The Structure and Absolute Configuration of $(+)_{450}$-*cis*-Dichlorobis(ethylenediamine)platinum(IV) Chloride, $[Pt(C_2H_8N_2)_2Cl_2]Cl_2$

By CHUI FAN LIU and JAMES A. IBERS

The crystal and molecular structure of $(+)_{450}$-*cis*-dichlorobis(ethylenediamine)platinum(IV) chloride, $[Pt(C_2H_8N_2)_2Cl_2]Cl_2$, has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques to a final R factor on F of 4.3% for 1564 reflections above background. The colorless crystals belong to space group C_2^3-C2 of the monoclinic system. The cell constants are: $a = 10.668$ (14), $b = 10.687$ (13), $c = 11.339$ (14) Å, and $\beta = 101.21$ (2)°. The calculated density of 2.44 g/cm^3 for four formula units in the unit cell agrees well with the observed density of 2.45 (1) g/cm^3. The structure of the complex ion is that of a slightly distorted octahedron. The coordinated chlorines occupy *cis* positions. The average Pt–Cl distance is 2.306 (4) Å and the average Pt–N distance is 2.057 (6) Å. The absolute configuration of the complex is Λ, and the conformations of the two chelate rings are $\lambda\lambda$.

Introduction

Although attempts have been made previously,[1] it was not until recently that the *cis*-dichlorobis(ethylenediamine)platinum(IV) ion had been prepared and resolved into optical isomers.[2] The resolved complex was found to be exceedingly stable toward racemization. Reactions between this complex ion and diamines are stereoselective. When $(+)_{450}$-*cis*-dichlorobis(ethylenediamine)platinum(IV) ion is treated with ethylenediamine, optically pure *d*-tris(ethylenediamine)platinum(IV) ion is obtained.[3] The optical stability of the resolved isomer and the stereoselectivity of its reactions distinguish the platinum(IV) complex from its cobalt(III) analog. This platinum(IV) compound seems quite desirable for certain reaction mechanism studies. Although the absolute configurations of a few cobalt(III) complexes have been determined by X-ray methods, no such determinations on the platinum(IV) compounds have appeared in the literature. In the present paper we report the solution of the structure and the determination of the absolute configuration of $(+)_{450}$-*cis*-dichlorobis(ethylenediamine)platinum(IV) chloride. The compound was prepared by a ring-closure reaction[3] and resolved into the optical isomers through the crystallization of the *l*-antimonyl tartrate salt.[2] The crystals used in the present investigation were analyzed. *Anal.* Calcd for PtC$_4$H$_{16}$N$_4$Cl$_4$: C, 10.50; H, 3.50; N, 12.25; Cl, 31.06; Pt, 42.68. Found: C, 10.83; H, 3.55; N, 12.00; Cl, 30.38; Pt, 43.24. The ORD curve of this isomer is shown in Figure 1.

Collection and Reduction of the X-Ray Data

Optical examination and preliminary X-ray photography indicated that the colorless crystals belong to the monoclinic system. The systematic absences that were observed on Weissenberg and precession photographs are *hkl*, $h + k \neq 2n$. Since the compound is optically active the space group must be C2, rather than Cm or C2/m. The lattice constants, obtained by

least-squares refinement[4] of the setting angles of 21 reflections which had been carefully centered on a Picker four-circle automatic X-ray diffractometer, are $a = 10.668$ (14), $b = 10.687$ (13), $c = 11.339$ (14) Å, $\beta = 101.21$ (2)° (λ(Mo Kα_1) 0.70930 Å, 25°). The calculated density of 2.44 g/cm^3 for four formula units in the cell agrees with the density of 2.45 $\pm$ 0.01 g/cm^3 measured by the flotation method in a mixture of carbon tetrachloride and carbon tetrabromide. Thus, no crystallographic symmetry conditions need be imposed on the ions.

