Preparation, Crystal Structure and Vibrational Spectra of N-benzylpiperazinium-pentahalodimercury(II) Complexes: (NbzpipzH)Hg$_2$X$_5$ (X = Cl, Br)

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The preparation of new mercury(II) compounds, (NbzpipzH)Hg$_2$X$_5$ (NbzpipzH = N-benzylpiperazinium monocation; X = Cl, Br) is reported. The determination of the structure of (NbzpipzH)Hg$_2$Cl$_5$ by three-dimensional single-crystal X-ray analysis is described. The structure contains two different mercury atoms. One of them binds covalently two chlorine atoms and two bridged chlorine atoms with long contacts. The coordination around the other mercury is tetrahedrically distorted and involves one terminal and two bridged chlorine atoms and one molecule of N-benzylpiperazinium monocation. Far-infrared and Raman spectra are interpreted on the grounds of the crystal structure of compounds suggesting a relation between the values of mercury–halogen stretching frequencies and the related bond distances.

Introduction

Our interest in the chemical behavior of the positively charged ligands derives from the fact that they may determine a wide variety of structural geometries of the metal ion, forming compounds having unusual structures. Although there are a few examples of complexes in which the ligand has a formal positive charge somewhat removed from the metal–ligand bond, these only involve the first transition metal ions [1, 2].

In this paper we report the mercury(II) halide complexes of the N-benzylpiperazinium monocation. All the synthesized compounds of the type (NbzpipzH)Hg$_2$X$_5$ (X = Cl, Br) and (NbzpipzH)HgBr$_3$ are investigated by means of far-infrared and Raman spectroscopy and for one of them, the (NbzpipzH)-

Hg$_2$Cl$_5$ complex, the crystal structure was also determined.

This work also takes on a great interest from the fact that, although some compounds of formula LHg$_2$Cl$_5$ are known [3], for this type of complexes no detailed structural data are available.

Experimental

Preparation of the Complexes

(NbzpipzH)Hg$_2$Cl$_5$: to a methanolic solution containing 0.01 mol of HgCl$_2$ maintained at 50 °C was slowly added a solution of 0.005 mol of N-benzylpiperazinium monohydrochloride. The solution was cooled slowly to room temperature. On standing for several hours colorless crystals precipitated. The compound was recrystallized from methanol. *Anal.* Calcd. for C$_{11}$H$_{17}$N$_2$Hg$_2$Cl$_5$: C, 17.47; H, 2.27; N, 3.71%. Found: C, 17.46; H, 2.44; N, 3.71%.

(NbzpipzH)Hg$_2$Br$_5$: was prepared as above starting from HgBr$_2$ and N-benzylpiperazinium monohydrobromide. *Anal.* Calcd for C$_{11}$H$_{17}$N$_2$Hg$_2$Br$_5$: C, 13.50; H, 1.75; N, 2.86%. Found: C, 13.64; H, 1.79; N, 2.86%.

(NbzpipzH)HgBr$_3$: to a methanolic solution containing 0.01 mol of (NbzpipzH)Br maintained at 50 °C a hot methanolic solution of 0.005 mol of HgBr$_2$ was slowly added. The solution was cooled slowly at room temperature. On standing for several hours colorless crystals precipitated. The compound was recrystallized from methanol. *Anal.* Calcd. for C$_{11}$H$_{17}$N$_2$HgBr$_3$: C, 21.83; H, 2.77; N, 4.54%. Found: C, 21.44; H, 2.78; N, 4.54%.

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TABLE I. Final Positional and Thermal Parameters. The e.s.d.'s are given in parentheses and refer to the last significant figure. The anisotropic temperature factors are expressed as $T = \exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg1	0.0396(4)	0.2518(6)	0.0222(7)	4.7(2)	2.7(2)	3.2(3)	1.0(2)	0.7(3)	−1.0(3)
Hg2	0.2405(4)	0.6202(6)	0.1378(7)	5.1(2)	2.5(2)	4.1(2)	−0.6(3)	1.0(4)	−0.6(3)

