Three-co-ordinate Mercury: Crystal Structure and Spectroscopic Properties of Trimethylsulphonium Trichloromercurate(II)

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The structure of the title compound has been solved from diffractometer data by the heavy-atom method and refined by least-squares techniques to *R* 8.24% for 890 independent reflections. Crystals are monoclinic, space group $P2_1/n$, with unit-cell dimensions: $a = 8.894(6)$, $b = 14.603(8)$, $c = 7.476(6)$ Å, $\beta = 97.85(5)°$, $Z = 4$. The structure consists of planar trigonal $[HgCl_3]^-$ anions and pyramidal $[Me_3S]^+$ cations. Two chloride ions bridge consecutive $[HgCl_3]^-$ anions, giving rise to infinite chains running along [001]. I.r. and Raman spectra between 3 500 and 50 cm^{-1} have been recorded and characteristic $[Me_3S]^+$ and $[HgCl_3]^-$ frequencies assigned. The spectral features agree with the planar trigonal structure of the anion. Raman data and molecular-weight measurements showed that $[HgCl_3]^-$ is strongly dissociated in aqueous solution.

In crystal-structure determinations of chloromercurate compounds, $L[HgCl_3]$, mercury atoms with 'characteristic' trigonal co-ordination have not so far been observed. In the compounds $Na[HgCl_3]$, $Na[HgCl_3]\cdot 2H_2O$, and $[NH_4][HgCl_3]$, distorted octahedra $[HgCl_6]$, containing linear Cl–Hg–Cl skeletons with Hg–Cl bonds shorter than the other four and a 'characteristic' digonal co-ordination on the mercury atoms, are present.[1] Only for $[NMe_4][HgCl_3]$ has a trigonal co-ordination in the

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[1] D. Grdenic, *Quart. Rev.*, 1965, **19**, 303, and refs. therein.

$[HgCl_3]^-$ group been suggested on the basis of its crystal structure being isomorphous with that of $[NMe_4][HgBr_3]$.[2] However, the existence of $[HgCl_3]^-$ anions in aqueous and organic solutions of mercury(II) chloride with added chlorine ions has been shown.[3-6] Raman lines were assigned to the vibrations of $[HgCl_3]^-$ groups in the spectra of methanol solutions or of molten $HgCl_2$ with added Cl^- ions.[7,8] However, from these mixtures a compound containing $[HgCl_3]^-$ has never been isolated and from spectral data it is not possible to assign with certainty to $[HgCl_3]^-$ a D_{3h} or a C_{3v} symmetry. To date, no i.r. data have been available for $[HgCl_3]^-$. The spectroscopic behaviour of $[Me_3S]^+$ has been extensively investigated. Vibrational spectra of the compound $[Me_3S]X$ (X = Cl, Br, I, or HgI_3),[9,10] have been reported and correlated with the configuration of the cation in the known crystal structure of $[Me_3S]I$ and $[Me_3S][HgI_3]$.[11,12] The aim of this work was to ascertain whether the crystal structure of $[Me_3S][HgCl_3]$ contains mercury atoms with digonal or trigonal co-ordination and to correlate the spectroscopic behaviour of the compound with its crystal and molecular structure. Raman spectra in solution have also been investigated in order to ascertain whether structural modifications are induced by the solvent on the $[Me_3S][HgCl_3]$ unit.

EXPERIMENTAL

Preparation.—Dimethyl sulphoxide and mercury(II) chloride (mole ratio 1 : 1) were warmed until white fumes appeared in the reaction flask (*ca.* 150 °C). The stoicheiometry of the reaction is still under investigation. The solid residue was extracted with methanol from which white crystals of trimethylsulphonium trichloromercurate(II) were obtained, m.p. 191—192 °C (Found: C, 9.5; H, 2.3; Cl, 27.2; Hg, 52.6; S, 8.3. $C_3H_9Cl_3HgS$ requires C, 9.4; H, 2.4; Cl, 27.7; Hg, 52.2; S, 8.3%). The n.m.r. spectrum [$(CD_3)_2SO$, $(CH_3)_4Si$] exhibits one signal at δ 2.88 p.p.m.

