

## Structure of the Mixed-Valence Compound Dipotassium Tribromo(pyridine)platinate(II) Pentabromo(pyridine)platinate(IV) Dihydrate\*

BY ANDRÉ L. BEAUCHAMP,† DHARANIDHAR LAYEK AND THEOPHILE THEOPHANIDES

Département de Chimie, Université de Montréal, CP 6210, Succursale A, Montréal, Québec, Canada H3C 3V1

(Received 6 November 1981; accepted 11 January 1982)

### Abstract

$K_2[PtBr_3(C_5H_5N)][PtBr_5(C_5H_5N)] \cdot 2H_2O$ ,  $2K^+ \cdot C_{10}H_{10}Br_8N_2Pt_2^{2-} \cdot 2H_2O$ ,  $M_r = 1301.9$ , belongs to the orthorhombic space group  $Cmcm$ , with  $a = 5.606$  (1),  $b = 26.651$  (3),  $c = 8.343$  (2) Å,  $V = 1246.5$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 3.468$  g cm<sup>-3</sup>;  $\lambda(Mo K\alpha) = 0.71067$  Å (graphite monochromator),  $T = 295$  K,  $\mu(Mo K\alpha) = 243.8$  cm<sup>-1</sup>,  $\mu(Cu K\alpha) = 393.6$  cm<sup>-1</sup>. The structure was refined by full-matrix least squares on 346 independent nonzero reflections to an  $R$  factor of 0.042. It consists of infinite chains of square-planar  $[Pt^{II}Br_3py]^-$  ions (py = pyridine) alternating with octahedral  $[Pt^{IV}Br_5py]^-$  ions. The Br atoms bridging consecutive Pt atoms along the chain are disordered on two positions. The water molecule forms two hydrogen bonds with terminal Br atoms on consecutive complex ions along the chain and a distorted tetrahedral environment about its O atom is completed by two  $K^+$  ions. The nine-coordinate  $K^+$  ion is at the center of an approximate trigonal prism, where the top and bottom planes consist of three terminal Br atoms from various chains. Extra contacts are established through the middle of the side faces with one bridging Br and two O atoms. The  $K^+$  ions and water molecules define infinite chains roughly parallel to the  $c$  axis. The py molecules are oriented at 55° from the  $PtBr_3N$  plane.

### Introduction

X-ray work has now been carried out on a number of linear-chain halide-bridged  $Pt^{II}$ – $Pt^{IV}$  mixed-valence compounds (Beauchamp, Layek & Theophanides, 1982, and references therein). In all cases, the data were interpreted in terms of a strictly periodic . . . Hal– $Pt^{IV}$ –Hal . . .  $Pt^{II}$  . . . Hal– $Pt^{IV}$ –Hal . . .  $Pt^{II}$  . . . chain. However, the periodicity is usually lost in the directions perpendicular to the chain axis. In the simplest cases, the effect is restricted to the relative positions of the

short Hal–Pt–Hal bonds in adjacent chains: these pairs of short bonds are shifted by one Pt–Pt distance along the chain in one half of the chains and in a random manner. This effect manifests itself by weak diffuse layer lines, in addition to the normal Bragg lines, in oscillation photographs of the crystal rotating about the chain axis. Only a few examples of three-dimensionally ordered compounds have been proposed (Matsumoto, Yamishita, Ueda & Kida, 1978; Endres, Keller, Martin, Traeger & Novotny, 1980; Matsumoto, Yamashita & Kida, 1978), some of which have been criticized (Beauchamp *et al.*, 1982).

In addition to the halogen, the coordination sphere of Pt in the compounds studied so far usually contained  $NH_3$  or small mono- or bidentate aliphatic amines. These ligands can form hydrogen bonds, which were found to play an important role in stabilizing the crystal. We felt that it would be interesting to study the effect of using a pyridine molecule (py), which cannot form hydrogen bonds and possesses a large and flat organic portion. The crystal structure of  $K_2[PtBr_3py][PtBr_5py] \cdot 2H_2O$  is reported in the present paper.

