

## Dinuclear Compounds with a $\mu$ -Cyano Ligand.

### Part XIII\*. Synthesis, Characterization and Solid State Kinetics of the Formation of ( $\mu$ -Cyano)(tricyanometal(II))pentaamminerhodium(III) and Iridium(III) (Metal(II) = Nickel, Palladium, Platinum). Influence of the Pt–Pt Interactions

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#### Abstract

Six new dinuclear complexes of ( $\mu$ -cyano)(tricyanometal(II))pentaamminerhodium(III) or iridium(III), metal(II) being nickel, palladium and platinum, have been obtained by solid state reaction of the tetracyanomethylate(II) of aquopentaamminerhodium(III) and iridium(III), respectively. All these complexes have been characterized by chemical analysis, electronic and IR spectra and TG measurements. The kinetics of the solid-state deaquation–anation has been studied by thermogravimetric measurements under both nonisothermal and isothermal conditions. The activation energies so obtained are 105.3 and 107.7 kJ/mol for the Ni compounds; 115.0 and 118.1 kJ/mol for the Pd compounds and 90.2 and 92.2 kJ/mol for the Pt compounds. These low values of activation energy can indicate an  $S_N1$  dissociative mechanism with an activated complex of square-based-pyramidal geometry. The marked difference in the kinetic parameters between the Ni, Pd compounds and Pt compounds may be explained in terms of Pt–Pt association in the crystal lattice, which causes distortion and allows the water molecules to escape easily from the crystal structure. These 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 and at about 330 nm and 300 nm in solution.

#### Introduction

In a previous work [2] the authors described the synthesis and characterization of ( $\mu$ -cyano)(tricyanometal(II))pentaamminecobalt(III), metal(II) being Ni, Pd, and Pt. On the other hand, the solid-state kinetic parameters for the deaquation–anation of the tetracyanonickelate(II), tetracyanopalladiate(II) and

tetracyanoplatinate(II) of aquopentaamminecobalt(III) were determined. We have found that the dehydration–anation mechanism for these three complexes and other aquaamine complexes of chromium(III) and cobalt(III) [3] with cyanocomplexes as entering ligands is always consistent with a dissociative mechanism.

If the process takes place by an  $S_N1$  pathway, the rate determining step is the loss of the water from  $[M(NH_3)_5(H_2O)]^{3+}$  and the activation energy should be almost invariant with the nature of the anion, provided that the structure of the complexes is very similar. Furthermore, the principal contribution to  $E_a$  must be, according to House [4], the  $Dq$  factor of M(III) (due to passing from hexacoordination to the intermediate square-pyramid).

For these reasons, it would be very interesting to synthesize the analogous complexes with Rh(III) and Ir(III) instead Co(III) and to compare the kinetic parameters for the dehydration–anation reaction to study the influence of the  $Dq$  parameter.

In this paper we synthesize and characterize the new complexes  $[Rh(NH_3)_5(H_2O)]_2[M(CN)_4]_3$  and  $[Ir(NH_3)_5(H_2O)]_2[M(CN)_4]_3$  (M = Ni, Pd, Pt); we propose a mechanism for its dehydration–anation reaction giving the corresponding dinuclear compounds with  $\mu$ -cyano ligand, and we explain the observed differences with the  $[Pt(CN)_4]^{2-}$  anion in terms of strong Pt–Pt interactions in the lattice, shown by UV spectra.

#### Experimental

##### Preparation of the New Compounds

(a)  $[M(NH_3)_5(H_2O)]_2[Ni(CN)_4]_3$  (M = Rh, Ir). 0.2 g of  $K_2[Ni(CN)_4]$  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 0.25 g of  $[Rh(NH_3)_5(H_2O)](ClO_4)_3$  [5] or  $[Ir(NH_3)_5(H_2O)](ClO_4)_3$  [6] in 10 ml of water. A pale yellow precipitate was obtained

\*For part XII of this series, see ref. 1.

