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 $[\mathrm{Co}(\mathrm{C_2H_8N_2})_3]\mathrm{Br_3}\cdot 0.5\mathrm{H_2O}$[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.

Acknowledgment.—Financial assistance by the National Institutes of Health is gratefully acknowledged. C. F. L. is also grateful to the National Institutes of Health for a Special Postdoctoral Fellowship under which this research was carried out.

[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.

[15] K. Matsumoto, Y. Kushi, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jap.*, **40**, 2988 (1967).

[16] K. Nakatsu, M. Shiro, Y. Saito and H. Kuroya, *ibid.*, **30**, 158 (1957).

[17] H. Iwasaki and Y. Saito, *ibid.*, **39**, 92 (1966).

[18] E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

[19] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842 (1968).

Contribution No. 2236 from the Institute of Atomic Research and
Department of Chemistry, Iowa State University, Ames, Iowa

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

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

Received February 24, 1969

The crystal structure of potassium trichloroammineplatinate(II) monohydrate, $\mathrm{K[PtCl_3NH_3]\cdot H_2O}$, 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 $\mathrm{Cmc2_1}$. 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] 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 $[\mathrm{PtCl_3NH_3}]^-$ ion should reveal whether the apparent

---

[1] (a) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. (b) Department de Chimie Inorganique, Faculte des Sciences, 38, Rue des Trente-six Ponts, Toulouse, 31, France. (c) Department of Chemistry, The University, Leicester, England.

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

chemical difference between Pt–Cl bonds *cis* and *trans* to an ammine group is reflected in a difference in the corresponding Pt–Cl bond lengths.

A single crystal electron diffraction structure determination of anhydrous potassium trichloroammineplatinate(II)[3] found the Pt–Cl bond *trans* to chloride to be 0.03 Å longer than the one *trans* to ammonia; however, this difference has an estimated standard deviation of ±0.03 and so cannot be regarded as significant. The present determination was undertaken at the suggestion of the late Professor R. E. Rundle to try to determine the Pt–Cl bond lengths in the $[PtCl_3NH_3]^-$ anion with greater accuracy.

Experimental Section

Crystals of $K[PtCl_3NH_3]\cdot H_2O$ which grow in large flat plates were generously supplied by Dr. D. S. Martin. Attempts were made to grind spherical crystals using an apparatus similar to that described by Bond.[4] The crystals were rather fragile and often shattered as they approached a suitable size; the best crystal finally selected was ellipsoidal in shape, $0.08 \times 0.08 \times 0.16$ mm.

Preliminary Laue and precession photographs showed the cell to be orthorhombic, with $a = 4.572 \pm 0.002$, $b = 21.025 \pm 0.009$, $c = 8.125 \pm 0.004$ Å, obtained by micrometering precession photographs of a very small crystal to ±0.04 mm. (Errors reflect internal consistency; the camera was previously calibrated using a NaCl crystal, $a = 5.6399$ Å, for Mo Kα, λ 0.7107 Å). This is in agreement with Bokii, *et al.*,[3] who found $a = 20.6$, $b = 8.0$, and $c = 4.5$ Å, and with Lyashenko,[5] who reported axial ratios 1.2910:1.0:0.8404 (corresponds to our $a:2b:3c = 1.294:1.0:0.8626$).

The density, measured by flotation in a mixture of methylene iodide and 1,2-dibromoethane, was found to be 3.181 ± 0.003 g/ml from four separate determinations. Calculated values of 3.04 for 4 molecules of $KPtCl_3NH_3$, and 3.19 for 4 molecules of $KPtCl_3NH_3\cdot H_2O$, indicated that the crystal examined had the latter formula.

Absences of $h + k = 2n$ for hkl and $l = 2n$ for $h0l$ reflections gave the possible space groups as Cmcm (no. 63, D_{2h}^{17}), Cmc2$_1$ (No. 36, C_{2v}^{12}), or C2cm (No. 40, C_{2v}^{16}) (Ama2 in standard setting).

A complete octant of three-dimensional intensity data out to $\sin\theta/\lambda = 0.75$ was collected for the crystal at room temperature using molybdenum radiation ($\lambda = 0.7107$ Å). A General Electric XRD-5 X-ray unit with single crystal orienter and scintillation counter was used with the moving-crystal–moving-counter technique and (θ, 2θ) coupling, a 3° take-off angle, and a 2° diffracted beam aperture fitted with a zirconium foil filter. Single crystal orienter settings were precalculated using a program sco-6 written for the IBM 7074 computer by D. E. Williams. A 200-sec scan at 1°/min (2θ) was used for each reflection, followed by a repeat scan for background with angle ω offset by 1.8° for about 40% of reflections. During the period of 8 days required for these measurements, three standard reflections (0, 0, 16; 0, 4, 6; 2, 1, 2) were checked daily and the intensities of these reflections remained constant over a period of 8 days to within $\pm 3\sigma$, which was ±3.5% of total counts. A total of 830 reflections were measured.

A graph of measured background counts *vs.* θ was plotted which showed the background to vary smoothly with θ; consequently, the background correction for each reflection was obtained by interpolation from a table as a function of θ. In view of the large absorption coefficient ($\mu = 203$ cm^{-1}), an absorption correction was applied approximating the crystal by a 26-face truncated prism and using a 216-point grid for the numerical integration.[6] A correction for the presence of noncharacteristic radiation along radial reciprocal lattice lines was made by a similar method to that described by Williams and Rundle,[7] adapted by J. E. Benson of this Laboratory. The intensity *vs.* θ profiles of the [0 0 1]* and [1 0 3]* lines were used.