### Experimental section

#### Crystallographic measurements

The compound was prepared as described by Werner (1896) and Werner & Fassbender (1897) and the crystals were grown directly in the reaction mixture. They consist of very long red plates, in which the long edge corresponds, as usual, to the chain direction ( $a$  axis). Films were taken with two specimens which yielded the same results. The crystal used for intensity measurements had the dimensions: 0.043 [between faces (001) and (00 $\bar{1}$ )]  $\times$  0.003 [(010) and (010)]  $\times$  0.55 mm [(100) and ( $\bar{1}00$ )].

Oscillation photographs of the crystal rotating about the  $a$  axis clearly showed a Laue mirror. Normal Bragg layers were interleaved with weak diffuse layers, which indicated a superstructure similar to those reported in most other mixed-valence compounds of this type. The structure deduced from the normal Bragg layers is

\* Potassium *catena- $\mu$ -bromo-tribromo(pyridine)platinate(II,IV) hydrate.*

† To whom correspondence should be addressed.

discussed here. Weissenberg photographs (levels 0, 1 and 2) showed the additional Laue mirror of the orthorhombic system. From the systematic absences ( $hkl$ ,  $h + k \neq 2n$  and  $h0l$ ,  $l \neq 2n$ ), a set of three space groups was retained:  $Cmcm$  (No. 63),  $Cmc2_1$  (No. 36) and  $C2cm$  (alternative definition for  $Ama2$ , No. 40).

The intensity data were recorded with an Enraf-Nonius CAD-4 diffractometer, following the procedure described previously (Beauchamp *et al.*, 1982). A set of 651 independent  $hkl$  reflections ( $2\theta \leq 50^\circ$ ,  $h + k = 2n$ ) was collected with  $Mo K\alpha$  radiation. Slow scans were performed only on the reflections found to have a net intensity  $I > \sigma(I)$  at the fast prescan. A total of 346 reflections considered to be significantly above background [ $I \geq 3\sigma(I)$ ] were retained for structure determination. These data were corrected for the effects of Lorentz-polarization and absorption (Gaussian integration, grid  $8 \times 8 \times 8$ , transmission coefficient: 0.53–0.92).

At a later stage, when it was realized that the structure was severely disordered in group  $Cmcm$ , the possibility that the compound might belong to a less symmetrical space group was considered and it became important to determine whether the conditions of systematic absence given above were strictly obeyed. A new set of data was collected with the same crystal, by using the stronger and cleaner  $Cu K\alpha$  radiation. All reflections of the  $hkl$  octant ( $2\theta \leq 140^\circ$ , including the  $h + k \neq 2n$  reflections) were measured by a slow scan. The  $\sim 600$  presumably absent reflections had intensities  $< 3\sigma(I)$  with only two exceptions: 010 [ $I/\sigma(I) = 8.0$ ] and 201 [ $I/\sigma(I) = 8.2$ ]. Both of these reflections showed very unsymmetrical backgrounds and their  $I/\sigma(I)$  ratio would drop below 4 if the higher backgrounds were used. Therefore, this was not considered to affect seriously the validity of the conditions deduced from the film work and the  $Mo K\alpha$  data set.

### Resolution of the structure

#### Space group $Cmcm$

A  $PtBr_3$  square-planar unit (with one corner missing) was deduced from the Patterson synthesis. In space group  $Cmcm$ , the Pt and the Br(2) atoms occupy equipoint 4(c) on the twofold axis at the intersection of two mirror planes. The two Br(1) atoms are symmetry equivalent and they occupy equipoint 8(f). Therefore the  $PtBr_3$  unit lies in a mirror plane and the site symmetry at Pt is  $2mm$ . In the two other space groups equally consistent with the systematic absences (*i.e.*  $Cmc2_1$  and  $C2cm$ ), some of the restrictions on the coordinates and the equivalence between the Br(1) atoms imposed in  $Cmcm$  would disappear, but the  $PtBr_3$  unit would have the same geometry and would be

similarly positioned in the cell. Consequently, this set of atomic positions was a suitable starting model to solve the structure, even if a lower-symmetry space group could eventually be adopted.

