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μ-Peroxo Dicobalt Complexes Containing an Unsymmetrical Dinucleating Ligand: Synthesis, Characterization, and Oxygen Affinity

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A new unsymmetric dinucleating ligand, Htpdb (Htpdb=1,4-bis[bis(2-pyridylmethyl)amino]-2-butanol), was synthesized. This is a hybrid of Htpdp (1,3-bis[bis(2-pyridylmethyl)amino]-2-propanol) and Htmdp (1,5-bis[bis-(2-pyridylmethyl)amino]-3-pentanol). Its dinuclear cobalt(II,II) complexes, $[Co_2(tpdb)(RCOO)](ClO_4)_2 \cdot nH_2O$ ($RCOO=CH_3COO$ (**1**) and C_6H_5COO (**2**)), were prepared. Their electronic spectra indicate that **1** and **2** have a five-coordinate structure with a bridging carboxylato group. The complexes reacted reversibly with molecular oxygen in acetonitrile to form dioxygen complexes $[Co_2(tpdb)(RCOO)(O_2)]^{2+}$. The structure of a dioxygen complex $[Co_2(tpdb)(CH_3COO)(O_2)](PF_6)_2 \cdot CH_3CN \cdot 0.5H_2O$ (**3**) was determined by X-ray crystallography. **3** cystallizes in orthorhombic space group $Pmn2_1$ with a=23.034 (6), b=17.352 (2), c=10.355 (2) Å, and Z=4. Two cobalt atoms are triply bridged by dioxygen, acetato, and alkoxo groups. Two cobalt atoms are triply bridged by dioxygen, acetato, and alkoxo groups. $P(O_2)_{1/2}$ of **1** is 720 Torr in acetonitrile at 20 °C; this value is in between those of the corresponding tpdp and tmdp complexes. The bridging skeleton of the dinucleating ligands contributes significantly to the oxygen affinities of the complexes. The complex **2**, $[Co_2(tpdb)(C_6H_5COO)]^{2+}$, underwent an oxidative degradation in methanol–water mixture (1 : 1) in the presence of C_6H_5COONa to produce a dinuclear mixed valence complex $[Co_2(tpdb)(C_6H_5COO)_2](ClO_4)_2 \cdot H_2O$ (**4**).

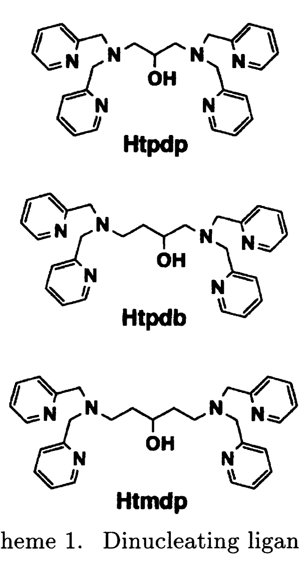
Dinuclear metal complexes with sterically and electronically controlled ligand environments are expected to bind molecular oxygen reversibly. In the previous studies, we have demonstrated that a series of dinucleating ligands (L=bpmp, bpmep, bpep, tpdp, and tmdp)[1] form the dinuclear five-coordinate cobalt(II, II) complexes $[Co_2(L)(CH_3COO)]^{2+}$, which react reversibly with molecular oxygen to from μ-peroxo complexes $[Co_2(L)(CH_3COO)(O_2)]^{2+}$. Their oxygen affinity and reversibility are highly dependent on the stereochemistry of the dinucleating ligands.[2] For example, $P(O_2)_{1/2}$ of the tmdp complex is ca. 3 Torr (1 Torr=133.322 Pa) at 20 °C, whereas the tpdp complex does not react with O_2 at 20 °C and reacts only at low temperature ($P(O_2)_{1/2}$=780 Torr at −15.6 °C,[2d] where $P(O_2)_{1/2}$ represents a partial oxygen pressure at which 50% of the complex is oxygenated. This result suggests that the chelate ring size of the bridging skeleton has a significant influence on the oxygen affinity: tmdp forms two six-membered chelate rings in bridging skeleton, whereas tpdp forms two five-membered chelate rings (Scheme 1). As an extension of our studies on the correlation between the stereochemistry of the dinucleating ligands and the oxygen affinity, we prepared a new unsymmetrical dinucleating ligand, Htpdb (1,4-bis[bis-(2-pyridylmethyl)amino]-2-butanol), which is a hybrid of Htpdp and Htmdp and forms five- and six-membered chelate rings in bridging skeleton. Although the ligand has an asymmetric carbon atom, we used racemate in this study. Here we will report the syntheses and oxygenation of dinuclear cobalt(II,II) complexes containing tpdb, and the crystal structure of a dioxygen complex $[Co_2(tpdb)(CH_3COO)(O_2)](PF_6)_2 \cdot CH_3CN \cdot 0.5H_2O$.

Experimental

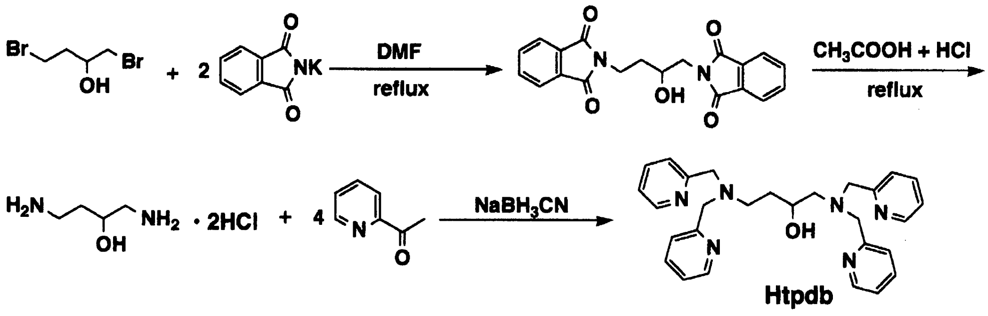
Preparation of Ligand. Scheme 2 outlines the synthetic route of Htpdb.

1,4-Bis(phtalimido)-2-butanol: To a suspension of potassium phthalimide (87.98 g, 475 mmol) in 300 cm^3 of dry DMF was added 1,4-dibromo-2-butanol (50 g, 216 mmol) with stirring. The resulting mixture was heated at 110 °C for 4 h. Most of DMF was evaporated under a reduced pressure to give white powder, which was collected by filtration and washed with a large amount of water and then with methanol. Yield: 75.23 g (206 mmol). Anal. Found: C, 65.56; H, 4.45; N, 7.67%. Calcd for $C_{20}H_{16}N_2O_5$: C, 65.93; H, 4.43; N, 7.69%.

1,4-Diamino-2-butanol Dihydrochloride: A suspension of 1,4-bis(phthalimido)-2-butanol (75.23 g, 206 mmol) in acetic acid (350 cm^3) and concentrated hydrochloric acid (225 cm^3) was heated at 120 °C for 3 d. During heating,



Scheme 1. Dinucleating ligands.



Scheme 2. Synthetic route of Htpdb.

five 10 cm^3 quantities of concentrated hydrochloric acid were added to the suspension. After cooling, the phthalic acid which deposited was removed by filtration and the filtrate was evaporated to dryness. The residue was taken up into 100 cm^3 of water and undissolved phthalic acid was removed by filtration. The filtrate was evaporated to dryness to give white powder. Yield: 33.7 g (190 mmol). ^{1}H NMR (D_2O, 400 MHz) δ=1.82 (1H, m, CH_2), 1.94 (1H, m, CH_2), 2.93—3.20 (4H, m, CH_2N), 4.01 (1H, m, CH).

