The Crystal Structure of Di-pyridino-mercuric Chloride

*D. Grdenić and I. Krstanović**

Laboratory for General and Inorganic Chemistry,
Faculty of Science, University of Zagreb, Zagreb, Croatia, Yugoslavia

Di-pyridino-mercuric chloride $HgCl_2 . 2C_5H_5N$ crystallizes in the space group C_{2h}^5 - $P2_1/a$ with the cell dimensions:

$$a = 17.70 \text{ Å} \qquad b = 8.62 \text{ Å} \qquad c = 3.90 \text{ Å} \qquad \beta = 93^0$$

with two formula units in the cell.

The structure was solved by means of the two-dimensional [001] Fourier-Bragg projection. Each mercury atom is surrounded by two nearer chlorine atoms at a distance of 2.34 Å, two farther chlorine atoms at a distance of 3.25 Å and two nitrogen atoms at a distance of 2.60 Å in a deformed octahedral coordination.

The compound is not to be considered as a complex compound but as mercuric chloride containing pyridine of crystallization, the pyridine molecules being held in the crystal similar to that of water molecules in many hydrates.

The long needle-like crystals of di-pyridino-mercuric chloride are formed by coolling a warm solution of mercuric chloride in pyridine as previously described by Pesci[1]. The crystals gradually lose pyridine, mercuric chloride being left over.

According to the present knowledge of the chemical behaviour and crystal structure of mercuric compounds, we may take into consideration three main possibilities for the structure of this compound: a) the compound might contain a complex cation [Py-Hg-Py]; b) the compound might be a neutral complex Py_2HgCl_2; c) the compound might be an aggregate of mercuric chloride and pyridine or, in other words, it might be mercuric chloride containing pyridine of crystallization.

a) Several mercury derivatives of ammonia are known, in which a mercury atom forms 2-coordination complex with nitrogen atom as a donor. The simplest and most common of them is fusible white precipitate $(H_3N)_2HgCl_2$ the crystal structure of which consists of linear $[H_3N\text{-}Hg\text{-}NH_3]^{++}$ cations and Cl^- anions[2]. The analogous structure may be assumed for ethylated fusible precipitate $(C_2H_5NH_2)_2HgCl_2$ [3] as well as for the methyl derivative $(CH_3NH_2)_2HgCl_2$ [4].

The ability of nitrogen atom to act as a donor is much smaller in the case of pyridine than in the case of ammonia or ammines, so that it seems quite unlikely that di-pyridino-mercuric chloride has a structure analogous to the structure of fusible precipitate.

---

* Present adress: Mineralogical Institute, Faculty of Science, The University, Beograd, Yugoslavia.

b) The mercury complexes containing four ligands in a tetrahedral coordination are known[5]. It is our opinion that in the present case such a coordination seems also very improbable, owing to the considerable difference in electronegativities between the nitrogen atom in pyridine and the chlorine atom.

c) Thus the most probable structure seems to be that one in which the mercuric chloride molecules retain their individuality and are packed in the crystal with the pyridine molecules in the most favourable position. The instability of the compound gives further evidence for this assumption.

The aim of this investigation was to establish the coordination around the mercury atom as well as to determine the mercury-chlorine bond lenght, especially the amount by which it differs from the value for this bond in pure mercuric chloride.

<center>EXPERIMENTAL</center>

Crystallographic and X-ray data.

The crystals gradually lose pyridine and disintegrate. In order to prevent disintegration during the measurements and photographie recording, the crystal was sealed in a quartz capillary with a small drop of pyridine to keep the atmosphere saturated with pyridine vapour.

Goniometric measurements showed that the crystalls were monoclinic holohedral elongated in [001] direction.

The cell dimensions were determined by means of oscillation photographs and are as follows:

$$a = 17.70 \text{ Å} \qquad b = 8.62 \text{ Å} \qquad c = 3.90 \text{ Å} \qquad \beta = 93^0$$

The density measured by suspension method amounted to 2.34 gcm.$^{-3}$, in good agreement with the calculated density (2.42 gcm.$^{-3}$) for two formula units in the elementary cell. The systematic absence of reflexions was observed only in the case of $0k0$ with k odd and $h0l$ with h odd, so that the space group is C_{2h}^5- $P2_1/a$. In the X-ray work nickel filtered CuKα radiation was used.

Intensity measurements.

