BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 169—175 (1973)

Derivatographic Studies on Transition Metal Complexes. IX.[1] Thermal CN-Bridging Reaction of Double Complex Salts in Solid Phase[2]

Ryokichi Tsuchiya, Shigeo Nakagawa,* Akira Uehara, and Eishin Kyuno
Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa
**Department of Chemical Engineering, Faculty of Technology, Kanazawa University, Kanazawa*

(Received June 3, 1972)

It was found by derivatography and spectral measurements that the double complex salts, $[Co(H_2O)_2N_4][Co(CN)_6]\cdot nH_2O$, where N_4 is $4NH_3$, two moles of ethylenediamine (en) or one mole of triethylenetetramine (trien), $[Co(NH_3)_2trien][Co(CN)_6]\cdot 2H_2O$, $[Co(NH_3)tepa][Co(CN)_6]\cdot 2H_2O$, where tepa is tetraethylenepentamine, and $[Co(H_2O)_2trien][Cr(CN)_6]\cdot 2H_2O$ underwent deaquation- or deammonation-CN-bridging formation reaction upon heating. The general tendency was observed to be as follows: the more stable the structural configuration of the coordination sphere, the higher the activation energy. In the case of the complex containing hexacyanochromate(III) as an anion, the activation energy for the bridging formation reaction is especially high as a result of possible flipping in CN bridging groups.

It is known that the hexaammine or aquopentaammine complexes of transition metals such as $[M(NH_3)_6]X_3$ or $[M(H_2O)(NH_3)_5]X_3$ liberate a part of ammonia or water by deammonation- or deaquation-anation upon heating, producing the corresponding acidopentaamine complexes as expressed by the fol-

---

[1] Part VIII in this series: see R. Tsuchiya, M. Suzuki, and E. Kyuno, This Bulletin, **45**, 3105 (1972).

[2] Presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April (1970).

lowing reactions:

$$[M(NH_3)_6]X_3(s) \xrightarrow{\Delta} [MX(NH_3)_5]X_2(s) + NH_3(g)$$

$$[M(H_2O)(NH_3)_5]X_3(s) \xrightarrow{\Delta} [MX(NH_3)_5]X_2(s) + H_2O(g),$$

where M is Co[3–6] or Cr[6,7] and X is halogens.

Thermal bridging reaction can be expected when X in the complexes of the above types is replaced by the relevant complex anions of the type $[M'X_6]^{3-}$ containing a ligand X which can form a bridge over two metals, *i.e.*, heating of some double complex salts will give the binuclear complexes as expressed by the following reactions:

$$[MA_nB_{6-n}][M'X_6] \xrightarrow{\Delta} [B_{6-n}M\text{-}X_n\text{-}M'X_{6-n}] + nA,$$

where M and M′ are central metal atoms, A is a volatile neutral ligand, B the ligand which can not be expelled by heating, X the ligand which can form the bridge between M and M′, and *n* the number of ligand A contained in the starting complexes.

It can be expected that the binuclear complexes produced have one, two or three bridges between two metals in the respective cases where *n* is 1, 2, or 3, the coordinated atoms forming two octahedrons holding a point, an edge or a face in common, respectively, as shown in Fig. 1.

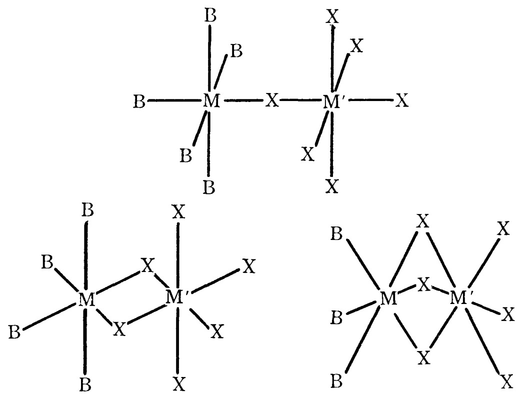


Fig. 1. Three possible types of bridged binuclear complexes.