1, 4-Bis[bis(2-pyridylmethyl)amino]-2-butanol (Htpdb): 1,4-Diamino-2-butanol dihydrochloride (17.7 g, 100 mmol) was dissolved into a small amount of water, to which was added 2-pyridinecarbaldehyde (45.0 g, 420 mmol) in 200 cm^3 of ethanol. To the resulting solution was dropwise added sodium cyanotrihydroborate (17.6 g, 280 mmol) with stirring. The solution was then stirred for three days at room temperature, it was subsequently acidified by addition of concentrated hydrochloric acid, and then evaporated almost to dryness under a reduced pressure. The residue was dissolved in 100 cm^3 of 0.1 mol dm^{-3} NaOH solution and extracted with three 50 cm^3-portions of chloroform. The combined extracts were dried over Na_2SO_4 and evaporated under a reduced pressure to give an oily product, which was then purified by silica gel column chromatography with chloroform/methanol. Yield: 12.5 g (27%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.64 (2H, m, CH_2), 2.60 (2H, m, CH_2N), 2.71 (2H, m, CH_2N), 3.72—3.92 (9H, m, CH and CH_2py), 7.11 (4H, m, pyH), 7.35 (2H, d, pyH), 7.44 (2H, d, pyH), 7.59 (4H, dd, pyH), 8.51 (4H, m, pyH).

Preparation of Complexes. The preparation of the cobalt(II,II) complexes were carried out under an argon atmosphere using a Schlenk apparatus. Racemic Htpdb was used for preparation.

[Co_2(tpdb)(CH_3COO)](ClO_4)$_2$·H_2O (1): To a solution of $Co(ClO_4)_2\cdot 6H_2O$ (1 mmol) and Htpdb (0.5 mmol) in 5 cm^3 of methanol was added a solution of triethylamine (0.5 mmol) and CH_3COONa (0.5 mmol) in 5 cm^3 of methanol–water (1 : 1) with stirring. The resulting purple solution was allowed to stand for one day. The deep purple crystals which formed were collected by filtration, washed with methanol and ether, and dried in vacuo. Yield: 272 mg. The compound was air-sensitive, so it formed a brown compound when exposed to the air. The elemental analysis was performed for the brown compound. Anal. Calcd for $C_{30}H_{36}N_6O_{14}Co_2Cl_2$ ([Co_2(tpdb)(CH_3COO)(O_2)](ClO_4)$_2$·H_2O): C, 40.33; H, 4.06; N, 9.41%. Found: C, 40.53; H, 3.90; N, 9.49%.

[Co_2(tpdb)(C_6H_5COO)](ClO_4)$_2$ (2): To a solution of $Co(ClO_4)_2\cdot 6H_2O$ (1 mmol) and Htpdb (0.5 mmol) in 5 cm^3 of methanol was added a solution of triethylamine (0.5 mmol) and C_6H_5COONa (0.5 mmol) in 5 cm^3 of methanol–water (1 : 1). The resulting purple solution was allowed to stand for one day. The violet crystals formed were collected by filtration, washed with methanol and ether, and dried in vacuo. The complex was converted into a brown compound, when exposed to the air. Yield: 287 mg. The elemental analysis was performed for the brown compound. Anal. Calcd for $C_{35}H_{37}N_6O_{13.5}Co_2Cl_2$ ([Co_2(tpdb) (C_6H_5COO)(O_2)](ClO_4)$_2$·0.5H_2O): C, 44.42; H, 3.94; N. 8.88%. Found: C, 44.38; H, 3.98; N, 8.74%.

[Co_2(tpdb)(CH_3COO)(O_2)](PF_6)$_2$·CH_3CN·0.5H_2O (3): To a solution of $Co(CH_3COO)_2\cdot 4H_2O$ (1 mmol) in 5 cm^3 of methanol was added a solution of Htpdb (0.5 mmol) in 15 cm^3 of methanol–acetonitrile (1 : 1). Then oxygen gas was bubbled for 5 min into the solution, to which a solution of NH_4PF_6 (2 mmol) in a minimum amount of methanol was added with stirring. Slow diffusion of diethyl ether into the resulting brown solution afforded dark brown crystals, which were collected by filtration, washed with ethanol and ether, and air-dried. Yield: 313 mg. Anal. Calcd for $C_{32}H_{38}N_7O_{5.5}Co_2F_{12}P_2$: C, 37.81; H, 3.77; N, 9.65%. Found: C, 37.82; H, 3.83; N, 9.39%.

[Co_2(tpdb)(C_6H_5COO)$_2$](ClO_4)$_2$·H_2O (4): To a solution of $Co(ClO_4)_2\cdot 6H_2O$ (1 mmol) in 10 cm^3 of methanol was added a mixture of Htpdb (0.5 mmol) and C_6H_5COONa (1.0 mmol) in 10 cm^3 of methanol. Oxygen gas was bubbled into the solution for 5 min and to the resulting solution was added 5 cm^3 of water. The brown solution was allowed to stand for several days at room temperature. The brown crystals which formed were collected by filtration, washed with methanol and ether, and dried in vacuo. Yield: 126 mg. Anal. Calcd for $C_{42}H_{43}N_6O_{14}Co_2Cl_2$: C, 48.29; H, 4.15; N, 8.05%. Found: C, 48.11; H, 4.01; N, 8.18.

Measurements. The electronic spectra were measured on a Hitachi U-3400 spectrophotometer equipped with an Otsuka Denshi optical glass fiber attachment. The infrared spectra were obtained by the KBr-disk method with a Horiba FT-200 spectrophotometer. The magnetic susceptibilities were measured with a SQUID susceptometer of QUANTUM DESIGN MPMS Model which was calibrated with Hg[Co(NCS)$_4$]. Diamagnetic correction was made by using Pascal's constants.$^{3)}$ 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 a reference electrode. Acetonitrile was used as the solvent, and *n*-tetrabutylammonium perchlorate as a supporting electrolyte. 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. X-band ESR spectra were measured at liquid-nitrogen temperature on a JEOL JES-RE1X ESR spectrometer. The band frequency was calibrated with 1,1-diphenyl-2-picrylhydrazyl (DPPH, $g=2.0036$). The molar conductivities were measured at 25 °C in acetonitrile (1×10^{-3} mol dm^{-3}) with a TOA CM-20S conductivity meter.

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

$$[Co_2] + O_2 \overset{K}{\rightleftharpoons} [Co_2(O_2)] \qquad (1)$$

was determined by spectrophotometric titration at 20 °C in acetonitrile. The measurements were carried out with a three necked vessel. A balloon was connected to the one neck to keep the inner pressure constant. The optical fiber attachment was attached to a second neck to measure the change in absorbance, and the third neck was sealed with a rubber septum to inject the oxygen gas by a syringe. The oxygen partial pressure was estimated from the O_2/N_2 ratio which was determined by a Hitachi 502 gas chromatograph with 3 m column of molecular sieves 5A and corrected with vapor pressure of acetonitrile at 20 °C. The reaction temperature was controlled with an ADVANTEC LAB THERMO COOL LCH-4V constant temperature circulation pump.

The equilibrium constant (K) was calculated by the following equation: $P(O_2)=C\cdot P(O_2)/\Delta A-K^{-1}$, where $P(O_2)$ is the partial pressure of O_2, ΔA is the difference between the absorbances of the solution at $P(O_2)$ and $P(O_2)=0$ Torr, and C is a constant. A plot of $P(O_2)$ vs. $P(O_2)/\Delta A$ gave a straight line, indicating a 1 : 1 (complex: O_2) stoichiometry for the oxygenation.