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TABLE I. Analytical Data, Colour and the Best Conditions to Obtain the Dinuclear Compounds in Solid State

Compound	T (°C)	t (min)	Colour	Anal. Calc (Found)			Water loss %
				C%	N%	H%	
Rh-Ni	110	20	Pale yellow	16.67(16.9)	35.65(35.8)	3.47(3.6)	4.00(4.04)
Rh-Pd	95	20	White	14.30(14.1)	30.59(30.3)	2.98(3.1)	3.45(3.48)
Rh-Pt	100	15	Deep yellow	11.31(11.2)	24.19(24.0)	2.36(2.3)	2.75(2.72)
Ir-Ni	110	15	Pale yellow	13.81(13.7)	29.54(29.3)	2.88(2.8)	3.34(3.37)
Ir-Pd	130	15	White	12.15(12.4)	25.98(26.1)	2.53(2.6)	2.95(2.98)
Ir-Pt	115	15	Deep yellow	9.92(10.1)	21.22(21.3)	2.07(2.1)	2.42(2.40)

by adding 2-propanol and ether or by putting the solutions in a freezing compartment. The products were filtered, washed with acetone and ether and air-dried.

(b)  $[\text{M}(\text{NH}_3)_5(\text{H}_2\text{O})]_2[\text{M}'(\text{CN})_4]_3$  (M = Rh, Ir; M' = Pd, Pt). We have used a similar method to obtain the Pd and Pt salts from  $\text{K}_2[\text{Pd}(\text{CN})_4]$  [7] and  $\text{K}_2[\text{Pt}(\text{CN})_4]$  (Johnson-Matthey), with the cation exchanger in the acid form. For Pt(II) a different behaviour was observed when the precipitation was attempted. A white precipitate was formed in an ice bath but a yellow product was obtained by precipitation with 2-propanol. Solutions of all these complexes have the same white color. The yellow salt is less soluble. The different behaviour of the Pt compound in the solid state is discussed below (Results and Discussion).

(c)  $[(\text{NH}_3)_5\text{M}-\text{NC}-\text{M}'(\text{CN})_3]_2[\text{M}'(\text{CN})_4]$  (M = Rh, Ir; 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 the aquocomplexes according to the conditions indicated in Table I. From the data, 0.3 g of the mixed salts was heated in an oven for 20 min. Under these conditions there was no signal of minimal decomposition. The analysis of the dinuclear compounds is also given in Table I.

### Techniques

Infrared spectra were recorded on a IR-20A spectrophotometer. Samples were prepared using the KBr technique. Electronic absorption spectra were recorded in solution and in the solid phase 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  $5^\circ \text{C min}^{-1}$ . The kinetic parameters were determined on the basis of the general kinetic relation

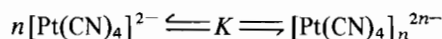
$$g(\alpha) = \int_{T_1}^{T_2} k(T) dt$$

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 [8, 9]. The  $g(\alpha)$  used were taken from literature data [10].

The kinetic parameters were calculated as previously described by us for  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]_2[\text{M}(\text{CN})_4]_3$  (M = Ni, Pd, Pt) [2]. All the calculations were made with a FORTRAN IV program.

### 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  $CA^{-1/n}$  versus  $A^{(n-1)/n}$  were linear, the slope giving the value of  $\epsilon$  and the intercept the value of  $K$ .

## Results and Discussion

### TG Measurements

The nonisothermal TG curves for the solid-phase thermal deauration of  $[\text{Rh}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{M}(\text{CN})_4]_3$  and  $[\text{Ir}(\text{H}_2\text{O})(\text{NH}_3)_5]_2[\text{M}(\text{CN})_4]_3$  (M = Ni, Pd, Pt) are given in Figs. 1 and 2. For the rhodium(III) complexes there is a mass loss corresponding to a molecular weight decrease of 36 a.m.u. between 100 and  $157^\circ \text{C}$ , 80 and  $120^\circ \text{C}$ , 35 and  $140^\circ \text{C}$  respectively. For the three Ir(III) complexes these temperatures are 95 to  $167^\circ \text{C}$ , 90 to  $155^\circ \text{C}$ , and 65 to  $165^\circ \text{C}$

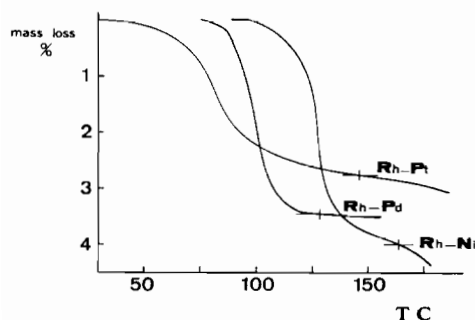


Fig. 1. Nonisothermal TG curves for  $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]_2\text{-}[\text{M}(\text{CN})_4]_3$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ), showing the great similarity between the Ni and Pd compounds and the difference in the Pt compound.

