

Crystal and Molecular Structure of Dichloronicotinemercury(II)

M. R. UDUPA* and B. KREBS

Anorganisch-Chemisches Institut der Universität Münster, Gievenbecker Weg 9, D-4400 Münster, F.R.G.

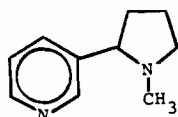
Received October 8, 1979

The crystal and molecular structure of dichloronicotinemercury(II) was determined from single crystal X-ray data collected by counter methods. The colourless crystals are orthorhombic with the space group $P2_12_12_1$. The unit cell parameters are $a = 11.210(2)$, $b = 15.166(4)$ Å, $c = 7.568(2)$ Å, $V = 1286$ Å³ and $Z = 4$. The structure was solved by heavy atom methods from 1338 reflections and was refined to an R index of 0.049.

Each nicotine molecule is bonded to two adjacent mercury atoms, one through the pyrrolidine nitrogen (Hg–N 2.397 Å) and the other through the pyridine nitrogen (Hg–N 2.454 Å), forming endless polymeric chains. The coordination around mercury is completed by two chlorine ligands (Hg–Cl 2.364 and 2.384 Å), resulting in a highly distorted tetrahedral arrangement.

Introduction

3-(2-N-Methylpyrrolidinyl)pyridine, called nicotine, is commonly well known as a stimulant and



poison, and naturally occurs in tobacco leaf. It is a base of moderate strength and readily forms several nicotinium metal double salts [1]. It can function as a monodentate and bidentate chelating and bridging ligand. Adducts of nicotine with copper(II) [2], zinc(II) [3] and cobalt(II) [4] halides have been isolated. However, not much structural information is available on the metal–nicotine complexes. In order to investigate the bonding and coordination of nicotine as an important naturally occurring base towards metal atoms, it was thought interesting to prepare a variety of metal–nicotine

complexes and study the ligating behaviour of the ligand. In this paper, we report the crystal and molecular structure of dichloronicotinemercury(II).

Experimental

Dichloronicotinemercury(II) was prepared by adding an ethanolic solution of nicotine to an acetone solution of mercury(II) chloride in a 1:1 molar ratio. The reaction mixture was stirred, and the precipitated crystalline product was filtered then washed with acetone and ether. Single crystals of the complex were obtained by slow evaporation of the alcoholic solution of the complex. *Anal.*: found, C 27.36, H 3.44, N 5.98, Cl 16.71, Hg 45.81; calcd. for $[C_{10}H_{14}N_2Cl_2Hg]$: C 27.69, H 3.36, N 6.46, Cl 16.35, Hg 46.24%.

A crystal of dimensions, $0.2 \times 0.5 \times 0.2$ mm³ was used of for the X-ray data collection. Preliminary Weissenberg and precession photographs suggested the crystals being orthorhombic. The systematic absences $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, $00l$, $l = 2n + 1$ indicated the space group $P2_12_12_1$ (D_2^2 , No. 19).

The unit cell parameters after least squares refinement of the diffractometer coordinates for 15 reflections are $a = 11.210(2)$, $b = 15.166(4)$, $c = 7.568(2)$ Å, $V = 1286$ Å³. There are four molecules per unit cell and the calculated and the measured densities are 2.240 and 2.23(2) g cm⁻³ respectively.

Data Collection and Reduction

The X-ray intensity data for the complex were collected on a Syntex $P2_1$ four-circle diffractometer using graphite monochromated $MoK\alpha$ radiation in the θ - 2θ mode ($K\alpha_1 = 0.70926$, $K\alpha_2 = 0.71354$ Å). The sampling interval in 2θ for every reflection was 1.0° below the $MoK\alpha_1$ maximum to 1.0° above the $MoK\alpha_2$ maximum. The rate of scanning was dependent on the intensity of the reflection and generally varied from 2 to 15° min⁻¹ in 2θ . The background measurements with the total time for back-

*Permanent address: Department of Chemistry, Indian Institute of Technology, Madras-600 036, India.