Molecular Weight.—This was determined cryoscopically in water and was found to be 150 (2.68×10^{-2} M), and 138 (1.04×10^{-2} M) (calc. 384.1).

Conductivity Measurements.—These were performed at 20 ± 0.1 °C (cell constant 0.047 cm^{-1}) in water (1.52×10^{-3} M) and in dimethyl sulphoxide solution (1.61×10^{-3} M) and gave molar conductivity values of 112.1 and 32.1 S cm^2 mol^{-1} respectively.

Spectra.—I.r. spectra were recorded on a Perkin-Elmer 180 spectrophotometer flushed with dry air in the range 3 500—50 cm^{-1} in Nujol and hexachlorobuta-1,3-diene mulls, thin Polythene films being placed between the mulls and the CsI windows to avoid halogen exchange. Raman spectra were recorded with a Cary 81 Raman spectrophotometer by use of a 4 880 Å argon-ion laser line. The sample was observed as powder in capillary tubes in the range 3 500—50 cm^{-1} and in water or dimethyl sulphoxide solution between 3 050 and 50 cm^{-1}.

Crystal Data.—$C_3H_9Cl_3HgS$, Monoclinic, $a = 8.894(6)$, $b = 14.603(8)$, $c = 7.476(6)$ Å, $\beta = 97.85(5)°$, $U = 961.8$ Å^3, $D_m = 2.70$, $Z = 4$, $D_c = 2.65$, $F(000) = 696$. Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) = 172.9 cm^{-1}. Space group $P2_1/n$ [non-standard orientation for C_{2h}^5 (No. 14)] from systematic absences = $h0l$, $h + l = 2n + 1$; $0k0 = 2n + 1$.

Preliminary unit-cell dimensions were determined from rotation and Weissenberg photographs. Accurate cell-parameters were obtained from single-crystal diffractometry by measurement of some high-angle reflections.

Data Collection.—Intensity data were collected from a thick prismatic crystal, mean radius 0.24 mm, aligned with its *c* axis parallel to the ϕ axis of a Siemens AED diffractometer. A total of 2 101 reflections were measured in the range $5 < 2\theta < 54°$, using Mo-K_α radiation and the ω—2θ scanning technique; 1 211 reflections were considered unobserved, having intensities $< 3\sigma(I)$, and were not used in the analysis. The intensity of a standard reflection monitored every 20 reflections did not vary significantly during data collection. Corrections for Lorentz and polarization effects, but not for absorption, were applied. Data were placed on an absolute scale by correlating observed and calculated structure amplitudes.

Structure Analysis.—The co-ordinates of the mercury atom were readily obtained from a Patterson map. The electron-density distribution calculated with the mercury phases gave the positions of the three chlorine and the sulphur atoms. Before location of the carbon atoms, the co-ordinates of the heavier atoms were refined by block-diagonal least-squares, first with isotropic, and then with anisotropic thermal parameters. Convergence was achieved after seven cycles at *R* 11.5%. At this stage a difference-Fourier map revealed four peaks of equivalent heights in the region of the sulphur atom. Three of these were interpreted as being carbon atoms of the sulphonium group, while the presence of the fourth peak could be explained only by considering the sulphur atom as disordered and distributed in two positions of different occupancy. Four further cycles of refinement were carried out in which the thermal parameters of the carbon atoms were treated isotropically and the occupancy factor of sulphur was also refined. Introduction of a weighting scheme * and exclusion from the refinement of ten reflections with rather large values of $|F_o - F_c|$ reduced *R* to its final value of 8.24%.

Atomic scattering factors employed in the calculations were taken from ref. 13 with corrections for the real and imaginary part of anomalous dispersion for mercury, chlorine, and sulphur from ref. 14. Final co-ordinates and thermal parameters are given in Table 1. Observed and calculated structure factors are listed in Supplementary

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* The function minimized was $\Sigma\omega|F_o - F_c|^2$, first with unit weights then the scheme $\omega^{-1} = A + B|F_o| + C|F_o|^2$ was assumed, with coefficients *A* 0.250, *B* −0.250, and *C* 0.062 5 being obtained by plotting ΔF *vs.* $|F_o|$.

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Publication No. SUP 21902 (10 pp., 1 microfiche).* All calculations were performed on the Cyber 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'-Italia Nord-Orientale.

