Crystal Structure and Spectroscopic Properties of Mercury(II) Halide Complexes. Part 4.[1] Crystal and Molecular Structure and Circular Dichroism Spectra of the Chiral 1 : 1 Adduct $(S)_s(S)_c(-)_{589}$-Methyl 2-phenylbutyl Thioether–Mercury(II) Chloride†

Paolo Biscarini *
Dipartimento di Chimica Fisica ed Inorganica dell'Universita', Viale Risorgimento 4, 40136 Bologna, Italy
Giancarlo Pelizzi
Istituto di Chimica Generale ed Inorganica Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Viale delle Scienze, 43100 Parma, Italy

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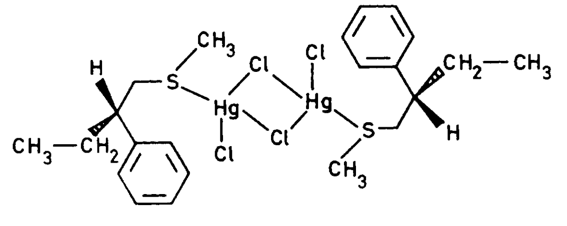
The crystal and molecular structure of $(-)_{589}[(S)_S(S)_C\text{-Me(EtCHPhCH}_2\text{)S}\cdot\text{HgCl}_2]_2$ has been determined by the heavy-atom method from three-dimensional *X*-ray data collected by counter methods and refined by least-squares techniques to *R* 0.0468 for 1 207 observed reflections. Crystals are monoclinic, space group $P2_1$, with two molecules in a unit cell of dimensions a = 8.457(3), b = 5.634(3), c = 14.667(6) Å, and β = 94.68(4)°. The S atom of the donor molecule and the non-bridging Cl(1) atom are strongly bonded to Hg [2.433(4) and 2.315(5) Å, respectively]. The overall co-ordination sphere of Hg also includes three crystallographically equivalent bridging Cl(2) atoms [2.677(5), 2.838(10), and 2.995(10) Å], and a very weakly π-bonded Ph ring (3.64 Å), thus completing an approximately octahedral array. The triply bridging action of Cl(2) leads to the formation of a polymeric structure in which the molecules are linked in chains and further into ribbons parallel to the *b* axis. I.r. spectroscopic data are consistent with a bent Cl–Hg–Cl moiety. The absolute configuration at both chiral centres of the diastereoisomer is *S*. The $(S)_S$ absolute configuration at the sulphur atom has been correlated with the negative Cotton effect assigned to a charge-transfer transition at 265 nm in the circular dichroism spectrum. The diastereoselective synthesis of the complex has been confirmed.

The diastereotopic sulphur atom of a chiral asymmetric thioether can bind to mercury(II) chloride from two different directions, creating two opposite absolute configurations, *S* or *R*, on the ligand sulphur atom.[2]

The chiral thioether, $(S)(-)\text{-Me(EtCHPhCH}_2\text{)S}$, and its 1:1 diastereoisomeric complex with mercury(II) chloride $(-)\text{-}[(S)_s(S)_c\text{-Me(EtCHPhCH}_2\text{)S}\cdot\text{HgCl}_2]_2$, (**1**), have been synthesized to show the diastereoselectivity of the formation reaction.[3] Circular dichroism (c.d.) spectra in ethanolic solution have shown that bond formation between the sulphur atom and mercury in this and similar types of complex may be diastereoselective.[2,3]



(**1**)

An *S* or *R* absolute configuration on the sulphide–mercury group can be envisaged from the respectively negative or positive Cotton effects assigned to a new charge-transfer (c.t.) transition observed during complex formation. Moreover there has been much interest in the problem of chiral discrimination.[4,5]

This new type of chiral thioether–mercury(II) adduct affords a chance to study the stereochemical and energy aspects of the induction of chirality through intermolecular associations.

