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Cobalt(III) Complexes Containing Large Chelate Rings. I. Syntheses and Properties of Bis(ethylenediamine)-1,ω-diaminoalkanecobalt(III) Complexes[1)]

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New cobalt (III) complexes, $[Co(en)_2(H_2N(CH_2)_nNH_2)]X_3$ (n=4, 10, 12 and 14), $[Co_2(en)_4(H_2N(CH_2)_nNH_2)_2]X_6$ (n=4, 5, 6, 8, 10 and 12), $[Co(en)_2(H_2N(CH_2)_4NH_3)_2]X_5$ and $[CoCl(en)_2(H_2N(CH_2)_{12}NH_3)]X_3$ were isolated from the products of reactions between $[CoCl_2(en)_2]Cl$ and 1,ω-diaminoalkane in dimethylsulfoxide, with the aid of SP-Sephadex column chromatography. For n=5, 6 and 8, no monomeric $[Co(en)_2(H_2N(CH_2)_nNH_2)]^{3+}$ was observed. This result is compatible with instability of the medium size rings in organic compounds. The elution behaviors on Sephadex column and the visible and ultraviolet absorption spectra of the new complexes were also described.

Although several reports on the isolation of metal complexes containing large chelate rings have been presented, no conclusive evidence for the ring formation has ever been obtained.[2)] Attempts to prepare metal complexes with 1,ω-diaminoalkanes, $H_2N(CH_2)_nNH_2$ ($n>3$) have also been made extensively.[3—10)] However, only Pfeiffer[11)] succeeded in isolating copper(II) complexes of bis(1,4-diaminobutane) and of bis- and tris-(1,6-diaminohexane), although his brief report did not give any evidence for the formation of seven- or nine-membered chelate rings. As shown later, these diamines tend to coordinate to a metal ion as a unidentate ligand or to two metal ions as a bridging ligand.

This paper will present the syntheses and properties of cobalt(III) complexes containing various 1,ω-diaminoalkanes. The diamines, $H_2N(CH_2)_nNH_2$, used in this work are as follows; n=2(en), 3(tn), 4(tmd), 5(pmd), 6(hxn), 8(ocn), 10(den), 12(don) and 14(tden). Some part of this work have been reported briefly in two communications.[12,13)] Very recently, Pryde *et al.*[14)] obtained platinum(II) and iridium(I) complexes containing $Bu^t_2P(CH_2)_nPBu^t_2$ (n=9 or 10).

Experimental

Materials. Guaranteed reagent grade dimethyl sulfoxide (DMSO) and 1,ω-diaminoalkanes (N–N) were obtained from Tokyo Kasei Co. and used without further purification. Column chromatography was carried out by use of SP-Sephadex C-25 (Pharmacia, Sweden).

Preparation of Cobalt(III) Complexes. All bis(ethylenediamine)-1,ω-diaminoalkanecobalt(III) complexes were obtained from the products of reactions of *cis*- or *trans*-$[CoCl_2(en)_2]Cl$ with N–N in DMSO. The *cis*-isomer of $[CoCl_2(en)_2]Cl$ seems to be a better starting material than the *trans*-isomer, because the *cis*-isomer is more soluble in DMSO.

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

1) $[Co(en)_2(tmd)]Br_3$ *and* $[Co_2(en)_4(tmd)_2]Br_6\cdot 6H_2O$: To 550 ml of DMSO containing 4.3 g of *cis*- or *trans*-$[CoCl_2(en)_2]Cl$ (0.015 mol) was added 1.4 g of tmd (0.016 mol). The solution was kept at 50 °C for 20 hr and then cooled to room temperature. The reddish orange solution resulted was neutralized with concd HCl and diluted to 3 l with water. This was poured on a Sephadex ion exchange column (ϕ 5×40 cm). After washing the column with water, 1 l of an 0.1 M KBr solution was passed through the column. At this stage, the column showed four bands; pink (very small amount), red (small amount), yellow and yellowish orange bands from bottom to top of the column. After the first and second bands had been eluted with an 0.2 M KBr solution, the third yellow band was eluted with an 0.4 M KBr solution. The eluate was concentrated with a rotary evaporator to a small volume. A mixture of yellowish orange crystals of $[Co(en)_2(tmd)]Br_3$ and solid KBr was collected on a glass filter and washed with a small amount of water to remove KBr. The crude product thus obtained was recrystallized from water by the addition of solid NaBr. Pure crystals were filtered off and washed with ethanol and then with ether. Yield: 5.4 g (70%).

The last yellowish orange band was eluted with a warm 1 M KBr solution. Yellowish orange crystals of $[Co_2(en)_4(tmd)_2]Br_6\cdot 6H_2O$ were obtained from the eluate by a procedure similar to the above. Yield: 0.3 g.

