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Spectroscopic Studies of Polynuclear Complexes. II.[1] Preparation and Optical Resolution of μ-Amido-μ-superoxo and μ-Amido-μ-peroxo Tetrakis(α-di-imine)dicobalt(III) Ions

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New binuclear cobalt(III) complexes of the type, $[L_2Co(\mu\text{-}NH_2,O_2)CoL_2](ClO_4)_n$, where L is 1,10-phenanthroline or 2,2′-bipyridyl, and $n=3$ and 4, correspond to the so-called μ-peroxo and μ-superoxo form, respectively, were prepared and resolved into their optical isomers. Their absorption spectra have been compared with those of analogous ethylenediamine complexes and the structures have been discussed. The absolute configuration of these complexes has been determined by their circular dichroism spectra. The μ-peroxo complexes seem to be more stable than the corresponding μ-superoxo complexes in aqueous solution.

It is well known that cobalt(II) salts in aqueous ammonia solutions react with molecular oxygen to form diamagnetic brown complex,[2] $[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{4+}$, which can be oxidized to paramagnetic green complex,[3] $[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{5+}$. Recently, House *et al.*[4,5] prepared many oxygen-bridged complexes of these types containing polyamines such as ethylenediamine (en) and triethylenetetramine. We have studied those complexes which have μ-amido group as a second bridge, and reported on optically active $[(l\text{-pn})_2Co(\mu\text{-}NH_2, O_2)Co(l\text{-pn})_2]^{4+}$ (l-pn$=l$-propylenediamine) and its derivatives.[1]

This paper concerns the preparation and optical resolution of $[(\alpha\text{-di-imine})_2Co(\mu\text{-}NH_2, O_2)Co(\alpha\text{-di-imine})_2](ClO_4)_n$ ($n=3$ and 4, α-di-imine$=$2,2′-bipyridyl (bip) and 1,10-phenanthroline (phen)), and their geometrical and optical structures were determined by absorption (AB) and circular dichroism (CD) spectroscopy. These are first examples of cobalt(III) binuclear complexes which contain oxygen bridge and aromatic ligands, and their optical spectra will provide useful information in elucidating the electronic state of binuclear complexes.

Experimental

Preparation of the complexes. (1) *μ-Amido μ-superoxo-octaammine-dicobalt(III) Perchlorate.* $[(NH_3)_4Co(\mu\text{-}NH_2, O_2)Co(NH_3)_4](ClO_4)_4$ (**1**). This complex was prepared from the corresponding sulfate dihydrate.[6] To a suspension containing 10 g of the sulfate dihydrate in 50 m*l* of water was added 50 m*l* of 60% perchloric acid slowly with frequent stirrings. The crude complex was precipitated by cooling in an ice bath, filtered off, washed with methanol-ether (1 : 1) and ether, and dried *in vacuo*. Dark green crystals, recrystallized from warm water acidified with perchloric acid, are soluble in water, methanol, ethanol and acetone, but insoluble in ether.

Nitrogen analysis of this complex gave always 1—2% over than the expected value, probably because of the instability of the complex. The dark green crystals changed into an unknown black product in a week. However, the absorption spectrum of this perchlorate in water was identical with that of the corresponding nitrate.[1]

(2) μ-Amido-μ-peroxo-tetrakis(1,10-phenanthroline)-dicobalt(III) Perchlorate Monohydrate, $[(phen)_2Co(\mu\text{-}NH_2,O_2)Co(phen)_2](ClO_4)_3\cdot H_2O$ (**2**). A mixture of 8 g of freshly prepared **1** and 10 g of 1,10-phenanthroline in 300 m*l* of methanol was warmed at 60°C for 10 hr with stirring and cooled in an ice bath. Brown precipitate obtained by adding 2 g of sodium perchlorate was filtered off, washed with cold methanol and ether, and air dried. The product was recrystallized from warm water (60°C) by adding sodium perchlorate. Yield: about 8 g.

Found: C, 47.75; H, 2.72; N, 10.29%. Calcd for $C_{48}H_{36}N_9O_{15}Co_2Cl_3$: C, 47.76; H, 3.01; N, 10.44%.

