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

Solid-State Kinetic Parameters and Mechanism for the Deaquation–Anation of Hexacyanochromate(III) and Nitrosylpentacyanochromate(I) of Aquopentaamminechromium(III), -cobalt(III), -rhodium(III), and -iridium(III)

JOAN RIBAS,* ALBERT ESCUER, and MONTSERRAT MONFORT

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Five new dinuclear complexes, $[(NH_3)_5MNCCr(CN)_5]$ (M = Rh, Ir) and $[(NH_3)_5MNCCrNO(CN)_4]$ (M = Co, Rh, Ir), have been obtained by solid-state reaction of the corresponding double complexes $[M(H_2O)(NH_3)_5][Cr(CN)_6]$ and $[M(H_2O)(NH_3)_5][CrNO(CN)_5]$. This solid-state deaquation–anation has been studied by thermogravimetric measurements in both nonisothermal and isothermal conditions. The activation energies so obtained are 104 ± 5 for $[Co(H_2O)(NH_3)_5][CrNO(CN)_5]$, 114.5 ± 2 for $[Rh(H_2O)(NH_3)_5][Cr(CN)_6]$, 118.6 ± 1 for $[Rh(H_2O)(NH_3)_5][CrNO(CN)_5]$, 132.5 ± 5 for $[Ir(H_2O)(NH_3)_5][Cr(CN)_6]$, and 127.8 ± 5 for $[Ir(H_2O)(NH_3)_5][CrNO(CN)_5]$ (all values in kJ/mol). These values are found on the basis of isothermal methods, applying all the expressions for the solid-state models (growth, nucleation, nucleation–growth, and diffusion). These low values indicate an S_N1 dissociative mechanism with an activated complex of square-based pyramidal geometry. The low values for the Rh(III) and Ir(III) compounds are explained in terms of the size ratio between cations and anions, which allows the water molecules to escape easily from the crystal lattice in the more voluminous $[Ir(H_2O)(NH_3)_5]^{3+}$ complexes.

Introduction

The solid-phase thermal reaction of the doubly complexed salts $[M(H_2O)(NH_3)_5][M'(CN)_6]$ (M, M' = Co, Cr) has been largely studied since Haim and co-workers prepared the dinuclear $[(NH_3)_5CoNCCo(CN)_5]$ from $[Co(H_2O)(NH_3)_5][Co(CN)_6]$.[1,2] One more systematic study has been recently reported by Uehara[3] and co-workers that discusses the results of the decomposition of nine doubly complexed salts of this type, under quasi-isothermal and dynamic conditions.

With respect to the first step of the decomposition process, i.e. the loss of the molecule of coordination water from $[M(H_2O)(NH_3)_5]^{3+}$ with formation of a dinuclear compound with cyano bridge $[(NH_3)_5MNCM'(CN)_5]$, the literature data indicate that when M = Cr, the decomposition is very complicated because, on heating, these complexes evolve water, ammonia, and hydrocyanic acid in a single step[3,4] and the corresponding dinuclear complex cannot be obtained;[5] when M = Co(III), this loss of the first water molecule is easy to separate from the next decomposition only in the $[Co(H_2O)(NH_3)_5][Co(CN)_6]$ compound.[1,2] Instead, in the doubly complexes salt $[Co(H_2O)(NH_3)_5][Cr(CN)_6]$ a rather steep weight loss can be seen at about 110–120 °C in the TG curve, which corresponds to the evolution of 1 mol of water, but the structure of the intermediate $[(NH_3)_5CoNCCr(CN)_5]$ cannot clearly be identified because of the subsequent decomposition.[3,4]

The mechanism of this dehydration–anation process has been only studied in $[Co(H_2O)(NH_3)_5][Co(CN)_6]$ by the calculation of the kinetic parameters in both nonisothermal and isothermal measurements.[6]

Taking into account the method described by the said authors, we think that the most accurate value for E_a is 143.8 ± 7 kJ/mol, calculated by House and Smith from isothermal measurements.[6] The mechanism may be explained in terms of an S_N1 process that supposes Frenkel defect formation by elimination of water molecules and subsequent formation of square-based pyramid activated complex.[7,8] If we assume this S_N1 mechanism, the activation energy must be almost independent of the entering anion and relatively small. On the other hand, according to the difference between the size of the cation and anion, the water molecule may be more or less able to slip into an interstitial position (Frenkel defect) and to escape from the crystal.