2) $[Co(en)_2(tmdH)_2]Br_5\cdot 4H_2O$: To 100 ml of DMSO containing 2.9 g of *cis*-$[CoCl_2(en)_2]Cl$ (0.01 mol) was added 1.9 g of tmd (0.02 mol). The solution was stirred for 3 hr at room temperature. The reddish orange solution resulted was treated by a method similar to 1). When 2 l of an 0.2 M NaBr solution and then 4 l of an 0.25 M NaBr solution were passed through the column, five bands were observed on the column; red, yellow, reddish orange, yellow and orange bands from bottom to top of the column. They were eluted with 0.3—1 M NaBr solutions successively. The second yellow band gave $[Co(en)_2(tmd)]Br_3$ (0.15 g) and the fourth yellow band, $[Co(en)_2(tmdH)_2]Br_5\cdot 4H_2O$ (1.5 g). When the fourth band was eluted from the column, the fifth band was found to be separated into several bands, from one of which $[Co_2(en)_4(tmd)_2]Br_6\cdot 6H_2O$ (0.6 g) was obtained. Species in eluates obtained from other bands were not characterized.

3) $[Co_2(en)_4(pmd)_2]Br_6\cdot 2H_2O$, $[Co_2(en)_4(hxn)_2]Br_6\cdot 4H_2O$, $[Co_2(en)_4(ocn)_2]Br_6\cdot 4H_2O$, $[Co(en)_2(den)]Br_3\cdot 2H_2O$ *and* $[Co_2(en)_4(den)_2]Br_6\cdot 3H_2O$: To 550 ml of DMSO containing 4.3 g of *cis*-$[CoCl_2(en)_2]Cl$ (0.015 mol) was added 0.015 mol of N–N (1.5 g for pmd, 1.7 g for hxn, 2.2 g for ocn and 2.6 g for den). The solution was kept at 65 °C for 30 hr and then treated in a similar way to 1). By developing the adsorbed band with an 0.3 M KBr solution, the column gave the following eight bands regardless of the kind of N–N used; pale pink (very small amount, characterized as Co^{2+} species), reddish violet, yellow (this band is refered to as A band), reddish orange, yellowish orange, reddish orange, yellowish orange (B band) and orange from bottom to top of the column. The last orange band seems to be a mixture of highly charged species, because the band was separated into several bands with progression of the elution.

After the pale pink and reddish violet bands had been

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Table 1. Summary of analytical data for the complexes prepared in this work

Complex	Formula	C, %		H, %		N, %	
		Calcd	Found	Calcd	Found	Calcd	Found
$[Co(en)_2(tn)]Br_3$	$[CoC_7H_{26}N_6]Br_3$	17.06	16.81	5.32	5.46	17.05	16.80
$[Co(en)(tn)_2]Br_3\cdot 4H_2O$	$[CoC_8H_{28}N_6]Br_3\cdot 4H_2O$	16.59	16.66	6.27	6.97	14.51	14.71
$[Co(en)_2(tmd)]Br_3$	$[CoC_8H_{28}N_6]Br_3$	18.95	18.71	5.57	5.76	16.58	16.58
$[Co(en)_2(den)]Br_3\cdot 2H_2O$	$[CoC_{14}H_{40}N_6]Br_3\cdot 2H_2O$	26.81	26.72	7.07	6.88	13.40	13.73
$[Co(en)_2(don)]Br_3\cdot H_2O$	$[CoC_{16}H_{44}N_6]Br_3\cdot H_2O$	30.16	29.91	7.28	7.31	13.19	13.04
$[Co(en)_2(tden)]Br_3\cdot 2.5H_2O$	$[CoC_{18}H_{48}N_6]Br_3\cdot 2.5H_2O$	31.23	31.35	7.72	7.61	12.14	12.37
$[CoCl(en)_2(donH)]Br_3\cdot 2.5H_2O$	$[CoClC_{16}H_{45}N_6]Br_3\cdot 2.5H_2O$	27.43	26.91	7.19	6.78	11.99	12.16
$[Co(en)_2(tmdH)_2]Br_5\cdot 4H_2O$	$[CoC_{12}H_{42}N_8]Br_5\cdot 4H_2O$	17.39	17.43	6.08	6.06	13.52	13.50
$[Co_2(en)_4(tmd)_2]Br_6\cdot 6H_2O$	$[Co_2C_{16}H_{56}N_{12}]Br_6\cdot 6H_2O$	17.12	17.01	6.11	6.16	14.98	15.09
$[Co_2(en)_4(pmd)_2]Br_6\cdot 2H_2O$	$[Co_2C_{18}H_{60}N_{12}]Br_6\cdot 2H_2O$	20.05	19.92	5.98	5.96	15.59	15.68
$[Co_2(en)_4(hxn)_2]Br_6\cdot 4H_2O$	$[Co_2C_{20}H_{64}N_{12}]Br_6\cdot 4H_2O$	21.03	20.95	6.35	6.35	14.72	14.30
$[Co_2(en)_4(ocn)_2]Br_6\cdot 4H_2O$	$[Co_2C_{24}H_{72}N_{12}]Br_6\cdot 4H_2O$	24.06	23.68	6.73	6.35	14.03	14.03
$[Co_2(en)_4(den)_2]Br_6\cdot 3H_2O$	$[Co_2C_{28}H_{80}N_{12}]Br_6\cdot 3H_2O$	27.20	26.92	7.01	6.74	13.59	13.83
$[Co_2(en)_4(don)_2]Cl_6\cdot 6.5H_2O$	$[Co_2C_{32}H_{88}N_{12}]Cl_6\cdot 6.5H_2O$	35.30	35.52	9.35	9.25	15.44	15.09

