

Dinuclear Cobalt(II) Complexes Containing 1,3-(or 1,5-)Bis[bis-(2-pyridylmethyl)amino]-2-propanolato (or -3-pentanolato): Preparation and Reaction with Molecular Oxygen

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Two dinuclear cobalt(II,II) complexes, $[\text{Co}_2(\text{tpdp})(\text{CH}_3\text{COO})](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ (**1**) and $[\text{Co}_2(\text{tmdp})(\text{CH}_3\text{COO})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**2**), were prepared, where Htpdp and Htmdp are 1,3-bis[bis(2-pyridylmethyl)amino]-2-propanol and 1,5-bis[bis(2-pyridylmethyl)amino]-3-pentanol respectively. Their electronic spectral and magnetic data revealed that **1** and **2** are five-coordinate in the high-spin state, in the same manner as $[\text{Co}_2(\text{bpmp})(\text{CH}_3\text{COO})]^{2+}$ (**3**) (Hbpmp=2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol). The complexes reacted with molecular oxygen to form μ -peroxo complexes in dichloromethane and acetonitrile. The oxygen affinity of the complexes decreased in the order of **3** > **2** > **1**. The relationships between the oxygen affinities and (1) the donor abilities of dinucleating ligands, (2) the energies of the charge-transfer bands (O_2^{2-} to Co^{3+}) of the μ -peroxo complexes, and (3) the redox potentials of the $\text{Co}^{3+}-\text{O}_2^- - \text{Co}^{3+}/\text{Co}^{3+}-\text{O}_2^{2-} - \text{Co}^{3+}$ couple indicated that a steric effect arising from the dinucleating ligands contributes significantly to the oxygen affinities of the complexes.

Dinuclear metal complexes with sterically and electronically controlled environment are expected to bind molecular oxygen reversibly. In the previous studies, we demonstrated that the dinuclear cobalt(II,II) complex with a dinucleating ligand bpmp, $[\text{Co}_2(\text{bpmp})(\text{CH}_3\text{COO})]^{2+}$, reacts reversibly with molecular oxygen to form a μ -peroxo complex $[\text{Co}_2(\text{bpmp})(\text{CH}_3\text{COO})(\text{O}_2)]^{2+}$,¹⁾ where Hbpmp is 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol (Fig. 1c). This complex was thermodynamically and thermally very stable both in a solid and in solution: $P(\text{O}_2)_{1/2}$ was less than 0.1 Torr (1 Torr $\approx$ 133.322 Pa) in acetonitrile at 20°C. The complex also showed an excellent reversibility toward oxygen binding. Such stability may stem from the geometry and the donor properties of bpmp. As an extension of our previous studies, here we will report on the preparation and oxygenation of dinuclear cobalt(II,II)

complexes containing two dinucleating ligands, tpdp and tmdp, where Htpdp and Htmdp are 1,3-bis[bis(2-pyridylmethyl)amino]-2-propanol and 1,5-bis[bis(2-pyridylmethyl)amino]-3-pentanol respectively (Fig. 1a and b).

Experimental

Preparation of the Dinucleating Ligands. Htpdp: To a cold solution of 1,3-diamino-2-propanol dihydrochloride (7.5 g, 0.046 mmol) and 2-pyridinecarbaldehyde (22.5 g, 0.21 mmol) in 250 cm³ of methanol was dropwise added sodium cyanotrihydroborate (8.68 g, 0.138 mmol) with stirring. The solution was then stirred for two days at room temperature, subsequently acidified by the addition of concentrated hydrochloric acid, and evaporated almost to dryness under a reduced pressure. The residue was taken up in 100 cm³ of 0.1 mol dm⁻³ of NaOH and extracted with three 30-cm³ of portions of chloroform. The combined extracts were dried over Na_2SO_4 and evaporated under reduced pressure to give an oily product, which was then partly purified by passing it through a silica gel column with methanol as the eluent.

Htmdp: This was prepared in a way similar to that used for the Htpdp, but by using 1,5-diamino-3-propanol dihydrochloride^{2,3)} instead of 1,3-diamino-2-propanol dihydrochloride.