The geometry of the addition compound is not known. Infrared and diffractometric studies of 1:1 adducts between mercury(II) chloride and various ligands such as thioethers or sulphoxides indicate that the structure consists of dimeric units with bridging chlorine atoms and ligands in *trans* positions.[1] Crystal structures of several adducts between mercury(II) chloride and ligands with donors such as oxygen atoms have shown the possibility of the mercury atom attaining a tetrahedral or a distorted-octahedral co-ordination according to the nature of the ligand. There has been no report of a chiral group obtained by the attack of mercury on the diastereotopic sulphur atom of a chiral ligand.

The complex (**1**) has now been investigated by *X*-ray crystallographic methods in order to define unequivocally the absolute configuration at the sulphur atom and to obtain information of use in correlating the c.d. and i.r. spectroscopic data with the structure. In particular, interest focuses on correlating the sign of the c.d. Cotton effect with the absolute configuration of the two chiral centres in the diastereoisomeric molecule of adduct (**1**). Also of interest is to ascertain the steric and/or electronic reasons for the higher thermodynamic stability of the diastereoisomer obtained.

Experimental

Preparation.—The adduct $(S)_s(S)_c(-)_{589}$-methyl 2-phenylbutyl thioether–mercury(II) chloride (1/1), $(-)[(S)_s(S)_c\text{-Me(EtCHPhCH}_2\text{)S}\cdot\text{HgCl}_2]_2$, (**1**), was obtained as described[3]

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† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

and slowly crystallized from 95% ethanol. Infrared, u.v., and c.d. spectra were recorded as reported.[3]

X-Ray Analysis.—All *X*-ray measurements were carried out at room temperature with a Siemens AED three-circle diffractometer in conjunction with a General Automation Jumbo 220 computer, using niobium-filtered molybdenum radiation ($\lambda = 0.710\,69$ Å). The crystal selected for data collection had approximate dimensions 0.10 × 0.23 × 0.25 mm. The crystal system and space group were obtained by use of peak search, centring, and indexing programs and by the systematic absences (0*k*0, *k* odd) observed during data collection. The choice of non-centric space group $P2_1$ in preference to $P2_1/m$ was based on the fact that the compound is known to be optically active. The absence of a centre of symmetry was also confirmed by the analysis of the intensity statistics.

Crystal data. $C_{11}H_{16}Cl_2HgS$, $M = 451.80$, monoclinic, $a = 8.457(3)$, $b = 5.634(3)$, $c = 14.667(6)$ Å, $\beta = 94.68(4)°$, $U = 696.5(5)$ Å^3, space group $P2_1$, $Z = 2$, $D_c = 2.154$ g cm^{-3}, $F(000) = 424$, Mo-K_α radiation, μ(Mo-K_α) = 115.5 cm^{-1}.

Unit-cell constants, with estimated standard deviations, were obtained by least-squares fitting to the diffractometer measured 2θ values for 19 reflections chosen in diverse regions of reciprocal space ($18.7 < 2\theta < 35.8°$). A total of 1 681 reflections were measured with the use of the θ-2θ step-scanning mode in the range $5.0 < 2\theta < 52.0°$. Equivalent data were averaged and the 1 207 reflections with $I > 2\sigma(I)$ were retained for structure analysis. A standard reflection monitored every 50 reflections to check for crystal decomposition or movement showed only slight intensity fluctuation. A diffraction profile analysis was performed on all reflections using the Lehmann and Larsen algorithm.[6] The intensities were converted into relative structure amplitudes after correction for Lorentz and polarization effects. Corrections for absorption and extinction were also made, using the empirical method of Walker and Stuart.[7]