eluted with an 0.3 M KBr solution, the A band was eluted with an 0.4 M KBr solution and its yellow eluate was concentrated. A small amount of yellow crystals of $[Co(en)_3]Br_3\cdot 3H_2O$ was obtained and no formation of $[Co(en)_2(N\text{–}N)]^{3+}$ was observed for all the diamines except the den. In the case of den, the eluate gave yellowish orange crystals of $[Co(en)_2(den)]Br_3\cdot 2H_2O$. They were recrystallized similarly from water by the addition of solid KBr. Yield: 0.24 g (2.5 %).

After the A band had been eluted from the column, the concentration of eluent was increased to 0.6 M and then 1 M or more with progression of the elution. However, the use of such KBr solutions caused sometimes crystallization of $[Co_2(en)_4(N\text{–}N)_2]Br_6\cdot nH_2O$ in the column, so that a warm KBr solution (40—70 °C) was used. In the case of the den system, it was still difficult to avoid the crystallization. Therefore, the layer of B band was transfered to a beaker and a colored species was extracted with a hot 0.6 M KBr solution repeatedly. Yellowish orange crystals which were obtained from each eluate or extract by concentration were $[Co_2(en)_4(pmd)_2]Br_6\cdot 2H_2O$, $[Co_2(en)_4(hxn)_2]Br_6\cdot 4H_2O$, $[Co_2(en)_4(ocn)_2]Br_6\cdot 4H_2O$ and $[Co_2(en)_4(den)_2]Br_6\cdot 3H_2O$. The yields of $[Co_2(en)_4(N\text{–}N)_2]^{6+}$ ranged from 30% (pmd) to 12% (den) depending on the length of the methylenic chain of the N–N.

4) $[CoCl(en)_2(donH)]Br_3\cdot 2.5H_2O$, $[Co(en)_2(don)]Br_3\cdot H_2O$ *and* $[Co_2(en)_4(don)_2]Cl_6\cdot 6.5H_2O$: These complexes were obtained from 4.3 g of *cis-* or *trans*-$[CoCl_2(en)_2]Cl$ (0.015 mol) and 3.0 g of don (0.015 mol) by a method similar to 3). By developing the reaction product on a Sephadex column with an 0.2 M NaBr solution, eight bands were observed; pink (small amount), red (A band), yellow (B band), yellowish orange, reddish orange, yellowish orange, yellowish orange (C band) and orange from bottom to top of the column. The last band seems also to be a mixture of several highly charged species. After the first pink band had been eluted with an 0.2 M NaBr solution, the red A band was eluted with an 0.3 M NaBr solution. By evaporating the eluate, reddish violet crystals of $[CoCl(en)_2(donH)]Br_3\cdot 2.5\,H_2O$ were obtained and recrystallized from water by the addition of NaBr. The eluate of the A band contained a small amount of $[Co(en)_3]^{3+}$, but it was separated easily from the desired complex by the recrystallization.

The B band was eluted with an 0.4 M NaBr solution and the eluate was concentrated. Yellowish orange crystals of $[Co(en)_2(don)]Br_3\cdot H_2O$ were obtained and recrystallized from water by the addition of solid NaBr. Yield: 0.87 g (9%).

Then the column was washed with water. The layer of C band was transfered to a beaker and a colored species was extracted with a hot 1 M NaCl solution repeatedly. Upon cooling the extract to room temperature, fine crystals of $[Co_2(en)_4(don)_2]Cl_6\cdot 6.5H_2O$ were precipitated, filtered off and recrystallized from water.

