Crystal and Molecular Structure of $[H_3N(CH_2)_2NH_2(CH_2)_2NH_3]_2HgCl_8$:† a Compound containing a Discrete Axially-compressed Trigonal-bipyramidal Pentachloromercurate Anion

Luigi P. Battaglia and Anna Bonamartini Corradi*
Istituto di Chimica Generale ed Inorganica dell'Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., via M. D'Azeglio 85, 43100 Parma, Italy
Luciano Antolini, Tiziano Manfredini, Ledi Menabue, and Gian Carlo Pellacani
Dipartimento di Chimica dell'Università di Modena, via G. Campi 183, 4100 Modena, Italy
Gustavo Ponticelli
Istituto di Chimica Generale dell'Università di Cagliari, via Ospedale 72, 09100 Cagliari, Italy

The compound $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]_2HgCl_8$ has been prepared and investigated by an *X*-ray structural analysis and vibrational spectroscopy. The compound crystallizes with two formula units in space group *P*2/*n* of the monoclinic system in a cell of dimensions a = 11.530(2), b = 6.638(1), c = 15.028(3) Å, β = 93.00(2)°, and Z = 2. The crystal structure was determined by three-dimensional *X*-ray diffraction and refined to R = 0.048, R' = 0.051. The structure consists of diethylenetriammonium cations, chloride anions and discrete $[HgCl_5]^{3-}$ anions. Co-ordination around the metal, which lies on the two-fold axis, can be described as a compressed trigonal bipyramid, where the equatorial positions are occupied by three weakly bonded chlorine atoms, two of them related by the two-fold axis [Hg–Cl(2) 3.029(3) Å]. The apices of the bipyramid are occupied by two shortly bonded chlorine atoms [Hg–Cl(1) 2.327(4) Å]. This is an example of a trigonal-bipyramidal d^{10} metal ion in which the axial bonds are significantly shorter than the equatorial bonds. Therefore it may be considered to consist of a linear $HgCl_2$ molecule, with a bond angle [Cl(1)–Hg–Cl(1′) 178.8(1)°] perturbed by the interaction of three weakly bonded chlorine atoms. Packing is determined by a network of hydrogen bonds involving the diethylenetriammonium cation and co-ordinated and unco-ordinated chlorine atoms. The vibrational spectra of the $[HgCl_5]^{3-}$ anion are rationalized in terms of D_{3h} symmetry and a correlation between the values of mercury–chlorine stretching frequencies and the related bond distances in $HgCl_2$ units is also discussed.

Five-co-ordination occupies a special position in inorganic chemistry, still presenting some unresolved problems. For example, although in the past few years a great number of five-co-ordinated molecules, possessing trigonal-bipyramidal or square-pyramidal, or any intermediate structures, have been reported,[1,2] the question of when to expect five-co-ordination and, for the transition metals, what form the stereochemistry will take, remains open. This is partly due to the fact that the large increase in the number of known five-co-ordinated compounds has mainly been determined by the production of ligands which by their specific stereochemical properties impose five-co-ordination on a metal ion.

From an electronic, structural, and theoretical viewpoint, discrete molecules containing a metal ion bound to five equivalent unidentate ligands, which are of the greatest potential interest, are still relatively few, including only some $[MCl_5]^{n-}$ (M = In^{III},[3] Tl^{III},[4] Cu^{II},[5,6] Cd^{II},[7] or Hg^{II}[8]) polyhedra. In particular, $[InCl_5]^{2-}$ and $[TlCl_5]^{2-}$, as their tetraethylammonium salts,[3,4] and $[CuCl_5]^{3-}$ as its *N*-2-ammonioethylpiperazine-1,4-dium salt[6] adopt a nearly regular square-based pyramidal structure, while $[CuCl_5]^{3-}$, $[CdCl_5]^{3-}$, and $[HgCl_5]^{3-}$, which are stabilized in the solid state by precipitation with large cations such as $[Co(NH_3)_6]^{3+}$ and $[Cr(NH_3)_6]^{3+}$, exist as regular trigonal bipyramids. It is worthy of note that only for $[CuCl_5]^{3-}$ have trigonal-bipyramidal[5] and square-pyramidal[6] forms been separately crystallized and therefore a convincing discussion on the preferred co-ordination geometry for d^9 cations has been reported,[9] based on experimental data and rationalized in terms of theoretical models.