The co-ordinates for the mercury atom were derived from a Patterson function and used as an initial phasing model for a Fourier difference synthesis, which clearly revealed the position of the remaining non-hydrogen atoms. Since $P2_1$ is a polar space group, the origin has to be defined with respect to the *b* direction. The *y* co-ordinate of Hg was therefore set arbitrarily at 0.75 and held invariant. Full-matrix least-squares refinement of positional and isotropic thermal parameters gave a residual *R* index of 0.0583 ($R' = 0.0748$). By introducing anisotropic thermal parameters for all atoms and continuing the refinement, *R* was reduced to 0.0468 ($R' = 0.0591$, goodness of fit = 0.5158) with a 9.8:1 data-to-parameter ratio. The phenyl group was refined as a rigid body possessing D_{6h} symmetry (C–C bond length 1.395 Å). The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The data were weighted with $w = 1$ at first, while in the last stage of refinement the weights were $w = 0.4792/[\sigma^2(F_o) + 0.004\,32\,F_o{}^2]$. Hydrogen atoms were ignored. A final difference map yielded three large peaks of *ca.* 1.9 e Å^{-3} near the mercury atom, but was otherwise featureless. Neutral scattering factors were employed and the anomalous dispersion terms for Hg, Cl, and S were included in F_c.[8]

Calculations were carried out on a GOULD-SEL 32/77 computer using the SHELX 76 crystallographic system of programs.[9] The other programs used in the structure determination have been cited elsewhere.[10]

The final atomic positional parameters are listed in Table 1, selected interatomic distances and angles in Table 2. The co-ordinates in Table 1 are those of the diastereoisomer with *S* configuration at both chiral centres, namely C(3) and S. The assignment was made on the basis of chemical arguments (see later). Although both possible diastereoisomers *SS* and *RR* were tried, no straightforward crystallographic distinction between them could be made in the refinement. On the contrary, by application of the Hamilton test, the incorrect diastereoisomer was judged to be, if anything, marginally more likely. It can be added, however, that a comparison of the Bijovet differences of a set of 12 sensitive *hkl* and $h\bar{k}l$ pairs, carried out with a different crystal when the structure determination was completed, favoured the initial choice, albeit only slightly.

Table 1. Fractional atomic co-ordinates (× 10^5 for Hg, × 10^4 for S, Cl, and C) of complex (**1**)

Atom	*X/a*	*Y/b*	*Z/c*
Hg	1 479(7)	75 000	11 414(4)
S	−2 666(5)	7 990(7)	1 326(3)
Cl(1)	2 768(6)	7 958(11)	1 704(4)
Cl(2)	299(6)	7 644(18)	−674(3)
C(1)	−3 443(23)	7 949(31)	120(13)
C(2)	−3 518(22)	5 128(40)	1 710(13)
C(3)	−3 404(22)	5 085(42)	2 767(12)
C(4)	−4 296(27)	2 909(50)	3 022(14)
C(5)	−4 409(32)	2 196(96)	4 028(15)
C(6)	−1 756(11)	5 159(27)	3 175(9)
C(7)	−1 274(11)	7 049(27)	3 746(9)
C(8)	289(11)	7 169(27)	4 130(9)
C(9)	1 369(11)	5 398(27)	3 943(9)
C(10)	887(11)	3 508(27)	3 372(9)
C(11)	−675(11)	3 388(27)	2 988(9)

Table 2. Selected interatomic distances (Å) and angles (°)

Hg–S	2.433(4)	S–C(1)	1.83(2)
Hg–Cl(1)	2.315(5)	S–C(2)	1.87(2)
Hg–Cl(2)	2.677(5)	C(2)–C(3)	1.55(3)
Hg–Cl(2^{I})	2.838(10)	C(3)–C(4)	1.50(3)
Hg–Cl(2^{II})	2.995(10)	C(4)–C(5)	1.54(3)
S–Hg–Cl(1)	149.8(2)	Cl(2^{I})–Hg–Cl(2^{II})	150.0(2)
S–Hg–Cl(2)	103.5(2)	Hg–Cl(2)–Hg^{I}	100.5(2)
S–Hg–Cl(2^{I})	91.4(2)	Hg–Cl(2)–Hg^{II}	104.7(2)
S–Hg–Cl(2^{II})	79.0(2)	Hg^{I}–Cl(2)–Hg^{II}	150.0(2)
Cl(1)–Hg–Cl(2)	103.2(2)	Hg–S–C(1)	99.7(6)
Cl(1)–Hg–Cl(2^{I})	107.3(2)	Hg–S–C(2)	109.9(7)
Cl(1)–Hg–Cl(2^{II})	94.2(2)	C(1)–S–C(2)	99.4(9)
Cl(2)–Hg–Cl(2^{I})	78.8(2)	S–C(2)–C(3)	108.8(14)
Cl(2)–Hg–Cl(2^{II})	76.0(2)		