5) $[Co(en)_2(tden)]Br_3\cdot 2.5H_2O$: This complex was prepared similarly by warming a DMSO (500 ml) solution containing 2.9 g of *cis*-$[CoCl_2(en_2)]Cl$ (0.01 mol) and 2.3 g of tden (0.01 mol) at 60 °C for 20 hr. The Sephadex column gave six bands on developing the product with an 0.2 M KBr; pale pink (small amount), yellow (small amount of $[Co(en)_3]^{3+}$), reddish violet, yellowish orange, reddish orange and brownish orange from bottom to top of the column. After the first three bands had been eluted with an 0.3 M KBr solution, the fourth yellowish orange band was eluted with a warm 0.6 M KBr solution. A gummy oil was separated from the solution by concentrating the eluate. The oil was dissolved into a small amount of warm water and the solution was cooled gradually to room temperature. Yellowish orange crystals of $[Co(en)_2(tden)]Br_3\cdot 2.5H_2O$ were precipitated, filtered off and recrystallized from water. Yield: 0.38 g (6%).

6) $[Co(en)_2(tn)]Br_3$: This complex was prepared by the procedure reported by Bailar and Work.[10] The product contained a considerable amount of $[Co(en)_3]Cl_3\cdot 3H_2O$. Pure crystals of $[Co(en)_2(tn)]Br_3$ were obtained by recrystallizing the product several times from water by the addition of a KBr solution.

Alternatively, a method similar to 1) was employed; to 100 ml of DMSO containing 2.9 g of *cis*-$[CoCl_2(en)_2]Cl$ (0.01 mol) was added 0.74 g of tn (0.01 mol). The solution was allowed to stand overnight at room temperature, neutralized with conc. HCl and subjected to Sephadex column chromatography. The fastest moving band seemed to be Co^{2+} species. The second band was pink and was followed by a yellow band. The yellow band was eluted with an 0.2 M KBr solution. Some bands remained on the column after elution of the yellow band. Evaporation of the yellow eluate gave crystals of $[Co(en)_2(tn)]Br_3$ which also contained $[Co(en)_3]Br_3\cdot 3H_2O$. They were recrystallized similarly from water by the addition of a KBr solution to give pure $[Co(en)_2(tn)]Br_3$. Yield: 1.2 g.

7) [Co(en)(tn)$_2$]Br$_3$·4H$_2$O: To 40 ml of an aqueous solution containing 12 g of $CoCl_2\cdot 6H_2O$ (0.05 mol) were added 11 g of tn (0.15 mol), 3 g of en (0.05 mol), 8.3 ml of 6 M HCl (0.05 mol) and 1 g of active carbon. Air was passed through the solution for 12 hr at room temperature. After removal of active carbon by filtration, solid KBr was added to the filtrate. A mixture of $[Co(en)_2(tn)]Br_3$ and $[Co(en)(tn)_2]Br_3\cdot 4H_2O$ was obtained. The latter was more soluble than the former and the desired complex was obtained by the fractional crystallization.

When solid $[CoCl_2(tn)_2]Cl$ was added in small portions to a DMSO solution containing equimolar amount of en, the desired complex was also formed together with $[Co(en)_3]^{3+}$ and $[Co(en)_2(tn)]^{3+}$

Apparatus. Visible and ultraviolet absorption spectra of aqueous solutions of the complexes were recorded on a Hitachi EPS-3 recording spectrophotometer.

Results and Discussion

Chromatographic Properties and Characterization of the Complexes. Both yellowish orange complexes of the monomeric $[Co(en)_2(N\text{–}N)]X_3$ and the dimeric $[Co_2(en)_4(N\text{–}N)_2]X_6$ obtained here have the same chemical composition, but their complex cations have different charges. The difference in the charge of the complex ion may be reflected on the chromatographic properties.

Sephadex resin charged with two kinds of complex ion was placed carefully on the top of a Sephadex column (ϕ 1.6×20 cm) by 1 mm thickness. The adsorbed complex ions were eluted with an 0.25 M KBr solution adjusted to pH 3 with HBr at a rate of about 1.6 ml/min. The relative R_f values to that of $[Co(en)_3]^{3+}$ are summarized in Table 2 where those of the authentic samples of the known charge are given for comparison. Table 2 shows that the R_f value increases by four to ten times as the charge of the complex ion decreases by one and that the complexes, $[Co(en)_2(N\text{–}N)]^{3+}$ give values expected for a monomeric tripositive ion, although a slight deviation from unity is observed for the complexes containing larger diamine chelate.

Table 2. The relative R_f values of various complexes

(Eluent: 0.25 M KBr solution adjusted to pH 3 with HBr.)

Complex ion	Relative R_f value
$[CoCl(NH_3)_5]^{2+}$	7.6[a]
$[Co(en)_3]^{3+}$	1[b]
$[Co(NH_3)_6]^{3+}$	0.65
$[CoCl(en)_2(donH)]^{3+}$	~1
$[Co(en)_2(tn)]^{3+}$	1.0
$[Co(en)_2(tmd)]^{3+}$	1.0
$[Co(en)_2(den)]^{3+}$	0.87
$[Co(en)_2(don)]^{3+}$	0.54
$[Co(en)_2(tden)]^{3+}$	0.43
$[Co(en)_2(tmdH)_2]^{5+}$	0.16
$[Co_2(en)_4(tmd)_2]^{6+}$	0.01_8
$[Co_2(en)_4(hxn)_2]^{6+}$	<0.02
$[Co_2(en)_4(don)_2]^{6+}$	<0.01
$[Cr\{(OH)_2Cr(en)_2\}_3]^{6+}$	~0.008

a) This value was determined by the elution of resins charged with $[CoCl(NH_3)_5]^{2+}$ and $[Co(en)_3]^{3+}$. (Eluent: 0.1 M KBr solution adjusted to pH 3 with HBr.) b) The R_f value of this complex ion is taken as unity.

