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MOLTEN $LiNO_2$–$NaNO_2$, $LiNO_2$–KNO_2, $LiNO_2$–$CsNO_2$, AND $NaNO_2$–KNO_2 EUTECTICS: THE REACTION OF $PdCl_2$, K_2PdCl_4, $K_2Pd(NO_2)_4$, $PtCl_2$, K_2PtCl_4, $K_2Pt(NO_2)_4$, $PtCl_4$, AND K_2PtCl_6 *

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ABSTRACT

The reaction of eight compounds of Pd(II), Pt(II) and Pt(IV) with four molten nitrite eutectics were studied and their stoichiometries were deduced using thermogravimetric analysis. Their behaviour revealed an interesting class of oxidation–reduction reactions in which the nitrite melt acted as the reducting agent. Infrared spectra and high-temperature absorption spectra were used to identify the complex species formed in these melts. At low temperatures, Pd(II) and Pt(II) dissolved in the nitrite melts forming clear yellow solutions of nitro/nitrito species of Pd(II) and Pt(II), respectively. These solutions decomposed at higher temperatures, evolving nitrogen dioxide and leaving black residues of Pd and Pt metals. Pt(IV) formed an insoluble nitro/nitrito species that reacted in two stages, first to Pt(II) and eventually to Pt metal.

INTRODUCTION

The chemistry of transition metal compounds in molten nitrites has revealed interesting chemical behaviour. Published work, although mainly confined to the first row transition series, demonstrated a wide variety of reactions. These reactions included acid–base [1–4], oxidation–reduction [5–12] and variation of stereochemistry and coordination, namely with the formation of nitro and/or nitrito complexes [13]. In more recent studies,

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* This article is dedicated to the memory of Dr. Sabah S. Al Omer, who passed away after this work was completed.

† Deceased.

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ruthenium(II), rhodium(III) and iridium(III) were found to form insoluble hexanitro complexes [14] and lanthanum(III), cerium(III), praseodymium(III) and europium(III) showed varied behaviours in these melts [15].

In the present work, the reactions of palladium(II), platinum(II) and platinum(IV) in molten nitrites have been studied systematically. The results provide further illustration of oxidation–reduction as well as the formation of nitro/nitrito complexes in these melts. Four different nitrite eutectics have been used to study the cation effect on the stability of these complexes and whether different complex species can be stabilized in the lower melting nitrite eutectics. Another reason was the possibility that the metal complex may precipitate out from one of these melts, which would lead to its separation and characterization.

EXPERIMENTAL

Materials

Analar $NaNO_2$ (Hopkin and Williams) and pure KNO_2 (Riedel-de Haen) were dried at 150°C. Pure K_2PdCl_4, K_2PtCl_4 and K_2PtCl_6 (Fluka) were used as received. Reagent grade $PdCl_2$ (BDH) and pure $PtCl_2$ (Fluka) were dried under 10^{-1} Torr pressure at 150°C. $PtCl_4$ was prepared by heating $H_2PtCl_6 \cdot H_2O$ at 275°C under a stream of chlorine gas [16]. $K_2Pd(NO_2)_4$ and $K_2Pt(NO_2)_4$ were prepared by mixing an aqueous solution of K_2PdCl_4 or K_2PtCl_4, respectively, with a solution of KNO_2 [17,18] and the products were recrystallized from hot water and dried at 100°C. (Analysis: K, 21.5; Pd, 28.5; NO_2, 50.4%. Calculated for $K_2Pd(NO_2)_4$: K, 21.1; Pd, 28.8; NO_2, 50.5%. Analysis: K, 17.3; Pt, 42.1; NO_2, 40.3%. Calculated for $K_2Pt(NO_2)_4$: K, 17.1; Pt, 42.7; NO_2, 40.2%). $LiNO_2$ and $CsNO_2$ were prepared as reported previously [19] and dried under vacuum at 110°C. $LiNO_2$–$NaNO_2$, $LiNO_2$–KNO_2 and $NaNO_2$–KNO_2 eutectics were prepared as described previously [14]. $LiNO_2$–$CsNO_2$ was prepared by mixing the constituent salts in the eutectic ratio (40 mole% $LiNO_2$) [20] and the melt at 120°C was dehydrated by bubbling dry nitrogen, filtered through a G4 sinter, and again dehydrated under reduced pressure. The clear melts were quenched in liquid nitrogen, broken into small pieces and stored in a dry box.