Roman numeral superscripts refer to the following equivalent positions relative to the reference set (*x*, *y*, *z*) given in Table 1: I $\bar{x}$, $y - \frac{1}{2}$, $\bar{z}$; II $\bar{x}$, $y + \frac{1}{2}$, $\bar{z}$.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond distances and angles.

Results and Discussion

Figure 1 shows a perspective drawing of the molecule along with the atom-numbering scheme. The compound has a polymeric structure, in which one of the two crystallographically independent chlorine atoms unsymmetrically bridges three adjacent symmetry-related mercury atoms.

The overall co-ordination around the mercury atom is not simple to interpret, as the ligand arrangement cannot be described in terms of a regular polyhedron. The metal atom is covalently co-ordinated by the sulphur atom [2.433(4) Å] and by the non-bridging chlorine atom [2.315(5) Å] (Table 2). The immediate co-ordination sphere of mercury appears to be mainly digonal with a large departure from linearity, the S–Hg–Cl angle being nearly 30° less than the 180° expected for

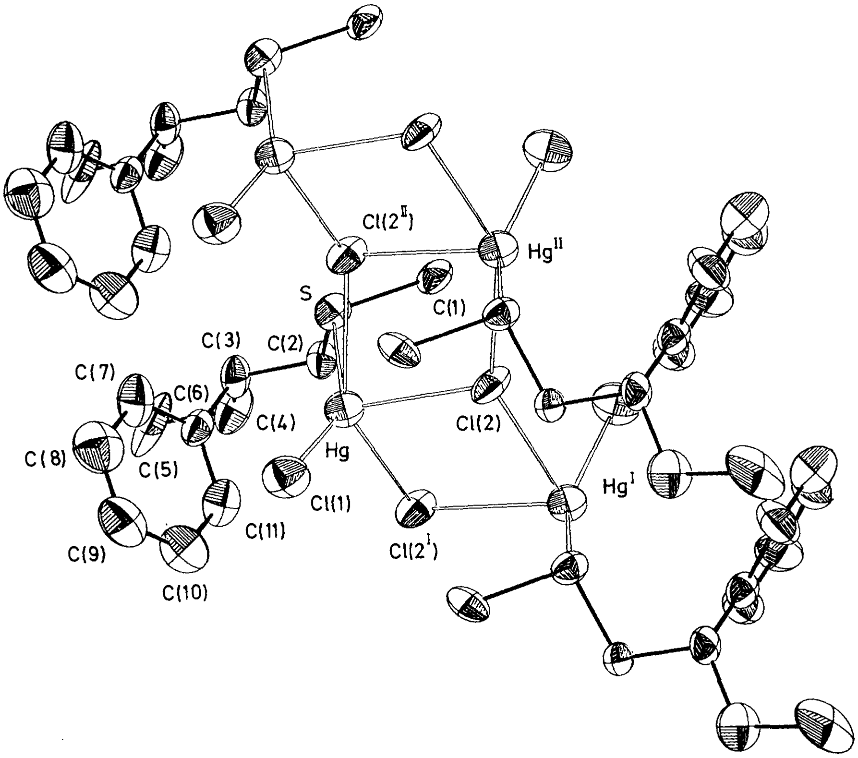


Figure 1. ORTEP drawing of the structure. Ellipsoids are drawn at 50% probability

