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The Crystal and Molecular Structure of *trans*-Bis(dimethylamine)diammineplatinum(II) Chloride

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The crystal structure of *trans*-bis(dimethylamine)diammineplatinum(II) chloride, *trans*-$[Pt(NH_3)_2(NH(CH_3)_2)_2]Cl_2$, has been determined by three-dimensional X-ray methods. The compound crystallizes in a triclinic unit cell of symmetry $P\bar{1}$ with dimensions $a = 7.414$ (3) Å, $b = 7.937$ (2) Å, $c = 5.481$ (2) Å, $\alpha = 92.32$ (2)°, $\beta = 110.40$ (4)°, and $\gamma = 106.72$ (4)°. There is one molecule per unit cell; the measured and calculated densities are 2.24 ± 0.04 and 2.26 g/cm³, respectively. A total of 1010 independently observed intensities were obtained by film methods. The structure was refined by the method of least squares to give a discrepancy factor of 0.108. The platinum atoms are located on a crystallographic center of symmetry. The approximately square-planar $Pt(NH_3)_2(NH(CH_3)_2)_2{}^{2+}$ cations form layers with the chloride ions by means of an extensive hydrogen-bonding system. There are no atoms immediately above or below the square-planar cations.

Introduction

A number of square-planar complexes of the type $Pt(A)_2(B)_2$ have been shown to undergo photochemical reactions leading to *cis–trans* isomerization.[3] As one phase of our investigation of the relationship of the spectral and photochemical properties of such complexes, the molecular and crystal structure of *trans*-bis(dimethylamine)diammineplatinum(II) chloride, *trans*-$[Pt(NH_3)_2(NH(CH_3)_2)_2]Cl_2$, has been determined.

Experimental Section

Preparation.—*trans*-$[Pt(NH_3)_2(NH(CH_3)_2)_2]Cl_2$ was prepared by the method of Jorgensen.[4] Single crystals suitable for the X-ray investigation were obtained by recrystallization from an ethanol–water solution on slow evaporation. *Anal.* Calcd for $[Pt(NH_3)_2(NH(CH_3)_2)_2]Cl_2$: C, 12.31; H, 5.13; N, 14.35. Found: C, 12.42; H, 4.93; N, 14.14. The crystals decompose slowly on exposure to a highly humid atmosphere.

X-Ray Diffraction.—A crystal of parallelepiped habit with dimensions of 0.14 × 0.16 × 0.20 mm (parallel to c) was mounted in a thin-walled glass capillary oriented on the c axis and was investigated using nickel-filtered Cu Kα radiation. Data from the $hk0$–$hk4$ layers were collected by equiinclination, multiple-film Weissenberg techniques. Two sets of films were obtained for each layer so that all data could be obtained from the lower half of the film. Kodak No-Screen Medical film was used to record data at about 25°. No special absences were observed on the film and a subsequent analysis of the cell dimensions by the method of Delaunay[5] showed the crystal to belong to one of the triclinic space groups.

The unit cell parameters at 25° are $a = 7.414 \pm 0.003$ Å, $b = 7.937 \pm 0.002$ Å, $c = 5.481 \pm 0.002$ Å, $\alpha = 92.32 \pm 0.02°$, $\beta = 110.40 \pm 0.04°$, and $\gamma = 106.72 \pm 0.04°$. These values were determined from a least-squares fit[6] for 40 values of sin θ measured from a set of Weissenberg photographs with superimposed Al powder lines. Ten reflections were chosen from each nonzero layer. The estimated error is the estimated deviation (σ) from this least-squares analysis.

The observed density, obtained by flotation in a mixture of iodomethane and carbon tetrachloride, was 2.24 ± 0.04 g/cm³ which agrees with a value of 2.265 g/cm³ calculated for $Z = 1$, $M = 390.18$, and $V = 285.9$ Å³. The choice of the $P\bar{1}$ rather than the $P1$ space group was assumed at first and verified by the refinement.