In the later stages of least-squares refinement, a weighting factor w was applied to each reflection, calculated from

$$\sigma F = 1/\sqrt{w} = [\sqrt{(I + \sigma I)} - \sqrt{I}]/(Lp\sqrt{A})$$

$$(\sigma I)^2 = [C_T + C_B + (K_TC_T)^2 + (K_BC_B)^2 + (K_SC_S)^2(K_AC_P)^2]/A^2$$

where C_T, C_B, and C_S are the counts for total peak, background, and streak, and $C_P = C_T - C_B - C_S$; K_T, K_B, K_S, and K_A are nonstatistical proportional errors in total peak, background, streak counts, and absorption correction and were taken to be 0.04, 0.04, 0.1, and 0.1, respectively; A is the absorption correction (actually a transmission factor); L is the Lorentz factor; and p is the polarization factor. The terms σI and σF represent the estimated errors in intensity and structure factor, respectively.

Atomic scattering factors were taken from Cromer and Waber,[8] and in the later stages of refinement were modified for the effects of anomalous dispersion using the coefficients of Cromer.[9]

Structure Determination

Since there are only four molecules per unit cell, and no systematically weak reflections were observed, the platinum atoms must lie on special positions c of Cmcm (0, y, $^1/_4$), a of Cmc2$_1$ (0, y, z), or b of C2cm (x, y, $^1/_4$), all of which have only one variable parameter y (in the last two space groups a second parameter may be arbitrarily chosen for 1 atom). For platinum only structure factor calculations were carried out with values of y incrementing by 0.025 from $y = 0$ to $y = 0.25$. The R factor showed a pronounced minimum at $y = 0.15$ and least-squares refinement improved this coordinate to 0.157. For convenience this was altered to the equivalent position of $y = 0.343$. In Cmcm the platinum has site symmetry mm, and coordinates for the two nonrelated chlorine atoms Cl(1) (on both mirror planes) and Cl(2) (one of the mirror related *trans* pair) were readily derived.

At this point structure factor calculations gave an R factor of 0.18. Attempts to place the potassium ion in the available fourfold sites of Cmcm were unsuccessful. A three dimensional observed Fourier synthesis calculated with Cmcm symmetry, and based on the platinum and chlorine positions, revealed the nitrogen atom at the expected position on the mirror plane at $z = {}^1/_4$, and also two mirror-related pairs of peaks at $x = 0$ whose peak heights corresponded to half-potassium and half-oxygen atoms. Two interpretations of the half-height peaks were considered. The four potassium and four oxygen atoms could occupy the eightfold sites f (0, y, z) in Cmcm, or c (x, y, z) in C2cm, in a random manner while the $[PtNH_3Cl_3]^-$ ion retains full mm symmetry. An alternative interpretation is that the true space group is Cmc2$_1$, which does not require a mirror plane at $z = {}^1/_4$ and consequently full K and O atoms may be placed one on either side of the now nonexistent mirror plane. In this case the $[PtCl_3NH_3]^-$ ion is only required to be planar.

---

[3] G. B. Bokii, B. K. Vainshtein, and A. A. Babareko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **6**, 667 (1951).

[4] W. L. Bond, *Rev. Sci. Instrum.*, **22**, 344 (1951).

[5] W. N. Lyashenko, *Tr. Inst. Kristallogr., Akad. Nauk SSSR*, **9**, 335 (1954).

[6] W. R. Busing and H. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

[7] D. E. Williams and R. E. Rundle, *J. Amer. Chem. Soc.*, **86**, 1660 (1964).

[8] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

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

TABLE I

REFLECTIONS REMOVED FROM FINAL REFINEMENT

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c
0	2	0	128	74	0	2	1	265	303
0	8	0	122	87	1	1	6	15	94
0	14	0	68	33	3	9	7	91	39