TABLE I. Coordinates of the Atoms in the Structure of Dichloronicotinemercury(II) with Standard Deviations.

| | x | y | z |
|-------|------------|------------|------------|
| Hg | 0.42543(6) | 0.29924(5) | 0.44714(9) |
| Cl(1) | 0.4128(5) | 0.1518(3) | 0.3395(7) |
| Cl(2) | 0.3249(5) | 0.4342(3) | 0.3997(7) |
| N(1) | 0.1213(10) | 0.1624(8) | 0.6754(17) |
| N(2) | 0.4911(9) | 0.2839(7) | 0.7470(17) |
| C(1) | 0.1408(15) | 0.0794(11) | 0.7235(22) |
| C(2) | 0.2393(15) | 0.0560(11) | 0.8230(25) |
| C(3) | 0.3198(14) | 0.1193(11) | 0.8736(24) |
| C(4) | 0.3033(12) | 0.2084(9) | 0.8222(19) |
| C(5) | 0.1995(13) | 0.2246(9) | 0.7258(22) |
| C(6) | 0.3893(13) | 0.2784(9) | 0.8781(19) |
| C(7) | 0.3425(15) | 0.3726(12) | 0.9000(25) |
| C(8) | 0.4458(19) | 0.4286(12) | 0.8603(30) |
| C(9) | 0.5496(15) | 0.3670(12) | 0.8088(25) |
| C(10) | 0.5712(14) | 0.2097(12) | 0.7538(26) |

ground counts being equal to the scan time were made both at the beginning and at the end of each scan with the counter stationary. A standard reflection was measured for every 50 reflections. A complete set of 1639 unique reflections was measured up to $(\sin \theta)/\lambda = 0.64 \text{ \AA}^{-1}$ out of which 1338 reflections were accepted as statistically above the background on the basis of $I > 1.96\sigma(I)$. The data reduction was done applying Lorentz and polarization corrections and a Wilson plot. The linear absorption coefficient was calculated to be 125.9

cm^{-1} , and the diffraction data were corrected for absorption effects.

Structure Determination and Refinement

The structure was solved by the heavy-atom method [5]. The coordinates of the Hg and Cl atoms were obtained by the Patterson map. After isotropic refinement of Hg and Cl, the other non-hydrogen atoms were located from the difference Fourier map. The coordinates of the hydrogen atoms were calculated and not refined. The atomic scattering factors for Hg, Cl, N, C and H, including anomalous scattering corrections for Hg, were taken from the International Tables [6]. Full-matrix least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms and fixed coordinates and isotropic temperature factors for the hydrogen atoms (4.0 \AA^2) resulted in residuals of $R_1 = 0.049$ for the correct absolute configuration (including unobserved data $R_1 = 0.060$), $R_2 = 0.049$ where $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme was based on counting statistics of the intensities. The shifts in the final cycle were below 0.02σ and the final difference Fourier map had no significant features. The absolute configuration was obtained without ambiguity from comparison of the R values after final refinement of both enantiomeric forms with all reflections measured. The wrong absolute configuration yielded a final R_1 of 0.065. The final positional and thermal parameters are given in Tables I and II. A Table of calculated and observed structure factors is available from the Editor.

