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Optically Active Ethylenediamine(1,4,8,11-tetraazacyclotetradecane)cobalt(III) and Ethylenediamine (1,4,7,10-tetraazacyclotridecane)cobalt(III) Complexes

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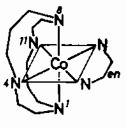
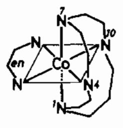
Complexes of macrocyclic ligands are an attractive subject of study in coordination chemistry. However, only a little is known about optical activity of the complexes [1]. The structure of the complex [Co(en)(cyclam)]$Cl_3 \cdot 3H_2O$ (en = ethylenediamine and cyclam = 1,4,8,11-tetraazacyclotetradecane) has been determined by X-ray [2]. The alternate distribution of five- and six-membered chelate rings of the coordinated cyclam produces chirality in the complex and the complex is expected to be resolved. We have succeeded in resolving it and the related one, [Co(en)([13]aneN_4)]$^{3+}$, where [13]aneN_4 is 1,4,7,10-tetraazacyclotridecane.



(I) [Co(en)(cyclam)]$^{3+}$



(II) [Co(en)([13]aneN_4)]$^{3+}$

The complex [Co(en)(cyclam)]$Cl_3 \cdot 3H_2O$ was prepared by the method in the literature [2] and chromatographically resolved [3] as follows. An aqueous solution of the complex was placed on an SP-Sephadex C-25 column (2.7 cm ϕ × 120 cm) and eluted with 0.2 *M* aqueous solution of sodium tartratoantimonate(III). Two bands, the $(+)_{589}$- and $(-)_{589}$-isomers, were eluted in this order. The $(+)_{589}$-isomer (I) was isolated as chloride (Table I). The complex $(+)_{589}$-[Co(en)([13]aneN_4)]$Cl_3 \cdot 2H_2O$ (II) was obtained similarly but from the slower eluting component. The complexes were characterized and the absorption (AB) and circular dichroism (CD) spectral data are given in Table II.

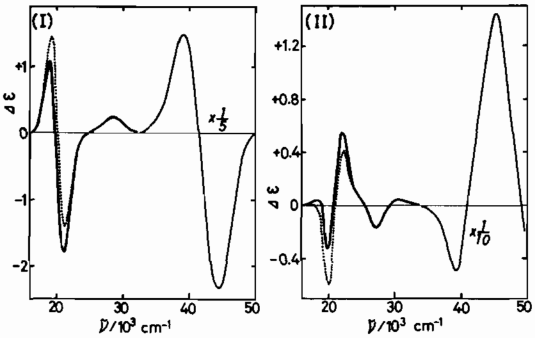


Fig. 1. CD spectra of (I) and (II) in H_2O (——) and in 0.1 *M* aqueous Na_2SO_4 (•••).

TABLE I. Analytical Data for the $(+)_{589}$-Complexes.

Complex	Analysis, found (calcd.), %		
	C	H	N
(I) [Co(en)(cyclam)]$Cl_3 \cdot 1\frac{1}{4}H_2O$	32.03(32.16)	7.64(7.76)	18.65(18.76)
(II) [Co(en)([13]aneN_4)]$Cl_3 \cdot 2H_2O$	29.69(29.51)	7.60(7.65)	18.70(18.77)

TABLE II. Absorption and Circular Dichroism Spectra of the Complexes in H_2O.

Complex	AB, $\tilde{\nu}_{max}/10^3$ cm^{-1} ($\log\epsilon$)	CD, $\tilde{\nu}_{ext}/10^3$ cm^{-1} ($\Delta\epsilon$)	
(I) [Co(en)(cyclam)]$Cl_3 \cdot 1\frac{1}{4}H_2O$	20.3(2.16)	19.0(+1.09)	39.1(+7.40)
	28.3(2.15)	21.2(−1.81)	44.6(−11.7)
	42.5(4.34)	28.5(+0.25)	
(II) [Co(en)([13]aneN_4)]$Cl_3 \cdot 2H_2O$	20.8(2.24)	18.3(+0.05)	39.1(−4.88)
	28.7(2.18)	19.9(−0.33)	44.3(+14.5)
	43.4(4.32)	22.1(+0.54)	
		27.2(−0.18)	
		30.4(+0.05)	

The absorption spectra of (I) and (II) are observed at lower wavenumbers and have enhanced intensities compared with that of $[Co(en)_3]^{3+}$ ($\tilde{\nu}_{max}$ 21.3 × 10^3 cm^{-1} (logϵ = 1.92) and 29.4(1.87)). The ligand fields of the complexes of the macrocyclic amines are weakened probably because the presence of additional five- and/or six-membered chelate rings may result in producing strains and/or distortions.

In the region of the ν_1 transition ($^1A_{1g} \rightarrow {}^1T_{1g}$ in O_h approximation), the intensity of the CD spectrum of Λ-$[Co(tn)_3]^{3+}$ ($\tilde{\nu}_{ext}$ 18.8 × 10^3 cm^{-1} ($\Delta\epsilon$ = +0.06) and 21.1(–0.13)) (tn = 1,3-diaminopropane) is very weak compared with that of Λ-$[Co(en)_3]^{3+}$ ($\tilde{\nu}_{ext}$ 20.3 × 10^3 cm^{-1} ($\Delta\epsilon$ = +1.89) and 23.4(–0.17)). Based on this fact, the contribution of a six-membered chelate ring to CD is inferred to be much smaller than that of a five-membered one [4]*. By considering only the five-membered chelate rings of cyclam, the absolute configuration of (I) can be tentatively assigned to be Λ based on the sign of the CD spectrum (Table II). In very gross terms, the CD spectra of (I) and (II) are similar in pattern though opposite in sign. This suggests that the absolute configurations of the two should be opposite to each other. The proposition is also supported by similar CD spectral changes observed upon addition of sodium sulfate (Fig. 1). Namely, the CD extremes at 19.0 × 10^3 cm^{-1} of (I) and at 19.9 of (II) ($^1A_1 \rightarrow {}^1E$) are similarly enhanced in strength and those at 21.2 of (I) and at 22.1 of (II) ($^1A_1 \rightarrow {}^1A_2$) reduced.

In contrast to Λ-$[Co(en)_3]^{3+}$, the complex(I) has the large $|\Delta\epsilon|$ value for the high energy component (A_2) in the ν_1 region and the same R configuration of all the four nitrogen atoms of cyclam [2] may be one of the origin. The $|\Delta\epsilon|$ values of (I) in the ν_1 region are about 3 times those of (II). The net number of skew chiral pairs of five-membered chelate rings of (I) is superior to that of (II). This may be reflected in the values. Isomers arising from different configurations of secondary nitrogen atoms may exist for the [13]aneN_4 complex like for *cis*-β-$[Co(gly)(trien)]^{2+}$ (gly = glycinate ion and trien = triethylenetetramine) which exits in the two forms, *cis*-β-S,R(R,S)- and *cis*-β-S,S(R,R)-configurations [5] (R and S represent the configurations of the secondary nitrogen atoms). This type of isomerism is now under detailed investigation.

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*Contribution of a six-membered chelate ring with a chair conformation to CD is known to be extremely small [4] and the chair conformation of the six-membered chelate rings of cyclam is confirmed by the X-ray analysis [2].

References

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