466 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 51 (2), 466—469 (1978) [Vol. 51, No. 2

Solid-phase Thermal Syntheses of Binuclear Chromium(III) and Cobalt(III) Complexes Containing *N*-(2-Sulfoethyl)iminodiacetic Acid[1)]

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(Received June 7, 1977)

The following four chromium(III) and cobalt(III) double complexes were prepared and the thermal reactions were investigated both isothermally and non-isothermally in the solid-phase: [(Cr or Co)(H_2O)(NH_3)$_5$][(Cr or Co)(sida)$_2$] where sida denotes *N*-(2-sulfoethyl)iminodiacetate ion. The double complexes were found to be thermally deaquated to form the homo- and hetero-metal binuclear complexes [(NH_3)$_5$(Cr or Co)(sida)(Cr or Co)(sida)] in which one of *N*-(2-sulfoethyl)iminodiacetate ions functions as the bridging ligand between two metal ions. The complexes thus obtained were purified from a 50% $HClO_4$ or a 1 M $NaClO_4$ solution in the forms of the hydrogen salts [(NH_3)$_5$(Cr or Co)(sida)(Cr or Co)(sidaH)]ClO_4 or the sodium salts [(NH_3)$_5$(Cr or Co)(sida)(Cr or Co)(sidaNa)]ClO_4.

Only a few complexes are known in which natural or artificial amino acids function as the bridging ligand: the homo-metal binuclear complexes[2)] such as [en_2Co(L-asp)$Co(H_2O)en_2$]$(ClO_4)_4 \cdot H_2O$[3)] and [$(NH_3)_5Co$(edta)-$Co(H_2O)$]$(ClO_4)_2$[4)] were recently isolated by means of column chromatography. When the solid-phase bridging[5–7)] and ligand-transfer[8)] reactions reported previously were applied to the preparation of the amino acid-bridging binuclear complexes, they were obtained easily.

The present study was therefore undertaken to prepare the amino acid-bridging homo- and hetero-metal binuclear complexes[2)] by the use of solid-phase thermal reactions. The preparative procedures of the present study are based on the following thermal reactions:

$$[(\text{Cr or Co})(H_2O)(NH_3)_5][(\text{Cr or Co})(\text{sida})_2] \xrightarrow[\Delta]{-H_2O}$$

$$[(NH_3)_5(\text{Cr or Co})(\text{sida})(\text{Cr or Co})(\text{sida})],$$

where sida denotes *N*-(2-sulfoethyl)iminodiacetate ion.

The thermal syntheses according to the above reaction have the following characteristics: firstly, the hetero-metal binuclear complexes can conveniently be synthesized by selecting the combination of metal ions in the starting double complexes. Secondly, amino acid-bridging binuclear complexes can be obtained with simpler processes. Thirdly, the complexes in which the $-SO_3$ group in sida is coordinated to a metal ion can be isolated, although they have not been isolated previously because of the weak coordination ability of a $-SO_3$ group.[9,10)]

Experimental

Preparation of the Starting Complexes for Obtaining Double Complexes. The starting complexes [$Cr(H_2O)(NH_3)_5$]$(NO_3)_3$,[11)] [$Co(H_2O)(NH_3)_5$]$(NO_3)_3$,[12)] *trans*(*N*)-K_3[Cr(sida)$_2$]$\cdot 4H_2O$[9)] and *trans*(*N*)-K_3[Co(sida)$_2$]$\cdot 4H_2O$[13)] were prepared by the same method as that reported in each literature, and they were identified by means of elemental analyses and spectrophotometric measurements.

*Preparation of Double Complexes. Aquapentaamminechromium(III) Bis(*N*-(2-sulfoethyl)iminodiacetato)chromate(III) Dihydrate, [Cr(H_2O)(NH_3)$_5$][Cr(sida)$_2$]$\cdot 2H_2O$ (Red) (I).* Ten and seven tenth grams (3.2×10^{-2} mol) of [$Cr(H_2O)(NH_3)_5$]$(NO_3)_3$ and 15.0 g (3.2×10^{-2} mol) of *trans*(*N*)-K_3[Cr(sida)$_2$]$\cdot 4H_2O$ were dissolved separately in about 50 ml of water and then they were mixed together. The mixture was stirred with a glass rod for a few minutes and allowed to stand in a refrigerator overnight, red crystals being obtained. They were collected by filtration, washed with small amounts of water, ethanol and ether, and air-dried. Yield about 16 g.

