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Thermal Reactions of Metal Complexes under Quasi-isothermal and -isobaric Conditions. 3.[1] Solid-Phase Thermal Reactions of the Doubly Complexed Salts of the Forms $[(Cr\ or\ Co)(NH_3)_6][(Cr\ or\ Co)(CN)_6]$, $[(Cr\ or\ Co)(H_2O)(NH_3)_5][(Cr\ or\ Co)(CN)_6]$, and *cis*-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$

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The following nine double complexes were prepared and their thermal reactions in the solid phase were investigated under quasi-isothermal and -isobaric conditions (Q conditions) and under dynamic conditions (D conditions): $[(Cr\ or\ Co)(NH_3)_6][(Cr\ or\ Co)(CN)_6]$, $[(Cr\ or\ Co)(H_2O)(NH_3)_5][(Cr\ or\ Co)(CN)_6]$ and *cis*-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$, where both the chromium and cobalt ions are tervalent. All the complexes were decomposed in complicated ways under D conditions, but under Q conditions each thermal reaction step was clearly detected and it was found that the thermal reaction patterns of the complexes are markedly different from each other depending upon the combination of the metal ions contained in the cation and anion moieties. All the compounds having the combinations of [Cr][Cr], [Cr][Co], and [Co][Cr] were finally converted into the species consisting of the rational formula $M(CN)_6M'$, where M and M′ denote Cr(III) and Co(III) ion. The compound $Cr(CN)_6Cr$ gave a considerably subnormal magnetic moment (2.4–2.6 μ_B), indicating the presence of metal–metal interaction between two Cr(III) ions. CN flipping was found in the thermal reaction of the complexes of [Co][Cr], which was supported by the fact that the final product is not $Co(NC)_6Cr$, but $Co(CN)_6Cr$. In the case of [Co][Co], the reduction of a part of Co(III) to Co(II) ion takes place along with the evolution of ammonia to yield the species $Co^{II}(CN)_6Co^{III}$. It was also found that the evolution of water precedes that of ammonia in the cationic cobalt(III) complexes $[Co(H_2O)(NH_3)_5][(Cr\ or\ Co)(CN)_6]$ and *cis*-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$ and vice versa in the cationic chromium(III) complexes $[Cr(H_2O)(NH_3)_5][(Cr\ or\ Co)(CN)_6]$.

Introduction

The cyano-bridged binuclear cobalt(III) complex $[(NH_3)_5Co(NC)Co(CN)_5]$ was first prepared by thermal dehydration in the solid phase:[3]

$$[Co(H_2O)(NH_3)_5][Co(CN)_6] \xrightarrow[\Delta]{} [(NH_3)_5Co(NC)Co(CN)_5] + H_2O$$

Ribas et al. applied the same idea to the preparation of $[(NH_3)_5Cr(NC)Co(CN)_5]$ from $[Cr(H_2O)(NH_3)_5][Co(CN)_6]$, but their attempt failed because the double complexed salt evolves water and ammonia in a single step.[4] We were also unsuccessful in obtaining $[(NH_3)_5Cr(NC)Cr(CN)_5]$ from $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$.[5] From these facts and others, we concluded that the thermal reactions of the complexes $[(Cr\ or\ Co)(H_2O)(NH_3)_5][(Cr\ or\ Co)(CN)_6]$ may be quite different from each other depending upon the combination of metal ions contained in the cation and anion moieties. The primary purpose of the present study is therefore to investigate the details of the thermal reactions of the doubly complexed salts in which the cation moiety consists of $[(Cr\ or\ Co)(NH_3)_6]^{3+}$ or $[(Cr\ or\ Co)(H_2O)(NH_3)_5]^{3+}$ and the anion moiety, $[(Cr\ or\ Co)(CN)_6]^{3-}$, and the complex *cis*-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$.

The presence of metal–metal interaction has been exemplified in the studies on the binuclear chromium(III) complexes containing μ-hydroxo[6,7] and μ-oxo[8,9] groups: e.g., $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Br_5$ and $[(NH_3)_5CrOCr(NH_3)_5]Br_4$ give considerably lower magnetic moments of 3.44 (294.5 K) and 1.29 μ_B (294.7 K) than that expected from the spin-only value for the Cr(III) ion. Earnshaw and Lewis[10] have pointed out from magnetic studies of the analogues of the above binuclear complexes that the degree of metal–metal interaction depends upon the nature of the bridging group and markedly upon the M–L–M′ bond angle: the greater the bonding ability of the bridging group and the larger the M–L–M′ bond angle is, the stronger the metal–metal interaction becomes (M and M′ are the same or different metal ions, and L is the bridging ligand). From this point of view, the chromium(III) complexes containing the μ-cyano group may be interesting candidates. Another purpose of the present study is to learn whether or not such a metal–metal interaction is present in the products obtained by the thermal reaction of $[Cr((NH_3)_6\ or\ (H_2O)(NH_3)_5)][Cr(CN)_6]$.

The complexes in the present study are divided into the following four groups in relation to the combination of metal ions contained in the cation and anion moieties: [Cr][Cr], [Cr][Co], [Co][Cr], and [Co][Co].[11]

Experimental Section

Preparation of the Starting Materials for Obtaining Double Complexes. $[Cr(NH_3)_6](NO_3)_3$,[12] $[Co(NH_3)_6]Cl_3$,[13] $[Cr(H_2O)(NH_3)_5](NO_3)_3$,[14] $[Co(H_2O)(NH_3)_5]Cl_3$,[15] *cis*-$[Co(H_2O)_2(NH_3)_4]Cl_3$,[16] $K_3[Cr(CN)_6]$,[17] and $K_3[Co(CN)_6]$[18] were prepared by the same

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[1] Part 2: Ueno, H.; Uehara, A.; Tsuchiya, R. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1821.

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[3] de Castellō, R. A.; Mac-Call, C. P.; Egen, N. B.; Haim, A. *Inorg. Chem.* **1969**, *8*, 699.

[4] Ribas, J.; Casabo, J.; Serra, M.; Coronas, J. M. *Inorg. Chim. Acta* **1979**, *36*, 41.

[5] Tsuchiya, R.; Nakagawa, S.; Uehara, A.; Kyuno, E. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 169.

[6] Cline, S. J.; Glerup, J.; Hodgson, D. J.; Jensen, G. S.; Pedersen, E. *Inorg. Chem.* **1981**, *20*, 2229.

[7] Thomson, M.; Connick, R. E. *Inorg. Chem.* **1981**, *20*, 2279.

[8] Glerup, J. *Acta Chem. Scand.* **1972**, *26*, 3775.

