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# Absorption and Circular Dichroism Spectra of Bis(ethylenediamine)(1,3-diamine)cobalt(III) Complexes

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**Synopsis.** New bis(ethylenediamine)cobalt(III) complexes containing various 1,3-diamines have been prepared and resolved (or separated) into optical isomers. The preferred conformations of six-membered 1,3-diamine chelate rings in these complexes seem to be reflected on the absorption and circular dichroism spectra.

In the previous papers,[2,3] we reported that the stable conformations of flexible six-membered chelate rings in some tris(1,3-diamine)cobalt(III) complexes can be elucidated from their absorption and circular dichroism(CD) spectra in the region of the first absorption band. In this note, we have extended such studies to cobalt(III) complexes of the type, [Co(en)$_2$(1,3-diamine)]$^{3+}$. The diamines used here are (*R*,*R*)- and (*R*,*S*)-2,4-pentanediamine(ptn), (*S*,*S*)- and (*R*,*S*)-1,3-diphenyl-1,3-propanediamine(dppn), (*S*)-1,3-butanediamine(bn), and (*S*)-1-phenyl-1,3-propanediamine(phtn).

## Experimental

*Ligands.* 1,3-Diamines were prepared by the methods described previously; (*R*,*R*)- and (*R*,*S*)-ptn,[4] (*S*,*S*)- and (*R*,*S*)-dppn,[5] (*S*)-bn,[6] and (*S*)-phtn.[7]

*Complexes.* The [Co(en)$_2$(1,3-diamine)]$^{3+}$ complexes were prepared from 1,3-diamine and *trans*-[CoCl$_2$(en)$_2$]Cl in dimethyl sulfoxide according to a method similar to that for [Co(en)$_2$(tn)]$^{3+}$ (tn = trimethylenediamine).[8] The separation (or resolution) of diastereomers (or enantiomers) except the *R*,*S*-dppn complex were achieved by SP-Sephadex column chromatography using a 0.2 mol·dm$^{-3}$ $Na_2SO_4$ or a 0.2 mol·dm$^{-3}$ sodium $(+)_{589}$-tartrate solution as the eluent. The racemic [Co(en)$_2$(*R*,*S*-dppn)]Br$_3$·3H$_2$O complex was resolved with K$_3$[Co(*S*-cysu)$_3$]·6H$_2$O(cysu = cysteinesulfinato(2−)-SN).[9] The addition of an aqueous solution (30 cm$^3$) of the resolving agent (1.4 g) to an aqueous solution (30 cm$^3$) of the complex(1.5 g) gave immediately orange precipitate, which was recrystallized from hot water several times. The product was suspended in water and 1 mol·dm$^{-3}$ hydrobromic acid(20 cm$^3$) was added to the suspension. The solution became orange and insoluble material ([Co(*S*-Hcysu)$_3$]) was filtered off. The filtrate was evaporated to dryness and the residue was recrystallized from water to give $\Lambda$-[Co(en)$_2$(*R*,*S*-dppn)]Br$_3$·3H$_2$O.

The results of elemental analysis are given in Table 1.

*Measurements.* Absorption and CD spectra were recorded on a Hitachi 323 spectrophotometer and a JASCO J-20 Spectropolarimeter, respectively.

TABLE 1. ANALYTICAL DATA OF THE COMPLEXES

| Complex | C/% | | H/% | | N/% | |
|---|---|---|---|---|---|---|
| | Found | Calcd | Found | Calcd | Found | Calcd |
| $\Delta$-[Co(en)$_2$(*R*, *R*-ptn)](ClO$_4$)$_3$ | 18.48 | 18.65 | 5.07 | 5.22 | 14.50 | 14.50 |
| $\Lambda$-[Co(en)$_2$(*R*, *R*-ptn)](ClO$_4$)$_3$ | 18.70 | 18.65 | 5.21 | 5.22 | 14.69 | 14.50 |
| $\Lambda$-[Co(en)$_2$(*R*, *S*-ptn)](ClO$_4$)$_3$ | 18.80 | 18.65 | 4.96 | 5.22 | 14.58 | 14.50 |
| $\Delta$-[Co(en)$_2$(*S*, *S*-dppn)]Br$_3$·3H$_2$O | 33.06 | 32.64 | 5.82 | 5.77 | 11.87 | 12.02 |
| $\Lambda$-[Co(en)$_2$(*S*, *S*-dppn)]Br$_3$·2.5H$_2$O | 32.81 | 33.06 | 5.20 | 5.70 | 12.10 | 12.18 |
| $\Lambda$-[Co(en)$_2$(*R*, *S*-dppn)]Br$_3$·3H$_2$O | 32.85 | 32.64 | 5.54 | 5.77 | 12.11 | 12.02 |
| $\Delta$-[Co(en)$_2$(*S*-bn)](ClO$_4$)$_3$·H$_2$O | 16.60 | 16.46 | 4.89 | 5.18 | 14.42 | 14.40 |
| $\Lambda$-[Co(en)$_2$(*S*-bn)](ClO$_4$)$_3$·H$_2$O | 16.59 | 16.46 | 5.21 | 5.18 | 14.37 | 14.40 |
| $\Delta$-[Co(en)$_2$(*S*-phth)]Cl$_3$·0.5H$_2$O | 35.32 | 35.11 | 7.16 | 7.02 | 19.11 | 18.90 |
| $\Lambda$-[Co(en)$_2$(*S*-phtn)]Cl$_3$·2.5H$_2$O | 32.47 | 32.48 | 7.40 | 7.34 | 17.37 | 17.48 |

