A Study of the Products obtained by crystallising $[NH_4]_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ or $K_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ from Acidic Chloride Solutions

By **David J. Wood** and **Allan E. Underhill**,* School of Physical and Molecular Sciences, University College of North Wales, Bangor, Gwynedd LL57 2UW

The products obtained by crystallising $[NH_4]_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ or $K_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ from solutions which contain high concentrations of chloride ions and protons have been studied. These products are shown to be isomorphous with the original compounds but contain extra chloride ions and protons in the lattice.

DURING the past few years studies have been made of compounds isomorphous with the one-dimensional conductor $K_2[Pt(CN)_4]Br_{0.30}\cdot 3H_2O$, (1). In these compounds chloride is present as the anion and potassium is replaced by other monovalent cations.[1-3] The initial report that crystals of ammonium tetracyanoplatinate chloride grown from solutions containing $[NH_4]Cl$ had unexpectedly high ammonium-ion contents was disproved by further work.[4,5] However, the presence of a high chloride to platinum mole ratio was confirmed.[5]

TABLE 1

Analyses (%) of ammonium tetracyanoplatinate chloride crystals

Crystallisation condition (see text)	K^+	$[NH_4]^+$	Pt^{total}	Pt^{IV}	Cl	C	N	H_2O	Oxidation state	Cl: Pt ratio
(*a*)		8.95 [a,b]	46.55 [c,d]	6.95 [e]	3.75 [f]	12.8	21.4	11.3 [g]	2.27 [h]	0.44
(*b*)	0.001	8.95 [b]	48.2 [d,j]	6.75 [e]	3.50 [f]	12.65	22.0		2.283 [h]	0.40
(*c*)		8.85 [b]	48.2 [d,i]		3.65 [j]	12.45	21.85			0.42
(*d*)		8.75 [b]	46.0 [j]	7.0 [e]	3.60 [j]	11.5	20.8	13.6 [g]	2.283 [h]	0.43
(*e*)			46.8 [d,i]		3.40 [j]	12.75	20.9			0.40
(*f*)			47.35 [d,i]		3.60 [j]	12.7	21.1			0.42
(*g*)		8.85 [a]	47.85 [c,f]	6.95 [e]	2.65 [f]	12.3	20.2	12.5 [g]	2.29 [k]	0.30 [f]
					2.70 [j]					0.31 [j]

[a] Gravimetric as $[NH_4][BPh_4]$. [b] Micro-Kjeldahl. [c] Atomic absorption. [d] Analysis by Johnson, Matthey Research Laboratories. [e] $KI-Na_2[S_2O_3]$ titration. [f] Analysis by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. [g] Thermal gravimetric analysis. [h] Calculated from values determined for total Pt and Pt^{IV} in the same solution by $KI-Na_2[S_2O_3]$ titration. [i] Gravimetric. [j] Analysis by Dr. Strauss, Microanalytical Laboratories, Oxford. [k] Calculated from values determined for total Pt and Pt^{IV} in different samples.

In compounds of this type the existence of incompletely occupied halide sites creates a random potential which may play a crucial role in determining the electrical conduction properties of the one-dimensional metallic strands of platinum atoms.[6] It is therefore very important to determine whether the occupancy of these halide sites can be varied. We now report the results of an investigation into the factors affecting the chloride-site occupancy in ammonium tetracyanoplatinate chloride, (2), and potassium tetracyanoplatinate chloride, (3).

EXPERIMENTAL

Preparation of (2).—Seven separate batches of crystals were obtained from five separate preparations and each batch of crystals was extensively analysed.