[9] Pedersen, E. *Acta Chem. Scand.* **1972**, *26*, 333.

[10] Earnshaw, A.; Lewis, J. *J. Chem. Soc.* **1961**, 396.

[11] For convenience, throughout this paper, the double complexes $[Cr((NH_3)_6\ or\ (H_2O)(NH_3)_5)][Cr(CN)_6]$ and $[Cr((NH_3)_6\ or\ (H_2O)(NH_3)_5)][Co(CN)_6]$ are simply abbreviated as [Cr][Cr] and [Cr][Co], respectively. The complexes $[Co((NH_3)_6\ or\ (H_2O)(NH_3)_5)][Cr(CN)_6]$ and $[Co((NH_3)_6, (H_2O)(NH_3)_5, or\ (H_2O)_2(NH_3)_4)][Co(CN)_6]$ are similarly designated as [Co][Cr] and [Co][Co].

[12] Mori, M. *Nippon Kagaku Zasshi* **1953**, *74*, 253.

[13] Bjerrum, J.; McReynolds, J. P. *Inorg. Synth.* **1946**, *2*, 216.

[14] Mori, M. *Inorg. Synth.* **1957**, *5*, 132.

[15] Jörgensen, S. M. *Z. Anorg. Chem.* **1898**, *17*, 461.

[16] Jörgensen, S. M. *Z. Anorg. Chem.* **1892**, *2*, 297.

[17] Bigelow, J. H. *Inorg. Synth.* **1946**, *2*, 203.

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Table I. Analytical Data for the Doubly Complexed Salts

	%H		%C		%N	
	found	calcd	found	calcd	found	calcd
$[Cr(NH_3)_6][Cr(CN)_6]$	5.26	4.97	19.50	19.89	46.32	46.41
$[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$	4.81	4.72	19.29	19.84	42.17	42.41
$[Cr(NH_3)_6][Co(CN)_6]$	5.05	4.87	19.50	19.51	45.02	45.53
$[Cr(H_2O)(NH_3)_5][Co(CN)_6]$	4.62	4.63	19.29	19.47	41.53	41.62
$[Co(NH_3)_6][Cr(CN)_6]$	4.96	4.87	19.61	19.51	44.98	45.53
$[Co(H_2O)(NH_3)_5][Cr(CN)_6]$	4.73	4.63	19.21	19.47	41.55	41.62
$[Co(NH_3)_6][Co(CN)_6]$	4.82	4.82	18.96	19.16	44.56	44.68
$[Co(H_2O)(NH_3)_5][Co(CN)_6]$	4.27	4.54	18.84	19.11	39.45	40.36
cis-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$	4.00	4.23	19.00	19.05	36.81	37.04

methods as those reported in the literature, and they were identified by means of elemental analyses and spectrophotometric measurements.

Preparation of Double Complexes. It should be noted that the double complexes obtained were not recrystallized because they are in general sparingly soluble in water and no other suitable solvent for them was found, and therefore the starting materials for use in the preparation of the double complexes must be fully purified beforehand.

$[(Cr\ or\ Co)((NH_3)_6\ or\ (H_2O)(NH_3)_5)][(Cr\ or\ Co)(CN)_6]$. A solution of 0.01 mol of $[Cr(NH_3)_6](NO_3)_3$, $[Co(NH_3)_6]Cl_3$, $[Cr(H_2O)(NH_3)_5](NO_3)_3$, or $[Co(H_2O)(NH_3)_5]Cl_3$ in 200 cm^3 of water was gradually added with continuous stirring to a solution of 0.01 mol of $K_3[Cr(CN)_6]$ or $K_3[Co(CN)_6]$ in 100 cm^3 of water. After a few minutes precipitates began to appear. The mixture was then allowed to stand in a refrigerator overnight to complete precipitation. The precipitates thus obtained were collected by filtration, washed several times with water, ethanol, and ether in turn, and air-dried.

cis-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$. The complex was prepared in a manner similar to that described above except that solutions of 0.01 mol of *cis*-$[Co(H_2O)_2(NH_3)_4]Cl_3$ in 50 cm^3 of water and 0.01 mol of $K_3[Co(CN)_6]$ in 50 cm^3 of water were used.

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

Preparation of Prussian Blue Analogues. Two Prussian blue analogues, $Co^{II}_3[Co(CN)_6]$ and $Co^{II}_3[Cr(CN)_6]$, and their derivatives $Cr^{III}(NC)_6Co^{III}$ and $Cr^{III}(NC)_6Cr^{III}$ were prepared by a modification of the procedure of Brown and Shriver.[19]

Derivatographic Measurements. The thermal reactions of the complexes were traced under quasi-isothermal and -isobaric conditions (Q conditions) and dynamic conditions (D conditions) by using Q and D derivatographs.[1,20] Sample weights of 0.3 and 0.4 g were used for Q and D derivatography, respectively. The measurements by D derivatograph were carried out under a constant flow of nitrogen at the heating rate of 2 °C min^{-1}.

Electronic Spectral Measurements. The electronic spectra of the samples in solution were monitored on a Jasco UVIDEC-505 UV/VIS recording digital spectrophotometer and those in powder state on a Hitachi EPU-2A spectrophotometer equipped with a standard Hitachi reflection attachment (Type R-3).

IR and Far-IR Spectral Measurements. IR spectra of the samples were measured by a KBr-disk method with a Jasco IR-F far-infrared spectrophotometer.

Magnetic Moments. The magnetic susceptibilities of the samples were measured by the Gouy method at room temperature. The effective magnetic moments (μ_{eff}) were corrected by the use of Pascal's constants for each component in the compound.

Results

For clarification, the following discussion will be held according to the complexes classified by the combination of metal ions contained in the cation and anion moieties. Unless otherwise specified, the chromium and cobalt ions are all in the tervalent state.

[Cr][Cr]. Derivatography. Figure 1 shows the Q and D derivatograms of $[Cr(NH_3)_6][Cr(CN)_6]$ and $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$. As seen from the D derivatograms of both complexes, a monotonic decrease takes place and no plateau is observed in the TG curves, indicating that the complexes decompose gradually in a complicated manner without formation of uniform products under D conditions. Since the same tendency was found in all the other complexes, their D derivatograms are omitted for simplification of the following discussion.