TABLE 2. DATA OF THE FIRST ABSORPTION AND CD BANDS OF THE COMPLEXES IN WATER

| [Co(en)$_2$(L)]$^{3+}$ | Configuration (Conformation of L)[a] | Absorption $\tilde{\nu}/10^3$ cm$^{-1}$ ($\varepsilon$) | CD $\tilde{\nu}/10^3$ cm$^{-1}$ ($\Delta\varepsilon$) |
|---|---|---|---|
| L = *R*, *R*-ptn | $\Delta(\lambda)$ | 21.19 (88.2) | 20.01 (−1.42)<br>22.88 (+0.16) |
| *R*, *R*-ptn | $\Lambda(\lambda)$ | 21.10 (98.8) | 20.49 (+1.61) |
| *R*, *S*-ptn | $\Lambda$(ch) | 21.05 (97.5) | 20.41 (+1.21) |
| *S*, *S*-dppn | $\Delta(\lambda)$ | 21.03 (98.1) | 20.04 (−1.71) |
| *S*, *S*-dppn | $\Lambda(\lambda)$ | 20.94 (129) | 20.70 (+1.82) |
| *R*, *S*-dppn | $\Lambda$(ch) | 20.90 (124) | 20.36 (+0.93) |
| *R*-bn[b] | $\Delta$(ch, $\lambda$) | 21.10 (92.9) | 20.28 (−1.18) |
| *R*-bn[b] | $\Lambda$(ch, $\lambda$) | 21.05 (94.6) | 20.28 (+1.05) |
| *S*-phtn | $\Delta$(ch, $\lambda$) | 21.00 (104) | 20.16 (−1.29) |
| *S*-phtn | $\Lambda$(ch, $\lambda$) | 20.94 (113) | 20.37 (+1.08) |

a) The conformations of L(1,3-diamine) are those with equatorially disposed substituents, and the $\lambda$ and ch represent the $\lambda$-skew and the chair conformations, respectively. b) The absolute configuration of *S*-bn used in the Experiment was changed to its enantiomorph, *R*-bn, since the skew conformations of the other 1,3-diamine chelate rings studied here are all stabilized in the $\lambda$-form.

## Results and Discussion

Table 2 shows that the peak positions of the first absorption bands for diastereomeric complexes of a given 1,3-diamine shift to higher energies in the order of the *meso*-diamine complex, $\Lambda$- and $\Delta$-isomers of the optically active diamine. The *meso* and active diamine chelates listed in Table 2 will be stabilized in the chair and the $\lambda$-skew conformations, respectively, since these conformers have substituents disposed equatorially. The *R*-bn and *S*-phtn chelate rings can also take the chair conformation with an equatorial substituent (*vide infra*). The $\lambda$-skew conformers in the $\Delta$- and $\Lambda$-configurations form the *lel* and the *ob* structures, respectively.[10] Thus, the order of the shift in the absorption bands corresponds to that of chair, $\Lambda(\lambda)$(*ob*), and $\Delta(\lambda)$(*lel*) structures. This order agrees with the results obtained for some tris(1,3-diamine)cobalt(III) complexes.[2,3] These findings will also be utilized for determining the absolute configuration of 1,3-diamine ligands.

The energy differences in the absorption bands between each pair of diastereomers of the *R*-bn and *S*-phtn complexes are smaller than those of cases of the ptn and dppn complexes. This fact suggests that the *R*-bn and *S*-phtn chelate rings are in equilibrium between the $\lambda$-skew and the chair conformations.