A difference Fourier ( $\Delta F$ ) map phased on  $PtBr_3$  provided information on the unknown portions of the cell:

(a) As expected, the missing corner of the square plane was found to be occupied by N of pyridine, which was positioned on the twofold axis already containing Pt and Br(2) [equipoint 4(c)]. Another peak on the twofold axis, further away from Pt, corresponded to C(3) of the pyridine ring. However, since the pyridine molecule as a whole was neither coplanar with  $PtBr_3$ , nor perpendicular to it, the mirror planes produced two overlapping images of the ring, with N and C(3) as common atoms. Thus, the side atoms C(1) and C(2) were considered as disordered on a general equipoint with half occupancy.

(b) The bridging Br(3) atoms were found on two positions along the Pt–Pt vector, symmetrically displaced from the midpoint between consecutive Pt atoms in the chain. This disordering is commonly observed in such compounds (Beauchamp *et al.*, 1982). It was anticipated from the diffuse layer lines in the oscillation photographs, by the short chain axis ( $a = 5.6 \text{ \AA}$ ) and by the fact that the four Pt atoms in group  $Cmcm$  have to be symmetrically equivalent. The Br(3) atoms were distributed on equipoint 8(g) with an occupancy factor of 0.5.

(c) The highest unexplained peak, found at 0, 0.47, 0.03, was obviously due to the  $K^+$  ion. From its coordinates,  $K^+$  had to sit on a mirror plane [equipoint 8(f)]. Since there are only four  $K^+$  ions per cell, half occupancy through disorder was indicated; this was also consistent with the fact that full occupancy of the eight 8(f) sites would place two  $K^+$  ions too close together. Another peak in the  $x = 0$  section of the map, weaker than the previous one, but with the same characteristics, was assigned to the water oxygen. Thus K and O were placed each on an equipoint 8(f) with half occupancy.

Refinement was carried out by full-matrix least squares. Individual weights based on counting statistics were applied. Isotropic refinement of all known atoms converged to  $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.091$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.107$  (nonzero reflections only). The Pt, Br and K atoms were then refined anisotropically and this reduced  $R$  to 0.045 and  $R_w$  to 0.058. The H atoms on pyridine were fixed at their calculated positions (isotropic  $B = 5.0 \text{ \AA}^2$ ). Their parameters were not refined, but their coordinates were recalculated after each cycle of refinement. The H atoms of the water molecule were not visible on the  $\Delta F$  map. In the last cycles, a secondary-extinction parameter was also included in the refinement. The final values of  $R$  and  $R_w$  were 0.042

Table 1. *Refined fractional coordinates* ( $\times 10^3$ , for Pt, Br, K  $\times 10^4$ ) *and equivalent isotropic temperature factors* ( $\times 10^3$ , for Pt  $\times 10^4$ )

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$ ( $\text{\AA}^2$ )
Pt	0	1135 (1)	2500	271 (6)
Br(1)	0	1144 (2)	5428 (4)	55 (1)
Br(2)	0	222 (2)	2500	48 (2)
Br(3) <sup>†</sup>	4425 (10)	1111 (3)	2500	58 (3)
K <sup>†</sup>	0	4733 (7)	318 (20)	59 (7)
N	0	192 (1)	250	24 (9)
C(1) <sup>†</sup>	167 (8)	215 (2)	174 (5)	41 (11)
C(2) <sup>†</sup>	171 (12)	269 (2)	168 (7)	91 (22)
C(3)	0	297 (2)	250	58 (16)
O <sup>†</sup>	0	441 (2)	158 (6)	69 (17)
H(1) <sup>*†</sup>	289	197	122	63
H(2) <sup>*†</sup>	291	286	107	63
H(3) <sup>*</sup>	0	333	250	63

\* Not refined.

