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Structural Studies of Precursor and Partially Oxidized Conducting Complexes. 13. A Neutron Diffraction and X-Ray Diffuse Scattering Study of the Dimerized Platinum Chain in Rubidium Tetracyanoplatinate Chloride (2:1:0.3) Trihydrate, $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3.0H_2O$[1]

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The crystal structure and molecular formula of the one-dimensional conductor $Rb_2[Pt(CN)_4]Cl_{0.30}\cdot 3.0H_2O$, RbCP(Cl), have been fully characterized using single-crystal neutron diffraction, x-ray diffuse scattering data, and thermogravimetric analysis. We have determined that RbCP(Cl) is isostructural with KCP(Cl) and KCP(Br) except that only one halide site can be identified; i.e., there does not appear to be any evidence for the presence of a "defect" water molecule in RbCP(Cl). From thermogravimetric analyses RbCP(Cl) is a 3.0 hydrate as is KCP(Br). RbCP(Cl) crystallizes in the tetragonal space group *P*4*mm*, with unit cell dimensions $a = 10.142$ (6) Å, $c = 5.801$ (4) Å, $V_c = 596.7$ Å^3, and $Z = 2$. A total of 1113 neutron diffraction data (594 independent) were collected to $(\sin\theta)/\lambda = 0.724$ and of these 511 had $F_o^2 > \sigma(F_o^2)$. The crystal structure was solved using MULTAN and a full-matrix least-squares refinement resulted in a final $R(F_o^2) = 0.063$ (all data) and $R(F_o^2) = 0.059$ for data with $F_o^2 > \sigma(F_o^2)$. Using x-ray diffuse scattering techniques we have established the Pt oxidation as +2.31 (2) from which the molecular formula $Rb_2[Pt(CN)_4]Cl_{0.31(2)}\cdot 3.0H_2O$ is obtained. The structure consists of nearly planar $Pt(CN)_4$ moieties stacked along the *c* axis forming a perfectly linear Pt–Pt chain. The crystal asymmetric unit contains two independent $Pt(CN)_4{}^{1.7-}$ groups, two H_2O sites, one Rb^+ site, and one Cl^- site. The asymmetric ordering of the Rb^+ ion and the H_2O molecules constitutes the main source of crystal asymmetry. The two-independent Pt–Pt chain distances are definitely *unequal* (2.877 (8) and 2.924 (8) Å) with the average intrachain separation (2.90 Å) being slightly longer than in KCP(Br) (2.88 Å) and KCP(Cl) (2.87 Å). Since RbCP(Cl) and KCP(Cl) are isostructural, it appears that the replacement of K^+ by Rb^+ results in lattice expansion along *c*, which produces larger Pt–Pt intrachain separations, simply because of the larger cation radius of Rb^+. Thus the unequal and slightly longer Pt–Pt separations in RbCP(Cl), compared to those in KCP(Br, Cl), apparently result in increased electron localization along the Pt-atom chain and a concomitant decrease in the electrical conductivity.

Introduction

Partially oxidized tetracyanoplatinate (POTCP) compounds have currently been of great interest due in part to Little's predictions[3] of high-temperature superconductivity in one-dimensional metals. The room temperature metallic conductivities of these POTCP salts are due to the formation of Pt–Pt chains along which electron transport occurs. Usually these POTCP salts have metal–metal spacings only ~0.02–0.2 Å longer than in Pt metal (2.78 Å). Experience has shown that the electrical transport properties of these salts depend not only on the specific compound under study but also on the crystalline environment of the metal conducting spine.[24] For example, the chemical environment about the $Pt^{(2+x)+}(CN)_4$ (x = 0.25–0.40) groups results in *bent* metal chains in $K_{1.75}[Pt^{2.25+}(CN)_4]\cdot 1.5H_2O$ (Pt–Pt = 2.96 Å)[4] and *linear* chains in $K_2[Pt^{2.33+}(CN)_4]Br_{0.3}\cdot 3.0H_2O$ (Pt–Pt = 2.88 Å).[5] It has been shown[6,7] that the degree of partial oxidation (DPO) and the Pt–Pt spacings are inversely related, such that it is possible to predict one if the other is known. In the two known cases with the highest DPO's[8] (~0.40), in $Cs_2[Pt^{2.39+}(CN)_4](FHF)_{0.39}$ and $Rb_2[Pt^{2.40+}(CN)_4](FHF)_{0.40}$, the Pt–Pt spacings are the shortest yet observed[9] in POTCP salts at 2.83 and 2.80 Å, respectively. Because metal–metal bonds between Pt atoms are reported[10] to be as short as ~2.5–2.6 Å, it is not unreasonable to assume that Pt–Pt spacings in POTCP salts may eventually be found which will be considerably *less* than in Pt metal (~2.78 Å) itself.

In this paper we discuss the detailed molecular structure of $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3.0H_2O$, RbCP(Cl), derived from a single-crystal neutron diffraction analysis. This study was undertaken to provide structural information which might assist in explaining why RbCP(Cl), which appears to be isostructural with KCP(Cl), has a maximum conductivity of ~0.1 that of KCP(Cl).[11] We also present new synthetic results which indicate that while RbCP(Cl) can be prepared, its Br^- analogue has yet to be synthesized. Therefore, as we previously postulated,[20] the report[23] of an x-ray diffuse scattering study of $Rb_2[Pt(CN)_4]Br_{0.25}\cdot 1.3H_2O$, RbCP(Br), may have actually been performed on $Rb_{1.75}[Pt(CN)_4]\cdot xH_2O$.