Analysis

Gravimetric procedures were used for the determination of palladium with dimethylglyoxime [21] and lithium as lithium potassium iron(III) paraperiodate [22]. Spectrophotometric methods were adopted for the determination of platinum as platinum(II) dithiozonate [23], nitrite as a diazonium compound (formed by diazotation of sulfanilic acid) coupled with α-naphthylamine hydrochloride [24], and nitrate (after destroying excess nitrite with sulfamic acid) by nitration of phenoldisulfonic acid [25]. Sodium and potassium were estimated by flame photometry.

Method

Reactions were carried out, using 10 g portions of the melt, in a pyrex tube closed with a silica gel drying tube and fitted snugly into a Stanton Redcroft vertical tube furnace connected to a temperature control unit. Melt samples for analysis were drawn, solidified and dissolved in water. Gaseous products were collected, via a vacuum line connected to the reaction tube, in an infrared gas cell fitted with KBr windows, and were identified by their bands at 750, 1320 and 1610 cm^{-1} for NO_2, 1875 cm^{-1} for NO, 590, 1290 and 2220 cm^{-1} for N_2O [26]. Thermogravimetry, on 0.5 g melt samples in 5 ml vitroecil crucibles, was carried out under nitrogen atmosphere on a Stanton Redcroft MF-H5 massflow thermobalance, using a heating rate of 5°C min^{-1}; all reactants were ground to fine powder and mixed well in a dry box. Weight losses were corrected for nitrate formation from the reaction [3],

$$NO_2 + NO_2^- \rightarrow NO_3^- + NO \qquad (1)$$

Weight losses corrected in this way were within 2% from those calculated from the stoichiometry of the reactions postulated by this study. High temperature visible and ultraviolet spectra of thin films of the melt solutions on a silica plate were measured on a Pye-Unicam SP1800 double-beam spectrophotometer modified for use up to 450°C [27]. Infrared spectra were taken of powdered solid of the reacted melts pressed into thin discs with KBr, on a Perkin-Elmer 377 spectrometer over the range 4000–450 cm^{-1}. The X-ray powder lines were obtained with a Philips 1410 diffractometer using nickel filtered Cu$K\alpha$ radiation.

RESULTS AND DISCUSSION

The rapid decomposition of the nitrite melts at high temperatures (Fig. 1), evolving, as expected [28], NO_2, NO, and N_2O, limited their use as solvents to the following temperature ranges: $LiNO_2$–$NaNO_2$, 150–450°C; $LiNO_2$–KNO_2, 110–470°C; $LiNO_2$–$CsNO_2$, 105–430°C; $NaNO_2$–KNO_2, 220–550°C. (The lower limit is the melting point of the eutectic.) The upper limit which marks the decomposition temperature of these melts is a measure of their relative thermal stability. This limit showed a trend that is expected from the polarizing power of the cations present in the melt, except in the case of $LiNO_2$–$CsNO_2$. However, the assumption that the nearest

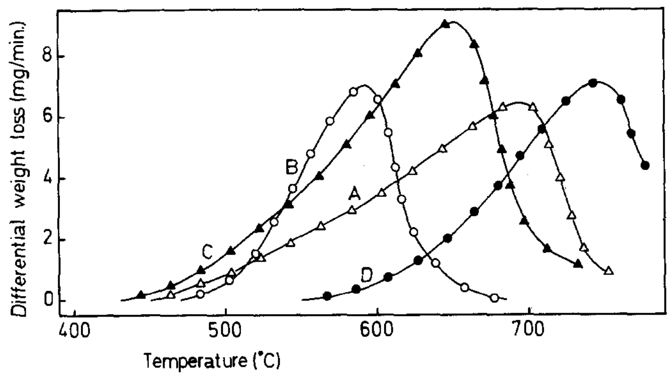

Fig. 1. Thermogravimetry of 1 mmol of nitrate eutectics. (A) $LiNO_2$-$NaNO_2$; (B) $LiNO_2$-KNO_2; (C) $LiNO_2$-$CsNO_2$; (D) $NaNO_2$-KNO_2.

sites of the nitrite ion are expected to be much more populated by the small lithium ions than by the much larger cesium ions, may explain the unexpected low thermal stability of the latter melt. The difference between the shape of the thermogravimetric curves (Fig. 1) or the observation that their peak position does not follow the same trend observed for the decomposition temperature, was attributed to kinetic factors.