All intensities from the two different orientations were estimated visually by comparison with a standard set of intensities prepared from the crystal used to collect the data. In a number of cases the reflections showed streaking parallel to the rotation axis; this streaking did not increase measurably during the collection of intensity data, and it did not prevent the obtaining of a reading for each reflection. A modification of one of the California Institute of Technology's CRYRM programs[7] was then applied to the two sets of data, resulting in corrections for Lorentz and polarization factors, assignment of standard deviations for each intensity, weighted averaging of multiple readings, interlayer scaling on a time basis, and intralayer scaling using $(3.85)^{\sec \nu_n}$, where ν_n is the equiinclination angle of nth layer and 3.85 is the film-to-film factor for the zero-layer films. Standard propagation of error methods were used to obtain the $\sigma(F)$ values from the σ for the average I values, which were in turn obtained from the σ's for the individual multiple readings. Equivalent reflections were averaged[8] to yield 1010 independent reflections. It should be noted that in the index range covered no reflections were too weak to be estimated, due to the symmetry-fixed presence of the Pt atom at (0, 0, 0).

For the purpose of calculating absorption effects, the crystal was considered to be a cylinder with $R = 0.0093$ cm. The resulting value of $\mu R = 2.54$ indicated that absorption was appreciable and consequently equiinclination absorption corrections[9] were applied to the intensities and their $\sigma(I)$'s. These absorption factors for F varied from about 2.8 to 6.3 for the zero layer and from 3.14 to 8.78 for the fourth layer.

Refinement was also done using a set of reflections which had been corrected for absorption by using the absorption factors for a spherical sample of radius 0.085 mm. This refinement did not change any of the positional parameters by more than one standard deviation. The parameters reported in this article are from the intensity data corrected with the cylindrical approximation.

Calculations were performed on the IBM 7040 using UACP[6] Fourier and bond distance programs and highly modified versions of the Gantzel–Sparks–Trueblood and Busing–Martin–Levy full-matrix, least-squares programs. Atomic scattering factors for neutral atoms were taken from "International Tables of X-Ray

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(1) Participant in Summer 1968 College Teacher Research Participation Program (NSF GY-4101).

(2) Alfred P. Sloan Research Fellow.

(3) P. Haake and T. A. Hylton, *J. Am. Chem. Soc.*, **84**, 3774 (1962); V. Balzani, V. Carassiti, L. Moggi, and N. Sabbatini, *Inorg. Chem.*, **4**, 1247 (1965); J. E. Martin, Ph.D. Dissertation, University of Arkansas, 1968.

(4) S. M. Jorgensen, *Z. Anorg. Allgem. Chem.*, **48**, 374 (1906).

(5) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965, p 530.

(6) University of Arkansas Crystallographic Program (UACP).

(7) D. J. Duchamp, "User's Guide to the CRYRM Crystallographic Computing Systems," California Institute of Technology, Pasadena, Calif., 1964. The equation for the standard deviations assigned to the intensity readings is given by B. D. Sharma and J. F. McConnell, *Acta Cryst.*, **19**, 797 (1965).

(8) $F_{av} = [\Sigma(F^2/\sigma^2(F^2))/\Sigma(1/\sigma^2(F^2))]^{1/2}$; $\sigma_{av} = [1/\Sigma(1/\sigma^2(F^2))]^{1/2}$.

(9) "International Tables of X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1965, p 295.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS ($\times 10$) FOR *trans*-$[Pt(NH_3)_2(NH(CH_3)_2)_2]Cl_2$

TABLE II

ATOMIC POSITIONAL AND THERMAL PARAMETERS FOR *trans*-$[Pt(NH_3)_2(NH(CH_3)_2)_2]Cl_2$[a]

	x	*y*	*z*	*B*, Å^2
Pt	0	0	0	
Cl	−0.2863 (11)	0.2702 (9)	−0.6051 (18)	
N(1)	−0.2677 (34)	0.0545 (32)	−0.1112 (55)	5.2 (4)
N(2)	0.1055 (24)[b]	0.2304 (25)[b]	−0.1317 (44)[b]	4.8 (3)
C(1)	0.2474 (24)[b]	0.2339 (25)[b]	−0.2654 (44)[b]	5.8 (5)
C(2)	0.1972 (24)[b]	0.3879 (25)[b]	0.0749 (44)[b]	5.8 (5)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.0229 (2)	0.0169 (2)	0.0390 (7)	0.0066 (2)	0.0128 (3)	0.0046 (2)
Cl	0.0364 (16)	0.0221 (10)	0.0657 (44)	0.0089 (10)	0.0121 (18)	0.0040 (15)

[a] Numbers in parentheses in all tables are estimated standard deviations in the least significant digits. The anisotropic temperature factor was in the form: $T_i = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}kh + 2\beta_{13}hl + 2\beta_{23}kl)_i]$. [b] Estimated standard deviations for the positional parameters of the atoms in the rigid group are those of the origin of the rigid group.