Hbpmp: This was prepared as has previously been described.^{1a)}

Preparation of Complexes. For the preparation of the tmdp and bpmp complexes, all the manipulations were carried out under an argon atmosphere using a Schlenk apparatus and a glovebag.

$[\text{Co}_2(\text{tpdp})(\text{CH}_3\text{COO})](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ (1**):** To a solution of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (1 mmol) and Htpdp (0.5 mmol) in 20 cm³ of methanol was added a solution of triethylamine (0.5 mmol) and NaClO_4 (3 mmol) in 10 cm³ of methanol with stirring. After filtration, the violet solution was allowed to stand overnight. The violet crystals which were thus formed were collected by filtration, washed with methanol and ether, and air-dried.

$[\text{Co}_2(\text{tmdp})(\text{CH}_3\text{COO})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (2**):** To a solution

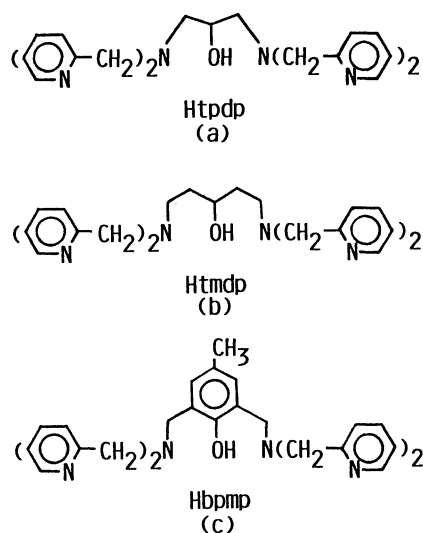


Fig. 1. Dinucleating ligands.

of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (1 mmol) and Htmdp (0.5 mmol) in 20 cm³ of methanol was added a solution of triethylamine (0.5 mmol) and NaClO_4 (2 mmol) in 20 cm³ of methanol. The resulting violet solution was concentrated to ca. 20 cm³ under a reduced pressure and then allowed to stand overnight. The violet crystals thus formed were collected by filtration, washed with methanol and ether, and dried in vacuo. The complex was air-sensitive and formed a brown compound when exposed to the air.

[Co(tmdp)(CH₃COO)(O₂)](BPh₄)₂ · 2H₂O (2a): Complex **2** (0.5 mmol) was dissolved in 5 cm³ of acetonitrile in air to give a brown solution, to which was added NaBPh₄ (2 mmol). To the resulting brown solution was added 5 cm³ of methanol in small portions to give a brown powder, which was collected by filtration, washed with methanol and ether, and air-dried.

[Co₂(bpmp)(CH₃COO)](ClO₄)₂ (3) and [Co₂(bpmp)(CH₃COO)(O₂)](ClO₄)₂ · 2H₂O (3a): The complexes were prepared in the way described previously.^{1c)}

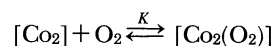
[Co₂(tmdp)Cl](ClO₄)₂ · 0.5CH₃OH (4): To a solution of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol), Htmdp (0.5 mmol), and LiCl (1 mmol) in 20 cm³ of methanol was added a solution of triethylamine (0.5 mmol) in 5 cm³ of methanol with stirring. The resulting solution was allowed to stand overnight to give violet crystals, which were collected by filtration, washed with methanol and ether, and dried in vacuo. The dried complex was stable in air. The presence of methanol was confirmed by ¹H NMR.

[Co₃(tmdp)Br](ClO₄)₂ (5): The complex was prepared in a way similar to that used for **4** except that (Bu₄N)Br was used instead of LiCl.

