Thermochimica Acta, 57 (1982) 283–291
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

DINUCLEAR COMPLEXES WITH MU-CYANO LIGAND. PART VI. CHARACTERIZATION AND THERMAL STUDIES OF *trans*-$K[CrF(H_2O)(aa')_2][Co(CN)_6]$ (aa' = en, tmd)

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(Received 26 February 1982)

ABSTRACT

The new complexes *trans*-$K[CrF(H_2O)(en)_2][Co(CN)_6]$ aq. and *trans*-$K[CrF(H_2O)(tmd)_2][Co(CN)_6]$ aq. (en = ethylenediamine; tmd = 1,3 diaminepropane) have been prepared. The anation reactions have been studied with TG and DSC techniques. The anation reaction gives the new dinuclear species *cis* $K[(aa')_2FCr\text{-}NC\text{-}Co(CN)_5]$ (aa' = en, tmd). The reaction enthalpy of bridge formation has been determined. The activation energy has been calculated by non-isothermal methods.

INTRODUCTION

A large number of thermal studies on the deaquation and anation reactions

$$[M(H_2O)L_5]X_3 \rightarrow [M(X)L_5]X_2 + H_2O$$

(L is generally NH_3 and M = Co, Cr, Ru, Rh) have been described [1–7].

Studies on amine loss and substitution of halides or pseudohalides in the presence of catalysts have also been described [8,9]. On the other hand few works have been carried out on the dehydration and anation reaction of Cr(III) complexes containing H_2O and bidentate amines as ligands [10].

Vaughn prepared the chloride and bromide of *trans*-$[CrF(H_2O)(aa')_2]^{2+}$ (aa' = en, tmd) from the perchlorate salt [11,12]. By heating the halides in the solid phase *cis*-$[CrF(X)(en)_2]X$ and *trans*-$[CrF(X)(tmd)_2]X$ were obtained. Further work by the same author dealt with analogous reactions with other amine ligands, including mixed combinations [$(aa')_2$ = en and tmd; pn and tmd; en and pn (pn = 1,2 diaminepropane)] [13,14].

Recently we have obtained and studied thermogravimetrically the compounds *trans*-$[CrF(H_2O)(aa')_2]S_2O_6$ (aa' = en, tmd). The reaction enthalpies

0040-6031/82/0000–0000/$02.75

and activation energies of both reactions have been estimated by DSC [15].

When X is a cyanocomplex the above anation–dehydration reaction may be used to prepare new dinuclear complexes with a mu-cyano bridge. We have prepared a number of dinuclear complexes by this method [16–19].

Recently we have also reported the thermochemical parameters for the thermal dehydration of the compounds *trans*-$[CrF(H_2O)(tmd)_2][Ni(CN)_4]$ [20].

The results of the preparation and solid-phase thermal dehydration of *trans*-$K[CrF(H_2O)(aa')_2][Co(CN)_6]$ (aa′ = en, tmd) under non-isothermal conditions are presented in this paper.

EXPERIMENTAL

Preparation of trans-$K[CrF(H_2O)(en)_2][Co(CN)_6]H_2O$

$K_3[Co(CN)_6]$ (2.07 g) was added to *trans*-$[CrF(H_2O)(en)_2](ClO_4)_2$ [21] (2.66 g) in ice-cold water (20 ml). After stirring for 5 min the precipitated $KClO_4$ was filtered off and the red solution was treated with cold ethanol (100 ml). The precipitate was filtered and recrystallized by dissolving it in cold water, filtering and adding ethanol. The product was filtered, washed with ethanol and acetone and air-dried. Analysis—Calcd: Cr, 10.21; Co, 11.58; C, 28.29; H, 4.75 and N, 27.50. Found: Cr, 10.2; Co, 11.6; C, 27.8; H, 4.6 and N, 26.8.

Preparation of trans-$K[CrF(H_2O)(tmd)_2][Co(CN)_6]H_2O$

The procedure was as above but starting from *trans*-$[CrF(H_2O)(tmd)_2](ClO_4)_2$ [22]. Analysis—Calcd: Cr, 10.17; C, 28.18; H, 5.08; N, 27.39. Found: Cr, 10.4; C, 28.5; H, 5.1; N, 27.8.