TABLE III

DISTANCES AND ANGLES FOR *trans*-$Pt(NH_3)_2(NH(CH_3)_2)_2^{2+}$

Atoms	Distance, Å	Atoms	Angle, deg
	Bonded distances		
Pt–N(1)	2.042 (27)	N(1)–Pt–N(2)	85.2 (10)
Pt–N(2)	2.038 (21)	Pt–N(2)–C(1)	117.0 (15)
N(2)–C(1)	1.472[a]	Pt–N(2)–C(2)	113.1 (8)
N(2)–C(2)	1.472[a]	C(1)–N(2)–C(2)	108.0[a]
	Nonbonded contacts		
Cl···N(1)	3.245 (30)	Cl–N(1)–Cl[b]	114.7 (4)
Cl···N(1)[b]	3.265 (30)	Cl–N(1)–Cl[c]	98.4 (4)
Cl···N(1)[c]	3.344 (30)	Cl[c]–N(1)–Cl[c]	107.2 (1)
Cl···N(2)	3.257 (30)		

[a] Parameter was fixed by the rigid-group assumption. [b] The coordinates of the chlorine atom are (x, y, $z + 1$) with respect to those reported. [c] The coordinates of the chlorine atom are ($-x - 1$, $-y$, $-z - 1$) with respect to those reported.

Crystallography," Vol. III. Pt and Cl scattering factors were corrected for the real portion ($\Delta f'$) of anomalous dispersion.[10]

In the least-squares refinement, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and w is the weight defined as $1/\sigma^2(F_o)$, where $\sigma(F_o)$ was the value assigned by the data processing program.

Solution and Refinement of the Structure

Since $Z = 1$, the Pt atom must be positioned on a crystallographic center of symmetry and the unique part of the molecule is half the formula unit. A three-dimensional Patterson function revealed the position of the chlorine atom and a three-dimensional Fourier map clearly revealed the position of the carbon and nitrogen atoms. A structure factor calculation at this point had

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[10] Values obtained from D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

an unweighted discrepancy index $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.23$.

Adjustment of the atomic parameters was made by calculating a three-dimensional difference-Fourier map and led to $R_1 = 0.201$. All subsequent refinements were carried out using a full-matrix least-squares procedure. The initial two-cycle calculation refined only atomic parameters and gave $R_1 = 0.185$. A two-cycle refinement of scale factor, atomic parameters, and isotropic temperature factors led to $R_1 = 0.154$. A similar two-cycle refinement with anisotropic temperature factors for Pt and Cl yielded $R_1 = 0.120$.

Up to this point the absorption corrections had not been made since absorption normally affects temperature factors more than atomic positions for structures of this type.[11]

After the approximate corrections described in the Experimental Section were made, further refinement using the corrected intensities led to $R_1 = 0.108$. The weighted discrepancy factor

$$R_2 = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$$

where $w = 1/\sigma(F)^2$, was 0.129. Inclusion of anisotropic temperature factors for the C and N atoms yielded $R_1 = 0.106$ and $R_2 = 0.127$ which, for the 1010 reflections used in the refinement, is no significant improvement if tested by the statistical method outlined by Hamilton.[12] The nitrogen and carbon atoms in the dimethylamine species were then treated as a rigid group and refinement was continued as follows. First, all atoms were considered to have isotropic temperature factors and different scaling factors were used for each layer. Except for the fourth layer, all of the layer scale factors were within 2% of the time-based factors. That for the fourth was approximately 11% higher. Then the scaling factors were held constant and the Pt and Cl atoms were assigned anisotropic temperature factors. The final values of R_1 and R_2 are 0.108 and 0.129, respectively. An analysis of the final least-squares cycle showed the weighting scheme to be reasonable; *i.e.*, there was no recognizable dependence on F or θ or combinations of the two. No attempt was made to determine the positions of the hydrogen atoms. The final parameters obtained from the rigid group refinement agreed within one standard deviation of those obtained from the unconstrained refinement, with the main exception being one N–C bond which was 0.06 Å shorter than expected in the unconstrained model.