Structure factors calculated from the platinum, chlorine, and nitrogen atom positions, and with potassium and oxygen positions with a population parameter of 0.5, in space group Cmcm gave an agreement factor $R = 0.15$, which rapidly converged to 0.13 with isotropic temperature factors, and to 0.068 (0.058 omitting zero reflections) with anisotropic temperature factors for all atoms. At this stage, the Cl(2) atom anisotropic thermal vibration component perpendicular to the molecular plane was very large, suggesting that the $[PtCl_3NH_3]^-$ ion was not strictly planar. Three cycles of refinement in space group C2cm, after arbitrarily displacing the Cl(2) atom out of the plane by 0.3 Å, did not improve the *R* factor, nor effectively cause any lowering of temperature factors.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS (SPACE GROUP $Cmc2_1$) IN ELECTRONS MULTIPLIED BY 10. RUNNING INDEX IS *k*, FOLLOWED BY F_{obsd} AND $|F_{calcd}|$

```
* H= 0 L= 0  30  49  48  24  52  59  17  75  83   3 243 243   5  25  16 * H= 2 L= 1  24  21  17   4  28  25  11  63  62  15  39  40 * H= 4 L= 1  14  54  57   7  60  57  15  23  20
  4 237 278 * H= 0 L= 4  26  31  32  19 197 198   5  45  41   7  57  57   2 227 218  26  59  56   6  16  10  13  89  85  17  35  39   2 130 128  16   5   3   9  54  52 * H= 5 L= 7
  6 350 374   0 349 334 * H= 0 L= 8  21  33  49   7 163 164   9  77  83   4 155 153  28  44  34   8  40  40  15  75  76  19  61  62   4  89  88  18  47  47  11  81  79   1  38  34
 10 405 411   2  82  81   0 103 100  23  91  86   9 207 212  11  23  19   6  73  64 * H= 2 L= 5  10  15   0  17  56  62  21  11   0   6  42  39  20  38  35  13  13   6   3   8   0
 12 176 205   4 142 140   2  27  31  25  87  84  11  30  34  13  47  42   8 233 237   2 119 119  12  29  31  19  98  96  23  31  30   8 132 133  22  17   0  15  46  44   5  42  46
 16 236 244   6 241 235   4  54  52  27   4  22  13 169 170  15  45  48  10  82  72   4  80  78  14  25  29  21  11   0 * H= 3 L= 7  10  47  40 * H= 4 L= 6  17  54  56   7  23  20
 18  90 107   8  29  30   6  70  66  29  84  82  15  95  92  17  23  25  12 127 129   6  44  43  16   7  16  23  42  44   1  78  77  12  77  76   0  64  87  19  15   4   9  20  19
 20 129 137  10 246 240   8  16  17  31  35  22  17  57  57  19  54  55  14 130 131   8 104 108  18  29  38  25  60  61   3  17  14  14  83  83   2  22  16  21  47  47  11  40  43
 22 117 120  12 113 109  10  77  74 * H= 1 L= 1  19 133 133  21   7   0  16  27  23  10  55  56 * H= 2 L=10  27  15  21   5  84  85  16  14   0   4  46  48 * H= 5 L= 2 * H= 5 L= 8
 24  47  52  14  18  18  12  50  46   1 301 288  21  27  18  23  21  14  18 133 138  12  79  84   0  56  56 * H= 3 L= 3   7  47  48  18  81  85   6  62  67   1  66  67   1  23  18
 26 104 107  16 162 165  14  15   0   3 112 109  23  61  62 * H= 1 L= 9  20  86  85  14  75  72   2   5   0   1 155 153  11  80  85  20  55  50   8  11   0   3  74  71   3  29  32
 28  61  60  18  78  73  16  54  51   5 159 167  25  73  69   1  43  34  22  38  29  16   8   0   4  26  28   3  31  20  13  13   0  22  24  14  10  67  73   5  20  19   5   8   0
 30  25  33  20  98  95  18  32  31   7 197 190  27   6   0   3  26  22  24  73  68  18  68  67   6  39  39   5 163 163  15  47  50  24  50  47  12  35  40   7  63  67   7  24  26
* H= 0 L= 1  22  83  81  20  35  36   9 166 173  29  60  53   5  26   0  26  41  39  20  55  56   8   8  11   7  91  88  17  50  51 * H= 4 L= 2  14  17  28   9  77  81 * H= 6 L= 0
  2 297 265  24  28  26  22  35  39  11 230 248 * H= 1 L= 5   7  38  34  28  49  49  22  27  24  10  46  53   9  89  91  19  11  11   0 129 123  16  50  53  11  27  18   0  80  76
  4 196 193  26  69  70  24   8   7  13  34  30   1 128 125   9  34  32  30  51  47  24  44  42  12  16  11  11 150 152  21  48  55   2  50  45  18  22  16  13  56  55   2  17   8
  6  89  87  28  53  55 * H= 0 L= 9  15 106 111   3  56  55  11  37  36 * H= 2 L= 2  26  25  32  14   9  14  13  24  18 * H= 3 L= 8   4  81  82  20  34  34  15  42  44   4  38  39
  8 297 307  30  20  24   2  42  39  17 154 155   5  69  71  13   5   0   0 198 188 * H= 2 L= 6  16  34  36  15  64  63   1  44  45   6 100 100 * H= 4 L= 7  17  32  34   6  55  51
 10 105  96 * H= 0 L= 5   4  29  25  19  46  43   7 117 118  15  20  14   2  82  80   0 137 131 * H= 2 L=11  17  95  93   3  51  51   8   4   0   2  68  69  19  56  58   8   5   0
 12 152 163   2 134 129   6  17   4  21 110 114   9 107 109  17  35  31   4 121 117   2  35  25   2  35  29  19  22   0   5  15   0  10 104 106   4  33  27  21   7  10  10  61  63
 14 152 157   4  87  86   8  43  43  23  65  64  11  98 100  19  19  28   6 141 135   4  70  74   4  18  15  21  90  90   7  42  40  12  71  75   6   8   0 * H= 5 L= 3  12  32  33
 16  35  37   6  50  47  10  15   0  25  31  32  13  12  11  21  22  24   8   6   0   6  94  98   6   4   0  23  37  34   9  55  56  14  33  34   8  72  78   1  74  72  14  10   4
 18 159 170   8 112 112  12  32  28  27  86  85  15  43  48 * H= 1 L=10  10 161 162   8  19   0   8  37  39  25  23  19  11  17  13  16  75  75  10  18  18   3  15   0 * H= 6 L= 1
 20 102  98  10  64  64  14  26  33  29   4   0  17 101 101   1  30  29  12 105 105  10 109 107  10  13  14  27  50  64  13  36  35  18  34  35  12  37  39   5  79  79   2  59  59
 22  45  44  12  89  92  16   6   0  31  39  32  19  42  36   3  51  45  14  56  56  12  49  46 * H= 3 L= 0 * H= 3 L= 4  15  32  31  20  54  54  14  39  39   7  45  41   4  42  42
 24  82  80  14  82  81  18  31  33 * H= 1 L= 2  21  57  56   5   8   0  16 106 107  14  27  13   1 113 111   1 102  98  17  19  20  22  53  55  16  12   9   9  43  43   6  20  17
 26  48  50  16  11  12  20  21  28   1 214 207  23  35  40   7  39  32  18  48  45  16  77  78   3 227 233   3 149 151  19  40  39  24   5   0  18  45  49  11  74  77   8  60  61