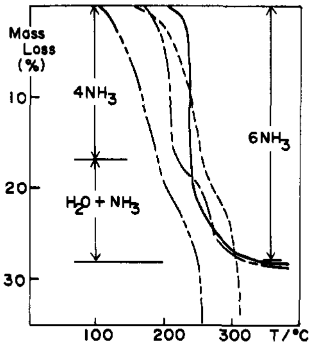

Figure 1. Q derivatograms of $[Cr(NH_3)_6][Cr(CN)_6]$ (—) and $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$ (— - —) together with D derivatograms of $[Cr(NH_3)_6][Cr(CN)_6]$ (---) and $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$ (— -- —).

On the other hand, the Q derivatogram of $[Cr(NH_3)_6][Cr(CN)_6]$ represents a sharp weight loss at 205–310 °C and then a plateau is obtained in the TG curve. The weight loss is due to the evolution of 6 mol of ammonia (found, 28.0%; calcd, 28.2%). The original yellow color became dark brown.

The Q derivatogram of $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$ exhibits two steps of the weight loss: the first is a steep loss corresponding to 4 mol of ammonia at 170–220 °C, and the second is a rather slow weight loss corresponding to 1 mol of ammonia plus 1 mol of water at 220–305 °C. The original reddish yellow complex turned light brown at the first step and then dark brown at the second step. The elemental analyses and IR spectral measurements of the first product indicate that the product still contains water, having the chemical formula $[(H_2O)(NH_3)Cr(NC)_4Cr(CN)_2]$. The final product was found to have a basic composition of $Cr(NC)_6Cr$.

IR Spectra. The IR and far-IR spectral bands due to the CN stretching vibration (ν_{CN}), MCN stretching vibration (ν_{MCN}), and CMC bending vibration (δ_{CMC})(M = metal ion) are diagnostically useful for distinguishing terminal-CN from bridging-CN groups.[21] Table II summarizes the IR and far-IR data for all the complexes and the products obtained at each thermal reaction step, together with those for some pertinent reference compounds such as $K_3[Cr(CN)_6]$, $Cr(NC)_6Cr$, and the like.

The bands at 2130 and 2135 cm^{-1} for $[Cr(NH_3)_6][Cr(CN)_6]$ and $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$ are assignable to the terminal-CN stretching vibration. The final products of both

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(18) Bigelow, J. H. *Inorg. Synth.* **1946**, *2*, 225.

(19) Brown, D. B.; Shriver, D. F. *Inorg. Chem.* **1969**, *8*, 37.

(20) (a) Tsuchiya, R.; Uehara, A.; Kobayashi, K. *Bull. Chem. Soc. Jpn.* **1981**, *53*, 921. (b) Tsuchiya, R.; Uehara, A.; Yoshikuni, T. *Inorg. Chem.* **1982**, *21*, 590.

(21) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds"; Wiley: New York, 1963; pp 178–186.

Table II. IR and Far-IR Spectral Data (cm^{-1}) due to the CN-Stretching Vibration (ν_{CN}), MCN-Stretching Vibration (ν_{MCN}), and CMC-Bending Vibration (δ_{CMC}) and Effective Magnetic Moments (μ_{eff}, μ_B)[a]

	terminal-CN bands			bridged-CN bands		
compds[b]	ν_{CN}	ν_{MCN}	δ_{CMC}	ν_{CN}	ν_{MCN} or δ_{CMC}[c]	μ_{eff} (temp, K)
ref compds						
$K_3[Cr(CN)_6]$	2135	458	337			
$K_3[Co(CN)_6]$	2130	562	414			
$Cr(NC)_6Cr$				2190	527	
$Cr(NC)_6Co$				2200	581, 505, 325	
$Co^{II}_3[Cr(CN)_6]_2$				2175	493, 377	
$Co^{II}_3[Co(CN)_6]_2$				2180	460	
$[Cr(NH_3)_6][Cr(CN)_6]$						
original	2130	454	344			3.8 (299)
final				2190	527	2.4 (299)
$[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$						
original	2135	455	345			3.8 (296)
first				2175	502	2.6 (290)
final				2190	525	2.5 (290)
$[Cr(NH_3)_6][Co(CN)_6]$						
original	2135	562	415			3.8 (288)
final				2200	600, 512, 321	3.8 (299)
$[Cr(H_2O)(NH_3)_5][Co(CN)_6]$						
original	2130	563	420			3.8 (289)
final				2200	597, 510, 320	3.8 (288)
$[Co(NH_3)_6][Cr(CN)_6]$						
original	2135	459	344			3.8 (289)
final				2200	596, 510, 317	4.2 (288)
$[Co(H_2O)(NH_3)_5][Cr(CN)_6]$						
original	2130	460	345			3.8 (288)
final				2200	596, 510, 317	4.0 (290)
$[Co(NH_3)_6][Co(CN)_6]$						
original	2130	562	417			diamag (296)
first				2175	455	4.9 (288)
final				2180	493	4.9 (289)
$[Co(H_2O)(NH_3)_5][Co(CN)_6]$						
original	2130	564	420			diamag (293)
first	2130	563	420	2200		diamag (289)
second				2175	457	4.9 (289)
final				2180	493	4.9 (288)
cis-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$						
original	2130	462	419			diamag (288)
first	2130	562	421	2200		diamag (289)
second				2170	455	4.9 (289)
final				2175	493	5.0 (287)

[a] Unless otherwise specified, the chromium and cobalt ions are tervalent. [b] Original stands for the original complexes before heating. First, second, and final mean the first, second, and final products obtained during heating, and they are identical with those in Table III. [c] The bands (ν_{MCN} and δ_{CMC}) due to bridged-CN groups are not adequately assignable, and the bands that appeared in these regions are all listed in the same column.

the complexes do not give the terminal-CN band but give a new band at 2190 cm^{-1}, which is attributable to the bridging-CN band. We also find appreciable differences in the far-IR spectral data: both the doubly complexed salts exhibit two peaks in the ν_{CrCN} region (454 cm^{-1} for $[Cr(NH_3)_6][Cr(CN)_6]$ and 455 cm^{-1} for $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$) and in the δ_{CCrC} region (344 cm^{-1} for $[Cr(NH_3)_6][Cr(CN)_6]$ and 345 cm^{-1} for $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$). These peaks are not detectable in the final products of both the salts, but instead only one peak appears at 527 cm^{-1} for $[Cr(NH_3)_6][Cr(CN)_6]$ and 525 cm^{-1} for $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$, which are exactly the same as that (527 cm^{-1}) of $Cr(NC)_6Cr$. These results indicate that the final product from neither salt contains any terminal-CN group and all CN^- groups are used to make bridges between two Cr(III) ions.

