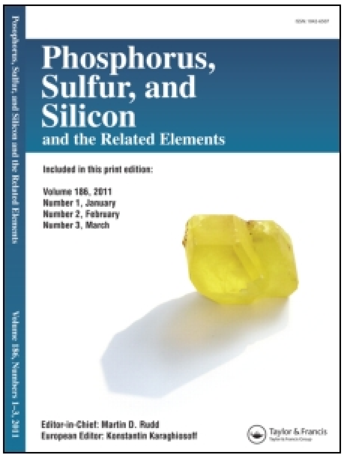

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Heterometallic Complexes of Sn(II)

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We report here some new approaches to heterometallic complexes containing Sn(II) and transition metals. These are exemplified by the syntheses and structures of the complexes $[Sn(mit)_6Cu_4]$ (1), $[\{Sn_4(NBu^t)_3O\}Cr(mit)Cl_2(NMe_2H)]$ (2) (mit= $CH_2N(MeC(\underline{...}S)\underline{...}N]$ and $[(thf)(Me_2NH)_2Cl_2Cr]_2\{ClSn(\mu\text{-}O)\}]_2$ (3).

Keywords: metal-metal bonds; oxo compounds; heterometallics; tin; chromium; copper

INTRODUCTION

There is currently a great deal of interest in the preparation and structures of heterometallic complexes containing main group and transition metals.[1] In particular, there is an opportunity to observe new forms of metal-metal bonding in these species and the formation and stabilisation of cluster and cage complexes of these metals is of considerable theoretical interest. In addition, heterometallic complexes containing tin-transition metal combinations (which are the focus of this paper) have been found to be active in various homogeneous and heterogeneous catalytic processes.[2]

Heterometallic tin/transition metals complexes have been known since the 1940's and there have been a variety of synthetic methods used in their preparation.[3] Perhaps the most widely used method involves the formation of a tin-transtion metal bond by reaction of an organo-Sn(II) anion with transition metal complexes (Scheme 1a) or by the reaction of an anionic transition metal complex with a neutral Sn complex (Scheme 1b). A second common method involves the elimination of small molecules such as an amine or hydrogen halide (an example of which is shown in Scheme 1c). Further methods which have been reported include oxidative addition (Scheme 1d) or oxidative elimination reactions, insertion reactions of tin(II) chloride and transmetalation of mercury compounds.

$$Me_3SnCl + Na[Mn(CO)_5] \longrightarrow [Me_3SnMn(CO)_5] + NaCl \quad ....(1a)$$

$$Ph_3SnLi + [(C_5H_5)_2HfCl_2] \longrightarrow [Ph_3SnHf(C_5H_5)_2Cl] + LiCl \quad ....(1b)$$

$$Ph_3SnH + [Ti(NEt_2)_4] \longrightarrow [Ti(SnPh_3)_4] + 4HNEt_2 \quad ....(1c)$$

$$Me_3SnCl + [Pt(PR_3)_2] \longrightarrow [Me_3SnPtCl(PR_3)_2] \quad ....(1d)$$

In this paper we report some new approches to heterobimetallic complexes containing Sn(II) and transition metals, in which metal centres of the complexes produced are associated by a combination of bridging ligand and metal···metal interactions.

HETEROMETALLIC Sn(II)/ TRANSITION METAL COMPLEXES

Synthesis and Structure of $[Sn(mit)_6Cu_4]$ (1)

One area of interest to us has been the application of a range of neutral and anionic p block metal based ligands in the preparation of mixed-metal complexes.[4] In particular, the organometallic anions of Group 14 metals ($[R_3E]^-$; E= Ge-Pb)[5] and their metallo-organic relatives ($[\{RY\}_3E]^-$; Y= O, S, N, P)[6] are a readily prepared and extensive class of ligands. Unfunctionalised tri(organo) metal anions have been employed as metal-centred monodentate ligands to a variety of main group[5] and transition metals,[7] giving heterobimetallic complexes containing metal-metal bonds. In contrast, the functionalised metallo-organic derivatives [e.g., tris(alkoxy) and tris(amido) stannates] generally act as bidentate or tridentate ligands, utilising the heteroatoms in their coordination to metal ions.[8] In the complexes $[\{(CO)_5MSn(\mu\text{-}O^tBu)_3\{Mo(CO)_5\}]$ (M= Cr, Mo), however, the trisalkoxy stannate fragment acts as a multifunctional (metal- and heteroatom-centred) ligand.[9]

