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The Chemistry of Some Group VIII Metals in Molten Cyanide.
Part II. Ni, Pd and Pt

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The chemistry of nickel, palladium and platinum in quenched (Na, K)CN eutectic melts has been investigated by diffuse-reflectance and infrared measurements. Nickel, when added as Ni(II), displays the characteristic spectra of Ni(II), and Ni(0) cyanide species. Only the latter species is formed when Ni(I) is added to the melt. A Ni(I) complex, $Ni_2(CN)_6^{4-}$ is formed when Ni(II) and Ni powder is added to the melt. Palladium, when added as Pd(II), displays the characteristic spectra of Pd(II) and Pd(I) cyanide compounds. A Pd(0) cyanide complex formed when sodium cyanamide (reducing agent) is added to the latter melt. Three species, characterised as Pt(II), Pt(I) and Pt(0) cyanide complexes are formed when Pt(II) compounds are added to the melt. The concentration of the Pt(0) species is increased by adding sodium cyanamide to the melt, while the concentration of the Pt(I) species is increased upon the addition of sodium dicyanamide (oxidising agent). The preparation and identification of a palladium cyanohydride complex is also described.

Introduction

Part I of this series [1] discussed the chemistry of ruthenium, osmium, rhodium and iridium in quenched cyanide melts. This publication is a sequel to that work and deals with nickel, palladium and platinum.

Low-oxidation-state complexes of nickel have been described by Von Winbush *et al.* [2], who prepared Ni(0) and Ni(I) cyanide complexes in molten KCN. The dimer $K_4Ni_2(CN)_6$ was further prepared in aqueous medium by sodium amalgam reduction [3] and also by reduction with potassium in liquid ammonia [4]. Its structure was derived from infrared data [5] and X-ray powder studies [6]. The electronic absorption spectrum has also been reported [7, 8]. A monomeric complex of Ni(I), $K_3Ni(CN)_4$, has also been prepared [9]. The Ni(0) complex, $K_4Ni(CN)_4$, was prepared in liquid ammonia [4], and its infrared spectrum was given [10].

Magnuson *et al.* [11] investigated the behaviour of palladium in molten KCN, and concluded that palladium is present as a Pd(II) cyanide polymer. Manchot *et al.* [12] reported the formation of a Pd(I) cyanide complex during the reduction of an aqueous solution of $K_2Pd(CN)_4$. The reduction of $K_2Pd(CN)_4$ and $K_2Pt(CN)_4$ by potassium in liquid ammonia is well known [13]. More recently, Nast *et al.* identified the zero-oxidation-state compounds $K_2Pt(CN)_2$ [14] and $K_2Pd(CN)_2$ [15].

Experimental

The experimental procedures followed have already been described in Part I [1]. Infrared spectra of palladium and platinum compounds reported here were recorded on a Perkin Elmer model 467 infrared spectrophotometer (Table I).

TABLE I. Infrared Spectra.

Compound	cm^{-1}	Medium
Alkali Cyanide	2085 vs	
$Ni_2(CN)_6^{4-}$	2040 vs 2065 s 2125 w	NH_3-isolated and Quenched Melt
$Ni(CN)_4^{3-}$	2055 br, vs 2125 s	Isolated
$Ni(CN)_4^{2-}$	2130 vs (d)	Isolated and Quenched Melt
$Ni(CN)_4^{4-}$	1967 vs	Quenched Melt
$Pd(CN)_4^{2-}$	2140 vs	Isolated and Quenched Melt
Pd(I)CN	2130 s	Quenched Melt
Pd(0)CN	2022 w 2038 w	Quenched Melt
Pd-H/CN	2095 s 1980 br, m 1952 br, m	Isolated
Pd–CN Deficient	2158 sh, s 2170 sh, w	Quenched Melt and Cyanohydride
$Pt(CN)_4^{2-}$	2140 vs	Isolated and Quenched Melt
Pt(I)CN	2130 s	Quenched Melt
Pt(0)CN	2022 w 2042 w	Quenched Melt
Pt–CN Deficient	2158 sh, s 2174 sh, w	Quenched Melt

Preparation of Complexes

$K_2Ni(CN)_4$ [16], $K_2Pd(CN)_4$ [17], $K_2Pt(CN)_4$ [18], $K_4Ni_2(CN)_6$ [19] and PdNOCl [20] were prepared according to known methods.

