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The Chemistry of Some Group VIII Metals in Molten Cyanide. Part I. Ru, Os, Rh and Ir

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The chemistry of ruthenium, osmium, rhodium and iridium in (Na, K)CN eutectic has been investigated by diffuse reflectance and infrared measurements on the quenched melts. Ruthenium and osmium are present as $Ru(CN)_6^{4-}$ *and* $Os(CN)_6^{4-}$ *ions. Rhodium, when added as Rh(III), displays characteristic spectra of Rh(III), Rh(I) and possibly a Rh(O) species. Only the latter two species are observed when Rh(I) is added to the melt or when the metal is anodically dissolved. Spectroscopic and NMR studies show that the low oxidation state rhodium compounds are oxidised to* $Rh(CN)_6^{3-}$ *through the formation of the intermediates* $RhH(CN)_5^{3-}$ *and* $RhH(CN)_4H_2O^{2-}$*. Low oxidation state iridium species in quenched melts are less stable than rhodium compounds, but otherwise follow the behaviour of rhodium closely.*

Introduction

Previous work on the extraction of platinum group metals from molten cyanide solutions into liquid metals [1], showed that further investigation on the nature of the species in the salt phase is essential for the formulation of extraction mechanisms. In an attempt to facilitate the interpretation of electronic spectra of molten cyanide solutions at present in progress, a study of the chemistry of quenched melts was initiated. The chemistry of ruthenium, osmium, rhodium and iridium in quenched cyanide melts is discussed in Part I of the series. Part II deals with nickel, palladium and platinum.

The formation of novel transition metal complexes in molten potassium cyanide has already been investigated [2, 3]. Von Winbush *et al.* reported the preparation, in molten cyanide, of Ni(O) and Ni(I) cyanide complexes, while Magnuson *et al.* reported the preparation of low oxidation state manganese and molybdenum complexes, as well as a novel palladium(II) cyanide polymer.

Low oxidation state cyanide complexes of the transition elements have also been prepared in liquid ammonia [4]. However, the reduction of rhodium and iridium cyanide complexes in this medium has not been thoroughly investigated.

A rhodium complex of formula $K_3Rh(CN)_4$ was prepared [5], and its characteristic electronic and infrared spectra were given. A further rhodium complex of formula $K_8Rh_2(CN)_8$ has been postulated [6], but no spectra have been given.

Experimental

The (Na, K) CN eutectic was purified according to a method described by Lessing [7]. All the samples were prepared in titanium crucibles and under anaerobic conditions within a High Integrity glove box. The oxygen and water content of the argon was maintained below 20 ppm by circulating the argon through molecular sieves and a manganese oxide column.

Diffuse reflectance spectra were recorded at room temperature on a Unicam SP 1 800 Ultraviolet spectrophotometer equipped with an SP 890 Diffuse Reflectance Accessory. The sample holder was a modified 2.5 cm diameter metal syringe. Samples were pressed between the front end of the stainless steel syringe piston and a removable quartz disc, which was fitted to the bottom end of the syringe tube. The tightness of fit between the piston and syringe tube enabled spectra to be recorded under acceptable anaerobic conditions. Magnesium oxide was used as a reference medium.

The infrared measurements were recorded on a Perkin–Elmer 237 Grating spectrophotometer (wavelength range 4000–625 cm^{-1}), which was kept in an argon-filled glove box. The mull technique was used. Sodium-dried GLC quality n-hexadecane and sodium chloride, dried by evacuation at 200 °C, were used in preparing the mull.

Reactions in Liquid Ammonia

Reactions in liquid ammonia to establish molar reacting ratios of K to Rh were carried out in a glass titrating flask which was attached to an ammonia purification unit as described by Herzog [8]. One of two side-arms on the cylindrical titrating flask was attached to a nitrogen cylinder and the other was coupled either to the sodium reservoir or a mercury manometer. The top of the container was connected to a vacuum line through a wide-necked glass stopper. A known weight of $K_3Rh(CN)_6$, contained in a filtering tube and dried overnight at 150 °C under vacuum, was added to approximately 100 ml of liquid ammonia. The ammonia was dried over sodium and distilled into the titrating flask.

The solvent was stirred with a magnetic stirrer. Small cubes of potassium, well cleaned of their oxide layer, were weighed in sodium-dried hexane, and added to the rhodium-ammonia solution until the intense blue–green colour persisted. Spectroscopic pure N_2 was used to maintain an inert atmosphere above the ammonia surface when the samples of rhodium and potassium were added. The weight of potassium was so chosen that it was not necessary to make more than three additions for each titration. A solution containing no rhodium needed practically no potassium (< 5 mg) when the same titration procedure was followed. The accuracy of titration was further checked by titrating $K_2Pd(CN)_4$ under the same conditions with potassium. It has previously been shown [9] that Pd(II) reacts with two equivalents of potassium under these conditions. An average of six determinations yielded a value of 2.25 ± 0.09 equivalents K to one equivalent of Pd. Using the Liebig method, the rhodium content of the prepared $K_3Rh(CN)_6$ salt was determined by titrating the excess cyanide.

