

greatly in their solvation characteristics. Depending on the local chemical environment of the redox partner, each reaction "prepares for" electron transfer in a different way, particularly as regards the extent of desolvation of  $O_2(H_2O)_n^-$ . Within a series of chemically similar oxidizing agents, however, consistency is obtained, but not when very diverse substances are considered. Thus the transition states may lie at quite different points along the reaction coordinate. To a first approximation an inverse correlation can be discerned between  $K_{eq}$  and the calculated value of  $k_{11}$ .

There are a number of other such pairs involving small molecules and their anions for which similar estimates of self-exchange rate constants have been made. These include  $ClO_2/ClO_2^-$  ( $4 \times 10^2 M^{-1} s^{-1}$ ),<sup>45</sup>  $NO_2/NO_2^-$  ( $10^{-2} M^{-1} s^{-1}$ ),<sup>46</sup> and  $I_2/I_2^-$  ( $\sim 10^2 M^{-1} s^{-1}$ ).<sup>47,48</sup> Each is derived from kinetic

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(46) Wilmarth, W. K.; Stanbury, D. M.; Byrd, J. E.; Po, H. N.; Chua, C.-P. *Coord. Chem. Rev.* **1983**, *51*, 155-179.

(47) Our estimate is based on published kinetic and equilibrium data for the reaction of  $Os(bpy)_3^{3+}$  with  $I_2^-$  (Nord, G.; Pederson, B.; Farver, O. *Inorg. Chem.* **1978**, *17*, 2233) and uses a self-exchange rate constant for the osmium complexes which is itself a Marcus-equation estimate made by the same group (Nord, G.; Pedersen, B.; Yan-Lovborg, E.; Pagsberg, P. *Ibid.* **1982**, *21*, 2327). Another estimate for  $I_2/I_2^-$  has not been included. It was based on reactions of  $Fe^{II}(edta)^{2-}$  (Woodruff, W. H.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2578), a reaction that is demonstrably inner sphere. Since  $IFe^{III}(edta)^{2-}$  and  $I^-$  are formed, or at best  $I_2^-$  within the coordination shell of the metal, and not free  $I_2^-$ , it seems to us unlikely that properties of the latter are calculable from these data.

data from only one or two reactions. It is *not* our contention that more inclusive data sets will *necessarily* lead to discrepancies like those for  $O_2/O_2^-$ . *On the other hand, it is important to anticipate that such might possibly be the case.* The situation clearly calls for the study of many additional systems of some diversity and for continued caution as to whether such parameters are clearly assignable to the authentic self-exchange reactions.

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**Registry No.**  $O_2^-$ , 11062-77-4;  $O_2$ , 7782-44-7;  $Fe(C_5H_5)_2^+$ , 12125-80-3;  $Co(NH_3)_6^{3+}$ , 14695-95-5;  $Co(en)_3^{3+}$ , 14878-41-2;  $Co(chxn)_3^{3+}$ , 41970-05-2.

(48) Values for  $Br_2/Br_2^-$  or  $Cl_2/Cl_2^-$  self-exchange are also discounted. That from  $Fe^{II}(edta)$  is not included for the reason stated above.<sup>47</sup> A second value was based on  $Fe(phen)_3^{2+}$  (Ige, J.; Ojo, J. F.; Oloboide, O. *Can. J. Chem.* **1979**, *57*, 2065), a reaction claimed to proceed by initial outer-sphere electron transfer:  $Fe(phen)_3^{2+} + X_2 = Fe(phen)_3^{3+} + X_2^-$ . The small equilibrium constant ( $\sim 10^{-11}$  for  $X = Br$ ) requires a very large reverse rate constant ( $\sim 10^{11} M^{-1} s^{-1}$ ), which not only may exceed the diffusion-controlled limit but also is likely to cause the subsequent reaction steps to influence the kinetic measurements, a point that was not included in analysis of the published kinetic data.

Contribution from the Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Barcelona, Spain

## Solid-State Kinetic Parameters for the Deaquation-Anation of the Tetracyanonickelate(II), Tetracyanopalladate(II), and Tetracyanoplatinate(II) of Aquopentaamminecobalt(III). Influence of the Metal-Metal Interactions on the Platinum Complex

JOAN RIBAS,\* MIQUEL SERRA, and ALBERT ESCUER

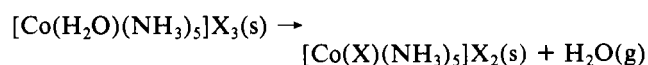
Received April 27, 1983

Three new dinuclear complexes of ( $\mu$ -cyano)(tricyanometal(II))pentaamminecobalt(III), metal(II) being nickel, palladium, and platinum, have been obtained by solid-state reaction of the tetracyanometalate(II) of aquopentaamminecobalt(III). This solid-state deaquation-anation has been studied by thermogravimetric measurements under both nonisothermal and isothermal conditions. The activation energies so obtained are  $117.4 \pm 6$  kJ/mol for the Ni compound,  $131.0 \pm 5$  kJ/mol for the Pd compound, and  $66.7 \pm 1$  kJ/mol for the Pt compound. These values are found on the basis of the agreement between nonisothermal and isothermal methods, by applying the expressions for the solid-state models (growth, nucleation, nucleation-growth, and diffusion). The marked difference in the kinetic parameters between the Ni and Pd compounds and the Pt compound may be explained in terms of Pt-Pt association in the crystal lattice, which causes distortions and allows water molecules to escape easily from the crystal structure. For this reason and because of the low values of activation energy, an  $S_N1$  dissociative mechanism is proposed with an activated complex of square-based-pyramidal geometry. The Pt-Pt interactions are shown in the electronic spectrum by the appearance of a very strong band at about 355 nm in the solid state, which does not belong to the parent compounds. The Pt-Pt interaction is also found in solution by the appearance of new bands at about 300 and 330 nm, which do not follow Beer's law. We attribute these new bands to the oligomeric association of the dinuclear cations. The conductivity measurements in the solid state for the Pt compound also indicate its special behavior, which may be explained in terms of Pt-Pt interactions that remove the Pt-Pt symmetrical packing typical of many cyano compounds of platinum(II).

### Introduction

In the literature there are a great number of papers on the kinetic parameters of aquoamine complexes of cobalt(III).<sup>1</sup>

Focusing our interest only on the kinetics of the deaquation-anation of the reaction



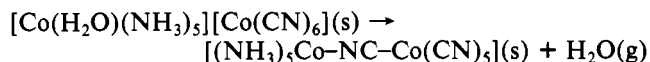
we find that there is a poor agreement in kinetic parameters reported in the literature, as has been indicated by LeMay.<sup>2</sup>

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In view of our interest in the solid-state deaquation-anation reactions of aquoamine complexes of chromium(III) with cyano compounds as entering ligands,<sup>3</sup> we consider it of interest to follow the research in this field with cobalt(III) analogues.

