

## THE CRYSTAL AND MOLECULAR STRUCTURE OF *N*-[2-(CHLOROMERCURI)ETHYL]DIETHYLAMINE

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### SUMMARY

The crystal structure of *N*-[2-(chloromercuri)ethyl]diethylamine,  $(\text{CH}_3\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{HgCl}$ , has been determined by X-ray diffraction. The crystals are monoclinic, of space group  $P2_1/n$ ; cell dimensions,  $a = 8.509(4)\text{ \AA}$ ,  $b = 17.052(7)\text{ \AA}$ ,  $c = 6.306(2)\text{ \AA}$ ,  $\beta = 95.82(15)^\circ$ . There are 4 molecules per unit cell. With refinement to give  $R = 0.056$ , the interatomic distances and angles are C-Hg,  $2.13(3)\text{ \AA}$ ; Hg-Cl,  $2.36(1)\text{ \AA}$ ; C-Hg-Cl =  $167.1(8)^\circ$ . The intermolecular N-Hg distance of  $2.77(2)\text{ \AA}$  is less than the Van der Waals contact distance.

### INTRODUCTION

The tendency for amines and other nucleophiles to coordinate with mercuric salts,  $\text{HgX}_2$ , (including those which have organic groups bonded to mercury via non-carbon atoms such as S, N and O) is well known<sup>1</sup>. On the other hand, the tendency of amines to coordinate with mercury in diorganomercury compounds,  $\text{R}_2\text{Hg}$ , is quite small. For an intermediate group of compounds, the organomercuric halides or pseudohalides,  $\text{RHgX}$ , there are almost no structural data to reveal either the tendency for nitrogen coordination to mercury or the structural effects of such coordination. To examine such an interaction the X-ray structure determination of *N*-[2-(chloromercuri)ethyl]diethylamine was undertaken.

### EXPERIMENTAL

The *N*-[2-(chloromercuri)ethyl]diethylamine was synthesized via the aminomercuration reaction<sup>2</sup> in which mercuric chloride and diethylamine are added to ethylene. Multiple recrystallizations, alternately from anhydrous ethanol and ether, yielded white crystals, m.p.  $47-48^\circ$ . (Found\*: C, 21.43; H, 4.22; Cl, 10.49; Hg, 59.75; N, 4.19.  $\text{C}_6\text{H}_{14}\text{ClHgN}$  calcd.: C, 21.43; H, 4.20; Cl, 10.54; Hg, 59.66; N, 4.17%.)

The crystals are susceptible to radiation damage which is strongly wavelength-dependent. When  $\text{Cu-K}_\alpha$  radiation was used the crystals were converted into a non-crystalline substance after 10-15 h of exposure. Using  $\text{Mo-K}_\alpha$  radiation an exposure

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of 70 h did not affect the intensity of moderate reflections, but increased the intensity of very strong reflections by diminishing primary extinction.

The symmetry of the crystal and its unit cell dimensions were determined using a Weissenberg camera and a Picker FACS diffractometer. During all these measurements crystals were kept in thin-walled glass capillaries because of their tendency to decompose in air. This circumstance caused high background in diffraction experiments which rendered it difficult to measure weak intensity reflections. The crystals are monoclinic, of space group  $P2_1/n$ . The unit cell dimensions,  $a = 8.509(4)$  Å,  $b = 17.052(7)$  Å,  $c = 6.306(2)$  Å,  $\beta = 95.82(15)^\circ$ , (standard errors given in parentheses) were determined by the least squares method from the  $2\theta$ ,  $\phi$  and  $\chi$  angles measured for 14 high angle reflections ( $2\theta$ ) on the diffractometer. The unit cell, containing 4 molecules, has a volume of  $910.40$  Å<sup>3</sup> and a calculated density of  $2.41$  g/cm<sup>3</sup>. The density of the crystal was not measured; the number of molecules per unit cell—determined from the symmetry, the volume of the unit cell and features of the Patterson functions—was confirmed by the success of the analysis.

Intensity measurement for the structure determination was performed on a 4-circle automatic diffractometer (Picker FACS) with filtered Mo- $K_\alpha$  radiation ( $2\theta$  scan, linear absorption coefficient =  $71.15$  cm<sup>-1</sup>). Altogether 2300 reflections were measured in a half of reciprocal space using a fragment of approximately cubic shape (maximum dimension =  $0.05$  mm, minimum dimension =  $0.035$  mm, maximum  $\mu \cdot \rho \cdot t = 0.36$ , minimum  $\mu \cdot \rho \cdot t = 0.26$ ); this led finally to 780 independent reflections, 586 of which had integrated intensities larger than their e.s.d. (determined in the usual way from the number of counts recorded for the peak and both background readings).