Found: C, 19.98; H, 5.02; N, 13.27%. Calcd for $C_{12}H_{37}O_{17}N_7S_2Cr_2$: C, 20.03; H, 5.19; N, 13.63%.

*Aquapentaamminechromium(III) Bis(*N*-(2-sulfoethyl)iminodiacetato)cobaltate(III) Dihydrate, [Cr(H_2O)(NH_3)$_5$][Co(sida)$_2$]$\cdot 2H_2O$ (Pink) (II).* This was prepared in a manner similar to that of complex I except that a solution of 15.3 g (3.2×10^{-2} mol) of *trans*(*N*)-K_3[Co(sida)$_2$]$\cdot 4H_2O$ in 50 ml of water was used in place of the solution of *trans*(*N*)-K_3[Cr(sida)$_2$]$\cdot 4H_2O$.

Found: C, 19.78; H, 5.03; N, 13.55%. Calcd for $C_{12}H_{37}O_{17}N_7S_2CrCo$: C, 19.83; H, 5.14; N, 13.50%.

*Aquapentaamminecobalt(III) Bis(*N*-(2-sulfoethyl)iminodiacetato)chromate(III) Dihydrate, [Co(H_2O)(NH_3)$_5$][Cr(sida)$_2$]$\cdot 2H_2O$ (Orange) (III).* The complex was also obtained by a method similar to that of complex I except that a solution of 10.9 g (3.2×10^{-2} mol) of [$Co(H_2O)(NH_3)_5$]$(NO_3)_3$ in 150 ml of water was used instead of the solution of [$Cr(H_2O)(NH_3)_5$]$(NO_3)_3$. Yield about 15 g.

Found: C, 19.49; H, 5.07; N, 13.12%. Calcd for $C_{12}H_{37}O_{17}N_7S_2CrCo$: C, 19.83, H, 5.14; N, 13.50%.

*Aquapentaamminecobalt(III) Bis(*N*-(2-sulfoethyl)iminodiacetato)cobaltate(III) Dihydrate, [Co(H_2O)(NH_3)$_5$][Co(sida)$_2$]$\cdot 2H_2O$ (Pale Red) (IV).* This was synthesized according to a procedure similar to that of complex I from 10.9 g (3.2×10^{-2} mol) of [$Co(H_2O)(NH_3)_5$]$(NO_3)_3$ and 15.3 g (3.2×10^{-2} mol) of *trans*(*N*)-K_3[Co(sida)$_2$]$\cdot 4H_2O$ in 150 ml and 50 ml of water, respectively.

Found: C, 19.66; H, 5.06; N, 13.48%. Calcd for $C_{12}H_{37}O_{17}N_7S_2Co_2$: C, 19.65; H, 5.09; N, 13.37%.

*Preparation of Binuclear Complexes. μ-*N*-(2-Sulfoethyl)iminodiacetatopentaamminechromium(III)(or cobalt(III))hydrogen(or sodium)-*N*-(2-sulfoethyl)iminodiacetatochromium(III)(or cobalt(III)) Perchlorates, [(NH_3)$_5$(Cr or Co)(sida)(Cr or Co)(sidaH or sidaNa)]ClO_4 (Reddish Violet) (V through XII).* For simplification, the procedures for preparing the binuclear complexes are schematically outlined in Fig. 1.