$K_3Ni(CN)_4$ was prepared by hydrazine reduction [9]. The precipitate which formed after the addition of H_2-saturated AR Ethanol to the aqueous solution of $K_2Ni(CN)_4$ was filtered and vacuum-dried under anaerobic conditions in a filtrating apparatus as described by Herzog [21].

The palladium cyanohydride complexes were prepared by sodium amalgam reduction of a concentrated aqueous solution of $K_2Pd(CN)_4$. AR Ethanol saturated with H_2 was slowly added, with vigorous stirring, to the solution containing sodium amalgam. A steady flow of N_2 was passed over the solution during the addition of ethanol. A white precipitate formed immediately, and turned black within a few minutes due to the formation of palladium metal. In order to retard the decay process, the precipitate was decanted into a Schlenk tube. The Schlenk tube was then immediately attached to a filtrating apparatus (described by Herzog [21]), which had previously been evacuated and then filled with spectrographic-quality N_2. The precipitate was collected on a glass frit and vacuum-dried. The colour of the isolated product changed from white to light orange upon drying. The preparation of the samples for measuring the infrared and diffuse-reflectance spectra was conducted in a high-purity glove box [1]. The light-orange solid rapidly turned black when exposed to the atmosphere. When added to water, H_2 was vigorously evolved, and the sample decomposed to palladium metal.

Very seldom, apparently when the preparation was not conducted under favourable anaerobic conditions, a yellow palladium solid was isolated. This product did not exhibit the same infrared spectrum as the orange product, and did not turn black when exposed to the atmosphere. The yellow product was therefore not identified as a reduced species, and was discarded.

Results and Discussion

Nickel

The diffuse-reflectance and infrared spectra recorded on the slightly coloured, quenched melt when anhydrous $NiCl_2$, $Ni(CN)_2$ or $K_2Ni(CN)_4$ (nickel concentration was varied within the molar ratio range 100–20, of (Na,K)CN to Ni) was added to the cyanide melt, are given in Figure 1(a) and Figure 2(a). The sample was very sensitive to air. Upon exposure to the atmosphere, the infrared band at 1967 cm^{-1} decreased in intensity with a simultaneous increase in intensity of the $Ni(CN)_4^{2-}$ band at 2130 cm^{-1}. Similarly, the intensity of the band at 270 nm, and of that at 220 nm, decreased overnight with a simultaneous increase in intensity of the $Ni(CN)_4^{2-}$ absorption bands at 310 nm, 280 nm and 260 nm; two bands characteristic of the Ni(I) cyanide complex (see later), also appeared as prominent shoulders at 470 nm and 340 nm. These spectral results are in agreement with the observations of Von Winbush *et al.* [2], who showed that both $K_2Ni(CN)_4$ and $K_4Ni(CN)_4$ are present in a KCN melt to which an Ni(II) compound was added. The peak at 1967 cm^{-1}

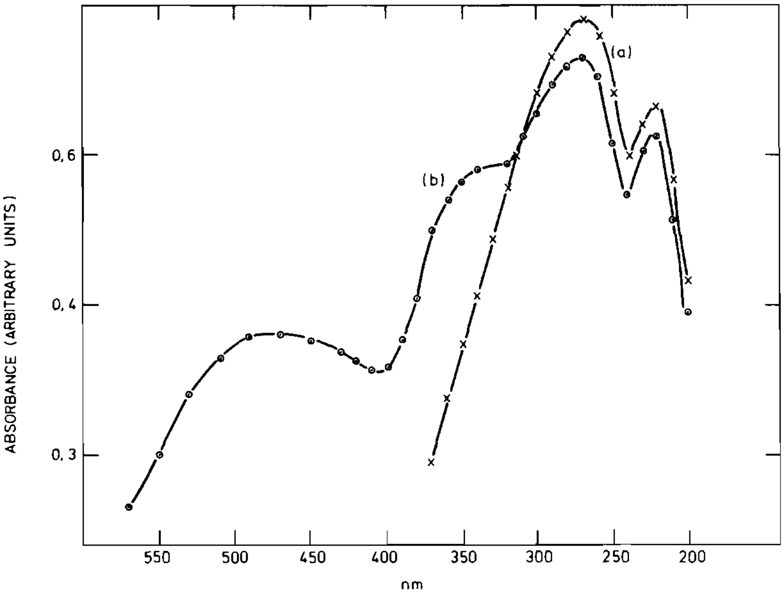

Figure 1. Diffuse-reflectance spectra of Ni-containing melts. (a) Dissolved as $NiCl_2$, (b) dissolved as $NiCl_2$ and Ni metal in a 1:1 molar ratio.

