Cobalt(III) Complexes Containing Large Chelate Rings. II.[1] Syntheses and Properties of Cobalt(III)-Ammine Complexes Containing α,ω-Alkanediamines

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(Received March 17, 1977)

Reactions of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ with $H_2N(CH_2)_nNH_2$ (N–N) in dimethyl sulfoxide were examined by changing the number of methylene groups in N–N (n=2—5, 7, 8, 10, 12, and 14). Complexes of the $Co(NH_3)_4(N–N)^{3+}$ type were found to be formed for n=2—4, 12, and 14, but, not for n=5, 7, 8, and 10. In addition to these products, a number of new cobalt(III) complexes were isolated.

In the previous paper, a number of new cobalt(III) complexes were isolated as products of the reactions of $[CoCl_2(en)_2]Cl$ with α,ω-alkanediamines $H_2N(CH_2)_nNH_2$ (N–N) in dimethyl sulfoxide (DMSO), where en denotes 1,2-ethanediamine.[1] Among them, complexes of the $[Co(en)_2(N–N)]X_3$ and $[Co_2(en)_4(N–N)_2]X_6$ types which contain large chelate rings were found.

Recently, $[Co(NH_3)_{6-2p}(en)_p]X_3$ (p=0, 1, 2, and 3) and $[Co(NH_3)_5(enH)]X_4$ were isolated as products of the reaction of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ with en in DMSO.[2] It seemed that it would be interesting and worthwhile to know, when this reaction is applied to various diamines, what kinds of products are formed. If a diamine with a long methylenic chan is used, the formation of the complexes containing large chelate rings might be expected. In this paper, the products of the reactions of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ with α,ω-alkanediamines (N–N) in DMSO are examined. The diamines, $H_2N(CH_2)_nNH_2$, used in this work are n= 2 (en), 3 (tn), 4 (tmd), 5 (pmd), 7 (hepn), 8 (ocn), 10 (den), 12 (don), and 14 (tden).

Several attempts have been made to prepare cobalt(III) complexes in non-aqueous solvents.[3] The results indicate that the non-aqueous solvents are useful for obtaining novel cobalt(III) complexes. The present study will also help to understand the features of the reactions of cobalt(III) complexes in such a solvent.

Experimental

Preparation of Cobalt(III) Complexes. All the cobalt(III) complexes were obtained from the products of the reactions of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ with N–N in DMSO. The species formed in the reactions were separated by the use of an SP-Sephadex C-25 column ($\phi 5\times 40$ cm). Usually, KBr solutions were used as the eluents. In order to isolate the products, each eluate was concentrated to a small volume by means of a rotary evaporator.

When it was difficult to obtain bromide salt because of its high solubility, the eluate was diluted with water and then poured into another SP-Sephadex column. The adsorbed species was then eluted with an appropriate eluent, *e.g.*, a HCl, $LiClO_4$, or NaI solution. When a $LiClO_4$ solution was used as the eluent, the column was washed first with a dilute HCl solution to remove potassium ions; otherwise, the deposition of insoluble $KClO_4$ crystals in the column was unavoidable. The eluate was then concentrated again. The addition of ethanol or ethanol-ether to the resulting solution was often necessary to ensure crystallization.

The elution of highly charged species with KBr solutions sometimes caused a crystallization of the bromide salt in the column. In such a case, the eluent was changed to a sodium acetate-acetic acid solution and the eluate was concentrated. Then, the bromide salt was obtained by the addition of an HBr solution to the concentrated eluate.

The analytical data for the complexes prepared in this work are summarized in Table 1.

1) Products of the Reaction of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ *with en.* To 100 ml of a DMSO solution containing 9.2 g of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ (0.02 mol) were added 1.2 g of en (0.02 mol). The solution was kept at 85 °C for 20 min. The resulting deep yellowish orange solution was neutralized with concd HCl and diluted to 1.5 l with water. This was poured into a Sephadex column, and then the column was washed with water. When the adsorbed bands were developed with NaBr solutions, the column showed three bands; reddish orange (a trace amount), yellow, and yellowish orange, in the order of elution. The first and second species were eluted with a 0.25 M NaBr solution. The first reddish orange species was found to be $Co(H_2O)(NH_3)_5^{3+}$. When the second yellow eluate was concentrated, crystals of $[Co(NH_3)_6]Br_3$ appeared; they were filtered off, and the filtrate was diluted with water and then poured into a Sephadex column. The adsorbed species were eluted with a 0.08 M Na_3PO_4 solution. The single band was progressively separated into three bands. The eluates were labeled F1, F2, and F3, in the order of elution. Each eluate was neutralized with a HCl solution and poured into a Sephadex column. The F1 species was eluted with a 0.3 M HCl solution. The concentration of the eluate gave yellow crystals, which were characterized as $[Co(en)_3]Cl_3\cdot 3H_2O$ by the measurements of the infrared, electronic, and PMR spectra. The F2 and F3 species were eluted out with 0.5 M KI solutions. The concentration of these eluates gave *cis*-$[Co(NH_3)_2(en)_2]I_3$ and $[Co(NH_3)_4(en)]I_3$ respectively. The *cis* configuration of $[Co(NH_3)_2(en)_2]I_3$ was confirmed by the measurement of the PMR spectrum.

