Organothiometallic Compounds. Crystal Structure and Spectroscopic Properties of (Isopropylthio)mercury(II) Chloride †

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The structure of the title compound was solved from diffractometer data by the heavy-atom method and refined by least-squares techniques to $R = 0.056$ for 585 observed reflections. Crystals are monoclinic, space group $C2$, with unit-cell dimensions $a = 21.424(6)$, $b = 4.668(2)$, $c = 6.734(3)$ Å, $\beta = 90.45(5)°$, and $Z = 2$. For each asymmetric unit there are two crystallographically independent mercury atoms. One of them bonds covalently to two sulphur atoms at 2.378 Å, and four chlorine atoms with long contacts (2.985 and 3.342 Å). The co-ordination around the other mercury atom involves two chlorine atoms at 2.534 Å and two sulphur atoms at 2.537 Å. The geometry of the polymeric structure is consistent with i.r. and Raman data. The low values of ν(Hg–S) (231 cm^{-1}) and ν(Hg–Cl) (218 cm^{-1}) reflect the interactions of ligand groups in the crystal. Spectroscopic results suggest two types of dissociation pathways on dissolving in pyridine, to form the species Hg(SPr^i)Cl, Hg(SPr^i)$_2$, and HgCl$_2$, and corresponding pyridine adducts.

Many ligands (L), of the type R^{1}R^{2}S, R^{1}R^{2}SO, RS$^-$(R,R^1,R^2 = alkyl or phenyl), react with mercury(II) halides HgX$_2$ (X = Cl, Br, or I) to give addition, (1) and (2), or substitution compounds (3) and (4), (see Scheme), with evident structural differences of the metal environment.[1,2]

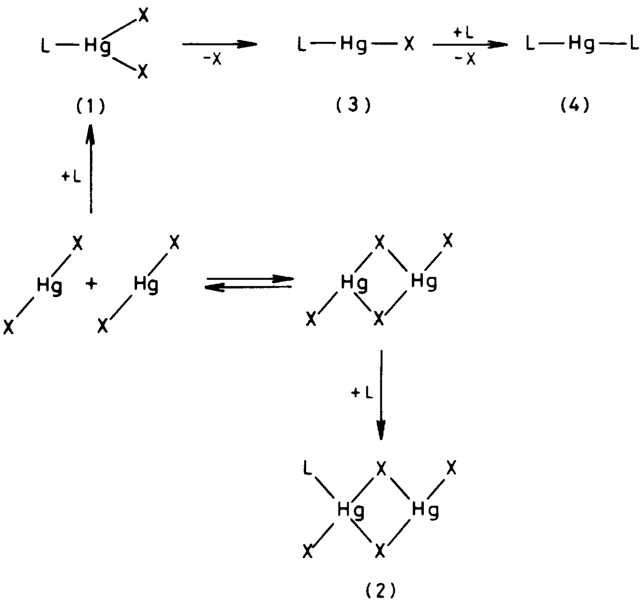
The bond lengths and bond angles, the hybridization on the metal, and the different co-ordination number reflect the character of the Hg–L and Hg–X interactions. In many cases vibrational spectroscopy has produced evidence of the various structural situations. From i.r. and Raman data the co-ordination mode of the metal and the particular interactions Hg–L, Hg–X, and Hg $\cdots$ X could be deduced. The crystal and molecular structures of some compounds have been correlated with their spectroscopic properties.[2] Ultraviolet photoelectron spectroscopy (u.v.p.s.) and calculation results suggested a double bond nature for Hg–S interactions in dialkylthiomercury(II) compounds, Hg(SR)$_2$.[3]

We are now studying the structural modifications realised in type (3) and (4) substitution compounds with L = RS$^-$ to explain the nature of the mercury–sulphur bond and the structural modifications revealed by vibrational spectroscopy. The i.r. and Raman spectra of Hg(SR)X (X = Cl, Br, or I; R = alkyl) suggested, in particular, structural differences between Me and Pr^i derivatives.[1e] The crystal structures of Hg(SMe)X (X = Cl or Br) have been reported and recently refined.[4,5]

Here the crystal and molecular structure of Hg(SPr^i)Cl is reported to investigate correlations with spectroscopic properties; in addition, a solid-state investigation of this compound would determine the influence of intermolecular interactions *via* halogen atoms on the spectroscopic behaviour, quite atypical if compared with several members of the same series.