A final difference Fourier map showed no peak >2.0 $e^-/Å^3$ except for a small region around the Pt atom. None of the observed peaks could be interpreted as unexpected or misplaced atoms. On the final cycle of least-squared refinement, the maximum shifts in positional and isotropic and anisotropic thermal parameters were 0.09σ, 0.04σ, and 0.03σ, respectively. The standard deviation of an observation of unit weight was 1.45.

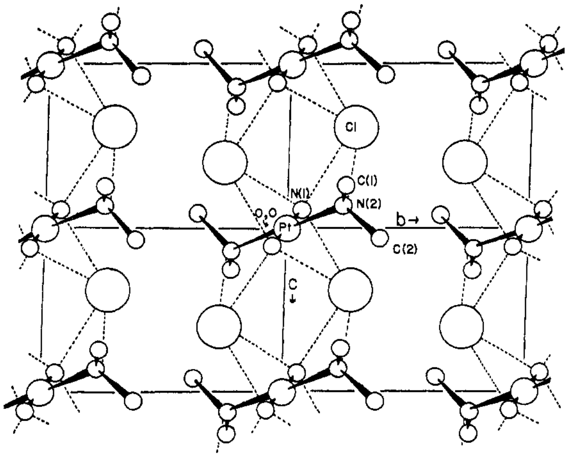

Figure 1.—The view of several unit cells down the *a* axis, showing the layered nature of the structure. The dotted lines indicate probable hydrogen bonds.

Table I lists the observed and calculated structure amplitudes (×10), F_o and F_c, respectively. Table II gives the positional and thermal parameters obtained from the last cycle of the least-squares refinement along with their standard deviations as estimated from the least-squares program.

Description of Structure

The bond distances and angles in the *trans*-$Pt(NH_3)_2(NH(CH_3)_2)_2^{2+}$ cation and their estimated standard deviations are listed in the first section of Table III. As expected, the nitrogen atoms are seen to vary only a few degrees from square-planar symmetry. The acute N–Pt–N angle may be related to the fact that both of the N atoms involved are likely H bonded to a common chloride ion (see below). The planarity of the square is fixed by symmetry and the Pt–N bond lengths agree with values previously reported.[13] Other nonbonded distances of interest are listed in the last section of Table III. The main feature of the structure is not the configuration of the platinum complex ion, which shows no significant deviation from expected angles and distances, but is the evidence for an extensive hydrogen-bonding system which creates a layered structure and the lack of any atoms immediately above and below the platinum atom. The chloride ion which appears to be directly above the Pt in Figure 1 is actually displaced along x to a distance of 4.29 Å from the Pt, as seen better in Figure 2.

The chlorine–nitrogen distances noted in Table III would indicate that considerable hydrogen bonding occurs between the chloride ions and the amino and dimethylamine groups. If all of the chlorine–nitrogen distances <3.4 Å are considered to contribute to such bonding, the crystal packing can be described as layers of cations and anions held together by extensive intralayer hydrogen bonding. These layers lie parallel to the [010] face of the crystal. Within these layers each chloride ion appears to be hydrogen bonded to four

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[11] R. C. Srivastava and E. C. Lingafelter, *Acta Cryst.*, **20**, 918 (1966); P. Werner, *Acta Chem. Scand.*, **18**, 1851 (1964).

[12] W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

[13] "Interatomic Distances Supplement," The Chemical Society, London, 1956–1959, p M57s; "Interatomic Distances," The Chemical Society, London, 1958, p M100.