No reports have been found on the above thermal reactions except for a study in which the complex $[(NH_3)_5Co\text{–}NC\text{–}Co(CN)_5]$ was prepared by isothermal heating and characterized by physical methods.[8]

We prepared a series of double complex salts containing water or ammonia as a volatile ligand A and CN^- as bridging group X, and examined the possibility of occurrence of these bridging formation reactions.

Experimental

Preparation of Double Complex Salts. 1) cis-*Diaquotetraamminecobalt(III) Hexacyanocobaltate(III) Monohydrate,* cis-*$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]\cdot H_2O$ (I).* To a 100 ml aqueous solution of 3.7 g of *cis*-diaquotetraamminecobalt(III) nitrate, *cis*-$[Co(H_2O)_2(NH_3)_4](NO_3)_3$,[9] a 100 ml of 3.3 g of potassium hexacyanocobaltate(III) $K_3[Co(CN)_6]$[10] was added. After a few minutes of stirring, red crystals were precipitated. After being filtered off, they were washed with water, ethanol and ether in turn and air dried.

Found: C, 18.16; H, 4.33; N, 35.89%. Calcd for $[Co(H_2O)_2(NH_3)_4][Co(CN)_6]\cdot H_2O$: C, 18.50; H, 4.66; N, 36.00%.

2) cis*-Diaquobis(ethylenediamine)cobalt(III) Hexacyanocobaltate(III) Trihydrate,* cis-*$[Co(H_2O)_2en_2][Co(CN)_6]\cdot 3H_2O$ (II).* When a solution of 4.9 g of *cis*-diaquobis(ethylenediamine)cobalt(III) bromide dihydrate, *cis*-$[Co(H_2O)_2en_2]Br_3\cdot 2H_2O$[11] in 20 ml of 1 N HNO_3 and a solution of 3.3 g of $K_3[Co(CN)_6]$ in 20 ml were mixed together and kept standing at room temperature for one day, fine red crystals were precipitated. They were treated and dried in a similar way to that described for 1).

Found: C, 24.77; H, 5.13; N, 29.13%. Calcd for $[Co(H_2O)_2en_2][Co(CN)_6]\cdot 3H_2O$: C, 24.80; H, 5.41; N, 28.91%.

3) cis*-α-Diaquotriethylenetetraminecobalt(III) Hexacyanocobaltate(III) Dihydrate,* cis-α-*$[Co(H_2O)_2trien][Co(CN)_6]\cdot 2H_2O$ (III).* The complex was obtained as pink crystals precipitated from a mixture of the two solutions, one containing 0.01 mol of *cis*-α-diaquotriethylenetetraminecobalt(III) salt, *cis*-α-$[Co(H_2O)_2trien]^{3+}$, and the other containing 3.3 g of $K_3[Co(CN)_6]$ in a similar manner to that for salt I, the former being prepared by the reaction of *cis*-α-carbonatotriethylenetetraminecobalt(III) perchlorate monohydrate, *cis*-α-$[CoCO_3trien]ClO_4\cdot H_2O$[12] (3.7 g) with 20% $HClO_4$ solution.

Found: C, 29.55; H, 5.25; N, 28.66%. Calcd for $[Co(H_2O)_2trien][Co(CN)_6]\cdot 2H_2O$: C, 29.28; H, 5.32; N, 28.45%.

4) cis*-β-Diaquotriethylenetetraminecobalt(III) Hexacyanocobaltate(III) Dihydrate,* cis-β-*$[Co(H_2O)_2trien][Co(CN)_6]\cdot 2H_2O$ (IV).* The double complex salt was prepared from 3.7 g of *cis*-β-$[CoCO_3trien]ClO_4$[12] as the starting complex cation in the same way as descrybed in 3). It was orange.

Found: C, 28.84; H, 5.13; N, 27.53%. Calcd for $[Co(H_2O)_2trien][Co(CN)_6]\cdot 2H_2O$: C, 29.28; H, 5.32; N, 28.45%

5) cis*-β-Diamminetriethylenetetraminecobalt(III) Hexacyanocobaltate(III) Dihydrate,* cis-β-*$[Co(NH_3)_2trien][Co(CN)_6]\cdot 2H_2O$ (V).* *cis*-β-diamminetriethylenetetraminecobalt(III) chloride, *cis*-β-$[Co(NH_3)_2trien]Cl_3$[13] and $K_3[Co(CN)_6]$ were used as starting materials for the preparation. The product was yellow crystals.