TABLE 1

Fractional atomic co-ordinates (× 10^4 for Hg, Cl, and S; × 10^3 for S* and C) and thermal parameters (Å^2),† with estimated standard deviations in parentheses

	x/a	y/b	z/c	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg	5 731(1)	−198(1)	2 636(1)	4.05(3)	7.35(4)	4.04(3)	0.69(3)	0.47(2)	0.73(3)
Cl(1)	3 548(5)	−859(4)	3 848(6)	4.8(2)	7.3(3)	4.1(2)	−1.5(2)	1.4(2)	−0.4(2)
Cl(2)	8 164(5)	−932(4)	3 178(6)	4.4(2)	8.7(3)	4.5(2)	2.1(2)	0.0(2)	0.7(2)
Cl(3)	5 231(5)	1 198(4)	918(6)	5.9(2)	7.2(3)	2.9(2)	−0.3(2)	−0.5(2)	0.9(2)
S	9 408(8)	1 246(5)	1 205(9)	3.2(3)	3.5(3)	4.2(3)	−0.4(2)	0.2(2)	−0.4(2)
S*	1 024(2)	192(1)	189(3)	12.5(9)	7.9(9)	10.7(9)	−0.5(7)	−0.9(8)	0.2(8)
C(1)	896(2)	179(1)	317(3)	5(1)					
C(2)	1 151(3)	114(1)	176(3)	9(1)					
C(3)	917(3)	214(2)	−41(4)	7(2)					

† Anisotropic thermal parameters are expressed in the form: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. Occupancy factor of S is 62%, and of S* 38%.

RESULTS AND DISCUSSION

The whole structure is built up from $[HgCl_3]^-$ anions and $[Me_3S]^+$ cations. As can be seen from the clinographic projection of Figure 1, in the anion the 'characteristic' co-ordination of mercury is trigonal, with the three chlorine atoms arranged at the vertices of an almost regular triangle. The metal atom lies in the plane of the triangle, so that its environment can be considered as planar and only slightly distorted from that expected for sp^2 hybridized mercury, on the basis of bond distances and angles at the metal atom (Table 2). The Hg–Cl bond lengths (2.399, 2.418, and 2.451 Å) are shorter than those observed in the trigonal planar chlorobis(thiourea)mercury(II) chloride (2.57 Å),[15] and intermediate between digonal (2.26—2.32 Å)[16] and tetrahedral (2.58 and 2.62 Å)[17] bonds.

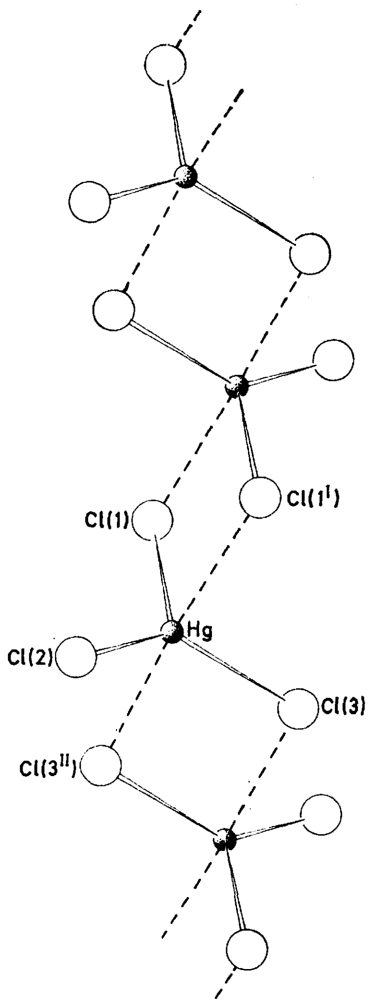

FIGURE 1 Chains of $[HgCl_3]^-$ anions

TABLE 2

Bond distances (Å) and angles (°)