Experimental Section

Crystal Preparation. Attempts to prepare RbCP(Br) in the conventional manner by mixing $Rb_2[Pt^{4+}(CN)_4Br_2]$ and $Rb_2[Pt^{2+}(CN)_4]\cdot xH_2O$ in a 1:5 ratio, or in any ratio, at 5[25] or 22 °C were not successful, even if excess RbBr was present (vide infra). Furthermore, we were unable to synthesize it by electrolysis (2 V dc) of a solution of RbBr and $Rb_2[Pt(CN)_4]\cdot xH_2O$. However, we were able to prepare RbCP(Cl) by either of the above mentioned methods. Chemical analysis[12] yielded a composition consistent with $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$, and iodine–thiosulfate titrations[13] established the metal oxidation state as $Pt^{2.30+}$. Emission spectrographic analyses revealed that only Pt and Rb were present with traces of K (~0.08%)

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and Na (~0.01%). The final least-squares structure refinement was consistent with the composition $Rb_2[Pt(CN)_4]Cl_{0.353(2)}{\cdot}3H_2O$ but more reliable (we feel) diffuse x-ray scattering measurements indicate the chemical formula to be $Rb_2[Pt(CN)_4]Cl_{0.31(2)}{\cdot}3H_2O$, in agreement with the iodine titrations.

Crystals were prepared by slow evaporation of a saturated aqueous solution which had to be >2 M in RbCl. The best specimen selected for neutron data collection had approximate dimensions 1.0 × 1.3 × 5.5 mm and weighed 14.9 mg. It was sealed in a Pb glass capillary for protection against dehydration during data collection.

Unit Cell and Space Group. Preliminary x-ray photographs indicated RbCP(Cl) to be isostructural, space group *P4mm*, with KCP(Br, Cl). The lattice parameters for the primitive tetragonal cell were established by centering 16 intense reflections, in the range $40 < 2\theta < 60°$, on the neutron diffractometer. The resulting least-squares fit of the angles 2θ, χ, and ϕ of these reflections, measured with a neutron wavelength of 1.142 (1) Å (22 °C), yielded $a = 10.142$ (6) Å, $c = 5.801$ (4) Å, and $V_c = 596.7$ Å^3. These may be compared with those for KCP(Br) and KCP(Cl) which are $a = 9.907$ (3), 9.883 (3) Å and $c = 5.780$ (2), 5.742 (2) Å, respectively.[5] The calculated crystal density for two formula units per unit cell is 2.98 g cm^{-3} and the observed value, determined by flotation, is 2.98 (1) g cm^{-3}.

Data Collection. After complete data collection with a tiny (1.4 mg) crystal,[26] a larger (14.9 mg) crystal was grown and used for data collection at the Argonne National Laboratory CP-5 reactor. The crystal was mounted in an arbitrary orientation, and data were collected using an Electronics-and-Alloys four-circle automated diffractometer under the remote control of a Sigma V computer.[14] The monochromatic beam (λ 1.142 (1) Å) results from use of a Be single-crystal monochromator, with monochromator angle $\theta_m = 30°$, which yields a neutron flux at the sample of $\sim 2.9 \times 10^6$ N cm^{-2} s^{-1}.

Based on the least-squares-determined orientation matrix, data were collected automatically using the θ–2θ step-scan method with 0.1° step intervals and preset scan ranges of 40–70 steps. At each extremity of the scan the background intensities were established with both crystal and detector in a stationary position. The total number of data collected was 1113 (594 independent) to $(\sin\theta)/\lambda = 0.724$. Of the 594 independent data 511 had $F_o^2 > \sigma(F_o^2)$. Instrument and crystal stability were monitored by remeasuring two reference reflections after every 80 regular data and their combined intensity did not vary more than 5% during data collection. Individual reflections were corrected for absorption ($\mu_{calcd} = 1.16$ cm^{-1}) and the calculated transmission factors ranged from 0.81 to 0.89. Using the integrated intensities, after correction for absorption, the F_o^2 were obtained by application of the following equation:[15] $F_o^2 = (\omega I \sin 2\theta)/I_0\lambda^3N^2V$, where ω is the angular rotation velocity of the crystal, I_0 the incident intensity, λ the wavelength, N the number of unit cells per unit volume, V the crystal volume, and θ the Bragg angle. A preshaped NaCl crystal, for which precise absorption and secondary extinction corrections had been calculated for all reflections, was used to obtain I_0 which allowed us to place the derived F_o^2 on an approximate "absolute scale"; i.e., $S \simeq 1.0$ in the least-squares refinement. All variances of F_o^2 were calculated from $\sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0.05F_o^2)$, where $\sigma_c^2(F_o^2)$ were determined from the counting statistics and the 0.05 added factor was deduced from the 5% maximum variation in the reference reflections integrated intensities.