Electrochemical Methods

Specpure rhodium and iridium wire were anodically dissolved in the cyanide melt. The value of the oxidation state that the metal assumes as it dissolves in the melt, was calculated from the number of coulombs required to dissolve a known weight of metal.

Nuclear Magnetic Resonance

High-resolution nuclear magnetic measurements were made with a Varian Associates spectrometer at 60 MHz, and using 5 mm od. spinning tubes.

Preparation of Complexes

$K_3Rh(CN)_6$ was prepared by adding $RhCl_3 \cdot xH_2O$ to an aqueous-saturated KCN solution, in the molar ratio of $Rh{:}CN \leqslant 10$.

Anhydrous $RhCl_3$ and $IrCl_3$ were prepared by chlorinating the metal sponge at high temperature.

The complexes $[Rh(CO)_2Cl]_2$ [10], $K_2RhH(CN)_4H_2O$ [11], $Ir(PPh_3)_2COCl$ [12], and $K_3Rh(CN)_4$ [5] were all prepared according to known methods. The hydride complex of possible formula $K_3RhH(CN)_3$ [13] was prepared free of excess cyanide by washing the complex several times with AR methanol under anaerobic conditions, using a filtrating apparatus as described by Herzog [8]. It was further dried under vacuum and immediately transferred to the glove box, since it is extremely sensitive to air.

The infrared spectra of all complexes were recorded after isolation.

Results and Discussion

Ruthenium and Osmium

Diffuse reflectance and the infrared spectra were recorded on quenched cyanide melts in which ruthenium and osmium chloride complexes were dissolved (the metal concentration was varied within the molar ratio range 20–50 of Na/KCN to metal). The position of the strongest infrared bands as given in Table I observed for osmium and ruthenium agree favourably with those reported for the complexes $K_4Os(CN)_6$ and $K_4Ru(CN)_6$ [14]. The position of two of the electronic absorption bands (215 nm and 315 nm) observed in the spectrum of the ruthenium cyanide melt, and the position of the band at 225 nm for osmium, agree favourably with the energy of the bands reported for the complexes $Ru(CN)_6^{4-}$ and $Os(CN)_6^{4-}$ [15]. A further lower energy band at 390 nm, which was observed in the ruthenium spectrum, was not observed in the solution spectrum of $Ru(CN)_6^{4-}$ [15]. However, the presence of this band can be successfully interpreted in terms of the spin-forbidden transition $^3T_{1g} \longleftarrow {}^1A_{1g}$. A band at 250 nm for ruthenium and osmium was also observed in other metal-containing melts and can be ascribed to the presence of dicyanamide. It has been shown [16] that dicyanamide is found in cyanide solutions when metals in normal oxidation states are dissolved in molten cyanide through reactions of the type shown in equation (1). All such melts also have an absorption peak at 2180 cm^{-1} in the infrared region.

Rhodium

The diffuse reflectance spectrum recorded on the greenish–yellow quenched melt (orange when molten) when anhydrous $RhCl_3$ (rhodium concentration was varied within the molar ratio range 100–20 of Na/KCN to Rh) was added to the melt, is given in Figure 1. The sample was very sensitive to air and the spectrum rapidly changed when exposed to the atmosphere, as shown in Figure 1 (a–c). Infrared measurements showed similar behaviour, as shown in Figure 2. Both spectra showed the presence of $Rh(CN)_6^{3-}$ (bands at 2145 cm^{-1} and 220 nm) and possibly two other species (bands at 2055 cm^{-1}, 390 nm and 310 nm; 2028 cm^{-1}, 444 nm and 360 nm respectively), which are probably rhodium cyanide complexes of lower oxidation states. The infrared bands of the decomposition products (Figure 2 (b,c))

TABLE I. IR spectra (vs, very strong; s, strong; m, medium).