One of the reactions previously studied from a kinetic point of view is



This reaction is not well-defined because there is a second step after the loss of water with HCN loss,<sup>4,5</sup> overlapped with the first. The activation energy found by various authors is 239,<sup>6</sup> 143.8 ± 7,<sup>5</sup> and 232 ± 40 kJ/mol.<sup>7</sup> Taking into account the methods described by the respective authors, we think that the most accurate value is 143.8 ± 7 kJ/mol (House and Smith).<sup>5</sup> In effect, the first paper does not specify the conditions and does not indicate the resolution of the overlapping with the decomposition processes; the third paper describes only nonisothermal thermogravimetric studies. Instead, the isothermal method has been employed by House<sup>5</sup> to find the 143.8 ± 7 kJ/mol value. In our work on amine complexes of chromium(III) we have seen, according to the literature,<sup>8</sup> that is not possible to find either an accurate value for the activation energy or the possible mechanism from only the nonisothermal TG curves. The more accurate activation energy is best determined with a series of isothermal TG curves, which gives a value of  $E_a$  almost independent of the physical model proposed (nucleation, growth, diffusion, or intermediates). Furthermore, the isothermal experiments are much less sensitive to variation in particle size, compactness, etc.

This disagreement between the experimental results has created a great deal of confusion about the chemical mechanism of the process (dissociative or associative). LeMay<sup>2</sup> suggests, for instance, that previous assignments of an  $S_N2$  associative-type mechanism based on the variation of activation parameters are "unwarranted". According to this author and House,<sup>9</sup> an  $S_N1$  process is more consistent with the true activation energies. This  $S_N1$  process is explained in terms of Frenkel defect formation by elimination of water molecules. Consequently, the activation energies must be independent of the entering anion; however, according to the difference between the size of the cations and anions, the water molecules may be more or less able to slip into an interstitial position and to escape from the crystal.

In this paper we describe the results achieved with isothermal and nonisothermal experiments on the new complexes  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{M}(\text{CN})_4]_3$  (M = Ni, Pd, Pt); we propose a mechanism, and we explain the observed differences with the  $[\text{Pt}(\text{CN})_4]^{2-}$  anion in terms of strong Pt-Pt interactions in the lattice,<sup>10</sup> shown by UV spectra and conductivity measurements in the solid. This Pt-Pt interaction is also shown in solution.

## Experimental Section

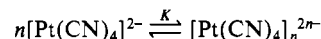
**Preparation of the New Compounds.** (a)  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{Ni}(\text{CN})_4]_3$ . One gram of potassium tetracyanonickelate(II) was dissolved in 4 mL of water, and the solution was passed through an Amberlite IR 20 cation exchanger in the ammonium form. This solution was added with constant stirring to an ice-cold solution formed by 1.2 g of  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5](\text{ClO}_4)_3$  in 10 mL of water. A pink-red precipitate was obtained by adding 2-propanol or by putting the solution in a freezing compartment. The product was filtered, washed with acetone and ether, and air-dried.

(b)  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{M}(\text{CN})_4]_3$  (M = Pd, Pt). We have used a similar method to obtain the Pd and Pt salts from  $\text{K}_2[\text{Pd}(\text{CN})_4]^{12}$  and  $\text{K}_2[\text{Pt}(\text{CN})_4]$  (Johnson Matthey), with the cation exchanger in the acid form. For Pt(II) a different behavior was observed when the precipitation was attempted. An orange-red precipitate is formed in an ice bath, but a deep yellow product, that becomes yellow-green in ether, was obtained by precipitation with 2-propanol. Solutions of all these products have the same light red color and the same electronic spectra (see Results and Discussion). The green salt is less soluble. The different behavior of the Pt compound in the solid state is discussed below.

(c)  $[(\text{NH}_3)_5\text{Co}-\text{NC}-\text{M}(\text{CN})_5]_2[\text{M}(\text{CN})_4]$  (M = Ni, Pd, Pt). Previous isothermal TG measurements indicated that the best conditions to obtain the dinuclear compounds were by heating in the solid state for 25–30 min at 110 °C for the Ni and Pd compounds and at 95 °C for the Pt compound. From these data, 0.3 g of the mixed salts was heated in an oven for 25 min. Under these conditions there was no sign of minimal decomposition. Anal. Calcd for the anhydrous Ni compound: C, 18.56; N, 39.70; H, 3.87; Co, 15.18; Ni, 22.70; water loss, 4.43%. Found: C, 18.4; N, 39.5; H, 3.8; Co, 15.2; Ni, 22.4; mass loss, 4.42%. Calcd for the Pd anhydrous compound: C, 15.67; N, 33.51; H, 3.26; Co, 12.82; water loss, 3.77%. Found: C, 15.6; N, 33.3; H, 3.3; Co, 12.9; mass loss, 3.75%. Calcd for the Pt anhydrous compound: C, 12.95; N, 25.99; Co, 9.94; H, 2.53; water loss, 2.95%. Found: C, 12.9; N, 25.7; Co, 9.7; H, 2.6; mass loss, 2.96%. Prolonged heating at temperatures over 120–130 °C causes decomposition of the product.

**Techniques.** Infrared spectra were recorded on a Beckman IR 20 A spectrophotometer purged with dry air. Samples were prepared by using the KBr technique. Electronic absorption spectra were recorded in solution and in the solid phase (KBr disk or diffuse reflectance) on a Beckman 5230 UV spectrophotometer. Thermogravimetric analyses were carried out on a Perkin-Elmer Model TGS-1 system, under nitrogen ( $10 \text{ cm}^3 \text{ min}^{-1}$ ), the sample size being in the range 4–7 mg. The heating rate for nonisothermal experiments was 5 °C/min. To resolve the nonisothermal TG curves we used the widely employed approximation of Coats and Redfern.<sup>13</sup> All the calculations were made with a Fortran IV program. Conductivity measurements on solid samples were determined on a Hewlett-Packard 3435 A Digital Multimeter, with the possibility of heating the sample.

**Molecular Association Constant.** If the long-wavelength feature is due to a single oligomer formed according to the equilibrium



then the association constant,  $K$ , was determined from the equation

$$CA^{-1/n} = n\epsilon^{-1}A^{(n-1)/n} + (K\epsilon)^{-1/n}$$

( $C$  = stoichiometric concentration of the dinuclear complex,  $A$  = measured absorbance at 300 nm,  $\epsilon$  = molar absorptivity of the oligomer complex at 300 nm, and  $K$  = association constant). The derivation of this equation is straightforward and assumes that 1-cm cells are used and that the absorption at 300 nm is due only to the oligomer. Plots of  $CA^{-1/n}$  vs.  $A^{(n-1)/n}$  were linear, the slope giving the value of  $\epsilon$  and the intercept the value of  $K$ .

