Spectroscopic Studies of Polynuclear Complexes. III.[1] Characteristics of Some μ-Peroxoammine Cobalt(III) Complexes.

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The spectroscopic and chemical properties of various μ-peroxo and μ-superoxo cobalt(III) complexes containing several kinds of polyamine including optically active *l*-propylenediamine (*l*-pn) have been studied. The single bridged μ-peroxo complexes have strong absorption peaks at *ca.* 300 nm, whereas the double-bridged μ-peroxo-μ-amido and μ-peroxo-μ-hydroxo complexes have peaks at *ca.* 350 nm. The μ-superoxo complexes have two absorption peaks in the visible region at *ca.* 700 and 480 nm. The former is remarkably stronger for single-bridged species, but both are of almost equal strength for double bridged species. The complexes $[LNH_3Co(\mu\text{-}O_2{}^{(2-)})CoNH_3L]^{4+}$ (L; 2en (ethylenediamine), 2*l*-pn, and trien(triethylenetetramine)) are spontaneously converted into $[LCo(\mu\text{-}O_2{}^{(2-)}, OH)CoL]^{3+}$ in water at room temperature. The en ligands in $[(dien)(en)Co(\mu\text{-}O_2{}^{(2-)})Co(en)(dien)]^{4+}$ (dien; diethylenetriamine) are replaced by *l*-pn in a few days in aqueous solutions containing an excess of *l*-pn. The absolute configuration of $[(l\text{-}pn)_2Co(\mu\text{-}O_2{}^{(2-)}, OH)\ Co(l\text{-}pn)_2]^{3+}$ is assigned to be $\Delta\Delta$ on the basis of circular dichroism spectrum.

As an extention of our preparative and spectroscopic studies of binuclear cobalt complexes bridged by peroxo or superoxo anions,[1,2] this paper deals with spectroscopic and chemical properties of some binuclear cobalt ammine complexes bridged by peroxo anions. Such complexes have been synthesized by many authors in various ways.[3] Fremy[4] passed air through an ammoniacal solution of cobalt(II) salt and obtained μ-peroxo-decaamminedicobalt(III) ions, $[(NH_3)_5Co(\mu\text{-}O_2{}^{(2-)})Co(NH_3)_5]^{4+}$, identified by Werner.[5] This compound is readily decomposed to cobalt(II) salt in a neutral solution with evolution of oxygen. Werner[6] prepared a double bridged dicobalt complex $[(NH_3)_4Co(\mu\text{-}O_2{}^{(2-)},NH_2)Co(NH_3)_4]^{3+}$ from well-known Vortmann's sulfate obtained by passing air through a warm ammoniacal solution of cobalt(II) salt and neutralizing with sulfuric acid. Mori *et al.*[7] obtained the same complex more conveniently and with better yield by warming Fremy's μ-peroxo complex[3] in aqueous ammonia. Recently Gainsford and House, and Duffy *et al.*[8] prepared polyamine derivative of Fremy's μ-peroxo complex,[4] *e.g.* $[(en)_2(NH_3)Co(\mu\text{-}O_2{}^{(2-)})Co(NH_3)(en)_2]^{4+}$ and $[(trien)(NH_3)Co(\mu\text{-}O_2{}^{(2-)})Co(NH_3)(trien)]^{4+}$ [9] by adding en or trien to an aqueous solution of $[(NH_3)_5Co(\mu\text{-}O_2{}^{(2-)})Co(NH_3)_5]^{4+}$ at room temperature. Foong *et al.*[10] obtained a double bridged dicobalt complex $[(en)_2Co(\mu\text{-}O_2{}^{(2-)},OH)Co(en)_2]^{3+}$ by passing air through an aqueous ethanol solution of cobalt(II) salt and en.

We prepared such binuclear complexes with aims of comparing the ultraviolet and visible absorption spectra with other binuclear complexes given previously,[1,2] and found that some of House's complexes with μ-peroxo bridges undergo rapid spectral change in aqueous solutions even at room temperature. The change seems to be related to an unusual lability of amine type ligands of binuclear complexes with μ-peroxo bridges.

Absorption Spectra of the Complexes. House *et al.*[8] prepared several binuclear complexes of cobalt containing polyamines with peroxo single bridge, including $[(tetren)Co(\mu\text{-}O_2{}^{(2-)}Co(tetren)]^{4+}$, $[(dien)(en)Co\text{-}$