<sup>†</sup> Atoms involved in the disorder.

and 0.055, respectively. The goodness-of-fit ratio was 1.56. The final  $\Delta F$  map was essentially featureless: five peaks in the range 0.7–1.4 e  $\text{\AA}^{-3}$  were found near Pt or Br, while the general background was  $< \pm 0.5$  e  $\text{\AA}^{-3}$ .

The coordinates refined in group *Cmcm* are listed in Table 1.\* The form factors used are those of Cromer & Waber (1965) except for H (Stewart, Davidson & Simpson, 1965). The  $f'$  and  $f''$  components of anomalous dispersion were included in the structure factor calculation for Pt, Br and K (Cromer, 1965).

### Lower symmetry

Refinement in space group *Cmcm* revealed three disordered regions in the asymmetric unit. As an ordered structure would appear to be disordered when refined in a space group containing symmetry elements absent from the 'true' cell, we decided that less symmetrical space groups should be considered, in spite of the low *R* factor in *Cmcm*. Indeed, the atoms involved in the disorder represent a small fraction of total electron density, compared with the ordered  $\text{PtBr}_3\text{N}$  unit. Therefore, improper description of some of these light-atom positions is not expected to produce dramatic effects on the *R* factor.

The Br(3) atoms were expected to remain disordered, irrespective of the space group, for the reasons given above. Thus, we tried to find space groups likely to generate ordered arrangements for the pyridine

ligands and/or the K–O chains. From the positions of the ordered  $\text{PtBr}_3\text{N}$  units, it was deduced that none of the *C*-orthorhombic space groups could make these two regions simultaneously ordered. Indeed, these space groups possess either a twofold axis or a mirror plane through the Br(2)–Pt–N bonds. The former symmetry element inevitably introduces disorder in the K–O chain, the latter in the pyridine ligand.

Space group *Cmc2*<sub>1</sub>, which has the same set of systematic absences as *Cmcm*, would be consistent with ordered K–O chains. Refinement in this non-centrosymmetric space group was undertaken. The atomic positions found in *Cmcm* were transposed to *Cmc2*<sub>1</sub>, with Pt on equipoint 4(*a*) at  $z = \frac{1}{4}$  to define the origin along *c*. The ordered K and O atoms occupied one 4(*a*) equipoint each, while Br(1), C(2) and C(3) were split into two nonequivalent sets. Least-squares refinement led to high correlations between the positional and thermal parameters of these two sets, but convergence was slowly attained. Attempts to refine Br(3) anisotropically resulted in imaginary thermal ellipsoids. In the final cycle [Pt, Br(1), Br(1'), Br(2) and K anisotropic, other nonhydrogen atoms isotropic], the *R* factor was 0.048. The overall geometry did not differ greatly from *Cmcm*, but unrealistic distances were found in the pyridine ring: C–N, 1.30 and 1.04  $\text{\AA}$ ; C–C, 0.93, 1.99, 1.66 and 1.87  $\text{\AA}$ . Therefore, the *Cmc2*<sub>1</sub> model was not considered as an improvement over *Cmcm*.

Group *C2cm*, the other noncentrosymmetric space group derived from *Cmcm*, would retain the simultaneous disorder in the pyridine region and in the K–O chains. This group was not investigated further.

The only *C*-orthorhombic group that could make pyridine ordered (but the K–O chains disordered) is *C222*<sub>1</sub>. Attempts similar to those described above were made in this space group, but the least-squares calculations failed to converge. This model differed from *Cmcm* only in the positions of some C atoms and this was clearly not sufficient to hold the structure in space group *C222*<sub>1</sub> (assuming that the compound belongs to this group). Furthermore, there were no nonzero reflections among the  $h0l$ ,  $l \neq 2n$  reflections, which should not be absent in *C222*<sub>1</sub>. We thus conclude that this model should not be retained.