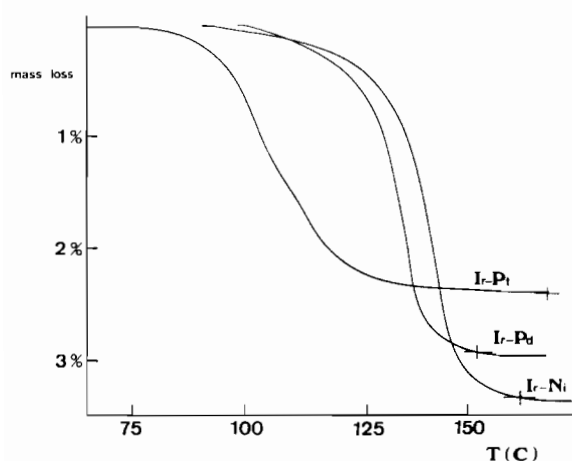


Fig. 2. Nonisothermal TG curves for  $[\text{Ir}(\text{NH}_3)_5(\text{H}_2\text{O})]_2\text{-}[\text{M}(\text{CN})_4]_3$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ), showing the great similarity between the Ni and Pd compounds and the difference in the Pt compound.

respectively. In both series the shape of the Pt compound is different from the Ni and Pd analogues. In all the six cases a new compound was obtained at the end of the curve, which corresponds to  $[(\text{NH}_3)_5\text{-Rh-NC-M}(\text{CN})_3]_2[\text{M}(\text{CN})_4]$  and  $[(\text{NH}_3)_5\text{Ir-NC-M}(\text{CN})_3]_2[\text{M}(\text{CN})_4]$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ). The Ir(III) TG runs can be prolonged up to 200–220 °C without significant decomposition; the Rh(III) compounds are less stable, especially the Ni complex. The Co(III) complexes previously studied [2] were much less stable, presenting considerable decomposition after the water loss.

#### IR Spectra

The IR spectra of the three new mixed salts are very similar. The bands due to the  $[\text{M}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$  cation ( $\text{M} = \text{Rh}, \text{Ir}$ ) are identical to those described for the same cations with other anions [11]. The spectra of the cyanide part show a very strong band around 2130  $\text{cm}^{-1}$ , depending on the metal, with a marked fine structure: 2120–2125

$\text{cm}^{-1}$  (sh), 2130–2135  $\text{cm}^{-1}$  (vs) and 2155–2160  $\text{cm}^{-1}$  (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  $[\text{M}(\text{CN})_4]^{2-}$  anions with simple cations [12].

When the cyano complex is coordinated in the deaquation–anation reaction a dinuclear compound with  $\mu$ -cyano ligand is formed. The IR spectra of the six new dinuclear complexes present a very intense and perfectly defined doublet in the  $\nu(\text{CN})$  region: 2130–2135  $\text{cm}^{-1}$  (vs) and 2200  $\text{cm}^{-1}$  (s). The clear splitting of the  $\nu(\text{CN})$  stretching frequency is good evidence for a bridging cyano group [13]. 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 [13]. 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 [12].

#### Electronic Spectra

In the Co(III) analogues, previously described [2], there were two relevant aspects in the electronic spectra: the d–d shift of the first cobalt(III) transition and the Pt–Pt interactions. In the Rh(III) and Ir(III) complexes, it is not possible to assign the d–d bands due to overlapping with the intense charge transfer bands of the cyano anions. For this reason we only studied the electronic spectra in order to understand the Pt–Pt interactions.

As indicated above, the solids  $[\text{M}(\text{NH}_3)_5(\text{H}_2\text{O})]_2\text{-}[\text{Pt}(\text{CN})_4]_3$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) show a different color (yellow or white) depending on the precipitation method. Independently of the color, the electronic spectra in KBr disk or diffuse reflectance show an intense band at 355 nm. Instead, in solution, only the bands due to  $[\text{Pt}(\text{CN})_4]^{2-}$  anion [14, 15] appear. This difference between the solid state and solution indicates that the Pt–Pt interaction is present only in the solid phase and is destroyed in solution.

