

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, SOUTHERN UNIVERSITY IN NEW ORLEANS, NEW ORLEANS, LOUISIANA 70126, AND LOUISIANA STATE UNIVERSITY IN NEW ORLEANS, NEW ORLEANS, LOUISIANA 70122

## The Crystal and Molecular Structure of Bis(2-imidazolidinone)mercury(II) Chloride

BY R. J. MAJESTE<sup>1a</sup> AND L. M. TREFONAS<sup>\*1b</sup>

Received October 18, 1971

The crystal and molecular structure of  $\text{HgCl}_2 \cdot 2(\text{C}_3\text{H}_6\text{N}_2\text{O})$  has been determined by single-crystal X-ray diffraction techniques using a GE 490 diffractometer system. The compound crystallizes in space group  $P\bar{1}$  with one formula weight in a unit cell of dimensions  $a = 5.098$  (1) Å,  $b = 8.150$  (1) Å,  $c = 10.659$  (1) Å,  $\alpha = 135.75$  (1)°,  $\beta = 92.14$  (1)°, and  $\gamma = 102.23$  (1)°. The structure was solved by means of a three-dimensional Patterson function and refined by block-diagonal least squares to a final  $R = 0.027$  for 736 statistically significant reflections. The crystal is composed of infinite chains of the complex with  $\text{HgCl}_2$  molecules as the basic units tied together by ethyleneurea ligands. The mercury has slightly distorted octahedral coordination and each ethyleneurea molecule is distorted asymmetrically due to bonding with two mercury atoms, one through the oxygen and the other through a nitrogen.

## Introduction

Along with the growing alarm over mercury contamination of our waters has come increased research into the mechanism by which mercury interferes with normal body functions.<sup>2,3</sup> It is often difficult to obtain information about bonding in such metal complexes with enzymes or proteins because of their large size. Consequently, the structures of model compounds are often used to aid in these studies.<sup>4</sup> In this study, in order to observe probable interactions of mercury with the amide linkages, urea complexes were chosen as representative models.

The ethyleneurea-mercury complex is of further interest since it affords an easy means of testing a hypothesis linking spectral information to structural details. In the literature it has been postulated that, for amide type ligands, the nature of the metal to ligand bond can be determined from a single spectral shift.<sup>5,6</sup> If the carbonyl absorption band shifts to a lower frequency than that of the free amide, a metal to oxygen bond is presumed, while a shift to higher frequency would indicate a metal to nitrogen bond. Recently, however, the validity of this method has been questioned.<sup>7</sup> This mercury-ethyleneurea complex (Mull and KBr disks) shows a strong shift of the carbonyl frequency from the  $1660 \text{ cm}^{-1}$  found in ethyleneurea itself to  $1709 \text{ cm}^{-1}$ , implying a metal to nitrogen bond as the predicted mode of complexation.

## Experimental Section

A sample of the compound was furnished to us by R. J. Berni of Southern Regional Research Laboratory, Department of Agriculture, and recrystallized from ethanol. A single crystal with dimensions  $0.11 \times 0.12 \times 0.15 \text{ mm}$  was mounted on a General Electric XRD-5 diffractometer with the (1, 3, 4) axis coincident with the  $\phi$  axis. The reciprocal lattice showed neither systematic absences nor evidence of a mirror plane, limiting the crystal to a triclinic system in space group  $P1$  or  $P\bar{1}$ . Lattice constants were determined by a least-squares fit of 30 carefully measured  $2\theta$  values of the  $\text{Cu K}\alpha_1$  and  $\text{Cu K}\alpha_2$  doublet for  $2\theta > 70^\circ$  under fine conditions ( $1^\circ$  takeoff angle and  $0.05^\circ$  slit). The

resultant lattice constants and their estimated standard deviations (esd) are  $a = 5.098$  (1) Å,  $b = 8.150$  (1) Å,  $c = 10.659$  (1) Å,  $\alpha = 135.75$  (1)°,  $\beta = 92.14$  (1)°, and  $\gamma = 102.23$  (1)°. The calculated density of  $2.51 \text{ g/cm}^3$  for one molecule per unit cell agrees well with the experimental density of  $2.53 \text{ g/cm}^3$  measured by flotation methods.

