Isolation and characterisation of transition and main group metal complexes supported by hydrogen-bonded zwitterionic polyphenolic ligands[†]

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Reaction of $Zr(O'Pr)_4$ or $Sn[N(SiMe_3)_2]_2$ with the tris-phenol amine ligand $H_3L^{(Me/Me)}$ results in the formation of zirconium or tin complexes containing the new C_3 -symmetric zwitterionic ammonium-trisphenolate ligand HL^{2-} , while increasing the steric bulk of the ligand results in the isolation of a zirconium complex containing the known trianionic ligand L^{3-} .

Trianionic, chelating amido and/or alkoxo ligands, which are capable of providing a range of stable steric and electronic environments for catalytically active metal centres, have been the subject of considerable research for some time, not least for their ability to bind metal centres in a C_3 -symmetric fashion.¹

We and others have recently been exploring the rich chemistry of amine trisphenolate ligands, **1**, and their use in the stabilisation of highly reactive, Lewis acidic $Ti^{(IV)}$ metal centres.^{2,3} For example, Kol *et al*.have shown that reaction of ligands **1a** and **1b** with one equivalent of titanium tetra(*iso*-propoxide) yields the corresponding monomeric [L]Ti(O'Pr) complexes **2a** and **2b**.^{3a} This is in contrast to the oligomeric systems formed using other tri-ol ligands.^{1f} We now report on complexes of **1** with both zirconium and tin which exhibit a new coordination mode for ligands of this type, which potentially increases their utility as scaffolds for reactive metal centres and provides a highly unusual hydrogen bonding environment.

Treatment of ligand **1a** with one equivalent of $[Zr(O'Pr)_4-(HO'Pr)]$ in toluene under ambient conditions yields the colourless complex $(HL^{(Me/Me)})_2Zr$, **3a**, whereas, a similar reaction with ligand **1b** yields the pale yellow complex $(L^{(Bu/Bu)})Zr(O'Pr)$, **3b** (Scheme 1).† Both complexes are readily soluble in a range of aromatic, and aliphatic solvents and can be crystallised from toluene solutions. In the case of complex **3a** these crystallisation which are gradually lost on standing. Complex **3b** shows some stability to hydrolysis,



† Electronic supplementary information (ESI) available: full synthetic and spectroscopic details. See http://www.rsc.org/suppdata/cc/b3/b303618a/ although small amounts of an insoluble white precipitate are formed over a period of hours after exposure of solutions to atmospheric moisture.

An X-ray crystallographic study[‡] reveals **3a** to be an unprecedented C_3 -symmetric zwitterionic complex, in which two formally trianionic [L^(Me/Me)] ligands are bound to a central 6-coordinate, octahedral, zirconium centre, resulting in a formal dianionic charge at the metal centre (Fig. 1). This charge is



Fig. 1 ORTEP (50% probability ellipsoids) diagrams of **3a**. Top: A view down the N–Zr–N vector showing the C_3 -symmetry of the complex. Bottom: A side view of **3a** showing H-bonding interactions. Selected bond lengths (Å): Zr(1)–O(1) 2.058(2), Zr(1)–O(2) 2.064(2), Zr(1)–O(3) 2.057(2), Zr(1)–N(1) 3.617(2), Zr(1)–H(1) 2.688(3), N(1)–H(1) 0.87(3), N(1)–O(1) 2.868(2) (O(1)–H(1) 2.21(3)), N(1)–O(2) 2.920(2) (O(2)–H(1) 2.29(2)), N(1)–O(3) 2.834(2) (O(3)–H(1) 2.15(3)); Bond angles (°): Zr(1)–O(1)–C(16) 157.23(15), Zr(1)–O(2)–C(26) 154.51(15), Zr(1)–O(3)–C(36) 160.04(15), N(1)–H(1)–O(1) 130.21(19), N(1)–H(1)–O(2) 129.51(19), N(1)–H(1)–O(3) 133.39(19). Toluene and remaining hydrogen atoms have been omitted for clarity.

