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Spectroscopic and Structural Investigation on Tetrahalomercurates(II). Crystal and Molecular Structures of Bis(N-ethylmorpholinium)tetrachloromercurate(II) and (N-ammoniumethylmorpholinium)tetrachloromercurate(II) Complexes

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Compounds of the type $[LH]_2HgX_4$ *and* $[LH_2]HgX_4$ *[LH = N-ethylmorpholinium cation;* LH_2 = *N-ammoniumethylmorpholinium dication; X = Cl, Br, I] were prepared and characterized by means of Raman and far-IR spectroscopies. For two compounds,* $[LH]_2HgCl_4$ *(A) and* $[LH_2]HgCl_4$ ***(B)****, the crystal structures were also determined. Crystals of both compounds show that they are composed of discrete monomeric* $[HgCl_4]^{2-}$ *units and counterions,* $[LH^+]$ *and* $[LH_2^{2+}]$*. Coordination around the mercury atoms is distorted tetrahedral, arising from hydrogen bonding. In compound (A) there is one long (2.559(5) Å) and three short (av. 2.456(15) Å) Hg–Cl distances, while in compound* ***(B)*** *a continuous range of Hg–Cl distances (2.395(3)–2.562(3) Å) is present. The deviations from tetrahedral geometry of the* $[HgCl_4]^{2-}$ *units do not play a significant role in vibrational spectra.*

Introduction

It is well known that Hg(II) has the ability of forming a variety of compounds with different coordination numbers and showing interesting physical and structural properties [1–5]. Thus, although a distinction between ligands 'bonded' and 'non-bonded' to mercury is not always easy to make, it may be assumed that Hg(II) halide complexes present structures with coordination numbers ranging from 2 to 6 [1–5].

Our interest in this field has focused on the halomercurates(II) containing discrete monomeric $[HgX_4]^{2-}$ units to examine possible correlations between Raman and IR spectra and structural parameters, in particular, the distortion of the tetrahedral geometry around the mercury atom induced by the crystal packing forces (*e.g.* hydrogen bonding). Therefore, extending a previous investigation [5], we have synthesized and determined the structures of tetrahalomercurates(II) containing as counterions, N-ethylmorpholinium ($NetmfH^+$) and N-ammoniumethylmorpholinium ($NametmfH_2^{2+}$), having different charges and therefore different crystal packing.

Experimental

The complexes $[NetmfH]_2HgX_4$ and $[NametmfH_2]HgX_4$ (where X = Cl, Br, I) were prepared by mixing the mercury halide and the appropriate amine in a concentrated hydrogen halide solution, having a metal to ligand molar ratio of 1:2 and 1:1, respectively. On standing, crystals separated. Nitrogen, carbon and hydrogen were analysed with a Carlo Erba Elemental Analyser Instrument Model 1106. Found: C, 24.99; H, 4.92; N, 4.87: Calc. for $C_{12}H_{28}N_2O_2HgCl_4$: C, 25.05; H, 4.91; N, 4.87. Found: C, 19.19; H, 3.74; N, 3.71. Calc. for $C_{12}H_{28}N_2O_2HgBr_4$: C, 19.03; H, 3.73; N, 3.70. Found: C, 15.23; H, 2.93; N, 3.01. Calc. for $C_{12}H_{28}N_2O_2HgI_4$: C, 15.31; H, 3.00; N, 2.98. Found: C, 15.12; H, 3.31; N, 5.90. Calc. for $C_6H_{16}N_2OHgCl_4$: C, 15.17; H, 3.39; N, 5.90. Found: C, 11.38; H, 2.51; N, 4.45. Calc. for $C_6H_{16}N_2OHgBr_4$: C, 11.04; H, 2.47; N, 4.28. Found: C, 8.66; H, 1.99; N, 3.26. Calc. for $C_6H_{16}N_2OHgI_4$: C, 8.57; H, 1.92; N, 3.33.

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TABLE I. Crystal Data and Data Collection Parameters for the $[NetmfH]_2HgCl_4$ (A) and $[NametmfH_2]HgCl_4$ (B) Compounds.