(a) In the $[HgCl_3]^-$ anion			
Hg–Cl(1)	2.451(5)	Hg–Cl(1^{I})	3.040(5)
Hg–Cl(2)	2.399(6)	Hg–Cl(3^{II})	3.049(5)
Hg–Cl(3)	2.418(6)		
Cl(1)–Hg–Cl(2)	120.2(2)	Cl(1)–Hg–Cl(3^{II})	89.5(2)
Cl(1)–Hg–Cl(3)	115.6(2)	Cl(2)–Hg–Cl(1^{I})	90.2(2)
Cl(2)–Hg–Cl(3)	124.2(2)	Cl(2)–Hg–Cl(3^{II})	94.1(2)
Cl(1^{I})–Hg–Cl(3^{II})	175.7(1)	Cl(3)–Hg–Cl(1^{I})	91.9(2)
Cl(1)–Hg–Cl(1^{I})	87.9(2)	Cl(3)–Hg–Cl(3^{II})	86.1(2)
(b) In the $[Me_3S]^+$ cation			
S–C(1)	1.77(2)	S*–C(1)	1.60(3)
S–C(2)	1.87(3)	S*–C(2)	1.61(4)
S–C(3)	1.76(2)	S*–C(3)	1.87(3)
C(1)–S–C(2)	101(1)	C(1)–S*–C(2)	121(2)
C(1)–S–C(3)	103(1)	C(1)–S*–C(3)	105(1)
C(2)–S–C(3)	104(1)	C(2)–S*–C(3)	110(2)

Superior Roman numerals denote the following equivalent positions: I $1 - x, \bar{y}, 1 - z$; II $1 - x, \bar{y}, \bar{z}$.

As frequently observed in mercury(II) compounds additional bonds to mercury allow the achievement of the 'effective' co-ordination.[1] In the present compound two chlorine atoms of neighbouring $[HgCl_3]^-$ groups approach the mercury atom at 3.040 and 3.049 Å in directions nearly perpendicular to the $HgCl_3$ plane, so that the overall co-ordination corresponds to a trigonal bipyramid.

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1976, Index issue.

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Three-co-ordinate mercury has been found in some mercury(II) compounds. In most of these the different nature of the atoms bonded to the metal seems to be responsible for the significant deviations from ideal trigonal geometry.[15,18-21] However, in a few compounds where mercury is surrounded by three atoms of the same kind, severe distortion in bond angles as in $Hg_3O_2Cl_2$ [22] or significant displacements of metal from the triangle plane as in $[NMe_4][HgBr_3]$ [2] have also been observed. Only in $[Me_3S][HgI_3]$ [12] and in $[HgI_3]^-$ (ref. 21) has a situation been found similar to that in our compound, with a planar arrangement of the HgI_3 moiety and two additional Hg···I contacts which realize the 'effective' co-ordination number of five.

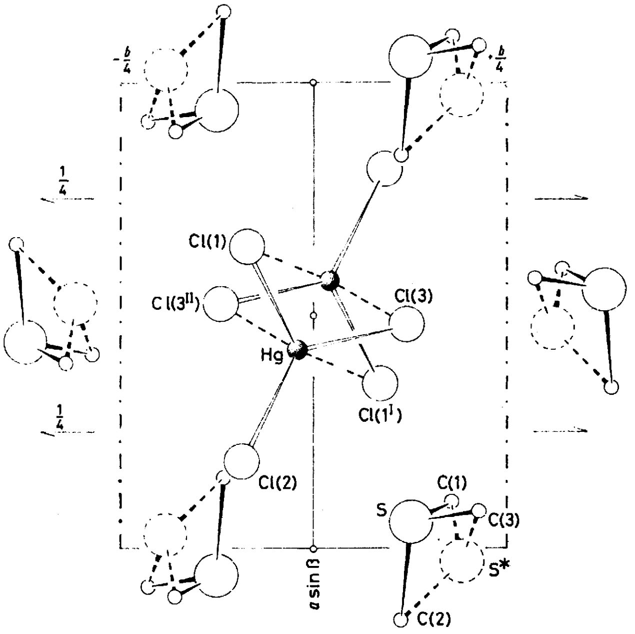

FIGURE 2 Projection of the structure along [001] showing the molecular packing

The configuration of the sulphonium ion is pyramidal as expected,[12,23] the sulphur atom lying 0.79 (S) and —0.48 Å (S*) out of the C(1)—(3) plane. Bond distances and angles in it, and in particular those concerning S*, show a poor degree of reliability, as they involve light atoms in the presence of much heavier atoms.