sp hybridization. The Hg–S and Hg–Cl bond lengths are both substantially shorter than expected from the sum of the respectively covalent radii and in a fairly good agreement with the corresponding distances observed for a similar nearly linear co-ordination of Hg in S–Hg–Cl systems *e.g.* Hg–S 2.40(2), Hg–Cl 2.30(2) Å in $HgCl_2 \cdot C_4H_8S$,[11] 2.41(2), 2.35(2) Å in $2HgCl_2 \cdot Et_2S$,[12] 2.42(1), 2.37(1) Å in $HgCl_2[MeS\text{–}CS\text{–}N(CH_2)_4]$,[13] and 2.32(1), 2.37(1) Å in $[\{HgSCMe_2CH(NH_3)CO_2\}_3(\mu_3\text{-}Cl)]^{2+}$.[14] The nearest neighbours to mercury are three crystallographically equivalent Cl(2) atoms at distances of 2.677(5), 2.838(10), and 2.995(10) Å, which implies a possible (2 + 3) co-ordination. All three bridged Hg–Cl bonds fall within the same range, 2.62—3.08 Å, as the Hg–Cl bonds reported for other chloride-bridged mercury systems.[11,14–16]

In addition, a very weak sixth bond is formed between the metal atom and the phenyl ring. The distance from Hg to the midpoint of the C(6)–C(11) bond is 3.64 Å, rather close to the value of 3.51 Å reported for $HgCl_2 \cdot Ph_2SO$,[17] but significantly longer than the 3.13 Å found in $[HgMe(dmbipy)]NO_3$ (dmbipy = 3,3′-dimethyl-2,2′-bipyridyl).[18] The Hg–C(6—11) vector is almost perpendicular to the phenyl ring plane, at an angle of 86.4(3)°, and is approximately *trans* to the Hg–Cl(2) bond. If this interaction is also considered as part of the co-ordination sphere, the 'effective' co-ordination number of mercury is raised to six and the ligand configuration may be described as a tetragonally distorted oblate octahedron having four long bonds in the equatorial sites and two short bonds at the apices. This octahedral (2 + 4) co-ordination is common for Hg^{II}.[19] The four equatorial ligands lie nearly in the same plane (maximum deviation 0.04 Å), with the mercury atom located 0.50 Å from this plane towards the non-bridging chlorine atom.

As a consequence of the bridging action of Cl(2) two chelation rhombi are formed. Within each of them, the two Hg–Cl–Hg angles are significantly obtuse and the two Cl–Hg–Cl angles are significantly acute. Both chelation rings are planar within 0.03 Å, and so exhibit no significant folding along the Cl • • • Cl vectors.

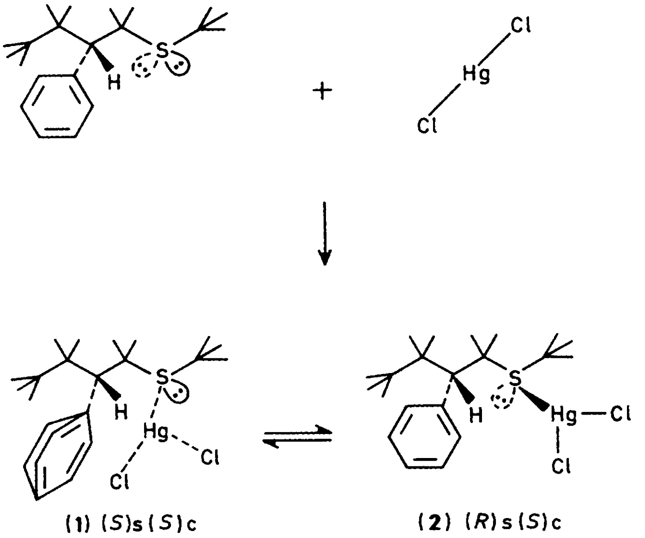
The conformation of the organic ligand displays several interesting features and seems to be a result of both bonding and steric effects. The relative position of C(1) across the S–C(2) bond is defined by the torsion angle C(1)–S–C(2)–C(3) −165(1)° thus indicating an antiperiplanar conformation.

