DALTON

Synthesis, multinuclear magnetic resonance spectroscopic studies and crystal structures of mono- and di-selenoether complexes of tin(IV) halides

Sandra E. Dann, Anthony R. J. Genge, William Levason and Gillian Reid

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

Reaction of SnX_4 (X = Cl or Br) with Me_2Se or diselenoether ligands in dry $CHCl_3$ produced white or yellow solids $[SnX_4L_2]$ in high yield [X = Cl, $L_2 = MeSe(CH_2)_nSeMe$, $PhSe(CH_2)_nSePh$ (n = 2 or 3), $C_6H_4(SeMe)_2$-*o* or $2Me_2Se$; X = Br, $L_2 = MeSe(CH_2)_nSeMe$ (n = 2 or 3), $C_6H_4(SeMe)_2$-*o* or $2Me_2Se$]. These compounds have been characterised by a combination of variable-temperature ^1H, ^{119}Sn-{^1H} and ^{77}Se-{^1H} NMR, IR spectroscopy and microanalyses. Single-crystal X-ray diffraction studies on *trans*-$[SnX_4(SeMe_2)_2]$, $[SnX_4\{C_6H_4(SeMe)_2\text{-}o\}]$ (X = Cl or Br) and $[SnCl_4\{MeSe(CH_2)_3SeMe\}]$ confirm distorted octahedral geometry at Sn^{IV} in each case, with the bidentate ligands chelating. The $C_6H_4(SeMe)_2$-*o* complexes adopt the *meso* arrangement, while the ligand is in the DL form in $[SnCl_4\{MeSe(CH_2)_3SeMe\}]$. The trends in d(Sn−X) and d(Sn−Se) reveal that the *trans* influence of halide is greater than that of selenium in these systems. In comparable systems d(Sn−Se) is longer in the bromo than in the chloro systems, consistent with the greater Lewis acidity of $SnCl_4$. The NMR studies revealed that pyramidal-inversion and ligand-dissociation processes are facile. In the $SeMe_2$ complexes both *cis* and *trans* isomers are present, while in the diselenoether systems the *meso* and DL forms are both apparent at low temperatures. The co-ordination shifts in the ^{77}Se-{^1H} NMR spectra are markedly dependent upon chelate-ring size; the first time this has been observed for complexes of a p-block metal.

The co-ordination chemistry of d-block metals has been one of the most active areas of inorganic chemistry in the last fifty years. Although p-block metals also form co-ordination complexes, these lack the characteristic UV/VIS spectra and magnetic properties, which provided much of the early impetus in the d-block work. p-Block metal complexes are often hydrolytically unstable and very labile in solution, which made them difficult to study and less suited to some spectroscopic techniques. The net result is that our knowledge of them is still very limited, although recent applications as precursors for metal chemical vapour deposition (MCVD) synthesis of new electronic materials have stimulated new investigations. In the case of tin(IV), nitrogen- and oxygen-donor ligand complexes have long been known[1] and phosphine complexes have recently been studied.[2] We recently reported a detailed study of dithioether complexes of tin(IV) halides using ^1H and ^{119}Sn-{^1H} NMR spectroscopy in solution and ^{119}Sn magic angle spinning (MAS) NMR in the solid state in conjunction with single-crystal X-ray diffraction.[3] Here we describe the first systematic study of the synthesis and properties of mono- and di-selenoether complexes of tin(IV) halides. The only prior reports of selenoether complexes are studies of $[SnX_4(R_2Se)_2]$ (X = Cl or Br, R = Me or Me_3SiCH_2) utilising ^1H NMR and vibrational spectroscopy.[4,5]

Results and Discussion

The reaction of SnX_4 (X = Cl or Br) with 2 molar equivalents of Me_2Se or 1 molar equivalent of diselenoether in dry $CHCl_3$ produced white or yellow solids $[SnX_4L_2]$ [X = Cl, $L_2 = MeSe(CH_2)_nSeMe$, $PhSe(CH_2)_nSePh$ (n = 2 or 3), $C_6H_4(SeMe)_2$-*o* or $2Me_2Se$; X = Br, $L_2 = MeSe(CH_2)_nSeMe$ (n = 2 or 3), $C_6H_4(SeMe)_2$-*o* or $2Me_2Se$]. Attempts to isolate complexes of $PhSe(CH_2)_nSePh$ (n = 2 or 3) with $SnBr_4$, or SnI_4 complexes with any of these ligands, were unsuccessful, although NMR evidence for their formation *in situ* was obtained in some cases (see below). As we observed previously with dithioethers,[3] no interaction between these selenoethers and a suspension of SnF_4 in chlorocarbons was apparent.

The solid complexes appear indefinitely stable in sealed tubes or in a dry-box, but decompose quickly in moist air, and are very easily hydrolysed by traces of water in solution. The complexes are more hydrolytically unstable than the dithioether analogues,[3] and all samples were handled in Schlenk equipment or in a glove-box (water levels < 10 ppm). Samples for solution NMR measurements were made up in rigorously anhydrous solvents in the glove-box, since trace amounts of water lead to some displacement of the neutral ligand. The IR spectra (Experimental section) show the presence of the selenium ligands and for the $[SnX_4$(diselenoether)$]$ complexes show several strong vibrations assignable as ν(SnX) (theory $2A_1 + B_1 + B_2$), and confirm the absence of water. The far-IR spectra of $[SnX_4(Me_2Se)_2]$ show single strong bands at 312 (X = Cl) and 220 cm^{-1} (X = Br) in agreement with the previous study[4] and consistent with the major isomer in the solid state being the *trans* form.

Prior to this study there were no reports of structural data on any tin(IV) selenoether complexes. Therefore, in order to enable comparisons with the thioether derivatives which we reported previously,[3] and to establish any trends between the solution NMR behaviour (below) and the solid-state structures, single-crystal structure analyses were undertaken on *trans*-$[SnX_4(Me_2Se)_2]$ and *cis*-$[SnX_4\{C_6H_4(SeMe)_2\text{-}o\}]$ (X = Cl or Br). For $[SnX_4(Me_2Se)_2]$ the structures show (X = Cl, Fig. 1, Table 1; X = Br, Fig. 2, Table 2) the central Sn^{IV} occupies a crystallographic inversion centre, co-ordinated *via* four precisely planar X atoms, with two mutually *trans* $SeMe_2$ ligands completing the slightly distorted octahedral geometry [X = Cl, Sn−X 2.413(2), 2.427(2), Sn−Se 2.7001(9); X = Br, Sn−X 2.576(2), 2.587(2), Sn−Se 2.731(2) Å]. In both cases the angles around the central Sn atom are very close to the 90 and 180° expected for a regular octahedron. The Sn−Se distances in the bromo derivative are significantly longer than in the chloro species, probably a consequence of $SnBr_4$ being a poorer acceptor than $SnCl_4$. McAuliffe and co-workers[6] have reported the structures of the thioether analogues *trans*- and *cis*-$[SnBr_4(SMe_2)_2]$. While the Sn−Br distances in these are very similar to those in *trans*-$[SnBr_4(SeMe_2)_2]$, the Sn−Se distances in this selenoether species are *ca.* 0.1 Å longer than d(Sn−S) in *trans*-$[SnBr_4(SMe_2)_2]$, consistent with the larger radius of Se over S.