The procedures used in data collection and processing parallel those described previously.[4,5] The crystal used in data collection was an irregular, thick plate with the approximate dimensions of 0.17 mm × 0.15 mm × 0.11 mm. The crystal was mounted and aligned along the *b* axis, but this orientation was changed by arbitrarily resetting the arcs of the goniometer head to zero before data collection began. Mo Kα radiation was used, and the takeoff angle of the X-ray tube was 1.3°. The diffracted beams were filtered through a 3.0-mil Zr filter. Data were collected by the θ–2θ scan technique. A symmetrical scan range of 2.6° in 2θ was used for all reflections. Stationary crystal, stationary counter background counts of 10 sec were taken at each end of the scan. The scan rate was 1° of 2θ/min. The scintillation counter was 31 cm from the crystal and had an aperture of 7 × 7 mm. The pulse height analyzer was set to admit about 90% of the Mo Kα peak.

Intensity data were collected for two members of the form (*hkl*) of this monoclinic crystal (*hkl*, $h\bar{k}l$) out to a 2θ value for Mo Kα of 45°. The hkl data set was collected first. A total of 1660 intensities were measured. As a general check on electronic and crystal stability the intensities of four standard reflections were measured periodically during the collection of the intensity data. After the collection of the hkl reflections was complete the (020) standard reflection slowly decreased in intensity, the total decrease being 26% of the original

(1) L. F. Heneghan and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **75**, 1840 (1953).
(2) C. F. Liu and J. Doyle, *Chem. Commun.*, 412 (1967).
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(4) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
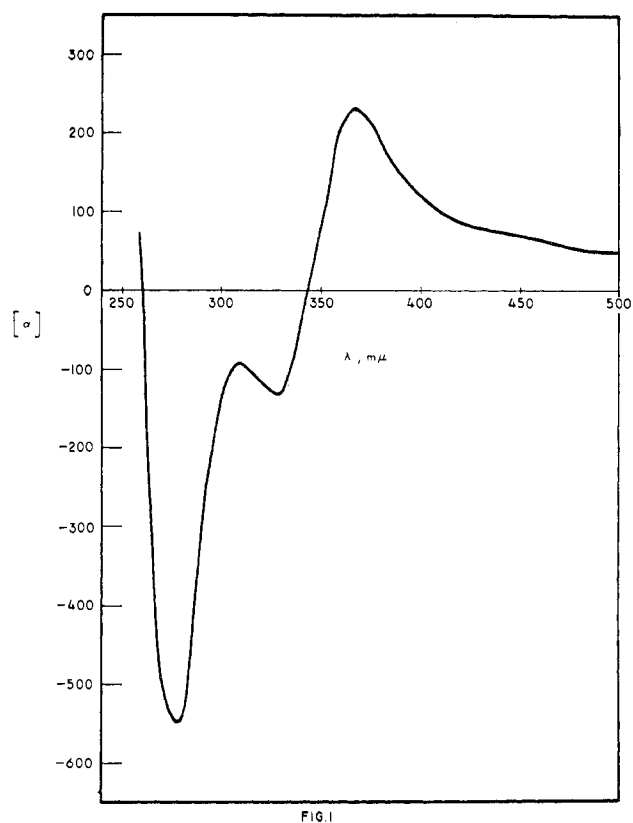(5) R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

Figure 1.—Specific rotation of $(+)_{450}$-*cis*-dichlorobis(ethyl-enediamine)platinum(IV) chloride.

intensity. The other standard reflections stayed essentially constant. This decrease in intensity was the result of crystal rather than electronic instability. Therefore, a necessarily approximate correction was made to bring the *hkl* reflections to the same scale. The percentage decrease in the standard (020) intensity at the time of collection of a particular reflection is readily obtained by graphical interpolation. The actual percentage decrease in intensity of this specific reflection as a result of decomposition and movement was taken to be that fraction of the decrease in (020) intensity which corresponds to the projection of the index vector of the reflection on the *b* axis. The data were processed in the manner previously described.[4,5] The value of *p* used in the estimation of standard deviations of the intensities was 0.05.

For an absorption correction, the ten crystal faces were indexed by optical goniometry and their dimensions were carefully measured. The ten crystal faces are 001, 00$\bar{1}$, $\bar{1}$1$\bar{1}$, $\bar{1}$11, 1$\bar{1}\bar{1}$, 11$\bar{1}$, $\bar{1}\bar{1}$1, 111, $\bar{2}\bar{2}$1, and 1$\bar{1}$1. The absorption correction was carried out by numerical methods[6] with a linear absorption coefficient of 111.8 cm^{-1}. The transmission coefficients were found to range from about 0.25 to 0.50. Of the 1660 reflections, 1564 were above background $(F^2 > 3\sigma(F^2))$ and only these reflections were used in the refinement.