## Results and Discussion

**IR Spectra.** The IR spectra of the three new mixed salts are very similar. The bands due to the  $[\text{CoH}_2\text{O}(\text{NH}_3)_5]^{3+}$

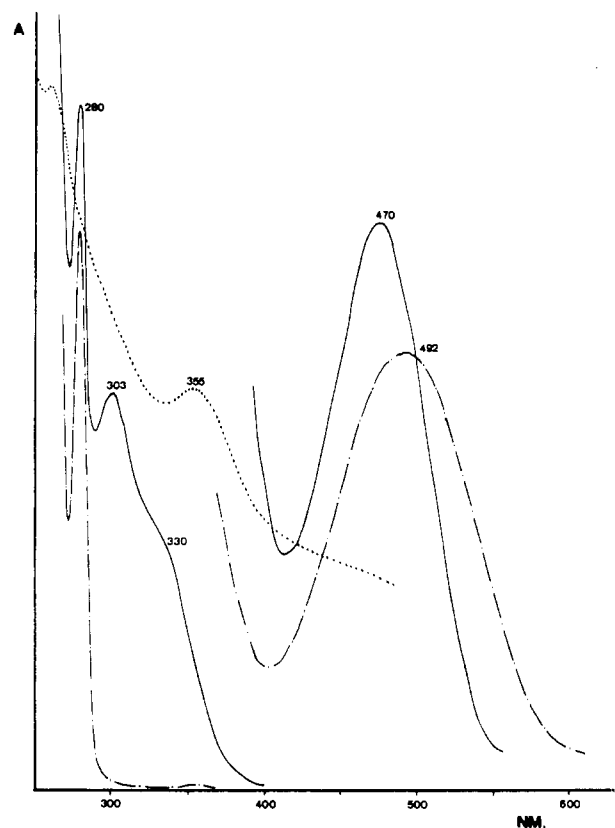
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- (13) Coats, A. W.; Redfern, J. P. *Nature (London)* **1964**, *201*, 68.

cation are identical with those described for the same cation with other anions.<sup>14</sup> The spectra of the cyanide part show a very strong band around 2130  $\text{cm}^{-1}$  (s), depending on the metal, with a marked fine structure: the Ni compound shows three bands at 2120 (sh), 2130 (vs), and 2155  $\text{cm}^{-1}$  (s); the Pd compound, bands at 2130 (sh), 2140 (vs), and 2160  $\text{cm}^{-1}$  (s); and the Pt compound, bands at 2130 (sh), 2140 (vs), and 2150  $\text{cm}^{-1}$  (s). These vibrations are due to the symmetric and asymmetric stretching  $\nu(\text{CN})$  and are in perfect agreement with those reported in the literature for the same  $[\text{M}(\text{CN})_4]^{2-}$  anion with simple cations.<sup>15</sup> Furthermore, we have observed in a series of analogous mixed salts of chromium(III) with these cyano complexes as anions<sup>3</sup> that the marked fine structure is good evidence of the nonexistence of water of crystallization in the lattice. This fact agrees with the analytical data and TG measurements.

When the cyano complex is coordinated in the deaqua-tion-anation reaction, a dinuclear compound with  $\mu$ -cyano ligand is formed. The IR spectra of these three new complexes show a significant difference with respect to the starting complexes, i.e. the presence of a very intense and perfectly defined doublet in the  $\nu(\text{CN})$  region: 2130 (vs) and 2200  $\text{cm}^{-1}$  (s) for the Ni compound, 2135 (vs) and 2200  $\text{cm}^{-1}$  (s) for the Pd compound, and 2135 (vs) and 2200  $\text{cm}^{-1}$  (s) for the Pt compound. The clear splitting of the CN stretching frequency is good evidence for a bridging cyano group.<sup>3,16</sup> According to the literature data, the component occurring at lower frequency may be assigned to  $\nu(\text{CN})$  of the terminal cyano group, while that appearing at high frequency (ca. 2200  $\text{cm}^{-1}$ ) may be attributed to  $\nu(\text{CN})$  of the bridging cyano group.<sup>3,16</sup> The bands attributable to the  $\nu(\text{M}-\text{C})$  vibrations at lower frequencies are not influenced by the coordination and are in agreement with the literature data.<sup>15</sup>

**Electronic Spectra.** There are two relevant aspects in the electronic spectra: the d-d shift of the first cobalt(III) transition and the Pt-Pt interaction. On the d-d shift, the mixed complex salts  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{M}(\text{CN})_4]_3$  (M = Ni, Pd, Pt) show in solution a first maximum at 492 nm ( $\epsilon = 47.1$ ) (Figure 1), in perfect agreement with the starting complex  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5](\text{ClO}_4)_3$ .<sup>17</sup> The second band at 345 nm ( $\epsilon = 43.0$ ), also typical of the  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{3+}$  cation, is not found in the Ni compound due to the very intense band at 310 nm, characteristic of  $[\text{Ni}(\text{CN})_4]^{2-}$ .<sup>15</sup> In the visible region, the three new dinuclear complexes (Figure 1) present a perfectly defined and symmetrical band centered at 470–472 nm (due to their great insolubility it was not possible to calculate the molar extinction with accuracy; however, the intensity is very similar to that of the parent aquoamminecobalt(III) cation). The shift of nearly 20 nm toward lower wavelengths has been observed in other dinuclear compounds with  $\mu$ -CN bridge derived from  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{3+}$ <sup>4,18</sup> and agrees with the position of  $-\text{NC}$  in relation to water in the spectrochemical series. The second d-d transition of cobalt(III) is observed only in the Pd compound: the intense 310-nm band of  $[\text{Ni}(\text{CN})_4]^{2-}$  completely obscures this second band in the Ni compound, and the Pt-Pt interactions (see below) also obscure this band in the Pt complex. In the Ni and Pd compounds the bands attributable to  $[\text{M}(\text{CN})_4]^{2-}$  are found in identical positions, which are described in the literature.<sup>15</sup> The Pt case is different due to the presence of the metal-metal interaction



**Figure 1.** Electronic spectra of  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{Pt}(\text{CN})_4]_3$  in solution (---) or in the solid state (---), showing the strong band at 355 nm (Pt-Pt interaction), and of  $[(\text{NH}_3)_5\text{Co}-\text{NC}-\text{Pt}(\text{CN})_3]_2[\text{Pt}(\text{CN})_4]$  in solution (—), showing the strong band at 330 and 303 nm due to Pt-Pt interactions (the solid-state spectrum is very similar).

in the solid state and solution.

The electronic spectrum of the  $[\text{Pt}(\text{CN})_4]^{2-}$  anion shows rather intense and diffuse bands with maxima at approximately 280, 258, 242, and 217 nm.<sup>15,19</sup> The new complex reported here shows these bands; moreover, due to Pt-Pt interaction, two new bands at high wavelengths occur in both the solid state and solution.