First of all the corresponding double complexes were triturated thoroughly in an agate mortar and were heated at given temperatures for a given period of time. The products [(NH_3)$_5$(Cr or Co)(sida)(Cr or Co)(sida)] were purified in

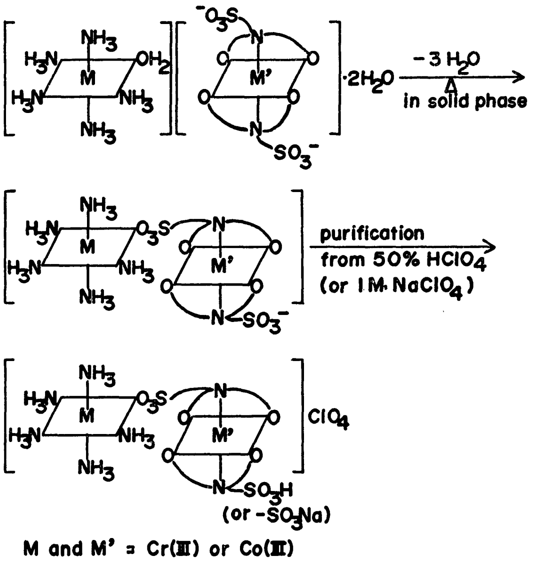

Fig. 1. Procedures for obtaining the binuclear complexes.

the forms of the hydrogen salts $[(NH_3)_5(Cr$ or $Co)(sida)(Cr$ or $Co)(sidaH)]ClO_4$ and the sodium salts $[(NH_3)_5(Cr$ or $Co)(sida)(Cr$ or $Co)(sidaNa)]ClO_4$ from a 50% $HClO_4$ solution and a 1 M $NaClO_4$ solution, respectively. The yields of the hydrogen salts and the sodium salts were about 40% and 30% based on the amounts of the double complexes used, respectively.

Table 1 summarizes the binuclear complexes obtained, their analytical data, the starting double complexes, and the heating conditions determined non-isothermally (derivatographically) and/or isothermally.

Derivatographic Measurements. The derivatograms of the samples were recorded on a MOM Derivatograph Typ-OD-102. All the measurements were carried out in a nitrogen stream at the heating rate of 1 °C min^{-1}, 0.4 g of the samples being used in each run.

Isothermal Measurements. For the determination of the heating conditions for obtaining the desired binuclear complexes, isothermal measurements were carried out by using a Shimadzu TM-1A Thermanobalance in a static air at various temperatures.

Spectral Measurements. Visible and ultra-violet, and IR absorption spectra of the samples were measured in aqueous solutions and in KBr disks with Union High-sens. Spectrophotometer SM-401 and with a JASCO A-3 Infrared Spectrophotometer, respectively.

Magnetic Susceptibilities. The magnetic susceptibilities of the samples were measured by Gouy method at room temperatures. The effective magnetic moments were evaluated from the magnetic susceptibilities measured above and corrected by the use of Pascal's constants for each component in the complexes.

Molar Conductivities. Molar conductivities were measured to determine the charges of the binuclear complexes with a YEW Universal Bridge TYPE BU-Z-13A.

Behaviors toward Ion Exchangers. The behaviors of the binuclear complexes toward ion exchangers were examined to find whether they were cationic complex species or not. Dowex 1-X8 (100—200 mesh) and Dowex 50W-X8 (50—100 mesh) were used as anion and cation exchangers, respectively.

Results and Discussion

For convenience, in the following discussion, the double complexes ($[Cr$ or $Co)(H_2O)(NH_3)_5][(Cr$ or $Co)(sida)_2]$) and binuclear complexes ($[NH_3)_5(Cr$ or $Co)(sida)(Cr$ or $Co)(sida)]$) will be abbreviated as [Cr or Co][Cr or Co] and [(Cr or Co)–(Cr or Co)], and the hydrogen salts ($[(NH_3)_5(Cr$ or $Co)(sida)(Cr$ or $Co)(sidaH)]ClO_4$) and the sodium salts ($[(NH_3)_5(Cr$ or $Co)(sida)(Cr$ or $Co)$–$(sidaNa)]ClO_4$) will be designated similarly as [(Cr or Co)–(Cr or Co)H] and [(Cr or Co)–(Cr or Co)Na], respectively.

(1) Determination of the Conditions for Thermal Syntheses of Binuclear Complexes. For the determination of preparative conditions (temperature and duration of heating) of the binuclear complexes, the thermal reactions of the corresponding double complexes were observed both derivatographically and isothermally.