Compound	cm^{-1}	Medium	Compound	cm^{-1}	Medium
Alkali Cyanide	2085 s		$K_3RhH(CN)_5$	2110 vs 1950 m	Isolated + Quenched Melt
$Ru(CN)_6^{4-}$	2045 vs 2025 m	Quenched Melt	$K_2RhH(CN)_4H_2O$	2115 vs 1990 s	Isolated + Quenched Melt
$Os(CN)_6^{4-}$	2040 vs 2020 s	Quenched Melt	$Ir(CN)_4^{3-}$?	2045 vs	Quenched Melt
$Rh(CN)_6^{3-}$	2145 vs	Isolated + Quenched Melt	$Ir_2(CN)_8^{8-}$?	2015 s	Quenched Melt
$Ir(CN)_6^{3-}$	2140 vs	Quenched Melt			
$Rh(CN)_4^{3-}$	2055 vs	Isolated + Quenched Melt	$IrH(CN)_5^{3-}$	2110 vs 1950 m	Quenched Melt
$Rh_2(CN)_8^{8-}$?	2028 s	Quenched Melt			

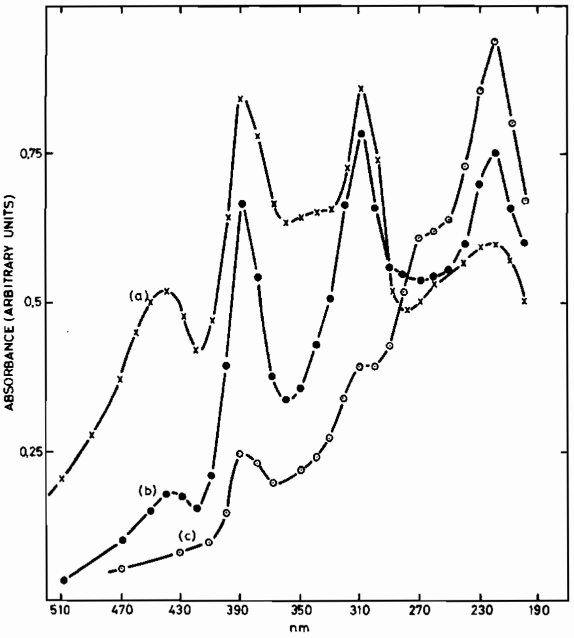

Fig. 1. Diffuse reflectance spectra of a quenched cyanide melt containing rhodium. (a) Spectrum of sample not exposed to atmosphere. (b) Spectrum of same sample as in (a) exposed to atmosphere for a few hours. (c) Spectrum of same sample as in (a) and (b) exposed to atmosphere for 24 hours.

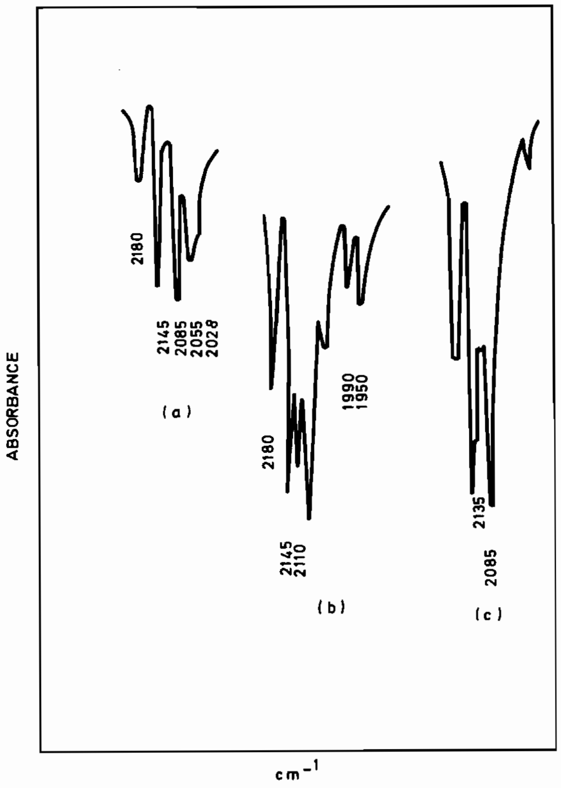

Fig. 2. Infrared spectra of a quenched cyanide melt containing rhodium (dissolved as $RhCl_3$). (a) Unexposed sample. (b) Same sample as in (a) exposed to atmosphere for a few minutes. (c) Same sample as in (a) exposed to atmosphere for 24 hours. Free cyanide absorbs at 2085 cm^{-1}. Band at 2180 cm^{-1}: decomposition product (see text under Ruthenium and Osmium).

will be discussed later. The presence of more than one oxidation state seems surprising at first, as molten cyanide at 500 °C represents fairly drastic conditions. Similar results have, however, been found during experiments on the extraction of platinum metals from molten cyanide, and it has also been shown that the reaction product, cyanogen, which forms upon oxidation of cyanide, is stabilised in the melt as dicyanamide and can thus cause imcomplete reduction of Rh(III) [16]

$$Rh(III) + 3\,CN^- \longrightarrow Rh(<III) + C_2N_3^- + C \qquad (1)$$

where $C_2N_3^-$ represents dicyanamide.

