

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

Anthony R. J. Genge, William Levason and Gillian Reid

Department of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ

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 PF₆⁻ or BF₄⁻ 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-MeOC₆H₄Te)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%). $\nu_{\max}/\text{cm}^{-1}$: 330 (br) (SnCl).

Compound [SnCl₄(MeSeCH₂SeMe)]: yellow solid (Found: C, 7.9; H, 2.0. C₃H₈Cl₄Se₂Sn requires C, 7.8; H, 1.7%). $\nu_{\max}/\text{cm}^{-1}$: 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

[†] X-Ray crystallography. In each case the selected crystal was coated with mineral oil, mounted on a glass fibre and immediately placed under a stream of cold nitrogen. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Systems cryostream operating at 150 K and graphite-monochromated Mo-Kα radiation (0.710 73 Å) using ω–2θ scans.

Crystal data for [SnCl₄(MeSCH₂SMe)]: *M* = 368.72, monoclinic, space group *P*2₁/*c*, *a* = 6.371(2), *b* = 13.456(4), *c* = 13.319(2) Å, β = 100.30(2)°, *U* = 1123.4(4) Å³, *Z* = 4, *D*_c = 2.180 g cm⁻³, μ(Mo-Kα) = 35.32 cm⁻¹, *F*(000) = 704. Colourless block (0.55 × 0.40 × 0.40 mm), 2075 unique reflections (*R*_{int} = 0.025) of which 1656 with *F* > 5σ(*F*) were used in all calculations. The structure was solved by direct methods.⁸ Iterative cycles of least-squares refinement and Fourier-difference synthesis on absorption corrected data (ψ scans) revealed the positions of all non-H atoms for one complete molecule in the asymmetric unit.⁹ All non-H atoms were refined with anisotropic thermal parameters and H atoms were included but not refined. At final convergence, *R* = 0.028, *R*' = 0.035, *S* = 1.98 for 91 parameters and the final Δ*F* synthesis showed Δρ in the range 0.65 to –1.17 e Å⁻³.

Crystal data for [SnCl₄(MeSeCH₂SeMe)]: *M* = 462.52, orthorhombic, space group *Pnma*, *a* = 11.839(1), *b* = 12.633(1), *c* = 7.634(2) Å, *U* = 1141.8(3) Å³, *Z* = 4, *D*_c = 2.690 g cm⁻³, μ(Mo-Kα) = 94.87 cm⁻¹, *F*(000) = 848. Yellow block (0.60 × 0.40 × 0.25 mm), 1194 reflections of which 815 with *F* > 5σ(*F*) were used in all calculations. The structure was solved using heavy-atom Patterson methods.¹⁰ Iterative cycles of least-squares refinement and Fourier-difference synthesis on absorption corrected data (ψ scans) revealed the positions of all non-H atoms for one half-molecule in the asymmetric unit, related to the other half by a crystallographic mirror plane.⁹ Anisotropic thermal parameters were refined for all non-H atoms except Cl(3) and C(2) for which unrealistic values were obtained (probably due to the ψ scans giving an imperfect absorption correction) and hence these were refined with isotropic thermal parameters. Hydrogen atoms were included but not refined. At final convergence, *R* = 0.041, *R*' = 0.053, *S* = 2.04 for 44 parameters and the final Δ*F* synthesis showed Δρ within the range 0.90 to –1.65 e Å⁻³. CCDC reference number 186/779.

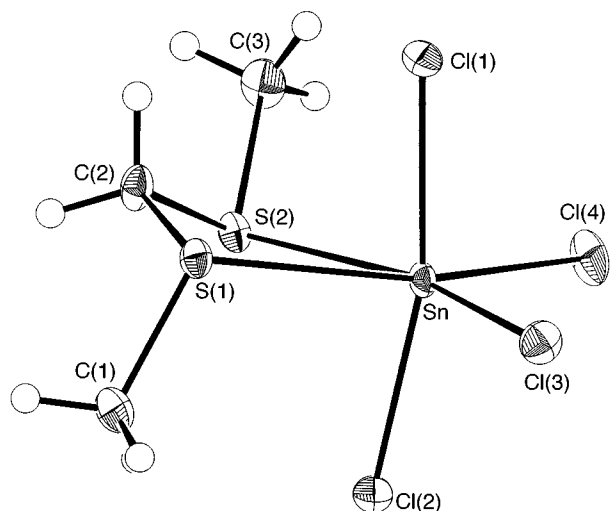


Fig. 1 View of the structure of $[\text{SnCl}_4(\text{MeSCH}_2\text{SMe})]$ with numbering scheme adopted. Ellipsoids are shown at 40% probability. Selected bond lengths (Å) and angles ($^\circ$): Sn–Cl(1) 2.402(2), Sn–Cl(2) 2.390(2), Sn–Cl(3) 2.343(2), Sn–Cl(4) 2.362(2), Sn–S(1) 2.710(2), Sn–S(2) 2.647(2); S(1)–Sn–S(2) 67.82(5), Cl(1)–Sn–Cl(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)

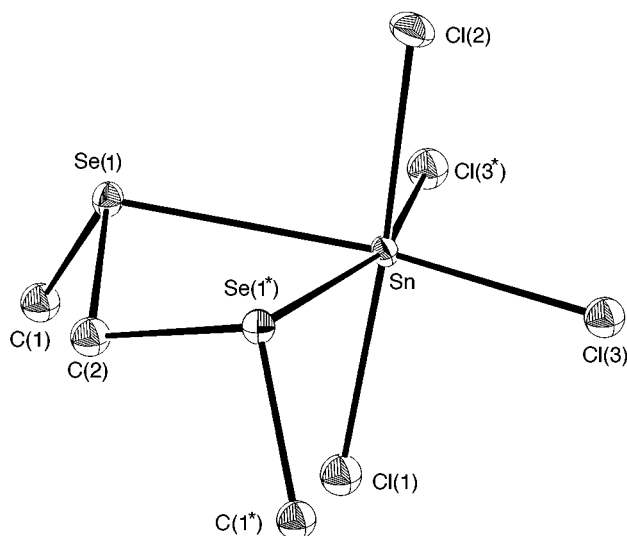


Fig. 2 View of the structure of $[\text{SnCl}_4(\text{MeSeCH}_2\text{SeMe})]$ with numbering scheme adopted. Ellipsoids are shown at 40% probability. Selected bond lengths (Å) and angles ($^\circ$): Sn–Cl(1) 2.406(4), Sn–Cl(2) 2.407(4), Sn–Cl(3) 2.376(3), Sn–Se(1) 2.782(1); Se(1)–Sn–Se(1*) 69.11(5), 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) $^\circ$, 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 $d(\text{Sn–Cl})$ *trans* to S or Se being shorter than $d(\text{Sn–Cl})$ *trans* to Cl.^{4–6}

Above 230 K no signal is observed in the $^{119}\text{Sn}\{-^1\text{H}\}$ NMR spectrum (CD_2Cl_2) of $[\text{SnCl}_4(\text{MeSCH}_2\text{SMe})]$. 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 $[\text{SnCl}_4(\text{L–L})]$ complexes, where L–L is a bidentate thioether.⁴ Variable-temperature $^{119}\text{Sn}\{-^1\text{H}\}$ and $^{77}\text{Se}\{-^1\text{H}\}$ NMR spectroscopy over the range 180–300 K revealed no signal, suggesting that the selenoether complex $[\text{SnCl}_4(\text{MeSeCH}_2\text{SeMe})]$ 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.

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