(3) μ-Amido-μ-peroxo-tetrakis(2,2′-bipyridyl)dicobalt (III) Perchlorate Dihydrate, $[(bip)_2Co(\mu\text{-}NH_2, O_2)Co(bip)_2](ClO_4)_3\cdot 2H_2O$ (**3**). This complex was prepared by the same method as that for **2** by use of 8 g of 2,2′-bipyridyl instead of 1,10-phenanthroline. Yield: about 8 g.

Found: C, 42.99; H, 3.31; N, 11.45%. Calcd

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[1] Part I of this series, Y. Sasaki, J. Fujita and K. Saito, This Bulletin, **42**, 146 (1969).

[2] A. Werner and A. Mylius, *Z. Anorg. Chem.*, **16**, 245 (1898).

[3] A. Werner, *Ber.*, **41**, 3915 (1908).

[4] A. R. Gainsfeld and D. A. House, *Inorg. Nucl. Chem. Lett.*, **4**, 621 (1968).

[5] D. L. Duffy, D. A. House and J. A. Weil, *J. Inorg. Nucl. Chem.*, **31**, 2053 (1969).

[6] M. Mori, J. A. Weil and M. Ishiguro, *J. Amer. Chem. Soc.*, **90**, 615 (1968).

for $C_{40}H_{38}N_9O_{16}Co_2Cl_3$: C, 42.71; H, 3.41; N, 11.21%.

(4) μ-Amido-μ-superoxo-tetrakis(1,10-phenanthroline)dicobalt(III) Perchlorate Dihydrate, $[(phen)_2Co(\mu\text{-}NH_2,O_2)Co(phen)_2](ClO_4)_4\cdot 2H_2O$ (**4**). To a solution of 2 g of **2** in 50 m*l* of 7 N nitric acid was added 3 g of solid sodium perchlorate, and the solution was cooled in an ice bath for an hour. Brown fine crystals were filtered off, washed with aqueous sodium perchlorate solution, cold methanol and ether, and dried. Yield: 1—1.5 g,

Found: C, 43.60; H, 2.94; N, 9.34%. Calcd for $C_{48}H_{38}N_9O_{20}Co_2Cl_4$: C, 43.66; H, 2.90; N, 9.55%.

This complex is unstable in water and gives the μ-peroxo complex **2** and other unidentified materials.

(5) μ-Amido-μ-superoxo-tetrakis(2,2′-bipyridyl)dicobalt(III) Perchlorate Monohydrate, $[(bip)_2Co(\mu\text{-}NH_2, O_2)Co(bip)_2](ClO_4)_4\cdot H_2O$ (**5**). This complex was obtained as green crystalline powder from the μ-peroxo complex **3** by a similar method to that for **4**. This complex also unstable in water, as **4**. Yield: 1—1.5 g.

Found: C, 39.69; H, 3.11; N, 10.50%. Calcd for $C_{40}H_{36}N_9O_{19}Co_2Cl_4$: C, 39.82; H, 3.10; N, 10.45%.

(6) (+)$_D$*-μ-Amido-μ-peroxo-tetrakis(1,10-phenanthroline)dicobalt(III) Perchlorate Hexahydrate,* $(+)_D$-$[(phen)_2Co(\mu\text{-}NH_2,O_2)Co(phen)_2](ClO_4)_4\cdot 6H_2O$ (**6**). Ten grams of **2** was converted into chloride with 50 m*l* of water and Dowex CG 400 ion-exchange resin in the chloride form by a batch method. The resin was filtered off, and washed with a small amount of water. To the filtrate silver antimonyl *d*-tartrate (12 g) was added, stirred for half an hour, and then silver chloride was filtered off. The filtrate was poured into 100 m*l* of methanol and stored in a refrigerator with occasional stirring. Addition of methanol to the solution gave an oily product which could not be crystallized. After a day, the precipitated crude antimonyl *d*-tartrate of $(+)_D$-isomer was filtered off, washed with a small amount of cold water, methanol and ether, and dried. The filtrate was stored to obtain $(-)_D$-isomer (filtrate *a*).