Magnetic Moments. The magnetic moments (μ_{eff}) for all the complexes and the products obtained in each reaction step are also listed up in Table II. As seen from the table, the μ_{eff}/Cr(III) ion value of $[Cr(NH_3)_6][Cr(CN)_6]$ and $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$ is 3.8 μ_B, which is almost equal to that expected for the spin-only value of the Cr(III) ion. The final product of $[Cr(NH_3)_6][Cr(CN)_6]$ gives 2.4 μ_B, and the first and the final products of $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$ give 2.6 and 2.5 μ_B, respectively. Such substantially lower values of μ_{eff}'s evidently support the proposal that the Cr–Cr interaction through the CN bridge is considerably strong in these products.

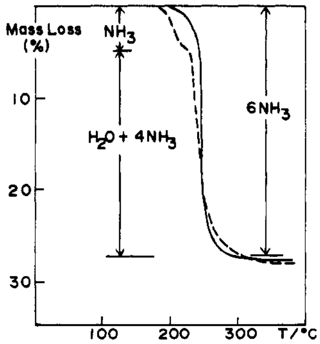

Figure 2. Q derivatograms of $[Cr(NH_3)_6][Co(CN)_6]$ (—) and $[Cr(H_2O)(NH_3)_5][Co(CN)_6]$ (- - -).

[Cr][Co]. Figure 2 shows the Q derivatograms of $[Cr(NH_3)_6][Co(CN)_6]$ and $[Cr(H_2O)(NH_3)_5][Co(CN)_6]$. For the first, a sharp weight loss can be seen at about 205–290 °C and then a plateau is obtained above 290 °C. The weight loss up to the plateau is 27.5%, which corresponds to the evolution of 6 mol of ammonia (27.6%). The color of the complex changed from yellow to brown. The TG curve of $[Cr(H_2O)(NH_3)_5][Co(CN)_6]$ displays a gradual weight loss at about

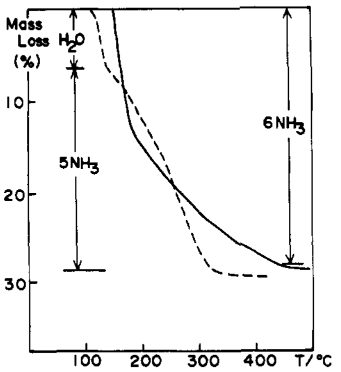

Figure 3. Q derivatograms of $[Co(NH_3)_6][Cr(CN)_6]$ (—) and $[Co(H_2O)(NH_3)_5][Cr(CN)_6]$ (---).

190–230 °C and then a steep weight loss up to 315 °C, reaching nearly a plateau. It was confirmed IR spectrophotometrically that the gradual weight loss is due to the evolution of ammonia but not of water. The overall weight loss (27.2%) agrees with the value (27.8%) calculated for the loss of 1 mol of water plus 5 mol of ammonia. The salt turned brown from reddish yellow. The final products from both complexes have the composition $Cr(NC)_6Co$.

$[Cr(NH_3)_6][Co(CN)_6]$ and $[Cr(H_2O)(NH_3)_5][Co(CN)_6]$ exhibit terminal ν_{CN} bands at 2135 and 2130 cm^{-1}, respectively. These bands are not detectable in the final products of both complexes, but instead the band due to the bridging-CN groups can be seen at 2200 cm^{-1}. The same situation is also true in the far-IR spectra. $[Cr(NH_3)_6][Co(CN)_6]$ and $[Cr(H_2O)(NH_3)_5][Co(CN)_6]$ give ν_{CoC} at 562 and 563 cm^{-1} and δ_{CCoC} at 415 and 420 cm^{-1}, respectively. On the other hand, the final products of both complexes give three bands in this region, which quite resemble those of the reference compound $Cr(NC)_6Co$. From these results, both the final products are believed to have the rational formula of $Cr(NC)_6Co$.

The magnetic moments of both complexes are almost the same (3.8 μ_B) as the spin-only value of the Cr(III) ion before and after heating, indicating that the cobalt(III) ion remains unchanged even after heating.

[Co][Cr]. Figure 3 depicts the Q derivatograms of $[Co(NH_3)_6][Cr(CN)_6]$ and $[Co(H_2O)(NH_3)_5][Cr(CN)_6]$. The Q derivatogram of $[Co(NH_3)_6][Cr(CN)_6]$ shows an unclear and smooth weight loss over the wide temperature range 150–440 °C, and a plateau is obtained above 440 °C. The net weight loss (27.8%) is very close to the evolution of 6 mol of ammonia (27.6%). The orange color of the original salt turned grayish green. In the TG curve of $[Co(H_2O)(NH_3)_5][Cr(CN)_6]$, a rather steep weight loss can be seen at about 110–120 °C, which corresponds to the evolution step of 1 mol of water. Then, a smooth curve appears up to 320 °C until a plateau is obtained. The net weight loss up to the plateau is approximately equal to the evolution of $H_2O + 5NH_3$ (found, 28.2%; calcd, 27.8%). The compound changed from reddish yellow to grayish green.

The IR bands at 2135 and 2130 cm^{-1} of $[Co(NH_3)_6][Cr(CN)_6]$ and $[Co(H_2O)(NH_3)_5][Cr(CN)_6]$ are due to the terminal-CN stretching vibration, which is shifted to a higher frequency region (2200 cm^{-1}) in the final products. The shift is ascribable to the CN-bridge formation. If both complexes are subject to simple bridge formation without the occurrence of CN flipping, the final products will have the Co(NC)Cr linkage. It should be mentioned, however, that the inspection of the IR and far-IR data in Table II reveals that both the final products do not coincide with the reference compound of $Co^{II}_3[Cr(CN)_6]_2$, but they resemble the compound of $Cr(NC)_6Co$. From this, it is believed that CN flipping may occur in any stage of the reaction without any substantial reduction of Co(III) ion.

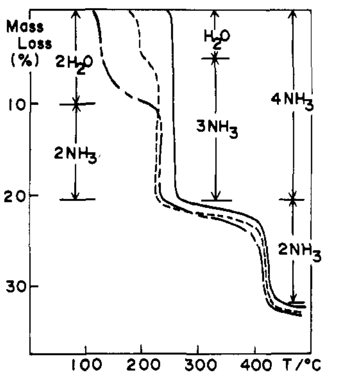

Figure 4. Q derivatograms of $[Co(NH_3)_6][Co(CN)_6]$ (—), $[Co(H_2O)(NH_3)_5][Co(CN)_6]$ (---), and *cis*-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$ (—-—).

