

parameter for O7 has the largest value of any refined atom and that there are no hydrogen-bonding contacts to O7 in this direction which would constrain its motion along z . The hydrogen-bonding network is illustrated in Figure 3.

Physical Properties of the Complex

The blue complex exhibits one broad d-d absorption at 14800 cm^{-1} either as a mullied solid or in nitromethane solution ($\epsilon 100$). Its nitromethane solution is nonconducting and upon evaporation yields crystals with the same ir spectrum as the original solute. After heating of the compound at 150° for 5 hr, it suffered no mass loss or ir spectral changes. The ir spectrum shows broad O-H absorptions with maxima at 3400 and 1650 cm^{-1} and three bands at 1170 , 1095 , and 1030 cm^{-1} attributed to the coordinated sulfate group. At room temperature the magnetic moment is 1.87 BM .

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Registry No. $[\text{Cu}(\text{tmen})\text{SO}_4(\text{OH}_2)_2]\cdot\text{H}_2\text{O}$, 57196-94-8.

Supplementary Material Available: Listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure by Neutron Diffraction of Potassium Tetracyanoplatinate(II) Trihydrate, the Starting Product for Partially Oxidized Conducting Cyanoplatinate Salts^{1a}

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Potassium tetracyanoplatinate(II) trihydrate, $\text{K}_2\text{Pt}(\text{CN})_4\cdot 3\text{H}_2\text{O}$, crystallizes in the orthorhombic space group $Pbcn$, with $a = 13.426(5)$, $b = 11.848(4)$, and $c = 6.956(2)\text{ \AA}$ with $Z = 4$. The strongly efflorescent crystals grown from aqueous solution were sealed in capillaries for three-dimensional neutron data collection. The structure was deduced from the neutron Patterson map and was refined by Fourier and full-matrix least-squares techniques to $R_p = 0.061$ ($R_F = 0.056$) for 587 reflections with $F^2 > \sigma(F^2)$. The structure consists of planar $\text{Pt}(\text{CN})_4^{2-}$ groups stacked parallel to c forming linear Pt chains with a Pt-Pt separation of $3.478(1)\text{ \AA}$. Alternate $\text{Pt}(\text{CN})_4^{2-}$ groups are rotated giving an eclipsed configuration with C-Pt-Pt-C torsion angles of $15.7(1)$ and $16.7(1)^\circ$. The $\text{Pt}(\text{CN})_4^{2-}$ plane is also tilted with respect to c by $\sim 3^\circ$. The two types of water molecules serve to link CN^- groups within a $\text{Pt}(\text{CN})_4^{2-}$ stack and to cross-link adjacent $\text{Pt}(\text{CN})_4^{2-}$ stacks. Comparisons are made with the structure of the mixed-valence compound $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\cdot 3\text{H}_2\text{O}$, $\text{KCP}(\text{Br})$.

Introduction

Square-planar platinum complexes with electron-rich ligands are the basic starting materials for the preparation of the novel mixed-valence, highly conducting, one-dimensional metallic salts such as $\text{K}_2\text{Pt}(\text{CN})_4\text{X}_{0.3}\cdot 3\text{H}_2\text{O}$, $\text{KCP}(\text{X})$ where X^- is Br^- or Cl^- . The preparation involves partial oxidation of a Pt^{II} compound such as $\text{K}_2\text{Pt}(\text{CN})_4\cdot 3\text{H}_2\text{O}$, KTCP hereafter, with a strong oxidizing agent such as Cl_2 , Br_2 , or H_2O_2 . Although the highly conducting compounds have been the subject of much experimental and theoretical investigation,^{2,3} there are few reliable physical and structural data available for the starting material, KTCP , and related complexes.⁴ The cyanoplatinate family displays many interesting chemical, optical, and spectroscopic properties.⁵ Insofar as electrical conductivity is concerned KTCP is an insulator; its conductivity is $\sim 10^{-9}$ that of $\text{KCP}(\text{Br})$. We have chosen to investigate the structure of KTCP by neutron diffraction in order to have accurate data for structural comparisons between the precursor, KTCP , and the partially oxidized products.

Experimental Section

Crystal Preparation. Single crystals of KTCP were prepared by evaporation from an aqueous solution of a sample purchased from K & K Laboratories. Single crystals of a size suitable for neutron diffraction grew within a few hours. The crystals are transparent, have a yellow-green tint when viewed perpendicular to c , give intense blue fluorescence when viewed down the c axis, and lose water very quickly when exposed to air. The crystal density was not measured because of the rapidity of water loss. The x-ray density is 2.589 g/cm^3 .