Experimental

Preparations and Spectra.—The compound was obtained as previously described and crystallized after extraction with absolute ethanol in a Soxlet apparatus.[1e] Infrared and Raman spectra were recorded in Nujol mulls and pyridine (py) solution as described previously.[1e]



Scheme. Reactions of sulphur donor ligands, L = R^{1}R^{2}S, R^{1}R^{2}SO, or RS$^-$ (R,R^1,R^2, = alkyl or phenyl), with mercury(II) halides (X = Cl, Br, or I)

Crystal Data.—Unit-cell parameters were determined from the least-squares fit to the $(\theta,\chi,\varphi)_{hkl}$ values of 25 reflections measured on a diffractometer. C$_6$H$_{14}$Cl$_2$Hg$_2$S$_2$, $M = 622.44$, monoclinic, $a = 21.424(6)$, $b = 4.668(2)$, $c = 6.734(3)$ Å, $\beta = 90.45(5)°$, $U = 673.43$ Å^3, $Z = 2$, $D_c = 3.07$ g cm^{-3}, $\mu_{Mo} = 226$ cm^{-1}, space group $C2$.

Intensity Data Collection.—Intensity data were collected on a Phillips PW 1100 single-crystal four-circle automated diffractometer, with graphite-monochromatized Mo-K_α radiation ($\lambda = 0.7107$ Å) up to $\theta = 25°$, using the θ—2θ scan technique.

During the data collection two standard reflections were

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† *Supplementary data available* (No. SUP 23869, 18 pp.): H-atom co-ordinates, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

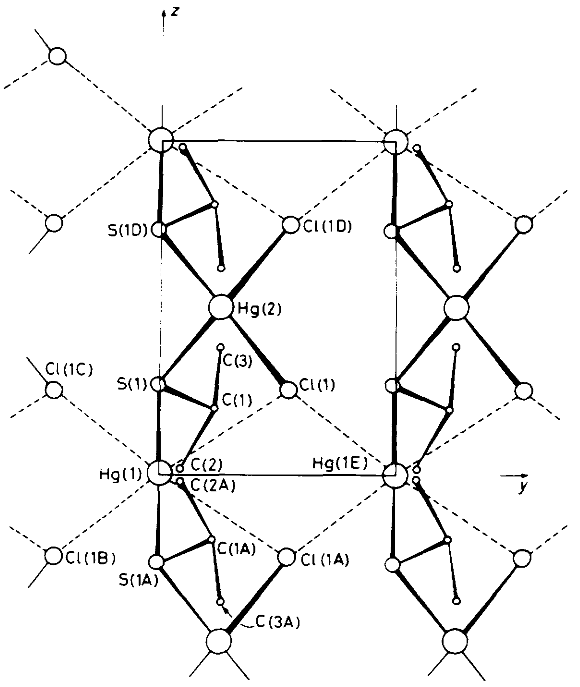

Figure 1. Projection of the (100) plane, with unit cell edges, showing the atom-numbering scheme and interatomic approaches between adjacent groups and chains in the sheet

measured every 180 min to check the stability of the crystal and the electronics. No systematic variation was detected. Intensities were corrected for Lorentz and polarization effects and were converted to an absolute scale by the Wilson method. Experimental absorption correction was applied following the method proposed by North *et al.*[6] Intensity data were collected from a crystal of approximate dimensions 0.06 × 0.06 × 0.6 mm.