Structure Solution and Refinement.[16] Although RbCP(Cl) appeared to be isostructural with KCP(Br), this information was not used and the structural solution was obtained using MULTAN which provided rapid location of the $Pt(CN)_4$ moiety. Complete structural solution was accomplished using Fourier and difference maps which allowed location of the remaining Rb, O, H, and Cl atoms. Initial full-matrix least-squares refinement of all atom positional parameters, with isotropic thermal parameters, yielded discrepancy indices as follows:

$$R(F_o) = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} = 0.20$$

$$R(F_o^2) = \frac{\Sigma|F_o^2 - F_c^2|}{\Sigma F_o^2} = 0.26$$

and

$$R_w(F_o^2) = \left[\frac{\Sigma w|F_o^2 - F_c^2|^2}{\Sigma w_i F_o^4}\right]^{1/2} = 0.31$$

Table I. Final Discrepancy Indices for $Rb_2[Pt(CN)_4]Cl_{0.3}{\cdot}3.0H_2O$[a]

Data selection	No. of reflections	$R(F_o)$	$R(F_o^2)$	$R_w(F_o^2)$	σ_1
All reflections	594	0.065	0.063	0.083	1.10
$F_o^2 > 1.0\sigma(F_o^2)$	511	0.051	0.059	0.080	1.17

[a] See Experimental Section for explanation of $R(F_o)$, $R(F_o^2)$, $R_w(F_o^2)$, and σ_1.

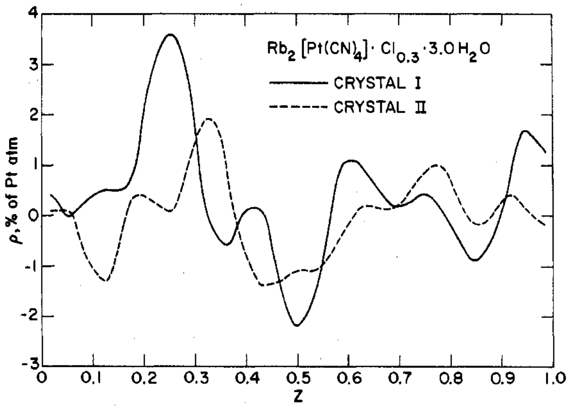

Figure 1. Difference Fourier density line (0.5, 0.5, z) from the neutron data.[26] A possible "second site" at $z \simeq 0.3$ could not be confirmed from least-squares analysis (see text).

After introduction of anisotropic thermal parameters the agreement factors were reduced dramatically and are given in Table I. The standard deviation of an observation of unit weight,

$$\sigma_1 = \left[\frac{w_i|F_o^2 - F_c^2|^2}{n - p}\right]^{1/2}$$

where n is the number of observations and p the number of parameters varied (69) in the least-squares refinement, was very good at 1.10. The final observation to parameter ratio was 8.6:1.

In order to provide a check of the final least-squares refinement, and examine the possibility of an additional water[17] or halide[5] site, a difference Fourier map was calculated. It revealed only two peaks slightly above background: one of intensity 2.0 times background with coordinates (0, 0, −0.39) and another at 1.7 times background and with coordinates (0.5, 0.5, 0.32). The former peak lies between Pt(1) and Pt(2) and cannot be assigned to any logical structural feature. However, the second peak might be assigned to a "second site" for Cl^- which would yield two Cl^- sites describing a vector parallel to c with a site separation of $\sim c/6$. Both neutron diffraction data sets[26] exhibited a peak at (0.5, 0.5, ~0.3) as illustrated in Figure 1. In the case of $K_2[Pt(CN)_4]Br_{0.3}{\cdot}3H_2O$, the "second site" separation was also $c/6$.[5] In either case a complicated disorder is involved and in the case of KCP(Br) the second site has been described as either a Br^- anion[5] or a highly disordered "defect water" molecule.[17] The "defect" H_2O description leads to a chemical formula of $K_2[Pt(CN)_4]Br_{0.3}{\cdot}3.2H_2O$ rather than that previously accepted, $K_2[Pt(CN)_4]Br_{0.3}{\cdot}3.0H_2O$. We have established (see section on Thermogravimetric Analyses) in this investigation that both KCP(Br) and RbCP(Cl) are indeed 3.0 hydrates.

In addition, there is no indication from the final difference map of the existence of H atoms near the second site if indeed a H_2O molecule is involved. It should be pointed out, however, that in RbCP(Cl) this possible second site is displaced *oppositely* to that in KCP(Br, Cl); i.e., this site lies in the portion of the unit cell ($z < 0.5$) populated by H_2O molecules rather than lying near the Rb^+ ions. Another factor which suggests that this site is spurious is that it is surrounded by four symmetry-related O(2) atoms with a very short X···O distance of 2.4 Å and no indication that H-atom peaks are present. Therefore, in an attempt to verify the existence of the second site as a Cl^- ion, its coordinates were used in a least-squares refinement (crystallographic occupancy factor 0.02). The $R(F_o^2)$ was only slightly reduced from 0.063 to 0.062, the occupancy factor converged to 0.0057

Table II. Positional[a] and Thermal[a] Parameters (Å^2) for $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3.0H_2O$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	0	0	0	163 (13)	163	97 (11)	0	0	0
Pt(2)	0	0	4960 (13)	172 (13)	172	103 (11)	0	0	0
C(1)	1971 (2)	0	−43 (16)	192 (8)	285 (9)	192 (9)	0	−22 (22)	0
C(2)	1397 (3)	1397	5009 (13)	233 (11)	233	189 (8)	−37 (6)	16 (29)	16
N(1)	3109 (2)	0	−92 (14)	191 (6)	517 (10)	371 (11)	0	22 (18)	0
N(2)	2198 (2)	2198	5052 (14)	350 (11)	350	379 (10)	−137 (6)	−2 (24)	−2
Cl(1)	5000	5000	4929 (28)	294 (36)	294	540 (37)	0	0	0
Rb	1970 (3)	5000	7400 (15)	432 (14)	381 (13)	531 (20)	0	12 (17)	0
O(1)	5000	0	3788 (15)	372 (29)	1006 (50)	265 (29)	0	0	0
O(2)	3406 (10)	3406	923 (16)	777 (46)	777	541 (35)	−103 (33)	149 (43)	149
H(1)	4276 (8)	0	2761 (20)	633 (43)	1023 (61)	501 (52)	0	−189 (44)	0
H(2)	2909 (22)	2909	1790 (34)	1172 (124)	1172	1455 (147)	−35 (78)	582 (160)	582
H(3)	3825 (31)	3825	1982 (30)	1788 (222)	1788	681 (94)	−95 (132)	75 (151)	75