X-Ray Crystallography. A single crystal of **3** was obtained by a slow diffusion of diethylether into an acetonitrile–methanol (1 : 1) solution of **3** under oxygen atmosphere at 5 °C. A single crystal was mounted inside a glass capillary with a small amount of mother liquor to prevent a decomposition by a loss of acetonitrile from the crystal. Data were collected on a Rigaku AFC-5R four circle automated diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.71073$ Å) at room temperature. Unit cell parameters were determined by a least-squares fit to 25 reflections having $30.0°<2\theta<37.0°$. Crystallographic data are summarized in Table 1. Three standard reflections were measured every 150 reflections; they showed no systematic decay throughout data collection. The data were corrected for Lorentz and polarization effects and an empirical absorption correction (Ψ scans) was also applied (transmission factors range from 0.926—1.000). The structure was solved by the standard heavy-atom techniques. The metal atom was located by Patterson syntheses using the program SHELX-86.[4] Full-matrix least-squares refinement and difference Fourier methods (SHELX-76)[5] were used to locate all remaining non-hydrogen atoms. The atomic scattering factors and anomalous dispersion coefficients were taken from the literature.[6]

Table 1. Crystallographic Data for Complex **3**

Formula	$C_{32}H_{38}N_7O_{5.5}Co_2F_{12}P_2$
Fw	1016.4
Space group	$Pmn2_1$
a/Å	23.034(6)
b/Å	17.352(2)
c/Å	10.355(2)
V/Å^3	4139(1)
Z	4
Crystal size/mm	0.3×0.3×0.4
ρ_{calcd}/g cm^{-3}	1.63
λ(Mo $K\alpha$)/Å	0.71073
Scan method	ω–2θ
Scan speed/° min^{-1}	6
Max scan times	3
No. of data collected	5423
No. of data used	2458($\lvert F_o\rvert \geq 3.5\sigma\lvert F_o\rvert$)
Range/deg	$3\leq 2\theta \leq 55$
T/°C	23
μ/cm^{-1}	9.11
R	0.075
R_w	0.079

A careful inspection of reflection data suggested that there are two possible space groups, $Pmmn$ and $Pmn2_1$. Only an analysis by using $Pmn2_1$ space group gave a chemically reasonable solution. It was found that the crystal contains two crystallographically independent dinuclear complex cations (**3a** and **3b**) and each complex cation has a mirror plane through O1a, C1a, and C2a for **3a** and O1b, C1b, and C2b for **3b** in Fig. 2. The presence of a mirror plane in the complex cations was found to be ascribed to disorder of five- and six-membered chelate rings in bridging skeleton ($NCH_2CH(O)CH_2CH_2N$ and $NCH_2CH_2CH(O)CH_2N$).

All the non-hydrogen atoms were refined anisotropically except for O1, O3, C3, C4, C5, and C6 atoms of **3a** and **3b** cations. Several cycles of refinement led to convergence with $R=0.075$ ($R_w=0.079$). A final difference Fourier map showed the largest peak of 0.86 eÅ^{-3}. Final atomic coordinates for the non-hydrogen atoms are given in Table 2. Tables of thermal parameters, and F_o and F_c are given in the supplementary materials, which are deposited as Document No. 67063 at the Office of the Editor of Bull. Chem. Soc. Jpn. All the calculations were carried out on a FACOM M760/20 computer at the Kanazawa University Information Processing Center.

Results and Discussion

Characterization of Complexes. Complexes **1** and **2** contain one acetato or benzoato group as the tpdp and tmdp complexes.[2d] IR spectra revealed that $\Delta\tilde{\nu}(COO^-)$ values ($\tilde{\nu}_{asymm}(COO^-)-\tilde{\nu}_{symm}(COO^-)$) of these complexes are in the range of 140—150 cm^{-1}, suggesting that the carboxylato groups function as bridging ligands in an O,O' syn–syn coordination mode.[7] The electronic spectra of **1** and **2** in acetonitrile show several d–d bands in the visible and near infrared regions (Fig. 1 and Table 3). The electronic spectra of the five-coordinate cobalt(II) complexes exhibit several d–d bands

Table 2. Fractional Atomic Coordinates and Isotropic Thermal Parameters of **3** with Their Standard Deviations in Parentheses

Atom	x	y	z	U_{eq}[a]	Atom	x	y	z	U_{eq}[a]
Co1a	0.9325(1)	0.0191(0)	0.0000(—)	0.040(1)	C5b[b]	0.4637(15)	0.3461(19)	0.0989(27)	0.071(3)
O1a[b]	1.0000(—)	0.0738(11)	0.0305(17)	0.074(3)	C6b[b]	0.4227(14)	0.4080(18)	0.0796(24)	0.056(3)
O2a	0.9521(6)	-0.0652(7)	0.1101(12)	0.061(3)	C7b	0.6472(8)	0.3579(13)	0.2561(20)	0.075(3)
O3a	0.9700(5)	-0.0191(6)	-0.1471(10)	0.050(2)	C8b	0.6340(8)	0.3492(11)	0.3892(19)	0.065(3)
N1a	0.8882(5)	0.0722(8)	0.1356(11)	0.043(3)	C9b	0.6553(10)	0.2905(12)	0.4677(23)	0.094(3)
N2a	0.9070(7)	0.0959(8)	-0.1223(13)	0.056(3)	C10b	0.6389(12)	0.2829(16)	0.5853(25)	0.127(3)
N3a	0.8622(7)	-0.0391(8)	-0.0236(13)	0.059(3)	C11b	0.5970(12)	0.3361(16)	0.6362(20)	0.112(3)
C1a[b]	1.0000(—)	-0.0935(16)	0.1414(23)	0.070(3)	C12b	0.5785(7)	0.3939(12)	0.5657(15)	0.060(3)
C2a[b]	1.0000(—)	-0.1597(16)	0.2309(23)	0.069(3)	C13b	0.6556(10)	0.4901(13)	0.1294(17)	0.085(3)
C3a[b]	0.9370(11)	0.1034(14)	0.2184(21)	0.032(3)	C14b	0.6759(7)	0.5331(11)	0.2487(16)	0.054(3)
C4a[b]	0.9822(11)	0.1386(15)	0.1285(22)	0.045(3)	C15b	0.7272(9)	0.5791(12)	0.2586(17)	0.065(3)
C5a[b]	1.0384(13)	0.1682(17)	0.1926(24)	0.054(3)	C16b	0.7468(10)	0.6108(12)	0.3639(19)	0.078(3)
C6a[b]	1.0820(13)	0.1137(16)	0.2516(22)	0.040(3)	C17b	0.7082(9)	0.6110(11)	0.4692(18)	0.067(3)
C7a	0.8477(9)	0.1308(10)	0.0716(17)	0.061(3)	C18b	0.6575(7)	0.5712(9)	0.4581(15)	0.046(3)
C8a	0.8692(8)	0.1463(9)	-0.0667(18)	0.058(3)	P1	0.8285(4)	0.8290(6)	0.4712(10)	0.070(3)
C9a	0.8450(11)	0.2091(14)	-0.1377(24)	0.122(3)	F11	0.8655(10)	0.8140(8)	0.5978(17)	0.124(3)
C10a	0.8638(10)	0.2107(15)	-0.2724(21)	0.105(3)	F12	0.7864(12)	0.7705(12)	0.5126(23)	0.179(4)
C11a	0.8973(12)	0.1603(15)	-0.3288(20)	0.101(3)	F13	0.8731(12)	0.7635(16)	0.4262(18)	0.185(4)
C12a	0.9251(12)	0.0952(13)	-0.2503(17)	0.097(3)	F14	0.7937(15)	0.8892(17)	0.5362(19)	0.205(4)
C13a	0.8491(7)	0.0212(9)	0.1836(14)	0.042(3)	F15	0.7896(11)	0.8467(17)	0.3667(19)	0.238(4)
C14a	0.8250(9)	-0.0303(10)	0.0798(16)	0.062(3)	F16	0.8748(7)	0.8976(8)	0.4363(13)	0.095(3)
C15a	0.7689(8)	-0.0613(10)	0.0898(18)	0.062(3)	P2	0.1703(5)	0.3281(6)	0.3542(9)	0.075(3)
C16a	0.7552(9)	-0.1093(11)	-0.0235(22)	0.089(3)	F21	0.2015(11)	0.3155(14)	0.4909(17)	0.180(4)
C17a	0.7880(9)	-0.1147(12)	-0.1265(17)	0.072(3)	F22	0.2088(12)	0.3991(10)	0.3261(23)	0.182(3)
C18a	0.8454(11)	-0.0807(10)	-0.1318(19)	0.089(3)	F23	0.2194(9)	0.2820(14)	0.2836(16)	0.130(3)
Co1b	0.5681(1)	0.4815(1)	0.3297(2)	0.043(1)	F24	0.1385(10)	0.3372(15)	0.2263(16)	0.178(3)
O1b[b]	0.5000(—)	0.4237(8)	0.2885(13)	0.028(3)	F25	0.1428(13)	0.2571(15)	0.3892(22)	0.203(4)
O2b	0.5484(5)	0.5563(7)	0.1993(11)	0.050(3)	F26	0.1289(9)	0.3644(10)	0.4415(17)	0.129(4)
O3b	0.5300(5)	0.5468(6)	0.4399(11)	0.049(2)	N4[b]	1.0000(—)	0.0182(23)	-0.5085(29)	0.148(4)
N1b	0.6167(7)	0.4234(9)	0.1981(15)	0.061(3)	C21[b]	1.0000(—)	-0.0381(20)	-0.4676(25)	0.079(4)
N2b	0.5960(6)	0.4027(9)	0.4398(14)	0.055(3)	C22[b]	1.0000(—)	-0.1236(30)	-0.4173(33)	0.229(4)
N3b	0.6414(5)	0.5338(6)	0.3488(12)	0.035(3)	N5[b]	0.0000(—)	0.3885(13)	0.2374(19)	0.056(3)
C1b[b]	0.5000(—)	0.5842(10)	0.1712(16)	0.020(3)	C23[b]	0.0000(—)	0.4508(29)	0.2880(32)	0.180(4)
C2b[b]	0.5000(—)	0.6584(19)	0.0862(26)	0.095(4)	C24[b]	0.0000(—)	0.5258(29)	0.3333(33)	0.200(4)
C3b[b]	0.5697(15)	0.3776(20)	0.1323(26)	0.067(3)	OW[b]	0.5000(—)	0.2056(22)	0.3953(30)	0.238(4)
C4b[b]	0.5112(17)	0.3677(21)	0.1918(27)	0.110(4)					