Ordered arrangements of the pyridine ligands and K–O chains would require a still lower symmetry, such as a *P*-orthorhombic cell. These space groups would produce nonzero reflections among the  $hkl$ ,  $h + k \neq 2n$  data and this was not detected. We conclude that *Cmcm* is the only satisfactory model to explain our results.

### Description of the structure

The crystal contains infinite chains of complex anions parallel to the *a* axis (Fig. 1). In the ideally ordered

\* Lists of structure factors, anisotropic thermal parameters and least-squares-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36726 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

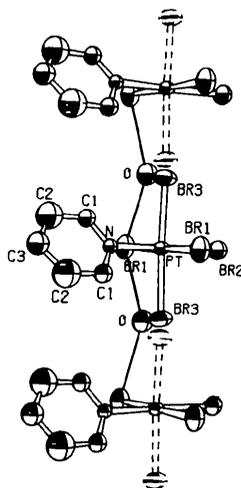


Fig. 1. Portion of the infinite chain of  $[PtBr_3py]^-$  and  $[PtBr_3py]^-$  ions along the  $a$  axis. The dotted lines correspond to the bridging Br atoms in one half of the chains. The thin bonds represent hydrogen bonds formed by the water molecule with Br(1) atoms in consecutive anions. The thermal ellipsoids correspond to 50% probability.

chain, square-planar  $[Pt^{II}Br_3py]^-$  ions alternate with octahedral  $[Pt^{IV}Br_3py]^-$  ions, two *trans* Br atoms in the latter anion acting as bridging groups between the metal atoms. Any given chain in such compounds is believed to be rigorously ordered. However, for one half of the chains and in a random manner, the pairs of short Br—Pt—Br bonds are displaced by one Pt—Pt distance along the chain axis (dotted bonds in Fig. 1). The same pattern would be produced if all the bridging Br atoms in a chain moved simultaneously away from the close  $Pt^{IV}$  atom, in the direction of  $Pt^{II}$ , which would become  $Pt^{IV}$  in the process. So, the average structure deduced from X-ray data makes all the Pt atoms symmetrically equivalent, with two half-bromine atoms at 2.481 (6) Å and two more at 3.126 (6) Å. This model is consistent with the presence of weak diffuse scattering layers in the oscillation photographs.

The Pt—Br distances along the chain (Fig. 2) are in the ranges (2.45–2.49 and 3.07–3.14 Å, respectively) observed for  $[PtBr_2(NH_3)_2][PtBr_4(NH_3)_2]$  (Keller, Keppler, Ledezma-Sanchez & Steiger, 1981),  $[PtBr_2(en)][PtBr_4(en)]$  (en = ethylenediamine, Ryan & Rundle, 1961) and  $[Pt(C_2H_5NH_2)_4][PtBr_2(C_2H_5NH_2)_4]Br_4$  (Craven & Hall, 1966; Brown & Hall, 1976). The difference between the Pt—Br distances is somewhat reduced (2.54–2.56 and 2.92–2.96 Å) in the trimethylenediamine (tn) complexes  $[Pt(tn)_2][PtBr_2(tn)_2]X_4$  ( $X = ClO_4^-$ ,  $BF_4^-$ , Matsumoto, Yamashita & Kida, 1978). The  $[Pt(en)_2][PtBr_2(en)_2](ClO_4)_4$  system, with Pt—Br distances of 2.71 (2) and 2.76 (2) Å (Endres *et al.*, 1980), seems to behave differently.