For the pentachlorometalates of d^{10} metal ions, all presenting trigonal-bipyramidal structures, there are some inconsistencies between experimental and theoretical results. In fact along with pentachloromercurate anions, which in agreement with theoretical models[10,11] exhibit equatorial bonds shorter than axial bonds,[8b,c] there are $[HgCl_5]^{3-}$ [8a] and $[CdCl_5]^{3-}$ [7] anions having axial bond lengths shorter than equatorial bond lengths. The axial compression is particularly unexpected in the case of d^{10} metal ions and has only recently been theoretically justified in terms of electronic effects under particular conditions.[12]

In any case, all the theoretical treatments are incomplete, being unable to take into consideration factors such as electrostatic, steric, and crystal packing effects, which are probably too important to be neglected. For d^9 systems, experimental results demonstrate that extensive and strong hydrogen bonding, on which the crystal packing depends, diminishing the charge density at the ligand atoms, minimizes ligand–ligand electron repulsion, stabilizing square-pyramidal geometry in pentachlorocuprate(II) with respect to the trigonal-bipyramidal one.[6]

Being particularly interested in this field, we have begun a systematic investigation on the importance of the combination of size and hydrogen-bonding effects of counter ions on the coordinaton geometry of pentachlorometalates(II) of the d^{10} metal ions. In this paper we discuss the structural and spectroscopic

---

† Bis(diethylenetriammonium) trichloride pentachloromercurate(II).

Supplementary data available (No. SUP 56576, 4 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Experimental data for the crystallographic analysis

Formula	$C_8H_{32}Cl_8HgN_6$
M	696.6
a/Å	11.530(2)
b/Å	6.638(1)
c/Å	15.028(3)
β/°	93.00(2)
U/Å^3	1 148.6(3)
Z	2
Space group	$P2/n$
D_c/g cm^{-3}	2.01
D_m/g cm^{-3}	1.99
F(000)	676
T/K	293
Crystal size (mm)	0.11 × 0.24 × 0.44
Diffractometer	Philips PW1100
μ/cm^{-1}	76.5
Scan speed (° s^{-1})	0.075
Scan width (°)	1.20
Radiation (λ/Å)	Mo-K_α($\bar{\lambda}$ = 0.710 688)
θ range (°)	3.0—26.0
Scan mode	θ–2θ
No. of measured reflections	2 546 (1 400 observed)
Condition for observed reflections	$I > 3\sigma(I)$
No. of reflections used	1 381
Min./max. height in final Δρ (e Å^{-3})	±0.6
No. of refined parameters	135
R	0.0483
R'	0.0510
k, g ($w = k/[\sigma^2(F_o) + gF_o^2]$)	0.66, 4.08 × 10^{-3}

properties of a compound having an unusual mercury–chlorine ratio of 1:8, in which the mercury atom adopts an unexpected truly axially-compressed trigonal-bipyramidal geometry.

We have been very encouraged by our previous results on the importance of the type of counter ions in determining the co-ordination geometry of chlorocuprates(II)[6,13] and its ineffectiveness with respect to the geometry of tetrachloromercurates.[14,15]

Table 2. Fractional atomic co-ordinates (×10^4) with e.s.d.s in parentheses

Atom	X/a	Y/b	Z/c
Hg	2 500	2 535(1)	2 500
Cl(1)	4 272(3)	2 573(6)	1 827(3)
Cl(2)	3 782(3)	3 804(5)	4 220(2)
Cl(3)	2 500	−1 927(8)	2 500
Cl(4)	7 500	2 151(5)	2 500
Cl(5)	3 644(2)	3 680(4)	−984(2)
N(1)	907(9)	4 206(16)	−1 770(7)
N(2)	1 923(8)	219(13)	−852(6)
N(3)	3 587(9)	−3 267(17)	719(7)
C(1)	546(12)	2 034(15)	−1 929(9)
C(2)	707(10)	806(18)	−1 079(8)
C(3)	2 097(11)	−1 193(19)	−80(8)
C(4)	3 413(9)	−1 594(20)	68(8)

