Speciation And Interconversion Mechanism Of Mixed Halo And O,O- And O,N-Bidentate Ligand Complexes Of Zirconium

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~~ Serenity is a state of being, not a state of mind ~~

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List of Abbreviations

Abbreviation Meaning		
NAC	thermal neutron absorption cross section	
acacH	cH acetyl acetone	
phacacH	diphenyl acetylacetone	
^t Bu acacH	di-tertiarybutyl acetylacetone	
tfacacH	trifluoro acetylacetone	
hfacacH	hexafluoro acetylacetone	
tropH	tropolone	
oxH	8-hydroxyquinoline	
ср	cyclopentadienyl	
IR	infra red	
UV/Vis	ultra violet/visible	
NMR	nuclear magnetic resonance	
KMR	kern magnetiese resonans	
XRD	x-ray diffraction	
Z	number of molecules in a unit cell	
Α	absorbance (theoretical)	
$A_{\sf obs}$	observed absorbance	
(L,L')	bidentate ligand	
k_{x}	rate constant for a forward equilibrium reaction	
<i>k</i> -x	rate constant for a backward equilibrium reaction	
K _x	equilibrium constant for an equilibrium reaction	
$k_{\sf obs}$	observed rate constant	
ppm	(unit of chemical shift) parts per million	
DMF	dimethyl formamide	
C_6D_6	deuterated benzene	
C_7D_8	deuterated toluene	
ν	IR stretching frequency	
λ	UV/Vis wavelength	
ΔH	Enthalpy of activation	
ΔS	Entropy of activation	
mg	milligram	
mmol	millimol	
М	mol.dm⁻³	
Å	angstrom	
0	degrees	
°C	degrees Celsius	
π	pi	

Abstract

Key words: Zirconium; hafnium; bidentate ligands; O,O'-donating ligands; synthesis; crystallographic characterisation; kinetic mechanistic study.

The aim of this project is to find significant chemical differences between the fluorinated O,O-bidentate ligand complexes of zirconium and hafnium which would allow the separation and purification of these metals. In the present investigation of zirconium complexes, different ratio's of bidentate ligands (L,L') have been used in synthesis, to study the variation in activity and selectivity of coordination of L,L' to zirconium halides, where L,L' = tfacacH, hfacacH and oxH.

Different synthetic procedures and characterization methods of these complexes are discussed. Optimal reaction conditions have been found for different substituted L,L'bidentate halo-zirconium complexes. The crystallographic characterization of tetrakis(1,1,1-trifluoroacetylacetonato- κ^2 -O,O') zirconium(IV) toluene solvate and tetrakis(quinolinolato- κ^2 -N,O)zirconium(IV) N,N-dimethyl-formamide solvate is presented and compared with literature. The former crystallizes in a monoclinic crystal system while the latter is triclinic. Both crystal structures were found to have solvent molecules as part of the basic molecular unit, though these solvent molecules are shown to not have a great impact on the steric packing for either basic organometallic group (consisting of the respective bidentate ligands coordinated to zirconium). It was also found that these structures show square anti-prismatic coordination polyhedra, with a small distortion towards a dodecahedral geometry in both cases. This is however not uncommon for zirconium-bidentate ligand structures.

A discussion of the principles of the kinetic approach employed is also included as well as experimental results. Specific reference is made to the advancement in setting standards for identifying reaction steps and defining reaction mechanisms. New conclusions about the coordination mechanism with regard to these systems are drawn from new observations made during the synthesis, characterization and preliminary kinetic studies. The initial coordination mechanism is postulated for the four observed steps of zirconium chelating reactions individually identified and analyzed with bidentate ligands. A step-wise substitution mechanism is proposed and discussed for this coordination reaction scheme, yielding interesting results concerning the theoretical assumptions for such a reaction proceeding to full coordination of zirconium, studied by time resolved stopped flow and slower UV/Vis spectroscopy. Other than traditional square-planar coordination reactions, this system proved to be independent of solvent effects, as also evident by the independence of crystallographic characterized structures shown to have no influence from steric effects of solvent molecules present in the formula unit.

Opsomming

Sleutelwoorde: Sirkonium; hafnium; bidentate ligande; O,O'-skenkende ligande; sintese; kristallografiese karakterisering; kinetiese meganistiese studie.

Die doel van hierdie projek is om beduidende chemiese verskille tussen die gefluorineerde O,O-bidentate ligandkomplekse van sirkonium en hafnium te vind wat die skeiding en suiwering van hierdie metale sal toelaat. In die huidige ondersoek van sirkonium komplekse is verskillende verhoudings van bidentate ligande (L,L') in sintese gebruik om die verskille in aktiwiteit en selektiwiteit van koördinasie van L,L' aan sirkonium haliede, waar L,L' = tfacacH, hfacacH en oxH, te bestudeer.

Verskillende sintetiese prosedures en karakteriseringsmetodes van hierdie bespreek. komplekse word Optimale reaksietoestande is vir verskillend gesubstitueerde L,L'-bidentate halo-sirkonium komplekse Die gevind. kristallografiese karakterisering van tetrakis(1,1,1-trifluoroasetielasetonato- κ^2 -O,O') sirkonium(IV) tolueen solvaat en tetrakis(kinolinolato- κ^2 -N,O)sirkonium(IV) N,Ndimetiel-formamied solvaat word voorgelê en vergelyk met beskikbare literatuur. Eersgenoemde kristalliseer in `n monokliniese kristalstelsel terwyl laasgenoemde triklinies is. Beide kristalstrukture bevat oplosmiddel molekule as deel van die basiese molekulêre eenheid, maar die oplosmiddel molekule het nie `n groot impak op die steriese pakking van enige van die twee basiese organometalliese groepe (bestaande uit die onderskeie bidentate ligande gekoördineer aan sirkonium) nie. Dit is ook vasgestel dat hierdie strukture vierkantig anti-prismatiese koördinasie polihedra vertoon, met `n klein uitwyking na dodekahedrale geometrie in beide Dit is egter nie `n ongewone verskynsel in sirkonium-bidentate gevalle. ligandstrukture nie.

`n Bespreking van die beginsels van die toegepaste kinetiese benadering is ingesluit, asook die eksperimentele resultate. Spesifieke verwysing word gemaak na die vooruitgang in standaardstelling om reaksiestappe te identifiseer en

-X-

reaksiemeganismes te definieer. Nuwe gevolgtrekkings aangaande die koördinasiemeganisme met betrekking to hierdie stelsels word gemaak vanaf nuwe waarnemings tydens die sintese, karakterisering en voorlopige kinetiese studies. Die aanvanklike koördinasiemeganisme is gepostuleer vir die vier waargenome stappe van sirkonium kilasiereaksies met bidentate ligande wat individueel geïdentifiseer en `n Stapsgewyse substitusiemeganisme vir hierdie koördinasie geanaliseer is. reaksieskema is voorgestel en bespreek, wat interessante resulte gelewer het ten opsigte van die teoretiese aannames vir hierdie tipe reaksie wat lei tot die volle koördinasie van sirkonium, soos bestudeer met gestopde-vloei en stadiger UV/Visspektroskopie. Anders as tradisionele vierkantig-planêre koördinasiereaksies is bewys dat hierdie stelsel onafhanklik is van oplosmiddel invloed, soos ook duidelik is uit die onafhanklikheid van kristallografies gekarakteriseerde strukture wat nie steries beïnvloed word deur oplosmiddel molekule in die formule eenheid nie.

Introduction

1.1. Zirconium and Hafnium

Zirconium and hafnium are two transition metals found in the titanium triad in the periodic table, with very similar chemical properties, and occur together in nature. Zirconium ore (commonly referred to as zircon) is a byproduct of mining and processing of the titanium minerals; ilmenite and rutile, as well as tin.¹ Zircon in itself always contains 1 - 3% hafnium,² and the separation of zirconium and hafnium is extremely difficult due to the almost identical chemical characteristics.

These two metals find a very important application in the nuclear industry, which is due to the large difference in the respective thermal neutron absorption cross section $(NAC)^3$ properties. The smaller the NAC, the less the affinity the metal has for absorbing thermal neutrons (nuclear energy); this cross section of an element is measured in barns (1 barn = 10^{-24} cm²). Zirconium has a NAC of 0.185 barn and this along with its anti-corrosive properties and high thermal stability, makes it an ideal applicant for cladding material of nuclear fuel rods. These rods usually contain uranium or plutonium oxides, called fuel pellets. Due to the intense reactivity in the reactor, these pellets are cladded with a metal that has

¹ R. Callaghan (2008). USGS Minerals Information. Available:

http://minerals.usgs.gov/minerals/pubs/commodity/zirconium. Last accessed 25 November 2008. ² L.O. Ivan; *Chem. Rev.*, **1928**, 5, 1, 17

³ A. Munter (2008). Neutron scattering lengths and cross sections. Available:

http://www.ncnr.nist.gov/resources/n-lengths. Last accessed 25 November 2008.

high anti-corrosive properties and has a low NAC to prevent leakage of nuclear reactive materials.⁴ Hafnium, on the other hand, has a NAC of 104.1 barn and is applied as control rods in some nuclear reactors. Control rods for nuclear reactors are components, used to soak up excess nuclear energy and control the amount of energy produced from the fuel rods.⁵

For the effective application of the respective metals mentioned above, it is imperative that the separation process applied on the base ore be as efficient as possible. A fractional impurity in either metal would seriously hamper the effectiveness of the metal's role in a nuclear reactor. It is also required that such a separation technique be as economically viable and environmentally friendly as possible. The industry naturally tends towards processes that produce an expensive product *via* an inexpensive process.

1.2. The Nuclear Industry

Currently, the nuclear industry is controversial at best. World trends towards the development of nuclear power production are divided into two camps. Some countries continue to have a ban in place for nuclear energy use while the larger part of the world actively researches new possibilities for application of nuclear energy in favor of consumption of hazardous fossil fuels.⁶ Since 2005, nuclear power provides 6.3% of the world's energy and 15% of the world's electricity, with Japan, France and the United States accounting for more than half of nuclear generated

⁴ Science Encyclopedia - Net Industries (2008). Nuclear Power - The Nuclear Power Plant. Available: http://science.jrank.org/pages/4743/Nuclear-Power-nuclear-power-plant.html. Last accessed 25 November 2008.

⁵ Science Encyclopedia - Net Industries (2008). Nuclear Reactor - Control Rods. Available: http://science.jrank.org/pages/4754/Nuclear-Reactor-Control-rods.html. Last accessed 25 November 2008.

⁶ J.A. Lake (2004). Nuclear Energy's Role in Responding to the Energy Challenges of the 21st Century. Available: http://nuclear.inl.gov/docs/papers-presentations/ga_tech_woodruff_3-4.pdf. Last accessed 25 November 2008.

electricity.⁷ The production of nuclear energy across the world is very diverse, with the percentage of electricity generated from nuclear reactors ranging from 78% in France to 2% in China. These are among the 30 countries with nuclear power generation capacity. Early in 2008, there were 439 nuclear power plants operational worldwide, while 35 more are under construction. The United States tops the list with 104 plants, followed by France (59), Japan (55) and Russia (31). The expansion in nuclear power generation is centered in Asia with a total of 20 out of the 35 plants under construction, while 28 of the last 39 plants connected to the grid are also in Asia.⁸ According to the World Nuclear Association, during the 1980's one new nuclear reactor was started up globally every 17 days on average, and by the year 2015 this rate could increase to one every 5 days.⁹

The economics of nuclear power is a sensitive subject, since multi-billion dollar investments hang in the balance of the choice of any energy source. Nuclear power plants typically have high capital costs for building the plant, but low operational costs. Thus by comparison to other power generation methods it is very dependent on projected financing and construction timelines. Cost estimates also need to take into account: plant decommissioning and nuclear waste storage costs. On the other hand, measures to mitigate global warming, such as carbon tax or carbon emissions trading, favours the development for nuclear energy *versus* traditional fossil fuel generated sources.

⁷ International Energy Agency (2007). Key world energy statistics. Available:

http://www.iea.org/textbase/nppdf/free/2007/key_stats_2007.pdf. Last accessed 25 November 2008.

⁸ Synergyst (2008). Exploring the Economics of Nuclear Power. Available:

http://www.marketresearch.com/product/display.asp?productid=1838750. Last accessed 25 November 2008.

⁹ World Nuclear Association (2008). Plans for New Reactors Worldwide. Available: http://worldnuclear.org/info/inf17.html. Last accessed 25 November 2008.

1.3. The Need for Improvement in Separation

All of the above considered, it becomes apparent that a global trend towards the effective shift to nuclear energy production will affect every linked aspect to the final nuclear power plant and its operation. An increase for the need of safe, clean and cheap energy sources breeds the need for a knowledgeable workforce and dependable operational setup. More importantly this trend increases the global demand for the components and base materials utilized in the nuclear power plants. Therefore, it can be expected that the world market price for pure zirconium and hafnium will greatly increase as the demand for their respective applications expand. As mentioned before, the concept of producing something expensive at an inexpensive cost, is after all the most economically sought after approach. Furthermore, research that can lead to such a process for zirconium and hafnium is a world-wide point of interest, as can be seen from several research publications that directly involve the study of the differences in chemical properties of identical moieties of zirconium and hafnium.^{10,11,12}

1.4. The Separation of Zirconium and Hafnium

There are several known methods of separation of zirconium and hafnium. The first known method involves the fractional crystallization of ammonium fluoride metal salts and the fractionated distillation of the metal chloride. These methods are however not suitable for an industrial scale production process. Methods currently used in the industry for separation are mentioned below.

¹⁰ T. J. Pinnavaia & R. C. Fay; *Inorg. Chem.*, **1968**, 7, 508 ¹¹ H. V. R. Dias, W. Jin & Z. Wang; Inorg. Chem., **1996**, 35, 6074

¹² M. J. Scott & S. J. Lippard; Inorg. Chim. Acta, **1997**, 263, 287

• Liquid-liquid extraction^{13,14}

Liquid-liquid extraction, also known as solvent extraction and partitioning, is a method used to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent. It involves an extraction of a substance from one liquid phase into another liquid phase. Solvent extraction is used in nuclear reprocessing, ore processing, the production of fine organic compounds, the processing of perfumes and other industries.

By utilizing the difference in density of the two metals, preferential solubility of one metal in one phase is enhanced by the addition of an acid and thus the two metals are separated.

• Extractive Distillation¹⁵

Extractive distillation is a process that involves distillation in the presence of a miscible, high boiling, relatively non-volatile component, and the solvent, which forms no azeotrope with the other components in the mixture. This method is used for mixtures, having a low value of relative volatility, nearing unity. Such mixtures cannot be separated by simple distillation, because the volatility of the two components in the mixture is nearly the same, causing them to evaporate at nearly the same temperature and at a similar rate, making normal distillation impractical.

• Kroll Process¹⁶

The Kroll process is a pyrometallurgical industrial process initially used to produce metallic titanium and later adapted to be used for the separation

¹³ R. Madhavan (2008). Optimize Liquid-Liquid Extraction. Available:

http://www.cheresources.com/extraction.shtml. Last accessed 25 November 2008.

¹⁴ W.F. Fischer, B. Deierling, H. Heitsch, G. Otto, H.P. Pohlmann & K. Reinhardt; *Angew. Chem. Int. Ed.*, **1966**, 5, 1, 15.

¹⁵ D.F.C. Yee (2008). In Depth Look at Extractive Distillation. Available:

http://www.cheresources.com/extrdist.shtml. Last accessed 25 November 2008.

¹⁶ The Columbia Electronic Encyclopedia (2000). Zirconium. Available:

http://www.infoplease.com/ce6/sci/A0853458.html. Last accessed 25 November 2008.

of zirconium and hafnium. During this process the zircon is treated with carbon in an electric furnace to form a cyanonitride, which is in turn treated with chlorine gas to form the volatile tetrachloride. The tetrachloride is then purified by sublimation in an inert atmosphere and is chemically reduced to metal sponge by reacting with molten magnesium.

1.5. The Aim of This Study

The key to the effective and easy separation of zirconium and hafnium is undoubtedly found in the differences in chemical properties of two similar organic chelated moieties of these metals. In the search for a unique chemical state difference, it is necessary to investigate metal compounds with ligands, which allow for characterization and evaluation of said metal complexes. The postulation of the reaction mechanism and step-wise analysis will also assist in the development of a process to clarify the chemical behaviour, which the metal itself undergoes during substitution with organic chelates.

Some examples of zirconium complexes with acetyl acetone-type ligands are found in literature, which provides significant scope for the investigation of the varied chemical properties of organometallic complexes of zirconium and hafnium in different stages of higher coordination. The step-wise proposed aims for this project can thus be summarized as follows:

 To synthesize new zirconium – bidentate ligand complexes, with a specific aim to control the extent of coordination. It is postulated that a chemical difference that will allow ease of separation between hafnium and zirconium, could be found in the different chemical properties of a certain coordination mode for these metals. This might mean, for example, that a bis-coordinated complex of zirconium might be less dense than its hafnium counterpart and thus allowing separation by some method exploiting the differences in density. The ligands proposed for this study are (Figure 1.1):

- 1,1,1-Trifluoro-acetylacetone (TfacacH)
- 1,1,1,5,5,5-Hexafluoro-acetylacetone (HfacacH)
- 8-Hydroxy Quinoline (OxH)



Figure 1.1 Proposed bidentate ligands for this project, from left to right: TfacacH, HfacacH and OxH

- 2. The characterization of these new complexes will be mostly focused on X-Ray Crystallography for its unique three dimensional functionality of characterization; but infrared-, Ultraviolet/Visible- and Nuclear Magnetic Resonance Spectroscopy will also be employed. The choice of fluorinated acac ligands is motivated due to the availability of ¹⁹F NMR-spectroscopic experiments.
- 3. Solution behavioural kinetic studies of successfully characterized crystallographic structures of zirconium bidentate ligand complexes, give valuable insight into the mechanism of coordination of these bidentate ligands, which ultimately produces the final product. Through the intimate understanding of the reaction mechanism, the chemical differences for a specific ligand system reaction event, can be identified and utilized in the separation of zirconium and hafnium. If, for instance, one metal reacts much faster with a specific ligand than the other, reaction time can be limited and the differences in the extent of coordination for these two metals can be exploited in separation *via* extraction or other physical means.

In the following section a brief literature review will be given on the application of zirconium as well as known complexes from literature.

Literature Review

2.1. Zirconium – A Brief History

Zirconium (from the Persian zargun, meaning gold like)¹ was first discovered by Martin Heinrich Klaproth, a German chemist, while analyzing the composition of the mineral jargon (ZrSiO₄) in 1789 and named the new element Zirkonerde (zirconia). The zirconium-containing mineral zircon, (also known as jargoon, hyacinth, jacinth, and ligure) was also mentioned in biblical writings. Zirconium was isolated in an impure form by Jöns Jacob Berzelius, a Swedish chemist, in 1824, by heating a mixture of potassium and potassium-zirconium fluoride by activating a decomposition process in an iron tube.² The first industrial process for the commercial production of pure metallic zirconium, the Crystal Bar Process (or Iodide process), was developed by Anton Eduard van Arkel and Jan Hendrik de Boer in 1925. The process was followed by the much cheaper pyrometallurgic process developed by William J. Kroll (also known as the Kroll Process), where zirconium tetrachloride is reduced by magnesium at 800 – 850 °C in a stainless steel retort.³

¹ A. Stwertka, 1996, A Guide to the Elements, Oxford University Press, 117

² M. Winter (1993). Zirconium - historical information. Available:

http://www.webelements.com/zirconium/history.html. Last accessed 25 November 2008.

³ Advameg Inc. (2007). Zirconium. Available: http://www.madehow.com/Volume-1/Zirconium.html. Last accessed 25 November 2008.

Zirconium is a lustrous, grey-white, strong, transition metal found in the titanium triad on the periodic table. This group of metals (including titanium and hafnium) most notably are favoured in industry for their good electrical conductivity as well as their tendency to form metallic salts.³ Zirconium is the nineteenth most abundant element in the earth's crust and is far more abundant than copper and lead. The melting point of zirconium is 2128 °C, while the boiling point is 4682 °C. Zirconium has an electronegativity of 1.33 on the Pauling scale, and has the fourth lowest electronegativity after yttrium, lutetium, and hafnium. It is found in abundance in S-type stars, and has been identified in the sun and meteorites. Lunar rock samples obtained by several Apollo program missions to the moon show a higher abundance of zirconium oxide content compared to terrestrial rocks.⁴ It is never found separately in nature, it always occurs with hafnium, which has very similar chemical properties.⁵

The principal commercial sources of zirconium, is the zirconium silicate mineral, zircon ($ZrSiO_4$) and baddeleyite (ZrO_2) and is also a by-product of the mining and processing of the titanium minerals ilmenite and rutile as well as tin mining.⁶ Zirconium also occurs in more than 140 other recognized mineral species⁷ and has no known biological role. Zirconium salts are of low toxicity. The human body contains, on average, only 1 milligram of zirconium, and intake is approximately 50 µg per day. The zirconium content in human blood is as low as 10 parts per billion. Aquatic plants readily take up soluble zirconium, but it is rare in land plants.²

⁴ University of California (2003). Zirconium. Available: http://periodic.lanl.gov/elements/40.html. Last accessed 25 November 2008.

⁵ The Columbia Electronic Encyclopedia (2007). Zirconium. Available:

http://www.infoplease.com/ce6/sci/A0853458.html. Last accessed 25 November 2008.

⁶ J. Gambogi (2008). Zirconium and Hafnium - Statistics and Information. Available:

http://minerals.usgs.gov/minerals/pubs/commodity/zirconium. Last accessed 25 November 2008. ⁷ J. Ralph & I. Ralph (2008). Minerals that include zirconium. Available:

http://www.mindat.org/chemsearch.php?inc=Zr%2C&exc=&sub=Search+for+Minerals. Last accessed 25 November 2008.

2.2. Application of Zirconium

Cubic zirconia (ZrO₂) is best known for its remarkable similarity to diamonds. It is widely applied in the jewellery industry as a cheaper, though equally durable, substitute. Cubic zirconia is hard, optically flawless and usually colourless, but may be manufactured in a variety of different colours. It is a commercially synthesised gem stone and should not be confused with zircon, which is a zirconium silicate (ZrSiO₄). The addition of certain metal oxide dopants, gives the final gem a vibrant colour. For instance; the addition of chromium produces green and titanium leads to golden brown gems.⁸

Due to its high anti-corrosion properties, it is also applied as an alloy in the manufacturing of surgical appliances, explosive primers, vacuum tube getters and filaments.⁹ Zirconium alloys are also used in space vehicle parts because of their resistance to heat and is used extensively as a refractory material in furnaces and crucibles, in ceramic glazes and in gas mantles.⁵

Zirconium compounds also find a wide range of applications in the chemical industry. These range from lotions to treatments for poison ivy (Zirconium carbonate), a component in some abrasives (grinding wheels and sandpaper), to uses in the dye, textile, plastics, and paint industries.⁵

Zirconium metal complexes can also be applied as catalysts in certain reactions. Most notably the metallocene complex of zirconium (Cp₂ZrHCl), also known as Schwartz's Reagent, is used in organic synthesis for various transformations of alkenes and alkynes. It reacts with alkenes and alkynes by

⁹ Mineral Information Institute (2000). Zirconium. Available:

⁸ J. Berg (2002). Cubic Zirconia. Available:

http://www.emporia.edu/earthsci/amber/go340/students/berg/cz.html. Last accessed 25 November 2008.

http://www.mii.org/Minerals/photozircon.html. Last accessed 25 November 2008.

hydrozirconation, which leads to the addition of the Zr-H bond across the C=C or C=C bond.^{10,11,12} Zirconium(IV) tetrapropanolate is also reportedly applied in heterogeneous catalysis to produce hydrocarbons that are easily converted to kerosene and gas oil (middle distillate fraction).¹³

The chief application of zirconium is found in the nuclear industry, where about 90% of zirconium produced worldwide, is used in this setting.⁴ Zirconium has a very low thermal neutron absorption cross-section (0.185 barn), and along with this property and its high thermal stability and anti-corrosive properties, makes it ideal for use as cladding material on fuel rods in nuclear reactors. These fuel rods typically contain uranium and plutonium, and need to be cladded to prevent the leakage or corrosion of these rods into the reactor itself. The form in which zirconium is used in nuclear reactors is an alloy called Zircaloy with a range of zirconium-metal mixes for various conditions.¹⁴

- **Zircaloy-1:** Zirconium and 2.5% tin. An increase in corrosion over time forced the development of alloys with addition of other elements.
- **Zircaloy-2 (Zry-2):** Zirconium (98.25%), tin (1.45%), chromium (0.10%), iron (0.135%), nickel (0.055%) and hafnium (0.01%).
- **Zircaloy-4 (Zry-4):** Zirconium (98.23%), tin (1.45%), iron (0.21%), chromium (0.1%) and hafnium (0.01%).

Zirconium has a high affinity to hydrogen, this absorption can lead to hydrogen embrittlement which causes local or total fuel element failure. Zircaloy is generally more corrosion-resistant and has better neutron transparency than other materials. Unfortunately the corrosion resistance of

¹⁰ D.W. Hart & J. Schwartz; *J. Am. Chem. Soc.*, **1974**, 96, 8115

¹¹ J. Schwartz & J.A. Labinger; *Angew. Chem. Int. Ed.*, **2003**, 15, 330

¹² D.W. Hart, T.F. Blackburn & J. Schwartz; *J. Am. Chem. Soc.*, **1975**, 97, 679

¹³ R.W. Joyner (2007). Zirconium in catalysis. Available:

http://www.zrchem.com/pdf/CATLIT7A.pdf. Last accessed 25 November 2008.

¹⁴ Revision history statistics (2008). Zircaloy. Available:

http://en.wikipedia.org/w/index.php?title=Zircaloy&oldid=249770137. Last accessed 25 November 2008.

the alloy may degrade significantly if some impurities (e.g. >300 ppm carbon or >40 ppm nitrogen) are present. The corrosion resistance of these materials are improved by intentional development of a thicker passivation layer of lustrous zirconium oxide or by coating with titanium nitride.¹⁴

Some other zirconium alloys contain quantities of niobium (1-5%). The main difference in reactor grade zirconium alloy application depends on where the reactor was built and by which technology it is maintained. Reactors constructed with assistance of Western corporations apply the zirconium-tin alloys, while reactors built by Soviet, Eastern Europe, or Chinese companies generally tend towards zirconium-niobium alloys.¹⁴

2.3. The Purification of Zirconium vs. Hafnium

Purification of zirconium is most importantly focused on the removal of hafnium. Hafnium has chemically very identical properties to zirconium, largely due to lanthanide contraction. In general, the similarity of radii of fifth-and sixth-period transition metals is accounted to this aspect. The lanthanide elements collectively are theorised to fill the 4*f*-electron sub shell of the atomic electron model. The covalent radius (predicted bond length for an atom bound to another) decreases in a steady trend from cerium to lutetium, with a substantial total decrease over the lanthanide series. At the point where the 4*f*-subshell is completely filled, the covalent radii of the transition elements from hafnium onwards are very similar to those elements of the preceding row in the periodic table. The covalent radius of hafnium (150 pm) is thus almost identical to that of zirconium (148 pm).¹⁵

¹⁵ D.D. Ebbing & S.D. Gammon; *General Chemistry*, 7th Ed, Houghtoun Mifflin Company, Boston New York, **2002**, 1006

These metals share many characteristics and are always found together in nature. The most notable differences amongst the chemical properties are the atomic masses, densities, melting and boiling points and thermal neutron absorption cross section (Table 2.1). The difference in densities is most notably applied during the separation technique via liquid-liquid extraction or extractive distillation.