Space Group. Preliminary x-ray precession and Weissenberg photographs gave the conditions for diffraction as $hk0$ ($h+k=2n$), $h0l$ ($h+l=2n$), and $0kl$ ($k+l=2n$) which would indicate space group P_{nm} . However, neutron observations gave the corrected conditions as $hk0$ ($h+k=2n$), $h0l$ ($l=2n$), and $0kl$ ($k=2n$) leading to the unique space group $Pbcn$. The apparent discrepancy is due to the dominance of Pt scattering in the x-ray case and the locations of Pt atoms $c/2$ apart in the cell.

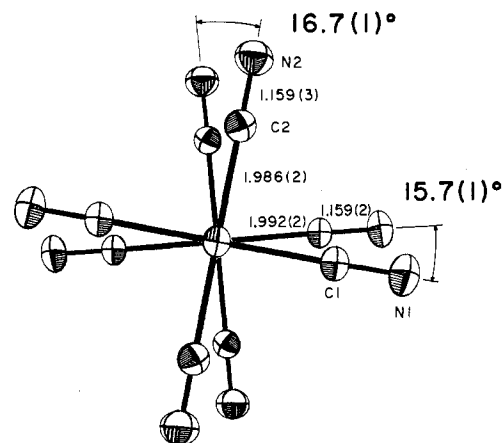
Neutron Data. The crystal selected for data collection was a rectangular parallelepiped $1.0 \times 1.7 \times 6.8\text{ mm}$. It was quickly sealed in a lead glass capillary and mounted for data collection on the Chemistry Division four-circle neutron diffractometer at the CP-5

Table I. Fractional Atomic Coordinates and Final Isotropic Temperature Factors for KTCP

Atoms	x	y	z	B, Å ²
Pt(1)	0	0	0	1.3 (2)
C(1)	-0.0203 (2)	0.1665 (2)	0.0003 (4)	1.3 (2)
C(2)	0.1461 (2)	0.0244 (2)	-0.0160 (4)	1.6 (2)
N(1)	-0.0299 (1)	0.2637 (1)	0.0006 (4)	2.4 (2)
N(2)	0.2314 (1)	0.0384 (2)	-0.0262 (3)	2.0 (2)
O(1)	0	0.4706 (4)	0.25000	3.1 (4)
O(2)	0.1987 (4)	0.2959 (4)	0.1809 (6)	2.1 (2)
H(1)	0.0115 (6)	0.4200 (5)	0.3507 (12)	6.1 (6)
H(2)	0.2189 (6)	0.3582 (7)	0.2593 (12)	4.1 (4)
H(3)	0.1419 (6)	0.2688 (7)	0.2389 (13)	5.7 (5)
K(1)	0.3438 (4)	0.1403 (4)	0.2959 (8)	2.2 (4)

reactor. This apparatus previously has been described in detail.⁶ The crystal remained clear and transparent throughout the study. The orientation was a general one with *c* approximately parallel to the ϕ axis of the goniometer. The cell parameters and orientation matrix were determined from precise angular measurement of 20 automatically centered reflections, chosen in the 2θ range 30–50°. The cell parameters are $a = 13.426$ (5), $b = 11.848$ (4), and $c = 6.956$ (2) Å at 22°C. The wavelength of 1.142 (1) Å was obtained with a Be crystal monochromator set at $\theta_M = 30^\circ$. Data were collected in the θ - 2θ step scan mode with 0.1° steps and scan width varying from 2.5 to 5°. Backgrounds were measured on both sides of the peak for times ca. 0.3–0.5 the peak scan time. Data collection was limited to $2\theta = 80^\circ$, beyond which few reflections were observable. A total of 1667 reflections in the two octants hkl and $\bar{h}\bar{k}l$ were collected. However, because of the rather severe extinction encountered with the hkl reflections due to crystal shape, the analysis was restricted to the $\bar{h}\bar{k}l$ group. A single standard reflection was checked repeatedly during the data collection and found to remain unchanged in intensity within the expected statistical variation. Standard errors were assigned to the data on the basis of counting statistics plus a $(0.03I)^2$ contribution to the variance of each reflection. The data were corrected for absorption ($\mu = 0.91 \text{ cm}^{-1}$) and were reduced to scaled F^2 values for structure solution and refinement. Transmission coefficients ranged from 0.86 to 0.95.