Measurements. The electronic spectra were measured on a JASCO UVIDECD 505 UV/VIS recording digital spectrophotometer and a Hitachi U-3400 spectrophotometer. The infrared spectra were obtained by the KBr-disk and the Nujol mull methods with a JASCO A-3 infrared spectrophotometer. The magnetic susceptibilities were measured with a Shimadzu torsion magnetometer MB-2 which was calibrated with Hg[Co(NCS)₄]. Diamagnetic correction was made by using Pascal's constant.⁴⁾ Cyclic voltammograms were obtained with a Hokuto Denko HA-301 potentiostat/galvanostat and a Hokuto Denko HB-104 function generator by using a three-electrode configuration, including a glassy carbon working electrode, a platinum-coil auxiliary electrode, and a saturated calomel electrode as the reference electrode. Acetonitrile was used as the solvent, and tetra-

butylammonium perchlorate, as the supporting electrolyte. Ferrocene was added for an internal check of the redox potential and the reversibility. The $E_{1/2}$ value of ferrocene was 0.39 mV vs. SCE with a peak-to-peak separation ($\Delta E = 70$ mV). Constant-potential electrolyses were performed with a Hokuto Denko HA-301 Potentiostat/Galvanostat by using a two compartmental H-type cell separated by a polypropylene film (JURAGUARD-2500), the cell was equipped with a platinum gauze working electrode, a platinum plate auxiliary electrode, and a saturated calomel electrode. The integration of the current was carried out by integrating the area of the current vs. time curve. The ESR spectra were measured on a JEOL JES-PE3X ESR spectrometer. The molar conductivities were measured at 25 °C in acetonitrile (1×10^{-3} mol dm⁻³) with a TOA CM-20S conductivity meter. In the case of **2**, the conductivity of the oxygenated complex was measured.

Oxygen-Uptake Measurement. The equilibrium constant (K) of **1** for the following reaction



was determined by spectrophotometric titration at -15.6 °C in acetonitrile. Nitrogen gases containing oxygen of various partial pressures, obtained with Koflac Model GM-3A gas mixing apparatus, were passed into an acetonitrile solution in a quartz cell (1-cm path length). The temperature was controlled with a Neslab Model RTE-8 constant temperature circulation pump.

The equilibrium constant (K) was calculated by the use of the following equation: $P(\text{O}_2) = C \cdot P(\text{O}_2)/\Delta A - K^{-1}$, where $P(\text{O}_2)$ is the partial pressure of O₂, ΔA is the difference in the absorbances of the solution at $P(\text{O}_2)$ and $P(\text{O}_2) = 0$ Torr, and C is a constant. The plot of $P(\text{O}_2)$ vs. $P(\text{O}_2)/\Delta A$ gave a straight line, indicating a 1:1 (complex: O₂) stoichiometry for the oxygenation.

In the case of **2**, an accurate K value could not be determined because of its high oxygen affinity and its degradation in acetonitrile and dichloromethane.

Results and Discussion

Characterization of Complexes. Complexes **1** and **2** contain one acetato group. It has been shown that the $\Delta\tilde{\nu}(\text{COO}^-)$ value ($\tilde{\nu}_{\text{asym}}(\text{COO}^-) - \tilde{\nu}_{\text{sym}}(\text{COO}^-)$) of the acetato group is a useful diagnostic tool for elucidating the coordination mode of carboxylato groups;

Table 1. Analytical Data, Molar Conductivities, and Effective Magnetic Moments

Complex	Found (Calcd) (%)			$\Lambda/\Omega^{-1} \text{ cm}^2 \text{ dm}^{-3}$	$\mu_{\text{eff}}/\text{BM}^{\text{a})}$
	C	H	N		
1 [Co ₂ (tpdp)(CH ₃ COO)](ClO ₄) ₂ · 0.5H ₂ O	41.57 (41.53)	4.03 (3.97)	10.22 (10.02)	303	3.86
2 [Co ₂ (tmdp)(CH ₃ COO)](ClO ₄) ₂ · H ₂ O	42.21 (42.53)	4.61 (4.37)	9.59 (9.60)	301 ^{b)}	3.49
2a [Co ₂ (tmdp)(CH ₃ COO)(O ₂)](BPh ₄) ₂ · 2H ₂ O	69.59 (69.51)	5.63 (5.91)	6.28 (6.16)		0.60
4 [Co ₂ (tmdp)Cl](ClO ₄) ₂ · 0.5CH ₃ OH	41.65 (41.69)	4.40 (4.15)	9.87 (9.89)	294	
5 [Co ₂ (tmdp)Br](ClO ₄) ₂	39.17 (39.66)	3.70 (3.79)	9.68 (9.57)	274	3.80

a) μ_{eff} per cobalt(II) ion at room temperature. b) Measured under an O₂ atmosphere.

