	ZnCl$_2$	ZnBr$_2$	ZnI$_2$
l(Zn–X), Å	0.061	0.063	0.066
K(Zn–X), Å	0.022	0.028	0.029

On the basis of these K values, the r_α bond angles for all three molecules are 180°, well within experimental error, viz. 179.7, 179.6, and 179.8° for ZnCl$_2$, ZnBr$_2$, and ZnI$_2$ with estimated total errors, 2.0, 1.4, and 1.4°, respectively.

Discussion

The molecular parameters of zinc dihalides, ZnX$_2$, X = Cl, Br, I, are well determined. It is noteworthy that the early results of Akishin and Spiridonov[12] are in good agreement with the present work if error limits are considered (Table II).

Our electron diffraction data in conjunction with available spectroscopic information from Loewenschuss and Givan[13,14] reveal the unambiguously linear configuration of ZnCl$_2$, ZnBr$_2$, and ZnI$_2$ molecules. This is not surprising in view of the [Ar]3d^{10}4s^2 electronic configuration of zinc and is also in agreement with the discussion of MX$_2$ structures including ZnX$_2$ molecules by Drake and Rosenblatt[24] and by Coulson.[25]

The present results and those on analogous calcium derivatives[10] well augment structural information on bond lengths of first-row transition-metal dichlorides and dibromides. The mean chloride/bromide difference is 0.140 Å with a standard deviation of 0.015 Å.

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Contribution from the Departament de Química Inorgànica, Universitat Autònoma de Barcelona, Bellaterra (Barcelona), Spain, and Departament de Química Inorgànica, Universitat de Barcelona, Barcelona, Spain

Solid-State Kinetic Parameters for the Deaquation–Anation of the Double-Complex Salts [CoH$_2$O(NH$_3$)$_5$][CoX(CN)$_5$] (X = CN, Cl, Br, I, NO$_2$, N$_3$) and the Preparation of Dinuclear Derivatives with μ-Cyano Bridges

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Double-complex salts of formula [CoH$_2$O(NH$_3$)$_5$][Co(CN)$_5$X] (X = CN, Cl, Br, I, NO$_2$, N$_3$) have been synthesized and characterized. Dinuclear μ-CN compounds [(NH$_3$)$_5$CoNCCo(CN)$_4$X] (X = CN, Cl, Br, I, NO$_2$, N$_3$) have been prepared by controlled heating of the aforementioned double-complex salts. These dinuclear compounds have been characterized by methods such as ^{59}Co NMR spectrometry and IR and UV–visible spectrophotometry. The double-complex salts have been proven by X-ray powder diffraction techniques to be isostructural with [Co(NH$_3$)$_6$][Co(CN)$_6$]. Several unit cell parameters have been calculated and discussed. The solid-phase thermal deaquation–anation of the double-complex salts has been studied by nonisothermal methods, and several kinetics parameters have been calculated. The activation energy values of these processes have been related to the unit cell parameters.

Introduction

The solid-phase thermal reaction of the double-complex salts [MH$_2$O(NH$_3$)$_5$][M'(CN)$_6$] (M, M' = Co(III), Cr(III)) has been largely studied since Haim et al. prepared the dinuclear compound [(NH$_3$)$_5$CoNCCo(CN)$_5$] from [CoH$_2$O(NH$_3$)$_5$][Co(CN)$_6$].[1,2] House[3] proposed general mechanisms for the solid-state dehydration–aquation of coordination compounds. In these, the generation of a Schottky or Frenkel type of point defect is considered in the formation of the transition state. The dehydration of [M(H$_2$O)(NH$_3$)$_5$]X$_3$ complexes as well as several double-complex salts such as [MH$_2$O(NH$_3$)$_5$][M'(CN)$_6$] has been shown to be consistent with an S$_N$1 dissociative mechanism with a Frenkel type defect generation.[4,5]

If the process takes place by an SN$_1$ pathway, the rate-determining step is the loss of the water from the cation [MH$_2$O-(NH$_3$)$_5$]$^{3+}$ and its location in an interstitial position in the lattice. The activation energy should be largely influenced by a crystal field component due to formation of a pentacoordinated transition state but almost invariant to the nature of the entering anion.

Several papers have been written pointing out the influence of the crystal field component in the activation energy.[5] Our aim is to show the influence of the different entering anions in the lattice energy component of the activation energy favoring or hindering the diffusion of the water molecule through the lattice.

We have chosen a family of *isostructural double-complex salts*, [CoH$_2$O(NH$_3$)$_5$][Co(CN)$_5$X] (X = CN, Cl, Br, I, NO$_2$, N$_3$), to prove this point. The unit cell parameters will be modified by the different X groups; consequently, varying the lattice free spaces allows a study of their influence in the activation energy of the solid-state process.