The primary purpose of the present work is, therefore, to investigate the kinetic parameters and the mechanism of the thermal dehydration–anation of the doubly complexed salts in which the cation moiety consists of $[M(H_2O)(NH_3)_5]^{3+}$ (M = Cr, Co, Rh, and Ir) and the anion moiety $[Cr(CN)_6]^{3-}$ and $[CrNO(CN)_5]^{3-}$ and to study the influence of these very similar anions on the ammine cations with increasing size (Co < Rh < Ir). We compare these results with those previously reported by us[9] for $[M(H_2O)(NH_3)_5][Co(CN)_6]$ (M = Co, Rh, and Ir), and we discuss the influence of the size ratio between cations of increasing volume and similar anions on the calculated kinetic parameters.

Experimental Section

Preparation of the Starting Materials for Obtaining Double Complexes. $[Cr(H_2O)(NH_3)_5](ClO_4)_3$,[10] $[Co(H_2O)(NH_3)_5](ClO_4)_3$,[11] $[Rh(H_2O)(NH_3)_5](ClO_4)_3$,[12] $[Ir(H_2O)(NH_3)_5](ClO_4)_3$,[13] $K_3[Cr(CN)_6]$,[14] and $K_3[CrNO(CN)_5]$[15] were prepared by the same methods as those reported in the literature, and they were identified by means of elemental analyses and spectrophotometric measurements.

Preparation of the Double Complexes. It should be indicated that the double complexes obtained were not recrystallized because they are sparingly soluble in water and in the more common solvents; therefore, the starting materials for use in the preparation of the double complexes must be fully purified beforehand.

A solution of 0.02 mol of $[M(H_2O)(NH_3)_5](ClO_4)_3$ (M = Cr, Co, Rh, Ir) in the minimum amount of ice-cold water is gradually added with continuous stirring to a solution of 0.02 mol of $K_3[Cr(CN)_6]$ and $K_3[CrNO(CN)_5]$ in the minimum amount of water, passed through an Amberlite cation-exchange resin in its ammonia form. After a few minutes precipitates began to appear. The mixture was then allowed to stand in a refrigerator overnight to complete its precipitation. The precipitate thus obtained was collected by filtration, washed several times with ice-cold water, ethanol, and ether, and air-dried.

All the double complexes were obtained in almost quantitative yields. Table I summarizes the analytical data for the complexes obtained.

IR Measurements. The IR spectra of the samples were measured with a Beckman IR-20-A spectrophotometer, purged with dry air, by the KBr disk method or Nujol suspension.

TG Studies. Themogravimetric studies were carried out on a Perkin-Elmer Model TGS-1 system in a nitrogen atmosphere, the sample

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Table I. Analytical Data

compd	% anal. found (calcd)				
	Cr	Co	C	N	H
$[CrH_2O(NH_3)_5][Cr(CN)_6]$ (I)	28.3 (28.65)		19.6 (19.83)	41.7 (41.62)	4.7 (4.68)
$[CrH_2O(NH_3)_5][CrNO(CN)_5]$ (II)	28.5 (28.33)		16.6 (16.34)	41.9 (41.98)	4.6 (4.63)
$[CoH_2O(NH_3)_5][Cr(CN)_6]$ (III)	14.3 (14.05)	15.8 (15.92)	19.3 (19.46)	41.7 (41.63)	4.5 (4.59)
$[CoH_2O(NH_3)_5][CrNO(CN)_5]$ (IV)	14.1 (13.90)	15.8 (15.76)	16.1 (16.09)	41.5 (41.17)	4.5 (4.54)
$[RhH_2O(NH_3)_5][Cr(CN)_6]$ (V)	12.8 (12.56)		17.2 (17.39)	37.8 (37.20)	4.1 (4.10)
$[RhH_2O(NH_3)_5][CrNO(CN)_5]$ (VI)	12.2 (12.44)		14.6 (14.35)	36.9 (36.84)	4.0 (4.06)
$[IrH_2O(NH_3)_5][Cr(CN)_6]$ (VII)	10.5 (10.33)		14.2 (14.31)	29.8 (30.60)	3.2 (3.37)
$[IrH_2O(NH_3)_5][CrNO(CN)_5]$ (VIII)	10.4 (10.25)		11.6 (11.83)	30.2 (30.36)	3.2 (3.35)
$[(NH_3)_5CoNCCrNO(CN)_4]$ (IX)	14.6 (14.61)	16.4 (16.56)	16.8 (16.86)	43.3 (43.27)	4.2 (4.21)
$[(NH_3)_5RhNCCr(CN)_5]$ (X)	13.4 (13.13)		18.2 (18.18)	38.7 (38.84)	3.6 (3.78)
$[(NH_3)_5RhNCCrNO(CN)_4]$ (XI)	13.2 (13.00)		15.1 (15.00)	38.4 (38.50)	3.7 (3.75)
$[(NH_3)_5IrNCCr(CN)_5]$ (XII)	10.6 (10.72)		14.7 (14.84)	31.8 (31.74)	3.1 (3.09)
$[(NH_3)_5IrNCCrNO(CN)_4]$ (XIII)	10.5 (10.63)		12.2 (12.26)	31.0 (31.18)	3.0 (3.07)

