Studies on the Cobalt(III) Complexes Containing Only One Chelate Ring. II.[1] *Syntheses and Properties of Monoethylenediamine-tetrammine-cobalt(III) Complexes,* $[\mathrm{Co\ en\ (NH_3)_4}]X_3$[2]

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No monoethylenediamine-tetrammine cobalt(III) complexes were hitherto known, while all the other members of ammine-ethylenediamine series of cobalt(III) complexes have thoroughly been studied. In the present paper, the syntheses of these missing luteo salts, $[\mathrm{Co\ en\ (NH_3)_4}]\mathrm{X_3}$, will be reported. And the absorption spectra of the cobalt(III) complexes which belong to the ammine-ethylenediamine series will be discussed.

Results and Discussion

Method of Syntheses.—For the syntheses of the monoethylenediamine-tetrammine complexes, after several preliminary attempts, the following scheme was adopted.

$$[\mathrm{Co\ en\ (NH_3)_2\ Cl_2}\left\{\begin{smallmatrix}(1)\\(6)\end{smallmatrix}\right.]\mathrm{Cl}\ \xrightarrow[\mathrm{KNCS}]{\text{(i)}}$$

$$[\mathrm{Co\ en\ (NH_3)_2\ (NCS)_2}]^{+}\ \xrightarrow[\mathrm{H_2O_2}]{\text{(ii)}}$$

$$[\mathrm{Co\ en\ (NH_3)_2\ (NH_3)_2}]^{3+}\ \xrightarrow[\mathrm{H_2SO_4}]{\text{(iii)}}$$

$$[\mathrm{Co\ en\ (NH_3)_4}]_2\ (\mathrm{SO_4})_3$$

The starting material, $[\mathrm{Co\ en\ (NH_3)_2\ Cl_2}\left\{\begin{smallmatrix}(1)\\(6)\end{smallmatrix}\right.]\mathrm{Cl}$, was prepared from $\mathrm{NH_4[Co\ en\ (NH_3)_2\ (SO_3)_2]\cdot H_2O}$ by Bailar and Pappard's method[3]. The possible three geometrical isomers of $[\mathrm{Co\ en\ (NH_3)_2\ (NCS)_2}]^{+}$ may result from the reaction i. The separation of these isomers, however, was not

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[1] Part I of this series: Y. Shimura, This Bulletin, **31**, 173 (1958).

[2] Partly presented at the Symposium on Co-ordination Compounds, Tokyo, October 28, 1956.

[3] J. C. Bailar, Jr. and D. F. Peppard, *J. Am. Chem. Soc.*, **62**, 105 (1940).

intended, because it was expected that all these isomers equally produce the desired complex by the reaction ii.

The reaction ii was carried out by a modification of the Werner's method[4], who prepared *trans*- and *cis*-$[Co\ en_2\ (NH_3)_2]X_3$ from the corresponding isothiocyanato-complexes by hydrolytic oxidation with chlorine or with hydrogen peroxide. These reactions leave the nitrogen atoms co-ordinated to the cobalt atom; the co-ordinated isothiocyanato-groups are transformed into co-ordinated ammonia molecules.

The crystals of the sulfate or the bromide of $[Co\ en\ (NH_3)_4]^{3+}$ are orange-colored and indistinguishable by the color from the other members of the ammine-ethylenediamine series. The monoethylenediamine-tetrammine complexes have rather high solubilities in water as compared with hexammine or trisethylenediamine complexes. For this reason, the purification of the chloride, $[Co\ en\ (NH_3)_4]Cl_3 \cdot xH_2O$, was not practical.

Unsuccessful Attempt on Optical Resolution.—Recently several X-ray[5,6] and infrared[7] studies have shown that the co-ordinated ethylenediamine molecule is not planar but takes so-called *gauche* form. This *gauche* configuration has a mirror image antipode. Therefore, it is very interesting to test the possibilities for the optical resolution of $[Co\ en\ (NH_3)_4]X_3$.