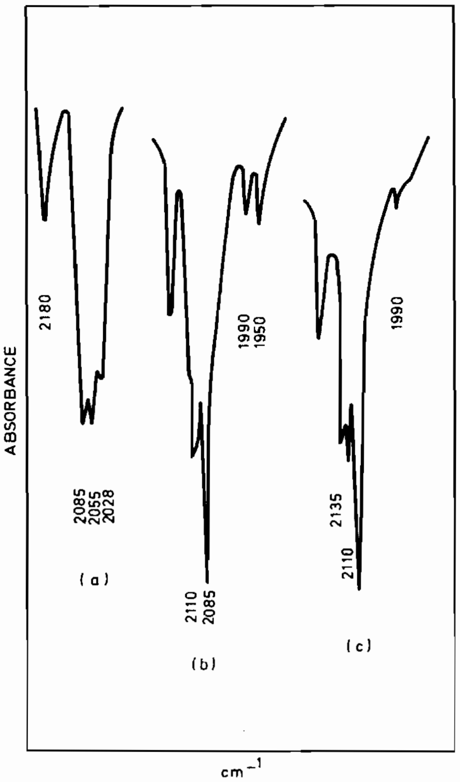

Fig. 3. Infrared spectra of a quenched cyanide melt containing rhodium (dissolved as $[Rh(CO)_2Cl]_2$). (a) IR spectrum of sample unexposed to atmosphere. (b) IR spectrum of same sample as in (a) exposed to atmosphere for a few minutes. (c) IR spectrum of sample as in (a) exposed to atmosphere for a few hours.

Solutions without any Rh(III) present, should therefore preferably be prepared from low oxidation state rhodium salts. The infrared spectrum shown in Figure 3 was obtained from a cyanide melt to which $[Rh(CO)_2Cl]_2$ (molar ratio of Na/KCN to Rh of 50) was added. No Rh(III) can be observed. Upon exposure to the atmosphere, the same spectral changes as in Figure 2 (a–c) were observed.

Solutions free of Rh(III) were also prepared by the anodic dissolution (current density 1.0–4.4 mA/cm^2) of rhodium wire in the melt. It was concluded from several experiments that rhodium dissolves as Rh(I) (within 2% error from the theoretical value calculated from the number of coulombs passed). The infrared and diffuse reflectance spectra were similar to those observed for melts in which $[Rh(CO)_2Cl]_2$ was dissolved.

From equation (1) and the following equilibrium suggested by Lessing [16]

$$\mathrm{Rh}(<\mathrm{III}) + C_2N_3^- \rightleftharpoons \mathrm{Rh}(\mathrm{III}) + CN_2^{2-} \qquad (2)$$

where CN_2^{2-} represents cyanamide it can be concluded that the addition of dicyanamide or cyanamide to rhodium containing cyanide melts, should result in a decrease or increase in the concentration of low oxidation state species respectively. This was indeed found to be the case since $RhCl_3$ containing melts (rhodium concentration was varied within the molar ratio range 20–50 of Na/KCN to Rh) to which up to 3% sodium cyanamide was added, showed increased intensities for the peaks at 444 nm and 360 nm. The effect of dicyanamide was even more pronounced, with the peaks at 444 nm and 360 nm falling sharply at 2% sodium dicyanamide concentration, and the peaks at 390 nm and 310 nm almost disappearing at 4% sodium dicyanamide concentration.

The two absorption bands at 390 nm and 310 nm can be compared to the bands characteristic of the complex $K_3Rh(CN)_4$ [5], except that the energy difference between the bands is larger in the melt. However, the infrared band at 2055 cm^{-1} measured for the complex $K_3Rh(CN)_4$ (Halpern [5] reported a value of 2065 cm^{-1} for the complex $[Cr(en)_3][Rh(CN)_4]$) has similar energy as one of the infrared bands observed in the rhodium - containing melt as shown in Figure 2. A similar effect on the positions of the absorption bands, with no difference in the infrared band, were observed on evaporated solutions of $K_3Rh(CN)_4$ containing an excess of cyanide (see Figure 4). Such an effect would be observed if the complex assumes a tetragonal distorted structure in a large excess cyanide medium, compared to the D_{4h} symmetry of the isolated $K_3Rh(CN)_4$ complex.