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balanced by the protonation of both nitrogen atoms to form acidic ($\delta_{\rm H} = 11.8$ ppm) cationic ammonium centres, which are involved in unusual trifurcated N–H…O₃ hydrogen bonding. Overall this arrangement represents a new binding mode for these ligands. Compound **3a** can be considered a 'truly zwitterionic' complex, as the formal charge separation cannot be modified by resonance of π -electrons.⁴

In contrast, the solid state molecular structure of 3b[‡] (as represented in Scheme 1) is very similar to analogous titanium complexes.^{2,3a} Comparison of **3a** with **3b** highlights a number of structural differences between the two bonding modes. The Zr metal centre in **3a** is displaced out of the plane of the oxygen atoms by 1.255 Å, compared to only 0.365 Å for the same parameter in **3b**. Furthermore, the Zr–O bonds in **3b**, are significantly shorter than the corresponding Zr–O bonds in **3a** (av. Zr–O 1.95 and 2.06Å, for **3b** and **3a** respectively). These features are consistent with significant steric repulsion between both the two ligands and the NH unit and the metal centre in **3a**.

In solution at room temperature, ¹H NMR spectra are consistent with the C_3 -symmetry of **3a** and **3b** being maintained, as indicated in both cases by the presence of an AB spin system for the CH₂ protons.^{3a}

These structural observations can be interpreted as follows. In the case of tetravalent metals, the formation of HL^{2-} complexes is dependant on two factors. First, the metal centre must be large enough to accommodate the N–H···O₃ structural motif without imposing repulsive NH····M interactions.⁵ Second, the steric demands of the ligand must not inhibit formation of the a stable metal HL^{2-} complex. Hence, we predict that Ti is too small to allow HL^{2-} coordination and L^{3-} complexes will always result.^{2,3} However, in the case of larger tetravalent metals, (*e.g.*, Zr and Hf), coordination of HL^{2-} is possible, but *only* provided that the ligand is sufficiently small (*e.g.*, *ortho*-methyl-substituted) to allow two ligands to approach the metal centre.

These results inspired us to explore other metal complexes in order to test the generality of the new HL^{2-} coordination mode. Thus, we speculated that a large, divalent metal such as $Sn^{(II)}$ should favour the zwitterionic bonding mode observed in **3a**. Reaction of one equivalent of $Sn[N(SiMe_3)_2]_2$ and **1a** yields the colourless complex **4**. The solid state molecular structure of $HL^{(Me/Me)}Sn$, **4**,‡ (Fig. 2) shows a monomeric complex with a very similar metal–ligand bonding motif to that found in **3a**. Indeed, the similarity between **3a** and **4** in terms of key structural parameters [*e.g.*, M–O distances: 2.064(2) and 2.081(2) Å. N–H····M distances: 2.688(3) and 2.689(4) Å in **3a** and **4**, respectively] suggests that a balance between attractive N–H···O and repulsive N–H···M interactions has been reached and that these impose an unusual rigidity on a normally flexible ligand. The monomeric nature of **4** is noteworthy considering

Fig. 2 ORTEP (50% probability ellipsoids) diagram of 4. Selected bond lengths/Å: Sn(1)-O(1) 2.081(2), Sn(1)-N(1) 3.631(3), Sn(1)-H(1N) 2.689(4), N(1)-H(1N) 0.97(4), O(1)-N(1) 2.893(3), (O(1)-H(1N) 2.17(2)); Bond angles/°:Sn(1)-O(1)-C(11) 136.25(16), N(1)-H(1N)-O(1) 130.8(8). Toluene and hydrogen atoms omitted for clarity.