a) $U_{eq}=1/3(U_{11}+U_{22}+U_{33})$. b) The occupancy factor of the atom is 0.5.

in the 5000—25000 cm^{-1} region.[8] Thus, the electronic and IR spectra indicate that **1** and **2** have a five-coordinate structure with a carboxylato bridge.

An oxygenated complex $[Co_2(tpdb)(CH_3COO)(O_2)](PF_6)_2 \cdot CH_3CN \cdot 0.5H_2O$ (**3**) was isolated by the reaction of $[Co_2(tpdb)(CH_3COO)]^{2+}$ with molecular oxygen. The complex has an intense brown color in acetonitrile. Heating the brown solution resulted in a decolorization to give a pink solution, whose spectrum is identical to that of **1**. IR spectrum of **3** showed a $\Delta\tilde{\nu}(COO^-)$ value ($\tilde{\nu}_{asymm}(COO^-)-\tilde{\nu}_{symm}(COO^-)$) of 116 cm^{-1}, indicating the presence of an acetato bridge.

Complex **2** reacts reversibly with molecular oxygen in acetonitrile to form an oxygenated complex $[Co_2(tpdb)(C_6H_5COO)(O_2)]^{2+}$ as **1**. In methanol–water mixture, however, an irreversible oxidation of only one of the two cobalt(II) ions took place during several days and a mixed valence complex $[Co_2(tpdb)(C_6H_5COO)_2]$-

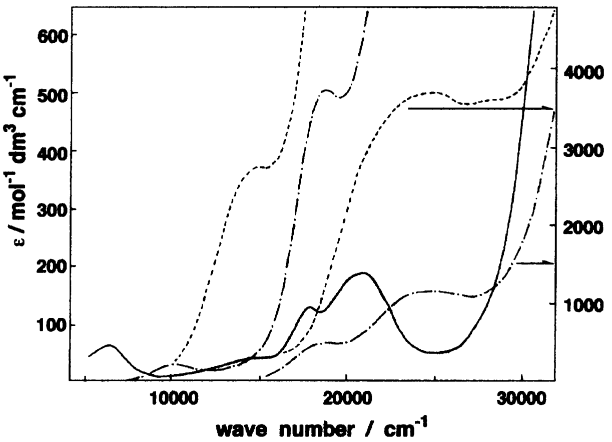
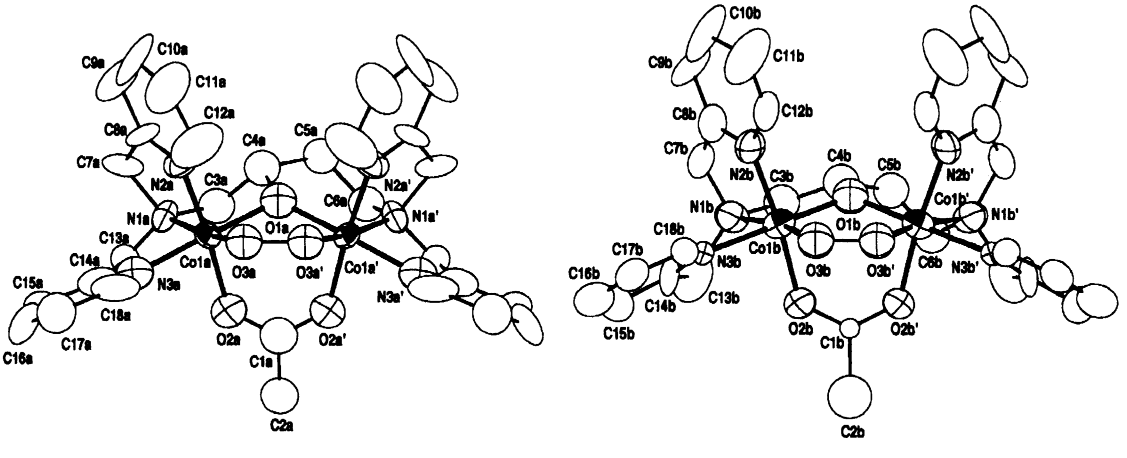


Fig. 1. Electronic spectra of **1** (——), **3** (- - -), and **4** (–·–) in acetonitrile.



3a **3b**

Fig. 2. Molecular structures of two isomers (**3a** and **3b**) of $[Co_2(tpdb)(CH_3COO)(O_2)](PF_6)_2 \cdot CH_3CN \cdot 0.5H_2O$ (**3**). Counterparts of the bridging skeletons of the disordered complex cations of **3a** and **3b**, respectively, are omitted for clarity.

Table 3. Electronic Spectral Data of **1**, **2**, **3**, and **4**[a)]

Complexes	Band maxima			
	$\tilde{\nu}/cm^{-1}$ (ε mol^{-1} $dm^3\,cm^{-1}$)			
$[Co_2(tpdb)(CH_3COO)]^{2+}$ (**1**)	21030(185)	17800(130)	14600(40)	6200(60)
$[Co_2(tpdb)(C_6H_5COO)]^{2+}$ (**2**)	21000(160)	17800(147)	14600(40)	6700(57)
$[Co_2(tpdb)(CH_3COO)(O_2)]^{2+}$ (**3**) [b)]	28000(3640)[c)]	24700(3720)[d)]	14600(360)[c)]	
$[Co_2(tpdb)(C_6H_5COO)_2]^{2+}$ (**4**)	24700(1160)	18900(510)	10100(30)	

a) Measured in acetonitrile. b) The spectrum was measured at room temperature under air atmosphere. Deoxygenation in this condition was very slow and the spectrum was almost constant within 1 h. c) Shoulder. d) Broad band.