[a] Multiplied by 10^4. Thermal parameters correspond to the expression $\exp[-8\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$.

Table III. Interatomic Distances (Å) and Bond Angles (deg) for $Rb_2Pt(CN)_4Cl_{0.3}\cdot 3.0H_2O$

(A) Distances around Platinum Atoms[a]

Pt(1)-C(1)	1.999 (2)	Pt(1)-Pt(2)	2.877 (8)
Pt(2)-C(2)	2.005 (2)	Pt(1)-Pt(2)^{I}	2.924 (8)

(B) Carbon-Nitrogen Distances in Cyanide Groups

C(1)-N(1)	1.155 (3)	C(2)-N(2)	1.149 (3)

(C) Water Molecule Distances

O(1)-H(1)	0.946 (10), 0.970 (11)[b]
O(2)-H(2)	0.873 (17), 0.969 (23)
O(2)-H(3)	0.859 (25), 0.958 (28)

(D) Hydrogen Atom Interactions

H(1)···N(1)	2.034 (9)	O(1)-H(1)-N(1)	164.6 (9)
H(2)···N(2)	2.149 (16)	O(2)-H(2)-N(2)	153.5 (18)
H(3)···Cl	2.401 (21)	O(2)-H(3)-Cl	179.8 (16)

(E) Rubidium Ion Interactions[a]

Rb-O(1)^{II}	2.895 (7)	Rb-N(2)	3.160 (3)
Rb-O(2)^{III}	2.985 (9)	Rb-Cl	3.391 (7)
Rb-N(1)^{IV}	3.128 (3)		

(F) Chloride Ion Interactions[a]

Cl-O(2)	3.260 (14)	Cl-Rb	3.391 (7)

(G) Angles (deg) of Pt Chain and Bonded Atoms

Pt(2)-Pt(1)-Pt(2)^{I}	180
Pt(1)-C(1)-N(1)	179.3 (5)
Pt(2)-C(2)-N(2)	179.6 (5)
C(1)-Pt-C(1)^{II}	89.991 (7)
C(2)-Pt-C(2)^{VI}	89.988 (12)
H(1)-O(1)-H(1)^{V}	101.9 (14)
H(2)-O(2)-H(3)	99.1 (17)

[a] Superscripts refer to symmetry positions listed below. If no superscript appears (X, Y, Z) is implied: (I) $x, y, z - 1$; (II) y, x, z; (III) $x, y, z + 1$; (IV) $y, x, z + 1$; (V) $1 - x, 1 - y, z$; (VI) $-x, -y, z$. [b] Corrected for thermal motion; hydrogen assumed to ride on oxygen.

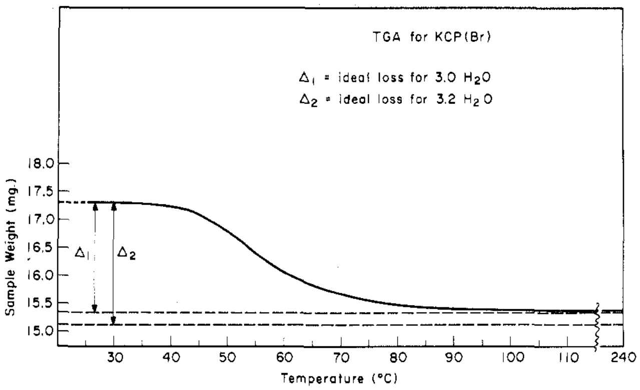

Figure 2. Thermogravimetric analysis of $K_2[Pt(CN)_4]Br_{0.3}\cdot 3.0H_2O$, KCP(Br), using a heating rate of 4 °C/min. Note that KCP(Br) is a 3.0 hydrate if prepared by the method of Saillant et al.[19] and is not a 3.2 hydrate.[17]

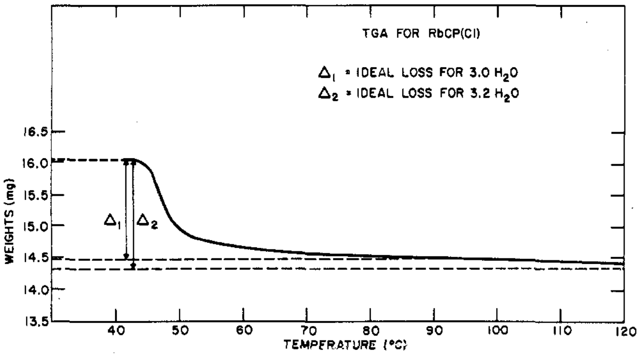

Figure 3. Thermogravimetric analysis of $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3.0H_2O$, RbCP(Cl) (heating rate 4 °C/min).