Experimental Section

Preparation of Starting Materials. K$_3$[Co(CN)$_5$X] (X = Cl, Br, I, NO$_2$) complexes were prepared from K$_3$[Co(CN)$_5$N$_3$] by a procedure already described by the authors.[6] K$_3$[Co(CN)$_5$N$_3$],[7] K$_3$[Co(CN)$_6$],[8] and [CoH$_2$O(NH$_3$)$_5$](ClO$_4$)$_3$[9] were prepared by procedures reported in the literature and identified by elemental analyses and spectrophotometric methods.

Preparation of the New Compounds [CoH$_2$O(NH$_3$)$_5$][Co(CN)$_5$X] (X = Cl, Br, I, NO$_2$, N$_3$). In a typical experiment, K$_3$[Co(CN)$_5$Cl] (1.2 g) was dissolved in a H$_2$O/glacial acetic acid (5:1) mixture. NaClO$_4$ (2 g)

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Table I. Analytical Data and Yields of All Compounds Synthesized[a]

compd	anal. found (calcd), %					yield, %	temp, °C	time, h
	C	N	H	Co	X	yield, %	temp, °C	time, h
$[CoH_2O(NH_3)_5][Co(CN)_5Cl]$	16.2 (15.5)	36.5 (36.2)	4.5 (4.4)	30.4 (30.5)	8.8 (9.2) (Cl)	70		
$[CoH_2O(NH_3)_5][Co(CN)_5Br]$	14.15 (14.0)	32.8 (32.5)	4.17 (4.0)	27.4 (27.4)	18.4 (18.6) (Br)	70		
$[CoH_2O(NH_3)_5][Co(CN)_5I]$	12.7 (12.5)	28.7 (29.3)	3.5 (3.5)	25.1 (24.7)	27.3 (26.6) (I)	62		
$[CoH_2O(NH_3)_5][Co(CN)_5N_3]$	15.51 (15.27)	47.87 (46.31)	4.33 (4.32)	29.6 (30.1)		65		
$[CoH_2O(NH_3)_5][Co(CN)_5NO_2]$	15.3 (15.1)	38.4 (38.8)	4.3 (4.3)	29.3 (29.7)		70		
$[(NH_3)_5CoNCCo(CN)_4Cl]\cdot H_2O$	15.2 (15.5)	36.3 (36.2)	4.6 (4.4)	30.3 (30.5)		72	120	8
$[(NH_3)_5CoNCCo(CN)_4Br]\cdot H_2O$	13.9 (13.9)	32.8 (32.5)	3.7 (3.9)	27.3 (27.4)		75	115	6
$[(NH_3)_5CoNCCo(CN)_4I]\cdot H_2O$	12.51 (12.56)	28.8 (29.3)	3.46 (3.56)	24.8 (24.7)		50	100	3
$[(NH_3)_5CoNCCo(CN)_4N_3]\cdot H_2O$	15.5 (15.3)	45.9 (46.3)	4.4 (4.3)	29.7 (30.0)		55	100	$2^{1}/_2$
$[(NH_3)_5CoNCCo(CN)_4NO_2]\cdot H_2O$	14.45 (15.12)	37.5 (38.8)	4.10 (4.28)	29.6 (29.7)		65	110	3

[a] Columns 8 and 9 give the heating conditions for the preparation of dinuclear compounds.

Table II. Selected IR Bands (cm⁻¹) of the Double-Complex Salts $[CoH_2O(NH_3)_5][Co(CN)_5X]$

	X = Cl⁻	X = Br⁻	X = I⁻	X = N₃⁻	X = NO₂⁻
$\nu_s(OH)$, $\nu_{as}(OH)$	3450–3500	3400–3500	3400–3600	3400–3500	3400–3600
$\nu(NH)$	3120–3280	3100–3280	3180–3280	3100–3280	3120–3260
$\nu(CN)$	2190	2190	2200	2180	2120
	2120	2120	2120	2115	
$\nu_a(NNN)^a$				2040	
$\delta_d(NH_3)$, $\delta(OH)$	1620	1600	1620	1610	1610
$\delta_s(NH_3)$, $\nu_{as}(NO_2)^b$	1395	1400	1390	1390	1380
$\nu_s(NO_2)^b$, $\delta_s(NH_3)$	1345	1350	1340	1340	1310–1340
$\nu_s(NNN)^a$				1290	
$\rho_r(NH_3)$, $\rho_r(H_2O)$	840	850	840	840	840
$\delta(NNN)^a$			660		
			575		
$\rho_w(NO_2)^b$					600–590
$\nu(CoC)$	410	410	415	405	410
$\delta(CoCN)$	360	360	360	360	360
$\delta(NCoN)$	300–310	320	310	310	310

[a] Bands due to coordinated azide group. [b] Bands due to coordinated nitro group.

was added and the resulting KClO₄ eliminated by filtration. With vigorous stirring [CoH₂O(NH₃)₅](ClO₄)₃ (1.6 g) was added in small portions. The stirring was continued until total dissolution was obtained.