	(A)	**(B)**
Molecular formula	$C_{12}H_{28}N_2O_2Cl_4Hg$	$C_6H_{16}N_2OCl_4Hg$
Mol. wt.	574.77	474.61
Crystal system	Orthorhombic	monoclinic
Space group	Pbca	$P2_1/c$
a, Å	18.750(3)	6.657(2)
b, Å	14.363(2)	13.790(3)
c, Å	15.131(3)	14.404(3)
α, deg	90	90
β, deg	90	91.48(8)
γ, deg	90	90
V, Å^3	4075(1)	1321.8(6)
Z	8	4
d_{calc}, g cm^{-3}	1.87	2.38
μ(Mo Kα), cm^{-1}	80.9	124.3
Crystal dimensions, mm	0.30 × 0.25 × 0.10	0.30 × 0.15 × 0.10
Radiation ($\bar{\lambda}$, Å)	0.71069 (Mo Kα) (graphite monochromated)	
Scan mode	$\omega/2\theta$	
Scan speed, deg·sec^{-1}	0.04	
Scan width, deg	1.3	1.1
Total background count, sec	14	
2θ range, deg	$5 \leqslant 2\theta \leqslant 50$	
Measured reflections	3566 (+h +k +l)	2454 (±h +k +l)
Observed reflections ($I \geqslant 3\sigma(I)$)	1994	1787
R factor[a]	0.073	0.042
R_{2w} factor[b]	0.099	0.064

[a] R factor $= \Sigma\|F_o| - 1/k|F_c\|/\Sigma|F_o|$. [b] R_{2w} factor $= \Sigma w\|F_o|^2 - 1/k^2|F_c|^2|/\Sigma w|F_o|^2$.

TABLE II. Final Positional and Thermal Parameters for Compounds (A) and (B). E.s.d.'s are given in Parentheses. Anisotropic Thermal Factors in the form: $T = \exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$.

Atom	x/a	y/b	z/c	B_{11} (B_{iso})	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Compound $[NetmfH]_2[HgCl_4]$ (A)									
Hg	0.12932(3)	0.20728(4)	0.21462(5)	3.45(2)	2.66(2)	7.10(3)	0.21(2)	0.67(3)	−0.32(2)
Cl(1)	0.06617(20)	0.14848(27)	0.35375(32)	3.46(16)	3.46(17)	7.11(25)	0.17(12)	0.08(16)	0.60(16)
Cl(2)	0.02465(26)	0.26888(35)	0.13490(37)	5.58(22)	5.75(25)	7.31(29)	1.50(18)	−1.34(21)	0.04(21)
Cl(3)	0.20859(22)	0.33312(29)	0.26491(37)	4.01(17)	3.01(15)	9.12(32)	−0.52(13)	0.03(19)	−0.84(19)
Cl(4)	0.19398(26)	0.07460(29)	0.15376(40)	5.83(23)	3.02(17)	12.13(37)	0.13(16)	3.95(25)	−1.61(21)
C(1)	−0.0259(9)	0.4499(12)	0.2898(11)	4.91(34)					
C(2)	0.0460(10)	0.4881(13)	0.3212(13)	5.36(37)					
C(3)	0.0505(9)	0.3941(12)	0.4436(12)	5.24(37)					
C(4)	−0.0246(9)	0.3548(11)	0.4271(11)	4.54(33)					
C(5)	−0.1120(10)	0.3184(13)	0.3030(12)	5.23(38)					
C(6)	−0.1254(10)	0.2203(13)	0.3363(13)	5.87(40)					
C(7)	0.1959(10)	0.1072(13)	0.5304(12)	5.70(38)					
C(8)	0.2293(11)	0.1996(14)	0.5088(14)	6.19(44)					
C(9)	0.3026(11)	0.1391(14)	0.4017(13)	6.17(43)					
C(10)	0.2690(11)	0.0451(14)	0.4132(14)	6.43(46)					
C(11)	0.1660(14)	−0.0482(18)	0.4694(17)	8.98(63)					