the tendency of Sn^(II) complexes containing *tris*-alkoxide ligands to form polymetallic clusters.⁶ As with complexes **3**, the three arms of the trisphenolate ligand in **4**, are orientated in a C_3 -symmetric propeller arrangement in the solid state, but unlike **3a**, the ¹H NMR spectrum of **4** shows only a single resonance for the CH₂ protons, indicating that rapid inversion of the structure occurs at room temperature. As a consequence of chelation by HL²⁻, the pyramidal geometry at Sn^(II) is reinforced, and the metal centre lies out of the plane of the three phenolic oxygen atoms by 1.259 Å. In spite of this apparent nakedness, complex **4** exhibits considerable stability and resistance to hydrolysis. For example, on addition of D₂O to a CDCl₃ solution of **4** the NH unit ($\delta = 10.7$ ppm) disappears rapidly but there is no further change to the NMR (¹H, ¹³C and ¹¹⁹Sn) spectra even after several weeks.

In conclusion, the new zwitterionic coordination mode of HL^{2-} observed in complexes **3a** and **4** appears to be a general feature of the metal chemistry of H_3L ligands which is dictated by the size of the metal centre and/or ligand-ligand repulsions.

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Notes and references

‡ *Crystal data* were collected on a Nonius KappaCCD diffractometer using Mo–Kα radiation ($\lambda = 0.71073$ Å), and all structures were solved by direct methods and refined on all F^2 data using the SHELX-97 suite of programs.⁷ Hydrogen atoms not involved in hydrogen bonding included in idealised positions and refined using a riding model.

3a: $C_{70}H_{81}N_2O_6Zr$, M = 1137.59, yellow blocks, crystal size $0.25 \times 0.20 \times 0.06$ mm, Triclinic, space group $P\bar{1}$, a = 11.338(3) Å, b = 11.768(3) Å, c = 12.886(4) Å, $\alpha = 82.058(1)^\circ$, $\beta = 83.645(1)^\circ$, $\gamma = 73.389(1)^\circ$, U = 1627.17(8) Å³, Z = 1, $D_c = 1.161$ g cm⁻³, T = 150(2) K, 19089 reflections measured, 7403 unique reflections ($2\theta_{max} = 27.52^\circ$, $R_{int} = 0.0290$) against 384 parameters gave $R_I = 0.0510$ and $wR_2 = 0.1392$ [$I > 2\sigma(I)$] ($R_1 = 0.0583$ and $wR_2 = 0.1462$ for all data). CCDC 207513.

3b: $C_{54}H_{87}N_1O_4Zr$, M = 905.47, colourless blocks, crystal size $0.25 \times 0.20 \times 0.17$ mm, Tetragonal, space group $P4_3$, a = b = 14.581(1) Å, c = 25.419(1) Å, U = 5404.27(7) Å³, Z = 4, $D_c = 1.113$ g cm⁻³, T = 150(2) K, 100213 reflections measured, 12336 unique reflections ($2\theta_{max} = 27.48^{\circ}$, $R_{int} = 0.0486$) against 768 parameters, with 55 restraints gave $R_1 = 0.0363$ and $wR_2 = 0.0901$ [$I > 2\sigma(I)$] ($R_I = 0.0450$ and $wR_2 = 0.0956$ for all data). CCDC 207514.

4: $C_{34}H_{39}N_1O_3Sn$, M = 628.35, colourless blocks, crystal size $0.32 \times 0.20 \times 0.16$ mm, Trigonal, space group $R\overline{3}$, a = b = 14.0560(4) Å, c = 25.9860(7) Å, $\gamma = 120^\circ$, U = 4446.2(2) Å³, Z = 6, $D_c = 1.408$ g cm⁻³, T = 150(2) K, 13702 reflections measured, 2246 unique reflections ($2\theta_{max} = 27.46^\circ$, *R*int = 0.0759) against 130 parameters gave $R_1 = 0.0354$ and $wR_2 = 0.0740$ [$I > 2\sigma(I)$] ($R_I = 0.0594$ and $wR_2 = 0.0812$ for all data). CCDC 207515

See http://www.rsc.org/suppdata/cc/b3/b303618a/ for crystallographic data in CIF format.

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