Evaluation of oxine-type ligand coordination to zirconium (IV)

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Synopsis

$[Zr(C_9H_6NO)_4]\cdot(HCON(CH_3)_2)\cdot(H_2O)$, where (C_9H_6NO) = 8-hydroxy quinoline (oxH), was synthesized and characterized. This tetrakis-coordinated zirconium complex crystallized in the triclinic crystal system ($P\bar{1}$, Z=2) along with water and N,N'-dimethylformamide (DMF) solvate in the asymmetric unit. The metal atom is surrounded by four N,O-donating bidentate ox-ligands that are arranged around the metal centre to give a square antiprismatic coordination polyhedron with a small distortion towards a dodecahedral geometry. Crystal packing is stabilized by intermolecular interactions of adjacent oxine ring systems in neighbouring molecules, as well as hydrogen bonding of the aqua and DMF solvate molecules, linking the molecular entities into a supramolecular three-dimensional network.

Keywords
zirconium, tetrakis coordination, quinolinato.

Introduction

Zirconium metal complexes have received moderate amounts of interest from research groups worldwide. The general focus of research concerning zirconium as coordinated metal revolves around structural defining studies with particular reference to coordination geometries[1–5]. Other research reports focus heavily on the development of new complexes for industrial applications in catalysis, with particular interest in polymerization catalytic processes[6–10]. Although many literature sources discuss in detail the similarities and differences between zirconium and their aimed investigative comparative metal(s), few ever focus in such detail on the specific associated zirconium formation/coordination chemistry processes.

This study forms part of ongoing research initiatives investigating the coordination behaviour of O,O'- and N,O-bidentate ligands with zirconium(IV) and hafnium(IV) for possible separation of these two metals from base ore sources.

Experimental

General considerations

All reagents used for the synthesis and characterization were of analytical grade and were purchased from Sigma-Aldrich, South Africa. Reagents were used as received, without further purification.

The reaction solvent used throughout, N,N'-dimethyl formamide (DMF), was dried by passing through alumina. Infrared spectra were recorded on a Bruker Tensor 27 Standard System spectrophotometer with a laser range of 4000–370 cm^{-1}, coupled to a computer. All ^{1}H NMR spectra were obtained in C_6D_6 on a Bruker 300 MHz nuclear magnetic resonance spectrometer.

Crystallography

The X-ray intensity data was collected on a Bruker X8 ApexII 4K Kappa CCD area detector diffractometer, equipped with a graphite monochromator and MoKα fine-focus sealed tube (λ = 0.71069 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 SMART software package[11]. The collected frames were integrated using a narrow-frame integration algorithm and reduced with the Bruker SAINT-Plus and XPREP software packages[12] 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[13] and the structure was solved by the direct methods package SIR97[14] and refined using the WinGX[15] software incorporating SHELXL[16].

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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 obtained with the DIAMOND17 program with 50 per cent probability ellipsoids for all non-hydrogen atoms.

Synthesis of [Zr(ox)$_4$]·(DMF)·(H$_2$O)

$ZrCl_4$ (0.1003 g, 0.430 mmol) and oxH (0.1413 g, 0.863 mmol) were each separately dissolved in 10 ml DMF. These reagent solutions were heated to ca. 40.0 °C before the ligand solution was added dropwiseto the metal solution while stirring. The final reaction solution was left to stir at the elevated temperature for 30 minutes before removal of the reaction vessel to a fume hood and allowing to stand for crystallization under slow evaporation over several days. (Yield: mass ca. 51%); IR (ATR): ν_{CO} = 1572 cm^{-1}; UV/Vis: λ_{max} = 382 nm, ε = 157 cm^{-1}.M^{-1}; 1H 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).

Results and discussion

Crystal data and details of the data collection and refinement are shown in Table I and selected geometric parameters are given in Table II. The numbering scheme for this DMF-solvated complex in its unit cell is given in Figure 1. Hydrogen atoms and/or solvent molecules are omitted in some molecular presentations for clarity.

The title compound is composed of an eight-coordinated zirconium metal centre, in which the four N,O-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 2). The ox-ligands are arranged in an approximately equally spaced placement in the three-dimensional space around the metal centre, with alternating placement of the coordinating O and N atoms from the ligand, i.e. approaching an inversion-centred coordination geometry.

