Direct-current Induced Oxidation–Reduction Reactions in Some Partially Oxidised Cyano- and Oxalato-platinate Crystals Containing Platinum–Platinum Chains

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The application of d.c. fields of greater than 200 V cm^{-1} to $K_{1\cdot74}Pt(CN)_4,1\cdot8H_2O$ and $K_{1\cdot64}Pt(C_2O_4)_2,pH_2O$ (where p indicates an unknown number of water molecules) induces an oxidation–reduction reaction which commences at the anode and spreads through the crystal towards the cathode. The products of the reactions appear to be $K_{1\cdot74}H_{0\cdot26}Pt(CN)_4,xH_2O$ and $K_{1\cdot64}H_{0\cdot36}Pt(C_2O_4)_2,gH_2O$ (where g indicates an unknown number of water molecules). $Mg_{0\cdot82}Pt(C_2O_4)_2,5\cdot3H_2O$ does not undergo this reaction at the anode up to 3000 V cm^{-1}. $K_{1\cdot64}Pt(C_2O_4)_2,pH_2O$ at 50 V cm^{-1} and $K_{1\cdot74}Pt(CN)_4,1\cdot8H_2O$ at 500 V cm^{-1} exhibit a colour change at the cathode. Evidence suggests that this is due to partial replacement of K^+ by H^+ ions.

THE electrical conduction properties of compounds which might behave as one-dimensional ' metals ' have recently received much study.[1-7] During the course of these studies, we reported the occurrence of a novel chemical reaction in the partially oxidised platinum atom chain compounds $K_2Pt(CN)_4Br_{0\cdot30},2\cdot3H_2O$ and $K_2Pt(CN)_4Cl_{0\cdot32},2\cdot6H_2O$ induced by d.c. fields of >120 V cm^{-1}.[3,4] In the reaction, halogen was expelled, and the partially oxidised platinum compound reduced to $K_2Pt(CN)_4,2H_2O$. The occurrence of this reaction clearly limits the size of the d.c. field that can be applied to crystals of these compounds. We have therefore extended our investigation to other types of partially oxidised platinum-atom chain compounds, to see if these also undergo a reaction under these conditions. The compounds we have selected for study are $K_{1\cdot74}Pt(CN)_4,1\cdot8H_2O$,[8]-$K_{1\cdot64}Pt(C_2O_4)_2,pH_2O$ [9] (where p indicates an unknown number of water molecules) and $Mg_{0\cdot82}Pt(C_2O_4)_2,5\cdot3H_2O$.[10] None of these compounds contains halide ions, and the partial oxidation of the platinum atom is achieved by a deficiency of cations. These compounds were selected to determine whether the presence of halide ions was necessary for a reduction reaction to occur, and if not, whether the reaction was affected by the nature of the ligands attached to the platinum atoms or by the cations in the lattice. During the course of our work, a short communication has been published on proton injection in $K_{1\cdot64}Pt(C_2O_4)_2,pH_2O$.[11]

RESULTS

$K_{1\cdot74}Pt(CN)_4,1\cdot8H_2O$.—$K_{1\cdot74}Pt(CN)_4,1\cdot8H_2O$ is obtained as very small triclinic crystals in which the square-planar $[Pt(CN)_4]^{1\cdot7-}$ units are stacked above one another along the c- (needle) axis of the crystal with a Pt–Pt distance of 2·960 Å.[8] It is expected that the potassium ions and the water molecules will occupy sites between these $[Pt(CN)_4]^{1\cdot7-}$ chains, although their exact positions are not known.