Zirconium Vs. Hafnium:				
Name zirconium hafnium				
Symbol	⁴⁰ Zr	⁷² Hf		
Standard atomic weight (g·mol ⁻¹)	91.224	178.49		
Density (near r.t.) (g⋅cm⁻³)	6.52	13.31		
Melting point (K)	2128	2506		
Boiling point (K)	4682	4876		
Principal oxidation states	4+	4+		
Atomic radius (pm)	155	155		
Atomic radius (calc.) (pm)	206	208		
Covalent radius (pm)	148	150		
Thermal neutron absorption cross section (barn)	0.185	104.1		

Table 2.1 Comparison of chamical & physical properties of ziroopium and hefpium

The purification of zirconium from hafnium, for its application in the nuclear industry is paramount, since hafnium has an approximately 600 times larger affinity for thermal nuclear energy than zirconium. Hafnium in itself is most notably applied as control rods in some nuclear reactors, to control the rate of production of energy and also in case of emergency, to soak up the excess nuclear particles (reducing the core temperature).



Figure 2.1 Graphical representation of a gas cooled nuclear reactor¹⁶

2.4. The Chemistry of Zirconium Organometallic Complexes

The key to effective and easy separation of zirconium and hafnium is undoubtedly found in the differences between chemical properties of all these metal complexes, containing similar ligands. In the search for a unique chemical state difference, it is necessary to investigate metal compounds with ligands that allow for characterisation and evaluation of said metal complexes, as well as allowing for the postulation of the reaction mechanism that the metal itself undergoes in substitution of one chelate with another.

Zirconium metal complexes have received moderate amounts of interest from research group's worldwide. The general focus of research concerning

¹⁶ Image of Nuclear Reactor adapted from:

http://commons.wikimedia.org/wiki/Image:Magnox_reactor_schematic.svg (25/09/08)

zirconium as coordinating metal revolves around structural defining studies with particular reference to coordination geometries. Other research reports focus heavily on the development of new complexes for industrial applications in catalysis, with particular interest in polymerisation catalytic processes.^{17,18,19,20,21}

2.4.1. Zirconium and β -diketones: An Overview of O,O-donors

The β -diketone family of bidentate ligands are a widely used type of conjugated ligand system in organometallic chemistry. In particular, the acetylacetone branch of this family is a special favourite in the world of organometallic chemistry. It is a well know ligand system employed for its ease of coordination to all known non-radioactive elements. Zirconium and hafnium are unique in this case as they are the only elements which have been reported to form β -diketonates in which the metal may exhibit coordination numbers of six, seven and eight.²² Another interesting aspect of the tetrakis(acetylacetonato) zirconium^{IV}-type complexes are classic examples of square-antiprismatic coordination geometries.²³

Research with regard to zirconium complexes of the acetylacetones and functionalised derivatives has found a fair amount of interest in literature, as discussed in the following sections. These complexes are prepared by many different synthetic procedures, but the general trend for synthesis requires anhydrous conditions, since these metal centres are strong Lewis acids and show strong hydrophilic tendencies during the reaction process.

¹⁷ R. Vollmerhaus, M. Rahim, R. Tomaszewski, S. Xin, N.J. Taylor & S. Collins, *Organometallics*, **2000**, 19, 2161

¹⁸ J. Kim, J.W. Hwang, Y. Kim, M.H. Lee, Y. Han, Y. Do; Journal of Organometallic Chemistry, **2001**, 620, 1

¹⁹ M.J. Scott & S.J. Lippard; Inorganica Chimica Acta, **1997**, 263, 287

²⁰ M. Rahim, N.J. Taylor, S. Xin & S. Collins, *Organometallics*, **1998**, 17, 1315

²¹ H. V. Rasika Dias, W. Jin & Z. Wang; *Inorg. Chem.*, **1996**, 35, 6074

²² T. J. Pinnavaia & R. C. Fay; *Inorg. Chem.*, **1968**, 7, 502

²³ W. Clegg; Acta Cryst., **1987**, C43, 789

A wide range of these type of tetrakis (O,O') complexes of zirconium have been published. Fictionalisation of the methyl groups at the 1st and 3rd carbon of the O-C-C-C backbone are most commonly found with a replacement of methyl (acetylacetone or 2,4-pentanedione) with favoured organic groups such as phenyl (1,3-diphenyl-1,3-propanedione), tertiarybutyl (2,2,7,7-tetramethyl-3,5-heptanedione) and trifluoromethyl acetylacetone/1,1,1,5,5,5-hexafluoro-2,4-pentanedione) (hexafluoro moieties. Unsymmetrical moieties are also produced such as the substitution of a single methyl group with trifluoro methyl (trifluoro acetylacetone/ 1,1,1-Trifluoro-2,4-pentanedione). Most notably these complexes are published in abundance as the 3- or 4-chelated complex, but very few examples of lesser coordinated complexes are available.



Figure 2.2 Graphic representation of basic Acac type ligand structure. For acac, R₁=R₂=CH₃; phacac, R₁=R₂=ph; ^tBu acac, R₁=R₂=^tBu; hfacac, R₁=R₂=CF₃; tfacac, R₁=CF₃ & R₂=CH₃.

2.4.2. Tetrakis(β -diketone) zirconium(IV) complexes



Figure 2.3 Graphic representation of a typical tetrakis(β -diketone) zirconium(IV) complex. R₁ and R₂ defined below in subsections 2.4.2.1–5.

2.4.2.1. Tetrakis(acetylacetonato)-zirconium(IV) ($R_1 = R_2 = CH_3$)

The first Zirconium(IV) acetylacetonato complex to be characterized by xray crystallography, was published in 1963 by Silverton et al.²⁴ The study was aimed at fully characterizing the coordination geometry of a tetrakis coordinated acetylacetonato moiety of zirconium. The final conclusions, with regard to the completed characterization, defined the distorted antiprismatic properties of the coordination sphere, setting the field for zirconium acac research for the future. Comparisons were drawn with molybdenum similar and tungsten complexes, previously only characterized by theoretical electron modeling.

2.4.2.2. Tetrakis(1,3-diphenyl-1,3-propanedionato)zirconium(IV) ($R_1=R_2=Ph$)

In 1979 Chun et al.²⁵ published the structure for the 4-coordinated phacac zirconium complex. The research paper discusses the packing effects of β -diketone ligands in zirconium complexes as 4-coordinated species. They set out to describe the exact crystal packing, prompted by reports from previous papers that suggested that zirconium(IV) β -diketone complexes would be similar to the 4-coordinated phacac complexes of Ce, Th, and U, which have a dodecahedral mmmm structure. In the final conclusions they reported that the phacac complex of zirconium, had in fact an ssss square-antiprismatic structure that closely resembles the structure of $[Zr(acac)_4]$. This then goes further to confirm that the 4-coordinated acac and derivative complexes all tend toward a anti-prismatic coordination geometry, as square postulated by Silverton *et al.*²⁴ and Clegg²³ in previous papers with regard to these type of complexes.

 ²⁴ J.V. Silverton & J.L. Hoard; *Inorg. Chem.*, **1963**, 2, 243
²⁵ H.K. Chun, W.L. Steffen & R.C. Fay; *Inorg.Chem.*, **1979**, 18, 2458

2.4.2.3. <u>Tetrakis(hexafluoroacetylacetonato)-zirconium(IV) ($R_1 = R_2 = CF_3$)</u>

In 1998 Calderazzo et al.²⁶ published the structure of a 4-coordinated zirconium complex with hfacac as bidentate ligand. Their interest in the total 8-coordinated (2 oxygens for each ligand coordination) species of zirconium and niobium stemmed from research on the differences for these types of coordinated complexes of metals with different oxidation states (Zr⁴⁺ & Nb⁵⁺). They intended to study and to verify the dependence of the coordination polyhedron on the bite angle of the ligand for these cations of early transition metals. They favoured hfacac over standard acac, in order to provide weaker intermolecular interactions and therefore presumably to give better solubility and higher vapour pressure. Their crystallographic characterization confirmed that the 4-coordinated hfacac molety of zirconium also packs in the distorted square anti-prismatic geometry, just like every other $[Zr(acac)_4]$ type of complex. Their conclusions on the dependence of coordination geometry on the bidentate ligand bite angle states that for smaller bite angles of bidentate ligands, a dodecahedral coordination geometry is observed, while for large bite angles such as acac-type ligands, the square anti-prismatic geometry is found.

2.4.2.4. <u>Tetrakis(trifluoroacetylacetonato)-zirconium(IV) ($R_1 = CF_3$; $R_2 = CH_3$)</u>

In late 2007 Kurat'eva *et al.*²⁷ published several structures of zirconium containing tfacac, hfacac and pivaloyltrifluoroacetone as replacement ligand. This research paper was inspired by research on metal oxides applied as coatings for industrial uses such as memory chips, solid oxide fuel cells, chemical engineering and more. They reported synthesis of

²⁶ F. Calderazzo, U. Englert, C. Maichle-Mössmer, F. Marchetti, G. Pampaloni, D. Petroni, C. Pinzino, J. Strähle & G. Tripepi; *Inorg. Chim. Acta*, **1998**, 270, 177

²⁷ N.V. Kurat'eva, I.A. Baidina, O.A. Stabnikov, I.K. Igumenov.; *J. Struct. Chem.*, **2007**, 48, 3, 513

these complexes as reactions of anhydrous zirconium(IV) chloride with an excess of the ligand in a boiling inert solvent under reflux. The molecule of the tfacac complex has the two-fold axial symmetry. A zirconium atom is coordinated by eight oxygen atoms of four β -diketonate ligands. For this structure, the unsymmetrical bidentate ligand shows different Zr—O bond lengths for the two sides of a specific acac-backbone set. The Zr—O bond on the fluorinated side of the ligand is shorter by an average of 0.033 Å than the methyl side. It is also reported that the complex shows intermolecular interactions between F and H atoms between molecular groups, forming a net-like structure.

2.4.2.5. <u>Isopropoxy-tris(2,2,7,7-tetramethyl-3,5-heptanedionato)</u> <u>zirconium(IV) & tetrakis(2,2,7,7-tetramethyl-3,5-heptanedionato)</u> <u>zirconium(IV) (R₁=R₂=^tBu)</u>

In 2006 Spijksma *et al.*²⁸ published a structure of 3- and 4-coordinated ¹Bu acac derivatives, synthesized from zirconium *n*-propoxide as starting reagent. Their research for this paper stems from the modification of zirconium and hafnium alkoxides for application in large scale integrated circuits and as a gate dielectric in metal-oxide semiconductors. Their synthesis of the 2-coordinated moiety yielded a dimeric complex with the remaining original *n*-propoxide ligands, from the starting material, in the bridging positions. The main interest for synthesis and structural characterization for the 4-coordinated complexes of zirconium and hafnium was to reveal the reasons for their unusual physicochemical properties. These complexes are known to be very poorly soluble in hydrocarbon solvents and have relatively poor volatility in comparison to other mononuclear ^tBu derivatives of transition metals. The slightly higher solubility in aromatic hydrocarbons can be attributed to a higher solvation

²⁸ G.I. Spijksma, H.J.M. Bouwmeester, D.H.A. Blank, A. Fischer, M. Henry & V.G.Kessler; *Inorg. Chem.*, **2006**, 45, 4938

ability of these solvents, compared to the aliphatic ones. The packing of the 4-coordinated complexes of zirconium and hafnium requires a bigger and less symmetric unit cell, compared to other known tetrakis derivatives of zirconium and hafnium, where a more regular and less-symmetric nature of ligands can permit a packing in a more-organized and lessuniform manner. Their final conclusion state that a 2-coordinated ^tBu acac cannot be prepared, or more specifically that such a modification cannot be performed from zirconium(IV) propoxides. According to them, the so called commercial product "[Zr(O'Pr)₂(^tBu acac)₂]" most commonly used for the metal-organic vapor deposition preparation of ZrO₂ does not exist. Furthermore, they concluded that no evidence was found for the presence of such a compound in either zirconium or hafnium-based systems. Formation of the dimeric hydroxo-bis(¹Bu acac)-substituted complex could be proved only for hafnium-based system and occurs on microhydrolysis. This then leads to the postulation that 2-coordinated bidentate complexes of zirconium will generally tend towards dimeric species as a preference to monomeric species.

2.4.3. Tris(β -diketone)halido zirconium(IV) complexes



Figure 2.4 Graphic representation of a typical tetrakis(β -diketone) zirconium(IV) complex. R₁, R₂ and X defined below in subsections 2.4.3.1–4.

2.4.3.1. <u>Chlorotris(1,3-diphenyl-I,3-propanedionato-O, O')zirconium(IV)</u> $(R_1=R_2=Ph, X=CI)$

In 1998 Janiak et al.²⁹ published the structure for a 3-coordinated phacac zirconium complex. The inspiration for the project arises from the application of Zirconium β -diketonate complexes being described as single-site catalysts for the polymerization of ethene and styrene. The use of these chelate ligands or complexes in catalysis was based on the idea that bis- or tris-chelate complexes can assume chiral \varDelta and Λ forms. Chiral catalytic centers are a prerequisite for the tailored stereo regular coordination polymerization of prochiral α -olefins. To verify this formation of enantiomeric forms in the pre-catalytic chelate complexes, the molecular and crystal structures of this compound were determined. The compound was prepared by reaction zirconium(IV) chloride, with a six molar equivalent of dibenzoylmethane and refluxing for 14 hours. Final remarks concluded that the structure contains three bidentate ligands arranged as propeller blades around the C₃ Zr--C₁ axis to give a chiral molecule. The centrosymmetric space group contains a racemic mixture of left and right-handed propellers and the coordination geometry around the seven-coordinate Zr metal atom is a capped octahedron.

2.4.3.2. <u>Chlorotris(2,2,6,6-tetramethyl-3,5-heptanedionato-0,0')</u> zirconium(IV) ($R_1=R_2=^tBu, X=CI$)

In 1995 Jardin *et al.*³⁰ published a structure of a 3-coordinated ^tBu acac derivative. The structural characterization showed that the zirconium metal centre is in a 7-coordinated state with 6 O and 1 Cl atom. These molecular groups are further tied together in the lattice by

 ²⁹ C. Janiak & T.G. Scharmann; *Acta Cryst., Sect.C: Cryst.Struct.Commun.*, **1998**, 54, 210
³⁰ M. Jardin, Y. Gao, J. Guery & C. Jacoboni; *Acta Cryst., Sect.C:Cryst.Struct.Commun.*, **1995**, 51,2230

interactions between CI of one molecular group and H of another, forming netted planes that stack reversed on top of one another. Final conclusions on the crystal structure confirm that the same type of hydrogen bonding behaviour is observed in the standard 3-coordinated acac moiety as reported by Von Dreele et al.³¹

2.4.3.3. Tris(hexafluoroacetylacetonato)- π -cyclopentadienyl-zirconium(IV) $(R_1 = R_2 = CF_3, X = cp)$

In 1969 M. Elder³² published a structure of a zirconium complex with 3 hfacac ligands and a cyclopentadienyl (cp) as a fourth ligand. Though not strictly an example of a tris(β -diketone) halido zirconium(IV) complex, it is a very interesting study. They claim that the zirconium atom is formally 11-coordinated, though this seems to be an incorrect assumption. Cp ring systems are accepted to formally occupy only 3 coordination sites, even though they are assigned by nomenclature as $\eta^{\rm b}$ -conjugated. It is thus suggested that it be accepted that the zirconium center be considered as formally 9 coordinated, which seems more plausible as far as coordination extent goes. The synthesis and characterization of this complex was undertaken as part of a correlation study between NMR and x-ray crystallographic techniques to assist in the prediction of zirconium structures, based solely on NMR spectra for ¹H and ¹⁹F NMR experiments as a comparison to known structures like the standard acac species. It was remarked that a rapid intramolecular rearrangement averages the expected ligand derivative substituent groups from all spectra. This then goes a long way to explain why very few kinetic studies have been reported for zirconium complexes.

 ³¹ R. Von Dreele, J. J. Stezowski & R. C. Fay; J. Am. Chem. Soc., **1971**, 93, 2887
³² M. Elder; *Inorg.Chem.*, **1969**, 8, 2103

2.4.3.4. <u>Dichlorobis(2,4-pentanedionato)zirconium(IV) and Chlorotris(2,4-pentanedionato)zirconium(IV) (R₁=R₂=CH₃, X=CI)</u>

In 1968, Pinnavaia et al.^{22,33} published a two part research paper on the infrared and Raman characterization of zirconium and hafnium acac complexes. They aimed to synthesis the 2- and 3-coordinated moieties of Zr acac complexes, containing halogens from the synthesis starting metal material zirconium (IV) halide. Synthesis of the different coordination states was controlled by using different reaction times and solvents, thought the reason why these methods yielded the intended products are unclear. The reaction conditions for the 3-coordinated complex are reported at 4 hours of refluxing in benzene, while the comparative for the 2-coordinated moiety is 12 hours refluxed in ether. The greater part of both papers is devoted to the infrared absorption characterization of the halide-acac-metal complexes and no specific mention is made as to the accuracy of the assumption that the different coordination modes have in fact been isolated. The melting points for the intended 3-coordinated species are reported in a range between 101 °C to 158 °C, while the melting point for the 2-coordinated species is reported at 185 °C. The final conclusions remark that they were able to discern between *cis*- and *trans*- coordinated moieties of all complexes. No 3-dimnesional structural characterization is reported.

2.4.4. Mono and $bis(\beta$ -diketone) halido zirconium(IV)

From a search on the Cambridge Structural Database³⁴ (CSD), no examples of traditional O,O-acac type ligand complexes of single and dual coordinated zirconium(IV) halido could be found. Zirconium(IV) complexes

³³ T. J. Pinnavaia & R. C. Fay; *Inorg. Chem.*, **1968**, 7, 508

³⁴ Cambridge Structural Database (CSD), Version 5.30, February 2009 update; F.H. Allen, *Acta Cryst.*, **2002**, B58, 380.

containing two or three halides are very limited, and the only examples that could be found contain acac derivative ligand groups with O,N or N,N-donor atoms.



Figure 2.5 Graphic representation of (a) Dichloro-bis(4-(phenylamido)pent-3-en-2-one)zirconium(IV) & (b) *cis*-Dichloro-bis(2,4-bis(phenylimino)pent-3-ene)-zirconium(IV)

2.4.4.1. Dichloro-bis(4-(phenylamido)pent-3-en-2-one)-zirconium(IV)

In 1998 Jones *et al.*³⁵ published the structure of a bis(O,N-acac) type zirconium(IV) dihalido complex (See Figure 2.5 (a)). Their research involves an adjustment of β -diketone ligands for zirconium complexes for application as catalyst systems for the conversion of ethylene into linear α -olefins. They report that the bis(ligand) complexes can be synthesized by the reaction of ZrCl₄ with the isolated ligand salt of tetrahydrofuran (THF), by *in situ* generation of the ligand salt, or from the bis(ligand) adduct and LiBuⁿ. The reaction proceeds at 60 °C for 4 hours before filtration separation and *in vacuo* drying of the filtrate product, yielding >90% product by this procedure.

³⁵ D. Jones, A. Roberts, K. Cavell, W. Keim, U. Englert, B.W. Skelton & A.H. White; *J.Chem.Soc.,Dalton Trans.*, **1998**, 255

2.4.4.2. cis-Dichloro-bis(2,4-bis(phenylimino)pent-3-ene)-zirconium(IV)

Also in 1998, Rahim et al.³⁶ published the structure of a bis(N,N-acac) type zirconium(IV) dihalido complex (see Figure 2.5(b)). Their research also involved investigation into the group 4 transition metals in connection with their use in olefin polymerization and related processes. Their synthetic technique involves reacting the desired ligand with the zirconium reagent in toluene at 80-90°C, with subsequent cooling and filtering and recrystallization of the precipitate to yield >75% product.

In both cases noted above, it could be postulated that the steric bulk afforded by the Ph-substituent on the N-donor atom, restricts the number of ligands that can effectively coordinate to the metal center. It is also interesting to note that in both cases the ligands are coordinated in a configuration, regardless of steric bulk. The cis-configuration is the most stable isomer, although the trans-configuration may sometimes be favourable due to steric effects on the O,O'-backbone. The reason for the higher stability of the *cis*- configuration can be attributed to the π -back donation into the three metal *d*-orbitals (d_{xy} , d_{xz} and d_x^2), whereas for the trans-configuration only two *d*-orbitals (d_{xy} and d_{xz}) are occupied.³⁷

³⁶ M. Rahim, N.J. Taylor, S. Xin & S. Collins; *Organometallics*, **1998**, 17, 1315 ³⁷ D.C. Bradley & C.E. Holloway; *J.Chem.Soc., Chem. Commun.*, **1965**, 284.
2.4.4.3. <u>Trichloro-(2-((2,6-di-isopropylphenyl)amino)-4-((2,6-di-isopropylphenyl)imino)-2-pentene)-zirconium(IV)</u>, <u>Dichloro-bis(4-p-isopropylphenyl)imino)-2-pentene)-zirconium(IV)</u> & <u>Dichloro-(2-(p-tolylamino)-4-(p-isopropylphenyl)-zirconium(IV)</u>)</u>



Figure 2. 6 Graphic representation of **(a)** Trichloro-(2-((2,6-di-isopropylphenyl)amino)-4-((2,6-di-isopropylphenyl)imino)-2-pentene)-zirconium(IV), **(b)** Dichloro-bis(4-ptoluidinopent-3-en-2-one)-zirconium(IV) & **(c)** Dichloro-(2-(p-tolylamino)-4-(p-tolylimino)-2-pentene)-zirconium(IV)

Further proof of the effect of steric bulk on the extent in coordination, is found in the published work of Kakaliou *et al.*³⁸ With the goal of studying compounds supported by monoanionic ligands which steric and electronic properties can easily be modified, they had examined the synthesis, structure, and reactivity of main-group and transition metal compounds stabilized by β -diketiminate ligands. They published the structure of a mono-substituted zirconium(IV) trihalido complex with a derivative acactype ligand containing N,N-donor groups. The substituents on these donor groups in turn are a derivative phenyl ring with iso-propyl groups on the sites nearest the acac ligand structure. They also published (in the same paper) the structures of bis-substituted zirconium(IV) dihalido complexes with a derivative acac-type ligand containing O,N and N,N-donor groups with tolyl substituents on the N-donor atoms. The steric bulk from these ligands clearly blocks coordination of more such ligands onto

³⁸ L. Kakaliou, W.J. Scanlon, B. Qian, S.W. Baek, & M.R. Smith; *Inorg.Chem.*, **1999**, 38, 5964.

the metal chelating sites available. Thus most Cl⁻ ligand groups remain unsubstituted on the metal center. Again, it should be noted that the bissubstituted complexes are coordinated in the *cis*-configuration, as in the examples mentioned above. Their synthesis technique involves converting the organic ligand to a lithium salt before reacting this salt with the zirconium reagent at room temperature for several hours. The reaction mixture is then filtered and the precipitate extracted with pentane before recrystallization at -80°C to produce yields of 50-80%.

2.4.5. Zirconium and other multidentates: Other O,O- and O,N-donors 2.4.5.1. Tetrakis(tropolonato) zirconium(IV) chloroform



Figure 2.7 Tetrakis(tropolonato) zirconium(IV) Chloroform/ Zr(trop)₄

In 1978 Davis *et al.* ³⁹ published the crystal structure for the 4-coordinated zirconium tropolone complex. To date, it is the only such crystal structure published. As part of research on structural characteristics of chelating reactions of trop structures, they reported the synthesis and characterisation of this complex as a comparison with the theory of high coordination from literature. The complex was prepared by the reaction of zirconium(IV) chloride with 4.5 molar equivalents of tropolone in chloroform, under reflux for 15 minutes.

³⁹ A.R. Davis & F.W.B. Einstein; *Acta Cryst*, **1978**, B34, 2110

The crystal structure showed a disordered dodecahedron coordination geometry, with one trop ligand disordered. The ligand had a disordered portion containing the entire 7 carbon ring and 1 oxygen atom bound to the metal. The disorder was solved to show the ligand had shifted up from the standard ligand plane at an angle of 21°. The structure crystallized with one chloroform solvent molecule in the unit cell that was disordered with the trop ligand. It was stated that the disorder of the ligand is dependent on the thermal movement of the chloroform molecule itself. From their comparison with literature they further confirmed that the size of the ligand bite angle is directly related to the coordination geometry for tetrakis(bidentate ligand) zirconium complexes. They state that as with the acac variation of O,O-donor ligands, smaller bite angles will result in dodecahedron geometries, while bite angles normally associated with 5 member bite configurations of acac and its derivatives, will result in square antiprismatic geometries.

2.4.5.2. 8-Hydroxyquinoline

a) <u>Tetrakis(8-quinolinolato)zirconium(IV)</u>



Figure 2.8 Tetrakis(8-quinolinolato)zirconium(IV)/ Zr(Ox)4

In 1974 Lewis *et al.*⁴⁰ published the structure for the 4-coordinated zirconium complex of 8-Hydroxyquinoline. As part of research covering the coordination geometries of 8-coordinated transition metals, they proposed to relate the structural characteristics of the zirconium moiety with that of tungsten and molybdenum. A comparison of only the M—O and M—N bonds was made as part of the direct correlation with other metal complexes. They report that for this ox ligand complex, the zirconium is situated in a dodecahedron geometry, which does not correspond with acac and trop ligand systems. Since the ligand has a large bite angle to the metal it would be expected to adopt a square anti-prismatic coordination geometry.

b) (MeOx)₂ZrR₂ and (MeBr₂Ox)₂ZrR₂⁴¹



Figure 2.9 Ox zirconium structures; (a) (MeOx)₂ZrR₂ & (b) (MeBr₂Ox)₂ZrR₂

The only other ox-Zr structures published, can be found in a paper from 1997 by Bei *et al.* Two ox-derivatives (2-Methyl-8-quinolinolato & 2-Methyl-5,7-dibromo-8-quinolinolato) where prepared, which was coordinated to ZrR_4 (R = CH₂Ph, CH₂CMe₃, CH₂SiMe₃). This extensive study was aimed at describing the synthesis, structures,

⁴⁰ D.F. Lewis & R.C. Fay; *J.C.S. Chem. Comm.*, **1974**, 1046

⁴¹ X. Bei, D.C. Swenson & R.F. Jordan; *Organometallics*, **1997**, 16, 3282-3302

bonding, reactivity and coordination geometries of all the complexes in comparison to each other and to literature. The main inspiration for the research is taken from olefin polymerization catalysts of zirconium chelated with cyclopentadienyl ligand groups. They intended to discover how coordination geometries influence the reactivity of catalysts. They reported that the neutral structures synthesised all conform to distorted dodecahedral coordination geometries, while cationic ligands tend towards square pyramidal geometries. They also concluded that in the cases of the Br-derivative ox ligand complexes, they found the reactivity, with regard to catalytic properties, to increase. They assigned this to the presence of the electron withdrawing Br-substituents, which increase the Lewis acidity of the metal centre, and thereby enhancing catalytic properties of the complex.

2.5. Conclusions

Very little is known about the mechanism of ligand coordination and the interchange for zirconium complexes especially from the above discussed literature sources, since most synthetic projects focus on merely characterizing certain aspects of a specific complex. A number of research projects on the coordination geometries and prediction of coordination from characterization by methods not using 3-dimensional structural analysis (X-ray diffraction) have been done,^{24,25,26} but very few literature references can fully confirm why certain methods of synthesis were used. The aspects involved for control of the extent of coordination (*i.e.* controlling a reaction to only produce a two- or three coordinated complex) are never discussed. This leaves a general feeling that the first steps of creating new zirconium bidentate complexes are truly 'a shot in the dark'. Many published works refer back to synthetic methods published by others, but no researcher ever

confirms that they produced the specific zirconium species coordinated, as intended.