As clearly depicted in Figure 1, the basic building elements of the crystal lattice are infinite –Hg–Cl(2)–Hg–Cl(2)– chains which run parallel to the *b* axis. Within the chains the Hg • • • Hg non-bonding distance is 4.367(2) Å. Furthermore, the chains are linked in pairs through the same Cl(2) atom, which thus acts as a triple bridge, to form endless ribbons. These ribbons are significantly puckered as the planes of two consecutive rhombi are at an angle of 16.4(1)° to one another.

The i.r. spectra of Nujol mulls between 1 300 and 200 cm^{-1} show the strongest band at 315 cm^{-1} assigned to $\nu_{asym.}(ClHgCl)$ of the $SHgCl_2$ group, with a shoulder at lower energy and a medium-intensity band at 358 cm^{-1} assigned to $\nu_{asym.}(ClHgCl)$ of mercury(II) chloride groups with a different effective co-ordination. This spectrum is very similar to those of analogous 1:1 adducts such as $HgCl_2 \cdot C_4H_8S$, 304 cm^{-1}, and $(HgCl_2 \cdot Et_2S)_2$, 306 and 338.5 cm^{-1}. The presence of a second medium-intensity band is attributable to a partial decomposition of the complex upon grinding.[20]

The addition of mercury(II) chloride to the chiral diastereotopic thioether, (*S*)(−)-Me(EtCHPhCH$_2$)S, may yield for each conformation two diastereoisomers, $(S)_s(S)_c$ and $(S)_s(R)_c$, where *R* or *S* refers to the configuration of the carbon C(3) and sulphur atom of the thioether. The metal could bind to the prochiral sulphur atom of each conformation from two different directions (Scheme).

The absolute configuration at the sulphur atom binding to mercury(II) chloride in diastereoisomer (**1**) is *S*, similar to that of the chiral carbon atom C(3) of the ligand. The assignment of the carbon configuration was made on the basis of chemical arguments based on the synthesis of (*S*)(−)-Me(EtCHPhCH$_2$)S, starting with optically pure (*S*)(+)-2-phenylbutanoic acid.[3] Since subsequent replacements on the chiral centre



Scheme. Formation reaction of the two $(S)_s(S)_c$ and $(R)_s(S)_c$ diastereoisomeric complexes of (*S*)(−)-Me(EtCHPhCH$_2$)S with mercury(II) chloride starting from an *anti* conformation of the thioaliphatic chain of the ligand

occurred with retention of the initial configuration, this knowledge allows assignment of the $(S)_c$ configuration at C(3) and, at the same time, after crystallographic resolution the chirality of sulphur can be fixed accordingly as $(S)_s$.

The conformation of the ligand could give rise to steric difficulties in forming one of the two possible diastereoisomers. Sometimes the conformation favours the interaction of the metal with other electron-donor groups present in the molecule of the ligand, stabilizing one of the two diastereoisomers. Among all the possible conformations of the sulphur ligand, the bonding and steric effects contribute to the stabilization of the antiperiplanar conformation of the C(1)SC(2)C(3)C(4)C(5) chain. In this case the free rotation of the phenyl group around the bond C(6)–C(3) and of the C(4)–C(5) group around C(3)–C(4) is favoured.

In this conformation the diastereotopic lone pair for addition to mercury(II) chloride is that lying almost parallel to the phenyl plane. A direct mercury–phenyl interaction is in this case possible at the same time as the S–Hg bond formation. The stereoselective formation of one of the two diastereoisomers seems driven by the phenyl group of the chiral C(3) centre which can interact electrostatically at long range with the mercury atom to which the sulphur is co-ordinated.

