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Preparation and crystal structures of $[SnCl_4(MeSCH_2SMe)]$ and $[SnCl_4(MeSeCH_2SeMe)]$: dithio- and diseleno-ether complexes incorporating highly strained four-membered chelate rings

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The preparation and crystal structures of $[SnCl_4(MeSCH_2SMe)]$ and $[SnCl_4(MeSeCH_2SeMe)]$, 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 $MeSCH_2SMe$ and $MeSeCH_2SeMe$ 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 η^1 co-ordination of these ligands are known (*e.g.* $[ML_2Cl_2]$, M = Pd or Pt; L = $PhSCH_2SPh$, $MeSCH_2SMe$, $PhSeCH_2SePh$ or $MeSeCH_2SeMe$),[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 C_1-linked ditelluroether, $[\{(4\text{-}MeOC_6H_4Te)_2CH_2\}PdCl_2]$ and $[\{(4\text{-}MeOC_6H_4Te)_2CH_2\}(Ph_2PCH_2CH_2PPh_2)Pd]^{2+}$.[7] Here we describe the products derived from reaction of $MeECH_2EMe$ (E = S, Se or Te) with $SnCl_4$ which to our surprise involve chelating $MeSCH_2SMe$ and $MeSeCH_2SeMe$.

Reaction* of $SnCl_4$ with 1 molar equivalent of $MeSCH_2SMe$ or $MeSeCH_2SeMe$ in anhydrous CH_2Cl_2 affords white or yellow solids respectively. These products are extremely sensitive to moisture (more so than the other dithio- and diseleno-ether complexes of $SnCl_4$ 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 $[SnCl_4(MeSCH_2SMe)]$ and $[SnCl_4(MeSeCH_2SeMe)]$ respectively. Attempts to isolate the analogous telluroether complex $[SnCl_4(MeTeCH_2TeMe)]$ from the reaction of $SnCl_4$ with $MeTeCH_2TeMe$ 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 CH_2Cl_2.† Surprisingly, the single-crystal structure of $[SnCl_4(MeSCH_2SMe)]$ shows (Fig. 1) a mononuclear Sn^{IV} species involving a highly distorted octahedral S_2Cl_4 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 SnS_2Cl_2 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 $[SnCl_4\{MeS(CH_2)_2SMe\}]$.[4] The structure of $[SnCl_4(MeSeCH_2SeMe)]$ shows (Fig. 2) a very similar arrangement. This molecule possesses crystallographic

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* The complexes were prepared using Schlenk techniques under a dry N_2 atmosphere by the same general method and this is detailed below for one example.

Compound $[SnCl_4(MeSCH_2SMe)]$: $SnCl_4$ (2 mmol) was added to a solution of the ligand (2 mmol) in anhydrous CH_2Cl_2 (10 cm^3). 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. $C_3H_8Cl_4S_2Sn$ requires C, 9.8; H, 2.2%). ν_{max}/cm^{-1}: 330 (br) (SnCl).

Compound $[SnCl_4(MeSeCH_2SeMe)]$: yellow solid (Found: C, 7.9; H, 2.0. $C_3H_8Cl_4Se_2Sn$ requires C, 7.8; H, 1.7%). ν_{max}/cm^{-1}: 326 (br) (SnCl).

† 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 $[SnCl_4(MeSCH_2SMe)]$: $M = 368.72$, monoclinic, space group $P2_1/c$, $a = 6.371(2)$, $b = 13.456(4)$, $c = 13.319(2)$ Å, $\beta = 100.30(2)°$, $U = 1123.4(4)$ Å^3, $Z = 4$, $D_c = 2.180$ 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 $F > 5\sigma(F)$ 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 ΔF synthesis showed $\Delta\rho$ in the range 0.65 to −1.17 e Å^{-3}.

Crystal data for $[SnCl_4(MeSeCH_2SeMe)]$: $M = 462.52$, orthorhombic, space group *Pnma*, $a = 11.839(1)$, $b = 12.633(1)$, $c = 7.634(2)$ Å, $U = 1141.8(3)$ Å^3, $Z = 4$, $D_c = 2.690$ 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 $F > 5\sigma(F)$ 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 ΔF synthesis showed $\Delta\rho$ within the range 0.90 to −1.65 e Å^{-3}. CCDC reference number 186/779.