Pure perchlorate of $(+)_D$-isomer was obtained as follows; the aqueous solution of the antimonyl *d*-tartrate salt was treated with a small amount of solid sodium perchlorate, and stirred for an hour in an ice bath. At this stage, the other enantioisomer was precipitated as less soluble racemate and filtered off. The $(+)_D$-isomer was obtained by adding excessive sodium perchlorate to the filtrate. This procedure was repeated to give a constant rotation.

Found: C, 44.63; H, 3.19; N, 9.49%. Calcd for $C_{48}H_{46}N_9O_{24}Co_2Cl_4$: C, 44.58; H, 3.59; N, 9.74%.

The $(-)_D$-isomer was obtained from the filtrate *a*. The filtrate was evaporated to 50 m*l* at about 40°C, and then a small amount of sodium perchlorate was added to remove less soluble racemate as stated above. Pure perchlorate of $(-)_D$-isomer was obtained from the filtrate by adding excessive sodium perchlorate.

(7) (+)$_D$*-μ-Amido-μ-peroxo-tetrakis(2,2′-bipyridyl)dicobalt(III) Perchlorate Trihydrate,* $(+)_D$-$[(bip)_2Co(\mu\text{-}NH_2,O_2)Co(bip)_2](ClO_4)_3\cdot 3H_2O$ (**7**). This isomer was prepared from **3** by a similar procedure to that for **6**. The antimonyl *d*-tartrate of $(+)_D$-isomer was precipitated by cooling at 0°C for 5 hr without adding methanol.

Found: C, 42.03; H, 3.53; N, 11.03%. Calcd for $C_{40}H_{40}N_9O_{17}Co_2Cl_3$: C, 41.96; H, 3.49; N, 10.83%.

The $(-)_D$-isomer was obtained also by the procedure as described for the $(-)_D$-isomer of the (phen) complex.

(8) (+)$_D$*-μ-Amido-μ-superoxo-tetrakis(1,10-phenanthroline)dicobalt(III) Perchlorate,* $(+)_D$-$[(phen)_2Co(\mu\text{-}NH_2,O_2)Co(phen)_2](ClO_4)_4$(**8**), *and* $(+)_D$*-μ-Amido-μ-superoxo-terakis(2,2′-bipyridyl)dicobalt(III) Perchlorate Monohydrate,* $(+)_D$-$[(bip)_2Co(\mu\text{-}NH_2,O_2)Co(bip)_2](ClO_4)_4\cdot H_2O$ (**9**). These $(+)_D$-isomers were prepared from **6** and **7**, by the procedures for **4** and **5**, respectively.

Found: C, 45.22; H, 3.05; N, 10.33%. Calcd for $C_{48}H_{34}N_9O_{18}Co_2Cl_4$: C, 44.88; H, 2.67; N, 9.81%. Found: C, 39.88; H, 3.27; N, 10.33%. Calcd for $C_{40}H_{36}N_9O_{19}Co_2Cl_4$: C, 39.82; H, 3.01; N, 10.45%.

Measurements. Visible and ultraviolet absorption spectra were obtained with a Hitachi 124 recording spectrophotometer. The CD curves were recorded with a Model ORD/UV-5 spectrophotometer of Japan Spectroscopic Co. with its CD attachment. The μ-peroxo complexes were measured in water, and the μ-superoxo complexes in 60% perchloric acid to avoid decomposition. Magnetic susceptibilities were measured with a magnetic balance of the Gouy type. The balance was calibrated with $HgCo(NCS)_4$. The effective magnetic moment, μ_{eff}, per one molecule was calculated from the expression $\mu_{eff}=2.83\sqrt{\chi_M\cdot T}$ B.M., where χ_M is the molar susceptibility corrected using Pascal's constant[7] and T absolute temperature. All the measurements were made at room temperature.