The *R* configuration on the sulphur atom is not achieved if the thioether has an antiperiplanar conformation of the chain with an *S* configuration on the carbon atom C(3), since the corresponding diastereotopic face does not sufficiently stabilize the incoming mercury(II) chloride group. So the 1:1 complex formation reactions seem stereochemically controlled by the chiral carbon atom.

It seems from Dreiding's model that the other possible conformations are excluded for steric reasons. Some of the possible conformers are unstable in solution, while for others diastereoisomer formation is sterically hindered. The most stable conformation adopted by a butane molecule or a long chain of –CH$_2$– is the *anti* or extended conformation. The presence of *gauche* arrangements in the methylthiobutyl chain involves severe hindrance and is thus ruled out. The phenyl group in position 3 and the sulphur-methyl group in position 2 can interact strongly with each other if the antiperiplanar conformation of the molecule is modified. We therefore conclude that a regular zigzag conformation favours the free rotation of the phenyl group, which stabilizes Hg–S bond formation more than occurs with the other diastereotopic face. These factors, together with packing requirements, cause the formation reaction to be stereoselective. The stereoselection depends on the stereo disposal of the phenyl group on the chiral C(3) atom.

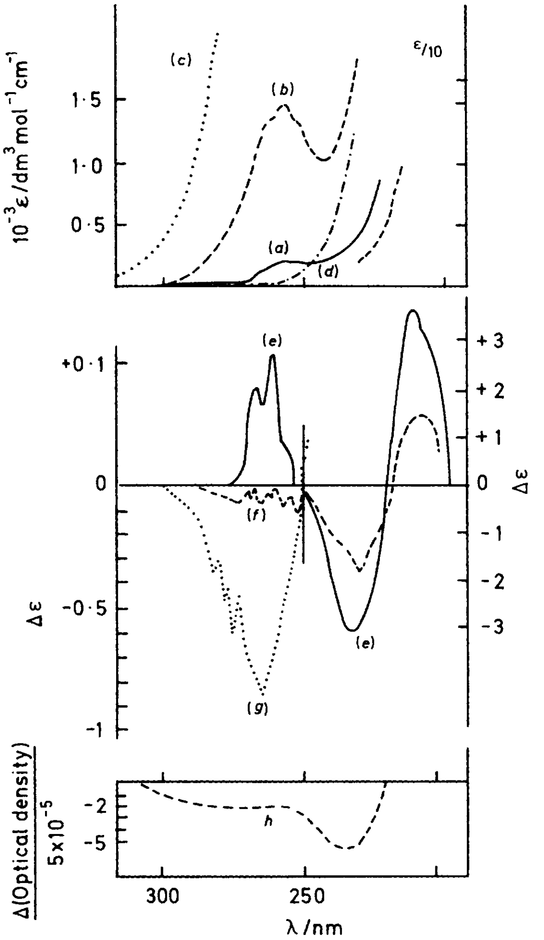


Figure 2. U.v. and c.d. spectra of the thioether, (*S*)(−)-Me(EtCHPhCH$_2$)S, in ethanol [(*a*) and (*e*) (——)] and of the complex [$(S)_s(S)_c$(−)-Me(EtCHPhCH$_2$)S·HgCl$_2$]$_2$, (**1**) (– – –) in ethanol ($c = 3.2 \times 10^{-2}$ mol dm^{-3}), (*b*) and (1.04×10^{-2} mol dm^{-3}) (*f*); with an excess of HgCl$_2$ (molar ratio ML:M = 1:200) [(*c*) and (*g*)]; and as a solid film (*h*). The absorbance spectrum of HgCl$_2$ (0.22 mol dm^{-3}) is reported for comparison (*d*)

Figure 2 reports the u.v. spectra of the ligand and complex, (**1**), respectively. The addition of mercury(II) chloride in excess to a solution of the 1:1 complex (**1**) strongly affects the u.v. and c.d. spectra.