	x/a	y/b	z/c	B (A^2)
Cl1	0.125(2)	−0.027(3)	0.177(4)	2.5(5)
Cl2	0.253(2)	0.259(4)	0.081(4)	3.7(6)
Cl3	−0.060(2)	0.394(4)	0.135(4)	2.8(5)
Cl4	0.192(2)	0.613(4)	0.411(4)	3.7(5)
Cl5	0.321(3)	0.614(4)	−0.095(5)	5.0(5)
C1	0.535(8)	0.655(11)	0.453(14)	5.4(10)
C2	0.530(7)	0.710(12)	0.634(12)	6.4(11)
C3	0.452(8)	0.859(9)	0.666(10)	4.6(12)
C4	0.484(7)	0.719(9)	0.304(9)	3.7(9)
C5	0.406(7)	0.866(10)	0.354(11)	5.7(11)
C6	0.392(6)	0.934(10)	0.524(10)	3.5(9)
C7	0.322(7)	1.098(10)	0.555(11)	2.5(10)
C8	0.153(6)	1.259(8)	0.572(10)	2.4(9)
C9	0.064(6)	1.257(9)	0.582(10)	2.9(9)
C10	0.121(6)	0.975(10)	0.678(11)	2.9(10)
C11	0.215(4)	0.980(9)	0.629(9)	3.1(9)
N1	0.228(4)	1.087(6)	0.548(7)	3.3(7)
N2	0.050(4)	1.157(6)	0.723(7)	2.5(7)

Analyses

Nitrogen, carbon and hydrogen were analysed with a Perkin Elmer 240 Elemental Analyzer.

Structural Determination

Crystal data: white prismatic crystals $Hg_2Cl_5N_2$-$C_{11}H_{17}$; M.W. = 755.716; D_{calcd} = 2.728, D_{obs} = 2.74(1). Triclinic; a = 14.747(9) Å; b = 8.839(8) Å; c = 7.501(6) Å; α = 95.64(6)°; β = 98.57(7)°; γ = 72.32(8)° (least squares refined using the 2θ values of 25 reflections); V = 919.82 A^3. Space group $P\bar{1}$; Z = 2. The data collection was eventually carried out using a crystal of approximate dimensions 0.15 × 0.24 × 0.29 mm, on a Philips PW 1100 single crystal diffractometer using graphite mono-chromatized Mo Kα radiation (λ = 0.71069 Å) up to a sin θ/λ value of 0.53 A^{-1}. The $\omega/2\theta$ scan mode was used with scan width 1.10° and scan speed 0.05° s^{-1}. Two background counts were measured at either side of the peak and the values obtained subsequently averaged. Of the 1267 independent reflections collected, 963 were considered as observed (having $I \geqslant 3\sigma(I)$) and used in the refinement. The data were corrected for Lorentz and polarization factors. An empirical absorption correction using azimuthal ϕ scan of 4 general reflections did not improve the data and the uncorrected set was used in the last stages of the refinement. During the data collection the stability of the crystals and of the experimental

TABLE II. Selected Interatomic Distances and Angles.[a]

Bond distances (A)		Bond Angles (°)	
		Hg1–Cl2–Hg2	106.1(11)
Hg1–Cl1	2.69(2)	Cl1–Hg1–Cl2	100.0(10)
Hg1–Cl2	2.40(2)	Cl1–Hg1–Cl3	94.5(10)
Hg1–Cl3	2.40(1)	Cl2–Hg1–Cl3	136.2(8)
Hg1–N2'	2.41(5)	Cl2–Hg2–Cl4	86.4(10)
Hg2···Cl2	3.13(2)	Cl2–Hg2–Cl5	94.3(9)
Hg2–Cl4	2.28(2)	Cl2–Hg2–Cl1'	151.6(9)
Hg2–Cl5	2.24(3)	Cl4–Hg2–Cl1'	82.5(10)
Hg2···Cl1'[b]	3.04(2)	Cl5–Hg2–Cl1'	101.8(8)
(C–C)aromatic[c]	1.39(9)	Cl4–Hg2–Cl5	168.2(9)
(C–N)	1.56(10)	N2'–Hg1–Cl1	96.1(9)

[a]Numbers in parentheses are the e.s.d.'s on the last significant figure. [b]Primed atoms are related to the unprimed by the symmetry operation (x; 1 + y; z). [c]Average values.

