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# OXIDATIVE ADDITION REACTIONS OF $[Pt(CN)_4]^{2-}$; A $^{13}C$ AND $^{195}Pt$ NMR STUDY

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## Summary

$^{13}C$ and $^{195}Pt$ NMR measurements show that complexes of the type *trans*-$[Pt(CN)_4X_2]^{2-}$ are formed on addition of $X_2$ (X = Br, Cl, I) to $M_2[Pt(CN)_4]$ (M = K or $NBu_4$) in aqueous and chloroform solution respectively. Addition of ICN to $K_2[Pt(CN)_4]$ (60% $^{13}CN^-$) in aqueous solution results in the formation of potassium pentacyanoiodoplatinate(IV) with complete $^{13}CN^-/^{12}CN^-$ scrambling. The reaction of equi-molar amounts of *trans*-$[PtX_2(CN)_4]^{2-}$ (X = Br and Cl), which was previously claimed to result in complete transformation into *trans*-$[PtBrCl(CN)_4]^{2-}$, is instead shown to result in an approximately statistical redistribution of halogens. A progressive shift of $\delta_{Pt}$ to high field is observed on successive replacement of $^{12}CN^-$ by $^{13}CN^-$ in $[Pt(CN)_4]^{2-}$.

## Introduction

$^{195}Pt$ Fourier Transform NMR is a powerful technique for examining systems which cannot be studied by INDOR. We have concentrated on mechanistic and structural investigation of such systems. For example we have shown that even at low temperatures $[Pt_9(CO)_{18}]^{2-}$ is fluctional [1] and undergoes at higher temperatures inter $Pt_3$-triangular exchange [1] with $[Pt_{12}(CO)_{24}]^{2-}$. Similarly $^{195}Pt$ NMR has been used to show that addition of bromine to tetrachloroplatinate(II) results in halogen scrambling with formation of 10 species of the type $[PtBr_nCl_{6-n}]^{2-}$ ($n$ = 0, 1—6) [2], although previous work [3] suggested the formation of a single product $[PtBr_2Cl_4]^{2-}$, which was assigned the *trans*-configuration on the basis of Raman spectroscopy. The preparation of neutral gold(III) and platinum(IV) complexes containing both bromine and chlorine *via* oxidative addition reactions has also been shown to result in halogen scrambling by $^{31}P-\{^1H\}$ [4,5], although previous work suggested otherwise [6], and we suspect that halogen scrambling in such reactions is quite general. It was therefore of

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interest to obtain $^{13}C$ and $^{195}Pt$ NMR data on products resulting from the addition of halogen to $[Pt(CN)_4]^{2-}$ since previous work, based on IR/Raman measurements, suggested the formation of a single product, *trans*-$[PtX_2(CN)_4]^{2-}$ (X = Br, Cl, I) [7]. NMR data on related cyanoplatinum complexes are also described.

## Results

Addition of halogen (1 mol) to either an aqueous solution of $K_2[Pt(CN)_4]$ (1 mol) or to a chloroform solution of $(NBu_4)_2[Pt(CN)_4]$ (1 mol) gives a product which analyses for $M_2[PtX_2(CN)_4]$ (M = K, $NBu_4$) (Table 1). Both $^{13}C$ and $^{195}Pt$ NMR spectra exhibit a single resonance (Table 2) consistent with the formation of a single species, as suggested earlier [7]: long-term accumulation gave $^{13}C$

