Studies of the Mixed Amino Acid Complexes of Cobalt(III). IV.[1] Magnetic Circular Dichroism Spectra of the $[Co(ox)_x(gly)_y(en)_z]$ Complexes

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Magnetic circular dichroism (MCD) spectra of a series of sixteen complexes of the $[Co(ox)_x(gly)_y(en)_z]$ type have been measured. The MCD intensity increases with increasing number of the coordinated carboxylato groups. A negative MCD band whose shape is similar to the corresponding absorption band was observed in the first d-d absorption band region. This negative band is assigned to the "B" term, in which the "A" term is swamped. A positive and a negative MCD band appear in the second d-d absorption band region. The origin of the positive band is discussed.

Only a few papers have reported the magnetic circular dichroism (MCD) spectra of cobalt(III) complexes; these results include $[Co(NH_3)_6]^{3+}$,[2,3] $[Co(CN)_6]^{3-}$,[2] $[CoCl(NH_3)_5]^{2+}$,[2] *trans*- and *cis*-$[CoCl_2(en)_2]^+$,[2] *cis*-$[Co(NH_3)_4(OH_2)_2]^{3+}$,[2] $[Co(en)_3]^{3+}$,[2,3] $[Co(ox)_3]^{3-}$,[2,4] $[Co(rac\text{-}pn)_3]^{3+}$,[3] $[Co(mal)_3]^{3-}$,[4] and $[Co(acac)_3]$.[5]* The purpose of the present work is to take a general view of the MCD spectra of a fundamental series of the sixteen cobalt(III) complexes, whose absorption spectra have been studied already.[6] The sixteen complexes form a complete series of the $[Co(ox)_x(gly)_y(en)_z]$ type,* where x, y, and z are 0, 1, 2, or 3 and $x+y+z$ equals 3. The oxalato, glycinato, and ethylenediamine ligands all produce a five-membered chelate ring; each complex is a tris(chelate) type and belongs to one of the $[Co^{III}(O)_n(N)_{6-n}]$ types (n=0—6).

Experimental

The complexes were prepared by the methods described in the available literature.[6-13]

Visible and near-ultraviolet absorption spectra were measured by a Shimadzu UV-200 spectrophotometer. MCD spectra were recorded in a magnetic field of 15000 gauss with a Jasco MOE-1 spectropolarimeter. The MCD intensity is expressed in terms of the molar ellipticity per unit magnetic field in the direction of the light beam, $[\theta]_M$, which has the units of degree m^{-1} dm^3 mol^{-1} $gauss^{-1}$.

Measurements were made at room temperature in aqueous solutions, except for *fac*-$[Co(gly)_3]$, which was studied in 3 M H_2SO_4 solution.

Results and Discussion

Band shapes of MCD spectra have been generally interpreted as composed from three terms, A, B, and C, whose shapes are either dispersion type (for A) or absorption type (for B and C). The "A" term arises when at least one of the ground or the excited states is degenerate, while a "B" term is present in principle for every electronic transition. A "C" term exists only when the ground state is degenerate. This term may be disregarded in the present case, since the ground state of an octahedral cobalt(III) complex is nondegenerate, $^1A_{1g}$.

The sixteen complexes of $[Co(ox)_x(gly)_y(en)_z]$ series can be classified into ten types with respect to the coordinated atoms. They are $[Co(N)_6]$, $[Co(N)_5(O)]$, *cis(O)*- and *trans(O)*-$[Co(N)_4(O)_2]$, *mer(N)*- and *fac(N)*-$[Co(N)_3(O)_3]$, *trans(N)*- and *cis(N)*-$[Co(N)_2(O)_4]$, $[Co(N)(O)_5]$ and $[Co(O)_6]$, in which only the *mer(N)*-$[Co(N)_3(O)_3]$ type has no degenerate excited state in any approximation. Thus, the A term may be expected in most of the complexes, except in *mer(N)*-$[Co(gly)_3]$ and *mer(N)*-$[Co(ox)(gly)(en)]$.