Paragraph Discussed	Reference	Structure	Coordination Number	Oxidation State
2.4.2.1	24	Zr(acac) ₄	8	Zr ⁴⁺
2.4.2.2	25	Zr(phacac)₄	8	Zr ⁴⁺
2.4.2.3	26	Zr(hfacac) ₄	8	Zr ⁴⁺
2.4.2.4	27	Zr(tfacac) ₄	8	Zr ⁴⁺
2.4.2.5	28	Zr(^t Bu acac) ₄	8	Zr ⁴⁺
2.4.2.5	28	Zr(O ⁱ Pr)(^t Bu acac) ₃	7	Zr ⁴⁺
2.4.3.1	29	ZrCl(phacac)₃	7	Zr ⁴⁺
2.4.3.2	30	ZrCl(^t Bu acac) ₃	7	Zr ⁴⁺
2.4.3.3	32	ZrCp(hfacac) ₃	9	Zr ³⁺
2.4.3.4	22, 33	ZrCl(acac) ₃	7	Zr ⁴⁺
2.4.3.4	22, 33	ZrCl ₂ (acac) ₂	6	Zr ⁴⁺
2.4.5.1	39	Zr(trop) ₄	8	Zr ⁴⁺
2.4.5.2 (a)	40	Zr(ox) ₄	8	Zr ⁴⁺
2.4.5.2 (b)	41	(Meox) ₂ ZrR ₂	6	Zr ⁴⁺
2.4.5.2 (b)	41	(MeBr ₂ ox) ₂ ZrR ₂	6	Zr ⁴⁺

Table 2.2: Summary of higher coordinated zirconium bidentate ligand complexes as discussed in this chapter.

Since mechanistic studies for zirconium bidentate systems are virtually unknown, and those available have yet to fully characterize the equilibrium states for every step of coordination process, the only conclusions about the coordination mechanism that can thus far be drawn from literature are (see Table 2.2):

• Ligand interchange occurs step-wise by replacement of single leaving (original) ligand with a single bidentate ligand, implying coordination increases integrally from 4 to 5 to 6 and so on.

- The oxidation state of the metal remains the same throughout the reaction (Zr^{4+}) .
- The zirconium halide systems are generally very sensitive to moisture and care needs to be taken in ensuring an anhydrous environment while studying these reactions.

Some vague conclusions can be drawn for differences in chemistries for zirconium and hafnium. From literature it seems that hfacac complexes of hafnium favour dimeric coordination modes while zirconium tends towards monomeric species. Some ligands (such as ^tBu acac) will produce hafnium complexes but no zirconium counterparts. Generally no explanation is reported for this behaviour.

In the following section the characterization techniques will be discussed in more detail.

Chapter 3

The Theory of Solid and Solution State Characterisation

3.1. Introduction

The characterisation of newly synthesised complexes in a research project, can be performed via several methods. The methods utilized, mostly depend on the specific composition of these complexes. These methods can be divided into two groups of characterisation, namely destructive and nondestructive techniques. Destructive techniques, as the name implies, will generally destroy a sample in the process of characterisation. Examples of such methods are Inductively Coupled Plasma (ICP)-, Elemental Mass (MS)and Atomic Absorption (AA) spectrometry as well as Gas Chromatography (GC). These methods are mostly used as quantitative as well as qualitative methods, and are favoured in situations where large quantities of sample are available. Non-Destructive methods, as implied, do not destroy a sample during characterisation but merely identifies the components via some form of Examples include Infrared Absorption (IR)-, Ultraviolet/Visible radiation. (UV/Vis) - and Nuclear Magnetic Resonance (NMR) - Spectrophotometry as well as X-Ray Diffraction Crystallography (XRD). These methods are often applied in situations where very small quantities of sample are available for characterisation. Most of these methods are generally only applied as a qualitative characterising method, though some, like XRD and UV/Vis, are extensively used for quantitative characterisation as well.

In this chapter, the basic theories of the methods used for characterisation in this research project will be discussed. Specific reference will be made to the choice of method, due to advantages concerned with inorganic synthesis product characterisation.

3.2. Infrared Absorption Spectroscopy (IR)

Infrared Absorption Spectroscopy is an invaluable tool for characterisation of organic and inorganic compounds. This is due to the fact that all molecular compounds (with the exception of some homonuclear molecules like O_2 and N_2) absorb infrared radiation. Furthermore, each molecular species has a unique infrared absorption, which allows for identification in the circumstance where an unknown compound can be compared to a known compound by matching their infrared spectra. This characteristic absorption spectrum is also commonly referred to as a molecular fingerprint and there is often made reference to the matching of fingerprint regions in newly synthesised complexes to determine whether or not the desired reaction has, in fact occurred, thus yielding the intended product. This method, though often criticised at not being 100% accurate, does find favourable application in situations where moderate accuracy is needed to identify the presence of select groups in a newly synthesised compound.¹

The basic process that takes place during the identification of a sample with this method entails the radiation of said sample with infrared radiation. The reflection of the radiation is then further reflected and captured in the

¹ D.A. Skoog, D.M. West, F.J. Holler & S.R. Crouch, Fundementals of Analytical Chemistry, 8th Ed., Brooks/Cole, Thomson Learning Inc., Belmont California, 2004, 811-819.

spectrophotometer itself, where it is then converted by a computer to a readable spectrum. Or more simply, it is the absorption measurement of IR radiation of a sample at set frequencies. The frequency here, implying the wavelength at which absorption is observed in terms of reciprocal centimetre (cm⁻¹) and is defined as the number of wave cycles in one centimeter. Frequency is defined as the number of wave cycles that pass through a point in one second, while wavelength is the length of one complete wave cycle.

From theory it is known that a chemical bond acts like a spring, connecting the parts (nuclei) of a molecule. The effect of this is that the nuclei within the molecule can vibrate and rotate, implying that they do not stay in fixed or frozen positions. This vibration and rotation of the nuclei in the molecule is what is observed with IR spectroscopy. Infra-red radiation energies can excite the molecule's vibration and rotational transitions, but does not translate enough energy to excite electronic transitions. Furthermore, the frequency of radiation absorbed equals the frequency of nuclear vibrations.²

The number of ways a molecule can vibrate is relative to the number of atoms and bonds within the molecule. Even though some vibrational effects can sometimes not be observed, the spectrum for even a simple molecule can become complex. As mentioned above, from theory many observed peaks have been classified to be characteristic of certain types of chemical bonds. Though IR is very useful for organic characterisation, it can also be applied for covalently bonded metal species. The specific regions generally assigned for metal bond frequencies range below 500 cm⁻¹ and require specialised equipment to be observed however. Numerous tables of organic bond identification regions are available for identification purposes. In general, each possible type of organic bonding mode is described in these tables, ranging from aromatic and aliphatic positions, specific concentration relations

² D.D. Ebbing & S.D. Gammon, General Chemistry, 7th Ed, Houghtoun Mifflin Company, Boston New York, 2002, 385-386

and the appearance of the peak that would be found on the spectra. These organic spectra occupy the range of 550-4000 cm⁻¹.¹

In organic synthesis characterisation, it is obvious that this method for characterisation is very valuable, though complex. For inorganic synthesis characterisation it is however most often applied for general identification of coordination of previously fingerprinted ligand systems with a metal atom. The exact metal bonding frequency is not always observed, but from the changes in the ligand fingerprint, the coordination reaction can be confirmed. Furthermore, the new molecular environment of coordinated ligand groups will also have an effect on the main fingerprint spectra, since intermolecular effects will affect the specific movement within the coordinated ligand. The withdrawal or donation of electron densities across bonds should theoretically shift the region in which these specific bonds are then observed.

3.3. Ultraviolet/Visible Spectroscopy (UV/Vis)

Molecular spectroscopy based on ultraviolet, visible and infrared radiation is widely used for identification and determination of many inorganic, organic and biochemical species.³ Molecular UV/Vis absorption spectroscopy is used primarily for quantitative analysis and is applied more extensively as internationally accepted method than any other. Since all complexes absorb light in some range of the broad spectrum of electromagnetic radiation, the application of a characterisation method that accurately measures the intensity of absorbance across the range or at specific frequencies has proven to be an invaluable tool in scientific experimentation.

³ D.A. Skoog, D.M. West, F.J. Holler & S.R. Crouch, Fundementals of Analytical Chemistry, 8th Ed., Brooks/Cole, Thomson Learning Inc., Belmont California, 2004, 784-793.

The technique of UV/Vis spectroscopy involves the radiation of a sample in a specific and definable form, followed by the recording of specific absorbance of this sample at either a pre-set frequency or range of frequencies. As with IR spectroscopy, this recording is also translated by a computer to a readable spectrum for further analysis. During the kinetic application of this method, advantage is taken of the fact that different complexes will absorb radiation at different frequencies with different intensities. For example, during the recording of a reaction of two compounds in solution, the absorption intensity of the solution would change at a specific frequency as the new product is formed in solution over time. This change in absorbance is recorded over time to give specific spectra, unique to this precise product's formation. The kinetic experiments are designed in such a way to optimise the results recorded from the reaction process. For a discussion of the application of UV/Vis data applied in kinetic mechanistic studies, see Paragraph 3.5.

3.4. Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance (NMR) is a physical phenomenon based upon the quantum mechanical magnetic properties of an atom's nucleus. The basic principles regarding to this principle was first described and measured in molecular beams by Isidor Rabi in 1938. By 1946, Felix Bloch and Edward Mills Purcell had refined the technique for use on liquids and solids, for which they shared the Nobel Prize in physics in 1952. Purcell had worked on the development and application of RADAR during World War II at the Massachusetts Institute of Technology's Radiation Laboratory. His work during that project on the production and detection of radiofrequency energy, and on the absorption of such energy by matter, preceded his discovery of NMR. They noticed that magnetic nuclei, like ¹H and ³¹P, could absorb RF energy when placed in a magnetic field of a strength specific to the identity of the nuclei. When this absorption occurs, the nucleus is described as being in resonance. Different atoms within a molecule resonate at different frequencies at a given field strength. The observation of the resonance frequencies of a molecule allows a user to discover structural information about the molecule.⁴

The basic theory of the actual characterisation technique starts on the IvI of the atom and its component itself. Protons and electrons in the atom shell move constantly, as such the electrons spin around an axis created by the positive centre made up of the protons and neutrons. This spin can be influenced if a larger magnetic field where to be applied on the atom, forcing the orientation of atomic spin in a specific direction. Now consider a multitude of these atoms all forced to spin in a specific direction by the external magnet, before the external magnetic field is removed. The energy radiated into this system of atoms is now released as they all return to spinning in their natural state. The principles of the spectroscopic method involved in NMR is based on the observation or recording of the release of this energy by forced atoms as they return to their natural spinning state. The theoretical guidelines involved in experimental use of this physical method become very complex.

The first considerations involve the chemical setup of the atom to be observed. The rules for determining the net spin of a nucleus are as follows:

- If the number of neutrons and the number of protons are both even, then the nucleus has NO spin.
- If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)
- If the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

⁴ I. Sillitoe (1998). History of NMR. Available: http://winter.group.shef.ac.uk/crystal/projectsug/sillitoe/html/history.htm. Last accessed 25 November 2008.

The overall spin, *I*, is important. Quantum mechanics tells us that a nucleus of spin *I* will have 2I + 1 possible orientations. A nucleus with spin 1/2 will have 2 possible orientations. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given a magnetic quantum number, *m*. Since the nucleus is positively charged and spinning, it generates its own magnetic field. This implies it has a magnetic moment (μ) which is proportional to its spin (*I*) as follows:

$$\mu = \frac{\gamma I h}{2\pi}$$
 Eq. 3.1

The constant, γ , is called the magnetogyric ratio and is a fundamental nuclear constant which has a different value for every nucleus.

At this point it might seem logical that all atoms of the same type would always experience the same energy from the applied magnetic field and thus all show up on a spectrum as a singular peak denoting that specific atom. This is however not the case due to the principle of nuclear shielding. This aspect of NMR is due to the fact that the electronic effects of some nuclei, generally nuclei with excess electron density, affects the effect of external magnetic field application on other nuclei by shielding them from the full effect of the external force. The inverse of this, is deshielding, which entails the removal of electron density from another nuclei by some electron poor nucleus, making the deshielded nuclei more heavily affected by the external field than it would have been if it had not been exposed. If the nucleus is more shielded, then it will be shifted upfield (lower chemical shift) and if it is

Nuclei in a molecule also have another effect on each other with regard to magnetic field experiments. This effect is often called spin-spin coupling or

⁵ Sheffield Hallam University (2006). NMR Spectroscopy - Theory. Available: http://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/nmr1.htm. Last accessed 25 November 2008.

simply coupling.⁶ This coupling arises from the interaction of different spin states through the chemical bonds of a molecule and results in the splitting of NMR signals. These splitting patterns can be complex or simple and likewise, can be straightforwardly interpretable or deceptive. This coupling provides detailed insight into the connectivity of atoms in a molecule. This effect is reported as *J*-coupling, in terms of numbers of Hz that measure the distance between the peaks on the NMR spectrum.

The structural data that can be obtained from a single NMR spectrum is astounding. The exact location of peaks, the pattern in which they are found together as well as the integrated area under the peaks themselves all fit together like a puzzle to give a unique perspective on the structural identification of the sample observed. Advanced techniques involve two dimensional NMR spectra that clearly show exact bonding locations for larger molecules when combined with multinuclear NMR spectroscopy. The most commonly used NMR observed nuclei are ¹H, ¹³C, ³¹P and ¹⁹F. This is due to the fact that the spectra are easy to obtain (¹H and ¹⁹F) or are unique identifiers for specific molecular compounds (¹³C and ³¹P).

⁶ William Reusch (2007). Nuclear Magnetic Resonance Spectroscopy. Available: http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/nmr/nmr1.htm. Last accessed 25 November 2008.

3.5. Theory of Kinetic Study Mathematical Modeling and Data Handling

The mathematical mechanistic interpretations of kinetic studies discussed in this paragraph are applied for IR, UV/Vis and NMR spectroscopic techniques across the board, though some basic starting assumptions may vary. The principals illustrated here are discussed in terms of the general approach for UV/Vis kinetic evaluations. The basic theory behind the kinetic study of a reaction by UV/Vis spectroscopy is described by the Beer-Lambert Law:⁷

 $A = \varepsilon cL$ Eq. 3.2 where *A* denotes the absorbance observed, *L* the path length through the sample, *c* the concentration of the observed species and ε the molar absorptivity or extinction coefficient. This constant is a fundamental molecular property in a given solvent, at a particular temperature and pressure. From this basic principle relating the absorbance of the product specie to its concentration, mathematical theory steps in to allow for the correlation of the recorded absorbance change with the increase in concentration of the product species. From this, the rate law for a reaction is described, defined and calculated.

For a simple equilibrium reaction:

$$xX + yY \xleftarrow{K,k_1}{k_{-1}} zZ$$
 Eq. 3.3

where *X*, *Y* & *Z* represent the species involved in the reaction; *x*, *y* & *z* represent the amount of each compound involved; *K* represents the equilibrium constant for the reaction; k_I and k_{-I} represents the reaction rate constant for the forward and reverse reactions, respectively. Reaction rate constants are unique for every reaction and the reaction conditions such as

⁷ Sheffield Hallam University (2006). Beer's Law. Available:

http://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/beers1.htm. Last accessed 25 November 2008.

temperature, pressure and solvent of solution kinetic experiments may influence this constant.

For this reaction, the rate law can be described as a derivative function of time including the concentrations of all species involved:⁸

$$rate = -\frac{1}{x} \frac{\delta[X]}{\delta t} = -\frac{1}{y} \frac{\delta[Y]}{\delta t} = \frac{1}{z} \frac{\delta[Z]}{\delta t}$$
 Eq. 3.4

This forward reaction rate law can also be defined as:

$$rate = k_1 [X]^{\alpha} [Y]^{\beta} [Z]^{\lambda}$$
 Eq. 3.5

where $\alpha \& \beta \& \gamma$ represent the reaction order in terms of *X*, *Y* & *Z*, respectively. This reaction order is related closely to the reaction mechanism and can be affected by the concentrations of the species involved in the reaction. Because the reaction order is difficult to determine experimentally, kinetic experiments are designed at the start to induce a simplified *pseudo* reaction order or *pseudo* first order mechanism. When considering the rate equation 3.2, it is possible to visualize the effect of changing the concentrations of these reactants to fit a *pseudo* mechanistic behaviour. If one reactant, e.g. *X*, is present in a concentration much larger than the other (*Y*), the change in concentration of *X* will not be that observable when compared to the change for *Y*, in the case of a stoichiometric reaction. Thus if [*X*] >> [*Y*], the rate can be written as:

$$rate = k_{obs}[Y]^{\beta}$$
 leading to $k_{obs} = k_1[X]^{\alpha}$ Eq. 3.6

From this we can derive the rate equation for the complete reaction:

$$rate = k_1[X][Y] + k_{-1}[Z]$$
 Eq. 3.7

and the pseudo first order conditions gives:

$$k_{obs} = k_1[X] + k_{-1}$$
 Eq. 3.8

By integration of the initial rate expression from the start of the reaction (t=0) to a random point of time (t), we obtain the equation:

⁸ M. Nic, J. Jirat & B. Kosata (2006). Compendium of Chemical Terminology - Rate of Reaction. Available: http://goldbook.iupac.org/R05156.html. Last accessed 25 November 2008.

$$\ln \frac{[Y]_{t}}{[Y]_{0}} = -k_{obs}t \quad \text{or} \quad [Y]_{t} = [Y]_{o}e^{-k_{obs}t}$$
 Eq. 3.9

From the basic principle that the absorbance of a species is directly proportional to its concentration and further mathematical manipulation of the derived equations above, we can completely simplify to:⁹

$$A_{abs} = A_{\infty} - (A_{\infty} - A_0)e^{-k_{abs}t}$$
 Eq. 3.10

where A_{obs} represents the experimentally observed absorbance at specific time *t*, A_{∞} is the absorbance maximum after the reaction has completed and A_0 represents the initial absorbance when the reaction was started.

Now mathematical kinetic theory can be reconciled with experimentally obtainable data. If a coordination experiment is designed in advance to uphold the *pseudo* first-order conditions (i.e. by having one component in great excess to the other) this mathematical model can be fitted to determine the rate constant for the forward and reverse reaction. If the reaction is repeated with varying concentrations of the excess component (for instance somewhere between 10 to 100 times the concentration of the other component) a graphical representation can be compiled where the observed rate constants are plot against the specific concentrations of the excess compound, at which the constant was obtained. In theory, a straight line should then be obtained with a slope representative of the forward reaction rate (k_{-1}).

From the plotted observed rate constants vs. excess component concentration, we can also postulate the reaction mechanism and reaction order. If the plotted graph does not give a straight line (within 95% experimental error), the shape of the curve can be indicative of another type

⁹ W. R. Salzman (2004). Pseudo First Order Reactions - Arrhenius Rate Theory. Available: http://www.chem.arizona.edu/~salzmanr/480a/480ants/pfo3oarr/pfo3oarr.html. Last accessed 25 November 2008.

of mechanism. Sloped curves may indicate larger order reactions and are generally verified by plotting the observed rate constants against higher powers of the excess compound concentration (e.g. $[X]^2$, $[X]^3$, etc).

From further kinetic theory we also know that the equilibrium constant (K) can be calculated from these results:

$$K = \frac{k_1}{k_{-1}}$$
 Eq. 3.11

By further application of experimentally obtained data, thermodynamic knowledge of the system under observation can also be gathered. By repeating the exact reaction experiment at different temperatures, different rate constants at the different temperatures should be obtained. This data is then furthermore plotted in accordance with the Eyring equation in linear form:¹⁰

$$\ln\frac{k}{T} = \frac{-\Delta H^{\neq}}{RT} + \ln\frac{k_B}{h} + \frac{\Delta S^{\neq}}{R}$$
 Eq. 3.12

A plot of $\left(\ln \frac{k}{T}\right)$ vs. $\left(\frac{1}{T}\right)$ would give a linear relation with a slope of $\left(\frac{-\Delta H^{\neq}}{R}\right)$

and intercept of $\left(\ln \frac{k_B}{h} + \frac{\Delta S^{\neq}}{R}\right)$. Here *k* is representative of the experimentally

determined rate constants at each temperature *T*. *R* is the Universal Gas Constant (8.314 J·K⁻¹·mol⁻¹), k_B is the Boltzmann Constant (1.381 J·K⁻¹) and *h* is Planck's Constant (6.626 J·s). Thus the only unknown variables from this equation remain the Enthalpy of Activation (ΔH^{\neq}) and the Entropy of Activation (ΔS^{\neq}), which is calculated from the experimental graph data.

¹⁰ P. Keusch (2003). Eyring Equation. Available: http://www.chemie.uniregensburg.de/Organische_Chemie/Didaktik/Keusch/eyr-e.htm. Last accessed 25 November 2008.

3.6. X-Ray Diffraction Spectroscopy (XRD)

X-ray Crystallography is an extremely precise technique utilised to characterise the exact molecular structures within a crystalline lattice. The method itself takes advantage of the fact that atoms in a molecule and in fact molecules themselves, tend to order themselves in specific arrangements when a substrate is forced into its solid crystalline state. This method is used to determine the arrangement of atoms within a crystal when a beam of X-rays irradiates a crystal sample and scatters into many different directions. From the angles and intensities of these scattered beams, it is possible to produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and sundry other information.¹¹

The reason why x-ray radiation is applied has to do with the size of the observed specie. For cellular observations, a normal microscope using visible light is sufficient. In order for an object to be seen, its size needs to be at least half the wavelength of the light being used to see it. Since visible light has a wavelength much longer than the distance between atoms it is not usable for structural analysis on molecular scale. In order to see molecules it is necessary to use a form of electromagnetic radiation with a wavelength on the order of bond lengths, such as x-rays. Unfortunately, unlike with visible light, there is no known way to focus x-rays with a lens. This means that building an x-ray microscope cannot be done. Thus this characterisation utilises the diffraction of x-rays from a crystalline lattice to create a diffraction pattern which can be interpreted mathematically by a computer. This turns the computer into a virtual lens allowing us to see the exact structure of molecules within the crystal.

¹¹ S.A. Nelson (2008). X-Ray Crystallography. Available:

http://www.tulane.edu/~sanelson/eens211/x-ray.htm. Last accessed 25 November 2008.

The ordered and symmetrical nature of crystals also makes them ideal for this identification technique, since this will show repeated patterns within the entire structure. The most basic identifying area of space within the crystal is commonly referred to as the unit cell. This unit cell is a representation of the entire crystal if it where to be duplicated in all directions. The x-ray diffraction from one unit cell would appear insignificant, but by symmetrical repetition of a singular unit cell amplifies the total and compound diffraction of the observed sample enough to give results that are useable as visual representations of said unit cell by interpretation *via* the computer attached to the diffractometer.¹²

X-ray crystallography is related to several other methods for determining atomic structures. Similar diffraction patterns can be produced by scattering electrons or neutrons, which are likewise interpreted as a Fourier transform. If single crystals of sufficient size cannot be obtained, various X-ray scattering methods can be applied to obtain less detailed information; such methods include fibre diffraction, powder diffraction and small-angle X-ray scattering (SAXS). In all these methods, the scattering is elastic; the scattered X-rays have the same wavelength as the incoming X-ray. By contrast, inelastic X-ray scattering methods are useful in studying excitations of the sample, rather than the distribution of its atoms.¹¹

3.6.1. X-Ray Diffraction Theory and Bragg's Law

A good understanding of the basic workings of x-ray diffraction is found by means of the Bragg model of diffraction. This principle was first derived by the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray

¹² St. Olaf College (2003). X-ray Crystallography. Available:

http://www.stolaf.edu/people/hansonr/mo/x-ray.html. Last accessed 25 November 2008.

beams at certain angles of incidence. ¹³ This model represents the reflection of a wave of radiation by the evenly spaced planes within the crystal structure. The specific orientation of a set of planes is represented by three units defined as h, k and l. The spacing between these planes is denoted by d. These units are called Miller indices which denote planes orthogonal to a direction in the basis of the reciprocal lattice vectors.¹⁴ The reciprocal lattice vectors represent the imaginary vectors generated from a set point in a lattice set to run at co-planar dimensions from each other to represent the 3 directions of 3 dimensional space. To define a point in space, one vector will have a finite length while the two others will have infinite length. Miller indices are thus representative of the position described by the inverse of the reciprocal vector.^{14, 15, 16} Bragg's law proposes that the incoming radiation is scattered and reflected by all planes with the same angle towards the reflected outgoing ray.



Figure 3.1 Diffraction of X-rays according to Bragg's Law

http://www.eserc.stonybrook.edu/ProjectJava/Bragg. Last accessed 25 November 2008. ¹⁴ P. Marchment & D. Brook (2008). Lattice Planes and Miller Indices. Available:

¹³ P.J. Schields (2007). Bragg's Law and Diffraction. Available:

http://www.doitpoms.ac.uk/tlplib/miller_indices/index.php. Last accessed 25 November 2008. ¹⁵ H. Föll (2008). Reciprocal Lattice. Available: http://www.tf.uni-

kiel.de/matwis/amat/semi_en/kap_2/basics/b2_1_2.html. Last accessed 25 November 2008. ¹⁶ V. Zamlynny (1997). Reciprocal Lattice. Available:

http://www.chembio.uoguelph.ca/educmat/chm729/recip/vlad.htm. Last accessed 25 November 2008.

From this it is assumed that x-rays scattered from adjacent planes will combine constructively (constructive interference) when the angle θ between the plane and the x-ray, results in a path-length difference that is an integer multiple n of the x-ray wavelength λ . Bragg's law refers to the equation:

$$n\lambda = 2d\sin\theta$$
 Eq. 3.13

A reflection is said to be indexed when its Miller indices (or its reciprocal lattice vector components) have been identified from the known wavelength and the scattering angle 2θ . This indexing then results the unit-cell parameters, the lengths and angles of the unit-cell, as well as its space group.

The only technicality not covered by this principle is accounting for the relative intensities of the reflections during scattering observations. Thus the actual arrangements of atoms or structure factor needs to be derived mathematically. For this a Fourier Transform method is applied to calculate the unknown data from inverse functionality.

3.6.2. Structure Factor

The possible reflections from a crystal are described by the reciprocal lattice points (*hkl*) whose reflection intensities depend on various factors of the content of the cell. The structure factor, F_j , is used to obtain a value which corresponds to the ability and intensity of X-rays to be diffracted from a specific plane. The position of the j^{th} atom within a unit cell expressed in terms of fractional coordinates is given by equation 3.14.

$$R_j = x_j a + y_j b + z_j c$$
 Eq. 3.14

with x_j , $y_j \& z_j$ as constants. A new set of basis vectors a^* , b^* and c^* can be used as a basis for a new lattice of which the vectors can be given by:

$$G_i = ha^* + kb^* + lc^*$$
 Eq. 3.15

Equation 3.15 is known as the *reciprocal lattice* and a^* , b^* and c^* the *reciprocal basis vectors*. The mathematical relationships between lattice and reciprocal basis are given as followed:

$$a^{*} a = 2\pi, \qquad a^{*} b = a^{*} c = 0,$$

 $b^{*} b = 2\pi, \qquad b^{*} a = b^{*} c = 0,$
 $c^{*} c = 2\pi, \qquad c^{*} a = c^{*} b = 0$ Eq. 3.16

If we consider an X-ray beam scattered from a one-dimensional monoatomic lattice, the overall scattering of all the atoms (*j*) in the unit cell relative to that of a single electron is expressed by the structure factor, F_{hkl} ,

$$F_{hkl} = \sum_{j=1}^{N} f_j \exp[i2\pi r.s]$$
 Eq. 3.17

By incorporating the reciprocal lattice equations into the overall scattering of all the atoms (j) in a three dimensional unit cell, the following equation is obtained.¹⁷

$$F_{hkl} = \sum_{j=1}^{N} f_j \exp[i2\pi(hx_j + ky_j + lz_j)]$$
 Eq. 3.18

And in the case of a cento symmetric unit cell, equation 3.18 can be rewritten as:

$$F_{hkl} = \sum_{j=1}^{N} f_j \cos[i2\pi(hx_j + ky_j + lz_j)]$$
 Eq. 3.19

¹⁷ M.F.C. Ladd & R.A. Palmer, *Structure Determination by X-ray Crystallography*, New York, Plenum Press, 1977.