Table 3. Bond distances (Å) and angles (°)*

Hg–Cl(1)	2.327(4)	Cl(1′)–Hg–Cl(2)	91.5(1)
Hg–Cl(2)	3.029(3)	Cl(1)–Hg–Cl(3)	90.6(1)
Hg–Cl(3)	2.962(5)	Cl(1)–Hg–Cl(2)	88.1(1)
		Cl(2)–Hg–Cl(3)	106.1(1)
		Cl(1′)–Hg–Cl(1)	178.8(1)
		Cl(2′)–Hg–Cl(2)	147.8(1)
C(1)–N(1)	1.52(1)	N(1)–C(1)–C(2)	100.9(9)
C(1)–C(2)	1.52(2)	C(1)–C(2)–N(2)	114.1(9)
C(2)–N(2)	1.48(1)	C(2)–N(2)–C(3)	115.5(9)
C(3)–N(2)	1.50(1)	N(2)–C(3)–C(4)	108.1(9)
C(3)–C(4)	1.55(2)	C(3)–C(4)–N(3)	108.7(1.0)
C(4)–N(3)	1.49(2)		

Torsion angles (°) in the diethylenetriammonium cation

N(1)–C(1)–C(2)–N(2)	−77.4(1.2)
C(1)–C(2)–N(2)–C(3)	−173.1(1.0)
C(2)–N(2)–C(3)–C(4)	−178.8(9)
N(2)–C(3)–C(4)–N(3)	−169.8(9)

* Primes denote atoms at $\frac{1}{2} - x, y, \frac{1}{2} - z$.

Experimental

Preparation of Bis(diethylenetriammonium) Trichloride Pentachloromercurate(II), $[H_3dien]_2HgCl_8$.—The complex was prepared by mixing mercury(II) chloride and the amine in concentrated hydrogen chloride in a metal to amine molar ratio from 1:1 to 1:3. On standing, white crystals separated (Found: C, 13.9; H, 4.75; Cl, 40.8; N, 12.0. Calc. for $C_8H_{32}Cl_8HgN_6$: C, 13.8; H, 4.65; Cl, 40.7; N, 12.05%). In the presence of an excess of metal ion another crystalline compound of formula $[H_3dien]_2Hg_3Cl_{12}$ precipitated (Found: C, 7.70; H, 2.65; Cl, 34.5; N, 6.75. Calc. for $C_8H_{32}Cl_{12}Hg_3N_6$: C, 7.75; H, 2.60; Cl, 34.35; N, 6.80%). This compound which gave unsuitable crystals for *X*-ray analysis and altered under laser irradiation is not dealt with in this paper, since it is unwise to discuss the metal ion geometry on the sole basis of far-i.r. spectroscopy.

Physical Measurements.—These were made as reported in ref. 14.

Crystallographic Data Collection and Structure Determination.—A crystal of $[H_3dien]_2HgCl_8$ was mounted on a Philips PW1100 four-circle diffractometer in a random orientation, using graphite-monochromated Mo-K_α radiation. Crystal data and details of parameters associated with data collection and refinement of the structure are given in Table 1. Cell dimensions were determined by diffractometry using 20 reflections in the range $16 \leqslant \theta \leqslant 20°$. The intensities of 2 546 reflections were collected using the θ–2θ scan technique with individual profile analysis.[16] One reflection was measured after 1 h as a check of the alignment of the crystal and instrument stability. 1 400 Reflections having $I > 3\sigma(I)$ were considered as 'observed' and used in the analysis. After the usual Lorentz and polarization reduction, the intensities were put on absolute scale by a least-squares method. Correction for absorption was carried out using the empirical method of North *et al.*[17] with minimum and maximum correction 1.01—1.48. Location of the mercury atom from the Patterson map led to the full structure by standard Fourier methods. Refinement, carried out by full matrix least-squares, anisotropically for Hg and Cl, isotropically for N and C gave a R value of 0.058. The hydrogen atoms were located in a ΔF map and introduced in a calculation of final structure factors. The refinement converged at R = 0.048, R' = 0.051. The function minimized in the refinement was $\Sigma w(|F_o| - |F_c|)^2$ using the weighting scheme $w = k/(\sigma^2 F_o + gF_o^2)$. 19 Reflections, affected by extinction or counting error were excluded from the final refinement (200, 110, 020, 121, −402, 602, 022, 402, 103, 013, 213, −933, 204, −404, 755, 206, 006, 717, 618). The atomic scattering factors and corrections for anomalous dispersion were applied using the values given in the International Tables.[18] Final atomic co-ordinates are reported in Table 2. Bond distances and angles are given in Table 3. All the calculations were performed on the CYBER 76 computer of the Centro di Calcolo dell'Italia Nord Orientale di Bologna with the SHELX system program,[19] with financial support from the University of Parma. An ORTEP view of the $[HgCl_5]^{3-}$ anion is shown in Figure 1, and a projection of the structure along the [100] axis in Figure 2.