Firstly, the chemical resolution by *d*-tartrate was tried. By the double decomposition of $[Co\ en\ (NH_3)_4]Br_3 \cdot H_2O$ and silver *d*-tartrate(tart), an oily product was obtained, the composition of which is perhaps $[Co\ en\ (NH_3)_4]Br \cdot (d\text{-tart}) \cdot xH_2O$. The oily product was dissolved in water and fractionally treated with ethanol. But no evidences for the separation of diastereoisomers were obtained. Secondly, the method of asymmetric adsorption on optically-active quartz[8,9] was applied. But the result was also negative. These negative results, however, are not improbable, since the puckered five-membered ethylenediamine-cobalt ring may be easily inverted into its antipode.

The last method tested, though it was also unsuccessful, is an equilibrium method with the aid of rotatory dispersion measurements. Very recently, Kirschner[10] succeeded to demonstrate that $K_2[Cu\ (edta)]$ is optically active by showing that the mixed aqueous solution of *l*-quinone hydrobromide and the copper complex exhibits an anomalous rotatory dispersion in the vicinity of the absorption band of the complex. This fact indicated that there was a shift in the equilibrium, $\text{D-}[Cu(edta)]^{=} \rightleftarrows \text{L-}[Cu(edta)]^{=}$, under the asymmetric influence of *l*-quinone hydrobromide.

Following the above method, the rotatory dispersion of the mixed aqueous solution of $[Co\ en\ (NH_3)_4]_2\ (SO_4)_3 \cdot 4H_2O$ and Rochelle salt was measured. In the region of 600~300 mμ, scarcely any anomalous rotatory dispersion was observed (Table I.).

TABLE I

OPTICAL ROTATION OF MIXED SOLUTION OF ROCHELLE SALT AND $[Co\ en(NH_3)_4]_2(SO_4)_3 \cdot 4H_2O$

λ(mμ)	ν(10^{13}/sec.)	α_1	α_2	$\alpha_2-\alpha_1$
577	52.0	0.643°	0.640°	−0.003°
546	54.9	0.723	0.715	−0.008
492	61.0	0.890	0.878	−0.012
436	68.8	1.148	1.142	−0.006
405	74.1	1.328	1.323	−0.005
365	82.2	1.607	1.598	−0.009
312.6	96.0	1.972	1.967	−0.005

α_1: Optical rotation of 0.1 F aq. soln. of $NaKC_4H_4O_6 \cdot 4H_2O$ (1 dm, 28°C).

α_2: Optical rotation of mixed aq. soln. of 0.1F $NaKC_4H_4O_6 \cdot 4H_2O$ and 0.001 F $[Co\ en\ (NH_3)_4]\ (SO_4)_{1\frac{1}{2}} \cdot 2H_2O$ (1 dm, 28°C).

This result may be considered to indicate that little of the asymmetric shift of the equilibrium, $\text{D-}[Co\ en\ (NH_3)_4]^{3+} \rightleftarrows \text{L-}[Co\ en\ (NH_3)_4]^{3+}$ occurred, or that the anomalous rotatory dispersion of this complex ion is very small. An alternative explanation is to postulate that the first and the second absorption band of this complex are optically inactive.

Absorption Spectra.—The absorption curves of the cobalt(III) complexes which belong to the ammine-ethylenediamine series are shown in Fig. 1. The numerical data of the first and the second absorption band are tabulated in Table II.

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[7] J. V. Quagliano and S. Mizushima, *J. Am. Chem. Soc.*, **75**, 6084 (1953); S. Mizushima, I. Ichishima, I. Nakagawa and J. V. Quagliano, *J. Phys. Chem.*, **59**, 293, (1955) etc.

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[10] S. Kirschner, *J. Am. Chem. Soc.*, **78**, 2372 (1956).