The double-complex salt was then precipitated with glacial acetic acid (≃10 mL), filtered, washed with H₂O, EtOH, and Et₂O, and air-dried (yield 70%). Table I summarizes the analytical data for these compounds.

Preparation of the New Dinuclear Compounds [(NH₃)₅CoNCCo-(CN)₄X] (X = Cl, Br, I, NO₂, N₃). All these compounds were synthesized by controlled heating of the corresponding double-complex salts.

In every case heating conditions were derived from TG and IR studies. In a typical experiment, [CoH₂O(NH₃)₅][Co(CN)₅Cl] (1.0 g) was heated in an oven for 8 h at 120 °C. The crude product was recrystallized by dissolving it in H₂O (5 mL), filtered, and poured into cold EtOH (0 °C). The solid obtained was collected, washed with EtOH and Et₂O, and air-dried (yield 72%).

Table I summarizes analytical data, yields, and heating conditions for these compounds.

Techniques. Co was determined by a complexometric method with EDTA after destroying the complex with H₂SO₄.[10] C, N, and H elemental analyses were performed in our miroanalysis laboratory with a Perkin-Elmer 240-B instrument.

IR spectra were measured on a Beckman IR-20A spectrophotometer by the KBr-disk method. Electronic spectra were recorded on a Shimadzu UV-240 or Beckman Acta III spectrophotometer in aqueous solution or KBr disk if the compound was not soluble.

X-ray powder diffraction spectra were recorded on a Philips diffractometer at the Department of Inorganic Chemistry of the University of Barcelona.

⁵⁹Co NMR spectra were recorded on a JEOL FX-90Q spectrophotometer at 21.4 MHz in D₂O solution at the Department of Chemistry of the University of Michigan (Ann Arbor, MI).

Thermogravimetric curves were carried out on a Perkin-Elmer Model TGS-2 instrument. The sample size was in the range of 3–10 mg, and the heating rate was 1.25, 5, and 20 °C/min in each case. Differential scanning calorimetry was performed on a Perkin-Elmer DSC-2 instrument with a sample weight of 3–7 mg and a heating rate of 4 °C/min. All these measurements were performed at the Department of Organic

Chemistry of the University of Zaragoza. Conductivity measurements were carried out in a Radiometer CDM 3 conductimeter, on a 10⁻³ M aqueous solutions.

Results and Discussion

IR Spectra. The IR spectra of the double-complex salts are very similar and show the typical bands of the coordinated CN, NH₃, and H₂O groups. Table II summarizes the more characteristic bands $\nu(CN)$, $\delta_s(NH_3)$, and $\rho(NH_3)$ in these salts. $\delta_s(NH_3)$ and $\rho(NH_3)$ are shifted 20–30 cm⁻¹ to higher frequencies with regard to the starting perchlorate complex, [CoH₂O(NH₃)₅]-(ClO₄)₃. These shifts are consistent with the existence of hydrogen bonding between anion and cation, as has been pointed out by several authors.[11,12] Hydrogen bonding has been observed in the [Co(NH₃)₆][Co(CN)₆] molecule[13] with a N···H···N distance of 3.0006 Å. The $\nu(CN)$ stretching mode appears as a very strong and well-defined band in the 2100–2200-cm⁻¹ region according to the literature data for the parent complexes K₃[Co(CN)₅X] (X = Cl⁻, Br⁻, I⁻, NO₂⁻, N₃⁻).[14] All these compounds show a very weak band in this region at slightly higher frequencies, also indicating the existence of interionic hydrogen bonding.[15] The most important frequency interval for the characterization of the dinuclear cyano complexes is the $\nu(CN)$ stretching mode between 2100 and 2200 cm⁻¹. The $\nu(CN)$ band appears as a very intense and perfectly defined doublet (Table III). The component occurring at a lower frequency is assigned to the $\nu(CN)$ terminal cyano group, while that appearing at higher frequency is attributed to the $\nu(CN)$ bridging cyano group.[1,16]

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Table III. Selected IR Bands (cm⁻¹) of the Dinuclear Compounds [(NH₃)₅Co–NC–Co(CN)₄X]·H₂O

	X = Cl⁻	X = Br⁻	X = I⁻	X = NO₂⁻	X = N₃⁻
ν_s(OH), ν_{as}(OH)	3400–3600	3400–3600	3400–3580	3400–3600	3400–3600
ν(NH)	3100–3300	3100–3300	3100–3300	3120–3320	3100–3350
ν(CN)	2180	2180	2160	2200	2180
	2120	2120	2000	2130	2120
ν_a(NNN)ᵃ					2030
δ_d(NH₃), δ(OH)	1610	1605	1600	1615	1630
δ_s(NH₃), ν_{as}(NO₂)ᵇ	1390	1370	1380	1390	
ν_s(NO₂),ᵇ ν_s(NH₃)	1325	1310	1320	1335	1350
ρ_r(NH₃), ρ_r(H₂O)				860	
	850	850	840		860
δ(ONO)ᵇ				840	
δ(NNN)ᵃ					650
ρ_w(NO₂)ᵇ				600	
ν(CoC)	415	415	410	420	420
δ(NCoN)	320	320	310	315	310

ᵃ Bands due to coordinated azide group. ᵇ Bands due to coordinated nitro group.