The observed MCD spectra of $[Co(ox)_x(gly)_y(en)_z]$ type complexes in the visible and near-ultraviolet region are shown in Figs. 1—6, together with their absorption spectra. The data are summarized in Table 1.

The First d-d Absorption Band Region. A negative band, whose shape resembles greatly the corresponding absorption band, appears in this region for all the present complexes. This result is in accordance with that from the magnetic rotatory dispersion studies of $[Co(en)_3]^{3+}$, $[Co(gly)(en)_2]^{2+}$, *etc.*[14] Thus it seems that only a negative B term is present, while the A

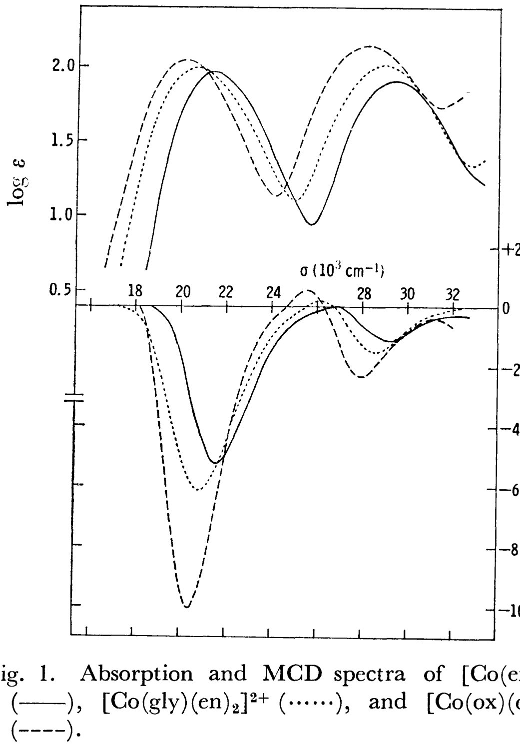

Fig. 1. Absorption and MCD spectra of $[Co(en)_3]^{3+}$ (——), $[Co(gly)(en)_2]^{2+}$ (……), and $[Co(ox)(en)_2]^+$ (----).

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* Abbreviation of ligands: en=ethylenediamine, pn=propylenediamine, ox=oxalate(2−) ion, mal=malonate(2−) ion, acac=acetylacetonate(1−) ion, gly=glycinate(1−) ion, and ala=alaninate(1−) ion.

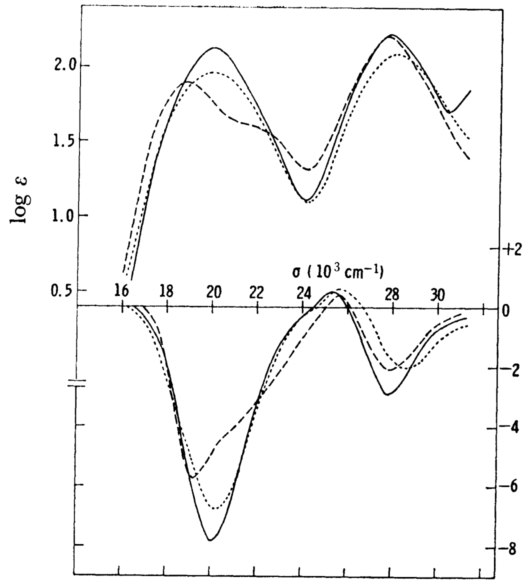

Fig. 2. Absorption and MCD spectra of three geometrical isomers of $[Co(gly)_2(en)]^+$: C_1-*cis(O)* (——), C_2-*cis(O)* (······), and *trans(O)* (----).