The terminal Pt—Br bonds are equal within experimental errors and their average value [2.440 (4) Å] is

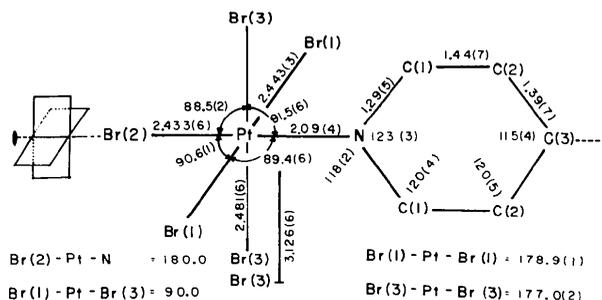


Fig. 2. Interatomic distances (Å) and bond angles ( $^\circ$ ) around Pt. The values not shown are related to those shown in the figure by the  $2mm$  symmetry at Pt (see diagram on the left).

in good agreement with those found for other Pt compounds (Keller *et al.*, 1981; Ryan & Rundle, 1961; Bokii & Kukina, 1965; Russell, Tucker & Whittaker, 1975; Messmer & Amma, 1966; Mélançon, Rochon & Hubert, 1979; Mélançon, Hubert & Rochon, 1975). The Pt—N distance [2.09 (4) Å] is also normal (Keeton, Mason & Russell, 1971; Colamarino & Orioli, 1975; Caira & Nassimbeni, 1975; Thiele & Wagner, 1978; Meester, Olie, Sint & Schenk, 1975). Space-group symmetry requires that the bonds to the four non-bridging ligands be in a crystallographic mirror plane. The angles not fixed by this symmetry are all close to the ideal values of 90 or 180° (Fig. 2).

The geometry of the pyridine ligand is normal (Fig. 2) and the ring is planar within 0.2 Å ( $0.3\sigma$ ). The rings make an angle of 55(2)° with the  $PtBr_3N$  plane and because of the mirror planes in the space group, they exist in two disordered orientations. As shown in the packing pattern (Fig. 3), the Pt chains are so oriented that the pyridines are restricted to layers parallel to  $ac$ , at  $y \sim \frac{1}{4}$  and  $\frac{3}{4}$ , in which the interactions are of the van der Waals type. Inspection of the inter-ring contacts

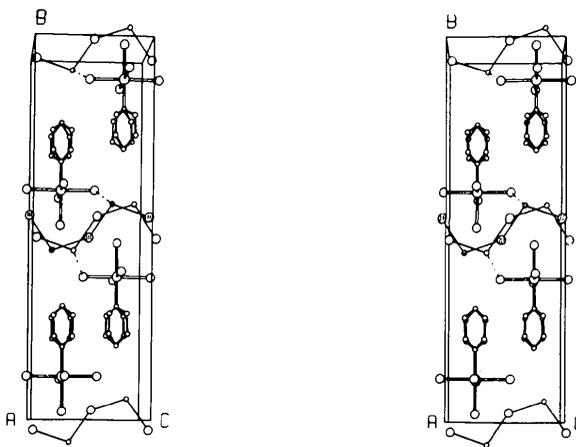


Fig. 3. Projection of the unit cell down the chain direction ( $a$  axis). The atoms are represented by spheres of arbitrary size and they can be identified by reference to Fig. 2. The two disordered patterns for the pyridine rings and K—O chains are illustrated.