Preparation of cis-$K[(en)_2FCr\text{-}NC\text{-}Co(CN)_5]$

Solid *trans*-$K[CrF(H_2O)(en)_2][Co(CN)_6]H_2O$ was heated at 140°C for 10–12 h. Except for the loss of the two water molecules, no other decomposition reaction was observed. Analysis—Calcd: Cr, 11.68; C, 26.97; H, 3.60; N, 31.46. Found: Cr, 11.6; C, 26.9; H, 3.6; N, 31.3.

Preparation of cis-$K[(tmd)_2FCr\text{-}NC\text{-}Co(CN)_5]$

The method was the same as that used to prepare the analogous en complex but the temperature was 120–130°C and the heating time 10 h.

Analysis—Calcd: Cr, 10.98; C, 30.45; N, 29.59; H, 4.23. Found: Cr, 10.9; C, 30.1; N, 29.8; H, 4.1.

Thermogravimetric studies

Thermogravimetric curves were taken on a Perkin Elmer model TGS-1 thermogravimetric system. Samples were heated under nitrogen at the rate of 10°C min^{-1}. Calculations were carried out on a programable calculator and a linear regression analysis was used to determine slopes, intercepts and standard deviations. In all cases, four TG curves were made.

Reaction enthalpy

Thermal dehydration studies were carried out on a Perkin Elmer Differential Scanning Calorimeter(DSC-2). Enthalpy values were calculated using the melting point of tin or indium as a standard. In all cases four DSC curves were made. Electronic spectra were recorded on a Beckman UV 5230 spectrophotometer. IR spectra (samples as KBr disks) were recorded on a Beckman IR 20A spectrophotometer.

RESULTS AND DISCUSSION

IR and electronic spectra

Both new compounds and starting materials were characterized by IR and electronic spectroscopy. Cyano bridge formation (formed during the dehydration process) may be conveniently studied by IR spectroscopy. The IR spectra of the two mixed salts show the presence of a very strong band at 2125 cm^{-1} due to the stretching vibration ν(CN) of ionic $[Co(CN)_6]^{3-}$ [23]. After heating (in the oven or in the TG or DSC apparatus) the two new dinuclear compounds show a perfectly defined doublet at 2175–2125 cm^{-1} for the en salt and at 2180–2125 cm^{-1} for the tmd salt. The clear splitting on the CN stretching vibration is good evidence for a bridging cyano group [16–19,24]. The bands of coordinated ethylenediamine or 1,3 diaminepropane are in perfect agreement with literature values [25,26].

Table 1 shows the electronic spectra of relevant compounds. The spectra of the dinuclear compounds obtained by isothermal heating in the oven or as TG and DSC residues are identical and correspond to a *cis* geometry in an octahedral environment around Cr(III). This *trans* → *cis* isomerization is proved by the visible spectra: the starting *trans* compounds show two maxima in the visible region around 500 nm (see Table 1) while the solids

TABLE 1

Electronic spectra

Compound	λ (in nm)					Ref.
$K_3[Co(CN)_6]$				310	257	23
trans-$[CrF(H_2O)(en)_2]^{2+}$	515	460	370			20
$K[CrF(H_2O)(en)_2][Co(CN)_6]$	515	455		310	255	
trans-$[CrF(H_2O)(tmd)_2]^{2+}$	533	457	375			22
$K[CrF(H_2O)(tmd)_2][Co(CN)_6]$	530	455	375(sh)	310	255	
cis-$[(en)_2FCr\text{-}NC\text{-}Co(CN)_5]^-$	490			310	230	
cis-$[(tmd)_2CrF\text{-}NC\text{-}Co(CN)_5]^-$	500		375(sh)	310	230	

subjected to thermal treatment show only one maximum (at 490 nm for the en compound and at 500 nm for the tmd compound). The presence of only one, well defined and symmetrical band in this zone is generally believed to be the best piece of evidence for the *cis* geometry. It has been known for a long time that ethylenediamine complexes can change their geometry from *trans* to *cis* by solid-phase heating or even by reaction in solution. On the other hand the data for tmd complexes is scarce and contradictory [20,22]. For our compounds there is no doubt about the isomerization due to the clarity of the visible spectra.