TABLE 1

ANALYTICAL DATA FOR Pt(II) AND Pt(IV) CYANO COMPLEXES

| Compound | Found (calcd.) (%) | | | |
|---|---|---|---|---|
| | C | H | N | Other |
| $(NBu_4)_2[Pt(CN)_4]$ | 55.3<br>(55.2) | 9.8<br>(9.3) | 10.6<br>(10.7) | |
| $K_2[Pt(CN)_4]H_2O$ | 12.1<br>(12.15) | 0.5<br>(0.5) | 14.0<br>(14.2) | |
| $(NBu_4)_2[PtCl_2(CN)_4]$ | 49.9<br>(50.6) | 8.0<br>(8.4) | 9.6<br>(9.8) | Cl, 7.9<br>(8.1) |
| $K_2[PtCl_2(CN)_4]$ | 10.7<br>(10.7) | | 11.7<br>(12.5) | Cl, 16.2<br>(15.85) |
| $(NBu_4)_2[PtBr_2(CN)_4]$ | 45.8<br>(45.8) | 7.7<br>(7.7) | 8.9<br>(8.9) | |
| $K_2[PtBr_2(CN)_4]$ | 8.9<br>(8.9) | | 10.0<br>(10.4) | Br, 29.8<br>(29.8) |
| "$(NMe_4)_2[PtBrCl(CN)_4]$" [a] | 25.4<br>(25.6) | 4.65<br>(4.3) | 15.1<br>(14.9) | |
| "$(NBu_4)_2[PtBrCl(CN)_4]$" [b] | 47.8<br>(48.0) | 7.6<br>(8.0) | 9.3<br>(9.3) | |
| $(NBu_4)_2[PtI_2(CN)_4]$ | 41.7<br>(41.6) | 7.2<br>(7.0) | 8.0<br>(8.1) | |
| $K_2[PtI_2(CN)_4]$ | 7.6<br>(7.6) | | 8.7<br>(8.9) | I, 39.7<br>(40.2) |
| $K_2[PtCl(CN)_5]2H_2O$ [c] | 13.0<br>(12.65) | 0.2<br>(0.6) | 14.9<br>(14.7) | Cl, 7.9; K, 16.5<br>(7.5) (16.4) |
| $Na_2[PtI(CN)_5]H_2O$ | 10.9<br>(10.9) | 1.2<br>(1.2) | 12.5<br>(12.7) | |
| $(NBu_4)_2[Pt(CN)_6]$ | 54.6<br>(54.6) | 8.8<br>(8.6) | 13.4<br>(13.4) | |
| $K_2[Pt(CN)_6]H_2O$ | 16.4<br>(16.4) | 0.2<br>(0.2) | 19.2<br>(19.2) | |

[a] From the reaction of $K_2[PtBr_2(CN)_4]$ + $K_2[PtCl_2(CN)_4]$ in water followed by the addition of $NMe_4Cl$ [10,11]. [b] Same reaction, but followed by addition of $NBu_4Cl$. [c] From $Na_2[PtCl_6]$ + 6 KCN in aqueous solution.

TABLE 2

$^{13}C$ AND $^{195}Pt$ NMR DATA FOR Pt(II) AND Pt(IV) CYANO COMPLEXES

$Na^+/K^+$ salts in $D_2O$ and $NBu_4^+$ salts in acetone-$d_6$

| Compound | $\delta$(CN) (ppm) [a] | $^1J$(PtC)(Hz) | $\delta$(Pt) (ppm) [b] | |
|---|---|---|---|---|
| | | | Observed | Predicted [c] |
| $(NBu_4)_2[Pt(CN)_4]$ | 123.2 | 1005.9 ± 2 | −174 | |
| $K_2[Pt(CN)_4]$ | 126.5<br>125.4[14] | 1029.3 ± 2<br>1035[15] | −213<br>−229[13 f] | |
| $(NBu_4)_2[PtCl_2(CN)_4]$ | 94.8 | 842 ± 6 | 2052 | 2070 |
| $K_2[PtCl_2(CN)_4]$ | 98.9 | 851 ± 6 | 1909 | 1940 |
| $(NBu_4)_2[PtBr_2(CN)_4]$ | 92.2 | 842 ± 6 | 1184 | 1427 |
| $K_2[PtBr_2(CN)_4]$ | 96.3 | 854 ± 6 | 935 | 1306 |
| $(NBu_4)_2[PtBrCl(CN)_4]$ | | | 1589 | 1618 [d] |
| $(NBu_4)_2[PtI_2(CN)_4]$ | 86.8 | 845 ± 6 | −185 | |
| $K_2[PtI_2(CN)_4]$ | 90.8 | 853 ± 6 | −257 | −164 |
| $K_2[PtCl(CN)_5]$ | 92.8(4)<br>75.8(1) | 821 ± 6<br>e | 1239 | 1303 |
| $(NBu_4)_2[PtI(CN)_5]$ | 84.4(4)<br>70.5(1) | 815 ± 6<br>e | 500 | |
| $Na_2[PtI(CN)_5]$ | 87.8(4)<br>74.6(1) | 827 ± 6<br>921 ± 6 | 319 | 252 |
| $(NBu_4)_2[Pt(CN)_6]$ | 83.4 | 796 ± 6 | 712 | |
| $K_2[Pt(CN)_6]$ | 85.5 | 806 ± 6 | 667<br>663[13 f] | |