Table II. Initial and Final Temperatures for the Dynamic Thermograms Corresponding to the Loss of Coordinated Water

compd	t_{in}, °C	t_f, °C	wt loss equiv
$[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$	80	contin wt loss	
$[Cr(H_2O)(NH_3)_5][CrNO(CN)_5]$	80	contin wt loss	
$[Co(H_2O)(NH_3)_5][Cr(CN)_6]$	100	170 (inflecn)	1 H_2O + $^1/_2$ HCN
$[Co(H_2O)(NH_3)_5][CrNO(CN)_5]$	100	145[a] (inflecn)	1 H_2O
$[Rh(H_2O)(NH_3)_5][Cr(CN)_6]$	90	150[b]	1 H_2O
$[Rh(H_2O)(NH_3)_5][CrNO(CN)_5]$	100	150[b]	1 H_2O
$[Ir(H_2O)(NH_3)_5][Cr(CN)_6]$	130	180[b]	1 H_2O
$[Ir(H_2O)(NH_3)_5][CrNO(CN)_5]$	130	180[b]	1 H_2O

[a] After the inflection the compound loses weight with a lower rate. [b] An almost horizontal line is observed after the water loss for these four salts; further decomposition starts at 200 °C.

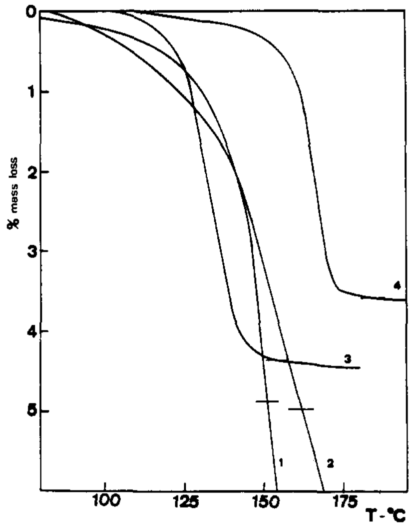

Figure 1. Nonisothermal TG curves for $[M(H_2O)(NH_3)_5][Cr(CN)_6]$ (M = Co (1); Cr (2); Rh (3); Ir (4). The horizontal lines indicate a mass loss corresponding to 1 mol of water.

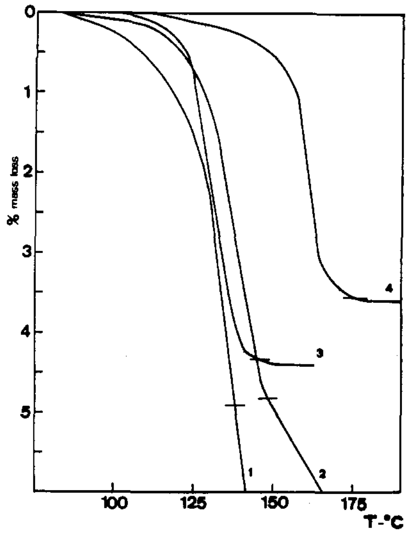

Figure 2. Nonisothermal TG curves for $[M(H_2O)(NH_3)_5][CrNO(CN)_5]$ (M = Cr (1); Co (2); Rh (3); Ir (4). The horizontal lines indicate a mass loss corresponding to 1 mol of water.

size being in the range of 5–7 mg. The heating rate for nonisothermal experiments was 5 °C/min. The kinetic parameters were determined on the basis of the general kinetic relation[16]

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

In this work we have used all the principal expressions of $f(\alpha)$ indicated in the literature,[16] following the four physical models of solid-state chemistry: nucleation, growth, nucleation–growth, and diffusion. To find the real kinetic parameters, we have compared the variable values obtained for nonisothermal measurements with the almost constant values for any model in the isothermal measurements and we have taken into account the best r^2 (regressions coefficient) value. In the nonisothermal measurements we employed the approximation of Coats and Redfern.[17] For the isothermal analysis, an isothermal preheating at low temperature (50–60 °C) was carried out until weight stabilization.

