Avirah, Cook & Malloy (1975) have reported an analysis of the microwave spectrum of 3-thietanone and have presented estimates for structural parameters. The values C(1)–C(2) = 1·528 (9) and C(2)–O(2) = 1·224 (18) Å (our numbering scheme) are in good agreement with those in the crystal. Their angle C(1)C(2)C(3) = 100·5 (8)° is somewhat smaller and their C–S distance 1·826 (13) is considerably shorter than that in (III). We suspect that their value is unrealistically short since the analogous C–C bond distance in cyclobutanone is 1·556 (1) Å (Table 5).

The Cr^0 atom of (III) displays a reasonable approximation to octahedral coordination geometry. The deviations from ideality are largely traceable to the steric repulsions mentioned above. There is clear indication of a *trans* effect in the Cr–C(11) and C(11)–O(11) distances which are respectively shorter and longer than their analogs in the equatorial plane. The presence of such an effect may be taken as evidence that ligand (I) is a good electron donor (n electrons) but a rather poor π-electron acceptor. The equatorial Cr–C distances are very similar to those reported for $Cr(CO)_6$ at 78 K (Jost, Rees & Yelon, 1975); the equatorial C–O distances are slightly, but possibly significantly, longer. The average values for riding-motion-corrected coordinates are $\langle Cr–C \rangle_e$ = 1·915 and $\langle C–O \rangle_e$ = 1·149 for (III) and $\langle Cr–C \rangle$ = 1·918 and $\langle C–O \rangle$ = 1·141 Å for $Cr(CO)_6$.

Two methyl groups, C(1M1) and C(3M2), display short intermolecular contact distances to two carbonyl O atoms, O(14) and O(12), respectively [3·171 (2) and 3·376 (2) Å]. Since the Fe complex described in the previous paper displays a similar contact distance with no apparent affect on the bonding geometry of either atom involved, these contact distances probably do not contribute significantly to the differences in bond angles between these methyl groups and the other two. We assign the differences to intramolecular interactions.

References

AVIRAH, T. K., COOK, R. L. & MALLOY, T. B. (1975). *J. Mol. Spectrosc.* **55**, 464–475.

BLACKWELL, C. S. & LORD, R. C. (1975). *J. Mol. Spectrosc.* **55**, 460–463.

BRAUMAN, J. I. & LAURIE, V. W. (1968). *Tetrahedron*, **24**, 2595–2602.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

CZAUDERNA, B. (1976). Thesis, Univ. Stuttgart.

JOGUN, K. H. & STEZOWSKI, J. J. (1979). *Acta Cryst.* B**35**, 2306–2310.

JOHNSON, C. K. (1971). *ORTEP* II. Report ORNL-TM-5138. Oak Ridge National Laboratory, Tennessee.

JOST, A., REES, B. & YELON, W. B. (1975). *Acta Cryst.* B**31**, 2649–2658.

MAYER, R. & FUNK, K. F. (1961). *Angew. Chem.* **73**, 578–579.

SCHARPEN, L. R. H. & LAURIE, V. W. (1968). *J. Chem. Phys.* **49**, 221–228.

SHIRRELL, C. D. & WILLIAMS, D. E. (1975). *Acta Cryst.* B**31**, 199–202.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STIGLIANI, W. M., LAURIE, V. W. & SCHARPEN, L. H. (1976). *J. Mol. Spectrosc.* **62**, 85–89.

ZBINDEN, R. & HALL, H. K. (1960). *J. Am. Chem. Soc.* **82**, 1215–1218.

The Molecular and Crystal Structure of Bis[2-(aminomethyl)pyridine]platinum(II) Dichloride Monohydrate

BY F. D. ROCHON AND R. MELANSON

Département de Chimie, Université du Québec à Montréal, CP 8888, Montréal, Canada H3C 3P8

Abstract

[Pt(C_6H_8N_2)_2]Cl_2.H_2O, [Pt(amp)_2]Cl_2.H_2O [amp = 2-(aminomethyl)pyridine], forms monoclinic crystals with $a = 8\cdot137$ (4), $b = 14\cdot617$ (7), $c = 13\cdot905$ (7) Å, $\beta = 110\cdot66$ (4)°, $Z = 4$ and space group $P2_1/c$. The structure was refined by block-diagonal least-squares analysis to a conventional R factor of 0·031 and R_w =

0·027. The coordination around the Pt atom is square-planar. Some deformations in the chelated rings are observed indicating considerable strain caused by the bidentate ligands. The packing in the crystal consists of alternate layers of [Pt(amp)$_2$]$^{2+}$ and chloride ions (containing also the water molecules) parallel to the bc plane. The different layers are held together by hydrogen bonds.

