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Zirconium complexes of amino(polyphenolic) ligands and their hydrolytic stability

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Abstract

Three amino(polyphenolic) ligands, N,N'-bis(5-*tert*-butyl-2-hydroxybenzyl)-1,2-diaminoethane **1**, tris(5-*tert*-butyl-2-hydroxy-3-methyl-benzyl)amine **3**, its 3-chloro analogue **4** and their Zr^{IV} complexes have been synthesised. The crystal structure of the Zr^{IV} complex of tris (5-*tert*-butyl-3-chloro-2-hydroxybenzyl)amine, shows this to be $[Zr(4-2H)_2]$ in which both ligands exists in a zwitterionic form with one alkylammonium and three phenolate groups. The complexes are stable in a two phase, chloroform/water, system at high pH, but the zirco-nium is stripped at pH < 2.5. The pH value needed to strip 50% of the Zr^{IV} from the complex [Zr(1-4H)] of the tetraphenolic ligand is ~2.0 whilst the complexes $[Zr(3-2H)_2]$ and $[Zr(4-2H)_2]$ of the triphenolic ligands are slightly more stable with $pH_{1/2}$ values of ~1.4. We were unable to use the ligands to extract zirconium from low pH aqueous zirconium oxychloride solutions into an organic phase under a variety of conditions.

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The high affinity of Zr^{IV} and Hf^{IV} for anionic oxygen has led us to consider polyphenolic ligands as solvent extractants to recover zirconium from aqueous solution. The only reports in the literature recording the use of phenols in zirconium extraction involve phenolic oximes similar to those used commercially for copper recovery [1,2].

The potentially sexadentate tetrakis(2-hydroxybenzyl)-1,2-diaminoethane ligands have been reported by Hefele et al. [3] to complex Ti^{IV}, V^{IV}, Mn^{IV} and Sn^{IV}. The crystal structure of a V^{IV} complex has also been reported [4]. Other metal complexes of this ligand type have included Zn^{II} [5], Fe^{III} [6], and Ga^{III} [7]. Tetraphenols of this type have been shown to extract gallium from strongly basic solutions containing aluminates [8], giving high selectivity for recovery of Ga^{III} over Al^{III}. In this paper we report the formation of the Zr^{IV} complex of N, N, N', N'-tetrakis(4-*tert*-butyl-2-hydroxybenzyl)-1,2-diaminoethane **1**.



The triphenol **2** has been shown to give a 2:1 complex with Zr^{IV} in which the ligand exists in a zwitterionic form [9], with phenolate groups defining a pseudo octahedral Zr^{IV} complex and the two bridgehead nitrogens being

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protonated to give an overall neutral complex $[Zr(2-2H)_2]$. The reported air-stability of this complex was of interest to us in relation to the hydrolytic stability of this type of complex and whether ligands of this type, in particular 3 and 4, would be useful extractants for zirconium.



Chloro-substitution of the triphenol (as in 4) was undertaken to investigate the effect of altering the pK_a of the ligand. The 4-*tert*-butyl substituted variants of the triphenol, 3 and 4, and the tetraphenol 1 were prepared as candidate extractants to enhance solubility in non-polar and/or hydrocarbon solvents.

In order to operate efficiently as 'pH-swing' extractants for Zr^{IV} , loading and stripping, e.g.,

$$\begin{split} L_{\text{org}} + Zr^{4+} &\rightleftharpoons \left[Zr(L\text{-}4H)\right]_{\text{org}} + 4H^+ \ (L = 1) \\ 2L_{\text{org}} + Zr^{4+} &\rightleftharpoons \left[Zr(L\text{-}2H)_2\right]_{\text{org}} + 4H^+ \ (L = 3 \text{ or } 4) \end{split}$$

must occur over a pH-range to allow the ligand to be fully loaded at a pH lower than that at which insoluble zirconium(IV) oxy/hydroxides precipitate from aqueous solution [10], and be fully stripped at a low pH which is conveniently accessible with hydrochloride or similar acids.

Ligand 1 was synthesised by a modified literature procedure [8] outlined in Scheme 1. 1,2-Diaminoethane was reacted with 4-*tert*-butlylsalicylaldehyde to give the double Schiffs' base which was subsequently reduced with sodium borohydride to give bis-phenol 5 in 93% yield. Reaction of 5 with 2-bromomethyl-4-*tert*-butylphenyacetate followed by removal of the acetate groups gave the desired product 1 in 35% yield.