Results

(a) Dynamic TG of the Double Complexes. The nonisothermal TG curves for the solid-phase thermal deaquation of $[M(H_2O)(NH_3)_5][Cr(CN)_6]$ and $[M(H_2O)(NH_3)_5][CrNO(CN)_5]$ are given in Figures 1 and 2, respectively. The initial and final temperatures and weight loss in each case is indicated in Table II. When M = Cr(III), there is a continuous mass loss from 80 °C, as has already been described by Uehara et al.[3]; when M = Co(III), if the anion is $[Cr(CN)_6]^{3-}$, there is simultaneous loss of H_2O and HCN, as has been described by House[2] and Uehara.[3] In the other five cases (IV–VIII) there is a mass loss corresponding exactly to 1 mol of water for each mole of product. In these five cases a new compound was obtained at the end of the curve (or at the end of the isothermal runs, which will be reported below). This new product corresponds to $[(NH_3)_5MNCCr(CN)_4L]$ (M = Co, Rh, Ir; L = CN, NO) according to analysis and IR measurements (see below).

After the water loss, the $[Co(H_2O)(NH_3)_5][CrNO(CN)_5]$ complex immediately begins to decompose. There is no horizontal region in the TG curve. Instead, the Ir runs can be prolonged until 200–220 °C without significant decomposition. The Rh compounds have an intermediate behavior (Figures 1 and 2; Table II).

(b) Characterization of the Double Complexes and Dinuclear Compounds Formed by Heating. All the compounds are isostructural and with $[Co(NH_3)_6][Co(CN)_6]$ and $[Co(NH_3)_6]$-$[Cr(CN)_6]$, whose structures are known.[18] Previous study of this

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Table III. Selected IR Spectral Bands (cm^{-1})

	ν(CN)	$\delta(NH_2)$	$\rho(NH_2)$
$[Cr(H_2O)(NH_3)_5](ClO_4)_3$		1315 (vs)	750 (vs)
$[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$	2120 (vs)	1345 (vs)	775 (vs)
$[Cr(H_2O)(NH_3)_5][CrNO(CN)_5]$	2130 (vs)	1340 (vs)	775 (vs)
$[Co(H_2O)(NH_3)_5](ClO_4)_3$		1310 (vs)	830 (s)
$[Co(H_2O)(NH_3)_5][Cr(CN)_6]$	2120 (vs)	1350 (vs)	840 (s)
$[Co(H_2O)(NH_3)_5][CrNO(CN)_5]$	2095 (vs)	1340 (vs)	835 (s)
$[(NH_3)_5CoNCCrNO(CN)_4]$	2100 (vs) 2150 (s)	1320 (s)	835 (m)
$[Rh(H_2O)(NH_3)_5](ClO_4)_3$		1335 (vs)	845 (vs)
$[Rh(H_2O)(NH_3)_5][Cr(CN)_6]$	2120 (vs)	1365 (vs)	860 (vs)
$[Rh(H_2O)(NH_3)_5][CrNO(CN)_5]$	2105 (vs)	1350 (vs)	855 (vs)
$[(NH_3)_5RhNCCr(CN)_5]$	2120 (vs) 2185 (s)	1340 (vs)	860 (vs)
$[(NH_3)_5RhNCCrNO(CN)_4]$	2105 (vs) 2160 (m)	1335 (vs)	850 (m)
$[Ir(H_2O)(NH_3)_5](ClO_4)_3$		1370 (vs)	850 (vs)
$[Ir(H_2O)(NH_3)_5][Cr(CN)_6]$	2115 (vs)	1390 (vs)	885 (s)
$[Ir(H_2O)(NH_3)_5][CrNO(CN)_5]$	2105 (vs)	1390 (vs)	885 (vs)
$[(NH_3)_5IrNCCr(CN)_5]$	2125 (vs) 2155 (s)	1355 (vs)	875 (s)
$[(NH_3)_5IrNCCrNO(CN)_4]$	2105 (vs) 2160 (m)	1355 (s)	880 (s)

isostructuralism has been already reported by us.[19] Taking into account the importance of this isostructuralism in order to discuss the variation in the kinetic parameters in the Co, Rh, Ir series, it will be very useful to summarize here the results: all the complexes belong to the spatial group $R\bar{3}$, with $Z = 1$; the M and M′ atoms are placed on the $\bar{3}$ axis. The structure consists of a pair of $[M(H_2O)(NH_3)_5]^{3+}$ and $[Cr(CN)_6]^{3-}$ or $[Cr(NO)(CN)_5]^{3-}$ ions placed in a rhombohedral cell having the CsCl structure type.