 28  58  56  18  74  72 * H= 0 L=10   3 118 116  25  19  27   9  41  40  20  86  82  18  31  32   5  46  42   5  28  24 * H= 3 L= 9 * H= 4 L= 3 * H= 4 L= 8  13  13   8  10  22  27
 30  58  56  20  61  65   0  71  67   5  52  57  27  55  56  11  16  25  22  75  74  20  57  59   7 170 172   7 107 105   1  36  34   2 133 133   0  52  51  15  45  45  12  36  39
* H= 0 L= 2  22  31  33   2   6   0   7 130 133 * H= 1 L= 6  13  41  44  24   5  11  22  43  44   9 167 166   9 130 134   3  18  16   4  63  61   2  15   0  17  49  51  14  41  45
  0 221 235  24  48  49   4  31  29   9 197 204   3 111 104  15  18  13  26  55  53  24  11   6  11  28  27  11  24  17   5  25  17   6  21   5   4  30  30  19  11   6 * H= 6 L= 2
  2  91 103  26  28  25   6  46  38  11 107 105   5  21   0  17  18  24  28  46  50  26  41  41  13 154 154  13 112 112   7  30  34   8 133 138   6  39  35 * H= 5 L= 4   0  62  66
  4 126 125  28  37  34   8  10  20  13 104 100   7  91  92 * H= 1 L=11 * H= 2 L= 3 * H= 2 L= 7  15  81  82  15  62  54   9  26  29  10  37  33   8   5   0   1  48  45   2  24  18
  6 142 135 * H= 0 L= 6  10  56  51  15  95 100   9 110 112   1  34  26   2 260 255   2 124 125  17  54  53  17  42  41  11  32  37  12  72  73  10  41  44   3  72  69   4  39  40
 10 184 195   0 161 157  12  19  12  17  81  83  11  49  53   3   9  19   4 107 103   4  57  60  19 129 127  19  91  91  13   4   0  14  75  76  12  27  34   5  14   9   6  50  53
 12 116 124   2  41  29  14  11   3  19 126 131  13  86  89   5  35  32   6  33  19   6  11   6  21  20  11  21  16  20  15  18  17  16  16   0  14  11   5   7  55  57   8   2   6
 14  69  69   4  81  78  16  41  39  21  18   0  15  49  46   7  25  18   8 248 249   8 131 140  23  65  61  23  46  44 * H= 3 L=10  18  82  85 * H= 4 L= 9   9  63  65  10  50  55
 16 115 120   6 108 108  18  17  23  23  52  47  17  49  50   9  17  21  10  67  62  10  31  20  25  60  57  25  51  52   1  21   9  20  42  38   2  30  34  11  13   0  12  35  40
 18  51  56   8  24   0 * H= 0 L=11  25  77  76  19  82  84  11  34  31  12 128 130  12  64  65  27   1   0 * H= 3 L= 5   3  35  34  22  17  21   4  21  20  13  57  56  14  15  14
 20 101 102  10 130 130   2  43  41  27  24   0  21  13   0  13   7  12  14 127 130  14  67  71 * H= 3 L= 1   1  99  99   5   6   8  24  49  50   6  11   0  15  31  31 * H= 6 L= 3
 22  82  83  12  53  55   4  21  26  29  60  65  23  42  46 * H= 1 L=12  16  31  27  16  24  25   1 179 165   3  39  34   7  27  35 * H= 4 L= 4   8  30  33  17  24  15   2  56  55
 24   6   0  14  33  35   6   4   5  31  23  26  25  45  44   1  17  10  18 142 139  18  79  83   3  60  55   5  67  67   9  29  29   0 134 134  10  12  16  19  48  48   4  31  31
 26  62  54  16  89  87   8  46  44 * H= 1 L= 3  27  19  18   3  10   0  20  68  68  20  38  38   5 129 131   7  84  87  11  10   9   2  33  25 * H= 4 L=10 * H= 5 L= 5   6  12  11
 28  51  53  18  34  25  10  16  21   1 263 259 * H= 1 L= 7 * H= 2 L= 0  22  26  31  22  13   5   7 122 119   9  75  82 * H= 3 L=11   4  65  62   0  34  32   1  55  56   8  57  62
 30  33  33  20  68  66  12  23  14   3  50  35   1 121 118   0 466 474  24  80  81  24  43  45   9 107 103  11  81  84   1  23  14   6  98  91 * H= 5 L= 0   3  19  12  10  17  12
* H= 0 L= 3  22  48  49  14  25  31   5 266 257   3  27  22   2  54  68  26  41  39 * H= 2 L= 8  11 155 158  13  11   0   3   6   0   8   9   0   1  54  46   5  45  48  12  32  27
  2 360 339  24  12   0 * H= 0 L=12   7 145 143   5 129 129   4 164 178  28  53  48   0  86  80  13  24  20  15  40  37 * H= 4 L= 0  10 105 110   3 101  97   7  44  45 * H= 6 L= 4
  4 136 123  26  49  53   0  16   4   9 142 144   7  72  72   6 245 260 * H= 2 L= 4   2  23  16  15  79  82  17  77  79   0 203 196  12  52  52   5  19  14   9  39  44   0  57  59
  6  41  39 * H= 0 L= 7   2   6   7  11 231 232   9  59  63   8  52  58   0 259 250   4  47  47  17 110 107  19  28  25   2  32  32  14  15   0   7  77  71  11  49  46   2  15   9
  8 326 311   2 157 154   4  11   0  13  37  35  11 122 128  10 294 307   2  61  55   6  60  59  19  32  17  21  48  46   4  85  86  16  76  80   9  78  74  13   8   0   4  30  30
 10  86  86   4  72  75   6  14   0  15 123 123  13  20   5  12 131 135   4 113 114   8  11   0  21  82  81  23  29  33   6 125 123  18  33  34  11  14   0  15  28  34   6  43  47
 12 161 163   6  13  17 * H= 1 L= 0  17 142 146  15  69  66  14  24  13   6 183 169  10  65  71  23  48  48  25  16  21   8  19  16  20  49  49  13  75  71  17  42  48   8  31  31
 14 157 160   8 165 162   1 214 231  19  31  29  17  75  73  16 187 188   8  71  74  12  42  44  25  25  29 * H= 3 L= 6  10 148 143  22  43  43  15  39  31 * H= 5 L= 6  10  46  47
 16  38  41  10  39  38   3 443 472  21 131 127  19  15  12  18  70  70  10 193 198  14  14  17  27  64  61   1  70  68  12  69  65 * H= 4 L= 5  17  30  24   1  35  42 * H= 6 L= 5
 18 174 174  12  78  79   5  97 116  23  52  46  21  70  74  20 106 106  12  90  89  16  47  47 * H= 3 L= 2   3  84  86  14  18   0   2  79  81  19  64  61   3  48  49   2  39  44
 20  82  88  14  83  85   7 307 337  25  31  27  23  31  27  22  95  92  14  18  14  18  27  27   1 135 130   5  17  13  16 104 101   4  56  56  21  10   0   5  10   0   4  28  32
 22  30  28  16  31  32   9 290 314  27  81  80  25  18  13  24  35  28  16 131 131  20  30  34   3 120 113   7  67  70  18  38  33   6  29  23 * H= 5 L= 1   7  38  44   6  15  13
 24  96  94  18  97  99  11  38  47  29  19  14 * H= 1 L= 8  26  87  83  18  61  59  22  30  36   5  38  33   9  81  85  20  63  58   8  74  76   1  87  83   9  44  53   8  38  45
 26  49  46  20  47  43  13 243 251 * H= 1 L= 4   1  62  58  28  50  48  20  82  79 * H= 2 L= 9   7 108 109  11  32  29  22  57  57  10  35  35   3  26  16  11  14  12 * H= 6 L= 6
 28  63  60  22  15  22  15 132 135   1 172 169   3  69  66  30  22  21  22  69  68   2  40  30   9 145 145  13  65  71  24  17  12  12  51  52   5  73  74  13  37  45   0  39  40
```