$(ClO_4)_2 \cdot H_2O$ (**4**) was isolated in the presence of C_6H_5COONa. Protic solvents such as water and methanol seem to be responsible for the irreversible oxidation of one of two cobalt(II) ions. Similar observations have been made for the $[Fe_2(tpdb)(RCOO)_2]^{2+}$ [9)] and $[Fe_2(bpmp\ or\ bzimp)(RCOO)_2]^{2+}$.[10)] IR spectrum of **4** exhibits $\tilde{\nu}_{asymm}(COO^-)$ at 1572, and $\tilde{\nu}_{symm}(COO^-)$ at 1398 and 1371 cm^{-1}, which resemble those of the analogous mixed valence complexes ($[M_2(bpmp)(C_6H_5COO)_2]^{2+}$ (M = Fe[10)] and Mn[11)])), suggesting that two benzoato groups bridge two cobalt ions in *O,O'* syn–syn coordination mode. Thus complex **4** has a six-coordinate structure bridged by alkoxo and two benzoato groups. The electronic spectrum of the complex exhibits three absorption bands in the near infrared and visible regions (Fig. 1 and Table 3). The band at 10100 cm^{-1} (ε=30 $mol^{-1}\,dm^3\,cm^{-1}$) is assigned to the d–d transition (${}^4T_{1g}({}^4F)$ to ${}^4T_{2g}({}^4F)$ in O_h symmetry) of six-coordinate cobalt(II) moiety.[12)] The band at 18900 cm^{-1} (ε=510 $mol^{-1}\,dm^3\,cm^{-1}$) is assigned to the first absorption band (${}^1A_{1g}$ to ${}^1T_{1g}$ transition in O_h symmetry) of a low-spin six-coordinate cobalt(III) moiety, which is overlapped with an intense band at 24700 cm^{-1} (ε=1160 $mol^{-1}\,dm^3\,cm^{-1}$). The presence of high-spin cobalt(II) (S=3/2) and low-spin cobalt(III) (S=0) ions is also supported by its magnetism. The effective magnetic moment of **4** is 4.7 B.M. at 300—80 K and gradually decreases to 4.1 B.M. at 6 K. Such magnetic behavior is in line with those of six-coordinate high-spin cobalt(II) complexes.[13)]

Electronic Spectrum of $[Co_2(tpdb)(CH_3COO)(O_2)](PF_6)_2 \cdot CH_3CN \cdot 0.5H_2O$ (3). The electronic spectrum of **3** displays an intense absorption band at 24700 cm^{-1} (ε=3720 $mol^{-1}\,dm^3\,cm^{-1}$) in acetonitrile; such a band is characteristic of the μ-peroxo cobalt complexes[14)] (Fig. 1). This intense band is assigned to the charge-transfer transitions (CT) from the peroxo π^* orbital to cobalt(III) d_σ^* orbitals, although it may also contain an absorption band observed at 24700 cm^{-1} for the mixed valence complex **4**. The complex exhibits a rather intense band at 14600 cm^{-1} (ε=360 $mol^{-1}\,dm^3\,cm^{-1}$) in both solid and solution. This band may not be assigned to the d–d transitions of the low-spin cobalt(III) moieties, since the mixed valence complex with the same N_3O_3 donor set, $[Co_2(tpdb)(C_6H_5COO)_2](ClO_4)_2 \cdot H_2O$ (**4**), has no absorption band in this region and has the first d–d band at 18900 cm^{-1} (ε=510 $mol^{-1}\,dm^3\,cm^{-1}$). Tuczek and Solomon[15)] reported that for *trans*-1,2-μ-peroxo complexes ($[Co(N_5)O_2(N_5)Co]^{4+}$) in which Co–O–O–Co is planar, the charge transfer transitions from the peroxo π_{v}^{*} orbital (non-bonding character) vertical with respect to the Co–O–O–Co plane to cobalt(III) d_{σ}^{*} orbitals appear at 17500—14500 cm^{-1}. However, for *cis*-1,2-μ-peroxo complexes ($[\mathrm{Co(N_4)(\mu\text{-}OH\ or\ \mu\text{-}NH_2)O_2(N_4)Co}]^{3+}$), such low energy charge transfer transitions are not observed, where Co–O–O–Co are not planar and the torsion angles of Co–O–O–Co are ca. 60 °. This mixes together π_{v}^{*} and π_{σ}^{*} ($\mathrm{O_2^{2-}}$) orbitals both of which have bonding character, so that the CT transition energy becomes higher in the *cis*-1,2-μ-peroxo complexes.[14,15] The band at 14600 cm^{-1} in **3** may be assigned to the CT of peroxo π_{v}^{*} orbital to cobalt(III) d_{σ}^{*} orbitals and the band at 24700 cm^{-1} to that of peroxo π_{σ}^{*} orbital to cobalt(III) d_{σ}^{*} orbitals. The presence of such a low energy CT transition at 14600 cm^{-1} suggests that the torsion angle of Co–O–O–Co in **3** must be small.

Description of the Structure of $[\mathrm{Co_2(tpdb)(CH_3COO)(O_2)}](\mathrm{PF_6})_2\cdot\mathrm{CH_3CN}\cdot0.5\mathrm{H_2O}$ (3). The crystal structure consists of two crystallographically independent dinuclear complex cations (**3a** and **3b**), $\mathrm{PF_6}$ anions, and lattice acetonitrile and water molecules. Although each complex cation is unsymmetric, disorder of five- and six-membered chelate rings in the bridging skeleton results in the presence of an apparent mirror plane in the complex cations. Large and anisotropic thermal parameters in bis(2-pyridylmethyl)amine side arms seem to reflect the disordered structures. The bond distances and angles obtained are those of the averaged structures of the disordered molecules (Table 4). Detailed discussion about the bond distances and angles may not be meaningful, but the present result is very useful for discussing the structural feature of the μ-peroxo complex cations.

Figure 2 shows the molecular structures of the complex cations (**3a** and **3b**), which are conformational isomers in the bridging chelate rings. The conformations of the bridging chelate rings in **3a** and **3b** are shown in Fig. 3. The presence of conformational isomers suggests that the five- and six-membered chetate rings in bridging skeleton ($\mathrm{NCH_2CH(O)CH_2CH_2N}$) have substantial stereochemical flexibility. Each cobalt moiety in both **3a** and **3b** has a distorted octahedral structure with *cis*,*cis*-$\mathrm{N_3O_3}$ donor set. Two cobalt atoms in dinuclear units are triply bridged by alkoxo, acetato, and peroxo groups. The oxygen atoms of peroxo group are trans to tertiary amine nitrogens. This arrangement differs from that found for $[\mathrm{Co_2(bpmp)(C_6H_5COO)(O_2)}]^{2+}$ in which two oxygen atoms are unsymmetrically coordinated to cobalt atoms; one oxygen is trans to a tertiary amine nitrogen, whereas the other is trans to a pyridyl nitrogen.[2b] This difference in the coordination mode of the peroxo groups is probably due to a steric requirement of the bridging skeleton.

Although the bond distances and angles are those of averaged structures of the disordered molecules as mentioned above, the O–O bond distances of **3a** and **3b** seem to be chemically reasonable (1.38(2) Å), which are in the range found for those of the peroxo complexes (1.31—1.53 Å).[16—18] The Col–O3–O3–Col are planar. The observed planar Co–O–O–Co structure is attributable to the result of disorder of the complex cations. Such a planar structure has not been observed for *cis*-1,2-μ-peroxo complexes so far reported. The torsion angles of Co–O–O–Co in *cis*-1,2-μ-peroxo complexes so far reported are in the range of 51—63° (Table 5), although several *trans*-1,2-μ-peroxo complexes with a planar Co–O–O–Co structure have been known. The Co···Co distances are 3.10—3.14 Å; this is comparable with that of $[\mathrm{Co_2(bpmp)(C_6H_5COO)(O_2)}]^{2+}$ (3.14 Å). The Co···Co distances of the dibridged complexes with a hydroxo or an amide bridge ($[\mathrm{Co_2(N_4)_2(\mu\text{-}OH\ or\ \mu\text{-}NH_2)(O_2)}]^{3+}$ type complexes) are 3.27—3.29 Å (Table 5). Thus the Co···Co distances are constrained in a relatively narrow range (3.10—3.3 Å) irrespective of the di- and tribridged cores.

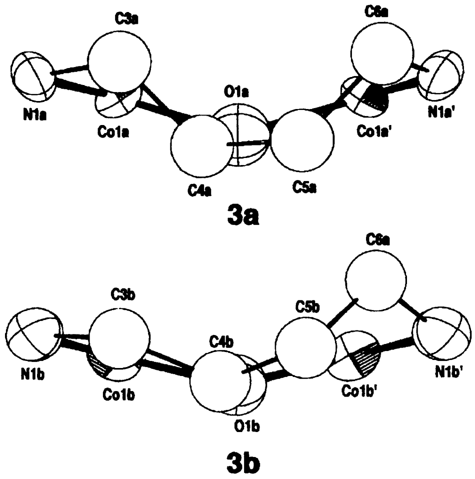


Fig. 3. Conformations of the bridging skeletons in **3a** and **3b**. Counterparts of the bridging skeletons of the disordered complex cations of **3a** and **3b**, respectively, are omitted for clarity.