(continued on facing page)

TABLE II. *(continued)*

Atom	*x/a*	*y/b*	*z/c*	B_{11} (B_{iso})	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(12)	0.0947(15)	−0.0501(19)	0.4914(19)	10.95(70)					
N(1)	−0.0381(7)	0.3533(9)	0.3321(8)	4.08(25)					
N(2)	0.1955(8)	0.0509(10)	0.4509(10)	5.60(32)					
O(1)	0.0560(6)	0.4883(8)	0.4046(8)	5.09(23)					
O(2)	0.3017(7)	0.1918(8)	0.4764(9)	5.86(27)					
Compound $[NametmfH_2][HgCl_4]$ **(B)**									
Hg	0.21555(6)	0.24671(3)	0.40257(3)	4.22(1)	2.87(1)	3.40(1)	0.45(1)	0.85(1)	−0.18(1)
Cl(1)	0.59829(36)	0.23183(19)	0.39381(18)	3.10(9)	3.99(10)	3.38(10)	0.53(8)	−0.36(7)	−0.79(8)
Cl(2)	0.16697(39)	0.22605(22)	0.23102(18)	3.47(10)	5.70(13)	2.70(9)	−0.10(9)	−0.52(8)	−0.76(9)
Cl(3)	0.15727(42)	0.40948(17)	0.46644(19)	4.82(11)	2.53(9)	3.97(11)	0.15(8)	1.46(9)	−0.15(8)
Cl(4)	0.06712(40)	0.12010(19)	0.49169(21)	3.86(10)	3.47(10)	5.50(14)	0.56(9)	1.33(10)	1.15(10)
C(1)	0.6084(14)	0.4856(7)	0.3054(7)	2.98(15)					
C(2)	0.7684(14)	0.4424(7)	0.2437(7)	3.28(17)					
C(3)	0.5515(16)	0.4409(8)	0.1137(8)	4.09(20)					
C(4)	0.3821(14)	0.4834(7)	0.1660(6)	2.85(15)					
C(5)	0.2921(13)	0.5862(6)	0.2983(6)	2.69(15)					
C(6)	0.3680(14)	0.6513(7)	0.3784(7)	3.13(16)					
N(1)	0.4641(10)	0.5439(5)	0.2462(5)	2.38(12)					
N(2)	0.1950(11)	0.7028(6)	0.4177(6)	3.19(14)					
O	0.6799(10)	0.3822(5)	0.1736(5)	3.49(12)					

Physical Measurements

Infrared spectra were recorded at low temperature in polythene pellets on a Perkin Elmer 180 spectrophotometer equipped with a liquid-nitrogen cell. Raman spectra were recorded at room temperature with a Jobin-Yvon Ramanor HG2S spectrometer. The spectra were excited by the 514.5 nm line of a Spectra-Physics 165 argon ion laser (incident power 60–150 mW). Plasma radiation was removed from the source by means of an interference filter.

Determination and Refinement of the Crystal Structures of Compounds $[NetmfH]_2HgCl_4$ (A) and $[NametmfH_2]HgCl_4$ (B)

Colourless crystals of bis(N-ethylmorpholinium)-tetrachloromercurate(II) **(A)** and (N-ammonium-ethylmorpholinium)tetrachloromercurate(II) **(B)** were mounted on a glass fiber in a general orientation. Data were collected using a Philips PW 1100 automated diffractometer. Crystallographic and data collection parameters are listed in Table I. Data were corrected for Lorentz and polarization factors and for absorption, and the integrated intensities were considered as observed when $I_{net} \geqslant 3\sigma(I_o)(\sigma(I_o)$ based on counting statistics). The structures were solved by Patterson and Fourier methods and refined by block-diagonal least-squares using anisotropic thermal factors for Hg and Cl atoms, isotropic for the others. The function minimized was $\Sigma w(|F_o| -$

TABLE III. Relevant Bond Lengths (Å) and Angles (deg). E.s.d's on last digit given in parenthesis.