The μ_{eff}'s of the final products are 4.2 μ_B for $[Co(NH_3)_6][Cr(CN)_6]$ and 4.0 μ_B for $[Co(H_2O)(NH_3)_5][Cr(CN)_6]$, which are slightly higher than the spin-only value of Cr(III) ion probably because a small portion of Co(III) ion is reduced to Co(II) ion in the final products.

[Co][Co]. Figure 4 shows the Q derivatograms of $[Co(NH_3)_6][Co(CN)_6]$, $[Co(H_2O)(NH_3)_5][Co(CN)_6]$, and *cis*-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$. The reactions of these complexes are characterized in that each thermal reaction step can be clearly detected. $[Co(NH_3)_6][Co(CN)_6]$ evolves 4 mol of ammonia at 240–270 °C and then 2 mol of ammonia at 390–430 °C. The complex turns deep blue from orange via purple blue. $[Co(H_2O)(NH_3)_5][Co(CN)_6]$ loses 1 mol of water at 165–205 °C to form yellow $[(NH_3)_5Co(NC)Co(CN)_5]$. Three moles of ammonia are then released sharply at 224 °C (purple blue), and finally 2 mol of ammonia are evolved at 380–430 °C (deep blue). *cis*-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$ evolves 2 mol of water at 115–150 °C and then 2 mol of ammonia at 228 °C and again at 383–430 °C.

The IR and far-IR spectra of the three final products resemble one another, which are identical with that of the reference material, $Co^{II}_3[Co(CN)_6]_2$.

From the measurements of magnetic moments, it was found that the first products obtained at the deaquation step (first step) of $[Co(H_2O)(NH_3)_5][Co(CN)_6]$ and *cis*-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$ are diamagnetic. The terminal-CN (2130 cm^{-1}) and the bridging-CN bands (2200 cm^{-1}) can be seen simultaneously in the IR spectra of both products. Therefore, it is thought that the deaquated products of $[Co(H_2O)(NH_3)_5][Co(CN)_6]$ and *cis*-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$ are $[(NH_3)_5Co(NC)Co(CN)_5]$ and $[(NH_3)_4Co(NC)_2Co(CN)_4]$, respectively, in which Co(III) stays intact.

On the other hand, the first product of $[Co(NH_3)_6][Co(CN)_6]$ and the second products of $[Co(H_2O)(NH_3)_5][Co(CN)_6]$ and *cis*-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$ give μ_{eff}'s of 4.9 μ_B. The final products of these three complexes also show nearly the same values (Table II). The value of 4.9–5.0 μ_B is reasonable for a cobalt(II) ion under a high-spin state in an octahedral ligand field.[22]

Discussion

The thermal reaction pathways of the complexes were found to differ considerably from one another depending upon the combination of metal ions in the cation and anion moieties and the ligands contained in the cation moiety. Table III summarizes the thermal reaction pathways of these complexes.

Reduction of Co(III) Ion. It is well-known that most Co(III) complexes have a tendency to undergo the reduction of Co(III) to Co(II) ion during thermal decomposition.[23] In our study,

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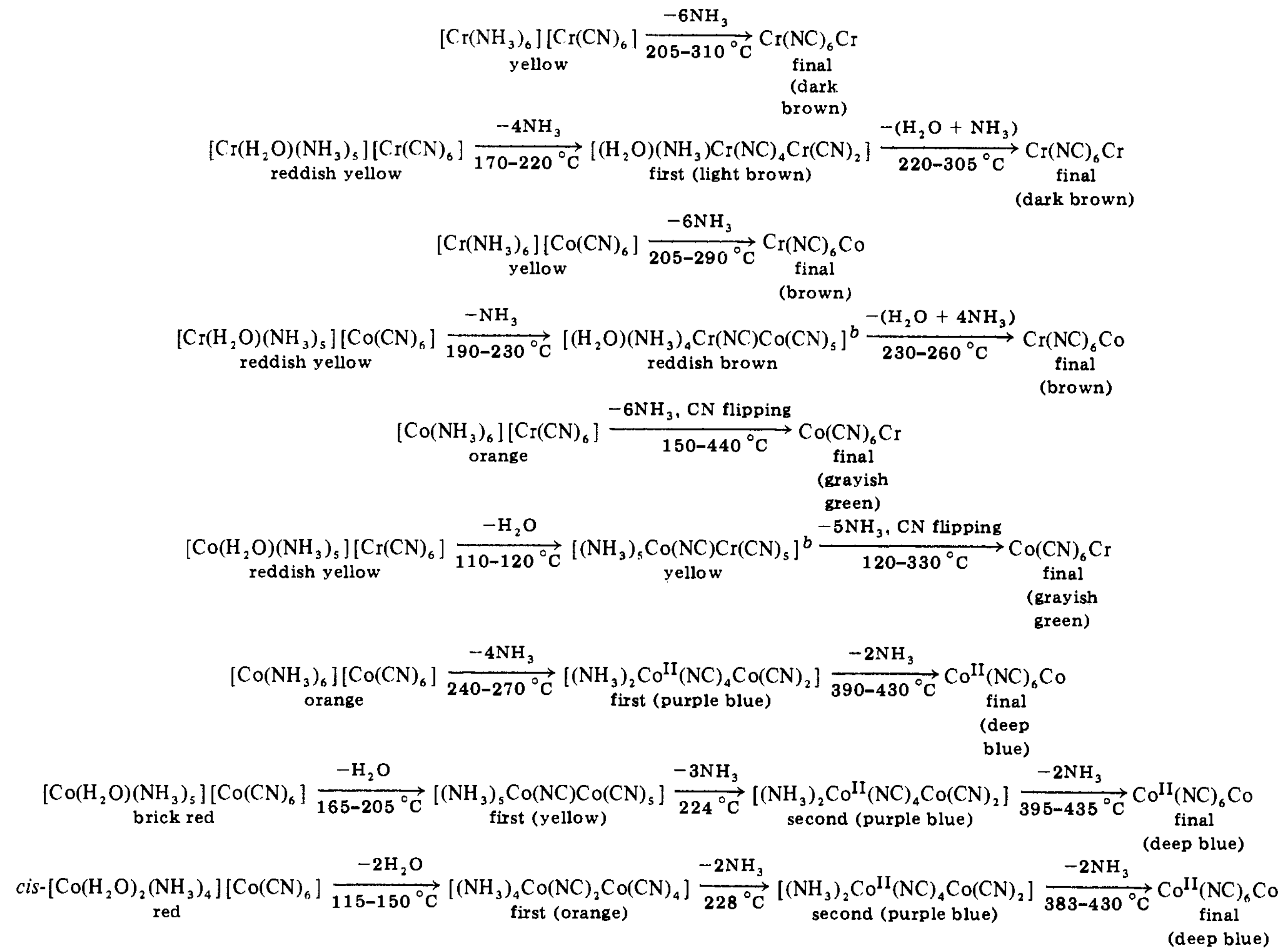
(22) It is well-known that the observed μ_{eff}'s for the octahedral Co(II) ion are on the order of 4.3–5.5 μ_B.