Results and Discussion

Description of the Structure.—The structure consists of diethylenetriammonium cations, chloride ions, and discrete pentachloromercurate anions.

The mercury atom, situated on a two-fold axis, is bonded to two chlorines in a linear arrangement [Hg–Cl(1) 2.327(4) Å, Cl(1)–Hg–Cl(1′) 178.8(1)°] with the Hg–Cl bond slightly elongated compared to that in gaseous $HgCl_2$ [2.252(5) Å].[20] In this way we may consider the mercury atom as possessing the 'characteristic'[21] two-co-ordinated structure, with two covalent bonds. Three chlorine atoms, two of them related by a two-fold axis [Cl(2) and Cl(2′)] and the third placed on the same axis, approach the mercury in the equatorial plane at 3.029(3) and 2.962(5) Å; thus we get the 'effective' co-ordination number for the mercury. Since five mercury–chlorine contacts are less than the sum of van der Waals radii,[21,22] the true co-ordination number is five.

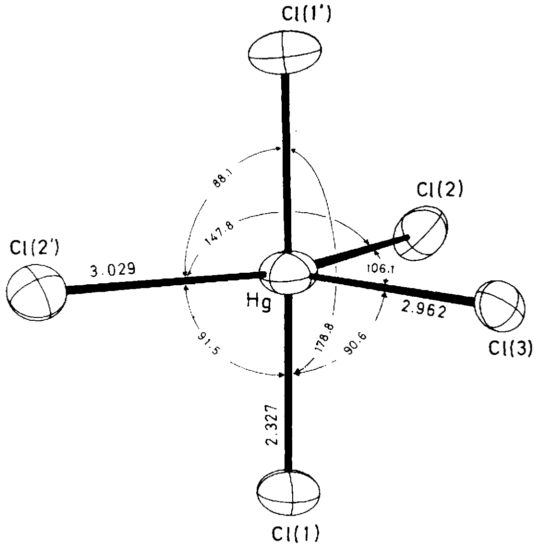

Figure 1. ORTEP view of the $[HgCl_5]^{3-}$ anion showing the atomic numbering and thermal motion ellipsoids (40%)

A precise description of the geometry is obtained by means of the criterion of Muetterties and Guggenberger,[23] evaluating the dihedral angles formed by the normals to adjacent triangular faces of the co-ordination polyhedron. The values of these angles are 38.7(1), 75.9(1), and 75.9(1)°, which correlate with the limiting forms (53.1° for the ideal trigonal bipyramid and 0° for the tetragonal pyramid), indicating an intermediate co-ordination geometry for the mercury atom.

The linear arrangement of Cl(1)–Hg–Cl(1′) and related Hg–Cl distances suggest that the structure can be classified as containing a discrete $HgCl_2$ unit, constrained by the symmetry and slightly perturbed by the longer equatorial Hg–Cl contacts. In fact Hg–Cl distances in $HgCl_2$ crystals are 2.284(12) and 2.301(14) Å, and the Cl–Hg–Cl angle 178.9(5)°.[24]

The shortness of the axial bond is evident from the fractional bond orders calculated from Pauling's empirical relationship $d(n) = d(1) - 0.60 \log n$, where $d(n)$ is the bond distance for fractional bond order n and $d(1)$ is the single bond distance.[25,26] The values obtained using $d(1) = 2.29$ Å[21] are 0.87 for the axial bond and 0.09 and 0.06 for the two different equatorial bonds. These values are compared in Table 4 with those of other $[HgCl_5]^{3-}$ moieties.