The red crystals of $PdCl_2$ dissolved, with difficulty, in the $NaNO_2$-KNO_2 at 230°C and in the other three melts at 180°C, forming intense yellow solutions. At higher temperatures, the melt solutions reacted forming a black residue with the evolution of NO_2, NO and N_2O. Gravimetric determination of palladium in the residue showed it to be pure palladium. Comparison of its powder pattern with that reported in the ASTM for palladium metal, supported that finding. Thermogravimetry (Fig. 2, curves A–D) showed a single stage of weight loss commencing at different temperatures in different melts. The overall weight loss, after correction for the nitrate formation from reaction (1), corresponded to the loss of 2N + 4O per $PdCl_2$ in all four melts, according to the stoichiometry,

$$Pd^{2+} + 2NO_2^- \rightarrow Pd + 2NO_2 \qquad (2)$$

In all four nitrite melts, K_2PdCl_4 dissolved faster and was much more soluble than $PdCl_2$ at the same temperature, forming intense orange solutions. The relatively low solubility of $PdCl_2$ may be attributed to the packing of its molecules as planar Pd_6Cl_{12} units in its crystal [29,30]. Solutions of K_2PdCl_4, however, reacted in a similar manner to those of $PdCl_2$ (Fig. 2, curves E–G) and the corrected overall weight loss corresponded to the loss of 2N + 4O per K_2PdCl_4, according to eqn. (2).

$K_2Pd(NO_2)_4$ reacted with the nitrite melts (Fig. 2, curve H) in a similar fashion to $PdCl_2$ and K_2PdCl_4 and the corrected overall weight loss corresponded to the loss of 2N + 4O per $K_2Pd(NO_2)_4$, according to eqn. (2).

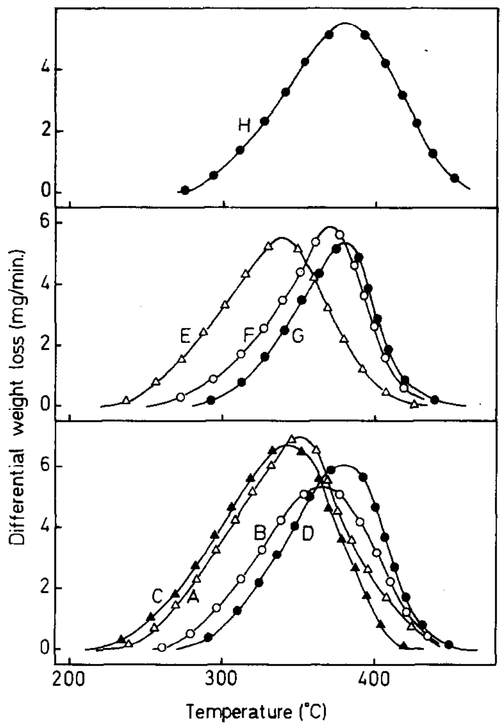

Fig. 2. Thermogravimetry of $PdCl_2$: (A) 0.18 *m* in $LiNO_2$-$NaNO_2$; (B) 0.12 *m* in $LiNO_2$-KNO_2; (C) 0.18 *m* in $LiNO_2$-$CsNO_2$; (D) 0.15 *m* in $NaNO_2$-KNO_2. Thermogravimetry of K_2PdCl_4: (E) 0.18 *m* in $LiNO_2$-$NaNO_2$; (F) 0.21 *m* in $LiNO_2$-KNO_2; (G) 0.18 *m* in $NaNO_2$-KNO_2. Thermogravimetry of $K_2Pd(NO_2)_4$: (H) 0.13 *m* in $NaNO_2$-KNO_2.

The yellowish brown powder of $PtCl_2$ dissolved in all four nitrite eutectics, at temperatures just above their melting points, forming clear yellow solutions. At higher temperatures, the melt solutions reacted forming a greyish black residue with the evolution of NO_2, NO and N_2O. Spectrophotometric determination of platinum in the residue showed it to be pure platinum and its powder pattern corresponded to that reported in the ASTM for platinum metal. Thermogravimetry (Fig. 3, curves A–D) showed a single stage of weight loss commencing at different temperatures in different eutectics. The overall weight loss, when corrected for the nitrate formation, corresponded to the loss of 2N + 4O per $PtCl_2$ in all four melts, according to the stoichiometry,

$$Pt^{2+} + 2NO_2^- \rightarrow Pt + 2NO_2 \qquad (3)$$

Both K_2PtCl_4 and $K_2Pt(NO_2)_4$ dissolved in the nitrite melts yielding clear yellow solutions. Thermogravimetry (Fig. 3, curves E–J) showed a single stage of weight loss, except in $LiNO_2$-$NaNO_2$ where two stages were