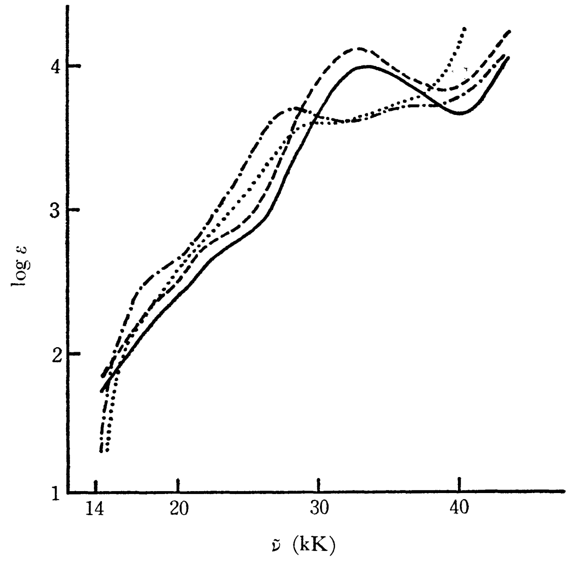

Fig. 1. Absorption spectra of several μ-peroxo dicobalt complexes in water.
——— $[(dien)(en)Co(\mu\text{-}O_2{}^{(2-)})Co(en)(dien)]^{4+}$
------ $[(tetren)Co(\mu\text{-}O_2{}^{(2-)})Co(tetren)]^{4+}$
—·—· $[(en)_2Co(\mu\text{-}O_2{}^{(2-)}, OH)Co(en)_2]^{3+}$
········ $[(en)_2Co(\mu\text{-}O_2{}^{(2-)}, NH_2)Co(en)_2]^{3+}$

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[1] Part II of this series, Y. Sasaki, J. Fujita, and K. Saito, This Bulletin, **43**, 3462 (1970).

[2] a) Y. Sasaki, J. Fujita, and K. Saito, *ibid.*, **42**, 146 (1969); b) **40**, 2206 (1967); c) Y. Sasaki and J. Fujita, *ibid.*, **42**, 2089 (1969).

[3] A. G. Sykes and J. A. Weil, *Progress Inorg. Chem.*, **13**, 1 (1970).

[4] E. Fremy, *Ann. Chim. Phys.*, **35**, 257 (1852).

[5] A. Werner and A. Mylius, *Z. anorg. Chem.*, **16**, 262 (1898).

[6] G. Vortmann, *Monatsh. Chem.*, **6**, 404 (1855); A. Werner, *Ann. Chem.*, **375**, 1 (1910).

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

[8] a: A. R. Gainsford and D. A. House, *Inorg. Nucl. Chem. Lett.*, **4**, 621 (1968); b: D. L. Duffy, D. A. House, and J. A. Weil, *J. Inorg. Nucl. Chem.*, **31**, 2053 (1969).

[9] Abbreviations used in this paper are as follows; en, ethylenediamine; *l*-pn, R(D)(−)D-propylenediamine; dien, diethylenetriamine; trien, triethylenetetramine; tetren, tetraethylenepentamine.

[10] S. W. Foong, J. D. Miller, and F. D. Oliver, *J. Chem. Soc.*, *A*, **1969**, 2847.

(μ-O$_2{}^{(2-)}$)Co(en)(dien)]$^{4+}$, [(en)$_2$(NH$_3$)Co(μ-O$_2{}^{(2-)}$)Co(NH$_3$)(en)$_2$]$^{4+}$ and [(trien)(NH$_3$)Co(μ-O$_2{}^{(2-)}$)Co(NH$_3$)(trien)]$^{4+}$, and gave absorption shoulders in water at 437, 420, 550, and 562 nm with extinction coefficients 619, 557, 247, and 230, respectively, We have prepared *l*-pn derivatives of the second and the third complex [(dien)(*l*-pn)Co(μ-O$_2{}^{(2-)}$)Co(*l*-pn)(dien)]$^{4+}$ and [(*l*-pn)$_2$(NH$_3$)Co(μ-O$_2{}^{(2-)}$)Co(NH$_3$)(*l*-pn)$_2$]$^{4+}$ in a similar manner, and measured the absorption spectra of all the six complexes in the region from 200 to 700 nm. All gave absorption maxima at *ca.* 300 nm in freshly prepared solutions. However, the complexes containing ammonia *i.e.* [(en)$_2$(NH$_3$)Co(μ-O$_2{}^{(2-)}$)Co(NH$_3$)(en)$_2$]$^{4+}$, [(trien)(NH$_3$)Co(μ-O$_2{}^{(2-)}$)Co(NH$_3$)(trien)]$^{4+}$ and [(*l*-pn)$_2$(NH$_3$)Co(μ-O$_2{}^{(2-)}$)Co(NH$_3$)(*l*-pn)$_2$]$^{4+}$ underwent rapid spectral change and the absorption maxima shifted to *ca.* 350 nm. The absorption pattern of the other three complexes remained unchanged as shown in Fig. 1.