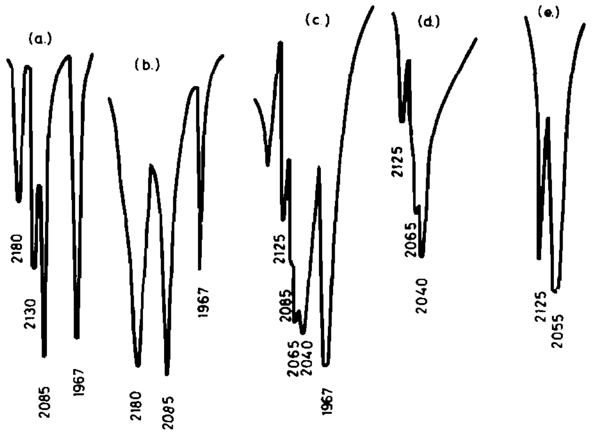

Figure 2. Infrared spectra of Ni-containing melts. (a) Dissolved as $NiCl_2$, (b) dissolved as $K_4Ni_2(CN)_6$, (c) dissolved as $NiCl_2$ and Ni metal in a 1:1 molar ratio, (d) & (e) infrared spectra of $K_4Ni_2(CN)_6$ and $K_3Ni(CN)_4$ respectively.

is thus probably due to $Ni(CN)_4^{4-}$ (El-Sayed *et al.* [10] reported a peak at 1985 cm^{-1} for $K_4Ni(CN)_4$), which is oxidised to $Ni(CN)_4^{2-}$ and an Ni(I) cyanide complex upon exposure to the atmosphere. The existence of species with different oxidation states of the same element in molten cyanide was also found for rhodium and iridium [1]. It is the result of incomplete reduction due to the limited reducing power of cyanide for high concentrations of metal salts (*cf.* eq(1) in ref. [1]), and implies that melts free of Ni(II) can be prepared from low-oxidation-state salts. This was indeed found to be the case, since the addition of $K_4Ni_2(CN)_6$ to a cyanide melt gave spectra in which the 2130 cm^{-1} band was absent (see Figure 2(b)). The same effect was observed when 3% sodium cyanamide by weight (with respect to cyanide; nickel concentration of 100:1 molar ratio of (Na,K)CN to Ni) was added to a melt prepared from $NiCl_2$. It was shown previously [1] that cyanamide promotes the formation of low-oxidation states.

A complex infrared band at 1985 cm^{-1} was always observed on quenched cyanide melts which contained 5%, or more, by weight of sodium cyanamide. The formation of this band limited the use of cyanamide in cyanide melts at concentrations higher than 5%.

The positions of the electronic absorption bands for $Ni(CN)_4^{4-}$ at 270 nm and 220 nm are similar to the spectrum reported for $Ni(CO)_4$ [22]. The bands can therefore also be categorised as being of the M→L charge-transfer type.

Von Winbush *et al.* [2] also prepared an Ni(I) complex in a potassium cyanide melt. From the results given in Figs. 1(b) and 2(c)–2(e) it appears, however, that Ni(I) is present as the dimer $Ni_2(CN)_6^{4-}$ and not as the monomer $Ni(CN)_4^{3-}$, as was concluded by these authors. Figs. 1(b) and 2(c) give the diffuse reflectance and infrared spectra of a quenched melt prepared by adding Ni powder and $Ni(CN)_4^{2-}$ to molten cyanide. The infrared spectra for $Ni_2(CN)_6^{4-}$ and $Ni(CN)_4^{3-}$ are given in Figs. 2(d) and 2(e) respectively. Comparison of the spectra shows that the species in the quenched melt (Fig. 2(c)) can be identified as $Ni_2(CN)_6^{4-}$. The additional bands in Fig. 2(c) are due to the presence of $Ni(CN)_4^{4-}$ (1976 cm^{-1}), alkali cyanide (2085 cm^{-1}), and a decomposition product of the melt (2180 cm^{-1}), which has been discussed previously [1]. The diffuse-reflectance