Two intense bands at 365 nm ($\epsilon = 5 \times 10^3$) and 325 nm ($\epsilon = \pm 9 \times 10^3$) along with a weak shoulder at ±340 nm were observed in the solution spectrum of $K_3Rh(CN)_4$, but a further weaker band at ±435 nm was observed in the spectrum of solid $K_3Rh(CN)_4$. The absorption bands can be assigned as metal-to-ligand charge transfer transitions, and can successfully be interpreted in terms of the molecular orbital energy level scheme for square-planar d^8 cyanide complexes, proposed by Piepho [17], when spin-orbit coupling is included. The bands at ±435 nm and 365 nm can be assigned as $a_{1g}\ (Z^2) \longrightarrow a_{2u}\pi^*$ transitions, $E_u3(^3A_{2u}) \longleftarrow {}^1A_{1g}$ and $A_{2u}^2\ (^1A_{2u}, {}^3E_u) \longleftarrow {}^1A_{1g}$ respectively. The lesser intensity of the 435 nm band is consistent with the spin-forbidden character of the transition $E_u3 \longleftarrow {}^1A_{1g}$. The shoulder at 340 nm and the intense band at 325 nm can be assigned to the transitions $e_g \longrightarrow a_{2u}\pi^*$, $A_{2u}1\ (^1A_{2u}) \longleftarrow {}^1A_{1g}$ and $E_u1\ (^1E_u) \longleftarrow {}^1A_{1g}$ respectively.

A tetragonal distortion (along the z-axis of the D_{4h} symmetry will tend to decrease the energy of the $a_{1g}\ (Z^2) \longrightarrow a_{2u}\pi^*$ transition and increase the energy of the $e_g \longrightarrow a_{2u}\pi^*$ transition as was indeed found (see Fig. 4).

The other two intense visible bands (at 444 nm and 360 nm) are probably characteristic of a rhodium complex of an even lower oxidation state than (I).

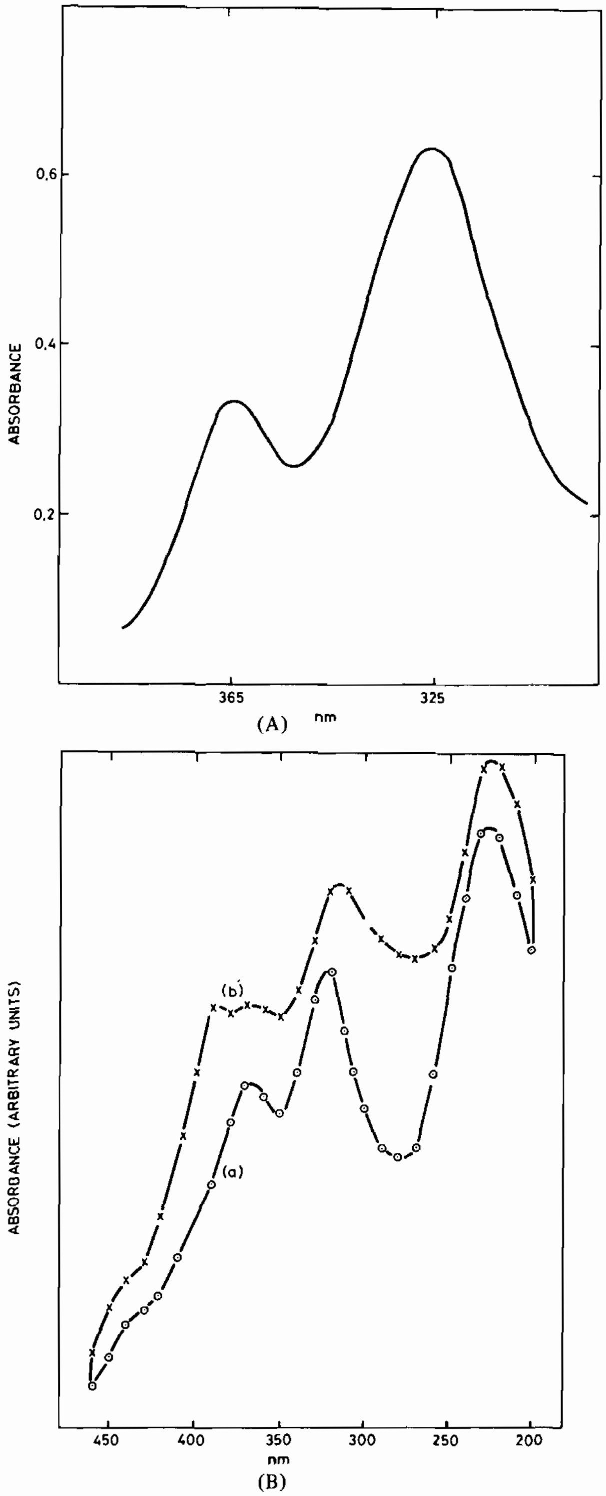

Fig. 4. Effect of excess cyanide on the position of the absorption bands of $Rh(CN)_4^{3-}$. A. Solution spectrum of $Rh(CN)_4^{3-}$ formed when $K_3RhH(CN)_5$ is added to a 3*M* KOH solution. B. (a) Diffuse reflectance spectrum of $K_3Rh(CN)_4$ free of excess cyanide. (b) Diffuse reflectance spectrum of $K_3Rh(CN)_4$ containing excess cyanide.