[a] Downfield from internal TMS. Figures in parentheses are relative intensities. [b] Chemical shift for a magnetic field such that the protons in TMS resonate at exactly 100 MHz. 21.4 MHz = 0 ppm and positive shifts are to high frequency (low field). [c] $\delta([PtX_n(CN)_{6-n}]^{2-}) = \delta([Pt(CN)_6]^{2-}) + n\{\delta([PtX_6]^{2-}) - \delta([Pt(CN)_6]^{2-})\}/6$ (X = Cl, Br or I; $n$ = 1 or 2). In aqueous solution, $\delta([PtX_6]^{2-})$ = 4484 (X = Cl); 2528 (X = Br); −1827 (X = I) ppm. In acetone-$d_6$ solution, $\delta([PtX_6]^{2-})$ = 4785 (X = Cl); 2585 (X = Br) ppm. [d] $\delta([PtBrCl(CN)_4]^{2-}) = \{\delta([PtBr_2(CN)_4]^{2-}) + \delta([PtCl_2(CN)_4]^{2-}\}/6$. [e] Not observed. [f] The data from ref. 13 have been converted to our scale using $\delta(Na_2PtCl_6)$ = +4484 ppm.

spectra exhibiting satellites due to $^1J$(PtC). Incremental shifts to high field are observed for $\delta$(Pt) on replacement of chloride with bromide in $[PtCl_6]^{2-}$ [2] and the predicted values of $\delta$(Pt) for $[PtX_2(CN)_4]^{2-}$ calculated on a similar basis are given in Table 2. In view of the enormous range of platinum chemical shifts, the observed values of $\delta$(Pt) are reasonably close to the predicted values, except when X = Br. We have no explanation for this discrepancy since $\delta$(Pt) for $[PtBr_2(CN)_4]^{2-}$ is anomalous for the product prepared in chloroform and particularly anomalous for that prepared in aqueous solution. Good analytical data were obtained for both these species before and after the NMR measurement and, although $[PtBr(OH_2)(CN)_4]^-$ has been claimed as an intermediate in the bromine oxidation of $[Pt(CN)_4]^{2-}$ in aqueous solution [8], we find no evidence for such species in our work. Furthermore, addition of $NBu_4[ClO_4]$ to an aqueous solution of $K_2[PtBr_2(CN)_4]$ gives the same species as that obtained by bromination of $(NBu_4)_2[Pt(CN)_4]$ in chloroform solution.

Addition of ICN (1 mol) to an aqueous solution of $Na_2[PtCl_4]$ (1 mol) gives $Na_2[Pt(CN)_3I]$ as previously reported [9]. However, in neither chloroform nor methanol solution, does ICN react with $(NBu_4)_2[Pt(CN)_4]$, although $(NBu_4)_2$-$[Pt(CN)_5I]$ has been prepared by addition of $NBu_4I$ to an aqueous solution of $Na_2[Pt(CN)_5I]$. Both the $^{13}C$ and $^{195}Pt$ NMR are consistent with the presence of $[Pt(CN)_5I]^{2-}$ in aqueous and acetone solutions (Table 2). Very fast $^{12}CN^-/^{13}CN^-$ scrambling occurs on carrying out the reaction of ICN with $Na_2[Pt(CN)_4]$ (ca. 60% $^{13}CN^-$) so that the product, which is formed within the time of mixing, contains cyanides with equal $^{13}C$-enrichment.