In the present compound the Cl(4) and Cl(5) anions complete the 1:8 stoicheiometric Hg:Cl ratio in the crystal for $Z = 2$. These ionic chlorine atoms and the diethylenetriamine triprotonated cation occupy the spaces between the pentachloromercurate anions.

The axial compression of the $[HgCl_5]^{3-}$ units may be rationalized on experimental bases, by considering the network of hydrogen bonding present in the molecule (Table 5). In fact diethylenetriammonium cations are bonded to co-ordinated and unco-ordinated Cl atoms *via* hydrogen bonds, in some cases strong and medium strong (H···Cl ranging from 2.06 to 2.17 Å) and in others weak (H···Cl ranging from 2.35 to 2.76 Å), these last corresponding to bifurcated hydrogen bonds. Only the Cl(1) atom, with a short bond to mercury, is not involved in hydrogen bonding. This again implies a distinct $HgCl_2$ unit in the molecule, which makes the approach of three equatorial ligands a low-energy process, thus the mercury–chlorine distances are predominantly determined by hydrogen bonding. Previous findings,[8c,27] with which our results apparently disagree, are not applicable to the present $[HgCl_5]^{3-}$ anion, which may be considered the first true example of a simple d^{10} metal, albeit distorted, in which axial bonds are markedly lower than equatorial bonds (see Table 6). On the other hand, two-co-ordination is common for mercury, probably deriving from the high promotional energy of $6s^2 \longrightarrow 6s6p$ for mercury (524 kJ mol^{-1}) involved in the formation of two covalent bonds[28] and the presence of pseudo-$HgCl_2$ molecules,

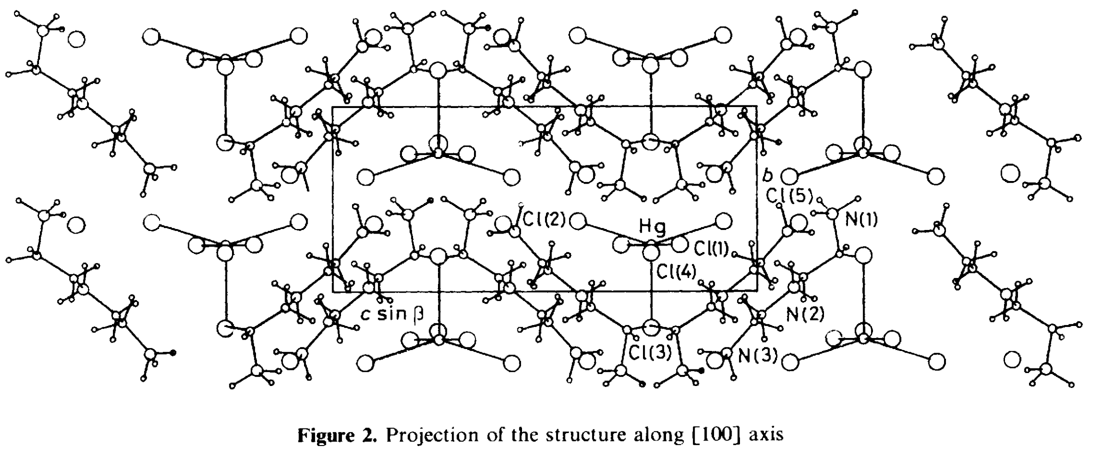

Figure 2. Projection of the structure along [100] axis

Table 4. Axial and equatorial bond distances and fractional bond orders (*n*) in $[HgCl_5]^{3-}$ moieties

	d(Hg–Cl)$_{ax.}$/Å	*n*	*d*(Hg–Cl)$_{eq.}$/Å	*n*
$[H_3dien]_2HgCl_8$[a]	2.327	0.87	2.962, 3.029	0.09, 0.06
$[Cr(NH_3)_6][HgCl_5]$[b]	2.518	0.42	2.640	0.26
$[Co(NH_3)_6][HgCl_5]$[c]	2.869, 3.158	0.11, 0.04	2.383, 2.447	0.70, 0.55
$[Co(NH_3)_6][HgCl_5]$[d]	2.871, 3.038		2.418, 2.431	

[a] This work; formulated as $[(H_3dien)_2Cl_3][HgCl_5]$. [b] Ref. 8*a*. [c] Ref. 8*c*; orthorhombic modification. [d] Ref. 8*b*; monoclinic form.

