Partially Oxidised Tetracyanoplatinate Complexes containing Both Divalent and Monovalent Cations

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A series of new one-dimensional metals based on partially oxidised tetracyanoplatinate complexes containing both monovalent and divalent cations is described. The complexes appear to be isostructural with $K_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ but with *ca.* 13% of the cation sites containing a divalent cation and with all the halide sites occupied. The small change in composition is shown to have a large effect on the electrical conduction properties of the compounds because the effect of the introduction of divalent cations results in an increased stiffness of the lattice. This leads to a reduction of λ, the electron phonon coupling constant, resulting in increased conductivity at low temperatures.

One-dimensional (1-D) metallic complexes containing partially oxidised tetracyanoplatinate (potcp) anions have been studied extensively over the past decade as examples of 1-D metals.[1] However, such studies have been restricted so far to the salts of monovalent cations. It has been found from studies of the partially oxidised bis(oxalato)platinate salts that the inclusion of divalent cations in the lattice produces compounds with very different structures and solid-state properties from those containing monovalent cations.[2] Thus there is great interest in the preparation and properties of potcp compounds with divalent cations.

In the 1860s, compounds of metallic appearance were reported with the empirical formula ' $MPt(CN)_5$ ' (where M is a divalent cation such as lead or magnesium).[3] This formula is not in accord with our modern knowledge of these materials, but does indicate that efforts should be made to prepare potcp salts of divalent cations. In 1968 Krogmann and Ringwald[4] reported the synthesis of $Mg[Pt(CN)_4]Cl_{0.28}\cdot H_2O$ by co-crystallising $Mg[Pt(CN)_4]\cdot 7H_2O$ and $Mg[Pt(CN)_4Cl_2]\cdot xH_2O$. However Williams and co-workers[5] later showed that the product was a mixed hydrate of the platinum(II) salt $Mg[Pt(CN)_4]\cdot xH_2O$ and not a potcp compound.[5] Attempts to synthesise other potcp complexes containing divalent cations such as Be^{2+} and Ba^{2+} were also unsuccessful.[5]

In this paper we outline experiments in which the original work carried out in the 1860s was repeated and new methods were developed to prepare and study the solid-state properties of a number of compounds of potcp which contain both monovalent and divalent cations. A brief report of some of this work has appeared elsewhere.[6]

Results and Discussion

The method for the preparation of ' $Pb[Pt(CN)_5]$ ' published in 1861 involved treating an aqueous solution containing equimolar quantities of lead(II) acetate or nitrate and $K_2[Pt(CN)_4]\cdot 3H_2O$ with nitric acid.[3] This procedure was repeated, but the product, $Pb_{0.77}K_{0.23}[Pt(CN)_4]\cdot 1.5H_2O$, always contained potassium as well as lead cations.[7] Attempts were made to oxidise aqueous solutions containing only $Pb[Pt(CN)_4]\cdot 3H_2O$, since this would avoid the possibility of potassium being incorporated into the product. However attempts using a variety of oxidising agents (H_2O_2, halogen, HNO_3) and conditions were not successful, yielding the platinum(II) compound, the platinum(IV) compound, or a mixture of the two. Electrolytic oxidation of an aqueous solution of $Pb[Pt(CN)_4]\cdot 3H_2O$ also failed to yield any partially oxidised product. Thus it does not appear possible to prepare a potcp salt containing only lead(II) as a cation by these conventional methods.

In an attempt to grow large crystals of $Pb_{0.77}K_{0.23}[Pt(CN)_4]\cdot 1.5H_2O$ the aqueous solution containing equimolar quantities of lead nitrate and $K_2[Pt(CN)_4]\cdot 3H_2O$ was electrolysed at 0.8 V. Large needle-shaped crystals (up to 20 × 1 × 1 mm) formed at the platinum anode in low yield. Chemical analysis showed the crystals to have the composition $Pb_{0.27}K_{1.73}[Pt(CN)_4]Cl_{0.5}\cdot 3H_2O$ (1; Pb/K). This is completely different from that of the crystals obtained by chemical oxidation. The presence of chloride in the product was unexpected, and presumably arose from the presence of potassium chloride impurities in the $K_2[Pt(CN)_4]\cdot 3H_2O$ starting material. The very low yield is due to the fact that the amount of material produced is limited by the amount of chloride impurity in the starting material. The low solubility of $PbCl_2$ also restricts the amount of product that can be obtained by adding more chloride ions to the solution. The preparation was repeated using various molar concentration ratios of Pb to K in the range 3 : 1 to 1 : 3, but the composition of the product remained unaltered.