a symmetrically bridging carboxylato group gives a $\Delta\tilde{\nu}$ value smaller than 200 cm^{-1} .⁵⁾ The $\Delta\tilde{\nu}$ values of **1** and **2** were in the range of $100\text{--}150\text{ cm}^{-1}$, indicating that the acetato groups function as bridging ligands. Judging from the dinucleating nature of the present ligands as well as the conductivity data and elemental analyses (Table 1), both complexes seem to have a dinuclear structure, with an alkoxo bridge of tdp or tmdp and an acetato bridge. Such a dinuclear unit has been found for various transition metal complexes with tdp⁶⁾ and such related dinucleating ligands as 1,3-bis[bis(2-benzimidazolylmethyl)amino]-2-propanolato.^{7,8)}

The effective magnetic moments of one cobalt(II) ion in **1** and **2** are 3.86 and 3.49 BM/Co respectively at room temperature, suggesting that cobalt(II) ions are in the high-spin state. The electronic spectra of **1** and **2** in acetonitrile are shown in Fig. 2, together with those of **4** and **5**. Both complexes show several d-d bands in the visible and near infrared regions. In general, five-coordinate cobalt(II) complexes exhibit several d-d bands in the $5000\text{--}25000\text{ cm}^{-1}$ range.⁹⁾ Thus, the electronic spectra in the figure indicate that **1** and **2** have a five-coordinate structure. A possible structure is illustrated in Fig. 3a.

Complex **2a** was obtained from an acetonitrile solution of **2** under an O_2 atmosphere by the addition of

NaBPh_4 and methanol. The complex is essentially diamagnetic (0.6 BM at room temperature) and has an intense absorption band at ca. 25000 cm^{-1} ($\epsilon=5750\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$) in dichloromethane which is characteristic of μ -peroxo cobalt complexes.¹⁰⁾ The intense absorption band at ca. 25000 cm^{-1} can be assigned to the charge-transfer transition from the π^* orbital of O_2^{2-} to the d_{z^2} orbital of Co^{3+} (LMCT).¹⁰⁾ That the complex has a μ -peroxo group is also supported by the ESR spectral change before and after the complex is electrochemically oxidized.

The results of the elemental analyses and the conductivity data of **4** and **5** suggest the coordination of the chloride and bromide ions respectively. The magnetic data (Table 1) and electronic spectra (Fig. 2) indicate that the cobalt(II) ions in the complexes are five-coordinate in the high-spin state. Although the structures of these complexes are not clear, it is possible that the chloride and bromide ions function as bridging ligands, as shown in Fig. 3a. The complexes have no reactivity with O_2 in the solid state, but gradually react with O_2 in solution to give a brown color. The electronic spectra of the oxidized compounds have no intense band in the visible and the near UV regions, implying that they do not form μ -peroxo complexes.

Oxygenation Reaction. Since all the oxygenated complexes have an intense brown color, the oxygenation can be monitored spectrophotometrically. Complex **1** did not react with O_2 either in a solid and in a solution at room temperature. However, upon exposure to O_2 at 0°C , a color change in an acetonitrile solution was observed from the original violet to brown; the brown color was then restored to the original violet color by bubbling argon gas. Figure 4 shows the spectral change of **1** at various partial oxygen pressures ($P(\text{O}_2)$) in acetonitrile at -15.6°C . The equilibrium constant (K) and $P_{1/2}(\text{O}_2)$ value