The application of a d.c. voltage of <200 V cm^{-1} in the direction of the metal atom chain to a single crystal of $K_{1\cdot74}Pt(CN)_4,1\cdot8H_2O$ produces a current which decays exponentially with time, and reaches a steady current after five minutes. This behaviour was also observed for the $K_2Pt(CN)_4X_{0\cdot3}xH_2O$ (X = Cl or Br) complexes.[4] The application of a succession of increasing d.c. voltages produces a steadily increasing initial current until, at a certain voltage, there is an exceptionally large rise in the current. The voltage necessary to produce this effect varies from crystal to crystal, but is generally in the range of 200—330 V cm^{-1}. The large increase in current is immediately accompanied by a change of colour of the crystal at the anode, from the metallic copper colour of $K_{1\cdot74}Pt(CN)_4,1\cdot8H_2O$ to a yellow-white colour with no metallic lustre. There is a sharp boundary between the two colours, and the boundary moves down the crystal to the cathode. The rate of movement of the boundary is initially extremely rapid, but decreases with time as the reaction moves across the crystal. The movement of the boundary is accompanied by a decrease in current. The decrease in the current and in the rate of movement of the boundary with time will be due, at least in part, to the much higher resistance of the product compared with the starting material. For a constant voltage applied to the complete crystal this will produce a decreasing field across the unchanged part of the crystal as the reaction proceeds.† The reaction occurs using silver paste, graphite, steel, or gelatine electrodes, and is irreversible. Reversal of the field before the crystal is completely changed causes the reaction to commence at the new anode.

All the behaviour described above is similar to that observed for $K_2Pt(CN)_4Br_{0\cdot30},2\cdot3H_2O$ and $K_2Pt(CN)_4Cl_{0\cdot32},2\cdot6H_2O$, except that the threshold field at which the reaction commences is higher.[3,4] Using the procedure previously described,[4] we have investigated the relationship between the rate of movement of the colour boundary after the initial period of very fast movement (*i.e.* 5 s) and the applied d.c. field. The results are shown in Figure 1. There is a much greater scatter of results for $K_{1\cdot74}Pt(CN)_4,1\cdot8H_2O$ compared with the $K_2Pt(CN)_4X_{0\cdot3}xH_2O$ compounds, possibly in part due to the much smaller crystals which

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† We thank a referee for his comments on this point.

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increase the errors associated with determining the size of the crystals. It can be seen, however, that whereas the behaviour of the two $K_2Pt(CN)_4X_{0.3}$ compounds was identical, that of $K_{1.74}Pt(CN)_4$ $1{\cdot}8H_2O$ is quite different. Not only is the threshold field much higher, but also the rate of movement of the boundary down the crystal is less dependent on the size of the d.c. field. This indicates that a different reaction mechanism occurs in this compound.

The yellow-white product of the reaction will not oxidise potassium iodide to iodine in contrast to the partially oxidised $K_{1.74}Pt(CN)_4,1{\cdot}8H_2O$. This indicates that reduction of the platinum atoms to Pt^{II} has taken place in the reactions. When small crystals (*ca.* 50 μg) of the reaction product are dissolved in drops (*ca.* 0·05 ml) of water, the resulting solution has a pH of *ca.* 2, suggesting that the crystals contain H^+ ions. Thus, it appears that the reaction taking place involves the reduction of the platinum atoms in the chain to Pt^{II}, and the simultaneous incorporation of protons into the lattice as the charge compensating species, to form $K_{1.74}H_{0.26}Pt(CN)_4,xH_2O$. The protons can arise either from a process of proton injection from the anode or from the breakdown of the water molecules already present in the crystal. Lecrone and Perlstein have suggested [11] that in the reaction observed at the anode in $K_{1.64}Pt(C_2O_4)_2,pH_2O$, the protons are injected into the crystal from the electrode material. We have carried out experiments on $K_{1.74}Pt(CN)_4xH_2O$ using gelatine electrodes of different pH in an attempt to determine whether or not proton injection occurs in this compound. Gelatine electrodes of pH 14 produce only a slightly slower rate of reaction than gelatine electrodes of pH 1 or silver paste electrodes. Therefore, it does not appear likely that proton injection plays an important part in the reaction, and it seems likely that the protons arise from the water molecules in the crystal. A possible mechanism will be discussed later. Electron probe analysis indicates that there is very little difference in the potassium contents of the partially oxidised $K_{1.74}Pt(CN)_4,1{\cdot}8H_2O$ and the reduction product, supporting the reaction scheme outlined above.