The value of c period showed that the pyridine molecules were only slightly inclined to the (001) plane. It was assumed, therefore, that the projection of the elementary cell along [001] direction would give sufficient information about the structure.

All possible $hk0$ reflexions (120 in total) were recorded by means of a Weissenberg goniometer with double film technique. The optical densities were measured at the centre of each spot by means of the microdensitometer and were transformed into the relative intensities using the characteristic blackening curve of the film. The linear absorption coefficient was 290 cm.$^{-1}$. The crystals had ten nearly equally developed prism faces of [001] zone and could be well approximated by a cylinder. This fact allowed the Classen's formula for absorption correction to be used[6]. Corrections for Lorentz and polarization factor were made in the usual way.

Determination of the structure.

The positions of the mercury atoms determined by the space group were centres of symmetry at (0, 0, 0); (½, ½, 0), while all the remaining atoms were located in general positions. The contribution of these atoms, i. e. of chlorine, nitrogen and carbon atoms, to the intensity of reflexions was generally small, which was also proved by the fact that only six $hk0$ reflexions with the odd sum $h + k$ had been recorded. The mercury contribution to these odd $hk0$ reflexions was zero and their intensity depended only upon the contributions of the chlorine, nitrogen and carbon atoms. It was assumed that the sign of the structure amplitudes of these reflexions

had been defined only by the chlorine atom position. The sign of all $hk0$ structure amplitudes with the even sum $h + k$ was defined by mercury atom owing to its large scattering factor and was throughout taken as positive. In order to determine the x,y-coordinates of chlorine atom, a $xy0$ Patterson projection was calculated (Fig. 1.).
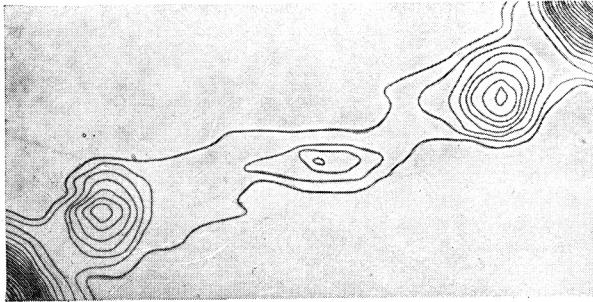

Fig. 1. The Patterson projection

The maxima corresponding to the mercury-chlorine and chlorine-chlorine vectors were clearly resolved. The resulting chlorine atom coordinates were: $x = 0.083$; $y = -0.150$. The Patterson projection indicated also the approximate position of the pyridine ring.
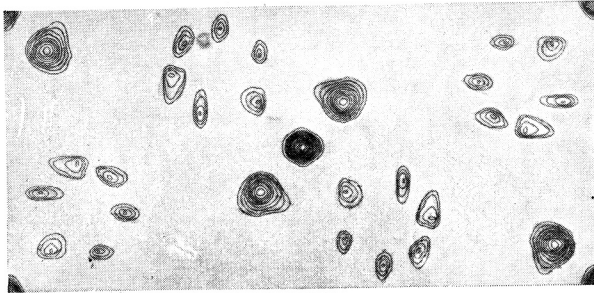

Fig. 2. The Fourier projection

TABLE I.

Atomic coordinates

	x	y	z
Hg	0	0	0
Cl	0.083	-0.150	-0.330
N	0.083	0.150	0.267
	(0.093)	(0.185)	(0.277)
C_1	0.166	0.150	
C_2	0.216	0.283	
C_3	0.183	0.416	
C_4	0.133	0.466	
C_5	0.066	0.366	

Using the above chlorine atom coordinates the signs of the structure amplitudes with odd $h + k$ sum were evaluated and the Fourier-Bragg projection along [001] was computed using Beevers-Lipson strips at 6⁰ intervals (Fig. 2.). All atoms were resolved better than it could be expected. However, the influence of the mercury atom in the centre of symmetry was very unfavourable. The pyridine ring appeared in the projection very deformed, so that it was immediately clear that such a distortion could not really exist. Besides, the heights of the carbon atom peaks have not equal numerical values, while the nitrogen atom peak is remarkably higher.