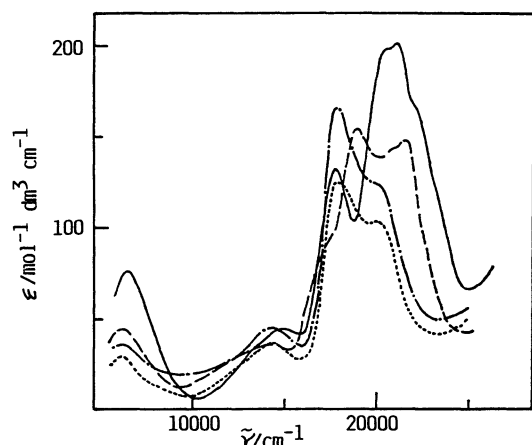


Fig. 2. Electronic spectra of **1** ($[\text{Co}_2(\text{tpdp})(\text{CH}_3\text{COO})]^{2+}$) (—), **2** ($[\text{Co}_2(\text{tmdp})(\text{CH}_3\text{COO})]^{2+}$) (---), **4** ($[\text{Co}_2(\text{tmdp})\text{Cl}]^{2+}$) (.....), and **5** ($[\text{Co}_2(\text{tmdp})\text{Br}]^{2+}$) (— · —) in acetonitrile.

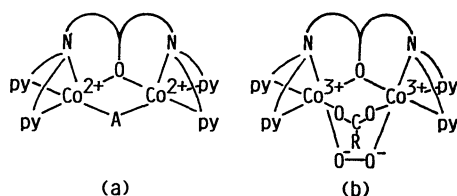


Fig. 3. Possible structures of dinuclear cobalt complexes.

A: CH_3COO^- , Cl^- , or Br^- .

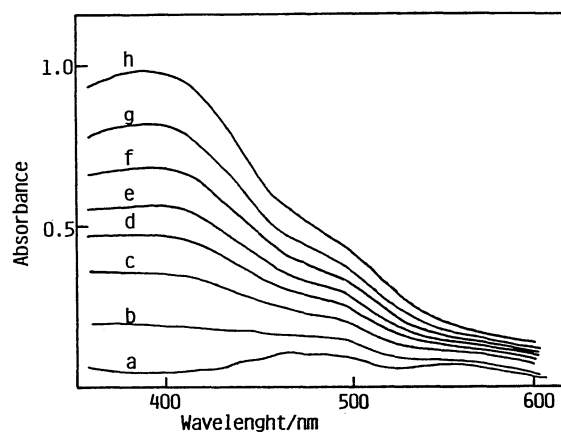


Fig. 4. Spectral change of **1** ($[\text{Co}_2(\text{tpdp})(\text{CH}_3\text{COO})]^{2+}$) at various oxygen pressures in acetonitrile at -15.2°C . Spectra of a—h are at the partial oxygen pressures: 0, 68, 149, 213, 280, 373, 497, and 756 Torr, respectively.

obtained were 1.28×10^{-2} Torr $^{-1}$ and 780 Torr respectively, where $P_{1/2}(\text{O}_2)$ represents the partial oxygen pressure at which 50% of the complex is oxygenated.

On the other hand, Complex **2** gradually changed in color from violet to brown upon exposure to O_2 in the solid state with a decrease in the magnetic moment. The complex instantaneously reacted with O_2 in acetonitrile or dichloromethane to give a brown solution, whose electronic spectrum is identical with that of Complex **2a**. Figure 5 shows the spectral change in **2** at various oxygen pressures in dichloromethane at 20°C. As may be seen from the figure, one cycle of oxygenation-deoxygenation in dichloromethane is almost reversible. The deoxygenation by bubbling Ar gas at room temperature was extremely slow, whereas it was much accelerated by boiling the solution under an Ar atmosphere. As has been mentioned above, the oxygenated complex has an intense LMCT band at ca. 25000 cm^{-1} . This LMCT band gradually decreased upon repeats of oxygenation-deoxygenation cycles or on prolonged standing (for several days) and finally disappeared as shown in Fig. 5e. Thus, the complex may undergo some type of oxidative degradation as found for many cobalt-oxygen complexes. Although the $P_{1/2}(\text{O}_2)$ of the complex could not be determined accurately because of its high-oxygen affinity and degradation, $P_{1/2}(\text{O}_2)$ was estimated roughly from Fig. 5 to be ca. 3 Torr.