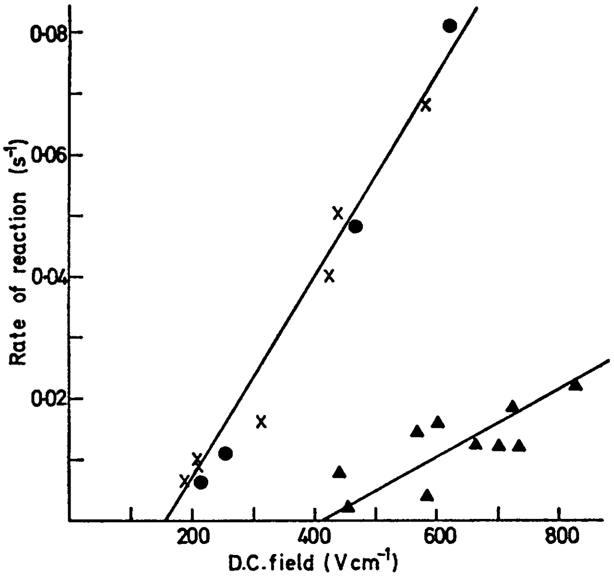

FIGURE 1 Variation of rate of reaction with applied d.c. field; ×, $K_2Pt(CN_4)Br_{0.30},2{\cdot}3H_2O$; ●, $K_2Pt(CN)_4Cl_{0.32},2{\cdot}6H_2O$; ▲, $K_{1.74}Pt(CN)_4,1{\cdot}8H_2O$

If large d.c. fields (>500 V cm⁻¹) are applied to the crystals using steel electrodes, the crystals turn to a blue-black colour at the cathode, as well as undergoing the reduction reaction at the anode as described above. Bubbles of a liquid can be seen on the surface of the crystal at the cathode and a white solid is deposited on the steel around the end of the crystal. A similar reaction has also been observed and investigated in detail for $K_{1.64}Pt(C_2O_4)_2,pH_2O$ (p indicates unknown number of water molecules), and will be discussed later.

$K_{1.64}Pt(C_2O_4)_2,pH_2O$.—Although a full *X*-ray structure determination of this compound has not been published, *X*-ray analysis of the related Mg salt (see later) indicates that the square-coplanar $[Pt(C_2O_4)_2]^{1.7-}$ units are stacked above one another with cations and water molecules occupying sites between the chains of $[Pt(C_2O_4)_2]^{1.7-}$ units. *X*-Ray powder studies indicate that the Pt–Pt distance in $K_{1.64}Pt(C_2O_4)_2,pH_2O$ varies from 2·83—2·85 Å, depending on the water content.[9]

The application of a sufficiently large field along the needle axis of single crystals of $K_{1.64}Pt(C_2O_4)_2,pH_2O$ produces a colour change at either (*a*) the anode, (*b*) the cathode (more frequently), or (*c*) at both the anode and cathode. This varied behaviour from crystal to crystal appears to be due to a combination of the size of the applied field and the presence of major crystal imperfections. Using silver paste as the electrode material, the colour change at the cathode may appear at a d.c. field as low as 50 V cm⁻¹, whereas that at the anode does not appear below 200 V cm⁻¹. Lecrone and Perlstein have reported [11] the colour change at the anode to appear at a field >200 V cm⁻¹, but do not mention a colour change at the cathode. If the crystal contains a major fault close to the cathode, then the colour change at the cathode will quickly stop, and may not readily be observed. In these circumstances, larger fields will then be applied before a reaction is observed, and this will then occur at the anode. If the crystals are placed across steel electrodes and fields of 500—600 V cm⁻¹ applied, then colour changes occur at both the anode and the cathode. The colour changes at the anode and the cathode will be discussed separately.