The bite angles of the bidentate ligands range from 70.11(1) to 70.84(1)°, with Zr—O bond distances averaging 2.106(2) Å and Zr—N bond distances averaging 2.420(2) Å. The opposite facing ox-ligands groups, however, do not 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

Table I

Crystallographic and refinement details for the title compound 1

Crystal formula	[Zr(ox)$_4$]·(DMF)·(H$_2$O)
Empirical formula	$C_{39}H_{32}N_5O_6Zr$
Formula weight (g.mol^{-1})	757.92
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions:	
a, b, c (Å)	11.342(5), 12.209(5), 12.538(5)
α, β, γ (°)	91.728(5), 103.419(5), 99.250(5)
Volume (Å^3), Z	1662.7(12), 2
Density (calculated) (g.cm^{-3})	1.514
Crystal morphology	cuboid
Crystal colour	orange
Crystal size (mm^3)	0.36 x 0.24 x 0.18
Absorption coefficient μ (mm^{-1})	0.389
F(000)	778
Theta range (°)	2.30 to 28.24
Index ranges	-14<=h<=14 -14<=k<=15 -16<=l<=15
Reflections collected, Independent Reflections, R_{int}	12828, 6786, 0.029
Completeness to 2υ (°, %)	27.00, 93.6
Max. and min. transmission	0.9333 and 0.8727
Data, restraints, parameters	6786, 2, 463
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R_1 = 0.0398 wR_2 = 0.0994
R indices (all data)	R_1 = 0.0478 wR_2 = 0.1053
Largest diff. peak and hole	0.9 and -0.588 e.Å^{-3}

Table II

Selected geometric parameters for [Zr(ox)$_4$]·(DMF)·(H$_2$O)

Selected bond lengths (Å)			
Zr—O$_1$	2.103(2)	Zr—N$_1$	2.424(2)
Zr—O$_2$	2.086(2)	Zr—N$_2$	2.415(2)
Zr—O$_3$	2.126(2)	Zr—N$_3$	2.411(2)
Zr—O$_4$	2.108(2)	Zr—N$_4$	2.431(2)
Selected bond angles (°)			
O$_1$—Zr—N$_1$	70.38(7)	O$_3$—Zr—N$_3$	70.18(7)
O$_2$—Zr—N$_2$	70.89(7)	O$_4$—Zr—N$_4$	70.27(7)

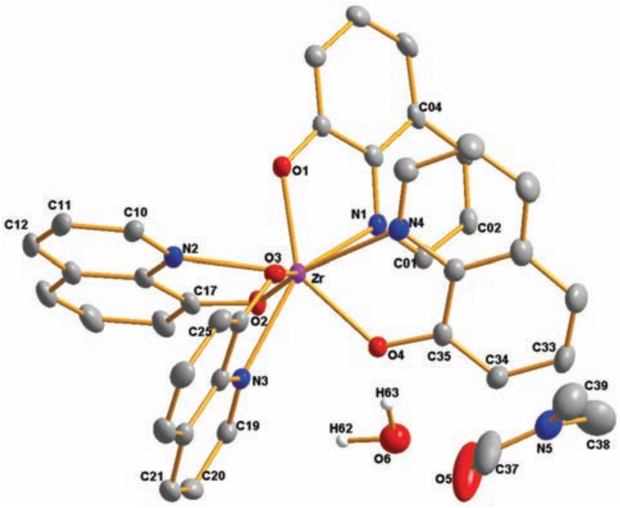

Figure 1—Representation of the [Zr(ox)$_4$]·(DMF)·(H$_2$O) compound, showing the numbering scheme and displacement ellipsoids (50% probability). The water and DMF solvate molecules are also shown. Hydrogen atoms are omitted for clarity. Ligand groups denoted by numbering of O and N atoms

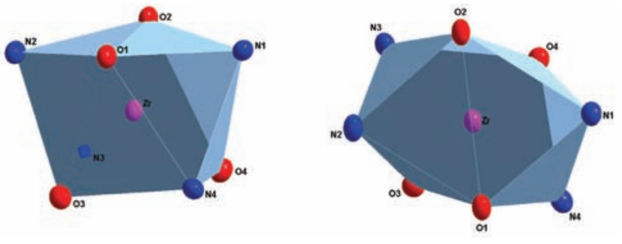

Figure 2—Illustration of square anti-prismatic coordination polyhedron as found for the title compound. (a) Side view showing a very small distortion towards dodecahedral geometry; (b) Top view showing staggered spacing of N,O-coordinating atoms