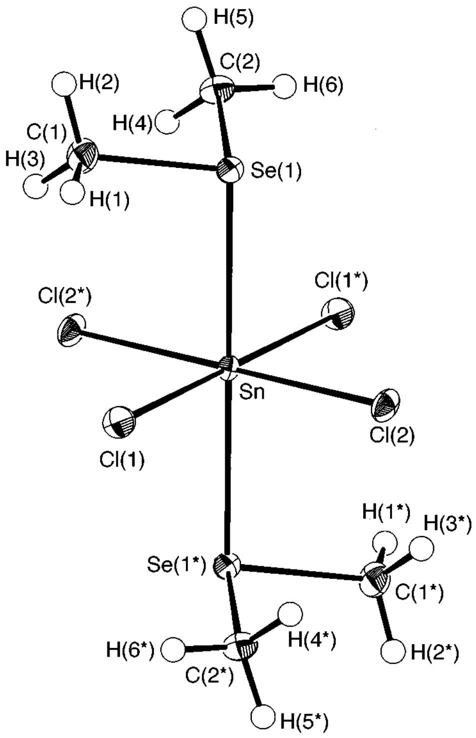

Fig. 1 View of the structure of *trans*-$[SnCl_4(Me_2Se)_2]$ with the numbering scheme adopted. Ellipsoids are shown at 40% probability and atoms marked with an asterisk are related by a crystallographic inversion centre

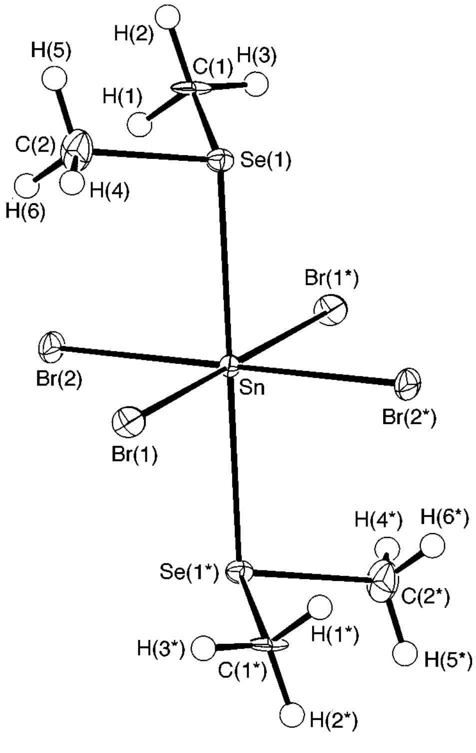

Fig. 2 View of the structure of *trans*-$[SnBr_4(Me_2Se)_2]$ with the numbering scheme adopted. Details as in Fig. 1

Table 1 Selected bond lengths (Å) and angles (°) for *trans*-$[SnCl_4(Me_2Se)_2]$

Sn–Se(1)	2.7001(9)	Se(1)–C(1)	1.957(10)
Sn–Cl(1)	2.413(2)	Se(1)–C(2)	1.952(9)
Sn–Cl(2)	2.427(2)		
Se(1)–Sn–Cl(2)	91.25(6)	Cl(1)–Sn–Cl(2)	89.54(8)
Se(1)–Sn–Cl(1)	89.40(6)	Sn–Se(1)–C(1)	100.7(3)
Sn–Se(1)–C(2)	100.2(3)	C(1)–Se(1)–C(2)	97.3(4)

Table 2 Selected bond lengths (Å) and angles (°) for *trans*-$[SnBr_4(Me_2Se)_2]$

Sn–Br(1)	2.576(2)	Se(1)–C(1)	1.96(2)
Sn–Br(2)	2.587(2)	Se(1)–C(2)	1.94(2)
Sn–Se(1)	2.731(2)		
Br(1)–Sn–Br(2)	90.47(5)	Br(1)–Sn–Se(1)	90.63(5)
Br(2)–Sn–Se(1)	88.46(5)	Sn–Se(1)–C(1)	100.9(4)
Sn–Se(1)–C(2)	102.2(5)	C(1)–Se(1)–C(2)	96.9(7)

The compounds $[SnX_4\{C_6H_4(SeMe)_2\text{-}o\}]$ (X = Cl or Br) both show distorted octahedral co-ordination at Sn^{IV} with the diselenoether chelating and adopting the *meso* arrangement (X = Cl, Fig. 3, Table 3; X = Br, Fig. 4, Table 4) [X = Cl, Sn–X (*trans* X) 2.389(3), 2.426(3), Sn–X (*trans* Se) 2.360(3), 2.364(3), Sn–Se 2.749(1), 2.787(2); X = Br, Sn–X (*trans* X) 2.512(1), 2.547(2), Sn–Br (*trans* Se) 2.600(2), Sn–Se 2.841(2) Å]. The trends apparent in *d*(Sn–X) with *trans* ligand parallel those observed for the thioether compounds,[3] *i.e.* *d*(Sn–X) *trans* X are consistently longer than *d*(Sn–X) *trans* Se. This suggests that the X ligands exert a greater *trans* influence than the Se (or S) donors in compounds of this type involving hard tin(IV) centres. Further evidence for this conclusion comes from a comparison of *d*(Sn–Se) in *trans*-$[SnX_4(SeMe_2)_2]$ *vs.* *d*(Sn–Se) in $[SnX_4\{C_6H_4(SeMe)_2\text{-}o\}]$. In the former the Se donor atoms are *trans* to each other, and *d*(Sn–Se) is noticeably shorter than in the latter where the greater *trans* influence of the X ligands leads to a significant elongation in *d*(Sn–Se).