Table IV. Electronic Spectra

compd	medium	λ, nm (ε)	assignt
[CoH₂O(NH₃)₅](ClO₄)₃	H₂O	490	$\{$ ¹A₁ → ¹E (C_{4v}) ¹A₁ → A₂ (C_{4v})
		342	¹A₁g → ¹T₂g (O_h)
[CoH₂O(NH₃)₅][Co(CN)₅Cl]	KBr (solid)	505	$\{$ ¹A₁ → ¹E (C_{4v}) ¹A₁ → ¹A₂ (C_{4v})
		385–390	¹A₁ → ¹E (C_{4v})
[CoH₂O(NH₃)₅][Co(CN)₅Br]	KBr (solid)	510	$\{$ ¹A₁ → ¹E (C_{4v}) ¹A₁ → ¹A₂ (C_{4v})
		395	¹A₁ → ¹E (C_{4v})
[CoH₂O(NH₃)₅][Co(CN)₅I]	H₂O	495	$\{$ ¹A₁ → ¹E (C_{4v}) ¹A₁ → ¹A₂ (C_{4v})
		440 (sh)	¹A₁ → ¹E (C_{4v})
		329	π → dz^2
[CoH₂O(NH₃)₅][Co(CN)₅NO₂]	KBr(solid)	490–500	$\{$ ¹A₁ → ¹E (C_{4v}) ¹A₁ → ¹A₂ (C_{4v})
		370	¹A₁ → ¹E (C_{4v})
		280	dπ → π*(NO₂⁻)
[CoH₂O(NH₃)₅][Co(CN)₅N₃]	H₂O	485–490	$\{$ ¹A₁ → ¹E (C_{4v}) ¹A₁ → ¹A₂ (C_{4v})
		378	¹A₁ → ¹E (C_{4v})
[(NH₃)₅CoNCCo(CN)₄Cl]·H₂O	H₂O	470 (67)	¹A₁g → ¹T₁g (O_h)
		388 (280)	¹A₁ → ¹E (C_{4v})
		330 sh (166)	¹A₁ → ¹A₂ (C_{4v})
[(NH₃)₅CoNCCo(CN)₄Br]·H₂O	H₂O	470 (80)	¹A₁g → ¹T₁g (O_h)
		395 (181)	¹A₁ → ¹E (C_{4v})
[(NH₃)₅CoNCCo(CN)₄I]·H₂O	H₂O	470 (200)	¹A₁g → ¹T₁g (O_h)
		333 (3350)	π → dz^2
[(NH₃)₅CoNCCo(CN)₄N₃]·H₂O	H₂O	485 sh	¹A₁g → ¹T₁g (O_h)
		377 (820)	¹A₁ → ¹E (C_{4v})
[(NH₃)₅CoNCCo(CN)₄NO₂]·H₂O	H₂O	473 (70)	¹A₁g → ¹T₁g (O_h)
		345 sh (437)	¹A₁ → ¹E (C_{4v})
		285 (2610)	dπ → π*(NO₂⁻)

All the compounds containing coordinated NO₂⁻ and N₃⁻ groups exhibit the corresponding IR bands in the spectra, according to the literature data.[17,18]

Electronic Spectra. Table IV summarizes the electronic spectra of these compounds and the parent compound [CoH₂O(NH₃)₅](ClO₄)₃. The electronic spectra of the double-complex salts display the features of the parent complexes, e.g. the amminated cation and the cyanurated anion.[19] The first band that appears at lower energies is attributed to the first d–d transition of the amminated Co(III) and the second band to the corresponding d–d transition of the cyanurated Co(III). The first band generally appears as a shoulder, overlapped to the more intense second band. So the values of the maxima for these transitions shown in Table IV have been found by a Gaussian analysis of this spectral region and they are in good agreement with the first maximum value found in the [CoH₂O(NH₃)₅]³⁺ ion.