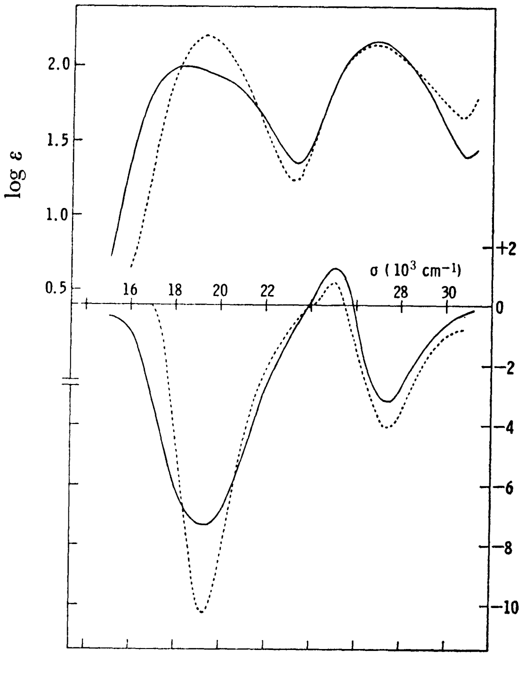

Fig. 3. Absorption and MCD spectra of two geometrical isomers of $[Co(gly)_3]$: *mer(N)* (——) and *fac(N)* (······).

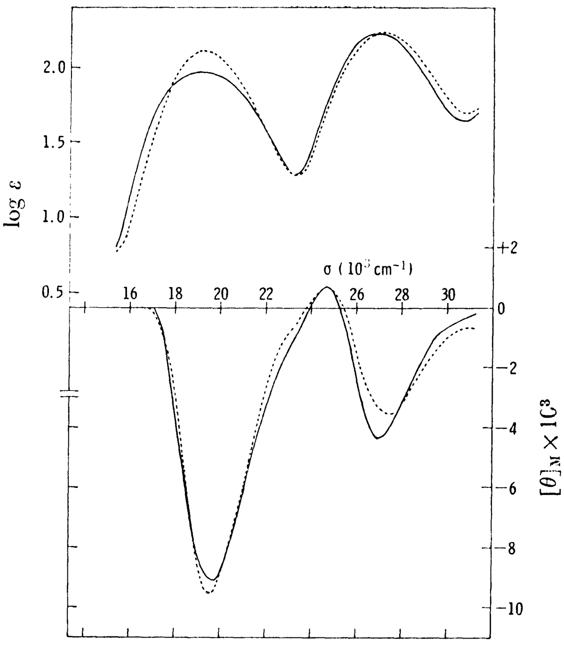

Fig. 4. Absorption and MCD spectra of two geometrical isomers of [Co(ox)(gly)(en)]: *mer(N)* (——) and *fac(N)* (······).

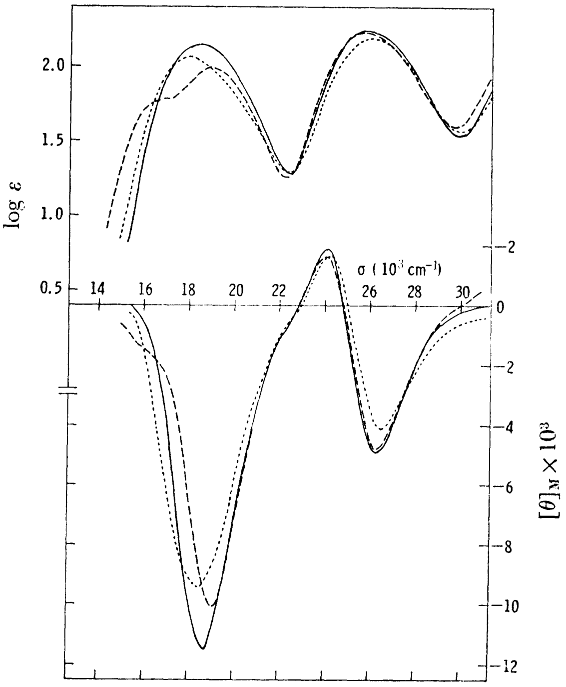

Fig. 5. Absorption and MCD spectra of three geometrical isomers of $[Co(ox)(gly)_2]^-$: *trans(N)* (----), C_2-*cis(N)* (······), and C_1-*cis(N)* (——).

term is not to be seen. This is in agreement with the results of earlier workers, who interpreted the unobservable A term as a quenching of the orbital angular momentum in the excited state.[2)]