As in the Me_2Se complexes discussed earlier, the Sn–Se distances in the bromo derivative are longer than in the chloro species, consistent with the relative acceptor strengths of the SnX_4 fragments. The angles involved in the chelate ring in $[SnX_4\{C_6H_4(SeMe)_2\text{-}o\}]$ are 76.08(4) for X = Cl and 71.60(6)° for X = Br, reflecting the restricted bite angle of the Se-(o-C_6H_4)Se linkage. This results in much more distorted overall stereochemistries for the bidentate ligand complexes compared to the monodentate species.

Data collection was also undertaken on a poorly diffracting crystal of $[SnCl_4\{MeSe(CH_2)_3SeMe\}]$* in an effort to establish whether the diselenoether is chelating or not. While the overall data quality was poor and the residuals rather high, preventing satisfactory refinement, the analysis was sufficient to confirm unambiguously that this compound does contain a chelating diselenoether ligand in the DL arrangement (Fig. 5). While there is no requirement that this structure is retained in solution, the solution NMR parameters suggest that at low temperature the $MeSe(CH_2)_3SeMe$ compounds are chelated (see below). While the high estimated standard deviations associated with the atomic positions and geometric parameters in this compound preclude any detailed comparisons with structural data on

---

* $C_5H_{12}Cl_4Se_2Sn$, $M = 490.6$, tetragonal $I4_1/a$, $a = 10.062(6)$, $c = 25.702(10)$ Å, $U = 2602(3)$ Å^3, $Z = 8$, $D_c = 2.504$ g cm^{-3}, $T = 150$ K, colourless prism, 0.25 × 0.24 × 0.15 mm, $\mu = 83.32$ cm^{-1}, $F(000) = 1824$; ω–2θ scans, 1187 unique reflections measured ($2\theta_{max} = 50°$), 836 with $I > 3\sigma(I)$ used in all calculations. The structure was solved by Patterson methods[7] and refined using iterative cycles of full-matrix least squares[8] which revealed one half $[SnCl_4\{MeSe(CH_2)_3SeMe\}]$ molecule (with the Sn atom lying on a two-fold axis) in the asymmetric unit. At isotropic convergence the data were corrected for absorption using DIFABS (maximum transmission factor 1.000, minimum 0.662),[9] and the Sn, Se and Cl atoms were then refined anisotropically and H atoms were included in fixed, calculated positions. This model refined to R, $R' = 0.106$, 0.159 respectively and $S = 6.83$ for 43 parameters. The final Fourier-difference map showed several residual electron-density peaks of up to 4.5 e Å^{-3}. Some of these occurred within 1 Å of the Sn or Se atoms, and attempts to refine the others as partially occupied O atoms (*e.g.* from H_2O solvate molecules) were not successful.

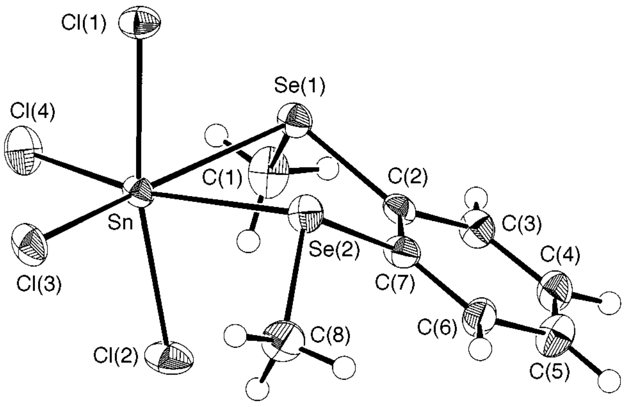

Fig. 3 View of the structure of [$SnCl_4\{C_6H_4(SeMe)_2\text{-}o\}$] with the numbering scheme adopted. 40% Probability ellipsoids are shown

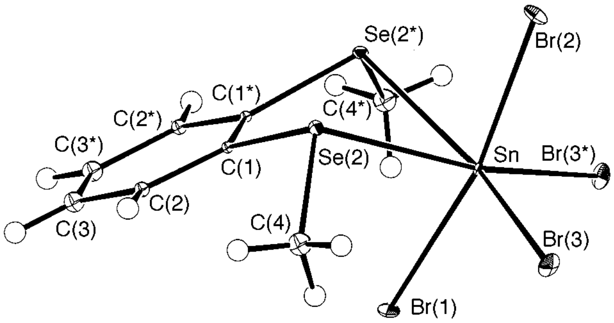

Fig. 4 View of the structure of [$SnBr_4\{C_6H_4(SeMe)_2\text{-}o\}$] with the numbering scheme adopted. 40% Probability ellipsoids are shown. Atoms marked with an asterisk are related by a crystallographic mirror plane

Table 3 Selected bond lengths (Å) and angles (°) for [$SnCl_4\{C_6H_4(SeMe)_2\text{-}o\}$]

Sn–Se(1)	2.749(1)	Sn–Se(2)	2.787(2)
Sn–Cl(1)	2.426(3)	Sn–Cl(2)	2.389(3)
Sn–Cl(3)	2.360(3)	Sn–Cl(4)	2.364(3)
Se(1)–C(1)	1.95(1)	Se(1)–C(2)	1.92(1)
Se(2)–C(7)	1.93(1)	Se(2)–C(8)	1.93(1)
C(2)–C(3)	1.39(2)	C(4)–C(5)	1.38(2)
C(2)–C(7)	1.41(2)	C(5)–C(6)	1.39(2)
C(3)–C(4)	1.38(2)	C(6)–C(7)	1.40(2)
Se(1)–Sn–Se(2)	76.08(4)	Se(1)–Sn–Cl(1)	82.41(8)
Se(1)–Sn–Cl(2)	91.27(9)	Se(1)–Sn–Cl(3)	166.60(9)
Se(1)–Sn–Cl(4)	90.50(9)	Se(2)–Sn–Cl(1)	83.16(8)
Se(2)–Sn–Cl(2)	87.40(9)	Se(2)–Sn–Cl(3)	91.41(9)
Se(2)–Sn–Cl(4)	166.37(9)	Cl(1)–Sn–Cl(2)	169.7(1)
Cl(1)–Sn–Cl(3)	91.4(1)	Cl(1)–Sn–Cl(4)	92.9(1)
Cl(2)–Sn–Cl(3)	93.0(1)	Cl(2)–Sn–Cl(4)	95.4(1)
Cl(3)–Sn–Cl(4)	101.7(1)	Sn–Se(1)–C(1)	104.2(4)
Sn–Se(1)–C(2)	100.3(3)	C(1)–Se(1)–C(2)	99.4(5)
Sn–Se(2)–C(7)	98.6(4)	Sn–Se(2)–C(8)	103.3(4)
C(7)–Se(2)–C(8)	100.2(6)	Se(1)–C(2)–C(3)	118.7(9)
Se(1)–C(2)–C(7)	121.7(9)	C(3)–C(2)–C(7)	119(1)
C(2)–C(3)–C(4)	120(1)	C(3)–C(4)–C(5)	120(1)
C(4)–C(5)–C(6)	120(1)	Se(2)–C(7)–C(2)	120.9(9)
C(5)–C(6)–C(7)	119(1)	C(2)–C(7)–C(6)	119(1)
Se(2)–C(7)–C(6)	119.4(9)		

related compounds, the trends in the bond lengths are similar to those already discussed. Also, it is not surprising that the six-membered chelate ring in this species, which results in a Se–Sn–Se angle of 85.9(2)°, leads to a considerably less strained octahedral geometry than in the *o*-phenylene derivatives discussed above.