If the water molecule and potassium ion occupy disordered sites, there is a possibility that the number of water molecules per potassium ion is less than one, especially in view of the similarity of the structure of this hydrated complex with the anhydrous compound. Therefore the population parameter for oxygen was made variable, but least-squares refinement led to a value corresponding to a full molecule of water per potassium ion, within the limit of error.

Refinement was then continued in space group $Cmc2_1$, with full potassium and oxygen atoms on opposite sides of the hypothetic mirror plane at $z = ^1/_4$, at first neglecting the imaginary part of the platinum scattering factor. A slight improvement in $\Sigma w\Delta^2$ was obtained together with small shifts of low significance, in atom positional parameters.

Since $Cmc2_1$ is a polar space group, the presence of anomalously scattering atoms could lead to systematic errors in atomic position,[10] particularly as only one octant of data was measured. Duplicate refinements were carried out, first assuming the octant was $+h$, $+k$, $+l$ and then $-h$, $-k$, $-l$. Ten cycles of refinement showed different behavior. The $+h$, $+k$, $+l$ case converged and on the last cycle the largest changes were for the U_{11} components of atoms Cl(2) and Cl(3), which amounted to $^1/_{30}$ of one standard deviation. The $-h$, $-k$, $-l$ case was consistently divergent and could not be refined to a stable set of parameters. This difference of behavior suggests that the measured octant was $+h$, $+k$, $+l$. However, a search through the calculated sets of structure factors revealed that for only 24 reflections was the difference $|F_{hkl}| - |F_{\bar{h}\bar{k}\bar{l}}|$ greater than 1.5σ for the measured value.

A comparison of the final $+h$, $+k$, $+l$ set of parameters with those obtained in $Cmc2_1$, neglecting $\Delta f''$ for platinum, revealed a shift of +0.037 (7) Å along the *z* direction for the potassium atom, relative to platinum. This shift is approximately that predicted by Cruickshank and McDonald.[10] Similar small shifts were observed for the other atoms, but in all other cases these were of the order of one standard deviation.

---

[10] D. W. J. Cruickshank and W. S. McDonald, *Acta Crystallogr.*, **23**, 9 (1967).

The final R factor was 0.069 for all reflections, and 0.056 for nonzero reflections. Six reflections (Table I) were removed from the final refinement as they appeared to contain large random errors ($\sqrt{w}\Delta > 3$). A three-dimensional difference Fourier synthesis revealed no significant features which could be attributed to hydrogen atoms. The observed and calculated structure-factor amplitudes are given in Table II. Table III lists the final atom position parameters, and Table IV gives the final atom vibration parameters obtained from the refinements in space groups Cmcm and $Cmc2_1$.

TABLE III

FRACTIONAL ATOMIC COORDINATES FOR REFINEMENT IN $Cmc2_1$ AND Cmcm[a]

	$Cmc2_1$		Cmcm	
	y	z	y	z
Pt	0.34338 (3)	1/4	0.34342 (3)	1/4
Cl(1)	0.4536 (2)	0.2506 (28)	0.4531 (2)	1/4
Cl(2)	0.3373 (9)	0.5311 (39)	0.3402 (2)	0.5316 (6)
Cl(3)	0.3425 (6)	−0.0306 (21)	0.3402 (2)	−0.0316 (6)
N	0.2467 (9)	0.2277 (63)	0.2449 (9)	1/4
K	0.0395 (3)	0.4640 (9)	0.0400 (3)	0.4595 (9)
O	0.0756 (11)	0.1374 (31)	0.0738 (9)	0.1300 (29)

[a] Standard deviation on last figure in parentheses. All atoms are at $x = 0$.

