

X-RAY DIFFUSE SCATTERING OF ONE-DIMENSIONAL TETRACYANOPLATINATE SALTS

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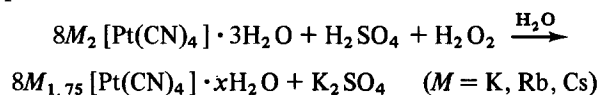
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We have observed and measured the X-ray diffuse scattering from several new partially oxidized tetracyanoplatinate, TCP, complexes. In all cases it is found that the superlattice associated with the diffuse sheets corresponds to the $2k_F$ wavevector derived from the chemical formula. The compounds which were prepared and studied are the cation deficient salts $M_{1.75}[\text{Pt}(\text{CN})_4] \cdot x\text{H}_2\text{O}$, $M(\text{def})\text{TCP}$ ($M = \text{K}, \text{Rb}, \text{Cs}$), where the Rb^+ and Cs^+ salts are newly synthesized, and the anion deficient guanidinium salt $[\text{C}(\text{NH}_2)_3]_2[\text{Pt}(\text{CN})_4]\text{Br}_{0.23} \cdot \text{H}_2\text{O}$, GCP(Br).

PARTIALLY OXIDIZED Tetracyanoplatinate, TCP, complexes have been of great interest recently due to their quasi-one-dimensional metallic behavior.² The prototype compound $\text{K}_2[\text{Pt}(\text{CN})_4]\text{Br}_{0.30} \cdot 3\text{H}_2\text{O}$, KCP(Br), undergoes a gradual transition from a room temperature one-dimensional conductor to a low temperature insulating state. The observation of a giant Kohn anomaly^{3,4} and a low temperature three-dimensional superlattice^{3,5,6} from various neutron and X-ray diffuse studies has been proposed as evidence for a Peierls transition in KCP(Br), although other data and interpretations have been reported.^{7,8} Since only anion deficient materials such as KCP(Br) have been studied, we have extended these investigations to all known cation deficient TCP salts, and to the only known TCP-bromine salt containing an organic cation. In this paper we report on their preparation and room temperature diffuse X-ray scattering.

The guanidinium complex $[\text{C}(\text{NH}_2)_3]_2[\text{Pt}(\text{CN})_4]\text{Br}_{0.23} \cdot \text{H}_2\text{O}$, GCP(Br), was prepared by co-crystallization of the platinum-(II) and platinum-(IV)-dibromo salts.⁹ The cation deficient salts, K(def)TCP, Rb(def)TCP, and Cs(def)TCP, were prepared by partial oxidation of the Pt(II) complex with hydrogen peroxide:¹⁰



In addition to elemental analyses on all complexes, the water content of GCP(Br) has been determined by thermal gravimetric analysis,¹¹ and the stoichiometry of K(def)TCP has been determined in detail from the

solution of its structure by neutron diffraction.¹² Attempts to prepare $\text{Rb}_2[\text{Pt}(\text{CN})_4]\text{Br}_{0.23} \cdot x\text{H}_2\text{O}$, RbCP(Br), by co-crystallization of $\text{Rb}_2[\text{Pt}(\text{CN})_4]$ and $\text{Rb}_2[\text{Pt}(\text{CN})_4\text{Br}_2]$ always yielded Rb(def)TCP.²² Comès *et al.*¹³ reported the diffuse scattering for RbCP(Br), which should be nearly equal to that for Rb(def)TCP (*vide infra*). However, since Comès *et al.* apparently based their formula on chemical analysis, we are puzzled by our contradictory results which clearly indicate that (Rb)CP(Br) cannot be prepared by co-crystallizing the appropriate Pt(II) and Pt(IV)Br₂ salts.

The diffuse scattering photographs were obtained in a manner similar to that described by Comès *et al.*¹³ In this work a non-bent graphite monochromator crystal (MoK α X-radiation $\lambda = 0.71069 \text{ \AA}$) was used. Exposure times of 3–4 days were required because of the moderate intensities obtained with our X-ray tube. Typical crystals were 1.5 mm long with 0.1 mm² cross-sections. The needle axes of the crystals, which always paralleled the Pt stacking direction, were aligned to within 2° of being coplanar with the film.