set up were checked measuring 3 standard reflections every 90 minutes; no significant variations were detected. The structure was solved by conventional Patterson and Fourier methods and refined by full matrix and block diagonal least-squares procedures with weights chosen after Cruickshank [4]. The scattering factors and the corrections for the real part of the anomalous dispersion were obtained from reference [5]. The refinement was carried out using aniso-
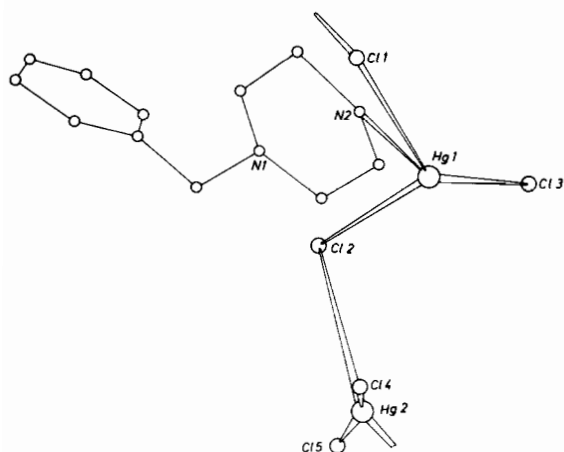
Fig. 1. A perspective view of the molecular structure of Hg$_2$-Cl$_5$N$_2$C$_{11}$H$_{17}$, showing the atoms numbering. Only the asymmetric unit is shown.

tropic thermal factors for Hg atoms and isotropic for Cl, C, N atoms; the final conventional R factor (R = $\Sigma(K|F_o| - |F_c|)/\Sigma K|F_o|$) was 0.104. The final Fourier difference map showed no significant features. The positional and thermal factors are listed in Table I (a list of observed and calculated structure factors is available on request from the authors). A list of selected bond lengths and angles is given in Table II.

Physical Measurements

The infrared spectra of KBr pellets were recorded with a Perkin Elmer 621 and the far-infrared spectra of nujol mulls with a Perkin Elmer 180 spectrophotometer. Raman spectra were recorded using solid samples on a Coderg PHO spectrophotometer equipped with an argon laser.

Results and Discussion

Molecular Structure

The unsatisfactory quality of the crystals affected to some extent the final agreement, as can be judged for example from relatively large e.s.d.'s, but without obscuring any significant geometrical information that was of interest.

A perspective view of the molecule is shown in Fig. 1. The molecule consists of tetra-coordinated Hg atoms bonded by a single bridging chlorine atom to form a chain running approximately parallel to the *a* axis. The coordination around each Hg shows pronounced distortions from the tetrahedral geometry which is a common feature in Hg(II) compounds [6]. The Hg(1)–Cl bond distances are of two different types: one being 2.69(2) Å (Hg(1)–Cl(1)) and two shorter at 2.40(1) Å (average value). These

values may be compared with an average of 2.5 Å for tetrahedrally coordinated Hg species [7]. Similar values have been found in (Me$_2$EtP)$_3$(HgCl$_2$)$_2$ [8]. An extensive collection of structural information on mercury(II) complexes has been reported in a recent review by Dean [9].

The coordination around Hg(1) is completed by the N-benzylpiperazinium monocation bonded via N(2) to the metal atom. The Hg(1)–N(2') distance of 2.41(5) Å is comparable with those reported for *cis*-dithiocyanatobis(1,10-phenanthroline)mercury(II) [10], Hg$_2$(Phen)(NO$_3$)$_2$ [11] and for Hg(en)(SCN)$_2$ [12], but it is significantly different from the value 2.60 Å found in the adduct bis(pyridine)dichloromercury(II) [13]. Moreover a Hg–N distance of 2.41(5) Å compared with the sum of the (approximate) tetrahedral radii [14] for Hg (1.48 Å) and N (0.70 Å) may indicate a reasonably strong interaction. Also the coordination around Hg(2) is characterized by two different sets of Hg–Cl distances. Two very short Hg–Cl bonds (2.26 (±0.02) Å), with a Cl–Hg–Cl angle of 168.2(9)°, may be compared with the values of 2.27 and 2.23 Å for HgCl$_2$ [9]. Two long contact distances, 3.04(2) and 3.13(2) Å, complete the tetrahedral coordination around Hg(2).

The value of 4.426(9) Å found for the distance between the two mercury atoms is considerably larger than the expected Van der Waals contacts.

The geometry of the N-benzylpiperazinium monocation does not show any particular features with average bond lengths in the expected range. The mean value for the angle in the phenyl ring is 119.2(9)° with C–C average of 1.39(9) Å. The piperazine ring is in the expected chair conformation [15, 16].

Infrared and Raman Spectra

Two types of mercury atoms, of different geometry, are present in the molecule of N-benzylpiperaziniumpentachlorodimercury(II). Hg(2) shows two covalently bonded chlorine atoms and two chlorine atoms at bond distances close to the sum of the Van der Waals radii [14]. Consequently it may be considered that a nearly linear HgCl$_2$ molecule, with a bond angle of 168°, should be present. This molecule is perturbed by the interaction of two weakly bonded chlorine atoms. Hg(1) is covalently coordinated in a highly distorted tetrahedral environment of one nitrogen and three chlorine atoms, two of which are at considerably shorter bond distances than the third.