The IR spectra of all these complexes show the typical bands of the CN, NH_3, and H_2O groups. The three more characteristic bands are ν(CN), $\delta_s(NH_3)$, and $\rho(NH_3)$ (Table III). The $\delta_s(NH_2)$ is shifted 20–30 cm^{-1} toward higher frequencies in the double salts, with regard to the starting perchlorate. The rocking band is also shifted toward higher frequencies, increasing about 30 cm^{-1} in the Ir(III) compounds.

These shifts are consistent with the existence of hydrogen bonding between anion and cation, as has been pointed out by Nakamoto[20] and Novak[21] in similar complexes. Such hydrogen bonding has been shown in the $[Co(NH_3)_6][Co(CN)_6]$ structure,[18] with an N···H···N distance of 3.0006 Å.

The more important region for the characterization of these cyano complexes is the ν(CN) stretching region between 2000 and 2200 cm^{-1}.[22] In the doubly complexed salts it appears as a very strong and defined band (Table III), according to the literature data for $[Cr(CN)_6]^{3-}$ and $[CrNO(CN)_5]^{3-}$ salts.[22] In the dinuclear complexes with the μ-CN ligand there is a significant difference with respect to the starting double complexes. There appears a very intense and perfectly defined doublet in the ν(CN) zone (Table III). The clear splitting of the CN stretching frequencies is a good evidence for a bridging cyano group.[23] According to the literature data, the component occurring at lower frequency is assigned to ν(CN) of the terminal cyano group, while that appearing at higher frequency is attributed to ν(CN) of the bridging cyano group.[23]

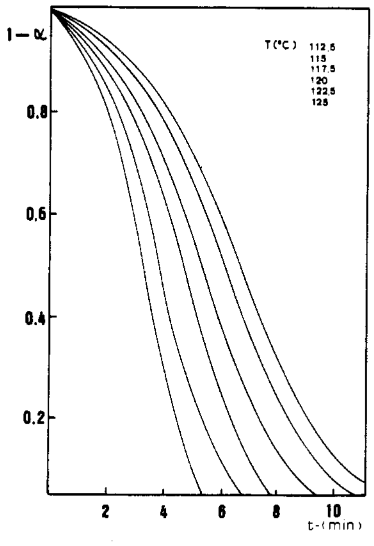

Figure 3. Isothermal TG curves (indicating the temperature) for $[Rh(H_2O)(NH_3)_5][CrNO(CN)_5]$. The other four complexes show very similar curves. The curves are cut at $\alpha = 0.05$ in order not to lengthen the abscissa (approximately 45 min may be necessary to arrive at $\alpha = 0$).

(c) Kinetic Parameters. Kinetic parameters are very difficult to calculate unambiguously from only nonisothermal TG curves,[24] due to the fact that the true $g(\alpha)$ expression of the solid-state model is not known. For this reason we have recorded not only the nonisothermal TG curves (Figures 1 and 2) for each compound but also the isothermal TG curves at several different temperatures (Figure 3) for each compound. In both methods (nonisothermal and isothermal) all the principal expressions of $g(\alpha)$ reported in the literature[16] 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 E_a and k_0 have been deduced from the isothermal curves, since the values so obtained are almost independent of the solid-state model proposed.[25] The average kinetic parameters taking into account the model proposed are given in Table IV.

With regards to the physical model (solid-state mechanism), many investigations made so far with nonisothermal methods accept or assume the reaction mechanism, i.e. a specific function $g(\alpha)$ or $f(\alpha)$. In order to avoid assumptions, we consider that the reaction mechanism may be established by comparing the dynamic and isothermal results, as also suggested by other authors.[26,27] The advantage of this method is the fact that one does not assume the mechanism and the order of the reaction, but all kinetic parameters are determined from experimentals results.

In the cases studied here, the comparison is not unequivocal. Effectively,[25] in all cases but $[RhH_2O(NH_3)_5][CrNO(CN)_5]$, which agrees unequivocally with the Avrami law with $n = 2–3$, there is a good correspondence for the Avrami–Erofeev law with $n = 1.5–3$ (according to the specific case) and power law with $n = 1–2$. There is no agreement for the growth model.