For both compounds, the strong band of $[Co(CN)_6]^{3-}$ at 310 nm overlaps part of the spectra due to the amine part of the dinuclear complex and neither the second nor the third *d–d* transition of the Cr(III) ion in a pseudooctahedral symmetry are observed. Only for the tmd compound is a shoulder observed in the 375 nm region (Table 1).

NON-ISOTHERMAL TG STUDIES

Figure 1 shows the TG curve for the solid phase deaquation of *trans*-$K[CrF(H_2O)(en)_2][Co(CN)_6]H_2O$ (10°C min^{-1}). A first mass loss with a decrease in formula weight of about 18 amu and corresponding to the loss of one molecule of water of crystallisation occurs at 320 K. A second mass loss of 18 amu, corresponding to the loss of coordinated water together with bridge formation, occurs at 425 K. The tmd compound has a similar TG curve, (340 K and 410 K, respectively) although the two weight losses are not so well resolved. Figure 2 is the same TG (Fig. 1) preheated to 355 K.

In order to characterize the TG curves, the so called kinetic parameters n(reaction order), E_a (activation energy) and k_0 (frequency factor) have been

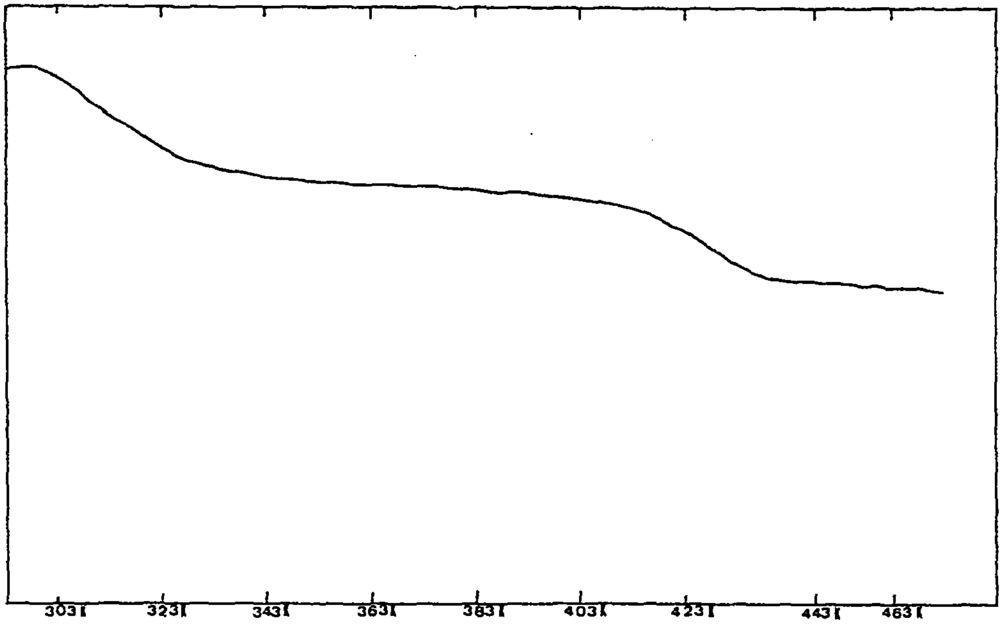

Fig. 1. TG curve of *trans*-$K[CrF(H_2O)(en)_2][Co(CN)_6]H_2O$.

determined using the general equations given below

$$dx/dt = k(T)f(x)$$

where $k(T)$ is assumed to follow Arrhenius' law

$$k(T) = k_0 \exp[-E_a/RT] \quad (k_0 = \text{frequency factor and } E_a = \text{ activation energy})$$

For simple decomposition reactions (as those dealt with in the present study) the following condition

$$f(x) = (1-x)^n$$

holds, which leads to

$$\int_0^x \frac{dx}{(1-x)^n} = \frac{k_0}{s} \int_0^T \exp[-E_a/RT] dT$$

(s = linear rate of heating)