It should be noted that the extremum of the MCD band has slightly higher energy than the maximum of the corresponding absorption band in most of the complexes (Table 1). This fact can be well explained by considering the presence of a small positive A term which is swamped by the large negative B term, as has been pointed out for $[Co(N)_6]$ type complexes by Russell and Douglas.[3)]

McCaffery and co-workers mentioned that the d-d bands are much more resolved in MCD than in the absorption of *cis*- and *trans*-$[CoCl_2(en)_2]^+$.[2] We cannot detect such an effect, however, for the present complexes in comparing the *cis* and *trans* isomers of $[Co(gly)_2(en)]^+$ or $[Co(ox)(gly)_2]^-$, and the *mer* and *fac* isomers of $[Co(gly)_3]$ or [Co(ox)(gly)(en)] (Figs.

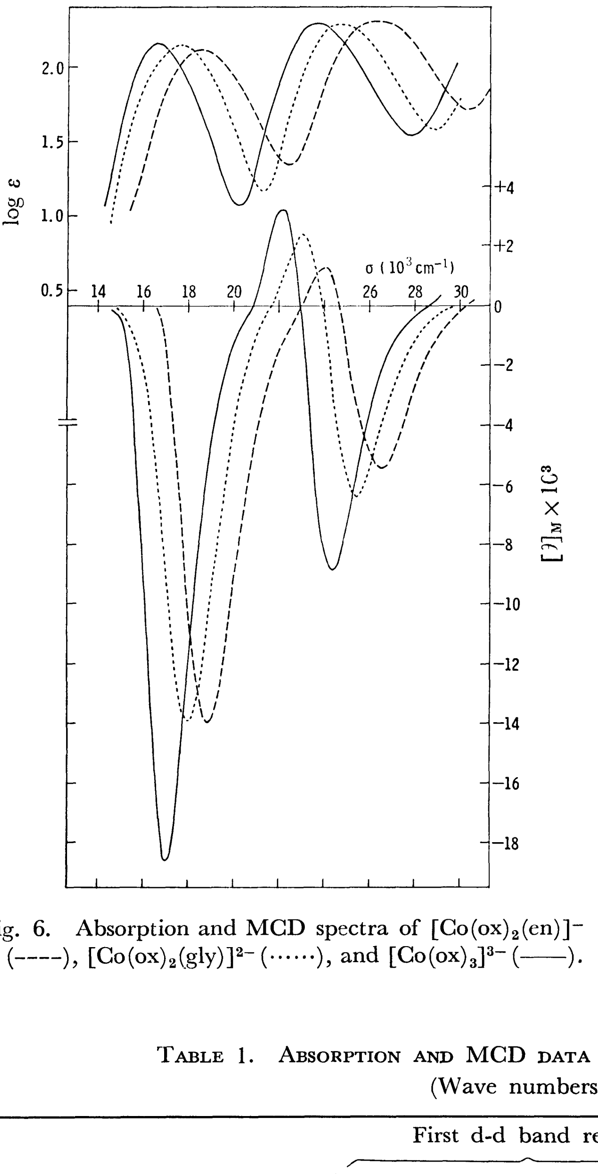

Fig. 6. Absorption and MCD spectra of $[Co(ox)_2(en)]^-$ (----), $[Co(ox)_2(gly)]^{2-}$ (······), and $[Co(ox)_3]^{3-}$ (——).