Found: C, 30.05; H, 5.68; N, 34.28%. Calcd for $[Co(NH_3)_2trien][Co(CN)_6]\cdot 2H_2O$: C, 29.37; H, 5.68; N, 34.28%.

6) Amminetetraethylenepentaminecobalt(III) Hexacyanocobaltate(III) Dihydrate, $[Co(NH_3)tepa][Co(CN)_6]\cdot 2H_2O$ (VI). One of the starting complexes, amminetetraethylenepentaminecobalt(III) bromide, $[Co(NH_3)tepa]Br_3$, was prepared from the corresponding bromo complex, $[CoBr\ tepa]Br_2$[14] in

---

3) M. Mori, R. Tsuchiya, and Y. Okano, This Bulletin, **32**, 1029 (1959).

4) N. Tanaka and M. Nanjo, *ibid.*, **37**, 1330 (1964).

5) M. Mori and R. Tsuchiya, *ibid.*, **33**, 841 (1960).

6) W. W. Wendlandt and J. L. Bear, *J. Inorg. Nucl. Chem.*, **22**, 77 (1961).

7) R. Tsuchiya, Y. Kaji, A. Uehara, and E. Kyuno, This Bulletin, **42**, 1881 (1969).

8) R. A. de Castelló, C. P. MacColl, N. B. Egen, and A. Haim, *Inorg. Chem.*, **8**, 699 (1969).

9) S. M. Jørgensen, *Z. Anorg. Chem.*, **2**, 281 (1892).

10) A. Benedetti-Pichler, *Z. Anal. Chem.*, **70**, 258 (1927).

11) A. Werner and K. R. Lange, *Ann. Chem.*, **386**, 88 (1912).

12) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967).

13) E. Kyuno and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **88**, 1125 (1966).

14) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

liquid ammonia. The aqueous solution containing 5.0 g of $[Co(NH_3)tepa]Br_3$ was mixed with a solution of 3.3 g of $K_3[Co(CN)_6]$ and cooled with ice in a similar manner to that described above. Yellow crystals were obtained and then treated as mentioned in 1).

Found: C, 32.18; H, 5.38; N, 31.75%. Calcd for $[Co(NH_3)tepa][Co(CN)_6]\cdot 2H_2O$: C, 32.54; H, 5.85; N, 32.53%.

7) cis-α-Diaquotriethylenetetraminecobalt(III) Hexacyanochromate(III) Dihydrate, cis-α-$[Co(H_2O)_2trien][Cr(CN)_6]\cdot 2H_2O$ (VII). The double complex salt was prepared from 3.7 g of *cis*-α-$[CoCO_3trien]ClO_4\cdot H_2O$[12] and 3.3 g of $K_3[Cr(CN)_6]$[15] in the same way as in the case of 3). The product was pink crystals.

Found: C, 30.72; H, 5.40; N, 28.98%. Calcd for $[Co(H_2O)_2trien][Cr(CN)_6]\cdot 2H_2O$: C, 29.70; H, 5.40; N, 28.86%.

8) μ-Cyanoaquobis(ethylenediamine)pentacyanodicobalt(III,III) Pentahydrate, $[(H_2O)en_2Co\text{-}NC\text{-}Co(CN)_5]\cdot 5H_2O$ (VIII). When one gram of *cis*-$[Co(H_2O)_2en_2][Co(CN)_6]\cdot 3H_2O$ was stirred in 400 ml of water, the compound gradually dissolved giving orange coloration. After being kept standing at room temperature for about a day, orange needle crystals appeared, which were dried after filtration.

Found: C, 23.86; H, 5.57; N, 27.87%. Calcd for $[Co_2en_2(H_2O)(CN)_6]\cdot 5H_2O$: C, 23.80; H, 5.60; N, 27.76%.