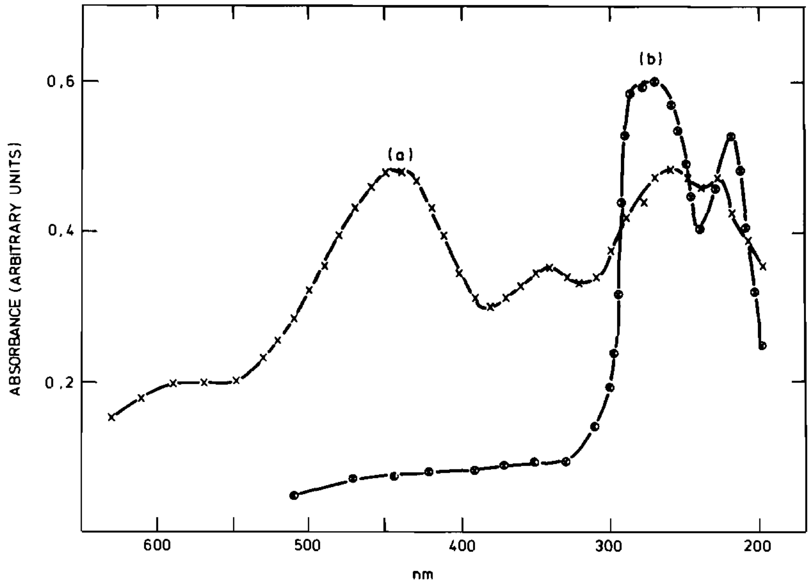

Figure 3. Diffuse-reflectance spectra of a Pd-containing melt, dissolved as $PdCl_2$. (a) Unexposed sample, (b) same sample as in (a) exposed to atmosphere overnight.

spectra of $Ni(CN)_4^{3-}$ and $Ni_2(CN)_6^{4-}$ are identical (absorption bands at 470, 340 and 310 nm), and are similar to that part of the quenched-melt spectrum which is not affected by the $Ni(CN)_4^{4-}$ bands (*i.e.* wavelengths lower than 300 nm).

Palladium

The diffuse-reflectance and infrared spectra recorded on the orange–yellow quenched melt when anhydrous $PdCl_2$ (palladium concentration was varied within the molar ratio range 100–20 of (Na,K)CN to Pd) was added to the melt, are given in Figs. 3(a) and 4(a) respectively. The same spectra were also obtained when palladium sponge and $PdCl_2$, in a molar ratio of one, were dissolved in the melt. It can be seen from Figs 3(a–b) that the bands at 580, 444 and 340 nm disappear when the quenched melt is exposed to the atmosphere. This is accompanied by the disappearance of an infrared band at 2130 cm^{-1}, and the formation of peaks at 260, 220 and 280 nm in the diffuse-reflectance spectrum, and an increase in the intensity of the peak at 2140 cm^{-1}, as well as the appearance of a peak at 2158 and at 2170 cm^{-1}. The addition of a freshly-prepared quenched melt to water resulted in the formation of palladium metal and the evolution of H_2 (the amount of H_2 which was evolved could not be correlated with the ratio of reduced to unreduced palladium species, but was visibly less than the H_2 evolved when a nickel-containing melt was added to water. This was not surprising since palladium, which formed as a decay product, has a large affinity for hydrogen). Spectra recorded on the sample which was evaporated to dryness revealed the absence of the bands at 280 nm and 2158 cm^{-1}, and 2170 cm^{-1}. As in the case of nickel, rhodium and iridium, the formation of a reduced species in the melt, characterised by the IR band at 2130 cm^{-1} and UV–Vis bands at 580, 444 and 340 nm, as well as $Pd(CN)_4^{2-}$ (bands at 260 and 220 nm, and 2140 cm^{-1}), seems very likely. The formation of the species with bands at 280 nm and 2158, 2170 cm^{-1} during the decomposition of the reduced species will be dealt with later. The similarity between the position of the UV–Vis absorption bands (444 and 340 nm) of the orange–yellow compound and those of Ni(I) (470 and 340 nm) suggests that it can be identified as a Pd(I) cyanide complex. The observation of a single IR band at 2130 cm^{-1} does differ from that of Ni(I) (2040, 2065 and 2125 cm^{-1}), but the concealment of additional peaks by the very intense alkali cyanide peak is likely.

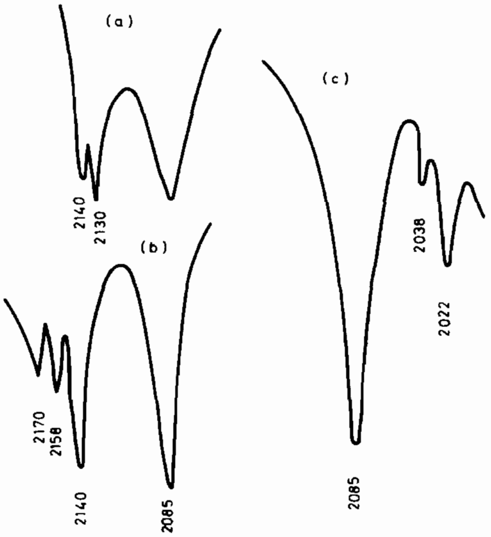

Figure 4. Infrared spectra of a quenched melt containing palladium, dissolved as $PdCl_2$. (a) Unexposed sample, (b) same sample as in (a) exposed to atmosphere overnight, (c) sodium cyanamide (5%).