The reaction of $[Sn(NMe_2)_2]$ with mitH (= $(CH)_2N(Me)C(\text{–}SH)\text{=}N]$) gives $[Sn(mit)_2]$ (Scheme 2), a neutral Sn(II) complex which can act as a multifunctional ligand.[10] The addition of [CuCl] to a suspension of this species gives a heterobimetallic cage complex $[Sn(mit)_6Cu_4]$ 1 which contains an unprecedented $[SnCu_4]$ cage arrangement. The synthesis of 1 can be conceived as occurring *via* the initial formation of $[Cu(mit)]_4$ which is then complexed by a $[Sn(mit)_2]$ monomer (Figure 1). This reaction can therefore be described as a *synergic complexation* reaction (i.e., resulting from a combination of N donation to Sn and lone pair donation from Sn to Cu).

$$3[Sn(mit)_2] + 4CuCl \longrightarrow [SnCu_4(mit)_6] + 2SnCl_2 \quad ....(2)$$

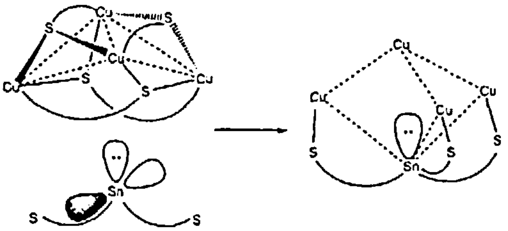


FIGURE 1 Formation of **1** from $[Cu(mit)]_4$ and $[Sn(mit)_2]$

The low-temperature X-ray structure of **1** is shown in Figure 2. The cage molecules of **1** are constructed from a C_3v symmetric hypho-hexagonal $[SnCu_4]$ metal core linked together by a combination of (N,S)- and (N,μ-S)-chelating mit ligands. The Sn(II) atom of **1**, which is bonded to the N centres of three mit ligands, adopts a typical pyramidal geometry [N(5A)–Sn–N(5AA) 90.0(2)°] which is symptomatic of the presence of a stereochemically active *endo* lone pair, which is directed along the major axis of the $[SnCu_4]$ core, towards Cu(3). Three symmetry related mit ligands form bridges between the Sn atom and each of the equatorial Cu atoms of the core [S(7A)–Cu(2) 2.266(2)Å], with the remaining mit ligands (N,μ-S)-chelating the three available Cu_3 faces of the Cu_4 pyramid. The arrangement of the mit ligands in **1** results in identical trigonal planar geometries for the equatorial Cu centres and in a pyramidal coordination geometry for the apical Cu atom [S(7B)–Cu(3)–S(7BA) 113.78(5)°]. The remaining vacant coordination site of the latter corresponds to the shortest Sn···Cu contact made with the Sn(II) lone pair [Sn(1)···Cu(3) 2.727(2)Å being close to the sum of the metallic radii 2.69Å, Sn(1)···Cu(3)–S(7B) 104.72(7)°]. In addition, the Sn centre also has longer interactions with the equatorial Cu atoms of the Cu_4 fragment [Sn(1)···Cu(2) 2.902(1)Å].

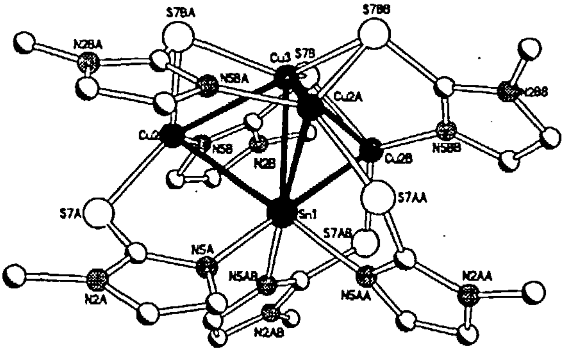


FIGURE 2 Structure of $[SnCu_4(mit)_6]$ (1)

Although there are no examples of structurally characterised complexes containing Ge–, Sn– or Pb–Cu(I) bonds, bonds between the heavier Group 14 elements and Au(I) have been observed in a number of simple σ bonded complexes.[11] The presence of relatively short Sn···Cu contacts in **1** and the geometries of Cu(3) and Sn(1) strongly indicate that Cu–Sn interactions help to supports the core.