The electronic spectra of the dinuclear complexes show a band at low energy attributable to the first d–d transition of the amminated moiety of the molecule. This band is shifted nearly 20 nm toward lower frequencies with respect to the band for [CoH₂O(NH₃)₅](ClO₄)₃. This is in accordance with other dinuclear

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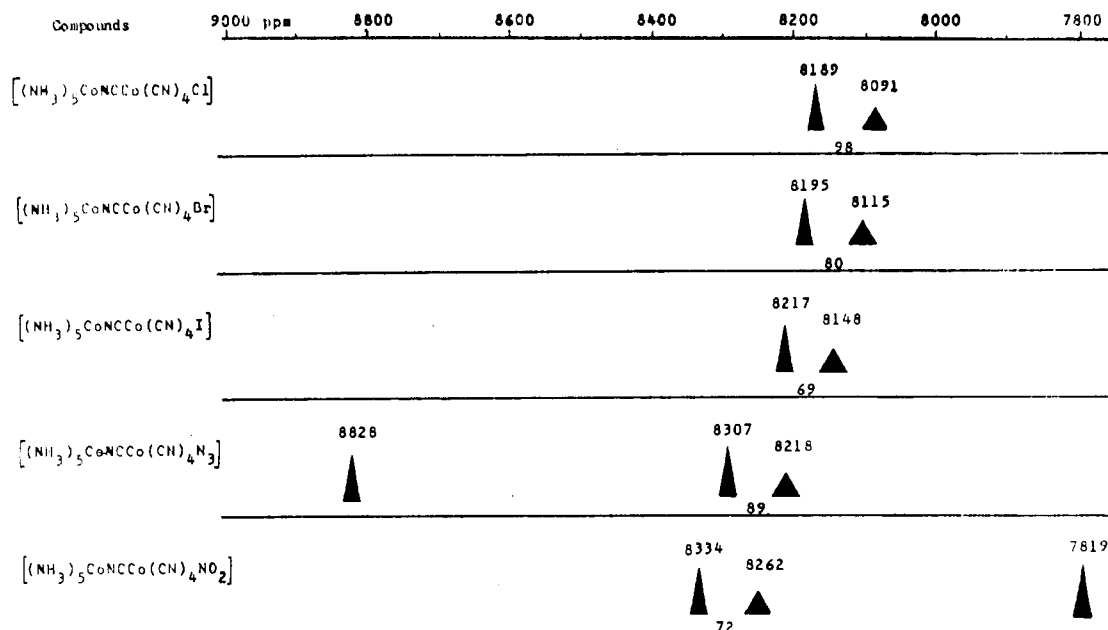**Figure 1.** ^{59}Co NMR spectra with schematic representations of the shapes of the observed absorptions.

complexes with μ-CN bridges derived from $[CoH_2O(NH_3)_5]^{3+}$ and agrees with the position of the μ-NC groups with regard to water in the spectrochemical series.[1]

Other bands at higher frequencies are assigned to the cyanurated moiety, and they agree with the values found in the parent compounds.[19]

Conductivity Measurements. All the dinuclear compounds present a molar conductivity between 20 and 30 Ω^{-1} mol^{-1} in 10^{-3} M aqueous solution. This suggests a nonelectrolyte behavior; however, the value of the conductivity measurement increases with time, indicating that an aquation phenomenon takes place in solution.

^{59}Co NMR Spectra. The ^{59}Co NMR spectra for all the dinuclear compounds $[(NH_3)_5CoNCCo(CN)_4X]$ (X = Cl, Br, I, NO$_2$, N$_3$) have been registered in D$_2$O solution with K$_3[Co(CN)_6]$ as an external reference. All of them exhibit bands only in the 7000–9000 ppm region, as is shown in Figure 1. According to the literature data,[20] these bands are assigned to the amminated moiety of the molecules. We have not found bands attributable to the cyanurated cobalt(III) ion. This is probably due to their typical large width.[21]

In the 8000–8500 ppm region there are two bands, one narrow and the other broader, in each spectrum. They are separated by 70–100 ppm. These bands present a shift to higher frequencies in the order Cl < Br < I < N$_3$ < NO$_2$. A similar shift but in the reverse order is observed in the series $[Co(NH_3)_5X]^{2+}$ (x = Cl, Br, I, NO$_2$, N$_3$).[22] These observations lead us to believe that the X groups attached to the cyanurated moiety are the reason for both peaks. On the other hand, the existence of two bands in close proximity is typical for a cis–trans isomer equilibrium.[22] Consequently, we have assigned these two bands to the cis and trans isomers (X group with respect to the CN bridge group). The narrow band is attributed to the cis isomer due to quadrupole relaxation effects. At this time it is not clear if both isomers are synthesized simultaneously or if they are formed via subsequent cis → trans isomerization. In fact, the NMR spectra were recorded 1 month after the dinuclear compounds were synthesized.