Structure Solution and Refinement.—The structure solution was performed by the heavy-atom method. The structure was refined by a full-matrix least-squares procedure; the final agreement factor R was 0.056 for 585 reflections having $F_o > 7\sigma(F_o)$, of the total 665 unique reflections. Ten reflections were omitted from the data set due to bad background statistics. The function minimized was $\Sigma w(\Delta F)^2$ in which $w = g/[\sigma^2(F_o) + kF_o]^2$; the g and k values found were 37.3680 and 0.000 137 respectively. Only Hg atoms were refined with anisotropic thermal parameters, the remaining non-hydrogen atoms were allowed to vibrate isotropically. Hydrogen atoms, geometrically located with a single thermal parameter, were treated as a fixed contributor. The largest peaks on a final F map were of height *ca.* 3.0 e Å^{-3} in regions near to the heavy-atom positions and at distances of 0.8—1.2 Å. The scattering factors were those for neutral Hg, Cl, S, C, and H atoms.[7] An anomalous dispersion correction for mercury was also included.[8] All calculations were carried out on the CYBER-76 of the CINECA (Casalecchio, Bologna) with the SHELX 76 system of crystallographic programs.[9] The final atomic co-ordinates are given in Table 1.

Results and Discussion

The whole structure is built up from parallel chains of $Hg(SPr^i)_2 \cdot HgCl_2$ groups. Figure 1 shows the molecular structure with the atom-numbering scheme. Table 2 lists interatomic distances and angles.

Table 1. Fractional co-ordinates, with estimated standard deviations in parentheses, obtained in the final least-squares refinement

*C*2; 2 Hg(1) in 2(a), 2 Hg(2) in 2(b); 4 Cl, 4 S, 12 C in 4(c) *

Atom	*X/a*	*Y/b*	*Z/c*
Hg(1)	0.0000	0.0000	0.0000
Hg(2)	0.0000	0.261 6(5)	0.5000
Cl(1)	0.061 3(4)	0.552 0(17)	0.250 4(10)
S(1)	−0.072 0(3)	−0.012 2(17)	0.267 0(8)
C(1)	−0.136 5(14)	0.227 6(58)	0.190 3(34)
C(2)	−0.167 0(17)	0.088 8(62)	0.014 2(43)
C(3)	−0.174 4(22)	0.267 2(79)	0.377 3(50)

* Space group *C*2: values indicate the number of atoms in positions 2(a), 2(b), and 4(c) (Wickoff notation, 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1952, vol. 1, p. 81).

Table 2. Interatomic distances * (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Hg(1) environment			
Hg(1)–S(1)	2.378(6)	S(1)–Hg(1)–S(1A)	178.2(2)
Hg(1) ··· Cl(1)	3.342(8)	S(1)–Hg(1)–Cl(1)	83.8(2)
Hg(1) ··· Cl(1B)	2.985(8)	S(1)–Hg(1)–Cl(1A)	98.4(2)
		S(1)–Hg(1)–Cl(1B)	97.2(2)
		S(1)–Hg(1)–Cl(1C)	80.9(2)
		Cl(1)–Hg(1)–Cl(1A)	79.1(2)
		Cl(1)–Hg(1)–Cl(1B)	174.1(2)
		Cl(1)–Hg(1)–Cl(1C)	94.9(2)
		Cl(1B)–Hg(1)–Cl(1C)	90.8(2)
(*b*) Hg(2) environment			
Hg(2)–S(1)	2.537(6)	S(1)–Hg(2)–Cl(1)	100.1(2)
Hg(2)–Cl(1)	2.534(8)	S(1)–Hg(2)–Cl(1D)	111.3(2)
		S(1)–Hg(2)–S(1D)	119.5(2)
		Cl(1)–Hg(2)–Cl(1D)	115.3(2)
(*c*) S environment			
S(1)–Hg(1)	2.378(6)	Hg(1)–S(1)–Hg(2)	93.5(2)
S(1)–Hg(2)	2.537(6)	Hg(1)–S(1)–C(1)	105.2(8)
S(1)–C(1)	1.85(3)	Hg(2)–S(1)–C(1)	108.5(9)
(*d*) Cl environment			
Cl(1) ··· Hg(1)	3.342(8)	Hg(1)–Cl(1)–Hg(2)	73.6(2)
Cl(1)–Hg(2)	2.534(8)	Hg(1)–Cl(1)–Hg(1E)	94.9(2)
Cl(1) ··· Hg(1E)	2.985(8)	Hg(2)–Cl(1)–Hg(1E)	121.4(2)
(*e*) C environment			
C(1)–S(1)	1.85(3)	S(1)–C(1)–C(2)	106(2)
C(1)–C(2)	1.50(4)	S(1)–C(1)–C(3)	104(2)
C(1)–C(3)	1.51(5)	C(2)–C(1)–C(3)	118(3)