In order to assess the extent to which Sn···Cu and Cu···Cu interactions support the cage of **1**, an Extended Hückel Molecular Orbital (EHMO) calculation was performed on its $[SnCu_4]^{6+}$ metal core. The lowest lying metal-metal bonding orbital involves the completely in-phase interaction of the Sn(II) lone pair with all four Cu centres (Figure 3a), with the corresponding out-of-phase interaction forming the LUMO (Figure 3b). The bonding between the metal centres is predominantly of *s* or *s/p* character, with less than 10% *d* character being contributed from the Cu centres. The strongest bonding interaction occurs between Sn and the apical Cu centre (overlap population 0.15), with weaker bonding occurring between the Sn and equatorial Cu atoms (overlap population 0.10) and with Cu···Cu interactions only being present between the apical and equatorial Cu ions (overlap population 0.07). The formation of the $[SnCu_4]^{6+}$ cluster is accompanied by the donation of charge from Sn(II) approximately equally to the Cu(I) centres (total 0.35e). Clearly, the geometric constraints and bonding preferences of the ligands are likely to have the largest effect on the metal core geometry of **1**. However, the structural and calculational findings support the view that weak Sn···Cu metal-metal cluster bonding reinforces the cage arrangement.

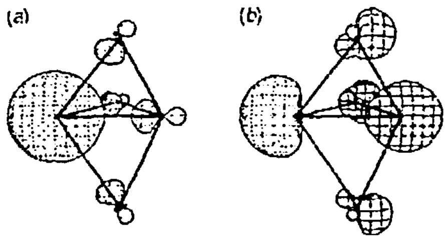


FIGURE 3 EHMO calculations on the $SnCu_4^{6+}$ core of 1.

Heterometallic Oxo Complexes of Sn(II); Syntheses and Structures of $[\{Sn_4(NBu^t)_3O\}Cr(mit)Cl_2(NMe_2H)]$ (2) and $[(thf)(Me_2NH)_2Cl_2Cr]_2\{ClSn(\mu\text{-}O)\}]_2$ (3)

In contrast to oxo complexes of Sn(IV), structurally characterised Sn(II) oxo complexes are rare and there are no general methods for their preparation.[12] The trapping of SnO units has been achieved by their incorporation into the frameworks of Sn(II)/Sn(IV) host complexes, by the formation of Lewis base/ Lewis base adducts and by coordination of transition metal carbonyls to the Sn(II) lone pairs. However, the oxo complexes of Sn(II) should consitute good ligand systems in their own right since the O centres are capable of donating to other metals. This behaviour was illustrated by Veith and coworkers who showed previously that the Sn(II) imido/oxo cubane $[(SnNBu^t)_3(SnO)]$ produces the adduct $[(SnNBu^t)_3(SnO)\cdot AlMe_3]$ with $AlMe_3$.[13] However, no further studies of the coordination chemistry of this type of 'ether-like' Sn(II) oxo complex have been reported.

We have discovered that $[(SnNBu^t)_3(SnO)]$ is accessible directly from the cubane $[SnN^tBu]_4$ by controlled hydrolysis with H_2O in ca. 80% yield, in contrast to the previously reported route to the same complex.[14] This new method therefore allows the direct preparation of this type of ligand in quantities sufficient for in-depth studies of the coordination chemistry with a large array of metals. The addition of $CrCl_3$ to a solution of $[(SnNBu^t)_3(SnO)]$ together with mitH (mit= $(CH)_2N(Me)C(\overset{\cdots}{-}S)\overset{\cdots}{-}N$) and $LiNMe_2$ gives the heterometallic Sn(II)/Cr(III) complex $[\{Sn_4(NBu^t)_3O\}Cr(mit)Cl_2(NMe_2H)]$ (2). The low-temperature X-ray structure of 2 (Figure 4) shows that the Cr^{3+} cation is complexed by a $[Sn_4(N^tBu)_3O]$ ligand. The major distortion in the geometry of the Cr^{3+} cation occurs in the equatorial plane as a result of the constraints imposed by the bidentate (N,S)-chelation of the cation by the mit ligand [S–Cr–N 69.18(14)°]. The observation of a N–H stretching band at 3073cm^{-1} in the IR spectrum of **2** indicates that there is a proton on the NMe$_2$ group.