The dinuclear complexes, on the other hand, show these Pt–Pt interactions in both the solid state and solution. Besides the intense bands due to the  $[\text{Pt}(\text{CN})_4]^{2-}$  [14, 15], two new, very intense bands at 330 nm(sh) and 300 nm(s) appear.

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. In order to clarify this question, the products were dissolved in water and passed through an anion-exchange resin in the chloride form. The UV spectrum or the eluted solution shows the very intense bands at nearly 300 nm, but the second band at 330 nm has almost disappeared

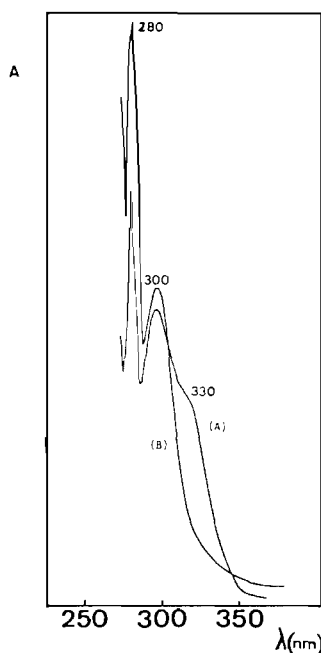


Fig. 3. Electronic spectra of the 400–250 nm zone of  $[(\text{NH}_3)_5\text{Rh-NC-Pt}(\text{CN})_3]_2[\text{Pt}(\text{CN})_4]$  in solution (A), showing two very intense bands at 330 and 300 nm, and of the same compound passed through an anion-exchange resin in the chloride form (B), showing only the very intense band at 300 nm (interpretation in the text).

(Fig. 3), 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) we investigated the concentration dependence for the 300 nm and 330 nm bands.

These two bands do not follow Beer's law. Both the appearance of the 300 nm 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  $[\text{Pt}(\text{CNR})_4][\text{Pt}(\text{CN})_4]$  [16] and  $\text{Ba}[\text{Pt}(\text{CN})_4]$  [17] by Isci and Adamson respectively.

Isci *et al.* [16] explained this new band by the presence of dimers; Adamson *et al.* [17] pointed out the possibility of higher oligomers and attributed the band at 305 nm to trimeric species and the band at 335 nm to tetramers. Assuming that the dinuclear complexes studied in this work contain dimers or trimers and assuming also that the band at 300 nm in the chloride solution is due to the association dinuclear complex, then a value for association constant ( $K$ ) can be obtained from the equation indicated in the 'Experimental', with  $n = 2$  or  $n = 3$ . The values of  $K$ ,  $\epsilon$  and  $r^2$  are given in Table II. The value of the linear regression coefficient,  $r^2$ , is higher if the formation of trimers is assumed, in agreement with Adamson theory and with our previous results

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

$[(\text{NH}_3)_5\text{Rh-NC-Pt}(\text{CN})_3]\text{Cl}$			
$A_{301}$	$A_{280}$	$C \times 10^{-4}$	$\epsilon_{\text{ap}}$
0.544	1.223	7.69	707.4
0.540	1.183	7.44	725.8
0.467	1.105	6.95	671.9
0.426	1.040	6.54	651.4
0.377	0.958	6.03	625.2
0.330	0.872	5.48	602.2
0.287	0.791	4.97	577.5
0.267	0.742	4.67	571.7
0.254	0.723	4.55	558.2
0.238	0.685	4.31	552.2
0.206	0.616	3.87	532.3
0.196	0.594	3.74	524.1
0.138	0.448	2.82	489.4
0.116	0.395	2.48	467.7
0.096	0.338	2.13	450.7
	Dimer association	Trimer association	
$K (\text{M}^{-1})$	$1.5 \times 10^3$	$4.3 \times 10^7$	
$\epsilon (\text{M}^{-1} \text{cm}^{-1})$	$2.46 \times 10^3$	$2.87 \times 10^3$	
$r^2$	0.9288	0.9776	

for Co(III) analogue [2]. These calculations could be made only for the Rh(III) dinuclear complex, because the interaction Pt–Pt in the Ir(III) analogue is lower and there is for this reason, a strong overlap of the 300 nm band with the 280 nm band due to free  $[\text{Pt}(\text{CN})_4]^{2-}$ .