Table 2. Environment of the  $K^+$  ion and the water molecule

Distances (Å)			
$K-O(1)^I$	2.78 (6)	$K-Br(3)^{viii,ix}$	3.27 (2)
$K-O(1)^{II}$	2.73 (6)	$O^I-K^x$	2.73 (6)
$K-Br(1)^{III,IV}$	3.65 (1)	$O^I-Br(1)^{xi,xii}$	3.31 (3)
$K-Br(2)^{V,VI}$	3.59 (1)		
$K-Br(2)^{VII,VIII}$	3.66 (1)		
Angles (°)			
$O^I-K-O^{II}$	143 (1)	$Br(2)^V-K-Br(2)^{VI}$	102.8 (4)
$O^I-K-Br(1)^{III,IV}$	123 (1)	$Br(2)^V-K-Br(2)^{VII}$	73.5 (3)
$O^I-K-Br(2)^{V,VI}$	89 (1)	$Br(2)^V-K-Br(2)^{VIII}$	155.8 (4)
$O^I-K-Br(2)^{VII,VIII}$	67 (1)	$Br(2)^V-K-Br(3)^{IX}$	133.8 (4)
$O^I-K-Br(3)^{X,IX}$	99 (1)	$Br(2)^V-K-Br(3)^{XII}$	122.5 (4)
$O^{II}-K-Br(1)^{III,IV}$	77 (1)	$Br(2)^{VII}-K-Br(2)^{VIII}$	99.9 (3)
$O^{II}-K-Br(2)^{V,VI}$	68 (1)	$Br(2)^{VII}-K-Br(3)^{VII}$	59.0 (3)
$O^{II}-K-Br(2)^{VII,VIII}$	128 (1)	$Br(2)^{VII}-K-Br(3)^{IX}$	68.7 (3)
$O^{II}-K-Br(3)^{X,IX}$	118 (1)	$K-O^I-K^x$	106 (1)
$Br(1)^{III}-K-Br(1)^{IV}$	100.3 (4)	$K-O^I-Br(1)^{XI,XII}$	102 (1)
$Br(1)^{III}-K-Br(2)^V$	67.7 (3)	$K^x-O^I-Br(1)^{XI,XII}$	115 (1)
$Br(1)^{III}-K-Br(2)^{VI}$	145.1 (4)	$Br(1)^{XI}-O^I-Br(1)^{XII}$	116 (1)
$Br(1)^{III}-K-Br(2)^{VII}$	56.6 (2)		
$Br(1)^{III}-K-Br(2)^{VIII}$	128.7 (4)		
$Br(1)^{III}-K-Br(3)^{IX}$	69.7 (3)		
$Br(1)^{III}-K-Br(3)^{VII}$	60.1 (3)		

Symmetry code: (i)  $x, 1-y, -z$ ; (ii)  $x, y, \frac{1}{2}-z$ ; (iii)  $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$ ; (iv)  $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$ ; (v)  $-\frac{1}{2}+x, \frac{1}{2}+y, z$ ; (vi)  $\frac{1}{2}+x, \frac{1}{2}+y, z$ ; (vii)  $-\frac{1}{2}+x, \frac{1}{2}-y, -z$ ; (viii)  $\frac{1}{2}+x, \frac{1}{2}-y, -z$ ; (ix)  $\frac{1}{2}-x, \frac{1}{2}-y, -z$ ; (x)  $x, 1-y, -\frac{1}{2}+z$ ; (xi)  $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (xii)  $-\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z$ .

shows that the rings cannot assume these two orientations at random. Two pyridine rings with the same orientation on adjacent chains would produce a very short  $H(1) \cdots H(2)$  contact of 2.01 Å (sum of the van der Waals radii, 2.40 Å) (Cotton & Wilkinson, 1972), whereas opposite orientations within the same chain would lead to a  $H(2) \cdots H(2)$  contact of 2.34 Å. The most likely arrangement is the one with the same orientation for all rings belonging to the same chain, but an alternance when moving from chain to chain. The resulting layer would then be ordered along the **a** and **c** directions. The periodicity is destroyed in the **b** direction, since there are apparently no restrictions for the next layer to assume the same pattern rather than its mirror image.

Although the H atoms of the water molecule were not positively identified in the Fourier map, it is clear that they are involved in hydrogen bonding with Br(1) atoms belonging to consecutive  $PtBr_3N$  units along the chain (Fig. 1 and Table 2). The  $O \cdots Br$  distance [3.31 (3) Å] is in the center of the range (3.17–3.38 Å) proposed by Stout & Jensen (1968) for  $O-H \cdots Br$  systems. Two  $K^+$  ions lying roughly along the lone pairs complete the distorted tetrahedral environment of oxygen.

