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PREPARATION AND ABSOLUTE CONFIGURATION OF L-TARTRATO-BIS(1,10-PHENANTHROLINE) COBALT(III) COMPLEXES

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Three complexes, Δ-,Λ-$[Co(phen)_2(L\text{-}tart)]^+$, and cis-$[Co(phen)_2(OH_2)(L\text{-}tart)]^+$, have been separated by ion-exchange Sephadex and characterized using the CD data. Two methods, empirical and nonempirical , have been used to assign the absolute configurations.

Recently, bis complexes containing conjugated bidentate ligands such as 1,10-phenanthroline(phen) or 2,2'-bipyridine(bipy) were prepared and their absolute configurations were determined by two methods ,namely, the empirical and nonempirical on the basis of their circular dichroism(CD) spectra.[1,2] In the former, the determination of the absolute configuration is performed by the comparison with the sign of the CD spectra in the d-d transitions of the related complexes. The nonempirical method, however, is based upon the sign of the CD spectra in the long-axis polarized $\pi \rightarrow \pi^*$ transitions of the conjugated bidentate ligands in the complexes, without reference to a standard molecule having a known absolute configuration. The purpose of this work is to isolate Δ-,Λ-$[Co(phen)_2(L\text{-}tart)]^+$ and cis-$[Co(phen)_2(OH_2)(L\text{-}tart)]^+$, and to compare the absolute configurations determined by empirical and nonempirical methods, and to evaluate the configurational effect and the vicinal effect in the CD spectra of these complexes.

Experimental

To a water solution (30 ml) containing 0.84 g of L-(+)$Na_2tart \cdot 2H_2O$, 1.6 g of cis-$[Co(phen)_2Cl_2]Cl \cdot 3H_2O$ were added, and the mixture was heated on a water bath (60°C) for half an hour. When the reaction was over, the solution was condensed almost to dryness in vacuo with a rotatory evaporator below 50°C. To the resulting viscous liquid, 30 ml of mixed solvent of ethanol and ether (1 : 1) was added. A crude deep-violet product was obtained.

About 0.5 g of this product was dissolved in 5 ml of 0.3 M aqueous solution of Na(+)SbOtart, and the solution was placed on the column [diameter (ϕ) = 2.7 cm, height of Sephadex(h) = 19.2 cm] containing SP-Sephadex C-25 ion-exchanger with 40-120 μ of particle size and 2.3 ± 0.3 meq/g of capacity.[3] The elution was carried out by 0.3 M aqueous solution of Na(+)SbOtart at a rate of 0.4-0.6 ml/min. To the eluate $NaClO_4$ solution was added. The mixture was evaporated to several ml in vacuo and stood for overnight in a refrigerator. The crystals deposited were purified by recrystallization from water. Analytical data of the complexes obtained are as follows. Anal. Calcd. for $[Co(phen)_2(L\text{-}tart)]ClO_4 \cdot 3H_2O$: C, 46.65; H, 3.64; N, 7.77. Found: C, 47.61; H, 3.47; N, 7.59. Anal. Calcd. for $[Co(phen)_2(L\text{-}tart)]ClO_4 \cdot 2H_2O$: C, 47.84; H, 3.44; N, 7.97. Found: C, 47.47; H, 3.69; N, 7.53. Anal. Calcd. for $[Co(phen)_2(OH_2)(L\text{-}tart)]ClO_4 \cdot 2H_2O$: C, 46.65; H, 3.64; N, 7.77. Found: C, 46.93; H, 3.47; N, 7.90.

The absorption (AB) and CD spectra were measured with a Shimadzu Recoding Spectrophotometer and a JASCO Model ORD/UV-5 Optical Rotatory Dispersion Recorder.

Results and Discussion

The five eluted bands appeared, as is shown in Figure 1.