In order to choose the appropriate solid-state mechanism it is necessary to take into account two things: (a) the best regression coefficient, r^2; (b) the shape of the isothermal curves. The Avrami–Erofeev model gives, in all our cases, a best r^2. Furthermore, due to the sigmoid shape of the isothermal curves it is probable that the solid-state model corresponds effectively to the nucleation-growth, according to the Avrami–Erofeev law. The literature[16] indicates that the sigmoid shape agrees with the Avrami law; the greater the sigmoid shape, the higher n value. In our cases, the sigmoid shape of the curves is rather pronounced and corresponds approximately to n(av) = 2.

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Table IV. Average Kinetic Parameters

compd	solid-state mech	E_a, kJ/mol	k_0
$[Co(H_2O)(NH_3)_5][CrNO(CN)_5]$	Avrami-Erofeev, $n = 1.5$	104.1 ± 5	0.66×10^{13}
$[Rh(H_2O)(NH_3)_5][Cr(CN)_6]$	Avrami-Erofeev, $n = 2$	114.5 ± 2	0.49×10^{15}
$[Rh(H_2O)(NH_3)_5][CrNO(CN)_5]$	Avrami-Erofeev, $n = 2$	118.6 ± 1	0.16×10^{16}
$[Ir(H_2O)(NH_3)_5][Cr(CN)_6]$	Avrami-Erofeev, $n = 2$	135.2 ± 5	0.11×10^{17}
$[Ir(H_2O)(NH_3)_5][CrNO(CN)_5]$	Avrami-Erofeev, $n = 2$	127.8 ± 5	0.30×10^{16}

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

mech	intermed	CFAE	$[Co(H_2O)(NH_3)_5]^{3+}$ $Dq = 25$ kJ/mol	$[Rh(H_2O)(NH_3)_5]^{3+}$ $Dq = 38$ kJ/mol	$[Ir(H_2O)(NH_3)_5]^{3+}$ $Dq = 45$ kJ/mol
dissociative	square-based pyramid	$4Dq$	100	152	180
	trigonal bipyramid	$11.48Dq$	287	436	516
associative	pentagonal bipyramid	$8.52Dq$	213	323	383
	octahedral wedge	$3.63Dq$	91	138	163

Discussion on the Mechanism of Solid-State Anation

House[7] has recently proposed several mechanisms in the thermal dehydration–anation reaction of solid complexes, determined by various types of defects: Schottky 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. Following the crystal field model of Basolo and Pearson[28] the transition stated (activated complexes) and the CFAE (crystal field activation energy) values for each metal are given in Table V (the Dq values for Co(III), Rh(III), and Ir(III) are those indicated by Huheey[29]). If the mechanism were associative, only the octahedral wedge transition state would give the CFAE values agreeing to the experimental data (the values for the pentagonal-bipyramidal transition state are too high). However, considering that in the S_N2 reaction the heptacoordination suggests a Shottky-type defect formation in an ionic crystal, it requires high energy ($E_{Shot} = 0.34U$, U being the lattice energy[30]). In our case, the ionic charge is 3^+ and 3^-; therefore, the lattice energy must be very large. Consequently, we should find a value of E_a greater than the values found by us (Table IV).

The mechanism, therefore, might be a S_N1 (dissociative) with the formation of a square-base pyramid activated complex. If we suppose a trigonal-bipyramidal activated complex, it would require a very large CFAE, incompatible with our experimental data. Consequently, the transition state is determined by the water loss and nonionic Frenkel defect formation. This implies, a priori, essentially no variation of the activation energy for a given cation, regardless of the anions, in which the mechanism would be identical. Effectively, for $[Cr(CN)_6]^{3-}$ and $[CrNO(CN)_5]^{3-}$ there is a good agreement in the kinetic parameters.

But there is no perfect agreement between our experimental results and the CFAE theory of the Basolo and Pearson. Effectively, according to this theory (Table V) the CFAE for Ir(III) is 180 kJ/mol, 152 kJ/mol for Rh(III), and 100 kJ/mol for Co(III). Therefore, the E_a for Rh(III) and Ir(III) complexes would be expected to increase by 1 order of magnitude. The experimental results are different. In the Co(III) case, the E_a value is greater than the contribution of CFAE (100 kJ/mol), which seems reasonable. But in the Rh(III) and Ir(III) complexes the E_a values are lower than the CFAE contribution (as compared in Tables IV and V).

Due to the repetition of TG measurements, this factor cannot be attributed to the experimental error, but it is constitutive of the compounds. On the other hand, we have found the same anomaly in the isostructural series $[M(H_2O)(NH_3)_5][Co(CN)_6]$ (M = Co, Rh, Ir).[9] In this case, this anomaly is more pronounced, because the E_a values are approximately 130, 120, and 100 kJ/mol, respectively. The Ir(III) compound presents the lowest E_a value.