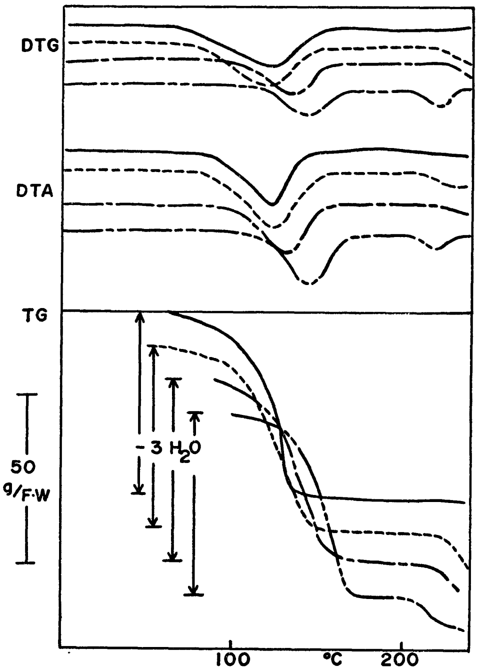

Fig. 2. Derivatograms of $[Cr(H_2O)(NH_3)_5][Cr(sida)_2]\cdot 2H_2O$ (——), $[Cr(H_2O)(NH_3)_5][Co(sida)_2]\cdot 2H_2O$ (······), $[Co(H_2O)(NH_3)_5][Cr(sida)_2]\cdot 2H_2O$ (·—·), and $[Co(H_2O)(NH_3)_5][Co(sida)_2]\cdot 2H_2O$ (··—··).

Derivatography. The derivatograms of the double complexes are depicted in Fig. 2. The TG curves show that all the double complexes evolve smoothly three moles of water (two moles of lattice water and one mole of coordinated water) in the temperature range of 60—135 °C ([Cr][Cr]), 50—150 °C ([Cr][Co]), 90—160 °C ([Co][Cr]), and 100—170 °C ([Co][Co]), remaining unchanged in weight losses up to 200—220 °C. The [Cr][Cr] complex was stable even at about 220 °C, but the other three ([Cr][Co], [Co][Cr] and [Co][Co]) were decomposed gradually in a complicated way above 200—210 °C with the reduction of Co(III) to Co(II) ions. These double complexes were initially orange or pink in color, but changed to reddish violet at the end of the evolution of three moles of water. The

Table 1. Binuclear complexes obtained, analytical data, starting double complexes, and heating conditions

Binuclear complex		Analytical data %[a] C	H	N	Starting double complex	Heating conditions[b] Temp (°C)	Time (min)
$[(NH_3)_5CrsidaCrsidaH]ClO_4$	(V)	19.09 (18.81)	4.39 (4.21)	12.53 (12.08)	$[CrH_2O(NH_3)_5]\cdot[Cr(sida)_2]\cdot 2H_2O$	122	120
$[(NH_3)_5CrsidaCrsidaNa]ClO_4$	(VI)	18.47 (18.29)	4.09 (3.97)	12.23 (12.44)			
$[(NH_3)_5CrsidaCosidaH]ClO_4$	(VII)	18.95 (18.64)	4.43 (4.18)	12.69 (12.69)	$[CrH_2O(NH_3)_5]\cdot[Co(sida)_2]\cdot 2H_2O$	122	120
$[(NH_3)_5CrsidaCosidaNa]ClO_4$	(VIII)	18.46 (18.13)	4.16 (3.94)	12.31 (12.34)			
$[(NH_3)_5CosidaCrsidaH]ClO_4$	(IX)	19.02 (18.64)	3.94 (4.18)	12.96 (12.69)	$[CoH_2O(NH_3)_5]\cdot[Cr(sida)_2]\cdot 2H_2O$	130	110
$[(NH_3)_5CosidaCrsidaNa]ClO_4$	(X)	18.25 (18.13)	4.01 (3.94)	12.27 (12.34)			
$[(NH_3)_5CosidaCosidaH]ClO_4$	(XI)	18.80 (18.49)	4.19 (4.14)	12.32 (12.57)	$[CoH_2O(NH_3)_5]\cdot[Co(sida)_2]\cdot 2H_2O$	142	210
$[(NH_3)_5CosidaCosidaNa]ClO_4$	(XII)	18.33 (17.97)	4.07 (3.90)	12.11 (12.23)			

a) The figures in parentheses are calculated values. b) The heating conditions were determined derivatographically and/or isothermally.

color changes are, as will be mentioned later, due to the liberation of the coordinated water in the complex cation ($[(Cr\ or\ Co)(H_2O)(NH_3)_5]^{3+}$) and the subsequent coordination of the $-SO_3^-$ group in the complex anion ($[Cr\ or\ Co)(sida)_2]^{3+}$).