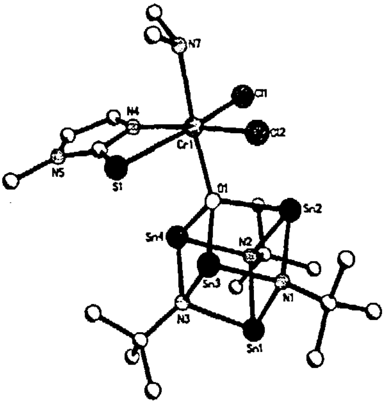


FIGURE 4 Structure of [{Sn$_4$(NBu^t)$_3$O}Cr(mit)Cl$_2$(NMe$_2$H)] (**2**).

As is usually observed in the structures of [SnNR]$_4$ cubanes,[15] the [Sn$_4$N$_3$O] cubane of **2** is distorted, the internal angles at the nitrogen centres being av. 100° and with those at the Sn centres being *ca.* 79°. This pattern reflects the reluctance of the heavy main group elements to hybridise. The Sn–N bond lengths are similar to those observed in related tin-imido cages.[15] Comparison of the bond lengths and angles found in the uncoordinated oxo-imido cubane [Sn$_3$(NBu^t)$_3$O][13] with **2** shows that major changes occur at the oxygen atom upon coordination, the Sn-O distances increasing significantly (range 2.168(9) to 2.130(7)Å in the free ligand, range 2.181(4) to 2.224(4)Å in **2**) as a result of donation of electron density to the Cr^{3+} cation. The Sn-O-Sn angles also become more acute (range 100.4(3) to 101.5(3)° in the free ligand,[5a] range 99.23(16) to 100.61(16)° in **2**) as a result of the O centre being pulled out of the cubane in order to engage the Cr^{3+} cation.

The Cr–O bond length in **2** (1.985(4)Å), is indicative of a single Cr–O bond. This bond is shorter than those seen in oxo alkyl chromiun complexes (such as 2.13(1)Å)[16] but similar to those in chromium (III) oxalate compounds (range from 1.954(5) to 1.969(13)Å).[17] The arrangement of the molecules of **2** in the crystal is of interest. They are linked together into loose dimers by a single Sn···Sn contact. The distance involved (4.261 Å) is slightly shorter than the sum of the van der Waals' radii (Sn···Sn 4.40Å) (Figure 5). Similar Sn···Sn contacts are common in Sn(II) imido compounds, in particular they are present in the oxo-imido cubane $[Sn_3(NBu^t)_3O]$ itself,[13] which is also associated into loose dimers in the solid state by more extensive Sn···Sn interactions (4.05Å).

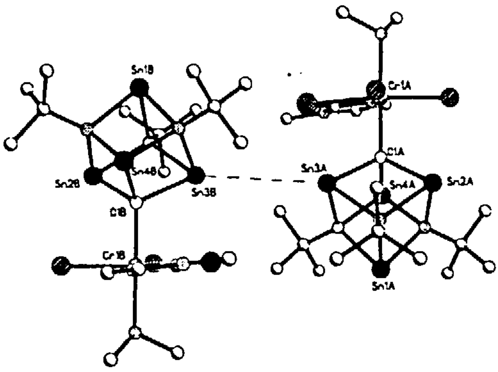


FIGURE 5 Association of molecules of **2** in the crystal.