Why this anomaly? According to the Basolo and Pearson theory[28] there are other unknown factors to add to Dq (these factors can be either positive or negative). House[6], on the other hand, already indicates that even the recent literature persists in trying to describe solid-state reactions in terms applicable to processes carried out in the homogeneous phase (gas or solution). And it is not correct: it is necessary to take into account the factors derived from the relative size of the ions, which was not possible, until now, to quantify. For a given size of anion (in our case $[Cr(CN)_6]^{3-}$ and $[CrNO(CN)_5]^{3-}$ are very similar), diffusion of interstitial defects depends on the size of the cation or on the comparative size of anion and cation.[30] In fact, interstitial diffusion of Frenkel defects is enhanced by a greater difference in size between ions (the volume of free space is greater). Thus, if water is set free from the complex ion in forming the transition state, the space of the water molecule will be facilitated for $[Ir(H_2O)(NH_3)_5]^{3+}$, the largest cation.[19] For this reason, the diffusion of water would be enhanced and the activation energy would be lower than the expected for the CFAE values.

Naturally, this reasoning will be valid only if the known structures are similar (isostructuralism), as is in our case. Consequently, the difference in the free space cannot be attributed to the structural differences but to the relataive size of the ions.

The importance of this concept of free space has already been studied and reported by us in several series of complexes like $[Co(H_2O)(NH_3)_5]_2[M(CN)_4]_3$[31] (M = Ni, Pd, Pt), three isostructural salts in which the E_a value of the Pt compound is lower due to the formation of strong Pt–Pt interactions in the crystal lattice.[31] These interactions allow the molecule of water to escape easily from the crystal. In the series *trans*-$[CrF(H_2O)(aa)_2][M(CN)_4]$ (aa = ethylenediamine, 1,3-diaminopropane, 1,2-diaminocyclohexane) we have also found that the greater the ligand volume, the lower the activation energy.[32]

Conclusions

A dissociative mechanism for the deaquation–anation reactions

$$[M(H_2O)(NH_3)_5][Cr(CN)_6] \rightarrow [(NH_3)_5MNCCr(CN)_5] + H_2O$$

$$[M(H_2O)(NH_3)_5][CrNO(CN)_5] \rightarrow [(NH_3)_5MNCCrNO(CN)_4] + H_2O$$

$$M = Co(III), Rh(III), Ir(III)$$

is proposed from TG measurements (isothermal and nonisothermal), but the calculated activation energy is not constant, being the Rh(III) and Ir(III) cases lower than the expected values taking into consideration the CFAE theory of Basolo and Pearson. We propose that it is due to the different size ratio between cations

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and anions, which allows the water molecule to escape easily from the crystal lattice in the more voluminous $[Ir(H_2O)(NH_3)_5]^{3+}$ complexes.

Since there are few studies of solid-state reactions of Rh(III) and Ir(III), we hope, in the future, to study this apparent anomaly in other complexes of $[Rh(H_2O)(NH_3)_5]^{3+}$ and $[Ir(H_2O)(NH_3)_5]^{3+}$ with several other entering anions to compare with the behavior of the known Co(III) analogues. It is hoped that such work will determine whether the relative size of the ions and the free space is effectively more important than the *Dq* contribution of the metal ion.

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Supplementary Material Available: Tables of computational parameters for $[M(H_2O)(NH_3)_5][Cr(CN)_6]$ (M = Rh, Ir) from both nonisothermal and isothermal measurements (2 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie de Coordination, Université de Provence, the Service de Cristallochimie, and the Laboratoire d'Électronique, Centre St. Jérôme, 13397 Marseille Cedex 13, France

Structure and Conductivity of Chloro(phthalocyaninato)zinc Single Crystals

MIREILLE MOSSOYAN-DENEUX,*[†] DAVID BENLIAN,[†] MARCEL PIERROT,[‡] ANDRÉ FOURNEL,[§] and JEAN PIERRE SORBIER[§]

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A new crystalline form of oxidized zinc phthalocyanine has been prepared by electrolysis in organic solvent. X-ray analysis of single crystals of ZnPcCl, grown at a Pt anode, shows helical stacks of bimolecular aggregates that allow, in different ways, inter-aromatic-ring overlaps. We can notice both an exceptionally large outward axial shift of the zinc and a rigorous planarity of the Pc ring. FT-IR spectra of both ZnPc and ZnPcCl confirm the structural differences between the two materials. The integral oxidation number and the structure are consistent with the intrinsic semiconductor properties demonstrated by the resistivity measurements. The new material, ZnPcCl, is characterized by a rather narrow gap and a transition point at ~230 K.