(6) In addition to various local programs for the CDC 6400 computer local modifications of the following programs were used in this work: FORDAP Fourier program by Zalkin, ORFLS and ORFFE least-squares and error function programs by Busing and Levy, ORTEP thermal ellipsoid plotting program by Johnson, and GONO9 absorption correction program by Hamilton.

Solution and Refinement of the Structure

Initial calculations were made using the 779 $\overline{hkl}$ intensities above background. Values of the atomic coordinates of the platinum atom and the two coordinated chlorine atoms were obtained from a three-dimensional Patterson function. These parameters were refined by usual full-matrix least-squares procedures with minimization of the function $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and where the weights w are taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors calculated by Cromer and Waber[7] were used. This refinement of the scale factor, positional parameters, and isotropic thermal parameters for the Pt and the Cl atoms led to a conventional R factor $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.15 and a weighted R factor $R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$ of 0.18. A difference Fourier map revealed the positions of one of the chlorine anions and the two ethylenediamine ligands. Refinement of the positional and the isotropic thermal parameters brought the conventional R factor down to 0.08 and the weighted R' factor down to 0.094. A further difference Fourier map at this point led to the position of the other chlorine anion. Next, the effects of anomalous dispersion were introduced in F_c to determine the absolute configuration of the complex.[8] The values of $\Delta f'$ and $\Delta f''$ for Pt and Cl were those given by Cromer.[9] Two refinements were carried out using the

Table I

Calculated and Observed Structure Amplitudes for the Two Absolute Configurations of $(+)_{450}$-*cis*-Dichlorobis(ethylenediamine)platinum(IV) Chloride

h	k	l	$|F_o|^a$	Λ confign $|F_c|^a$	Δ confign $|F_c|$
-2	-2	-3	73.07	77.52	56.91
2	2	3	56.81	61.25	73.08
-1	-3	-3	62.84	62.61	75.33
1	3	3	74.78	70.89	67.18
-3	-5	-1	100.77	102.01	93.06
3	5	1	96.08	95.81	99.56
-3	-1	-6	81.34	83.34	74.54
3	1	6	72.80	73.88	83.57
-2	-6	-4	54.81	54.95	62.34
2	6	4	62.55	60.41	57.70
-7	-3	3	99.07	97.25	106.14
7	3	-3	104.63	103.58	100.35
-2	-2	-9	66.26	65.23	71.04
2	2	9	72.32	70.41	66.17

^{a} At this stage in the refinement no anisotropy in thermal vibrations had been introduced and no account had been taken of contributions from the hydrogen atoms. Hence, these numbers differ slightly from those in Table III.

1564 $\overline{hkl}$ and *hkl* reflections. In the first refinement no change was made in the model. This refinement converged to an R factor of 0.075 and a weighted R' factor of 0.101. In the second refinement the y coordinates of all atoms were reversed in sign in order to test the other possible configuration. This refinement converged to

(7) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(8) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

(9) D. T. Cromer, *ibid.*, **18**, 17 (1965).