In all the preparations the initial solution of partially oxidised ammonium tetracyanoplatinate chloride, (2), was prepared in the same way. The compound $K_2[PtCl_4]$, obtained from Johnson, Matthey and Co. Ltd., was treated with K[CN] to give $K_2[Pt(CN)_4]\cdot 3H_2O$. This was converted into $H_2Pt(CN)_4$, under N_2, using a Dowex 50W-X8 cation-exchange resin. The free acid was rotary evaporated to an oil, with gentle warming, to remove any HCl or HCN impurities. The temperature was restricted to a maximum of 30 °C to prevent decomposition. The oil was neutralised with dilute analytical grade ammonia solution and a sixth of the solution was saturated with chlorine. Both this solution and the remainder of the original solution were then separately rotary evaporated to dryness, with gentle heating (<30 °C) to remove excess of chlorine and ammonia respectively. The resulting solids were dissolved in a little deionised water at room temperature, to give almost saturated solutions. The concentrated solutions were mixed and filtered without suction through a No. 4 Sinta-glass crucible.

In all the preparations crystals were obtained by allowing a concentrated solution to evaporate slowly at room temperature. The conditions used for each crystallisation are given below and the analysis obtained for each product is given in Table 1.

Crystallisation.—(*a*) The solution was initially 3.7 mol dm^{-3} in $[NH_4]Cl$ and 0.55 mol dm^{-3} (2). Crystals were collected after 7 d when the concentration of $[NH_4]Cl$ was >3.7 mol dm^{-3}.

(*b*) The mother-liquor from (*a*) was filtered through a 0.45 μm Millex filter and the filtrate seeded with several good quality crystals. Two large crystals (0.65 g, 1.7 × 0.6 × 0.6 cm and 0.47 g, 1.5 × 0.4 × 0.4 cm) slowly grew from the solution. The solution was almost saturated in $[NH_4]Cl$ when the crystals were removed. The analyses recorded in Table 1 were determined on a portion of the larger (0.65 g) crystal.

(*c*) The mother-liquor from (*b*) was allowed to evaporate further and yielded a third crop of crystals. These were heavily contaminated with solid $[NH_4]Cl$. The crystals were washed with cold water to remove the $[NH_4]Cl$ before analysis. (Saturated $[NH_4]Cl$ solution is 5.44 mol dm^{-3}.)

(*d*) The conditions were similar to (*a*).

(*e*) Compound (2) was crystallised from a solution initially 6 mol dm^{-3} in HCl instead of $[NH_4]Cl$.

(*f*) The preparation of (2) was carried out using fully deuteriated materials. The crystallisation conditions were the same as in (*a*) except that $[ND_4]Cl$ and D_2O were used. Evaporation was allowed to take place in a desiccator containing silica gel.

(*g*) Compound (2) was allowed to crystallise from aqueous solution at 4 °C without the addition of any other chemical species.

TABLE 2

Analysis (%) of potassium tetracyanoplatinate chloride (3)

	From 0.1 mol dm^{-3} KCl, 1 mol dm^{-3} urea solution	From 3 mol dm^{-3} HCl solution	Calc. for $K_2[Pt(CN)_4]$-$Cl_{0.32}\cdot 3H_2O$
Total Pt	43.0 [a]	42.8 [b]	44.1
K	16.3 [c]		17.7
C	10.0	11.5	10.8
N	12.8	12.6	12.7
Cl	2.50 [d]	3.90 [d]	2.55
Pt Oxidation state	2.31 [e]	2.33 [f]	2.32

[a] KI–$Na_2[S_2O_3]$ titre. [b] Analysis by Johnson, Matthey Research Laboratories. [c] Flame emission. [d] Dr. Strauss, Microanalytical Laboratories, Oxford. [e] Calculated from total Pt and Pt^{IV} measured on different samples. [f] Calculated from total Pt and Pt^{IV} measured on same solution.

Preparation of (3).—$K_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ was prepared and allowed to crystallise using the conditions (0.1 mol dm^{-3} KCl, 1 mol dm^{-3} urea) described by Saillant *et al.*[7] A sample of this product was recrystallised from a solution initially made 3 mol dm^{-3} in HCl. The analyses of both products are given in Table 2. Further samples of (3) were obtained from solutions containing different initial concentrations of KCl or HCl and these samples were analysed for their chloride content. The conditions used for each crystallisation and the chloride content of the product are shown in Table 3.