Results and Discussion

Synthetic Method and the Structure of the Complexes. As stated in the experimental section, the complexes **2** and **3** of the type, $[(\alpha\text{-di-imine})_2Co(\mu\text{-}NH_2,O_2)Co(\alpha\text{-di-imine})_2]^{3+}$, can be prepared easily from $[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4](ClO_4)_4$ (**1**) and 1,10-phenanthroline and 2,2′-bipyridyl, respectively, by substitution reactions in methanol. The complex **1** is useful for a reaction in a non-aqueous solution, since it is soluble in organic solvents such as methanol or ethanol. The reaction in water always produced a large amount of tris-(phen) or -(bip) complex. It will be interesting to note, however, that the reaction between phenanthroline and nitrate of the complex **1** in water gives an insoluble dark green crystalline product with the formula $[Co_2(phen)_2(NH_3)_4(\mu\text{-}NH_2,O_2)](NO_3)_4$ in a few minutes. Detailed studies of this product will be published later.

Table 1. Magnetic moment of the complexes (solid)

Complex	Magnetic moment
2	diamag.
3	diamag.
4	1.92 B. M.
5	1.80 B. M.

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[7] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," ed. by J. Lewis and R. G. Wilkins, Interscience Publishers, New York (1960), p. 400.

TABLE 2. NUMERICAL DATA OF ABSORPTION (AB) AND CIRCULAR DICHROISM (CD) $\tilde{\nu}$ IN 10^3 cm^{-1}, ($\log \varepsilon$) AND ($\varepsilon_l - \varepsilon_r$)

Complex		$\tilde{\nu}$	$\tilde{\nu}$	$\tilde{\nu}$	$\tilde{\nu}$	$\tilde{\nu}$
$(+)_D$ form of **2**	AB	15.4(2.78)			37.0(4.99)	
(in water)	CD	15.6(−10.6)	21.5(+39.4)	27.9(+23.8)	34.7(−158) 37.0(+111)	44.1(−119)
$(+)_D$ form of **3**	AB	15.6(2.67)			32.6(4.62)	40.0(4.74)
(in water)	CD	15.9(−8.6)	21.8(+34.5)	28.6(+9.5)	31.5(−34.5) 36.8(+50.9)	45.5(−68)
$(+)_D$ form of **4**	AB	14.4(2.71)	20.7(3.07)		36.2(5.08)	46.1(5.18)
(in 60% $HClO_4$)	CD		19.5(−11.8)	28.5(+58.0)	35.0(−138) 36.0(+96) 37.9(−59)	43.5(−150)
$(+)_D$ form of **5**	AB	14.5(2.64)	20.9(2.98)		32.7(4.84)	45.5(5.19)
(in 60% $HClO_4$)	CD		20.3(−11.9)	29.9(+54.5)	32.3(+68.0) 34.3(−53.5) 38.8(+46.3)	45.5(−123)

As Table 1 shows, the μ-superoxo complexes have a magnetic moment corresponding to one unpaired electron, while the μ-peroxo complexes are diamagnetic. The elementary analyses and the fact that the formers derived from the latters by oxidation with nitric acid are paramagnetic indicate that all the complexes contain bridging μ-dioxygen group.[8,9]

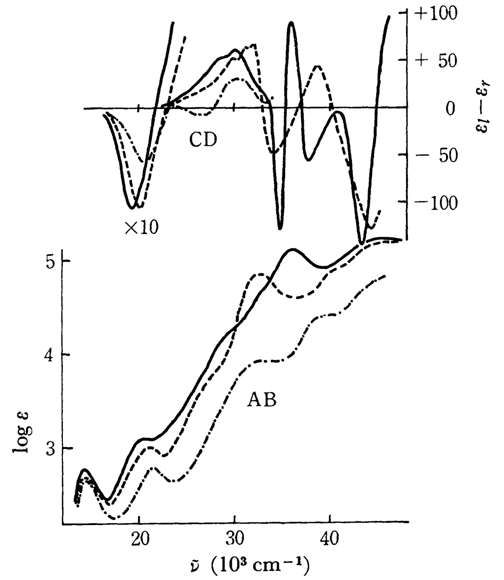

Fig. 1. The AB and CD spectra of $(+)_D$-$[(phen)_2Co(\mu\text{-}NH_2, O_2)Co(phen)_2](ClO_4)_4$ (——), $(+)_D$-$[(bip)_2Co(\mu\text{-}NH_2, O_2)Co(bip)_2](ClO_4)_4 \cdot H_2O$ (----) in 60% perchloric acid and $\Delta\Delta$-$[(en)_2Co(\mu\text{-}NH_2, O_2)Co(en)_2](NO_3)_4$ (—·—·) in water.