The chemical composition of the product indicates that the oxidation state of the platinum is 2.23, corresponding to a degree of partial oxidation (d.p.o.) of 0.23. This was confirmed by $KI/Na_2S_2O_2$ titrations. *X*-Ray diffuse scattering experiments have been reported for this compound, and from the position of the diffuse line a value for the Fermi wavevector k_F of $0.885\pi/d_{Pt-Pt}$ was obtained.[8] Using the formula

$$\text{d.p.o.} = 2[1 - k_F(d_{Pt-Pt})/\pi] \qquad \text{(i)}$$

(i) yields a value for the d.p.o. of 0.23, in agreement with the values obtained by chemical methods.

Oscillation and Weissenberg *X*-ray photographs show that the unit cell is orthorhombic with $a = b = 9.88$ Å; $c = 5.80$ Å. The Weissenberg photographs indicate that (1; Pb/K) is isostructural with the prototype 1-D conductor $K_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ (2; K) ($a = b = 9.883$ Å; $c = 5.748$ Å).[9] The structure of (2; K) contains columnar stacks of $[Pt(CN)_4]^{1.7-}$ anions with a linear Pt-atom chain aligned along the *c* axis of the unit cell.[9] The $[Pt(CN)_4]^{1.7-}$ anions are staggered, with an intra-chain torsion angle of 45° to minimise steric hindrance. The intra-chain Pt–Pt separation (d_{Pt-Pt}) is 2.874 Å. The Cl^- ions are located at the centre of the unit cell, but only 60% of the available crystallographic sites are occupied. The K^+ ions are located in one half of the unit cell whilst the water molecules occupy the other half. The water molecules form a hydrogen-bonded network between the cyanide ligands and either the chloride ion at the centre of the unit cell or the cyanide ligand of a $[Pt(CN)_4]^{1.7-}$ anion in an adjacent chain.

In the structure of complex (2; K) there is one Cl^- site at the centre of the unit cell per two platinum atoms. Thus in (1; Pb/K), unlike (2; K), the chemical analysis indicates that all these sites are occupied. Previous studies on (2; K) have shown that it is possible to increase the Cl^- occupancy of the sites up to *ca.* 100% but only by incorporating additional protons into the lattice as H_3O^+ and thus maintaining the d.p.o. at 0.30.[10] It is clear from the stoicheiometry and structure of (1; Pb/K) that Pb^{2+} and K^+ ions both occupy the K^+ site of the structure of (2; K) and that all these sites are occupied. The partial substitution of Pb^{2+} for K^+ is facilitated by the similar size of these cations (ionic radii: K^+, 1.33 Å; Pb^{2+}, 1.21 Å).[11] The extent of replacement of K^+ by Pb^{2+} will be governed by the total occupation of the Cl^- sites and the need to achieve a fixed d.p.o. representating a minimum energy state for the system. This will then govern the K^+ to Pb^{2+} molar ratio. Knowledge of the detailed arrangement of K^+ and Pb^{2+} ions within the potassium cation sites must await the results of further structural studies, in progress.[12]

Compounds Related to $Pb_{0.27}K_{1.73}[Pt(CN)_4]Cl_{0.5}\cdot 3H_2O$ (1; Pb/K).—It has been observed previously that in a small number of compounds isostructural with $K_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ (2; K), potassium is completely replaced by another monovalent cation. These include $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ (3; Rb) and $[NH_4]_2[H_3O]_{0.17}[Pt(CN)_4]Cl_{0.47}\cdot 2.83H_2O$.[13,14] No isostructural compounds with smaller cations such as Na^+ or Li^+ have been reported.