The atomic coordinates are listed in Table I. This table needs the following explanation. The z coordinates of the chlorine atom as it is given in Table I. has been obtained by the usual trial and error procedure using $00l$ and $0kl$ reflexions. This is not difficult, since the value of this coordinate is limited by Cl...Hg Van der Waals contact of the adjacent molecules along [001] direction, which amounts to 3.25 Å, being in good agreement with the value of the sum of Van der Waals radii (the values of 1.75 Å and 1.50 Å being taken for chlorine and mercury atoms respectively[7, 8]). Therefore, the accuracy of this chlorine z coordinate can be taken to be about ± 0.03 Å.
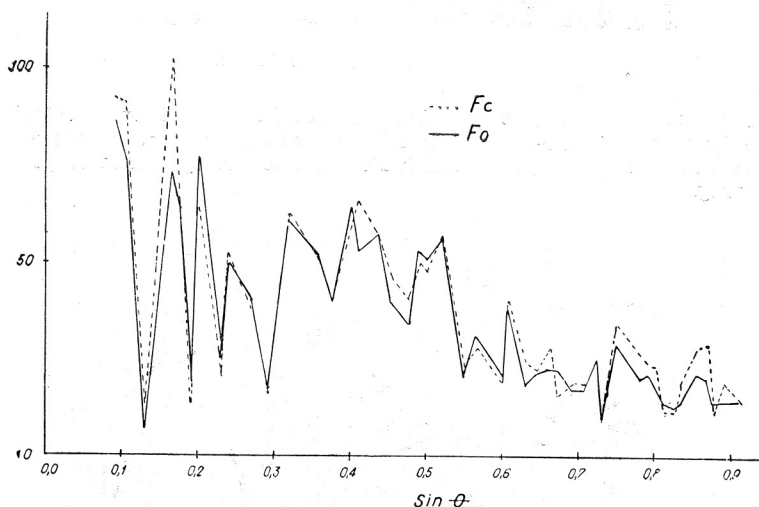

Fig. 3.

The position of the nitrogen atom is considerably influenced by the heavy mercury atom. This influence came to evidence: a) in the large N—C_5 distance value and b) in the length of the pyridine ring from nitrogen to C_3 carbon atom, which amounted to 2.90 Å but should be 2.50 Å, owing to the inclination of the ring towards (001) plane. This inclination was calculated from the value for the c period and from the thickness of pyridine ring (assumed 3.44 Å) and amounts to 28⁰ (it is the angle between N...C_3 axis of the ring and (001) plane; the inclination of the axis normal to the former one seemed to be insignificant).

An attempt was made to establish the position of nitrogen atom more reliably from the projection data with the help of known interatomic distances. The position obtained in this way is defined by the coordinate values given in brackets in Table I. These values differ from those obtained directly from the projection by about 0.2 Å. The nitrogen z coordinate has been obtained under the assumption that the mercury atom lies in the same plane as the pyridine ring which is very probable but not necessary. The angle ClHgN, amounting to 85 ± 5⁰, and N...Cl Van der Waals approaches, amounting to 3.2 Å and 3.6 Å, may be used as criteria for the reliability of nitrogen atom position obtained by trial method described.

The coordinates of the carbon atoms given in Table I. have been obtained directly from the projection data and do not correspond to the suggested nitrogen

coordinates. The reliability of these coordinates may be estimated by comparison of the obtained interatomic distances with the known ones in the pyridine ring. It follows that the mean deviation amounts to ± 0.1 Å. The reliability of the position of the pyridine ring itself may be estimated by using the intermolecular aproaches as criteria. They have the values of 4.20 Å to 4.90 Å for HC...CH approaches and 3.80 Å for Cl...C approach, which is in agreement with values usually observed in similar cases.

In Fig. 3. the graphical comparison of observed F_o and calculated F_c structure amplitudes is given. The calculated structure amplitudes were obtained by taking into account only mercury and chlorine atom contributions. The appropriate atomic factors[9] were multiplied by a temperature factor with parameter $B = 3.5$ Å^2.

DISCUSSION OF THE STRUCTURE

Interatomic distances resulting from the given data and which are significant for the nature of this structure are the following ones:

$$
\begin{array}{ll}
\text{Hg} - \text{Cl} & 2.34 \pm 0.03 \text{ Å} \\
\text{Hg} - \text{N} & 2.60 \pm 0.20 \text{ Å} \\
\text{Hg} \ldots \text{Cl} & 3.25 \pm 0.03 \text{ Å}
\end{array}
$$

The Hg-N distance value is larger than the sum of covalent radii and is also larger than the values found previously for the Hg-N distance in such compounds as fusible white precipitate[2] (2.03 Å), infusible precipitate[10] (2.05 Å), Millon base[11, 12] (2.07 Å, 2.04 Å) and mercuric immido-bromide[13] (2.13 Å). Therefore, it can be concluded that in di-pyridinomercuric chloride Hg-N bond is not covalent as it is in the compound just quoted. Even if the value Hg-N distance obtained directly from the projection (which amounts to 2.20 Å) is taken there is no evidence for covalent nature of this bond.