	$(NetmfH)_2HgCl_4$	$(NametmfH_2)HgCl_4$
Hg–Cl(1)	2.559(5)	2.562(2)
Hg–Cl(2)	2.468(5)	2.500(3)
Hg–Cl(3)	2.461(4)	2.460(2)
Hg–Cl(4)	2.439(5)	2.395(3)
$\langle C–C\rangle_{av}$	1.49(6)	1.52(2)
$\langle C–N\rangle_{av}$	1.51(4)	1.50(2)
$\langle C–O\rangle_{av}$	1.39(9)	1.43(2)
Cl(1)–Hg–Cl(2)	98.8(2)	92.6(1)
Cl(1)–Hg–Cl(3)	105.5(2)	104.9(1)
Cl(1)–Hg–Cl(4)	106.4(1)	113.1(1)
Cl(2)–Hg–Cl(3)	111.6(1)	117.1(1)
Cl(2)–Hg–Cl(4)	119.4(1)	113.7(1)
Cl(3)–Hg–Cl(4)	113.0(1)	113.2(1)
$\langle C–C–N\rangle_{av}$[a]	111(2)	109.6(1.1)
$\langle C–N–C\rangle_{av}$[a]	111(3)	111.3(2.5)
$\langle C–C–O\rangle_{av}$[a]	113(3)	111.1(1)
C–O–C	111(2)	108.9(7)

[a] Average values; the number in parenthesis refers to the estimated standard deviation of the mean.

TABLE IV. Relevant Packing Distances (Å). The e.s.d.'s for distances not involving H atoms are 0.01 Å or less.

	(A)	(B)
Cl(1)···N(1)	3.55 $^{\mathrm{i}}$	3.30 $^{\mathrm{ii}}$
Cl(1)···HN(1)	2.74 $^{\mathrm{i}}$	2.63 $^{\mathrm{ii}}$
Cl(1)···N(2)	3.16 $^{\mathrm{i}}$	3.14 $^{\mathrm{iii}}$
Cl(1)···HN(2)	2.21 $^{\mathrm{i}}$	
Cl(1)···H(3)N(2)		2.18 $^{\mathrm{iii}}$
Cl(2)···N(1)	3.43 $^{\mathrm{i}}$	3.52 $^{\mathrm{ii}}$
Cl(2)···HN(1)	2.68 $^{\mathrm{i}}$	2.82 $^{\mathrm{ii}}$
Cl(2)···N(2)		3.20 $^{\mathrm{iv}}$
Cl(2)···H(1)N(2)		2.62 $^{\mathrm{iv}}$
Cl(3)···N(2)		3.30 $^{\mathrm{v}}$
Cl(3)···H(2)N(2)		2.60 $^{\mathrm{v}}$
Cl(4)···N(2)		3.29 $^{\mathrm{v}}$
Cl(4)···H(3)N(2)		2.77 $^{\mathrm{v}}$
O···N(2)		2.93 $^{\mathrm{ii}}$
O···H(1)N(2)		2.38 $^{\mathrm{ii}}$

Roman numeral superscripts refer to the following symmetry operations applied to the second atom of the list:

i $x, y, z,$
ii $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$
iii $1 - x, 1 - y, 1 - z$
iv $\bar{x}, y - \frac{1}{2}, \frac{1}{2} - z$
v $\bar{x}, 1 - y, 1 - z$