(i) *Colour Change at the Cathode.*—The application of a field >50 V cm⁻¹ causes the copper-coloured crystals of $K_{1.64}Pt(C_2O_4)_2,pH_2O$ to change to a blue-black colour at the cathode. In well formed crystals, there is a sharp boundary between the two colours which moves down the crystal towards the anode. At the actual interface, there is a very narrow orange-coloured portion of the crystal separating the two colours. The movement of the colour boundary is initially very fast, but quickly slows down as the boundary moves down the crystal (see Figure 2). It is clear from Figure 2 that the rate of movement increases with increasing field. The movement of the boundary after the initial very fast period does not appear to obey the same rate relationship to the applied field as the anode reactions observed in $K_2Pt(CN)_4X_{0.3},xH_2O$ and $K_{1.74}Pt(CN),1{\cdot}8H_2O$. If a reaction also occurs at the anode, then the rate of movement of the blue-black boundary is inhibited (see Figure 2). The intensity of the blue-black colour is greatest adjacent to the cathode, and decreases as the reaction proceeds further down the crystal. The movement of the colour boundary is much slower than that observed for the anode reaction in crystals of $K_2Pt(CN)_4X_{0.3}$.

Bubbles of liquid appear on the outside of the crystal near the cathode, and when steel electrodes are used, a liquid is observed around the point of contact of the crystal. This liquid dries to a white solid which is deposited on the outside of the crystals near the electrodes, and on the electrodes themselves. The white solid gives an alkaline solution in water. It does not appear on the surface of the blue-black crystals away from the cathode. The presence of droplets suggests that some of the water of hydration is being expelled from the crystals.

The blue-black product is much more soluble in water than $K_{1.64}Pt(C_2O_4)_2,pH_2O$, indicating that some form of chemical change has taken place. When similar sized crystals of the blue-black compound and $K_{1.64}Pt(C_2O_4)_2,pH_2O$ are added to drops of KI solution, the former compound appears to liberate more iodine. Attempts to determine this quantitatively, using a sensitive spectrophotometer method [12] were unsuccessful, as the starch iodine complex produced underwent a further reaction, to give a species with $\lambda_{max.}$ 495 mμ instead of $\lambda_{max.}$ 575 mμ. The intensity of this absorption peak did, however, indicate that the blue-black product may be slightly more oxidising than $K_{1.64}Pt(C_2O_4)_2,pH_2O$. Thus, the platinum atoms in the blue-black product must be in an oxidation state of at least +2·3.

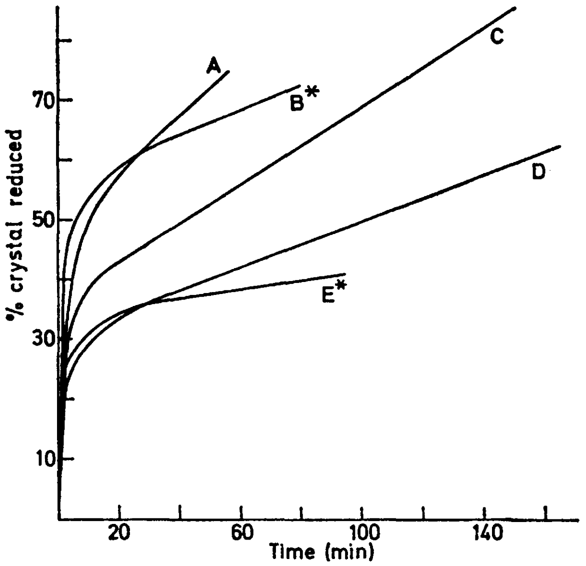

FIGURE 2 $K_{1.64}Pt(C_2O_4)_2,pH_2O$,reaction at cathode, % of crystal reduced with time. * Change inhibited by simultaneous reaction at anode. A, 377, B, 528; C, 286; D, 185; and E, 202 V cm^{-1}

Electron probe microanalysis indicated no large change in the K^+ content of the crystals on traversing the blue-black/copper-coloured boundary. This analysis did, however, indicate that the white alkaline powder which is deposited at the cathode has a very much higher K^+ content than either the blue-black or copper-coloured parts of the crystal (crystal K^+ content; 52 × 10^3 c.p.s./microamp; white powder K^+ content; 166 × 10^3 c.p.s./microamp). The high K^+ content and the alkaline nature of the white compound suggest that it is KOH and/or K_2CO_3.