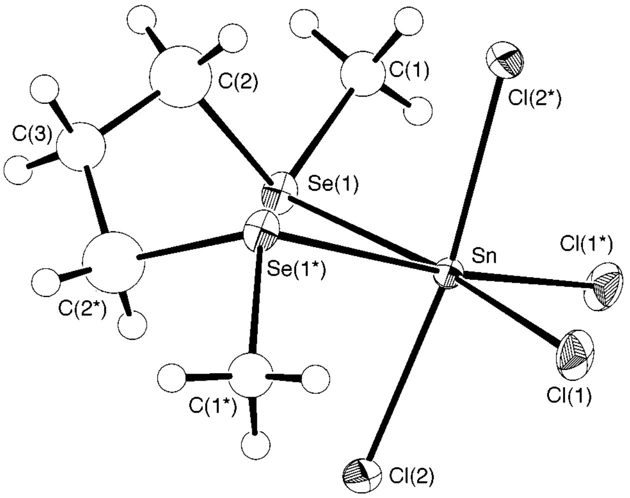

Fig. 5 View of the structure of [$SnCl_4\{MeSe(CH_2)_3SeMe\}$] with the numbering scheme adopted. 40% Probability ellipsoids are shown. Atoms marked with an asterisk are related by a crystallographic two-fold operation. Sn–Cl(1) 2.385(9), Sn–Cl(2) 2.427(9), Sn–Se(1) 2.766(4) Å; Se(1)–Sn–Se(1*) 85.9(2)°

Table 4 Selected bond lengths (Å) and angles (°) for [$SnBr_4\{C_6H_4(SeMe)_2\text{-}o\}$]

Sn–Br(1)	2.600(2)	Sn–Br(2)	2.547(2)
Sn–Br(3)	2.512(1)	Sn–Se(2)	2.841(2)
Se(2)–C(1)	1.93(1)	Se(2)–C(4)	1.95(1)
C(1)–C(1*)	1.36(2)	C(1)–C(2)	1.40(2)
C(2)–C(3)	1.42(2)	C(3)–C(3*)	1.36(2)
Br(1)–Sn–Br(2)	169.12(7)	Br(1)–Sn–Br(3)	92.44(5)
Br(2)–Sn–Se(2)	83.38(5)	Br(1)–Sn–Se(2)	87.81(5)
Br(3)–Sn–Se(2)	93.15(4)	Br(2)–Sn–Br(3)	94.40(5)
Br(3)–Sn–Se(2*)	164.74(5)	Br(3)–Sn–Br(3*)	102.08(7)
Se(2)–Sn–Se(2*)	71.60(6)	Sn–Se(2)–C(1)	96.5(3)
Sn–Se(2)–C(4)	100.9(4)	C(1)–Se(2)–C(4)	99.8(5)
Se(2)–C(1)–C(1*)	120.6(3)	Se(2)–C(1)–C(2)	119.4(8)
C(1*)–C(1)–C(2)	120.0(7)	C(1)–C(2)–C(3)	120(1)
C(2)–C(3)–C(3*)	119.5(7)		

The SnX_4/Me_2Se (X = Cl or Br) systems have previously been examined by Ruzicka and co-workers[4] *via* ^1H NMR spectroscopy. At 300 K in CD_2Cl_2, [$SnCl_4(Me_2Se)_2$] exhibits a single δ(Me) resonance with no evidence of $^{119/117}Sn$ satellites, but on cooling to 250 K the resonance splits and ill defined satellites appear. At 180 K two resonances are present (Table 5) in the ratio *ca.* 1.5 : 1 due to *trans* and *cis* isomers, with $^{119/117}Sn$ couplings of *ca.* 50–60 Hz. The behaviour of [$SnBr_4(Me_2Se)_2$] is similar, although the *trans* : *cis* ratio is *ca.* 3 : 1. The ^1H NMR spectra of the [SnX_4(diselenoether)] complexes are summarised in Table 5. As in our previous study of dithioether complexes,[3] NMR studies of the diselenoether complexes were carried out in anhydrous CD_2Cl_2 solution. The complexes of $MeSe(CH_2)_nSeMe$ are poorly soluble in CD_2Cl_2, especially at low temperatures, resulting in relatively poor quality spectra. Solubilities are higher in tetrahydrofuran or acetone, but the spectra obtained were significantly different and it is probable that these oxygen donors provide alternative ligands for the tin, hence these studies were not pursued. At 180 K the complexes of $MeSe(CH_2)_nSeMe$ each show two δ(Me) resonances (Table 5) due to DL and *meso* invertomers, which coalesce on warming due to the onset of pyramidal inversion and reversible ligand dissociation. Owing to the very poor solubility, convincing tin satellites were not observable. Resonances due to both invertomers were present in the ^1H NMR spectrum of [$SnCl_4\{MeSe(CH_2)_2SeMe\}$] below *ca.* 250 K, and below *ca.* 225 K in the corresponding spectrum of the bromide. The resonances of the invertomers were observed at lower temperatures for complexes of $MeSe(CH_2)_3SeMe$, and for [$SnCl_4\{PhSe(CH_2)_3SePh\}$] the expected second-order CH_2 resonances were very broad even at 180 K. The complex

Table 5 Proton NMR data[a]