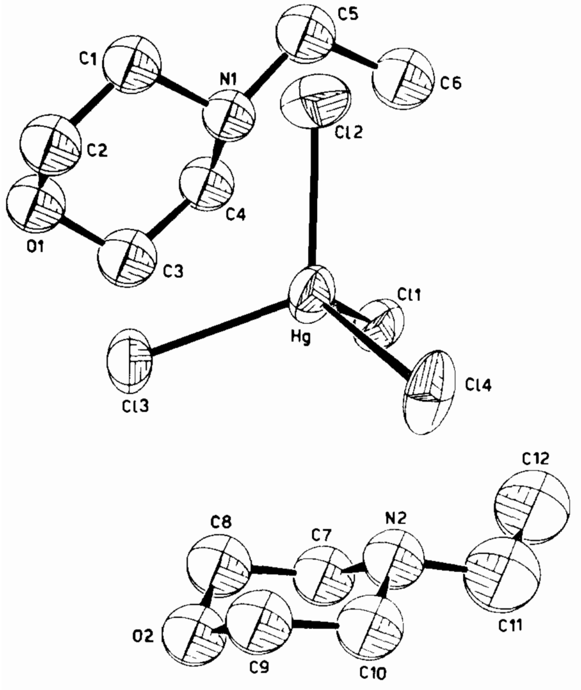

Fig. 1 An ORTEP view of the $(\mathrm{NetmfH})_2\mathrm{HgCl}_4$ (A) compound with the numbering scheme.

$1/k|F_c|)^2$ with weights chosen after Cruickshank [6]. Scattering factors were taken from ref. [7] and a correction for the real part of the anomalous dispersion was applied for Hg and Cl atoms [7].

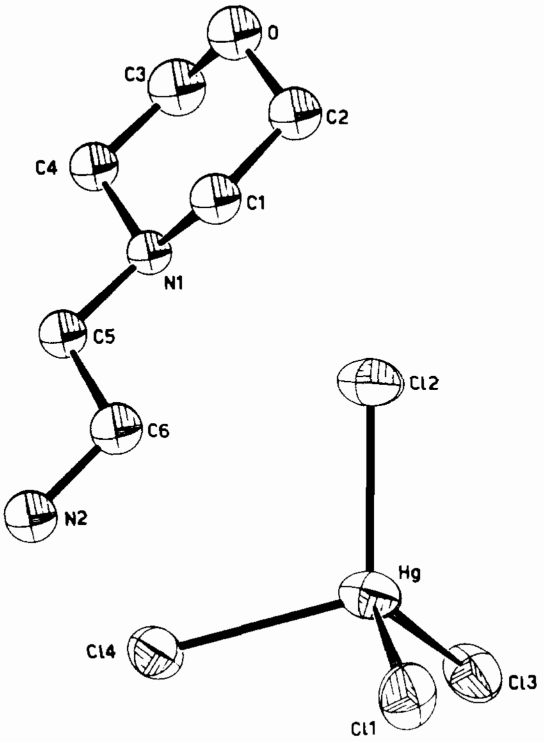

Fig. 2. An ORTEP view of the $(\mathrm{NametmfH_2})\mathrm{HgCl}_4$ (B) compound with the numbering scheme.

Final atomic coordinates are given in Table II. Relevant bond lengths and angles and packing distances are shown in Tables III and IV.

Structural Study of (A)

From systematic absences the space group was determined as Pbca. Cell constants were obtained from a least squares fit of the 2θ values of 16 high angle reflections ($2\theta > 20°$) accurately centered on the diffractometer. Three standard reflections ($2\ 3\ 1$, $\bar{2}\ 3\ \bar{1}$, $\bar{2}\ \bar{3}\ \bar{1}$) were measured every 120 min.; no significant variation in the experimental condition or in the crystal were detected. An empirical absorption correction was applied using azimuthal (ψ) scans of reflections: $1\ \bar{1}\ \bar{6}$, $1\ \bar{1}\ \bar{8}$, $1\ \bar{1}\ \overline{10}$. Only the positions of some hydrogen atoms were located in the final difference Fourier map; therefore all hydrogen atoms were placed in idealized positions (C–H 1.08 Å) and their contribution, held fixed in the last cycles of the refinement, was taken into account (using isotropic B = 7.0 Å^2). Upon convergence the maximum ratio shift/e.s.d.'s for the parameters was 0.39.