As indicated above, the solid  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{Pt}(\text{CN})_4]_3$  shows a different color (yellow to green-yellow) depending on the precipitation method. Independently of the color, the electronic spectra in KBr disk or diffuse reflectance show a very new intense band at 355 nm (Figure 1), which completely obscures the second d-d transition of cobalt(III) (at 345 nm) and masks the first d-d transition of cobalt(III) (at 492 nm). This mixed complex salt has a pink color in solution, characteristic of the aquopentaamminecobalt(III) cation. The electronic spectrum (Figure 1) shows a first maximum at 492 nm (see above) and a second maximum at 345 nm (not shown in Figure 1 in order to indicate only the more prominent features). The bands due to the  $[\text{Pt}(\text{CN})_4]^{2-}$  anion are identical with those reported in the literature (Figure 1 only indicates the very intense 280-nm band).

This difference between solid state and solution indicates that the Pt-Pt interaction is present only in the solid phase but it is destroyed in solution.

The dinuclear complex, on the other hand, shows the Pt-Pt interactions in both the solid state and solution. Besides the 470-nm band due to the  $[\text{Co}(\text{NH}_3)_5-\text{NC}-]$  group, two new very, intense bands at 330 (sh) and 303 nm (s) appear (Figure 1 gives only the spectrum in solution).

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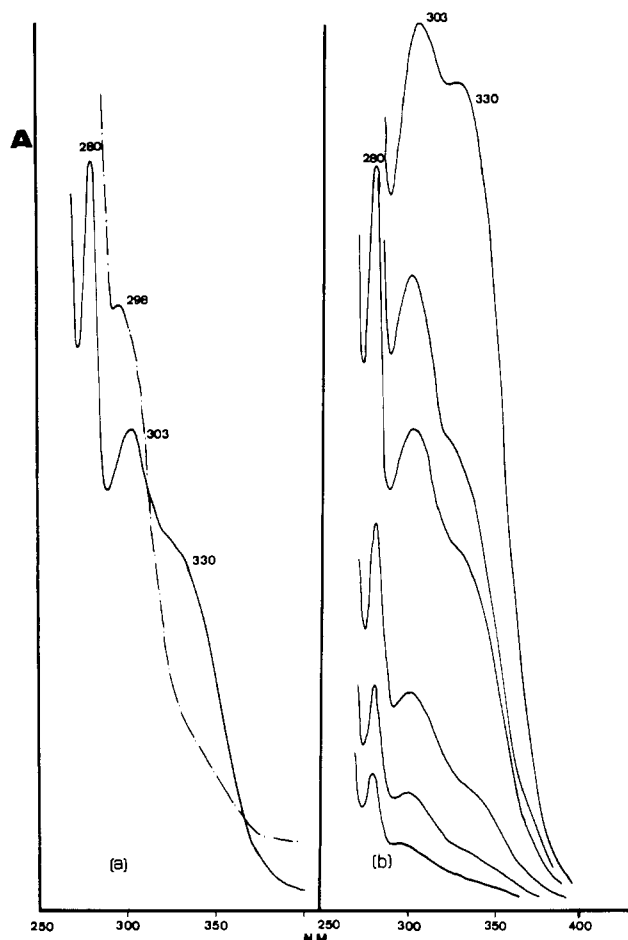
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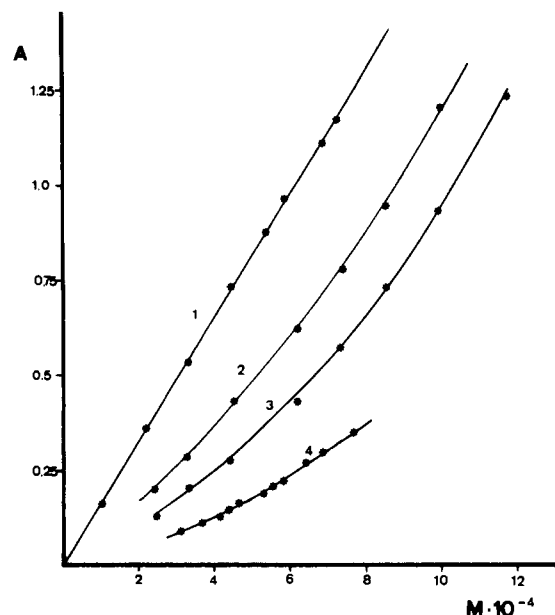


**Figure 2.** (a) Electronic spectra of the 400–250-nm zone of  $[(\text{NH}_3)_5\text{Co-NC-Pt}(\text{CN})_3]_2[\text{Pt}(\text{CN})_4]$  in solution (—), showing two very intense bands at 330 and 303 nm, and of the same compound passed through an anion-exchange resin in the chloride form (---), showing only the very intense band at 298 nm (interpretation in the text). (b) Comparison between the intensity of the 280-nm band (due to isolated  $[\text{Pt}(\text{CN})_4]^{2-}$ , which follows Beer's law) and the two other bands due to Pt–Pt interactions, showing the nonlinearity of  $A$  vs.  $[C]$  (indicating that Pt–Pt interactions vary with the concentration).

The problem that arises with these complexes is the possibility of Pt–Pt interactions between Pt atoms of the dinuclear cationic moiety, between Pt atoms of the  $[\text{Pt}(\text{CN})_4]^{2-}$  free ions, or between cationic and anionic parts (formula proposed:  $[(\text{NH}_3)_5\text{Co-NC-Pt}(\text{CN})_3]_2[\text{Pt}(\text{CN})_4]$ ). In order to clarify this question, the product was dissolved in water (it is very slightly soluble) and passed through an anion-exchange resin in the chloride form. The UV spectrum of the eluted solution shows the very intense band at nearly 300 nm, but the second band at 330 nm has almost disappeared (Figure 2a), indicating that the Pt–Pt interactions of both moieties are distinguishable.

Furthermore, taking into account the linearity of the 280-nm absorption band of  $[\text{Pt}(\text{CN})_4]^{2-}$  with the concentration (Beer's law) (Figure 2b), we investigated the concentration dependence for the 300- and 330-nm bands. Figure 2b and Figure 3 clearly indicate the failure of Beer's law for the two new bands.

Both the appearance of the 300- and 330-nm bands and the failure of Beer's law can be interpreted in terms of an oligomer association equilibrium in solution, like that reported in  $[\text{Pt}(\text{CNR})_4][\text{Pt}(\text{CN})_4]^{20}$  and  $\text{Ba}[\text{Pt}(\text{CN})_4]^{21}$ . Isci et al.<sup>20</sup> explained this new band by the presence of dimers; more recently, Adamson et al.<sup>21</sup> pointed out the possibility of higher oligomers



**Figure 3.** Absorbance ( $A$ ) vs. molar concentration ( $\times 10^{-4}$ ) of  $[(\text{NH}_3)_5\text{Co-NC-Pt}(\text{CN})_3]_2[\text{Pt}(\text{CN})_4]$ : (1) 280-nm band due to isolated  $[\text{Pt}(\text{CN})_4]^{2-}$ ; (2) 303-nm band due to Pt–Pt interactions; (3) 330-nm band due to Pt–Pt interactions; (4) 298-nm band due to the same compound passed through an anion-exchange resin in the chloride form.