TABLE II. Coefficients of the Anisotropic Temperature Factors.^a

| | B ₁₁ | B ₂₂ | B ₃₃ | B ₁₂ | B ₁₃ | B ₂₃ |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Hg | 2.90(2) | 3.87(2) | 4.43(2) | -0.02(3) | 0.29(3) | 0.11(3) |
| Cl(1) | 7.93(32) | 4.74(21) | 5.71(23) | -2.04(24) | -0.47(27) | -1.33(21) |
| Cl(2) | 5.89(25) | 5.88(25) | 7.26(34) | 2.79(22) | -0.19(22) | 0.46(23) |
| N(1) | 2.4(5) | 3.9(6) | 3.6(5) | 0.5(4) | -0.4(4) | 1.0(5) |
| N(2) | 1.9(4) | 2.9(5) | 3.7(5) | -0.7(4) | -0.5(4) | 0.4(4) |
| C(1) | 4.2(7) | 4.1(8) | 4.0(7) | 0.6(6) | 0.9(6) | -0.9(6) |
| C(2) | 3.6(7) | 5.4(9) | 4.9(8) | 0.4(7) | 0.1(7) | -1.0(7) |
| C(3) | 3.2(6) | 4.4(8) | 4.9(8) | 1.2(6) | 1.0(6) | -0.6(7) |
| C(4) | 3.3(6) | 2.1(5) | 3.3(6) | 0.5(6) | 0.2(5) | 0.9(6) |
| C(5) | 3.0(5) | 2.9(6) | 4.5(7) | -0.7(5) | -0.5(5) | 0.9(5) |
| C(6) | 3.4(6) | 3.6(7) | 2.7(5) | -0.3(5) | -0.3(5) | -0.5(5) |
| C(7) | 3.4(7) | 5.9(10) | 6.3(11) | -0.8(7) | 0.1(7) | -2.5(8) |
| C(8) | 6.0(11) | 4.5(8) | 7.3(11) | -1.5(7) | -1.0(9) | -0.2(8) |
| C(9) | 4.2(9) | 6.2(9) | 5.2(8) | -3.3(7) | -1.2(7) | -0.7(7) |
| C(10) | 2.0(5) | 5.9(9) | 7.6(9) | 1.8(8) | 0.7(7) | -0.4(8) |

^aThe temperature factors are defined as $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}kbl^*c^*)]$.

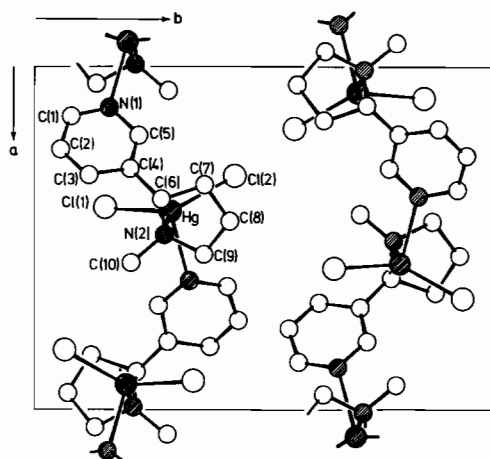


Fig. 1. Dichloronicotinemercury(II): projection of the unit cell parallel *c* with atomic designations.

Results and Discussion

The structure of dichloronicotinemercury(II) consists of four-coordinated Hg(II) in polymeric chains linked by Hg–nicotine–Hg bridges. A view of the unit cell showing the atomic labelling of all the non-hydrogen atoms is reproduced in Fig. 1.

The mercury atom in the molecule is strongly bonded to both chlorine atoms. Each nicotine molecule coordinates to two different mercury atoms through the pyrrolidine and the pyridine nitrogen atoms. Thus, nicotine acts as a bidentate bridge ligand. The nearest Hg–Hg distance is found to be 5.886 Å. The interatomic distances and bond angles are given in Table III. Generally, Hg(II) assumes a variety of structural arrangements [7], namely linear, triangular planar, tetrahedral, square pyramidal, trigonal bipyramidal, octahedral and square antiprismatic. The tetrahedral angles in the present complex vary from 96.1 to 137.0° suggesting the geometry around mercury to be highly distorted. The bond distances, Hg–Cl(1) and Hg–Cl(2) (2.384(5) and 2.364(6) Å) are significantly less than the sum of the covalent tetrahedral radii (2.47 Å) given by Pauling [8]. In several known chloro-complexes of Hg(II) [9–14] the Hg–Cl bond lengths vary from 2.29 to 2.56 Å. The bond angle Cl(1)–Hg–Cl(2) (137.0°) is far greater than that normally expected for a four-coordinated Hg(II). The large deviation from tetrahedral geometry towards a more linear Cl–Hg–Cl arrangement favours the stronger Hg–Cl interactions indicated by the bond length data. The bond lengths Hg–N(1) and Hg–N(2) (2.45 and 2.40 Å) are normal. Hg–N bond distances are found in the range 2.37–2.97 Å in N-ligated Hg(II) complexes [10, 15–17], and the observed values in the present complex are in agreement with the reported