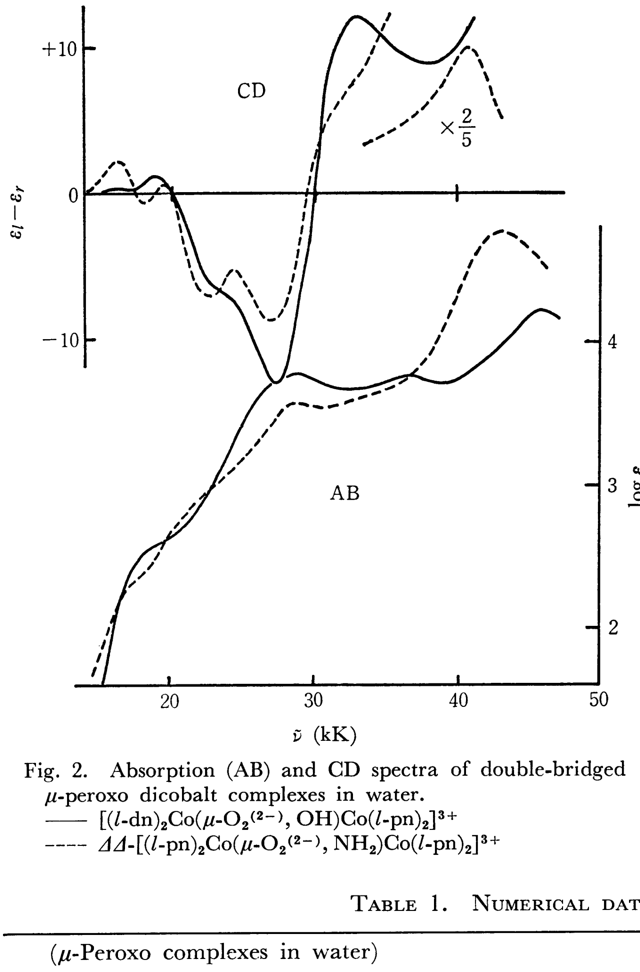

Fig. 2. Absorption (AB) and CD spectra of double-bridged μ-peroxo dicobalt complexes in water.
—— [(*l*-dn)$_2$Co(μ-O$_2{}^{(2-)}$, OH)Co(*l*-pn)$_2$]$^{3+}$
---- $\Delta\Delta$-[(*l*-pn)$_2$Co(μ-O$_2{}^{(2-)}$, NH$_2$)Co(*l*-pn)$_2$]$^{3+}$

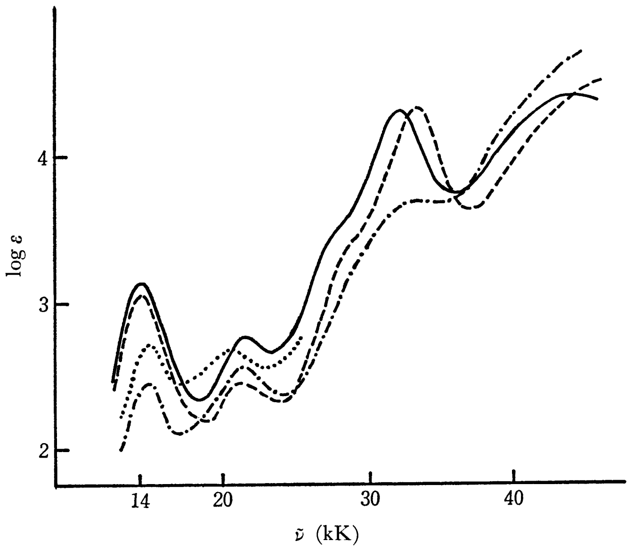

Fig. 3. Absorption spectra of several μ-superoxo dicobalt complexes in 0.01 N perchloric acid.
——— [(tetren)Co(μ-O$_2{}^{(-)}$)Co(tetren)]$^{5+}$
------ [(en)$_2$(NH$_3$)Co(μ-O$_2{}^{(-)}$)Co(NH$_3$)(en)$_2$]$^{5+}$
—·—· [(en)$_2$Co(μ-O$_2{}^{(-)}$, NH$_2$)Co(en)$_2$]$^{4+}$
········ [(en)$_2$Co(μ-O$_2{}^{(-)}$, OH)Co(en)$_2$]$^{4+}$ (approximate curve)

The double bridged complexes with peroxo and hydroxo bridges, [(*l*-pn)$_2$Co(μ-O$_2{}^{(2-)}$,OH)Co(*l*-pn)$_2$]$^{3+}$ and [(en)$_2$Co(μ-O$_2{}^{(2-)}$,OH) Co(en)$_2$]$^{3+}$ were prepared according to the method of Foong *et al.*[10] and the absorption spectra were recorded in water. They remained unchanged for more than 24 hr with maxima at *ca.* 350 nm, as seen in Figs. 1 and 2.