TABLE IV

ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$ Å^2) FOR REFINEMENT IN $Cmc2_1$ AND Cmcm, WITH STANDARD DEVIATIONS IN PARENTHESES[a]

	$Cmc2_1$ refinement				Cmcm refinement			
	U_{11}	U_{22}	U_{33}	U_{23}	U_{11}	U_{22}	U_{33}	U_{23}
Pt	291 (3)	224 (3)	454 (3)	−52 (10)	292 (3)	226 (3)	447 (4)	0
Cl(1)	495 (21)	269 (23)	414 (26)	−78 (70)	510 (25)	287 (18)	423 (24)	0
Cl(2)	1406 (210)	470 (67)	775 (134)	182 (78)	1200 (47)	499 (22)	492 (24)	203 (20)
Cl(3)	997 (115)	403 (67)	297 (47)	−121 (44)	1200 (47)	499 (22)	492 (24)	−203 (20)
N	412 (89)	246 (67)	1300 (284)	−70 (104)	449 (98)	382 (90)	990 (167)	0
K	515 (30)	358 (23)	444 (30)	9 (26)	481 (30)	377 (28)	431 (33)	38 (30)
O	654 (142)	360 (90)	611 (144)	−26 (95)	715 (144)	216 (76)	607 (143)	9 (88)

[a] The form of the temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{23}klb^*c^*)]$.

TABLE V

MOLECULAR GEOMETRY OF $[PtCl_3NH_3]^-$ ANION

	$Cmc2_1$ refinement		Cmcm refinement	
Atoms	Dist, Å	Dist, Å, cor for thermal vibration	Dist, Å	Dist, Å, cor for thermal vibration
Pt-Cl(1)	2.317 ± 0.007	2.321 ± 0.007	2.306 ± 0.005	2.310 ± 0.005
Pt-Cl(2)	2.288 ± 0.027	2.315 ± 0.027	2.289 ± 0.006	2.315 ± 0.006
Pt-Cl(3)	2.280 ± 0.014	2.300 ± 0.014		
Pt-N	2.042 ± 0.019	2.060 ± 0.019	2.07 ± 0.02	2.09 ± 0.02
Atoms		Angle, deg		Angle, deg
Cl(1)-Pt-Cl(2)		93.1 ± 0.6		91.7 ± 0.1
Cl(1)-Pt-Cl(3)		90.6 ± 0.5		
Cl(2)-Pt-N		91.9 ± 0.9		88.3 ± 0.1
Cl(3)-Pt-N		84.4 ± 0.7		

Discussion

Figure 1 shows the intramolecular geometry of the $[PtNH_3Cl_3]^-$ ion, which is crystallographically required to be planar in $Cmc2_1$. Table V gives bond lengths and angles for the parameters obtained from the $Cmc2_1$ refinement, and for the Cmcm refinement where K^+ and the oxygen from a water molecule are assumed to be in disordered positions. Distances are also given after correction for anisotropic thermal motion by the method of Busing and Levy.[11]

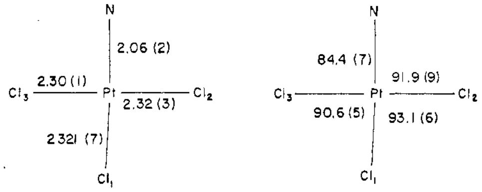

Figure 1.—Molecular geometry in the $[PtCl_3NH_3]^-$ anion. Standard deviation of last figure in parentheses.

A clear choice between the results obtained from space groups Cmcm and $Cmc2_1$ is not easily made. Refinement in both space groups leads to a similarly low R factor, and in the case of $Cmc2_1$ the presence of a polar dispersion effect does not completely clarify the situation. The Hamilton R factor ratio test suggests that the $Cmc2_1$ refinement is highly significant ($\mathcal{R} = 0.68/0.63 = 1.080$ using the weighted R factor for all reflections, $\mathcal{R}_{11,782,.005} = 1.035$). However, the reliability of this test under similar circumstances of pseudo symmetry has been questioned.[12]

However, it can be concluded from the structure that Cmcm cannot be the true space group symmetry of an individual unit cell since this would lead to the improbable situation of having two potassium ions per platinum in some cells, and two water molecules per platinum in others. Impossible contact distances arise from this situation. The crystal could, of course, be disordered in such a way that the two possible $Cmc2_1$ ar-

---

[11] W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).

[12] A. Whitaker and J. W. Jeffrey, *ibid.*, **23**, 984 (1967).