From the above equation it is obvious that the structure factor is only dependent on the relative position of the atoms in the cell and their scattering factors. Each term in Equation 3.19 describes a wave with amplitude of f_j and phase of $2\pi(hx_j + ky_j + lz_j)$, meaning that the position of the atoms in a crystal determines the phase dependence between the diffracted rays from each atom contributing to the diffraction.¹⁸ The intensities of the diffracted X-rays are directly proportional to F^2 because the energies in cosine waves are proportional to the square of the amplitudes of the waves, and therefore:

$$I_0(hkl) \propto [F_0(hkl)]^2$$
 Eq. 3.20

with I_{θ} and F_{θ} as the experimentally observed quantities. This phenomena makes is possible to link and compare the intensities of reflected X-rays, I_{θ} , to the structure properties of a crystal by F_{θ} . Reflected X-rays is caused by electrons associated within the atoms in a crystal which makes it possible to determine a crystal structure.

Electron density can be expressed as a function of position, $\rho(X,Y,Z)$ since atoms with higher atomic numbers yields greater concentration of electrons than atoms with lower atomic numbers. Due to the relation between electron density and structure factor, Equation 3.21 is obtained:

$$F_{hkl} = \int \rho(x, y, z) \exp[i2\pi(hx_n + ky_n + lz_n)]dV$$
 Eq. 3.21

3.6.3. 'Phase Problem'

The determination of a crystal structure requires both the amplitude, f_j , and the phase of the structure factor as described in Eq. 16. Due to limitations on X-ray technology, it is only possible to emit monochromatic X-rays and

¹⁸ L.V. Azaroff, *Elements of X-ray Crystallography*, New York, McGraw-Hill, Inc., 1968.

not coherent X-rays. Consequently the X-rays emitted starts out with dispersed phases, making it impossible to acquire the phases of the reflected X-rays. Unfortunately these phases contribute more to the informational content of X-ray diffraction patterns than the corresponding amplitudes. This inability to determine the phase is commonly known as the "phase problem" or "lost phases" and can easily be overcome by utilizing a number of different methods. There are two main methods to recover the phases using the data obtained by standard equipment; e.g.

3.6.3.1. Direct Method

The direct method estimates the initial- and expanding phases from measured X-ray intensities by using mathematical formulae e.g. a triple relation. This method yields the best results for compounds where only light atoms are present.

3.6.3.2. Patterson Function

The Patterson Function is only applied for compounds containing heavier atoms or when a major part of the structure is already known. The Patterson Function or Patterson Map resembles a map of electron density with positive electron density peaks in various positions which is defined as:

$$P(u, v, w) = V^{-1} \sum_{h} \sum_{k} \sum_{l} (F_{hkl})^{2} \exp[-2\pi i (hu + kv + lw)]$$
 Eq. 3.22

with V representing the volume of the unit cell.¹⁹ The positions of these peaks are not the positions of the atoms in the structure but a function of vectors between pairs of atoms in the structure, implying

¹⁹ G.H. Stout & L.H. Jensen, *X-ray Structure Determination: A Practical Guide*, London, The Macmillan Company, 1968.

that the Patterson Function only produces information where the atoms lie relative to each other and not relative to the unit cell origin. The Patterson Function will provide the position of one or two of the heavier atoms in the unit cell and then the rest of the structure can be analyzed by other techniques.

3.6.4. Least Squares Refinement

The least square refinement is a method used to compare experimental data with calculated data to obtain a degree of similarity between them. For crystal structure refinement the similarities between the experimental (observed) structural factor, $|F_0|$, and calculated structural factor, $|F_c|$, is compared in term of the *residual index* or *R-factor*¹⁹ by equation 3.23:

$$R = \frac{\sum \|F_0\| - |F_c\|}{\sum |F_0|}$$
 Eq. 3.23

R-factor values below 1 indicate that a well defined crystal structure has been obtained from the data collected. An even better refinement can be obtained by incorporating a weighting factor for each reflection, *w*, which is a reliability factor of the different measured data. This gives rise to a new residual factor which is extensively used for determining crystal structures.

$$wR^{2} = \frac{\sum w(F_{0}^{2} - F_{c}^{2})^{2}}{\sum w(F_{0}^{2})^{2}}$$
 Eq. 3.24

3.6.5. Bravais Lattice

Crystallographic unit cells are always reported and characterised by the type of crystalline lattice it represents. In geometry and crystallography, a Bravais lattice is an infinite set of points generated by a set of discrete translation operations. A crystal is made up of one or more atoms (the basis) which are repeated at each lattice point. The crystal then looks the same when viewed from any of the lattice points. In all, there are 14 possible Bravais lattices that fill three-dimensional space. Related to Bravais lattices are crystallographic point groups of which there are 32 and Space groups of which there are 230.

The 14 Bravais lattices are arrived at by combining one of the seven crystal systems (or axial systems) with one of the lattice centerings. Each Bravais lattice refers to a distinct lattice type. Not all combinations of the crystal systems and lattice centerings are needed to describe the possible lattices. There are a total of 42 possible combinations of lattice types, but many of them can be shown to be equivalent. Thus the conventional number of Bravais lattices account to 14 basic types (see Table 3.1).²⁰

The lattice centerings are:

- Primitive centering (P): lattice points on the cell corners only
- Body centered (I): one additional lattice point at the centre of the cell
- Face centered (F): one additional lattice point at centre of each of the faces of the cell
- Centered on a single face (A, B or C centering): one additional lattice point at the centre of one of the cell faces.

²⁰ B.J. Van Zeghbroeck (1997). Bravais lattices. Available: http://ecewww.colorado.edu/~bart/book/bravais.htm. Last accessed 25 November 2008.

Crystal System	Conditions			
Crystal System	Side Lengths	Corner Angles		
Cubic	a = b = c	$\alpha = \beta = \gamma = 90^{\circ}$		
Tetragonal	a = b ≠ c	$\alpha = \beta = \gamma = 90^{\circ}$		
Orthorombic	a≠b≠c	$\alpha = \beta = \gamma = 90^{\circ}$		
Monoclinic	a≠b≠c	$\alpha = \beta = 90^{\circ} \neq \gamma$		
Triclinic	a≠b≠c	$\alpha \neq \beta \neq \gamma$		
Trigonal	a = b = c	$\alpha = \beta = \gamma < 120^\circ \neq 90^\circ$		
Hexagonal	a = b ≠ c	$\alpha = \beta = 90^{\circ}; \ \gamma = 120^{\circ}$		

Table 3.1: Summary of Identification Conditions for Crystal Lattice Types.

3.7. Conclusions

In conclusion, the advantages of the methods for characterisation to be used during this project have been presented in this chapter. Infrared absorption spectroscopy is a well defined and often used method for structural characterisation over a wide range of desired outcomes. The effective application in inorganic metal complex synthesis for this method is internationally accepted as accurate and complete in justifying structural characteristics. The main advantage of unique fingerprinting of select groups outweighs the disadvantages of complex spectral analysis and supposed less than complete accuracy. It is therefore a sufficient method for preliminary synthesised characterisation of newly zirconium bidentate ligand complexes.²¹

²¹ William Reusch (2007). Infrared Spectroscopy. Available:

http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/InfraRed/infrared.htm. Last accessed 25 November 2008.

Furthermore, a great number of reaction information can be gathered from kinetic experiment studies utilizing UV/Vis spectroscopy. Valuable information regarding reaction mechanism, specific changes in a reaction that occur over time and methods of reaction coordination, especially with regard to metal-ligand coordination reactions, thermodynamic information and the times required to complete different steps of a reaction are amongst the most important. The actual experimental process is simple enough to allow for good accuracy, and the processing of data can be done with great certainty based on sound mathematical modeling proven by many over the years. All of these factors combined prove this method a great tool for kinetic reaction study for this project.

NMR spectroscopy can be greatly applied to test for the extent for coordination for certain reactions. If, for instance, Trifluoroacetylacetone ligands were employed in a reaction, ¹⁹F NMR experiments can be used to quantitatively measure the coordination that has occurred. This is performed by measuring the peak intensity of the experimental product sample against a standard compound such as α -Trifluoro toluene. The result would give a peak integration of product *vs.* standard, where standard would be accepted as one (since it contains one CF₃ group). The ratio of the product peak *vs.* standard peak can tell us how many CF₃ groups are present on the product sample and thus how many tfacac ligands have been coordinated.

Finally, X-ray crystallography is an invaluable tool for determination of complex structure. Since organometallic complexes can be relatively easily characterized by this method, it will allow for correlation of new Zr-complexes with similar moieties from literature.

IR and NMR data will be reported in Chapter 4 as part of synthesis results. Chapter 5 will discuss crystallographic results for this project. Chapter 6 will discuss the results from kinetic experiments where UV/Vis will be applied.

Chapter 4

Synthesis and Attempted Spectroscopic Characterisation of Zirconium(IV) Bidentate Complexes

4.1. Introduction

In this chapter all methods applied for zirconium complex synthesis are discussed. As mentioned in Chapter 2, previous literature research did not yield much information regarding the control of ligand coordination during a reaction. As was also mentioned, very little definite proof of effective synthetic technique was found. Many references report synthetic methods without fully discussing the choice of method and the effectiveness of method for the intended aims of the respective projects.

Since this project is aimed at the investigation of the complete coordination chemistry and reaction mechanism for zirconium coordination by bidentate O,O- and O,N-donating ligands, it was imperative to identify synthesis techniques that would yield different types of complexes by selective adjustment of the variables that play a role in a chemical reaction. These factors are specific reaction conditions such as reaction solvent, reaction temperature, reaction time and ligand and metal compound

quantities. Since no literature method was found that specifically investigated and describes the dependence of zirconium complex formation on the specific reaction conditions, a range of methods were attempted and evaluated during this study. Each method reported and discussed in this chapter is essentially an improvement on the previous one attempted that was initiated to counter the disadvantages of previous methods.

A specific problem that was encountered from the start, was the insolubility of the zirconium(IV) chloride in most organic solvents. The main problem faced while working with this reagent, was its affinity for moisture, i.e. hydrolysis of the chloride ligands. Even though it showed moderate solubility in alcohols, the concern for solvent interaction/ coordination instead of favoured bidentate ligand coordination was ultimately the largest pitfall for the development of effective and easy synthetic techniques. Since alcohol solvents are known to often act as a source of hydroxyl groups in organometallic reactions, it was deemed unfavourable to use these types of solvents. The progress of solvent effects observed is discussed later in this chapter.

4.2. General Considerations

All reagents used for the synthesis and characterization were of analytical grade and were purchased from Sigma-Aldrich, South Africa, unless otherwise stated. Reagents were used as received, without further purification and stored in inert atmospheric storage vessels. All organic solvents were dried by passing through alumina and then further distilled over sodium before use, except for N,N'-dimethyl formamide (DMF) which was used as received.

All the infrared spectra of the complexes were recorded on a Bruker Tensor 27 Standard System spectrophotometer with a laser range of 4000 – 370 cm⁻¹, coupled to a computer. All samples were analyzed as solid state species *via* ATR infrared spectrophotometry and all data was recorded at room temperature. No solution or KX (where X = I, CI, Br) solid salt pellets were utilized since halogen interaction was expected from the solution cell and the KX pellet preparation technique.

All ¹H NMR spectra were obtained in C_6D_6 (deuterated Benzene), referenced to the C_6D_6 solvent peak – 7.16 ppm, on a Bruker 300 MHz nuclear magnetic resonance spectrometer, while ¹⁹F NMR spectra were obtained in C_7D_8 (deuterated toluene), referenced to α, α, α -Trifluorotoluene – 564.77 MHz, on a Bruker 600 MHz spectrometer.

It should be noted that yields are reported throughout as approximations, since the heat sensitivity of the crystals have hampered the processing of the final product to weighable samples.

4.3. Synthesis Program – Phase 1: Direct Bench top Synthesis

The first synthetic method applied was an attempt to identify the specific hazards and sensitivities of the compounds that would be utilized throughout this project. As indicated in Chapters 1 and 2, the most important/common oxidation state of zirconium is 4+, thus no special precautions are necessary to avoid oxidation or reduction reactions. However the moisture sensitivity/ease of hydrolysis of the Cl⁻ ligands needs to be taken into account. No specific precautions were made at this

stage to maintain anhydrous conditions. Glassware and other apparatus were cleaned and dried in an oven for 2 hours at 110 °C.

- The synthetic method basically involves the addition of the solid ZrCl₄ to the solvent at room temperature to create a slurry of the metal reagent.
- ii. The solvent used in this phase was toluene, applied as received from suppliers without further purification or drying.
- iii. To this metal-slurry, the ligand was added directly, in varying molar ratios for different reaction runs (see a-d below).
- iv. The reaction mixture was then heated to 80 °C and stirred overnight (*ca.* 16 h).
- v. The resultant product mixture was then dried under vacuum, washed with pentane and filtered.
- vi. The precipitate was dissolved in diethyl ether and recrystallised at -23 °C.

The results from this program are as follows:

4.3.a) ZrCl₄ & tfacacH – 1:1

 $ZrCl_4$ (0.2141 g, 0.919 mmol) reacted with tfacacH (0.12 ml, 0.992 mmol) in 10 ml toluene. Intense yellow colour observed upon addition of ligand to solution, fades to ivory colour at completion. (Yield: *ca.* 23%)

IR (ATR): $v_{CO} = 1537 \text{ cm}^{-1}$

¹**H NMR (Benzene-** d_6): δ = 1.64 (s, 1H), 5.83 (s, 3H).

4.3.b) ZrCl₄ & tfacacH – 1:2

 $ZrCl_4$ (0.1348 g, 0.578 mmol) reacted with tfacacH (0.14 ml, 1.158 mmol) in 10 ml toluene. Intense yellow colour observed upon addition of ligand to solution, fades to ivory colour at completion. (Yield: *ca.* 47%)

IR (ATR): $v_{CO} = 1537 \text{ cm}^{-1}$ ¹**H NMR (Benzene-***d*₆**):** $\delta = 1.64$ (s, 1H), 5.83 (s, 3H).

4.3.c) ZrCl₄ & tfacacH – 1:3

 $ZrCl_4$ (0.1034 g, 0.444 mmol) reacted with tfacacH (0.16 ml, 1.323 mmol) in 10 ml toluene. Intense yellow colour observed upon addition of ligand to solution, fades to ivory colour at completion. (Yield: *ca.* 71%)

IR (ATR): $v_{CO} = 1537 \text{ cm}^{-1}$

¹**H NMR (Benzene-** d_6): δ = 1.64 (s, 1H), 5.83 (s, 3H).

4.3.d) ZrCl₄ & tfacacH – 1:4

 $ZrCl_4$ (0.5112 g, 2.194 mmol) reacted with tfacacH (1.07 ml, 8.847 mmol) in 10 ml toluene. Intense yellow colour observed upon addition of ligand to solution, fades to ivory colour at completion. (Yield: *ca.* 89%)

IR (ATR): $v_{CO} = 1537 \text{ cm}^{-1}$

¹**H NMR (Benzene-** d_6): δ = 1.64 (s, 1H), 5.83 (s, 3H).

This program yielded valuable information about the use of $ZrCl_4$ as reagent. The significant moisture sensitivity leads to easy contamination of the starting material with water, hydrochloric acid and other impurities carried by atmospheric moisture. The reaction process also revealed that simple bench top reaction conditions are not sufficient for yielding pure and complete reaction products. Upon direct addition of the ligand to the $ZrCl_4$ -slurry, it was also observed that large volumes of HCl are produced by the reaction mixture itself. This is due to moisture contamination as well as the substitution reaction by-product from deprotonation of the ligand and the liberation of a Cl^- from the metal starting reagent.

The next phase was therefore designed to counter the effect of moisture on the reaction, since these impurities undoubtedly affected the yields for all products. It was concluded that effective synthesis of zirconium complexes of these ligands could only be performed under more strict anhydrous conditions, spanning the entire range of components involved.

4.4. Synthesis Program – Phase 2: Argon Atmosphere Sodium-Ligand Salt Synthesis

During the first synthesis program, a concern noted was the production of large volumes of HCI from the reaction mixture. For Zr-complex synthesis with $ZrCl_4$ as a metal source, the acid (HCl) produced is not a too significant problem and can easily be removed from the system with a few setup adjustments. These adjustments could be some form of halogen trap added to the reaction solution itself, a drying tube or gas bubbler trapping the mineral acid gas in a liquid. If however this same synthesis was performed with ZrF₄ as metal source, the resultant HF gas produced would lead to far greater problems. In a laboratory setup where glassware, workspace and chemicals are shared amongst several chemists, the dangers of free HF gas can be fatal. Thus it was proposed to counter the production of mineral acids from reaction solutions entirely. The ligand applied was converted to the corresponding sodium-salt by simply combining equimolar amounts of ligand and NaOH and drying the resultant solid *in-vacuo* before application in a Zr-coordination reaction. This specific synthesis phase was also used to study the effect of change in reaction variables (as mentioned in Paragraph 4.1) on the outcome of the reaction. Reaction temperature and metal-to-ligand ratios were varied to determine if different products could be obtained by varying one specific variable for these systems.
The general procedure for each of these synthesis reactions were as follows:

- i. To a slurry of ZrCl₄ in dried toluene, tfacacNa is added (different ratios listed below at the specific procedure results).
- The system is evacuated by modified a Schlenk technique whereby the reaction vessel is attached to a double line manifold, incorporating a vacuum line and an argon gas line. The system is repeatedly flushed by argon and then evacuated by vacuum. This process of evacuation is repeated three times.
- iii. The reaction vessel setup is then heated to the desired reaction temperature (exact temperatures listed below), under reflux conditions.
- iv. This setup is then left to stir for 16 hours under an argon atmosphere.
- v. After accepted completion of the reaction, the reaction vessel is purged once more, and removed from the setup.
- vi. The reaction solution is then filtered through celite and captured in a clean vessel for recrystallization at -23 °C.

The results from this program are as follows:

4.4.a) ZrCl₄ & tfacacNa – 1:2, 80 °C

 $ZrCl_4$ (0.2692 g, 1.155 mmol) reacted with tfacacNa (0.4102 g, 2.330 mmol) in 5 ml toluene. The slight yellow colour observed upon addition of ligand to solution, fades to off-white colouring at completion. (Yield: *ca.* 52%)

IR (ATR): $v_{\rm CO} = 1533 \text{ cm}^{-1}$

UV/Vis: *λ*_{max} = 324 nm

¹⁹**F NMR (Toluene-***d*₈): δ = -75.33 (s, 3H).

¹**H NMR (Benzene**- d_6): δ = 1.66 (s, 1H), 5.86 (s, 3H).

4.4.b) ZrCl₄ & tfacacNa – 1:3, 80 °C

ZrCl₄ (0.2033 g, 0.872 mmol) reacted with tfacacNa (0.4678 g, 2.657 mmol) in 5 ml toluene. The slight yellow colour observed upon addition of ligand to solution, fades to off-white colouring at completion. (Yield: *ca.* 67%) **IR (ATR):** $\nu_{CO} = 1533$ cm⁻¹

UV/Vis: *λ*_{max} = 324 nm

¹⁹**F NMR (Toluene-***d*₈**):** δ = -75.34 (s, 3H).

¹**H NMR (Benzene-** d_6 **):** δ = 1.66 (s, 1H), 5.86 (s, 3H).

4.4.c) ZrCl₄ & tfacacNa – 1:4, 80 °C

 $ZrCl_4$ (0.2188 g, 0.939 mmol) reacted with tfacacNa (0.6634 g, 3.768 mmol) in 5 ml toluene. The slight yellow colour observed upon addition of ligand to solution, fades to off-white colouring at completion. (Yield: *ca.* 86%)

IR (ATR): $v_{\rm CO} = 1533 \text{ cm}^{-1}$

UV/Vis: *λ*_{max} = 324 nm

¹⁹**F NMR (Toluene-***d*₈): δ = -75.34 (s, 3H).

¹**H NMR (Benzene-** d_6): δ = 1.66 (s, 1H), 5.86 (s, 3H).

4.4.d) ZrCl₄ & tfacacNa – 1:4, 60 °C

ZrCl₄ (0.2308 g, 0.990 mmol) reacted with tfacacNa (0.6934 g, 3.938 mmol) in 5 ml toluene. The slight yellow colour observed upon addition of ligand to solution, fades to off-white colouring at completion. (Yield: *ca.* 81%) **IR (ATR):** ν_{CO} = 1533 cm⁻¹ **UV/Vis:** λ_{max} = 324 nm

¹⁹**F NMR (Toluene-***d*₈**):** δ = -75.34 (s, 3H).

¹**H NMR (Benzene-** d_6 **):** δ = 1.66 (s, 1H), 5.86 (s, 3H).

4.4.e) ZrCl₄ & tfacacNa – 1:4, Room Temperature

 $ZrCl_4$ (0.2206 g, 0.947 mmol) reacted with tfacacNa (0.6640 g, 3.771 mmol) in 5 ml toluene. The slight yellow colour observed upon addition of ligand to solution, fades to off-white colouring at completion. (Yield: *ca.* 79%)

IR (ATR): $v_{\rm CO} = 1533 \, {\rm cm}^{-1}$

- **UV/Vis:** $\lambda_{max} = 324 \text{ nm}$
- ¹⁹**F NMR (Toluene-***d*₈): δ = -75.35 (s, 3H).
- ¹**H NMR (Benzene-** d_6): δ = 1.66 (s, 1H), 5.86 (s, 3H).

After completion of this synthesis phase, little information about the effectiveness of temperature and metal-to-ligand ratio variation on the extent of coordination to zirconium and corresponding yields could be obtained. Crystallographic results (see Chapter 5.3 for discussion of the crystallographic characterization of product 4.4.c) proved that a tetrakis coordinated Zr-tfacac complex was formed in all cases, but the difficulty in producing crystals suitable for XRD characterization hampers the confirmation of lower coordinated complex synthesis. The crystals which were obtained were very sensitive to atmospheric conditions and temperatures higher than -15 °C. The products from this phase could therefore not be submitted for other forms of characterization since the decomposition and loss of solvation from crystals would not give results accurate for actual synthesis results.

The main benefit of this method was the ease of reaction mixture handling after the reaction is stopped. Both the metal and ligand salt reagents are insoluble in the reaction solvent (toluene), but the product is soluble. Thus, when the reaction is halted, the reaction mixture is filtered and recrystallization is done from the original reaction solvent. This results in less contamination of the sensitive components involved.

4.5. Synthesis Program – Phase 3: Drop-Wise Ligand Addition Synthesis – Schlenk Conditions

As discussed in Paragraph 4.4, the pitfall of ligand coordination control was still hampering the production of lower coordinated species for applied ligands, up to this point. It was proposed that the fact that all of the ligand starting material is added at once at the start of the reaction, may be countering all attempts to control the extent of coordination. The reaction preparation setup was then adjusted to allow for slower addition of ligand starting material, in an attempt to allow all zirconium metal to react with smaller quantities of ligand over time, rather than forcing a smaller percentage of available metal starting material to full coordination and resulting in wasted unreacted ZrCl₄ in the work-up process of filtering. It was also suggested that the liberation of free Cl⁻ from the metal starting reagent will occur at a slower pace, thus allowing the HCl gas liberated to dissolve in the reaction solvent instead of being liberated as free gas in the atmosphere.

This modified technique thus involved the same modified Schlenk technique discussed in Paragraph 4.4, with the addition of a dropper funnel to the reaction vessel as part of the purged setup before the reaction is started:

- The ligand is dissolved in the reaction solvent and this ligand solution is then added drop-wise to the ZrCl₄-slurry over a period of 30 minutes. Exact quantities of all components listed below.
- ii. The reaction is then allowed to react under reflux for 4 hours at 80 °C.

- iii. The reaction solution is then filtered after completion through celite to remove unreacted components and washed with a small quantity of clean reaction solvent.
- iv. This filtrate is then recrystallized at -23 °C.

The results from this program are as follows (ratios of metal:ligand again indicated at respective headings):

4.5.a) ZrCl₄ & tfacacH – 1:2

ZrCl₄ (0.2149 g, 0.922 mmol) reacted with tfacacH (0.223 ml, 1.844 mmol) in 5 ml Toluene. The feint yellow colouration observed during addition of ligand to solution, forming a slight slurry, which fades to clear light yellow solution at completion. (Yield: *ca.* 48%) **IR (ATR):** $v_{CO} = 1534$ cm⁻¹

UV/Vis: $\lambda_{max} = 324 \text{ nm}$

¹**H NMR (Benzene-** d_6): δ = 1.67 (s, 1H), 5.85 (s, 3H).

4.5.b) ZrCl₄ & tfacacH – 1:3

 $ZrCl_4$ (0.2236 g, 0.959 mmol) reacted with tfacacH (0.347 ml, 2.869 mmol) in 5 ml Toluene. The feint yellow colouration observed during addition of ligand to solution, forming a slight slurry, which fades to clear light yellow solution at completion. (Yield: *ca.* 69%)

IR (ATR): $v_{\rm CO} = 1534 \text{ cm}^{-1}$

UV/Vis: *λ*_{max} = 324 nm

¹**H NMR (Benzene-***d*₆): δ = 1.67 (s, 1H), 5.85 (s, 3H).

4.5.c) ZrCl₄ & hfacacH – 1:1

ZrCl₄ (0.2088 g, 0.896 mmol) reacted with hfacacH (0.125 ml, 0.895 mmol) in 5 ml Toluene. The feint orange-yellow colouration observed during addition of ligand to solution, forming a slight slurry,

which fades to clear light yellow solution colouring at completion. (Yield: *ca.* 17%) **IR (ATR):** $v_{CO} = 1549 \text{ cm}^{-1}$ **UV/Vis:** $\lambda_{max} = 319 \text{ nm}$ ¹**H NMR (Benzene-***d*₆): $\delta = 1.67$ (s, 1H).

4.5.d) ZrCl₄ & hfacacH – 1:2

 $ZrCl_4$ (0.5090 g, 2.184 mmol) reacted with hfacacH (0.600 ml, 4.292 mmol) in 5 ml Toluene. The feint orange-yellow colouration observed during addition of ligand to solution, forming a slight slurry, which fades to clear light yellow solution colouring at completion. (Yield: *ca.* 37%)

IR (ATR): $v_{\rm CO} = 1549 \text{ cm}^{-1}$

UV/Vis: $\lambda_{max} = 319 \text{ nm}$

¹**H NMR (Benzene-***d*₆): δ = 1.67 (s, 1H).

It was observed during this approach that the final crystalline products are even more sensitive to handling than the products from the synthesis program discussed in Paragraph 4.4. Crystalline products showed decomposition by merely removing the recrystallization vessel from the crystal fridge. The crystals obtained here, especially those of the hfacacH synthesis attempts, where unsuitable for crystallographic characterization, since these crystals are lost due to loss-of-solvent when they are handled at room temperature. The low yields obtained from the hfacacH syntheses also indicate that the attempted slower ligand coordination control was not successful. The low yields again indicated tetrakis coordination of zirconium, though this could not be confirmed by IR or NMR spectroscopic characterization.