Ligands 3 and 4 were synthesised via a modified literature procedure [11] (Scheme 2) in which either 4-*tert*butyl-2-methylphenol or 4-*tert*-butyl-2-chlorophenol is reacted with hexamethylenetetramine in the presence of a catalytic amount of *p*-toluenesulfonic acid. After chromatography, ligands 3 and 4 were isolated in 76% and 66% yield, respectively.

Compound 4 was recrystalised from acetonitrile to yield crystals suitable for X-ray structure determination (Fig. 1). The free ligand, in contrast to its Zr^{IV} complex (*vide infra*), does not exist in its zwitterionic form. It displays an *anti*-conformation of the phenolic groups in relation to the bridgehead amine. An intramolecular H-bond (1.86 Å) exists between one of the phenolic protons and the nitrogen atom. A second phenolic proton forms an intermolecular H-bond (2.07 Å), linking molecules in a 1D chain through the crystal structure.

The complexes were synthesised by reacting chloroform solutions of the ligand and zirconium(IV) isopropoxide in the appropriate ligand to metal ratio. Water was added to hydrolyse and extract any unreacted zirconium isopropoxide allowing the chloroform solution of the complex to be separated, dried over magnesium sulphate, and evaporated. The proposed formula for each of the complexes in supported by high resolution FAB mass spectrometry.

The complex [Zr(1-4H)] displays a lack of rotational flexibility in the ¹H NMR spectrum at 25 °C in chloroform. Severe broadening of all signals is observed, especially for the benzylic protons which become non-equivalent. Two



Scheme 1.



Fig. 1. Crystal structure of 4 (50% probability ellipsoids) showing H-bonding interactions. The remaining hydrogen atoms have been omitted for clarity.

signals are also observed for the aromatic protons that are *ortho* to the phenolic oxygen. The spectrum sharpens significantly at 80 °C in DMSO- d_6 , but the signals for the benzylic protons fail to coalesce. Apart from the signals relating to the *tert*-butyl groups, the ¹³C NMR spectrum could not be assigned as it consisted of severely broadened signals due to restricted rotation of the bonds.

The ¹H NMR spectrum of $[Zr(3-2H)_2]$ is similar to that reported [9] for the zirconium complex of **2**. The ammonium proton appears as a broad signal at δ 11.8. The benzylic CH₂ protons appear as an AB spin system which is attributed [9] to the C_3 -symmetry observed in the solid state being retained in solution, with slow interconversion of structures.

The crystal structure of $[Zr(4-2H)_2]$, crystallised from benzene, is shown in Fig. 2. The complex is isostructural with the reported [9] $[Zr(2-2H)_2]$ complex, displaying the same pseudo C_3 -symmetric coordination mode. Two trianionic ligands are bound to the Zr^{IV} metal centre in an octahedral arrangement of the phenolic oxygen donors. Charge neutrality is obtained by protonation of the two bridgehead amines, such that the ligands exist in a zwitterionic form. As for $[Zr(2-2H)_2]$, the same trifurcated N–H···O₃ hydrogen bonding between the ammonium proton and the phenolic oxygens is observed. The average Zr–O bond length, 2.0457(11) Å, is the same as that, 2.059(9) Å, in the complex of the dimethyl-substituted ligand **2** [9].



Fig. 2. Crystal structure of $[Zr(4-2H)_2]$ (50% probability ellipsoids) showing H-bonding interactions. The Zr^{IV} atom lies on an inversion centre. Selected bond lengths (Å): Zr1–O11 2.0446(11), Zr1–O12 2.0424(11), Zr1–O13 2.0501(11), N1–H1 0.93(0), O11–H1 2.17(9), O12–H1 2.17(3), O13–H1 2.06(9). The benzene solvent molecules and the remaining hydrogen atoms have been omitted for clarity.

Despite the similarity between the crystal structures of $[Zr(2-2H)_2]$ and $[Zr(4-2H)_2]$, the ¹H NMR spectrum of $[Zr(4-2H)_2]$ is much more complicated (and severely broadened) compared to that of $[Zr(2-2H)_2]$. This suggests that in solution the ligands of $[Zr(4-2H)_2]$ can exist in a number of conformations. While heating the solution began to sharpen the signals slightly, even at 110 °C in DMSO- d_6 the different conformations were not inter-converting rapidly enough on the NMR-time scale to see only one species. Likewise, the ¹³C NMR spectrum could not be assigned.