TABLE 1. NUMERICAL DATA OF THE ABSORPTION SPECTRUM

(μ-Peroxo complexes in water)	kK (log ε)	kK (log ε)	kK (log ε)
[(dien)(en)Co(μ-O$_2{}^{(2-)}$)Co(en)(dien)]$^{4+}$		24.0 (2.78) s	33.3 (3.98)
[(dien)(*l*-pn)Co(μ-O$_2{}^{(2-)}$)Co(*l*-pn)(dien)]$^{4+}$		24.0 (2.73) s	33.2 (4.00)
[(tetren)Co(μ-O$_2{}^{(2-)}$)Co(tetren)]$^{4+}$		24.0 (2.87) s	32.2 (4.10)
[(en)$_2$Co(μ-O$_2{}^{(2-)}$, OH)Co(en)$_2$]$^{3+}$		19.0 (2.59) s	28.0 (3.69)
[(*l*-pn)$_2$Co(μ-O$_2{}^{(2-)}$, OH)Co(*l*-pn)$_2$]$^{3+}$		19.3 (2.58) s	28.6 (3.76)
[(en)$_2$Co(μ-O$_2{}^{(2-)}$, NH$_2$)Co(en)$_2$]$^{3+}$ [a]		20 (2.6) s	29.8 (3.59)
(μ-Superoxo complexes in 0.01 N HClO$_4$)			
[(NH$_3$)$_5$Co(μ-O$_2{}^{(-)}$)Co(NH$_3$)$_5$]$^{5+}$ [a]	14.9 (2.92)	20.8 (2.43)	33.6 (4.35)
[(en)$_2$(NH$_3$)Co(μ-O$_2{}^{(-)}$)Co(NH$_3$)(en)$_2$]$^{5+}$	14.1 (3.05)	21.0 (2.48)	33.1 (4.29)
[(trien)(NH$_3$)Co(μ-O$_2{}^{(-)}$)Co(NH$_3$)(trien)]$^{5+}$	14.1 (3.11)	21.3 (2.66)	32.5 (4.29)
[(dien)(*l*-pn)Co(μ-O$_2{}^{(-)}$(Co(*l*-pn)dien)]$^{5+}$	14.0 (3.19)	21.4 (2.79)	32.6 (4.36)
[(tetren)Co(μ-O$_2{}^{(-)}$)Co(tetren)]$^{5+}$	14.1 (3.15)	21.5 (2.78)	31.9 (4.28)
[(en)$_2$Co(μ-O$_2{}^{(-)}$, OH)Co(en)$_2$]$^{4+}$	14.8 (2.72)	20.3 (2.67)	
[(*l*-pn)$_2$Co(μ-O$_2{}^{(-)}$, OH)Co(*l*-pn)$_2$]$^{4+}$	14.9 (2.71)	20.7 (2.67)	
[(en)$_2$Co(μ-O$_2{}^{(-)}$, NH$_2$)Co(en)$_2$]$^{4+}$ [a]	14.3 (2.45)	20.8 (2.50)	

s, shoulder. a) from Ref. 2a. (in water)

The spectral data of peroxo bridged complexes are summarized in Table 1. It is seen that the absorption peaks in the ultraviolet region depend on the structure of the bridging part. The single bridged μ-peroxo complexes have absorption maxima at *ca.* 300 nm, whereas the double bridged complexes, μ-peroxo-μ-hydroxo and μ-peroxo-μ-amido, at *ca.* 350 nm.

The absorption spectra of the μ-superoxo complexes corresponding to the μ-peroxo complexes are also shown in Fig. 3 and the data summarized in Table 1. Single bridged μ-superoxo complexes were isolated by the method of House *et al.* Double bridged μ-superoxo-μ-hydroxo complexes were not isolated and their approximate absorption spectra in the visible region were recorded by use of aqueous solutions of the corresponding μ-peroxo-μ-hydroxo complexes in the presence of excessive free chlorine.

The spectral pattern of these μ-superoxo complexes seems to be dependent also on the structure of the bridging part. Single bridged complexes have a distinctive absorption peak at *ca.* 300 nm. They also give absorptions at *ca.* 700 nm (log ε *ca.* 3) and *ca.* 480 nm (log ε, 2.8), the former being stronger. On the other hand, double bridged complexes give absorption peaks at *ca.* 700 and *ca.* 480 nm and their intensities are almost equal (log ε, 2.5). The absorption pattern at *ca.* 300 nm is not clear because of the presence of chlorine.

So far as the complexes given in Table 1 are concerned, the pattern of absorption spectra appears useful for discriminating the structure of the bridging part for both μ-peroxo and μ-superoxo complexes.

Lability of Coordinated Ammines and Amines. As stated previously, the absorption spectrum of $[(\text{en})_2(\text{NH}_3)\text{Co}(\mu\text{-O}_2{}^{(2-)})\text{Co}(\text{NH}_3)(\text{en})_2]^{4+}$ in water changed rapidly and became identical with that of $[(\text{en})_2\text{Co}(\mu\text{-O}_2{}^{(2-)}, \text{OH})\text{Co}(\text{en})_2]^{3+}$ prepared by the method of Foong *et al.* within 20 min at room temperature. Such a change indicates that the coordinated ammonia molecules in the single bridged μ-peroxo complexes are easily replaced by water molecules to give double bridged complexes. A similar spectral change was also observed with the corresponding *l*-pn complex. The absorption spectrum of $[(\text{trien})(\text{NH}_3)\text{Co}(\mu\text{-O}_2{}^{(2-)})\text{Co}(\text{NH}_3)(\text{trien})]^{4+}$ in water converges to a pattern with a band at 350 nm with an ε value 5760 (per one complex ion) within *ca.* 40 min, and shows an approximate isosbestic point as seen in Fig. 4. Fallab,[11] Miller and Wilkins[12] reported that $[(\text{trien})\text{Co}(\mu\text{-O}_2{}^{(2-)}, \text{OH})\text{Co}(\text{trien})]^{3+}$ showed a band at *ca.* 350 nm, although they did not isolate such species. We also examined the absorption spectrum of this double bridged complex by passing oxygen into an aqueous solution containing trien and cobalt(II) in various molar ratios. The apparent ε values at 350 nm increased with increase in the molar ratio, and approached a constant value 6800, when the ratio was more than 2. Thus it seems that $[(\text{trien})(\text{NH}_3)\text{Co}(\mu\text{-O}_2{}^{(2-)})\text{Co}(\text{NH}_3)(\text{trien})]^{3+}$ also liberates ammonia to form $[(\text{trien})\text{Co}(\mu\text{-O}_2{}^{(2-)}, \text{OH})\text{Co}(\text{trien})]^{3+}$ in water at room temperature. All these complexes have various geometrical isomers, but they cannot be distinguished by conventional absorption spectrum measurement.