Figure 1 shows that the AB spectra of the μ-superoxo complexes (**4**, **5**) in the visible region are very similar to that of the ethylenediamine analog reported previously.[1] This result suggests that these complexes have a similar structure to one another. On the other hand, such a similarity in spectral pattern is not seen among the μ-peroxo complexes (**2**, **3**) and ethylenediamine analog, as shown in Fig. 2. The present μ-peroxo complexes exhibit a distinct absorption maximum at about 15500 cm^{-1}, whereas the ethylenediamine analog does not. Further consideration with

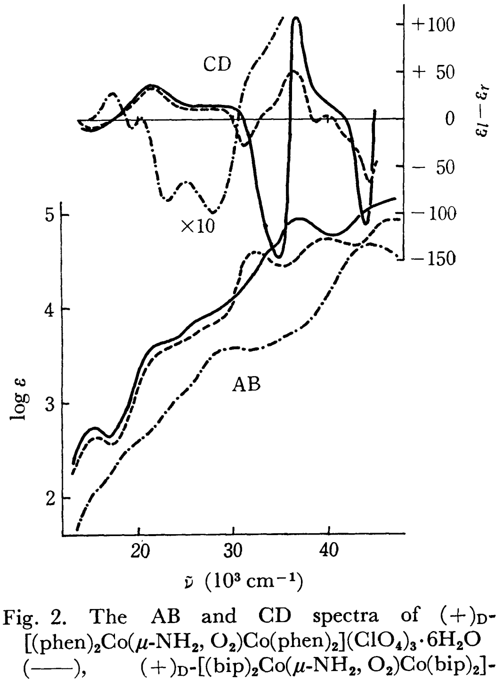

Fig. 2. The AB and CD spectra of $(+)_D$-$[(phen)_2Co(\mu\text{-}NH_2, O_2)Co(phen)_2](ClO_4)_3 \cdot 6H_2O$ (——), $(+)_D$-$[(bip)_2Co(\mu\text{-}NH_2, O_2)Co(bip)_2](ClO_4)_3 \cdot 3H_2O$ (----) and $\Delta\Delta$-$[(en)_2Co(\mu\text{-}NH_2, O_2)Co(en)_2]I_3$ (—·—·) in water.

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[8] L. R. Thompson and W. K. Wilmarth, *J. Phys. Chem.*, **56**, 5 (1952).

[9] M. Mori and J. A. Weil, *J. Amer. Chem. Soc.*, **89**, 3732 (1967).

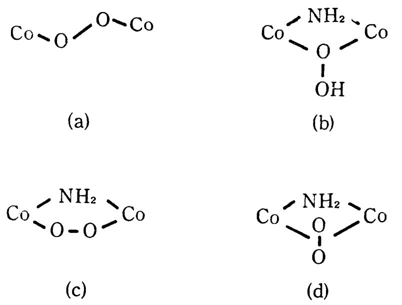

Fig. 3. Possible structures of μ-peroxo bridges.

reference to the structure of the bridge part would be needed.

Although no X-ray analysis has been made on a double bridged complex containing μ-peroxo group, the result for $[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5](SO_4)_2\cdot 4H_2O$[10] revealed that each oxygen atom of the μ-peroxo group coordinates to each cobalt ion forming the σ-type bonding as shown in Fig. 3(a).