TABLE 3

Chloride content (%) of samples of potassium tetracyanoplatinate chloride

Crystallisation conditions	Time after preparation of analysis	Cl *
KCl (0.1 mol dm^{-3}), urea (0.1 mol dm^{-3})		2.50
KCl (0.2 mol dm^{-3})	*ca.* 1 week	2.35
(3 mol dm^{-3})	*ca.* 1 week	2.45
HCl (3 mol dm^{-3})	*ca.* 1 week	3.90
	4 months	3.10
(3 mol dm^{-3})	*ca.* 1 week	3.30
	3 months	2.90
(4 mol dm^{-3})	*ca.* 1 week	3.65
(concentrated)	*ca.* 10 d	3.65

* Determined by Dr. Strauss, Microanalytical Laboratories, Oxford.

DISCUSSION

The crystals of (2) obtained from aqueous solutions containing no additional $[NH_4]Cl$ [crystallisation (*g*)] have analyses consistent with the formulation $[NH_4]_2$-$[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ (Found: see Table 1. Calc. for $C_4H_{14}Cl_{0.3}N_6O_3Pt$: C, 12.0; Cl, 2.65; N, 21.1; $[NH_4]^+$, 9.0; Pt (total), 48.8; Pt^{IV}, 7.3%). This is very similar to the composition of (3) obtained from aqueous solution.

Crystals of (2) obtained from solutions containing high (>3.7 mol dm^{-3}) $[NH_4]Cl$ or HCl concentrations have very similar C, N, $[NH_4]^+$, Pt (total), and Pt^{IV} content to those observed above but the Cl content is consistently higher, varying between 3.5 and 3.75% compared with an average of 2.70% observed for crystals obtained from aqueous solution. The Cl : Pt mol ratio is 0.42 ± 0.02 : 1 compared with 0.30 : 1. Further confirmation of the high chloride content in these crystals comes from the neutron-diffraction study of one of these crystals. The total Cl^- occupancy factor of 0.41(18) is in good agreement with the chemical value of 0.42 although the uncertainty in the neutron data is high.[3] From these results it would be expected that the Pt would be in an oxidation state of 2.42 in comparison with the properties of (1). However, the platinum(IV) content and the ratio of Pt^{IV} to total Pt determined on the same solution of the complex shows that the oxidation state is 2.28. This is further supported by *X*-ray diffuse scattering at room temperature which shows $2k_F = 1.75\ c^*$ (where k_F is the Fermi wave vector and $c^* = 2\pi/c$), *i.e.* oxidation state of 2.25.[8] The reason for the small difference in these values is unknown.

The most probable explanation of the apparent conflict between a Pt : Cl mol ratio of 1 : 0.42 and an oxidation state of the Pt of *ca.* 2.25 is the presence of additional cations in the lattice compared with $[NH_4]_2$-$[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ (2) obtained from aqueous solution. The structural studies, which indicate that the compound is isomorphous with (1), clearly rule out the presence of any additional large cations in the lattice.[3] However, it is well known that solutions of $[NH_4]Cl$ are strongly acidic and therefore it is proposed that protons are present in the lattice to compensate for the additional chloride ions. This suggestion is supported by the observation that crystals of the same composition can be obtained from 6 mol dm^{-3} HCl instead of 4 mol dm^{-3} $[NH_4]Cl$. Direct evidence of these additional protons is very difficult to obtain since only one additional proton per eight molecular units is required. Presumably the additional protons will be attached to water molecules in the lattice to form $[H_3O]^+$ ions.

The presence of such a small number of $[H_3O]^+$ ions would not be detected in the structural studies. We therefore propose that compound (2) obtained from concentrated solutions of $[NH_4]Cl$ or HCl should be formulated as $[NH_4]_2[H_3O]_{0.17}[Pt(CN)_4]Cl_{0.42}\cdot 2.83H_2O$.

All the compounds which contain the extra chloride ions have very similar Pt : Cl ratios of 1 : 0.42 ± 0.02. Within the structure of (2) there are sufficient Cl^- sites for a ratio of 1 : 0.5. The constancy of the observed ratio may reflect the fact that all the solutions from which crystals were obtained had similar chloride-ion concentrations (*ca.* 4—6 mol dm^{-3}) or it may indicate some preference for this amount of additional H^+ and Cl^- in the lattice.