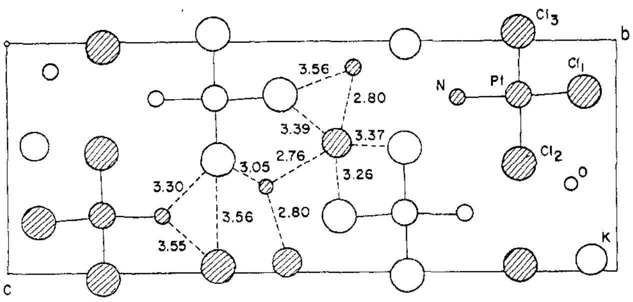

Figure 2.—Crystal packing of $K[PtCl_3NH_3]\cdot H_2O$, projected down the *a* axis. Open circles show atoms at $x = 0$, shaded circles are atoms at $x = 1/2$. Distances shown are in ångström units.

rangements, one with K^+ on the left and H_2O on the right of the pseudo mirror, the other *vice versa*, both occur equally in the crystal. This would lead to an apparent crystal symmetry of Cmcm. Refinement of such a structure would lead to a set of atom positions which would be the average of the two $Cmc2_1$ arrangements and would naturally have Cmcm symmetry. These positions would not necessarily correspond to the actual geometry of any individual molecule, however. It should be possible to distinguish between a Cmcm (disordered) lattice and an ordered $Cmc2_1$ lattice using the Pt anomalous dispersion effect. However, although some indication was gained from the parallel refinements of F_{hkl} and $F_{\bar{h}\bar{k}\bar{l}}$ data that the former rather than the latter had been measured, the magnitude of the effect is not sufficiently large for an unequivocal assignment to be made.

Nevertheless, we favor the results of the $Cmc2_1$ refinement for both crystallographic and chemical reasons. The $Cmc2_1$ refinement did successfully converge to the structure presented here from a number of different starting models. Also, the resulting crystal lattice bears a striking resemblance to that of $K[PtCl_3\cdot C_2H_4]\cdot H_2O$,[13] whose structure has recently been reinvestigated. The formation of this ordered lattice (discussed later) may provide additional stability over a disordered structure.

In view of the expected interactions between the $[PtCl_3NH_3]^-$ anion and the potassium ions and water molecules, it was not felt that the $PtCl_3NH_3$ group would behave as an independent rigid body in the lattice for a molecular vibration analysis to be applicable. In the $Cmc2_1$ refinement the very high correlation between corresponding parameters of Cl(2) and Cl(3) unfortunately lowers the accuracy of the two *trans* Pt–Cl bond lengths. The smaller errors for the Cmcm refinement cannot be taken at face value, either, for the reasons given above. The anomalously high component of the thermal vibration normal to the molecular plane for these two atoms also increases the uncertainty in these Pt–Cl bond lengths. It is apparent that there is no significant difference between the Pt–Cl bond lengths with or without any correction for thermal motion, although the limits of error are unavoidably high.

This result appears to conflict with the prediction of the polarization theory of Grinberg[14] for the *trans* effect. This theory assumes that a strongly *trans*-directing group actually weakens the metal–ligand bond opposite to itself by an electrostatic polarization mechanism, thus enabling *trans* substitution to occur more easily than in the *cis* position. In the $[PtCl_3NH_3]^-$ complex ion, the Pt–Cl bond *trans* to chlorine is expected to be weaker, and presumably longer, than the Pt–Cl bond *trans* to ammonia. If there is any weakening, it is apparently not accompanied by any appreciable lengthening (>0.05 Å) of the Pt–Cl bond.

An alternative explanation of the *trans* effect by Chatt[15] and Orgel[16] which suggests π-bond stabilization of a five-coordinate transition state does not seem applicable in this case because of the very low π-bonding ability of the ammine and chloro ligands.

A similar result has been recently found by Milburn and Truter[17] for the *cis* and *trans* isomers of dichlorodiammineplatinum(II), where the Pt–Cl bonds are not significantly different in the two compounds: 2.32 ± 0.01 Å for *trans*, 2.33 ± 0.01 Å for *cis*.

In contrast, an appreciably longer Pt–Cl bond (2.422 ± 0.009 Å) *trans* to a hydrido ligand has been observed in *trans*-hydridochlorobis(diphenylethylphosphine)platinum(II).[18] The hydrido ligand shows a very much greater *trans* effect than chloride or ammonia,[19] and the lack of any significant difference in Pt–Cl bond lengths in amminechloroplatinum(II) complexes may show that the effect is too small to be detected. It is interesting to note that there is no significant difference in the rate of exchange of isotopically labeled chloride ions with the *cis* and *trans* chlorine atoms in the $[PtCl_3NH_3]^-$ ion.[20]

In *cis*-dichlorobis(triethylphosphine)platinum(II), long Pt–Cl bond lengths of 2.364 and 2.388 Å have been observed.[21] However, no lengthening of the Pt–Cl bond occurs in a corresponding *trans* compound, *trans*-dichlorobis(trimethylphosphine)platinum(II).[22] Furthermore, the bond length of 2.294 Å found is very close to the average length, 2.289 Å, of the two uncorrected Pt–Cl(2) and Pt–Cl(3) distances in the present structure; this suggests there is no *cis* effect.[23]

The crystal packing and intermolecular contacts are shown in Figure 2 and Table VI. The crystal structure of the hydrated complex is quite similar to that of the anhydrous compound determined by Bokii, *et al.*[3] In the latter structure, the potassium is on the center of symmetry at the origin in space group Cmcm ($a =$

---

(13) M. Black, R. H. B. Mais, and P. G. Owston, private communication.

(14) A. A. Grinberg, *Acta Physicochim. URSS*, **3**, 573 (1935).

(15) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4456 (1955).

(16) L. E. Orgel, *J. Inorg. Nucl. Chem.*, **2**, 137 (1956).

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

(18) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

(19) F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 2207 (1961).

(20) T. S. Elleman, J. W. Reishus, and D. S. Martin, *J. Amer. Chem. Soc.*, **81**, 10 (1959).

(21) G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, **6**, 725 (1967).

(22) G. G. Messmer and E. L. Amma, *ibid.*, **5**, 1775 (1966).

(23) P. G. Owston, J. M. Partridge, and J. M. Rowe, *Acta Crystallogr.*, **13**, 246 (1960).