* Capital letters in the atom number denote the following equivalent positions: A $\bar{x}, y, \bar{z}$; B $\bar{x}, y - 1, \bar{z}$; C $x, y - 1, z$; D $\bar{x}, y, 1 - z$; E $x, y + 1, z$.

The major stereochemical feature of the structure is the presence of two kinds of co-ordination geometries around the Hg atoms. The two independent mercury atoms, Hg(1) and Hg(2), of the unit cell have the same point symmetry, 2.

The Hg(1) atom is almost linearly co-ordinated by two sulphur atoms (Hg–S 2.378 Å, S–Hg–S 178.2°) and the so-called 'characteristic' co-ordination number is two.[10] Two chlorine atoms from groups of the same chain at 3.342 Å and two others belonging to an adjacent chain at 2.985 Å form a plane orthogonal to the S–Hg–S axis with weaker bonds to Hg(1), so that the whole co-ordination polyhedron is a

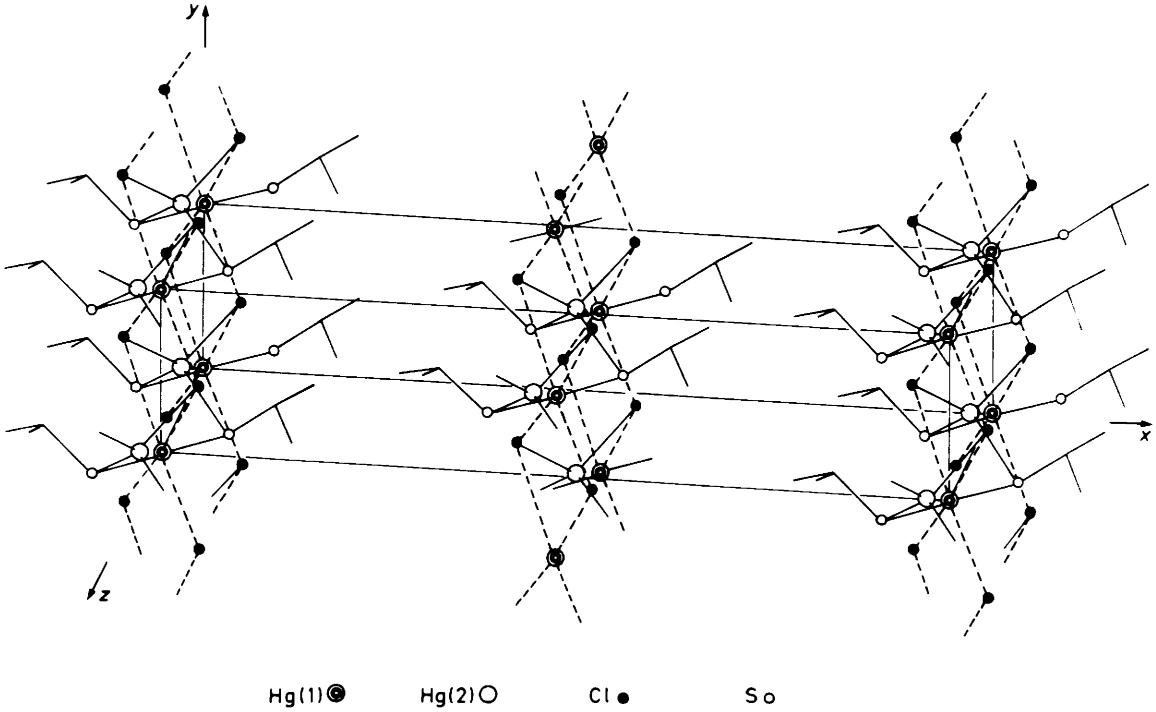

Figure 2. Packing arrangement of the structure in the unit cell

distorted octahedron. Many structures show mercury atoms with 'effective' co-ordination number six and mixed nitrogen, oxygen, or sulphur and halogen ligands at the edges of an octahedron.[11] In fact this kind of co-ordination with four long and two short contacts, corresponding to covalent bonds, is typical of mercury(II) compounds.[10]

The Hg(2) atom has a characteristic effective co-ordination number four, showing a tetrahedral co-ordination with two chlorine atoms at 2.534 Å and two sulphur atoms at 2.537 Å. The metal atom lies at the centre of the tetrahedron and its environment is slightly distorted from that expected for an sp^3-hybridized mercury atom (see Table 2 for bond lengths and angles). Tetrahedral co-ordination around mercury is common. In particular, in the 1 : 2 adduct between *cis,cis*-1,6-dithiacyclodeca-3,8-diene and mercury(II) chloride, the mercury atom exhibits a distorted $\mathrm{HgCl_2S_2}$ unit, as in the present case, with Cl–Hg–Cl and S–Hg–S angles of 99 and 109° respectively.[12]

To our knowledge, however, the contemporaneous presence of tetrahedral and octahedral polyhedra in $\mathrm{Hg^{II}}$ compounds has seldom been so clearly observed, even if the presence of two types of Hg co-ordination was seen, for example, in the dimethyl sulphoxide–mercury(II) chloride (2 : 3) adduct [2c] and in thioether–mercury(II)–chloride adducts.[13,14]