The last yellowish orange species was eluted with a 0.7 M NaBr solution. When the eluate was concentrated with a rotary evaporator, yellowish orange crystals of $[Co(NH_3)_5(enH)]Br_4$ were obtained. Yield: 0.6 g.

The yield of the products was found to be in the order: $Co(NH_3)_6^{3+} > Co(NH_3)_4(en)^{3+} > Co(NH_3)_2(en)_2^{3+} > Co(NH_3)_5(enH)^{4+} > Co(en)_3^{3+}$

When a mixture of 0.6 g of en (0.01 mol) and 2.6 g of $en\cdot 2HClO_4$ (0.01 mol) was used in place of 1.2 g of en, 0.8 g of $[Co(NH_3)_5(enH)]Br_4$ was obtained. The other products were found to be $[Co(NH_3)_{6-2p}(en)_p]Br_3$ (p=0—3).

When 100 ml of a DMSO solution containing 6.8 g of $[Co(NH_3)_6](ClO_4)_3$ and 0.9 g of en was kept at 90 °C for 10 min, 30 mg of $[Co(NH_3)_5(enH)]Br_4$ was obtained from the reaction products.

2) $[Co(NH_3)_5(en)]Br_3$. Crystals of $[Co(NH_3)_5(enH)]Br_4$ (0.2 g) were dissolved into 4 ml of 1.5 M aqueous ammonia. Solid NaBr was added to the solution until a small amount

TABLE 1. SUMMARY OF ANALYTICAL DATA FOR THE COMPLEXES PREPARED IN THIS WORK

Complex	C, %		H, %		N, %	
	Calcd	Found	Calcd	Found	Calcd	Found
$[Co(NH_3)_6]Br_3$[a]	0	—	4.53	4.54	20.97	21.19
$[Co(NH_3)_4(en)]I_3$	4.23	4.12	3.55	3.64	14.80	14.60
$[Co(NH_3)_2(en)_2]I_3$	8.09	7.84	3.73	4.00	14.15	14.04
$[Co(NH_3)_5(enH)]Br_4$	4.58	4.37	4.61	4.53	18.68	18.78
$[Co(NH_3)_5(enH)](ClO_4)_4$	3.98	4.27	4.01	4.09	16.26	16.02
$[Co(NH_3)_5(en)]Br_3$	5.41	5.68	5.22	5.34	22.09	21.82
$[Co(NH_3)_4(tn)](ClO_4)_3$	7.21	7.16	4.44	4.68	16.82	16.64
$[Co(NH_3)_2(tn)_2](ClO_4)_3$	13.36	13.08	4.86	5.12	15.57	15.74
$[Co(tn)_3](ClO_4)_3 \cdot H_2O$	18.08	17.90	5.39	5.67	14.06	14.25
$[Co(NH_3)_5(tnH)]Br_4$	6.69	6.98	4.86	5.15	18.20	18.10
$[(NH_3)_5Co(tn)Co(NH_3)_5]Br_6$[b]	4.21	4.68	4.79	5.28	19.97	19.66
$[Co(NH_3)_4(tmd)](ClO_4)_3$	9.36	9.60	4.71	4.90	16.36	16.43
$[Co(NH_3)_5(tmdH)]Br_4$	8.69	8.82	5.10	5.24	17.73	17.73
$[Co(NH_3)_4(tmdH)_2](ClO_4)_5$	11.97	12.14	4.77	5.00	13.96	13.77
$[Co(NH_3)_4(tmdH)_2]I_5$	10.22	10.01	4.07	4.07	11.92	11.97
$[(NH_3)_5Co(tmd)Co(NH_3)_5]Br_6$[b]	5.61	5.87	4.95	5.80	19.63	18.16
$[Co(NH_3)_5(pmdH)]Br_4$	10.59	10.63	5.33	5.48	17.30	17.62
$[Co(NH_3)_5(pmdH)](ClO_4)_4$	9.31	9.41	4.69	4.75	15.20	14.95
$[Co(NH_3)_4(pmdH)_2](ClO_4)_5$	14.46	14.08	5.10	5.12	13.49	13.28
$[(NH_3)_5Co(pmd)Co(NH_3)_5]Br_6 \cdot 3H_2O$	6.50	6.59	5.46	5.36	18.19	18.25
$[Co(NH_3)_5(hepnH)]Br_4$	14.13	14.14	5.76	5.86	16.49	16.80
$[Co(NH_3)_5(hepnH)](ClO_4)_4$	12.49	12.62	5.09	5.20	14.57	14.38
$[Co(NH_3)_4(hepnH)_2]Cl_5 \cdot 2H_2O$	27.89	27.90	9.03	9.12	18.59	18.58
$[Co(NH_3)_5(ocnH)]Br_4$	15.78	16.10	5.96	6.23	16.10	16.28
$[Co(NH_3)_4(ocnH)_2]Cl_5 \cdot 3H_2O$	29.62	29.32	9.32	8.95	17.27	17.49
$[Co(NH_3)_4(ocnH)_2]I_5 \cdot 2H_2O$	17.66	17.37	5.37	5.02	10.30	10.57
$[Co(NH_3)_5(denH)]Br_4$	18.85	19.14	6.33	6.55	15.39	15.48
$[Co(NH_3)_4(denH)_2]Br_5$	27.51	27.40	7.16	7.20	12.83	12.72
$[Co(NH_3)_3(denH)_3]Cl_6 \cdot 2H_2O$	41.00	40.98	10.09	10.01	14.35	14.18
$[(NH_3)_5Co(den)Co(NH_3)_5]Br_6 \cdot 2H_2O$	12.31	12.36	5.99	5.91	17.22	17.00
$[(NH_3)_4Co(den)_2Co(NH_3)_4]Br_6 \cdot 3H_2O$	21.22	21.45	6.94	7.03	14.85	14.76
$[Co_2(NH_3)_8(den)(denH)_2]Br_8 \cdot 2H_2O$	24.88	24.72	7.10	6.99	13.54	13.31
$[Co(NH_3)_4(don)]Br_3$	25.41	25.45	7.11	7.33	14.82	14.84
$[Co(NH_3)_5(donH)]Br_4$	21.67	21.73	6.67	6.71	14.74	15.02
$[Co(NH_3)_5(donH)](ClO_4)_4$	19.39	19.47	5.97	6.04	13.19	12.91
$[Co(NH_3)_4(donH)_2](ClO_4)_5$	28.07	28.26	6.87	6.69	10.91	10.45
$[(NH_3)_5Co(don)Co(NH_3)_5]Br_6$	14.89	15.06	6.04	6.30	17.36	17.31
$[Co(NH_3)_4(tden)]Br_3 \cdot 1.5H_2O$	27.07	27.11	7.63	7.58	13.53	13.64
$[Co(NH_3)_5(tdenH)]Br_4$	24.26	24.35	6.98	7.29	14.15	14.20