9) μ-Dicyanotriethylenetetraminetetracyanodicobalt(III,III) Pentahydrate, $[trien\ Co\text{-}(NC)_2\text{-}Co(CN)_4]\cdot 5H_2O$ (IX). When one gram of *cis*-α-$[Co(H_2O)_2trien][Co(CN)_6]\cdot 2H_2O$ was suspended in 200 ml of water and heated on a water bath, the double complex salt was completely dissolved with yellow color. The solution was concentrated to about half its volume on a water bath and kept standing at room tempetature, yellow crystals being precipitated. The complex was dried in a similar manner to that described above.

Found: C, 28.49; H, 5.46; N, 27.80%. Calcd for $[Co_2trien(CN)_6]\cdot 5H_2O$: C, 28.25; H, 5.53; N, 27.45%.

Derivatographic Measurements. The derivatograms were obtained with a MOM Derivatograph Typ-OD-102. All the measurements were carried out in a constant flow of nitrogen under the heating rate of 1°C/min. 0.4 or 0.5 g of sample was used in each run. The activation energies (E_a) and enthalpy changes (ΔH) were calculated by analysis of the DTA curves in the derivatograms.

Spectral Measurements. In order to examine the structural change during the course of the thermal reaction, the electronic spectra and IR spectra were measured with a Hitachi EPS and EPU-2A Spectrophotometers in both solution and powdered state and with a JASCO Model IR-E Spectrophotometer in mull state, respectively.

Isothermal Measurements. Isothermal determination of the deaquation or deammonation accompanied by bridging reaction was carried out by use of a Shimadzu TM-1A Thermobalance in static air at the desired temperature.

Results and Discussion

Derivatography. It was found that most of the salts do not show any distinct evidence for the bridging formation in the TG curve, except for some salts. As an example, the double complex salt, $[Co(H_2O)(NH_3)_5][Co(CN)_6]$, the simplest compound anticipated to give the binuclear complex, decomposed at 190°C without giving any plateau in the TG curve suggesting the bridging formation, as shown in Fig. 2.

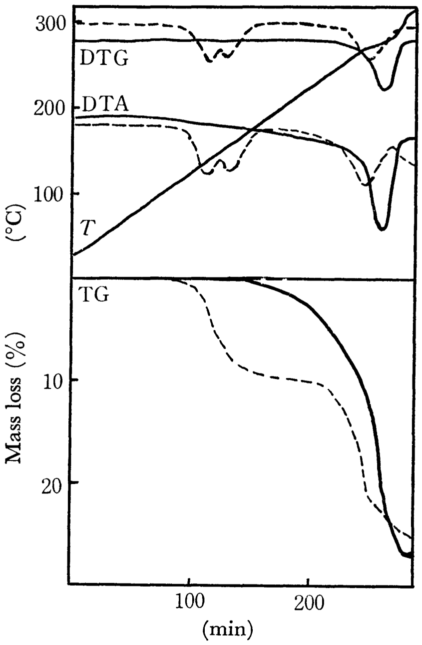


Fig. 2. Derivatograms of the double complex salts, $[Co(H_2O)(NH_3)_5][Co(CN)_6]$ (——) and I (----).

In several salts, however, distinct thermal reactions for the formation of the stable complexes containing CN bridges between two central metal atoms were found by the presence of one or two steady steps of the liberation of neutral ligands involved. The derivatograms of the diaquotetraammine-type double complex salt I, the diaquobis(ethylenediamine)-type one II. and the diaquotriethylenetetramine-type one III are shown in Figs. 2, 3, and 4, respectively.

In the double complex salt I, the DTA and DTG curves split into two peaks are observed in the temperature range 90—150°C, where the mass loss corresponding to two moles of water or to the sum of one mole of water and one mole of ammonia appears in

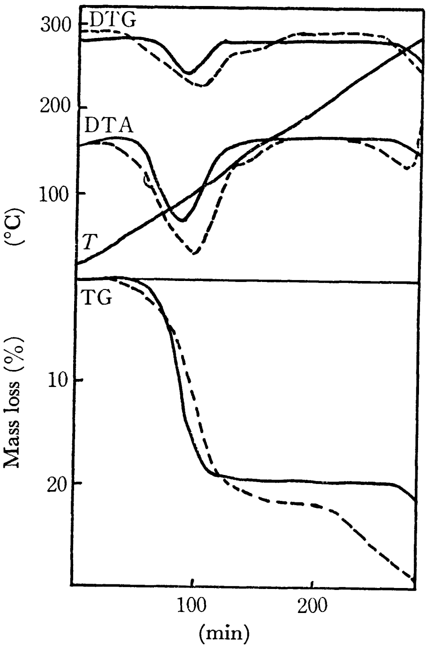


Fig. 3. Derivatograms of II (——) and VIII (----).