**Table I.** Calculated Values of  $K$ ,  $\epsilon$ , and  $r^2$  for the Oligomeric Association of  $[(\text{NH}_3)_5\text{Co-NC-Pt}(\text{CN})_3]^+$  Cation with Chloride as Counteranion

$10^4 [C], \text{M}$	$A$ (absorbance)	$10^4 [C], \text{M}$	$A$ (absorbance)
3.377	0.083	5.553	0.180
3.386	0.096	5.899	0.196
4.101	0.113	6.635	0.225
4.428	0.127	6.899	0.260
4.836	0.148	7.748	0.322
5.296	0.166		
		dimer assn	trimer assn
$K, \text{M}^{-1}$		$4.3 \times 10^2$	$2.7 \times 10^6$
$\epsilon, \text{M}^{-1} \text{cm}^{-1}$		2540	2260
$r^2$		0.9330	0.9760

and attributed the band at 305 nm in  $[\text{Pt}(\text{CN})_4]^{2-}$  to trimeric species and the band at 335 nm to tetramers. Both Isci and Adamson indicated that the assignments involving oligomers are necessarily qualitative. Assuming in the first place that the dinuclear complexes studied in this work contain dimers and assuming also that the band at 300 nm in the chloride solution is due to the associated dinuclear complex, then a value for association constant ( $K$ ) can be obtained from the equation indicated in the Experimental Section, with  $n = 2$ . Assuming, according to the Adamson theory,<sup>21</sup> that the species present in solution is mainly a trimer and applying the same equation with  $n = 3$ , we obtained a different value for the association constant. The values of  $K$ ,  $\epsilon$ , and  $r^2$  are given in Table I. The value of the linear regression coefficient,  $r^2$ , is higher if the formation of trimers is assumed, in better agreement with Adamson's theory.

The Pt–Pt interactions in the solid state have been explained by several authors. Day, for example, has studied them in a number of salts of the anion  $[\text{Pt}(\text{CN})_4]^{2-}$ ,<sup>22</sup> Martin et al., have studied them in  $[\text{PtCl}_2(\text{en})]$ ,<sup>23</sup> and Isci et al. have studied them

(20) Isci, H.; Mason, W. R. *Inorg. Chem.* **1974**, *13*, 1175.

(21) Schindler, J. W.; Fukuda, R. C.; Adamson, A. W. *J. Am. Chem. Soc.* **1982**, *104*, 3596.

(22) Day, P. *ACS Symp. Ser.* **1974**, *No. 5*, Chapter 17.

(23) Martin, D. S.; Hunter, L. D.; Kroening, R.; Coley, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 5433.

Table II. Computational Kinetic Parameters for  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{M}(\text{CN})_4]_3$  (M = Ni, Pd, Pt), from the Equations for Growth and Nucleation-Growth Mechanisms<sup>a</sup>

	growth model				nucleation-growth model <sup>b</sup>			
	$g(\alpha) = [1 - (1 - \alpha)^{1-n}]/(1 - n)$				(a) $g(\alpha) = [-\ln(1 - \alpha)]^{1/n}$			(b) $g(\alpha) = \ln[\alpha/(1 - \alpha)]$
	$n = 0$	$n = 1/3$	$n = 1/2$	$n = 2/3$	$n = 1$	$n = 2$	$n = 3$	
	$[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{Ni}(\text{CN})_4]_3$							
$E_a^c$	86.5	96.5	103.7	111.3	123.6	58.6	36.9	
$\ln K_0$	21.09	24.34	26.67	29.13	33.10	12.40	7.59	
$r^2$	0.9962	0.9989	0.9997	0.9998	0.9990	0.9989	0.9988	
$E_a^d$	114.6	114.6	114.6	114.6	114.8	114.9	115.0	115.2
$\ln K_0$	34.20	34.41	34.59	34.76	35.06	34.53	34.21	35.85
$r^2$	0.9940	0.9892	0.9850	0.9797	0.9701	0.9874	0.9915	0.9913
	$[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{Pd}(\text{CN})_4]_3$							
$E_a^c$	113.1	126.5	135.5	145.4	161.4	77.5	49.5	
$\ln K_0$	30.26	34.56	37.63	40.87	46.07	18.87	9.67	
$r^2$	0.9963	0.9982	0.9987	0.9986	0.9976	0.9974	0.9972	
$E_a^d$	125.1	124.4	124.1	123.7	123.1	124.8	125.5	125.8
$\ln K_0$	37.34	37.37	37.42	37.47	37.56	37.50	37.35	39.04
$r^2$	0.9926	0.9937	0.9944	0.9948	0.9953	0.9925	0.9910	0.9898
	$[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{Pt}(\text{CN})_4]_3$							
$E_a^c$	97.7	109.7	117.1	125.6	139.5	66.6	42.3	
$\ln K_0$	25.24	29.06	31.79	34.68	39.32	15.55	7.44	
$r^2$	0.9941	0.9974	0.9988	0.9996	0.9996	0.9996	0.9996	
$E_a^d$	66.1	66.7	67.2	67.7	68.3	66.8	66.3	66.2
$\ln K_0$	19.49	19.94	20.25	20.55	21.01	19.97	19.45	21.01
$r^2$	0.9945	0.9950	0.9954	0.9957	0.9960	0.9947	0.9941	0.9938

<sup>a</sup>  $E_a$  values in kJ/mol. <sup>b</sup> For nucleation-growth model: (a) Avrami-Erofeev' law; (b) Prout-Tompkins law. <sup>c</sup> Nonisothermal measurements. <sup>d</sup> Isothermal measurements.

in the compounds mentioned above.<sup>20</sup> All these authors explain the interactions by the approximate treatment of Davydov, i.e. in terms of the charge-transfer bands of the isolated molecules shifted to lower frequencies by specific interactions among molecules in the crystal.

The Pt-Pt interactions in solution have been less studied. Authors dealing with solution association, particularly Gray,<sup>24</sup> have discussed this phenomenon in terms of molecular orbital theory. The splitting of the isolated levels into several components due to the Pt-Pt interactions causes a shift of the charge-transfer transitions toward lower frequencies (red-shift transition). In our case, and assuming the formation of a dimer, the  $d_{z^2}$  and  $\pi^*$  orbitals of each  $[\text{Pt}(\text{CN})_4]^{2-}$  are split, and if we suppose a  $C_{2h}$  symmetry for the dimer, then the splitting is  $[(1a_g)^2(2b_u)^2(3a_g)^0(4b_u)^0]$ . The transition  $2b_u \rightarrow 3a_g$  [ $^1A_g \rightarrow ^1B_u$ ] is dipole-allowed in this symmetry and will produce the strong new band at 300 nm (red shift with respect to  $d_{z^2} \rightarrow \pi^*$  of starting  $[\text{Pt}(\text{CN})_4]^{2-}$ ). If formation of trimers is assumed, the reasoning is the same and the red shift is even greater.

