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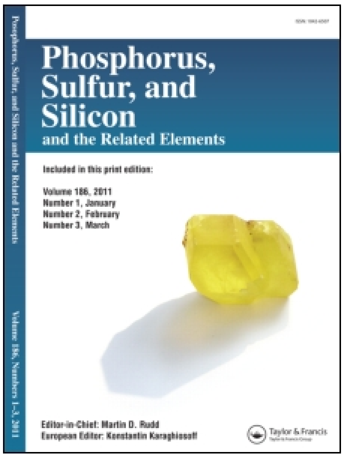

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The Co-Ordination Chemistry of TIN(IV) Halides with Chelating Group 16 Donor Ligands

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SnX_4 reacts with thio-, seleno- and telluro-ethers in dry $CHCl_3$ solution to give the six coordinate species $[SnX_4(Me_2E)_2]$ [X = Cl, Br or I; E = S, Se or Te] or $[SnX_4(L\text{-}L)$ [L-L = $RE(CH_2)_nER$ or $o\text{-}C_6H_4(EMe)_2$ where R = Me or Ph, n = 1–3 for E = S or Se, and n = 1 or 3 for E = Te] in high yields as pale white or yellow powdered solids. The ditelluroether compounds are very unstable, but their poor solubility aided isolation. X-Ray structural studies of the complexes formed confirm an E_2X_4 donor set with the bidentate ligand chelating. Variable-temperature solution NMR studies show the complexes are extremely labile and ligand dissociation and pyramidal inversion are fast except at low temperatures.

Keywords: tin; thioether; selenoether; telluroether; NMR; X-ray

The co-ordination chemistry of the d-block metals has been studied extensively in inorganic chemistry over the last fifty years. The contrasts with the p-block metals, which have been much less studied due to their lack of characteristic electronic and magnetic properties, which provided much of the early impetus in the d-block work. The complexes formed by the by the p-block metals are often hydrolytically unstable and very labile in solution, which made them difficult to study and less suited to some spectroscopic techniques. In the case of tin(IV), nitrogen- and oxygen-donor ligand complexes have long been known[1,2] and phosphine complexes have also been studied.[3-11] Studies with the softer neutral group 16 donor ligands are extremely limited.[6,12-16] Of these the majority are studies of the monodentate complexes of the type $[SnX_4(R_2E)_2]$[12-14] (X = Cl or Br, E = S or Se, R = Me or Me_3SiCH_2) examining the *cis/trans* isomerisation using ^1H NMR and vibrational spectroscopy. The only examples of chelating systems were reported by Willey and co-workers[16] involving thioether macrocyclic ligands, and

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Abel and co-workers[14] who studied the 3,4-bis(methylthio)toluene complex of tin(IV) chloride and the complex [$PhSnCl_3\{MeS(CH_2)_2SMe\}$] which was studied in preference to the less soluble [$SnCl_4\{MeS(CH_2)_2SMe\}$] which had been synthesised previously.[15] Chelating bi- and poly-dentate telluroethers were first reported about ten years ago,[17,18] and subsequently complexes with various transition metals including Pd^{II}, Pt^{II},[19] Co^{III},[20] Cu^{I} and Ag^{I} [21,22] were characterised. In contrast to Group 15 donor ligands, relatively little attention has been devoted to the study of the metal-Group 16 donor element bond (ref. 23 is a significant exception), and while RTe-Sn bonds are established,[24] no tin telluroether complexes appear in the literature. With a view to exploring some of the factors involved in the metal-Group 16 donor element bond we have undertaken a study of the complexes of thio-,[25,26] seleno-[26,27] and telluro-ethers[28] with the hard Lewis acid tin(IV) halides.