(3), and B_{iso} was 0.6 Å^2. The introduction of an anisotropic temperature factor for "Cl(2)" invariably resulted in nonpositive definite temperature factors. For these reasons it was decided, in the absence of any positive indications, to describe the RbCP(Cl) structure in terms of only one Cl$^-$ site.

The final positional and thermal parameters are given in Table II and the important bond distances and angles in $Rb_2[Pt(CN)_4]Cl_{0.31}\cdot 3.0H_2O$ are given in Table III. For the least-squares refinements, the coherent neutron scattering amplitudes used for Pt, N, C, O, H, and Rb were, respectively, 0.950, 0.940, 0.665, 0.580, −0.374, and 0.70, all in units of 10^{-12} cm.[18]

Thermogravimetric Analyses of $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ and $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$. In an attempt to establish and compare the hydration states of KCP(Br) and RbCP(Cl), we have performed TGA analyses using an automatic recording Mettler TGA/DTA apparatus. The KCP(Br) sample was prepared in the identical manner described by Saillant et al.[19] and stored above a 75% relative humidity bath (saturated $KNO_3\cdot NH_4Cl$ solution). The RbCP(Cl) samples were prepared in a similar manner. The TGA sample chamber was continuously purged with 75% relative humidity N_2, which made it impossible to dehydrate the samples, prior to heating at a rate of 4°/min. The results for KCP(Br) (nine samples) and RbCP(Cl) (three samples) are shown in Figures 2 and 3. Clearly, there is absolutely no evidence that either compound is anything other than a trihydrate, which is in complete agreement with independent results obtained elsewhere[27] for KCP(Br). This strongly suggests that the work of Peters and Eagen[17] and Deiseroth et al.,[17] who have an opposing interpretation regarding the lattice location of the "excess" H_2O molecule, requires reinterpretation.

X-Ray Diffuse Scattering. The x-ray diffuse scattering photograph of a RbCP(Cl) crystal was obtained, in a manner previously described,[20] on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator. A modified film holder with Ilford film was mounted on the bracket on the detector arm, which is normally used with a Polaroid cassette for crystal orientation purposes. In order to reduce Bragg scattering, the c axis of the crystal was offset 10° from being exactly perpendicular to the incident beam. The stationary crystal–stationary film photograph was obtained with Mo Kα x radiation

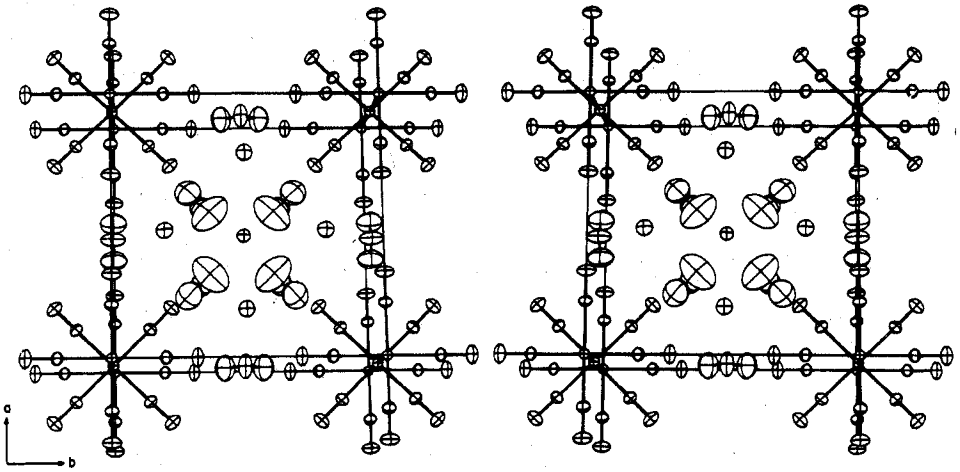

Figure 4. Stereodrawing of the structure of tetragonal $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3.0H_2O$ as viewed down *c*. The linear Pt atom chain is parallel to *c*. The *single* Cl^- site is located in the center of each stereopair. All ellipsoids are scaled to 50% probability.

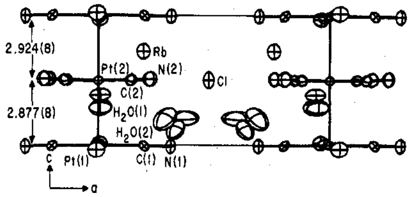

Figure 5. Drawing of the unit cell (50% probability ellipsoids) of $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3.0H_2O$ showing the linear Pt atom chain, which contains *un*equal Pt–Pt separations, and the asymmetric location of the Rb^+ ion and the H_2O molecules. The average Pt–Pt distance in RbCP(Cl) is ~0.03 Å longer than in KCP(Cl) or KCP(Br).

(λ 0.71069 Å) after an exposure of 40 h with the x-ray tube at 1000 W.

The photograph was similar in appearance to those obtained with other POTCP materials, with diffuse lines observable about each row of Bragg reflections. The lines exhibited increasing scattering intensity at higher diffraction angles indicative of sinusoidal displacements of the platinum atoms along each chain, with phases not correlated to those in neighboring chains. The superlattice calculated from the diffuse lines is 6.5 (3)*c′*, where *c′* is the average Pt–Pt separation. This corresponds to a wave vector $k = 2\pi(1 - 1/6.5)c' = 1.69\pi/c'$, which is equal to twice the Fermi wave vector $2k_F$ for a Peierls-type distortion. Therefore, based on the diffuse scattering, the Pt oxidation state is +2.31 (2), which yields a chemical stoichiometry of $Rb_2[Pt(CN)_4]Cl_{0.31(2)}\cdot 3.0H_2O$.