Under the same elution condition, other yellowish orange complexes assignable to $[Co_2(en)_4(N\text{–}N)_2]^{6+}$ show such slow flow rates that their R_f values are determined with difficulty. However, these ions flow with an 0.5 M KBr solution at rates similar to that of $[Cr\{(OH)_2Cr(en)_2\}_3]^{6+}$, indicating that they are dimeric with hexapositive charge.

The R_f value of the yellowish orange complex whose elemental analysis gives correct value for $[Co(en)_2(tmdH)_2]Br_5\cdot 4H_2O$ is 0.16 and the complex ion can be concluded to be pentapositive. This complex will be the first example of cobalt(III) complex containing two unidentate diamines.

For the $[Co(en)_2(N\text{–}N)]^{3+}$, two nitrogen atoms of the N–N can occupy *cis* or *trans* positions as shown in Fig. 1A, if the methylenic chain of the N–N is long enough. However, all the N–N used in this work will occupy only *cis* positions. Molecular models reveal that the non-bonding interaction between the en and the N–N chelates make *trans* spanning difficult even in the case of tden with 14 methylenes. This will be supported by the fact that $[Co(en)_2(tmd)]^{3+}$ and $[Co(en)_2(don)]^{3+}$ were resolved into optical isomers by SP-Sephadex column chromatography using an 0.15 M potassium tartratoantimonate(III) solution as an eluent.[12,15)]

Many isomers are possible for the dimeric complexes, $[Co_2(en)_4(N\text{–}N)_2]^{6+}$. As shown later, the formation of $[Co_2(en)_6]^{6+}$ was never observed, indicating that en will be unfavorable as a bridging ligand. Molecular models suggest that the structures in Fig. 1B are most probable. The catenane structures of which one example is shown in Fig. 1C are also possible, if the methylenic chain of

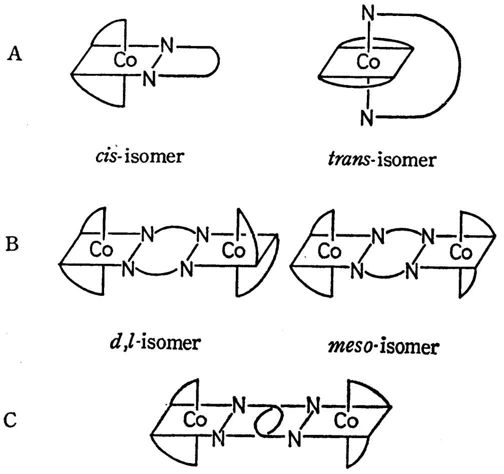


Fig. 1. Possible structures for the monomer ($[Co(en)_2(N\text{-}N)]^{3+}$) and the dimer ($[Co_2(en)_4(N\text{-}N)_2]^{6+}$). ⌒ and N⌒N denote en and N-N, respectively.

A: Possible structure of the monomer.
B: Most probable structures of the dimer.
C: One example of the catenane structures for the dimer.

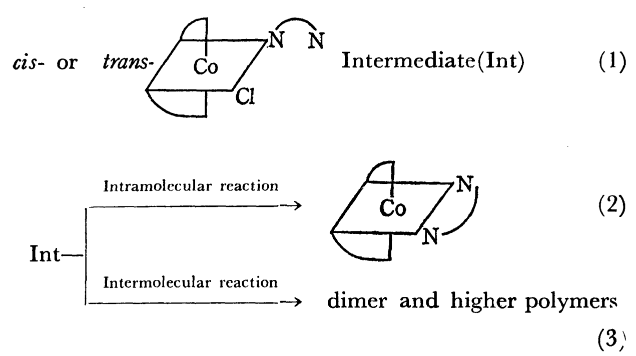
the N–N becomes long enough.