Though quite different, the Hg(1)–S and Hg(2)–S distances show common values for di-covalent and tetra-covalent mercury respectively.[10] Thus it appears that strong intermolecular contacts are present, giving rise to a co-ordination polymer involving sulphide bridges.

The alkyl sulphide groups $\mathrm{Pr^iS^-}$ act as bidentate ligands with geometries indicating sp^3 hybridization at the sulphur atom (see Table 2). The shorter distance S–Hg(1) compared to S–Hg(2) could reflect a higher bond order in the first case, due to the presence, in addition to the S–Hg σ bond, of a synergic π interaction between the filled 3*p* sulphur orbital and the empty 6*p* Hg(1) orbital, in agreement with data obtained by u.v.p.s. spectra for $\mathrm{Hg(SPr^i)_2}$.[3] In fact a partial double-bond character of S–Hg interactions should be attributed to S–Hg(1), due to the lower charge density on the metal; on the other hand, the contemporaneous co-ordination of two chlorine atoms on Hg(2) causes a higher electronic charge density, thus reducing the capacity to accept further negative charge from sulphur atoms.

One chlorine atom also bonds to two consecutive Hg(1) and Hg(2) atoms, contributing to the formation of infinite chains along [001] with the sulphur and chlorine mixed bridges between mercury atoms. Each chlorine atom is also shared by another Hg(1) atom of a parallel chain at 2.985 Å, bridging consecutive Hg(1) atoms along [010]. The chlorine atoms form the bridging connections between the chains. The angles values seem to indicate the use of pure *p* orbitals by chlorine atoms. The Cl–Hg(2) distance appears to be normal for tetrahedrally co-ordinated mercury but it is slightly longer than the sum of the covalent radii, $r(\mathrm{Hg_{tet.}}) = 1.48$ and $r(\mathrm{Cl}) = 0.99$ Å respectively.[10,15] The slight elongation is attributed to the simultaneous $\mathrm{Cl^-}$ interaction with two other mercury atoms, and to the consequent lower charge density on the ligand.