Structural Study of (B)

From the systematic absences the space group was determined to be $P2_1/c$. Cell constants were obtained from a least-squares fit of 24 accurately-centered reflections having $2\theta > 16°$. Three standard reflec-

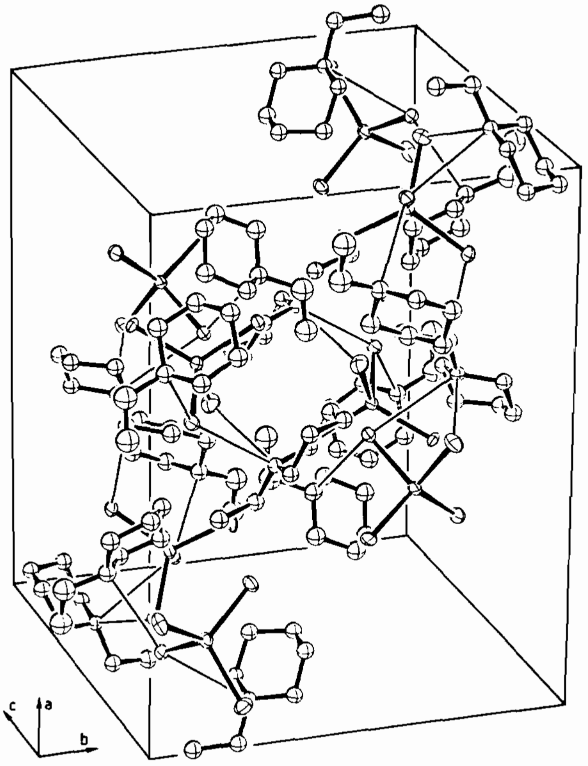

Fig. 3. Packing diagram of the $(NetmfH)_2HgCl_4$ (**A**) compound.

tions $(\bar{3}\,6\,4,\ 3\,\bar{6}\,\bar{4},\ 1\,\bar{4}\,4)$ measured every 180 min did not show any significant variation. Data were empirically corrected for absorption using an azimuthal (ψ) scan of reflections $\bar{2}\,\bar{1}\,1$, $\bar{3}\,\bar{1}\,2$, and $\bar{4}\,\bar{1}\,2$. All the hydrogen atoms were located from a final difference Fourier map and their contribution, held fixed during the refinement, was taken into account. The final maximum shift/e.s.d.'s for refined parameters was 0.27.

Results and Discussion

An ORTEP view of the two molecules is given in Figs. 1 and 2. Both compounds consist of discrete $HgCl_4^{2-}$ units hydrogen-bonded to the nitrogen atoms of the counterions. However the packing of the anions in the two compounds is very different, and its effect on the Hg–Cl bond lengths somewhat subtle; in compound (**A**) each single charged counterion $[NetmfH]^+$ is only hydrogen-bonded to one $HgCl_4^{2-}$ anion, while in compound (**B**) a tridimensional network is present due to the interactions of each $[NametmfH_2]^{2+}$ ligand with different symmetry-related mercuric units (see Figs. 3 and 4).

In both cases the Hg(II) atom shows a distorted tetrahedral coordination. This is a common feature found in Hg(II) complexes [1, 2] containing isolated monomeric units of $HgCl_4^{2-}$ [5, 8, 9]; deviations from T_d symmetry due to packing interactions have already been discussed [5].

In compound (**A**) there is one long (2.559(5) Å) and three short (av. 2.456(15) Å) Hg–Cl distances (see Table III), while in compound (**B**) a more continuous range of Hg–Cl bond lengths (2.395(3)–2.562(3) Å) is present. It may be noted that in N(2-