Such a species $K_8Rh_2(CN)_8$, comparable to $K_8Co_2(CN)_8$, had been suggested [6], although the reported infrared bands are similar to those of a sample containing $K_3Rh(CN)_4$ and $K_3Rh(CN)_6$. The existence of a Rh(O) cyanide complex is further supported by the molar reacting ratios of rhodium to potassium (1:3.29 ± 0.15), when $K_3Rh(CN)_6$ was titrated with K in liquid ammonia. As no Rh metal was formed during the titration, it was concluded that the reduction product is probably a Rh(O) cyanide complex. Unfortunately, due to its instability it was not possible to record the diffuse reflectance spectrum of the pure Rh(O) cyanide complex as prepared in liquid ammonia. Spectra obtained from the isolated species displayed the characteristic bands of $K_3Rh(CN)_4$.

Decomposition Products of the Rhodium Melt Hydrides

Infrared measurements on the quenched melt, which was left open to the atmosphere (see Figure 2 and 3), revealed that two intermediate compounds were formed. These compounds have bands at 2110 cm^{-1}, 1950 cm^{-1} and 2115 cm^{-1}, 1990 cm^{-1} respectively, which compares favourably with the spectra of $K_3RhH(CN)_5$ and $K_2RhH(CN)_4H_2O$ as

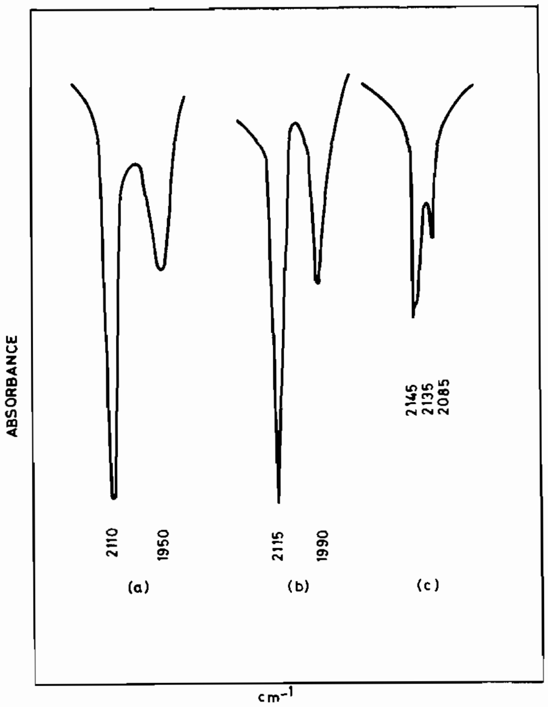

Fig. 5. (a) IR spectrum of $K_3RhH(CN)_5$. (b) IR spectrum of $K_2RhH(CN)_4H_2O$. (c) IR spectrum of a sample prepared by evaporating an aqueous solution of $K_3RhH(CN)_5$. KCN, in excess of the stoichiometric amount necessary to form $Rh(CN)_6^{3-}$, was dissolved in the aqueous solution of $K_3RhH(CN)_5$.

shown in Figure 5a and 5b respectively. The latter hydride was very stable and could even be separated from an aqueous solution to which the freshly prepared melt had been added. Further evidence for the formation of hydrides was the strong NMR signal (doublet) at –946 Hz relative to water, which was observed on freshly prepared aqueous solutions of the melts.

The intermediate formation of hydrides, along with their stability, could explain why a vigorous evolution of H_2 was not observed as expected when a low oxidation state cyanide complex is added to water [2].

Cyanide-deficient Coumpounds

When a freshly prepared melt was dissolved in water and heated on a hot plate, the solution assumed a light yellow colour. The evaporated salt was characterised by an infrared band at 2135 cm^{-1} and electronic absorption bands 370, 310 and 280 nm. Although the rhodium cyanide quenched melt which was left open overnight, assumed a white colour, an infrared band at 2135 cm^{-1} also formed as is shown in Figure 2 and 3. Similar bands were observed when $K_3RhH(CN)_5$, a white salt, was dissolved in water and evaporated to dryness (see Figure 5c). The possible formation of $K_3Rh(CN)_4$ from $K_3RhH(CN)_5$ [5] was ruled out since the characteristic band at 2055 cm^{-1} was absent. However, it is known that aqueous solutions of rhodium tetracyanohydride react with oxygen to form peroxycyanide complexes [11, 18] and tetracyanobisaquorhodate(III) [18]. Although the latter also has an infrared band at 2135 cm^{-1}, it is colourless. On the otherhand, it has been shown [19] that hydroxyl compounds, $K_3Co(CN)_4(OH)_2$ or $K_2Co(CN)_4(OH)$, are formed as intermediates in the preparation of $K_3Co(CN)_6$. Both hydroxyl compounds are characterised by intense colours; the former having two absorption bands at 310 nm and 380 nm. Although the available data is not sufficient for clarification, the possible formation of similar hydroxyl species for rhodium seems likely.