TABLE III. Interatomic Distances (Å) and Bond Angles (deg.) in the Structure of Dichloronicotinemercury(II) with Standard Deviations.

| <i>Hg Coordination</i> | | | |
|--------------------------|-----------|-----------------|-----------|
| Hg–Cl(1) | 2.384(5) | Cl(1)–Hg–Cl(2) | 137.0(2) |
| Hg–Cl(2) | 2.364(6) | Cl(1)–Hg–N(1) | 98.4(4) |
| Hg–N(1) | 2.454(13) | Cl(1)–Hg–N(2) | 104.5(3) |
| Hg–N(2) | 2.397(14) | Cl(2)–Hg–N(1) | 99.4(4) |
| | | Cl(2)–Hg–N(2) | 112.0(3) |
| | | N(1)–Hg–N(2) | 96.1(4) |
| <i>Nicotine Molecule</i> | | | |
| N(1)–C(1) | 1.33(2) | Hg–N(1)–C(1) | 118.4(11) |
| N(1)–C(5) | 1.34(2) | Hg–N(1)–C(5) | 121.6(10) |
| C(1)–C(2) | 1.38(2) | C(1)–N(1)–C(5) | 118.8(14) |
| C(2)–C(3) | 1.37(2) | N(1)–C(1)–C(2) | 121.6(15) |
| C(3)–C(4) | 1.42(2) | C(1)–C(2)–C(3) | 119.8(16) |
| C(4)–C(5) | 1.40(2) | C(2)–C(3)–C(4) | 120.3(15) |
| C(4)–C(6) | 1.50(2) | C(3)–C(4)–C(5) | 114.9(13) |
| N(2)–C(6) | 1.51(2) | C(3)–C(4)–C(6) | 121.0(13) |
| N(2)–C(9) | 1.50(2) | C(5)–C(4)–C(6) | 124.0(13) |
| N(2)–C(10) | 1.44(2) | C(4)–C(5)–N(1) | 124.6(13) |
| C(6)–C(7) | 1.53(2) | C(4)–C(6)–N(2) | 109.9(11) |
| C(7)–C(8) | 1.47(3) | C(4)–C(6)–C(7) | 118.2(12) |
| C(8)–C(9) | 1.54(3) | N(2)–C(6)–C(7) | 106.1(11) |
| | | C(6)–C(7)–C(8) | 104.4(13) |
| | | C(7)–C(8)–C(9) | 107.2(15) |
| | | C(8)–C(9)–N(2) | 105.0(13) |
| | | Hg–N(2)–C(6) | 113.2(8) |
| | | Hg–N(2)–C(9) | 110.4(9) |
| | | Hg–N(2)–C(10) | 107.5(9) |
| | | C(6)–N(2)–C(9) | 99.9(11) |
| | | C(6)–N(2)–C(10) | 113.8(11) |
| | | C(9)–N(2)–C(10) | 111.9(12) |

values of similar complexes. The polymeric structure of the present complex is caused by the steric requirements of the ligands which do not allow bonding of both the N-atoms of the ligand to the same Hg with formation of a 6-membered chelate ring. The bond distance Hg–N(2) (pyrrolidine) is slightly shorter than Hg–N(1) (pyridine). This is explained by the fact that the pyrrolidine nitrogen is more basic than the pyridine nitrogen as evidenced by the reported [18] pK_a values (8.02 and 3.12). However, it is interesting to note that according to NMR studies of paramagnetic shift reagents pyridine nitrogen is preferentially bonded in these metal chelates [19].