This is not in support of the findings of Magnuson *et al.* [11] who concluded that palladium is present as Pd(II) in molten KCN. An infrared absorption band at 2180 cm^{-1} was assigned [11] to a Pd(II) cyanide polymer. This peak has since been identified as a decomposition product of cyanide [1], and is present in all melts containing group VIII elements.

Fig. 5(a) shows the diffuse-reflectance spectrum obtained when 5% sodium cyanamide was added to a palladium-containing melt (molar ratio eutectic to palladium = 100). The spectrum of the colourless quenched melt differs completely from that observed in the absence of cyanamide (Fig. 3(a)). The bands at 580, 444 and 340 nm, as well as the infrared bands at 2130 and 2140 cm^{-1}, disappear (Fig. 4(c)), and new bands at 250 and 225 nm (infrared bands at 2022 and 2038 cm^{-1}) appear. The two infrared bands at 2022 and 2038 cm^{-1}, together with a weak band at 2130 cm^{-1}, were also observed for a sample of a melt to which the zero-oxidation-state compound, PdNOCl, was added. The colourless quenched mėlt was even more sensitive to air than the orange–yellow melt (Fig. 3(a)) and, as shown in Fig. 5(a–b), the bands at 444 and 340 nm reappeared within a few minutes, followed by the spectral changes shown in Figs. 3(a–b) and Figs. 4(a–b). This result indicates that the addition of the reducing agent, sodium cyanamide, may lead to the formation of another low-oxidation-state species of palladium, probably Pd(0).

The formation of Pd(0) cyanide compounds by potassium reduction in liquid ammonia had been described previously [15], and the infrared spectrum of $K_2Pd(CN)_2$ (band at 2055 cm^{-1} [15]) was given. Due to the instability of the reduced product in liquid ammonia, it was not possible to record the diffuse-reflectance spectrum.

The similarity in the diffuse-reflectance spectra, and general behaviour upon exposure to the atmosphere, between nickel and palladium in quenched melts suggest that, as in the case of nickel, $Pd(CN)_4^{4-}$ is also formed in the melt.

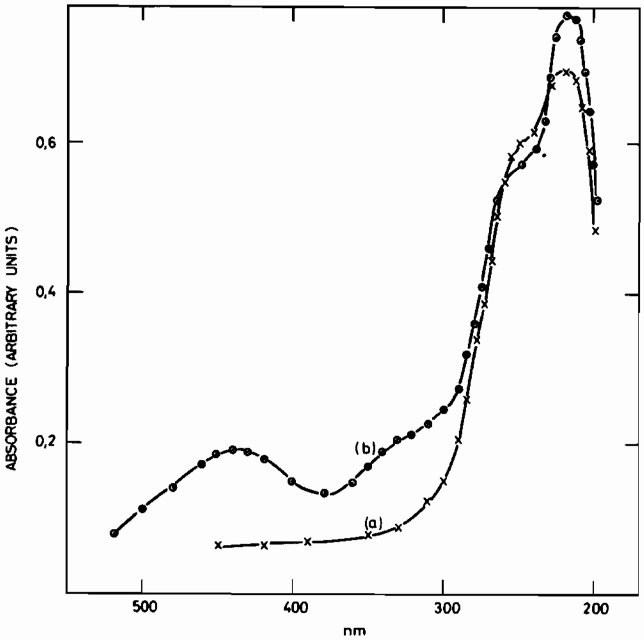

Figure 5. Diffuse-reflectance spectra of a quenched melt containing palladium, dissolved as $PdCl_2$, and sodium cyanamide (5%). (a) Unexposed sample, (b) same sample as in (a), exposed to atmosphere for a few minutes.