Table 1. Results of electrolysing aqueous solutions containing combinations of monovalent cation tetracyanoplatinates and divalent cation chlorides (radii taken from ref. 11)

Monovalent cation, radius in Å	Divalent cation, radius in Å	Formation of partially oxidised product
Na^+, 0.95	Ca^{2+}, 0.99	No
	Cd^{2+}, 0.97	No
	Mn^{2+}, 0.80	No
	Hg^{2+}, 1.10	No
	Fe^{2+}, 0.76	No
	Co^{2+}, 0.74	No
K^+, 1.33	Sr^{2+}, 1.13	No
	Ba^{2+}, 1.35	Yes
	Pb^{2+}, 1.21	Yes
Rb^+, 1.48	Ba^{2+}, 1.35	Yes

The partial replacement of Pb^{2+} for K^+ in the structure of (2; K) is thought to be due to the similar size of these two cations. An investigation was therefore carried out to see if other mixed divalent–monovalent cation salts of potcp compounds could be made, using the concept of similar ionic radii as a guideline. Electrolytic oxidations of aqueous solutions of sodium, potassium, or rubidium tetracyanoplatinate(II) and a suitable divalent metal chloride were performed. The results are given in Table 1. Experiments were carried out in which the sizes of the two cations were approximately the same. Table 1 shows that no compounds involving Na^+ were obtained. However two new compounds, $Ba_{0.29}K_{1.71}[Pt(CN)_4]Cl_{0.5}\cdot 3H_2O$ (4; Ba/K) and $Ba_{0.27}Rb_{1.73}[Pt(CN)_4]Cl_{0.5}\cdot 3H_2O$ (5; Ba/Rb), were obtained.

These compounds have a similar stoicheiometry to (1; Pb/K) and hence a similar d.p.o. It appears that substitution of divalent cations into the monovalent cation sites in the structure of (2; K) is achieved when the divalent cation is the same size as or slightly larger than but not when smaller than the monovalent cation. The unit-cell dimensions of the compounds are shown in Table 2. The dimensions are identical with those of complex (1; Pb/K). This is unexpected since $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ (3; Rb) has a larger unit cell than (2; K).[13] Attempts to prepare compounds containing divalent cations substituted for some of the K^+ ions in $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ were not successful.

Electrical Conductivity Studies.—The electrical conduction properties of all three compounds have been studied in the platinum atom chain direction ($\sigma_{\parallel}$) by means of 4-probe d.c. measurements.

The room temperature conductivities are shown in Table 2. All three compounds exhibit conductivities at room temperature similar to those found for complex (2; K).[1] The absolute values found for compounds of this type are very dependent on crystal quality. These results suggest that the partial replacement of K^+ or Rb^+ with Pb^{2+} or Ba^{2+} has in no way impaired the conduction properties of these materials.

Figure 1 shows the temperature dependence of the conductivity of (1; Pb/K). As the temperature decreases from room temperature the conductivity slowly rises and passes through a broad maximum at *ca.* 250 K. Below 150 K the conductivity falls rapidly. Figure 2 shows a plot of $\ln\sigma_{\parallel}$ *versus* reciprocal temperature. This indicates that below 60 K (1; Pb/K) is behaving as a semiconductor with an activation energy of 27 meV. The temperature dependence of $\sigma_{\parallel}$ for (4; Ba/K) and (5; Ba/Rb) is almost identical with that just described; they both show semiconductor behaviour with an activation energy of *ca.* 30 meV at low temperatures. Figure 3 compares the temperature dependence of the conductivity of (1; Pb/K)

Table 2. Unit cell and conductivity data together with the 1-D and 3-D parameters for the new mixed cation systems $Pb_{0.27}K_{1.73}[Pt(CN)_4]Cl_{0.5}\cdot 3H_2O$ (1; Pb/K), $Ba_{0.29}K_{1.71}[Pt(CN)_4]Cl_{0.5}\cdot 3H_2O$ (4; Ba/K), and $Ba_{0.27}Rb_{1.73}[Pt(CN)_4]Cl_{0.5}\cdot 3H_2O$ (5; Ba/Rb) together with the parameters for $K_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ (2; K) and $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ (3; Rb), for comparison