a) This sample was isolated from the products of the reaction of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ with en in DMSO.
b) The analytical results were not improved by repeated crystallizations. The salt might contain a small amount of $[(NH_3)_4Co(N\text{-}N)_2Co(NH_3)_4]Br_6$.

of crystals of $[Co(NH_3)_5(en)]Br_3$ appeared. Ethanol and then ether were added to insure the crystallization.

3) Products of the Reaction of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ *with tn, tmd, pmd, hepn, ocn, den, don, or tden.* To a DMSO solution containing $[Co(H_2O)(NH_3)_5](ClO_4)_3$ were added the title N–N. The solution was then treated with the way described in 1). The species adsorbed on a Sephadex column were eluted with KBr solutions.

a) Products of the Reaction with tn: To 100 ml of a DMSO solution containing 9.2 g of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ (0.02 mol) were added 1.5 g of tn (0.02 mol). Four bands were observed on a Sephadex column. The lowest reddish orange species was found to be a small amount of $Co(H_2O)(NH_3)_5^{3+}$. The upper three bands were of yellowish orange colors. The eluates were labeled F1, F2, and F3 in the order of elution. F1 was found to contain a mixture of $Co(NH_3)_{6-2p}(tn)_p^{3+}$ ($p=0$, 1, 2, and 3). The concentration of the eluate yielded crystals of $[Co(NH_3)_6]Br_3$. The filtrate was diluted, and then the solution was poured into a Sephadex column. After the column had been washed with dil HCl, the adsorbed species were eluted out with a 0.5 M $LiClO_4$ solution. The concentration of the solution gave crystals of $[Co(NH_3)_{6-2p}(tn)_p](ClO_4)_3$ ($p=1$, 2, and 3). The separation of $[Co(NH_3)_4(tn)](ClO_4)_3$, $[Co(NH_3)_2(tn)_2](ClO_4)_3$, and $[Co(tn)_3](ClO_4)_3 \cdot H_2O$ was achieved by fractional crystallization. From F2, crystals of $[Co(NH_3)_5(tnH)]Br_4$ were obtained. The concentration of F3 gave orange crystals which were considered to contain $[(NH_3)_5Co(tn)Co(NH_3)_5]Br_6$ as the main component (see Table 1).