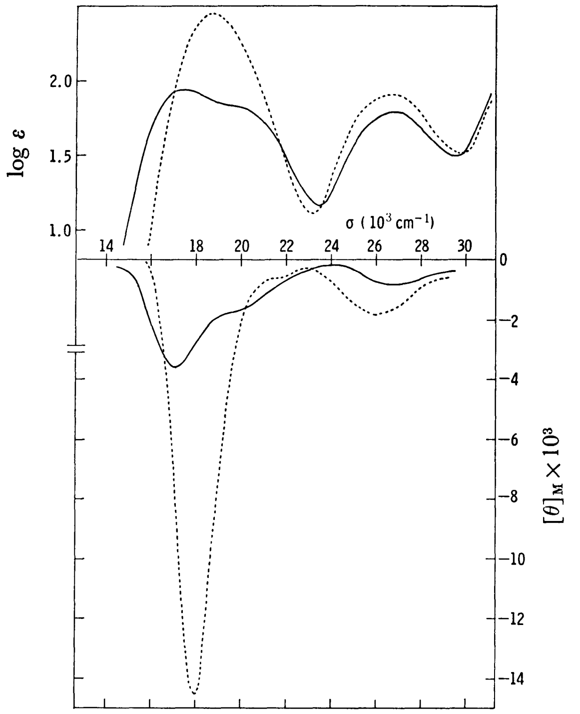

Fig. 7. Absorption and MCD spectra of two geometrical isomers of $[Co(\beta\text{-ala})_3]$: *mer*(*N*) (——) and *fac*(*N*) (······).

2—5). Our sensitivity for the splitting into the component bands seems to be of the same order for both the MCD and the absorption spectra.

The Second d-d Absorption Band Region. It is a unique behavior of the present $[Co(ox)_x(gly)_y(en)_z]$

TABLE 1. ABSORPTION AND MCD DATA OF THE $[Co(ox)_x(gly)_y(en)_z]$ TYPE COMPLEXES
(Wave numbers are given 10^3 cm^{-1})

Complex	First d-d band region			Second d-d band region		
	Absorption σ_{max}	MCD $\sigma_{ext}([\theta]_{Mext})$	$\frac{\lvert[\theta]_{Mext}\rvert}{\varepsilon_{max}}$ a)	Absorption σ_{max}	MCD $\sigma_{ext}([\theta]_{Mext})$	MCD $\sigma_{ext}([\theta]_{Mext})$
1. $[Co(en)_3]Br_3$	21.4	21.6(−0.0053)	5.8	29.3		29.2(−0.0011)
2. $[Co(gly)(en)_2](ClO_4)_2$	20.6	20.8(−0.0061)	6.3	28.8	26.0(+0.0002)	28.6(−0.0015)
3. $[Co(ox)(en)_2]Cl$	20.1	20.4(−0.0101)	9.2	28.1	25.6(+0.0005)	28.0(−0.0023)
4. C_1-*cis*-$[Co(gly)_2(en)]ClO_4\cdot 2H_2O$	19.9	20.1(−0.0079)	5.9	27.8	25.3(+0.0005)	27.8(−0.0030)
5. C_2-*cis*-$[Co(gly)_2(en)]I$	19.0	20.2(−0.0068)	7.4	28.1	25.6(+0.0006)	28.6(−0.0021)
6. *trans*-$[Co(gly)_2(en)]Br\cdot H_2O$	18.8	19.2(−0.0057)	7.3	27.7	25.6(+0.0004)	27.9(−0.0021)
7. *mer*-$[Co(ox)(gly)(en)]$	19.1	19.7(−0.0091)	9.8	27.0	24.7(+0.0007)	27.0(−0.0044)
8. *mer*-$[Co(gly)_3]\cdot 2H_2O$	18.4	19.4(−0.0074)	7.3	26.8	25.0(+0.0013)	27.4(−0.0033)
9. *fac*-$[Co(gly)_3]\cdot H_2O$	19.3	19.3(−0.0103)	6.5	26.7	25.0(+0.0008)	27.4(−0.0041)
10. *fac*-$[Co(ox)(gly)(en)]$	19.2	19.5(−0.0096)	7.5	27.2	24.7(+0.0007)	27.4(−0.0036)
11. *trans*-$Na[Co(ox)(gly)_2]$	19.0	19.1(−0.0101)	10.3	25.7	24.1(+0.0016)	26.3(−0.0048)
12. C_2-*cis*-$Na[Co(ox)(gly)_2]$	17.9	18.5(−0.0094)	8.2	26.0	24.2(+0.0017)	26.5(−0.0041)
13. C_1-*cis*-$Na[Co(ox)(gly)_2]$	18.4	18.8(−0.0115)	8.2	25.8	24.1(+0.0018)	26.3(−0.0049)
14. $Na[Co(ox)_2(en)]\cdot H_2O$	18.5	18.9(−0.0140)	10.9	26.1	24.1(+0.0013)	26.5(−0.0055)
15. $Na_2[Co(ox)_2(gly)]\cdot 1.5H_2O$	17.7	18.0(−0.0139)	10.1	24.8	23.0(+0.0024)	25.5(−0.0064)
16. $K_3[Co(ox)_3]\cdot 3H_2O$	16.6	17.0(−0.0186)	13.2	23.7	22.2(+0.0032)	24.4(−0.0089)