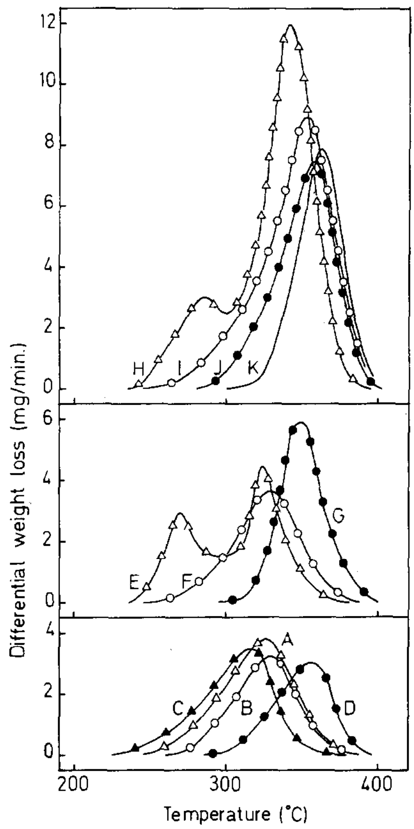

Fig. 3. Thermogravimetry of $PtCl_2$: (A) 0.15 *m* in $LiNO_2$–$NaNO_2$; (B) 0.13 *m* in $LiNO_2$–KNO_2; (C) 0.14 *m* in $LiNO_2$–$CsNO_2$; (D) 0.13 *m* in $NaNO_2$–KNO_2. Thermogravimetry of K_2PtCl_4: (E) 0.15 *m* in $LiNO_2$–$NaNO_2$; (F) 0.15 *m* in $LiNO_2$–KNO_2; (G) 0.13 *m* in $NaNO_2$–KNO_2. Thermogravimetry of $K_2Pt(NO_2)_4$: (H) 0.25 *m* in $LiNO_2$–$NaNO_2$; (I) 0.18 *m* in $LiNO_2$–KNO_2; (J) 0.18 *m* in $NaNO_2$–KNO_2; (K) alone.

observed. The corrected overall weight loss corresponded to the loss of 2N + 4O per K_2PtCl_4 and $K_2Pt(NO_2)_4$, according to eqn. (3). Although the two stages observed in the $LiNO_2$–$NaNO_2$ melt were reproducible, attempts to separate them by using a lower heating rate (2° min^{-1}) resulted in a thermogravimetric curve that shows a single stage of weight loss similar to that of $PtCl_2$ in the same melt. These two stages were attributed to a lower solubility of K_2PtCl_4 and $K_2Pt(NO_2)_4$ in this melt than in the other melts. Thus, at a slower heating rate the complex was allowed to dissolve and react steadily in a single stage.

The brown $PtCl_4$ did not appear to react when added to molten $LiNO_2$–KNO_2 at 120°C. After an induction period of 10–15 min, however, a white precipitate started to form. Infrared spectra (Table 1) of the quenched, reacted $LiNO_2$–KNO_2 at 120°C and of the white solid separated

TABLE 1

Infrared spectra (cm^{-1}) of quenched melt solutions after reaction in molten $LiNO_2$–KNO_2 at 120°C

	Nitro				Nitrito		Ref.
	$\nu_a(NO_2)$	$\nu_s(NO_2)$	$\delta(ONO)$	$\rho_w(ONO)$	$\nu(N{=}O)$	$\nu(NO)$	
$K_4Ni(NO_2)_4(ONO)_2$	1347	1325		414	1387	1206	33
$PdCl_2$ in $LiNO_2$-KNO_2 at 120°C [a]	1385 vs 1440 s	1350 s	822 vs		1470 sh 1490 sh	1185 s 1200 s	
$K_2Pd(NO_2)_4$	1380 vs 1402 1430	1340 vs	827 vs 834 vs	548 s 552 580 s 587			32
$PtCl_2$ in $LiNO_2$-KNO_2 at 120°C [a]	1370 vs 1380 vs 1430 s,sh	1345 vs	825 vs 850 sh		1500 s,sh	1190 s 1210 s	
$K_2Pt(NO_2)_4$	1385 vs 1412 1435	1340 vs	831 vs 834 840	613 617 s 638 s 646 w			32
$PtCl_4$ in $LiNO_2$-KNO_2 at 120°C [a]	1470 s	1340 s	822 s	627 m	1375 s	1190 s 1235 s	
$PtCl_4$ in $LiNO_2$-KNO_2 at 120°C [b]	1468 m 1490 s	1305 sh 1333 s	820 m 837 m	615 w		1245 vs,br	
$PtCl_4$ in $NaNO_2$-KNO_2 at 230°C [b]	1470 m 1490 s	1307 m 1333 s	820 m 838 m	615 w		1240 vs,br	
$K_2Pt(NO_2)_6$	1458 vs	1328 vs	834 vs	621 m			31

[a] Quenched melt.