Mori and Weil,[9] on the basis of kinetic and spectroscopic measurements, inferred the isomerization scheme as shown in Fig. 4 for the $[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{3+}$ ion. In this figure, [B] corresponds to the ordinarily prepared brown μ-amido-μ-peroxo-tetrakis-ethylenediamine complex. The [AH] was isolated as red nitrate[9,11] and its structure was determined by X-ray analysis.[12] This complex involves three bonded oxygen atom, as shown in Fig. 3(b). For the brown [B] form, Mori and Weil suggested the σ-type structure which is similar to that in $[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{4+}$ (Fig. 3(c)), They further considered that the [BH] and the [A] were intermediate species, and that their bridging structures would be similar to those of the [B] and [AH], respectively. In these arguments, however, there remain some ambiguities about the bridging structure of [A], for which a possibility of the π-type bonding structure (Fig. 3(d)) can not be excluded, since the interconversion between the Fig. 3(c) type and the π-type (Fig. 3(d)) seems to be easy.

From the analysis of kinetic data, Mori and Weil[9] obtained absorption spectra of the three species, [B], [BH] and [AH]. The spectra of the present μ-peroxo complexes (**2**, **3**) in water do not seem to correspond to any of these species.

In order to make clear the structure of the present μ-peroxo complexes, we have measured the spectra in the solid state and in various solvents at different pH's. As Fig. 5 shows, the solid spectra of the μ-peroxo complexes (**2**, **3**) show a peak at about 15400 cm^{-1} which seems to correspond to the band at about 15500 cm^{-1} in aqueous solution. No significant difference was either observed between the spectra in water and in a basic solution. These results may indicate that each complex ion exists as a single chemical species under the given conditions, in solid state and in neutral and basic solutions. In acid solutions, on the other hand, the spectra vary remarkably according to the acid concentration, and have no isosbestic point. (Fig. 6). At acid concentrations

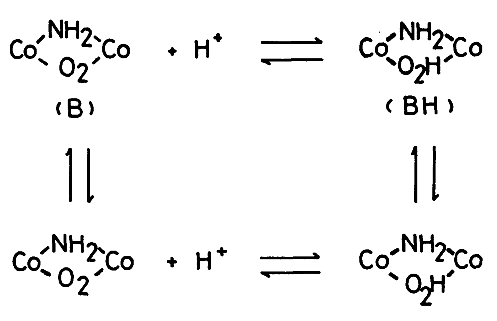

Fig. 4. Reaction scheme of μ-peroxo dicobalt ions. (From Ref. 9).

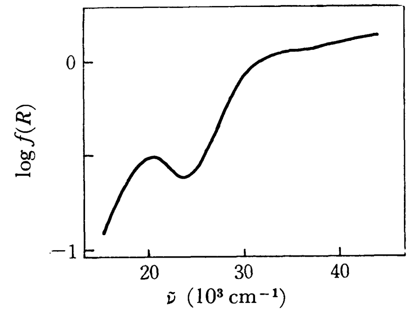

Fig. 5. Diffuse reflectance spectrum of $[(bip)_2Co(\mu\text{-}NH_2, O_2)Co(bip)_2](ClO_4)_3\cdot 2H_2O$ diluted with magnesium oxide.

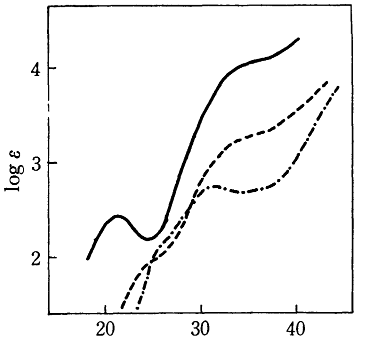

Fig. 6. The AB spectra of $[(bip)_2Co(\mu\text{-}NH_2, O_2)Co(bip)_2](ClO_4)_3\cdot 2H_2O$.
(——) in water and in 0.1 N KOH
(----) in 30% $HClO_4$
(·—·) in 60% $HClO_4$ and in 60% H_2SO_4.

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[10] W. P. Schaefer, *Inorg. Chem.*, **7**, 725 (1968).

[11] A. Werner, *Ber.*, **46**, 3674 (1913).

[12] U. Thewalt and R. Marsh, *J. Amer. Chem. Soc.*, **89**, 6364 (1967).

over 12 N, a constant curve is observed with an absorption maximum at 20400 cm^{-1}, and is similar to that of the μ-hydroperoxo ethylenediamine complex, [AH] (Fig. 1 in Ref. 9). Therefore, we can conclude that the complexes exist as μ-hydroperoxo form corresponding to the [AH] in strong acid solutions.