Measured intensities were corrected for Lorentz and polarization factors in a standard way. The irregular shape of the crystal and its instability made the absorption correction unacceptably difficult; therefore it was not applied. This was later justified by the progress of the analysis. The internal consistency of the intensity scale was maintained by using two reflections of moderate intensity as standards (reflections 4 0 0 and 0 10 0 were measured after each group of 20 reflections).

The initial positions of Hg atoms were determined from 2 projections of the Patterson function. Most calculations were performed using the system of crystallographic programs from University of Maryland (X-Ray 70). The position of the Cl atom was easily established from 3-D Fourier maps (using phases based on Hg positions only). The approximate positions of carbon and nitrogen atoms were obtained from difference Fourier maps (using phases based on Hg and Cl positions).

Approximate coordinates of all atoms were further refined using a least squares method. A weighting scheme with weights inversely proportional to the squares of the standard deviations of the structure factors for reflections with structure factors smaller than 60 (on absolute scale) and with weights inversely proportional to the squares of the structure factors for reflections with structure factors above 60, was found satisfactory. The refinement proceeded fairly quickly; after a few cycles of least squares calculations with individual, isotropic temperature factors, the  $R$  factor dropped to 0.11, and after two additional cycles of least squares calculations (full matrix) with anisotropic temperature factors for Hg and Cl atoms the  $R$  factor dropped to 0.056 and the maximum shift in the error ratio became 0.3. The weighting scheme was checked by evaluating the dependence of group averages of  $w(F_o - F_c)^2$

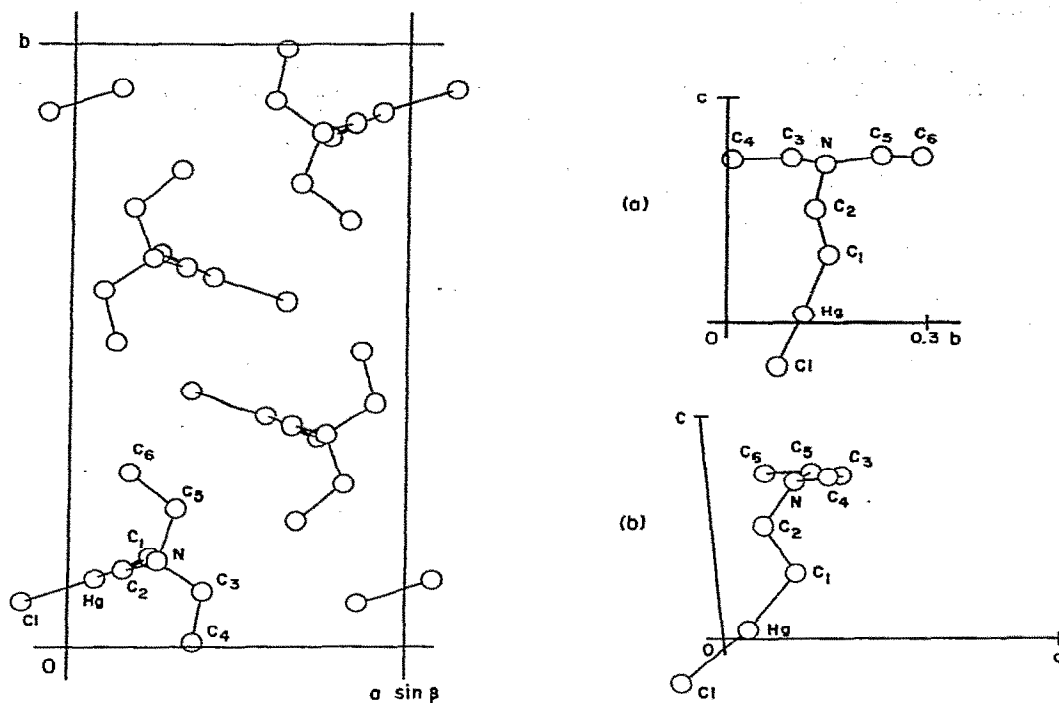


Fig. 1. Projection of the unit cell of the *N*-[2-(chloromercuri)ethyl]diethylamine crystal along the *C* axis.

Fig. 2. Projections of one molecule of *N*-[2-(chloromercuri)ethyl]diethylamine. (a) Along the *A* axis. (b) Along the *B* axis.

vs.  $F_o$  and the overall reliability of the model by calculating the difference map. No attempt was made to locate hydrogen atoms, nor to include their contributions in the structure factor calculations\*. Projections of the structure are shown in Figs. 1 and 2.