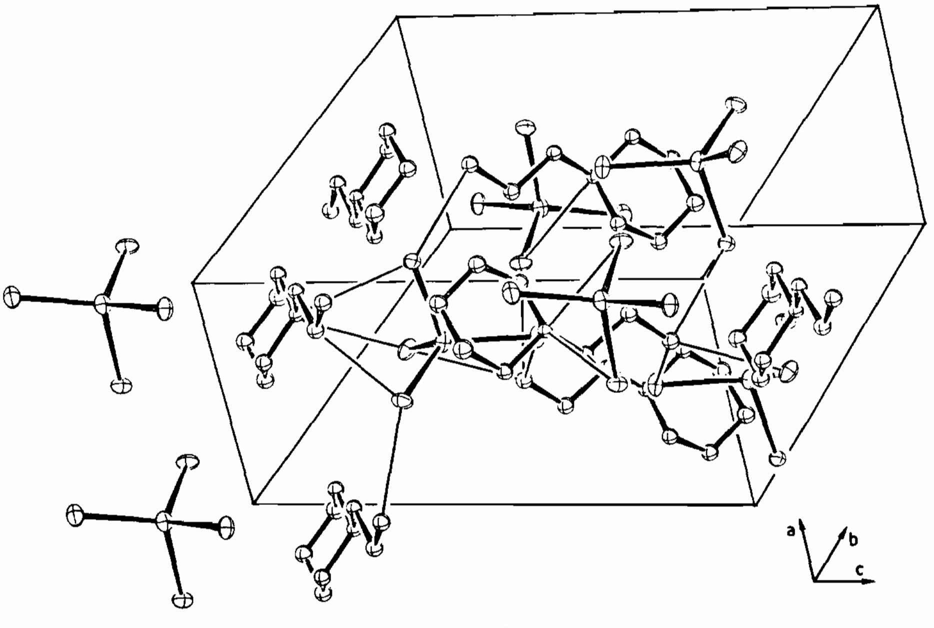

Fig. 4. Packing diagram of the $(NametmfH_2)HgCl_4$ (**B**) compound.

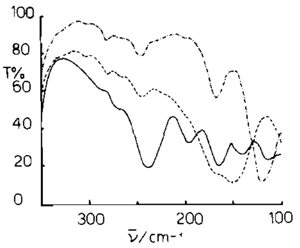

Fig. 5. IR spectra of solid $[NetmfH]_2[HgCl_4]$ (———), $[NetmfH]_2[HgBr_4]$ (------) and $[NetmfH]_2[HgI_4]$ (–·–·–).

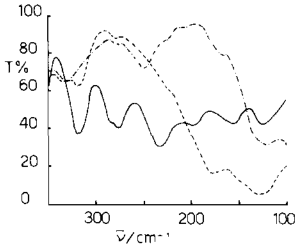

Fig. 7. IR spectra of solid $[NametmfH_2][HgCl_4]$ (———), $[NametmfH_2][HgBr_4]$ (------) and $[NametmfH_2][HgI_4]$) (–·–·–).

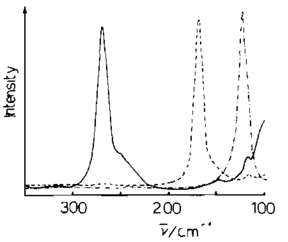

Fig. 6. Raman spectra of solid $[NetmfH]_2[HgCl_4]$ (———), $[NetmfH]_2[HgBr_4]$ (------) and $[NetmfH]_2[HgI_4]$ (–·–·–).

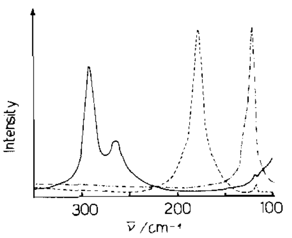

Fig. 8. Raman spectra of solid $[NametmfH_2][HgCl_4]$ (———), $[NametmfH_2][HgBr_4]$ (------) and $[NametmfH_2]$-$[HgI_4]$ (–·–·–).

ammoniumethyl)piperazinium monochloride tetrachloromercurate(II) [5] two longer (av. 2.556(9) Å) and two shorter (av. 2.440(9) Å) distances are found, while in bis(3,5-diphenyl-1,2-dithiolium)tetrachloromercurate(II) [9], distances in the range 2.441(5)–2.535(4) Å are present: a pattern very similar to (**B**).

These bond length differences are reflected in the large angular deviations from ideal values: the smaller angles (see Table III) are in both cases defined by the longer bonds.