The red complex assigned to $[CoCl(en)_2(donH)]Br_3 \cdot 2.5H_2O$[16] gives the R_f value almost the same as that of $[Co(en)_3]^{3+}$. This complex shows the first and the second absorption band at 18900 cm^{-1} with a shoulder at 21300 cm^{-1}, and at 27400 cm^{-1}, respectively. This spectral pattern is characteristic of a $[CoClN_5]$ type.[17,18] The complex is converted into aqua complex $[Co(H_2O)(en)_2(donH)]^{4+}$ when treated with silver nitrate in an acidic aqueous solution. The aqua complex exhibits a symmetrical first absorption band at 20400 cm^{-1}. Alexander and Spillert[19] prepared $[CoCl(en)_2(enH)]Cl_3 \cdot H_2O$ and assigned it to *cis* configuration. The present chloro complex may have the same *cis* structure.

Mechanism of the Reaction of $[CoCl_2(en)_2]Cl$ *with N–N in DMSO.* In order to elucidate the mechanism of the reaction of $[CoCl_2(en)_2]Cl$ with N–N, the preparations have been carried out under various conditions. The change of concentration of the reactants affects the distribution of products considerably. The yield of $[Co(en)_2(tmd)]^{3+}$ amounts to 70%, when 0.015 mol of tmd is allowed to react with an equivalent amount of $[CoCl_2(en)_2]Cl$ in 550 ml of DMSO. However, when the solvent DMSO is reduced to 50 ml, the yield of this monomer decreases to a few percent and that of the $[Co_2(en)_4(tmd)_2]^{6+}$ increases. In this case, formation of $[Co(en)_2(tmdH)_2]^{5+}$ and other very highly charged species than the hexapositive dimer is observed, some of the latter species remaining on the Sephadex column even after washed with a 1 M KBr solution. The mole ratio of $[CoCl_2(en)_2]Cl$ to N–N also affects the distribution of the products. As stated in the experimental section, the reaction of 0.01 mol of $[CoCl_2(en)_2]Cl$ with 0.02 mol of tmd in 100 ml of DMSO gives a small amount of $[Co(en)_2(tmd)]^{3+}$ and a large amount of $[Co(en)_2(tmdH)_2]^{5+}$ and $[Co_2(en)_4(tmd)_2]^{6+}$.

From these experimental results, the following mechanism can be deduced for the reaction of $[CoCl_2(en)_2]Cl$ with N–N:

$$cis\text{- or } trans\text{-}[CoCl_2(en)_2]^+ + \text{N-N} \xrightarrow{\text{fast}}$$



The reaction of $[CoCl_2(en)_2]Cl$ with N–N gives an intermediate species (Int) rapidly. The formation of the Int will be supported by the isolation of $[CoCl(en)_2(donH)]Br_3 \cdot 2.5H_2O$. An intramolecular ring closure of the Int leads to the formation of the monomer, while an intermolecular reaction of the Int results in the formation of the dimer and higher polymers. The former reaction is of the first-order and the half-time of the reaction should be independent of the concentration of the Int. On the other hand, the intermolecular reaction is bimolecular, so that the half-time of this reaction should decrease with increase of the concentration of the Int. Therefore, the reaction in a dilute solution favors the formation of the monomer in agreement with the experimental results.

The formation of $[Co(en)_2(tmdH)_2]^{5+}$ in a concentrated solution can be interpreted by a mechanistic consideration similar to that mentioned above; the bimolecular reaction of the Int with tmd would yield $[Co(en)_2(tmd)_2]^{3+}$ containing two unidentate tmd. The half-time of this reaction in a concentrated solution will be shorter than that in a dilute solution and hence the yield of $[Co(en)_2(tmdH)_2]Br_5 \cdot 4H_2O$ would increase with increase of the concentration of reactants.

A partial reduction of cobalt(III) to cobalt(II) were found for almost all the reactions in DMSO. The formation of a small amount of $[Co(en)_3]^{3+}$ may be related to this reduction reaction.

Relation between the Yield of $[Co(en)_2(N\text{–}N)]^{3+}$ *and the Size of the Chelate Ring formed by N–N.* The yields of monomeric complexes, $[Co(en)_2(N\text{–}N)]^{3+}$ are markedly dependent on the methylenic chain length of the N–N. In Fig. 2 is plotted the yield of $[Co(en)_2(N\text{–}N)]^{3+}$ obtained from $[CoCl_2(en)_2]Cl$ (0.015 mol), N–N (0.015 mol) and 550 ml of DMSO, against the number of ring members of the N–N in the complex ion. The reaction of $[CoCl_2(en)_2]Cl$ with en gives $[Co(en)_3]^{3+}$ almost quantitatively and no dimeric complex is detected even under the reaction in a highly concentrated solution. The yield of the monomer decreases sharply at pmd, which should form an eight membered chelate ring. The formation of the monomer is virtually zero for pmd, hxn and ocn. However, the monomer is again formed when the number of methylene groups becomes more than nine. The yield increases with increase of the number of methylene groups and seems to show a maximum at don, forming a fifteen membered chelate ring. This tendency is strikingly similar to that observed in the syntheses of organic ring