RESULTS AND DISCUSSION

Isolable complexes are prepared with several monodentate and bidentate ligands of group 16 by stoichiometric reaction of SnX_4 with ligand in non-coordinating solvents such as anhydrous $CHCl_3$ or anhydrous CH_2Cl_2. Reaction of SnX_4 (X = Cl, Br or I) with two molar equivalents of monodentate ligand, Me_2E (E = S, Se or Te) gives the six-co-ordinate species [$SnX_4(Me_2E)_2$] [X = Cl or Br, E = S, Se or Te; X = I, E = Te] in high yield as white or yellow powdered solids. Similar reaction of SnI_4 with excess Me_2Se did not yield an isolable product, although the tin(IV) selenoether adduct was observed *in situ* using $^{77}Se-\{^1H\}$ NMR spectroscopy (see below). Reaction of SnX_4 with 1 molar equivalent of bidentate ligand, L-L, in anhydrous non-coordinating solvent gives the six-coordinate species [$SnX_4(L\text{-}L)$] [X = Cl or Br, L-L = $MeE(CH_2)_nEMe$ where n = 1, 2 or 3 for E = S or Se, n = 1 for E = Te; L-L = $PhE(CH_2)_nEPh$ where n = 2 or 3 for E = S or Se and n = 3 for E = Te; L-L = $o\text{-}C_6H_4(EMe)_2$ where E = S, Se or Te] which were isolated as yellow or orange solids. The preparation of the analogous tin(IV) iodide complexes were all attempted, with the telluroether complexes forming as solids probably due to their insolubility rather than their stability. The thioether complexes appear almost indefinitely stable, hydrolysing only slowly in air. The selenoether derivatives hydrolysed rapidly in moist air and are easily hydrolysed by traces of water in solution but the solids seem indefinitely stable when stored in sealed tubes or in a dry-box. The telluroethers could only be handled in a dry-box and even then the solids decomposed over a period of weeks.

The ν(Sn-X) region of the IR spectra of the monodentate ligand systems show a single strong band consistent with the major isomer in the solid state being the *trans* form. The IR spectra of the bidentate complexes showed the presence of ligand as well as very strong vibrations assignable as ν(SnX_4) (theory $2A_1 + B_1 + B_2$), confirming the C_{2v} symmetry expected for the *cis*-SnX_4 configuration. Attempts to observe molecular ions in the mass spectra either by electrospray or FAB techniques were not successful.

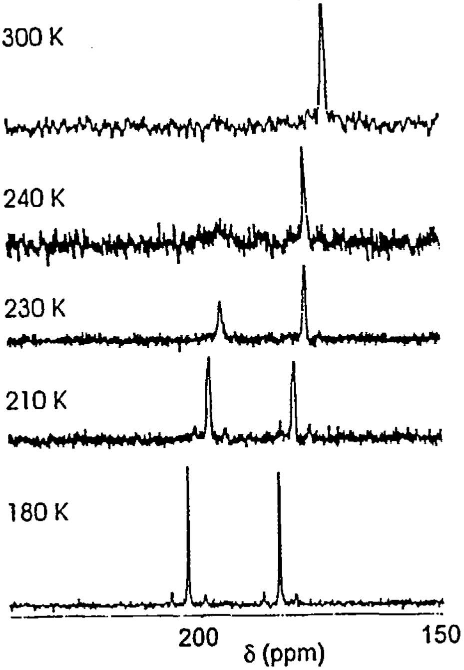

FIGURE 1 Variable temperature ^{77}Se-{^{1}H} NMR study of [$SnCl_4(Me_2Se)_2$] from 300-180 K

