

Synthesis and structure of $[\text{Sn}(\text{mit})_6\text{Cu}_4]$; a $[\text{SnCu}_4]$ cage supported by Sn–Cu cluster bonding [mit = $(\overline{\text{C}}\text{H})_2\text{N}(\text{Me})\text{C}(\ddot{\text{S}})\ddot{\text{N}}$]

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The reaction of $[\text{Sn}(\text{mit})_2]_n$ with CuCl gives the heterobimetallic complex $[\text{Sn}(\text{mit})_6\text{Cu}_4]$ **1**, in which the *hypho*-hexagonal-bipyramidal $[\text{SnCu}_4]$ core is stabilised by $\text{Sn}^{\text{II}}\text{--Cu}^{\text{I}}$ cluster bonding between the *endo* lone pair of the Sn centre and the tetrahedral Cu_4 fragment.

Much of our recent research has focused on the applications of a range of neutral and anionic p-block metal based ligands in the preparation of mixed-metal complexes.^{1,2} The organometallic anions of group 14 metals ($[\text{R}_3\text{E}]^-$; E = Ge–Pb)^{2b,3} and their metallo-organic relatives ($[\{\text{RY}\}_3\text{E}]^-$; Y = O, S, N, P)^{1a,4} 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-group³ and transition metals,⁵ giving heterobimetallic complexes containing metal–metal bonds. In contrast, the 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.^{4,6} However, the ability of these species to behave as multifunctional (metal- and heteroatom-centred) ligands has been utilised in the construction of mixed-metal complexes such as $[\{\text{CO}\}_5\text{MSn}(\mu\text{-OBu})_3\text{In}\{\text{Mo}(\text{CO})_5\}]$ (M = Cr, Mo).⁷

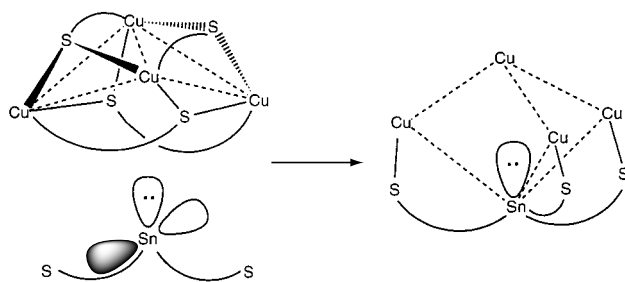
We report here that the addition of $[\text{CuCl}]$ to a suspension of $[\text{Sn}(\text{mit})_2]_n$ ⁸ [mit = $(\overline{\text{C}}\text{H})_2\text{N}(\text{Me})\text{C}(\ddot{\text{S}})\ddot{\text{N}}$] in thf gives the novel heterobimetallic cage complex $[\text{Sn}(\text{mit})_6\text{Cu}_4]$ **1**.[†] The complex contains an unprecedented SnCu_4 cage arrangement in which a tris(amido) stannate unit supports the cluster by a combination of heteroatom and metal-centred donation. The synthesis of **1** can be conceived as occurring *via* the initial formation of $[\text{Cu}(\text{mit})_4]^{9e}$ which is then complexed by a $[\text{Sn}(\text{mit})_2]$ monomer (Scheme 1). The latter can 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).

A low-temperature (173 K) crystallographic study of **1**[‡] shows it to be the heterobimetallic $\text{Cu}^{\text{I}}\text{Sn}^{\text{II}}$ complex $[\text{Sn}(\text{mit})_6\text{Cu}_4]$ (Fig. 1), which has crystallised with four molecules of thf. The cage molecules of **1** are constructed from a C_{3v} symmetric *hypho*-hexagonal $[\text{SnCu}_4]$ metal core linked together by a combination of N,S- and N, μ -S-chelating mit

ligands.⁹ The Sn^{II} atom of **1**, which is bonded to the N centres of three mit ligands [Sn(1)–N(5a) 2.202(6) Å], 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 $[\text{SnCu}_4]$ core, toward 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 2.69 Å,¹⁰ 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].