The packing arrangement in the structure is illustrated in Figure 2. Two chloride ions bridge consecutive $[HgCl_3]^-$ anions giving rise to infinite chains which run along [001]. Each chain is surrounded by six sulphonium cations, which interact with the chloride atoms of the anionic part with normal van der Waals contacts (Table 3).

Observed i.r. and Raman lines in the range 3 500—50 cm^{-1} for $[Me_3S][HgCl_3]$ are listed in Table 4. The assignment has been made by considering the two ionic units, $[Me_3S]^+$ and $[HgCl_3]^-$, as vibrating independently.

TABLE 3

Some significant interactions (Å) between anions and cations in the structure

Cl(3) ··· C(1)	3.62(2)	Cl(3) ··· C(2^{III})	3.45(2)
Cl(3) ··· S	3.69(1)	Cl(1) ··· S^{*IV}	3.49(2)
Cl(3) ··· S	3.74(1)	Cl(1) ··· C(1^{I})	3.63(2)

Roman numeral superscripts (see Table 2) refer to the following equivalent positions: III $x - 1, y, z$; IV $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

The point-group of $[Me_3S]^+$ is C_{3v} and its fundamental modes of vibration $7a_1$ (i.r. and Raman), $4a_2$ (inactive), and $11e$ (i.r. and Raman) can be correctly described in terms of conventional groups and skeletal modes.[9]

TABLE 4

Vibrational frequencies (cm^{-1}) and assignments for $[Me_3S][HgCl_3]$

I.r.	Raman			
Solid	Solid	Aq. soln.	Me_2SO	Assignments
3 010vs	3 009m	3 025w, dp		Me str. (a_1 and e)
2 924s	2 919vs	2 934m, p		Me sym. str. (a_1)
1 427vs	1 423w, sh	1 440vw		Me asym. def. (e)
1 418s, sh	1 409w			
1 407s		1 432vw		Me asym. def. (a_1)
1 351m				Me sym. def. (e)
1 312w				Me sym. def. (a_1)
1 044vs	1 046vw			Me rock (a_1 and e)
938m				Me rock (e)
729vw	731m	738w, dp		C–S asym. str. (e)
651m	653vs	658m, p		C–S sym. str. (a_1)
		320s, p		$HgCl_2$ sym. str. (Σ_g^+)
310vw, sh	309vw, sh			C–S–C def. (a_1)
258vw, sh				C–S–C def. (e)
	273vs	280w, br, p	279vs, p	$HgCl_3$ sym. str. (a'_1)
263vs, br				$HgCl_3$ asym. str. (e')
235vw, sh				Me torsion (e)
113s, sh				$HgCl_3$ def. (a_2'')
100vs	100vw, sh			$HgCl_3$ def. (e')
	75w			Lattice

p = polarized, dp = depolarized, vs = very strong, s = strong, m = medium, w = weak, vw = very weak, and br = broad.

The vibrational frequencies of the $[Me_3S]^+$ group have been easily assigned by comparison with spectra and assignments for the compounds $[Me_3S]X$ (X = Cl, Br, I, and HgI_3).[9,10]

The point-group of $[HgCl_3]^-$ is D_{3h} and its normal modes of vibrations can be described as $1a_1'$ (Raman) [sym. $\nu(HgCl_3)$], $1a_2''$ (i.r.) [$\delta'(HgCl_3)$], and $2e'$ (i.r. and Raman) [asym. $\nu(HgCl_3)$ and $\delta(HgCl_3)$]. The strong

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Raman line at 273 cm^{-1} for solid [Me$_3$S][HgCl$_3$] was ascribed to the symmetric stretching mode (a_1') of the [HgCl$_3$]$^-$ ion. In fact, the Raman spectrum <400 cm^{-1} in dimethyl sulphoxide solution exhibits, besides the bands of the solvent, only one strong polarized band at 279 cm^{-1}. Moreover the addition of LiCl to this solution causes the progressive disappearance of the 279 cm^{-1} and the appearance of a new strong polarized line at 261 cm^{-1}, assigned to the symmetric stretching mode of the [HgCl$_4$]$^{2-}$ ion, which is the only species present when there is a large excess of Cl$^-$ ions. A Raman line at 282 cm^{-1} was assigned to the symmetric stretching of [HgCl$_3$]$^-$ in the spectrum of molten HgCl$_2$–KCl.[8]

