Dichloro(tetramethylthiourea)selenium(II): Stabilization of the $SeCl_2$ Molecule *via* Co-ordination

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Summary The stabilization of the $SeCl_2$ molecule as the tetramethylthiourea complex $SeCl_2$(tmtu) is reported.

FROM vapour density,[1a,b] electron diffraction,[2] and Raman spectroscopic[3] studies it is known that $SeCl_4$ is completely dissociated into $SeCl_2$ and Cl_2 in the gas phase from 200—600°. The only known chemistry of $SeCl_2$ is the disproportionation to Se_2Cl_2 and $SeCl_4$ in the liquid or solid states, and the reaction with Cl_2 to give $SeCl_4$[1]

We have recently reported the preparation of methyltrihalogeno(tetramethylthiourea)tellurium(IV) complexes[4] from the reaction of $MeTeCl_3$ and $MeTeBr_3$ with tetramethylthiourea (tmtu). In extending our studies we found that the reaction of methylselenium trichloride with tmtu gave the unexpected complex $SeCl_2$(tmtu).

$MeSeCl_3$ reacted with tmtu to give, after work-up, a yellow solid. Recrystallization ($CHCl_3$) gave bright yellow moisture-sensitive crystals, m.p. 137—139°. Analytical results were consistent with the formula $SeCl_2$(tmtu). An average molecular weight of 255 was determined cryoscopically in $PhNO_2$ compared with the formula weight of 282.

From these results it was apparent that a redox reaction had occurred between tmtu and $MeSeCl_3$ presumably according to equation (1).

$$MeSeCl_3 + tmtu \rightarrow SeCl_2(tmtu) + MeCl \quad .. \quad (1)$$

This was supported by a ^1H n.m.r. spectrum of the reaction solution which showed the presence of MeCl. In contrast to $MeTeCl_3$(tmtu) which is stable for days in CH_2Cl_2 solution, our results are consistent only with the transient existence of the corresponding Se^{IV} complex. Some precedence for the reduction of a Se^{IV} species in the presence of a thiourea is found in the reported reduction of selenium(IV) in concentrated acid solution by thiourea to a suggested bis(thiourea)selenium(II) species, but no compound was isolated.[5]

The methyl groups in tmtu are equivalent in the n.m.r. spectrum with peaks at δ 3·02 p.p.m. in both $PhNO_2$ and $CHCl_3$ (*vs.* Me_4Si). For tmtu in $SeCl_2$(tmtu) a downfield shift to δ 3·29 in $CHCl_3$ and δ 3·46 p.p.m. in $PhNO_2$ was observed as predicted by simple inductive effects and consistent with our molecular weight data which indicated that the equilibrium (2)

$$SeCl_2(tmtu) \rightleftharpoons SeCl_2 + tmtu \quad .. \quad (2)$$

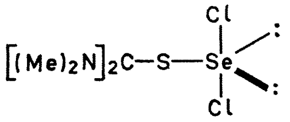
lay far to the left. In addition, our n.m.r. results were important in establishing that no measureable decomposition of $SeCl_2$(tmtu) occurred in $PhNO_2$ during the cryoscopic molecular weight determinations. However, it was found that decomposition was appreciable after *ca.* 4 h as evidenced by the appearance of a peak at δ 3·5 p.p.m. which we assigned to the $(tmtu)_2^{2+}$ ion.[6,7] Addition of tmtu to $SeCl_2$(tmtu) in $CHCl_3$ gave rise to one sharp peak of intermediate chemical shift indicating rapid exchange between unco-ordinated and co-ordinated tmtu. It was also noted that the presence of excess tmtu caused rapid decomposition of the complex.

I.r. spectra of $SeCl_2$ (tmtu) *and* tmtu[a]

$SeCl_2$ (tmtu)		tmtu
$CHCl_3$ solution	Nujol mull	Nujol mull
		45 m
		95 m
	128 sh, m	
	138 m	
160 sh, w	170 w	
204 m	210 s	200 w
233 w		
248 w	252 m-s	
273 w	270 sh, m	280 m
	325 sh, w	320 m
375 w	375 w	400 m
		490 m-s

[a] From 33—500 cm^{-1}.

The i.r. data (Table) suggest that no gross structural changes occur in going from solution to the solid state. Although neither our i.r. nor other data provide *direct* information concerning molecular structure, the T-shaped molecule (Figure) seems a reasonable structural model for $SeCl_2$(tmtu) in solution and the solid state. This structure is analogous to that found for $TeCl_2$(tmtu),[6] and is also in accord with the disposition of the five electron pairs around selenium.[8] Our i.r. data are at least consistent with this view as it seems reasonable to assign the peaks at 252 cm^{-1} in the solid, and 233 and 248 cm^{-1} in solution to axial Se–Cl frequencies. These are close to the values observed for symmetric and assymmetric Se–Cl stretches in Me_2SeCl_2 (244 and 280 cm^{-1})[9]† which has a linear $SeCl_2$ group and contains an Se atom formally isoelectronic with that in $SeCl_2$(tmtu). A shift in the antisymmetric N–C–N stretching region from 1535 in tmtu to 1585 cm^{-1} in $SeCl_2$ (tmtu) is consistent with donor bonding through sulphur.[12]



FIGURE

The Figure implies *sp*^{3}*d* hybridization of Se, but we prefer a bonding picture utilizing mainly *p*-orbitals on selenium. We favour a bonding scheme consisting of two-centre two-electron S–Se and three-centre four-electron[13] Cl–Se–Cl bonds.

Our "trapping" of the $SeCl_2$ molecule suggests it may be an important intermediate in the decomposition of alkyl-selenium trihalides. The Lewis base stabilization of $SeCl_2$ is reminiscent of the stabilization of the S_2O molecule in $S_2O\cdot(NMe_3)$.[14]

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† Note values for $SeCl_2$ symmetric and asymmetric stretching frequencies previously reported (ref. 10) are incorrect, probably because the spectrometer was not purged with dry air. The 270 cm^{-1} peak may therefore have been caused by strong water absorptions at 275—82 cm^{-1}, giving rise to a spurious doublet.

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