Structure Description

The Linear Pt Atom Chain. The structure of RbCP(Cl) is isostructural with KCP(Cl, Br) and consists of nearly planar $Pt(CN)_4{}^{1.7-}$ groups stacked along the tetragonal *c* axis thereby forming a perfectly linear Pt chain as shown in Figures 4 and 5. The noncentrosymmetric space group (*P*4*mm*) allows independent Pt(1)–Pt(2) distances, and this is the first example of a POTCP complex in which these distances are measurably different (2.877 (8) and 2.924 (8) Å).[5] As in the case of KCP(Br)[5] and KCP(Cl),[5] the TCP groups are bound by H_2O molecules and Rb^+ ions indicating that the main binding forces involve $Rb^+\cdots{}^-N{\equiv}C$ Coulombic attraction in addition to dipolar $HO{-}H\cdots N{\equiv}C$ interactions. The $Rb^+\cdots{}^-N{\equiv}C$ interactions, which result in CN^- canting toward Rb^+, are given in Figure 6, which presents the Rb^+ ion coordination sphere. The $Rb^+\cdots N$ distances are 3.128 (4) and 3.160 (3) Å in length and are ~0.15 Å longer than the van der Waals sum. The Cl^- coordination sphere is presented in Figure 7 from which it appears that the $Rb^+\cdots Cl^-$ distance is very nearly the sum of the two van der Waals radii.

The crystal asymmetric unit contains two crystallographically independent and slightly nonplanar $Pt(CN)_4{}^{1.7-}$ groups, two H_2O sites, one Rb^+ site, and one Cl^- site (see Figure 4).

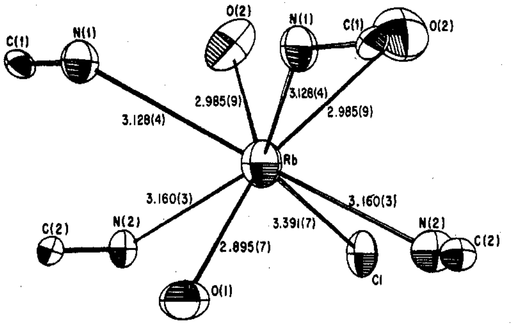

Figure 6. Diagram showing the rubidium ion interactions in $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3.0H_2O$. All $Rb^+\cdots{}^-N{\equiv}C$ distances are 3.14 (1) Å in length and are ~0.14 Å longer than the van der Waals sum.

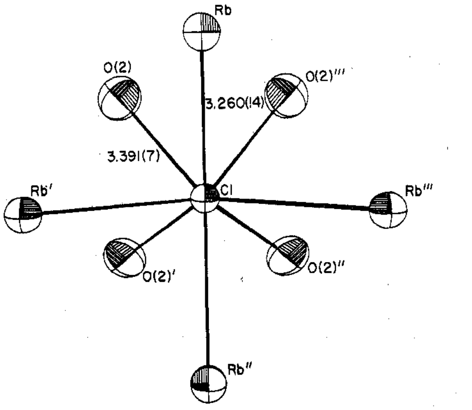

Figure 7. Drawing indicating the chloride ion interactions in $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3.0H_2O$. The $Rb^+\cdots Cl^-$ separations are essentially equal to the sum of the van der Waals radii.

As in KCP(Br, Cl), the alkali metal cations and halide anion occupy the top half of the unit cell ($z > {}^1/_2$) while the water molecules are all located in the lower half ($z < {}^1/_2$) of the unit cell. The slight but significant nonplanarity of the $Pt(CN)_4{}^{1.7-}$ groups is indicated by the deviation from *z* = 0.0 and 0.5 of the C and N *z* coordinates. It is the asymmetric ordering of the Rb^+ ion and the H_2O molecules which constitutes the main source of crystal asymmetry. The independent Pt–C distances (1.999 (2) and 2.005 (2) Å) and C–N distances (1.155 (3) and 1.149 (3) Å), respectively, show excellent internal agreement within less than two esd's (Table IIIA,B). The water molecule O–H distances, uncorrected for thermal motion, range between 0.86 and 0.95 Å. The water molecule hydrogen bonding is illustrated in Figures 8 and 9. While $H_2O(1)$ H-bonds to CN^- only, $H_2O(2)$ forms similar bonds

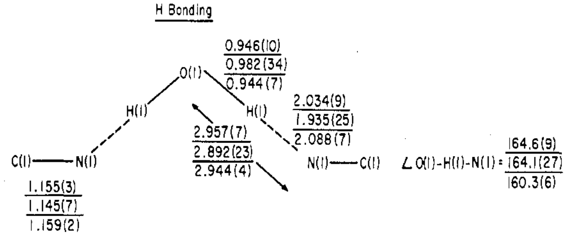

Figure 8. Composite drawing showing the $H_2O(1)$ molecule hydrogen bonding interactions in $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot3.0H_2O$ (top), in $(NH_4)_2[Pt(CN)_4]Cl_{0.3}\cdot3H_2O^{21}$ (middle), and in $K_2[Pt(CN)_4]Br_{0.3}\cdot3.0H_2O$ (bottom). The isostructural nature of all three compounds is evident from the nearly equal hydrogen bonding patterns (see also Figure 9).

