Preparation and crystal structures of [SnCl₄(MeSCH₂SMe)] and [SnCl₄(MeSeCH₂SeMe)]: dithio- and diseleno-ether complexes incorporating highly strained four-membered chelate rings

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The preparation and crystal structures of [SnCl₄(MeSCH₂SMe)] and [SnCl₄(MeSeCH₂SeMe)], the first examples showing bidentate chelation of these methylene bridged dithio- and diseleno-ethers, have been described.

We have been investigating the complexation of various Group 16 donor acyclic and macrocyclic ligands with d- and p-block ions.[1–6] In the course of this work we recently showed that the single methylene-bridged thio- and seleno-ether ligands MeSCH₂SMe and MeSeCH₂SeMe react with Cu^I or Ag^I to yield highly unusual three-dimensional networks incorporating channels which can host PF_6^- or BF_4^- anions.[2] In these materials the ligands bridge adjacent tetrahedrally co-ordinated metal centres generating extended arrays, and we believe that the single methylene interdonor linkage leads to a preference for ligand bridging over chelation since the latter would give rise to a highly strained chelate ring. Although examples which involve η¹ co-ordination of these ligands are known (*e.g.* [ML₂Cl₂], M = Pd or Pt; L = PhSCH₂SPh, MeSCH₂SMe, PhSeCH₂SePh or MeSeCH₂SeMe),[3] these Cu^I and Ag^I species were the first examples of network polymers based on this type of ligand, and a database search revealed that there are no structurally characterised examples of methylene bridged dithio- or diseleno-ethers functioning as chelating ligands. In fact, there are only two compounds involving a chelating C₁-linked ditelluroether, [{(4-MeOC₆H₄Te)₂CH₂}PdCl₂] and [{(4-MeO-C₆H₄Te)₂CH₂}(Ph₂PCH₂CH₂PPh₂)Pd]²⁺.[7] Here we describe the products derived from reaction of MeECH₂EMe (E = S, Se or Te) with SnCl₄ which to our surprise involve chelating MeSCH₂SMe and MeSeCH₂SeMe.

Reaction* of SnCl₄ with 1 molar equivalent of MeSCH₂SMe or MeSeCH₂SeMe in anhydrous CH₂Cl₂ affords white or yellow solids respectively. These products are extremely sensitive to moisture (more so than the other dithio- and diseleno-ether complexes of SnCl₄ which we have reported), fuming noticeably upon exposure to moist air. The IR spectra show strong broad peaks in the range 200–400 cm⁻¹ assigned to Sn–Cl stretching vibrations. This, together with microanalytical data, confirms the empirical formulations for the products as [SnCl₄(MeSCH₂SMe)] and [SnCl₄(MeSeCH₂SeMe)] respectively.

* The complexes were prepared using Schlenk techniques under a dry N₂ atmosphere by the same general method and this is detailed below for one example.
Compound [SnCl₄(MeSCH₂SMe)]: SnCl₄ (2 mmol) was added to a solution of the ligand (2 mmol) in anhydrous CH₂Cl₂ (10 cm³). Stirring at room temperature followed by concentration of the solution *in vacuo*, afforded a white precipitate which was collected by filtration and dried *in vacuo* (Found: C, 9.5; H, 2.4. C₃H₈Cl₄S₂Sn requires C, 9.8; H, 2.2%). ν_max/cm⁻¹: 330 (br) (SnCl).
Compound [SnCl₄(MeSeCH₂SeMe)]: yellow solid (Found: C, 7.9; H, 2.0. C₃H₈Cl₄Se₂Sn requires C, 7.8; H, 1.7%). ν_max/cm⁻¹: 326 (br) (SnCl).

Attempts to isolate the analogous telluroether complex [SnCl₄(MeTeCH₂TeMe)] from the reaction of SnCl₄ with MeTeCH₂TeMe were not successful.

In view of the highly unusual structural motifs identified for the Cu^I and Ag^I complexes with these ligands, it was essential to establish unequivocally the stereochemistry at Sn^{IV}. Single crystals of both complexes were obtained by slow evaporation from a solution of the appropriate complex in CH₂Cl₂.† Surprisingly, the single-crystal structure of [SnCl₄(MeSCH₂SMe)] shows (Fig. 1) a mononuclear Sn^{IV} species involving a highly distorted octahedral S₂Cl₄ donor set, with the dithioether ligand co-ordinated in a bidentate fashion to give a four-membered chelate ring, Sn–S(1) 2.710(2), Sn–S(2) 2.647(2), Sn–Cl(1) 2.402(2), Sn–Cl(2) 2.390(2), Sn–Cl(3) 2.343(2), Sn–Cl(4) 2.362(2) Å. The co-ordinated dithioether adopts the DL configuration, with the Me groups directed to opposite sides of the SnS₂Cl₂ plane. The S(1)–Sn–S(2) angle is 67.82(5)°, very significantly more acute than in the other chelating dithioether complexes of Sn^{IV} which we have studied, *e.g.* 84.2(4)° in [SnCl₄{MeS(CH₂)₂SMe}].[4] The structure of [SnCl₄(MeSeCH₂SeMe)] shows (Fig. 2) a very similar arrangement. This molecule possesses crystallographic