TABLE VI

NONBONDED ATOM DISTANCES (Å) LESS THAN 4 Å WITH STANDARD DEVIATION OF LAST FIGURE IN PARENTHESES

Cl(1)–Cl(2)	3.34 (2)	Cl(2)–O[c]	3.05 (2)
–Cl(3)	3.27 (2)	Cl(3)–N	2.91 (4)
–K[d]	3.26 (2)	–N[d]	3.55 (3)
–K[b]	3.39 (1)	–K[d]	3.37 (11)
–O[b]	3.56 (2)	–O[d]	3.98 (2)
Cl(2)–Cl(3)[e]	3.56 (2)	K–O[a]	2.76 (2)
–N	3.12 (6)	–O	2.80 (2)
–N[c]	3.30 (4)		

[a] Atom at 0, $-y$, $^1/_2 + z$. [b] Atom at $^1/_2$, $^1/_2 + y$, z. [c] Atom at $^1/_2$, $^1/_2 - y$, $^1/_2 + z$. [d] Atom at $^1/_2$, $^1/_2 - y$, $z - {}^1/_2$. [e] Atom at 0, y, $1 + z$.

4.19, b = 17.6, c = 8.84 Å), and is surrounded by eight chlorine atoms in a distorted cubic coordination. In the monohydrate, the potassium is displaced from the origin to a site which has six chlorine atoms at the corners of a trigonal prism and two water molecules in the centers of two of the rectangular faces. Thus water can be relatively easily lost from the lattice without much disruption of the structure, particularly in the $Cmc2_1$ model where the water molecules all lie above each other along the x axis, but the featureless difference Fourier synthesis and normal thermal parameters for oxygen confirm that the crystal examined here was fully hydrated. The potassium–oxygen distances (2.76 (2) and 2.80 (2) Å) are normal, the three potassium–chlorine distances (3.26 (2), 3.37 (1), 3.39 (1) Å) are somewhat longer than is commonly found (3.20–3.30 Å).[23]

The water molecule has an approximately tetrahedral environment, consisting of two potassium ions and two chlorine atoms [(angle Cl–O–Cl 97°, K–O–K 104°)]. The oxygen–chlorine distance of 3.05 (2) Å is slightly less (0.15 Å) than the sum of the van der Waals radii for oxygen and chlorine, and it is tempting to suggest that the water hydrogen atoms lie on these directions with a weak hydrogen bond between them. This is also a favorable electrostatic configuration of the oxygen atom with respect to the potassium ions.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

The Crystal and Molecular Structure of Bis(3,3′,5,5′-tetramethyldipyrromethenato)nickel(II)[1]

BY F. A. COTTON, B. G. DEBOER, AND J. R. PIPAL[2]

Received June 23, 1969

The crystal and molecular structure of bis(3,3′,5,5′-tetramethyldipyrromethenato)nickel(II), $Ni(C_{13}N_2H_{15})_2$, has been determined by single-crystal X-ray diffraction methods. The crystal data are: space group A2/a (C_{2h}^6, no. 15); cell dimensions $a = 22.352 \pm 0.007$ Å, $b = 7.337 \pm 0.005$ Å, $c = 31.496 \pm 0.008$ Å, $\beta = 114.70 \pm 0.05°$, $V = 4692.7$ Å^3; density 1.29 ± 0.02 g/cm^3 (by flotation), 1.294 g/cm^3 (calcd for $Z = 8$). The intensities of 1616 reflections collected on a manually operated counter diffractometer with Cu Kα radiation were used in solution and refinement. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares methods to final unweighted and weighted residuals of 0.068 and 0.097, respectively. The molecule possesses distorted D_2 symmetry, and the dihedral angle between the least-squares planes formed by the two ligands (including the nickel atom in each case) is 76.3°. The nickel–nitrogen bond lengths (1.948 (7)–1.957 (8) Å) are identical within experimental error. The bond lengths among the ring atoms indicate that electron delocalization occurs over each planar ring system.

Introduction

Metal complexes of dipyrromethenes are of interest because of their close relation to the biologically important metalloporphyrins. Several papers have appeared in the literature in which the preparation, spectra, magnetic properties, and possible structures of metal complexes of substituted dipyrromethenes are discussed. Much of this work centers on ligands containing methyl substituents in the 5 position of each ring. Porter[3] dealt with bivalent metal complexes (Co, Ni, Cu, Zn, Cd, Pd) and concluded on the basis of models that a planar configuration of the ligands was impossible due to steric repulsions between the 5- and 5′-methyl groups on one ligand and those on the other. Even with hydrogen atoms in the 5,5′ positions, there would probably be sufficient repulsion that true planarity (D_{2h}) could not be achieved.

Recent work by Ferguson and Ramsey[4] and Ferguson and West[5] favors a tetrahedral or distorted tetrahedral arrangement of the ligands. However, their work as well as that of Murakami and Sakata[6] seems to indicate that removal of one or both substituents in the 5 positions on the rings allows a twisting toward planarity, especially in a coordinating solvent.

In view of the uncertainty as to the detailed structure of this type of complex and as a basis for our further

---

[1] Research supported by the U. S. Atomic Energy Commission.

[2] NDEA Predoctoral Fellow, 1967–1969.

[3] C. R. Porter, *J. Chem. Soc.*, 368 (1938).

[4] J. E. Ferguson and C. A. Ramsey, *ibid.*, 5222 (1965).

[5] J. E. Ferguson and B. O. West, *ibid.*, *A*, 1565 (1966).

[6] Y. Murakami and K. Sakata, *Inorg. Chim. Acta*, **2**, 273 (1968).