a) In the units of 10^{-5}.

complexes, except $[Co(en)_3]^{3+}$, that a positive MCD band is observed on the lower energy side of the main negative MCD band in the second d-d absorption band region (Figs. 1—6). No such positive band was reported for the cobalt(III) complexes studied previously, except for $[Co(ox)_3]^{3-}$.[2,4]

Alternative interpretations may be presented for the origin of the positive MCD band in the second d-d absorption band region. The first would to postulate that this band is a longer wavelength wing of an A term. McCaffery and co-workers interpreted the MCD spectrum of $[Co(ox)_3]^{3-}$ in this region by postulating an A term of trigonal splitting E transition in D_3 symmetry.[2] However, the fact that the *mer(N)*-$[Co(N)_3(O)_3]$ type complexes also have the positive band cannot be so explained, because these complexes do not have a degenerate excited state.

In the second explanation, the positive band is attributed to a positive B term arising from one of the splitting components of the $T_{2g}(O_h)$ transition in the lower symmetry. In this case, it is expected that the energy separation between the two components of the *trans* isomer of $[Co(N)_4(O)_2]$ or $[Co(N)_2(O)_4]$ type is larger than that of the *cis* isomer. This energy separation is $1/2\delta_\sigma - 1/2\delta_\pi$ for the *trans* isomer, and $1/4\delta_\sigma - 1/4\delta_\pi$ for the *cis*, using Yamatera's parameters.[15] Nevertheless, the observed separation between the positive and negative bands is virtually invariant for both isomers (Table 1).

It should be noted that the maximum of the second d-d absorption band is located at slightly higher energy than the negative MCD band for the complexes of $[Co(N)_6]$ and $[Co(N)_5(O)]$ type, while it lies in the intermediate region between the positive and negative MCD bands for the complexes having more carboxylato groups, *e.g.*, for the $[Co(N)_2(O)_4]$, $[Co(N)(O)_5]$, and $[Co(O)_6]$ type complexes. Moreover, the intensity ratio of the positive to the negative band increases in the above order, and in the limiting case the positive MCD band does not appear in the $[Co(en)_3]^{3+}$ complex. These results seem to indicate that the positive MCD band is related to the presence of coordinated carboxylato groups.

In order to confirm the above assumption, MCD spectra of the other complexes were measured. Unexpectedly, no positive band is observed in *mer(N)*- and *fac(N)*-$[Co(\beta\text{-ala})_3]$ (Fig. 7). Also $[Co(mal)_3]^{3-}$ and *cis*-$[Co(NH_3)_4(OH_2)_2]^{3+}$ did not exhibit this band, as was reported in the previous papers.[2,4] From these facts, it is concluded that the positive band is characteristic for the complex having a planar carboxylato chelate ring. It has been well established that the β-ala[16] and mal[17] chelate rings are not planar.

Intensity. It is interesting that the values of $|[\theta]_{Mext}|$ and also $|[\theta]_{Mext}|/\varepsilon_{max}$ increase with increasing number of coordinated carboxylato groups, in both the first and second d-d absorption band regions, as can be seen from Table 1.

The value of $|[\theta]_{Mext}|$ in the first d-d absorption band region is greater than that in the second d-d absorption band region for all the present complexes, although some exceptional complexes, such as $[CoCl(NH_3)_5]^{2+}$ and *cis*-$[CoCl_2(en)_2]^+$, have been reported previously.[2]

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