Introduction

In recent years, we have been studying the interaction between Pt compounds and amine ligands, since the antitumour properties of the Pt complexes were related to an interaction with the bases of DNA. We have undertaken a programme of synthesizing new complexes and of studying their reactions and structures in solution and in the solid state. Here we report the crystal structure of [Pt(amp)$_2$]Cl$_2$.H$_2$O [amp = 2-(aminomethyl)pyridine].

[Pt(amp)$_2$]Cl$_2$ was prepared by the following method. K$_2$PtCl$_4$ and amp were dissolved in 1:1 proportions in water and heated. The precipitate [Pt(amp)Cl$_2$] was filtered out. It was then mixed with amp in a 1:1 proportion in water and heated. When the solution was clear, the water was evaporated and the residue washed with ether. The resulting compound [Pt(amp)$_2$]Cl$_2$ was then recrystallized from water. Crystals of [Pt(amp)$_2$]Cl$_2$.H$_2$O were then obtained.

A set of precession photographs showed that the $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ reflections were systematic absences indicating the space group $P2_1/c$. The cell parameters were obtained by least-squares refinement from the setting angles of 15 automatically centred reflections on a Syntex $P\bar{1}$ diffractometer using graphite-monochromatized Mo $K\alpha$ radiation.

Crystal data

C$_{12}$H$_{18}$Cl$_2$N$_4$OPt, $M_r = 500\cdot28$, monoclinic, $P2_1/c$, $a = 8\cdot137$ (4), $b = 14\cdot617$ (7), $c = 13\cdot905$ (7) Å, $\beta = 110\cdot66$ (4)°, $V = 1548$ (1) Å^3, $Z = 4$, $D_x = 2\cdot147$, $D_m = 2\cdot14$ (2) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 9·88 mm^{-1} and $T = 295$ K.

Collection and reduction of intensity data

The intensity data were collected from a crystal measuring 0·172 × 0·134 × 0·418 mm, elongated along the a axis. 3660 independent reflections were measured in the region of $2\theta < 60°$ by the $2\theta/\theta$ scan technique using Mo $K\alpha$ radiation. During the data collection, three standard reflections were measured after every 47 reflections. Their variations were less than 2% from their respective means. The reflections

(907) for which the intensities were less than $2\cdot5\sigma(I)$ were considered as unobserved. The standard deviation $\sigma(I)$ was calculated as already described (Melanson & Rochon, 1975). An absorption correction based on the equations of the crystal faces was applied to all the reflections. The transmission factors varied from 0·149 to 0·355. The data were then corrected for the Lorentz and polarization effects. The scattering factors of Cromer & Waber (1965) were used for Pt, Cl, O, N and C, those of Stewart, Davidson & Simpson (1965) were used for H. The anomalous-dispersion terms (Cromer & Liberman, 1970) of Pt and Cl were included in the calculations.

Structure determination

The position of the Pt atom was easily located from the three-dimensional Patterson map. The positions of all the other atoms, except the H atoms, were obtained by structure factor and Fourier map calculations. A residual peak was identified as a water molecule. The refinement of the parameters was carried out by block-diagonal least-squares methods. In the early stages of refinement, unit weight was assigned to all observed reflections. Later, individual weights w according to the equation $1/w = a + bF_o + cF_o^2$ were calculated. The constants of the equation were adjusted to make the distribution of $w|\Delta F|^2$ almost constant with respect to $|F_o|$ and $\sin\theta/\lambda$ ($a = 21\cdot622$, $b = -0\cdot3546$ and $c = 0\cdot0015$). All the H atoms, except those in the water molecule, were fixed at their calculated positions (C—H = 0·95 Å and N—H = 0·85 Å) and assigned isotropic temperature factors of 7·0 Å^2. The refinement of the scale factor, the coordinates and anisotropic temperature factors of all the non-hydrogen atoms converged to $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0\cdot031$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2} = 0\cdot027$.* The two H atoms of the water molecule were located on the difference Fourier map and their positional parameters refined. The final difference Fourier map did not show peaks higher than ~0·7 e Å^{-3}.

The calculations were carried out with a Cyber 73 computer and the programs used have already been described (Melanson & Rochon, 1975).