TABLE II

FINAL PARAMETERS FOR $(+)_{450}$-*cis*-DICHLOROBIS(ETHYLENEDIAMINE)PLATINUM(IV) CHLORIDE

Positional and Isotropic Thermal Parameters

Atom	x	y	z	B, Å²
Pt	0.23162 (5)[b]	0	0.21409 (5)	
Cl1[c]	0.1901 (6)	0.1930 (6)	0.2880 (6)	
Cl2[c]	0.1807 (6)	0.0686 (6)	0.0175 (5)	
ClA[d]	0.3228 (9)	−0.3948 (10)	0.3146 (9)	
ClB[d]	$1/2$	0.1090 (7)	$-1/2$	
ClC[d]	$1/2$	0.2308 (7)	0	
N1	0.4177 (15)	0.0504 (14)	0.2203 (14)	1.69 (28)
N2	0.0471 (16)	−0.0598 (15)	0.2138 (14)	2.01 (28)
N3	0.2848 (15)	−0.1652 (15)	0.1468 (13)	1.69 (28)
N4	0.2666 (19)	−0.0706 (19)	0.3869 (17)	3.23 (37)
C1	0.4921 (22)	−0.0626 (21)	0.2056 (19)	2.73 (39)
C2	0.0511 (22)	−0.1471 (21)	0.3145 (20)	2.82 (41)
C3	0.4123 (23)	−0.1466 (22)	0.1098 (21)	2.94 (42)
C4	0.1398 (23)	−0.0940 (22)	0.4255 (21)	3.31 (44)
N1H1	0.4221	0.1137	0.1536	1.7
N1H2	0.4532	0.0908	0.3032	1.7
N2H1	−0.0115	0.0166	0.2251	1.7
N2H2	0.0075	−0.1022	0.1329	1.7
N3H1	0.2944	−0.2354	0.2130	1.7
N3H2	0.2200	−0.1943	0.0738	1.7
N4H1	0.3185	−0.1523	0.3931	3.0
N4H2	0.3194	−0.0057	0.4471	3.0
C1H1	0.5193	−0.1130	0.2901	3.0
C1H2	0.5798	−0.0361	0.1737	3.0
C2H1	0.0891	−0.2372	0.2897	3.0
C2H2	−0.0443	−0.1622	0.3323	3.0
C3H1	0.3986	−0.1013	0.0253	3.0
C3H2	0.4610	−0.2356	0.1096	3.0
C4H1	0.1008	−0.0078	0.4555	3.5
C4H2	0.1517	−0.1621	0.5007	3.5

Anisotropic Thermal Parameters

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.00353 (7)	0.00360 (7)	0.00408 (6)	−0.00008 (9)	0.00042 (4)	0.00054 (9)
Cl1[c]	0.0068 (6)	0.0063 (6)	0.0113 (7)	0.0017 (5)	0.0010 (5)	−0.0024 (5)
Cl2[c]	0.0069 (6)	0.0096 (6)	0.0064 (5)	−0.0022 (5)	−0.0012 (4)	0.0031 (5)
ClA[d]	0.0138 (10)	0.0216 (13)	0.0152 (9)	0.0103 (10)	0.0079 (8)	0.0118 (10)
ClB[d]	0.0056 (7)	0.0075 (7)	0.0044 (6)	0	−0.00002 (56)	0
ClC[d]	0.0060 (8)	0.0066 (7)	0.0052 (6)	0	0.0005 (5)	0

[a] The form of the anisotropic thermal ellipsoid is $\exp[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. [b] Numbers in parentheses here and in succeeding tables are the estimated standard deviations in the least significant digits. [c] Coordinated chlorine. [d] Chloride ions.

an R factor of 0.060 and a weighted R' factor of 0.082. From the calculated and the observed structure amplitudes the absolute configuration of the complex was unambiguously determined to be the one with the y coordinates reversed. All subsequent calculations were done with this configuration. Table I gives the calculated and the observed structure amplitudes of a series of representative reflections of the two mirror image absolute configurations from these two refinements. At this point idealized positions of the hydrogen atoms were calculated by using an N–H distance of 1.03 Å, a C–H distance of 1.11 Å, and H–N–H and H–C–H angles of 109° 28'. These hydrogen atoms were introduced into the refinement but their positional and thermal parameters were held constant. Next, anisotropic thermal parameters were introduced for all atoms other than hydrogen, but the temperature factor of one of the nitrogen atoms became nonpositive-definite (though not significantly). It was decided that fur-