---

15) J. H. Bigelow and J. C. Bailar, Jr., "Inorganic Syntheses," Vol. 2, (1946), p. 203.

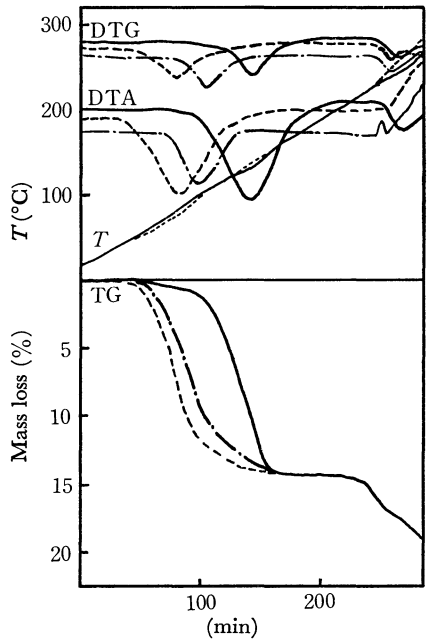


Fig. 4. Derivatograms of III (——), IV (----) and VII (–-–)

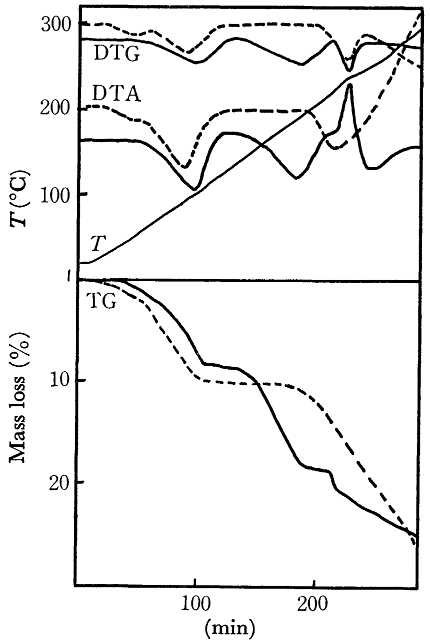


Fig. 5. Derivatograms of V (——) and VI (----).

the TG curve. However, since the ammonia evolution was not sufficient for detection in this step, the mass loss might be attributed to one mole of lattice water and one mole of coordinated water.

Salt II showed the mass loss corresponding to five moles of water in the region 50—120°C, and after that the weight of the sample remained constant till 260°C. The elemental analysis for the salt taken out from the furnace at 150°C was as follows: Found: C, 30.22; H, 4.90; N, 35.58%. Calcd for $[en_2Co_2(CN)_6]$: C, 30.47; H, 4.90; N, 35.53%. Thus, the thermal reaction product seems to be a binuclear complex containing two CN bridges as $[en_2Co(CN)_2Co(CN)_4]$.

The derivatogram of complex VIII which has one CN bridge is also included in Fig. 3. It is seen from the DTA and DTG curves that five moles of the lattice water are liberated from 60 to 120°C and then one mole of the coordinated water is continuously expelled to 160°C. Despite the loss of the coordinated water in complex VIII, the binuclear complex having the same two CN bridges as those obtained from complex II could not be found, the reason being not clear.

Salts III, IV, and VII give similar derivatograms to each other irrespective of the difference of the initiation dehydration temperatures, 90°C for III, 45°C for IV, and 75°C for VII, respectively, as seen in Fig. 4: two steps of the mass losses corresponding to two moles of the lattice water and to two moles of the coordinated water can not be distinguished from each other both in DTA and DTG curves. We also see that the *cis-β*-form double complex salt IV undergoes CN-bridging formation more easily than the corresponding *cis-α*-form one III and the complex containing $[Cr(CN)_6]^{3-}$ VII gives more readily the bridging formation than the corresponding cobaltate(III), III.