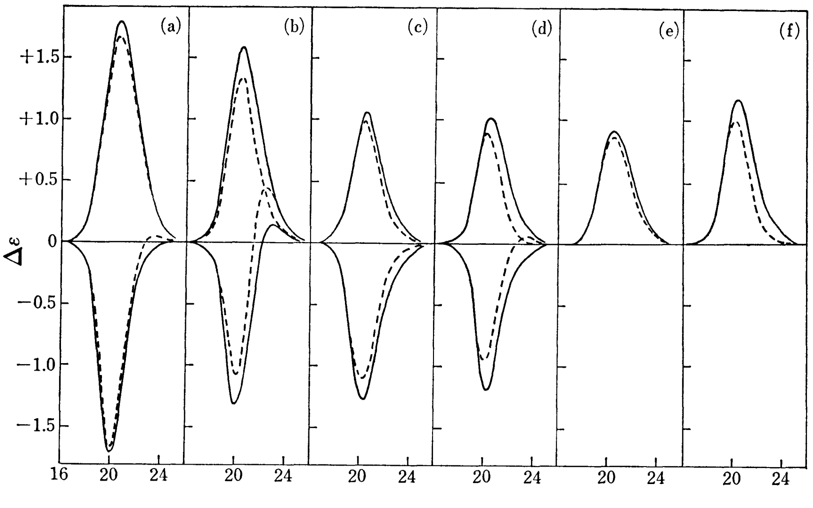

Fig. 1. CD spectra of $[Co(en)_2(L)]^{3+}$ in water (——) and in 0.2 mol·dm$^{-3}$ $Na_2SO_4$ (----). L; (a) *S*,*S*-dppn, (b) *R*,*R*-ptn, (c) *S*-phtn, (d) *R*-bn, (e) *R*,*S*-dppn, and (f) *R*,*S*-ptn.

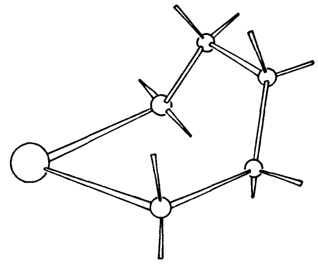

Fig. 2. The envelope conformation of a 1,3-diamine chelate ring.

As stated above, these chelate rings can also take the chair conformation. Molecular models suggest that the difference in the structure between the $\Delta$(*ch*) and $\Lambda$(*ch*) isomers is smaller than that between the $\Lambda(\lambda)$(*ob*) and $\Delta(\lambda)$(*lel*) isomers. Hence, the former two isomers give the first absorption bands with a small energy difference from each other.

In Fig. 1 are shown the CD spectra in water in the absence or the presence of sulfate ions. All the complexes show a typical CD pattern for a tris-diamine complex, and their absolute configurations can be assigned on the basis of the CD sign as shown in Table 2. In the presence of sulfate ions, all the complexes diminish the CD strength. Such a phenomenon is known to be caused by increase in the amounts of the *lel*$_3$($\Delta(\lambda\lambda\lambda)$ or $\Lambda(\delta\delta\delta)$) conformer due to ion-association between a complex and a sulfate ion; the *lel*$_3$ conformer is the most effective structure in forming an ion-pair through hydrogen bonding between the amino protons and the sulfate ion,[11] and since the CD sign due to the vicinal effect of a $\lambda$ ligand is positive opposite to that due to the configurational effect of a $\Delta$ isomer, the CD strength of the *lel*$_3$($\Delta(\lambda\lambda\lambda)$) conformer should be smaller than those of other conformers such as *lel*$_2$*ob* ($\Delta(\lambda\lambda\delta)$) or *lelob*$_2$($\Delta(\lambda\delta\delta)$).[2] For the present complexes of the optically active diamines, the $\Delta$-isomers will be stabilized in the $\Delta(\lambda\lambda\lambda)$(*lel*$_3$) conformer and reduced their CD strengths in the presence of sulfate ions. On the other hand, the $\Lambda$-isomers can form the $\Lambda(\delta\delta\delta)$(*lel*$_3$) conformer with difficulty, since the $\delta$ forms of the present 1,3-diamine chelate rings involve axially disposed substituents. Similar conformers with one axial substituent are fomed for the *meso*-diamine complexes in the *lel*$_3$ form. These conformers will be unstable because of large steric interactions between the substituent and the ethylenediamine ligand. However, when these 1,3-diamine chelate rings take a conformation as shown in Fig. 2, the complex can have the same set of three N–H bonds as that in the *lel*$_3$ conformer, and can form a stable ion-pair with a sulfate ion. Such a conformer involves a *cis* form around a skeletal carbon-carbon bond (envelope type), and will be unstable compared with typical chair and skew forms. However, it seems to be much more stable than conformers with axial substituents in an octahedral complex. Although the vicinal contribution of this conformer to CD is unknown at present, the CD change of the $\Lambda$- and *meso*-diamine complexes caused by the addition of sulfate ions will also be related to such a conformational change of the 1,3-diamine chelate rings.

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