Intensity data were collected on a General Electric XRD-490 fully automated diffractometer by the stationary-crystal, stationary-counter method using balanced zirconium and yttrium filters and Mo  $\text{K}\alpha$  radiation. A total of 796 reflections were measured to a  $2\theta$  maximum of  $50^\circ$  ( $d = 0.841$  Å). Using the criterion  $[I_{Zr} - 2\sigma(I_{Zr})] - [I_Y - 2\sigma(I_Y)] > 100$  ( $\sigma$  based entirely on counting statistics), a total of 735 (92%) reflections were considered observed.<sup>8</sup> The intensities were corrected for Lorentz-polarization effects in the usual manner. Normalized transmission factors ranged from 1.00 to 1.33 and so an absorption correction was made as a function of the polar angle  $\phi$  (linear absorption coefficient  $\mu = 139.8 \text{ cm}^{-1}$  for Mo radiation).

## Structure Determination

A three-dimensional Patterson function was used to find all of the nonhydrogen atoms. Since the unique peaks of suitable height found on the map represented only half of the mercury to ligand vectors in one empirical formula, the space group was assumed to be  $P\bar{1}$  with the mercury fixed at the origin. The structure was refined isotropically by block-diagonal least squares<sup>9</sup> to a value of  $R = 0.16$ . The isotropic temperature factors were then converted to anisotropic temperature factors and the structure was further refined to  $R = 0.04$ .

A difference electron density map was calculated in an attempt to locate the six unique hydrogens. This map contained only eight peaks with electron densities greater than  $0.5 \text{ e}/\text{Å}^3$ . Of these peaks, one was less than  $0.01$  Å from the Hg, one was less than  $0.20$  Å from the Cl, and the other six were used as the initial hydrogen coordinates in subsequent refinements. In these refinements all nonhydrogen atoms had anisotropic temperature factors while the hydrogens were initially assigned isotropic temperature factors of  $3.0 \text{ Å}^2$ . All parameters were varied with the exception of the Hg coordinates and the refinement continued until the shifts were less than one-tenth the estimated standard deviation of the respective parameters. The final value of the reliability index was  $R = 0.027$  using unit weights in the refinement.

## Results and Discussion

Table I lists the final coordinates and temperature factors together with their estimated standard deviations.

(8) A listing of the values of the observed and calculated structure factors has been deposited as Document No. 1747 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington, 25, D. C. 20540. A copy may be secured by citing the document number and by remitting \$5.00 for photoprints or \$2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(9) Scattering factors for all nonhydrogen atoms are from D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965), and those for hydrogen are from J. Stewart, R. Davidson, and A. Simpson, *J. Chem. Phys.*, **48**, 3175 (1965).

(1) (a) Southern University in New Orleans. (b) Louisiana State University in New Orleans.

(2) (a) N. Platonow, *Occup. Health Rev.*, **20**, 9 (1968); (b) J. W. Daniel and J. C. Gage, *Biochem. J.*, **111**, 20 (1969).

(3) M. A. Verity and W. J. Brown, *Amer. J. Pathol.*, **61**, 57 (1970).

(4) J. A. Carrabine and M. Sundaralingam, *Biochemistry*, **10**, 292 (1971).

(5) J. A. Costamaga and R. Levitus, *J. Inorg. Nucl. Chem.*, **28**, 2685 (1966).

(6) S. K. Madan and H. H. Denk, *ibid.*, **27**, 1049 (1965).

(7) J. N. Brown, A. G. Pierce, Jr., and L. M. Trefonas, *Inorg. Chem.*, **11**, 1830 (1972).