	δ	
Complex	300	180 K[b]
$[SnCl_4(Me_2Se)_2]$	2.51	2.44, 2.54 (1 : 1.5)
$[SnBr_4(Me_2Se)_2]$	2.36	2.26, 2.40 (1 : 3)
$[SnCl_4\{MeSe(CH_2)_2SeMe\}]$	2.48 (3 H), 3.30 (2 H)	2.40, 2.46, 3.10, 3.40 (1 : 1)
$[SnBr_4\{MeSe(CH_2)_2SeMe\}]$	2.25 (3 H), 3.15 (2 H)	2.21, 2.30, 3.10, 3.30 (2 : 1)
$[SnCl_4\{MeSe(CH_2)_3SeMe\}]$	2.30 (1 H), 2.46 (3 H), 3.2 (2 H)	2.40, 2.45, 2.51, 3.11, 3.42 (1 : 5)
$[SnBr_4\{MeSe(CH_2)_3SeMe\}]$	2.41 (1 H + 3 H), 3.1 (2 H)	2.38, 2.44, 3.05, 3.25 (1 : 3)
$[SnCl_4\{C_6H_4(SeMe)_2\text{-}o\}]$	2.83 (3 H), 7.5, 7.65 (2 H)	2.99, 2.79, 7.55 (5 : 1)
$[SnBr_4\{C_6H_4(SeMe)_2\text{-}o\}]$	2.45 (3 H), 7.25, 7.38 (2 H)	2.76 [2.55 (sh)], 7.47
$[SnCl_4\{PhSe(CH_2)_2SePh\}]$	3.39 (2 H), 7.2–7.7 (5 H)	3.5, 3.8, 7.0–7.8 (1 : 1)
$[SnCl_4\{PhSe(CH_2)_3SePh\}]$	2.10 (1 H), 3.25 (2 H), 7.2–7.7 (5 H)	Ill defined (see text)

[a] In CD_2Cl_2 relative to internal $SiMe_4$. [b] For Me_2Se complexes the ratio refers to the relative abundances of the geometric isomers, whereas for the bidentate ligand, it shows the abundances of the invertomers (*meso* and DL) obtained from integrating Me or CH_2 resonances.

$[SnCl_4\{C_6H_4(SeMe)_2\text{-}o\}]$ was more soluble in CD_2Cl_2 and at 180 K two sharp methyl resonances with clearly resolved $^{117/119}Sn$ satellites (^3J *ca.* 40 Hz) were observed, attributable to the expected invertomers, although the relative intensities were quite disparate (>5 : 1). On warming to *ca.* 210 K the lines coalesced, and above this temperature only a singlet δ(Me) resonance was present with no satellites. The corresponding spectrum of $[SnBr_4\{C_6H_4(SeMe)_2\text{-}o\}]$ at 180 K contained a broad line at δ 2.76 with a weak shoulder at 2.55, suggesting that even at this temperature the low-temperature-limiting spectrum was not achieved. Although the poor spectral quality resulting from the low solubilities, and complications introduced by ligand dissociation, preclude a more detailed treatment of the inversion processes, it is clear that qualitatively inversion barriers decrease in the order Se > S for analogous ligands.

The $^{77}Se\text{-}\{^1H\}$ and $^{119}Sn\text{-}\{^1H\}$ NMR spectra of $[SnCl_4(Me_2Se)_2]$ in CH_2Cl_2 contained single resonances at 300 K due to fast exchange between the isomers, but on cooling to *ca.* 250 K separate resonances for the *cis* and *trans* isomers are resolved which sharpen on further cooling, and at 180 K clear ^1J couplings appear (Table 6). [The $\gamma(^{119}Sn):\gamma(^{117}Sn)$ ratio is 0.956 : 1 and separate couplings to the two tin isotopes were not resolved.] In contrast, CH_2Cl_2 solutions of $[SnBr_4(Me_2Se)_2]$ show neither $^{77}Se\text{-}\{^1H\}$ nor $^{119}Sn\text{-}\{^1H\}$ resonances at room temperature, but single resonances appear at *ca.* 280 K and on further cooling resonances due to the *cis* and *trans* isomers are resolved. A solution of $[SnCl_4(Me_2Se)_2]$ containing an excess of Me_2Se in CH_2Cl_2 at 180 K shows sharp $^{77}Se\text{-}\{^1H\}$ resonances for *cis* and *trans* isomers and free Me_2Se (Fig. 6), showing exchange is slow on the NMR time-scale. On warming to *ca.* 230 K the resonance of the *cis* isomer broadens and then disappears, but that of the *trans* form broadens only near ambient temperatures. Corresponding changes occur in the $^{119}Sn\text{-}\{^1H\}$ spectra as a function of temperature. The NMR spectra of the system $[SnBr_4(Me_2Se)_2]$–excess Me_2Se in CH_2Cl_2 had generally similar behaviour, but with the onset of exchange at lower temperatures. The behaviour of these complexes is qualitatively similar to that observed in the $[SnX_4(Me_2S)_2]$–Me_2S systems by Knight and Merbach.[11]

None of the $[SnX_4$(diselenoether)$]$ complexes exhibited a $^{119}Sn\text{-}\{^1H\}$ NMR resonance at 300 K (probably due to reversible ring opening), and only $[SnCl_4\{MeSe(CH_2)_2SeMe\}]$ exhibited a $^{77}Se\text{-}\{^1H\}$ resonance and even this was very weak and broad. On cooling resonances from both nuclei were observed, initially as single broad peaks which sharpened on cooling and in most cases resolved into two signals by 180 K (Table 6), consistent with the presence of the *meso* and DL invertomers. Poor solubility of the diselenaalkane complexes (see above) at low temperatures resulted in spectra with relatively poor signal-to-noise ratios even after long accumulations, and prevented identification of satellites and the spectral data in Table 6 should be viewed with these qualifications in mind. Nonetheless the behaviour with X and ligand structure observed in the spectra from the different nuclei (^1H, ^{77}Se and ^{119}Sn) are internally consistent.