Electrochemistry. Cyclic voltammograms (CV) of **3** and **3a** in acetonitrile at 20°C are shown in Fig. 6. The oxygenated complex **3a** exhibits a reversible

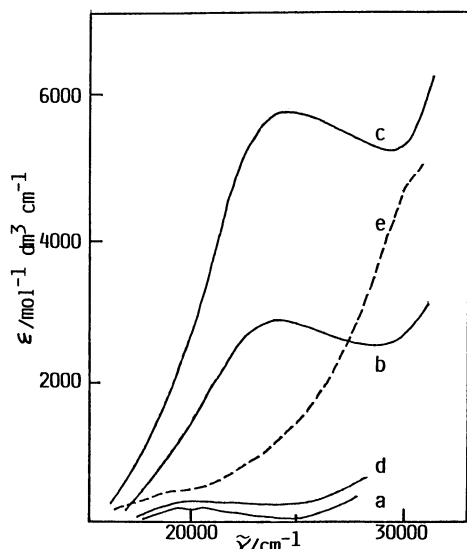


Fig. 5. Spectral change of **2** ($[\text{Co}_2(\text{tmdp})(\text{CH}_3\text{COO})]^{2+}$) at various oxygen pressures in dichloromethane at 20°C. The spectra of a–c are at the partial oxygen pressures: 0, 3, 700 Torr, respectively. The spectrum d is at 0 Torr after one oxygenation-deoxygenation cycle. The spectrum e is the one measured under the air after standing the oxygenated solution for 4 days (----).

redox couple at 0.93 V vs. SCE. The constant potential coulometry revealed that the redox couple corresponds to a one-electron transfer (1.05 electron for the oxidation at 1.05 V vs. SCE). The CV's of all the complexes were measured at -42°C in acetonitrile, since Complex **1** did not form the oxygen complex at higher temperature. All the complexes exhibited a reversible redox couple at from 0.76 to 0.89 V vs. SCE (Table 2).

ESR Spectra. In order to confirm the formation of μ -peroxo complexes for **1** and **2**, we measured the ESR spectra of the electrochemically oxidized forms of the oxygenated complexes (Fig. 7). The oxygenated complex **1** has no ESR signal, whereas the electrochemically oxidized form shows a signal at $g \approx 2$ with a slight anisotropy ($g_{\parallel} = 2.09$ and $g_{\perp} = 2.00$) at the temperature of liquid N_2 . More than 13 hyperfine lines ($A_{\parallel} = 20$ gauss) due to the ^{59}Co nuclei ($I = 7/2$) are observed in the $g_{\parallel}$ region. Such a small g -anisotropy and a small A value indicate the formation of the O_2^-

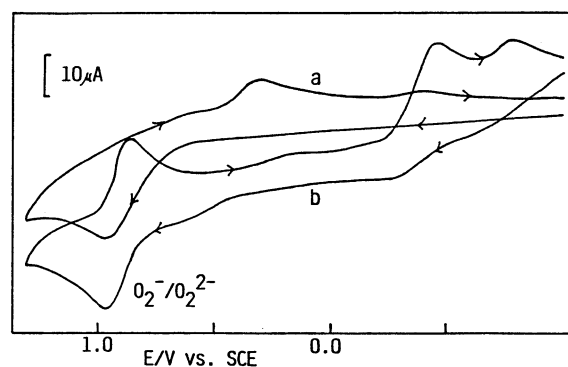


Fig. 6. Cyclic voltammograms of **3** ($[\text{Co}_2(\text{bpm})-(\text{CH}_3\text{COO})]^{2+}$) (a) and **3a** ($[\text{Co}_2(\text{bpm})(\text{CH}_3\text{COO})(\text{O}_2)]^{2+}$) (b) in acetonitrile (0.1 mol dm^{-3} tetrabutylammonium perchlorate) at a glassy carbon electrode at scan rate of 100 mV s^{-1} .