ther refinement would be carried out with only the platinum atom and the chlorine atoms refined anisotropically. The final refinement converged to a conventional R factor of 0.043 and a weighted R' factor of 0.062. Table II summarizes the final values of the positional and thermal parameters with their standard deviations as derived from the inverse matrix. Based on the parameters of Table II the values of $|F_o|$ and $|F_c|$ (in electrons $\times$ 10) for the 1564 reflections above background are given in Table III. A total of 96 reflections which had $F_o^2 < 3\sigma(F_o^2)$ were omitted from the refinement and are omitted from Table III. For these reflections $|F_o^2 - F_c^2| < 2.5\sigma$ (F_o^2). In Table IV we give the root-mean-square amplitudes of vibration for those atoms which were refined anisotropically. An indication of the directions of the vibrations may be obtained from the figures. A final difference Fourier map showed electron densities no higher than 1.4 electrons/Å³ (about 50% of a nitro-
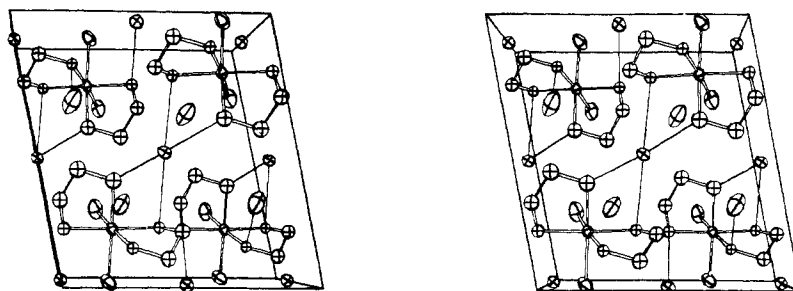
TABLE III

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES ($\times 10$) IN ELECTRONS FOR
$(+)_{450}$-*cis*-DICHLOROBIS(ETHYLENEDIAMINE)PLATINUM(IV) CHLORIDE

TABLE IV

ROOT-MEAN-SQUARE AMPLITUDE OF VIBRATION (Å)

Atom	1	2	3
Pt	0.138 (2)	0.139 (2)	0.168 (2)
Cl1	0.157 (9)	0.206 (8)	0.282 (8)
Cl2	0.161 (9)	0.181 (9)	0.285 (8)
C1A	0.184 (10)	0.219 (10)	0.451 (13)
C1B	0.156 (12)	0.192 (11)	0.208 (10)
C1C	0.174 (11)	0.193 (11)	0.196 (11)

gen atom) in the vicinity of the platinum atom. No abnormal features were observed. A refinement of the same model but employing only the hkl intensities converged to a conventional R factor of 0.036 and a weighted

R' factor of 0.047. However, the final positional and thermal parameters from this refinement are not significantly different from those of the refinement using the entire set of data. There were also no significant differences in the bond distances and bond angles. This lower R factor probably arises because the intensities of the $\overline{hkl}$ reflections were measured first, and data collection for these was complete before any significant decomposition occurred.

Description and Discussion of the Structure

There are four *cis*-dichlorobis(ethylenediamine)platinum(IV) ions and eight ionic chlorides per unit cell.

Figure 2.—A stereoscopic pair of views of the contents of a unit cell of cis-[Pt(C$_2$H$_8$N$_2$)$_2$Cl$_2$]Cl$_2$ viewed down the b axis. For clarity, no hydrogens are included, but Cl···H–N hydrogen bonds within the cell are depicted by the light lines between Cl and N atoms.

For each molecular unit one chloride ion (Cl A) occupies a general position and two other chloride ions (Cl B and Cl C) occupy special positions. Figure 2 gives a stereoscopic pair of views of the contents of a unit cell of this structure. The closest cation–anion distances are those between the anionic chlorides and the amine nitrogens.

TABLE V

POSSIBLE A–H···B BONDS

A	H	B	A–B, Å	H···B, Å	A–H···B, deg
N1	N1H2	ClB	3.184	2.198	159.14
N2	N2H2	ClC	3.266	2.327	149.89
N3	N3H1	ClA	3.083	2.046	168.19
N4	N4H2	ClB	3.207	2.264	147.85

Four Cl–N distances are found to be shorter than 3.30 Å and these possible Cl···H–N hydrogen bonds are summarized in Table V. Hydrogen bonding of this type was also observed in [Co(C$_2$H$_8$N$_2$)$_3$]Cl$_3$·3H$_2$O.[10]

The structure of the complex ion is represented by a perspective drawing in Figure 3. The platinum atom is