The pH of a solution of the blue-black compound (50 μg in 0·05 ml H_2O), free of the white alkaline material, was found to be *ca.* 2, while the comparable pH of $K_{1.64}H_{0.36}Pt(C_2O_4)_2,pH_2O$ formed at the anode is *ca.* 1. Thus, the blue-black product contains slightly less than 0·36 proton per platinum atom.

These results suggest that the chemical changes at the cathode involve the removal of some of the K^+ ions from the lattice, and their replacement (or partial replacement) by protons. It would appear that *ca.* 0·3 K^+ ions per platinum atom are being removed, and that the oxidation state of the platinum remains at *ca.* +2·3. The deep blue-black colour is presumably due to the presence of the protons in the lattice in close proximity to the partially oxidised $[Pt(C_2O_4)_2]^{1\cdot7-}$ chain. It has previously been observed that solutions of the partially oxidised acid $H_{1.6}Pt(C_2O_4)_2$ are deep blue.[13]

A similar reaction at the cathode has been observed in crystals of $K_2Pt(CN)_4X_{0.3}2\cdot3H_2O$, but is much more limited in extent, and only occurs at very much higher fields.

(ii) *Reaction at the Anode.*—The colour change observed at the anode for d.c. fields of >200 V cm^{-1} is from the copper colour of the original crystal with a metallic lustre, to a greenish-black colour with no metallic lustre. The colour varies somewhat from crystal to crystal, and with the viewing angle. The colour boundary moves down the crystal with a fairly sharp boundary between the two colours at a rate comparable to that observed at the cathode, and much slower than the anode reaction observed in $K_2Pt(CN)_4X_{0.3},xH_2O$. During the course of this work, Lecrone and Perlstein reported [11] observing this reaction, and suggested a proton-injection mechanism. Their suggestion was based on the variation of the rate of movement of the colour boundary with the pH of gelatine electrodes, and with the observation that the product has a pH of 1. In agreement with this, we have found the pH of a solution of the greenish-black product to be *ca.* 1, compared with about 5 for $K_{1.64}Pt(C_2O_4)_2,pH_2O$, suggesting that protons are present in the greenish-black compound.

The product does not oxidise KI solution, indicating that all the platinum atoms are in oxidation state II. The crystals bend outwards from the electrodes as the reaction proceeds, indicating expansion of the crystal as expected, since Pt^{II} compounds have Pt–Pt distances >3·1 Å, compared with *ca.* 2·85 Å in $K_{1.64}Pt(C_2O_4)_2,pH_2O$. Thus, it appears that the reduction of the platinum to oxidation state II is accompanied by the incorporation of protons into the lattice as the charge compensating species, resulting in the formation of $K_{1.64}H_{0.36}Pt(C_2O_4)_2,xH_2O$ as suggested by Lecrone and Perlstein.[11] It was suggested that the protons are injected from the organic binder of the silver paste, and on one occasion, the crystal was observed to return to the copper colour from the anode.[11] We have observed the reaction to occur with the crystals resting on steel electrodes in the absence of any proton containing material except atmospheric moisture. Unfortunately, experiments cannot be performed under a ' dry ' atmosphere, because the crystals lose water and break up. These results suggest that the protons involved in the reaction may arise from the water of hydration present in the crystal. Under the influence of the d.c. field in the crystal, the water could break down according to the equation,

$$2H_2O = 4H^+ + O_2 + 4e$$

The electrons released would be available to reduce the platinum atoms to Pt^{II}, the protons produced would

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[13] T. W. Thomas, Che-hsiung Hsu, M. M. Labes, P. S. Gomm, A. E. Underhill, and D. M. Watkins, *J.C.S. Dalton*, 1972, 2050.