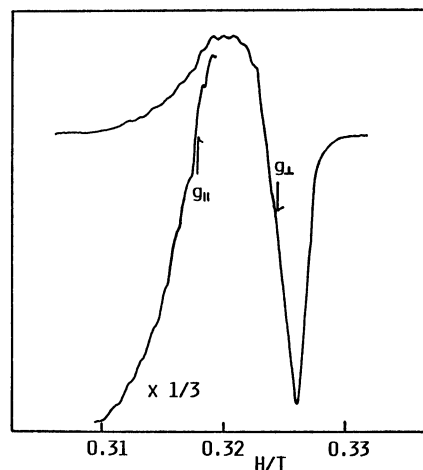


Fig. 7. ESR spectrum of the electrochemically oxidized form of the oxygenated complex **1** ($[\text{Co}_2(\text{tpdp})(\text{CH}_3\text{COO})(\text{O}_2)]^{2+}$) in acetonitrile at liquid N_2 temperature.

ion. In addition, the appearance of at least 13 hyperfine lines implies that an unpaired-electron on O_2^- couples with two ^{59}Co nuclei ($\text{Co}^{3+}-O_2^--\text{Co}^{3+}$). The ESR spectra of the oxidized forms of **2a** and **3a** were almost identical with that of the electrochemically oxidized form of the oxygenated complex **1**.

Oxygen Affinity. The oxygen affinity of cobalt(II) complexes has been shown to correlate with the electron-donor ability of the ligand which influences the electron density on a cobalt center: the stronger the electron-donor ability of the ligands, the greater the electron density on the cobalt center, and the higher the oxygen affinity.^{11,12} The oxygen affinities of **1**, **2**, and **3** were highly dependent on the kinds of dinucleating ligands; the order of their oxygen affinities was **3**>**2**>**1**. The order of the electron-donor abilities of the ligands may be estimated by comparing the donor atoms and the chelate-ring sizes of the ligands. Although tdpdp, tmdp, and bpmp have the same donor set (N_6O), they are basically different in that: (1) tdpdp and tmdp have a bridging alkoxo group, whereas bpmp has a bridging phenolato group, and (2) tdpdp forms only 5-membered chelate rings, while tmdp and bpmp form four 5-membered plus two 6-membered chelate rings. It is apparent that the bridging alkoxo group is a stronger base (stronger electron donor) than the bridging phenolato group. It has been reported that the chelate-ring size also has a significant effect on the electron-donor ability: the electron-donor ability of a 5-membered chelate ring is greater than that of a 6-membered chelate ring with the same donor set.^{10,13,14} Thus, the order of the electron-donor abilities of the present dinucleating ligands is presumed to be tdpdp>tmdp>bpmp. In fact, this order is proved to be valid by comparing the $\tilde{\nu}_{\text{max}}$ LMCT values or the redox potentials of $\text{Co}^{3+}-O_2^--\text{Co}^{3+}/\text{Co}^{3+}-O_2^--\text{Co}^{3+}$ (μ -hyperoxo/ μ -peroxo) of three μ -peroxo complexes (Table 2). A linear correlation has been found between the oxygen affinities of the cobalt(II) complexes and the $\tilde{\nu}_{\text{max}}$ LMCT values of their μ -peroxo complexes; namely, the stronger the donor ability of a ligand, the larger the $\tilde{\nu}_{\text{max}}$ LMCT value and the greater the oxygen affinity.^{12,14} In addition, further correlations have been found between the oxygen affinities and the redox potentials of $\text{Co}^{3+}/\text{Co}^{2+}$ of the original Co(II) complexes and between the oxygen affinities and the redox potentials