	Unit cell										
Compound	a (= b)/Å	c/Å	d_{Pt-Pt}/Å	σ_{RT}/Ω^{-1} cm^{-1}	$2k_F$ (π/d_{Pt-Pt})	ΔE/meV	ε_F/eV	T_p/K	T_{3D}/K	η	λ
(1; Pb/K)	9.88	5.80	2.90	10—220	1.77[a]	27	3.50	178	85	0.015	0.24
(4; Ba/K)	9.88	5.80	2.90	20—480	1.70[a]	*ca.* 30	3.23	197	85	0.0156	0.235
(5; Ba/Rb)	9.88	5.80	2.90	*ca.* 80	1.77[b]	*ca.* 30	3.50	197	85	0.0144	0.247
(2; K)[c]	9.883	5.748	2.874	200	1.70[a]	70	3.21	461	95	0.020	0.29
(3; Rb)[c]	10.142	5.80	2.90[d]	10	1.69[a]	75	3.20	494	110	0.022	0.30

[a] From diffuse *X*-ray scattering experiment. [b] From chemical analysis. [c] Values taken from ref. 16. [d] Average value.

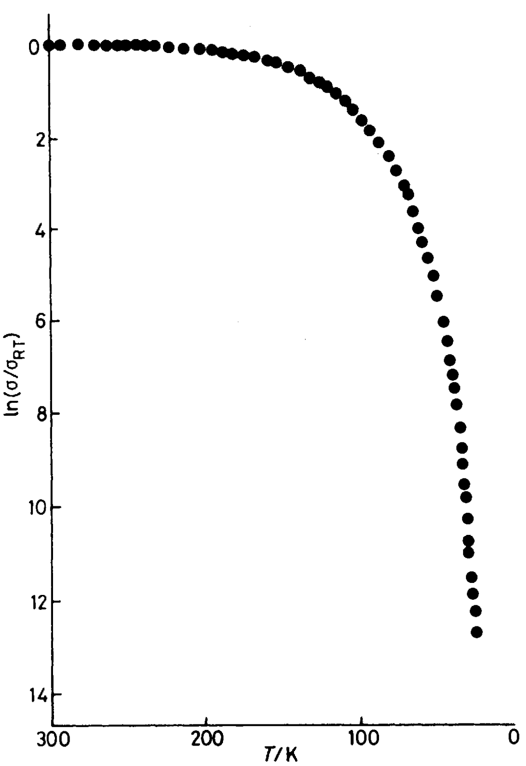

Figure 1. Variation of $\ln\sigma_{\parallel}/\sigma_{\parallel RT}$ with temperature for a single crystal of $Pb_{0.27}K_{1.73}[Pt(CN)_4]Cl_{0.5}\cdot3H_2O$ (1; Pb/K) (RT = room temperature)

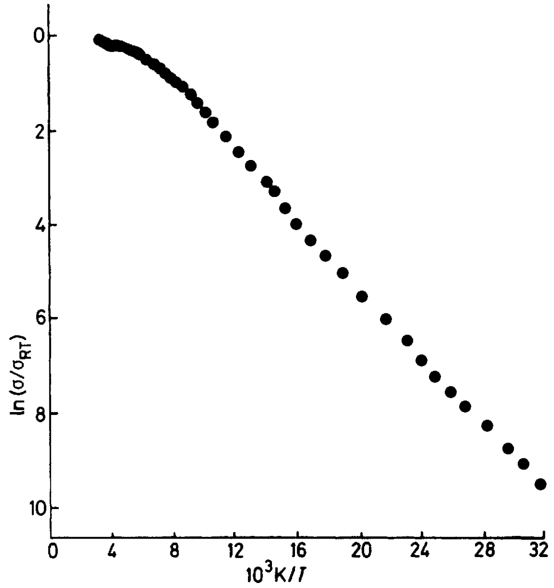

Figure 2. Variation of $\ln(\sigma_{\parallel}/\sigma_{\parallel RT})$ with inverse temperature for $Pb_{0.27}K_{1.73}[Pt(CN)_4]Cl_{0.5}\cdot3H_2O$ (1; Pb/K)

with those of (2; K) and two other anion-deficient tetracyanoplatinates.