The reaction of $[PtCl_6]^{2-}$ (1 mol) with cyanide (6 mol) gives $[PtCl(CN)_5]^{2-}$, which has been completely characterised by elemental analysis (Table 1) and NMR measurements (Table 2). The $^{195}Pt$ NMR spectrum, using short-term accumulation (1000 scans), exhibits a single resonance, which is in reasonable agreement with the predicted value of $\delta(Pt)$, and the $^{13}C$ NMR spectrum is consistent with the presence of 4 equivalent equatorial and 1 unique axial cyanide ligands. Longer-term accumulation (50,000 scans) gives a $^{195}Pt$ NMR spectrum showing an additional weak doublet due to $^1J(PtC)$ caused by one $^{13}C$-labelled equatorial cyanide. The centre of this doublet, which is $\delta(Pt)$ for $[PtCl(^{12}CN_{eq})_3$-$(^{13}CN_{eq})(^{12}CN_{ax})]^{2-}$, is 16.5 Hz to high field of $\delta(Pt)$ for $[PtCl(^{12}CN)_5]^{2-}$.

In order to prepare $[Pt(CN)_6]^{2-}$ it is necessary to irradiate an aqueous solution of $[Pt(CN)_5I]^{2-}$ containing cyanide [10]. The reaction of equimolar amounts of $K_2[PtBr_2(CN)_4]$ and $K_2[PtCl_2(CN)_4]$ in aqueous solution at 80°C, followed by[ addition of tetra-alkylammonium chloride, has been claimed to result in complete conversion to $(NR_4)_2[PtBrCl(CN)_4]$ (R = Me) [11]. Only analytical data were used to characterise this species, which was subsequently used for kinetic measurements [12]. We find that repetition of this procedure using $(NR_4)Cl$ (R = Me, $n$-Bu) gives a product with the expected analysis for the mixed bromo/chloro species but $^{195}Pt$ NMR shows equally intense resonances due to the presence of both reactants as well as a peak, which is twice as intense as the peaks due to the reactants, due to $(NR_4)_2[PtBrCl(CN)_4]$ (Table 2). It follows that approximately statistical redistribution of halogens occurs and not complete reaction as was originally thought [11,12].

$$trans\text{-}[PtBr_2(CN)_4]^{2-} + trans\text{-}[PtCl_2(CN)_4]^{2-} \overset{K=ca.4}{\rightleftharpoons} 2\ trans\text{-}[PtBrCl(CN)_4]^{2-} \quad (1)$$

The $^{13}C$ NMR spectra of $K_2[Pt(CN)_4]$ (1.1 and 60% $^{13}CN^-$) are, as expected, simple 1 : 4 : 1 triplets and the values of $\delta(CN)$ and $^1J(PtC)$ agree quite well with previously published data [14,15] (Table 2). Significantly different values of $^1J(PtC)$ are found for $[Pt(CN)_4]^{2-}$ in aqueous and acetone solutions and this must be due to the different degrees of solvation of the anion in the vacant octahedral positions and/or on the periphery of the square-plane. The former postulate is probably the more important since $^1J(PtC)$ for $[Pt(CN)_6]^{2-}$ in aqueous and non-aqueous solutions are, within experimental error, the same (Table 2).

The $^{195}Pt$ NMR spectrum of $[Pt(CN)_4]^{2-}$ (1.1% $^{13}CN^-$) consists of a single line [*] whereas the spectrum of this ion with ca. 60% $^{13}CN^-$ is quite complex but may be deconvoluted into spectra which arise from the different isotopomers [**] $[Pt(^{12}CN)_x(^{13}CN)_{4-x}]^{2-}$ ($x$ = 0, 1—4). For increasing values of $x$,

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[*] Pesek and Mason [13] have recently reported the $^{195}Pt$ spectrum of unenriched $[Pt(CN)_4]^{2-}$ ion (Table 2).

[**] Isotopomers are defined as species which contain different isotopic distributions of their constituent elements but otherwise have the same chemical and geometrical formulation.