b) Products of the Reaction with tmd: To 100 ml of a DMSO solution containing 9.2 g of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ (0.02 mol) were added 1.8 g of tmd (0.02 mol). The Sephadex column showed six bands. The lowest species was found to be a small amount of Co^{2+}. Then, the band of a small amount of $Co(H_2O)(NH_3)_5{}^{3+}$ followed. The eluates of the other four bands were labeled F1, F2, F3, and F4 in the oder of elution. The concentration of F1 gave $[Co(NH_3)_6]Br_3$. The filtrate contained $Co(NH_3)_4(tmd)^{3+}$, which could be crystallized as the perchlorate salt. When F2 was concentrated, crystals of $[Co(NH_3)_5(tmdH)]Br_4$ were obtained. The KBr medium in F3 was replaced by $LiClO_4$ with the aid of a Sephadex column. Upon the evaporation of the solution, crystals of $[Co(NH_3)_4(tmdH)_2](ClO_4)_5$ were precipitated. The concentration of F4 gave yellowish orange crystals, which were considered to consist of $[(NH_3)_5Co(tmd)Co(NH_3)_5]Br_6$ and a small amount of $[(NH_3)_4Co(tmd)_2Co(NH_3)_4]Br_6$ (see Table 1).

c) Products of the Reaction with den: To 750 ml of a DMSO solution containing 9.2 g of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ (0.02 mol) were added 3.4 g of den (0.02 mol). The Sephadex column showed the presence of a small amount of Co^{2+}, $Co(H_2O)(NH_3)_5{}^{3+}$, and many yellow-to-orange species. From the fractions with yellow to orange colors, the following salts were obtained, in the order of elution (the yield (%), based on $[Co(H_2O)(NH_3)_5](ClO_4)_3$, is given in parentheses): $[Co(NH_3)_6]Br_3$ (25), $[Co(NH_3)_5(denH)]Br_4$ (26), $[Co(NH_3)_4(denH)_2]Br_5$ (9), $[Co(NH_3)_3(denH)_3]Cl_6\cdot 2H_2O$ (0.3),[4] $[(NH_3)_5Co(den)Co(NH_3)_5]Br_6\cdot 2H_2O$ (7),[5] and $[(NH_3)_4Co(den)_2Co(NH_3)_4]Br_6\cdot 3H_2O$ (9).[5]

Even after these species had been eluted out, several species remained in the column. These species could be crystallized as bromides. One of the species was found to be $[Co_2(NH_3)_8(den)(denH)_2]Br_8\cdot 2H_2O$. Yield: 3%.[5]

d) Products of the Reaction with don: To 700 ml of a DMSO solution containing 6.9 g of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ (0.015 mol) were added 3.0 g of don (0.015 mol). The Sephadex column showed many bands. Crystals of $[Co(NH_3)_6]Br_3$, $[Co(NH_3)_4(don)]Br_3$, $[Co(NH_3)_5(donH)]Br_4$, $[Co(NH_3)_4(donH)_2](ClO_4)_5$,[4] and $[(NH_3)_5Co(don)Co(NH_3)_5]Br_6$ were obtained, in that order of elution. Even after these species had been eluted out, several species remained in the column.

e) Products of the Reaction with pmd, hepn, ocn, or tden: To 1000 ml of a DMSO solution containing 4.6 g of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ (0.01 mol) were added 0.01 mol of N–N (1.0 g for pmd, 1.3 g for hepn, 1.4 g for ocn, and 2.3 g for tden). From the eluates, various complexes containing pmd, hepn, ocn, or tden, which are shown in Table 1, were isolated as crystals. $[Co(NH_3)_6]Br_3$ was also obtained, regardless of the kind of N–N used. No formation of $Co(NH_3)_4(N\text{–}N)^{3+}$ was observed for any of the diamines except the tden. The $[Co(NH_3)_4(tden)]^{3+}$ ions moved faster than $Co(NH_3)_5(tdenH)^{4+}$, but slower than $Co(NH_3)_6{}^{3+}$. The formation of more positively charged species than six was not observed in any of the diamines under the conditions employed.

Apparatus. The electronic spectra were recorded with a Union Giken SM-401 or a Hitachi EPS-3 recording spectrophotometer. The PMR spectra were recorded with a Varian A-60 spectrometer.