Oxygenation Reaction. Complex **1** reacts reversibly with molecular oxygen in both solid and solution. Upon exposure to $\mathrm{O_2}$, a color change occurred from violet to brown in acetonitrile. Heating the brown solution restored the original violet color under argon atmosphere. The oxygenation–deoxygenation process is very slow compared with those of the other complexes $[\mathrm{Co_2(L)(RCOO)}]^{2+}$ (L = bpmp, bpmep, tpdp, tmdp). Complete oxygenation of **1** takes at least a few hours, whereas those of the other complexes take several minutes. Figure 4 shows the spectral change of **1** at various oxygen pressures ($P(\mathrm{O_2})$) in acetonitrile at 20 °C. The equilibrium constant (K) and $P(\mathrm{O_2})_{1/2}$ are estimated to be 1.4×10^{-3} Torr^{-1} and 720 Torr, respectively.

Electrochemistry. Cyclic voltammograms (CV) of **1**, **3**, and **4** in acetonitrile are shown in Fig. 5. Complex **1** exhibits no oxidation wave up to 1.0 V vs. SCE,

Table 4. Selected Bond Distances (l/Å) and Angles (ϕ/°) of **3**

Bond distances			
Molecule **3a**		Molecule **3b**	
Co1a–O1a	1.85(1)	Co1b–O1b	1.911(8)
Co1a–O2a	1.91(1)	Co1b–O2b	1.93(1)
Co1a–O3a	1.87(1)	Co1b–O3b	1.83(1)
Co1a–N1a	1.97(1)	Co1b–N1b	2.03(2)
Co1a–N2a	1.93(1)	Co1b–N2b	1.89(1)
Co1a–N3a	1.92(2)	Co1b–N3b	1.93(1)
O3a–O3a	1.38(2)	O3b–O3b	1.38(2)
Co1a···Co1a	3.110(4)	Co1b···Co1b	3.139(5)
Bond angles			
Molecule **3a**		Molecule **3b**	
O1a–Co1a–O2a	95.3(5)	O1b–Co1b–O2b	90.2(4)
O1a–Co1a–O3a	86.1(5)	O1b–Co1b–O3b	94.0(4)
O1a–Co1a–N1a	94.2(5)	O1b–Co1b–N1b	92.4(5)
O1a–Co1a–N2a	90.8(5)	O1b–Co1b–N2b	91.9(5)
O1a–Co1a–N3a	177.4(6)	O1b–Co1b–N3b	171.8(4)
O2a–Co1a–O3a	96.1(5)	O2b–Co1b–O3b	84.7(5)
O2a–Co1a–N1a	93.2(5)	O2b–Co1b–N1b	89.7(6)
O2a–Co1a–N2a	173.3(6)	O2b–Co1b–N2b	171.4(6)
O2a–Co1a–N3a	82.7(6)	O2b–Co1b–N3b	87.8(5)
O3a–Co1a–N1a	170.6(5)	O3b–Co1b–N1b	171.5(6)
O3a–Co1a–N2a	81.4(5)	O3b–Co1b–N2b	103.5(6)
O3a–Co1a–N3a	95.7(6)	O3b–Co1b–N3b	93.7(5)
N1a–Co1a–N2a	89.2(6)	N1b–Co1b–N2b	81.9(6)
N1a–Co1a–N3a	84.2(6)	N1b–Co1b–N3b	79.6(6)
N2a–Co1a–N3a	91.3(6)	N2b–Co1b–N3b	88.9(6)
Co1a–O1a–Co1a	114.0(1.0)	Co1b–O1b–Co1b	110.4(7)
Co1a–O3a–O3a	117.5(8)	Co1b–O3b–O3b	118.6(9)

Table 5. Comparison of Structural Data of Dinuclear Di- and Tribridged μ-Peroxo Complexes

Complexes	Co–O (l/Å)	O–O (l/Å)	Co···Co (l/Å)	Co–O–O–Co (ϕ/°)	Co–O–O (ϕ/°)	Ref.
$[Co_2(en)_4(NH_2)O_2](SCN)_3 \cdot H_2O$	1.87	1.46	3.28	62.7	110	16d
$[Co_2(en)_4(OH)O_2](NO_3)(S_2O_3) \cdot 2H_2O$	1.86	1.47	3.27	60.7	110	16e
$[Co_2(tren)_2(OH)O_2](ClO_4)_3 \cdot 3H_2O$	1.87	1.46	3.29	60.7	109	16f
$[Co_2(tpdb)(CH_3COO)O_2](PF_6)_2 \cdot CH_3CN \cdot 0.5H_2O$	1.87	1.38	3.11	0	118	Present work
	1.83		3.14		119	
$[Co_2(bpmp)C_6H_5COO)O_2](BF_4)_2 \cdot 2H_2O$	1.88	1.43	3.15	51	110	2b
$[Co_2(Bidhx)_2(OH)O_2](NO_3)_3$	1.88	1.38		60.2	111	16g

which implies that the five-coordinate cobalt(II) species resists the oxidation to cobalt(III) one, since cobalt(III) tends to form six-coordinate species. The oxygenated complex **3**, however, exhibits a reversible redox couple at 0.72 V vs. SCE at room temperature. The constant potential electrolysis revealed that this redox couple corresponds to a one-electron transfer process (1.01 e^- for the oxidation at 0.8 V vs. SCE). The ESR spectrum of a one-electron oxidized species of **3** indicated that this couple is ascribed to O_2^-/O_2^{2-} (vide infra). In contrast to **1**, **4** shows two sets of oxidation and reduction waves, although they are not reversible (Fig. 5). Such a remarkable change in redox properties is attributable to the difference in the coordination numbers of **1** (five-coordinate) and **4** (six-coordinate).

ESR Spectra. The oxygenated complex **3** is ESR silent, indicating the Co^{3+}–O^-–O^-–Co^{3+} formulation, whereas a one-electron oxidized species shows an ESR signal at $g=2.0$ with a slight anisotropy ($g_{\parallel}=2.07$ and $g_{\perp}=1.99$) at liquid N_2 temperature (Fig. 6). Fifteen hyperfine lines ($A=20$ 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 clearly indicate the formation of O_2^- species. The appearance of 15 hyperfine lines in the $g_{\parallel}$ region implies that an unpaired-electron is mainly localized on O_2^- moiety and weakly couples with two equivalent ^{59}Co nuclei (Co^{3+}–O_2^-–Co^{3+}). Such an observation has also been made for the corresponding tpdp and tmdp complexes.[2d)]

Oxygen Affinity. It has been shown that the oxygen affinity of cobalt(II) complexes correlates with the electron donor ability of the ligand: the stronger

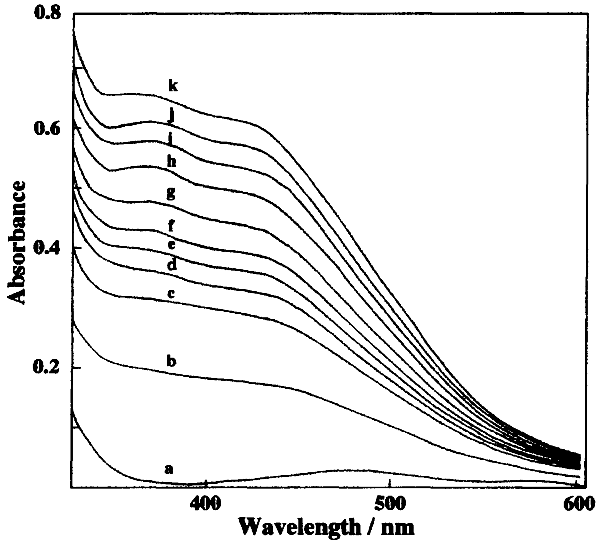


Fig. 4. Spectral changes of **1** at various partial pressures of oxygen in acetonitrile at 20 °C. Spectra of a—k are at the partial pressures of oxygen: 0, 98, 182, 210, 238, 263, 298, 369, 421, 471, and 535 Torr, respectively.

