tables of structure factors (18 pages). Ordering information is given on any current masthead page.

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Facile Synthesis and Structural Principles of the Strontium Phenoxide $Sr_4(OPh)_8(PhOH)_2(THF)_6$

The current knowledge of composition and structure of aryloxides and alkoxides of divalent metals throughout the periodic table remains underdeveloped:[1] only compounds of germanium,[2] tin,[2] chromium,[3] cobalt,[4] and zinc[5] have been structurally characterized. The propensity of binary alkoxides of the heavier metals derived from low molecular weight alcohols to be polymeric,[6] involatile, and insoluble has led to recent emphasis on bulky R groups, including ortho-disubstituted phenoxides.[7] To avoid several characteristics of such elaborate aryloxides, we have examined unsubstituted phenoxide as a ligand for strontium in the presence of Lewis bases.[8,9] Our goal is molecular phenoxides that are volatile and/or hydrolyzable.[10] Our choice of strontium[11] is dictated by its importance as a constituent of materials valued for their structural[12] ($SrTiO_3$ or $SrNb_2O_6$) and superconducting ($La_{2-x}Sr_xCuO_4$[13] or $Pb_2Sr_2LnCu_3O_{8+x}$[14]) properties.

Reaction of strontium metal with phenol in THF at reflux, followed by crystallization by the addition of hexane, gives a 90% yield of a material[15] of empirical formula $Sr(OPh)_2(PhOH)_{0.5}(THF)_{1.5}$. Although this gives a ligand:metal ratio of 4:1, the curious stoichiometry and the incorporation of two *different* neutral ligands require explanation.

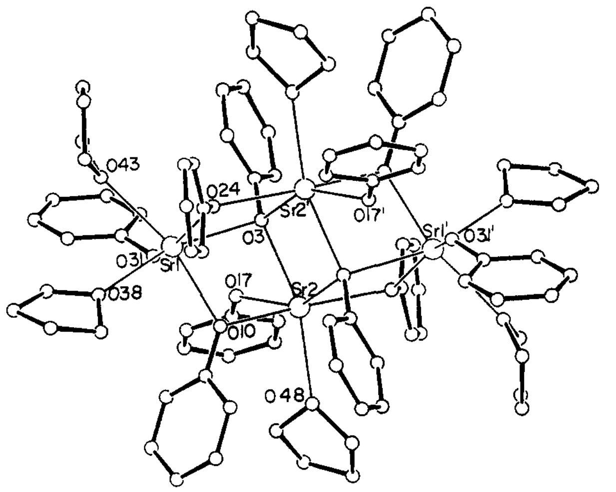

Figure 1. ORTEP drawing of the non-hydrogen atoms of $Sr_4(OPh)_8$-$(PhOH)_2(THF)_6$. Unlabeled atoms are carbon, and primed atoms are related to those not primed by a center of symmetry. Selected structural parameters: Sr1–O31, 2.450 (7) Å; Sr2–O17, 2.548 (7) Å; Sr–(μ_2-O), 2.404 (7)–2.495 (7) Å; Sr–(μ_3-O), 2.512 (7)–2.558 (6) Å; Sr–OC_4H_8, 2.548 (8)–2.584 (8) Å.

The solid state structure[16] of this compound (Figure 1) shows it to contain four metals in a centrosymmetric structure of formula $Sr_4(\mu_3\text{-}OPh)_2(\mu_2\text{-}OPh)_4(OPh)_2(THF)_6(PhOH)_2$. This structure results in a coordination number of 6 for each metal (yet the metals Sr1 and Sr2 have different environments) and approximate octahedral geometry. It is rare to find phenoxide as a μ_3-ligand.[17] The compound possesses the generic $M_2M'_2(\mu_3\text{-}X)_2(\mu_2\text{-}X)_4L_n$ stoichiometry and structure also adopted by $Li_2Sn_2(O^tBu)_6$[18] and $Mo_4O_{10}(OMe)_6^{2-}$.[19] When n (the number of terminal ligands) equals 10, this structure contains both edge- and face-shared octahedra and is thus highly suited to a metal like Ti(IV) in $Ti_4(OMe)_{16}$.[1] The generality of the structure,[20] however, rests in its ability to accommodate a variety of different terminal ligands (n values) and thus metals in oxidation states other than +4. For example, the Grignard-derived material of empirical formula $MgEt_{0.5}Cl_{1.5}(THF)_{1.5}$ is in fact[21] $Mg_4Et_2Cl_6(THF)_6$ with the same $Mg_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_4$ core structure and terminal ethyl and THF ligands that give two 6- and two 5-coordinate Mg^{2+} ions.

The incorporation of only two phenol molecules and the site they occupy in the structure are controlled by hydrogen bonding. The two phenol ligands occupy coordination sites that place their Sr–O bonds approximately parallel to the Sr–O bonds of the only two *terminal* phenoxides in the structure. Such a parallel alignment of M–O(H)R and M–OR bonds is clearly optimal for intramolecular hydrogen bonding. The hydrogen bonding in $Sr_4(OPh)_8(PhOH)_2(THF)_6$ is unusually strong.[22] This is evident

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(16) Crystallographic data for $C_{84}H_{100}O_{16}Sr_4$ (grown from toluene/pentane) at −100 °C: $a = 25.296$ (4) Å, $b = 14.477$ (2) Å, $c = 22.649$ (4) Å, $\beta = 100.36$ (1)° with $Z = 4$ in space group $C2/c$. $R(F) = 0.0891$ and $R_w(F) = 0.0836$ for 4417 observed ($F \geq 3\sigma(F)$) reflections.