From Table 2 it is clear that the chloride content of

(3) can be increased by crystallising the compound from 3 mol dm^{-3} HCl. Thus (3) behaves in a similar way to (2). Table 3 shows that the chloride content of (3) is not increased if the solution is 3 mol dm^{-3} in KCl. This confirms the suggestion made earlier for (2) that additional chloride ions are only incorporated into the lattice when crystallisation occurs from solutions that contain high concentrations of both chloride ions and protons. We therefore propose that crystals of (3) obtained from HCl solutions contain $[H_3O]^+$ ions to compensate for the additional halide ions. A single-crystal *X*-ray study of a crystal of (3) grown from 3 mol dm^{-3} HCl solution confirms that these products are isomorphous with the crystals obtained from KCl solution. It has previously been shown that crystals of (1) grown from acidic solutions have the same structure as those grown from neutral solution.[9] However no halide analyses of the products were reported.[9]

Table 3 also shows that there is a considerable variation in the chloride content of crystals of (3) obtained from HCl solution. It is also clear that re-analysis of the crystals after a period of several months showed a decrease in the chloride content. No such decrease was observed for crystals of (2) with a high chloride content. The crystal quality of all the crystals of (2) containing additional halide was very good and much superior to crystals of (2) grown from aqueous solutions which did not contain added ammonium chloride. The reverse is true concerning the crystals of (3). It seems likely that the poor quality of the crystals of (3) obtained from HCl solutions may be due to the break-up of the lattice as the HCl is slowly lost with time.

The highest chloride content obtained for (3) (3.9%) corresponds to a site occupancy of 98% as opposed to *ca.* 62% for samples obtained from KCl solution. However, the combination of poor crystal quality and slow loss of HCl make a detailed study of the variation of electrical conduction properties with halide-site occupancy very difficult. Preliminary studies on both (2) and (3) suggest, however, that changing the halide-site occupancy does not produce very large changes in the electrical conduction properties.[10] Larger effects, however, might be expected if the random potential was completely removed by 100% occupancy of the halide sites.

It seems likely that additional halide ions and protons will be incorporated into (1) and any of the compounds isomorphous with (1) if these compounds are recrystallised from solutions containing high concentrations of protons and the appropriate halide ion. Care must therefore be taken in using the halide to platinum mol ratio to determine the degree of partial oxidation in this type of compound.

We are indebted to Johnson, Matthey and Co. Ltd. for the loan of platinum salts and for platinum analyses and to the S.R.C. for a maintenance grant (to D. J. W.).

[9/282 *Received, 22nd February,* 1979]

REFERENCES

[1] A. E. Underhill and D. J. Wood, *Ann. New York Acad. Sci.*, 1978, **313**, 516.

[2] J. M. Williams, P. L. Johnson, A. J. Schultz, and C. C. Coffey, *Inorg. Chem.*, 1978, **17**, 834.

[3] P. L. Johnson, A. J. Schultz, A. E. Underhill, D. M. Watkins, D. J. Wood, and J. M. Williams, *Inorg. Chem.*, 1978, **17**, 839.

[4] A. E. Underhill, D. M. Watkins, and D. J. Wood, *J.C.S. Chem. Comm.*, 1976, 805.

[5] A. E. Underhill, D. M. Watkins, and D. J. Wood, *J.C.S. Chem. Comm.*, 1977, 392.

[6] H. Fukuyama, *J. Phys. Soc. Japan*, 1978, **45**, 1266.

[7] R. B. Saillant, R. C. Jaklevic, and C. D. Bedford, *Mater. Res. Bull.*, 1974, **9**, 289.

[8] K. Carneiro, A. S. Pederson, A. E. Underhill, D. J. Wood, D. M. Watkins, and G. B. Mackenzie, *Phys. Rev.* (*B*), 1979, **19**, 6279.

[9] A. H. Reis, S. W. Peterson, N. Enright, and J. M. Williams, *Mater. Res. Bull.*, 1975, **10**, 921.

[10] D. J. Wood and A. E. Underhill, unpublished work.