Palladium Cyanohydride Compound

Stable cyanohydride complexes of rhodium and iridium [1] formed as intermediates during the decomposition of reduced rhodium and iridium species to $Rh(CN)_6^{3-}$ and $Ir(CN)_6^{3-}$ respectively [1]. Although an analogous cyanohydride complex of palladium could not be identified, its formation as an intermediate during the decomposition of low-oxidation-state palladium complexes cannot be ruled out. The complex nature of the infrared spectra which were recorded on the quenched melts could conceal the infrared bands characteristic of such a compound. This possibility was further investigated through an attempt to synthesize palladium cyanohydride complexes in aqueous solution by sodium-amalgam reduction.

A species (see Experimental) with a UV band at 305 nm and infrared bands at 2095, 1980 and 1952 cm^{-1} (Fig. 6(a)), which could be identified as a cyanohydride complex of palladium, was isolated. This follows from NMR measurements on Na/Hg-reduced aqueous $K_2Pd(CN)_4$ solutions which showed a strong peak at −912 Hz relative to water. It was also observed that when the Na/Hg reduction was carried out in D_2O, the isolated solid did not absorb at 1980 and 1952 cm^{-1} (Fig. 6(b)). These two bands in the sample isolated from water can therefore be assigned to Pd–H stretching vibrations of a palladium cyanohydride complex. The position of the Pd–D stretching vibrations in the deuterated compound could not be established with certainty. The intense peak at 2095 cm^{-1}, which is not affected by deuteration can be assigned to the C–N stretching vibration of the palladium cyanohydride complex.

The palladium cyanohydride complex could never be isolated free of unreduced $K_2Pd(CN)_4$ and a further species with IR band at 2125 cm^{-1} (see Fig. 6(a)). The latter peak disappeared first, Fig. 6(c), followed by three peaks at 2095, 1980 and 1952 cm^{-1} and complete decomposition after 48 hours of exposure to the atmosphere, to $K_2Pd(CN)_4$ (Fig. 6(d)) and to palladium metal. Frequently the appearance of two IR bands (Fig. 6(e)) analogous to those observed for the quenched melt, were observed at 2158 and 2170 cm^{-1}. The diffuse-reflectance spectrum of the isolated orange-coloured solid revealed a band at 305 nm (probably associated with the cyanohydride complex), a band at 290 nm (probably associated with the IR bands at 2158 and 2170 cm^{-1}) and two bands at 475 and 340 nm (associated with the IR band at 2125 cm^{-1}). The similarity in the positions of the latter two UV–Vis bands and IR band 2125 cm^{-1} to those for the orange–yellow palladium-containing quenched melt, suggests that a Pd(I) cyanide complex was isolated together with the cyanohydride complex. The slight differences in the positions of the IR (2130 and 2125 cm^{-1}) and visible bands (444 and 475 nm) of the palladium complexes prepared from the melt and from aqueous media could be accounted for if some distortion of the complex, which was prepared in the aqueous medium, took place due to incomplete removal (by evacuation) of coordinate water molecules.

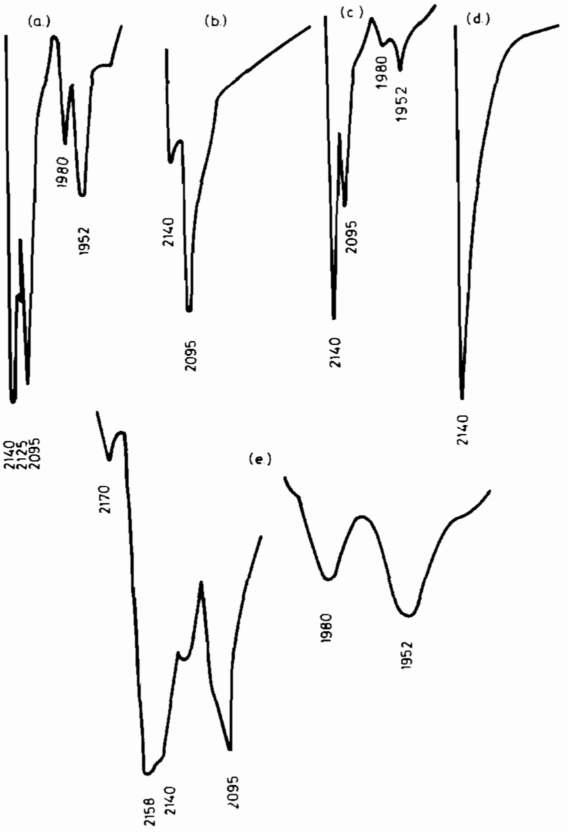

Figure 6. Infrared spectra of isolated cyanohydride compound. (a) Unexposed sample, (b) unexposed sample prepared from D_2O solution. (c) same sample as in (a) exposed to atmosphere for 1.5 h, (d) same sample as in (a) exposed to atmosphere for 48 h, or immediately added to water and evaporated to dryness, (e) same sample as in (a), kept in the mull form, exposed to the atmosphere for 1 h.