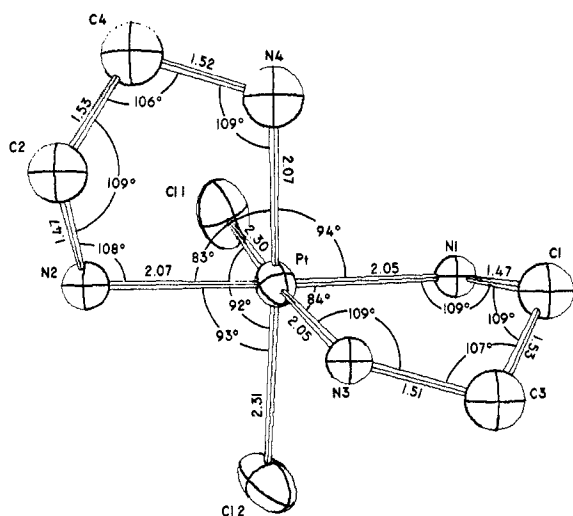Figure 3.—The [Pt(C$_2$H$_8$N$_2$)$_2$Cl$_2$]$^{2+}$ cation showing its bond distances and ellipsoids of thermal motion. The ellipsoids have been scaled to 50% probability distributions. For clarity, no hydrogen atoms are included.

situated at the center of a slightly distorted octahedron. The two coordinated chlorines (Cl1 and Cl2) occupy cis positions. The bond distances in this complex ion are given in Table VI and the bond angles are summa-

TABLE VI

SELECTED INTRAMOLECULAR DISTANCES (Å)

Interaction	Dist	Av dist
Pt–Cl1	2.302 (6)	2.306 (5)[a]
Pt–Cl2	2.309 (6)	
Pt–N1	2.045 (16)	
Pt–N2	2.068 (17)	
Pt–N3	2.047 (15)	2.057 (12)
Pt–N4	2.066 (19)	
N1–C1	1.472 (25)	
N2–C2	1.468 (28)	
N3–C3	1.512 (29)	1.493 (27)
N4–C4	1.521 (31)	
C1–C3	1.534 (32)	1.532 (3)
C2–C4	1.530 (34)	

[a] The standard deviations here are those for a single observed distance on the assumption that the distances within a given group are equivalent. The fact that these are smaller than those obtained from the inverse matrix shows that the distances are indeed equivalent.

TABLE VII

SELECTED INTERATOMIC ANGLES

Interaction	Angle, deg
Cl1–Pt–Cl2	92.4(3)
Cl1–Pt–N1	90.3(5)
Cl1–Pt–N2	91.5 (5)
Cl1–Pt–N3	174.6 (5)
Cl1–Pt–N4	89.6 (6)
Cl2–Pt–N1	89.6 (5)
Cl2–Pt–N2	92.9 (5)
Cl2–Pt–N3	86.8 (5)
Cl2–Pt–N4	175.9 (6)
N1–Pt–N2	176.7 (6)
N1–Pt–N3	84.4 (6)
N1–Pt–N4	93.9 (7)
N2–Pt–N3	93.8 (6)
N2–Pt–N4	83.4 (7)
N3–Pt–N4	91.5 (7)
Pt–N1–C1	108.7 (1.1)
N1–C1–C3	108.9 (1.8)
C1–C3–N3	106.6 (1.7)
C3–N3–Pt	108.7 (1.3)
Pt–N2–C2	108.2 (1.3)
N2–C2–C4	108.9 (1.8)
C2–C4–N4	105.5 (1.8)
C4–N4–Pt	109.0 (1.4)

rized in Table VII. The mean Pt–Cl distance of 2.305 (4) Å may be compared with the Co–Cl distances of 2.29 (1) Å found in trans-dichlorobis(propylenediamine)-cobalt(III)[11] and the Pt–Cl distance of 2.31 (1) Å found in cis- and trans-dichlorodiamineplatinum(II).[12]

(10) K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, Bull. Chem. Soc. Jap., 30, 158 (1957).

(11) Y. Saito and H. Iwasaki, ibid., 35, 1131 (1962).

(12) G. H. W. Milburn and M. R. Truter, J. Chem. Soc., 1609 (1966).