The explanation of these Pt–Pt interactions, both in solid state or in solution, has been extensively commented on in our previous work [2] and, consequently, will not be repeated here.

#### Mechanism

The kinetic parameters calculated are given in Table III. Taking into account the possible deviation

TABLE III. Average Kinetic Parameters Calculated from the Nonisothermal Measurements

Compound	$E_a$ (kJ/mol)	$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (cal/mol)	$\Delta G^\ddagger$ (kJ/mol)	$\ln K_0$
Rh–Ni	105.3	102.2	1.9	99.0	31.68
Rh–Pd	115	112.0	11.7	94.0	36.56
Rh–Pt	90.2	86.8	–2.9	91.3	29.16
Ir–Ni	107.7	104.5	4.4	97.4	32.94
Ir–Pd	118.0	115.1	6.7	103.8	33.94
Ir–Pt	92.2	86.4	–7.2	98.0	27.52

TABLE IV. CFAE (Crystal Field Activation Energies) for  $[M(H_2O)(NH_3)_5]^{3+}$  cations [ $M = Co(III), Rh(III), Ir(III)$ ]

Mechanism	Intermediate	CFAE	$[CoH_2O(NH_3)_5]^{3+}$ ( $Dq = 25$ kJ/mol)	$[RhH_2O(NH_3)_5]^{3+}$ ( $Dq = 38$ kJ/mol)	$[IrH_2O(NH_3)_5]^{3+}$ ( $Dq = 45$ kJ/mol)
Dissociative	Square based pyramid	$4 Dq$	100	152	180
	Trigonal bipyramid	$11.48 Dq$	287	436	516
Associative	Pentagonal bipyramid	$8.52 Dq$	213	323	383
	Octahedral wedge	$3.63 Dq$	91	138	163

and error of these values, we can affirm that the corresponding activation energy for the Ni and Pd compounds is of the same magnitude (110–120 kJ/mol) but the Pt compounds have an activation energy of only 80–90 kJ/mol.

The Co(III) analogues, previously reported by us [2], had the following activation energy: *ca.* 120 kJ/mol for the Ni; 130 kJ/mol for the Pd and only 65 kJ/mol for the Pt complex. Therefore the activation energy of the three complexes of Pt(II) is lower than the Ni and Pd analogues; moreover, the activation energy of Rh(III) and Ir(III) compounds is equal or lower than the Co(III) analogues.

House [4] has recently proposed several mechanisms in the thermal dehydration–anation reactions of solid complexes, determined by various types of defects: Shottky defects with an  $S_N2$  associative mechanism or Frenkel-type defects with an  $S_N1$  dissociative mechanism. According to this theory, high values of  $E_a$  have a better correspondence with an  $S_N2$  mechanism while low values have a better correspondence with  $S_N1$ .

The compounds studied here have a  $d^6$  configuration. Following the Crystal Field model of Basolo and Pearson [18], the CFAE (Crystal Field Activation Energy) of the Co(III), Rh(III) and Ir(III) are given in Table IV for the four principal possible intermediates [19].

In our case, in an  $S_N2$  reaction, the formation of a seven-bonded complex requires either  $8.52 Dq$  (greater than the  $E_a$  found) or  $3.63 Dq$  (similar to the  $E_a$  found). However, considering that in the  $S_N2$  reaction the heptacoordination suggests a Schotky-type defect formation in an ionic crystal, it requires high energy ( $E_{\text{defect}} = 0.34 U$ ;  $U$  = lattice energy) [20]. Consequently, we should find a value greater than 110–120 kJ/mol.

The mechanism, therefore, might be dissociative, with the formation of a square-base-pyramid activated complex requiring only  $4.00 Dq$  (for a trigonal-bipyramid activated complex it would require  $11.49 Dq$ ) [18].