If the complexes had a structure corresponding to the [A] form in the solid state and in basic solutions, the predominant species in acid solutions should be two, [A] and [AH], and the spectra at various acid concentrations should have isosbestic points. Thus, the most probable bridging structure in the present μ-peroxo complexes (**2**, **3**) will be the σ-type as shown in Fig. 3(c), although their spectra in the visible region are different from that of ethylenediamine analog. More detailed studies, however, would be necessary to elucidate the structure of such μ-dioxygen complexes.

Chemical Behavior of the Complexes. The present μ-superoxo complexes, (**4**, **5**) decompose gradually in water and in basic solutions, giving the μ-peroxo complexes in 60—70% yield. The other 30—40% products were not characterized. The yield of the μ-peroxo ions was determined by their absorption intensities at 15500 cm^{-1}. The reduction with iodide ions in water produced the μ-peroxo complexes almost quantitatively. Thompson and Wilmarth[8] considered that $[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{4+}$ in a basic solution is reduced to the μ-peroxo complex by hydroxide ion. Garbett and Gillard[13] examined the yield of this reduction and gave about 60%. However, the fact that the present μ-superoxo complexes are reduced in a neutral aqueous solution, in which the concentration of hydroxide ions is only 10^{-7} mol/*l*, suggests that in our case, the hydroxide ion would not be a main reducing agent. This suggestion will be supported further by the results that the yields of the μ-peroxo complex reduced in a neutral and in a basic solution are almost equal, 60—70%, but the reduction with another reducing agent such as the iodide ion proceeds almost quantitatively. However, we could not give a definite conclusion about such reductions at present.

It should be noted that when the reduction of racemic μ-superoxo complexes (**4**, **5**) is caused to proceed in water containing a large excess of potassium antimonyl *d*-tartrate, the resulting solution shows similar CD spectra to those of the $(-)_D$-μ-peroxo complexes. From their CD intensites, the optical purity of the products is known to be about 10%. The aqueous solutions of racemic μ-peroxo complexes containing potassium antimonyl *d*-tartrate exhibit very weak CD which originates probably from the second sphere coordination.[14,15] Therefore, such a phenomenon may suggest that the antimonyl *d*-tartrate ion interacts with reaction species stereoselectively in the reduction process.

d-Tartaric acid and *d*-bromocamphorsulfonate ions have no such effect.

Spectra and Absolute Configurations of the Complexes. The AB spectra of the μ-superoxo complexes (**4**, **5**) in the visible region are similar to that of ethylenediamine analog, as stated previously. The band at about 14000 cm^{-1} which is characteristic of μ-superoxo complexes might owe to the charge transfer transitions between the μ-superoxo group and the cobalt(III) ions.[1] The band at about 21000 cm^{-1} may correspond to the first band of a uninuclear cobalt(III) complex.[1] These bands, however, are located from the longer to shorter wavelength in the order of phenanthroline, bipyridyl and ethylenediamine complex (Fig. 1). This order is the reverse order of the spectrochemical series.[16] On the other hand, the location of the bands in the ammine and ethylenediamine analogs is in accord with this series.

As Fig. 1 shows, the $(+)_D$-μ-superoxo complexes show a fairly strong negative CD band in the first band region, which can be compared well with that of the $\Delta\Delta$[*1] isomer of ethylenediamine analog. This result indicates that these isomers have $\Delta\Delta$ configuration. Both $(+)_D$-isomers of the μ-peroxo complexes, from which the $\Delta\Delta$-μ-superoxo complexes were prepared, therefore, should have also $\Delta\Delta$ configuration, since it is very unlikely that inversion would take place during the oxidation. The CD spectra of these μ-peroxo complexes in the *d-d* transition region are very similar to each other, but are entirely different from that of the $\Delta\Delta$ isomer of ethylenediamine analog.[1]

All the complexes prepared here show strong absorption bands in the region 30000 to 40000 cm^{-1}, which can be assigned to the long-axis π–π^* transitions of the coordinated aromatic ligands.[17,18] It is known that these transitions are not largely modified from those of the free ligands.[18] According to the theory,[19–22] when two or three such

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13) K. Garbett and R. D. Gillard, *J. Chem. Soc.*, *A*, **1968**, 1725.