## RESULTS

Atomic coordinates (fractional) for all atoms considered in this study and isotropic temperature coefficients  $B$  [the temperature factor has the form  $\exp(-B \cdot \sin^2 \theta / \lambda^2)$ ] for carbon and nitrogen atoms are given in Table 1. Anisotropic temperature coefficients  $B_{ij}$  for Hg and Cl atoms are also listed in Table 1 [ $B_{ij}$  is defined as  $4\beta_{ij} / (a_i^* \cdot a_j^*)$ , where  $\beta_{ij}$  is the coefficient used in the ordinary anisotropic temperature factor  $\exp(-\sum \beta_{ij} \cdot h_i \cdot h_j)$  and  $a_i^*$  is the edge of the reciprocal cell].

Bond distances and angles are summarized in Table 2 and the shortest intermolecular contacts (below 3.5 Å) in Table 3.

\* The table of structure factors has been deposited as NAPS Document No. 1974, with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 866 Third Avenue, New York, New York 10022. A copy may be secured by citing the document number and by remitting \$2.00 for a microfiche or \$5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

TABLE 1

FRACTIONAL ATOMIC COORDINATES ( $X$ ,  $Y$ ,  $Z$ ), ISOTROPIC TEMPERATURE COEFFICIENTS ( $B$ ), AND ANISOTROPIC TEMPERATURE COEFFICIENTS ( $B_{ij}$ )<sup>a</sup>

Atom	$X$	$Y$	$Z$	$B$		
Hg	0.0797(1) <sup>a</sup>	0.1147(1)	0.411(2)			
Cl	0.3609(10)	0.4241(6)	0.3047(13)			
C(1)	0.238(3)	0.152(2)	0.304(5)	2.6(6) Å <sup>2</sup>		
C(2)	0.158(3)	0.131(2)	0.511(5)	2.7(6)		
C(3)	0.403(3)	0.094(2)	0.737(5)	3.1(7)		
C(4)	0.366(4)	0.007(2)	0.729(6)	4.5(8)		
C(5)	0.317(3)	0.229(2)	0.745(5)	3.0(7)		
C(6)	0.176(4)	0.289(2)	0.742(6)	4.6(8)		
N	0.261(2)	0.146(1)	0.710(3)	1.9(4)		
	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Hg	4.46(7)	2.56(7)	1.75(7)	0.04(6)	0.13(4)	-0.18(6)
Cl	4.6(4)	5.2(5)	2.7(4)	1.2(4)	-0.4(3)	0.4(4)

<sup>a</sup> Standard errors shown in parentheses; temperature coefficients in Å<sup>2</sup>.

TABLE 2

BOND LENGTHS AND ANGLES

Bond	Length (Å)	Atoms	Angle (°)
Cl-Hg	2.36(1)	Cl-Hg-C(1)	167.1(8)
Hg-C(1)	2.12(3)	Hg-C(1)-C(2)	107(2)
C(1)-C(2)	1.57(4)	C(1)-C(2)-N	114(2)
C(2)-N	1.48(3)	C(2)-N-C(3)	113(2)
N-C(3)	1.50(4)	C(2)-N-C(5)	116(2)
N-C(5)	1.50(4)	C(3)-N-C(5)	108(2)
C(3)-C(4)	1.52(5)	N-C(3)-C(4)	114(2)
C(5)-C(6)	1.58(5)	N-C(5)-C(6)	113(2)

TABLE 3

INTERMOLECULAR CONTACTS LESS THAN 3.5 Å

Contact	Distance (Å)
N...Hg <sup>a</sup>	2.77(2)
C(2)...Hg <sup>a</sup>	3.49(3)
C(5)...Hg <sup>a</sup>	3.42(1)
Cl...Hg <sup>b</sup>	3.42(1)

<sup>a</sup> Between molecules separated by the  $c$  translation. <sup>b</sup> Between molecules related by the inversion center.

The conformation of the [(chloromercuri)ethyl]amine group (Cl-Hg-C<sub>1</sub>-C<sub>2</sub>-N) is approximately planar. The standard deviation of the atoms from the best fit plane as determined by the least squares method is 0.05 Å. Similarly, the group of five

atoms consisting of the nitrogen atom and the carbon atoms in both ethyl groups is also approximately planar (standard deviation = 0.06 Å; maximum deviation = 0.09 Å for the N atom). The angle between both planes is 83°, the angle between the axis of the [(chloromercuri)ethyl]amine group and the plane of both ethyl groups is 124°.