The derivatograms of the two double complex salts V and VI containing ammine as the labile ligand against heating are shown in Fig. 5.

Salt V shows two steps of mass losses at 50—120°C and 140—190°C, and then decomposes at 220°C. From the results of IR spectra and detection of ammonia, the first step is due to the liberation of two moles of the lattice water and the second to the deammonation reaction accompanied by the two CN-bridging formation.

Salt VI loses one mole of ammonia at 100—170°C, giving a complex containing one CN-bridge.

Electronic Spectra. On heating these double complex salts in the solid phase, the deaquation-bridging reaction accompanied by a distinct color change from red to yellow was observed, but scarcely in the deammonation-bridging reaction.

In the double complex salts, the first absorption bands of the complex cations $[Co(H_2O)_2N_4]^{3+}$ give a maximum in the neighborhood of 500 nm, whereas those of the complex anions $[Co(CN)_6]^{3-}$ and $[Cr(CN)_6]^{3-}$ give a maximum at 311 and 300 nm, respectively. Since the bands resulting from the hexacyanometallate anions are situated in the near-ultraviolet region, they scarcely affect the visible bands of the complex cations contained in the double complex salts. Therefore, the first absorption maxima of the cations constituting the double complex salts are considered to be those of the complexes themselves.

The numerical values for the first absorption bands of all the complexes prepared in the experimental section and those heated are listed in Table 1. The spectra of salts III and IV and those heated at 170°C, including VII heated at 170°C, are shown as representatives in Fig. 6, the spectra being measured by the diffuse reflectance method.

As seen in Table 1, the absorption bands of the double complex salts, when heated, are found to shift to the higher frequency region except for salts V and VI, *e.g.*, those of the complexes II, III, and IV are shifted to the neighborhood of 470 nm, which is almost similar

Table 1. Change of the absorption maxima upon heating of the double complex salts

Salts	λ_{max} (nm)	$\xrightarrow[\Delta]{}$	λ_{max} (nm)
I	510		485
II	504		467
III	505		472
IV	486		472
V	476		472
VI	476		474
VII	505		420
VIII	480		468
IX	462		

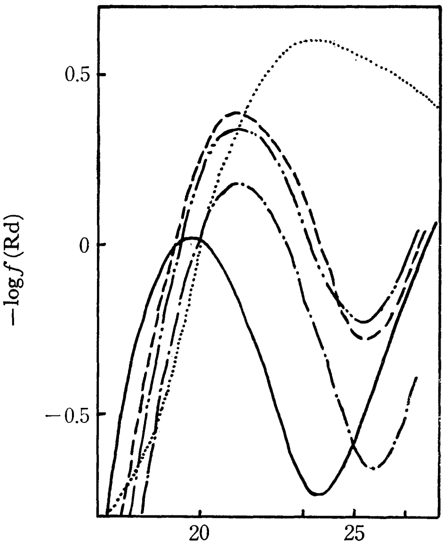


Fig. 6. Absorption spectra by the diffuse reflectance method of III at room temperature (——), III heated at 170°C (– – –), IV at room temperature (——), IV heated at 170°C (–·–), and VII heated at 170°C (······).

to that of hexaamminecobalt(III) complex, and above all, the wavenumber of the band of the thermal product from III is approximately close to that of IX. It is obvious that complex III undergoes the two-CN-bridging formation reaction upon heating to be converted into the binuclear complex IX.

Salt I liberates two moles of water upon heating, and the absorption band is shifted to 485 nm. Complex VIII has an absorption band at 480 nm, both bands coinciding with the band of aquopentaamminecobalt(III) complex. It seems that both the complex formed by heating I and complex VIII have one CN-bridge between two central metals and the cationic part has CoN_5O-type coordination. Complex VIII was found to give the absorption peak at 468 nm after the liberation of one mole of the coordinated water. The peak is close to that of the thermal bridging product of II. This suggests that complex VIII is converted into the two CN-bridging complex of CoN_6-type.