The packing arrangement in the crystal is shown in Figure 2. The resulting structure corresponds to two-dimensional networks stacked parallel to the (100) plane (interlayer mean distance *ca.* 5 Å). The alkylic tails are interposed between the layers and perhaps determine the observed packing arrangement. From a geometrical point of view the whole structure of the compound is built up of chains of octahedra sharing an equatorial edge. These chains are bridged together by tetrahedra through opposite edges.

The i.r. and Raman spectra in the solid state show halide mass-independent strong bands at 231 (Raman, 235) $\mathrm{cm^{-1}}$ which have been assigned to the stretching vibrations ν(Hg–S) of the polymeric chains $(-\overset{|}{\mathrm{S}}-\mathrm{Hg}-\overset{|}{\mathrm{S}}-\mathrm{Hg}-\overset{|}{\mathrm{S}}-)_n$. The i.r.- and Raman-active band at 218 (Raman, 220) $\mathrm{cm^{-1}}$ has been assigned to the stretching vibration ν(Hg–Cl) in tetrahedrally

Table 3. Distances and angles within the compound and associated i.r. and Raman (in parentheses) frequencies

		ν(Hg–S)/cm^{-1}				ν(Hg–Cl)/cm^{-1}	
Compound	d(Hg–S)/Å	solid	py solution	d(Hg–Cl)/Å	Cl–Hg–Cl/°	solid	py solution
$HgCl_3^-$ [a]				2.40—2.45	115.6—124.2	263	
						(273)	
$HgCl_4^{2-}$				2.50 [b]			(261) [c]
$Hg(SPr^i)Cl$	2.378, 2.537	231	240, 256	2.534	115.3	218	303
		(235)	(240)			(220)	(284)
$Hg(SPr^i)_2$ [d]		256	352, 260				
		(232)	(323), (257)				
Hg(SMe)Cl [e]	2.43 [f]	326, 282	349	2.71 [f]		178	295
		(296), (248)	(340), (318)			(170)	(293)

From ref. 2*a*. [b] Ref. 18. [c] In dimethyl sulphoxide solution, ref. 2*a*. [d] Ref. 1*d*. [e] Ref. 1*e*. [f] Ref. 5.

co-ordinated Hg(2). These spectra agree with the absence of a symmetry centre in the crystal and in the molecule. The low values of the stretching frequencies with respect to those of similar Hg–S and Hg–Cl in other compounds confirm the strong interactions of the ligand groups with other neighbouring metal atoms (see Table 3). The spectra are clearly different even from those of $Hg(SPr^i)_2$ and Hg(SMe)Cl and should reflect the substantial differences existing in the molecular structure.[1e,4,5] For example, the lower value of the ν(Hg–S) vibration, 231 cm^{-1}, for $Hg(SPr^i)Cl$ with respect to 256 cm^{-1} for $Hg(SPr^i)_2$ is indicative of a lower Hg–S bond strength. The i.r. and Raman band assigned to the ν(Hg–S) could then be considered to be due to the coupling of the various S–Hg group vibrations in the polymer having different distances, bond order, and consequently a different strength constant.