Table III. Thermal Reaction Pathways of the Complexes[a]



$$\underset{\text{yellow}}{[\mathrm{Cr(NH_3)_6}][\mathrm{Cr(CN)_6}]} \xrightarrow[205\text{–}310\ ^\circ\mathrm{C}]{-6\mathrm{NH_3}} \underset{\substack{\text{final}\\ \text{(dark brown)}}}{\mathrm{Cr(NC)_6Cr}}$$

$$\underset{\text{reddish yellow}}{[\mathrm{Cr(H_2O)(NH_3)_5}][\mathrm{Cr(CN)_6}]} \xrightarrow[170\text{–}220\ ^\circ\mathrm{C}]{-4\mathrm{NH_3}} \underset{\text{first (light brown)}}{[\mathrm{(H_2O)(NH_3)Cr(NC)_4Cr(CN)_2}]} \xrightarrow[220\text{–}305\ ^\circ\mathrm{C}]{-(\mathrm{H_2O} + \mathrm{NH_3})} \underset{\substack{\text{final}\\ \text{(dark brown)}}}{\mathrm{Cr(NC)_6Cr}}$$

$$\underset{\text{yellow}}{[\mathrm{Cr(NH_3)_6}][\mathrm{Co(CN)_6}]} \xrightarrow[205\text{–}290\ ^\circ\mathrm{C}]{-6\mathrm{NH_3}} \underset{\substack{\text{final}\\ \text{(brown)}}}{\mathrm{Cr(NC)_6Co}}$$

$$\underset{\text{reddish yellow}}{[\mathrm{Cr(H_2O)(NH_3)_5}][\mathrm{Co(CN)_6}]} \xrightarrow[190\text{–}230\ ^\circ\mathrm{C}]{-\mathrm{NH_3}} \underset{\text{reddish brown}}{[\mathrm{(H_2O)(NH_3)_4Cr(NC)Co(CN)_5}]^b} \xrightarrow[230\text{–}260\ ^\circ\mathrm{C}]{-(\mathrm{H_2O} + 4\mathrm{NH_3})} \underset{\substack{\text{final}\\ \text{(brown)}}}{\mathrm{Cr(NC)_6Co}}$$

$$\underset{\text{orange}}{[\mathrm{Co(NH_3)_6}][\mathrm{Cr(CN)_6}]} \xrightarrow[150\text{–}440\ ^\circ\mathrm{C}]{-6\mathrm{NH_3},\ \text{CN flipping}} \underset{\substack{\text{final}\\ \text{(grayish green)}}}{\mathrm{Co(CN)_6Cr}}$$

$$\underset{\text{reddish yellow}}{[\mathrm{Co(H_2O)(NH_3)_5}][\mathrm{Cr(CN)_6}]} \xrightarrow[110\text{–}120\ ^\circ\mathrm{C}]{-\mathrm{H_2O}} \underset{\text{yellow}}{[\mathrm{(NH_3)_5Co(NC)Cr(CN)_5}]^b} \xrightarrow[120\text{–}330\ ^\circ\mathrm{C}]{-5\mathrm{NH_3},\ \text{CN flipping}} \underset{\substack{\text{final}\\ \text{(grayish green)}}}{\mathrm{Co(CN)_6Cr}}$$

$$\underset{\text{orange}}{[\mathrm{Co(NH_3)_6}][\mathrm{Co(CN)_6}]} \xrightarrow[240\text{–}270\ ^\circ\mathrm{C}]{-4\mathrm{NH_3}} \underset{\text{first (purple blue)}}{[\mathrm{(NH_3)_2Co^{II}(NC)_4Co(CN)_2}]} \xrightarrow[390\text{–}430\ ^\circ\mathrm{C}]{-2\mathrm{NH_3}} \underset{\substack{\text{final}\\ \text{(deep blue)}}}{\mathrm{Co^{II}(NC)_6Co}}$$

$$\underset{\text{brick red}}{[\mathrm{Co(H_2O)(NH_3)_5}][\mathrm{Co(CN)_6}]} \xrightarrow[165\text{–}205\ ^\circ\mathrm{C}]{-\mathrm{H_2O}} \underset{\text{first (yellow)}}{[\mathrm{(NH_3)_5Co(NC)Co(CN)_5}]} \xrightarrow[224\ ^\circ\mathrm{C}]{-3\mathrm{NH_3}} \underset{\text{second (purple blue)}}{[\mathrm{(NH_3)_2Co^{II}(NC)_4Co(CN)_2}]} \xrightarrow[395\text{–}435\ ^\circ\mathrm{C}]{-2\mathrm{NH_3}} \underset{\substack{\text{final}\\ \text{(deep blue)}}}{\mathrm{Co^{II}(NC)_6Co}}$$

$$\underset{\text{red}}{cis\text{-}[\mathrm{Co(H_2O)_2(NH_3)_4}][\mathrm{Co(CN)_6}]} \xrightarrow[115\text{–}150\ ^\circ\mathrm{C}]{-2\mathrm{H_2O}} \underset{\text{first (orange)}}{[\mathrm{(NH_3)_4Co(NC)_2Co(CN)_4}]} \xrightarrow[228\ ^\circ\mathrm{C}]{-2\mathrm{NH_3}} \underset{\text{second (purple blue)}}{[\mathrm{(NH_3)_2Co^{II}(NC)_4Co(CN)_2}]} \xrightarrow[383\text{–}430\ ^\circ\mathrm{C}]{-2\mathrm{NH_3}} \underset{\substack{\text{final}\\ \text{(deep blue)}}}{\mathrm{Co^{II}(NC)_6Co}}$$

[a] First, second, and final have the same meanings as those in Table II. [b] The structures of the intermediates cannot clearly be identified because of the subsequent decomposition, and therefore the most plausible structures are given.