The four Pt–N distances found in the complex are not significantly different from one another. There is no evidence of any *trans* effect. The average Pt–N distance of 2.057 (6) Å is similar to those reported for *cis*- and *trans*-dichlorodiamineplatinum(II) (2.05 (4) Å).[12] The nitrogen–platinum–nitrogen angles are within the usual range found in other ethylenediamine chelate compounds. Though there seem to be small differences in the nitrogen–carbon distances, the differences are not significant. A measure of the degree of nonplanarity of the ethylenediamine chelate ring is the dihedral angle of the two planes defined by the two carbon atoms and one of the donor nitrogen atoms, and the two carbon atoms and the other donor nitrogen in the ring. This dihedral angle is found to be 53° and 55° in the two chelate rings of the complex. The analogous angles in $[Co(C_2H_8N_2)_3]Br_3 \cdot 0.5H_2O^{13}$ are 43–51°.

From the anomalous dispersion studies the absolute configuration of the complex is found to be Λ. This absolute configuration assignment is based on the following convention.[14] The planes each determined by the central metal atom and the two donor atoms of the bidentate ligand in a *cis*-bis-bidentate complex define a twofold axis and helix. A right-hand helix is labeled Δ while a left-hand helix is labeled Λ. The conformations of the chelate rings are labeled according to a similar convention.[14] When the chelate ring is viewed along the axis through the two donor atoms the sequence of bonds in the chelate ring defines a static screw. If it is right-handed the conformation is labeled δ. The mirror image is labeled λ.

The conformations of the two chelate rings, based on this convention, are λλ. This is different from that of (+)-*d*-*cis*-dicyanobis(ethylenediamine)cobalt(III), where the absolute configuration of the chelate rings is opposite that of the C_2 chirality of the complex ion.[15] However, it is analogous to the configuration found in tris(ethylenediamine)cobalt(III) chloride[16] and tris-(*l*-propylenediamine)cobalt(III) bromide.[17] This combination of the absolute configuration of the complex and the conformations of the chelate rings is also the thermodynamically stable species in solution according to the conformational analysis of Corey and Bailar.[18] In investigations of tris(ethylenediamine)-chromium(III) complexes Raymond, *et al.*,[19] found other combinations of absolute configuration of the complex and the conformations of the ethylenediamine chelate rings. They explained the existence of otherwise thermodynamically less favorable conformations on the basis of more extensive hydrogen bonding between the amine hydrogens and the cyanide groups. The fact that there are very few strong hydrogen bonds in the present structure is consistent with that explanation.

(13) K. Nakatsu, *Bull. Chem. Soc. Jap.*, **35**, 832 (1962).

(14) Y. Saito, "Spectroscopy and Structure of Metal Chelate Compounds," K. Nakamoto and P. J. McCarthy, Ed., John Wiley & Sons, New York, N. Y., 1968, p 26.

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The Crystal Structure of Potassium Trichloroammineplatinate(II) Monohydrate[1a]

By Y. P. JEANNIN[1b] AND D. R. RUSSELL[1c]

The crystal structure of potassium trichloroammineplatinate(II) monohydrate, $K[PtCl_3NH_3] \cdot H_2O$, has been determined at room temperature by three-dimensional X-ray crystallographic techniques using intensity data measured by scintillation counter. After correction for absorption, refinement by the full-matrix least-squares method, using anisotropic temperature factors, converged to an R factor of 0.056. The compound crystallizes in an orthorhombic unit cell; $a = 4.572 \pm 0.002$, $b = 21.025 \pm 0.009$, $c = 8.125 \pm 0.004$ Å with four molecules per unit cell and possible space groups Cmcm or $Cmc2_1$. The latter is preferred. The anion is planar and the three Pt–Cl bond lengths of 2.321 ± 0.007, 2.315 ± 0.027, and 2.300 ± 0.014 Å, after correction for thermal motion, are equal within one standard deviation.

Introduction

Substitution reactions of platinum(II) complexes with ammine and chloro ligands are often cited as examples of the so-called *trans* effect in metal complexes.[2]

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(2) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1963).

Thus the reaction of ammonia with the trichloroammineplatinate(II) ion gives only *cis*-dichlorodiammineplatinum(II), the chloro ligand opposite another chloro ligand is replaced in preference to that opposite ammonia, and chloride is said to have a higher *trans* effect than ammonia.

An accurate determination of the structure of the $[PtCl_3NH_3]^-$ ion should reveal whether the apparent