In the Raman spectrum of [Me$_3$S][HgCl$_3$] in aqueous solution (10^{-2}M) and <400 cm^{-1} both a strong polarized line at 320 cm^{-1} and a broad weak band at 280 cm^{-1} are present, whose intensity increases with the salt concentration. The former can be assigned to the symmetric stretching vibration of HgCl$_2$ molecules, due to dissociation of the trichloromercurate ions. The observed value is only slightly lower than that reported (325 cm^{-1}).[24] Molecular-weight determinations confirmed that [Me$_3$S][HgCl$_3$] is strongly dissociated in aqueous solution. The values obtained (150 and 138) at concentrations similar to those used for the Raman spectra were much lower than the theoretical (384.1), and indicate the presence in solution of at least three species. The other weak band at 280 cm^{-1}, polarized and at the same wavenumber as in dimethyl sulphoxide solution, was assigned to the symmetric stretching of the undissociated [HgCl$_3$]$^-$ ion. The spectrum of a methanol solution of HgCl$_2$ and LiCl, [Cl]/[Hg] = 3, the same as in the aqueous solution of [Me$_3$S][HgCl$_3$], showed a Raman line at 292 cm^{-1} which was ascribed to the symmetric ν(HgCl$_3^-$).[7] By increasing the [Cl]/[Hg] ratio, a single line at 268 cm^{-1} was observed and assigned to the symmetric ν(HgCl$_4^{2-}$). A Raman line at 269 cm^{-1} was assigned to the same vibration in the spectrum of an aqueous solution of HgCl$_2$ and KCl, [Cl]/[Hg] $\geqslant$ 4.[25] However, molar conductivity values for [Me$_3$S][HgCl$_3$] in water and in dimethyl sulphoxide solution (112.1 and 32.1 S cm^2 mol^{-1}) are of the same order of magnitude as those observed for uni-univalent electrolytes and do not agree with the presence of bivalent [HgCl$_4$]$^{2-}$ ions in the solutions. We conclude that dissociations (1) and (2) seem to be present in aqueous solutions:

$$[\mathrm{Me_3S}][\mathrm{HgCl_3}] \longrightarrow [\mathrm{Me_3S}]^+ + [\mathrm{HgCl_3}]^- \qquad (1)$$

$$[\mathrm{HgCl_3}]^- \rightleftharpoons \mathrm{HgCl_2} + \mathrm{Cl}^- \qquad (2)$$

The strong broad i.r. band with a maximum at 263 cm^{-1} for solid [Me$_3$S][HgCl$_3$] was assigned to the asymmetric stretching mode of [HgCl$_3$]$^-$ (e'). The observed value is lower than that reported for the same vibration (287 cm^{-1}), in the Raman spectrum of molten HgCl$_2$ with added Cl$^-$ ions.[8] The corresponding active Raman line, probably hidden under the strong 273 cm^{-1} band, was not observed.

The i.r. shoulder at 113 cm^{-1} (δ', a_2''), and the strong i.r. absorption at 100 cm^{-1} with a corresponding Raman shoulder at nearly 100 cm^{-1} (δ, e') were assigned to the bending vibrations of [HgCl$_3$]$^-$ ions. The broad Raman line at 75 cm^{-1} is probably due to a lattice vibration. Below 200 cm^{-1} no band was observed in the Raman spectrum of aqueous and dimethyl sulphoxide solutions.

The results of the present investigation show, as expected, that the attack of the nucleophilic Cl$^-$ ion on the linear HgCl$_2$ molecule induces a change in the hybridization of the mercury atom. The significant lengthening of the Hg–Cl bonds and the change in the Cl–Hg–Cl angles cause a relevant shift of the stretching frequencies, involving Hg–Cl bonds, with respect to the values observed for HgCl$_2$. As already suggested,[16] the observed frequencies can be taken as an indication of the different interactions between mercury(II) chloride and the Cl$^-$ ion or other ligands as, for instance, sulphoxides and sulphides.

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