Structure Solution and Refinement. The structure was solved directly from the neutron Patterson map. The Pt atom and one CN⁻ group were located from the Patterson analysis and the remaining atoms were placed utilizing Fourier and difference-Fourier methods. The structure was refined by full-matrix least-squares methods from $R_F = 0.24$ without H atoms and with isotropic temperature factors to $R_F = 0.088$ ($R_p = 0.068$) for all atoms with anisotropic temperature factors and anisotropic type 1 extinction.⁷ The quantity minimized in the refinement is $\sum w(F_o^2 - F_c^2)^2$ where F_o and F_c are the observed and calculated structure amplitudes and the weights w are given by $1/\sigma^2(F_o)^2$. For $F_o^2 < 0$, F_o^2 was set equal to zero. The agreement indices are defined as $R_F = \sum |F_o| - |F_c| / \sum F_o$, $R_p = \sum |F_o^2 - F_c^2| / \sum F_o^2$, and $\sigma_2 = \sum [w(F_o^2 - F_c^2)^2 / (N_o - N_r)]^{1/2}$ where N_o is the number of independent observations and N_r the number of parameters varied. The above R values include all the reflections, many of which were quite weak. The agreement indices $R_{F>\sigma} = 0.056$ and $\sigma_2 = 1.12$ are perhaps more representative in indicating the excellence of the refinement. Since the exact H₂O molecule multipliers were varied in one of the final refinements. The multipliers for H₂O(1) and H₂O(2)

Figure 1. Stacking configuration of the $\text{Pt}(\text{CN})_4^{2-}$ ions. View is down the *c* axis. Bond distances are in angstroms.

converged to 0.53 (3) and 1.00 (4) with no significant change in the R factor. This corresponds to 3.06 (5) molecules of H₂O in the cell which is in excellent agreement with expectation. The atomic coordinates and final isotropic temperature values are listed in Table I, and the anisotropic temperature factors and root-mean-square components of thermal displacement, in Table II. The neutron scattering amplitudes used were as follows: $b_{\text{Pt}} = 0.950$, $b_{\text{C}} = 0.6648$, $b_{\text{N}} = 0.940$, $b_{\text{O}} = 0.575$, $b_{\text{H}} = -0.374$, and $b_{\text{K}} = 0.370$, all in units of 10^{-12} cm^3 .

The raw neutron data were reduced using the program DATALIB⁹ for input into the Fourier and least-squares refinement programs SSFOUR¹⁰ and SSXFLS,¹⁰ respectively. All distances, angles, and planes were calculated using the program SSFFE.¹⁰ Molecular drawings were made using the program ORTEP.¹¹

Structure Description

The crystal structure consists of nearly square planar $\text{Pt}(\text{CN})_4^{2-}$ groups stacked parallel to *c* thus forming linear Pt atom chains. All Pt atoms are equivalent and are located in the fourfold sites, *a*, with site symmetry $\bar{1}$. The *c* glide plane perpendicular to *b* requires that two Pt atoms be located *c*/2 apart yielding a single Pt-Pt distance of 3.478 (1) Å in the chain. The $\text{Pt}(\text{CN})_4^{2-}$ groups are nearly square planar though not required to be so by symmetry. The bond distances in the $\text{Pt}(\text{CN})_4^{2-}$ group are given in Table III, the bond angles are given in Table IV, and the deviations from planarity are presented in Table V. The plane of the $\text{Pt}(\text{CN})_4^{2-}$ group is tilted 3.3 (1)° with respect to *c* as is evident from the bond angles in Table IV. Two of the carbon atoms of $\text{Pt}(\text{CN})_4^{2-}$ lie in the *xy* plane whereas the other two lie above and below the plane giving a C(1)-Pt(1)-Pt(1)' angle of 93.21 (8)°. Adjacent $\text{Pt}(\text{CN})_4^{2-}$ groups along *c* are in nearly eclipsed configuration with C-Pt-Pt-C torsion angles of 15.7 (1) and 16.7 (1)° as shown in Figure 1. The overall structure shown in Figure 2 is seen to consist of stacks of $\text{Pt}(\text{CN})_4^{2-}$ groups located at the edges and center of the cell. The stacks are stabilized by hydrogen-bonded water molecules which link

Table II. Anisotropic Temperature Factors^a ($\times 10^4$) and the Rms Component of Thermal Displacement along Each Principal Axis^b in KTCP