The [$SnCl_4(Me_2S)_2$]/Me_2S system has been studied in considerable detail by Knight and Merbach[13] using variable pressure proton NMR and variable temperature ^{119}Sn magnetization transfer NMR spectroscopy to establish the rates of *cis/trans* isomerisation in the 2:1 adducts. In our experiments at room temperature in CH_2Cl_2 solution the $^{119}Sn-\{^1H\}$ NMR spectrum of $[SnCl_4(Me_2S)_2]$ exhibits two resonances at δ –572 and –578 attributable to the *cis* and *trans* isomers respectively (table 1).[25] In the presence of an excess of Me_2S the processes occurring are (in order of decreasing rate) Me_2S exchange with the *cis* isomer, *cis-trans* isomerisation, and Me_2S exchange with the *trans* isomer.[13] The corresponding $SnBr_4$ compound exhibited the same behaviour with the onset of exchange at lower temperature. This was not achieved for the SnI_4 analogue, although a similar pattern was also seen in the $^{119}Sn-\{^1H\}$ NMR spectra and the $^{77}Se-\{^1H\}$ NMR spectra of the analogous selenoether complexes.[27] The $^{77}Se-\{^1H\}$ NMR spectra of SnI_4 in CH_2Cl_2 with an excess of Me_2Se exhibited a resonance at δ +152 at 180 K that may indicate the formation of a weak adduct {possibly *trans*-$[SnI_4(Me_2Se)_2]$} in solution at low temperatures. The systems $[SnX_4(Me_2Te)_2]$ proved insoluble in chlorinated solvents and too readily hydrolysed to provide useful data.[28]

Complex	$\delta(^{77}Se-\{^1H\})^*$	$\delta(^{119}Sn-\{^1H\})^\dagger$
$[SnCl_4(Me_2S)_2]$	-	-561, -572
$[SnBr_4(Me_2S)_2]$	-	-1174, -1222
$[SnCl_4(Me_2Se)_2]$	185 (460), 204 (490)	-691 (468), -695 (490)
$[SnBr_4(Me_2Se)_2]$	204 (555), 219 (500)	-1296 (500), -1319 (550)
$[SnI_4(Me_2Se)_2]$	152	not observed

TABLE 1 $^{77}Se-\{^1H\}$ and $^{119}Sn-\{^1H\}$ NMR data at 180 K for the systems $[SnX_4(Me_2E)_2]$

* Relative to external neat Me_2Se, $^1J(^{77}Se-^{117/119}Sn)$/Hz in parentheses. †Relative to external neat $SnMe_4$, $^1J(^{77}Se-^{119}Sn)$.

For complexes of the type $[SnX_4(L\text{-}L)]$, where L-L is a chelating group 16 donor ligand, two diastereoisomers (invertomers) are expected, *meso* and *DL* forms, which interconvert *via* pyramidal inversion at the donor atoms. Providing pyramidal inversion and ligand dissociation are slow on the NMR timescale, such diastereoisomers are readily distinguishable by ^1H NMR techniques.[29] Using variable temperature ^1H and $^{119}Sn-\{^1H\}$ NMR spectroscopy it was possible to reach the temperatures at which inversions processes were slowed sufficiently to observe two resonances for the *meso* and *DL* invertomers. In the proton spectra the presence of invertomers was observed from the splitting in the δ(Me) and δ(CH_2) resonances for methyl- and phenyl-substituted ligands respectively. As for the monodentate complexes, the selenoether complexes exhibit similar behaviour although the onset of ligand dissociation occurs at lower temperatures. The bidentate telluroether complexes proved too insoluble to provide useful data for the systems [SnX_4{RTe(CH_2)$_3$TeR}] (X = Cl, Br or I; R = Me or Ph) and it is most likely this insolubility which allowed $SnBr_4$ complexes of PhTe(CH_2)$_3$TePh to be isolated where we were unable to isolate analogous selenoether complexes.

Complex	δ(^{1}H)*	δ(^{119}Sn-{^{1}H})†
[$SnCl_4${MeS(CH_2)$_2$SMe}]	2.48, 2.61	-548.5, -549.0
[$SnBr_4${MeS(CH_2)$_2$SMe}]	2.26, 2.41	-1123.1, -1124.0
[$SnCl_4${MeSe(CH_2)$_2$SeMe}]	2.40, 2.46	-680, -682
[$SnBr_4${MeSe(CH_2)$_2$SeMe}]	2.21, 2.30	-1283, -1288
[$SnCl_4${*o*-C_4H_6(SMe)$_2$}]	2.80, 3.05	-504.2, -504.9
[$SnBr_4${*o*-C_4H_6(SMe)$_2$}]	2.86	n.o.
[$SnCl_4${*o*-C_4H_6(SeMe)$_2$}]	2.79, 2.99	-632, -635(?)
[$SnBr_4${*o*-C_4H_6(SeMe)$_2$}]	2.76, [2.55 (sh)]	n.o.