4.6. Synthesis Program – Phase 4: Bench Top Synthesis in N,N'-Dimethyl Formamide (DMF)

Up to this point, the insolubility of starting reagents in applied solvents has been a major concern. The ultimate goal, as far as this project goes, was after all to investigate solution behavioural kinetics of the synthesized products of zirconium and various O,O- and O,N- donating bidentate ligands. Coordination solution kinetic studies, requires complete homogenous solutions to investigate, and even though some solvents (such as alcohols, as mentioned in Paragraph 4.1) give moderate solubility, it was still not sufficient for kinetic study purposes. A wide range of solvents were continuously investigated for effective solubility without interaction in coordination reactions, and at different conditions (elevated temperature, increased volume, etc.), but no viable candidates were found at first. When the investigations on 8-hydroxyquinoline zirconium complex synthesis was started. it was discovered that N,N-dimethylformamide (DMF) allows for the complete dissolving of all This discovery not only allowed for less strict starting materials. anhydrous reaction conditions, but also greatly increases the possibilities for solution kinetic studies for these systems under investigation.

The new synthesis program that was set up to employ DMF as reaction solvent, allowed for bench-top synthesis once more. The advantage of this is that for an industrial process of separation of zirconium and hafnium by selective coordination with some specific bidentate ligand, a less strenuous/strict reaction environment is more desirable, since it would definitely be less expensive. The exact procedure applied was as follows:

i. ZrCl₄ and the ligand (specific details listed below) is separately dissolved in 5 ml of DMF and stirred until complete homogenization is reached.

- ii. These two solutions are heated to *ca.* 40°C.
- iii. The ligand solution is then added drop-wise to the metal solution over a 15 minute period, while stirring vigorously.
- iv. The reaction mixture is then left to stir at *ca.* 40°C for 30 minutes before removing from heated.
- v. Recrystallization takes place in a fume hood at atmospheric conditions for 3-5 days as the DMF slowly evaporates.

The results from this program are as follows (ratios of metal:ligand again indicated at respective headings):

4.6.a) ZrCl₄ & oxH – 1:2

ZrCl₄ (0.1003 g, 0.430 mmol) reacted with oxH (0.1413 g, 0.863 mmol) in 10 ml DMF. Bright yellow colour observed immediately after addition of ligand, colour intensity increases over time. Solution remains clear throughout. (Yield: *ca.* 61%)

IR (ATR): $v_{CO} = 1572 \text{ cm}^{-1}$

UV/Vis: $\lambda_{max} = 382 \text{ nm}$

¹**H NMR (Benzene-***d*₆**):** δ = 6.70 (d, 1H, *J* = 6 Hz), 7.29 (dd, 2H, *J* = 7.8 Hz, 6 Hz), 7.36 (t, 2H, *J* = 7.8 Hz), 8.13 (d, 1H, *J* = 7.2 Hz).

4.6.b) $ZrCl_4 \& oxH - 1:3$

ZrCl₄ (0.1016 g, 0.436 mmol) reacted with oxH (0.2149 g, 1.312 mmol) in 10 ml DMF. Bright yellow colour observed immediately after addition of ligand, colour intensity increases over time. Solution remains clear throughout. (Yield: *ca.* 76%)

IR (ATR): $v_{CO} = 1572 \text{ cm}^{-1}$

UV/Vis: *λ*_{max} = 382 nm

¹**H NMR (Benzene-***d*₆**):** δ = 6.70 (d, 1H, *J* = 6 Hz), 7.29 (dd, 2H, *J* = 7.8 Hz, 6 Hz), 7.36 (t, 2H, *J* = 7.8 Hz), 8.13 (d, 1H, *J* = 7.2 Hz).

4.6.c) ZrCl₄ & tfacacH – 1:2

ZrCl₄ (0.1091 g, 0.468 mmol) reacted with tfacacH (0.113 ml, 0.934 mmol) in 10 ml DMF. Yellow colouration observed during addition of ligand to solution, which fades to light yellow solution at completion. Solution remains clear throughout. No usable crystals obtained. (Yield: *ca.* 54%) **IR (ATR):** ν_{CO} = 1531 cm⁻¹

UV/Vis: *λ*_{max} = 325 nm

¹**H NMR (Benzene-***d*₆): δ = 1.66 (s, 1H), 5.86 (s, 3H).

4.6.d) ZrCl₄ & tfacacH – 1:3

 $ZrCl_4$ (0.2011 g, 0.863 mmol) reacted with tfacacH (0.313 ml, 2.588 mmol) in 10 ml DMF. Yellow colouration observed during addition of ligand to solution, which fades to light yellow solution at completion. Solution remains clear throughout. No usable crystals obtained. (Yield: *ca.* 68%)

IR (ATR): $v_{CO} = 1531 \text{ cm}^{-1}$

UV/Vis: *λ*_{max} = 325 nm

¹H NMR (Benzene- d_6): $\delta = 1.66$ (s, 1H), 5.86 (s, 3H).

Zirconium oxine complex crystals were successfully obtained from this program and these crystals were completely stable under atmospheric conditions. No decomposition was observed over time and no specific storage precautions (such as inert atmosphere, temperature control, etc.) needed to be taken. Crystallographic results (see Chapter 5.4 for discussion of the crystallographic characterization of product 4.6.a) proved that a $[Zr(ox)_4]$ complex was produced, even though it was intended to be a bis-coordinated complex. All though in all cases different ratios of metal:ligand were used, only the tetrakis complex was isolated in the

majority of cases, suggesting that the crystallization energy of the tetrakis complex is quite low in this typical symbiotic system.¹

By the time this specific program was started, it was already certain that reaction time and reaction temperature played no significant role in the coordination events for zirconium or hafnium. Reaction time and temperature was significantly decreased here and proved this point well. The tfacac products presumably require different recrystallization conditions, but IR and NMR spectroscopic results indicate that product formation did take place, since this data correlates with products from previous synthesis programs. It was also noted from this program that the intense colour change over time that forms part of the reaction of oxH with ZrCl₄ in reaction solution, would make an ideal candidate to study the kinetics of ligand coordination reactions by UV/Vis spectroscopy. This kinetic study is discussed in detail in Chapter 6.

4.7. Final Remarks

The synthetic program of this project has produced some valuable information. The aim was to synthesize new complexes, of which many have very little literature references to work from, and yielded good results. Two new crystallographic structural determinations could be produced, which ultimately gave valuable information as to the final mechanism and chemical behaviour of zirconium – bidentate ligand coordination reactions.

It was observed that the typical preference for crystallization composition tends toward the maximum extent of coordination for both zirconium and

¹ J,E, Huheey, E.A. Keiter & R.L. Keiter; *Inorganic Chemistry: Principles of Structure and Reactivity*, **4**th **Ed**, New York, 1993.

hafnium.² IR-, NMR- and UV/Vis spectroscopy also produced near identical results for all the hafnium and zirconium isomorphous complexes. This then illustrates that these methods are difficult to use under these circumstances to distinguish between products; especially if the coordination modes are so similar for both the hafnium and zirconium synthesis. Furthermore, this explained why so few examples of lower coordinated moieties are available in literature. From the synthetic methods that were applied, it became clear that to isolate any lower coordinated zirconium complex, intervention into the reaction process will have to be made shortly after it has started.

Several methods were attempted to determine which physical aspects of a reaction, control coordination. Unfortunately these attempts were unsuccessful. It rather seems that zirconium coordination reactions favour maximum coordination, suggesting that the crystallization energy of the tetrakis complex is quite low in this typical symbiotic system.¹ It is also possible (as discussed in Chapter 6) that throughout the reaction, all possible coordination species exist in the reaction system. But ultimately the species that is isolated as crystalline product will most likely be a tetrakis complex. It might however be possible to isolate other species *via* other crystallization techniques. A possible sublimation crystallization approach could produce crystals of lower coordinated complexes if samples of the reaction solution are withdrawn in an early stage of the reaction.

As mentioned in Paragraph 4.4 and 4.6, Chapter 5 discusses in detail the crystallographic structural determination of the products from Zr-tfacac (Paragraph 4.4.c) and Zr-ox (Paragraph 4.6.a) syntheses performed. Chapter 6 discusses the kinetic solution study for the reaction of $ZrCl_4$ and oxH.

² T. Viljoen, *M.Sc. Dissertation*, University of the Free State, **2009**.

Chapter 5

Crystallographic Characterisation of Zirconium Bidentate Complexes

5.1. Introduction

This chapter contains a detailed discussion of two crystal structures of zirconium bidentate ligand complexes prepared during the course of this project. The crystallographic structure determination of tetrakis(1,1,1-trifluoracetylacetonato- κ^2 -O,O')zirconium(IV) toluene solvate (Figure 5.1 a) and tetrakis(quinolinolato- κ^2 -N,O)zirconium(IV) N,N-dimethyl-formamide solvate (Figure 5.1 b) is presented in detail as well as the correlation of each structure with similar structures of zirconium and hafnium from literature.

Detailed information of the exact synthetic procedures that yielded these crystals can be found in Chapter 4.4.c and 4.6.a, respectively. The theory of X-ray crystallography has been discussed in detail in chapter 3.5. For reference (as discussed in chapter 2.4) the abbreviations tfacac and ox refer to the coordinated bidentate ligands trifluoroacetylacetonato and 8-hydroxyquinolinato.

5.2. Experimental

The X-ray intensity data was collected on a Bruker X8 ApexII 4K Kappa diffractometer, equipped CCD area detector with а araphite monochromator and MoK α fine-focus sealed tube ($\lambda = 0.71073$ Å, T = 100(2) K) operated at 2.0 kW (50 kV, 40 mA). The initial unit cell determinations and data collections were done by the SMART¹ software package. The collected frames were integrated using a narrow-frame integration algorithm and reduced with the Bruker SAINT-Plus and XPREP software packages² respectively. Analysis of the data showed no significant decay during the data collection. Data was corrected for absorption effects using the multi-scan technique SADABS,³ and the structure was solved by the direct methods package SIR97⁴ and refined using the WinGX⁵ software incorporating SHELXL.⁶ The final anisotropic full-matrix least-squares refinement was done on F^2 . The methine, methylene and aromatic protons were placed in geometrically idealized positions (C–H = 0.93 - 0.98 Å) and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. Non-hydrogen atoms were refined with anisotropic displacement parameters. The graphics were done using the DIAMOND' program with 50% probability ellipsoids for all non-hydrogen atoms.

¹ Bruker SMART-NT Version 5.050. *Bruker AXS Inc. Area-Detector Software Package;* Madison, WI, USA, **1998**.

 ² Bruker SAINT-Plus Version 6.02 (including XPREP), *Bruker AXS Inc. Area-Detector Integration Software*, Madison, WI, USA, **1999**.
 ³ Bruker SADABS Version 2004/1. *Bruker* 4XO Inc. Area Detector Integration

³ Bruker SADABS Version 2004/1. *Bruker AXS Inc. Area Detector Absorption Correction Software*, Madison, WI, USA, **1998**.

⁴ A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna; *J. Appl. Cryst.*, **1999**, 32, 115.

⁵ L.J. Farrugia; *J. Appl. Cryst.*, **1999**, 32, 837.

⁶ G.M. Sheldrick, SHELXL97. *Program for crystal structure refinement,* University of Göttingen, Germany, **1997**.

⁷ K. Brandenburg & H. Putz; *DIAMOND*, Release 3.0e, Crystal Impact GbR, Bonn, Germany, **2006**

Crystal Formula	$[Zr(tfacac)_4] \cdot (C_6H_7) \qquad [Zr(ox)_4] \cdot (HCON(CH_3)_2) \cdot (HCON(CH_3)_2)$		
Empirical formula	C ₃₄ H ₃₂ F ₁₂ O ₈ Zr	C ₃₉ H ₃₃ N ₅ O ₆ Zr	
Formula weight (g.mol ⁻¹)	887.82	758.92	
Crystal system, Space Group	Monoclinic, C2/c	Triclinic, $P\overline{1}$	
Unit cell dimensions:			
a, b, c (Å)	22.537(5), 8.054(5), 22.786(5)	11.342(5), 12.209(5), 12.538(5)	
α, β, γ (°)	90.000, 118.383(5), 90.000	91.728(5), 103.419(5), 99.250(5)	
Volume (ų), Z	3639(3), 4	1662.7(12), 2	
Density (calculated)	1.621 g.cm ⁻³	1.516 g.cm ⁻³	
Crystal morphology	cuboid	cuboid	
Crystal Colour	yellow	orange	
Crystal size	0.33 × 0.22 × 0.20 mm	0.36 x 0.24 x 0.18 mm	
Absorption coefficient μ	0.413 mm ⁻¹	0.389 mm ⁻¹	
F(000)	1792	780	
Theta range	2.73 to 28.27°	1.67 to 27.00°	
	-28<=h<=25	-14<=h<=14	
Index ranges	-10<=k<=7	-14<=k<=15	
	-28<=l<=29	-16<=l<=15	
Reflections collected,	14807 2075 0.0280	12820 6788 0.020	
Independent Reflections, R _{int}	14097, 3975, 0.0209	12030, 0700, 0.029	
Completeness to 2θ (°, %)	27.0, 100.0	27.0, 93.6	
Max. and min. transmission	0.8757 and 0.9219	0.8727 and 0.9333	
Data, restraints, parameters	3975, 0 , 249	6788, 5, 468	
Goodness-of-fit on F ²	1.054	1.092	
Einal P indicos [I>2sigma/I)]	$R_1 = 0.0285,$	$R_1 = 0.0380$	
Final R indices [I>2Sigma(I)]	$wR_2 = 0.0661$	$wR_2 = 0.1020$	
P indicos (all data)	$R_1 = 0.0338,$	$R_1 = 0.0468$	
n indices (all uala)	$wR_2 = 0.0697$	$wR_2 = 0.1171$	
Largest diff. peak and hole	0.496 and -0.448 e.Å ⁻³	0.935 and -0.440 e.Å ⁻³	

Table 5.1 Crystallographic and Refinement Details for structures discussed in this chapter

5.3. Crystal Structure of [Zr(tfacac)₄]·(C₇H₈)

5.3.1.Introduction

The published this fully coordinated structure of zirconiumtrifluoroacatylacetone complex⁸ is a unique example of such a structure crystallized with toluene solvent forming part of the main molecular unit cell. Very few examples of Zr-tfacac crystal structures are available from literature, the only other⁹ being a non-solvated structure. Synthesis of the compound and the resulting yellow crystals obtained from this was discussed in Chapter 4.4.c. A summary of the general crystal data is given in Table 5.1, while the numbering scheme of the solvated complex is shown in the perspective drawing in Figure 5.1. Table 5.2 presents selected bond lengths and angles of the title solvated complex. Atomic coordinates, anisotropic displacement parameters, all bond distances and angles and hydrogen coordinates, are given in the supplementary data (Appendix I). Hydrogen atoms and/or solvent molecules are omitted in some molecular presentations for clarity.

⁸ M. Steyn, A. Roodt & G. Steyl, Acta Crystallogr., 2008, E64, m827

⁹ N.V. Kurat'eva, I.A. Baidina, O.A. Stabnikov, I.K. Igumenov.; *J. Struct. Chem.*, **2007**, 48, 3, 513



Figure 5.1 DIAMOND representation of the $[Zr(C_5H_4F_3O_2)_4] \cdot (C_7H_8)$ compound, showing the numbering scheme and displacement ellipsoids (50% probability). Hydrogen atoms are omitted for clarity. Numbering scheme assigned by 1st digit denoting ligand group number and 2nd digit denoting atom position. Note symmetry generated molecular portion denoted by accent after numbering.

Selected Bond Lengths (Å)			
Zr—O ₀₁	2.1633(13)	Zr—O ₀₂	2.1973(15)
Zr—O ₁₁	2.1679(13)	Zr—O ₁₂	2.2079(15)
Selected Bond Angles (°)			
O ₀₁ '—Zr—O ₀₁	142.07(7)	O ₁₁ —Zr—O ₀₂	76.85(5)
O ₀₁ —Zr—O ₁₁	80.66(5)	O ₀₁ —Zr—O ₁₂	76.90(5)
O ₁₁ —Zr—O ₁₁ '	142.56(7)	O ₁₁ — Zr — O ₁₂	75.27(5)
O ₀₁ —Zr—O ₀₂	75.41(5)		
Symmetry codes: (') -x+1, y, -z+3/2.			
Selected Torsion Angles (°)			
O_{01} — C_{02} — C_{03} — O_{02}	4.88(3)	$O_{11} - C_{12} - C_{13} - O_{12}$	3.37(4)
O_{02} — C_{04} — C_{03} — O_{01}	-1.75(1)	O_{12} — C_{14} — C_{13} — O_{11}	-3.43(1)

Table 5.2: Selected Geometric Parameters for [Zr(C₅H₄F₃O₂)₄]•(C₇H₈)

5.3.2. Results and Discussion

The title compound is composed of an eight-coordinated zirconium metal centre in which the four O,O'-donating bidentate tfacac-ligands are arranged around the metal centre to give an approximate square antiprismatic coordination polyhedron of the O,O'-coordination ligand atoms, with a small distortion towards dodecahedral geometry.



Figure 5.2 Illustration of a Square Anti-Prismatic Coordination Polyhedron as found for the title compound. (a) Side view showing a very small distortion towards dodecahedral geometry; (b) Top view showing staggered spacing of O,O'-coordinating atoms.



Figure 5.3 Graphical representation of molecular packing within the unit cell for the title compound. Hydrogens omitted for clarity, 50% probability displacement ellipsoids.

The molecule has a two-fold rotation axis on the metal, with two bidentate ligands on either side, including a non-disordered toluene solvate molecule found in a 1:1 ratio to the zirconium complex. The bidentate ligands are coordinated in an alternating configuration with respect to the CF_3 groups. This ligand interchange can be visualized as four fins or propeller blades around the metal centre.

The ligand "fins" are found to bend at the intersection of the two planes formed by the ligand-backbone (O—C—C—O) and the O—Zr—O bite angle, with symmetry generated ligands bending towards each other at an angle of $19.84 - 20.23^{\circ}$ (see Figure 5.4).



Figure 5.4 Illustration of ligand "fin" bending as found in the title compound. The two planes intersect at the O,O'-coordination site.

Within the bidentate ligand structural representation, the Zr— O_1 (CF₃-side bond) and Zr— O_2 (CH₃-side bond) bond distances are unequal, varying by 0.034 – 0.040 Å. The bite angles of the bidentate ligands to the metal centre are 75.27(5) and 75.4(5)°, respectively.



Figure 5.5 Graphical illustration of π - π stacking within the unit cell for the title compound. (Only a portion of the unit cell shown, hydrogens omitted for clarity, 50% probability displacement ellipsoids)

 π - π Stacking is observed between the two toluene solvate molecules C_{100} — C_{106} and C_{100} — C_{106} ($-\frac{1}{2}$ +x, $\frac{1}{2}$ -y, $-\frac{1}{2}$ +z) with an interplanar distance of 3.548 Å and a centroid-to-centroid distance of 4.933 Å.



Figure 5.6 Graphical illustration of CH₃—CF₃ interaction within the unit cell for the title compound. (Only a portion of the unit cell shown, hydrogens omitted for clarity, 50% probability displacement ellipsoids)

Interactions between the CF₃ group on ligand 1 and the toluene CH₃ group is also observed: C_{01} — F_{03} to C_{106} – 3.078 Å, 127.63°. Weak C—H— π intermolecular interactions are observed between the toluene solvate and the tfacac-moiety: C_{105} — H_{105} to C_{12} (3.786 Å, 172.96°) and C_{106} — H_{10D} to C_{14} (3.702 Å, 67.74°), respectively.

Bond Distances (A): OZr			
Atom	Solvated	Non-Solvated	
O ₁₁	2.1633(1) 2.165(2		
O ₁₂	2.1973(2)	2.200(2)	
O ₀₁	2.1679(1)	2.179(2)	
O ₀₂	2.2079(2)	2.210(2)	
Plane Angles(°)			
Fins	Solvated	Non-Solvated	
Fins (L,L')₀₁	Solvated 19.84	Non-Solvated 21.39	
Fins (L,L') ₀₁ (L,L') ₀₂	Solvated 19.84 20.23	Non-Solvated 21.39 19.59	
Fins (L,L') ₀₁ (L,L') ₀₂	Solvated 19.84 20.23	Non-Solvated 21.39 19.59	
Fins (L,L') ₀₁ (L,L') ₀₂	Solvated 19.84 20.23 Bite Angles(°)	Non-Solvated 21.39 19.59	
Fins (L,L') ₀₁ (L,L') ₀₂ Fins	Solvated 19.84 20.23 Bite Angles(°) Solvated	Non-Solvated 21.39 19.59 Non-Solvated	
Fins (L,L') ₀₁ (L,L') ₀₂ Fins (L,L') ₀₁	Solvated 19.84 20.23 Bite Angles(°) Solvated 75.27(5)	Non-Solvated 21.39 19.59 Non-Solvated 75.27(8)	

Table 5.3: Geometrical data for Tetrakis(1,1,1-trifluoroacetylacetonato- κ^2 -O,O') zirconium^{IV}toluene solvate compared with the Non-Solvated moiety¹⁰

Compared to a recently published structure¹⁰ of the non-solvated complex, the deviation in characteristics between the solvated and non-solvated species are minimal (see Table 5.3). The Zr—O bond length on the CF₃-side of the acetylacetonato group, is shorter than the CH₃-side bond by an average of 0.035 Å. The angles at which the ligands bend out of the O—Zr—O plane show the most notable difference, with the steric interaction of the toluene molecule distorting the two fins formed on the zirconium complex. An exact molecular unit cell overlay cannot be

¹⁰ N.V. Kurat'eva, I.A. Baidina, O.A. Stabnikov, I.K. Igumenov.; *J. Struct. Chem.*, **2007**, 48, 3, 513

achieved however, since the non-solvated molecular unit packs much tighter than the solvated counterpart (Unit cell volume 2512 Å³ vs. 3638 Å³, respectively). This results in a different packing of the bidentate ligand "fins" around the metal centre along the *a* and *c* axes of the unit cells.

5.4. Crystal Structure of [Zr(ox)₄]·(HCON(CH₃)₂)·(H₂O)

5.4.1.Introduction

of The bench-top synthesis method complexes zirconium in N,N-Dimethylformamide discussed in Chapter 4.6.a yielded red crystals suitable for crystallographic characterization. This section will discuss the results of the characterization of the tetrakis(8-hydroxyquinolinato) zirconium^{IV} complex obtained. It should be mentioned again that the specific product crystal characterized, was obtained from synthesis intended to produce a bis(8-hydroxyquinolinato) zirconium^{IV} complex (or two ligand coordinated complex). The result as obtained yet again sheds light onto the absence of the lesser coordinated moieties of zirconium in literature. With each step in the investigation of zirconium syntheses, it becomes more justifiable to postulate that zirconium – bidentate ligand complexes naturally tend towards a maximum state of coordination. Though different ratios of metal ligand were used, the tetrakis complex was isolated in the majority of cases, suggesting that the crystallization energy of the tetrakis complex is quite low in this typical symbiotic system.¹¹

A summary of the general crystal data is given in Table 5.1 above. The numbering scheme for this DMF solvated complex in its unit cell is given in Figure 5.7 and Table 5.4 presents selected bond lengths and angles of the title solvated complex. Atomic coordinates, anisotropic displacement

¹¹ J,E, Huheey, E.A. Keiter & R.L. Keiter; *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th Ed, New York, **1993**.

parameters, all bond distances, angles and hydrogen coordinates are given in the supplementary data (Appendix II). Hydrogen atoms and/or solvent molecules are omitted in some molecular presentations for clarity.



Figure 5.7 Representation of the [Zr(ox)₄]·(HCON(CH₃)₂)·(H₂O) compound, showing the numbering scheme and displacement ellipsoids (50% probability). Hydrogen atoms are omitted for clarity.

Selected Bond Lengths (Å)			
Zr—O ₁	2.109(2)	Zr—N₁	2.431(2)
Zr—O ₂	2.103(2)	Zr—N ₂	2.423(2)
Zr—O₃	2.0850(19)	Zr—N ₃	2.415(2)
Zr—O ₄	2.1272(19)	Zr—N ₄	2.411(2)
Selected Bond Angles (°)			
O ₁ —Zr—N ₁	70.26(7)	O ₃ —Zr—N ₃	70.85(8)
O_2 — Zr — N_2	70.38(8)	O ₄ —Zr—N ₄	70.11(8)
Selected Torsion Angles (°)			
$N_1 - C_{09} - C_{08} - O_1$	-1.125(33)	$N_3 - C_{27} - C_{26} - O_3$	-1.0317(33)
$N_2 - C_{18} - C_{17} - O_2$	-1.231(33)	$N_4 - C_{36} - C_{36} - O_5$	-1.247(32)

Table 5.4 Selected Geometric Parameters for $[Zr(ox)_4] \cdot (HCON(CH_3)_2) \cdot (H_2O)$

5.4.2. Results and Discussion

The title compound is composed of an eight-coordinated zirconium metal centre, in which the four O,N-donating bidentate ox-ligands are arranged around the metal centre to give a square antiprismatic coordination polyhedron with a small distortion towards a dodecahedral geometry (see Figure 5.9). The ox-ligands are arranged in an approximately equally spaced placement in the 3 dimensional space around the metal centre, with alternating placement of the coordinating O and N atoms from the ligand, i.e. approaching an inversion centered coordination geometry.



Figure 5.8 Illustration of descriptive convention adopted throughout the discussion with regard to ligand groups and their nomenclature. Ligand groups identified by the number following the O or N coordinating ligand atom. C and H numbering systematically applied and have no direct reference to the ligand group it is part of.



Figure 5.9 Illustration of Square Anti-Prismatic Coordination Polyhedron as found for the title compound. (a) Side view showing a very small distortion towards dodecahedral geometry;

(b) Top view showing staggered spacing of O,N'-coordinating atoms.

Opposite facing ligand groups have their O and N coordinating groups placed on the same side of the metal centre. The bite angles of the bidentate ligands range from 70.11 to 70.84°, with Zr—O bond distance averaging 2.106 Å and Zr—N 2.420 Å. The opposite facing ox-ligand groups do not however form part of the same plane. These planes created by each ligand group respectively, lie at an angle to each other with an average of 42.52° with its opposite facing ligand group. Each plane of ox-ligand group also shows the O-coordination atom bent out of the main ligand plane in a range of $6.46 - 9.82^{\circ}$.



Figure 5.10 Illustration of out-of-plane bend of the O-coordination atom from the ox ligand, as found in the title compound.



Figure 5.11 Graphical representation of molecular packing within the unit cell for the title compound. Most hydrogens omitted for clarity, 50% probability displacement ellipsoids.

Each unit cell contains 2 molecular units consisting of a Zr-molecule, a DMF solvent molecule and a water molecule (See Figure 5.11). The metallic portion of the molecular units is placed at the center of the unit cell and the solvent molecules span the corners of the unit cell. A distortion of the methyl group *trans* to the carbonyl functionality on the DMF solvent molecule is observed. Within the unit cell, interactions between the metallic molecular groups are observed on the outermost carbons for the 3^{rd} and 4^{th} ligand groups on mirrored counterparts within the unit cell: C_{25} — H_{25} to C_{28} (sym. code: 1-x, 1-y, 1-z) – 2.214 Å, 123.82°.