Using the commonly employed Coats and Redfern's approximation [28] to solve the right-hand side integral, the following equations are obtained

$$\ln\left[\frac{1-(1-x)^{(1-n)}}{T^2(1-n)}\right] = \ln \frac{k_0 R}{SE_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{RT}$$

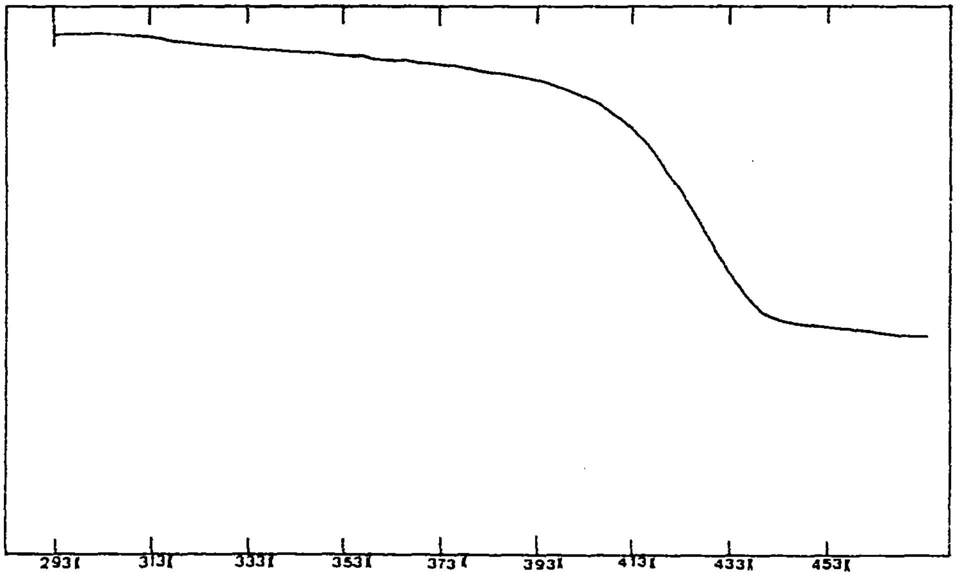

Fig. 2. TG curve of *trans*-$K[CrF(H_2O)(en)_2][Co(CN)_6]H_2O$ preheated to 355 K in order to eliminate the water of crystallization.

for all values of n, except $n = 1$, in which case the equation becomes

$$\ln\left[-\ln\frac{(1-x)}{T^2}\right] = \ln\frac{k_0}{S}\frac{R}{E_a}\left[1-\frac{2RT}{E_a}\right]-\frac{E_a}{RT}$$

For each run the curves were analysed assuming $n = 0$, $1/2$, $2/3$ and 1 to determine how much effect the order has on the derived kinetic parameters. The results of the numerical analysis of the three curves in the range $0.1 \leqslant x \leqslant 0.8$ are given in Tables 2 and 3.

Tables 2 and 3 indicate that the best fit (as determined by the average correlation coefficient) corresponds to the use of 1/2 and 2/3 order equations. Activation energies are about 21 ± 2 kcal mole^{-1} and 15 ± 1.5 kcal

TABLE 2

Numerical results of the TG curve of *trans*-$K[CrF(H_2O)(en)_2][Co(CN)_6]$

Parameters[a]	$n=0$	$n=1/2$	$n=2/3$	$n=1$
r^2	0.9889	0.9910	0.9902	0.9868
E_a	11.8 ± 1.0	14.59 ± 1.3	15.63 ± 1.4	17.91 ± 1.9
k_0	3.2×10^3	1.51×10^5	6.2×10^5	1.38×10^7

[a] Average of four TG values. E_a = kcal mole^{-1}.