General Discussion.—The solid state properties of $K_2[Pt(CN)_4]Br_{0.3}\cdot3H_2O$ and other isostructural potcp salts have been studied extensively and are relatively well understood.[15,16] The new compounds described here will be discussed using the same model.

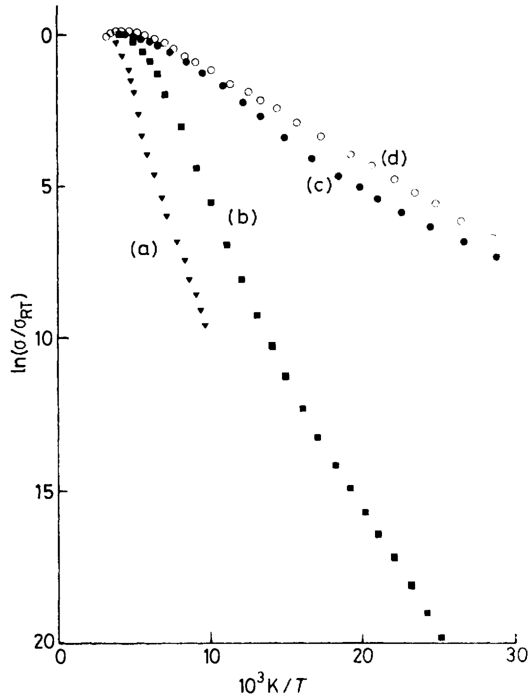

Figure 3. Variation of $\ln(\sigma_{\parallel}/\sigma_{\parallel RT})$ with inverse temperature for (a) $[NH_4]_2[H_3O]_{0.17}[Pt(CN)_4]Cl_{0.47}\cdot2.83H_2O$ (K. Carneiro, A. Steen Petersen, A. E. Underhill, D. J. Wood, D. M. Watkins, and G. A. Mackenzie, *Phys. Rev. B*, 1979, **19**, 6279); (b) $K_2[Pt(CN)_4]Cl_{0.30}\cdot3H_2O$ (2; K); (c) $Rb_2[Pt(CN)_4][HF_2]_{0.4}$ (D. J. Wood, A. E. Underhill, A. J. Schultz, and J. M. Williams, *Solid State Commun.*, 1979, **30**, 501); (d) $Pb_{0.27}K_{1.73}[Pt(CN)_4]Cl_{0.5}\cdot3H_2O$ (1; Pb/K)

In this type of compound overlap of the $5d_z{}^2$ orbitals on the platinum atoms within the chain leads to the formation of a $5d_z{}^2$ band which is only partially filled owing to the d.p.o. of the compound. The extent of band filling depends on the d.p.o., and for complex (1; Pb/K) the band is 0.885 filled. However 1-D metals are unstable, with respect to a lattice distortion of period $2k_F$ which will produce a band gap at the Fermi surface (the Peierls instability). One-dimensional metallic complexes are however only pseudo-one-dimensional, and the 1-D chains of platinum atoms interact with each other *via* the crystal lattice.

The temperature behaviour of the conductivity of (2; K) and the mixed cation compounds can be explained in terms of the Peierls instability. Around room temperature $\sigma_{\parallel}$ is almost temperature independent and is associated with metallic behaviour. At lower temperatures there is a transition into a semiconducting state with characteristic activated behaviour of $\sigma_{\parallel}$ which is directly associated with the low-temperature Peierls semiconducting state. The temperature behaviour of the conductivity between these two regions is complicated and it has been suggested that it may be described by a temperature dependent gap $\Delta(T)$ together with a power law dependence of the mobility[16] [equation (ii), where k = Boltzmann constant].