Figure 5.12 Graphical illustration of carbon-hydrogen interactions within the unit cell for the title compound. Only a portion of the unit cell is presented, hydrogens on metallic molecules omitted for clarity, 50% probability displacement ellipsoids.

Further interactions are observed (see Figure 5.13) between the O from the solvent water molecule to the O on the DMF carbonyl from a neighboring unit cell – O_6 — H_{62} to O_5 (sym. code: 2-x, -y, 2-z) – 1.653 Å, 163.61°. This water molecule O also interacts with the O from group 4 ox-ligand within the same unit cell – O_6 — H_{63} to O_4 – 1.880 Å, 171.01°.



Figure 5.13 Graphical illustration of O—O interactions within the unit cell for the title compound. Only a portion of the unit cell is presented, hydrogens on metallic and DMF solvent molecules omitted for clarity, 50% probability displacement ellipsoids.



Figure 5.14 Graphical illustration of stacking between group 1 and 3 and their mirror image counterparts. Ligand group coloration as described in Figure 5.6.

 π - π Stacking is observed between ligand groups 1 and 3 with their mirror images from neighbouring unit cells (see Figure 5.14). Ligand group 1 stacks with an interplanar distance of 3.136 Å and centroid-to-centroid distance of 3.645 Å. Ligand group 3 shows stacking with an interplanar distance of 3.271 Å and centroid-to-centroid distance of 3.585 Å. These ligand groups span the outermost edge of the unit cell (as seen in Figure 5.11) and as such, every unit cell shows two of these sets of stacked ligand group partnerships. This π - π stacking is a complete overlaying of quinoline ligand group for each pair.

Further quinoline ligand group interaction is observed for the group 2 ligand portions and its mirror image on neighbouring unit cells. This interaction is however not a π - π stacking interaction, but simply an interaction between carbons from each quinoline group: C₁₁ to C₁₃ (sym. code: 2-x, 1-y, 1-z) and C₁₃ to C₁₁ (sym. code: 2-x, 1-y, 1-z) – 3.263 Å.



Figure 5.15 Illustration of hydrogen bonded molecular building blocks. Blue dotted lines represent hydrogen bonding, C_{37} — H_{37} to $O_6 = 3.316$ Å, 160.65°; O_6 — H_{62} to $O_5 = 2.755$ Å, 163.61°.

The most noteworthy aspect visible in the crystal packing, is the evidence of molecular building block groups structured around a backbone of the solvent molecules (see Figure 5.15). Hydrogen bonding is observed between solvent molecules of neighbouring unit cells. These units constructed from two molecular units, consisting of an organometallic portion and a solvation portion, form the building blocks for the entire structure.

As mentioned in Chapter 2, Lewis *et al.*¹² published the first $[Zr(ox)_4]$ structure in 1974. However, the only structural information given in this publication is the zirconium-to-coordinating ligand atom distances, which was compared to the identical distances for other metal complexes. As can be seen in Table 5.5, the distances they reported are near identical to the solvated structure discussed in this section. Though little information can be gathered from this comparison, it does seem to correlate with the tfacac-crystal packing behaviour as mentioned in the previous section, that showed solvent contributions to zirconium complex packing are negligible if not non-existent.

Zr-coordination bond lengths (Å)		
Bond	Solvated	Non-Solvated
Zr—O₁	2.106	2.106
Zr—N₁	2.42	2.405

Table 5.5 Geometrical data for $[Zr(ox)_4] \cdot (HCON(CH_3)_2) \cdot (H_2O)$ compared with the Non-Solvated moiety¹².

¹² D.F. Lewis & R.C. Fay; *J.C.S. Chem. Comm.*, **1974**, 1046

5.5. Comparisons with Hafnium counterparts

As discussed in previous chapters, the chemical similarities between zirconium and hafnium have lead to difficulties in separation and purification of both metals. In 2008 J.A. Viljoen published the structure of $[Hf(tfacac)_4] \cdot (C_6H_7)^{13}$, as part of his research on hafnium systems.



Figure 5.16 Representation of the $[Hf(C_5H_4F_3O_2)_4] \cdot (C_7H_8)$ compound, showing the numbering scheme and displacement ellipsoids (50% probability). Hydrogen atoms are omitted for clarity.

When this isomorphous structure is superimposed on the zirconium counterpart discussed in Section 0, the intense chemical similarity between these two metals is visually evident. An RMS overlay error of less than 1 Å (1.53x10⁻² Å, excluding F atoms) is observed, demonstrating the strong similarities between hafnium and zirconium's coordination geometry modes.

An overlay of $[Zr(ox)_4] \cdot (HCON(CH_3)_2) \cdot (H_2O)$ and its identical hafnium counterpart could not however be clearly defined. These two crystal structures show different crystal packing modes, even though the

¹³ J.A. Viljoen, A. Roodt & A.J. Muller, *Acta Cryst.*, **2008**, E64, m838.

geometries around the metal centers are the same. The zirconium complex (as discussed earlier) shows a ligand out-of-plane bend at the O-coordinating atom only, whereas the hafnium complex shows an out-of-plane bend of the entire aromatic duel-ring system (similar to the bend discussed with the [$Zr(tfacac)_4$] complex). This difference in crystal structure leaves a lot of room for speculation as to different reaction mechanistics for the ox-ligand coordination events. Specific kinetic studies (see Chapter 6) reveal much about such speculations.

5.6. Final Conclusions

Two new zirconium crystal structures have been successfully characterized, one of which has already been published⁸. Comparisons were drawn with similar structures from literature and the structures from this study were found to conform well to known theories of zirconium – bidentate ligand coordination crystallography.

Very few structures of this type (tfacac & ox) of bidentate ligand organometallic structures are known in literature though, leaving large scope for future studies on the same ligands and derivatives. The zirconium structures discussed in this chapter also conform to what is generally accepted as the blue-print of zirconium – acac type ligand coordination geometry, namely the square antiprismatic coordination mode as well as general structural characteristics such as bond lengths and bonding bite angles (see Table 5.6 for correlative information). Even though direct coordination geometries for zirconium and hafnium counterparts may be identical, the crystal packing of polymorphs may still show enough variance to imply differences in chemical reaction mechanism, leading to the final coordination state in the crystalline form.

	Zr—O Bond Length Range (Å)	O—Zr—O Bite Angle Range (°)	Ref.
[Zr(acac) ₄]	2.181 - 2.218	74.92 - 74.97	14
[Zr(acac)₄]	2.176 - 2.201	74.62 - 75.07	15
[Zr(hfacac)₄]	2.140 - 2.225	74.56 - 78.03	16
[Zr(hfacac)₄]	2.141 - 2.205	74.11 - 78.63	17
[Zr(phacac)₄]	2.139 - 2.205	74.25 - 74.85	18
[Zr(tBu acac)₄]	2.119 - 2.223	73.71 - 75.03	19
[Zr(tfacac)₄]	2.165 - 2.210	75.27 - 75.47	17
[Zr(tfacac) ₄]	2.163 - 2.208	75.27 - 75.41	This Work

 Table 5.6 Correlation of selected tetrakis coordinated zirconium complexes with O,O'-donating bidentate acac-type ligands, as found in literature.

From this study, it can be hypothesized that solvent molecule interaction in the reaction mechanism, may be negligible. The crystal structures discussed here (and their hafnium counterparts as discussed by Mr. J.A. Viljoen, M.Sc. Chemistry Thesis 2009) is seemingly not significantly influenced by the presence of solvent molecules (bulky or not) in their final crystalline form. The main organometallic portion of zirconium and hafnium crystal structures show near identical dimensions within the structure when compared to the non-solvated moieties of the structures.

The next chapter will cover a detailed discussion on the reaction mechanism for the $[Zr(ox)_4]$ crystal structure as well as a proposed mechanism for the entire step wise reaction, involving the coordination of four ligands at different stages of the entire reaction leading up to the final four-coordinated organometallic crystal structure.

¹⁴ J.V. Silverton & J.L. Hoard; *Inorg. Chem.*, **1963**, 2, 235

¹⁵ W. Clegg; Acta Cryst., **1987**, C43, 789

¹⁶ F. Calderazzo, U. Englert, C. Maichle-Mössmer, F. Marchetti, G. Pampaloni, D. Petroni, C. Pinzino, J. Strähle & G. Tripepi; *Inorg. Chim. Acta*, **1998**, 270, 177

¹⁷ K.V. Zherikova, N.B. Morozova, N.V. Kurat'eva, I.A. Baidina, P.A. Stabnikov & I.K. Igumenov; *Zh.Strukt.Khim .(Russ.) (J.Struct.Chem.)*, **2007**, 48, 555

¹⁸ H.K. Chun, W.L. Steffen & R.C. Fay; *Inorg.Chem.*, **1979**, 18, 2458

¹⁹ G.I. Spijksma, H.J.M. Bouwmeester, D.H.A. Blank, A. Fischer, M. Henry & V.G. Kessler; *Inorg.Chem.*, **2006**, 45, 4938

Chapter 6

Preliminary Kinetic Study of the Formation of 8-Hydroxy Quinolinato Complexes of Zirconium(IV)

6.1. Introduction

The synthesis programme of zirconium(IV) – 8-hydroxyquinolinato (oxH), showed that the ox-ligand exhibits good solution properties to be further exploited by a kinetic investigation. Solubility was no longer an issue with N,N-dimethyl formamide as reaction solvent. During the synthesis experiments described in Chapter 4, an intense colour change over time was observed upon the reaction of oxH with $ZrCl_4$, which would make it an ideal candidate for the monitoring of the ligand coordination reactions via UV/Vis spectroscopy.

Since one of the main aims of this project has been to identify and clarify the ligand coordination mechanism for zirconium and bidentate ligands, this setup grants a unique opportunity to investigate the factors responsible for the difficulties encountered during attempts at crystallization of lower coordinated zirconium complexes than the tetrakis examples, of which there are such an abundance of (see Chapter 2). As discussed in Chapter 5, it was hypothesised that crystalline zirconium complexes seem to generally tend towards a maximum extent of coordination, as this seems to be the state of lowest crystallization energy requirement. By investigation a reaction of bidentate ligand coordination *in solution*, rather than merely characterising the solid state product, one might obtain valuable information of the exact zirconium reaction steps of ligand coordination. This can only be possible if the exact mechanism of coordination and characterization of different species associated for both metals are known. A principal interest for defining the exact mechanism lies in the possibility to isolate the mono- and bis-coordinated species.

This chapter includes the results and discussion of the mechanistic coordination investigation of zirconium(IV) experiments with 8-hydroxyquinoline as entering ligand. The process of mathematical prediction of reaction rate conditions is discussed along with the observations from the kinetic experiments. It is important to note that this kinetic study was started with very little background information to work from. All initial assumptions with regard to reaction rate and rate orders where merely suggested as a basis to start data processing from. The results portion of this chapter will be interlaced with a clarification of how the mechanistic principles applied in the mathematical treatment of data, was constantly adjusted as new properties for this system were identified.

6.2. General Considerations and Procedures

All reagents and chemicals were of analytical grade. ZrCl₄, OxH and tetraphenylphosphonium chloride were used as received from Sigma Aldrich and the solvent (DMF) was dried by passing through alumina. Kinetic measurements were performed on a Varian Cary 50 Conc UV/Vis-(slower reactions) or Applied Photophysics Stopped-flow (fast reactions)

spectrophotometers. Temperature control of the reaction solutions was maintained to within \pm 0.1 °C by means of a circulating water bath system. The kinetics involve time resolved scanning a sample over a range of preset wavelengths to determine absorption changes of the sample in this range. The sample in this case would be a mixture of a metal complex solution and a ligand solution with known concentrations. All the kinetic runs were performed with the ligand in excess of at least ten-fold to ensure *pseudo* first-order reaction conditions in each case, with the ligand concentration varied by ca. one order of magnitude. The software program Scientist¹ from Micromath was used to fit, *by mathematical calculations*, the data to selected kinetic equations for a single, two- and three consecutive step reactions as discussed below in Par. 6.4.

6.3. Kinetic Experimental Procedures

Initial investigations require that stability tests of the reagent solutions be performed. This involves scanning these solutions for a longer period of time than the reaction would occur, to establish that the reagents themselves do not undergo any changes (such as decomposition and coordination) while in solution, since these side reactions could significantly complicate the modeling of the kinetics. If these reagents do undergo changes in solution, kinetic data are void since the changes observed and applied in further calculations are not strictly from the product formation one intends to study. No significant decomposition or interaction between the solvent and starting reagents was observed (see Figure 6.1), and a more detailed kinetic study, employing these reagents, could be undertaken.

¹ MicroMath Scientist for Windows, Version 2.01, Copyright © 1986 – 1995, MicroMath, Inc.



Figure 6.1 Stability test UV/Vis spectral scans of an overnight study of: (a) $ZrCl_4$ (2.6mg, 1.12 x10⁻⁴M) – DMF; (b) oxH (2.6mg, 1.12 x10⁻²M) – DMF

Reaction solutions were prepared to comply with *pseudo* first-order conditions. The metal solution was prepared throughout to maintain a final concentration of 5.578×10^{-5} M (ZrCl₄: 26 mg, 0.112 mmol, dissolved in 100 ml DMF) whereas the ligand solution was prepared as stock solution of 5.610×10^{-3} M final concentration and dilution was carried out across a series of 7 solutions with minimum final concentration solution of 5.610×10^{-4} M (oxH Stock Solution: 163.8 mg, 1.128 mmol, dissolved in 100 ml DMF). Fresh solutions were prepared for separate days of kinetic experiments. Even though stability of solutions were confirmed for *ca.* 24 hour periods, it was considered unwise to apply solutions older than that time.

A full discussion of the basic kinetic principles applied during this study, can be found in Chapter 3.5.
6.4. Results and Discussion

6.4.1. Introduction

Since the initiation of this project, a principle obstacle to evaluate chemical differences in coordinated complexes of zirconium and hafnium, has been the absence of general coordination chemistry data, and specific kinetic data, in literature (see discussion in Chapter 2) for both these metals. A properly-defined stepwise coordination mechanism for the process of bidentate ligand(s) reacting with zirconium(IV) halides could not be found. This provided scope for a complete solution mechanistic investigation.

The main aim for this kinetic investigation was, as indicated previously, to identify the different steps involved during the chloride substitution from $ZrCl_4$ by oxH, to evaluate the exact rates, times, equilibria and factors influencing the reaction.

In Figure 6.2, different steps of the total coordination are thus postulated, but are as yet unconfirmed. It must be noted that the individual steps shown might well be more complicated than the simple equilibria indicated, since each reaction step involves initial coordination and the substitution of the halide via ring closure. The deprotonation of the hydroxyl moiety, normally expected to be fast and potentially also influencing the process, is not considered at all during the interpretations below, and will form the basis of future investigations.

The synthesis of $[Zr(ox)_4]$ as final product in the overall process, was already discussed in detail in Chapter 4.6 and the crystallographic characterization given in Chapter 5.4.



Figure 6.2 Proposed stepwise ligand substitution process for the formation of [Zr(ox)₄].

6.4.2. Preliminary Analysis of Rate Data obtained by Slow UV/Vis Spectroscopy

Figure 6.3 shows the typical results obtained from a kinetic run evaluated by UV/Vis spectroscopy in the minute to hour range, illustrating the change in absorbance over time.



Figure 6.3 Graphical representation of data obtained from UV/Vis Spectroscopic Kinetics for the formation of $[Zr(ox)_n]$: **(a)** Wavelength scans over time [3h]; **(b)** Absorbance vs. time trace at 380 nm. $[ZrCI_4] = 5.578 \times 10^{-5}$ M, [oxH] range = 5.61 x 10⁻⁴ to 5.61 x 10⁻³M, Solvent: DMF, Temp: 25°C

This kinetic data obtained for a ligand solution concentration range of 10 to 100 times that of the metal solution concentration, is then fitted to a mathematical model according to the theoretically postulated reaction mechanism.

The data was firstly evaluated in terms of a simple first-order exponential, as illustrated in Figure 6.4 A, based on a simple *pseudo* first-order reversible one step reaction:

$$Zr + (LL') \xrightarrow{K_1, k_1} [Zr(LL')]$$
 Eq.6.1

For this process the simplified rate equation is:

$$k_{\rm obs} = k_1 [LL'] + k_{-1}$$
 Eq.6.2

The absorbance *vs.* time data, illustrated in Figure 6.4A, was fitted to Eq. 6.3, which represents a first-order observed absorbance change from the kinetic experiments according to the following equation:

$$A_{\rm obs} = A_{\infty} - (A_{\infty} - A_0) e^{-kobs.t}$$
 Eq. 6.3

For Eq. 6.3 the variables are defined as:

 A_{obs} – Observed absorbance as found in kinetic data.

 A_0 – Initial absorbance at the start of the experiment.

 A_{∞} – Infinite final product absorbance as found in kinetic data.

t - time (s).

 k_{obs} – observed rate constant for a single step first-order process

When the experimental data, observed for the reaction between $ZrCl_4$ and 8-Hydroxyquinoline, is plotted against the above model, it is clear that the data does not give a good fit to the simple first-order relationship, represented by Eq. 6.3 (see Figure 6.4 A).

It was therefore concluded that there is clearly more than one reaction defined by the absorbance vs. time data obtained.

It is further clear that the model in Eq. 6.1 is an over simplification for the total process, and that some of the subsequent reactions in the stepwise ligand coordination (see Figure 6.2) are contributing to the total absorbance change observed. It is to be expected, since the total process involves the liberation of four chloride ligands from the metal centre as well as the coordination of four bidentate ligands and the ring closure of these ligands.

Thus, below, two sets of experiments, monitored by <u>slow</u> UV/vis spectroscopy and evaluated by selected multi-exponentials, are reported,

which include the effect of ligand variation, both in the (i) absence and (ii) presence of free chloride ions.

6.4.2.1. Experiments <u>without additional chloride</u> added to the reactant solution.

In general, the liberation of the chloride ligands from the Zr-metal centre and the ring closure reaction steps might not be observable, but this still leaves at least four reactions to be accounted for, namely the coordination of the four bidentate ligands.

From the spectral changes observed (Figure 6.3), the initial portion of the reaction is lost on the slow UV/Vis Spectrophotometer since the first 20 seconds of the reaction is spent on manually mixing the samples. This is simply a mechanical technicality in the process that cannot be avoided.

It was therefore proposed to investigate these exact reactions on a Stopped-Flow Spectrophotometer, which allows for the observation of reactions with rates in the order of milliseconds. It was postulated that the first ligand coordination step occurs in this initial phase where rapid Stopped-Flow techniques are required to observe it (see Par 6.4.3 for detailed discussion on this aspect).

The data obtained from the slower experiments in the minute to hour time scale as studied on the slower UV/Vis experiments were thus further evaluated.

The data was fitted to mathematical models (Eqs. 6.4 and 6.5 respectively; using two and three exponentials) that represent two-step *pseudo* first-

order (see Figure 6.4 B) and three-step *pseudo* first-order reactions (see Figure 6.4 C), respectively.

$$A_{\rm obs} = (A_0 - B_0) e^{(-kAB.t)} + (B_0 - B_1) e^{(-kBC.t)} + B_{\rm I}$$
 Eq. 6.4

$$A_{\rm obs} = (A_0 - B_0)e^{(-kAB.t)} + (B_0 - C_0)e^{(-kBC.t)} + (C_0 - C_{\rm I})e^{(-kCD.t)} + C_{\rm I}$$
 Eq. 6.5

For Eqs. 6.4 and 6.5 the following applies:

 A_{obs} – Observed absorbance as found in kinetic data.

 A_0 – Initial absorbance at the start of the experiment.

 B_0 – Theoretical/calculated initial absorbance of the 2nd product.

 B_I – Infinite 2nd/final product absorbance as found in kinetic data.

 C_0 – Theoretical/calculated initial absorbance of the 3rd product.

 C_I – Infinite 3rd/final product absorbance as found in kinetic data. *t* – time (s).

 k_{xy} – observed rate constant for the specific step; k_{AB} represents k_{obs} for the 1st slow reaction; k_{BC} for the second, k_{CD} for the third.

It is clear from Fig. 6.4 that the kinetic data fit these models much better. More specifically, since Eq. 6.5 describes the total absobance vs. time data for the slow process the best, and the data for the variation of [ox] were therefore analysed using this expression, yielding rate constants for the <u>three</u> consecutive steps and allowing the evaluation of these steps on [ox].

The data obtained is summarized in Table 6.1.



Figure 6.4 UV/Vis data fitted to a (A) single step, Eq. 6.2; (B) two step; (C) a three-step reaction. (● ● ● observed UV/Vis data; solid line calculated using Eqs. 6.3, 6.4 and 6.5 for (A), (B) and (C), respectively);
[ZrCl₄] = 5.578 x10⁻⁵M, [oxH] = 5.61 x 10⁻⁴M, Solvent: DMF, Temp: 25°C.

Table 6.1 Comparison of observed rate constants for three consecutive steps ^{a)} of slow UV/VIS kinetics for two experiments where Tetraphenylphosphonium Chloride (0.112 mmol) was added to the metal solution in one case; $[ZrCl_4] = 5.578 \times 10^{-5}$ M, Solvent: DMF, Temp: 25°C. A = 1st slow reaction, B= second slow reaction; C= third slow reaction. k_{xy} – observed rate constant for the specific step; k_{AB} represents k_{obs} for the 1st slow reaction; k_{BC} for the second, k_{CD} for the third.

Ligand	Observed rate constants (k_{XY}) for three consecutive steps (s ⁻¹)							
	1 st step): $k_{ m AB \ obs}$	2^{nd} step: $k_{BC obs}$		3^{rd} step: $k_{CD obs}$			
[ox] (M)	No Cl ⁻	Cl ⁻ added	No Cl ⁻	Cl ⁻ added	No Cl ⁻	Cl ⁻ added		
0	2.50 x 10 ⁻³	2.50 x 10 ⁻³	0	0	0	0		
5.61 x 10 ⁻⁴	4.44 x 10 ⁻³		8.26 x 10 ⁻⁴		5.16 x 10 ⁻⁵			
1.12 x 10 ⁻³	5.06 x 10 ⁻³		1.66 x 10 ⁻³		2.04 x 10 ⁻⁴			
2.25 x 10 ⁻³	6.43 x 10 ⁻³		1.90 x 10 ⁻³		1.80 x 10 ⁻⁴			
2.81 x 10 ⁻³	8.05 x 10 ⁻³	6.91 x 10 ⁻³	1.80 x 10 ⁻³	2.99 x 10 ⁻⁴	2.05 x 10 ⁻⁴	4.00 x 10 ⁻⁵		
3.37 x 10 ⁻³	8.61 x 10 ⁻³	9.85 x 10 ⁻³	1.71 x 10 ⁻³	2.50 x 10 ⁻⁴	2.52 x 10 ⁻⁴	4.94 x 10 ⁻⁵		
3.93 x 10 ⁻³	9.38 x 10 ⁻³	9.29 x 10 ⁻³	1.73 x 10 ⁻³	3.22 x 10 ⁻⁴	2.50 x 10 ⁻⁴	5.30 x 10 ⁻⁵		
4.49 x 10 ⁻³	9.88 x 10 ⁻³	1.05 x 10 ⁻²	1.88 x 10 ⁻³	3.61 x 10 ⁻⁴	2.54 x 10 ⁻⁴	5.62 x 10 ⁻⁵		
5.61 x 10 ⁻³	1.01 x 10 ⁻²	1.07 x 10 ⁻²	1.85 x 10 ⁻³	4.25 x 10 ⁻⁴	2.38 x 10 ⁻⁴	6.03 x 10 ⁻⁵		

(^{a)} NOTE: It is clear that the Abs vs Time data fitted to Eq. 6.5 requires seven parameters to be determined, therefore large estimated standard deviations for the individual parameters were obtained. These are not listed, but may have relative values of ca. 20%.)

The data for the three consecutive steps were further all graphically evaluated as a function of ligand concentration, and the influence is illustrated in Figure 6.5A to C, respectively. It is clear from Figure 6.5 that in the case of no added chloride ions, all three steps observed by the slow UV/vis data collection technique, limiting kinetics is obtained.

The simple rate equation for a rapid pre-equilibrium, followed by a slower second reaction, see Eq. 6.6, is therefore assumed to hold for all three these steps.

$$K_{XY obs} = (k_{XY}K_{XY}[ox])/(1 + K_{XY}[ox]) + k_r$$
 Eq.6.6





In Eq. 6.6,

 $k_{XY obs}$ = observed rate constant for step X to Y (AB, BC and CD respectively;

 K_{XY} = Pre-equilibrium constant for step X to Y (AB, BC and CD respectively;

 k_{XY} = observed second order limiting rate constant (n=1,2 or 3 for steps AB, BC and CD respectively);

 $k_{\rm r}$ = reverse/ parallel reaction indicated by intercept.

The first-order rate constants (indicated by k_{AB} , k_{BC} and k_{CD}) and equilibrium constants, obtained for the three consecutive reactions upon fitting the data given in Table 6.1 to Eq. 6.6 [illustrated in Figure 6.5 (lines fitted Data; <u>points</u>: experimental data)] are summarized in Table 6.2.

It is important to note that no evidence other than the kinetics as obtained from this study, is available to conclude this, and that significant future work is required to confirm this further.

6.4.2.2. Experiments <u>with additional chloride</u> added to the reactant solution.

The rate laws above do not take into account that the chloride ligands being substituted as indicated by Figure 6.5, might contribute to the observed kinetics. To preliminary evaluate the possible effect of free chloride ions on the rate, a set of kinetic runs, similar to those above in Par. 6.4.2.1, were done, but with a ten fold excess of chloride added. The effect of added chloride ions is graphically illustrated in Figure 6.6 below.



Figure 6.6 Plot of Aobs vs time fitted to Eq. 6.5; line represents the fit; points the experimental data: A= approximately 1 h; B= after 3 h. $[ZrCl_4] = 5.578 \times 10^{-5}$ M, $[Cl-Salt] = 5.60 \times 10^{-4}$ M, $[oxH] = 4.49 \times 10^{-3}$ M, Solvent: DMF, Temp: 25°C

The observed rate constants for the three consecutive reactions (indicated by $k_{AB obs}$, $k_{BC obs}$ and $k_{CD obs}$) as described above, in the presence of added chloride ions, were again obtained from fitting the data for the range of [ox]

to Eqs. 6.5 and 6.8 (summarized in Table 6.1; illustrated in Figure 6.5) and are reported in Table 6.2.

It is clear (visually, by comparing the difference in data; Figure 6.5) that:

(i) A significant <u>decrease</u> is observed for the 2nd and 3rd reactions (k_{BC} and k_{CD});

(ii) The 1st slow reaction is not really influenced.

(iii) These observed rate constants for the three consecutive steps in all three cases clearly still showed limiting kinetics (as was the case in the absence of added chloride ions), as again quantitatively evaluated by fitting the data to Eq. 6.6.

The rate constants thus obtained are listed in Table 6.2.

	Constant	No Cl ⁻ added	Cl ⁻ added
	k _{AB} (s⁻¹)	0.017±0.006	0.019±0.012
1 st Reaction	K_{AB} (M ⁻¹)	141±101	161±154
	$k_{\rm r} ({\rm s}^{-1})$	0.0029±0.0007	0.0021, Fixed
	_		
	$k_{\rm BC} ({\rm S}^{-1})$	0.0021±0.0001	0.0011±0.0006
2 nd Reaction	$K_{ m BC}({ m M}^{-1})$	1877±667	107±91
	<i>k</i> _r (s⁻¹)	0, Fixed	0, Fixed
	$k_{\rm CD}$ (s ⁻¹)	0.00032±0.00005	0.00011±0.00002
3 rd Reaction	$K_{\rm CD}$ (M ⁻¹)	797±385	221±62
	$k_{\rm r}~({\rm s}^{-1})$	0, Fixed	0, Fixed

 Table 6.2 Comparative rate and equilibrium results obtained by fitting values from Table 6.1 (no Cl⁻ added, and Cl⁻ added) to Eq. 6.6

6.4.2.3. Comparison of kinetic data for the consecutive three reactions, in presence and absence of chloride ions

Upon comparison of the results given in Table 6.2, interesting observations are made.