TABLE 3

$^{195}$Pt NMR DATA FOR $(NBu_4)_2[Pt(^{12}CN)_x(^{13}CN)_{4-x}]$

($x$ = 0, 1—4) (ca. 60% $^{13}CN^-$) in acetone-$d_6$

| | $x$ | | | | |
|---|---|---|---|---|---|
| | 0 | 1 | 2 | 3 | 4 |
| $\delta$(Pt) (ppm) | −174.39 | −174.67 | −174.95 | −175.23 | −175.51 |
| $^1J$(PtC) (±2 Hz) | — | 1007.8 | 1007.8 | 1007.8 | — |

the isotopomers are present with the following relative abundances 1 : 6 : 13.5 : 13.5 : 5 : 1, at this level of $^{13}$C-enrichment, and give rise to a singlet, doublet, quartet and quintet respectively, with the appropriately weighted relative intensities. Furthermore, the spectrum due to each isotopomer is progressively displaced to high field (6 Hz; 0.28 ppm) with each successive replacement of $^{12}CN^-$ by $^{13}CN^-$. The value of $^1J$(PtC) is independent of $x$ (Table 3).

## Discussion

A variety of redox/substitution mechanisms are involved in $Cl^-/Br^-$ randomisation on oxidation of $[PtCl_4]^{2-}$ with bromine [2] whereas the formation of a single product, *trans*-$[PtX_2(CN)_4]^{2-}$ (X = Br, Cl, I), on oxidation of $[Pt(CN)_4]^{2-}$ with halogen suggests a much simpler sequence of reactions, which is probably similar to the reactions involved in the oxidative-addition of ICN to $[Pt(CN)_4]^{2-}$ in aqueous solution. In this case, the experimental observations, vide supra, suggest that oxidative-addition occurs because of dissociation of ICN in aqueous solution:

$$ICN \rightleftharpoons I^+ + CN^- \qquad (2)$$

Since it is known that $[Pt(CN)_4]^{2-}$ is very labile towards nucleophilic substitution [16], it is proposed that rapid $^{12}CN^-/^{13}CN^-$ randomisation takes place before oxidation. This could occur via pseudo-rotation of the 5-coordinate intermediate or by $k_1$ and $k_{-1}$ both being large with $k_{-1} \geqslant k_1$ (Scheme 1). As a result, it is difficult to decide whether the oxidation involves electrophilic attack of $I^+$ on a 4- or 5-coordinate complex. Nevertheless, the above ideas provide an explanation for the statistical redistribution of $^{13}CN^-/^{12}CN^-$ on reaction of $I^{12}CN$ with $[Pt(^{13}CN)_4]^{2-}$.

SCHEME 1

POSSIBLE REACTIONS INVOLVED IN THE ADDITION OF ICN TO $[Pt(CN)_4]^{2-}$

$$\begin{tikzcd}
{[Pt(CN)_4]^{2-}} \arrow[r, "I^+"] \arrow[d, shift left, "k_1(+CN^-)"] & {[PtI(CN)_4]^-} \arrow[d, "+CN^-"] \\
{[Pt(CN)_5]^{3-}} \arrow[u, shift left, "(-CN^-)k_{-1}"] \arrow[r, "I^+"] & {[PtI(CN)_5]^{2-}}
\end{tikzcd}$$

The $^{13}$C chemical shifts of all the platinum cyano complexes (Table 2) are between those of NaCN (165.1 ppm) and ICN (37.8 ppm), which have been measured in aqueous and $CDCl_3$ solutions respectively. The potassium platinum(II) and platinum(IV) salts have δ(CN) at consistently lower fields (2—4 ppm) and δ(Pt) at higher fields than the analogous tetrabutylammonium salts. This probably arises because of the different solvents used for the NMR measurements but the reasons for these opposite shifts are not obvious. NMR measurements were generally carried out on ca. 0.2 *M* solutions but in some cases, because of low solubility, more dilute solutions had to be used and this may account for the nonsystematic differences in δ(Pt) for the same anion in different solvents.