TABLE 2 Selected ^{1}H and ^{119}Sn-{^{1}H} NMR data at 180 K for the systems [SnX_4(L-L)]

*In CD_2Cl_2 relative to internal $SiMe_4$. †Relative to external neat $SnMe_4$.

No resonances were observed in the ^{125}Te-{^{1}H} NMR spectra. While this may be due to poor solubility, addition of readily soluble free telluroethers to the NMR experiments still showed no resonances. This shows that exchange is fast on the NMR time-scale in these systems.[28]

Although ligand dissociation occurring at similar energies to pyramidal inversion precludes more detailed measurements,[14] qualitatively it is clear that inversion barriers in these tin(IV) complexes decrease with ligand substituents Me > Ph, (CH_2)$_2$ > *o*-C_6H_4, and with the *trans* ligand Cl > Br > I; the same trends as observed with many d-block metal complexes. In view of the small number of well characterised examples of dithioether complexes of Sn(IV) and the absence of any examples of selenoether or telluroether complexes of Sn(IV), we undertook single-crystal X-ray analyses on several of the products in an atempt to identify trends in their geometric parameters, and to correlate these with their solution behaviour. All of the structures obtained displayed a distorted octahedral arrangement at Sn(IV) with the dithio-,

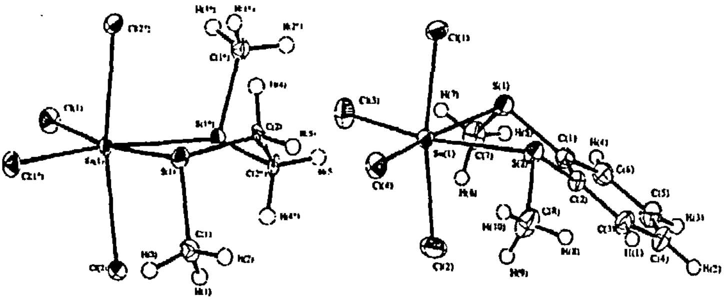

FIGURE 2 Structures of [$SnCl_4\{MeS(CH_2)_2SMe\}$] and [$SnCl_4\{o\text{-}C_6H_4(SMe)_2\}$]. Atoms marked with an asterisk are related by a crystallographic two-fold axis at (½, 0, z).

and macrocyclic systems.[16] In all cases the Sn-X_{transE} and SnX_{transX} bond lengths varied. When *trans* to a donor atom (E) the Sn-X distance was markedly shorter than the Sn-X distance for a halide atom *trans* to another halide atom. This presumably reflects the greater *trans* influence of X over the donor atom (E) in these Sn(IV) systems. Also common to all structures examined is a variation in Sn-E distance. These distances vary with ligand substituent, halide species and chelate ring-size. Sn-E bond distances increase with softening Lewis acid (Cl < Br < I), representative of the weaker binding to be expected. Sn-E are also seen to increase when a Me-substituent is replaced by a Ph-substituent. The size of the chelate ring also affects the Sn-E distances, with the highly strained four-membered chelate containing the longest Sn-E distance and the favoured five-membered chelate containing the shortest distance.

CONCLUSIONS

These results show that bidentate group 16 ligand adducts of certain tin(IV) halides can be readily prepared, and, the NMR spectroscopic data show that examples involving phenyl substituents are typically less stable than those involving methyl groups, with the complex stability decreasing with the SnX_4 acceptor: X = Cl > Br > I, and also with chelate ring size: 5 > 6 > 4. This is supported by the trends in the Sn-X and Sn-E bond lengths derived from the X-ray crystallographic studies. Furthermore, ^{1}H, $^{119}Sn-\{^{1}H\}$ and, where applicable, $^{77}Se-\{^{1}H\}$ and $^{125}Te-\{^{1}H\}$ NMR spectroscopic studies show that the $[SnX_4(L-L)]$ systems are extremely labile in solution, with the ligand-exchange and pyramidal-inversion processes both of low energy.