The nitro and azido derivatives show one more band at 7819 and 8828 ppm, respectively. The positions of these bands, very similar to those of the bands observed[20] for $[Co(NH_3)_5NO_2]^{2+}$

Table V. X-ray Powder Diffraction Data for the Double-Complex Salts

compd	2θ, deg	d, Å	hkl	$100I/I_0$
[CoH₂O(NH₃)₅][Co(CN)₆]	16.43	5.40	10$\bar{1}$	95
	18.04	4.92	110	40
	30.25	2.95	21$\bar{1}$	100
[CoH₂O(NH₃)₅][Co(CN)₅Cl]	16.53	5.36	10$\bar{1}$	100
	19.13	4.64	110	50
	30.38	2.94	21$\bar{1}$	65
[CoH₂O(NH₃)₅][Co(CN)₅Br]	16.40	5.41	10$\bar{1}$	100
	18.95	4.68	110	55
	30.15	2.95	21$\bar{1}$	64
[CoH₂O(NH₃)₅][Co(CN)₅I]	16.25	5.46	10$\bar{1}$	99
	18.75	4.73	110	80
	28.93	3.09	21$\bar{1}$	100
[CoH₂O(NH₃)₅][Co(CN)₅NO₂]	16.55	5.36	10$\bar{1}$	100
	18.60	4.77	110	33
	30.25	2.97	21$\bar{1}$	33
[CoH₂O(NH₃)₅][Co(CN)₅N₃]	16.1	5.51	10$\bar{1}$	100
	19.15	4.64	110	73
	29.95	2.98	21$\bar{1}$	78

Table VI. Unit Cell Parameters for the Double-Complex Salts [CoH₂O(NH₃)₅][Co(CN)₅X]^a

	X = CN$^-$	X = Cl$^-$	X = Br$^-$	X = NO$_2^-$	X = N$_3^-$	X = I$^-$
α, deg	97.28	97.23	97.20	95.54	98.37	97.20
a, Å	7.18	7.14	7.20	7.21	7.27	7.26
V, Å^3	359.88	354.12	364.1	367.69	371.2	373.1

^{a} Error estimates: α, 0.03°; a, 0.005 Å; for V, 0.78 Å^3.

(7625 ppm) and $[Co(NH_3)_5N_3]^{2+}$ (8680 ppm), suggest to us a migration process of the NO$_2$ and N$_3$ groups from the cyanurated to the amminated Co(III) ion, showing the complexity of the solution and solid-state chemistry of these compounds.

X-ray Powder Diffraction Spectra. Table V summarizes the Bragg angles (2θ) and relative intensities of the most important lines of the X-ray powder diffraction spectra of the double-complex salts. The values for the most symmetrical complex [Co(NH₃)₆][Co(CN)₆] are also included. As can be observed from the data shown in Table V, all of the complexes are isostructural, which can be explained by a random orientation at room temperature of H₂O and X (X = Cl, Br, I, NO₂, N₃) groups in the lattice. This behavior has been found by the authors in other double-complex salt families.[23]

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(21) Harris, Robin K.; Mann, Brian E. *NMR and the Periodic Table*; Academic: New York, 1978; p 243.

(22) Harris, Robin K.; Mann, Brian E. *NMR and the Periodic Table*; Academic: New York, 1978; p 239.

(23) Carlin, R. L.; Burriel, R.; Pons, J.; Casabó, J. *Inorg. Chem.* **1983**, *22*, 2832.

The crystalline structure of $[Co(NH_3)_6][Co(CN)_6]$ is rhombohedral,[13a] space group $R\bar{3}$, with $Z = 1$. Co atoms are occupying spatial positions on the $\bar{3}$ axis. The structure is a CsCl type that is trigonally distorted. Table V also includes distances (d) and Miller indices for each line calculated from the known structure of $[Co(NH_3)_6][Co(CN)_6]$. Table VI summarizes some cell parameters of these compounds derived from the powder diffraction spectra. In particular, values of unit cell volumes are given. In order to discuss below the chemical mechanism in the solid state of the deaquation–anation reaction that takes place during the heating of the double-complex salts, prior to the dinuclear μ-CN compound formation, it is of interest to discuss more about cell parameters.

Assuming a CsCl structure and anion–cation contact (as a first approach), it is straightforward to express the unit cell volume, V, as a function of the cation and anion radii, r_+ and r_-:

$$V = \frac{8(3^{1/2})}{9}(r_+ + r_-)^3$$

For the double-complex-salt family that we have studied, $[CoH_2O(NH_3)_5][Co(CN)_5X]$ (X = CN, Cl, Br, I, NO$_2$, N$_3$), r_+ is always constant so the increase in unit cell volume reflected in Table VI is attributable to r_-. In our case it is possible to order the apparent anionic radii in the form $I^- > N_3^- > NO_2^- > Br^- > CN^- > Cl^-$.

On the other hand, one can defined a space-filling factor,[24] ϕ, which for a CsCl structure is

$$\phi = \frac{(4\pi/3)(r_+^3 + r_-^3)}{V}$$

and hence

$$\phi = \frac{\pi 3^{1/2}}{2} \frac{r_+^3 + r_-^3}{(r_+ + r_-)^3}$$

or, if we define

$$\sigma = \frac{r_-}{r_+}$$

then

$$\phi = \frac{\pi 3^{1/2}}{2} \frac{1 + \sigma^3}{(1 + \sigma)^3}$$

In the aforementioned anion–cation contact region (0.731 < σ < 1.365)[24] the above expression has a minimum value for $\sigma = 1$, so the space-filling factor, ϕ, always decreases when r_- increases provided $\sigma < 1$ and r_+ is constant as it is in these compounds.