Atoms	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	Rmsd 1	Rmsd 2	Rmsd 3
Pt(1)	31 (1)	31 (1)	72 (4)	0 (1)	1 (2)	-6 (3)	0.128 (5)	0.152 (4)	0.168 (3)
C(1)	42 (1)	29 (2)	114 (5)	0 (1)	-3 (3)	-1 (3)	0.144 (4)	0.167 (4)	0.196 (4)
C(2)	34 (1)	42 (2)	101 (6)	1 (1)	2 (2)	-7 (3)	0.152 (5)	0.176 (4)	0.177 (3)
N(1)	59 (1)	35 (1)	167 (5)	6 (1)	-10 (3)	5 (3)	0.153 (3)	0.201 (3)	0.237 (3)
N(2)	41 (1)	60 (2)	168 (6)	-2 (1)	1 (2)	-11 (3)	0.192 (3)	0.194 (3)	0.216 (3)
O(1)	54 (3)	53 (6)	279 (18)	0	16 (7)	0	0.194 (1)	0.216 (7)	0.266 (9)
O(2)	63 (3)	54 (3)	178 (9)	-5 (2)	-6 (4)	-11 (5)	0.186 (7)	0.215 (6)	0.242 (5)
H(1)	84 (5)	79 (6)	343 (23)	6 (5)	4 (9)	24 (9)	0.228 (10)	0.277 (8)	0.297 (9)
H(2)	108 (6)	74 (6)	352 (24)	8 (4)	-51 (10)	-56 (10)	0.200 (11)	0.273 (9)	0.350 (10)
H(3)	67 (5)	115 (7)	417 (28)	-3 (5)	21 (10)	36 (11)	0.239 (9)	0.277 (9)	0.334 (11)
K(1)	48 (3)	62 (4)	149 (12)	-2 (3)	1 (5)	21 (6)	0.175 (8)	0.208 (6)	0.224 (8)

^a The anisotropic thermal parameter, T , is defined as $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$. ^b The Rms component of thermal displacement along each principal axis is in angstroms.

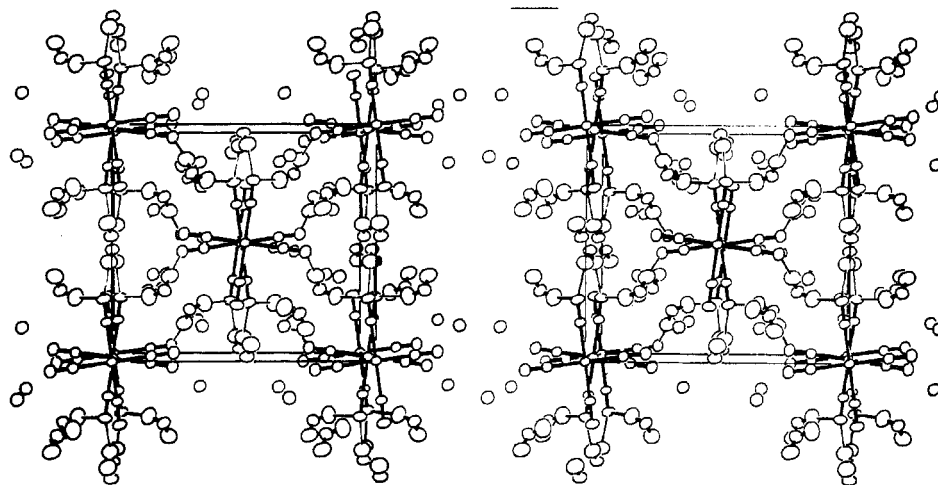


Figure 2. Stereopacking drawing of KTCP viewed down c . The a axis is horizontal and b is vertical. Hydrogen bonds are indicated by the lighter lines.

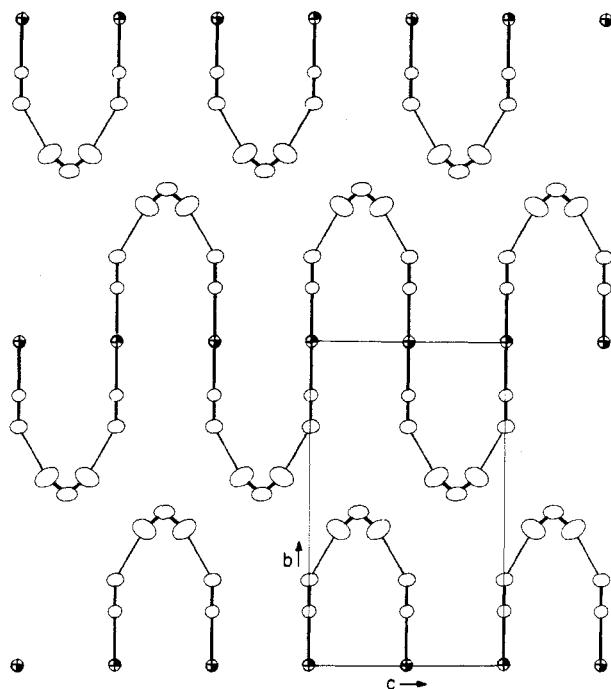


Figure 3. Hydrogen-bonding network within the bc plane. A similar network displaced $b/2$ is found at the $1/2a$ level of the unit cell.