The suggested Hg-N distance value (2.60 Å) is smaller than the expected Van der Waals approach of 3.00 Å (1.50 Å being taken for mercury as well as for nitrogen atom intermolecular radius). Therefore the bond between mercury and nitrogen atom can be considered as the result of polarizing activity of mercury atom in mercuric chloride. Against the assumption of covalency speaks also the steric relation, since the chlorine and nitrogen atoms are in the same plane with mercury atom in a nearly quadratical coordination.

The correctness of the above conclusion may be also proved by the comparison of Hg-Cl distance values in fusible and infusible precipitate, which amount to 2.87 Å and 3.18 Å respectively, with those obtained for di-pyridino-mercuric chloride. It is evident that chlorine atoms in the former compounds are bonded ionically. In the present compound the opposite is true; the chlorine atoms are bonded to mercury essentially in the same way as in mercuric chloride, the bond length value being only slightly larger but just equal to that found earlier in the crystal of NH_4HgCl_3.[14]

It follows, therefore, that the structure of di-pyridinomercuric chloride is to be considered as built up of the mercuric chloride and pyridine molecules. Each mercury atom has a octahedral coordination: two chlorine atoms at 2.34 Å, two nitrogen atoms at 2.60 Å and two chlorine atoms at 3.25 Å. The most favourable packing is achieved in the [001] direction. In this direction the coordination octahedra are arrayed by sharing their Cl...Cl edge. The packing at the pyridine side is much weaker.

It follows, therefore, that the compound should be included in class c) and that it should be considered as mercuric chloride containing pyridine of crystallization with $HgCl_2 \cdot 2Py$ as correct formula.

REFERENCES

1. A. P e s c i, *Gazz. chim. ital.* **25** (1895) 429.
2. C. H. M a c g i l l a v r y and J. M. B i j v o e t, *Z. Krist.* **94** (1936) 240.
3. K. A. H o f m a n n and M a r b u r g, *Ann.* **305** (1899) 196.
4. D. G r d e n i ć, unpublished data.
5. A. F. W e l l s, *Structural Inorganic Chemistry*, 2nd Ed., Oxford 1950, pp. 631—4.
6. *Internationale Tabellen zur Bestimmung der Kristalstrukturen*, Leipzig 1935, Bd. 2. p. 583.
7. H. B r a e k k e n and W. S c h o l t e n, *Z. Krist.* **89** (1934) 488.
8. D. G r d e n i ć, *Arhiv kem.* **22** (1950) 14.
9. *Internationale Tabellen zur Bestimmung der Kristalstrukturen*, Leipzig 1935, Bd. 2. p. 571.
10. W. N. L i p s c o m b, *Acta Cryst.* **4** (1951) 266.
11. W. N. L i p s c o m b, *Acta Cryst.* **4** (1951) 156.
12. W. R ü d o r f f und K. B r o d e r s e n, *Z. anor. allg. Chem.*, **274** (1953) 324.
13. K. B r o d e r s e n und W. R ü d o r f f, *Z. Naturforsch,* **9b** (1954) 164.
14. E. J. H a r m s e n, *Z. Krist.* **100** (1938) 208.

IZVOD

Kristalna struktura di-piridino-živina klorida

D. Grdenić i I. Krstanović

Di-piridino-živin klorid $HgCl_2 \cdot 2C_5H_5N$ kristalizira u prostornoj grupi $C_{2h}^5 - P2_1/a$. Dimenzije su elementarne ćelije ove:

$$a = 17.70 \text{ Å} \qquad b = 8.62 \text{ Å} \qquad c = 3.90 \text{ Å} \qquad \beta = 93^0$$

Elementarna ćelija sadrži 2 stehiometrijske jedinice. Struktura je određena s pomoću dvodimenzionalne Fourier-Braggove sinteze elektronskoga rasporeda projiciranog uzduž [001].

Spoj nije kompleks, nego ga treba shvatiti kao živin klorid, koji sadrži kristalizacijski piridin.