Reports, including X-ray crystal structure studies, have been published on molecular conductors and molecular semiconductors. Some of these compounds are metal phthalocyanines modified by oxidative insertion of iodine.[1-4]

Among these, few attempts of crystal growth at an electrode are mentioned, in spite of the well-known electrochemistry of macrocyclic complexes. The present paper describes an original compound obtained by electrooxidation from an organic solution. This compound has remarkable electronic properties, comparable to those of halogen-doped phases. The X-ray structure of the material shows striking similarities to that of the metallic conductor NiPcI.[1] The vibrational spectra and the conductivity data of the new material are discussed in accordance with the structural features and in comparison with other results published on similar compounds.

Experimental Section

Preparation. ZnPc, obtained by the usual synthesis,[5] was purified by repetitive sublimation and precipitation from a H_2SO_4 solution. Electrolysis was performed on a two-electrode system. Amperostatic regulation was maintained for about 200 h, to collect large enough crystals from the anode. Some pulverulent material with identical properties settled on the bottom of the vessel.

No elemental analysis could be done, but sweeping microscopic examination showed well-formed crystals on which X-ray analysis by energy gave invariably the ratio Zn/Cl = 1.

Crystal Structure. A 0.4 × 0.15 × 0.6 mm³ crystal with no particular feature was selected, and a precession chamber study (Mo Kα, λ = 0.70 Å) gave the space group $P4/nnc$ (No. 126[6]). Systematic extinctions are found for $hk0$ ($h + k = 2n + 1$), $0kl$ ($k + l = 2n + 1$), and hhl ($l = 2n + 1$). Parameters have been refined on an automatic diffractometer (Enraf-Nonius CAD4 with a graphite monochromator). The unit cell dimensions and volume are a = 13.85 (1) Å, c = 13.09 (1) Å, and V = 2511 Å³. With the theoretical formula $ZnC_{32}H_{16}N_8Cl$ and for four molecules per unit cell, the calculated density of 1.62 agrees with the observed density of 1.58 obtained by flotation of the crystal in $ZnCl_2$ solutions. Data were collected with a ω–2θ scan (θ_{max} = 27°). Intensity was controlled (maximum deviation <1%) on three standard reflections checked at 3600-s intervals. The orientation of the crystal was verified every 100 measurements. A total of 1200 data having $F_o^2 > 3\sigma(F_o^2)$ were used for initial refinements. A total of 1014 reflections *hkl*, *khl* were

Table I. Summary of Crystal Data and Intensity Collection

compd	$ZnC_{32}H_{16}N_8Cl$
cryst dimens, mm	0.4 × 0.15 × 0.6
space group	$P4/nnc$ (No. 126)
a, Å	13.85 (1)
c, Å	13.09 (1)
V, Å³	2511
Z	4
density, g/cm³	1.62 (calcd) 1.58 (obsd)
radiation	graphite–monochromated Mo Kα (λ = 0.707 Å)
μ, cm⁻¹	110
scan	ω–2θ, θ_{max} = 27°
scan angle	0.8 + 0.35 tan θ
slit aperture	2.0 + 0.5 tan θ
t_{max}, s	120
unique data with $F_o^2 > 3\sigma F_o^2$	665 (after averaging Friedel pairs)
R_I	0.098
R_w	0.11

Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z
Zn(1)	0.250	0.250	0.5840 (4)
Cl(1)	0.250	0.250	0.4041 (6)
N(1)	0.189 (1)	0.123 (1)	0.630 (2)
N(2)	0.332 (1)	0.020 (1)	0.628 (2)
C(1)	0.237 (1)	0.036 (1)	0.629 (2)
C(2)	0.165 (1)	−0.043 (1)	0.627 (2)
C(3)	0.176 (1)	−0.142 (1)	0.627 (2)
C(4)	0.092 (2)	0.197 (1)	0.632 (3)
C(5)	0.002 (2)	0.155 (1)	0.630 (2)
C(6)	−0.011 (1)	−0.055 (1)	0.629 (2)
C(7)	0.072 (1)	−0.000 (1)	0.628 (2)
C(8)	0.092 (1)	0.104 (1)	0.630 (1)

[†] Laboratoire de Chimie de Coordination, Université de Provence.

[‡] Service de Cristallochimie.

[§] Laboratoire d'Electronique.

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