Results and Discussion

Product Distribution. The analytical results given in Table 1 are in good agreement with the formulas assigned to the products isolated in this work. All these products are yellow to yellowish orange in color; hence, they must be of the CoN_6 type (*vide infra*). This is also consistent with the assigned formulas. Furthermore, these complex ions show reasonable flow rates on Sephadex columns.[1]

A semi-quantitative determination of the product distribution of the reactions in question was also carried out; the results are shown in Table 2. Complex ions, $Co(NH_3)_6{}^{3+}$ and $Co(NH_3)_5(\underline{N}\text{–}NH)^{4+}$,[6] were always formed as the products, regardless of the kind of N–N. The pH titration of the solutions containing $Co(NH_3)_5(\underline{N}\text{–}NH)^{4+}$ with standard NaOH solutions reveals that the complex ions are mono-basic acid. The value of p*K* increases with the increase in the number of methylene groups in the N–N.[7]

Table 2 shows that the change in the concentration of the reactants affects the product distribution considerably. The formation of highly charged species becomes significant with the increase in the concentration of the reactants. This is a trend similar to that found in the reactions of $[CoCl_2(en)_2]Cl$ with N–N in DMSO.[1]

TABLE 2. PRODUCT DISTRIBUTION OF THE REACTIONS OF $[Co(H_2O)(NH_3)_5](ClO_4)_3$ WITH N-N IN DMSO[a)]

	N-N used	en	tn[b,c)]	tn	tmd[b,d)]	tmd	pmd	hepn	ocn	den[e)]	don[e)]	tden
	Concentration of reactants/M ($[Co(H_2O)(NH_3)_5{}^{3+}]=[N\text{-}N]$)	0.20	0.010	0.20	0.010	0.20	0.010	0.010	0.010	0.027	0.021	0.010
Products	Co^{2+}	0	0	0	25	f	f	f	f	f	f	f
	$Co(NH_3)_6{}^{3+}$	f } 90	42	f } 80	26	18	18	26	23	25	27	29
	$Co(NH_3)_4(N\text{-}N)^{3+}$	f	f } 41	f	22	21	0	0	0	0	5	6
	$Co(NH_3)_2(N\text{-}N)_2{}^{3+}$	f	f	f	0	0	0	0	0	0	0	0
	$Co(N\text{-}N)_3{}^{3+}$	f	f	f	0	0	0	0	0	0	0	0
	$Co(NH_3)_5(\underline{N}\text{-}NH)^{4+}$	6	6	16	8	29	36	33	26	26	30	48
	$Co(NH_3)_4(\underline{N}\text{-}NH)_2{}^{5+}$	0	0	0	1	6	1	3	5	9	7	—[g)]
	$(NH_3)_5Co(N\text{-}N)Co(NH_3)_5{}^{6+}$[h)]	0	0	1[f)]	0	6[f)]	0.8	—[g)]	—[g)]	7	17	—[g)]

a) The reactants were allowed to react at 85 °C for 20 min, unless otherwise stated. The numerical values given in this table denote the yield (%) based on $[Co(H_2O)(NH_3)_5](ClO_4)_3$. The f symbol denotes that the product indicated is formed. b) The reactants were allowed to react at 92 °C for 20 min. c) The recovered $Co(H_2O)(NH_3)_5{}^{3+}$ amounted to 8% of the initial $Co(H_2O)(NH_3)_5{}^{3+}$. d) The recovered $Co(H_2O)(NH_3)_5{}^{3+}$ amounted to 14% of the initial $Co(H_2O)(NH_3)_5{}^{3+}$. e) The species with charges higher than 6+ were formed in considerable amounts. f) The product is not sufficiently pure (see Table 1). g) The product indicated is considered to be formed, but no pure sample has been isolated. h) The yield was calculated by means of the following relation: Yield $=2\times$ (mol of the indicated product) $\times 100/$(mol of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ used as the starting material).

The formation of $\mathrm{Co(NH_3)_4(N{-}N)^{3+}}$, which contains an N–N chelate ring, is observed for en, tn, tmd, don, or tden, but not for pmd, hepn, ocn, or den. These facts support the previous conclusion in which the medium-size chelate ring is unstable.1)

In the en and tn systems, $\mathrm{Co(NH_3)_2(N{-}N)_2^{3+}}$ and $\mathrm{Co(N{-}N)_3^{3+}}$ were formed, and the formation of complexes more positively charged than four was not significant. The yield of $\mathrm{Co(NH_3)_5(\underline{N}{-}NH)^{4+}}$ was also low. However, when the diamines with more methylene groups than tn were used, the formation of appreciable amounts of $\mathrm{Co(NH_3)_5(\underline{N}{-}NH)^{4+}}$ was observed. Furthermore, the formations of $\mathrm{Co(NH_3)_4(\underline{N}{-}NH)_2^{5+}}$ and $\mathrm{(NH_3)_5Co(N{-}N)Co(NH_3)_5^{6+}}$ were also significant. These tendencies become notable with the increase in the number of methylene groups, as is shown in Table 2. These facts indicate that, when the methylenic chain of N–N is long, the N–N tends to coordinate to a cobalt(III) ion as a unidentate ligand, or to two cobalt(III) ions as a bridging ligand, rather than as a chelate ligand. In the systems of the diamines higher than tn, $\mathrm{Co^{2+}}$ ions were always formed during the reactions in DMSO. Their amounts increased with the increase in the reaction time and with the elevation of the reaction temperature. In the en and tn systems, the formation of $\mathrm{Co^{2+}}$ ions was found to be negligible.