Only a slight shift of the band can be observed in V and VI (Table 1). It is obvious that in their thermal bridging reaction product, N atoms in CN^- bridges are coordinated to cobalt in the cationic part and C atoms participate in cobalt in anionic part; *i.e.*, the cationic part consists of CoN_6-type coordination, giving similar spectra to that of hexaamminecobalt(III) complex.

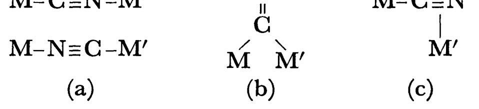
Complex VII heated at 170°C gives a broad absorption band in the wavelength region 430—390 nm in contrast to the case of Co–CN–Co type salts as shown in Fig. 6. It suggests that in contrast to the Co–CN–Co type salts which consist of CoN_6- and CoC_6-type coordination spheres combined with CN-bridges, the Co–CN–Cr type salt thermally obtained from VII consists of CoC_2N_4- and CrC_4N_2-type coordination spheres formed by the flipping of CN-bridges[8,16] and the overlap of their spectra appearing at 410 and 405 nm gives a broad band.

IR Spectra. IR spectra of the double complex salts we prepared except for those of VIII and IX show, in the frequency region of ν_{CN} stretching, one clear band at 2143—2149 or 2130 cm^{-1}, which is assigned to the terminal CN stretching vibration in $[Co(CN)_6]^{3-}$ or $[Cr(CN)_6]^{3-}$, respectively. With the progress of deaquation- or deammonation-anation, a new band whose extinction increases gradually appears at *ca.* 2190 cm^{-1} in addition to the original peak due to terminal-CN stretching. This is assigned to the stretching of CN bridging. The IR spectral data concerned with ν_{CN} for all the double complex salts and those heated are given in Table 2. As a typical example for the change of ν_{CN} bands, the spectra in the neighborhood of 2100—2200 cm^{-1} of salt IV at several steps of heating are shown in Fig. 7.

Table 2. Change of ν_{CN} in IR spectra of the double complex salts

Salts	ν_{CN}	$\xrightarrow[\Delta]{}$	ν_{CN}
I	2143		2143, 2190
II	2143		2143, 2190
III	2149		2149, 2196
IV	2149		2149, 2196
V	2143		2143, 2196
VI	2143		2143, 2190
VII	2130		2130, 2170
VIII	2143, 2220		
IX	2143, 2212		

The following three possible modes are considered for bridging structure:



(a) would be the most possible mode, because the frequency of CN stretching vibration in both (b) and (c) should be lower than that of the terminal CN group in $[M(CN)_6]^{3-}$ and the possibility of the flipping reaction was observed as shown in the section of electronic spectra. However, if mode (a) is accepted, the complexes containing two CN-bridges in *cis* position

---

[16] D. B. Brown and D. F. Shriver, *Inorg. Chem.*, **8**, 37 (1969).

Table 3. Enthalpy changes, ΔH, and activation energies, E_a, in the thermal bridging reactions of the double complex salts

Double complex salts	ΔH kcal/mol	E_a kcal/mol[a]	E_a kcal/mol[b]	E_a kcal/mol[c]
I	9.6	59.0	57.7	(99.5)
	9.4	48.5	49.4	
II	12.5	23.9	23.7	
III	12.9	30.9	31.1	31.3
IV	11.2	18.8	19.2	
V	14.9	42.5	42.8	42.7
VI	3.1	20.9	39.0	
VII	6.7	44.9	43.5	45.7
VIII	8.4	32.0	32.0	

a) Estimated by analysis of the DTA curve.
b) Estimated by analysis of the DTG curve.
c) Calculated from the Arrhenius plots in the isothermal measurements.