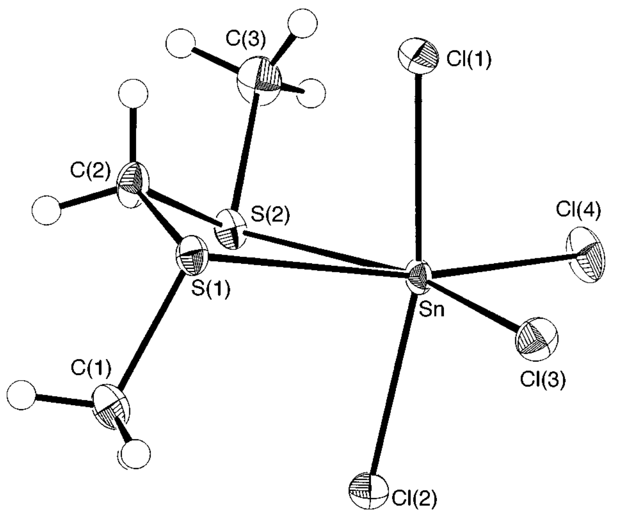

Fig. 1 View of the structure of [$SnCl_4(MeSCH_2SMe)$] with numbering scheme adopted. Ellipsoids are shown at 40% probability. Selected bond lengths (Å) and angles (°): Sn–Cl(1) 2.402(2), Sn–Cl(2) 2.390(2), Sn–Cl(3) 2.343(2), Sn–Cl(4) 2.362(2), Sn–S(1) 2.710(2), Sn–S(2) 2.647(2); S(1)–Sn–S(2) 67.82(5), Cl(1)–Sn–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)

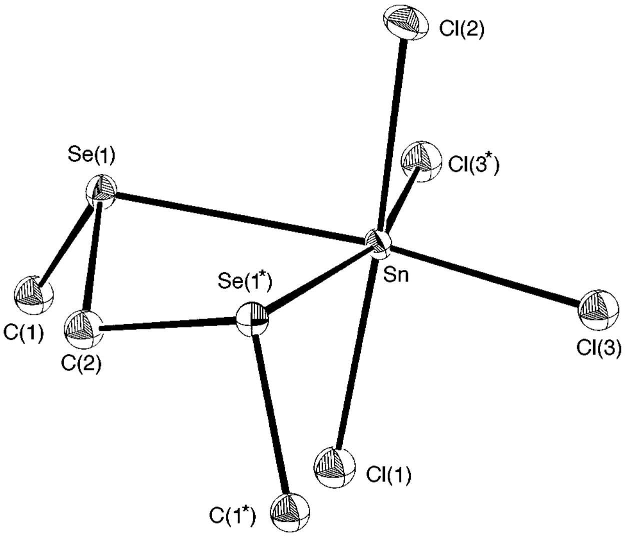

Fig. 2 View of the structure of [$SnCl_4(MeSeCH_2SeMe)$] with numbering scheme adopted. Ellipsoids are shown at 40% probability. Selected bond lengths (Å) and angles (°): Sn–Cl(1) 2.406(4), Sn–Cl(2) 2.407(4), Sn–Cl(3) 2.376(3), Sn–Se(1) 2.782(1); Se(1)–Sn–Se(1*) 69.11(5), Cl(1)–Sn–Cl(2) 175.5(1), Se(1)–Sn–Cl(2) 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 $^{119}Sn\text{-}\{^1H\}$ NMR spectrum (CD_2Cl_2) of [$SnCl_4(MeSCH_2SMe)$]. 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 [$SnCl_4$(L–L)] complexes, where L–L is a bidentate thioether.[4] Variable-temperature $^{119}Sn\text{-}\{^1H\}$ and $^{77}Se\text{-}\{^1H\}$ NMR spectroscopy over the range 180–300 K revealed no signal, suggesting that the selenoether complex [$SnCl_4(MeSeCH_2SeMe)$] 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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