The information obtained here implies that all the complexes are highly stable even after the liberation of water and hence the desired binuclear complexes are obtained by the use of the thermal reaction in the solid-phase without controlling conditions.

Isothermal Measurements. On the basis of the above results, preliminary experiments were carried out to determine the effective heating conditions for the thermal syntheses. Figure 3 shows the change in the weight losses of the double complexes with time at the given temperatures.

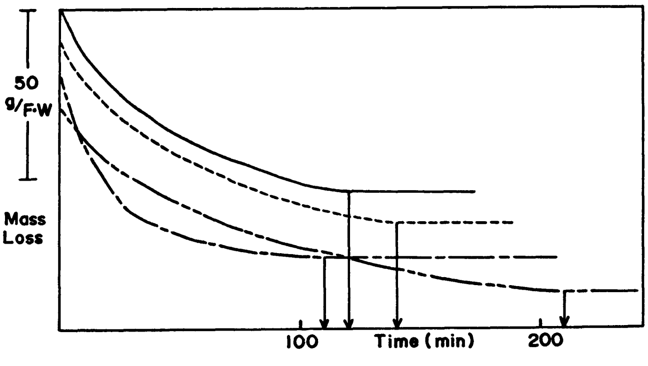

Fig. 3. Changes in weight losses with time of $[Cr(H_2O)(NH_3)_5][Cr(sida)_2]\cdot 2H_2O$ at 122 °C (——), $[Cr(H_2O)(NH_3)_5][Co(sida)_2]\cdot 2H_2O$ at 122 °C (······), $[Co(H_2O)(NH_3)_5][Cr(sida)_2]\cdot 2H_2O$ at 130 °C (·—·), and $[Co(H_2O)(NH_3)_5][Co(sida)_2]\cdot 2H_2O$ at 142 °C (··—··).

The [Cr][Cr] double complex gradually and monotonously loses the weight of 54 g/*F.W.* (*F.W.*=Formula Weight) which corresponds to 3 mol of water, no further weight change being found even after prolonged heating. From this result, 122 °C and 120 min were selected as the optimal heating temperature and the time duration for the thermal synthesis of the [Cr–Cr] binuclear complex. Similarly, the heating conditions for the other three complexes were determined as specified in Table 1.

(2) Properties of the Binuclear Complexes. *Magnetic Susceptibilities*: The [Cr][Cr] double complex gave the value of 3.9 B.M. (290 K) per one chromium ion. The values 3.9 B.M. (291 K) and 3.8 B.M. (291 K) were observed for the [Cr][Co] and [Co][Cr] double complexes, respectively. The [Co][Co] double complexes were found to be diamagnetic (291 K).

On the other hand, the values for the binuclear complexes are, in general, slightly smaller as compared with those for the corresponding double complexes: 3.6 B.M. (291 K) for [Cr–CrH], 3.7 B.M. (291 K) for [Cr–CoH] and 3.5 B.M. (291.5 K) for [Co–CrH]. The [Co–CoH] binuclear complex was diamagnetic (292 K). These results suggest that the cobalt and chromium ions are all tervalent in both the double and binuclear complexes.

Molar Conductivities: Table 2 lists the molar conductivities. The binuclear complexes of the hydrogen and

Table 2. Molar conductivities (25 °C) of the binuclear complexes

Complex			Molar Conductivities (mho cm^{-1})[a]
Hydrogen salts	[Cr–CrH]	(V)	432
	[Cr–CoH]	(VII)	321
	[Co–CrH]	(IX)	406
	[Co–CoH]	(XI)	359
Sodium salts	[Cr–CrNa]	(VI)	145
	[Cr–CoNa]	(VIII)	137
	[Co–CrNa]	(X)	142
	[Co–CoNa]	(XII)	133

a) 1.0×10^{-3} mol/l of aqueous solution was used.