In the Co(III) cases, the value of 120 kJ/mol is greater than the contribution of  $Dq$  (100 kJ/mol), which seems reasonable. Therefore, the  $E_a$  of Rh and Ir complexes would be expected to increase by an

order of magnitude. The experimental results are to the contrary, *i.e.*, the lower value is found for the Ir complexes.

To explain this result we have to take into account that in a dissociative mechanism the transition state is determined by the water loss and a non-ionic Frenkel defect formation. Therefore, the water will be able to escape into the interstitial sites of the lattice when the free space in the net is greater. We can expect that the free space will be greater with the more voluminous cation  $[Ir(NH_3)_5(H_2O)]^{3+}$  than in the Co(III) analogue, with respect to the same anion  $[M(CN)_4]^{2-}$  ( $M = Ni, Pd, Pt$ ) For this reason, the diffusion of the water would be enhanced and the activation energy would be lower than that expected for the CFAE values.

This same concept can also explain the differences between the kinetic parameters of the Pt complexes compared with the Ni and Pd analogues. In the Pt compounds there is a rearrangement in the lattice to permit the Pt–Pt interactions; this rearrangement creates more free space and allows the water molecule to escape easily. Effectively only when we find Pt–Pt interactions in the UV spectra (as in our case and in the Co(III) analogue [2]) is the  $E_a$  lower. When there is no Pt–Pt interaction, as in *trans*-[CrF(amine)<sub>2</sub>(H<sub>2</sub>O)] [Pt(CN)<sub>4</sub>] [21] the activation energy is very similar to the Ni and Pd analogues.

Furthermore, the entropy of activation calculated from the expression

$$\ln[(Kh)/(K_B T)] = \Delta S^\ddagger/R - \Delta H^\ddagger/RT$$

( $K$  = rate constant)

may also indicate the differences between the Ni, Pd and Pt compounds (Table III and Fig. 4). According to House [4] the entropy effect may be explained by the relative sizes of the ions and the free volume: where there is a large space between the cations and anions (as we suppose in the Pt compounds) the water molecule may be able to slip into an 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

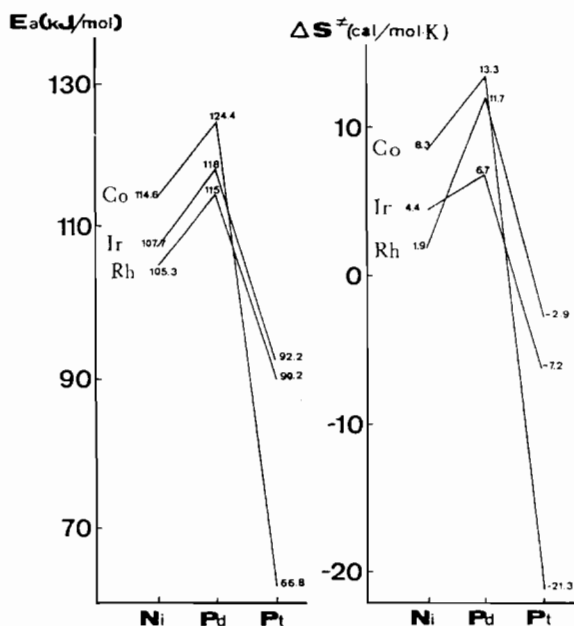


Fig. 4. Variation of  $E_a$  and  $\Delta S^\ddagger$  in the nine new products  $[M(NH_3)_5(H_2O)]_2[M'(CN)_4]_3$  ( $M = Co, Rh, Ir; M' = Ni, Pd, Pt$ ) (interpretation in the text).

interstitial position only with considerable lattice expansion so that the entropy of activation is positive.

Finally, the DSC runs also indicate a difference in the Pt cases. In the Co(III) series, the Pt compound presents a small endothermic peak ( $\Delta H = 3-4$  kJ/mol) between 55–75 °C before the dehydration–anation reaction. This peak can indicate a variation in the specific heat produced by the previous rearrangements to the main reaction (dehydration–anation). In the Rh(III) and Ir(III) complexes there is no previous peak but only a great difference in the slope, indicating also a difference in the specific heat of the components. This difference is less marked in the Ir(III)–Pt compound. Consequently, the DSC runs clearly indicate that the Pt–Pt interaction diminishes in the  $Co > Rh > Ir$  order, which agree with the electronic and TG measurements (see above).

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