Synthesis and structure of the heterobimetallic oxo complex $[(thf)(Me_2NH)_2Cl_2Cr^{III}]_2\{ClSn^{II}(\mu\text{-}O)\}_2$

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The reaction of $[Sn(NMe_2)_2]$ with a suspension of $CrCl_3$ and H_2O in thf gives the molecular $Cr^{III}Sn^{II}$ oxo complex $[(thf)(Me_2NH)_2Cl_2Cr]_2\{ClSn(\mu\text{-}O)\}_2$ 1, in which the O atoms of a central Sn_2O_2 ring coordinate two Cr^{III} cations.

Oxo complexes of Sn are an extensive and highly structurally varied class of compounds. Organotin(IV) oxo complexes are commonly prepared by hydrolysis of organotin(IV) halides or carboxylates or by the oxidation of organotin(II) complexes.[1] The functionality and steric bulk of the organic groups is crucial in dictating the geometries of the metal cores in these species and the nuclearity of the resulting cage arrangements. In contrast, structurally characterised tin(II) oxo complexes are rare and there are no general methods for their preparation.[2] The trapping of SnO fragments into molecular arrangements has been achieved by their incorporation into the frameworks of tin(II)/(IV) host complexes,[2a,c,e] by the formation of Lewis acid/base adducts with tin(II) complexes,[2b,d] or by coordination of transition metal carbonyls to the Sn lone pairs.[2f,g] In previous studies we showed that the low-temperature reactions of primary amines with dimethylamido p block metal reagents $\{[E(NMe_2)_x]$; E = Sn (x = 2), Sb (x = 3)$\}$ furnishes a simple route to imido and phosphinidene cage compounds [Scheme 1(*a*)].[3] We describe here the discovery that the analogous reactions of metal aqua complexes with dimethylamido p block reagents provide a new route to heterometallic oxo-complexes [Scheme 1(*b*)].

$$(a)\quad R{-}NH_2 + [E(NMe_2)_x] \longrightarrow [R{-}N\{E(NMe_2)_{x-2}\}] + 2Me_2N$$

$$(b)\quad M{-}OH_2 + [E(NMe_2)_x] \longrightarrow [M{-}O\{E(NMe_2)_{x-2}\}] + 2Me_2N$$

Scheme 1

The reaction of $[Sn(NMe_2)_2]$ with Bu^tNH_2–NH_3–1,4-dioxane in thf followed by addition of $CrCl_3$ was initially undertaken with a view to preparing a heterometallic Sn^{II}/Cr^{III} imido/nitrido complex. However, the product is a mixture of Sn^{II}/Cr^{III} oxo complexes $[(Me_2NH)_2(thf)CrCl_2]_2\{ClSn(\mu\text{-}O)\}_2\cdot L$ (L = 1,4-dioxane or Bu^tNH_2), the oxo ligand arising as a result of partial hydrolysis of the precursor $CrCl_3$. Further studies revealed that basic conditions catalyse this reaction and the stoichiometric reaction of a mixture of $CrCl_3$ and H_2O (1 : 1 equiv.) in thf–Bu^tNH_2 (1 equiv.) with $[Sn(NMe_2)_2]$ (1 equiv.) affords $[(Me_2NH)_2(thf)CrCl_2]_2\{ClSn(\mu\text{-}O)\}_2\cdot Bu^tNH_2$ ($\mathbf{1}\cdot Bu^tNH_2$) as the sole product (Scheme 2).‡

$$2CrCl_3 + 2\,H_2O \xrightarrow[\text{base}]{2[Sn(NMe_2)_2]} \underset{\mathbf{1}}{[\{(thf)(Me_2NH)_2CrCl_2\}_2\{ClSn(\mu\text{-}O)\}_2]}$$

Scheme 2

An X-ray crystallographic study of **1**§ as the 1,4-dioxane solvate reveals that the complex is composed of bimetallic molecules $[(Me_2NH)_2(thf)CrCl_2]_2\{ClSn(\mu\text{-}O)\}_2$ (Fig. 1) which are loosely associated by lattice-bound 1,4-dioxane molecules into a hydrogen-bonded network *via* C–H···O hydrogen bonds to the terminal thf ligands. Although a few examples of mixed transition metal–p block metal oxo complexes have been structurally characterised, all of these have relied on alkoxide functionalities to support the association of the metals, *e.g.* in $[Pb_2Ti_2(\mu_4\text{-}O)(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_4(OPr^i)_4]$.[4] The molecular arrangement of **1**, effectively resulting from the trapping of a central $[ClSn(\mu\text{-}O)]_2$ fragment by the coordination of the O centres to two Cr^{III} cations, is unique among main group oxo compounds. The closest analogy is found in the tin(II) complex $[\{Me_3Si(NBu^t)_2Sn_2O\}SnCl_2]$ in which a $SnCl_2$ molecule is coordinated by the O atom of a $[Me_3Si(NBu^t)_2\{Sn_2(\mu\text{-}O)\}]$ ligand.[2b]