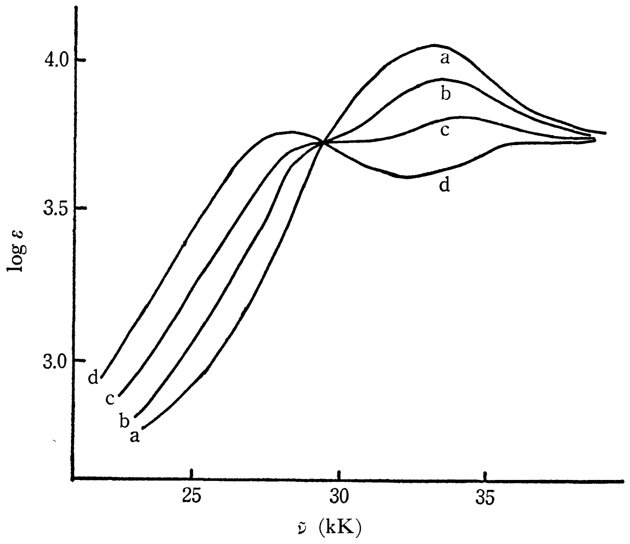

Fig. 4. Change in absorption spectrum of an aqueous solution of $[(\text{trien})(\text{NH}_3)\text{Co}(\mu\text{-O}_2{}^{(2-)})\text{Co}(\text{NH}_3)(\text{trien})]^{4+}$ at room temperature.
a : immediately b : after 5 min
c : after 15 min d : after 45 min

When a large excess of *l*-pn was added to an aqueous solution of $[(\text{dien})(\text{en})\text{Co}(\mu\text{-O}_2{}^{(2-)})\text{Co}(\text{en})(\text{dien})]^{4+}$ at room temperature, circular dichroism

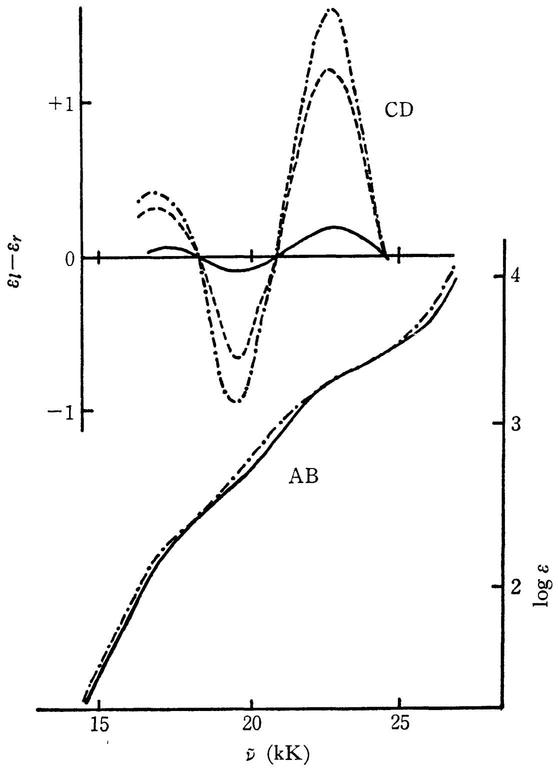

Fig. 5. Change in absorption (AB) and CD spectrum of $[(\text{dien})(\text{en})\text{Co}(\mu\text{-O}_2{}^{(2-)})\text{Co}(\text{en})(\text{dien})](\text{ClO}_4)_4$ in water containing an excess of *l*-propylenediamine.
—— after 3 hr ---- after 2 days —·—· after 5 days

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[11] S. Fallab, *Chimia*, **23**, 177 (1969); **24**, 76 (1970).

[12] F. Miller and R. G. Wilkins, *J. Amer. Chem. Soc.*, **92**, 2687 (1970).

(CD) appeared as shown in Fig. 5. The CD curve became constant after ten days, while the absorption spectrum remained almost unchanged. When an aqueous solution of synthesized $[(\text{dien})(l\text{-pn})\text{Co}(\mu\text{-O}_2{}^{(2-)})\text{Co}(l\text{-pn})(\text{dien})]^{4+}$ was treated with a large excess of en, the CD peak decreased gradually and eventually no CD was observable. These reactions are understood to be ligand substitutions of bidentate en or *l*-pn.

When *l*-pn was added to an aqueous solution of $[(\text{en})_2(\text{NH}_3)\text{Co}(\mu\text{-O}_2{}^{(2-)})\text{Co}(\text{NH}_3)(\text{en})_2]^{4+}$, the absorption and the CD spectrum changed rapidly at room temperature and became identical with those of $[(l\text{-pn})_2\text{Co}(\mu\text{-O}_2{}^{(2-)}, \text{OH})\text{Co}(l\text{-pn})_2]^{3+}$ synthesized by modified Foong *et al.*[10] within 20 min. The reaction is much faster than that of the substitution of bidentate ligands mentioned above. On the other hand, substitution of *l*-pn for en in the double bridged complex $[(\text{en})_2\text{Co}(\mu\text{-O}_2{}^{(2-)}, \text{OH})\text{Co}(\text{en})_2]^{3+}$ proceeds much slower than that in single bridged μ-peroxo complexes.