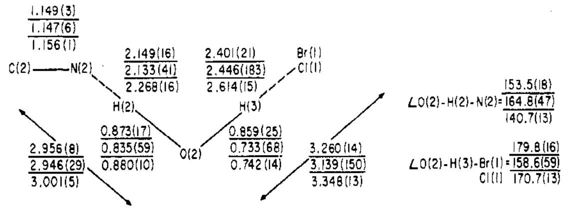

Figure 9. Composite drawing indicating the $H_2O(2)$ molecule hydrogen bonding interactions in RbCP(Cl) (top), NH_4CPCl^{21} (middle), and KCP(Br) (bottom).

to both CN^- and Cl^-. Since H(3) of $H_2O(2)$ is bound to Cl^-, the latter not always being present in the crystal site due to the compound nonstoichiometry, it follows that H(3) has increased thermal motion compared to H(2). Thus, a comparison of the O–H distances in $H_2O(1)$ (O–H ~ 0.95 Å) and $H_2O(2)$ (O–H ~ 0.87 and 0.86 Å) clearly indicates that $H_2O(2)$ does undergo larger thermal motion.

It can be seen from Figure 4 that although the environments about Pt(1) and Pt(2) are noncentrosymmetric, the Rb^+ ion placement (the 4*mm* site symmetry requires Rb^+ to be equally distributed on each side of the Pt atoms) is such that the $Rb^+\cdots{}^-N{\equiv}C$ Coulombic forces tend to alternately compress and expand the Pt–Pt chain as illustrated in Figure 10. We discussed this previously and pointed out that this could promote Pt chain dimerization resulting in two distinct Pt–Pt separations.[4] RbCP(Cl) is the first case in which measurable chain dimerization occurs, apparently because of $M^+\cdots{}^-N{\equiv}C$ interactions. The average Pt–Pt distance in the chain (2.90 Å) is slightly longer than that in KCP(Br) (2.88 Å)[5] and KCP(Cl) (2.87 Å).[5] We believe that the unequal and slightly longer Pt–Pt separations in RbCP(Cl), compared to those in KCP(Cl), result in decreased electron delocalization along the Pt atom chain and a concomitant decrease in the conductivity of RbCP(Cl).

As we pointed out elsewhere,[6] it is possible to calculate the Pt–Pt separations in one-dimensional salts using Pauling's theory[22] of the metallic bond. Using the equation $D(1) - D(n) = 0.6 \log n$, where the distance to be calculated is $D(n)$ (n = degree of partial oxidation and $D(1) = 2.59$ Å for Pt), we calculate a Pt–Pt distance of 2.87 Å if $n = 0.353$ (2) (from the least-squares refinement) or 2.90 Å if $n = 0.30$. From the diffuse x-ray scattering experiments we derived $n = 0.31$ which yields Pt–Pt = 2.90 Å. We feel that the DPO obtained from the diffuse scattering experiments is more reliable in this case than that from the least-squares refinements. The calculated Pt–Pt separations are therefore in good agreement with the experimental values.

Finally, as illustrated in Figures 8 and 9, the H-bonding schemes in RbCP(Cl), KCP(Br), and $NH_4CP(Cl)^{21}$ are essentially identical. Therefore it appears that the conductivity variations observed in these salts possibly result from subtle crystal binding changes due to the different cations and anions, or the slightly longer Pt–Pt separation, but not from any radical structural differences.

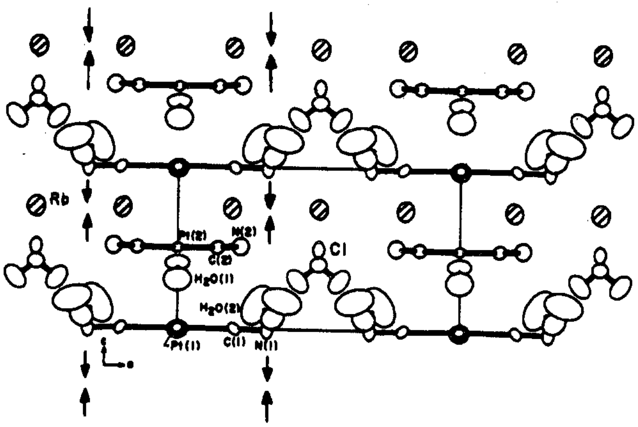

Figure 10. Diagram showing the $CN^-\cdots Rb^+$ interactions (indicated by arrows) which result in canting of the cyanide groups toward the cation and dimerization of the Pt atom chain in $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot3.0H_2O$.

In summary, it appears at this time that increasing the size of the cation ($K^+ \rightarrow Rb^+$), in the case of $K_2[Pt(CN)_4]Cl_{0.3}\cdot3H_2O$ vs. $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot3H_2O$ results in longer and unequal Pt–Pt separations while maintaining the same molecular structure. To this end we have prepared $Cs_2[Pt(CN)_4]Cl_{0.3}\cdot xH_2O$ and its structure and conductivity are now under investigation.

Registry No. $Rb_2[Pt(CN)_4]\cdot3H_2O$, 56372-18-0; $K_2[Pt(CN)_4]\cdot3H_2O$, 14323-36-5.

Supplementary Material Available: A listing of structure factor amplitudes for RbCP(Cl) (3 pages). Ordering information is given on any current masthead page.