Table 5. Possible hydrogen bonds*

N–H ··· Cl	H ··· Cl/Å	N ··· Cl/Å	N–H ··· Cl/°
N(1)–H(1) ··· Cl(2^{i})	2.13	3.22(1)	177
N(1)–H(2) ··· Cl(4^{i})	2.51	3.26(1)	126
N(1)–H(2) ··· Cl(5^{ii})	2.67	3.46(1)	130
N(1)–H(3) ··· Cl(5)	2.35	3.33(1)	150
N(2)–H(8) ··· Cl(5)	2.06	3.05(1)	164
N(2)–H(9) ··· Cl(4^{iii})	2.08	3.04(1)	169
N(3)–H(14) ··· Cl(5^{iv})	2.17	3.21(1)	164
N(3)–H(15) ··· Cl(3)	2.16	3.14(1)	160
N(3)–H(16) ··· Cl(2^{v})	2.76	3.36(1)	120
N(3)–H(16) ··· Cl(5^{vi})	2.59	3.27(1)	127

* Symmetry codes: i $-\frac{1}{2} + x$, $1 - y$, $-\frac{1}{2} + z$; ii $-x$, y, $-\frac{1}{2} - z$; iii $-\frac{1}{2} + x$, $-y$, $-\frac{1}{2} + z$; iv $1 - x$, $-y$, $-z$; v $\frac{1}{2} - x$, $y - 1$, $\frac{1}{2} - z$; vi x, $y - 1$, z.

only perturbed by interactions with some weakly bonded chlorine atoms, is well ascertained.[29,30]

The network of hydrogen bonds also influences the conformation of the diethylentriammonium cation, which can be described by using the torsion angles quoted in Table 3. Furthermore, chloromercurate units are connected along the *b* axis by weak van der Waals contacts Hg ··· Cl(3′) (′*x*, 1 + *y*, *z*) = 3.676(5) Å.

Vibrational Spectra.—The far-i.r. and Raman spectra of the $[HgCl_5]^{3-}$ anion are interpreted on the basis of D_{3h} symmetry. This type of symmetry allows three Raman-active and two i.r.-active mercury–chlorine stretching vibrations [$2A'_1$(R) + A''_2(i.r.) + E'(i.r.)].

The structural feature of the present compound is such that it may be considered as comprising two units, one linear $HgCl_2$ and one trigonal $HgCl_3$, which could present distinct vibrations. In particular those arising from axial $HgCl_2$ [A'_1(R) and A''_2(i.r.)] must appear at higher energies than those arising from equatorial $HgCl_3$ [A'_1(R) and E'(i.r., R)]

Table 6. Comparison of bond lengths (Å) in related structures

Anion	M–Cl$_{eq.}$	M–Cl$_{ax.}$	Difference
$[CdCl_5]^{3-}$[a]	2.561	2.526	0.036
$[CdCl_5]^{3-}$[b]	2.3912	2.2964	0.0948
$[HgCl_5]^{3-}$[c]	2.640	2.518	0.122
$[HgCl_5]^{3-}$[d]	2.995	2.327	0.668

[a] Ref. 7. [b] Ref. 5. [c] Ref. 7*a*. [d] This work; M–Cl$_{eq.}$ 2.995 Å is the mean value.

By comparing the vibrational spectra of $[H_3dien]_2HgCl_8$ with those of the triprotonated amine hydrochloride and of $[H_3dien]_2Hg_3Cl_{12}$, the i.r. bands appearing at 334 and 265 cm^{-1} may be assigned to Hg–Cl vibrations in axial nearly linear $HgCl_2$ and equatorial trigonal $HgCl_3$ units, respectively. Other bands appear in the i.r. spectrum at too low energy (*ca.* 200 cm^{-1}) to be assigned to terminal Hg–Cl bonds.