The photographs from the four complexes are shown in Fig. 1. As is true of KCP(Br),¹³ the diffuse lines are visible surrounding only the rows of Bragg reflections corresponding to the average Pt–Pt repeat distance, and not the true c-axis. It should be noted that the structural studies of KCP(Br)¹⁵ and K(def)TCP^{12,16} have shown that the crystallographically independent Pt–Pt distances are equal at room temperature, while GCP(Br) is the only known TCP salt where all Pt–Pt distances are crystallographically constrained to be equivalent.¹⁷ In the case of Rb(def)TCP and Cs(def)TCP,

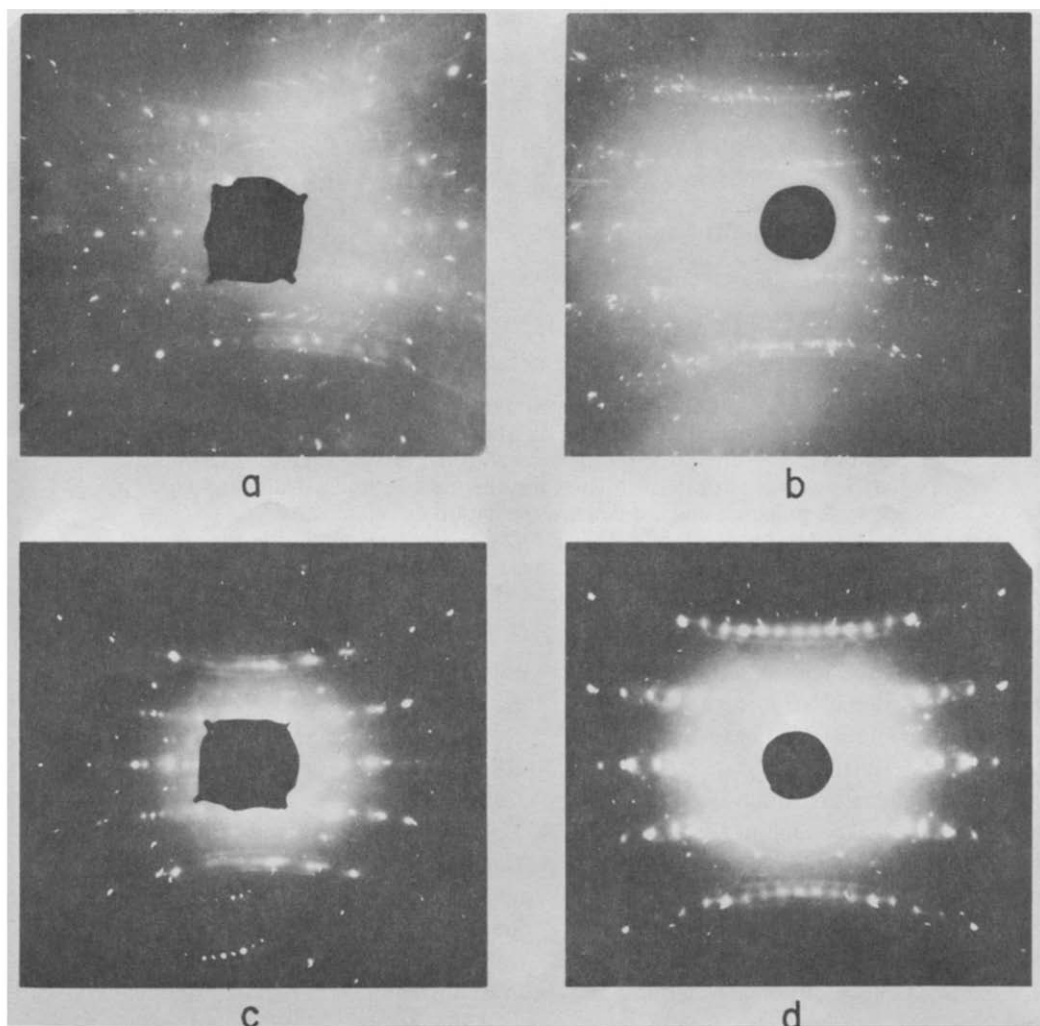


Fig. 1. Diffuse scattering photographs of (a) K(def)TCP, (b) Rb(def)TCP, (c) Cs(def)TCP and (d) GCP(Br).