Hydrogen bond distances may roughly be divided into two groups: on the one hand Cl···N distances less than 3.30 Å, *i.e.* shorter than the sum of the van der Waals radii (assuming as radii 1.75 Å for Cl and 1.55 Å for N [10]), on the other hand longer van der Waals contacts in the range 3.30–3.60 Å. In both compounds the shortest Cl···N distances (3.14–3.16 Å) are those involving atoms Cl(1) and N(2) (*cf.* Table IV); it is noteworthy that these two interactions may be those responsible for the increase of the Hg–Cl(1) distance to an average value of 2.560(2) Å compared to an average value of 2.457(9) for 'non hydrogen bonded' distances. It may also be noted that packing distances around 3.3 Å are in the upper end of the assumed van der Waals interactions and the 'lengthening' effect on Hg–Cl distances may be small: in fact to a Cl···N distance of 3.20 Å (*e.g.* Cl(2)···N(2)^{iv} (Table IV)) corresponds a Hg–Cl(2) bond length of 2.500(3) Å in (**A**) and in (**B**) to a Cl···N contact of 3.29 Å corresponds a 'short' Hg–Cl bond of 2.395(3) Å.

The two counterions have, as expected, a different coordination ability, primary amines being much more effective in achieving a complex pattern of hydrogen bonds than tertiary amines. However, it should be noted that the effect on the structural parameters of the interactions between the two amines and the $[HgCl_4]^{2-}$ units are approximately the same.

The morpholinium ring is in the expected chair conformation with a geometry comparable to that already found [11].

Vibrational Spectra

Due to the distorted tetrahedral coordination of the Hg(II) atoms in compounds (**A**) and (**B**), more Hg–Cl stretching bands than those calculated for T_d symmetry should be expected in the Raman and IR spectra. In fact, while assuming a T_d symmetry two Raman bands (A_1 and F_2) and one infrared band (F_2) only should be present for the Hg–Cl stretching vibrations: by lowering the symmetry at least three infrared and Raman active bands are calculated. This implies that in the latter case the F_2 vibration, triply-degenerate in T_d, is at least split into two vibrations, both infrared- and Raman-active.

The infrared spectra of compounds (**A**) and (**B**), even recorded at liquid nitrogen temperature, show only one strong and broad Hg–Cl stretching band; in the Raman spectra one strong and one weak band are observed, the latter found at the same frequency of the strong infrared band. Therefore it can be

TABLE V. Vibrational Stretching Frequencies (cm^{-1}) of $[HgX_4]^{2-}$ Anions.[a]

Compound	(A_1)	(F_2)	
	Raman	Infrared	Raman
$(NetmfH)_2HgCl_4$	270vs	240vsb	250sh
$(NetmfH)_2HgBr_4$	168vs	150vsb	160sh
$(NetmfH)_2HgI_4$	123vs	120vsb	
$(NametmfH_2)HgCl_4$	293vs	274m	265m
$(NametmfH_2)HgBr_4$	180vs	180sh	
$(NametmfH_2)HgI_4$	122vs	122vsb	132sh

[a] s = strong; m = medium; v = very; b = broad, sh = shoulder.

assumed that the splitting of F_2 stretch is low and that the bands expected, lowering the symmetry, are included in the strong broad IR band and in the corresponding weak Raman band. In conclusion it is reasonable to assign the strong infrared and Raman bands to the F_2 and A_1 stretching vibrations respectively.

The far-IR and Raman spectra of compounds (**A**) and (**B**) together with those of the corresponding bromo- and iodo-derivatives are shown in Figs. 5–8. The vibrational stretching frequencies attributed to the $[HgX_4]^{2-}$ (X = Cl, Br, I) groups, and their most probable assignments are reported in Table V.

On the basis of the vibrational spectra a tetrahedral structure can also be assigned to the $[HgX_4]^{2-}$ (X = Br, I) anions; in fact both their IR and Raman spectra show only one strong Hg–X stretching band, in agreement with the spectra of all the tetrabromo- and tetraiodomercurate(II) anions, whose tetrahedral structures have been confirmed by X-ray investigations [12, 13].

Even though the structural results obtained for the present compounds and those already reported in the literature [5, 8, 9] suggest that distortions from the tetrahedral geometry are a common feature for $[HgX_4]^{2-}$ anions, these deviations from the ideal symmetry do not play any significant role in the vibrational spectra.

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