In order to assess the viability of using ligands of the types 1, 3 and 4 as pH-swing extractants for Zr^{IV} we first undertook stripping of the neutral complexes,

$$\begin{split} \left[Zr(L-4H) \right]_{\text{org}} + 2HCl + H_2O &\rightleftharpoons L_{\text{org}} + ZrOCl_2 \ (L=1) \\ \left[Zr(L-2H)_2 \right]_{\text{org}} + 2HCl + H_2O &\rightleftharpoons 2L_{\text{org}} + ZrOCl_2 \ (L=3 \text{ or } 4) \end{split}$$

to establish the $pH_{1/2}$ values (the pH for 50% loading) for the ligands. We judged that a viable system should have a $pH_{1/2}$ significantly less than 2.8 because we had found that aqueous zirconium(IV) oxychloride solutions become cloudy at a pH of above 2.8.

The $pH_{1/2}$ values for stripping with aqueous HCl were determined by stirring aliquots of a 0.005 M solution of the complex in chloroform with aqueous solutions at various pH values which had a constant (0.8 M) chloride concentration for 16 hours.

The stripping curve for the tetraphenolate complex [Zr(1-4H)] is less steep than that of the bistriphenolates and has a $pH_{1/2}$ of ca. 2.0 (see Fig. 3). The shallower



Fig. 3. The pH dependence of zirconium stripping of 0.005 M chloroform solutions of $[Zr(1-4H)] \blacklozenge$, $[Zr(3-2H)_2] \blacksquare$ and $[Zr(4-2H)_2] \blacktriangle$ by aqueous HCl.

S-curve may be a consequence of regeneration of the free ligand requiring four independent reprotonation equilibria for 1 compared with only two to regenerate 3 or 4. A pH_{1/2} of ca. 2.0 for 1 suggests that recovery of Zr^{IV} could not be accomplished efficiently from aqueous solutions which are sufficiently acidic (pH < 2.8, *vide supra*) to prevent hydroly-sis/precipitation of Zr^{IV} compounds.

Stripping of the triphenolate complex of ligand 3, [Zr(3-2H)₂], into 0.8 M aqueous chloride gave a pH_{1/2} of \approx 1.4, close to a value which could provide a practical recovery process, provided that loading/stripping S-curves are steep and that loading behaviour mirrors that shown by the stripping experiments. On this basis we undertook the synthesis of ligand 4 in the expectation that the incorporation of the chloro-substituents would increase the acidity of the phenolic groups (the pK_a of 4-*tert*-butyl-2-chlorophenol is 8.58 [12] versus 10.59 for 4-*tert*-butyl-2-methylphenol [13]) and thus increase its strength as a pH-swing extractant. In practice, the strength of the tri-chloro-substituted ligand 4 (pH_{1/2} for Zr^{IV} stripping of \approx 1.4) is very similar to that of the tri-methyl-substituted analogue 3.

When extraction experiments in which 0.01 M chloroform solutions of these ligands were contacted with 0.005 M zirconium oxychloride solutions at pH values from 0 to 2.5 for 16 hours, no extraction of zirconium was detected. To determine whether high chloride concentration could promote zirconium extraction the experiment was repeated for ligand **3** with zirconium oxychloride solutions containing 0.8 M chloride ion. Again no zirconium uptake was detected in the organic phase.

As the kinetics of complex formation can be an important factor in extraction processes, an experiment was performed in which a 0.01 M chlorobenzene solution of ligand **3** was intimately stirred with a 0.005 M aqueous solution of zirconium oxychloride at 60 °C. Even after 5 days, no zirconium was detected in the organic phase. The failure of these ligands to extract zirconium could be attributed to the lack of an available mechanism for the zirconium species present in aqueous solution in the pH ranges studied to react with the ligand at the interface to give the Zr^{IV} complex. The fact that no zirconium is extracted also indicates that ZrO^{2+} is also not extracted by these ligands.

In conclusion, we have been able to synthesise Zr^{IV} complexes of both amino tetraphenolate and amino triphenolate ligands. These complexes are stable in a two phase aqueous system at high pH while the zirconium can be stripped from the complex at low pH. The present ligands were unsuitable for the recovery of zirconium by solvent extraction from aqueous zirconium(IV) oxychloride solutions.

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Appendix A. Supplementary material

Cryatallographic data has been deposited at the Cambridge Crystallographic Data Centre with the Deposition Numbers 646827 and 646828. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http:// www.ccdc.cam.ac.uk). Experimental data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.06.004.

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