The stretching vibration ν(Hg–Cl) (218 cm^{-1}), which is lower than the analogous stretching values of Hg–Cl terminal groups (350—286 cm^{-1}), but higher than the stretching frequencies associated with bridging Hg–Cl–Hg groups (below 200 cm^{-1}), could be due to the particular environment of each chlorine atom, as well as the hybridization at the mercury atom of the Cl–Hg–Cl group.[1e,16] As shown above the halogen atom interacts with three mercury atoms of two adjacent chains, interacting strongly with the tetrahedral Hg(2) atom at 2.534 Å and more weakly with two other Hg(1) atoms at 2.985 and 3.342 Å. These last interactions evidently are sufficient to determine a lowering of the charge density on the halogen atom and consequently to reduce the availability for interaction with the Hg(2) atom. In fact the Hg(2)–Cl bond distance is slightly higher than in similar tetrahedral $HgCl_2S_2$ groups (2.51 Å),[12] and in the $HgCl_4^{2-}$ tetrahedral anion (2.50 Å) of 6-(3,4-dimethoxyphenyl)-3,4-dihydro-4-oxobenzo[*c*][2,7]naphthyridinium mercury(II) tetrachloride.[17] This distance is even longer than in the trigonal $HgCl_3^-$ group (2.40—2.45 Å),[2a] but shorter than the Hg–Cl bridging bond, as in Hg(SMe)Cl (2.71 Å) [5] (see Table 3).

The Raman stretching frequency ν(Hg–Cl) (220 cm^{-1}) is lower than the symmetric stretching mode of the tetrahedral $HgCl_4^{2-}$ and the trigonal $HgCl_3^-$ groups in solution (261 and 280 cm^{-1},[2a] respectively) and higher than that of the bridging Hg–Cl in Hg(SMe)Cl (170 cm^{-1}).[1e] The spectra in pyridine (py) solution of $Hg(SPr^i)_2 \cdot HgCl_2$ differ substantially from those in the solid state and are consistent with the spectra of the independently vibrating molecules, $Hg(SPr^i)Cl$ and $Hg(SPr^i)_2$, even if an interaction of these species with the solvent cannot be excluded. The solubility of the title compound, only in pyridine or dimethyl sulphoxide, could be ascribed to its polymeric nature, and to a strong interaction of these solvents with the component groups of the compound.

A broad halide mass-independent Raman band at 240 cm^{-1}, barely resolved in the i.r., is assigned to the Hg–S stretching mode of $Hg(SPr^i)Cl$. An i.r. shoulder at 256 cm^{-1} could be assigned to the asymmetric stretching ν(S–Hg–S) of the corresponding compound $Hg(SPr^i)_2$, the symmetric mode of this vibration being hidden by the broad Raman band at 240 cm^{-1}. A strong, very broad band is registered at higher frequencies, 303 (Raman, 284) cm^{-1}, in the typical range of terminal halogen–mercury groups. This band is assigned to ν(Hg–Cl) and indicates the presence in solution of species with independently vibrating halogen–mercury groups. In the solution i.r. spectra of $Hg(SPr^i)Cl$ ν(Hg–Cl) of free $HgCl_2$ is not measureable because it occurs beyond the window of the solvent, but the shoulders to higher and lower frequencies of the maximum could be due to the presence of adducts of mercury(II) compounds with pyridine. In fact some mercury(II) halide–pyridine adducts were recently structurally and spectroscopically characterised, and give ν(Hg–Cl) frequencies in the solid state between 350 and 287 cm^{-1}.[18,19]

However, bearing in mind that in solutions of $Hg(SPr^i)Br$ and similar compounds, an equilibrium of the free compounds $Hg(SPr^i)Br$, $Hg(SPr^i)_2$, and $HgBr_2$ interacting with pyridine was observed,[1e] it could be suggested that the crystal dissociation in pyridine solution gives rise to some equilibria of the monomeric species, $Hg(SPr^i)Cl$, $Hg(SPr^i)_2$, and $HgCl_2$, and the corresponding adducts with the solvent.

The presence of these species in solution indicates also some different dissociation pathways of the polymeric crystal structure, which are determined by the strong interaction with pyridine.

In addition, these results suggest that the resolved crystal structure of $Hg(SPr^i)Cl$ could be considered as a model of a hypothetical 'intermediate' in the substitution reaction [(3)$\rightarrow$(4) of the Scheme], from (isopropylthio)mercury(II) chloride to di(isopropylthio)mercury(II).

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