Although no Ge-, Sn- or Pb– Cu^{I} bonded complexes have been structurally characterised, 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 bonding supports the core. In addition, the involvement of the Sn centre results in a large rearrangement in the Cu_4 core from the folded-square arrangement present in $[\text{Cu}(\text{mit})_4]$ {Cu...Cu range 2.671(2)–3.132(2) Å in $[\text{Cu}(\text{mit})_4]^{9e}$ Cu(2)...Cu(3) 2.683(1) in **1**; cf. 2.56 Å in Cu metal}.¹⁰

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)¹² calculation was performed on its $[\text{SnCu}_4]^{6+}$ metal core. § The lowest lying metal–metal bonding



Scheme 1

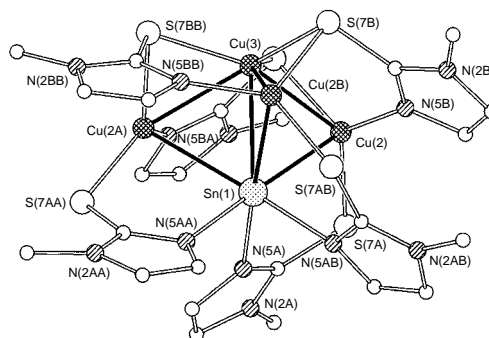


Fig. 1 Cage structure of **1**, showing the SnCu_4 arrangement. Key bond lengths (Å) and angles (°); Sn(1)...Cu(2) 2.902(1), Sn(1)...Cu(3) 2.727(2), Cu(2)...Cu(3) 2.683(1), Sn(1)–N(5a) 2.202(6), Cu(2)–S(7a) 2.266(2), Cu(2)–S(7ba) 2.300(2), Cu(3)–S(7a) 2.315(2), Cu(2)–N(5b) 1.967(6), C(6a)–S(7a) 1.731(7), C(6a)–N(5a) 1.335(9), C(6b)–S(7b) 1.736(8), C(6b)–N(5b) 1.34(1); S(7b)–Cu(3)–S(7ba) 113.78(5), Sn(1)...Cu(3)–S(7b) 104.72(7), N(5a)–Sn–N(5aa) 90.0(2).

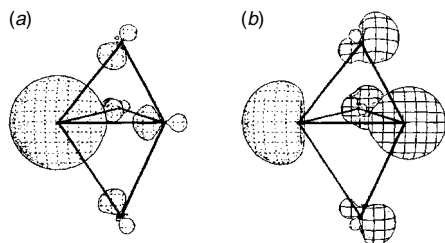


Fig. 2 Extended Hückel molecular orbital calculation (EHMO) of $[\text{SnCu}_4]^{6+}$; (a) lowest metal-metal bonding MO, (b) the out-of-phase combination (LUMO)

orbital involves the totally in-phase interaction of the Sn^{II} lone pair with all four Cu centres [Fig. 2(a)], with the corresponding out-of-phase interaction forming the LUMO [Fig. 2(b)]. 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 $[\text{SnCu}_4]^{6+}$ cluster is accompanied by the donation of charge from Sn^{II} approximately equally to the Cu^{I} centres (total 0.35 e). The magnitudes of the Cu...Cu interactions in **1** are similar to those calculated by Hoffman for naked $[\text{Cu}]_4^{4+}$ using the same EHMO parameters.¹³ The small attraction between the Cu centres in the latter arises from mixing of the s and p orbitals with the d orbitals.¹³ The cluster MO of **1** corresponds to a similar combination of Cu atomic orbitals as in $[\text{Cu}]_n^{n+}$ with the s orbital of Sn. 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.