$$\sigma_{\parallel}(T) = \sigma_m(T/T_m)^{-\alpha}\exp[-\Delta(T)/kT] \qquad \text{(ii)}$$

The derivative of the conductivity with temperature [equation (iii)] has been shown to give a maximum at $D(T)$

$$D(T) = \partial\ln\sigma_{\parallel}\delta/(1/T) = \Delta(T) - \partial\Delta(T)/\partial T - \alpha T \qquad \text{(iii)}$$

which corresponds to the transition temperature, T_{3D}, of the Peierls instability. The value of T_{3D} deduced from $D(T)$ for the compounds discussed here is shown in Table 2.

Within the $5d_z{}^2$ band the electrons in $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ have been shown to move along the chain with an effective mass very close to that of the free electron.[17] A detailed treatment of the 1-D characteristics has been published.[15,16] Based upon the values of the parameters k_F, Δ, and T_{3D} it is possible to calculate the Fermi energy by the equation (iv), where m = free electron mass. The scale temperature T_p is related to Δ by the relation $T_p = \Delta/1.76k$. The dimensionless electron–phonon coupling constant, λ, can be calculated from equation (v).

$$\varepsilon_F = \hbar^2 k_F{}^2/2m \qquad \text{(iv)}$$

$$T_p = 4.52\,\frac{1 - k_F d_{\|}/\pi}{1 + k_F d_{\|}/\pi}\,\varepsilon_F e^{-1/\lambda} \qquad \text{(v)}$$

Finally the interchain coupling constant η (defined as the electronic band-width anisotropy) may be calculated from the expression (vi).[18] The values of ε_F, T_p, λ, and η deduced for the mixed cation compounds are given in Table 2, together with those of (2; K) and $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ (3; Rb) for comparison.[16]

$$T_{3D}/T_p = \exp\,[-2.5(kT_p/\varepsilon_F)/\eta] \qquad \text{(vi)}$$

It has been observed previously [16,19] that for the tetracyanoplatinate salts of monovalent cations there is a smooth relationship (vii) between the d.p.o. and d_{Pt-Pt}. The mixed cation salts discussed here do not follow this relationship in spite of their being isostructural with (2; K).[1] The d.p.o. is much less (0.23) than that expected (*ca.* 0.28) from the observed d_{Pt-Pt} using the above relationship. It is also clear from Table 2 that the values of Δ and T_{3D} determined experimentally for these compounds are quite different from those expected by comparison with (2; K). Thus these mixed divalent–monovalent cations should be considered as compounds in which the solid-state properties have been extensively modified.

$$d_{Pt-Pt} = 2.56 - 0.62 \log (\text{d.p.o.}) \qquad \text{(vii)}$$

The mixed divalent/monovalent cation salts differ from previously prepared compounds isostructural with (2; K) in two important respects: (*a*) some 13.5% of the cation sites are occupied by a divalent cation; and (*b*) all the halide sites at the centre of the unit cell are occupied. Thus the Pb/K salt differs from (2; K) in that there will be no random potential arising from the halide sites; but a new random potential will be present from the Pb^{2+} and K^+ in the cation sites. The most likely explanation for the increased low temperature conductivity observed in these salts as compared with those of monovalent ions lies in the effect of the replacement of monovalent K^+ ions by divalent Pb^{2+} ions on the lattice stiffness in these compounds. This is demonstrated when the values of λ derived from the conductivity data (Table 2) are analysed using the microscopic expression (viii),[16] where c^* is the reciprocal unit-cell dimension of direction c, ω_D is the Debye frequency, and M the mass of the $[Pt(CN)_4]$ moiety. By inserting the experimentally determined values from Table 2, the ratio for the Debye frequencies in (1; Pb/K) as compared with (2; K) is found to be 1.45 : 1. The Debye frequency of a compound is related to the elastic stiffness constant, C, *via* the relation (ix), where ρ is the density.