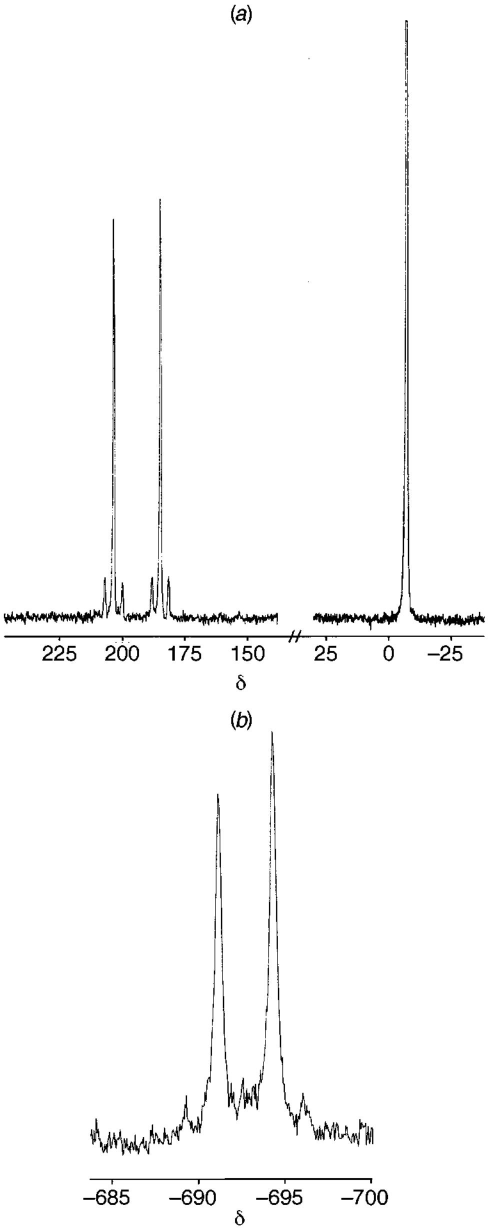

Fig. 6 (*a*) $^{77}Se\text{-}\{^1H\}$ and (*b*) $^{119}Sn\text{-}\{^1H\}$ NMR spectrum of $[SnCl_4(Me_2Se)_2]$ containing an excess of Me_2Se in CH_2Cl_2 at 180 K

A solution of $[SnCl_4\{C_6H_4(SeMe)_2\text{-}o\}]$ containing free $C_6H_4(SeMe)_2\text{-}o$ showed separate $^{77}Se\text{-}\{^1H\}$ NMR resonances for the free selenoether and *meso* and DL forms of the co-

Table 6 ^{77}Se-{^{1}H} and ^{119}Sn-{^{1}H} NMR data at 180 K [a]

Complex	δ(^{77}Se-{^{1}H})[b]	δ(^{119}Sn-{^{1}H})[c]
$[SnCl_4(Me_2Se)_2]$[d]	185 (460), 204 (490) [1:1]	−691 (468), −695 (490)
$[SnBr_4(Me_2Se)_2]$	204 (555), 219 (500) [2:1]	−1296 (500), −1319 (550)
$[SnCl_4\{MeSe(CH_2)_2SeMe\}]$[e]	482, 487 [1:1]	−680, −682
$[SnBr_4\{MeSe(CH_2)_2SeMe\}]$	493, 496 [2:1]	−1283, −1288
$[SnCl_4\{MeSe(CH_2)_3SeMe\}]$	231, 232 [5:1]	−685, −686.5
$[SnBr_4\{MeSe(CH_2)_3SeMe\}]$	261, 263 [1:2]	−1305, −1308
$[SnCl_4\{C_6H_4(SeMe)_2$-*o*$\}]$	323, 338 [1:5]	−632, −635?
$[SnBr_4\{C_6H_4(SeMe)_2$-*o*$\}]$	355	−1258 (br)
$[SnCl_4\{PhSe(CH_2)_2SePh\}]$	436	—

Free selenoether: δ(^{77}Se) Me_2Se, O; $MeSe(CH_2)_2SeMe$, 121; $MeSe(CH_2)_3SeMe$, 74; $PhSe(CH_2)_2SePh$, 340; $C_6H_4(SeMe)_2$-*o*, 202.[10] [a] In anhydrous CH_2Cl_2–CD_2Cl_2 containing $[Cr(acac)_3]$ (acac = acetylacetonate). [b] Relative to external neat Me_2Se, ^1J(^{77}Se–$^{117/119}$Sn)/Hz in parentheses, approximate ratios in square brackets. [c] Relative to external neat $SnMe_4$, ^1J(^{77}Se–^{119}Sn). [d] δ(^{77}Se-{^{1}H}) 176, δ(^{119}Sn-{^{1}H}) −695 at 300 K. [e] δ(^{77}Se-{^{1}H}) 486 at 300 K.

ordinated selenoether at 180 K. The signals were clearly broadened by 220 K and had disappeared by 235 K showing fast ligand exchange at this temperature. The $[SnCl_4\{PhSe(CH_2)_n$-$SePh\}]$ ($n = 2$ or 3) complexes failed to show ^{119}Sn resonances even at 180 K, presumably due to exchange, and only the $n = 2$ complex exhibited a ^{77}Se resonance at 180 K.

A solution of SnI_4 in CH_2Cl_2 containing a large excess of Me_2Se exhibited a ^{77}Se-{^{1}H} NMR resonance at δ + 152 at 180 K. This disappeared on warming and was not present unless a large excess of Me_2Se was used. It seems likely that this may indicate the formation of a weak adduct {possibly *trans*-$[SnI_4(Me_2Se)_2]$} in solution at low temperatures. In contrast, a CH_2Cl_2 solution of SnI_4 containing an excess of $MeSe(CH_2)_2$-SeMe showed no evidence for adduct formation over the temperature range 180–300 K. No evidence for complex formation was observed in Ph_2Se–SnX_4 systems. The $SnBr_4$–$PhSe(CH_2)_2SePh$–CH_2Cl_2 mixtures showed both ^{119}Sn and ^{77}Se resonances at low temperatures indicative of complex formation, but the solid complex could not be isolated.

Several consistent trends can be discerned in these data. The ^{119}Sn-{^{1}H} NMR resonances for the complexes show similar patterns of behaviour in *cis*/*trans*-$[SnX_4(Me_2E)_2]$ (E = S or Se) and in $[SnX_4(L$–$L)]$ for dithioether and diselenoether analogues with δ shifted by 110–150 ppm to low frequency on changing S for Se. In the ^{77}Se-{^{1}H} NMR spectra of $[SnX_4$-$(Me_2Se)_2]$ large high-frequency co-ordination shifts Δ (= $\delta_{complex} - \delta_{ligand}$) are observed of approximately +200 with the resonance of the *cis* isomer slightly to high frequency of the *trans*. For transition-metal complexes containing chelating diselenoether ligands the magnitude of the co-ordination shifts vary greatly with the chelate-ring size.[12] Following the approach of Garrou[13] first used for diphosphine complexes, one calculates first the co-ordination shift as above, and then the chelate-ring parameter (ΔR) defined as Δ(chelate complex) − Δ(equivalent monodentate complex). For our purposes for the complexes of $MeSe(CH_2)_nSeMe$, the 'equivalent monodentate complexes' are *cis*-$[SnX_4(Me_2Se)_2]$. For free $MeSe(CH_2)_2SeMe$ δ 121,[10] leading to Δ 365 for the tin chloride complex and 374 for the bromide and corresponding ΔR 161 (Cl) and 155 (Br), that is large positive ΔR values for the five-membered-ring species. In contrast, for $MeSe(CH_2)_3SeMe$ δ 74, Δ 158 (Cl) and 188 (Br) and ΔR −46 (Cl) and −31 (Br), *i.e.* negative ΔR values for the six-membered-ring complexes. This is clear evidence for the presence of a chelate-ring-parameter effect in the selenium chemical shift values, and is the first time this has been observed in complexes of a main-group metal. The trends are similar to those established with d-block metal complexes.[12] The origin of the chelate-ring effect is unclear even in the much studied diphosphine systems,[14] but the observation of such an effect in the tin complexes here, where the metal is behaving as a simple σ acceptor, supports the suggestion that it involves the strain in different size rings.[10]