## DISCUSSION

The values obtained in this study for the C–Hg and Hg–Cl bond lengths are comparable to those in the recent literature, as listed in Table 4. The distance 2.77(2) Å between Hg and N in adjacent molecules (related by the *c* translation) is less than the sum of the Van der Waals radii (3.0 Å, using 1.5 for Hg<sup>1</sup> and 1.5 for N<sup>9</sup>) indicating some intermolecular coordination of nitrogen to mercury. Similar coordination was observed in Hg(CN)<sub>2</sub> crystals, where the intermolecular Hg–N distance was found to be 2.74 Å<sup>8</sup>. It is interesting that in the case of CH<sub>3</sub>HgCN, where a methyl ligand replaces one of the cyano groups on mercury, the Hg–N intermolecular distance is not less than 3.15 Å<sup>5</sup>. Evidently the introduction of the alkyl group decreases the positive charge on Hg, and lessens its ability to interact with the weakly coordinating cyano

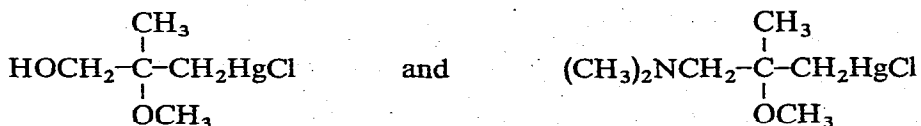
TABLE 4

## COMPARISONS WITH RECENT DATA

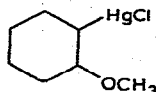
Atoms	This study	Literature value	Compound	Ref.
C–Hg	2.12(3) Å	2.06(2) Å	CH <sub>3</sub> HgCl (gas)	3
		2.07(2)	CH <sub>3</sub> HgBr (gas)	3
		2.08(2)	( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Hg	4
		2.08(2)	CH <sub>3</sub> –HgCN	5
		2.09	CH <sub>3</sub> HgI (gas)	6
Hg–Cl	2.36(1) Å	2.282(5) Å	CH <sub>3</sub> HgCl (gas)	3
		2.37	<i>cis</i> -C <sub>6</sub> H <sub>5</sub> COCH=CHHgCl	7
C–Hg–Cl	167.1(8)°	180°	CH <sub>3</sub> HgCl (gas)	3
		180(2)	CH <sub>3</sub> HgCN	5
		173	<i>cis</i> -C <sub>6</sub> H <sub>5</sub> COCH=CHHgCl	7
N····Hg	2.77(2) Å	2.742(3) Å	NCHgCN	8
		3.15(1)	CH <sub>3</sub> HgCN	5
Cl····Hg	3.42(1) Å	3.24 Å	<i>cis</i> -C <sub>6</sub> H <sub>5</sub> COCH=CHHgCl	7

nitrogen. By comparison in *N*-[2-(chloromercuri)ethyl]diethylamine, the greater polarity of the Hg–Cl bond and the greater coordinating ability of the aliphatic nitrogen favor Hg–N interaction.

The absence of intramolecular Hg–N coordination in (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>HgCl is expected on the basis of typical bond angles and lengths. The failure to observe such coordination is in accord with observations from NMR studies in the compounds:



Although strong coordination was found between the  $\gamma$  nitrogen and oxygen substituents and mercury, no evidence was obtained for coordination between the  $\beta$ -oxygen substituent and mercury<sup>10</sup>. In the only crystal structure reported for a  $\beta$ -heteroatom-substituted alkylmercuric halide, *viz.*:



the intramolecular O–Hg distances were 3.06 Å and greater<sup>11</sup>, indicating no O–Hg coordination. In that system one would expect ring strain and conformational effects to oppose the O–Hg coordination; whereas such inhibiting effects would not be present in the acyclic system studied here.

The value of 167(1)° found in this study for the C–Hg–Cl angle differs from the 180° angle typically reported for alkylmercuric salts<sup>3,5,11</sup>. Presumably this is due to the intermolecular Hg–N coordination which results in non-bonded atom repulsions and perhaps an alteration of the hybridization at mercury. The 173° C–Hg–Cl angle found by Kuz'mina, *et al.*<sup>7</sup>, may represent another instance of distortion by coordination to the mercury, since the authors suggest that there is intermolecular Cl–Hg coordination, and possible weak Hg–O intramolecular coordination.

The structures of additional nitrogen-containing alkylmercuric halides are being determined in these laboratories to further explore inter- and intramolecular N–Hg coordination.

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