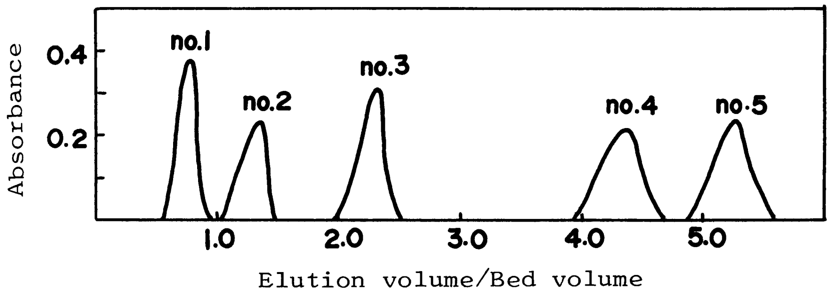


Fig. 1 Elution curve with 0.3 M Na(+)SbOtart solution as an eluent

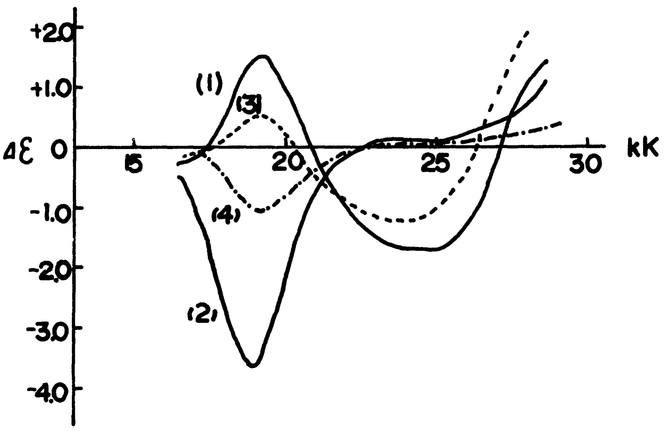
From the bands of no. 1,2, and 3, the complexes containing L-tartrate were isolated, and the spectroscopic data are summarized in Table I. The AB and the CD spectra are shown in Figure 2 together with the configurational effect and the vicinal effect evaluated.

Table I Spectroscopic data for the complexes

		AB^b		CD^b		
Band no.	Complexes^a	$\tilde{\nu}_{max}$	log ε	$\tilde{\nu}_{max}$	Δε	Trans.
1	$(-)\text{-}[Co(phen)_2(L\text{-}tart)]$	19.23	2.03	18.87	-2.19	
	$ClO_4 \cdot 3H_2O$	36.70	4.67	35.97	-47.8	A
				37.59	+38.2	B
2	$(+)\text{-}[Co(phen)_2(L\text{-}tart)]$	19.08	2.05	19.05	+5.05	
	$ClO_4 \cdot 2H_2O$	36.70	4.74	35.97	+45.8	A
				37.74	-43.2	B
3	$cis\text{-}[Co(phen)_2(OH_2)$	19.23	2.05	18.87	+0.50	
	$(L\text{-}tart)]ClO_4 \cdot 2H_2O$	36.90	4.73	-----		

a) The signs refer to the rotation at 589 mμ.

b) The data for the d-d transition region and the long-axis polarized $\pi \rightarrow \pi^*$ ligand band region are given. All frequencies in $cm^{-1} \times 10^{-3}$.



(1) Vicinal effect (ΔL+ ΛL)/2 and (2) Configurational effect (ΔL- ΛL)/2 for Δ-form

(3) The CD spectrum for complex of no.3 (Vicinal effect x 2)