In the Raman spectrum (difficult to record, since the compound decomposes under laser radiation) a strong intense band at 290 cm^{-1}, by its shape and position, is assigned to the A'_1 vibration arising from the $HgCl_2$ unit. In fact, owing to a small distortion from linearity of the $HgCl_2$ unit as in the compound studied, the antisymmetric Hg–Cl stretching mode should be very strong in the i.r., but weak in the Raman spectrum. On the other hand, the symmetric mode will be at lower frequency and show a reversed intensity in the i.r. and Raman spectra.

Our assignments of the Hg–Cl vibrations of the $HgCl_2$ unit agree well with the values reported in the literature for

Table 7. Comparison of Hg–Cl distances, Cl–Hg–Cl angles, and Hg–Cl_2 stretching frequencies in compounds containing nearly linear $HgCl_2$ units

	d(Hg–Cl)/Å	Cl–Hg–Cl/°	ν$(HgCl_2)_{asym}$/ cm^{-1} (i.r.)	ν$(HgCl_2)_{sym}$/ cm^{-1} (Raman)	Ref.
$HgCl_2$ (gas)			413	358	33
$HgCl_2$ (molten)	2.26	*ca.* 180	378, 372	313	33
$[NEt_4]_2[Cl_2HgCl_2MCl_2HgCl_2]HgCl_2$[a]	2.26, 2.25	180	371		*b*
$[Hbzpipz][Hg_2Cl_5]$[c]	2.28(3), 2.24(3)	168.2(9)	363	318	30
$Ph_2SO{\cdot}HgCl_2$	2.291(4), 2.289(4)	172.4(1)	362	308	*d*
heg·$2HgCl_2$[e]	2.298, 2.319	175.9	353		*f,g*
$2Me_2SO{\cdot}3HgCl_2$	2.309(6), 2.310(6)	166.0(2)	345, 339	288	*d*
$(H_4ttf)(HgCl_2)_3$[h]	2.307(5), 2.319(5)	169.7(2)	345	290	*i*
$Bu^n{}_2SO{\cdot}HgCl_2$	2.33(1), 2.35(1)	167.0(5)	348	298	*d*
$[H_3dien]_2HgCl_8$	2.327(4)	178.8(1)	334	290	*j*
pyo·$HgCl_2$[k]	2.316(16), 2.339(15)	163.1(9)	338, 314		*l*
$[Co(NH_3)_6][HgCl_5]$	2.870, 3.158			260	8*c*

[a] M = Pd or Pt. [b] R. M. Barr, M. Goldstein, T. N. D. Hairs, N. McPartlin, and A. J. Markwell, *J. Chem. Soc., Chem. Commun.*, 1974, 221. [c] $[Hbzpipz]^+$ = *N*-benzylpiperazinium cation. [d] P. Biscarini, L. Fusina, G. Nivellini, and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1981, 1024. [e] heg = $MeO(CH_2CH_2O)_6Me$. [f] R. Iwamoto, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 1123. [g] G. Wulfsberg, *Inorg. Chem.*, 1976, **15**, 1791. [h] H_4ttf = tetrahydrotetrathiafulvalene. [i] M. D. Glick, W. H. Ilsley, and A. R. Siedle, *Inorg. Chem.*, 1981, **20**, 3819. [j] This work. [k] pyo = pyridine *N*-oxide. [l] T. B. Brill and D. W. Wertz, *Inorg. Chem.*, 1970, **9**, 2692.

compounds containing nearly linear $HgCl_2$ groups (Table 7). A close correlation between the frequencies of vibrations and distances of Hg–Cl bonds has been well established for other chloromercurates(II).[26,30–33]

Acknowledgements

We thank the Ministero della Pubblica Istruzione of Italy for financial support.

