A Comparative Study in Metalloorganic Structural Chemistry: the X-ray Crystal Structures of [HB{C3N2H-3,5-(CH3)2}3Zr(OC6H5)3] and [HB{C3N2H-3,5-(CH3)2}3Zr(OC6H4-2-F)3]

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Abstract – The complexes $[ZrL(OC_6H_4-2-X)_3]$ ($L^- = HB\{3,5-Me_2C_3HN_2\}_3^-$, X = H (1), F (2)) are compared structurally with analogous precedents. Whilst the $\{LZr\}^{3+}$ moiety possesses formal or pseudo- $C_{3\nu}$ symmetry in both cases, the phenoxide ligands adopt a wide variety of attitudes thereto, which appear to be driven mainly by packing forces.

Keywords – hydridotris(dimethylpyrazolyl)borate, zirconium, crystal structure, fluorophenoxide ligands, X-ray crystal structure, disorder.

Introduction

Since its discovery in the mid-1960s [1], the ligand L (L⁻ = HB {3,5-Me₂C₃HN₂}₃) has been of interest due to its ability to direct pseudo-octahedral coordination about a metal. There are many examples of this tendency [2]. Of only a few known L complexes with Zr and phenoxide ligands produced, three have been characterised structurally up until the present, namely [ZrL(OC₆H₄-4-NO₂)₃] [3], [ZrL(OC₆H₃-2,6-Me₂)₃] and [ZrLCl(OC₆H₃-2,6-Me₂)₂] [4] (3, 4 and 5 respectively). These do indeed possess a near-octahedral coordination geometry, but in all cases the phenoxide ligand seems to be oriented into the cleft between the pyrazolyl rings of the L ligand. This might be thought to be due to some weak π -stacking interactions with the L dimethylpyrazolyl rings.

We were prompted by some recent developments in supramolecular design to consider the $\{ZrL\}^{3+}$ moiety as a flexible 'cornerstone' building block for supramolecular assemblies also containing phenoxide components. The tendency of the L ligand to demand an octahedral coordination geometry at the chelated metal results in the other ligands adopting orientations which are approximately orthogonal. However, if a large degree of phenoxide deviation into the interpyrazolyl cleft is endemic to these systems, this might mitigate against the use of phenoxide linkers to these supramolecular 'cornerstones'. We sought more crystallographic examples of $[ZrL(phenoxy)_3]$ complexes, aiming to synthesise and characterise structurally $[ZrL(OC_6H_4-2-X)_3]X = H(1), F(2)$, both of which contain sterically undemanding phenoxide ligands.

Results and Discussion

Complexes 1 and 2 were acquired by the treatment of ZrLCl₃ with 3 equivalents of the appropriate phenol and then 3 equivalents of triethylamine. Crystals were obtained by slow evaporation of hexane/dichloromethane solutions.

The structures of 1 and 2 are depicted in Figs. 1 and 2 respectively, their rings being labelled consistently for comparison. Salient structural details are given in Table 1, and a summary of experimental details is shown in Table 2.

Table 1.

Summary of Sciected Sond rengins (ii) and angles () for completes i							
	1	2	3	4	5		
Zr-O	1.9734(17)	1.9538(18)	1.978(1)	1.973(4)	1.949(3)		
	1.9670(20)	1.9755(20)	1.978(1)	1.978(4)	1.948(3)		
	1.9433(19)	1.9796(19)	1.978(1)	1.967(3)	-		
Zr-N	2.3368(21)	2.3220(24)	2.300(2)	2.327(4)	2.317(4)		
	2.3290(25)	2.3243(23)	2.300(2)	2.342(4)	2.334(4)		
	2.3148(22)	2.2996(25)	2.300(2)	2.333(5)	2.289(4)		
Zr-O-C	155.19(17)	174.4(2)	161.4(1)	176.8(4)	172.3(3)		
	161.35(18)	159.72(19)	161.4(1)	173.5(4)	176.8(3)		
	169.16(19)	158.45(19)	161.4(1)	174.9(3)	-		
BZr-O-C	147.1(4)	-16.8(18)	12.9(8)	$-53(6)^{a}$	33(2) ^a		
	3.0(6)	164.7(5)	12.9(8)	$72(2)^{a}$	$46(3)^{a}$		
	-5.4(10)	17.3(6)	12.9(8)	$-31(3)^{a}$	-		
twist angle ^b	36.6(1)	20.6(1)	6.3(2)	16.8(3)	13.6(1)		
	2.3(2)	26.8(2)	6.3(2)	16.8(3)	16.6(2)		
	17.9(1)	11.8(2)	6.3(2)	12.8(2)	-		

Summary of selected bond lengths (Å) and angles (°) for complexes 1 - 5.

^a The large uncertainties arise from near-linear Zr-O-C angles. ^b Defined as the angle between the planes of the 6 phenyl C atoms and the 7 {N₂C₅} atoms of the *trans*-pyrazolyl ring.