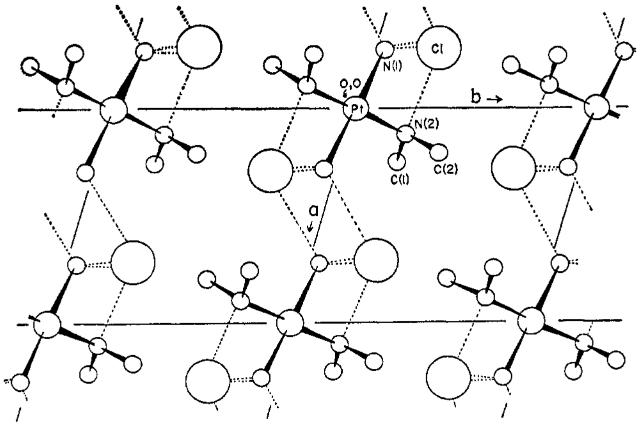

Figure 2.—The view of several unit cells down the *c* axis, showing the layered nature of the structure. The dotted lines indicate probable hydrogen bonds. The chloride ions are almost exactly midway in elevation between the N(1) atoms. The double dotted line between Cl and N(1) indicates probable hydrogen bonds to the nitrogen from chloride ions above and below.

different nitrogen atoms of three different cations. All three hydrogen atoms of the ammonia ligand and the lone hydrogen of the amine nitrogen appear to participate in hydrogen bonding. A careful study of a model of the structure showed that for one orientation of the ammonia ligand all of these hydrogen bonds have reasonable geometries. The Cl–N–Cl bond angles of the H-bonded system are given in Table III. Interlayer interaction appears to be of the weaker van der Waals type. This description is substantiated by the observation that a cleavage plane lies parallel to the [010] face, which is usually the well-developed face of the crystal. The structure can be visualized by examining Figures 1 and 2 which present projections along the *a* and *c* axes respectively.

Table IV

Angles Made by Pt–N Bonds with the Crystal Axes[a]

Bond	Angle (deg) with— *a* axis	*b* axis	*c* axis
Pt–N(1)	158.3 (8)	59.8 (8)	88.2 (8)
Pt–N(2)	75.6 (6)	36.8 (6)	121.6 (6)

[a] All angles are measured from positive axes.

Finally, since the major purpose of this investigation is to provide information for the interpretation of oriented single-crystal experiments, the angles that the Pt–N bonds in the cation make with the respective crystal axes are presented in Table IV. The lack of significant intermolecular interactions along the axial direction of the square-planar cation would suggest that the molecular cation be treated as an "oriented-gas" ion in subsequent spectroscopic investigations.

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The Chemistry of Alane. XIV.[1]
The Synthesis of Dimethylaminodichloroalane[2]

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Dimethylaminodichloroalane was prepared by a variety of methods. Careful purification of the product prepared by the reaction of $(CH_3)_2NAlH_2$ with $HgCl_2$ in diethyl ether showed that $(CH_3)_2NH_2Cl$ was a by-product impurity. This suggests that the evolution of H_2 in this reaction is the result not of the decomposition of unstable HgH_2 but of the reaction of HCl, produced in the decomposition of an intermediate HHgCl, with the hydridic alane hydrogens.

During the course of the attempted synthesis of various alane derivatives it became necessary to prepare dimethylaminodichloroalane as an intermediate. Utilizing a variation of one of the two procedures reported in the literature,[4] however, did not produce material with the reported properties. In order to clarify this situation, the synthesis of dimethylaminodichloroalane was reexamined in detail.

Experimental Section

All reagents were handled and all filtrations were performed in a nitrogen-atmosphere vacuum drybox, and all reactions were conducted under dry nitrogen. All solvents were purified and dried by refluxing with $LiAlH_4$, distilling, and storing over $LiAlH_4$ (benzene) or over LiH (diethyl ether and tetrahydrofuran). Dimethylamine and HCl were used directly from the cylinders. Lithium dimethylamide was obtained from K & K Laboratories, Plainview, N. Y. All melting points are uncorrected. Quanti-

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[1] Paper XIII: R. Ehrlich and A. R. Young, II, *J. Inorg. Nucl. Chem.*, **30**, 53 (1968).

[2] (a) Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968. (b) This investigation was supported under DA Project No. 1LO13001A91A, AMCMS 5016.11.844.

[3] Industrial Chemicals Research Laboratory, Allied Chemical Corp., Morristown, N J. 07960.

[4] J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 1798 (1961).