Despite the planarity of the O centres of **1** and the possibility of a degree of multiple bond character in the Cr–O bonds, the pattern of bond lengths and angles found in the $[Sn(\mu\text{-}O)]_2Cr_2$ portion of **1** is consistent with its formulation as a coordination complex between a $[ClSn(\mu\text{-}O)]_2^{2-}$ dianion and two Lewis base solvated $CrCl_2^+$ cations $\{$rather than the alternative resonance extreme involving $[Cl_2Cr{=}O]^-\}$. The central, planar $[Sn(\mu\text{-}O)]_2$ ring of **1** is rhombic shaped, with the internal angles at Sn and O [Sn–O–Sn 104.2(2), O–Sn–O 75.8(2)°] being similar to those present in the dimeric units of more elaborate tin(II) oxo compounds.[2e] In addition, the Sn–O bonds fall in the expected range (Sn–O av. 2.11 Å in **1**; *cf. ca.* 2.05–2.10 Å[2]). Significantly, the Cr–O bonds [1.893(4) Å] are only marginally below the value expected for single Cr–O bonds (*ca.* 1.93 Å)[5] and noticeably longer than those found for Sn–O–Cr linkages in organotin(IV) chromates.[6] In addition to their coordination by the O centres of the $[Sn(\mu\text{-}O)]_2$ ring, each of the Cr^{III} ions is also coordinated by two *trans*-Me_2NH ligands, by two *trans*-Cl^- ions and by one thf ligand, giving an octahedral geometry which is typical of Cr^{III}. The orientation of the Me_2NH groups, whose

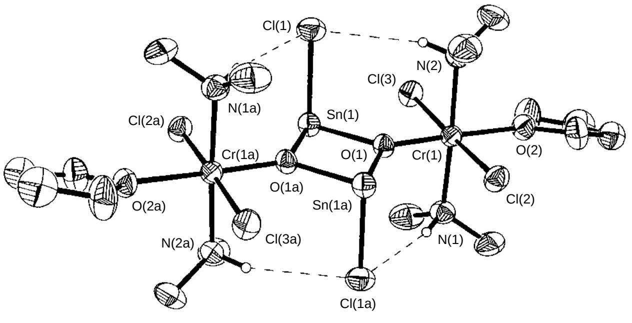

Fig. 1 ORTEP drawing of centrosymmetric molecular structure of $\mathbf{1}\cdot$1,4-dioxane. Thermal ellipsoids are at the 40% probability level. Selected bond lengths (Å) and angles (°); Sn(1)–Cl(1) 2.541(2), Sn(1)–O(1) 2.108(4), Sn(1)–O(1a) 2.103(4), Cr(1)–O(1) 1.893(4), Cr(1)–N(1) 2.140(5), Cr(1)–N(2) 2.135(5), Cr(1)–Cl(2) 2.327(2), Cr(1)–Cl(3) 2.334(2), Cr(1)–O(2) 2.108(4), H(2)···Cl(1) 2.59, H(1)···Cl(1a) 2.77, O(1)–Sn(1)–O(1a) 75.8(2), Sn(1)–O(1)–Sn(1a) 104.2(2), Cr(1)–O(1)–Sn(1, 1a) mean 127.9, O(1)–Cr–O(2) 178.4(2), N(1)–Cr(1)–N(2) 176.9(2), Cl(2)–Cr(1)–Cl(3) 177.94(8). Symmetry transformations used to generate equivalent atoms, a $-x + 1, -y - 1, -z + 1$.

H atoms are directed toward the Sn-bonded Cl^- ligands, and the presence of relatively short H$\cdots$Cl contacts [H(2)$\cdots$Cl(1) 2.59, H(1)$\cdots$Cl(1a) 2.77 Å] indicates that the molecular arrangement of **1** is partially supported by hydrogen bonding. Further evidence for hydrogen bonding is the slight axial distortion of the Me_2NH groups towards the Cl atoms [N(2)–Cr(1)–N(3) 176.9(2)°]. These interactions give a reason for the *trans* coordination of the Cr^{III} cations by the Me_2NH and Cl^- ligands (as opposed to the alternative *cis* isomer).

Further studies are in hand to determine the generality of similar deprotonation reactions in the synthesis of heterometallic oxo and nitrido complexes containing a variety of mixed-metal compositions.