(4) The CD spectrum for Δ-$[Co(phen)_2(ox)]^+$

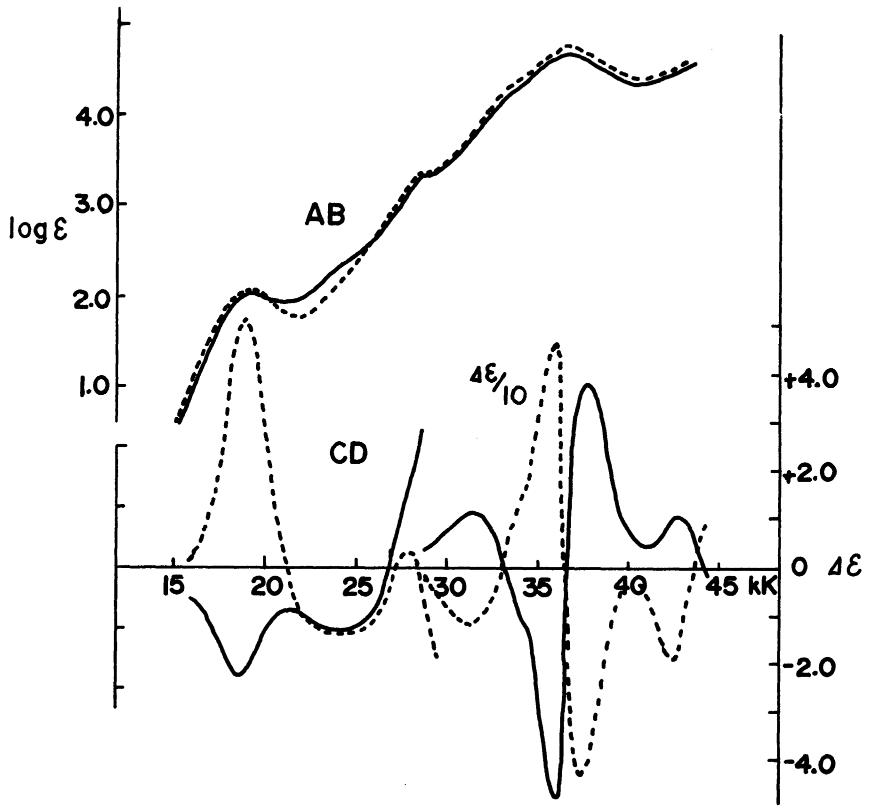


Fig. 2 The AB and the CD of $(-)_{589}$-$[Co(phen)_2(L\text{-}tart)]ClO_4\cdot 3H_2O$ (——) and $(+)_{589}$-$[Co(phen)_2(L\text{-}tart)]ClO_4\cdot 2H_2O$ (-------)

The major component with E trigonal parentage seems to dominate the configurational effect of the CD in the d-d transitions. On this basis, the absolute configuration of no. 1 with a dominant negative peak of configurational effect should be related to Δ-$[Co(en)_3]^{3+}$. This absolute configuration assigned seems to be supported also by the CD curve similar to the CD for Δ-$[Co(phen)_2(ox)]ClO_4 \cdot H_2O$.[2]

For the complex of no. 1, the CD of the long-axis polarized $\pi \rightarrow \pi^*$ band at around 37 kK are found to be strongly negative at low energies and strongly positive at higher energies in agreement with the predictions of the exciton theory for Δ-form. On the other hand, the CD curve of no. 2 in this region is almost enantiomeric to that of no. 1 and, indicationg the Λ configuration, as can be seen in Figure 2. This assignment agrees with that determined by the empirical method.

The CD spectrum of no. 3 is similar to the vicinal effect of no. 1 and no. 2 though the magnitude is smaller. This small CD component is characteristic of the CD for the unidentate complex of the ligand containing the asymmetric carbon atom. Then, the complex may be the cis structure because the trans structure results in the steric interference between the two phen molecules.[4]

The complexes of no. 4 and 5 were found to be optically inactive by-products. The products might be expected to be $[Co(phen)_2Cl(OH_2)]^{2+}$ and/or $[Co(phen)_2(OH_2)_2]^{3+}$ for no. 4 and to be $[Co(phen)_3]^{3+}$ for no. 5 on the basis of the AB spectra.

Thus, it can be concluded that $(-)_{589}$ complex of no. 1 is assigned to be Δ-form, $(+)_{589}$ complex of no. 2 to be Λ-form and the complex of no. 3 to be the cis unidentate complex of L-tartrate, respectively.

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