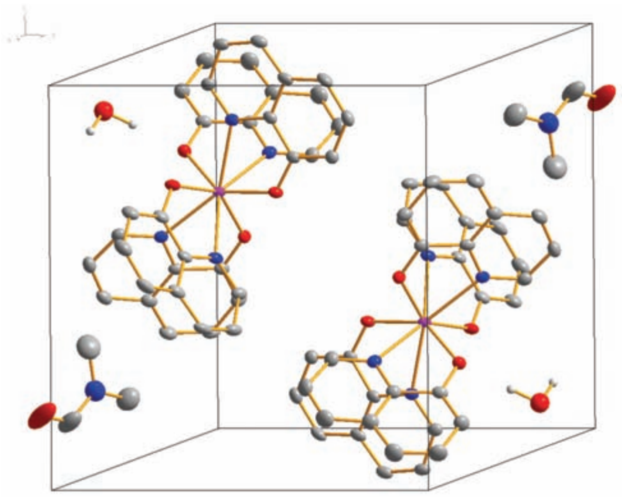

Figure 3—Graphical representation of molecular packing within the unit cell for the title compound. Most hydrogens omitted for clarity, 50% probability displacement ellipsoids

unit cell contains two molecular units consisting of a Zr-complex, a DMF solvent molecule, and a water molecule (See Figure 3).

The metallic portion of the molecular units is positioned at the centre of the unit cell and the solvent molecules span the corners of the unit cell. Within the unit cell, interactions between the metallic molecular groups are observed on the outermost carbons for the 3rd and 4th ligand groups on mirrored counterparts (Figure 4) within the unit cell: C_{25}—H_{25} to C_{28}(sym. code: 1-x, 1-y, 1-z) – 2.214 Å, 123.82°. Further interactions are observed (see Figure 5) between the O from the solvent water molecule to the O on the DMF carbonyl from a neighbouring unit cell – O_6—H_{62} to O_5 (sym. code: 2-x, -y, 2-z) – 1.653 Å, 163.61°.

π–π stacking is observed between ligand groups 1 and 3 with their mirror images from neighbouring unit cells (see Figure 6) as reported in Table III. These ligand groups span the outermost edge of the unit cell (as seen in Figure 3) and as such, every unit cell shows two of these sets of stacked ligand group partnerships. This π–π stacking show a complete overlay of quinoline ligand groups for each pair.

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 7). 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.

Lewis *et al.*[18] published the first $[Zr(ox)_4]$ structure in 1974. The only structural information given in this publication is the zirconium to coordinating ligand atom distances, which were compared to the identical distances for other metal complexes. As can be seen in Table IV, the distances they reported are near identical to the solvated structure discussed in this section. This indicates that solvent contributions to zirconium complex packing are negligible, if not non-existent.

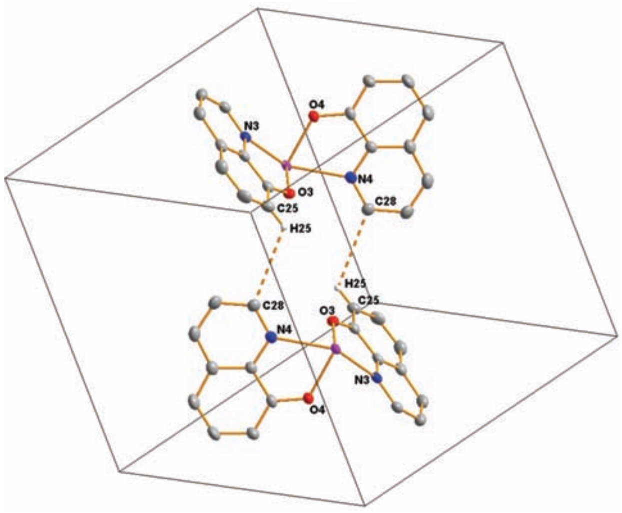

Figure 4—Graphical illustration of carbon-hydrogen interactions within the unit cell for the title compound. Only a portion of the unit cell is presented, hydrogens on metallic molecules omitted for clarity, 50% probability displacement ellipsoids