[b] White precipitate from the aqueous solution of a quenched melt.

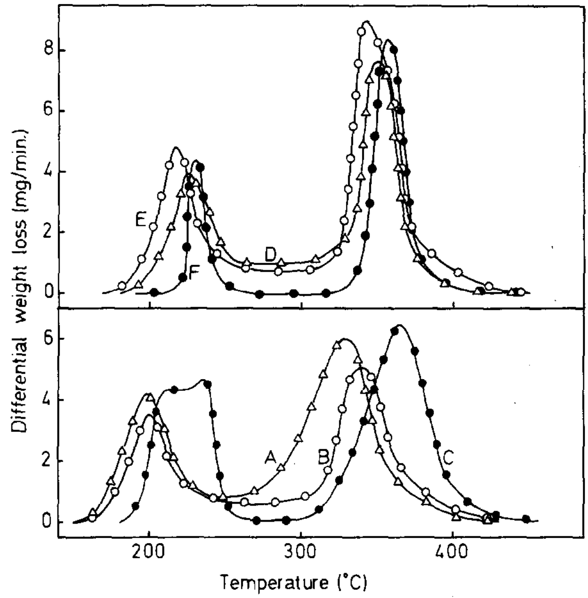

Fig. 4. Thermogravimetry of $PtCl_4$: (A) 0.16 *m* in $LiNO_2-NaNO_2$; (B) 0.14 *m* in $LiNO_2-KNO_2$; (C) 0.20 *m* in $NaNO_2-KNO_2$. Thermogravimetry of K_2PtCl_6: (D) 0.09 *m* in $LiNO_2-NaNO_2$; (E) 0.12 *m* in $LiNO_2-KNO_2$; (F) 0.11 *m* in $NaNO_2-KNO_2$.

from its aqueous solutions, however, were similar to that reported for $Pt(NO_2)_6^{4-}$ [31] plus an additional band assigned to the nitrito group. On prolonged heating at this temperature the white particles disappeared, with the evolution of more NO_2 and NO, leaving a clear yellow solution. The yellow melt solution reacted further at higher temperatures forming platinum metal and NO_2, NO and N_2O gases. Thermogravimetry of $PtCl_4$ (Fig. 4, curves A–C) showed two very well separated stages of weight loss in all three nitrite eutectic mixtures studied. The overall weight losses at the end of the first and the second stage, when corrected for nitrate formation, corresponded to the loss of 2N + 4O and 4N + 8O per $PtCl_4$, respectively, in agreement with the stoichiometry,

$$Pt^{4+} + 2NO_2^- \rightarrow Pt^{2+} + NO_2 \qquad (4)$$

followed by eqn. (3). A small depression in the first stage of the $NaNO_2-KNO_2$ thermogravimetric curve (Fig. 4, curve C) occurred around the melting point of the eutectic and was, thus, attributed to a difference in the rate of reaction when the reaction mixture changed from the solid to the molten state.

Thermogravimetry of K_2PtCl_6 in three nitrite eutectics (Fig. 4, curves D–F) showed two very well separated stages of weight loss, similar to those of $PtCl_4$. The overall weight losses at the end of these two stages, when corrected for nitrate formation, corresponded to the loss of 2N + 4O and

4N + 8O per K_2PtCl_6, respectively, also in agreement with stoichiometry (4) followed by (3).

The similarity between the thermogravimetric curves of Pd(II) compounds and also between those of Pt(II) compounds indicates the presence of the same Pd(II) and Pt(II) complex species, respectively, in these melt solutions. Thus attempts were made to characterize these species by studying infrared spectra (Table 1) of solids from melt solutions of $PdCl_2$ and $PtCl_2$ in $LiNO_2$–KNO_2 at 120°C and their high temperature electronic absorption spectra (Table 2) measured at 120°C.