Ammonia and amines in uninuclear cobalt(III) complexes are generally believed to be substitution inert.[13] Hence all the observations mentioned above would be understood by considering that the ammonia and amines in the binuclear complexes are unusually labile. Such a lability is not significant in double bridged μ-peroxo-μ-hydroxo complexes and seems to be characteristic of single bridged μ-peroxo complexes. Such a change in lability is more marked for ammonia than for multidentate amines.

Recently Taylor and Sykes[14] reported that $[(\text{NH}_3)_4\text{Co}(\mu\text{-OH}, \text{NH}_2)\text{Co}(\text{NH}_3)_4]^{4+}$ liberates ammonia in an aqueous solution at a rate 0.46×10^{-4} sec^{-1} (half time 250 min) at 35°C. It was found that the binuclear chromium(III) complex $[(\text{NH}_3)_5\text{Cr}(\mu\text{-O})\text{Cr}(\text{NH}_3)_5]^{4+}$ (rhodochromic salt) liberates one of its ammonia molecules very rapidly at room temperature,[15] and this fact was interpreted as an effect of π-bonding character of chromium oxygen bond.

A more detailed discussion on such an unusual change in lability cannot be made because of insufficient kinetic data. However, some of the properties of binuclear μ-peroxo complexes given in literature[5,8] would be understood by considering the ligand labilising effect in μ-peroxo complexes.

Other Properties of the μ-Peroxo Complexes. All the binuclear μ-peroxo complexes can be oxidized almost quantitatively to the corresponding μ-superoxo complexes by treatment with a slightly acidic aqueous solution containing chlorine. The single bridged μ-superoxo complexes were isolated as perchlorates,[8b] but the double bridged μ-superoxo-μ-hydroxo complexes were not isolated. μ-Peroxo complexes are also oxidized with nitric acid to the corresponding μ-superoxo complexes, but the yield is low.

The μ-peroxo complexes decomposed to cobalt(II) salts in perchloric and sulfuric acid, but always gave small amounts of the μ-superoxo complexes (*ca.* 10% at most). The yield was determined by measuring the intensity of absorption bands at *ca.* 700 nm, which are characteristic of μ-superoxo complexes. When single bridged μ-peroxo complexes were treated with concentrated hydrochloric acid, uninuclear chloropentaamine type complexes were formed.[8,16] On the other hand, μ-peroxo-μ-hydroxo double bridged complexes produced *trans*-dichlorotetraammine type complexes by a similar treatment.

Optical Activity of the Complexes Containing l-Propylenediamine. The absorption and the CD spectra of $[(l\text{-pn})_2\text{Co}(\mu\text{-O}_2{}^{(2-)}, \text{OH})\ \text{Co}(l\text{-pn})_2]^{3+}$ synthesized by a modified Foong *et al.* method[10] and of $\Delta\Delta$-$[(l\text{-pn})_2\text{Co}(\mu\text{-O}_2{}^{(2-)}, \text{NH}_2)\text{Co}(l\text{-pn})_2]^{3+}$ [2a] are shown in Fig. 2. From a comparison of their well-coinciding CD curves, the μ-peroxo-μ-hydroxo complex seems to have an asymmetric center around both cobalt ions and its absolute configuration can be determined to be $\Delta\Delta$. Hence the $\Delta\Delta$-$[(l\text{-pn})_2\text{Co}(\mu\text{-O}_2{}^{(2-)}, \text{OH})\text{Co}(l\text{-pn})_2]^{3+}$ seems to be formed stereospecifically under the given conditions. The CD curve of this complex produced by the hydrolysis of $[(l\text{-pn})_2(\text{NH}_3)\text{Co}(\mu\text{-O}_2{}^{(2-)})\text{Co}(\text{NH}_3)(l\text{-pn})_2]^{4+}$ also suggests a similar stereospecific formation. Further, the $\Delta\Delta$-configuration of this complex is supported by the CD spectrum of its μ-superoxo derivative which was obtained in a slightly acidic solution containing chlorine. We discussed such a stereospecificity of $[(l\text{-pn})_2\text{Co}(\mu\text{-O}_2{}^{(2-)}, \text{NH}_2)\ \text{Co}(l\text{-pn})_2]^{3+}$ in a previous paper.[2a] The same steric regulation appears to operate in the formation of μ-peroxo-μ-hydroxo complex.

The complex $[(\text{dien})(l\text{-pn})\text{Co}(\mu\text{-O}_2{}^{(2-)})\text{Co}(l\text{-pn})(\text{dien})]^{4+}$ prepared by the method of House *et al.* gives a CD spectrum in water as shown in Fig. 6. The CD changes as indicated and becomes constant

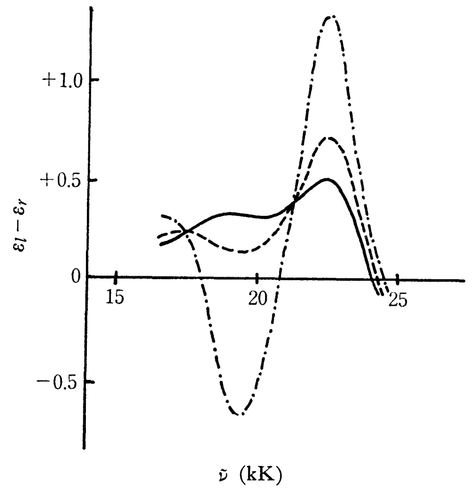

Fig. 6. Change in CD spectrum of an aqueous solution of $[(\text{dien})(l\text{-pn})\text{Co}(\mu\text{-O}_2{}^{(2-)})\text{Co}(l\text{-pn})(\text{dien})]^{4+}$ (see text)
—— immediately after solution
---- after 3 hr —·—· after 2 days

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[13] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd Ed., John Wiley and Sons, New York (1967).