The bond distances within the nicotine molecule have normal values. The pyridine ring together with the contact carbon atom of the pyrrolidine ring constitutes a plane. The least-squares equation for this plane containing the atoms N(1), C(1), C(2), C(3), C(4), C(5) and C(6) is 0.8534 – 0.2325 *y* – 0.4665 *z* + 4.4200 = 0 where *x*, *y* and *z* are related to the crystal axes. The maximum deviation from the

mean plane (0.016 Å) is to C(4). N(1) assumes a planar arrangement with Hg, C(1) and C(5) as neighbours, the N(1)–C(1) and N(2)–C(2) distances being as expected for N(sp²)–C distances. The N(2) atom, on the other hand, has a tetrahedral arrangement of the bonded neighbours Hg, C(6), C(9) and C(10). The bond lengths N(2)–C(6) and N(2)–C(9) are as expected for N(sp³)–C. The N(2)–C(10) distance is slightly shorter than the C(sp³)–N(sp³) value.

The pyrrolidine ring can assume two conformers [20], an envelope form and a half-chair form. The analysis of the dihedral angles suggests that it favours the envelope form (*cf.* Fig. 1) as observed also in the NMR studies [19].

Acknowledgment

The authors express their thanks to the Alexander von Humboldt Foundation for the award of a senior fellowship to M.R.U. and to the Fonds der Chemischen Industrie for financial support.

References

- 1 C. R. Smith, *J. Am. Chem. Soc.*, **75**, 2010 (1953).
- 2 S. F. Babak and G. B. Kagramanova, *Zhur. Obshchei Khim.*, **24**, 1690 (1954).
- 3 S. F. Babak and I. A. Kondrashov, *Zhur. Obshchei Khim.*, **24**, 1759 (1954).
- 4 S. Prasad, V. N. Garg and Y. M. Reddy, *J. Proc. Inst. Chemists*, **37**, 167 (1965).
- 5 The calculations were carried out on a Data General Eclipse computer, using, besides own programmes, the programmes of the Syntex EXTL System and on an IBM 360/50 using C. Johnson's ORTEP programme.
- 6 'International Tables for X-ray Crystallography', Vol. IV, Kynoch Press, Birmingham (1974) pp. 99 ff.; R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- 7 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', III. ed., Wiley, New York (1972) p. 505.
- 8 L. Pauling, 'The Nature of Chemical Bond', Cornell Univ. Press, Ithaca (1960).
- 9 R. D. Ellison, H. A. Levy and K. W. Fung, *Inorg. Chem.*, **11**, 833 (1972).
- 10 A. D. Redhouse, *Chem. Comm.*, 1119 (1972).
- 11 P. Biscarini, L. Fusina, G. D. Nivellini, A. Mangia and G. Pelizzi, *J. Chem. Soc. Dalton*, 159 (1973).
- 12 I. W. Nowell and D. R. Russell, *J. Chem. Soc. Dalton*, 2396 (1972).
- 13 J. A. Carrabine and M. Sunderalingan, *Biochem.*, **10**, 292 (1971).
- 14 W. J. Kozarek and Q. Fernando, *Chem. Comm.*, 604 (1972).
- 15 A. J. Canty and B. M. Gatehouse, *Acta Cryst.*, **B28**, 1872 (1972).
- 16 A. L. Beauchamp, B. Saperas and R. Rivest, *Can. J. Chem.*, **49**, 3579 (1971).
- 17 M. Frey and M. Ledéser, *Acta Cryst.*, **B27**, 2119 (1971).
- 18 'Handbook of Chemistry and Physics', Ed. R. C. Weast, CRC Press, Ohio (1976) p. D-148.
- 19 M. Ohashi, I. Morishima and T. Yonezawa, *Bull. Chem. Soc. Japan*, **44**, 576 (1971).
- 20 E. L. Eliel, 'Stereochemistry of Carbon Compounds', McGraw-Hill, New York (1962) p. 251.