Infrared spectra of Pd(II) and Pt(II) solutions were similar to those reported for $Pd(NO_2)_4^{2-}$ and $Pt(NO_2)_4^{2-}$ [32], respectively, plus additional bands which were compared to those of, and thus similarly assigned to, the nitrito ligand in $Ni(NO_2)_4(ONO)_2^{4-}$ [33]. However, complications in the spectra of those solutions due to solvent bands prevented any further information, regarding the number of nitro and nitrito ligands, to be drawn from these spectra.

Visible and ultraviolet spectra of $PdCl_2$ and $PtCl_2$ solutions in molten $LiNO_2$–KNO_2 at 120°C (Table 2) showed three intense charge transfer bands compared to those obtained for $K_2Pd(NO_2)_4$ and $K_2Pt(NO_2)_4$ in water, respectively.

In order to have some idea about the nature of the nitro/nitrito species present, the tetragonally distorted octahedral configuration that has been adopted for the Pd(II) and Pt(II) chloro complexes in the chloride melts [34,35] was accepted as the basis for further treatment. None of the three spin allowed *d-d* bands that are anticipated for a d^8 tetragonally distorted octahedral or square-planar configuration were observed. The lowest energy of the three bands is due to the transition $^1A_{1g} \rightarrow {}^1A_{2g}$. This transition is expected to exhibit no or only slight change when moving the two trans ligands along the z-axis ligands [34,35] and, thus, its energy should remain constant for any extent of tetragonal distortion to square planar. The frequency of this transition was calculated for all the possible nitro/nitrito species as follows, and the results of these calculations for the Pd(II) complex are shown in Table 3. First, this transition frequency for the Pd(II) nitro complex was calculated [36] as 1.02–1.10 times that (39000 cm^{-1}) of

TABLE 2

Visible and ultraviolet spectra (cm^{-1}) of solutions in molten $LiNO_2$–KNO_2 at 120°C

$PdCl_2$ in melt	28100 (s)	35100 (s)	42900 (vs)
$K_2Pd(NO_2)_4$ [a]	25700 ($\epsilon = 2000$)	36760 ($\epsilon = 4800$)	47620 ($\epsilon = 1.7 \times 10^4$)
$PtCl_2$ in melt	28750 (s)	35100 (s)	41000 (vs)
$K_2Pt(NO_2)_4$ [a]	30770 (sh, $\epsilon = 750$)	35460 (sh, $\epsilon = 1450$)	51815 ($\epsilon = 7 \times 10^4$)

[a] Aqueous solution of the complex.

TABLE 3

Calculated frequencies (cm^{-1}) of the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition for various hypothetical nitro/nitrito complexes of Pd(II)

$Pd(NO_2)_6^{4-}$	39780–42900
$Pd(NO_2)_5(ONO)^{4-}$	37679–40279
$Pd(NO_2)_4(ONO)_2^{4-}$	35578–37658
$Pd(NO_2)_3(ONO)_3^{4-}$	33477–35037
$Pd(NO_2)_2(ONO)_4^{4-}$	31378–32416
$Pd(NO_2)(ONO)_5^{4-}$	29275–29795
$Pd(ONO)_6^{4-}$	27174

the transition $^1A_{1g} \rightarrow {}^1T_{1g}$ in $[Rh(NO_2)_6]^{3-}$ [37]. Second, the transition frequency for the nitrito complex was taken to be approximately equal to that (27174 cm^{-1}) of the square-planar $[Pd(OH)_4]^{2-}$ complex [38]. Third, the frequency of this transition for all the possible nitro/nitrito species as calculated from the values obtained in the previous two steps using the rule of average environment [36],

$$\nu_{[M(NO_2)_n(ONO)_{(6-n)}]^{4-}} = \frac{n}{6}\nu_{[M(NO_2)_6]^{4-}} + \frac{n}{(6-n)}\nu_{[M(ONO)_6]^{4-}} \qquad (5)$$

where M is Pd or Pt.

The results of these calculations show that all the *d-d* bands were masked by the charge transfer bands. Therefore, the formation of any of the nitro/nitrito complexes cited is possible. Similar calculations for the Pt(II) species gave results that bear the same conclusion.

Finally, the presence of NO among the gaseous products of the reaction may be attributed to reaction (1), while N_2O may have been the product of slight decomposition of the melt itself [28] catalysed by the presence of the Pd and Pt metals produced by these reactions. The latter suggestion is supported by the absence of N_2O among the gaseous products of the first stage reaction of the Pt(IV) compounds which occurred at much lower temperatures and where no Pd or Pt metal was formed.

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