the reduction was not observed in the complexes except for [Co][Co]. Despite the fact that $[\mathrm{Co(NH_3)_6}][\mathrm{Co(CN)_6}]$, $[\mathrm{Co(H_2O)(NH_3)_5}][\mathrm{Co(CN)_6}]$, and *cis*-$[\mathrm{Co(H_2O)_2(NH_3)_4}][\mathrm{Co(CN)_6}]$ yield the same final product of $\mathrm{Co^{II}(NC)_6Co}$, their thermal reaction sequences are somewhat different from one another. $[\mathrm{Co(NH_3)_6}][\mathrm{Co(CN)_6}]$ undergoes reduction even at the beginning of the deammination step: viz., the diamagnetic original complex evolves 4 mol of ammonia to convert first into the paramagnetic species $[\mathrm{(NH_3)_2Co^{II}(NC)_4Co(CN)_2}]$ (4.9 μ_B) and then into the final product. On the other hand, in the cases of $[\mathrm{Co(H_2O)(NH_3)_5}][\mathrm{Co(CN)_6}]$ and *cis*-$[\mathrm{Co(H_2O)_2(NH_3)_4}][\mathrm{Co(CN)_6}]$, reduction was not detected in the water-evolution step: they deaquate without the reduction to form the diamagnetic species $[\mathrm{(NH_3)_5Co(NC)Co(NH_3)_5}]$ and $[\mathrm{(NH_3)_4Co(NC)_2Co(CN)_4}]$, respectively. In the next step, $[\mathrm{(NH_3)_5Co(NC)Co(CN)_5}]$ and $[\mathrm{(NH_3)_4Co(NC)_2Co(CN)_4}]$ lose 3 and 2 mol of ammonia, respectively, to yield the paramagnetic species $[\mathrm{(NH_3)_2Co^{II}(NC)_4Co(CN)_2}]$ (4.9 μ_B), which is identical with the first product of $[\mathrm{Co(NH_3)_6}][\mathrm{Co(CN)_6}]$. The species then liberates 2 mol of ammonia to form the final $\mathrm{Co^{II}(NC)_6Co}$ product.

The idea that it is the cobalt(III) ion in the cation moiety that undergoes reduction may be reasonably acceptable from the following facts. (1) The μ_{eff}'s of the final products are all on the order of 4.9–5.0 μ_B, which is close to the magnetic moment of a cobalt(II) ion under a high-spin state in an octahedral ligand field.[22] (2) In the case of the [Cr][Co] complexes, the cobalt(III) ion in the anion moiety was never reduced, even after reaction. (3) IR spectrophotometry verified that the final products are exactly the same as the Prussian blue analogue having a $\mathrm{Co^{II}(NC)Co^{III}}$ linkage.

Evolution of Water and Ammonia. Which ligand (water or ammonia) is preferentially evolved from the complexes containing both the ligands is also dependent upon the combination of metal ions. The water evolution precedes the ammonia evolution in the cationic Co(III) complexes $[\mathrm{Co(H_2O)(NH_3)_5}][(\mathrm{Cr\ or\ Co})(\mathrm{CN})_6]$ and *cis*-$[\mathrm{Co(H_2O)_2(NH_3)_4}][\mathrm{Co(CN)_6}]$, while the reverse is true in the cationic Cr(III) complexes $[\mathrm{Cr(H_2O)(NH_3)_5}][(\mathrm{Cr\ or\ Co})(\mathrm{CN})_6]$. This implies that in the solid state the Co(III)–N bond is stronger than the Co(III)–O bond, whereas the Cr(III)–O bond is stronger than the Cr(III)–N bond. This implication is parallel to the fact that in solution chemistry the Co(III) ion prefers to form complexes with nitrogen-donor rather than with oxygen-donor ligands, whereas the Cr(III) ion favors oxygen-donor over nitrogen-donor ligands.[24]

From the fact that the ammonia evolution precedes the water evolution in the thermal reaction of $[\mathrm{Cr(H_2O)(NH_3)_5}][(\mathrm{Cr\ or\ Co})(\mathrm{CN})_6]$, it is easily understandable why the previous attempts to get $[\mathrm{(NH_3)_5Cr(NC)}(\mathrm{Cr\ or\ Co})(\mathrm{CN})_5]$ always failed.[4,5]

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(23) (a) Wendlandt, W. W.; Smith, J. P. "The Thermal Properties of Transition-Metal Ammine Complexes"; Elsevier: Amsterdam, 1967; Chapters 3–5. (b) Tanaka, N.; Nagase, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 546.

(24) Garner, C. S.; House, D. A. *Transition Met. Chem.* (*N.Y.*) **1970**, *6*, 59–294.

CN Flipping. As mentioned in the preceding section, the final products of $[Co(NH_3)_6$ or $Co(H_2O)(NH_3)_5][Cr(CN)_6]$ were found to be $Co(CN)_6Cr$ but not $Co(NC)_6Cr$. This suggests that CN flipping takes place during the reaction. A similar CN flipping has been reported in the studies of the solid-state reaction of Prussian blue analogues such as $Co_3[Cr(CN)_6]_2$[24] and $Fe_3[Cr(CN)_6]_2$.[25]

Metal-Metal Interaction. The CN^- ion is rich in π electrons and capable of forming a M-NC-M′ bond (M and M′ are the same or different metal ions). The final products obtained in this study are therefore expected to have some extent of metal-metal interaction. The final products of the [Cr][Cr] reaction have a magnetic moment of 2.4-2.5 μ_B, which is remarkably low as compared with that expected from the spin-only value of the Cr(III) ion. Such subnormal magnetic moments are indicative of the presence of appreciable metal-metal interaction. As for the other complexes, a similar situation might be expected, but unfortunately we have insufficient evidence to bear out the expectation.

Registry No. $[Cr(NH_3)_6][Cr(CN)_6]$, 23540-70-7; $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$, 75058-08-1; $[Cr(NH_3)_6][Co(CN)_6]$, 39963-01-4; $[Cr(H_2O)(NH_3)_5][Co(CN)_6]$, 62534-93-4; $[Co(NH_3)_6][Cr(CN)_6]$, 38670-48-3; $[Co(H_2O)(NH_3)_5][Cr(CN)_6]$, 60897-44-1; $[Co(NH_3)_6][Co(CN)_6]$, 15556-03-3; $[Co(H_2O)(NH_3)_5][Co(CN)_6]$, 22622-91-9; *cis*-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$, 49732-16-3; $[Cr(NH_3)_6](NO_3)_3$, 15363-28-7; $[Co(NH_3)_6]Cl_3$, 10534-89-1; $[Cr(H_2O)(NH_3)_5](NO_3)_3$, 19683-62-6; $[Co(H_2O)(NH_3)_5]Cl_3$, 13820-80-9; $K_3[Cr(CN)_6]$, 13601-11-1; $K_3[Co(CN)_6]$, 13963-58-1; *cis*-$[Co(H_2O)_2(NH_3)_4]Cl_3$, 21264-85-7; $Co^{II}_3[Co(CN)_6]_2$, 14123-08-1; $Co^{II}_3[Cr(CN)_6]_2$, 14049-80-0; $Cr(NC)_6Co$, 26248-18-0; $Cr(NC)_6Cr$, 41751-48-8; $(H_2O)(NH_3)Cr(NC)_4Cr(CN)_2$, 86688-57-5; $(NH_3)_2Co^{II}(NC)_4Co(CN)_2$, 86688-58-6; $(NH_3)_5Co(NC)Co(CN)_5$, 86709-24-2; $(NH_3)_4Co(NC)_2Co(CN)_4$, 86688-60-0.