TABLE 3

Numerical results of the TG curve of *trans*-K[CrF(H_2O)(tmd)$_2$][Co(CN)$_6$]

Parameters [a]	$n=0$	$n=1/2$	$n=2/3$	$n=1$
r^2	0.9948	0.9968	0.9969	0.9947
E_a	16.18± 2.2	20.2± 2.2	21.84± 2.3	25.45± 2.5
k_0	1.59×10^5	9.97×10^7	8.28×10^8	8.52×10^{10}

[a] Average of four TG values. E_a = kcal mole^{-1}.

mole^{-1} for the en and tmd compounds, respectively. The values of 1/2 or 2/3 correspond to a contracting disk or contracting sphere reaction interface [29]. Regarding the activation energy, there is no considerable variation in this magnitude when a given order is assumed.

The pre-exponential or frequency factor has been calculated from the intersection of Coats and Redfern's numerical equations. The dispersion of the values obtained is low. The mean values found for the en and tmd compounds are 10^8 and 10^5, respectively. According to Cordes [30] and Shannon [31] the frequency factor is related to the freedom degrees of the activated complex and may vary between 10^5 and 10^{18}. Small values (as for the tmd complex) often indicate a rigid activated complex, without freedom degrees; on the contrary, high values indicate a flexible activated complex. The value found for the en compound (10^8) is larger than that for the tmd complex, which means that the activated complex of the latter compound has more freedom or less rigidity, agreeing with the larger volume of tmd as compared with en.

DSC

As expected, the two deaquation reactions observed in the TG curves are also observed with the DCS techniques. Two well defined peaks for the en compound and two, somewhat overlapped peaks for the tmd compounds are observed.

The two peaks of the en compound appear at 127 and 217°C. The first peak which corresponds to the loss of hydration water gives an enthalpy reaction $\Delta H = 10.6 \pm 1$ kcal mole^{-1}; and the second peak which corresponds to the anation reaction gives $\Delta H = 11.8 \pm 1$ kcal mole^{-1}. The value of E_a for the anation reaction using the Thomas and Clarke method [32] is 21.8 ± 2 kcal mole^{-1}, in agreement with the non-isothermal TG results.

The DSC curves of the tmd compound show two endothermic and poorly resolved peaks at 97 and 172°C. The reaction enthalpies are about 5 ± 0.5 kcal mole^{-1} for the first peak and 10 ± 1 kcal mole^{-1} for the second peak (loss of coordinated water). The activation energy for the anation reaction, determined using the method of Thomas and Clarke is about 40.2 ± 2 kcal mole^{-1}, a value much larger than that found by the TG technique. The difference may in this case be attributable to the low resolution of the peaks.

POSSIBLE MECHANISM

It is very difficult from E_a data to draw definite conclusions regarding a possible mechanism. House, Jr. [33] has recently proposed several mechanisms for the thermal reactions of anation of solid complexes based on the formation of Schottky or Frenkel defects.

House suggests that a high value of E_a corresponds better with an S_N2 mechanism while a low value of E_a means an S_N1 mechanism. For an S_N2 mechanism the contribution of the ligand field in the formation of a heptacoordination (activated complex) can vary from 4.26 Dq to 1.8 Dq for a pentagonal bipyramid or octahedral wedge, respectively [34]. Since for our Cr(III) complexes Dq is about 2000 cm^{-1} (about 6 kcal mole^{-1}) the ligand field contribution will be 25 kcal mole^{-1} or 11 kcal mole^{-1}, respectively. Furthermore, other contributions must be added as indicated by Basolo [34]. On the other hand, an associative mechanism involves the formation of an ionic Schottky defect which demands a larger amount of energy (about 0.4 U_0; U_0 = lattice energy) [35]. The sum of all these contributions gives values higher than those found by us for both complexes (about 20 kcal mole^{-1}). On the other hand, a dissociative mechanism (formation of a non-ionic Frenkel defect by loss of a water molecule which goes to the interstices in the crystal lattice and is eventually eliminated, would imply a very low contributon of E_a. The ligand field contribution for the two most likely geometries of a pentacoordinated activated complex are 2 Dq (12 kcal mole^{-1}) (square pyramid) and 5.74 Dq (34 kcal mole^{-1}) (trigonal bipyramid) [34]. By comparison with the experimental values we may eliminate an activated complex with a trigonal bipyramid geometry and are left with an associative S_N1 mechanism involving a square-pyramid activated complex.

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