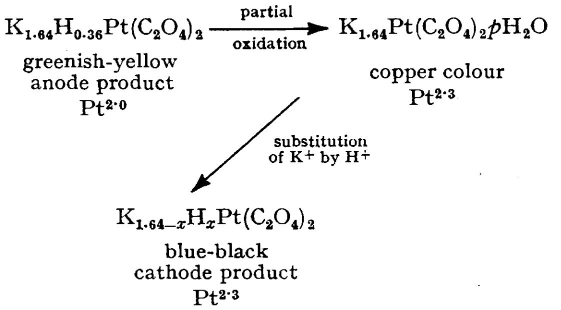
enter the lattice as the charge compensating species, and the oxygen would be released to the atmosphere.

If reactions proceed from both ends of the crystal, and the colour boundaries from the anode and cathode meet, then the blue-black colour from the cathode continues to move through the anode product towards the anode with a small copper-coloured portion between the two colours. Eventually, all the crystal is converted to the blue-black cathode product.

A similar effect is observed when the field is reversed on a crystal in which the colour boundary has moved half way down the crystal from the cathode. The blue-black colour fades to the green-yellow colour of the anode product without the appearance of any coppery colour. Reversal of the field yet again, causes the green-yellow part to be converted back to the blue-black colour. This occurs at different parts of the crystal at the same time, and proceeds through a transitory copper colour. To produce each successive colour change, an increased field was required.

These observations may be readily understood from the nature of the reaction products deduced earlier.

(*a*) conversion of anode product to cathode product



(*b*) conversion of cathode product to anode product

$$\underset{\text{cathode product}}{K_{1.64-x}H_xPt(C_2O_4)_2} \xrightarrow{\text{reduction}} \underset{\text{anode product}}{K_{1.64-x}H_{0.36+x}Pt(C_2O_4)_2}$$

Although the oxidation of the anode product to the cathode product goes through the original $K_{1.64}Pt(C_2O_4)_2pH_2O$ as an intermediate step, the reverse reaction cannot, as protons are already present in the lattice in the oxidised form.

$Mg_{0.82}Pt(C_2O_4)_2,5{\cdot}3H_2O$.—A complete *X*-ray structure determination of $Mg_{0.82}Pt(C_2O_4)_2,5{\cdot}3H_2O$ has been published.[10] In the orthorhombic crystals, the $Pt(C_2O_4)_2$ units are stacked above one another along the *c*-(needle) axis with a separation of 2·85 Å. Each successive cation is skew above another to reduce steric repulsions. Eight sites are available for the Mg^{2+} ions, but only 40% of the sites are occupied. Each Mg^{2+} ion is surrounded by an octahedral arrangement of six water molecules.

The application of d.c. fields appears to have far less effect on crystals of $Mg_{0.82}Pt(C_2O_4)_2$, $5{\cdot}3H_2O$ than on those of the other partially oxidised platinum compounds. No reaction has been observed at the anode up to a field of 3000 V cm^{-1}, and only a very limited reaction observed at the cathode at these high fields. If a d.c. field of *ca.* 500 V cm^{-1} is suddenly applied to the crystal, then the crystal disintegrates. If, however, the field is built up gradually in 100 V cm^{-1} steps, then at *ca.* 3000—4000 V cm^{-1} a very narrow blue-black band moves out from the cathode to approximately $\frac{1}{20}$ the length of the crystal.

DISCUSSION

The results described in this and previous papers [3,4,11] show that several different types of partially oxidised platinum atom chain compounds will undergo an oxidation–reduction under the influence of an applied d.c. field to yield platinum(II) compounds. This reaction occurs whether the platinum atom chain consists of $Pt(CN)_4^{x-}$ or $Pt(C_2O_4)_2^{x-}$ units. In compounds containing an excess of halide ions as the charge compensatory species, the reduction is accompanied by the expulsion of halogen,[3,4] but in those compounds which contain a deficiency of cations, the reduction is accompanied by the incorporation of protons into the lattice.