Finally, the Pt-Pt interactions in the solid have been supported by conductivity measurements on pellets of the new substances compared with those on  $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ . The values obtained are as follows:  $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ ,  $3.5 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$  (in agreement with literature data<sup>25</sup>);  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{Pt}(\text{CN})_4]_3$  (pink color),  $6.5 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ ;  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{Pd}(\text{CN})_4]_3$  (yellow-green color),  $1.29 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$ ;  $[(\text{NH}_3)_5\text{Co}-\text{NC}-\text{Pt}(\text{CN})_3]_2[\text{Pt}(\text{CN})_4]_3$ ,  $2.9 \times 10^{-14} \Omega^{-1} \text{cm}^{-1}$ ; the Ni and Pd dinuclear compounds have values of  $(3-4) \times 10^{-12} \Omega^{-1} \text{cm}^{-1}$ . These measurements indicate that upon reaction there are greater Pt-Pt interactions; therefore, distortion is also greater and conductivity lower.

Table III. Average Kinetic Parameters Calculated from the Correspondence of Isothermal and Nonisothermal Measurements<sup>a</sup>

	M = Ni	M = Pd	M = Pt
$E_a$ , kJ/mol	$117.4 \pm 6$	$131.0 \pm 5$	$66.7 \pm 1$
$\Delta H^\ddagger$ , kJ/mol	112.5	120.8	63.7
$\Delta S^\ddagger$ , cal/mol	$8.3 \pm 10$	$13.3 \pm 11$	$-21.3 \pm 9$
$\Delta G^\ddagger$ , kJ/mol	98.2	99.5	96.8
$\ln K_0$	$33.0 \pm 3$	$36.7 \pm 1$	$17.8 \pm 3$

<sup>a</sup> See text for the model proposed.

**Kinetic Parameters.** The kinetic parameters were determined on the basis of the general kinetic relation<sup>26,27</sup>

$$d\alpha/dt = f(\alpha) k(T)$$

or

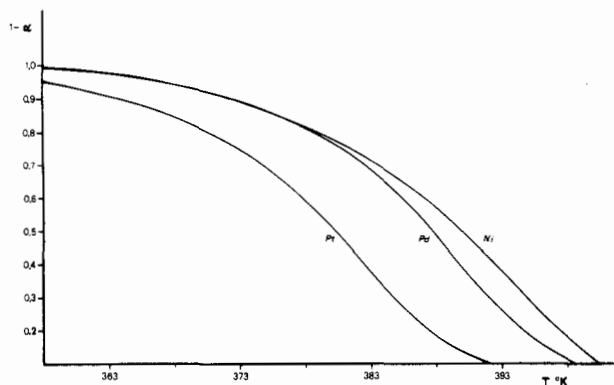
$$\int_0^1 d\alpha/f(\alpha) = \int_{T_1}^{T_2} k(T) dt = g(\alpha)$$

where  $\alpha$  is the fraction decomposed and  $k(T)$  follows the Arrhenius law [ $k(T) = K_0 \exp(-E_a/RT)$ ], with  $K_0$  being the frequency factor and  $E_a$  the activation energy. The expression  $g(\alpha)$  depends on the mechanism of the solid-state reaction: diffusion, nucleation, growth, or nucleation-growth.<sup>8</sup> Each process can be studied by several expressions of  $g(\alpha)$  depending on  $\alpha$  and  $n$  (reaction order).

Kinetic parameters are very difficult to calculate by only nonisothermal TG curves<sup>8</sup> due to ignorance of the true  $g(\alpha)$  expression. It is necessary to compare the results obtained by nonisothermal and isothermal TG measurements for all the  $g(\alpha)$  expressions in order to calculate the true activation energy and to know the physical mechanism of the solid-state process. For this reason we have recorded not only the nonisothermal TG curves (Figure 4) for each compound but also the isothermal TG curves at five different temperatures (Figure 5) for each compound. In both methods (nonisothermal and

- (24) (a) Mann, K. R.; Gordon, J. G.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3553. (b) Mann, K. R.; Lewis, N. S.; Williams, R. M.; Gray, H. B. *Inorg. Chem.* **1978**, *17*, 828. (c) Mann, K. R.; Bell, R. A.; Gray, H. B. *Ibid.* **1979**, *18*, 2671. (d) Mann, K. R.; Dipierro, M. J.; Gill, T. P.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 3965.
- (25) (a) O'Neil, J. H.; Underhill, A. E. *Solid State Commun.* **1979**, *29*, 557. (b) Hara, Y.; Shirohara, I.; Onodera, A. *Ibid.* **1975**, *17*, 827.

- (26) Young, D. A. "Decomposition of Solids"; Pergamon Press: Oxford, 1966; Chapter 1.
- (27) Garner, W. E. "The Chemistry of the Solid State"; Butterworths: London, 1955; Chapter 5.



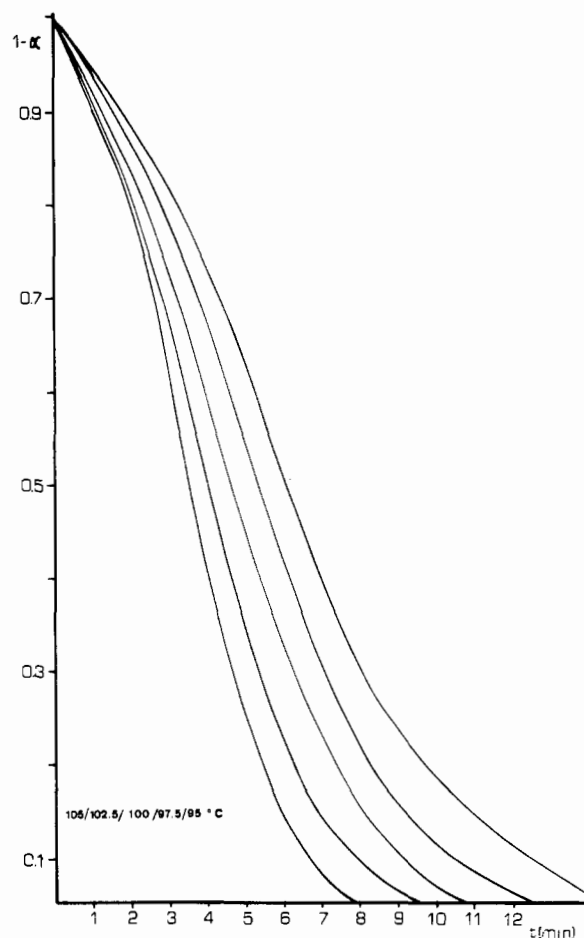
**Figure 4.** Nonisothermal TG curves for  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{M}(\text{CN})_4]_3$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ), showing the great similarity between the Ni and Pd compounds and the marked difference in the Pt compound (the curves are cut at  $\alpha = 0.1$  in order not to lengthen the abscissa).

isothermal) all the principal expressions of  $g(\alpha)$  reported in the literature<sup>8</sup> have been used. The computation for each  $g(\alpha)$  and for each  $n$  has been carried out with an ad hoc Fortran IV program.