Palladium Cyanide Compounds Deficient in Cyanide

The species associated with the peaks at 2158 and 2170 cm^{-1} and UV band at 280 nm, which were observed during the decomposition of the palladium-containing quenched melts and Na/Hg-reduced samples, are possibly cyanide-deficient compounds (*i.e.* CN: Pd ratio less than four). The formation of such compounds is conceivable when dimeric $Pd_2(CN)_6^{4-}$ is oxidised in the absence of excess free cyanide, for example in samples isolated after Na/Hg reduction or when free cyanide is not readily available for coordination as in the case of quenched melts where it will become available only when the sample becomes very moist or upon dissolution. Similar behaviour was observed for rhodium [1], where the oxidation of $Rh(CN)_4^{3-}$ probably also leads to the formation of cyanide-deficient Rh(III) complexes under the same conditions.

Platinum

The diffuse-reflectance spectrum recorded on the yellow-coloured quenched melt, when anhydrous K_2PtCl_4 (platinum concentration was varied within the molar ratio range 100–20 of (Na,K)CN to Pt) was added to the melt, is given in Fig. 7(a). The corresponding infrared spectrum, shown in Fig. 8(a), was more complex than those observed for nickel and palladium; bands were observed at 2140, 2130, 2085 cm^{-1}, and also two bands of weak intensity at 2042 and 2022 cm^{-1}. The same spectra were also obtained when platinum sponge and K_2PtCl_4, in a molar ratio of one, were dissolved in the melt. Upon exposing the quenched melt to the atmosphere, the complex band observed in the visible region (Fig. 7(a)) is resolved into three bands ~410, ~380 and 340 nm, while the shoulder at 310 nm appeared as a peak (Fig. 7(b)). This is accompanied by the disappearance of the infrared bands at 2042 and 2022 cm^{-1}. Similar spectral changes [Fig. 7(a) to Fig. 9(a) and Fig. 8(a) to Fig. 8(c)] were also observed when 3% sodium dicyanamide (oxidising agent) was added to the platinum-containing melt. On the otherhand, the addition of 3% sodium cyanamide to the platinum-containing melt leads to a decrease in intensity of the broad complex band in the visible region (Fig. 9(b); only a shoulder remaining at 350 nm, while the infrared bands at 2022 and 2042 cm^{-1} increased in intensity (Fig. 8(d)). When the sample containing cyanamide was exposed to the atmosphere, the complex band in the visible region reappeared and was resolved as shown in Fig. 7(b) while the infrared bands at 2042 and 2022 cm^{-1} disappeared. Furthermore, when any of the abovementioned platinum-

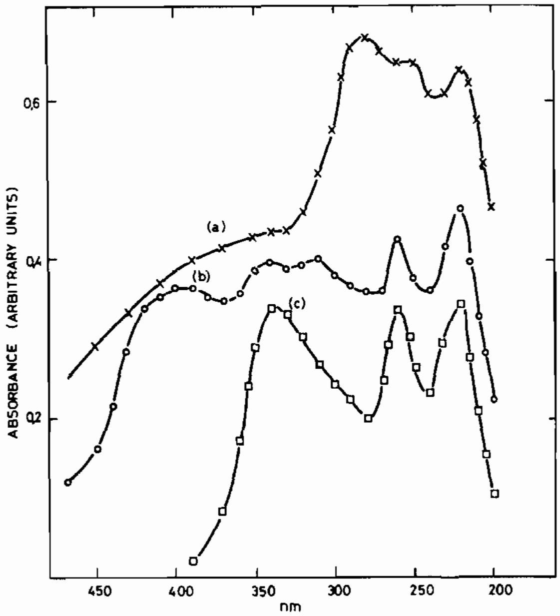

Figure 7. Diffuse-reflectance spectra of a Pt-containing melt, dissolved as K_2PtCl_4. (a) Unexposed sample, (b) same sample as in (a) exposed to atmosphere for a few hours, (c) same sample as in (a) exposed to the atmosphere overnight.