Table 3. IR data for the starting double complexes and the hydrogen salts of binuclear complexes obtained (cm^{-1})

Complex			H_2O ν(O–H)	ClO_4^- ν(Cl–O)	R–SO_3^- $\nu(SO_3^-)$
Double complexes	[Cr][Cr]	(I)	3450	—	642, 1035, 1053, 1190
	[Cr][Co]	(II)	3460	—	648, 1040, 1058, 1210
	[Co][Cr]	(III)	3450	—	641, 1035, 1054, 1194
	[Co][Co]	(IV)	3480	—	653, 1042, 1059, 1208
Binuclear complexes	[Cr–CrH]	(V)	—	1095	638, 1030, 1047, 1180
	[Cr–CoH]	(VII)	—	1100	643, 1032, 1049, 1185
	[Co–CrH]	(IX)	—	1095	638, 1032, 1047, 1182
	[Co–CoH]	(XI)	—	1085	648, 1037, 1052, 1189

the sodium salts exhibited 320—430 mho cm^{-1} and 130—145 mho cm^{-1}, respectively. These values may correspond to the conductivities of $HClO_4$ (hydrogen salts) and $NaClO_4$ (sodium salts) in solutions.

Both the hydrogen and sodium salts were adsorbed on neither cation nor anion exchangers at pH 7, but were adsorbed on cation exchanger at pH 3. These results indicate that at pH 7 the complexes are dissociated into $[(NH_3)_5$(Cr or Co)(sida)(Cr or Co)(sida)$]^0+Na^++ClO_4^-$, and at pH 3, $[(NH_3)_5$(Cr or Co)(sida)(Cr or Co)(sidaH)$]^++ClO_4^-$.

IR Data. The IR data of the double and binuclear complexes are summarized in Table 3. The characteristic band due to H_2O (3450—3480 cm^{-1}) is seen in the double complexes, but not in the binuclear complexes. The band due to ClO_4^- (1085—1100 cm^{-1}) is detected in the binuclear complexes. The characteristic bands due to the $-SO_3^-$ group of the binuclear complexes appear in the lower wavenumber region as compared with those of the double complexes. The shifts probably result from the coordination of a $-SO_3^-$ group in the cationic moiety of the double complexes.

Table 4. Visible and UV spectral data for the starting double complexes and the hydrogen salts of binuclear complexes obtained

Complex			$\tilde{\nu}_1$ 10^{-3} cm^{-1} (log ε_1)	$\tilde{\nu}_2$ 10^{-3} cm^{-1} (log ε_2)
Double complexes	[Cr][Cr]	(I)	19.53(2.13)	26.95(2.09)
	[Cr][Co]	(II)	19.34(2.17)	26.60(2.13)
	[Co][Cr]	(III)	19.38(2.15)	26.67(2.11)
	[Co][Co]	(IV)	19.19(2.19)	26.32(2.15)
Binuclear complexes	[Cr–CrH]	(V)	18.02(2.15)	25.38(2.10)
	[Cr–CoH]	(VII)	17.86(2.18)	25.06(2.15)
	[Co–CrH]	(IX)	17.89(2.17)	25.13(2.12)
	[Co–CoH]	(XI)	17.73(2.20)	24.81(2.16)

Electronic Spectra. Table 4 summarizes the absorption maxima in the region of d-d transitions. The absorption bands of the binuclear complexes appear at lower wavenumber regions than those of the corresponding double complexes. The shifts may be due to the fact that the coordinated water in the complex cation ([(Cr or Co)$(H_2O)(NH_3)_5]^{3+}$) is expelled and replaced by the $-SO_3^-$ group in the complex anion ([(Cr or Co)(sida)$_2]^{3-}$).

When the aqueous solutions of the binuclear complexes were allowed to stand at room temperature overnight, their absorption maxima were shifted to those of the corresponding double complexes. Thus the binuclear complexes are hydrolyzed gradually in aqueous media changing from $[(NH_3)_5$(Cr or Co)(sida)(Cr or Co)(sida)] into [(Cr or Co)$(H_2O)(NH_3)_5]^{3+}$+[(Cr or Co)(sida)$_2]^{3-}$.

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