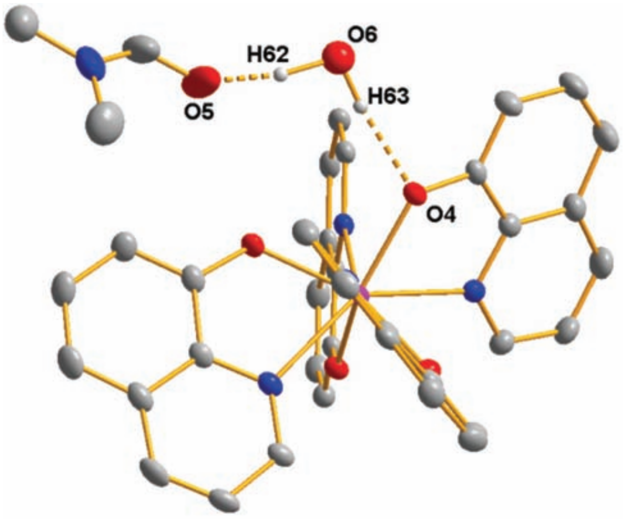

Figure 5—Graphical illustration of O—O hydrogen bonding interactions within the unit cell for the title compound. Only a portion of the unit cell is presented, hydrogens on metallic and DMF solvent molecules omitted for clarity, 50% probability displacement ellipsoids

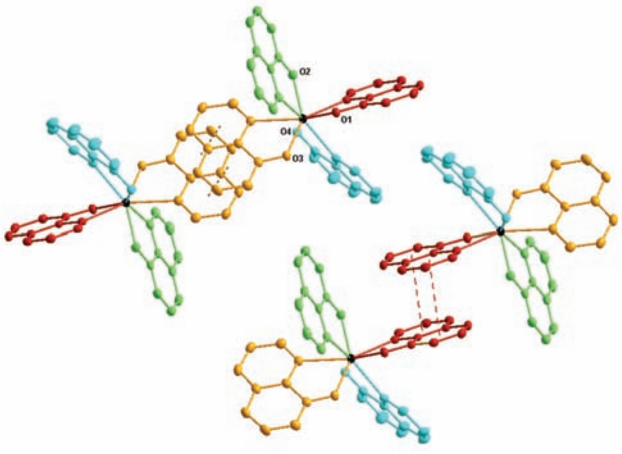

Figure 6—Graphical illustration of stacking between group 1 and 3 and their mirror image counterparts. Ligand groups identified by the number following the O or N coordinating ligand atom

Table III

-π-π stacking interactions in the title compound

	π-π stacking	
Ligand group	Interplanar distance (Å)	Centroid-to-centroid distance (Å)
1	3.136(2)	3.645(1)
3	3.271(7)	3.585(1)

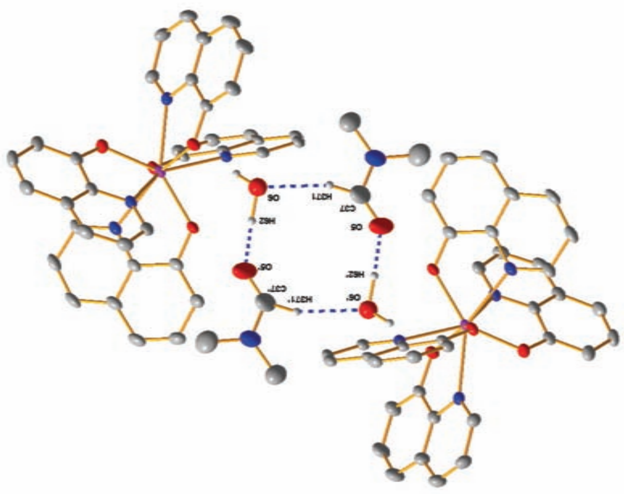

Figure 7—Illustration of hydrogen bonded molecular building blocks. Blue dotted lines represent hydrogen bonding, C_{37}—H_{37} to O_6 = 3.316 Å, 160.65 °; O_6—H_{62} to O_5 = 2.755 Å, 163.61°

Table IV

Geometrical data for $[Zr(ox)_4]\cdot(DMF)\cdot(H_2O)$ compared with the non-solvated moiety

Zr-coordination bond lengths (Å)		
Bond	Solvated	Non-solvated
Zr—O_1	2.106	2.106
Zr—N_1	2.42	2.405

Conclusion

The new zirconium crystal structure ($[Zr(ox)_4]\cdot(DMF)\cdot(H_2O)$) has been successfully characterized. Comparisons were drawn with similar structures from the literature and the structure from this study was found to conform well known theories of zirconium – bidentate ligand coordination crystallography. The zirconium structure discussed here also conforms to what is generally accepted as the blueprint of zirconium – bidentate type ligand coordination geometry, namely the square antiprismatic coordination mode as well as general structural characteristics such as bond lengths and bonding bite angles. Very few structures of this type (ox) of bidentate ligand organometallic structures are known in the literature though, leaving large scope for future studies on the same ligands and derivatives.

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