The above anionic radii ordering suggests an opposite space-filling-factor order and a unit cell "free space" order identical with that of the anion radius. This fact will be commented on later.

Dinuclear μ-CN compounds do not exhibit X-ray powder diffraction spectra, evidencing a noncrystalline structure due to the synthetic procedure.

Thermal Measurements. Thermogravimetric measurements carried out on the compounds $[CoH_2O(NH_3)_5][Co(CN)_5X]$ (X = CN, Cl, Br, I, NO$_2$, N$_3$) show a first weight loss corresponding to one water molecule and attributable to the deaquation–anation reaction $[CoH_2O(NH_3)_5][Co(CN)_5X] \rightarrow H_2O + [(NH_3)_5CoNCCo(CN)_4X]$. Table VII summarizes the aforementioned weight losses and the corresponding enthalpy values found from DSC measurements. These nonisothermal thermogravimetric curves performed at various heating rates served to calculate in each case the kinetics parameters of these reactions, as will be commented on later.

Table VII. Weight Loss and Thermodynamic and Kinetic Parameters for the Reaction $[CoH_2O(NH_3)_5][Co(CN)_5X] \rightarrow [(NH_3)_5CoNCCo(CN)_4X] + H_2O$

	% wt loss found (calcd)	ΔH, kcal mol^{-1}	n	E_a, kJ mol^{-1}	K_0
X = CN$^-$	4.75 (4.78)	35.46	1.5	124.0 ± 2	4.865×10^{14}
X = Cl$^-$	4.63 (4.66)	24.72	1.5	120.5 ± 2	5.722×10^{14}
X = Br$^-$	4.10 (4.18)	32.44	1.5	91.8 ± 8	1.3942×10^{12}
X = NO$_2^-$	4.24 (4.54)	17.16	1.5	84.0 ± 8	3.332×10^{12}
X = N$_3^-$	4.12 (4.58)	16.83	2.5	70.2 ± 3	5.146×10^9
X = I$^-$	3.46 (3.77)	12.98	1.5	63.5 ± 3	1.632×10^9

Kinetic Parameters. The kinetic parameters were determined on the basis of the kinetic relation[25,26]

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

or

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

where α is the fraction decomposed and $K(T)$ follows the Arrenhius 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).[27]

Each process can be studied by several expressions of $g(\alpha)$ depending on α and n (the reaction order). Kinetics parameters are very difficult to calculate by only nonisothermal TG curves due to ignorance of the true $g(\alpha)$ expression.[28] In order to calculate the true activation energy and to discern the physical mechanism of the solid-state process, it is necessary either to compare the results obtained by nonisothermal and isothermal TG measurements for every $g(\alpha)$ expression[28] or to compare with the known results of other isostructural compounds in which the physical model can be supposed to be the same. Recently one of us has reported a complete thermal study for the compound $[CoH_2O(NH_3)_5][Co(CN)_6]$,[29] which is isostructural with our series. Nonisothermal and isothermal measurements have been carried out, and for both methods all the principal expressions of $g(\alpha)$ reported in the literature[27] have been used. The physical mechanism and the corresponding kinetic parameters for the process are assigned on the basis of agreement in the activation energy, frequency factor, and r^2 (correlation coefficients) in both nonisothermal and isothermal methods. The best model formed for this compound is nucleation–growth (Avrami–Erofeev law: $g(\alpha) = -\ln (1 - \alpha)^{1/n}$) with a reaction order $n = 1.5$, $E_a = 128.6 \pm 2$ kJ/mol, and $K_0 = 4.865 \times 10^{14}$.

In a similar way, we have tried the principal expressions of $g(\alpha)$ on the compounds we are concerned with. As was expected due to their isoestructuralism with $[CoH_2O(NH_3)_5][Co(CN)_6]$, the model that fits the experimental results best is the nucleation–growth model. Table VII summarizes the best activation energy, frequency factor, and reaction order for each compound with the assumption of a Avrami–Erofeev model. These values are averaged over the values obtained in different experiments with heating rates of 1.27 and 4 °C/min. As can be observed from this table, the activation energies follow the order CN $\simeq$ Cl > Br > NO$_2$ > N$_3$ > I. This order will be discussed below.

Reaction Mechanism. House[3] and LeMay[4] have recently proposed several mechanisms on the thermal dehydration–anation reactions of solid complexes.

These are characterized by the formation of various types of defects: Schottky type defects with an S_N2 associative mechanism or Frenkel type defects with an S_N1 dissociative mechanism.

