Polarized Specular Reflectance of the New One-dimensional 'Metals' $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$, $Rb_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$, and $Cs_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$

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Summary Polarized specular reflectance data are presented which demonstrate that the platinum chain-forming compounds of the type $M_{1\cdot 75}[Pt(CN)_4]\cdot 1\cdot 5H_2O$, where $M = K^+$, Rb^+, and Cs^+, are new one-dimensional conductors.

THE partially oxidized tetracyanoplatinate (POTCP) compounds $K_2[Pt(CN)_4]Br_{0\cdot 3}\cdot 3H_2O$ [KCP(Br)], and K_2-$[Pt(CN)_4]Cl_{0\cdot 3}\cdot 3H_2O$ [KCP(Cl)], have been shown to be one-dimensional metals by several techniques, including electrical conductance measurements and polarized specular reflectance spectroscopy.[1] Reflectance spectra exhibiting high values in the i.r. region, with a plasma edge dropping to very low reflectivities at higher energies, have been cited as evidence of metallic conductivity in these compounds.[2]

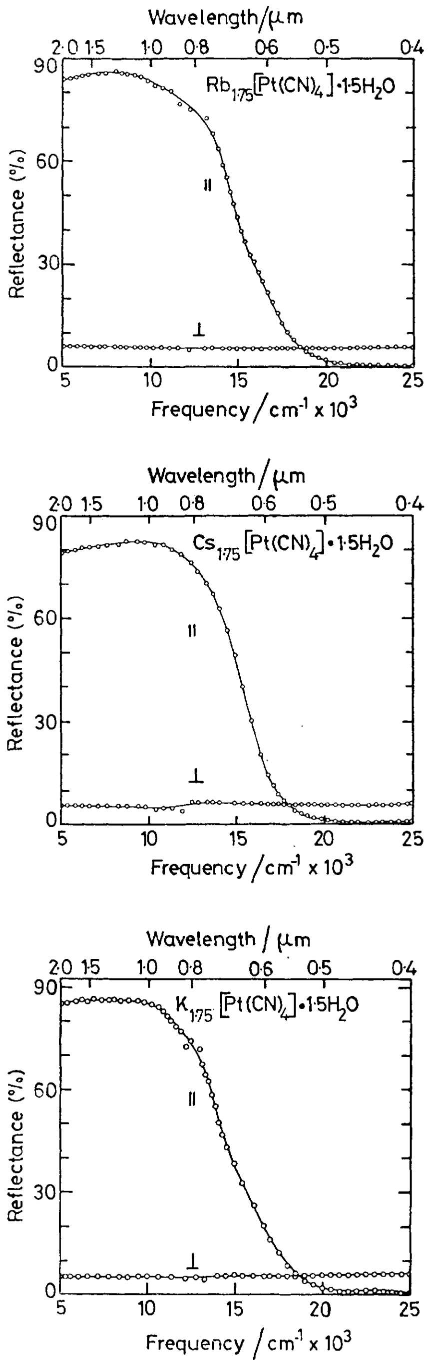

Figure. Polarized specular reflectance from $K_{1·75}[Pt(CN)_4]·1·5H_2O$, $Rb_{1·75}[Pt(CN)_4]·1·5H_2O$, and $Cs_{1·75}[Pt(CN)_4]·1·5H_2O$. Reflectance parallel and perpendicular to the Pt chains are labelled as ‖ and ⊥, respectively. The Pt chain in $K_{1·75}[Pt(CN)_4]·1·5H_2O$ is bent [Pt(1)–Pt(2)–Pt(3) bond angle 173·2°].

Recently the structure of the related cation-deficient compound $K_{1·75}[Pt(CN)_4]·1·5H_2O$ [K(def)TCP], has been reported[3] showing this crystal structure to be similar to one-dimensional KCP(Br) and KCP(Cl), but with longer Pt–Pt separations and a prominent 'zig-zag' to the platinum-atom chains. In addition, samples of $Rb_{1·75}[Pt(CN)_4]·1·5H_2O$, Rb(def)TCP,[4] and $Cs_{1·75}[Pt(CN)_4·1·5H_2O$, Cs(def)-TCP,[5] have recently been prepared in this laboratory. We report here a preliminary study of the polarized specular reflectance of K(def)TCP, Rb(def)TCP, and Cs(def)TCP.

Single crystals of K(def)TCP[6] were selected for moderate size (*ca.* 0·5 × 0·5 × 2 mm) and highest reflectivity, and spectra were recorded for the naturally grown faces. The samples of Rb(def)TCP[4] were *ca.* 0·3 × 0·3 × 1 mm and those of Cs(def)TCP[5] were thin needles, *ca.* 0·02 × 0·02 × 0·5 mm. The crystals were maintained at *ca.* 80% humidity at all times to prevent loss of water and subsequent crystal decomposition. Even slight surface decomposition would have a major influence on the reflectance values.

The use of a microspectrophotometer, based on an instrument described elsewhere,[7] enabled selection of small crystal regions having a high degree of planarity. A tungsten–halogen lamp was used as a source, a Glan-Thompson prism as a polarizer, and a photomultiplier and lead selenide as detectors. Measurements were made relative to an aluminium mirror and corrected for Al reflectivity.[8] Spectra were obtained with the electric vector of the polarized light oriented both parallel and perpendicular to the direction of the platinum chains (crystal needle axis).

The spectra shown in the Figure are typical of the best results. Corresponding spectra from adjacent faces were indistinguishable. The high reflectivity (up to 86%) in each case in the parallel spectra, in the i.r. region with the plasma edge in the red, is characteristic of a metallic conductor. The similarity of the spectra suggests similar optical conductivities as well. Values of conductivity were calculated using simple Drude theory, with a lattice dielectric constant of *ca.* 1·4, as determined through Kramers–Kronig analysis. The calculated optical conductivities were as follows: K(def)TCP, 4·8 × 10^3; Rb-(def)TCP, 5·0 × 10^3; and Cs(def)TCP, 4·2 × 10^3 Ω^{-1} cm^{-1}. Single-crystal conductivity measurements (four probe) are now in progress.[9] The metallic character in K(def)TCP has also recently been indicated by observation, from a neutron scattering study,[10] of a Kohn anomaly at low temperatures and an electrical conductivity study.[11] The very low reflectivity throughout the spectra in the perpendicular direction, which, as noted, occurs on adjacent faces and thus in the two perpendicular directions, clearly indicated non-conduction. Thus, all crystals appear to be new one-dimensional metallic conductors.

It has been predicted[12] that all POTCP salts will have similar metallic reddish-bronze colours and plasma frequencies. While this is true for the cation and anion deficient salts reported to date, we have prepared[13] new POTCP salts, $M_2[Pt(CN)_4]$ $(FHF)_{0·39}·H_2O$, M = Cs and Rb, which have a lustrous metallic gold colour and the shortest Pt–Pt separations yet observed (2·83 and 2·80 Å, respectively). Studies are underway to determine in what manner the plasma edge has been shifted and the conductivity modified.

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