Table III. Bond and Interaction Distances (Å) within the $\text{Pt}(\text{CN})_4^{2-}$ Ions

Atoms	Distance, Å	Atoms	Distance, Å
Pt(1)-C(1)	1.992 (2)	Pt(1)-Pt(1)'	3.478 (1)
Pt(1)-C(2)	1.986 (2)	C(1)···C(1)'	3.517 (6), 3.524 (6)
C(1)-N(1)	1.159 (2)	C(2)···C(2)'	3.526 (1)
C(2)-N(2)	1.159 (3)	N(1)···N(1)'	3.562 (5), 3.577 (5)
		N(2)···N(2)'	3.595 (2)

Table IV. Bond Angles within the $\text{Pt}(\text{CN})_4^{2-}$ Ions

Atoms	Angle, deg	Atoms	Angle, deg
Pt(1)-C(1)-N(1)	178.5 (2)	C(1)-Pt(1)-Pt(1)'	89.94 (8)
Pt(1)-C(2)-N(2)	179.7 (2)	C(2)-Pt(1)-Pt(1)'	93.21 (3)
C(1)-Pt(1)-C(2)	89.51 (8)		

CN^- groups within a stack and also cross-link between CN^- groups of adjacent stacks. There are two types of H_2O molecules; type 1 molecules in fourfold special positions are tetrahedrally coordinated by two N atoms and two K^+ ions.

The N atoms are hydrogen bonded to O atoms by weak

Table V. Least-Squares Planes and Dihedral Angles in KTCP
 $\text{Pt}(\text{CN})_4^{2-}$ Anion Plane: $-0.7675X - 0.0742Y - 6.944Z = 0.00$

Atom	Dev, Å	Wt	Atom	Dev, Å	Wt
Pt(1)	0.000 (1)	1.0	C(2)	-0.003 (3)	1.0
C(1)	0.002 (3)	1.0	N(2)	0.002 (3)	1.0
N(1)	-0.001 (3)	1.0			

Dihedral angle	Value, deg
$\text{Pt}(\text{CN})_4^{2-}$ plane with xy plane of the unit cell	3.3 (1)
$\text{Pt}(\text{CN})_4^{2-}$ plane with xz plane of the unit cell	89.6 (1)
$\text{Pt}(\text{CN})_4^{2-}$ plane with yz plane of the unit cell	86.7 (1)

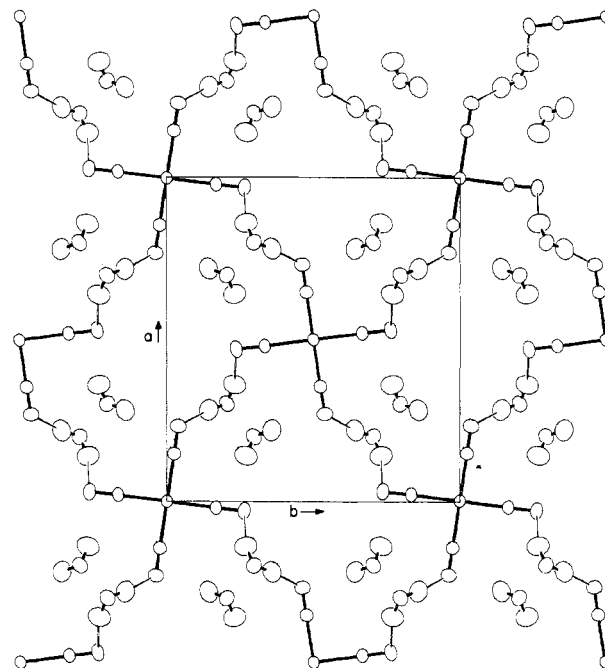


Figure 4. Interstack hydrogen bonding as viewed along c .