The physical mechanism is assigned and the corresponding kinetic parameters are calculated on the basis of agreement in the activation energy, frequency factor, and  $r^2$  values in both nonisothermal and isothermal methods (the physical mechanism, however, can remain ambiguous). As found in the literature<sup>1</sup> the solid-state deauration-anation of  $[\text{M}(\text{H}_2\text{O})(\text{NH}_3)_5]^{3+}$  and similar cations behaves according to growth or nucleation-growth models. In effect, the values of  $E_a$ ,  $K_0$ , and  $r^2$  found by us with diffusion or nucleation models are inconsistent. For this reason, in Table II only the values found for each compound with the growth and nucleation-growth models are reported. The activation energy values calculated are (Table III)  $117.4 \pm 6$  kJ/mol for the Ni compound (growth mechanism with  $n = 2/3$  or 1),  $131.0 \pm 5$  kJ/mol for the Pd compound (growth mechanism with  $n = 1/3$  or  $1/2$ ), and  $66.7 \pm 1$  kJ/mol for the Pt compound (nucleation-growth mechanism with  $n = 2$ ; Avrami's law). Taking into account the possible deviation and error of these values, we can affirm that the corresponding activation energy for the Ni and Pd compounds is of the same magnitude (120–130 kJ/mol) but the Pt compound has an activation energy of only 65–70 kJ/mol. This surprising result was confirmed by repetition of TG measurements on the Pt compound.

The agreement between the  $E_a$  values of the Ni and Pd compounds and the markedly different value for the Pt compound confirm the hypothesis of House<sup>9</sup> and LeMay<sup>2</sup> on the  $\text{S}_{\text{N}}1$  mechanism in these deauration-anation reactions.

House<sup>9</sup> has recently proposed several mechanisms in the thermal dehydration-anation reactions of solid complexes, determined by various types of defects: Schottky defects with an  $\text{S}_{\text{N}}2$  associative mechanism or Frenkel-type defects with an  $\text{S}_{\text{N}}1$  dissociative mechanism. According to this theory, high values of  $E_a$  have a better correspondence with an  $\text{S}_{\text{N}}2$  mechanism while low values have a better correspondence with  $\text{S}_{\text{N}}1$ . In our case, in an  $\text{S}_{\text{N}}2$  reaction the formation of a seven-bonded complex (pentagonal bipyramid) based on a crystal field model requires  $8.52Dq^{28}$  ( $Dq$  being about 25 kJ/mol for the aquopentaamminecobalt(III) ion),<sup>29</sup> which alone would be about 200 kJ/mol, greater than the  $E_a$  found. If the activated complex was an octahedral wedge, the energy required would be only  $3.63Dq$  (nearly 90 kJ/mol, similar to the  $E_a$  found). However, considering that in the  $\text{S}_{\text{N}}2$  reaction



**Figure 5.** Isothermal TG curves (indicating the temperature) for  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{Pt}(\text{CN})_4]_3$  (the Ni and Pd compounds show very similar curves). The curves are cut at  $\alpha = 0.05$  in order not to lengthen the abscissa (approximately 45 min may be necessary to arrive at  $\alpha = 1$  at 95 °C).

the heptacoordination suggests a Schottky-type defect formation in an ionic crystal, it requires high energy ( $E_{\text{defect}} = 0.24U$ ;  $U =$  lattice energy).<sup>30</sup> Consequently, we should find a value greater than 110–120 kJ/mol.

The mechanism, therefore, might be  $\text{S}_{\text{N}}1$  (dissociative mechanism) with the formation of a square-base-pyramid activated complex, requiring only  $4.00Dq^{28}$  (activation energy about 100 kJ/mol) (for a trigonal-bipyramid activated complex it would require  $11.49Dq$ ).<sup>28</sup> Consequently, the transition state is determined by the water loss and a nonionic Frenkel defect formation. This implies no variation of the activation energy regarding similar anions in which, a priori, the mechanism would be identical.

Why are the energy values in the Ni and Pd compounds so different from that in the Pt compound? Taking into account the similar size of  $[\text{M}(\text{CN})_4]^{2-}$  anions ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ), the  $E_a$  should be of the same order of magnitude if the three compounds had the same structure. However, due to the above mentioned Pt–Pt interactions, the Pt compound is not isostructural with the Ni and Pd analogues (as X-ray powder diffraction has shown).<sup>31</sup> This difference between the activation energy of the Pt compound and those of the Ni and Pd compounds is not found in other series studied by us, like *trans*- $[\text{CrF}(\text{H}_2\text{O})(\text{en})_2][\text{M}(\text{CN})_4]$ <sup>32</sup> and *trans*- $[\text{CrF}(\text{H}_2\text{O})-$

(28) Basolo, F.; Pearson, R. G. "Mechanism of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; Chapter 3.

(29) Huheey, J. E. "Inorganic Chemistry"; Harper and Row: London, 1975; p 309.

(30) Schmalzreid, H. "Solid State Reactions"; Verlag Chemie: New York, 1974; p 23.

(31) All the attempts to obtain crystals suitable for x-ray structural determination have failed, since the freshly prepared crystals change color (see text) and lose crystallinity in a few hours.

(tn)<sub>2</sub>][M(CN)<sub>4</sub>]<sup>3-</sup> (en = ethylenediamine; tn = 1,3-diaminopropane; M = Ni, Pd, Pt). In both cases the three salts are isostructural (X-ray powder diffraction), and there is no Pt-Pt interaction in the mixed salts. Consequently, the differences may be attributed to Pt-Pt interactions in the mixed complex salts that produce distortion in the lattice due to the packing, there is more free space, and the escape of a water molecule will be easier.

The *E*<sub>a</sub> values for the Ni and Pd compounds agree with the described value<sup>5</sup> for [Co(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>5</sub>][Co(CN)<sub>6</sub>], 143.8 ± 7 kJ/mol, where interstitial diffusion of water molecules as Frenkel defects is not enhanced by the similarity of the two ions. The values reported by LeMay<sup>2</sup> for chloride, bromide, and nitrate compounds (about 85–90 kJ/mol) are intermediate between our values found for the Ni and Pd compounds and that for the Pt compound. We can conclude that the proposed S<sub>N</sub>1 mechanism is more accurate in complexes of the aquopentaamminecobalt(III) cation; the activated complex is a square-based pyramid, and the action energy can vary depending on the crystal structures and relative sizes of the anion and cation.