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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 an S_N1 mechanism.

On the basis of a crystal field model, the formation of a seven-coordinate complex (pentagonal bipyramidal; S_N2 mechanism) requires $8.52Dq^{30}$ (Dq being close to 25 kJ mol^{-1} for the $[CoH_2O(NH_3)_5]^{3+}$ ion), which would be about 100 kJ mol^{-1}, similar to the E_a value found. In addition, the heptacoordination in the S_N2 reaction suggests the formation of a Schottky type defect in an ionic crystal. This process requires high energy ($E_{def} = 0.24U$; U = lattice energy);^{32} consequently, the E_a value expected should be larger than 110–120 kcal mol^{-1}.

The mechanism, therefore, might be S_N1 (dissociative mechanism) with the formation of a square-base-pyramid activated complex, requiring only $4.0Dq$ (for a trigonal-bipyramidal activated complex it would require $11.49Dq$).^{30} The transition state is, then, determined by the water loss and the formation of a nonionic Frenkel type defect.

The activation energy for this type of process in an isostructural family of compounds should be nearly constant, especially if they have a common cation and similar anions.

However, our experimental results show a significant variation in the E_a values for the deaquation–anation process (Table VII):

$$[CoH_2O(NH_3)_5][Co(CN)_5X] \rightarrow$$
$$H_2O + [(NH_3)_5CoNCCo(CN)_4X]$$
$$X = CN, Cl, Br, I, NO_2, N_3$$
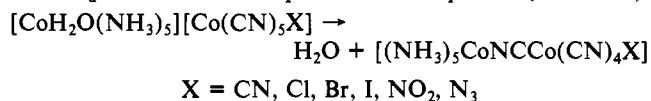
To explain the results we propose the concept of "lattice free space" as an important parameter to discuss these solid-state

reactions. The ordering in E_a values is in good agreement with the "unit cell free space" (see X-ray powder diffraction results). In the cases where there is a large space between the cations and anions (as may be supposed in the I and N_3 compounds), the water molecule may be able to slip into an interstitial position causing little or no lattice distortion. In these situations low values of E_a are expected. On the other hand, where there is a smaller space between the ions (as may be supposed in the CN and Cl compounds), the water molecules can occupy an interstitial position only with considerable lattice expansion; consequently, larger E_a values should result.

It can be concluded that in an S_N1 process the activation energy is determined by the crystal field component as well as the lattice component as is evident in this paper. The lattice component can be envisaged as the "free space" in the crystalline structure. The importance of the lattice component has been pointed out by some of us in several families of double-complex salts such as $[CoH_2O(NH_3)_5]_2[M(CN)_4]_3$ (M = Ni, Pd, Pt)^{33} and $[MH_2O-(NH_3)_5][M'(CN)_6]$ (M = Co, Rh, Ir; M' = Cr).^{34}

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Low-Dimensional Bimetallic Ordered Systems: Synthesis and Characterization of the Isomorphous Series CoxNi2-xEDTA·2H2O. Crystal Structure of Co2EDTA·2H2O and Preferential Site Occupation in CoNiEDTA·2H2O

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Four members of the isomorphous series of empirical formula Co$_x$Ni$_{2-x}$EDTA·2H$_2$O have been prepared (x = 2.0, 1.5, 1.0, 0.7), and the crystal structure has been solved for Co$_2$EDTA·2H$_2$O (space group $C2/c$, a = 26.967 (3) Å, b = 9.495 (1) Å, c = 11.154 (1) Å, β = 92.395 (8)°, Z = 8). These solids are crystalline polymers with three crystallographically independent metal centers corresponding to chromophores MN$_2$O$_4$, MO$_4$, and MO$_6$, bridged through carboxylate groups from EDTA. Metals in the MO$_4$ and MO$_6$ moieties occupy special positions (2 and $\bar{1}$, respectively). The electronic spectra of the complexes are consistent with preferential occupation of the MN$_2$O$_4$ site by Ni in the complex CoNiEDTA·2H$_2$O. Magnetic susceptibility measurements down to 4 K show no appreciable intermetallic magnetic interactions in CoNiEDTA·2H$_2$O, while some small antiferromagnetic coupling is detected for Co$_2$EDTA·2H$_2$O. According to their structural features these materials may be viewed as ferrimagnetic two-dimensional systems.

Introduction

The study of low-dimensional materials has been the subject of increasing interest over the past few years with linear chains having been the most extensively studied, both experimentally and theoretically.^{1,2} While homometallic linear-chain systems are

most frequently found in the literature, the coordination asymmetry present in the complex Zn$_2$EDTA·6H$_2$O^3 encouraged us to prepare an isomorphous series of heterometallic compounds of formula [M(H$_2$O)$_4$O$_I$O$_{II}$][M'EDTA]·2H$_2$O, where M = Mg,

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