Fig. 1 View of the structure of [SnCl₄(MeSCH₂SMe)] with numbering scheme adopted. Ellipsoids are shown at 40% probability. Selected bond lengths (Å) and angles (°): Sn–Cl(1) 2.402(2), Sn–Cl(2) 2.390(2), Sn–Cl(3) 2.343(2), Sn–Cl(4) 2.362(2), Sn–S(1) 2.710(2), Sn–S(2) 2.647(2); S(1)–Sn–S(2) 67.82(5), Cl(1)–Sn–S(2) 167.15(5), Cl(1)–Sn–S(1) 78.70(5), Cl(1)–Sn–S(2) 88.08(5), Cl(2)–Sn–S(1) 89.90(5), Cl(2)–Sn–S(2) 82.09(5), S(1)–C(2)–S(2) 111.1(3)
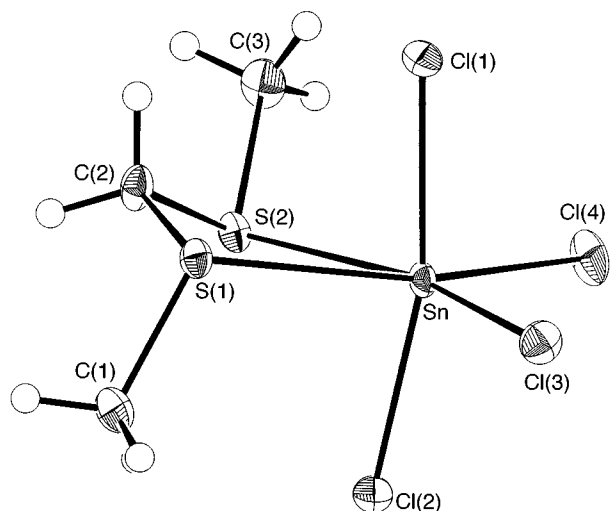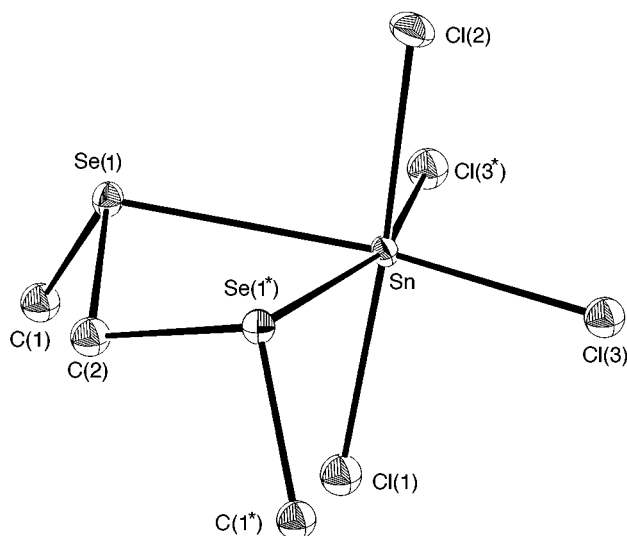

Fig. 2 View of the structure of [SnCl₄(MeSeCH₂SeMe)] with numbering scheme adopted. Ellipsoids are shown at 40% probability. Selected bond lengths (Å) and angles (°): Sn–Cl(1) 2.406(4), Sn–Cl(2) 2.407(4), Sn–Cl(3) 2.376(3), Sn–Se(1) 2.782(1); Se(1)–Sn–Se(1*) 69.11(5), Cl(1)–Sn–Cl(2) 175.5(1), Se(1)–Sn–Cl(2) 88.75(8), Se(1)–Sn–Cl(1) 87.53(8), Se(1)–C(2)–Se(1*) 107.2(2)

m symmetry with Sn, Cl(1) and Cl(2) lying on the mirror plane. Again the compound incorporates a four-membered chelate ring, although in this case the Me substituents adopt the *meso* configuration, Sn–Se(1) 2.782(1), Sn–Cl(1) 2.406(4), Sn–Cl(2) 2.407(4), Sn–Cl(3) 2.376(3) Å. In this case the angle involved in the chelate ring is marginally larger, 69.11(5)°, a result of the Sn–Se bond lengths being longer than Sn–S, hence leading to a slightly less strained four-membered ring. The Sn–S and Sn–Se

bond lengths in these species are in accord with those in other thio- and seleno-ether complexes of Sn^IV, and the Sn–Cl bond lengths exhibit similar trends, with *d*(Sn–Cl) *trans* to S or Se being shorter than *d*(Sn–Cl) *trans* to Cl.[4–6]

Above 230 K no signal is observed in the ¹¹⁹Sn-{¹H} NMR spectrum (CD₂Cl₂) of [SnCl₄(MeSCH₂SMe)]. Below 230 K a broad resonance is observed which splits at 180 K giving two signals of approximately equal intensity at δ 585.3 and 585.7, indicating fast exchange and/or ring-opening at high temperature with the chelated species present in solution at low temperature as a mixture of *meso* and DL forms. Importantly, this suggests that chelation is not just a consequence of crystallisation. These resonances occur at similar chemical shifts to other [SnCl₄(L–L)] complexes, where L–L is a bidentate thioether.[4] Variable-temperature ¹¹⁹Sn-{¹H} and ⁷⁷Se-{¹H} NMR spectroscopy over the range 180–300 K revealed no signal, suggesting that the selenoether complex [SnCl₄(MeSeCH₂SeMe)] is more labile than its thioether analogue in solution.

These complexes are the first structurally characterised examples incorporating chelating methylene-bridged dithio- or diseleno-ethers.

Acknowledgements

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