[14] R. S. Taylor and A. G. Sykes, *J. Chem. Soc., A*, **1970**, 1991.

[15] W. K. Wilmarth, H. Graff, and S. T. Gustin, *J. Amer. Chem. Soc.*, **78**, 2683 (1956).

[16] A. R. Gainsford and D. A. House, *Inorg. Chim. Acta*, **3**, 33, 367 (1969).

TABLE 2. ELEMENTARY ANALYSIS OF THE COMPLEXES

Formulae		C	H	N
$[(en)_2NH_3Co(\mu\text{-}O_2^{(2-)})CoNH_3(en)_2](ClO_4)_4$	Found	12.17	4.53	17.02
$C_8H_{38}N_{10}O_{18}Cl_4Co_2$	Calcd	11.68	4.65	17.04
$[(l\text{-}pn)_2NH_3Co(\mu\text{-}O_2^{(2-)})CoNH_3(l\text{-}pn)_2](ClO_4)_4$	Found	16.52	5.81	15.98
$C_{12}H_{46}N_{10}O_{18}Cl_4Co_2$	Calcd	16.41	5.28	15.95
$[(trien)NH_3Co(\mu\text{-}O_2^{(2-)})CoNH_3(trien)](ClO_4)_4$	Found	16.47	4.95	15.81
$C_{12}H_{42}N_{10}O_{18}Cl_4Co_2$	Calcd	16.49	4.84	16.02
$[(dien)(en)Co(\mu\text{-}O_2^{(2-)})Co(en)dien)](ClO_4)_4$	Found	16.53	5.21	16.18
$C_{12}H_{42}N_{10}O_{18}Cl_4Co_2$	Calcd	16.49	4.84	16.02
$[dien(l\text{-}pn)Co(\mu\text{-}O_2^{(2-)})Co(l\text{-}pn)dien](ClO_4)_4\cdot 5H_2O$	Found	16.89	5.01	15.11
$C_{14}H_{56}N_{10}O_{23}Cl_4Co_2$	Calcd	16.96	5.68	14.12
$[(tetren)Co(\mu\text{-}O_2^{(2-)})Co(tetren)](ClO_4)_4$	Found	20.84	5.51	14.98
$C_{16}H_{46}N_{10}O_{18}Cl_4Co_2$	Calcd	20.75	5.01	15.12
$[(en)_2Co(\mu\text{-}O_2^{(2-)}, OH)Co(en)_2](ClO_4)_3$	Found	13.66	4.63	15.77
$C_8H_{33}N_8O_{15}Cl_3Co_2$	Calcd	13.62	4.71	15.88
$[(l\text{-}pn)_2Co(\mu\text{-}O_2^{(2-)}, OH)Co(l\text{-}pn)_2](ClO_4)_3$	Found	18.37	5.35	14.81
$C_{12}H_{41}N_8O_{15}Cl_3Co_2$	Calcd	18.92	5.43	14.70
$[(en)_2NH_3Co(\mu\text{-}O_2^{(-)})CoNH_3(en)_2](ClO_4)_5$	Found	10.75	4.46	15.50
$C_8H_{38}N_{10}O_{22}Cl_5Co_2$	Calcd	10.43	4.16	15.20
$[(trien)NH_3Co(\mu\text{-}O_2^{(-)})CoNH_3(trien)](ClO_4)_5\cdot H_2O$	Found	14.73	4.80	13.91
$C_{12}H_{44}N_{10}O_{23}Cl_5Co_2$	Calcd	14.54	4.88	14.12
$[(dien)(l\text{-}pn)Co(\mu\text{-}O_2^{(-)})Co(l\text{-}pn)(dien)](ClO_4)_5$	Found	17.26	5.14	13.78
$C_{14}H_{46}N_{10}O_{22}Cl_5Co_2$	Calcd	16.79	4.63	13.98
$[(tetren)Co(\mu\text{-}O_2^{(-)}Co(tetren)](ClO_4)_5\cdot 2H_2O$	Found	18.04	5.08	12.89
$C_{16}H_{50}N_{10}O_{24}Cl_5Co_2$	Calcd	18.10	4.75	13.19

after *ca.* 2 days at room temperature. The final spectrum is identical with the final pattern (broken line with dot) in Fig. 5, which was formed by the reaction of *l*-pn with $[(dien)(en)Co(\mu\text{-}O_2^{(2-)})Co(en)(dien)]^{4+}$. This μ-peroxo complex can have various geometrical and diastereomeric isomers according to varying chelation of the bi- and terdentate ligand. They have all N_5O type coordination, and change in absorption spectra is not always expected among the isomers. No change in absorption pattern does not deny isomeric change of the complex. It appears, however, that the crystalline $[(dien)(l\text{-}pn)Co(\mu\text{-}O_2^{(2-)})Co(l\text{-}pn)(dien)]^{4+}$ obtained (see Experimental) has different isomeric composition from its most stable form in aqueous solution, and the CD change in Fig. 6 can be understood as due to some kind of rearrangement in the binuclear complex.