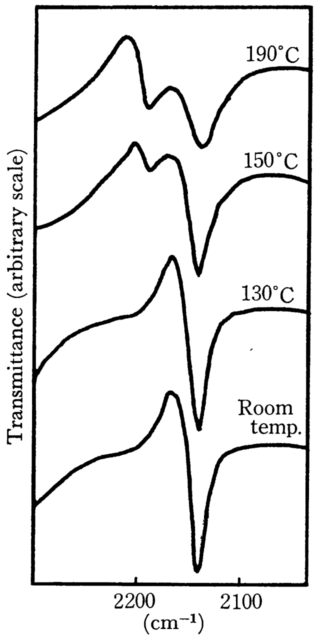


Fig. 7. Change of IR spectra in the frequency region of ν_{CN} of V at several steps of heating.

produced by the thermal reaction would not be binuclear but have the structure of either tetramer or polymer, since the bond M–C≡N–M′ or M–N≡C–M′ should be linear.

On the other hand, X-ray diffraction for the single crystal of $[(NH_3)_5Co–N≡C–Co(CN)_5]\cdot H_2O$[17] shows that the angle of Co–C–N is 172.4° and that of Co–N–C 159.8°. Thus, it is not unreasonable to consider the possibility of the presence of the binuclear complexes having structure (a) with bending M–C≡N–M′ or M–N≡C–M′ bonds in *cis* position, not (b) or (c). However, the presumption could not be verified, since the molecular weight determination could not be made because of the small solubility of the salts in many solvents.

Thermochemical Data. The data of the enthalpy changes ΔH and the activation energies E_a for the thermal reaction of the double complex salts are summarized in Table 3, the former being estimated from the analysis of DTA and the latter from the analysis of DTA or DTG curve in a similar manner to that described previously.[7]

The values of the enthalpy change for these thermal reactions of I through V are close to those for the general deaquation- or deammonation-anation reactions, but those for VI, VII, and VIII are remarkably small. This may be due to the large contribution of exothermic bridging formation throughout the reactions. It is found that the activation energies for the liberation of two neutral molecules increase in the order, IV<II<III<V<VII. This sequence can be explained as follows.

1. The α-trien chelate stabilizes the complex to a greater extent than ethylenediamine chelate, so that the coordinated water in salt III is not so easily liberated as in salt II.
2. Since β-trien chelate has a larger strain than α-trien chelate, the former expels the coordinated water more easily than the latter, making the activation energy in IV lower than in III.
3. The activation energy of V is larger than that of IV, which may be due to the greater difficulty of evolution of ammonia than water.
4. Salt VII has a larger activation energy than salt III. This might be due to the possibility of the flipping reaction in VII.

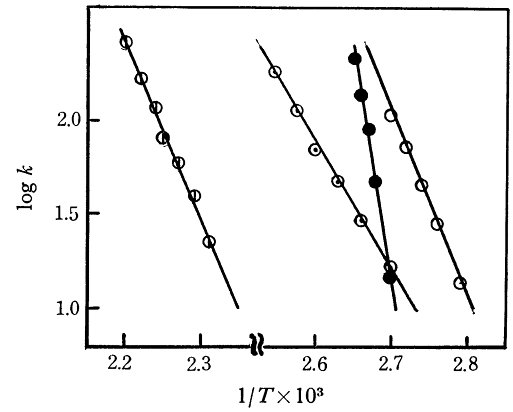


Fig. 8. Arrhenius plots for the bridging reaction of the double complex salts: I (●—●), III (⊙—⊙), V (⦶—⦶) and VII (○—○).

---

[17] O. Hassel and J. R. Salvesen, *Z. Phys. Chem.*, **128**, 345 (1927).

Isothermal Measurements and Reaction Mechanism. The Arrhenius plots, log *k* *vs.* $1/T$, estimated by the isothermal measurements of the thermal bridging formation reactions of salts I, III, V, and VII are shown in Fig. 8, where *k* is the rate constant of the reaction calculated on the basis of the presumption of the first order. The activation energies obtained from the plots are also given in Table 3. They are in fairly good agreement with those obtained by derivatography except for I.

Taking into account the results from derivatography, isothermal measurements and the UV and IR absorption spectral measurements, it was concluded that, in the thermal bridging formation reaction of Co–Co double complex salts, the CN groups in the anionic part coordinate to cobalt in cationic part with *N*-atoms, but in that of Co–Cr salts, they coordinate to cobalt with C-atom as a result of CN flipping.