Mechanism of the Reaction of $[\mathrm{Co(H_2O)(NH_3)_5}](\mathrm{ClO_4})_3$ *with N-N in DMSO.* When a DMSO solution containing $[\mathrm{Co(H_2O)(NH_3)_5}](\mathrm{ClO_4})_3$ is heated, the aqua ligand in $\mathrm{Co(H_2O)(NH_3)_5^{3+}}$ is known to be replaced by DMSO.3g) Here, it is assumed tentatively that the formation of $\mathrm{Co(DMSO)(NH_3)_5^{3+}}$ occurs prior to the attack of $\mathrm{Co(H_2O)(NH_3)_5^{3+}}$ by N–N; that is, the reaction occurs in the following sequence:

$$\mathrm{Co(H_2O)(NH_3)_5^{3+} + DMSO} \longrightarrow \mathrm{Co(DMSO)(NH_3)_5^{3+} + H_2O}, \quad (1)$$

$$\mathrm{Co(DMSO)(NH_3)_5^{3+} + N{-}N} \longrightarrow \mathrm{Co(NH_3)_5(\underline{N}{-}N)^{3+} + DMSO}. \quad (2)$$

Upon the acidification of the solution, the $\mathrm{Co(NH_3)_5(\underline{N}{-}N)^{3+}}$ complex should be converted into $\mathrm{Co(NH_3)_5(\underline{N}{-}NH)^{4+}}$. This explains the formation of $[\mathrm{Co(NH_3)_5(\underline{N}{-}NH)}]\mathrm{X_4}$.

As has been mentioned above, the product distributions of the en and tn systems are quite different from those for the higher N–N systems. The products indicate that the predominant reactions in the systems of en and tn can be expressed as follows:

$$\mathrm{Co(NH_3)_5(\underline{N}{-}N)^{3+}} \rightarrow \mathrm{Co(NH_3)_4(N{-}N)^{3+} + NH_3}, \quad (3)$$

$$\mathrm{Co(DMSO)(NH_3)_5^{3+} + NH_3} \rightarrow \mathrm{Co(NH_3)_6^{3+} + DMSO}, \quad (4)$$

$$\mathrm{Co(NH_3)_4(N{-}N)^{3+} + N{-}N} \rightarrow \mathrm{Co(NH_3)_2(N{-}N)_2^{3+} + 2NH_3}, \quad (5)$$

$$\mathrm{Co(NH_3)_2(N{-}N)_2^{3+} + N{-}N} \rightarrow \mathrm{Co(N{-}N)_3^{3+} + 2NH_3}, \quad (6)$$

$$\mathrm{Co(NH_3)_6^{3+} + N{-}N} \rightarrow \mathrm{Co(NH_3)_5(\underline{N}{-}N)^{3+} + NH_3}. \quad (7)$$

Reaction 7 was comfirmed by the product survey of the direct reaction of $\mathrm{Co(NH_3)_6^{3+}}$ with en in DMSO (see Experimental section). The occurrence of Reactions 3, 5, and 6 reveals that the successive substitution of the ammonia molecules from $\mathrm{Co(NH_3)_5(\underline{N}{-}N)^{3+}}$ with en or tn molecules leads to the formation of $\mathrm{Co(NH_3)_{6-2p}(N{-}N)_p^{3+}}$ containing the diamine chelate(s), where $1 \leq p \leq 3$. In the systems of the higher N–N's, however, Reactions 5 and 6 are absent. The successive substitution of ammonia molecules from $\mathrm{Co(NH_3)_5(\underline{N}{-}N)^{3+}}$ with these N–N molecules leads to the formation of

TABLE 3. ELECTRONIC SPECTRAL DATA FOR THE COMPLEXES PREPARED IN THIS WORK

Wave numbers are in $10^3\ \mathrm{cm^{-1}}$, while the intensities are given by $\log \varepsilon$ in parentheses.