The isotropic absorbance increases considerably in the range 250—290 nm indicating that new absorbing species have been formed ($\varepsilon \gg$ 1 000 dm^3 mol^{-1} cm^{-1}) [Figure 2(*c*)]. In this range the absorbance of mercury(II) chloride alone is very low [Figure 2(*d*)].

The growth of a new band with the characteristic shape of a c.t. transition band is observed at 265 nm overlapping the B_{2u}, benzene-like, transition band of the thioether, (*S*)(−)-Me(EtCHPhCH$_2$)S. At the same time the solid-film c.d. spectrum of complex (**1**) shows a broad negative Cotton effect at 270 nm and another negative signal at 230—240 nm [Figure 2(*h*) and (*i*)].

The c.d. spectra in ethanol solution change drastically from the thioether [Figure 2(*e*)] to the complex [Figure 2(*f*)]. In the latter spectrum a negative vibrationally structured band is registered between 250 and 290 nm which is indicative of the overlapping of a new band on the positive, originally benzene-like, B_{2u} transition band of the ligand. The addition of an excess of mercury(II) chloride [Figure 2(*g*)] clearly results in a strong negative Cotton effect at 265 nm, assigned to the new c.t. transition.[3]

These spectra confirm the results obtained with similar mercury(II) chloride chiral complexes.[2,3] However, the c.t. transition band can be positive or negative depending on the stereochemical aspects of the molecules involved in the formation of the S–Hg bond. The negative sign of this c.t. transition can now be correlated with the $(S)_s$ configuration on the sulphide–mercury group, confirming the correlation predicted from c.d. spectra in solution.[3]

Determination of the structure of complex (**1**) contributes to the correlation of the absolute configuration on a chiral centre and the c.d. signals obtained for this particular class of adducts. This relation is confirmed by the c.d. spectra of the (+)-$[(R)_s(S)_c(M)\text{ebt}\cdot\text{HgCl}_2]_2$ complex, where the positive Cotton effect of the c.t. transition at 270 nm has been correlated to the $(R)_s$ absolute configuration in the sulphide–mercury group of this molecule and to the *M* conformation of the saturated ring of the (*S*)(+)-4-ethyl-3,4-dihydro-1*M*-2-benzothi-ine (ebt) ligand.[2]

Solid-state c.d. and *X*-ray examination shows that the stereoselectivity of the addition reaction is maintained in the solid state and perhaps favoured by the crystal packing.

The higher thermodynamic stability of the $(-)[(S)_s(S)_c\text{-Me(EtCHPhCH}_2\text{)S}\cdot\text{HgCl}_2]_2$ diastereoisomer as compared with the $(R)_s(S)_c$ diastereoisomer may be due to the stereoassistance of the phenyl group in β position to the ether atom which undergoes electrophilic attack by the mercury(II) chloride.

The formation of the 1:1 adduct, (**1**), is stereoselectively achieved and can be represented by an equilibrium (Scheme) from which the diastereoisomeric complex (**2**) precipitates when its concentration reaches saturation point as an excess of mercury(II) chloride is added.

Conclusions

The stereoselectivity of the formation reaction has been demonstrated by resolving the crystal and molecular structure of complex (**1**). The molecular structure shows the existence of an $(S)_s$ absolute configuration on the new chiral centre obtained with the S–Hg bond formation. Long-range interaction between the phenyl group of the ligand and the mercury atom of the dimeric co-ordinating group probably stabilizes complex (**1**) better in the $(S)_s(S)_c$ than in the $(R)_s(S)_c$ diastereoisomeric form. C.d. spectra confirm that the $(S)_s(S)_c$ diastereoisomer has been preferentially synthesized. A relationship between the c.d. negative sign of the c.t. cotton effect at lower energies and the $(S)_s$ absolute configuration on the sulphur atom of the chiral thioether after the addition of mercury(II) chloride has been found.

Acknowledgements

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