The environment of the  $K^+$  ion includes two water O and seven Br atoms (Fig. 4 and Table 2). Two sets of

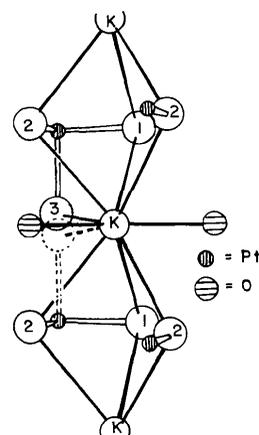


Fig. 4. Environment of the  $K^+$  ion in the cell. Bromine is represented by the numbers used in Fig. 2. The dashed portion represents the alternative position of the disordered Br(3) atom.

three coplanar terminal Br atoms define a trigonal prism with  $K^+$  at the center ( $K \cdots Br = 3.59-3.66$  Å,  $\sigma = 0.01$  Å). Extra contacts are established through the middle of the lateral faces, with two molecules at 2.73 (6) and 2.78 (6) Å, respectively, and with a bridging Br atom at 3.27 (2) Å in one of the two disordered positions. This geometry is found in a number of nine-coordinate species (Cotton & Wilkinson, 1972). The  $K \cdots O$  distances compare well with those found in carboxylates (Wyckoff, 1969) and in hydrated compounds such as Zeise's salt (Love, Koetzle, Williams, Andrews & Bau, 1975). The  $K-Br$  contacts are in the normal range (Bokii & Kukina, 1965), but it is noteworthy that the interaction with the bridging Br atom is particularly short [3.27 (2) Å]; this value corresponds to the sum of the radii of  $K^+$  and  $Br^-$  (Cotton & Wilkinson, 1972).

The water molecules and  $K^+$  ions define infinite chains parallel to the **c** axis (Fig. 3). These chains are found in two disordered patterns, related by a twofold axis. The interactions in the chain and with the rest of the structure remain the same in both orientations.

## Discussion

The model proposed for this structure involves twofold disorder in three regions of the asymmetric unit. It is interesting to speculate on whether these three regions can assume independently either pattern, or these disordered regions are correlated.

From packing considerations, it was possible to propose a likely arrangement of the pyridine rings within any given layer. However, there seems to be no particular interaction with the rest of the structure which would force the next layer to assume the same or

the opposite pattern. The arrangement adopted in one layer probably depends on the way the first units of this layer were assembled at the time the chains started to grow. Thus, the disorder of the pyridine rings seems to result from a non-periodic repetition of two-dimensionally ordered layers and this part of the structure is probably independent of the disorder affecting other regions.

The situation is not so clear with the bridging halogen and the K—O chains. There is a short contact between  $K^+$  and the bridging Br atom [3.27 (2) Å] (Fig. 4). However, the overall coordination geometry of  $K^+$  is not improved by using one possible position of Br(3) instead of the other: both K—Br(3) distances are symmetry equivalent and the angles around either  $K^+$  or Br(3) are just as favorable in both cases. So, there are no clear indications of strong correlations between the sets of atomic positions and we felt that these two regions should be considered independently.

It is interesting to examine whether this structure could participate in a disorder of dynamic origin. Reorganization of the pyridine layer is unlikely, since it would require rotation about the Pt—N bond for all the rings in this layer. Similarly, the atoms in the K—O chains would have to move around considerably to reach the alternative pattern. In particular, the  $K^+$  ion, which bridges a pair of Br(1) atoms, and the water molecule bridging the other pair, would have to exchange their role in the process. Therefore, we do not expect the disorder in these two regions to result from rapid exchange of positions in the crystal. On the other hand, the bridging Br atoms in a chain could probably all move, in a concerted manner, to the alternative positions, leading to a change of oxidation state in all Pt atoms in that chain. This process is more likely to take place, because it requires no reorganization of the rest of the structure.

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