Complex	I band	II band
$[\mathrm{Co(NH_3)_6}](\mathrm{ClO_4})_3$ a)	21.0(1.76)	29.5(1.67)
$[\mathrm{Co(NH_3)_4(en)}]\mathrm{I_3}$	21.2(1.87)	—
$[\mathrm{Co(NH_3)_4(en)}](\mathrm{SO_4})_{1.5}\cdot 2\mathrm{H_2O}$ a)	21.2(1.83)	29.5(1.76)
cis-$[\mathrm{Co(NH_3)_2(en)_2}]\mathrm{I_3}$	21.4(1.89)	—
cis-$[\mathrm{Co(NH_3)_2(en)_2}](\mathrm{ClO_4})_3\cdot \mathrm{H_2O}$ a)	21.5(1.79)	29.8(1.74)
trans-$[\mathrm{Co(NH_3)_2(en)_2}](\mathrm{ClO_4})_3\cdot \mathrm{H_2O}$ a)	21.4(1.77)	29.7(1.73)
$[\mathrm{Co(en)_3}](\mathrm{ClO_4})_3$ b)	21.3(1.94)	29.6(1.89)
$[\mathrm{Co(NH_3)_4(tn)}](\mathrm{ClO_4})_3$	20.9(1.82)	29.1(1.76)
$[\mathrm{Co(NH_3)_4(tn)}]\mathrm{Br_3}\cdot \mathrm{H_2O}$ c)	20.9(1.79)	29.2(1.78)
$[\mathrm{Co(NH_3)_2(tn)_2}](\mathrm{ClO_4})_3$	20.7(1.86)	28.9(1.83)
$[\mathrm{Co(tn)_3}](\mathrm{ClO_4})_3$ b)	20.3(1.88)	28.5(1.87)
$[\mathrm{Co(NH_3)_4(tmd)}](\mathrm{ClO_4})_3$	20.7(1.84)	29.0(1.77)
$[\mathrm{Co(tmd)_3}]\mathrm{Br_3}$ d)	19.9(1.89)	27.9(1.85)
$[\mathrm{Co(NH_3)_4(don)}]\mathrm{Br_3}$	20.6(1.86)	29.0(1.81)
$[\mathrm{Co(NH_3)_4(tden)}]\mathrm{Br_3}\cdot 1.5\mathrm{H_2O}$	20.7(1.88)	29.0(1.83)
$[\mathrm{Co(NH_3)_5(enH)}](\mathrm{ClO_4})_4$	20.8(1.80)	29.2(1.71)
$[\mathrm{Co(NH_3)_5(tnH)}](\mathrm{ClO_4})_4$	20.8(1.83)	29.2(1.75)
$[\mathrm{Co(NH_3)_5(tmdH)}](\mathrm{ClO_4})_4$	20.8(1.82)	29.2(1.74)
$[\mathrm{Co(NH_3)_5(pmdH)}](\mathrm{ClO_4})_4$	20.8(1.82)	29.2(1.74)
$[\mathrm{Co(NH_3)_5(hepnH)}](\mathrm{ClO_4})_4$	20.8(1.86)	29.2(1.80)
$[\mathrm{Co(NH_3)_5(ocnH)}](\mathrm{ClO_4})_4$	20.8(1.85)	29.2(1.81)
$[\mathrm{Co(NH_3)_5(denH)}]\mathrm{Br_4}$	20.8(1.83)	29.2(1.77)
$[\mathrm{Co(NH_3)_5(donH)}](\mathrm{ClO_4})_4$	20.8(1.87)	29.2(1.81)
$[\mathrm{Co(NH_3)_5(tdenH)}]\mathrm{Br_4}$	20.8(1.87)	29.2(1.83)
$[\mathrm{Co(NH_3)_4(tmdH)_2}](\mathrm{ClO_4})_5$	20.6(1.88)	29.0(1.83)
$[\mathrm{Co(NH_3)_4(pmdH)_2}](\mathrm{ClO_4})_5$	20.7(1.88)	29.0(1.82)
$[\mathrm{Co(NH_3)_4(hepnH)_2}]\mathrm{Cl_5}\cdot 2\mathrm{H_2O}$	20.7(1.91)	29.0(1.85)
$[\mathrm{Co(NH_3)_4(ocnH)_2}]\mathrm{Cl_5}\cdot 3\mathrm{H_2O}$	20.7(1.90)	29.0(1.84)
$[\mathrm{Co(NH_3)_4(denH)_2}]\mathrm{Br_5}$	20.7(1.89)	29.0(1.84)
$[\mathrm{Co(NH_3)_4(donH)_2}](\mathrm{ClO_4})_5$	20.7(1.91)	29.2(1.99)
$[\mathrm{Co(NH_3)_3(denH)_3}]\mathrm{Cl_6}\cdot 2\mathrm{H_2O}$	20.4	28.6
$[\mathrm{(NH_3)_5Co(tn)Co(NH_3)_5}]\mathrm{Br_6}$ e)	20.8	29.2
$[\mathrm{(NH_3)_5Co(tmd)Co(NH_3)_5}]\mathrm{Br_6}$ e)	20.8	29.2
$[\mathrm{(NH_3)_5Co(pmd)Co(NH_3)_5}]\mathrm{Br_6}\cdot 3\mathrm{H_2O}$ f)	20.9(2.13)	29.3(2.06)
$[\mathrm{(NH_3)_5Co(den)Co(NH_3)_5}]\mathrm{Br_6}\cdot 2\mathrm{H_2O}$ f)	20.8(2.11)	29.4(2.07)
$[\mathrm{(NH_3)_5Co(don)Co(NH_3)_5}]\mathrm{Br_6}$ f)	20.8(2.11)	29.2(2.07)
$[\mathrm{(NH_3)_4Co(den)_2Co(NH_3)_4}]\mathrm{Br_6}\cdot 3\mathrm{H_2O}$ f)	20.6(2.20)	29.1(2.15)
$[\mathrm{Co_2(NH_3)_8(den)(denH)_2}]\mathrm{Br_8}\cdot 2\mathrm{H_2O}$ f)	20.7(2.18)	29.1(2.15)