Since we do not have data for complexes of PhMeSe which would be the 'equivalent monodentate ligand' for $PhSe(CH_2)_2$-SePh or $C_6H_4(SeMe)_2$-*o*, similar calculations of ΔR cannot be carried out for complexes of these bidentate compounds, although for the latter the substantial co-ordination shifts in themselves strongly suggest that the chelate structures identified by X-ray crystallography for solid $[SnX_4\{C_6H_4(SeMe)_2$-*o*$\}]$ are also retained in solution.

Experimental

Physical measurements were made as described previously.[3] The ^{77}Se-{^{1}H} NMR spectra were obtained from anhydrous CH_2Cl_2–10% CD_2Cl_2 solutions as described.[10] The selenium ligands were made by literature methods.[10,15]

Syntheses

The complexes $[SnX_4L_2]$ were all made by the same general method. The tin(IV) halides are moisture sensitive, therefore all of the reactions were carried out under an atmosphere of dry nitrogen, using standard Schlenk, vacuum-line and dry-box techniques.

$[SnCl_4(Me_2Se)_2]$. Tin(IV) chloride (0.26 g, 1 mmol) was added to a solution of Me_2Se (0.22 g, 2 mmol) in chloroform (10 cm^3). The complex formed immediately as a white precipitate which was filtered off and dried *in vacuo*. Yield 0.44 g, 92% (Found: C, 9.75; H, 2.7. Calc. for $C_4H_{12}Cl_4Se_2Sn$: C, 10.05; H, 2.5%); $\tilde{\nu}_{max}$/cm^{-1} (Sn–Cl) 312.

$[SnBr_4(Me_2Se)_2]$. A saturated solution of tin(IV) bromide (0.44 g, 1 mmol) in chloroform (5 cm^3) was added dropwise to a solution of Me_2Se (0.22 g, 2 mmol) in chloroform (5 cm^3). On reducing the volume *in vacuo* the complex slowly formed as yellow crystals which were filtered off and dried *in vacuo*. Yield 0.54 g, 82% (Found: C, 7.4; H, 1.9. Calc. for $C_4H_{12}Br_4Se_2Sn$: C, 7.3; H, 1.85%); $\tilde{\nu}_{max}$/cm^{-1} (Sn–Br) 220.

The same general method was used for the synthesis of all of the complexes involving bidentate ligands, and this is detailed for one example of each of X = Cl and X = Br.

$[SnCl_4\{MeSe(CH_2)_2SeMe\}]$. Tin(IV) chloride (0.26 g, 1 mmol) was added to a solution of the selenoether (0.22 g, 1 mmol) in chloroform (10 cm^3). The complex precipitated as a white powder which was filtered off and dried *in vacuo*. Yield 0.45 g, 72% (Found: C, 10.3; H, 2.5. Calc. for $C_4H_{10}Cl_4Se_2Sn$: C, 10.1; H, 2.1%); $\tilde{\nu}_{max}$/cm^{-1} (Sn–Cl) 339, 331, 320 and 312.

$[SnCl_4\{MeSe(CH_2)_3SeMe\}]$. White precipitate. Yield 0.72 g, 93% (Found: C, 12.5; H, 2.6. Calc. for $C_5H_{12}Cl_4Se_2Sn$: C, 12.25; H, 2.45%); $\tilde{\nu}_{max}$/cm^{-1} (Sn–Cl) 336, 331, 325 and 313.

$[SnCl_4\{PhSe(CH_2)_2SePh\}]$. Yellow crystalline precipitate. Yield 0.59 g, 81% (Found: C, 27.2; H, 2.5. Calc. for

Table 7 Crystallographic data

	trans-[$SnCl_4(Me_2Se)_2$]	*trans*-[$SnBr_4(Me_2Se)_2$]	[$SnCl_4\{C_6H_4(SeMe)_2$-*o*}]	[$SnBr_4\{C_6H_4(SeMe)_2$-*o*}]
Formula	$C_4H_{12}Cl_4Se_2Sn$	$C_4H_{12}Br_4Se_2Sn$	$C_8H_{10}Cl_4Se_2Sn$	$C_8H_{10}Br_4Se_2Sn$
M	478.56	656.36	524.59	702.39
Colour, morphology	Colourless block	Yellow, rhomb	Colourless, block	Yellow, block
Crystal dimensions/mm	0.25 × 0.10 × 0.10	0.45 × 0.40 × 0.20	0.30 × 0.15 × 0.12	0.30 × 0.20 × 0.20
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/m$
a/Å	6.539(2)	6.768(3)	8.419(2)	6.826(3)
b/Å	12.610(3)	13.000(3)	11.323(3)	11.324(2)
c/Å	8.111(2)	8.373(3)	8.251(1)	9.936(2)
α/°			90.32(2)	
β/°	107.67(2)	108.47(3)	98.17(2)	100.67(2)
γ/°			109.68(2)	
U/Å^3	637.2(2)	698.7(4)	731.8(3)	754.7(3)
Z	2	2	2	2
$F(000)$	444	588	488	632
D_c/g cm^{-3}	2.494	3.119	2.380	3.119
μ(Mo-Kα)/cm^{-1}	85.04	184.63	73.85	184.63
Transmission factors (maximum, minimum)	1.000, 0.694	1.000, 0.645	1.000, 0.717	1.000, 0.645
No. of unique observed reflections	1189	1289	2563	1402
R_{int} (based on F^2)	0.031	0.132	0.028	0.043
Unique observed reflections with $I_o > 2.5\sigma(I_o)$	925	1039	1763	1143
No. parameters	52	52	136	50
Goodness of fit	2.29	4.35	1.97	3.49
$R(F_o)$	0.036	0.050	0.045	0.049
$R'(F_o)$	0.043	0.057	0.052	0.062
Maximum residual peak,	1.19	1.66	1.33	2.49
trough/e Å^{-3}	−1.66	−2.15	−2.10	−2.91

$R = \Sigma(|F_o|_i - |F_c|_i)/\Sigma|F_o|_i$, $R' = [\Sigma w_i(|F_o|_i - |F_c|_i)^2/\Sigma w_i|F_o|_i^2]^{\frac{1}{2}}$ and $w^{-1} = \sigma^2(F)$. Goodness of fit $= [\Sigma(|F_o|_i - |F_c|_i - |F_c|)/\sigma_i]/(n - m) \approx 1$ where n = no. of data, m = no. of parameters.