$$\lambda = \frac{\varepsilon_F}{4\omega_D}\,\frac{(c^*)^2}{M\omega_D}\,\frac{1}{\sin^2(k_F d_{Pt-Pt})} \qquad \text{(viii)}$$

$$C \propto \rho\omega_D{}^2 \qquad \text{(ix)}$$

After allowance for the small differences in ρ, the difference in ω_D corresponds to an increase in the elastic constant of (1; Pb/K) over that of (2; K) by a factor of 2.3. This compares favourably with an estimate based on the fact that the elastic constants of divalent ionic salts are *ca.* 10 times those of monovalent salts.[20] Given the concentrations of Pb^{2+} and K^+ ions in the lattice this would lead to the value of $\simeq 2.2$ by equation (x). This shows that there is good agreement with the increase in ω_D deduced both from the experimentally determined values of Δ and from that expected on replacing monovalent K^+ ions with heavier divalent Pb^{2+} ions.

$$\frac{C[(1;\ \text{Pb/K})]}{C[(2;\ \text{K})]} \simeq 2.2 \qquad \text{(x)}$$

Thus it is clear that the solid state properties of the potassium tetracyanoplatinate type compounds are profoundly affected by this inclusion of divalent ions into the lattice, owing to the effect of these ions on the bare phonon frequency. This produces a very significant reduction in λ.

Experimental

$Pb_{0.27}K_{1.73}[Pt(CN)_4]Cl_{0.5}\cdot 3H_2O$ (1; Pb/K).—$K_2[Pt(CN)_4]\cdot 3H_2O$ (1 g) and $PbCl_2$ (0.65 g) were mixed with distilled water (10 cm³) and conc. HNO_3 (0.5 cm³). The solution was filtered using a 0.22 μm Millipore filter, and placed in an electrolysis cell fitted with platinum wire electrodes. A constant voltage of 0.8 V was applied, and after a few days crystals of the product had formed at the anode. The crystals were filtered off, washed with ice-cold water, and air-dried (Found: C, 9.8; H, 1.4; Cl, 3.6; K, 13.75; N, 10.6; Pb, 11.5; Pt, 38.7. $C_4Cl_{0.5}K_{1.73}N_4Pb_{0.27}Pt\cdot 3H_2O$ requires C, 9.7; H, 1.2; Cl, 3.6; K, 13.7; N, 11.3; Pb, 11.3; Pt, 39.45%).

$Ba_{0.29}K_{1.71}[Pt(CN)_4]Cl_{0.5}\cdot 3H_2O$ (4; Ba/K).—This was prepared by a similar procedure (Found: C, 10.25; H, 1.1; Ba, 8.3; Cl, 3.75; K, 14.3; N, 11.55; Pt, 41.2. $C_4Ba_{0.29}Cl_{0.5}K_{1.71}N_4Pt\cdot 3H_2O$ requires C, 10.0; H, 1.25; Ba, 8.35; Cl, 3.7; K, 14.0; N, 11.75; Pt, 40.85%).

$Ba_{0.27}Rb_{1.73}[Pt(CN)_4]Cl_{0.5}\cdot 3H_3O$ (5; Ba/Rb).—This was also prepared by a similar procedure (Found: C, 8.8; Ba, 6.8; Cl, 3.2; N, 9.85; Pt, 35.6; Rb, 25.9. $C_4Ba_{0.27}Cl_{0.3}N_4PtRb_{1.73}\cdot 3H_2O$ requires C, 8.65; Ba, 6.65; Cl, 3.2; N, 10.1; Pt, 35.1; Rb, 26.6%).

Analyses.—Rb, K, and Ba were determined by atomic emission and Pb by atomic absorption. Pt was determined by atomic absorption (by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn). C, H, and N were determined by microanalysis, and chloride was determined by Dr. F. B. Strauss (Oxford) or Dr. F. Pascher (Bonn).

Physical Measurements.—Electrical conductivity measurements were made on high quality single crystals by the 4-probe d.c. technique using aquadag as the contact material between the crystal and 0.001-in gold wires. All the crystals gave ohmic behaviour under the conditions of measurement. *X*-Ray studies were made using a Stoe Weissenberg camera and Cu-K_α radiation.

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