Results and discussion

The refined atomic parameters are listed in Table 1. A labelled diagram of the [Pt(amp)$_2$]$^{2+}$ ion is shown in

Table 1. *Final positional parameters* ($\times 10^4$) *with estimated standard deviations in parentheses*

|	x	y	z
Pt	786·1 (3)	1204·3 (1)	2060·4 (1)
Cl(1)	5802 (3)	−50 (1)	2031 (1)
Cl(2)	6671 (3)	3170 (1)	1246 (1)
N(1)	578 (6)	1142 (3)	3451 (3)
N(2)	3370 (7)	1139 (3)	2915 (3)
N(3)	983 (6)	1316 (3)	662 (3)
N(4)	−1798 (6)	1229 (4)	1201 (3)
C(1)	3606 (8)	724 (4)	3924 (4)
C(2)	2093 (8)	938 (4)	4239 (4)
C(3)	2113 (9)	952 (5)	5240 (4)
C(4)	630 (11)	1155 (6)	5436 (5)
C(5)	−852 (9)	1380 (5)	4647 (5)
C(6)	−862 (9)	1356 (5)	3656 (5)
C(7)	−2094 (9)	962 (5)	115 (4)
C(8)	−528 (8)	1168 (4)	−127 (4)
C(9)	−543 (10)	1232 (5)	−1126 (4)
C(10)	1001 (11)	1467 (5)	−1290 (5)
C(11)	2514 (10)	1634 (5)	−477 (5)
C(12)	2429 (9)	1553 (4)	489 (4)
O	4926 (8)	2873 (3)	2871 (4)
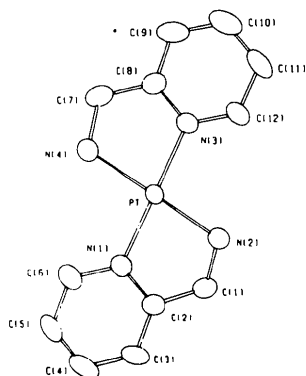
Fig. 1. Labelled diagram of the $[Pt(amp)_2]^{2+}$ ion.
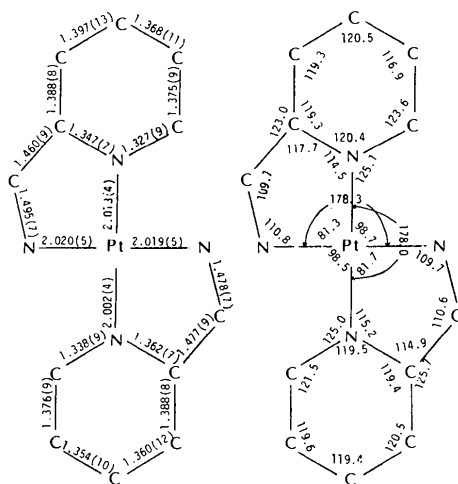
Fig. 2. Bond lengths (Å) and bond angles (°) within the $[Pt(amp)_2]^{2+}$ cation. The standard deviations are 0·2 to 0·4° for angles involving the Pt atom and 0·4 to 0·7° for other atoms.

Fig. 1. The bond lengths and angles within the ion are shown in Fig. 2.

As expected, the bidentate ligands are bonded to the Pt atom through the two N atoms forming a chelate. The coordination around the Pt atom is square-planar. The weighted best plane was calculated through the five atoms. The deviations from this plane are: Pt 0·0000 (2), N(1) −0·0368 (5), N(2) 0·0298 (5), N(3) −0·0336 (4), and N(4) 0·0300 (5) Å. The angles around Pt are close to the expected 90 and 180° but there are some distortions. The N(1)–Pt–N(2) and N(3)–Pt–N(4) angles (81·7, 81·3°) are smaller than the N(1)–Pt–N(4) and N(2)–Pt–N(3) angles (98·5, 98·7°). A considerable strain caused by the bidentate ligands is responsible for these deviations from the ideal square-planar coordination. Similar deformations around the Pt atom have been observed in other five-membered chelated rings (Iball, MacDougall & Scrimgeour, 1975; Drew, Riedl & Rodgers, 1972; Melanson & Rochon, 1975).

The Pt–N bond lengths (2·00–2·02 Å) are normal and agree well with the published data (Milburn & Truter, 1966; Melanson & Rochon, 1975, 1976, 1977, 1978*a,b*).