$C_{14}H_{14}Cl_4Se_2Sn$: C, 28.0; H, 2.35%); $\tilde{\nu}_{max}$/cm^{-1} (Sn−Cl) 330, 324, 319 and 313.

[$SnCl_4\{PhSe(CH_2)_3SePh\}$]. Orange crystalline precipitate. Yield 0.53 g, 86% (Found: C, 29.5; H, 2.7. Calc. for $C_{15}H_{16}Cl_4Se_2Sn$: C, 29.8; H, 2.65%); $\tilde{\nu}_{max}$/cm^{-1} (Sn−Cl) 330, 324, 315 and 304.

[$SnCl_4\{C_6H_4(SeMe)_2$-*o*}]. White crystalline precipitate. Yield 0.49 g, 94% (Found: C, 18.35; H, 2.0. Calc. for $C_8H_{10}Cl_4Se_2Sn$: C, 18.3; H, 1.9%); $\tilde{\nu}_{max}$/cm^{-1} (Sn−Cl) 338, 328, 323 and 317.

[$SnBr_4\{MeSe(CH_2)_2SeMe\}$]. A saturated solution of tin(IV) bromide (0.44 g, 1 mmol) in chloroform (5 cm^3) was added dropwise to a solution of the selenoether (0.22 g, 1 mmol) in chloroform (5 cm^3). A pale yellow precipitate formed immediately which was filtered off and dried *in vacuo*. Yield 0.50 g, 69% (Found: C, 7.5; H, 1.8. Calc. for $C_4H_{10}Br_4Se_2Sn$: C, 7.35; H, 1.55%); $\tilde{\nu}_{max}$/cm^{-1} (Sn−Br) 220, 218, 216 and 214.

[$SnBr_4\{MeSe(CH_2)_3SeMe\}$]. Yellow precipitate. Yield 0.48 g, 81% (Found: C, 9.3; H, 1.9. Calc. for $C_5H_{12}Br_4Se_2Sn$: C, 9.0; H, 1.8%); $\tilde{\nu}_{max}$/cm^{-1} (Sn−Br) 219, 214, 206 and 201.

[$SnBr_4\{C_6H_4(SeMe)_2$-*o*}]. Orange crystals. Yield 0.67 g, 86% (Found: C, 13.9; H, 1.7). Calc. for $C_8H_{10}Br_4Se_2Sn$: C, 13.65; H, 1.4%); $\tilde{\nu}_{max}$/cm^{-1} (Sn−Br) 230, 228, 224 and 222.

X-Ray crystallography

Single crystals of [$SnCl_4(Me_2Se)_2$], [$SnBr_4(Me_2Se)_2$], [$SnCl_4\{C_6H_4(SeMe)_2$-*o*}] and [$SnBr_4\{C_6H_4(SeMe)_2$-*o*}] were obtained from a solution of the appropriate complex in $CHCl_3$. The compounds were extremely sensitive to hydrolysis on exposure to moist air. Therefore, in each case the selected crystal was coated with mineral oil, mounted on a glass fibre using silicone grease as adhesive, and immediately placed in a stream of cold nitrogen gas and cooled to 150 K. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Cryostreams low-temperature attachment, and graphite-monochromated Mo-Kα X-radiation (λ_{max} = 0.710 73 Å); T = 150 K, ω–2θ scans. The intensities of three standard reflections were monitored every 150. No significant crystal decay or movement was observed. As there were no identifiable faces the raw data for the compounds [$SnCl_4(Me_2Se)_2$] and [$SnCl_4\{C_6H_4(SeMe)_2$-*o*}] were corrected for absorption using ψ-scans. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses in each case. Crystallographic data are present in Table 7.

All four structures were solved by direct methods,[16] and then developed by iterative cycles of full-matrix least-squares refinement (based on F) and Fourier-difference syntheses which located all non-H atoms in the asymmetric unit.[8] For [$SnBr_4(Me_2Se)_2$] and [$SnBr_4\{C_6H_4(SeMe)_2$-*o*}] an empirical absorption correction using DIFABS[9] was applied to the raw data at isotropic convergence. All non-H atoms in the structures were refined anisotropically (with the exception of [$SnBr_4\{C_6H_4(SeMe)_2$-*o*}] for which the C atoms were refined isotropically), and H atoms were placed in fixed, calculated positions with d(C−H) = 0.96 Å.

Atomic co-ordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/498.

Acknowledgements

We thank the University of Southampton and the EPSRC for support, and the latter for a grant to purchase the diffractometer.

References

1 I. R. Beattie, *Q. Rev. Chem. Soc.*, 1963, **17**, 382.
2 N. C. Norman and N. L. Pickett, *Coord. Chem. Rev.*, 1995, **145**, 27.

3 S. E. Dann, A. R. J. Genge, W. Levason and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1996, 4471.

4 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.

5 E. W. Abel, S. K. Bhargava, K. G. Orrell and V. Sik, *Inorg. Chim. Acta*, 1981, **49**, 25.

6 N. Bricklebank, S. M. Godfrey, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1994, 695.

7 PATTY, The DIRDIF Program System, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.

8 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1992.

9 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

10 D. J. Gulliver, E. G. Hope, W. Levason, S. G. Murray, D. M. Potter and G. L. Marshall, *J. Chem. Soc., Perkin Trans 2*, 1984, 429.

11 C. T. G. Knight and A. E. Merbach, *Inorg. Chem.*, 1985, **24**, 576.

12 E. G. Hope and W. Levason, *Coord. Chem. Rev.*, 1993, **122**, 109.

13 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.

14 J. G. Verkade and L. D. Quin (Editors), *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, VCH, Deerfield Beach, FL, 1987.

15 E. G. Hope, T. Kemmitt and W. Levason, *J. Chem. Soc., Perkin Trans. 2*, 1987, 487.

16 G. M. Sheldrick, SHELXS 86, program for crystal structure solution, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

Received 19*th February* 1997; *Paper* 7/01181D