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(1) Work performed under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy. A N.A.T.O. research grant (No. 1276) enabled J.M.W. to communicate with foreign scientists on numerous occasions.

(2) Undergraduate research participant sponsored by the Argonne Center for Educational Affairs from Mercyhurst College, Erie, Pa.

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Structural Studies of Precursor and Partially Oxidized Conducting Complexes. 15. A Combined Neutron and X-Ray Diffraction Study of Ammonium Tetracyanoplatinate Chloride Trihydrate, $(NH_4)_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$[1]

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The crystal and molecular structure of one-dimensional ammonium tetracyanoplatinate chloride trihydrate, $(NH_4)_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$, $NH_4CP(Cl)$, has been elucidated in detail using single-crystal neutron and x-ray diffraction techniques. The compound $NH_4CP(Cl)$ crystallizes with two molecules in the tetragonal cell $C_{4v}{}^1$-$P4mm$ of (neutron, x ray) dimensions $a = 10.048$ (7), 10.087 (5) Å and $c = 5.861$ (4), 5.840 (2) Å, respectively. The x-ray diffraction study was undertaken in order to alleviate the problem of large $NH_4{}^+$ ion thermal motion and resultingly large esd's obtained for the Pt–Pt intrachain distances derived in the neutron diffraction study. It is likely that only a low-temperature neutron diffraction investigation will reduce the $NH_4{}^+$ ion motion sufficiently to allow us to derive more precise Pt–Pt distances. In the neutron diffraction experiment, a total of 811 reflections were averaged to yield 390 independent reflections (312 with $F_o{}^2 > 1\sigma(F_o{}^2)$). The x-ray diffraction data set consisted of 340 independent reflections of which 307 had $F_o{}^2 > 1\sigma(F_o{}^2)$. The structure is isomorphous with that of the prototype one-dimensional conductor $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$, KCP(Br). Using full-matrix least-squares techniques, the final refinement yielded $R(F_o{}^2)$ values (neutron, x ray) of 0.131 and 0.122. The structure consists of linear Pt–Pt chains arising from the stacking of square-planar $Pt(CN)_4{}^{1.7-}$ groups. Adjacent $Pt(CN)_4{}^{1.7-}$ moieties have a staggered configuration yielding a C–Pt–Pt–C torsion angle of 45°. The Pt–Pt spacings are *different* at 2.914 (26) and 2.947 (26) Å (neutron) and (more precise) 2.910 (5) and 2.930 (5) Å (x rays). The average Pt–Pt separation (2.92 Å) in $NH_4CP(Cl)$ is ~0.04 Å longer than that observed in KCP(Br). The combined effects of the increased, and now *unequal*, intrachain Pt–Pt separations in $NH_4CP(Cl)$ appear to be the main cause of its diminished conductivity compared to KCP(Br). From the neutron diffraction data, we find that three of the four $NH_4{}^+$ group hydrogen atoms participate in hydrogen bonding interactions thereby resulting in formation of $NH\cdots{}^-N{\equiv}C$ and one NH···O bonds. The neutron and x-ray diffraction data yield different results regarding placement of the Cl^- ion. The neutron data may be interpreted in terms of a "two-site" model for the Cl^- ion, at (0.5, 0.5, 0.4838) and (0.5, 0.5, 0.6055), which yields a derived total Cl^- occupancy factor of 0.41 (18). This value is not significantly different from the accepted value of 0.30 for KCP(Br), KCP(Cl), and RbCP(Cl) and therefore a value of 0.30 has been adopted for this study (vide infra). The x-ray data provide evidence for only one Cl^- ion at (0.5, 0.5, 0.5). However, the Cl^- occupancy factor could not be refined, using least-squares techniques, to a reasonable value.

Introduction

One-dimensional partially oxidized tetracyanoplatinate (POTCP) conductors continue to be of interest not only because they have anisotropic electrical properties but also because metal bond formation produces short metal–metal spacings (typically ~0.1–0.2 Å longer than in Pt metal).[3] However, the crystalline environment about the metal-atom chains influences the one-dimensional conduction properties and associated phenomena, such as Peierls' distortions and charge density wave formation. By varying the ligands, cations, anions, and degree of lattice hydration, one should observe a discernible, logical, and predictable pattern of varying electrical conductivity.

Variable-temperature conductivity studies of four such closely related POTCP compounds have been reported by Underhill et al.,[4] viz., $M_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$, $M^+ = K^+$, Rb^+, and $NH_4{}^+$, and "$(NH_4)_{2.2}[Pt(CN)_4]Cl_{0.5}\cdot 3H_2O$". Although it was assumed that these one-dimensional salts all possess similar crystal structures and because Rb^+ and $NH_4{}^+$ have nearly identical ionic radii (~1.48 Å), the conductivity studies indicated a surprising trend, viz., K > Rb > NH_4 in MCP(Cl). $NH_4CP(Cl)$ is of additional interest because of the distinct possibility that it contains *unequal* intrachain Pt–Pt separations as we have recently observed in $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$.[6] As reported elsewhere the $NH_4{}^+$ ion containing materials pose troublesome synthetic problems.[4,5,15] Finally the possibility of hydrogen bond formation between $NH_4{}^+$ ions and lattice water molecules is of interest because such interactions might serve to increase interchain coupling thereby rendering thermal breakdown of the correlated Peierls distortion more difficult.

In this paper we report the results of a combined neutron and x-ray diffraction single-crystal structural investigation of $(NH_4)_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$. The structural results provide

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