The kinetic rate constants show that:

- The 1st slow process is virtually <u>independent</u> of added chloride ions (k_{AB} of 0.017±0.006 vs. 0.019±0.012 s⁻¹).
- The 2nd slow reaction is influenced by the addition of free chloride ions, i.e., an approximate <u>two-fold</u> decrease is observed (k_{BC} of 0.0021±0.0001 vs. 0.0011±0.0006 s⁻¹).
- The 3rd reaction is even more significantly influenced, and shows an approximate <u>three-fold</u> decrease (0.00032±0.00005 vs 0.00011±0.00002 s⁻¹).

The equilibrium constants follow a similar pattern:

- K_{AB} of 141±101 vs. 161±154 M⁻¹ (ca. <u>independent</u> of added chloride), for the 1st reaction;
- K_{BC} of 1877±667 vs. 107±91 M⁻¹ (more than <u>ten-fold</u> decrease), for the 2nd reaction;
- K_{CD} 797±385 vs. 221±62 M⁻¹ (ca. <u>three-fold</u> decrease), respectively.

A result from this, although not conclusively confirmed by the current data in hand, suggests that as the number of bidentate ligands around the Zr centre are increased, so does the steric demand, and:

- Both the thermodynamic equilibria of the higher coordinated oxine complexes [tris and tetrakis moieties] are then significantly more influenced;
- The forward rates for the formation of the tris and tetrakis moieties are significantly more affected.

6.4.3. Fast Stopped-Flow Spectroscopy

By returning to Figure 6.3, it is clear that there is a large increase of absorbance in the initial few seconds of the reaction after mixing the zirconium and oxine solutions, which is too fast to monitor on the conventional UV/Vis spectrometer used. For this portion of the reaction, fast stopped-flow spectroscopy was therefore utilized to evaluate the kinetics. The reactions performed on the slow UV/Vis experiments described in the previous paragraph, were thus repeated with exact solution concentrations and temperature on the stopped-flow instrument, with the first portion of the ligand coordination reaction monitored for *ca*. 200 seconds. The mechanics of the stopped-flow spectrophotometer become unreliable after this time, due to fluctuation in applied pressure and possible backflow of reaction solutions.

Two clear steps were identified by the data from the stopped-flow spectrometer.

The first reaction observed on the stopped-flow spectrometer, were fitted directly on the spectrophotometer via onboard software, using a *pseudo* first-order reaction (Eq. 6.3, fitted data in Table 6.3). Upon plotting the observed rate constants thus obtained *vs.* [ox], yielded the relationship as illustrated in Figure 6.7 below. This is typical for the simple reversible reaction of which the observed rate equation is given by:

$$k_{\rm AB} = k_1 [\rm LL'] + k_{-1}$$
 Eq.6.7

The slope of this relation is representative of the forward reaction rate (k_I) and the y-intercept by the backward reaction rate (k_I) . For this reaction step the rates are as follows:

- $k_1 = 23 \pm 3 \text{ M}^{-1} \cdot \text{s}^{-1}$
- $k_{-1} = 0.005 \pm 0.009 \text{ s}^{-1}$; which approximates to zero within standard deviation.



Figure 6.7 Plot of the observed rate constants for the 1st observable reaction on the Stopped Flow Experiment (See Table 6.1: Column 3); $[ZrCl_4] = 5.578 \times 10^{-5}$ M, [oxH] range = 5.61 x 10⁻⁴ to 5.61 x 10⁻³M, Solvent: DMF, Temp: 25°C.

Table 6.3 Observed rate constants from the fast Stopped-Flow Study (no chloride added); $[ZrCl_4] = 5.578 \times 10^{-5} M$, Solvent: DMF, Temp: 25°C.

Ligand	Observed rate constants, k _{obs} , for 2 consecutive steps (
[ox] (M)	1 st step	2 nd step			
5.61 x 10 ⁻⁴	0.015(3)	0.0035(3)			
1.12E x 10 ⁻³	0.027(2)	0.0071(2)			
2.25 x 10 ⁻³	0.056(3)				
2.81 x 10 ⁻³	0.074(1)	0.0111(1)			
3.37 x 10 ⁻³	0.092(2)	0.0116(2)			
3.93 x 10 ⁻³	0.106(2)	0.0128(2)			
4.49 x 10 ⁻³	0.090(2)				
5.61 x 10 ⁻³		0.0127(3)			

The second reaction monitored by the stopped-flow spectrometer, when the observed rate constant *vs.* [ox] is evaluated, shows a limiting relationship that is generally associated with a two-step reaction which becomes independent of ligand concentration at high [ox] values (Using Eq. 6.6; see Figure 6.8). It was also used to describe the three consecutive slower reactions described above in Par 6.4.2.



Figure 6.8 Plotted Reaction Rates of the 2nd observable reaction on Stopped Flow Experiment (See Table 6.3);

It was expected that this second reaction step, observed by stopped-flow kinetics, will be comparable to the 1st observable step from the slower UV/Vis kinetics. By fitting the observed rate constants to [ox] in Eq.6.6, the results in fact proved the assumption correct, see Table 6.4. It is also confirmed visually, by comparing Fig. 6.5A with Fig. 6.8.

It is therefore clear from the above that the pre-equilibrium constant (K_{xy}) as well as the observed second order limiting rate constant (k_{xy}) for the separately observed reactions are near identical within estimated error.

	Fast Stop	Slow UV/Vis		
1 st Reaction		2 nd Reaction	1 st Reaction ^{a)}	
$k_1 (M^{-1}s^{-1})$	23±3			
$k_{-1}(s^{-1})$	0.005±0.009			
$k_{xy} (M^{-1}s^{-1})$		0.017±0.003	0.017±0.006	
$K_{xy}(M^{-1})$		342±141	141±101	
$k_r (s^{-1})$		0.002, Fixed	0.0029±0.0007	

 Table 6.4 Comparative rate and equilibrium constants for reaction steps from

 Stopped Flow and UV/Vis Kinetics

^{a)} Data from Table 6.2; 1st reaction; XY = AB

The difference can be attributed to the fact that the 2nd reaction step kinetics observed by stopped-flow, is not fully completed by the time absorbance data collection is stopped (due to mechanical technically of the apparatus – see Par. 6.2) and thus this step is not as accurately defined by mathematical modeling as the that of the slower UV/Vis experiment.

The following simplified mechanism is therefore currently assumed for the two-step process monitored by fast stopped-flow spectroscopy:

Step 1: $ZrCl_4 + ox$ $\underbrace{K_1, k_1}_{k_{-1}}$ $[ZrCl_3(ox)]$ $[ZrCl_3(ox)] + ox$ $\underbrace{K_{2a}, k_{2a}}_{k_{-2a}}$ $[ZrCl_3(ox)(ox')]$ Step 2: $[ZrCl_3(ox)(ox')]$ $\underbrace{k_{2b}}_{k_{2b}}$ $[ZrCl_2(ox)_2]$

Scheme 6.1: Mechanistic presentation of the 1st and 2nd Reactions of the reaction between ZrCl₄ and OxH as observed on the Stopped-Flow spectrometer. (L,L' = oxine; halide ligands omitted for simplicity)

6.4.4. Combining Data: Final Mechanistic Observations

Unfortunately there are still unknown factors involved in the mechanism for these four occurring reactions. However, from the plots of reaction rate data against the corresponding ligand concentration, the trend of the relation may be estimated.

The initial reaction occurs rapidly and is:

- difficult to control, as well as
- isolate such an intermediate product in the solid state.

It is however possible, from the above, to more reliably confirm that a minimum of five reactions (probably seven, assuming that the coordination of the 3rd and 4th oxine ligands each enters via a two-step, rate-limiting process) are observed for the overall reaction, as illustrated in Scheme 6.2.

- The first step detected of the total process (as discussed in Par. 6.4) involves the coordination of the first ox ligand and concurrent replacement of the first chloride.
- The second step, which is observed as the 2nd step via stoppedflow spectroscopy and as the 1st step by the slower UV/Vis experiments, is defined by limiting kinetic behaviour. This is indicative of a two-phase process in itself, where an intermediate form is found after the fast initial equilibrium, which then undergoes a ring-closure/ chloride liberation process to yield the final step product, [ZrCl₂(ox)₂], after the slower rate determining second phase. The intermediate, [ZrCl₃(ox)(ox')] indicated in Scheme 6.2, has as yet an uncertain constitution, since the preliminary kinetic experimental data cannot yield information with regard to interchange products. This interchange phase can also occur via a

dissociative process of the leaving Cl⁻-ligand (followed by rapid ring-closing coordination of the entering ox ligand) or via an associative mechanism where the ox-ligand coordinates first, thus forcing the Cl⁻-ligand out of the coordination sphere. Future experiments will be designed to investigate this intermediate phase product specifically, since by controlling certain intermediates, separation of different coordinates might possibly be induced.



Scheme 6.2: Proposed overall scheme for the observed coordination of four oxine ligands to tetrachloridozirconium(IV) [free chloride ligands omitted for simplicity]

The coordination of the 3rd and 4th oxine ligands are observed as complete two-step coordination events, similar to Step 2, where intermediate phase products are formed [postulated to be [ZrCl₂(ox)₂(ox')] and [ZrCl(ox)₃(ox'), in Scheme 6.2, respectively] via fast initial equilibrium processes, followed by rearrangement to the final step seven and eight coordinate products, [ZrCl(ox)₃] and [Zr(ox)₄], respectively.

As mentioned throughout this chapter, the first phase of the reaction occurs so rapidly that it is clear why a *mono* coordinated zirconium bidentate ligand complex is difficult to isolate in the solid state. Within the first 3 minutes of the reaction, the second bidentate ligand has already started coordinating to the metal center. This implies that to even attempt to isolate the mono substituted complex, would require some form of intervention after less than two minutes of reaction time, and then even it may not be possible to isolate a solid structure, since the entire system by preference tends towards maximum coordination state.

6.5. Final Remarks

The mechanistic information gathered from this basic kinetic study could prove invaluable for the design of more specialized approaches to kinetic investigations for zirconium bidentate ligand complexes. No examples of this type of experimentation are currently available from literature (as discussed in Chapter 2), with regard to mechanistic study for the entire process of ligand coordination to a zirconium metal centre.

By clearly identifying intermediate species, exact mechanistic theory can be identified and further utilized for separation processes. From this preliminary work, it already is evident that the presence of excess original halide ligand (in this case Cl⁻), can limit the rate at which higher coordination takes place. By gathering more information on the same reaction ($ZrCl_4 + oxH$), along with other bidentate coordination reactions (tfacacH and hfacacH), more accurate theory about exact reaction mechanisms, for specific families of ligands, can be made. All of this is planned for future project work where ligands will also be tailored to investigate the effect of the size of the ligand on the exact rates and crystallization preferences for zirconium complex species.

In conclusion, the mechanistic information obtained so far proves to be a very important stepping stone for understanding exactly how zirconium(IV) coordination reactions proceed. With this blueprint, future studies could likely show the elusive chemical state difference between zirconium and hafnium, which could lead to more effective and less expensive separation techniques.

Chapter 7

Evaluation of this Study

7.1. Study Success and Perspective

This study was aimed at investigating the intimate chemical nature of zirconium in an environment of O,O- and O,N-donor bidentate ligands, particularly for the acetylacetonato (acac) - type family. It was intended to do this via synthesis, characterisation and solution behavioural evaluation of new complexes, to form part of parallel projects of the chemical differences between zirconium and hafnium. The aim of this comparative study is to ultimately discover a new method to separate these two metals more effectively and efficiently for application in industry.

This aim has partially been met. A significant amount of new information with regard to the formation kinetics of the tetrakis complexes, and the unpredictable nature of these two metals, was discovered. However, the frustration on the significant similarities still exists.

Two new crystal structures of zirconium bidentate ligand complexes have been produced along with fairly interesting comparative results from examples from literature (Chapter 5). It was discovered that solvent interactions in the crystallization process does not greatly affect the final steric properties at the zirconium metal centre in the crystalline state. A comparison between a solvated [Zr(tfacac)₄] complex and a non-solvated polymorph from literature, showed that as far as the coordination polyhedron goes, the bulky solvent molecule has little influence. The expected square anti-prismatic coordination polyhedron was confirmed for this acac family crystal structures, along with the slight distortion towards a dodecahedral geometry. The crystal packing for the larger volume of the solvated moiety did however show a difference from the non-solvated specie.

The crystal structure for the $[Zr(ox)_4]$ complex that was characterised could not fully be compared to literary references, since there are no complete references, but the synthesis of this complex provided scope for kinetic solution behavioural studies, since the conditions observed during synthesis are ideal for such studies. These kinetic investigations lead us to a proposed mechanism for the zirconium-oxine set of reaction events.

This project is a good example of why kinetic studies should feature as paramount importance in synthetic projects in coordination and organometallic chemistry. In spite of failing at the characterisation of lower coordinated products via all other methods available, kinetic experimentation yielded significant results. Apart from identifying intermediate product formation steps in a preliminary but scientifically sound mechanistic scheme, a method for limiting higher coordination product formation was discovered. By introducing an excess of halide ligand (present on the metal reagent, in this case CI), it is possible to restrain the rate at which the tris- and tetrakis- complexes were formed. This specific set of characterisation experiments then goes a long way to advance the search for new separation methods of zirconium and hafnium. With future studies, this isolation of lower coordinated products can be better studied and the metal counterparts compared to yield information about possible seperative properties.

When considering the scope of research work yet to be done, this project has been a successful preliminary study to identify the way for the future. Standards have been set and the guess-work involved with the specific aim has been resolved. Now, one can focus on specific subjects rather than the broader complex design concept. Specific kinetic experimentation will undoubtedly feature as most important tools for in situ product characterisation.

7.2. Aimed Future Research

Based on the results obtained from this study, a set of different aspects have been identified and will be covered in future, in an attempt to resolve the complete solution behaviour in a more detailed way and are the following:

- (i) The further solution studies of other bidentate ligands investigated in this study. The reaction mechanism for acac-family ligands could differ entirely from that of 8-hydroxyquinoline.
- (ii) The advancement of kinetic study techniques to allow for the identification of intermediate phase products.
- (iii) The investigation of tridentate ligand reaction effects. Since zirconium can easily form a formally eight-coordinated molecule, it will be interesting to investigate the effects of the metal being occupied by only two tri-dentate ligands. The mystery here is what will happen to the last two coordination sites. Can they be left occupied by halides? Will another tridentate ligand forcefully coordinate to the metal center? All these questions will be investigated in future.

- (iv) Specific tailoring of standard O,O-donating ligands to be adjusted for N,N-hybrids and the subsequent variation of the side groups attached to the 3rd position on the N donor atom. This will enable the investigation of the effects of larger steric hindrances closer to the metal centre.
- (v) The tailoring of ligand "backbones" to the study the effects of steric "rear-ends" of ligands on effective coordination and the extent thereof.
- (vi) Solution studies on the most interesting cases observed in synthesis.
 Only species that show definite variation in the products produced would be kinetically observed.
- (vii) Ultimately the goal of all of this would then be to find a successful method of separation from all this chemical knowledge. Therefore, specific separation studies will be undertaken to yield this method. Prospective methods under scrutiny so far, include ionization separation and liquid-liquid extraction techniques.

Appendix

I. Supplementary Crystallographic Data – [Zr(tfacac)₄]·(C₆H₇)

Table I.A Fractional atomic coordinates and isotropic or equivalent isotropic

 displacement parameters (Å²)

	x	У	z	U _{iso} */U _{eq}	Occ. (<1)
Zr	0.5000	0.16714 (3)	0.7500	0.01245 (7)	
F13	0.26810 (6)	-0.05226 (14)	0.66176 (6)	0.0295 (3)	
F11	0.31909 (6)	-0.06998 (14)	0.76862 (6)	0.0287 (3)	
F03	0.51411 (7)	0.40573 (15)	0.95310 (6)	0.0340 (3)	
F02	0.45468 (7)	0.22014 (15)	0.96764 (6)	0.0368 (3)	
O11	0.39952 (6)	0.08075 (15)	0.72452 (6)	0.0158 (3)	
O02	0.51936 (6)	-0.05446 (15)	0.81277 (6)	0.0166 (3)	
O01	0.49399 (6)	0.25443 (15)	0.83681 (6)	0.0169 (3)	
F12	0.24250 (6)	0.11472 (15)	0.71971 (7)	0.0366 (3)	
O12	0.43558 (6)	0.38983 (15)	0.71261 (6)	0.0171 (3)	
F01	0.40934 (7)	0.38633 (18)	0.88399 (6)	0.0431 (4)	
C13	0.33615 (9)	0.3227 (2)	0.71690 (10)	0.0200 (4)	
C02	0.48042 (9)	0.1790 (2)	0.87851 (9)	0.0174 (4)	
C05	0.50748 (11)	-0.2801 (2)	0.87225 (10)	0.0244 (4)	
H05A	0.5085	-0.3440	0.8372	0.037*	
H05B	0.4693	-0.3129	0.8774	0.037*	
H05C	0.5481	-0.2994	0.9132	0.037*	
C12	0.34797 (9)	0.1566 (2)	0.72089 (8)	0.0160 (3)	
C01	0.46413 (10)	0.2976 (2)	0.92118 (9)	0.0230 (4)	
C11	0.29404 (9)	0.0373 (2)	0.71787 (10)	0.0214 (4)	
C14	0.38103 (9)	0.4351 (2)	0.70992 (9)	0.0182 (4)	
C03	0.47956 (10)	0.0124 (2)	0.88819 (9)	0.0200 (4)	
C04	0.50208 (9)	-0.1001 (2)	0.85506 (9)	0.0174 (4)	
C102	0.67683 (12)	0.0133 (3)	1.07100 (11)	0.0402 (6)	
H102	0.6803	-0.0134	1.1122	0.048*	
C15	0.36143 (10)	0.6138 (2)	0.69579 (11)	0.0257 (4)	
H15A	0.4003	0.6786	0.7036	0.039*	
H15B	0.3440	0.6517	0.7246	0.039*	
H15C	0.3274	0.6260	0.6501	0.039*	
C105	0.66546 (11)	0.0938 (4)	0.94967 (11)	0.0403 (6)	
H105	0.6612	0.1195	0.9080	0.048*	
C104	0.67351 (12)	-0.0692 (3)	0.96984 (12)	0.0428 (6)	
H104	0.6748	-0.1519	0.9420	0.051*	

C100	0.66358 (10)	0.2198 (3)	0.98939 (11)	0.0337 (5)	
C101	0.66888 (11)	0.1768 (3)	1.05052 (11)	0.0352 (5)	
H101	0.6671	0.2593	1.0782	0.042*	
C103	0.67966 (12)	-0.1103 (3)	1.03094 (13)	0.0411 (6)	
H103	0.6857	-0.2203	1.0450	0.049*	
C106	0.65652 (13)	0.3975 (4)	0.96634 (16)	0.0586 (8)	
H10A	0.6561	0.4691	0.9998	0.088*	0.5
H10B	0.6151	0.4103	0.9255	0.088*	0.5
H10C	0.6938	0.4262	0.9590	0.088*	0.5
H10D	0.6540	0.4013	0.9231	0.088*	0.5
H10E	0.6949	0.4601	0.9974	0.088*	0.5
H10F	0.6162	0.4442	0.9639	0.088*	0.5
H03	0.4677 (11)	-0.027 (3)	0.9208 (10)	0.024 (6)*	
H13	0.2975 (12)	0.361 (3)	0.7144 (11)	0.028 (6)*	

Table I.B Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zr	0.01529 (12)	0.00880 (12)	0.01714 (12)	0	0.01087 (9)	0
F13	0.0252 (6)	0.0253 (6)	0.0364 (6)	-0.0084 (5)	0.0133 (5)	-0.0067 (5)
F11	0.0325 (6)	0.0214 (6)	0.0384 (7)	-0.0030 (5)	0.0221 (6)	0.0069 (5)
F03	0.0518 (8)	0.0227 (6)	0.0398 (7)	-0.0104 (6)	0.0318 (6)	-0.0121 (5)
F02	0.0681 (9)	0.0251 (6)	0.0407 (7)	-0.0054 (6)	0.0450 (7)	-0.0025 (5)
O11	0.0164 (6)	0.0125 (6)	0.0217 (6)	0.0012 (5)	0.0116 (5)	0.0004 (5)
O02	0.0188 (6)	0.0140 (6)	0.0206 (6)	0.0007 (5)	0.0123 (5)	0.0025 (5)
O01	0.0222 (6)	0.0131 (6)	0.0199 (6)	-0.0008 (5)	0.0136 (5)	0.0003 (5)
F12	0.0295 (7)	0.0204 (6)	0.0776 (10)	0.0012 (5)	0.0399 (7)	0.0000 (6)
O12	0.0193 (6)	0.0134 (6)	0.0231 (6)	0.0016 (5)	0.0136 (5)	0.0024 (5)
F01	0.0451 (8)	0.0518 (9)	0.0367 (7)	0.0246 (7)	0.0229 (6)	-0.0001 (6)
C13	0.0184 (9)	0.0161 (9)	0.0311 (10)	0.0030 (7)	0.0163 (8)	0.0012 (8)
C02	0.0192 (9)	0.0182 (9)	0.0173 (8)	-0.0009 (7)	0.0106 (7)	-0.0008 (7)
C05	0.0343 (11)	0.0156 (9)	0.0300 (10)	-0.0006 (8)	0.0208 (9)	0.0034 (8)
C12	0.0164 (8)	0.0158 (9)	0.0192 (8)	0.0001 (7)	0.0113 (7)	-0.0005 (7)
C01	0.0319 (11)	0.0205 (10)	0.0228 (9)	0.0012 (8)	0.0180 (8)	0.0014 (7)
C11	0.0203 (9)	0.0160 (9)	0.0342 (10)	0.0017 (7)	0.0180 (8)	0.0001 (8)
C14	0.0217 (9)	0.0146 (9)	0.0202 (9)	0.0034 (7)	0.0115 (7)	0.0012 (7)
C03	0.0260 (10)	0.0186 (9)	0.0212 (9)	-0.0010 (7)	0.0159 (8)	0.0023 (7)
C04	0.0163 (9)	0.0164 (9)	0.0194 (8)	-0.0018 (7)	0.0084 (7)	0.0020 (7)
C102	0.0378 (13)	0.0551 (16)	0.0294 (11)	-0.0099 (11)	0.0174 (10)	0.0037 (11)
C15	0.0268 (10)	0.0148 (9)	0.0406 (11)	0.0043 (8)	0.0202 (9)	0.0043 (8)
C105	0.0264 (11)	0.0699 (18)	0.0234 (10)	-0.0085 (11)	0.0108 (9)	-0.0024 (11)
C104	0.0286 (12)	0.0546 (17)	0.0453 (14)	-0.0078 (11)	0.0177 (11)	-0.0252 (12)
C100	0.0176 (10)	0.0387 (13)	0.0346 (11)	-0.0053 (9)	0.0040 (9)	0.0047 (10)
C101	0.0305 (12)	0.0414 (14)	0.0330 (11)	-0.0061 (10)	0.0145 (9)	-0.0128 (10)
C103	0.0284 (12)	0.0329 (13)	0.0552 (15)	-0.0059 (10)	0.0144 (11)	-0.0016 (11)
C106	0.0288 (13)	0.0518 (17)	0.0718 (19)	-0.0054 (12)	0.0048 (13)	0.0233 (15)

Table I.C Geometric parameters (Å, °)

Zr—O01i	2.1633 (13)	001i—Zr—012i	76.90 (5)
C05—H05C	0.9600	C14—C15—H15B	109.50
Zr—001	2.1633 (13)	001—Zr—012i	72.46 (5)
C12—C11	1.525 (3)	H15A—C15—H15B	109.50
Zr—011	2.1679 (13)	011—Zr—012i	140.87 (5)
C14—C15	1.496 (3)	C14—C15—H15C	109.50
Zr—O11i	2.1679 (13)	011i—Zr—012i	75.27 (5)
C03—C04	1.419 (3)	H15A—C15—H15C	109.50
Zr—O02i	2.1973 (15)	002i—Zr—012i	143.29 (5)
C03—H03	0.95 (2)	H15B-C15-H15C	109.50
Zr—002	2.1973 (15)	002—Zr—012i	121.20 (5)
C102—C103	1.372 (4)	C104—C105—C100	121.7 (2)
Zr—O12i	2.2079 (15)	001i—Zr—012	72.46 (5)
C102—C101	1.381 (4)	C104—C105—H105	119.10
Zr—012	2.2079 (15)	001—Zr—012	76.90 (5)
C102—H102	0.9300	C100—C105—H105	119.10
F13—C11	1.336 (2)	011—Zr—012	75.27 (5)
C15—H15A	0.9600	C103—C104—C105	120.2 (2)
F11—C11	1.335 (2)	011i—Zr—012	140.87 (5)
C15—H15B	0.9600	C103—C104—H104	119.90
F03—C01	1.333 (2)	002i—Zr—012	121.20 (5)
C15—H15C	0.9600	C105—C104—H104	119.90
F02—C01	1.330 (2)	002—Zr—012	143.29 (5)
C105—C104	1.374 (4)	C105—C100—C101	117.6 (2)
O11—C12	1.280 (2)	012i—Zr—012	71.35 (7)
C105—C100	1.374 (4)	C105—C100—C106	120.2 (2)
O02—C04	1.254 (2)	C12—O11—Zr	131.65 (12)
C105—H105	0.9300	C101—C100—C106	122.2 (2)
O01—C02	1.281 (2)	C04—O02—Zr	134.45 (12)
C104—C103	1.373 (4)	C102—C101—C100	120.9 (2)
F12—C11	1.337 (2)	C02—O01—Zr	131.67 (12)
C104—H104	0.9300	C102—C101—H101	119.50
O12—C14	1.256 (2)	C14—O12—Zr	134.72 (12)
C100—C101	1.384 (3)	C100—C101—H101	119.50
F01—C01	1.326 (2)	C12-C13-C14	120.47 (17)
C100—C106	1.506 (4)	C102—C103—C104	119.1 (2)
C13—C12	1.359 (3)	C12-C13-H13	119.8 (15)
C101—H101	0.9300	C102—C103—H103	120.50
C13—C14	1.421 (3)	C14—C13—H13	119.4 (15)
C103—H103	0.9300	C104—C103—H103	120.50
C13—H13	0.90 (2)	O01—C02—C03	127.88 (17)
C106—H10A	0.9600	C100—C106—H10A	109.50
C02—C03	1.362 (3)	O01-C02-C01	112.97 (16)
C106—H10B	0.9600	C100—C106—H10B	109.50
C02—C01	1.527 (3)	C03—C02—C01	119.15 (16)
C106—H10C	0.9600	H10A—C106—H10B	109.50
C05—C04	1.492 (3)	C04—C05—H05A	109.50

C106—H10D	0.9600	C100-C106-H10C	109.50					
C05—H05A	0.9600	C04—C05—H05B	109.50					
C106—H10E	0.9600	H10A—C106—H10C	109.50					
C05—H05B	0.9600	H05A—C05—H05B	109.50					
C106—H10F	0.9600	H10B—C106—H10C	109.50					
		C04—C05—H05C	109.50					
001i—Zr—001	142.07 (7)	C100—C106—H10D	109.50					
F13—C11—C12	111.10 (15)	H05A—C05—H05C	109.50					
001i—Zr—011	111.77 (5)	H10A—C106—H10D	141.10					
F12—C11—C12	112.97 (15)	H05B-C05-H05C	109.50					
001—Zr—011	80.66 (5)	H10B—C106—H10D	56.30					
O12-C14-C13	122.83 (16)	O11-C12-C13	128.12 (17)					
001i—Zr—011i	80.66 (5)	H10C—C106—H10D	56.30					
O12-C14-C15	118.18 (16)	O11-C12-C11	112.42 (15)					
001—Zr—011i	111.77 (5)	C100—C106—H10E	109.50					
C13—C14—C15	118.94 (17)	C13-C12-C11	119.40 (16)					
011—Zr—011i	142.56 (7)	H10A—C106—H10E	56.30					
C02-C03-C04	120.48 (17)	F01—C01—F02	107.98 (17)					
001i—Zr—002i	75.41 (5)	H10B—C106—H10E	141.10					
C02-C03-H03	118.7 (13)	F01—C01—F03	106.60 (17)					
001—Zr—002i	141.24 (5)	H10C—C106—H10E	56.30					
C04—C03—H03	120.5 (13)	F02—C01—F03	106.60 (15)					
011—Zr—002i	72.91 (5)	H10D—C106—H10E	109.50					
O02-C04-C03	122.81 (17)	F01—C01—C02	111.26 (16)					
011i—Zr—002i	76.85 (5)	C100—C106—H10F	109.50					
O02-C04-C05	118.06 (16)	F02—C01—C02	113.01 (16)					
001i—Zr—002	141.24 (5)	H10A—C106—H10F	56.30					
C03—C04—C05	119.11 (16)	F03—C01—C02	111.06 (16)					
001—Zr—002	75.41 (5)	H10B—C106—H10F	56.30					
C103—C102—C101	120.5 (2)	F11—C11—F13	106.99 (15)					
011—Zr—002	76.85 (5)	H10C—C106—H10F	141.10					
C103—C102—H102	119.80	F11—C11—F12	106.91 (15)					
011i—Zr—002	72.91 (5)	H10D—C106—H10F	109.50					
C101—C102—H102	119.80	F13—C11—F12	106.87 (15)					
002i—Zr—002	71.36 (7)	H10E—C106—H10F	109.50					
C14—C15—H15A	109.50	F11—C11—C12	111.66 (15)					
	Symmetry codes: (i) $-x+1$, y , $-z+3/2$.							