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Notes and References

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‡ *Synthesis of* **1**$\cdot Bu^tNH_2$: to a suspension of anhydrous $CrCl_3$ [0.31 g, 2.5 mmol, (Aldrich 99.9%)] in thf (20 ml) was added degassed H_2O (0.05 ml, 2.5 mmol). The mixture was stirred for 24 h at 25 °C. Bu^tNH_2 (0.26 ml, 2.5 mmol) was added and after stirring at 25 °C (20 min) the temperature was lowered to −78 °C and $[Sn(NMe_2)_2]$ (0.52 g, 2.5 mmol) in thf (10 ml) was added slowly. The mixture was allowed to warm to room temperature and the green solution produced was filtered to remove a white precipitate. The filtrate was reduced to *ca.* 20 ml under vacuum and storage at 5 °C (48 h) gave light brown crystals of **1**$\cdot Bu^tNH_2$. Yield 0.38 g, 31%. decomp. >255 °C to black solid. IR (Nujol), ν_{max}/cm^{-1} 3352w, 3166w (N–H str), other bands at 1288w, 1256m, 1118s, 1080m, 1018s, 922m, 871m, 800m, 721w. ^1H NMR $[(CD_3)_2SO$, +25 °C, 250 MHz], 5.80 (br s, Me_2NH), 3.59 (s), 1.76 (s, thf), 2.32 (s, *Me*$_2$NH), 1.21 (s, *Bu*^{t}NH$_2$), overlapping of the resonances due to paramagnetic broadening made accurate integration impossible. Anal. calc. for **1**$\cdot Bu^tNH_2$, C, 24.5; H, 5.2; N, 7.2; Cl, 21.8. Found; C, 23.8; H, 5.3; N, 7.2; Cl, 20.4%.

The reaction of $[Sn(NMe_2)_2]$ (0.53 g, 2.5 mmol) in thf (20 ml) with NH_3 (1.27 ml solution of 0.5 mol dm^{-3} in dioxane, 0.64 mmol) and Bu^tNH_2 (0.20 ml, 1.91 mmol) was aimed at the formation of the cubane $[Sn_4(NBu^t)_3NH]$. A red–brown solid formed after a few minutes. To this was added $CrCl_3$ (0.10 g, 0.81 mmol, 'anhydrous'). The mixture was stirred (1 h) giving a dark green solution. The insoluble material was filtered off and the filtrate concentrated to *ca.* 10 ml. Et_2O (3 ml) was added and storage at 5 °C (48 h) gave **1**$\cdot$1,4-dioxane and **1**$\cdot Bu^tNH_2$ as a mixture in low yield. The ^1H NMR spectrum is identical to that obtained separately for **1**$\cdot Bu^tNH_2$ (δ 1.19, Bu^t) but with a dioxane resonance at δ 3.60. Only **1**$\cdot$1,4-dioxane could be obtained as crystals from the mixture and repeated attempts to obtain single crystals of **1**$\cdot Bu^tNH_2$ have so far failed.

§ *Crystal data* for **1**: $C_{10}H_{26}Cl_3CrN_2O_3Sn$, $M = 998.74$, monoclinic, space group $P2_1/n$, $a = 8.002(1)$, $b = 14.956(2)$, $c = 15.855(2)$ Å, $\beta = 99.81(1)°$, $U = 1869.9(5)$ Å^3, $Z = 2$, $D_c = 1.77$ Mg m^{-3}, $\lambda = 0.710\,73$ Å, $T = 223(2)$ K, μ(Mo-Kα) = 2.351 mm^{-1}, $F(000) = 996$. Data were collected on a Siemens P4 diffractometer using an oil-coated rapidly-cooled crystal of dimensions 0.30 × 0.30 × 0.30 mm by the ω–2θ method ($1.88 \leqslant \theta \leqslant 25.00°$). Empirical absorption corrections were applied after initial refinement with isotropic displacement parameters.[7] Of a total of 4391 collected reflections, 3295 were independent ($R_{int} = 0.027$). The structure was solved by direct methods and refined by full-matrix least squares on F^2 to final values of $R1[F > 4\sigma(F)] = 0.040$ and $wR2 = 0.114$ (all data) [$R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{0.5}$, $w = 1/[\sigma^2(F_o{}^2) + (0.0535P)^2 + 2.9000P]$, $P = F_o{}^2 + (2F_c{}^2/3)$];[8] largest peak and hole in the final difference map 0.60 and −0.58 e Å^{-3}. Two of the C atoms of the Cr-bonded thf ligands are disordered. These were modelled with 1 : 1 occupancy. CCDC 182/869.

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