(3.03 Å) N-H...O bonds which serve to link the nearly eclipsed CN^- groups in the $\text{Pt}(\text{CN})_4^{2-}$ stacks into chainlike configurations shown in Figure 3. The second type of water molecule located in the eightfold general positions is also approximately tetrahedrally coordinated with two N atoms and two K^+ ions. There are two distinct hydrogen bonds of lengths 2.98 and 3.19 Å linking O(2) to N(2) and N(1), respectively. These serve to cross-link the $\text{Pt}(\text{CN})_4^{2-}$ groups which lie in the center of the cell to the four similar groups lying along the cell edges. This can be seen quite readily in Figure 4. K^+ ions are found near H_2O and CN^- , located

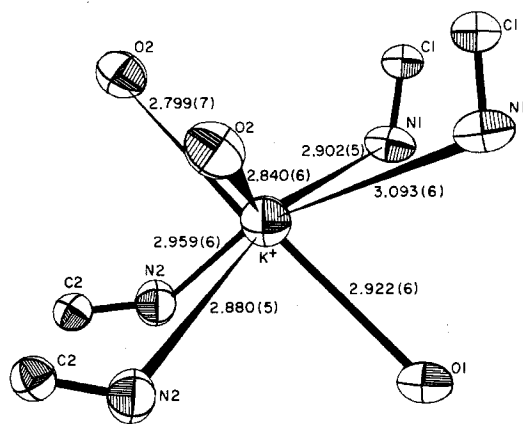


Figure 5. Coordination sphere of the potassium ion. Bond distances are in angstroms.

within voids in the structure. The coordination of K^+ is sevenfold with four N and three O near neighbors and is probably best described as a distorted capped trigonal prism (Figure 5).

Discussion

It is well-known that Pt^{II} forms planar complexes with most ligands. This is attributed to the d^8 electron configuration in which the $d_{x^2-y^2}$ orbital, which is favorably directed toward the ligands, forms dsp^2 hybrid orbitals which share the ligand bonding electrons. The structure of KTCP presented here is well suited to this description. The $Pt(CN)_4^{2-}$ group is precisely planar and nearly square, although not required to be so by symmetry, in accord with the dsp^2 hybridization. The linear Pt chains with a Pt-Pt separation of 3.478 Å are indicative of a weak metal-metal interaction along c . Since the d_{z^2} orbital which has maximum extension along c is fully occupied, additional hybridization (e.g., $5d-6p$) is required to account for the weak bonding interaction. However, it is interesting to note that the $Pt(CN)_4^{2-}$ groups are tilted by 3.3° with respect to c , which would tend to imply the existence of a repulsive interaction. There is also evidence of an interaction between the π -electron clouds of CN^- since the vertically stacked $Pt(CN)_4^{2-}$ groups are found in an eclipsed configuration with C-Pt-Pt-C torsion angles equal to $\sim 16^\circ$. The magnitude of the torsion angle has been shown previously^{4b} to be related to the metal-metal distance for a series of related transition metal complexes.

The structure of the partially oxidized derivative compound, KCP(Br), has recently been redetermined³ and is now quite accurately known over a wide temperature range.¹²⁻¹⁴ The structural changes which occur as a result of partial oxidation of Pt^{2+} to an average $Pt^{2.3+}$ are as follows. The point group symmetry is changed from mmm to $4mm$ and thus from centro- to noncentrosymmetric. The site symmetry of Pt is changed from $\bar{1}$ to $4mm$. The $Pt(CN)_4^{2-}$ group is nearly square planar in KTCP while it is square but distinctly nonplanar in KCP(Br). The K^+ ion and H_2O are distributed in opposite halves of the cell in noncentrosymmetric KCP(Br) while they are symmetrically distributed in KTCP. The most striking changes, of course, are the shortening of the Pt-Pt separation from 3.478 (1) to 2.890 (1) Å and the configurational change of the two vertically stacked $Pt(CN)_4^{2-}$ groups from a nearly eclipsed ($\sim 16^\circ$ torsion angle) to a staggered (45°) configuration. In addition while the four Pt atoms in the cell of KTCP are equivalent, there are two distinct Pt atoms in KCP(Br) with slightly different separations. The shortened Pt-Pt separation has been previously explained^{2a} to be due to a partial removal of d_{z^2} electrons from Pt upon oxidation, which allows substantially improved d_{z^2} orbital overlap and stronger metal-metal bonding. The $Pt(CN)_4^{2-}$

group configurational change is undoubtedly due to the increased π -orbital repulsion of the CN^- groups brought into closer contact in KCP(Br). The occurrence of nonequivalent Pt ions in the oxidized compound is intriguing and it is tempting to relate this to Pt in different valence states; however evidence from ESCA experiments^{15,16} tends to refute this. The difference in the two Pt-Pt separations in KCP(Br) is slight and does not provide strong evidence for different valence states. However, this difference appears to increase with decrease in temperature.^{13,14} The C-N bond distances are almost identical (1.158 Å in KCP(Br)) in the two compounds which does not support the suggestion of an extra transfer of electrons from cyanide to Pt in the oxidized compound.¹⁵