14) S. F. Mason and B. J. Norman, *Chem. Commun.*, **1965**, 335.

15) K. Ogino and U. Saito, This Bulletin, **40**, 826 (1967).

16) Y. Shimura and R. Tsuchida, *ibid.*, **29**, 311 (1956).

[*1] We use the symbols Δ and Λ in the sense of Piper's designation, in accord with the recommendation of IUPAC (1968); *Inorg. Chem.*, **9**, 1 (1970).

17) A. J. McCaffery, S. F. Mason and B. J. Norman, *Proc. Chem. Soc.*, **1964**, 259.

18) J. Hidaka and B. E. Douglas, *Inorg. Chem.*, **3**, 1180 (1964).

19) B. Bosnich, *ibid.*, **7**, 178 (1968).

20) J. Ferguson, C. J. Hawkins, N. A. P. Kane-Maguire and H. Lip, *ibid.*, **8**, 771 (1969).

21) A. J. McCaffery, S. F. Mason and B. J. Norman, *J. Chem. Soc.*, *A*, **1969**, 1428.

conjugated ligands are present in an octahedral complex, the CD spectrum corresponding to their transitions consists of two strong components with different signs. For a Δ configuration, their signs are minus and plus from longer to shorter wavelength. As Fig. 1 shows, the $(+)_D$-μ-superoxo-(phen) complex exhibits two strong, sharp CD peaks with minus and plus sign from longer to shorter wavelength in the π-π^* transition region, indicating that the absolute configuration around each cobalt(III) ion is Δ. This result agrees with the previous assignment obtained from the sign of CD band in the *d-d* transition region. The $(+)_D$-μ-peroxo-(phen) complex shows also such a CD pattern in this region, although the bands are somewhat broader than those of the μ-superoxo complex.

Neither $(+)_D$-isomer of the bipyridyl complexes, on the other hand, gives such a CD for the bands corresponding to the π-π^* transitions. In the bipyridyl complexes, the bands due to these transitions are at a longer wavelength region as compared with those of the phenanthroline complexes, and overlap with the so-called polynuclear bands.[1] Accordingly, it is supposed that the CD bands due to the π-π^* transitions of coordinated bipyridyl might be cancelled by overlapping or interacting with the other CD bands due to such polynuclear bands.

All the $(+)_D$-(bip) and -(phen) complexes exhibit strong negative CD bands at about 45000 cm^{-1}. In particular, those of (phen) complexes are strong and sharp. Mason and Norman[23] measured the CD spectrum of $(+)_D$-$[Co(phen)_3]^{3+}$ and claimed to have only a weak CD in this region. As Fig. 7 shows, however, this tris complex shows a strong negative CD band at 44600 cm^{-1}. Although the origin of such a discrepancy is not clear at present, there seems to be an optically active transition in this region for a cobalt(III) complex containing two or three phenanthroline molecules.

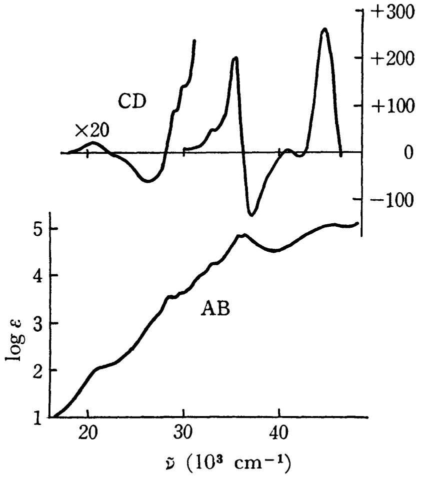

Fig. 7. The AB and CD spectra of $(+)_D$-$[Co(phen)_3](ClO_4)_3\cdot 2H_2O$ in water.

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[23] S. F. Mason and B. J. Norman, *Inorg. Nucl. Chem. Lett.*, **3**, 285 (1967).