Table 1

Chemical formula	$2k_F$ from formula	c' (Å) ^a	Superlattice ^b	$2k_F$ from superlattice
$K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$	$1.75\pi/c'$	2.958 ^d	$8.2c'$	$1.76\pi/c'$
$Rb_{1.75}Pt(CN)_4 \cdot xH_2O$	$1.75\pi/c'$	2.94 ^e	$7.3c'$	$1.73\pi/c'$
$Cs_{1.75}Pt(CN)_4 \cdot xH_2O$	$1.75\pi/c'$	2.88 ^e	$7.1c'$	$1.72\pi/c'$
$[C(NH_2)_3]_2Pt(CN)_4Br_{0.23} \cdot H_2O$	$1.77\pi/c'$	2.924 ^f	$7.9c'$	$1.75\pi/c'$
$K_2Pt(CN)_4Br_{0.30} \cdot 3H_2O$ ^g	$1.70\pi/c'$	2.88	$6.67c'$	$1.70\pi/c'$

^a c' is equal to *average* Pt–Pt distance along the chain.

^b Estimated errors are ± 0.5 . ^c Estimated errors are ± 0.02 .

^d References 12 and 16.

^e This work. Determined from oscillation photographs.

^f References 9 and 17.

^g KCP(Br) results from reference 3(c).

oscillation photographs exhibit weak rows of Bragg reflections corresponding to c-axes 2 or 4 times the average Pt–Pt repeat distance.

The diffuse lines in the photographs in Fig. 1 appear as symmetrical satellites about each row of Bragg reflections and exhibit greater intensity at higher diffraction angles. As pointed out by Comès and coworkers for KCP(Br),³ these observations indicate sinusoidal displacements of the platinum atoms along each chain, which, at room temperature, are not correlated to those in neighboring chains. Diffraction due to these one-dimensional distortions produces diffuse sheets in reciprocal space, which appear as curved lines upon intersection with the film. The lower quality of the Rb(def)TCP photograph is due to the crystalline sample actually being a bundle of thin fibers only approximately aligned; however, the diffuse scattering is still evident.

As seen in Table 1, the superlattice associated with the diffuse lines corresponds to the stoichiometry of each complex. Using K(def)TCP as an example, and with Krogmann's model¹⁸ of overlapping $5d_{z^2}$ orbitals in mind, one would expect the conduction band to be 0.25 electron deficient per Pt atom. A filled band would have two electrons per Pt atom, and therefore, the Fermi wavevector $k_F = (1.75/2)\pi/c' = 0.875\pi/c'$. Regardless of which theory^{3–8} one uses to interpret the data on KCP(Br), a phonon mode with wavevector $2k_F$ is required. For K(def)TCP, the wavevector k associated with the superlattice is $k = 2\pi/8.1c'$, or $k = 2\pi(1 - 1/8.1)/c' = 1.75\pi/c'$, in agreement with $2k_F$ predicted from its chemical stoichiometry.

Finally, as seen in Table 1, in comparison to KCP(Br), k_F is closely commensurate with the lattice

for all four complexes. In these cases, one finds the superlattice should be 8 times the average Pt–Pt repeat distance c' , while for KCP(Br) it is $6.67c'$. A slightly different approach is to consider the true c-axis as the repeat distance in determining the Fermi level. Carneiro *et al.*¹⁹ observe a Kohn anomaly in the neutron inelastic scattering of K(def)TCP at $2k_F = 3.5(2\pi/c)$, which is equivalent to $2k_F = 1.75\pi/c'$, where $c = 4c'$. Though one model leads to a half-filled conduction band, and the other to a 7/8 filled band, they are both commensurate with the lattice.

It should be emphasized that in this work we have not shown the existence of a soft phonon mode, but only the observation of a one-dimensional superlattice with the same wavevector as $2k_F$. Furthermore, the conductivities of K(def)TCP²⁰ and GCP(Br)⁹ have been measured and they appear to be orders of magnitude less than that for KCP(Br).² This may be due to the longer Pt–Pt distances, or the possibility that these compounds are below the Peierls transition at room temperature.⁹ The higher commensurability of their $2k_F$ wavevectors with the lattice would certainly add support to the latter proposal, since the electron–phonon coupling should be greater in these compounds than for the incommensurate KCP(Br).²¹ Additional studies, particularly at low temperatures, are needed in order to better understand these complexes.

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