TABLE II

ABSORPTION DATA OF $[Co\ (en)x\ (NH_3)_{6x-2x}]^{3+}$ SERIES

Complex Ion	First Absorption Band				Second Absorption Band					
	ν_{max} (10^{13}/ sec.)	$\log \varepsilon_{max}$	l* (10^{13}/ sec.)	δ** (10^{13}/ sec.)	ν_{max} (10^{13}/ sec.)	$\log \varepsilon_{max}$	l* (10^{13}/ sec.)	δ** (10^{13}/ sec.)	$\Delta(\nu_{max})$***	$\Delta(\log \varepsilon_{max})$****
$[Co\ (NH_3)_6]^{3+}$	62.9	1.68	10.3	0.45	88.3	1.60	12.5	0.35	25.4	−0.08
$[Co\ en\ (NH_3)_4]^{3+}$	63.6	1.83	10.7	0.55	88.4	1.76	13.1	0.55	24.8	−0.07
trans-$[Co\ en_2\ (NH_3)_2]^{3+}$	64.2	1.77	10.8	0.8	89.2	1.73	12.3	0.55	25.0	−0.04
cis-$[Co\ en_2\ (NH_3)_2]^{3+}$	64.4	1.79	10.7	0.65	89.4	1.74	12.6	0.5	25.0	−0.05
$[Co\ en_3]^{3+}$	63.9	1.94	10.4	0.55	88.4	1.90	12.0	0.4	24.5	−0.04

* l = half-value width. This corresponds to $\{\delta(+)+\delta(-)\}$ in Jørgensen's notation[13].

** δ = inclination parameter[14] or Inklination (in German)[15]. This parameter corresponds to $\frac{1}{2}\{\delta(+)-\delta(-)\}$ in Jørgensen's notation[13], and is defined by the equation $\delta=\frac{1}{2}\{\nu_k+\nu_l\}-\nu_{max}$, where ν_k and ν_l are the two frequencies where the formal extinction coefficients are equal to the half of ε_{max}.

*** Frequency difference between the maxima of the second and the first absorption band.

**** Difference between $\log \varepsilon_{max}$'s of the second and the first band.

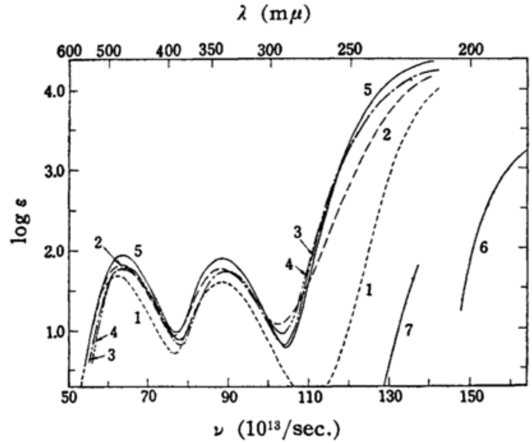

Fig. 1. Absorption curves of:
1, $[Co\ (NH_3)_6](ClO_4)_3$;
2, $[Co\ en\ (NH_3)_4](SO_4)_{1\frac{1}{2}}\cdot 2H_2O$;
3, *trans*-$[Co\ en_2\ (NH_3)_2](ClO_4)_3\cdot H_2O$;
4, *cis*-$[Co\ en_2\ (NH_3)_2](ClO_4)_3\cdot H_2O$;
5, $[Co\ en_3](ClO_4)_3$;
6, NH_3[11];
7, en[12].

From these data, the following conclusions are drawn.

i) Ethylenediamine has a higher position in the spectrochemical series [16,17] than that of ammonia.

ii) The successive substitution of ammonia molecules by ethylenediamine causes somewhat irregular shifts of band maxima. The change of the intensity by such a substitution is also irregular. Thus, for example, the first band of $[Co\ en\ (NH_3)_4]^{3+}$ is higher than that of *cis*- and *trans*-$[Co\ en_2(NH_3)_2]^{3+}$.

iii) The first or the second band of *cis*-$[Co\ en_2\ (NH_3)_2]^{3+}$ are at shorter wave lengths than those of the corresponding *trans* isomer. This fact coincides very well with the general rule which was reported previously by the present author[18].

iv) Generally speaking, the half-value width and the inclination parameter[14] are in the order of

$$trans\text{-}(NH_3)_2 > (NH_3)_4 > cis\text{-}(NH_3)_2 > en_3 > (NH_3)_6 .$$

The larger half-value width and the larger inclination parameter of the first three members in the above series are possibly explained by the slight splitting of the bands owing to the lower symmetry of those ions.

v) For all the complexes studied, the intensity of the second band is lower than that of the first band.

vi) The mean value of the frequency difference between the maxima of the second and the first band, is 24.94×10^{13}/sec.

vii) The intense ultraviolet bands are perhaps due to the co-ordinated ammonia and ethylenediamine molecules. Roughly speaking, an additive nature can be seen in the intensities of these bands. But the quantitative curve analysis was abandoned since only a part of the long wave length side of the band is available.