II. Supplementary Crystallographic Data – [Zr(ox)₄]·(HCON(CH₃)₂)•(H₂O)

	x	У	z	$U_{\rm iso}$ */ $U_{\rm eq}$	Occ. (<1)		
Zr1	0.71931 (2)	0.32600 (2)	0.694746 (19)	0.01535 (10)			
O2	0.89414 (16)	0.28000 (16)	0.73775 (14)	0.0197 (4)			
O4	0.64050 (16)	0.19991 (16)	0.78350 (15)	0.0191 (4)			
O3	0.57063 (16)	0.32655 (15)	0.56099 (14)	0.0184 (4)			
O1	0.77354 (16)	0.50002 (16)	0.70123 (14)	0.0183 (4)			
N3	0.6881 (2)	0.15723 (19)	0.57870 (18)	0.0180 (5)			
N1	0.80233 (19)	0.39843 (19)	0.88483 (17)	0.0171 (5)			
N2	0.8217 (2)	0.36040 (19)	0.54649 (17)	0.0187 (5)			
N4	0.56150 (19)	0.3902 (2)	0.76757 (18)	0.0184 (5)			
C02	0.8637 (2)	0.3987 (3)	1.0805 (2)	0.0212 (6)			
H02	0.8728	0.3569	1.1438	0.025*			
C18	0.9341 (2)	0.3286 (2)	0.5675 (2)	0.0184 (5)			
C04	0.8761 (2)	0.5737 (2)	0.9975 (2)	0.0195 (6)			
C09	0.8299 (2)	0.5116 (2)	0.8948 (2)	0.0174 (5)			
C27	0.5980 (2)	0.1569 (2)	0.4854 (2)	0.0188 (6)			
C36	0.5164 (2)	0.3198 (2)	0.8354 (2)	0.0196 (6)			
C22	0.5649 (2)	0.0698 (2)	0.4023 (2)	0.0216 (6)			
C07	0.8384 (2)	0.6792 (2)	0.7990 (2)	0.0197 (6)			
H07	0.8259	0.7167	0.733	0.024*			
C26	0.5355 (2)	0.2500 (2)	0.4773 (2)	0.0194 (6)			
C31	0.4328 (3)	0.3448 (3)	0.8967 (2)	0.0257 (6)			
C11	0.8535 (3)	0.4208 (2)	0.3739 (2)	0.0249 (6)			
H11	0.8225	0.4526	0.3071	0.030*			
C06	0.8835 (2)	0.7413 (2)	0.9009 (2)	0.0231 (6)			
H06	0.9001	0.8202	0.9023	0.028*			
C28	0.5232 (2)	0.4865 (3)	0.7553 (2)	0.0237 (6)			
H28	0.5528	0.5354	0.7061	0.028*			
C25	0.4422 (2)	0.2533 (2)	0.3854 (2)	0.0229 (6)			
H25	0.3984	0.3139	0.3789	0.027*			
C17	0.9713 (2)	0.2840 (2)	0.6716 (2)	0.0198 (6)			
C16	1.0851 (3)	0.2524 (3)	0.6982 (2)	0.0247 (6)			
H16	1.1116	0.2212	0.7663	0.030*			
C01	0.8195 (2)	0.3440 (2)	0.9755 (2)	0.0187 (6)			
H01	0.8011	0.265	0.9691	0.022*			
C10	0.7832 (3)	0.4053 (2)	0.4531 (2)	0.0211 (6)			
H10	0.7051	0.4281	0.4386	0.025*			
C23	0.4697 (3)	0.0773 (3)	0.3083 (2)	0.0253 (6)			
H23	0.4466	0.0201	0.2506	0.030*			
C03	0.8936 (2)	0.5121 (3)	1.0920 (2)	0.0215 (6)			
H03	0.926	0.5494	1.163	0.026*			

Table II.A Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

C05	0.9041 (2)	0.6909 (2)	0.9983 (2)	0.0229 (6)	
H05 0.9371 0.73		0.7344	1.0659	0.027*	
C15	1.1627 (3)	0.2664 (3)	0.6242 (2)	0.0286 (7)	
H15	1.2414	0.2452	0.6446	0.034*	
C20	0.7178 (3)	-0.0202 (2)	0.5144 (2)	0.0240 (6)	
H20	0.7608	-0.0810	0.5272	0.029*	
C24	0.4115 (3)	0.1672 (3)	0.3012 (2)	0.0254 (6)	
H24	0.3484	0.172	0.2376	0.030*	
C08	0.8122 (2)	0.5646 (2)	0.7938 (2)	0.0171 (5)	
C13	1.0118 (3)	0.3414 (2)	0.4930 (2)	0.0230 (6)	
C37	0.9300 (4)	0.0192 (4)	1.1584 (4)	0.0596 (13)	
C35	0.5614 (2)	0.2164 (2)	0.8442 (2)	0.0193 (6)	
C19	0.7463 (2)	0.0714 (2)	0.5924 (2)	0.0216 (6)	
H19	0.8095	0.0714	0.6572	0.026*	
N5	0.8721 (3)	0.0608 (3)	1.2265 (3)	0.0394 (7)	
C34	0.5215 (3)	0.1421 (3)	0.9139 (2)	0.0257 (6)	
H34	0.5502	0.0731	0.9211	0.031*	
O5	1.0309 (3)	-0.0102 (4)	1.1892 (3)	0.0922 (14)	
C29	0.4397 (3)	0.5197 (3)	0.8127 (3)	0.0283 (7)	
H29	0.4136	0.5895	0.8019	0.034*	
C30	0.3973 (3)	0.4500 (3)	0.8837 (3)	0.0320 (7)	
H30	0.3435	0.4726	0.9246	0.038*	
C14	1.1281 (3)	0.3094 (3)	0.5241 (2)	0.0279 (7)	
H14	1.1822	0.3176	0.4763	0.034*	
C12	0.9666 (3)	0.3896 (3)	0.3940 (2)	0.0255 (6)	
H12	1.0149	0.4004	0.3414	0.031*	
C33	0.4379 (3)	0.1679 (3)	0.9750 (3)	0.0324 (7)	
H33	0.4111	0.1154	1.0225	0.039*	
C32	0.3948 (3)	0.2659 (3)	0.9674 (3)	0.0332 (7)	
H32	0.3392	0.2813	1.0098	0.040*	
C21	0.6282 (3)	-0.0213 (3)	0.4202 (2)	0.0251 (6)	
H21	0.6086	-0.0828	0.3672	0.030*	
C38	0.9286 (4)	0.0694 (4)	1.3432 (3)	0.0556 (11)	
H38A	0.8761	0.1012	1.3833	0.083*	
H38B	1.0094	0.1175	1.3577	0.083*	
H38C	0.9386	-0.0048	1.3677	0.083*	
C39	0.7561 (3)	0.0973 (4)	1.1887 (3)	0.0522 (10)	
H39A	0.7294	0.1249	1.2518	0.078*	0.5
H39B	0.6945	0.0347	1.1492	0.078*	0.5
H39C	0.7653	0.157	1.1392	0.078*	0.5
H39D	0.7301	0.0861	1.1083	0.078*	0.5
H39E	0.7649	0.1764	1.2109	0.078*	0.5
H39F	0.6942	0.0541	1.2209	0.078*	0.5
06	0.7807 (2)	0.0489 (2)	0.90380 (19)	0.0387 (6)	
H37	0.854 (3)	0.029 (3)	1.079 (3)	0.046*	
H63	0.856 (2)	0.046 (3)	0.870 (3)	0.046*	
H62	0.726 (3)	0.106 (3)	0.853 (3)	0.046*	

	U ¹¹	U^{22}	U ³³	U ¹²	U ¹³	U^{23}
Zr1	0.01761 (14)	0.01695 (16)	0.01167 (14)	0.00135 (10)	0.00500 (10)	0.00076 (10)
O2	0.0207 (9)	0.0261 (11)	0.0136 (9)	0.0042 (8)	0.0065 (7)	0.0007 (8)
O4	0.0213 (9)	0.0182 (10)	0.0192 (9)	0.0025 (7)	0.0084 (7)	0.0015 (8)
O3	0.0222 (9)	0.0151 (10)	0.0171 (9)	0.0022 (7)	0.0039 (7)	0.0010 (8)
01	0.0212 (9)	0.0194 (10)	0.0136 (9)	0.0002 (7)	0.0054 (7)	-0.0006 (8)
N3	0.0210 (11)	0.0182 (12)	0.0153 (10)	0.0017 (9)	0.0065 (9)	0.0025 (9)
N1	0.0150 (10)	0.0209 (13)	0.0160 (11)	0.0029 (9)	0.0054 (8)	0.0016 (9)
N2	0.0217 (11)	0.0184 (13)	0.0150 (11)	-0.0015 (9)	0.0062 (9)	-0.0019 (9)
N4	0.0163 (11)	0.0217 (13)	0.0157 (11)	0.0014 (9)	0.0020 (8)	0.0016 (9)
C02	0.0193 (13)	0.0307 (17)	0.0156 (13)	0.0063 (11)	0.0067 (10)	0.0029 (12)
C18	0.0215 (13)	0.0170 (14)	0.0160 (12)	-0.0012 (10)	0.0069 (10)	-0.0046 (11)
C04	0.0144 (12)	0.0274 (16)	0.0172 (13)	0.0033 (11)	0.0060 (10)	-0.0046 (11)
C09	0.0134 (12)	0.0211 (15)	0.0183 (13)	0.0032 (10)	0.0054 (10)	-0.0021 (11)
C27	0.0202 (13)	0.0216 (15)	0.0140 (12)	-0.0013 (11)	0.0060 (10)	0.0018 (11)
C36	0.0183 (13)	0.0207 (15)	0.0189 (13)	0.0011 (11)	0.0042 (10)	0.0008 (11)
C22	0.0230 (13)	0.0220 (16)	0.0193 (13)	-0.0021 (11)	0.0085 (11)	0.0002 (12)
C07	0.0184 (13)	0.0210 (15)	0.0209 (13)	0.0047 (10)	0.0060 (10)	0.0021 (11)
C26	0.0209 (13)	0.0201 (15)	0.0168 (13)	-0.0018 (11)	0.0071 (10)	0.0021 (11)
C31	0.0203 (14)	0.0314 (18)	0.0265 (15)	0.0043 (12)	0.0082 (11)	0.0020 (13)
C11	0.0363 (16)	0.0221 (16)	0.0156 (13)	-0.0023 (12)	0.0101 (12)	0.0008 (12)
C06	0.0235 (14)	0.0195 (15)	0.0280 (15)	0.0061 (11)	0.0086 (12)	-0.0022 (12)
C28	0.0220 (14)	0.0255 (17)	0.0241 (14)	0.0072 (12)	0.0041 (11)	0.0034 (12)
C25	0.0240 (14)	0.0227 (16)	0.0202 (14)	0.0008 (11)	0.0036 (11)	0.0048 (12)
C17	0.0203 (13)	0.0206 (15)	0.0174 (13)	-0.0009 (11)	0.0065 (10)	-0.0058 (11)
C16	0.0236 (14)	0.0305 (17)	0.0188 (13)	0.0043 (12)	0.0040 (11)	-0.0057 (12)
C01	0.0164 (12)	0.0228 (15)	0.0188 (13)	0.0043 (10)	0.0071 (10)	0.0031 (11)
C10	0.0256 (14)	0.0196 (15)	0.0168 (13)	-0.0023 (11)	0.0070 (11)	0.0003 (11)
C23	0.0256 (14)	0.0278 (17)	0.0199 (14)	-0.0015 (12)	0.0051 (11)	-0.0053 (12)
C03	0.0163 (12)	0.0314 (17)	0.0170 (13)	0.0034 (11)	0.0053 (10)	-0.0031 (12)
C05	0.0211 (13)	0.0257 (16)	0.0214 (14)	0.0036 (11)	0.0060 (11)	-0.0081 (12)
C15	0.0223 (14)	0.0345 (19)	0.0293 (16)	0.0059 (12)	0.0075 (12)	-0.0094 (14)
C20	0.0282 (14)	0.0189 (15)	0.0288 (15)	0.0067 (11)	0.0127 (12)	0.0023 (12)
C24	0.0265 (14)	0.0299 (17)	0.0149 (13)	-0.0017 (12)	-0.0004 (11)	0.0022 (12)
C08	0.0157 (12)	0.0204 (15)	0.0162 (12)	0.0029 (10)	0.0063 (10)	0.0002 (11)
C13	0.0263 (14)	0.0215 (16)	0.0214 (14)	-0.0028 (11)	0.0118 (11)	-0.0058 (12)
C37	0.065 (3)	0.080 (3)	0.055 (3)	0.038 (2)	0.035 (2)	0.040 (2)
C35	0.0165 (12)	0.0241 (15)	0.0163 (12)	0.0000 (11)	0.0049 (10)	-0.0009 (11)
C19	0.0233 (14)	0.0240 (16)	0.0193 (13)	0.0043 (11)	0.0084 (11)	0.0056 (12)
N5	0.0356 (15)	0.0373 (18)	0.0488 (18)	0.0004 (13)	0.0211 (14)	0.0060 (15)
C34	0.0308 (15)	0.0224 (16)	0.0268 (15)	0.0029 (12)	0.0132 (12)	0.0044 (12)
O5	0.085 (2)	0.151 (4)	0.086 (2)	0.083 (3)	0.058 (2)	0.079 (3)
C29	0.0239 (14)	0.0305 (18)	0.0335 (16)	0.0133 (13)	0.0066 (12)	0.0047 (14)
C30	0.0249 (15)	0.041 (2)	0.0350 (17)	0.0114 (14)	0.0130 (13)	0.0026 (15)
C14	0.0278 (15)	0.0310 (18)	0.0268 (15)	0.0010 (12)	0.0143 (12)	-0.0093 (13)
C12	0.0340 (16)	0.0251 (17)	0.0180 (13)	-0.0050 (12)	0.0150 (12)	-0.0044 (12)
C33	0.0358 (17)	0.0351 (19)	0.0324 (17)	0.0042 (14)	0.0207 (14)	0.0099 (15)
C32	0.0307 (16)	0.037 (2)	0.0379 (18)	0.0063 (14)	0.0206 (14)	0.0051 (15)
C21	0.0311 (15)	0.0208 (16)	0.0246 (14)	0.0006 (12)	0.0126 (12)	-0.0036 (12)

Table II.B Atomic displacement parameters (Å²)

C38	0.046 (2)	0.053 (3)	0.059 (3)	0.0005 (19)	0.0027 (19)	-0.007 (2)
C39	0.041 (2)	0.059 (3)	0.057 (2)	0.0078 (19)	0.0127 (19)	0.013 (2)
O6	0.0410 (13)	0.0445 (16)	0.0341 (13)	0.0121 (11)	0.0117 (11)	0.0085 (11)

Table II.C Geometric parameters (Å, °)

Zr1—O3	2.0851 (19)	C25—C24—H24	119.00
C25—C24	1.409 (4)	01—Zr1—N1	70.28 (7)
Zr1—O2	2.102 (2)	O1—C08—C07	124.5 (2)
C25—H25	0.9500	O4—Zr1—N1	77.26 (8)
Zr1—O1	2.108 (2)	O1—C08—C09	117.7 (2)
C17—C16	1.376 (4)	N4—Zr1—N1	69.75 (7)
Zr1—O4	2.1283 (19)	C07—C08—C09	117.9 (2)
C16—C15	1.415 (4)	N3—Zr1—N1	140.94 (8)
Zr1—N4	2.412 (2)	C14—C13—C12	125.1 (3)
C16—H16	0.9500	N2—Zr1—N1	125.36 (8)
Zr1—N3	2.415 (2)	C14—C13—C18	118.5 (3)
C01—H01	0.9500	C17—O2—Zr1	124.30 (17)
Zr1—N2	2.424 (2)	C12—C13—C18	116.4 (3)
C10—H10	0.9500	C35—O4—Zr1	123.32 (17)
Zr1—N1	2.432 (2)	O5—C37—N5	123.4 (4)
C23—C24	1.364 (4)	C26—O3—Zr1	124.31 (17)
O2—C17	1.335 (3)	O5—C37—H37	142.5 (18)
C23—H23	0.9500	C08—O1—Zr1	123.94 (16)
O4—C35	1.337 (3)	N5—C37—H37	94.1 (18)
C03—H03	0.9500	C19—N3—C27	118.6 (2)
O3—C26	1.327 (3)	O4—C35—C34	124.8 (3)
C05—H05	0.9500	C19—N3—Zr1	129.66 (19)
O1—C08	1.326 (3)	O4—C35—C36	116.8 (2)
C15—C14	1.372 (4)	C27—N3—Zr1	111.73 (18)
N3—C19	1.321 (4)	C34—C35—C36	118.4 (2)
C15—H15	0.9500	C01—N1—C09	118.4 (2)
N3—C27	1.363 (3)	N3—C19—C20	122.2 (3)
C20—C21	1.365 (4)	C01—N1—Zr1	129.27 (19)
N1—C01	1.326 (3)	N3—C19—H19	118.90
C20—C19	1.408 (4)	C09—N1—Zr1	112.30 (16)
N1—C09	1.362 (4)	C20—C19—H19	118.90
C20—H20	0.9500	C10—N2—C18	118.7 (2)
N2—C10	1.319 (3)	C37—N5—C39	122.5 (4)
C24—H24	0.9500	C10—N2—Zr1	128.72 (18)
N2-C18	1.361 (3)	C37—N5—C38	118.3 (3)
C13—C14	1.407 (4)	C18—N2—Zr1	112.62 (17)
N4—C28	1.318 (4)	C39—N5—C38	119.2 (3)
C13—C12	1.413 (4)	C28—N4—C36	118.5 (2)
N4—C36	1.352 (4)	C35—C34—C33	120.3 (3)
C37—O5	1.235 (5)	C28—N4—Zr1	127.82 (18)
C02—C03	1.367 (4)	C35—C34—H34	119.90
C37—N5	1.326 (5)	C36—N4—Zr1	113.49 (17)
C02—C01	1.401 (4)	C33—C34—H34	119.90
C37—H37	1.18 (4)	C03—C02—C01	120.0 (3)

C02—H02	0.9500	C30—C29—C28	119.1 (3)
C35—C34	1.375 (4)	C03—C02—H02	120.00
C18—C13	1.421 (3)	C30—C29—H29	120.40
C19—H19	0.9500	C01—C02—H02	120.00
C18—C17	1.428 (4)	C28—C29—H29	120.40
N5—C39	1.438 (5)	N2-C18-C13	122.9 (3)
C04—C05	1.413 (4)	C29—C30—C31	120.4 (3)
N5-C38	1.448 (5)	N2—C18—C17	115.5 (2)
C04—C03	1.415 (4)	C29—C30—H30	119.80
C34—C33	1.416 (4)	C13—C18—C17	121.5 (2)
C04—C09	1.417 (4)	C31—C30—H30	119.80
C34—H34	0.9500	C05—C04—C03	124.9 (3)
C09—C08	1 426 (4)	C15-C14-C13	119.5 (3)
$C_{29} - C_{30}$	1,364 (4)	C_{05} C_{04} C_{09}	118.4 (3)
C27-C22	1 408 (4)	C15-C14-H14	120.30
C29_H29	0.9500	C03 - C04 - C09	116.6 (3)
C27_C26	1 427 (4)	C13 - C14 - H14	120.30
C30_H30	0.9500		123.0 (2)
C36_C31	1,415,(4)	$C_{11} - C_{12} - C_{13}$	120.0 (2)
C_{14} H_{14}	0.9500	N1 - C09 - C08	120.1 (2)
C14—1114 C26 C25	1 434 (4)	$C_{11} C_{12} = U_{12}$	13.4 (2)
$C_{12} = U_{12}$	0.9500		120.00
C12—I112	0.9300	C04 - C09 - C08	121.0 (3)
C22 - C21	1.415 (4)		120.00
C_{22}	1.301 (3)	$N_3 = C_2 T = C_2 Z_2$	123.0 (3)
C22 - C23	1.418 (4)	N2 C27 C26	121.0 (3)
	0.9500	N3-027-026	115.9 (2)
	1.379 (4)	C32—C33—H33	119.10
C32—H32	0.9500		121.1 (2)
	1.409 (4)	C34—C33—H33	119.10
C21—H21	0.9500	N4-C36-C31	123.7 (3)
C07—H07	0.9500	C33-C32-C31	120.1 (3)
C38—H38A	0.9800	N4—C36—C35	115.4 (2)
026-025	1.378 (4)	C33—C32—H32	120.00
C38—H38B	0.9800	C31—C36—C35	120.9 (3)
C31—C30	1.410 (5)	C31—C32—H32	120.00
C38—H38C	0.9800	C27—C22—C21	116.9 (3)
C31—C32	1.412 (4)	C20—C21—C22	119.4 (3)
C39—H39A	0.9800	C27—C22—C23	118.7 (3)
C11—C12	1.366 (4)	C20—C21—H21	120.30
C39—H39B	0.9800	C21—C22—C23	124.4 (3)
C11—C10	1.409 (4)	C22—C21—H21	120.30
C39—H39C	0.9800	C08—C07—C06	120.8 (3)
C11—H11	0.9500	N5—C38—H38A	109.50
C39—H39D	0.9800	C08—C07—H07	119.60
C06—C05	1.373 (4)	N5—C38—H38B	109.50
C39—H39E	0.9800	C06—C07—H07	119.60
C06—H06	0.9500	H38A—C38—H38B	109.50
C39—H39F	0.9800	O3—C26—C25	124.7 (3)
C28—C29	1.414 (4)	N5—C38—H38C	109.50
O6—H63	1.044 (18)	O3—C26—C27	116.9 (2)
C28—H28	0.9500	H38A—C38—H38C	109.50
O6—H62	1.121 (17)	C25—C26—C27	118.4 (3)
		H38B—C38—H38C	109.50
03—Zr1—O2	141.96 (7)	C30—C31—C32	125.5 (3)

N1-C01-H01	118.80	N5—C39—H39A	109.50
O3—Zr1—O1	92.68 (7)	C30—C31—C36	115.9 (3)
C02-C01-H01	118.80	N5—C39—H39B	109.50
02—Zr1—01	99.07 (8)	C32—C31—C36	118.6 (3)
N2-C10-C11	122.6 (3)	H39A—C39—H39B	109.50
O3—Zr1—O4	100.07 (7)	C12—C11—C10	119.4 (3)
N2—C10—H10	118.70	N5—C39—H39C	109.50
O2—Zr1—O4	93.26 (7)	C12—C11—H11	120.30
C11—C10—H10	118.70	H39A—C39—H39C	109.50
01—Zr1—O4	140.90 (7)	C10—C11—H11	120.30
C24—C23—C22	119.5 (3)	H39B—C39—H39C	109.50
O3—Zr1—N4	73.76 (8)	C05—C06—C07	121.7 (3)
C24—C23—H23	120.20	N5—C39—H39D	109.50
O2—Zr1—N4	144.01 (7)	C05—C06—H06	119.10
C22-C23-H23	120.20	H39A—C39—H39D	141.10
01—Zr1—N4	78.48 (7)	C07—C06—H06	119.10
C02—C03—C04	119.5 (3)	H39B—C39—H39D	56.30
04—Zr1—N4	70.11 (8)	N4—C28—C29	122.4 (3)
C02-C03-H03	120.30	H39C—C39—H39D	56.30
O3—Zr1—N3	70.83 (8)	N4—C28—H28	118.80
C04—C03—H03	120.30	N5—C39—H39E	109.50
O2—Zr1—N3	78.43 (8)	C29—C28—H28	118.80
C06—C05—C04	119.7 (3)	H39A—C39—H39E	56.30
O1—Zr1—N3	143.18 (7)	C26—C25—C24	120.3 (3)
C06—C05—H05	120.20	H39B—C39—H39E	141.10
O4—Zr1—N3	75.62 (8)	C26—C25—H25	119.90
C04—C05—H05	120.20	H39C—C39—H39E	56.30
N4—Zr1—N3	124.47 (8)	C24—C25—H25	119.90
C14—C15—C16	122.3 (3)	H39D—C39—H39E	109.50
O3—Zr1—N2	78.36 (8)	O2—C17—C16	124.8 (3)
C14—C15—H15	118.90	N5—C39—H39F	109.50
02—Zr1—N2	70.41 (8)	O2—C17—C18	117.0 (2)
C16—C15—H15	118.90	H39A—C39—H39F	56.30
01—Zr1—N2	74.34 (7)	C16—C17—C18	118.1 (2)
C21—C20—C19	119.8 (3)	H39B—C39—H39F	56.30
04—Zr1—N2	144.35 (7)	C17—C16—C15	120.1 (3)
C21—C20—H20	120.10	H39C—C39—H39F	141.10
N4—Zr1—N2	139.70 (8)	C17—C16—H16	119.90
C19—C20—H20	120.10	H39D—C39—H39F	109.50
N3—Zr1—N2	70.24 (8)	C15—C16—H16	119.90
C23—C24—C25	122.0 (3)	H39E—C39—H39F	109.50
03—Zr1—N1	142.03 (7)	N1—C01—C02	122.4 (3)
C23—C24—H24	119.00	H63—O6—H62	105 (2)
O2—Zr1—N1	75.61 (7)		