The rate of reduction of the crystal depends not only on the size of the applied d.c. field, but also on the mechanism of the reaction, since although the $K_2Pt(CN)_4X_{0.3},yH_2O$ compounds both react at the same rate, the cation deficient compounds react at a much slower rate. The latter compounds also have a higher threshold field below which the reaction does not occur.

The mechanism of the reaction must involve at least two steps.

(*a*) The addition of electrons to the platinum atoms $Pt^{2.3+} + 0{\cdot}3e \longrightarrow Pt^{2+}$

and

(*b*) Alterations to the number of anions or cations in the lattice to balance the charges in the product, and at the same time release the electrons for reaction (a).

(*i*) In $K_2Pt(CN)_4X_{0.3}xH_2O$, this reaction is $X^- \longrightarrow \frac{1}{2}X_2 + e$ and leads to the expulsion of halogen.

(*ii*) In cation deficient compounds, this reaction involves the addition of protons to the lattice which can arise either from the electrode material or from the breakdown of water molecules in the crystal.

It is not clear whether (*a*) or (*b*) is the rate controlling step. The identical rates observed for the $K_2Pt(CN)_4X_{0.3},xH_2O$ compounds,[3,4] and the differences between these and the cation deficient molecules suggests that step (*b*) is important. However, recent results [6] suggest that the band structures (localised or delocalised) in all these compounds will be different, due to the differing random potential created by the cations (or anions) along the platinum atom chains. These differences in band structure could affect reaction (*a*). The big difference in the behaviour of the partially oxidised magnesium and potassium oxalates could reflect either the effect of the relative cations on the platinum atom chain, thus affecting reaction (*a*), or the differences in the affinities of the cations for water, affecting reaction (*b*).

The reaction at the cathode appears to be due to the partial replacement of the cation by H^+, without producing any large change in the oxidation state of the platinum. This occurs more readily for $K_{1.64}Pt(C_2O_4)_2,pH_2O$ than for $K_2Pt(CN)_4X_{0.3},xH_2O$ or $K_{1.74}Pt(CN)_4,1{\cdot}8H_2O$, and may be a consequence of larger channels in the oxalate structure which enables the K^+ ions to migrate more easily to the cathode, but more detailed

X-ray studies are required before this can be substantiated. The very high fields required to induce this effect in the magnesium compound probably reflect the presence of six strongly co-ordinated water molecules around the cation.

EXPERIMENTAL

Crystals of $Mg_{0.82}Pt(C_2O_4)_2,5{\cdot}3H_2O$, $K_{1.74}Pt(CN)_4,1{\cdot}8H_2O$, and $K_{1.64}Pt(C_2O_4)_2,pH_2O$ were prepared as previously described.[13] The X-ray diffraction pattern of powdered samples confirmed the products as Phase A of $Mg_{0.82}Pt(C_2O_4)_2$, $5{\cdot}3H_2O$ and $K_{1.74}Pt(CN)_4$, $1{\cdot}8H_2O$.[8,10] The more perfectly formed crystals were selected for study. The average sizes of the crystals were as follows:

$K_{1.64}Pt(C_2O_4)_2,pH_2O$ *ca.* 0·1 × 0·01 × 0·01 cm
$K_{1.74}Pt(CN)_4,1{\cdot}8H_2O$ *ca.* 0·1 × 0·04 × 0·03 cm
$Mg_{0.82}Pt(C_2O_4)_2,5{\cdot}3H_2O$ *ca.* 0·15 × 0·03 × 0·03 cm

The reaction studies were carried out by mounting the crystals in the cells as previously described.[4] The movement of the colour boundaries across the crystal were recorded by photomicrography. Electron probe analyses and X-ray powder photographs were determined, as previously described.[4,13]

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