Iridium

The diffuse reflectance spectrum recorded on the quenched melt (reddish-brown colour) when an anhydrous $IrCl_3$ was dissolved in the cyanide melt (iridium concentration was varied within the molar ratio range 20–50 of Na/KCN to Ir) is shown in Figure 6. The spectrum observed when the Ir(I) compound, $Ir(PPh_3)_2COCl$, was dissolved in the melt, is shown in Figure 7. The quenched melt now assumed a purple colour. The infrared spectrum of the latter melt showed the absence of Ir(III), while the relative

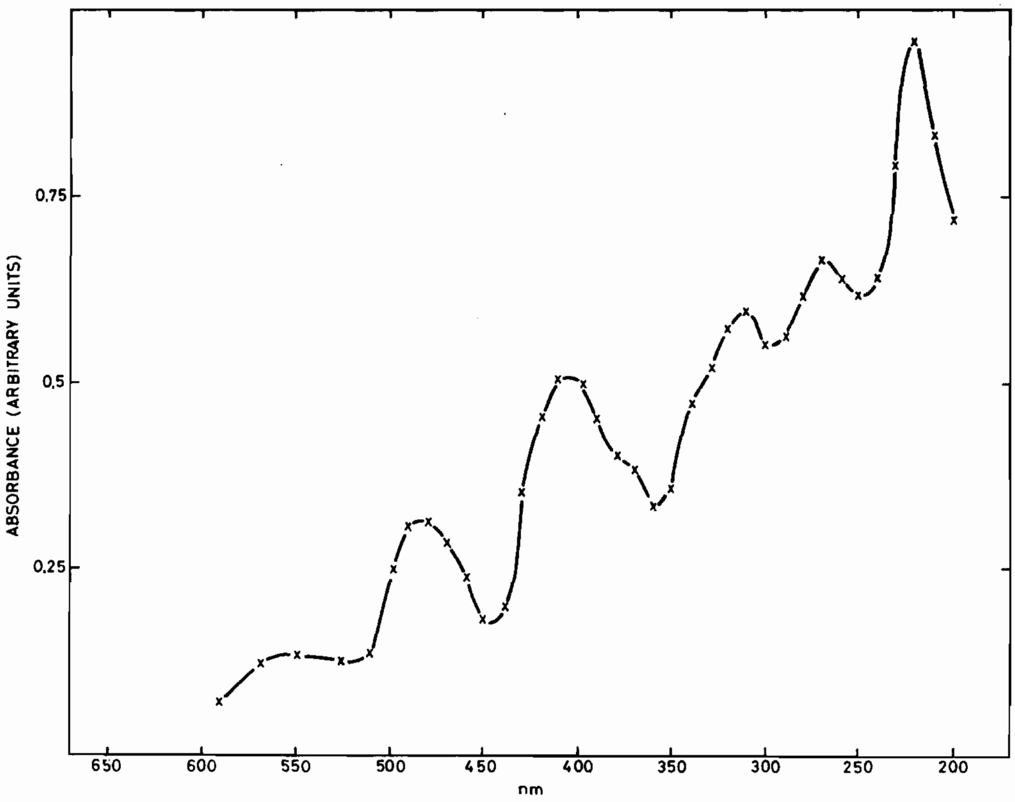

Fig. 6. The diffuse reflectance spectrum of a quenched cyanide melt containing iridium (dissolved as $IrCl_3$).