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Footnotes and References

† *Synthesis of 1*: $[\text{Bu}^{\text{t}}\text{NH}_2]$ (0.26 ml, 2.5 mmol) was added to a solution of $[\text{Sn}(\text{NMe}_2)_2]$ (0.52 g, 2.5 mmol) in toluene (20 ml). After bringing briefly to reflux, a yellow solution of $[\text{SnNBu}^{\text{t}}]_4$ was produced to which was added Hmit (0.28 g, 2.5 mmol). Stirring at room temp. (10 min) gave a white precipitate [later confirmed by elemental analysis and ^1H NMR to be $[\text{Sn}(\text{mit})_2]_n \cdot x\text{C}_6\text{H}_5\text{Me}$ ($x = 0.4\text{--}0.5$)] The solvent was removed under vacuum and thf was added (20 ml). CuCl (0.125 g, 1.25 mmol) was added and, after stirring the mixture at reflux (5 min), a clear yellow solution was produced. Removal of ca. 10 ml of solvent under vacuum and subsequent storage at room temp. (2 d) gave colourless cubic crystals of **1** (0.17 g, 52% with respect to CuCl supplied). Decomp. ca. 200 °C with final melting at ca. 320 °C; IR (Nujol), $\nu_{\text{max}}/\text{cm}^{-1}$ 1541w, 1524m (C=C and C=N str), 1294s, 1280s, 1143s, 1124s, 1063s, 743s, 716s, 697s, 679s; ^1H NMR [250 Mz, $(\text{CD}_3)_2\text{SO}$, +25 °C], δ 6.89 (s, CH of mit), 3.58 (m, thf), 3.43 (s, Me of mit), 1.78 (m, thf); ^{119}Sn [149.1 MHz, $(\text{CD}_3)_2\text{SO}$, +25 °C, relative to $\text{SnCl}_2\text{-D}_2\text{O}$], δ 317.3 (s); analytical results indicate that only ca. 1.5 thf molecules are retained in the lattice when **1** is isolated under vacuum (0.1 atm, 10 min). Found C, 31.2; H, 3.7; N, 14.2. Calc. for $[\text{Sn}(\text{mit})_6\text{Cu}_4] \cdot 1.5\text{thf}$: C, 31.1; H, 3.6; N, 14.5%.

‡ *Crystal data for 1-thf*: $\text{C}_{40}\text{H}_{72}\text{Cu}_4\text{N}_{12}\text{O}_4\text{S}_6\text{Sn}$, $M = 1340.23$, rhombohedral, space group $R\bar{3}$, $a = 16.0538(6)$, $c = 39.001(3)$ Å, $U = 8704.8(8)$ Å³, $Z = 6$, $D_c = 1.552$ Mg m⁻³, $\lambda = 0.71073$ Å, $T = 173(2)$ K, $\mu(\text{Mo-K}\alpha) = 2.15$ mm⁻¹, $F(000) = 4080$. Data were collected on a Siemens P4 diffractometer using an oil-coated rapidly cooled crystal¹⁴ of dimensions $0.32 \times 0.30 \times 0.28$ mm by the $\theta\text{-}2\theta$ method ($1.55 \leq \theta \leq 24.92^\circ$). Of a total of 4144 collected reflections, 3363 were independent ($R_{\text{int}} = 0.0791$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R_1[F > 4\sigma(F)] = 0.062$ and $wR_2 = 0.192$

(all data);^{15,16} largest peak and hole in the final difference map 1.299 and -1.318 e Å⁻³. Three symmetry related molecules of thf had slight configurational disorder and a fourth thf molecule was equally disordered over two sites of C_3 symmetry. CCDC 182/583.

§ Calculations were carried out using the same arrangement as found in the solid-state structure of **1**. Parameters utilised- Sn, ζ_s 2.120, H_s -16.16, ζ_p 1.820, H_p -8.32; Cu ζ_s 2.200, H_s -11.40, ζ_p 2.200, H_p -6.06, ζ_{d1} 5.950, H_{d1} -14.00, c_1 0.5933, ζ_{d2} 2.300, c_2 0.5744.

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