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in the 2.504-Å O···O distance, in the severe bending at these oxygens (∠C–O–Sr = 135.2° for O17 and 137.8° for O31), and in the acute Sr–Sr–O angles of 70.46° (O17)) and 78.29° (O31), as these ligands try to decrease the distance between their lone pairs. These latter bond angles and the longer distance to O17 mark it as the phenol ligand.

Solution spectroscopic studies (^{1}H and ^{13}C NMR) at 25 °C in THF-d_8 show evidence for only a single phenyl environment. Even at −90 °C, some rapid fluxional process time averages the structurally inequivalent phenyl sites.

Visually, this compound appears to melt at 96–99 °C. Thermal analysis of this solid under helium reveals well-defined transformations. DSC shows an endotherm (41 J/g) centered at 98 °C, which is evident in the TGA profile as the weight loss of all six THF molecules. Further weight loss continues so that, by 200 °C, all phenol has been lost. Additional weight loss accompanies further heating to 1000 °C.

The above findings serve to demonstrate that the oxygen donor Lewis base THF, when combined with strontium and phenoxide/phenol, is sufficient to afford a discrete and soluble molecular aggregate in which Sr^{2+} attains a pseudooctahedral environment. The Lewis base is sufficiently strongly bound to prevent polymer formation in solution but too labile to give volatile molecular species. A donor substituent on the phenoxide might avoid this difficulty.

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Supplementary Material Available: A listing of positional and thermal parameters for $Sr_4(OPh)_8(PhOH)_2(THF)_6$ (3 pages). Ordering information is given on any current masthead page.

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Articles

Contribution from the Chemistry Department, Université du Québec à Montréal,
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Hydrolysis and Dimerization of Nitrile to Diacetamide and Crystal Structures of Chloro(2,2,2,2′,2′,2′-hexachlorodiacetamido)(dimethyl sulfoxide)platinum(II) and *cis*-Aquadichloro(dimethyl sulfoxide)platinum(II)

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The reaction of K[Pt(DMSO)Cl_3] with trichloroacetonitrile in aqueous solution adjusted to pH ≈ 7 with NaOH produces, after 24 h, a blue solution from which blue crystals were grown and analyzed by X-ray diffraction. The compound is a monomeric chelate Pt(II) species containing a deprotonated imide ligand, formed from the dimerization of trichloroacetonitrile. The crystals of Pt(DMSO)Cl($C_4NO_2Cl_6$) are monoclinic, $P2_1/n$ space group, with a = 11.214 (9) Å, b = 11.555 (11) Å, c = 13.841 (9) Å, β = 107.18 (5)°, V = 1714 (2) Å^3, and Z = 4. The structure was refined to R = 0.040 and R_w = 0.039. The bond distances are Pt–Cl = 2.301 (2), Pt–S = 2.217 (2), Pt–O(1) = 2.002 (5), and Pt–O(2) = 1.950 (5) Å. The imide ligand is planar, and its dihedral angle with the Pt(II) coordination plane is 1.7°. After being exposed to air more than 7 months, the crystal became yellow. The blue color was probably caused by a coating on the surface by a blue amorphous Pt complex. When the pH of the aqueous solution is not adjusted (pH ≈ 2), K[Pt(DMSO)Cl_3] reacts with trichloroacetonitrile to give a yellow powder and very pale yellow crystals, identified by diffraction methods as *cis*-Pt(DMSO)(H_2O)Cl_2. The crystals are orthorhombic, $P2_12_12_1$ space group, with a = 8.900 (3) Å, b = 9.020 (3) Å, c = 10.493 (4) Å, and Z = 4, and the structure was refined to R = 0.044 and R_w = 0.052. The Pt–Cl bonds are 2.337 (5) and 2.292 (5) Å, and the Pt–S distance is 2.191 (4) Å, while the Pt–O bond is 2.076 (16) Å. The crystal is stabilized by hydrogen bonds between the aqua ligand and one Cl ligand and O of DMSO.

Introduction

We have recently reported[1] the molecular and crystal structure of an analogue of "platinblau" reported in 1907,[2] whose exact structure is still unknown. It was suggested[3] that platinblau contained deprotonated acetamide anions bound to platinum(II), the acetamide ligand being obtained by reaction of water with coordinated acetonitrile. But attempts to obtain platinblau by direct combination of platinum(II) with acetamide were not successful. It has been assigned a variety of monomeric and polymeric structures of platinum(II) and -(IV).[4-8]

More recently, "platinum blues" have been obtained from the reaction of cisplatin (*cis*-Pt(NH_3)Cl_2) with pyrimidines, especially uracil derivatives.[9] It has been suggested that platinum blues might be promising as second generation platinum antitumor drugs. But these compounds have shown to be difficult to characterize. *cis*-Diammineplatinum pyrimidine blues were suggested to be amorphous polymers of varying chain lengths.[9,10]

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