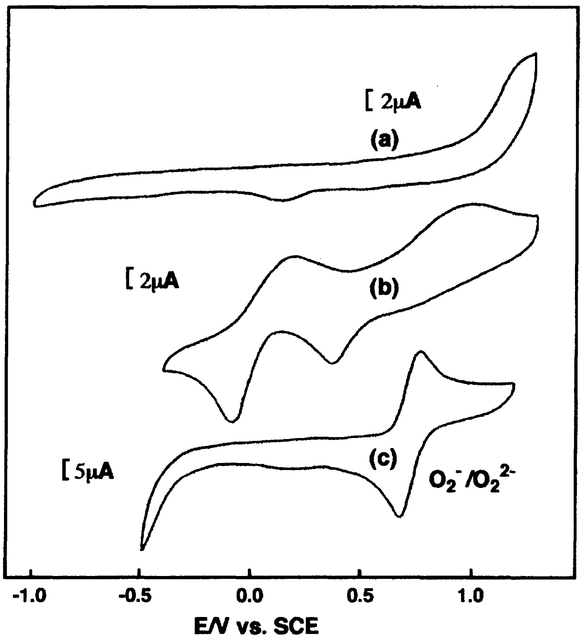


Fig. 5. Cyclic voltammograms of **1** (a), **4** (b), and **3** (c) in acetonitrile (0.1 mol dm^{-3} tetra-*n*-butylammonium perchlorate) at a glassy carbon electrode with scan rate 100 mV s^{-1}.

the electron donor ability of the ligand, the greater the electron density on cobalt center, the easier the electron drift from cobalt to dioxygen, and the higher the oxygen affinity.[17,18] In the previous studies, however, we found that the oxygen affinities of $[Co_2(L)(RCOO)]^{2+}$ type complexes are not simply correlated with the electron donor abilities of the dinucleating ligands (Table 6).

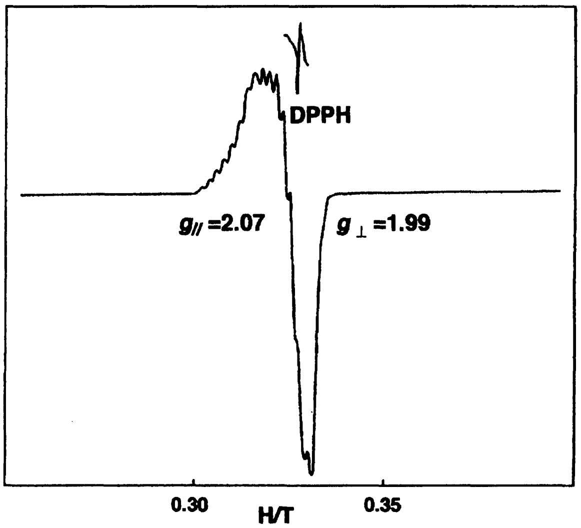


Fig. 6. ESR spectrum of the one-electron oxidized species of the oxygenated complex **3** in acetonitrile at liquid N_2 temperature.

For a series of the present type of dinucleating ligands (tpdp, tpdb, tmdp, bpmp, bpmep, and bpep) the order of the electron donor abilities may be anticipated by considering the donor atoms and the numbers of five- and six-membered chelate rings formed. Although tpdp, tpdb, tmdp, bpmp, bpmep, and bpep have the same N_6O donor set, the former three have a bridging alkoxo group, whereas the latter three have a phenolato group. It is reasonable to assume that the bridging alkoxo group is a stronger donor than the bridging phenolato group. It has been shown that a chelate ring size also has a significant influence on the electron donor ability: The electron donor ability of a five-membered chelate ring is stronger than that of six-membered chelate ring with the same donor set.[19] Thus the order of the electron donor abilities of the present type of ligands can be assumed to be tpdp > tpdb > tmdp > bpmp > bpmep > bpep by considering the bridging group (alkoxo or phenolato) and the numbers of the 5- and 6-membered chelate rings. This is supported by comparing the energies of the LMCT ($O_2^{2-} \rightarrow Co^{3+}$) of the present complexes. It has been observed that there is a correlation of the electron donor ability of ligand with the energy of LMCT($O_2^{2-} \rightarrow Co^{3+}$).[20] The order of the energies of LMCT for the present complexes is in accord with that of the electron donor abilities, as mentioned above (Table 6). There is also a rough correlation between $E_{1/2}$ (Co^{3+}–O_2^-–Co^{3+}/Co^{3+}–O_2^{2-}–Co^{3+} (hyperoxo/peroxo)) and the electron donor ability (Table 6). $E_{1/2}$ (Co^{3+}–O_2^-–Co^{3+}/Co^{3+}–O_2^{2-}–Co^{3+} (hyperoxo/peroxo)) seems to be a measure of the electron density on the peroxo group: the greater the electron density, the easier the oxidation of peroxo to hyperoxo.

Figure 7 shows the observed order of the oxygen affinities of the present type complexes depending on the dinucleating ligands (bpmp > tmdp > bpmep > tpdb >

Table 6. Oxygen Affinities ($P(O_2)_{1/2}$), Energies of LMCT, and Electrochemical Data of the Dinuclear Complexes

Complex	$P(O_2)_{1/2}^{a)}$ (P/Torr)	LMCT ($\tilde{\nu}_{max}$ /nm)	$E_{1/2}$ (O_2^-/O_2^{2-})$^{b)}$ (E/V vs. SCE)	Ref.
$[Co_2(tpdp)(CH_3COO)(O_2)]^{2+}$	$780^{c)}$	390	0.76	2d
$[Co_2(tpdb)(CH_3COO)(O_2)]^{2+}$	720	405	0.70	Present work
$[Co_2(bpmep)(CH_3COO)(O_2)]^{2+}$	24			2c
$[Co_2(tmdp)(CH_3COO)(O_2)]^{2+}$	$3^{d)}$	410	0.87	2d
$[Co_2(bpmp)(CH_3COO)(O_2)]^{2+}$	>0.1	470	0.89	2c,2d

a) Measured in acetonitrile at 20 °C. b) Measured in acetonitrile at −42 °C where all the complexes were fully oxygenated. c) The complex does not react with O_2 at 20 °C. The oxygen affinity was measured at −15.6 °C. d) Measured in dichloromethane at 20 °C.

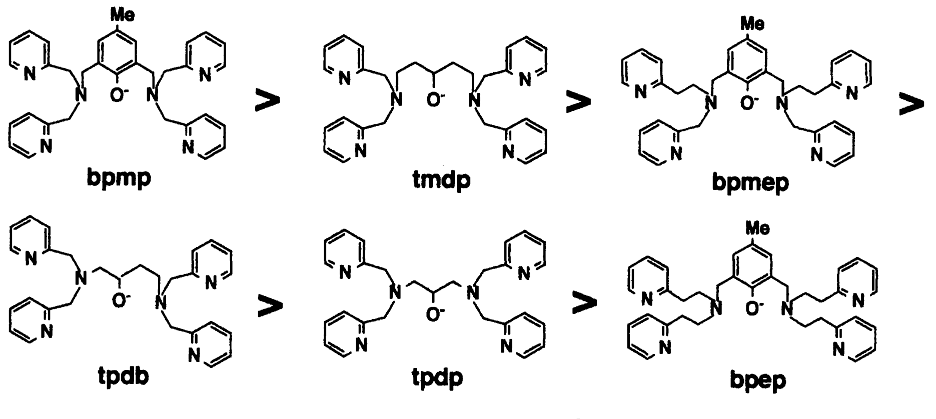


Fig. 7. The order of the oxygen affinities of $[Co_2(L)(CH_3COO)]^{2+}$ depending on the dinucleating ligands (L).