The $^{13}C$ chemical shift for $[Pt(CN)_4]^{2-}$ is at much lower field than for $[Pt(CN)_6]^{2-}$ (Table 2) and similar trends in $^{13}C$ NMR data have been observed for carbonyl complexes [17], carbonyl clusters [18] and for a series of organic compounds containing either a carbon—oxygen double bond (e.g. aldehydes, ketones, esters, etc.) [19] or a carbon—nitrogen triple bond (nitriles) [20]. Thus increasing the oxidation state of the metal or increasing the electronegativity of the substituent attached to the carbon atom of the functional group ($C{\equiv}N$ or $C{=}O$) results in a shift of the $^{13}C$ resonance to high field and, in the case of organic nitriles, $^{14}N$ NMR data show a concomittant deshielding of the nitrogen atom [20].

The trends observed in the $^{195}Pt$ chemical shifts are largely in accord with those noted elsewhere [2,21—29]: the $^{195}Pt$ resonance for Pt(IV) complexes occurs at lower field than analogous Pt(II) complexes and increasing "heavy-atom" substitution (Cl, Br, I) results in increased shielding of the $^{195}Pt$ nucleus.

The variations in $^1J(PtC)$ in the present work are similar to those observed for $^1J(PtP)$ [30]. Thus, increasing the oxidation state of platinum from II to IV results in a reduction of the "*s*-character" of the Pt—CN bond with the associated decrease in $^1J(PtC)$. Similarly, in $[Pt(CN)_5I]^{2-}$, $^1J(PtC)$ is greater when the cyanide is *trans* to iodide than when *trans* to cyanide due to the much greater *trans*-influence of cyanide compared to that of iodide [31].

Isotopic substitution ($^{12}CN^-/^{13}CN^-$) in $[Pt(CN)_4]^{2-}$ and $[PtCl(CN)_5]^{2-}$ results in a significant shift of the frequency of the $^{195}Pt$ resonance and similar shifts of the $^{59}Co$ resonance in $K_3[Co(CN)_6]$ have been observed [32]. Heavy isotopic substitution results in the $^{195}Pt$ and $^{59}Co$ resonances shifting to lower frequency, consistent with a lower zero-point vibrational frequency and a shortening of the average length of the bond holding the isotope which results in increased shielding of the metal nuclei. Comparison of the shift in the $^{195}Pt$ resonance brought about by replacement of $^{12}CN^-$ with $^{13}CN^-$ of a cyanide *trans* to cyanide in Pt(IV) and Pt(II) complexes shows that the shift is greater in $[PtCl(CN)_5]^{2-}$ (16.5 Hz) than in $[Pt(CN)_4]^{2-}$ (6 Hz). This probably results because of a lengthening of the Pt—CN bond on decreasing the oxidation state and hence isotopic substitution in Pt(IV) complexes produces a bigger perturbation than in Pt(II) complexes. Support for the above rationalisation comes from a study of the $^{195}Pt$ NMR of *trans*-$[Pt(H/D)X(PEt_3)_2]$ (X = Cl, CN), which will be reported in detail separately [33]. H/D substitution produces much larger shifts in the position of the $^{195}Pt$ resonance and the magnitude of these shifts depends on the nature of the *trans* ligand. Thus, cyanide, which has a strong *trans*-influence, produces a small isotope shift (187 Hz) whereas the low *trans*-influence group, $Cl^-$, produces a large isotope shift (265 Hz).

## Experimental

Carbon-13 and platinum-195 NMR spectra were recorded on a JEOL PS-100 Fourier transform spectrometer, using an internal deuterium lock.

Elemental analyses were carried out by Mr. G. Powell, The University of Kent Microanalytical Laboratory.

Cyanogen iodide was prepared as described previously [34].

### *Preparation of complexes*

Standard procedures were used to prepare $K_2[Pt(CN)_5I]$ [9] and $K_2[Pt(CN)_6]$ [10].