References

1 S. J. Wood, *Prog. Inorg. Chem.*, 1972, **16**, 227 and refs. therein.

2 R. R. Holmes, *Prog. Inorg. Chem.*, 1984, **32**, 119 and refs. therein.

3 D. S. Brown, F. W. B. Einstein, and D. G. Tuck, *Inorg. Chem.*, 1969, **8**, 14.

4 D. F. Shriver and I. Wharf, *Inorg. Chem.*, 1969, **8**, 2167.

5 K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1111; I. Bernal, J. D. Korp, E. O. Schlemper, and M. S. Hussain, *Polyhedron*, 1982, **1**, 365.

6 L. Antolini, G. Marcotrigiano, L. Menabue, and G. C. Pellacani, *J. Am. Chem. Soc.*, 1980, **102**, 1303.

7 (*a*) T. V. Long, A. W. Herlinger, E. F. Epstein, and I. Bernal, *Inorg. Chem.*, 1970, **9**, 459; (*b*) E. F. Epstein and I. Bernal, *J. Chem. Soc. A*, 1971, 3628.

8 (*a*) W. Clegg, D. A. Greenhalgh, and B. P. Straughan, *J. Chem. Soc., Dalton Trans.*, 1975, 2591; (*b*) W. Clegg, *ibid.*, 1982, 593; (*c*) A. W. Herlinger, J. N. Brown, M. A. Dwyer, and S. F. Pavkovic, *Inorg. Chem.*, 1981, **20**, 2366.

9 D. Reinen and C. Friebel, *Inorg. Chem.*, 1984, **23**, 791.

10 J. K. Burdett, *Inorg. Chem.*, 1975, **14**, 375.

11 A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 365.

12 E. Shustorovich, *Inorg. Chem.*, 1978, **17**, 2648.

13 See, for example, L. Antolini, L. Menabue, G. C. Pellacani, M. Saladini, G. Marcotrigiano, and W. Porzio, *J. Chem. Soc., Dalton Trans.*, 1981, 1753 and refs. therein; L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano, L. Menabue, and G. C. Pellacani, *Inorg. Chem.*, 1982, **21**, 3919 and refs. therein.

14 L. Menabue, G. C. Pellacani, A. Albinati, F. Ganazzoli, F. Cariati, and G. Rassu, *Inorg. Chim. Acta*, 1982, **58**, 227 and refs. therein.

15 I. M. Vezzosi, A. Benedetti, A. Albinati, F. Ganazzoli, F. Cariati, and L. Pellicciari, *Inorg. Chim. Acta*, 1984, **90**, 1 and refs. therein.

16 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.

17 A. C. T. North, D. C. Phillips, and F. Scott Mathews, *Acta Crystallogr., Sect A*, 1968, 351.

18 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

19 G. M. Sheldrick, 'SHELX-76, Program for Crystal Structure Determination,' University Chemical Laboratory, Cambridge, 1976.

20 K. Kashiwabara, A. Konaka, and M. Kimura, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 410.

21 D. Grdenic, *Q. Rev.*, 1965, **19**, 303.

22 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

23 E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1974, **96**, 1748.

24 V. Subramanian and K. Seff, *Acta Crystallogr., Sect. B*, 1980, **36**, 2132.

25 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, 1960, p. 255.

26 D. E. Scaife, *Aust. J. Chem.*, 1971, **24**, 1753.

27 J. K. Burdett, *Inorg. Chem.*, 1975, **14**, 931.

28 F. A. Cotton and G. Wilkinson, 'Chimica Inorganica,' 2nd edition, ed. E. Ambrosiana, Milano, Italy, 1974, p. 565.

29 A. Ben Salah, J. W. Bats, R. Kalus, H. Fuess, and A. Daoud, *Z. Anorg. Allg. Chem.*, 1982, **493**, 178.

30 A. Albinati, S. V. Meille, F. Cariati, G. Marcotrigiano, L. Menabue, and G. C. Pellacani, *Inorg. Chim. Acta*, 1980, **38**, 221 and refs. therein.

31 H. Poulet and J. P. Mathieu, *J. Chim. Phys.*, 1963, **60**, 442.

32 S. T. R. Dunsmuir and A. P. Lane, *J. Inorg. Nucl. Chem.*, 1971, **33**, 4363.

33 P. A. W. Dean, *Prog. Inorg. Chem.*, 1978, **24**, 109.

Received 28th October 1985; *Paper* 5/1877