a) From Ref. 8. b) From Ref. 1. c) From Ref. 10. d) From Ref. 3i. e) The sample is not pure (see Table 1). f) The intensities are given per complex ion, *i.e.*, per two cobalt(III) ions.

$Co(NH_3)_{6-p}(\underline{N}\text{-}N)_p{}^{3+}$:

$$Co(NH_3)_5(\underline{N}\text{-}N)^{3+} + (p-1)N\text{-}N \longrightarrow Co(NH_3)_{6-p}(\underline{N}\text{-}N)_p{}^{3+} + (p-1)NH_3, \quad (8)$$

where $p>1$. Upon the acidification of the solution, the $Co(NH_3)_{6-p}(\underline{N}\text{-}N)_p{}^{3+}$ complex should be converted into the highly charged $Co(NH_3)_{6-p}(\underline{N}\text{-}NH)_p{}^{(3+p)+}$ complex. This would explain the formation of $Co(NH_3)_4(\underline{N}\text{-}NH)_2{}^{5+}$ and $Co(NH_3)_3(denH)_3{}^{6+}$. Reaction 8 is absent in the systems of en and tn, This result and the occurrence of Reactions 3, 5, and 6 show the remarkable tendency for the en or tn to take the chelate form.

The formation of the dimeric complex can be expressed as:

$$Co(DMSO)(NH_3)_5{}^{3+} + Co(NH_3)_5(\underline{N}\text{-}N)^{3+} \longrightarrow (NH_3)_5Co(N\text{-}N)Co(NH_3)_5{}^{6+} + DMSO. \quad (9)$$

The amount of the dimer becomes appreciable with the increase in the number of methylene groups in the N–N. In the N–N with a long methylenic chain, a close approach between two positively charged cobalt(III) ions is not necessary. This would favor the formation of the dimer.

Spectral Properties of the Complexes. The numerical data for electronic absorption spectra of the complexes are summarized in Table 3. The positions of the first absorption bands of all the complexes prepared in this work are located around 21000 cm^{-1}. Therefore, it can be concluded that all the complexes have CoN_6 moieties. The increase in the number of en chelate(s) in $Co(NH_3)_{6-2p}(en)_p{}^{3+}$ causes shifts in the absorption maxima to shorter wavelengths,[9] while those of the other N–N chelate(s) shift to longer wavelengths. The absorption bands of $Co(NH_3)_4(N\text{-}N)^{3+}$ shift to longer wavelengths as the methylenic chain of the N–N becomes longer; hence, the ligand-field strength for N–N chelates is in this order: en$>(NH_3)_2>$tn$>$tmd$\simeq$don$\simeq$tden. The successive substitution of ammonia molecules in $Co(NH_3)_6{}^{3+}$ with monoprotonated diamines causes shifts in the absorption maxima to longer wavelengths. However, the absorption positions for $Co(NH_3)_5(\underline{N}\text{-}NH)^{4+}$ and $Co(NH_3)_4(\underline{N}\text{-}NH)_2{}^{5+}$ are almost independent of the kind of diamine. The absorption positions of the dimeric complexes are also insensitive to the kind of diamine.

The author wishes to thank Professor Nobuyuki Tanaka, Tohoku University, and Professor Junnosuke Fujita, Nagoya University, for their encouragement and support.

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4) As it was difficult to separate the bromide complex from KBr, the complex was converted to the chloride or perchlorate with the aid of a Sephadex column.

5) The yield in % was calculated by means of the following equation:

Yield = 2× (mol of the indicated product) × 100/(mol of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ used as the starting material)

6) $Co(\underline{N}\text{-}NH)$ denotes that the ω-aminoalkylammonium ion $N\text{-}NH^+$ is coordinated to the cobalt moiety through the ω-amino group. Similarly, $Co(\underline{N}\text{-}N)$ denotes that the N–N acts as the monodentate ligand.

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