TABLE I  
 FRACTIONAL COORDINATES AND THERMAL PARAMETERS<sup>a</sup>

Atom	X	Y	Z	$\beta_{11}$ or $B$ , Å <sup>2</sup>	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Hg	0.0000 (0)	0.0000 (0)	0.0000 (0)	710 (3)	238 (2)	165 (1)	249 (2)	216 (2)	143 (1)
Cl	-0.0116 (7)	0.3891 (4)	0.2674 (4)	922 (20)	265 (8)	215 (6)	297 (11)	295 (9)	166 (6)
Ox	0.3748 (15)	0.2328 (12)	-0.0407 (10)	625 (42)	359 (26)	320 (20)	299 (28)	308 (24)	241 (20)
C1	0.5231 (19)	0.1543 (16)	-0.1503 (13)	378 (49)	269 (32)	192 (22)	156 (32)	99 (27)	137 (23)
N1	0.6467 (17)	0.2605 (14)	-0.1946 (12)	603 (49)	332 (30)	251 (21)	277 (32)	229 (27)	221 (22)
N2	0.5876 (17)	-0.0582 (14)	-0.2419 (12)	562 (49)	288 (29)	290 (22)	232 (31)	244 (27)	213 (23)
C2	0.7115 (21)	-0.1210 (17)	-0.3883 (13)	495 (55)	324 (36)	163 (21)	236 (36)	118 (28)	136 (24)
C3	0.8151 (22)	0.1283 (18)	-0.3195 (15)	563 (60)	398 (40)	235 (25)	283 (40)	202 (32)	226 (28)
H1	0.9980 (55)	0.2128 (36)	-0.2572 (04)	2.1 (0)					
H2	0.8004 (71)	0.1194 (53)	-0.4323 (17)	3.5 (0)					
H3	0.8644 (76)	-0.1746 (58)	-0.3861 (20)	3.8 (0)					
H4	0.5843 (80)	-0.2430 (62)	-0.5112 (23)	4.0 (0)					
H5	0.4717 (84)	-0.1597 (62)	-0.2687 (23)	4.0 (0)					
H6	0.6559 (89)	0.3947 (69)	-0.1410 (28)	4.5 (0)					

<sup>a</sup> Anisotropic thermal parameters  $\times 10^4$ ; estimated standard deviations in parentheses refer to last decimal place. Anisotropic temperature factors of the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . Hydrogen isotropic temperature factors of the form  $\exp[-(\beta_{11}(\sin^2 \theta)/\lambda)]$ .

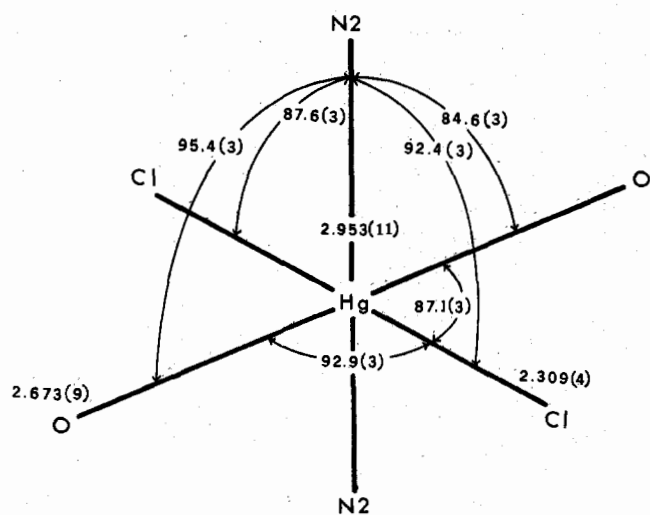


Figure 1.—Schematic drawing of the coordination sphere about the mercury.

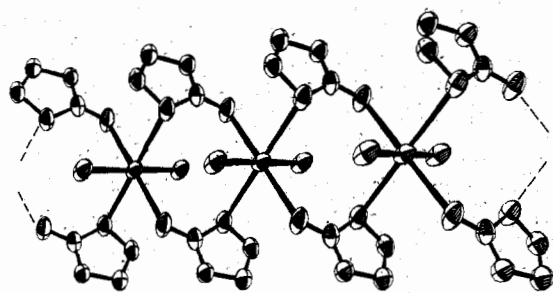


Figure 2.—ORTEP diagram of the molecular chain structure.

tions. The nonhydrogen atoms all have anisotropic temperature factors and the hydrogen atoms have isotropic temperature factors.