In many respects the structures of KTCP and KCP(Br) are quite similar in spite of the differences in symmetry. The K^+ ions in KTCP have sevenfold coordination with four N and three O near neighbors while in KCP(Br) the neighbors include one Br plus four N and three O atoms giving an eightfold antiprism coordination. There are two kinds of H_2O molecules in each structure. The $H_2O(1)$ molecules link $Pt(CN)_4^{2-}$ groups lying along the cell edges in both cases while the $H_2O(2)$ molecules cross-link essentially along cell diagonals between nonequivalent CN^- ions attached to $Pt(CN)_4^{2-}$ groups located diagonally across the cell. In both cases H_2O is given up readily but the crystals retain their integrity over a substantial composition range.

Conclusions

The production of one-dimensional metal atom chains through crystallization of square-planar molecular complexes which stack in pancake-like arrays is now well known. There are a number of factors which limit or determine the closeness of metal-metal atom approach and thus the extent to which metallic properties develop. One of these is the electronic configuration of the central metal atom. The d^8 Pt configuration is particularly suited, when influenced by strong-field ligands, to producing the desired square-planar complex. The nature of the ligands is a second important factor. Thus bulky ligands such as phenyl rings, methyl or ethyl groups, etc. bonded to the central metal atoms may be expected to force rather large metal-metal stacking distances. On the other hand CN^- , CO, NO^+ , and $(C_2O_4)^{2-}$ ligands are favorable in regard to size, electron-withdrawing tendency, and the capacity to cause orbital splitting and produce square-planar configurations. The factor which appears to be of major significance, however, is the removal of electrons from the metal atom by partial oxidation. The present structure analysis of KTCP provides strong supporting evidence for the major role played by electron removal through oxidation. Thus the change in Pt-Pt distance from 3.48 Å in KTCP to 2.89 Å in KCP(X) does not appear to be related to any significant difference in metal-ligand bonding; hence, it must be rationalized essentially solely in terms of electron configuration on Pt.

Registry No. $K_2Pt(CN)_4 \cdot 3H_2O$, 14323-36-5.

Supplementary Material Available: Listing of structure factor amplitudes (2 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) (a) Work performed under the auspices of the U.S. Energy Research and Development Administration. (b) Participant in the Undergraduate Research Participation Program sponsored by the Argonne Center for Educational Affairs.
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Synthesis, Properties and X-Ray Characterization of Aquo and Hydroxo Complexes of Cobalt(II) and Nickel(II) with Poly(tertiary phosphines)

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Cobalt(II) and nickel(II) aquo cations deriving from $[M(H_2O)_6](BF_4)_2$ ($M = Co, Ni$) reacting with poly(tertiary phosphines) (L_n) such as tris(2-diphenylphosphinoethyl)amine ($N(CH_2CH_2PPh_2)_3$; np_3), tris(2-diphenylphosphinoethyl)phosphine ($P(CH_2CH_2PPh_2)_3$; pp_3), and tris(*o*-diphenylphosphinophenyl)phosphine ($P(C_6H_4PPh_2)_3$; QP), according to the nature of the solvent form a series of hydroxo complexes $[M(OH)L_n]Y$ ($Y = BF_4, BPh_4$) and a series of aquo complexes $[M(H_2O)L_n](BF_4)_2$. All the nickel complexes are low spin and trigonal bipyramidal. The cobalt complexes with np_3 are high spin and are assigned a tetrahedrally distorted TBP geometry. The other cobalt complexes are low spin with distorted square-pyramidal geometry. This assignment comes from the results of x-ray structure determinations, performed on the complexes $[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$ and $[Co(H_2O)(pp_3)](BF_4)_2 \cdot CH_3COCH_3$. Both the crystals are triclinic, space group $P\bar{1}$, with the following cell constants for the $[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$ and $[Co(H_2O)(pp_3)](BF_4)_2 \cdot CH_3COCH_3$ respectively: $a = 11.826$ (2) Å, $b = 12.293$ (2) Å, $c = 16.690$ (4) Å, $\alpha = 92.72$ (3)°, $\beta = 90.88$ (3)°, $\gamma = 117.27$ (4)°; $a = 17.897$ (3) Å, $b = 12.237$ (2) Å, $c = 12.116$ (2) Å, $\alpha = 63.19$ (3)°, $\beta = 78.05$ (3)°, $\gamma = 83.57$ (3)°. Counter methods were used and least-squares refinements gave final R factors of 0.089 and 0.081, respectively.