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Experimental

Ethylenediamine - tetrammine - cobalt (III) Sulfate Tetrahydrate, [Co en $(NH_3)_4]_2$ $(SO_4)_3 \cdot 4H_2O$—Ten grams of *trans*-[Co en $(NH_3)_2$ $Cl_2]Cl \cdot \frac{1}{2}H_2O$[3] is dissolved in 100 ml. of warm water and to this solution 10 g. of potassium thiocyanate in 20 ml. of water is added. The resulting green mixture is heated for 20 min. at 75～80°C on a water bath and for more 3 min. at 85°C. The dark red mixture is allowed to cool and acidified by a few drops of dilute sulfuric acid. Fifty milliliters of 30% hydrogen peroxide is next added drop by drop to the mixture. After being allowed to stand for several hours, the resulting dark orange solution is concentrated to about 75 ml. by evaporation, and cooled. Twenty five milliliters of dilute sulfuric acid and 150 ml. of ethanol is added to the solution. The crude complex separates in voluminous precipitates. The product is treated with a small amount of water and any less soluble materials are filtered off. Ethanol-water mixture is then added to the filtrate. The desired complex precipitates as orange-colored plates. The crystals were washed by ethanol and dried in air. For purification, the salt was recrystallized from ethanol-water mixture. The yield was 7 to 8 g. (about 50～60%). The crystals effloresced on exposure to the air. The crystals freshly dried were analyzed for water of crystallization. The analyses for the other components were performed by making use of the salts dehydrated at 100～110°C.

Anal. Found: H_2O, 9.93%. Calcd. for $[Co(C_2H_8N_2)(NH_3)_4]_2(SO_4)_3 \cdot 4H_2O$: H_2O 9.84%.

Found: Co, 17.7; C, 7.29; H, 6.16; SO_4^{--}, 43.83%. Calcd. for $[Co(C_2H_8N_2)(NH_3)_4]_2(SO_4)_3$: Co, 17.79; C, 7.25; H, 6.09; SO_4^{--}, 43.50%.

Ethylenediamine - tetrammine - cobalt (III) Bromide Monohydrate, [Co en $(NH_3)_4]Br_3 \cdot H_2O$ —A solution of the above sulfate is treated with a solution of the equivalent amount of barium chloride and the resulting barium sulfate is filtered off. The filtrate is concentrated by evaporation. To this solution solid ammonium bromide is added. The desired bromide monohydrate separates as orange prismatic crystals. They are recrystallized from water containing a small amount of ethanol, washed with ethanol and dried in air.

Anal. Found: Br, 53.38; H_2O, 3.64%. Calcd. for $[Co(C_2H_8N_2)(NH_3)_4]Br \cdot H_2O$: Br, 53.88; H_2O, 4.05%.

The corresponding chloride, [Co en $(NH_3)_4]Cl_3 \cdot xH_2O$ was also prepared, but its purification was impractical because it is very soluble in water or in water-ethanol mixtures.

Absorption and Rotation Measurements.— The absorption measurements were made in aqueous solutions by a Beckman DU Spectrophotometer at room temperature. The concentration of the solutions varied from 1.0×10^{-2} to 1.0×10^{-4} gram complex-ion per liter. The measurements of optical rotation were made by a Rudolph photoelectric spectropolarimeter, Model 200S-80.

Summary

A new cobalt(III) luteo ion, [Co en $(NH_3)_4]^{3+}$, has been prepared by the hydrolytic oxidation of [Co en $(NH_3)_2$ $(NCS)_2]^+$. The sulfate and the bromide of the new complex ion have been isolated. Several attempts to resolve the ion were unsuccessful.

The visible and the ultraviolet absorption spectra of all the members of the cobalt(III) ammine-ethylenediamine series have been measured and discussed.

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