The slightly distorted octahedral coordination of the mercury is shown in Figure 1. The Hg-Cl distance of  $2.309 \pm 0.004$  Å is close to that of 2.25 Å found in HgCl<sub>2</sub> itself. The Hg-O distance of  $2.67 \pm 0.01$  Å and the Hg-N distance of  $2.95 \pm 0.01$  Å seem excessively long for normal bonds even to a mercury atom. However, the addition of ligands to increase coordination number, forming two short and four long

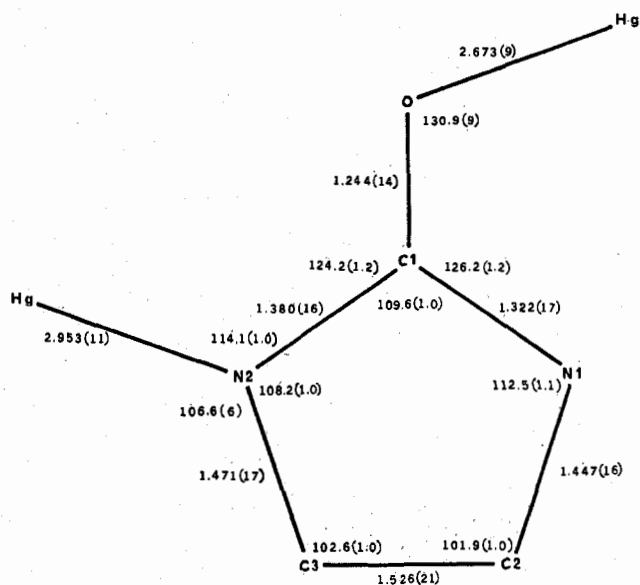


Figure 3.—Schematic drawing of the bond distances and angles within an ethyleneurea group.

bonds, is typical in mercury complexes.<sup>10</sup> It has also been established by Grdenic that mercury has an effective van der Waals radius of 1.73 Å. Using the van der Waals radii for oxygen and nitrogen of 1.40 and 1.71 Å, respectively, it is clear that the observed lengths correspond to moderate to strong mercury-ligand bonds.

The crystal is composed of infinite chains of the complex, as shown in Figure 2, with no close contact distances between atoms on different strands. The basic unit of the chain is the HgCl<sub>2</sub> molecule. These units are then bridged through the ethyleneurea ligands. In most of the mercury chloride chain complexes studied before, the bridging was found to occur through chlorine atoms.<sup>4,11,12</sup> One HgCl<sub>2</sub> unit, having an average Hg-Cl distance of 2.29 Å, would be tied to two other HgCl units by Cl-Hg distances averaging 3.07 Å. In this structure, however, each HgCl<sub>2</sub> unit is tied to the next by two ethyleneurea molecules. The first mercury is bonded to an oxygen in one ethyleneurea and to a

(10) D. Grdenic, *Quart. Rev., Chem. Soc.*, **19**, 303 (1965).

(11) F. Aubry and H. Pandrand, *C. R. Acad. Sci.*, **260**, 6613 (1965).

(12) A. McPhail and G. Sim, *Chem. Commun.*, 21 (1966).

nitrogen in the other. The ethyleneurea with the Hg-O bond in turn bonds to the second mercury through one of its nitrogen atoms, while the ethyleneurea, with the Hg-N bond to the first mercury, bonds through its oxygen to the second. This pattern is continued down the length of the chain. It is interesting to note that the HgCl<sub>2</sub> unit can cause such an ordering of amide-containing molecules when one considers that mercury taken into the body, even in the form of methylmercury salts, is converted to inorganic mercury.<sup>2b, 13</sup>

The ethyleneurea groups are distorted asymmetrically as shown in Figure 3, due to bonding with two mercury atoms. The average nitrogen to carbonyl carbon distance in ethyleneurea is 1.34 Å.<sup>7</sup> In this structure this carbon to nitrogen distance is lengthened when the nitrogen is in turn bonded to a mercury (C1-N2 = 1.38 ± 0.01 Å) while the other carbon to nitrogen distance not involving coordination to the mercury (N1-C1 = 1.32 ± 0.02 Å) is significantly shorter than this average. This is most easily rationalized by assuming that the electron pair on the mercury-coordinated nitrogen is involved in the coordination decreasing the electronic delocalization on that nitrogen whereas the uncoordinated nitrogen

attempts to delocalize further its nonbonding pair. The other distances and angles compare well with those found in urea and ethyleneurea.<sup>7, 14</sup>

The shift in the carbonyl stretching frequency in this compound would imply Hg-N coordination exclusively, in terms of the aforementioned hypothesis. However, the coordination occurs through both the oxygen and the nitrogen with the Hg-O distance (2.67 ± 0.01 Å) shorter than the Hg-N distance (2.95 ± 0.01 Å). It is thus obvious that, in this case at least, the assignment is even qualitatively incorrect and that the reliance on a single spectral band shift as a structure indicator is inadequate to describe even a moderately complex system. Additional studies are now under way to test further the validity of this criterion in cases where the coordination involves only one type of ligand and in which the spectral shifts are of such magnitude that the prediction must stand on its own merits.