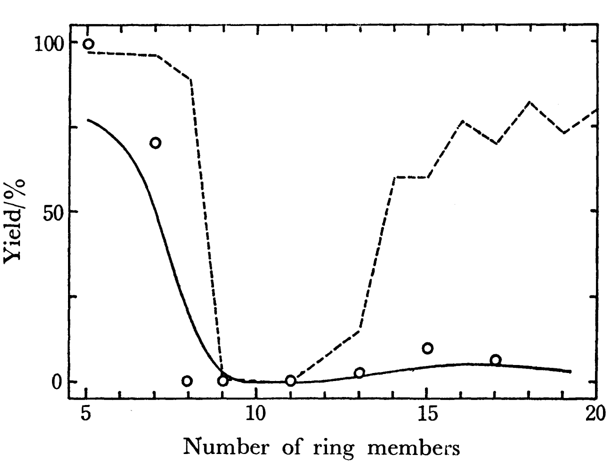


Fig. 2. Relation between the yield of compounds and the number of ring members. Open circles indicate the yields of $[Co(en)_2(N\text{–}N)]^{3+}$. Solid line and dashed line indicate the yield of ring ketones[22] obtained by Ruzicka and Ziegler, respectively.

TABLE 3. ABSORPTION SPECTRAL DATA FOR THE COMPLEXES PREPARED IN THIS WORK AND THE RELATED COMPLEXES
Wave numbers are in 10^3 cm^{-1} and the intensities given by log ε in parentheses.

Complex	I Band	II Band	Charge Transfer Band
$[Co(en)_3](ClO_4)_3$	21.3 (1.94)	29.6 (1.89)	47.5 (4.36)
$[Co(en)_2(tn)](ClO_4)_3$	21.0 (1.98)	29.2 (1.97)	45.9 (4.37)
$[Co(en)(tn)_2](ClO_4)_3$	20.7 (1.91)	28.8 (1.91)	44.4 (4.34)
$[Co(tn)_3](ClO_4)_3$	20.3 (1.88)	28.5 (1.87)	43.5 (4.36)
$[Co(en)_2(tmd)]Cl_3\cdot H_2O$	20.9 (1.95)	29.1 (1.94)	45.9 (4.35)
$[Co(tmd)_3]Br_3$[a)]	19.9 (1.89)	27.9 (1.85)	43.1 (4.35)
$[Co(en_2)(den)]Br_3\cdot 2H_2O$	20.8 (2.00)	28.9 (1.98)	45.5 (4.43)
$[Co(en)_2(don)]Br_3\cdot H_2O$	20.8 (2.01)	29.0 (2.00)	
$[Co(en)_2(tden)]Br_3\cdot 2.5H_2O$	20.8 (2.01)	29.0 (2.00)	45.5 (4.33)
$[Co(en)_2(tmdH)_2]Br_5\cdot 4H_2O$	20.7$_5$ (2.00)	28.8 (1.97)	45.5sh(4.45)
$[Co_2(en)_4(tmd)_2]Br_6\cdot 6H_2O$[b)]	20.8 (2.29)	28.9 (2.36)	46sh (4.72)
$[Co_2(en)_4(pmd)_2]Br_6\cdot 2H_2O$[b)]	20.8 (2.26)	28.9 (2.26)	45.$_5$ (4.72)
$[Co_2(en)_4(hxn)_2]Br_6\cdot 4H_2O$[b)]	20.8 (2.28)	28.9 (2.28)	45.2 (4.41)
$[Co_2(en)_4(ocn)_2]Br_6\cdot 4H_2O$[b)]	20.7$_5$ (2.31)	29.0 (2.29)	45.0 (4.74)
$[Co_2(en)_4(den)_2]Br_6\cdot 3H_2O$[b)]	20.8 (2.29)	29.0 (2.27)	45.0 (4.71)
$[Co_2(en)_4(don)_2]Cl_6\cdot 6.5H_2O$[b)]	20.8 (2.34)	29.0 (2.31)	45.0 (4.75)
$[CoCl(en)_2(donH)]Br_3\cdot 2.5H_2O$	18.9 (1.89), 21sh(1.74)	27.4 (1.98)	44 (4.38)

a) From ref. 13. b) The intensities are given per one complex ion, *i.e.*, per two cobalt(III) ions.

ketones from bifunctional aliphatic molecules.