The two pyridine rings are planar. C(1) is also in the plane containing N(1), but C(7) is slightly out of the plane containing N(3) (0·07 Å). The two methylene C atoms are on the same side of the Pt square plane (0·54 and 0·52 Å). The angles between the Pt plane and the two pyridine planes are 15·0 and 164·9°. The angle between the two pyridine rings is 150·2°. Therefore the whole ion is close to being planar.

The bond lengths in the ligands agree well with the published data on Pt–pyridine complexes (Melanson & Rochon, 1976, 1977, 1978*b*). It is interesting to observe that the C–C (1·477, 1·460 Å) and C–N (1·478, 1·495 Å) bonds involving the methylene groups are of the same length. Exocyclic C–C distances of 1·47–1·50 Å were also observed in the references mentioned above.

The bond angles within the pyridine rings are normal but there are some deformations in the chelated rings indicating considerable strain caused by the bidentate ligands. The Pt–N(1)–C(2) and Pt–N(3)–C(8) angles (115·2, 114·5°) are smaller than the Pt–N(1)–C(6) and Pt–N(3)–C(12) angles (125·0, 125·1°). The angles around C(2) and C(8) also show the same deformations.

A packing diagram of the crystal is shown in Fig. 3. The complex ions which are almost planar are parallel to the *ac* plane. The packing consists of rows of cations which are parallel to the *bc* plane and separated by rows containing the water molecules and the chloride ions. The environments of the water molecules and of the −NH₂ groups were closely examined for possible hydrogen bonding. N(2) is not involved in hydrogen bonds, but the two H atoms of N(4) are hydrogen

Table 2. *Distances and angles involved in hydrogen bonds*

	Transformation (on third atom)	Distance (Å)		Angle (°)
N(4)—H···Cl(1)	$-x,y,z$	3·199 (6)	Pt—N(4)···Cl(1)	114·6 (2)
			C(7)—N(4)···Cl(1)	108·1 (4)
N(4)—H···Cl(2)	$-x,y,z$	3·108 (6)	Pt—N(4)···Cl(2)	110·2 (2)
			C(7)—N(4)···Cl(2)	109·6 (4)
O—H···Cl(1)	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	3·103 (5)	O—H···Cl(1)	173·1 (3)
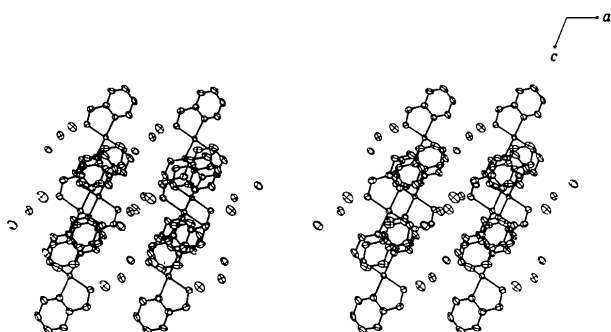
Fig. 3. Stereoscopic diagram of the packing in the [Pt(amp)₂]-Cl₂.H₂O crystal.

bonded to the Cl atoms. The N···Cl distances are 3·108 and 3·199 Å (Table 2) and the angles are favourable (~109°). The water molecules form hydrogen bonds with Cl(1) only. The O···Cl distance is 3·103 Å. Therefore the structure consists of alternate layers of cations and anions. The latter layers also contain the water molecules. The layers are parallel to the *bc* plane and are held together by hydrogen bonds.

References

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

DREW, M. G. B., RIEDL, M. J. & RODGERS, J. (1972). *J. Chem. Soc. Dalton Trans.* pp. 234–237.

IBALL, J., MacDOUGALL, M. & SCRIMGEOUR, S. (1975). *Acta Cryst.* B**31**, 1672–1674.

MELANSON, R. & ROCHON, F. D. (1975). *Can. J. Chem.* **53**, 1139–1143.

MELANSON, R. & ROCHON, F. D. (1976). *Can. J. Chem.* **54**, 1002–1006.

MELANSON, R. & ROCHON, F. D. (1977). *Acta Cryst.* B**33**, 3571–3573.

MELANSON, R. & ROCHON, F. D. (1978a). *Acta Cryst.* B**34**, 941–943.

MELANSON, R. & ROCHON, F. D. (1978b). *Acta Cryst.* B**34**, 1125–1127.

MILBURN, G. H. W. & TRUTER, M. R. (1966). *J. Chem. Soc. A*, pp. 1609–1616.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.