tpdp>bpep). This order is not in line with that anticipated from the electron donor ability. These results suggest that the oxygen affinity of the present type of complexes depends on the structural fitness of the bridging skeleton, where the $Co\cdots Co$ distances may be constrained to be ca. 3.1—3.3 Å. The metal–metal distances of the complexes with bpmp and tmdp analogs which have two six-membered chelate rings in the bridging skeleton are in the wide range 2.94—4.13 Å, ($[Cu_2(bpmp)Cl_2]^+$, 4.13 Å;[21] $[Fe_2(5\text{-}Me\text{-}HXTA)(\mu\text{-}OH)(H_2O)_2]$, 3.137 Å;[22] $[Fe_2(bpmp)(C_2H_5COO)_2]^+$, 3.365 Å;[23] $[Mn_2(1,5\text{-}bis(salicylidenamino)\text{-}3\text{-}pentanolato)(CH_3O)(CH_3COO)(CH_3OH)_2]^+$, 2.943 Å;[24]). This suggests that such dinucleating ligands have a substantial structural flexibility for formation of a tribridged core with a peroxo bridge, without any significant steric hindrance. The ligands (L-5) containing two five-membered chelate rings in the bridging skeleton tend to expand the metal–metal distances. In fact, there is no complex of the type $[M_2(L\text{-}5)X]^{n+}$ having X in one-atom bridging mode; the metal–metal distances of the complexes of tpdp or its analogs are constrained to be longer than 3.45 Å.[25] Such a stereochemical constraint seems to bring about a steric hindrance of a tribridged core upon oxygenation. The order of the oxygen affinity suggests that the structural fitness of the bridging skeleton of tpdb is in between tmdp and tpdp.

Concluding Remarks. An unsymmetrical dinucleating ligand tpdb forms five-coordinate dinuclear cobalt(II,II) complexes $[Co_2(tpdb)(RCOO)]^{2+}$. The complexes react reversibly with molecular oxygen to form $[Co_2(tpdb)(RCOO)(O_2)]^{2+}$ in acetonitrile. $P(O_2)_{1/2}$ of **1** is 720 Torr, which is in between those of the tmdp and tpdp complexes. The oxygen affinity of the present type complexes are highly dependent on the stereochemistry of the bridging structure.

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References

1) Abbreviations of ligands: Hbpmp, 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol; Hbpmep, 2,6-bis[(2-pyridylmethyl)(2-pyridylethyl)aminomethyl]-4-methylphenol; Hbpep, 2,6-bis[bis(2-pyridylethyl)aminomethyl]-4-methylphenol; Htpdp, 1,3-bis[bis(2-pyridylmethyl)amino]-2-propanol; Htmdp, 1,5-bis[bis(2-pyridylmethyl)amino]-3-pentanol; Htpdb, 1,4-bis[bis(2-pyridylmethyl)amino]-2-butanol.

2) a) M. Suzuki, H. Kanatomi, and I. Murase, *Chem. Lett.*, **1981**, 1745; b) M. Suzuki, I. Ueda, H. Kanatomi, and I. Murase, *Chem. Lett.*, **1983**, 185; c) M. Suzuki, H. Kanatomi, and I. Murase, *Bull. Chem. Soc. Jpn.*, **57**, 36 (1984); d) M. Suzuki, T. Sugisawa, and A. Uehara, *Bull.*

Chem. Soc. Jpn., **63**, 1115 (1990).

3) F. E. Mabbs and D. J. Marchin, "Magnetisms and Transition Metal Complexes," Chapman and Hall, London (1975), p. 5.

4) G. M. Sheldrick, "SHELXS-86. A Program for Crystal Structure Determination," University of Göttingen, FRG (1986).

5) G. M. Sheldrick, "SHELX-76. A Program for Crystal Structure Determination," Cambridge University, Cambridge, UK (1976).

6) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England (1974), Vol. IV.

7) G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, **23**, 227 (1980).

8) M. Ciampolini and I. Bertini, *J. Chem. Soc. A*, **1961**, 2241.

9) M. Suzuki, Y. Hayashi, M. Suzuki, Y. Maeda, H. Hori, and A. Uehara. To be published.

10) a) M. Suzuki, A. Uehara, H. Oshio, K. Endo, M. Yanaga, S. Kida, and K. Saito, *Bull. Chem. Soc. Jpn.*, **60**, 3547 (1987); b) M. Suzuki, H. Oshio, A. Uehara, K. Endo, M. Yanaga, S. Kida, and K. Saito, *Bull. Chem. Soc. Jpn.*, **61**, 3907 (1988).

11) M. Suzuki, M. Mikuriya, S. Murata, A. Uehara, H. Oshio, S. Kida, and K. Saito, *Bull. Chem. Soc. Jpn.*, **60**, 4305 (1987).

12) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

13) P. W. Ball and A. B. Blake, *J. Chem. Soc., Dalton Trans.*, **1974**, 852; P. Chaudhuri, J. Querbach, K. Wieghardt, B. Nuber, and J. Weiss, *J. Chem. Soc., Dalton Trans.*, **1990**, 271.

14) A. B. P. Lever and H. B. Gray, *Acc. Chem. Res.*, **11**, 348 (1978).

15) F. Tuczek and E. I. Solomon, *Inorg. Chem.*, **31**, 944 (1993).

16) a) B. C. Wang and W. P. Schaeher, *Science*, **166**, 1404 (1969); b) M. Calligaris, G. Nardis, L. Randaccio, and A. Ripamonti, *J. Chem. Soc. A*, **1970**, 1069; c) T. Shibahara, S. Koda, and M. Mori, *Bull. Chem. Soc. Jpn.*, **46**, 2070 (1973); d) U. Thewalt, *Z. Anorg. Allg. Chem.*, **393**, 1 (1972); e) U. Thewalt and G. Struckmeier, *Z. Anorg. Allg. Chem.*, **419**, 163 (1976); f) M. Zehnder, U. Thewalt, and S. Fallab, *Helv. Chim. Acta*, **59**, 2290 (1976); g) E. Bouwman and W. L. Driessen, *J. Am. Chem. Soc.*, **110**, 4440 (1988).

17) R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, **79**, 139 (1979), and the references cited therein.

18) E. C. Niederhoffer, J. H. Timmons, and A. E. Martell, *Chem. Rev.*, **84**, 137 (1984), and the references cited therein.

19) W. R. Harris, I. Murase, J. H. Timmons, and A. E. Martell, *Inorg. Chem.*, **17**, 889 (1978); S. R. Pickens and A. E. Martell, *Inorg. Chem.*, **19**, 15 (1980).

20) S. R. Pickens and A. E. Martell, *Inorg. Chem.*, **19**, 15 (1980).

21) Y. Nishida, H. Shimo, H. Maehara, and S. Kida, *J. Chem. Soc., Dalton Trans.*, **1985**, 1945.

22) B. P. Murch, F. C. Bradley, P. D. Boyle, V. Papaefthymiou, and L. Que, Jr., *J. Am. Chem. Soc.*, **109**, 7993 (1987).

23) A. S. Borovik, V. Papaefthymiou, L. F. Taylor, O. P. Anderson, and L. Que, Jr., *J. Am. Chem. Soc.*, **111**, 6183 (1989).

24) M. Mikuriya, Y. Yamato, and T. Tokii, *Bull. Chem. Soc. Jpn.*, **65**, 2624 (1992).

25) D. L. Jameson, C. L. Xie, D. N. Hendrickson, J. A. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, **109**, 740 (1987); Q. Chen, J. B. Lynch, P. G. Romero, A. B. Hussein, G. B. Jameson, C. J. O'Conner, and L. Que, Jr., *Inorg. Chem.*, **27**, 2673 (1988); M. Suzuki, T. Sugisawa, H. Senda, H. Oshio, and A. Uehara, *Chem. Lett.*, **1989**, 1091; M. Suzuki, H. Senda, M. Suenaga, T. Sugisawa, and A. Uehara, *Chem. Lett.*, **1990**, 923; S. Menage, B. A. Brennan, C. J. Garcia, E. Münck, and L. Que, Jr., *J. Am. Chem. Soc.*, **112**, 6423 (1990); Y. Hayashi, M. Suzuki, A. Uehara, Y. Mizutani, and T. Kitagawa, *Chem. Lett.*, **1992**, 91; S. Kawata, M. Nakamura, Y. Yamashita, K. Asai, K. Kikuchi, I. Ikemoto, M. Katata, and H. Sano, *Chem. Lett.*, **1992**, 135.