Furthermore, the entropy of activation calculated from the expression

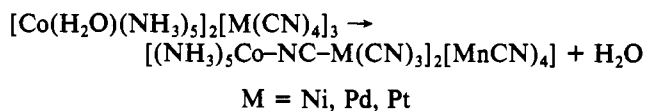
$$(\ln K)h/(k_B T) = \Delta S^\ddagger / R - \Delta H^\ddagger / RT \quad (K = \text{rate constant})$$

also may indicate the differences between the Ni and Pd compounds and the Pt compound (Table III). According to House<sup>9</sup> the entropy effect may also be explained by the relative sizes (in our case the relative packing) of the ions and the free volume: where there is a large space between the cations and anions (as we suppose in the Pt compound), the water molecule may be able to slip into a interstitial position, causing little or no lattice distortion. Therefore the entropy of activation may be small or slightly negative. Where there is a smaller space between the ions (as we can suppose in the Ni and Pd

compounds), the water molecules can occupy an interstitial position only with considerable lattice expansion so that the entropy of activation is positive. Although this entropy reasoning of House is speculative and not supported by any facts, we believe that it gives an intuitive comprehension of the process.

### Conclusions

A dissociative mechanism for the deaquation-anation reaction



is proposed from TG measurements (isothermal and nonisothermal), but the calculated activation energy is of the same magnitude only for the Ni and Pd compounds, being very different in the Pt compound. To explain this difference, and taking into account the similarity of the anions, we propose a different structure in the Pt case that allows the water molecule to escape easily from the crystal lattice. This difference may be due to Pt-Pt interactions in the solid state as shown by the appearance of the new, very intense band at 355 nm in the electronic spectrum (a similar band also appears in dilute solution). The Pt-Pt interactions can produce distortions in the lattice (similar to Peierls distortions) which would be responsible for the different behavior on heating.

**Registry No.** [Co(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>5</sub>]<sub>2</sub>[Ni(CN)<sub>4</sub>]<sub>3</sub>, 90269-67-3; [Co(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>5</sub>]<sub>2</sub>[Pd(CN)<sub>4</sub>]<sub>3</sub>, 90269-68-4; [Co(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>5</sub>]<sub>2</sub>[Pt(CN)<sub>4</sub>]<sub>3</sub>, 90269-69-5; [(NH<sub>3</sub>)<sub>5</sub>Co-NC-Ni(CN)<sub>3</sub>]<sub>2</sub>[Ni(CN)<sub>4</sub>], 90269-71-9; [(NH<sub>3</sub>)<sub>5</sub>Co-NC-Pd(CN)<sub>3</sub>]<sub>2</sub>[Pd(CN)<sub>4</sub>], 90269-73-1; [(NH<sub>3</sub>)<sub>5</sub>Co-NC-Pt(CN)<sub>3</sub>]<sub>2</sub>[Pt(CN)<sub>4</sub>], 90269-75-3; [Co(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>5</sub>](ClO<sub>4</sub>)<sub>3</sub>, 13820-81-0; K<sub>2</sub>[Ni(CN)<sub>4</sub>], 14220-17-8; K<sub>2</sub>[Pd(CN)<sub>4</sub>], 14516-46-2; K<sub>2</sub>[Pt(CN)<sub>4</sub>], 562-76-5.

**Supplementary Material Available:** A listing of kinetic parameters calculated for each compound (both nonisothermal and isothermal methods) for all the principal expressions for growth, nucleation, nucleation-growth, and diffusion mechanisms (71 pages). Ordering information is given on any current masthead page.

(32) Ribas, J.; Serra, M., to be submitted for publication. The activation energy for the three compounds is about 120–130 kJ/mol.

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Indian Association for the Cultivation of Science, Calcutta 700032, India

## Hydroxamates of Bis(2,2'-bipyridine)ruthenium: Synthesis, Protic, Redox, and Electroprotic Equilibria, Spectra, and Spectroelectrochemical Correlations

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The synthesis and characterization of pink complexes of the type Ru<sup>II</sup>(bpy)<sub>2</sub>(RX)ClO<sub>4</sub>·2H<sub>2</sub>O are reported (bpy = 2,2'-bipyridine; RX = RN(O)C(O)C<sub>6</sub>H<sub>4</sub>-*p*-X; R = H, Me; X = OMe, Me, H, Cl, NO<sub>2</sub>). The HX complexes act as weak acids in aqueous media; the pK values (8–11) correlate linearly with σ, the Hammett substituent constant of X. The green deprotonated complex Ru<sup>II</sup>(bpy)<sub>2</sub>(X)·H<sub>2</sub>O has been isolated. All species show highly reversible ruthenium(III)–ruthenium(II) couples in acetonitrile with formal potentials, *E*<sup>o</sup><sub>298</sub>, that vary (–0.3 to 0.5 V) linearly with σ but with a relatively small reaction constant (~0.08 V). The *E*<sup>o</sup><sub>298</sub> values of the deprotonated complexes are unusually low; the complexes also display a reversible ruthenium(IV)–ruthenium(III) couple (*E*<sup>o</sup><sub>298</sub> ~ 0.9 V). The ruthenium(IV) complex is, however, relatively unstable. In aqueous media spontaneous proton dissociation occurs on metal oxidation. The resultant electroprotic equilibrium Ru(bpy)<sub>2</sub>(X)<sup>+</sup> + e<sup>-</sup> + H<sup>+</sup> ⇌ Ru(bpy)<sub>2</sub>(HX)<sup>+</sup> has been characterized (*E*<sup>o</sup><sub>298</sub> ~ 0.5 V) by using variable-pH cyclic voltammetry in 60:40 water-dioxane. The complexes Ru<sup>III</sup>(bpy)<sub>2</sub>(MeMe)(ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (blue) and Ru<sup>III</sup>(bpy)<sub>2</sub>(H)ClO<sub>4</sub>·2H<sub>2</sub>O (brownish yellow) are isolated by oxidation of the ruthenium(II) counterparts with cerium(IV) in neutral aqueous acetonitrile. All ruthenium(II) complexes have an MLCT band system in the visible region (530–720 nm). Deprotonation markedly affects the MLCT band energy as it does metal redox potentials. The linear correlation of the MLCT frequency with the difference of *E*<sup>o</sup><sub>298</sub> of metal oxidation (Ru(II) → Ru(III)) and bpy reduction (bpy → bpy<sup>-</sup>) is noted.

### Introduction

The structure and stereochemistry and formation and stability as well as transport and reactivity of the hydroxamates of transition-metal ions have been the subject of many recent

studies.<sup>1–4</sup> This interest originates from several factors such as the analytical usefulness of hydroxamates<sup>5</sup> and particularly

(1) Smith, W. L.; Raymond, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 3341.