**Acknowledgments.**—The authors wish to express their gratitude to the National Science Foundation (Grant GU-2632) for financial assistance to support this study, for a summer fellowship for R. M. (Grant GY 8528), and for a Petroleum Research Fund starter grant (No. 2496-G2) for R. M. Thanks are also extended to the computation center at Louisiana State University in New Orleans.

(13) T. Norseth and T. W. Clarkson, *Biochem. Pharmacol.*, **19**, 2775 (1970).

(14) A. Caron and J. Donohue, *Acta Crystallogr., Sect. B*, **25**, 404 (1969).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LOUISIANA STATE UNIVERSITY IN NEW ORLEANS, NEW ORLEANS, LOUISIANA 70122

## Crystal and Molecular Structure of the Dimer Complex $\mu$ -Bis[2(1H)-tetrahydropyrimidinone]-octakis[2(1H)-tetrahydropyrimidinone]-dicobalt(II) Perchlorate

BY M. E. BROWN, J. N. BROWN, AND L. M. TREFONAS\*

Received November 29, 1971

The crystal and molecular structure of the dimer complex  $\mu$ -bis[2(1H)-tetrahydropyrimidinone]-octakis[2(1H)-tetrahydropyrimidinone]dicobalt(II) perchlorate, (CoC<sub>20</sub>H<sub>40</sub>O<sub>13</sub>Cl<sub>2</sub>)<sub>2</sub>, has been determined by a single-crystal X-ray diffraction study. The compound crystallizes in the space group *P* $\bar{1}$  with unit cell constants  $a = 11.835 \pm 0.001$  Å,  $b = 13.827 \pm 0.001$  Å,  $c = 12.871 \pm 0.001$  Å,  $\alpha = 101.72 \pm 0.01^\circ$ ,  $\beta = 107.94 \pm 0.01^\circ$ , and  $\gamma = 117.83 \pm 0.01^\circ$ . The calculated density of 1.56 g/cm<sup>3</sup> assuming one dimer formula weight per unit cell is in agreement with the experimentally measured density of  $1.55 \pm 0.02$  g/cm<sup>3</sup>. The structure was solved by the heavy-atom method and refined by block-diagonal least squares to a final *R* value of 0.053 for the 1911 statistically significant reflections. Coordination occurs through the oxygen atoms with the cobalt having approximately octahedral symmetry. Each cobalt has four unique ligands and shares two others to complete the six-coordinate sphere.

### Introduction

Stable complexes of metal salts with substituted ureas have been isolated for some time, but there have been many arguments in the literature about the site of coordination, either oxygen or nitrogen or both. Many references in the literature have suggested that the mode of bonding can be deduced from the position of the carbonyl stretching frequency of the complex relative to that of the free ligand.<sup>1-3</sup> A shift of the

carbonyl absorption to lower frequency is presumed to indicate oxygen to metal bonding, while a shift to higher frequency would indicate nitrogen to metal bonding. For example, based on infrared spectral data, Penland and coworkers<sup>4</sup> postulated oxygen to metal bonding in urea complexes of Cr(III), Fe(III), Zn(II), and Cu(II), and nitrogen to metal bonding with Pt(II) and Pd(II). Costamagna and Levitus<sup>5</sup> used similar arguments to demonstrate oxygen to

(1) B. B. Kedzia, P. X. Armendarez, and K. Nakamoto, *J. Inorg. Nucl. Chem.*, **30**, 849 (1968).

(2) A. W. McLellan and G. A. Melson, *J. Chem. Soc. A*, 137 (1967).

(3) A. R. Katritzky and R. A. Y. Jones, *Chem. Ind. (London)*, 722 (1961).

(4) R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, **79**, 1575 (1957).

(5) J. A. Costamagna and R. Levitus, *J. Inorg. Nucl. Chem.*, **28**, 2685 (1966).