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[25] House, J. E.; Bailar, J. C., Jr. *Inorg. Chem.* **1969**, *8*, 672.

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Solvent Exchange and Anation on Five-Coordinate (*N*,*N*-Dimethylformamide)(2,2′,2″-tris(dimethylamino)triethylamine)copper(II)

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Proton NMR studies show that *N*,*N*-dimethylformamide exchange on five-coordinate $[Cu(Me_6tren)dmf]^{2+}$ (where Me_6tren = 2,2′,2″-tris(dimethylamino)triethylamine) is characterized by $k_{ex}(298.2\ K) = 555 \pm 39\ s^{-1}$, $\Delta H^{\ddagger} = 43.3 \pm 1.1\ kJ\ mol^{-1}$, $\Delta S^{\ddagger} = -47.0 \pm 3.1\ J\ K^{-1}\ mol^{-1}$, and $\Delta V^{\ddagger}(365\ K) = 6.1 \pm 0.1\ cm^3\ mol^{-1}$. These data suggest a dissociative (d) activation mode for dmf exchange. Anation of $[Cu(Me_6tren)dmf]^{2+}$ by NCS^-, N_3^-, and Br^- is characterized by kinetic data consistent with the operation of a dissociative interchange (I_d) mechanism.

Introduction

The coordination of the tetradentate ligand 2,2′,2″-tris(dimethylamino)triethylamine (Me_6tren) to copper(II) produces a five-coordinate copper(II) species in which solvent in the fifth cordination site exhibits a $\sim 10^5$ reduction in lability by comparison to that exhibited by hexakis(solvent)copper(II) species.[1-6] In consequence of this it is found that in *N*,*N*-dimethylformamide (dmf) $[Cu(Me_6tren)dmf]^{2+}$ undergoes solvent exchange and anation reactions at rates that fall conveniently into the NMR and stopped-flow spectrophotometric time scales. This facilitates a detailed kinetic characterization of simple ligand substitution processes on this example of five-coordinate copper(II)—a state that for copper(II) in particular and metal ions in general has not been subjected to the intensive mechanistic scrutiny afforded six-coordinate species.[3]

Experimental Section

Materials. *N*,*N*-Dimethylformamide was distilled under vacuum from anhydrous copper sulfate and was dried and stored over Linde 4A molecule sieves under nitrogen. Cyclohexane used as a reference was distilled at atmospheric pressure and was dried and stored as for dmf.

The 2,2′,2″-tris(dimethylamino)triethylamine (Me_6tren) ligand was prepared as previously described, as was the complex $[Cu(Me_6tren)ClO_4]ClO_4$.[5] This complex (3.7 g) was dissolved in dmf (10 cm^3) at 340 K, 13.4 g of triethyl orthoformate was added, and heating at 340 K was continued for 1 h. On cooling the blue crystalline $[Cu(Me_6tren)dmf](ClO_4)_2$ precipitated, and a further crop was obtained on addition of ether. The combined products were filtered off and washed with ether under dry nitrogen prior to pumping down under vacuum for 6 h. Anal. Calcd for $[Cu(Me_6tren)dmf](ClO_4)_2$: Cu, 11.2. Found: Cu, 11.2. $[Zn(Me_6tren)dmf](ClO_4)_2$ was similarly prepared. Anal. Calcd for $[Zn(Me_6tren)dmf](ClO_4)_2$: Zn, 11.5. Found: Zn, 11.6. Sodium azide, bromide, perchlorate, and thiocyanate were recrystallized from water prior to drying at 355 K for 5 days prior to pumping under vacuum for 1 day. The infrared spectra of these salts exhibited no water bands after this treatment. All chemicals used were from BDH.

Perchlorate salts of metal complexes may be explosive under some circumstances and should be handled with caution. No explosion hazard was encountered under the conditions of this study.

All solution preparations were carried out in a dry nitrogen atmosphere. Solutions for equilibrium studies by Job's method of continuous variations[7] and general spectrophotometric studies were contained in tightly stoppered quartz spectrophotometric cells. The solutions for stopped-flow spectrophotometric studies were transferred to storage syringes under dry nitrogen. Solutions for NMR studies were sealed under vacuum in 2-mm diameter NMR tubes, which were positioned concentrically in 5-mm diameter NMR tubes containing CD_3NO_2 or $(CD_3)_2SO$ (Stohler), depending on the temperature range studied.

Spectrophotometric Studies. The stoichiometry of the complex formed between $[Cu(Me_6tren)dmf]^{2+}$ and X^- (Br^-, N_3^-, or NCS^-) was investigated by Job's method of continuous variations in the $[[Cu(Me_6tren)dmf]^{2+}]$ and $[X^-]$ ranges of 2.8×10^{-5}–4.2×10^{-3} and 2.9×10^{-5}–4.0×10^{-3} mol dm^{-3}, respectively, at 298.2 K. The wavelengths employed were 315 and 330, 410, and 700 nm, respectively, for Br^-, N_3^-, and NCS^- at which substantial differences in molar

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[1] Poupko, R.; Luz, Z. *J. Chem. Phys.* **1972**, *57*, 3311.
[2] West, R. J.; Lincoln, S. F. *J. Chem. Soc., Dalton Trans.* **1974**, 281.
[3] Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. "Coordination Chemistry"; Martell, A. E., Ed.; American Chemical Society: Washington, DC, 1978; Vol. 2.
[4] Rablen, D. P.; Dodgen, H. W.; Hunt, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 1771.
[5] DiVaira, M.; Orioli, P. L. *Acta Crystallogr., Sect. B* **1968**, *B24*, 595.
[6] Coates, J. H.; Collins, P. R.; Lincoln, S. F. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 1236.

[7] Job, P. *Ann. Chim. (Paris)* **1928**, *9*, 113.

0020-1669/83/1322-2869$01.50/0