The values of the frequencies of vibrations involving Hg–Cl bonds in mercury(II) chlorine complexes, are strictly related to the mercury–chlorine distances. Poulet and Mathieu [17] have reported that the frequency of the symmetric stretching of the HgCl$_2$ unit in a series of chloromercurates(II) decreases, as expected, with increasing Hg–Cl bond length. A similar variation was observed [3, 18] in the anti-

TABLE III. Relation between Average Hg–Cl Stretching Frequency (cm^{-1}) and Average Hg–Cl Bond Distance.

Compound	d (A) (average)	Ref.	ν(HgCl) (average)	Ref.
$HgCl_2$	2.25	(9)	345	(9)
$CsHgCl_3$	2.29	(9)	302	(15)
αNH_4HgCl_3	2.34	(9)	304	(19)
$(PyO)_2Hg_2Cl_2$	2.33	(9)	310	(20)
$K_2HgCl_4 \cdot H_2O$	2.43	(9)	286	(19)

TABLE IV. Infrared and Raman Mercury–Halogen Stretching Frequencies (cm^{-1}).

Compound	d^a (A)	ν(Hg–Cl) i.r.	ν(Hg–Cl) Raman	Assignment
Hg_2Cl_5L	2.26	363s	363vw	$\nu(HgCl_2)^b$
	2.26		318s	
	2.40	280m	280sh	$\nu(HgCl_2)$
	2.40		266s	
	2.69	178m		$\nu(HgCl)$
Hg_2Br_5L		254s	251vw	$\nu(HgBr_2)^b$
			198s	
		194m		$\nu(HgBr)$
		174m	171s	

^{a}Hg–Cl average bond distance. ^{b}Nearly linear HgX_2 unit; s, strong; m, medium; vw, very weak; sh, shoulder.

Fig.2. Infrared spectra of nujol mull samples: (NbzpipzH)-Hg_2Cl_5 (———), (NbzpipzH)Hg_2Br_5 (------), [NbzpipzH] Cl (–·–·–), [NbzpipzH] Br (······).

symmetric stretching mode. In the studied compound we must consider that the vibrators corresponding to very different bond lengths are separated by heavy Hg atoms and joined by a long bond. As a consequence, the coupling between Hg–Cl stretching vibrations, which corresponds to very different bond lengths, may be considered negligible. Therefore one can independently treat the Hg–Cl stretching vibrations of Hg(2) from those of Hg(1).

The infrared and Raman ν(Hg–Cl) stretching vibrations that appear at higher frequency should be those of the nearly linear $HgCl_2$ structural unit. For a strictly linear $HgCl_2$ geometry, one should expect only a symmetric Raman active $\nu_1(\Sigma_g^+)$ stretching vibration, and only one antisymmetric, infrared active, $\nu_3(\Sigma_u^+)$ stretching vibration.

For a small distortion from linearity, as in the compound studied, the antisymmetric mercury–chlorine stretching mode should be very strong in the infrared but weak in the Raman spectrum. On the other hand, the symmetric mode will be at a lower frequency and show a reversed intensity in the i.r. and Raman spectra. Taking into account the values reported in the literature one can expect to find frequencies of mercury–chlorine stretching vibrations of the nearly linear $HgCl_2$ structural unit. In Table III we have reported the average values of symmetric and antisymmetric stretching vibrations of several $HgCl_2$ units together with the average values of Hg–Cl bond distances [19, 20]. Assuming an almost linear $HgCl_2$ structural unit, it seems possible to assign the strong infrared band at 363 cm^{-1} and the strong Raman band at 318 cm^{-1} to the anti-symmetric and symmetric stretching vibrations respectively. In fact these frequencies are consistent with an average mercury–chlorine bond distance of 2.26 Å. The Hg(1) atom of the compound reported here shows two short and one long Hg–Cl bonds in a tetrahedral configuration. One expects two coincident infrared and Raman bands corresponding to the stretching vibrations of the two shorter Hg–Cl bonds, and one infrared and Raman active band corresponding to the stretching vibration of the longer Hg–Cl bond. These two different types of covalent distances

may be related respectively to the ν(Hg–Cl) frequencies that occur in the 280–270 cm^{-1} and the 180–170 cm^{-1} regions of infrared and Raman spectra. In fact these values are in agreement with those reported [21] for $(PPh_3HgCl_2)_2$ which has Hg–Cl bond distances [22] similar to those found in our compound. Therefore the most probable assignments of Hg–Cl stretching vibrations of Hg_2Cl_5(NbzpipzH) are those reported in Table IV.