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References

[1] I. R. Beattie, *Q. Rev. Chem. Soc.*, 1963, **17**, 382.
[2] J.-M. Dumas and M. Gomel, *Bull. Chem. Soc. Fr.*, 1974, **10**, 1885.
[3] W. Levason and C. A. McAuliffe, *Coord. Chem. Rev.*, 1976, **19**, 173.
[4] P. G. Harrison, B. C. Lane and J. J. Zuckerman, *Inorg. Chem.*, 1972, **11**, 1537.
[5] D. Cunningham, M. J. Frazer and J. D. Donaldson, *J. Chem. Soc. (A)*, 1971, 2049.
[6] N. Bricklebank, S. M. Godfrey, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc. Chem. Commun.* 1994, 695; N. Bricklebank, S. M. Godfrey, C. A. McAuliffe and K. C. Molloy, *J. Chem. Soc., Dalton Trans.*, 1995, 1593.
[7] F. Kunkel, K. Dehnicke, H. Goesmann and D. Fenske, *Z. Naturforch. Teil B.*, 1995, **50**, 848.
[8] F. Sarikahya. *Synth. React. Inorg. Met. Org. Chem.*, 1989 **19**, 641.
[9] R. Colton, D. Daktemieks and C-A. Harvey, *Inorg. Chim. Acta*, 1982, **61**, 1.
[10] V. S. Petrosyan, N. S. Yahina and E. J. Gefel, *Silicon, Germanium, Tin and Lead Compounds*, 1985, **9**, 1387.
[11] W. McFarlane and N. H. Rees, *Polyhedron*, 1989, **8**, 2047.
[12] S. J. Ruzicka and A. E. Merbach, *Inorg. Chim. Acta*, 1976, **20**, 221; 1977, **22**, 191; S. J. Ruzicka, C. M. P. Favez and A. E. Merbach, *Inorg. Chim. Acta*, 1977, **23**, 239.
[13] C. T. G. Knight and A. E. Merbach, *Inorg. Chem.*, 1985, **24**, 576.
[14] E. W. Abel, S. K. Bhargava, K. G. Orrel and V. Sik, *Inorg. Chim. Acta*, 1981, **49**, 25.
[15] G.T. Morgan and W. Ledbury, *J. Chem. Soc.*, 1922, 2882.
[16] G. R. Willey, A. Jarvis, J. Palin and W. Errington, *J. Chem. Soc., Dalton Trans.*, 1994, 255.
[17] E. G. Hope, T. Kemmitt and W. Levason, *Organometallics*, 1988, **7**, 78.
[18] T. Kemmitt and W. Levason, *Organometallics*, 1989, **8**, 1303.
[19] T. Kemmitt, W. Levason and M. Webster, *Inorg. Chem.*, 1989, **28**, 692; T. Kemmitt and W. Levason, *Inorg. Chem.*, 1990, **29**, 731.
[20] J. L. Brown, T. Kemmitt and W. Levason, *J. Chem. Soc., Dalton Trans.*, 1990, 1513.
[21] J. R. Black and W. Levason, *J. Chem. Soc., Dalton Trans.*, 1994, 3225.
[22] J. R. Black, N. R. Champness, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1995, 3439; *Inorg. Chem*, 1996, **35**, 1820.
[23] H. Schumann, A. A. Arif, A. L. Rheingold, C. Janiak, R. Hoffmann and N. *Kuhn*, *Inorg. Chem.*, 1991, **30**, 1618.
[24] T. Chivers, *J. Chem. Soc., Dalton Trans.*, 1996, 1185 and refs. therein.
[25] S. E. Dann, A. R. J. Genge, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1996, 4471.
[26] A. R. J. Genge, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1997, 4479.
[27] S. E. Dann, A. R. J. Genge, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1997, 2207.
[28] A. R. J. Genge, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1997, 4549.
[29] E. W. Abel, S. K. Bhargava and K. G. Orrell, *Prog. Inorg. Chem.*, 1984, **33**, 1.