Introduction

In a large number of papers published by Venanzi¹ and by Meek,² various series of 3d metal complexes, mostly five coordinated, containing polyfunctional ligands (L_n) with group 5 donor atoms, have been described. These complexes of general formula $[MX_mL_n]Y$ contain in the coordination sphere one or more rarely two anions (halides, pseudohalides, nitrate, perchlorate) besides the polyfunctional ligands.

No hydroxo complexes, however, have resulted, even from preparations starting from hydrated metal salts. Thus the only examples known to date of hydroxo-phosphino metal complexes remain those of Fe(I), Rh(I), and Ir(I).³⁻⁵

In very few cases, with ligands containing arsenic as the donor atoms, have nickel(II) complexes with a molecule of water as the fifth ligand been formed.⁶⁻⁸

In a previous paper we described the formation of a dimeric hydroxo complex of cobalt(II), $[(p_3)Co(OH)_2Co(p_3)](BPh_4)_2$, where p_3 is the poly(tertiary phosphine) 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2PPh_2)_3$, which was obtained starting from $[Co(H_2O)_6](BF_4)_2$ in acetone solution. The fact that such a hydroxo species was formed under these circumstances was attributed to the basic nature of the phosphine, which is capable of taking protons from water molecules of the aquo cation to form phosphonium cations.⁹

This novel observation induced us to undertake a systematic study of the behavior of the tripod poly(tertiary phosphine) ligands toward the salts $[Ni(H_2O)_6](BF_4)_2$ and $[Co(H_2O)_6](BF_4)_2$ under conditions in which the only anion present in the reaction mixture could be the ion BF_4^- , which is believed to have very low coordinating power. The poly(tertiary phosphines) used were the following: tris(2-diphenylphosphinoethyl)amine ($N(CH_2CH_2PPh_2)_3$; np_3), tris(2-diphenylphosphinoethyl)phosphine ($P(CH_2CH_2PPh_2)_3$; pp_3), and the tris(*o*-diphenylphosphinophenyl)phosphine named by Venanzi (QP, $P(C_6H_4PPh_2)_3$).

Under such conditions two types of complexes have been

isolated, both for nickel and for cobalt, the hydroxo complexes $[M(OH)L_n]Y$ ($Y = BF_4, BPh_4$) and the aquo complexes $[M(H_2O)L_n](BF_4)_2$.

All these complexes were characterized by means of magnetic, spectrophotometric, and conductivity measurements.

The structures of two of these complexes, $[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$ and $[Co(H_2O)(pp_3)](BF_4)_2 \cdot CH_3COCH_3$, have been determined by means of x-ray diffraction.

Experimental Section

Reagents and Physical Measurements. The syntheses of the ligands np_3 and QP appear elsewhere.^{10,11} The ligand pp_3 was acquired from the Pressure Chemical Co., Pittsburgh, Pa. Ethanol, acetone, and petroleum ether solvents were used without further purification, but the tetrahydrofuran was purified by distillation over $LiAlH_4$. The $NaBPh_4$ was A.R. grade. Both the perchlorates and tetrafluoroborates of cobalt and nickel were released from the metal carbonate by addition of the corresponding acid and then recrystallized from aqueous solutions.

The physical measurements were executed by the previously described method.¹² See Table I for analytical, magnetic, and conductivity data.

Preparation of the Complexes. All preparative operations were carried out in an atmosphere of dry nitrogen and complexes were dried off by standing in dry nitrogen current. Almost invariably the experimental quantities of ligand or aquo complex dissolved in the appropriate solvent were 1 mmol of solid in 20 ml of solvent. To avoid unnecessary repetition these ratios will be assumed throughout unless stated otherwise.

$[Co(OH)(np_3)]ClO_4 \cdot C_2H_5OH$. Room-temperature solutions of the ligand in acetone and aquo complex $[Co(H_2O)_6](ClO_4)_2$ in ethanol (40 ml) were mixed and concentrated by means of a stream of dry nitrogen. On standing overnight red-brown crystals separated which were filtered off and washed with alcohol and petroleum ether.

$[Co(OH)(pp_3)]BF_4 \cdot C_2H_5OH$. The orange colored crystalline product was prepared by an analogous procedure to the perchlorate above, starting from $[Co(H_2O)_6](BF_4)_2$ and concentrating the mixture by heating to ca. 10 ml.

$[Co(OH)(np_3)]BPh_4$. An ethanolic solution of $[Co(H_2O)_6](BF_4)_2$