The intensity of CD is of the order of $\Delta\varepsilon = ca. +1.3$ which can be accounted for by either vicinal effect coming from *l*-pn, or by asymmetric configuration in this complex. Apparently the CD indicates some kind of inversion with lapse of time, and this fact may support stereoselective coordination of the ligand. However, the band assignment in this complex still remains uncertain, and nothing decisive as to whether the optically active ligand exhibits stereoselectivity in such a single bridged complex or not can be stated at the present stage.

Experimental

Preparation of the Complexes. The preparation methods of all the complexes are essentially the same as those given in literature.[8,10] The results of elementary analysis are summarized in Table 2.

1) $[(en)_2(NH_3)Co(\mu\text{-}O_2^{(2-)})Co(NH_3)(en)_2](ClO_4)_4$ *and* $[(trien)(NH_3)Co(\mu\text{-}O_2^{2-})Co(NH_3)(trien)](ClO_4)_4$*:* These complexes were prepared by the method of House *et al.*[8] involving substitution of en and trien for ammonias of $[(NH_3)_5Co(\mu\text{-}O_2^{(2-)})Co(NH_3)_5]^{4+}$. They were also prepared directly as follows; cobalt(II) nitrate hexahydrate (2.9 g) and sodium perchlorate (10 g) were dissolved in water (10 m*l*), mixed with ethylenediamine hydrate (2 g) or trien (2 g) in concentrated aqueous ammonia solution (30 m*l*) and bubbled with air for *ca.* 30 min. The brown precipitate was washed with ethanol and ether and air dried (yield *ca.* 3 and 2.5 g, respectively).

2) $[(l\text{-}pn)(dien)Co(\mu\text{-}O_2^{(2-)})Co(dien)(l\text{-}pn)](ClO_4)_4$*:* Cobalt(II) nitrate hexahydrate (2.9 g) and sodium perchlorate (10 g) were dissolved in water (10 m*l*), treated with dihydrochloride of *l*-pn (3 g), dien (1 g) and sodium hydroxide (1.6 g) in water (20 m*l*), and bubbled with air for *ca.* 30 min. The brown precipitate was similarly washed and dried (yield *ca.* 3 g).

3) $[(l\text{-}pn)_2(NH_3)Co(\mu\text{-}O_2^{(2-)})Co(NH_3)(l\text{-}pn)](ClO_4)_4$*:* $[(NH_3)_5Co(\mu\text{-}O_2^{(2-)})Co(NH_3)_5](NO_3)_4\cdot 2H_2O$[5] (1.3 g) was added to a solution of dihydrochloride of *l*-pn (1.5 g), sodium hydroxide (0.8 g) and sodium perchlorate (1.5 g) in water (7.5 m*l*) under constant passage of air. A brown precipitate was formed after 30 min, which was washed and dried in a similar way (yield 0.9 g).

4) $[(dien)(l\text{-}pn)Co(\mu\text{-}O_2^{(-)})Co(l\text{-}pn)(dien)](ClO_4)_5$*:* Crude $[(dien)(l\text{-}pn)Co(\mu\text{-}O_2^{(2-)})Co(l\text{-}pn)(dien)](NO_3)_4$ was prepared by a similar method to the perchlorate[6] without sodium perchlorate. The brown nitrate was collected after 5 days. This salt (0.6 g) was added to a solution of concentrated hydrochloric acid (1.5 m*l*) and zinc chloride dihydrate (2.5 g) in water (3 m*l*), warmed at 80°C for 30 min and cooled to room temperature. It appears that the peroxo bridge was oxidized to superoxo in the hydrochloric acid solution by the nitrate and precipitated as tetrachlorozincate. The green powder was washed with ethanol, dissolved in a small amount of water containing a trace of nitric acid, and treated with a saturated sodium perchlorate solution. The green crystals were washed with ethanol and ether and air dried (yield 0.4 g).

5) $[(\mathrm{l}\text{-}pn)_2Co(\mu\text{-}O_2{}^{(2-)}, OH)Co(\mathrm{l}\text{-}pn)_2](ClO_4)_3$: Cobalt(II) perchlorate (2.4 g) was dissolved in water (10 m*l*) and mixed with *l*-pn (1.5 g) in ethanol (10 m*l*) and water (30 m*l*). Oxygen was passed through this solution for *ca.* 30 min. Yellow crystals precipitated initially dissolved during the course of bubbling. The solution was filtered and kept in a refrigerator for a day. The dark brown crystals were washed with ethanol and ether and air dried (yield *ca.* 1 g).

Propylenediamine was resolved by Dwyer's method.[17]

Measurements. The absorption and the circular dichroism spectra were recorded with a Hitachi 124 double beam recording spectrophotometer and Jasco ORD/UV-5 spectrophotometer with appropriate accessories, respectively.

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[17] E. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, **81**, 2955 (1959).