The 253 cm^{-1} infrared frequency (see Fig. 2) could arise from the Hg–N stretching vibration, which, according to reference [23], should appear where we find the stretching vibrations assigned to the two shorter mercury–chlorine bonds of the tetrahedral mercury atom.

The infrared Raman spectra of (NbzpipzH)Hg_2Br_5 are reported in Figs. 2 and 3.

From the analysis of these spectra we conclude that this compound has the same geometrical structure of the corresponding chloro derivative.
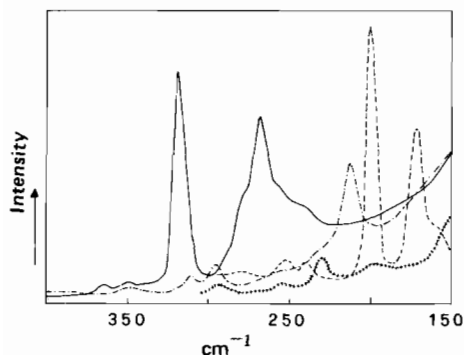
Fig. 3. Raman spectra of solid samples: (NbzpipzH)Hg$_2$Cl$_5$ (———), (NbzpipzH)Hg$_2$Br$_5$ (------), [NbzpipzH]Cl (—·—·—), [NbzpipzH]Br (·······).
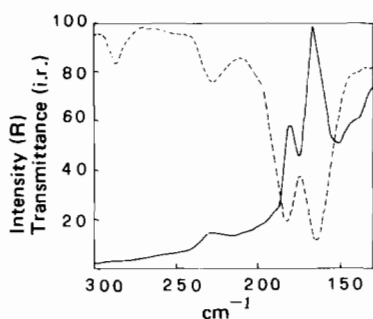

Fig. 4. Vibrational spectra of (NbzpipzH)HgBr$_3$: ——— Raman spectrum of solid sample. ------ Infrared spectrum of nujol mull sample.

The assignments of vibrational Hg–Br stretching frequencies are also listed in Table IV.

The infrared spectra of both compounds (KBr pellets) show in the high frequency region two bands at 3215 and 2730 cm^{-1} which, according to the literature [24, 25], were assigned to ν(NH) and ν(NH$^+$) stretching vibrations respectively. The ν(NH) stretching frequency is shifted to a lower value compared to that of the free ligand [16, 26], as expected for the coordination of amine ligand.

As described in the experimental section HgBr$_3$-(NbzpipzH) was obtained by the reaction of HgBr$_2$ and N-benzylpiperazinium monohydrobromide salt in molar ratio 1:2. In this compound the amine ligand is coordinated to the metal atom, as indicated by the infrared spectrum, which shows the lowering of the ν(NH) stretching frequency compared to that of the free amine [16, 26]. From the far-i.r. and Raman spectra (Fig. 4) we may regard this compound as having a distorted tetrahedral structure. In fact infrared and Raman spectra show two coincident bands corresponding to symmetric and antisymmetric ν(Hg–Br) stretching vibrations of a compound having C$_{3v}$ symmetry. The frequencies of these bands are

in the same ν(Hg–Br) region as the tetrahedral mercury atom of (NbzpipzH)Hg$_2$Br$_5$. Therefore it may be proposed that the reaction between HgBr$_2$ and N-benzylpiperazinium monohydrobromide salt proceeds in two following stages:

$$2HgBr_2 + [NbzpipzH]\,Br = Hg_2Br_5(NbzpipzH)$$

$$H_2Br_5(NbzpipzH) + [NbzpipzH]\,Br =$$
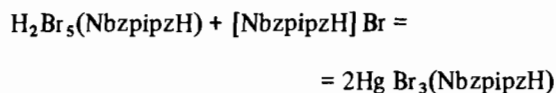
$$= 2Hg\,Br_3(NbzpipzH)$$

In the latter, the monohydrobromide salt reacts breaking the bridged bonds that are present in Hg$_2$-Br$_5$(NbzpipzH) giving HgBr$_3$(NbzpipzH). The same mononuclear chloroderivative was not obtained even in the presence of an excess of N-benzylpiperazinium monohydrochloride. We suggest that this feature should be attributed to the stronger bridged bonds formed by chlorine atoms.

Acknowledgment

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