#### *Potassium tetracyanoplatinate(II), $K_2[Pt(CN)_4]$ (ca. 60% $^{13}CN^-$)*

An aqueous solution of potassium cyanide (4 mol) (ca. 60% $^{13}CN^-$) was added to a solution of potassium tetrachloroplatinate(II) (1 mol) in water. The resulting solution was warmed (ca. 40°C) until it became colourless. Concentration under vacuum, followed by cooling in ice/salt gave colourless crystals which were filtered off, recrystallised from water and dried in vacuum (0.01 mmHg at 25°C) for 3 h (yield 75%).

#### *Tetrabutylammonium tetracyanoplatinate(II), $(NBu_4)_2[Pt(CN)_4]$*

Addition of an aqueous solution of tetrabutylammonium hydroxide (5 ml of 40% w/v) to a solution of potassium tetracyanoplatinate(II) (1 g) in water (30 ml) gave an immediate colloidal precipitate. The solution was concentrated to ca. 10 ml whereupon some oil appeared. On cooling in ice and scratching the flask, the oil became a colourless crystalline solid which was filtered off and recrystallised from acetone/water (1 : 2, 30 ml). The resulting crystalline solid was obtained in 80% yield. The $^{13}C$-enriched complex was prepared similarly starting from $K_2[Pt(CN)_4]$ (ca. 60% $^{13}CN^-$).

#### *Potassium dihalotetracyanoplatinate(IV), $K_2[PtX_2(CN)_4]$ ($X$ = Br, Cl, I)*

A solution of halogen (1 mol) in carbon tetrachloride was added to an aqueous solution of $K_2[Pt(CN)_4]$ (1 mol). After shaking for 1 h, when X = Br, Cl, concentration gave the product which was recrystallised from water to give pale yellow and colourless crystals respectively. When X = I, it was necessary to shake the solution for 7 days to get a good yield of the dark brown product.

#### *Tetrabutylammonium dihalotetracyanoplatinate(IV), $(NBu_4)_2[PtX_2(CN)_4]$ ($X$ = Br, Cl, I)*

The two methods used to prepare the above complex gave products with identical spectroscopic properties.

*(a) From $K_2[PtX_2(CN)_4]$.* An acetone solution of $(NBu_4)ClO_4$ was added to a vigorously stirred aqueous solution of $K_2[PtX_2(CN)_4]$ whereupon an immediate precipitate was produced. This was filtered off, dried and recrystallised from (X = Br) acetone/petroleum ether (60/80) and (X = Cl, I) from acetone/water.

*(b) From $(NBu_4)_2[Pt(CN)_4]$.* A solution of halogen (1 mol) in carbon tetrachloride was added to a solution of $(NBu_4)_2[Pt(CN)_4]$ (1 mol) in chloroform. After shaking for 30 min, concentration produced either an oil or a solid which, in all cases (X = Br, Cl, I) was recrystallised from acetone/carbon tetrachloride.

*Potassium chloropentacyanoplatinate(IV),* $K_2[PtCl(CN)_5] \cdot 2\,H_2O$

Addition of an aqueous solution of potassium cyanide (6 mol) to an aqueous solution of $Na_2[PtCl_6]$ (1 mol) produced an immediate yellow colloidal precipitate which slowly dissolved on stirring at room temperature for 5—6 h to give a colourless solution. Concentration of this solution, followed by cooling in ice, gave a solid which was recrystallised from water to give colourless crystals of the product (yield 65%).

*Tetrabutyl pentacyanoiodoplatinate(IV),* $(NBu_4)_2[Pt(CN)_5I]$

This compound was prepared by addition of an acetone solution of $(NBu_4)I$ to an aqueous solution of $K_2[Pt(CN)_5I]$ [9]. The resulting yellow precipitate was filtered off, dried and recrystallised from acetone solution by the slow addition of water.

*Tetrabutyl hexacyanoplatinate(IV),* $(NBu_4)_2[Pt(CN)_6]$

Slow addition of an aqueous solution of $(NBu_4)Cl$ to a well stirred aqueous solution of $K_2[Pt(CN)_6]$ [10] gave a precipitate which was filtered off, dried and recrystallised from acetone to give colourless crystals of the product (yield 80%).

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