Fig. 1. Two views of [ZrL(OC₆H₅)₃] (1); shown are a general view and a view along the B-Zr axis, respectively. The H atoms are omitted for clarity, and anisotropic thermal ellipsoids are depicted [5] at the 50% level.

Both of the new structures 1 and 2 possess phenoxide ligands adopting a novel orientation, as might be seen from Table 1 which compares structures 1 - 5. If the torsion angle B...Zr-O-C is measured for each phenoxide ligand, an angle of zero might be interpreted as the

phenoxide being directly oriented into the interpyrazolyl cleft. The torsion angles of published precedents 3-5 are all are nearer to zero than the 180° which would indicate an orientation away from the interpyrazolyl cleft: in each case they are oriented into the cleft. Both 1 and 2 seem to break this pattern in that both possess two phenoxide ligands oriented into the cleft, and one oriented away (torsion angles of 147.1(4)° and 164.7(5)° respectively). This orientation away from the interpyrazolyl cleft allows a greater scope for the twisting of the phenoxide ring out of the plane of the *trans*- oriented pyrazolyl ring. This twisting (angles of $36.6(1)^{\circ}$ and $26.8(2)^{\circ}$ respectively) is unprecedentedly large. Both structures 1 and 2 show a larger variation in Zr-O-C angles between chemically equivalent phenoxides than do 3-5. In 2, this difference is almost 16°, which is a situation previously seen in [Zr{HB(N₂C₃H₃)₃}(C₅H₅)(OC₆H₄-2-C₆H₅)₂] [6] or [{(4-Cl-C₆H₄O)Zr(C₅H₅)₂}₂O] [7].



Fig. 2. Two views of [ZrL(OC₆H₄-2-F)₃] (2); shown are a general view and a view along the B-Zr axis, respectively. The minor occupancy site F1' and all H atoms are omitted for clarity, and anisotropic thermal ellipsoids are depicted [5] at the 50% level.

Experimental

Samples of 1 and 2 were prepared according to previously reported procedures [3] and recrystallised from dichloromethane-hexane mixtures by slow evaporation, affording colourless needle-shaped crystals in both cases. Data were collected by the EPSRC National Crystallography Service at the University of Southampton using previously described procedures [8], [9]. Metal atom positions were estimated using Patterson methods [10]. All remaining non-H atom positions were obtained through subsequent Fourier syntheses interspersed with occasional least-squares refinements [11] which were by full-matrix least-squares on F² data. To achieve the converged model all non-H atoms were refined anisotropically, and all H atoms were refined at calculated idealised positions ($CH_3 = 0.98$ Å, CH = 0.95Å, BH = 1.00Å) being assigned group-specific common refined isotropic displacement parameters. In 1, five low-angle reflections with $F_{0}^{2} \ll F_{c}^{2}$ were suppressed. There was slight disorder in the structure of 2, with a 12% F occupancy on C42. Upon convergence, H-atom displacement parameters for 1 and 2 respectively were 0.08281(297) and 0.06216(283)Å² (CH₃); 0.06005(245) and 0.04058(244)Å² (CH); and 0.01690(622) and 0.02649(790)Å² (BH). Molecular graphics were generated using ORTEP [5], [12].

Conclusions

The phenoxide ligands in 1 and 2 did not conform to the previously observed tendency to be oriented into the interpyrazolyl cleft of the L ligand. It seems that the orientations of such phenoxide ligands can be rather variable, and likely dictated by intermolecular packing effects as much as steric or electronic intramolecular effects. These results add weight to the proposition that the $\{ZrL\}^{3+}$ moiety might indeed be suitable as a 'cornerstone' building block for supramolecular assemblies also containing phenoxide components.

Table 2.

	1	2		1	2
М	667.7	721.7	Crystal habit	Needle	Needle
System	Monoclinic	Orthorhombic	T/K	150	120
Space group (no.)	$P2_1/n$ (14)	$P_{\rm na}2_1$ (33)	μ/mm^{-1}	0.38	0.39
Z	4	4	$\rho/g \text{ cm}^{-3}$	1.353	1.446
a/Å	8.0578(2)	20.9823(42)	Data measured	38317	30262
b/Å	20.4916(7)	19.6979(39)	Unique data	7633	4287
c/Å	19.8719(8)	8.0203(16)	$R_{\rm int}(\%)$	7.47	5.56
ß/°	92.6715(12)	90	$R\sigma(\%)$	9.15	5.83
$V/Å^3$	3277.6(2)	3314.85(11)	$R[I > 2\sigma(I)](\%)$	4.80	3.69
Crystal size/mm ³	0.3×0.04×0.04	0.3×0.1×0.1	wR_2 (all data)(%)	11.45	8.98

Crystal data and experimental details for complexes 1 and 2.

Acklowledgments

We are grateful to the EPSRC National Crystallography Service at Southampton, UK and its Chemical Database Service at Daresbury, UK.

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