The formation of **2** provides a model for the potential stabilisation of $[SnO]_n$ cage fragments by the coordination of transition metals to the oxo functionality. We have previously reported that the low-temperature reactions of primary amines with dimethylamido p block metal reagents $[E(NMe_2)]_x$ (E= As-Bi) furnishes a simple route to imido compounds (Scheme 3a).[4] The analogous reactions of metal aqua complexes with $[E(NMe_2)]_x$ provides a potential new route to heterometallic complexes in which transition metal stabilisation of the main group metal oxo fragments occurs (Scheme 3b).

$$R\text{-}NH_2 + [E(NMe_2)_x] \longrightarrow [R\text{-}N\{E(NMe_2)_{x-2}\}] + 2Me_2NH \quad ...(3a)$$

$$M\text{-}OH_2 + [E(NMe_2)_x] \longrightarrow [M\text{-}O\{E(NMe_2)_{x-2}\}] + 2Me_2NH \quad ...(3b)$$

Reaction of partially hydrolised chromium chloride with $[Sn(NMe_2)_2]$ leads to the mixed tin-chromium complex $[(thf)(Me_2NH)_2Cl_2Cr]_2\{ClSn(\mu\text{-}O)\}]_2$ (**3**) (as shown in Scheme 4).

$$2CrCl_3 + 2H_2O \xrightarrow[\text{base}]{2[Sn(NMe_2)_2]} [\{(thf)(Me_2NH)_2CrCl_2\}_2\{ClSn(\mu\text{-}O)\}_2] \quad ...(4)$$

The structure of this compound was determined by an X-ray crystallographic study (Figure 6). The molecular arrangement results from the trapping of a central $[ClSn(\mu\text{-}O)]_2$ fragment by the coordination of the O centres to two Cr(III) cations; a unique arrangement among main group oxo compounds. 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*-chloride ions and by one thf ligand, giving an octahedral geometry which is typical of Cr(III). The orientation of the amino groups, whose hydrogens are directed toward the Sn-bonded chlorine ligands and the presence of relatively short H···Cl contacts (2.59 and 2.77Å) suggests that the molecular arrangement of this compound is partially supported by hydrogen bonding. These interactions give a reason for the *trans* coordination of the Cr(III) cations by the amine and chlorine ligands, as opposed to the alternative *cis* isomer.

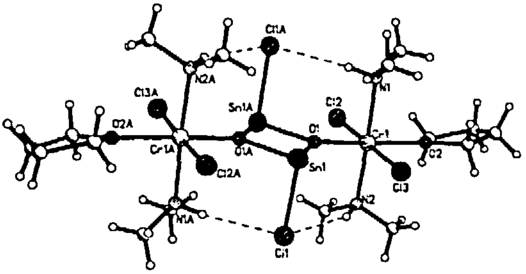
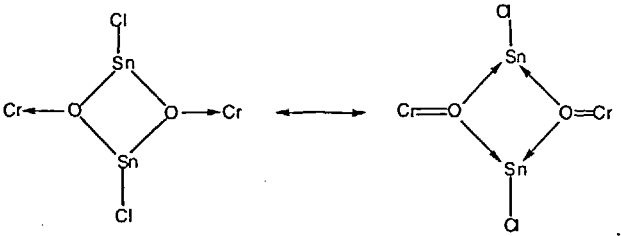


FIGURE 6 Structure of $[(thf)(Me_2NH)_2Cl_2Cr]_2\{ClSn(\mu\text{-}O)\}]_2$ (3).

Despite the planarity of the O centres in this compound 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 $[ClSn(\mu\text{-}O)]_2$ fragment of 3 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 $[ClCr{=}O]^-$ (Scheme 5). The central, planar $[Sn(\mu\text{-}O)]_2$ ring in 3 compound is rhombic, with the internal angles at Sn and O being similar to those present in the dimeric units of more elaborate Sn(II) oxo compunds.[12] In addition, the Sn–O bonds fall in the expected range (av. 2.11Å; cf *ca.* 2.05-2.10Å[12]). The Cr–O bonds are only marginally below the value expected for single Cr–O bonds (*ca.* 1.93Å) and noticeably longer than those found for Sn–O–Cr linkages in organo Sn(IV) chromates.[18]



....(5)

3. Conclusions and Closing Remarks

The syntheses and structures of the heterometallic Sn(II)/transition metal complexes described in this work provide some promising new approaches to heterometallic main group/ transition metal complexes in general. Future studies will be aimed at the preparation of a broad range of mixed-metal complexes of this type. In particular, using a similar methodology to that described in the formation of 3 we hope to prepare nitrido and phosphido complexes of various main group metals.

Acknowledgements

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