Ruzicka[20)] succeeded in preparing large ring ketones by pyrolysis of metal salts of dicarboxylates. Ziegler *et al.*[21,22)] improved Ruzicka's method and obtained the same compounds from dinitriles by employing the high dilution method. The relations between the yields of ring ketones prepared by both methods and the ring size are also given in Fig. 2. In organic chemistry, medium size ring compounds which correspond to eight to eleven membered ring systems are known to be less stable owing to such strains as bond angle deformations, bond opposition forces and trans-annular interactions.[23,24)] Larger ring compounds than eleven members will be released from such strains sterically and becomes more stable than the medium size compounds. Existence of a minimum in the yields of the ring ketones in Fig. 2 has been interpreted in terms of such strains and entropy factor in the ring closure process.[23-26)] Similar situation must exsist in the present complexes containing N–N. Molecular models reveal that the complexes containing pmd, hxn or ocn are seriously strained. With more increase of the ring members, the complex is formed but its yield decreases again over fifteen ring members. This second decrease can be understood by a concept similar to that widely accepted for the ring closure process of bifunctional organic compounds; the longer the chain the smaller probability of encounter between the cobalt(III) center and the terminal nitrogen atom of diamine in the Int. Parallelism between the chelate ring complexes and the ring ketones provides an additional support for the formulation of the present monomeric complexes containing a large chelate ring.

Spectral Properties of the Complexes. Numerical data for visible and ultraviolet absorption spectra of the complexes are summarized in Table 3.

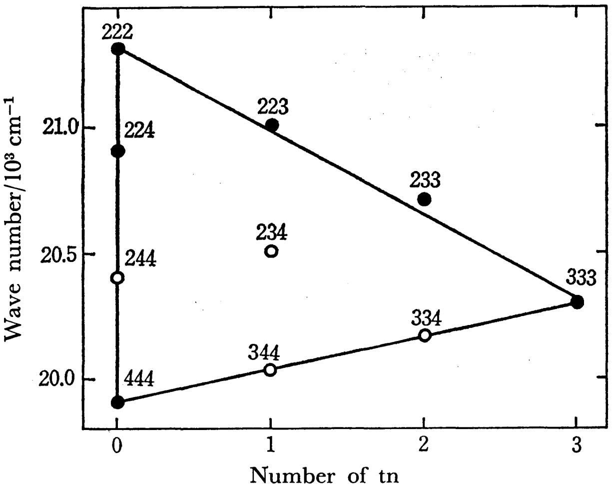


Fig. 3. Positions of the first absorption bands of $[Co(en)_a(tn)_b(tmd)_{3-a-b}]^{3+}$.
In the figure, 2, 3 and 4 indicate en, tn and tmd in the complex, respectively. For example, 234 denotes $[Co(en)(tn)(tmd)]^{3+}$. Open circles are the estimated values.

The successive substitution of en in $[Co(en)_3]^{3+}$ with tn or tmd causes shifts in the first and second absorption bands to longer wave length. In Fig. 3 are plotted the positions of the first absorption band maxima of $[Co(en)_a(tn)_b(tmd)_{3-a-b}]^{3+}$ against the number of tn in the complexes. The magnitude of the shifts is additive. Hence, the positions of the first absorption maxima of unknown complexes consisting of en, tn or tmd can be estimated from Fig. 3.

Figure 4 compares the maximum positions of the first absorption bands of various tris(diamine)cobalt(III) complexes. The absorption bands of $[Co(en)_2(N{-}N)]^{3+}$ shift to longer wave-length as the methylenic chain of the N–N becomes longer. However, the magnitude of the shifts becomes smaller with increase of the number of methylenic chain. A similar trend is observed for $[Co(en)(N{-}N)_2]^{3+}$ and $[Co(N{-}N)_3]^{3+}$.

Table 3 shows that the $[Co_2(en)_4(N{-}N)_2]^{6+}$ give the

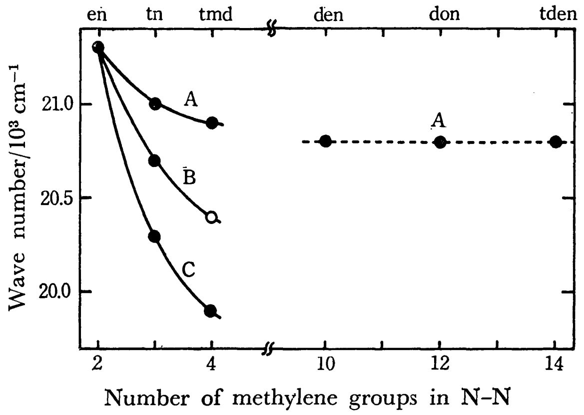


Fig. 4. Relation between the maximum potitions of the first absorption bands and the methylenic chain length of the N-N in $[Co(en)_2(N\text{-}N)]^{3+}$ (A), $[Co(en)(N\text{-}N)_2]^{3+}$ (B) and $[Co(N\text{-}N)_3]^{3+}$ (C). Absorption maximum of $[Co(en)(tmd)_2]^{3+}$ is taken from Fig. 3 (open circle).

absorption bands at almost the same positions as those of $[Co(en)_2(N\text{-}N)]^{3+}$. Their molar extinction coefficients are approximately 2 times larger than those of the monomeric complexes, the intensities of the dimeric complexes per one cobalt(III) ion being almost the same as those of the monomeric complexes.

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