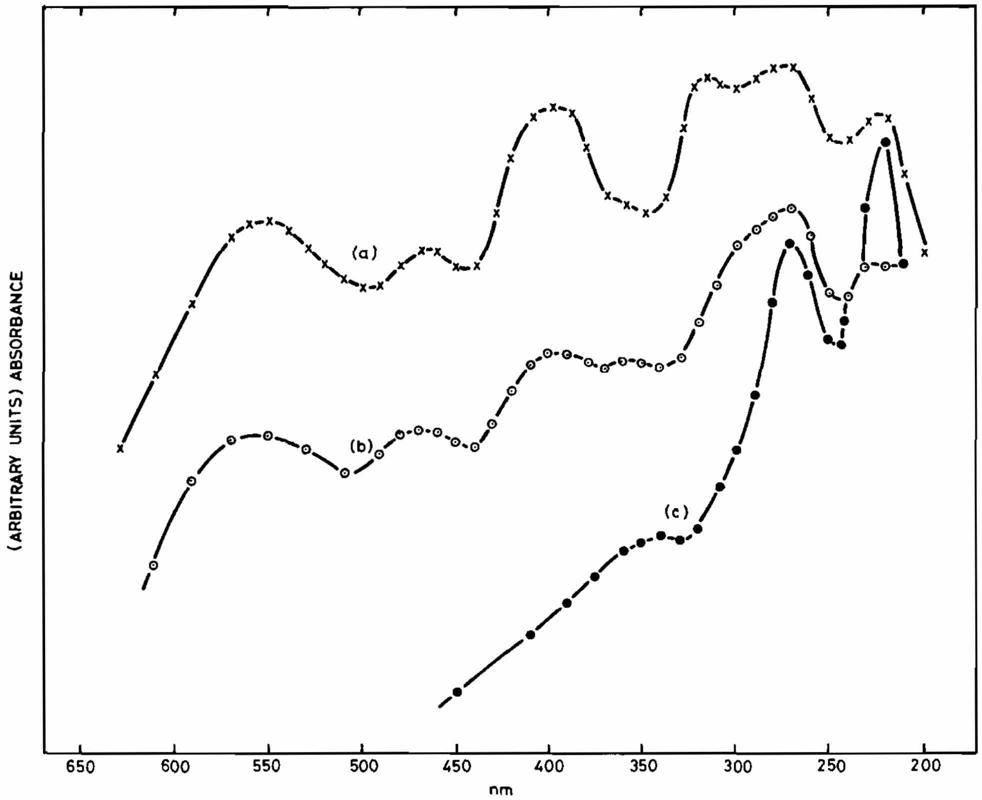

Fig. 7. The diffuse reflectance spectrum of a quenched cyanide melt containing iridium (dissolved as $Ir(PPh_3)_2COCl$). (a) Spectrum of sample not exposed to the atmosphere. (b) Spectrum of same sample as in (a) exposed to the atmosphere for a few minutes. (c) Spectrum of same sample as in (a) exposed to the atmosphere for approximately 1 hr.

intensities of the absorption bands are completely different from those shown in Figure 6. This effect became even more pronounced when 1% sodium cyanamide, with respect to cyanide, was added to the latter melt. Although the iridium complexes present in the melt were much more sensitive to the atmosphere than those of rhodium, a difference in the rate of decomposition of the low oxidation state complexes are again observable as is shown in Figure 7 (a–c).

The data confirmed, as found for rhodium, that two species of different oxidation states and probably of structure $Ir(CN)_4^{3-}$ (470, ±365, 340 and 270 nm, and 2045 cm^{-1}) and $Ir_2(CN)_8^{8-}$ (560, 400 and 315 nm, and 2015 cm^{-1}) have been formed in the melt (Figs. 6 and 7; Table I). A further absorption band in the region of 530 nm for the Ir(I) complex cannot be excluded, considering the broadening of the band at 560 nm, when the sample was exposed to the atmosphere. The strong absorption band at 220 nm which becomes prominent after exposure to the atmosphere is due to $Ir(CN)_6^{3-}$, which absorbs strongly at this wavelength. The larger number of bands observed for iridium, relative to those observed for rhodium, is consistent with the larger spin–orbit coupling of iridium. Although the intensity of the bands is unknown, the bands are probably also due to charge-transfer transitions of the metal-to-ligand type.

In direct contrast to rhodium, iridium anodically dissolved as Ir(I) at a current density of 1 mA/cm^2, but when the current density was increased, the tendency to dissolve as Ir(III) increased; so much so that it dissolved as Ir(III) within an error of 5%, at a current density of 5 mA/cm^2 in a cyanide melt, to which $Zn(CN)_2$ (10% by weight with respect to cyanide) had been added. The addition of $Zn(CN)_2$ is known to decrease the reduction potential of the cyanide melt [16]. The above measurements were confirmed by infrared and diffuse reflectance measurements which showed the absence of Ir(III) in the first case, but indicated that Ir(III) was formed exclusively in the latter.

Hydrides of Iridium

Infrared measurements on the quenched melt, which was exposed to the atmosphere, revealed that at least one intermediate compound had formed (IR bands at 2110 cm^{-1} and 1950 cm^{-1}), as the low oxidation state iridium compounds decomposed to $Ir(CN)_6^{3-}$. Furthermore, a freshly prepared aqueous solution of the iridium cyanide melt showed an

NMR signal (singlet) at −1142 Hz relative to water. Krogman *et al.* [20] also prepared a hydride complex, but the infrared bands (2110 cm^{-1} and 2043 cm^{-1}) differ from those found in this work.

Acknowledgement

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