of $\text{Co}^{3+}-O_2^--\text{Co}^{3+}/\text{Co}^{2+}-O_2^--\text{Co}^{2+}$ (and/or $\text{Co}^{3+}-O_2^--\text{Co}^{2+}$) of their μ -peroxo complexes.^{11,12,15} Unfortunately, for the present dinuclear complexes, the redox potentials of $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Co}^{3+}-O_2^--\text{Co}^{3+}/\text{Co}^{2+}-O_2^--\text{Co}^{2+}$ (and/or $\text{Co}^{3+}-O_2^--\text{Co}^{2+}$) could not be determined by cyclic voltammetry because of their irreversible behavior. The redox potentials of $\text{Co}^{3+}-O_2^--\text{Co}^{3+}/\text{Co}^{3+}-O_2^--\text{Co}^{3+}$ were, however, determined. The redox potentials of μ -hyperoxo/ μ -peroxo may be expected to be a measure of the electron density on O_2^- , which may depend on the electron donor ability of the ligand. A stronger electron donor should promote the electron transfer from Co(II) to O_2 , resulting in a negative shift of the redox potential of μ -hyperoxo/ μ -peroxo. The data are in line with the above order of the electron-donor abilities of ligands. However, the situation is reversed for the observed order of the oxygen affinity of the present dinuclear complexes, for which other effects (e.g. the stereochemical effect) than the effect of the electron-donor abilities must be taken into account.

For the present type of μ -peroxo complexes, it is important that the two cobalt(II) ions held by bridging phenolato or alkoxo and bridging acetato groups are in a suitable position for O_2 binding. An X-ray analysis of **3a** containing 6-membered chelate rings in the bridging moiety showed that the distance between two Co atoms is 3.15 Å.^{1b)} The structures of the tetranuclear manganese complex of tdpdp and the tetranuclear iron complexes of the related dinucleating ligands which have a dinuclear unit with 5-membered chelate rings in the bridging moiety reveal that the distance between two metal atoms are longer than 3.5 Å; in some cases, coordination geometries are not suitable for the formation of a μ -peroxo bridge along with the acetato bridge.⁶⁻⁸⁾ In the case of the cobalt tdpdp complex, it is reasonable to assume that the distance between two Co atoms is also longer than 3.5 Å. This probably requires a large stereochemical distortion and/or a rearrangement of the coordination geometry for the formation of both μ -peroxo and acetato bridges. Thus, the steric effect of tdpdp may be of key importance for the observed low oxygen affinity.

The oxygen affinity of the tmdp complex is much lower than that of the bpmp complex, although both

Table 2. The ν_{max} Values of LMCT Bands,^{a)} Cyclic Voltammetric Data of O_2^-/O_2^{2-} Redox Couples, and Oxygen Affinities ($P_{1/2}(O_2)$)

Complex	$\nu_{\text{max}}/\text{cm}^{-1}$	$E_{1/2}(O_2^-/O_2^{2-})$ (E/V vs. SCE) ^{b)}	$P_{1/2}(O_2)/\text{Torr}$
1 $[\text{Co}_2(\text{tpdp})(\text{CH}_3\text{COO})]^{2+}$	25640	0.76	780 ^{c)}
2 $[\text{Co}_2(\text{tmdp})(\text{CH}_3\text{COO})]^{2+}$	24390	0.87	≈ 3 ^{d)}
3 $[\text{Co}_2(\text{bpmp})(\text{CH}_3\text{COO})]^{2+}$	21280	0.89	<0.1 ^{e)}

a) The charge-transfer transitions from O_2^- to Co^{3+} . b) Measured at -42°C . c) Measured at -15.6°C . d) Measured at 20°C . e) Measured at 20°C . Ref. 1c.

tmdp and bpmp form 6-membered chelate rings in the bridging moiety and the electron-donor ability of the alkoxo bridge in tmdp appears to be larger than that of the phenolato bridge in bpmp. Although we have no structural information, there seems to be some stereochemical disadvantage in **2a** compared with **3a**.

In our previous studies, we reported that Complex **3** shows an excellent reversibility for oxygen binding; no degradation was observed, even after 10 cycles of oxygenation-deoxygenation in acetonitrile, where deoxygenation was carried out by boiling the acetonitrile solution under N₂. It should be noted that some type of oxidative degradation (irreversible oxidation to cobalt(III) ion) is much more pronounced in **2a** than in **3a**. This may be attributable to the stronger electron donor ability of tmdp compared with that of bpmp. For the present dinuclear cobalt(II) complexes, the stereochemical effect may play an important role for the oxygen affinity and the oxidative degradation.

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