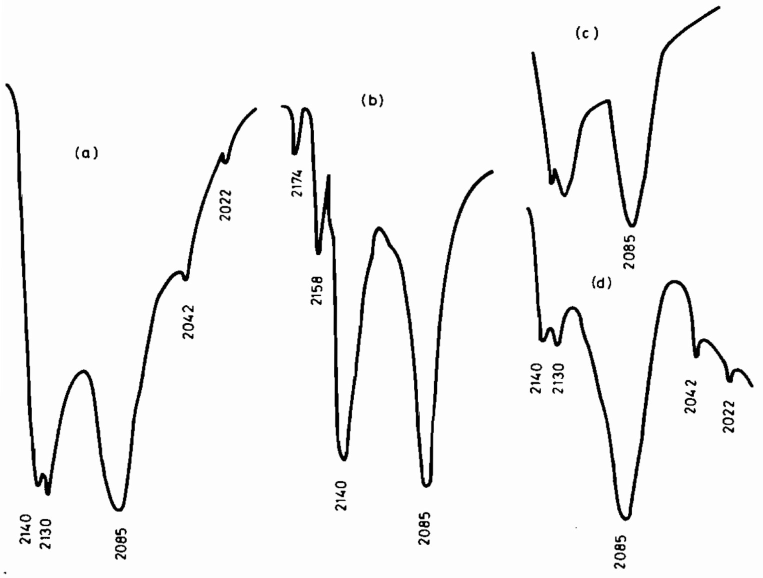

Figure 8. Infrared spectra of quenched melt containing platinum, dissolved as K_2PtCl_4. (a) Unexposed sample, (b) same sample as in (a) exposed to the atmosphere overnight, (c) sodium dicyanamide (3%), (d) sodium cyanamide (3%).

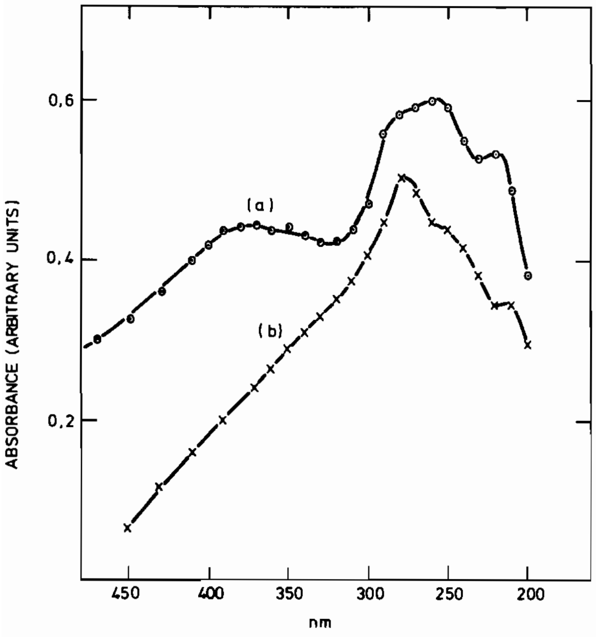

Figure 9. Diffuse-reflectance spectra of quenched melts containing platinum, dissolved as K_2PtCl_4. (a) Sodium dicyanamide (3%), (b) sodium cyanamide (3%).

containing melts were exposed overnight to the atmosphere, a very intense band (Fig. 7(c) at 345 nm with accompanying IR bands 2158 and 2174 cm^{-1} (Fig. 8(b)) appeared. It also led to an increase in the intensity of the characteristic bands of $Pt(CN)_4^{2-}$ at 260 and 220 nm, and at 2140 cm^{-1} in the infrared region.

As in the case of palladium, the addition of a solid sample of a freshly-prepared quenched melt containing platinum liberates H_2, while free platinum metal is formed.

The similarity in the chemistry of platinum- and palladium-containing cyanide melts suggests that platinum closely follows the behaviour of palladium. That is, a Pt(I) cyanide complex which is yellow-coloured (characterised by the bands at ~410 and ~380, 340 (?) and 310 nm, and 2130 cm^{-1}), and a colourless Pt(0) cyanide complex (characteristic bands at 280, 350 (?), 2022 and 2042 cm^{-1}) can form in a cyanide melt.

As in the case of palladium, the formation of a platinum cyanohydride in aqueous solution when a concentrated solution of $K_2Pt(CN)_4$ was reduced with sodium amalgam, was confirmed by a strong NMR signal at −809 Hz relative to water. No platinum cyanohydride compound could, however, be isolated.

The decomposition species (bands at 345 nm, and 2158 and 2174 cm^{-1}) observed when the quenched melts were exposed overnight can thus probably also be ascribed to cyanide-deficient compounds, as was found in the case of palladium.

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