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Dinuclear Cobalt(II) Complexes with Various Dinucleating Ligands and Their Dioxygen Complexes

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Various types of dinuclear cobalt(II) complexes, $[Co_2L(CH_3COO)_2]ClO_4$, $[Co_2L(CH_3COO)](ClO_4)_2$, $[Co_2L(OH)](ClO_4)_2$, $[Co_2L(C_3H_3N_2)](ClO_4)_2(C_3H_3N_2^-$=pyrazolate), and $[Co_2LX_2](ClO_4)_n$, were prepared, where HL represents 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol(Hbpmp), 2,6-bis[*N*-(2-pyridylmethyl)-2-(2-pyridyl)ethylaminomethyl]-4-methylphenol(Hbpmep), 2,6-bis[bis[2-(2-pyridyl)ethyl]aminomethyl]-4-methylphenol(Hbpep), and 2,6-bis[bis(2-benzimidazolylmethyl)aminomethyl]-4-methylphenol(Hbbimp), and X is N_3^-, NCS^-, Cl^-, Br^-, H_2O, or py(pyridine). The electronic spectra and magnetic moments of the complexes revealed that $[Co_2L(CH_3COO)_2]ClO_4$ (L=bpmp, bpmep, or bpep) are high-spin octahedral, whereas the other complexes have five-coordinate structure of high-spin configuration. Some of the bpmp and the bpmep complexes reacted reversibly with molecular oxygen more or less. The $P_{1/2}$ of some complexes were determined spectrometrically. The oxygen affinities of the complexes are highly dependent on the natures of the dinucleating ligands and additional bridging or unidentate ligands.

It has been demonstrated that a number of metal complexes with sterically and electronically controlled ligand environment reversibly bind molecular oxygen. Dinuclear metal complexes in which two metal ions are in suitable positions can bind molecular oxygen to form 2:1 (metal:O_2) dioxygen adducts.[1,2]

In biological system, hemocyanine and hemerythrin contain two metal ions (copper for hemocyanine and iron for hemerythrin) at each oxygen binding site and form 2:1 dioxygen adducts. For those complexes, it has been postulated that two metal ions are linked by such bridging ligands as phenolate, carboxylate, hydroxide, or oxide.[3,4]

In the previous studies,[5,6] we demonstrated that dinuclear cobalt(II) complexes having phenolate and carboxylate bridges, $[Co_2(bpmp)(CH_3COO)_2]ClO_4$ and $[Co_2(bpmp)(CH_3COO)](ClO_4)_2$, react with molecular oxygen to form 2:1 dioxygen adduct, $[Co_2(bpmp)(CH_3COO)(O_2)](ClO_4)_2\cdot 2H_2O$. The X-ray analysis of $[Co_2(bpmp)(benzoato)(O_2)](BF_4)_2\cdot 2H_2O$ showed that two cobalt ions are linked by three bridging ligands, *viz.* dioxygen, phenolate, and benzoate, and the O-O bond distance is 1.43 Å which is in the range of those of the μ-peroxo complexes.[6]

As an extension of the above studies, we have synthesized various types of dinuclear cobalt(II) complexes with the dinucleating ligands shown in Fig. 1, and their reactivities toward molecular oxygen have been investigated spectrometrically.

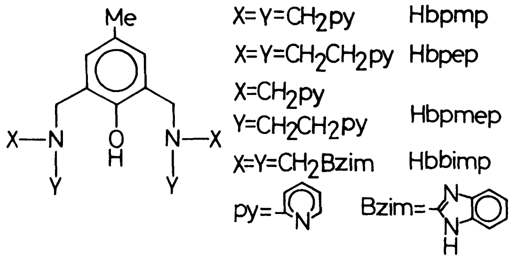

Fig. 1. Dinucleating ligands.

Experimental

Preparation of Ligands. Bis[2-(2-pyridyl)ethyl]amine was prepared according to the literature.[7] Bis(2-benzimidazolylmethyl)amine was synthesized by heating a mixture of iminodiacetic acid and *o*-phenylenediamine at 200 °C. *N*-(2-pyridylmethyl)-2-(2-pyridyl)ethylamine was prepared as follows. An ethanol solution of 2-(2-pyridyl)ethylamine (0.1 mol) and 2-pyridinecarbaldehyde (0.1 mmol) was refluxed for 30 min. The resulting Schiff base was hydrogenated under 4 atm pressure (1 atm=1.013×10^5 Pa) at room temperature using 1 g of 5% Pd-C catalyst. Approximately one molar equivalent of hydrogen was absorbed during 2 h. The filtered solution was distilled and fraction, bp 155—160 °C (133 pa), was collected. This was used for the preparation of Hbpmep without further purifications.

Hbpmep and Hbpep were prepared in the same way as that of Hbpmp.[5] Those ligands were used without further purifications. Hbbimp was prepared as follows. To a dimethylformamide solution (200 cm^3) of bis(2-benzimidazolylmethyl)amine (0.1 mol) and triethylamine (0.1 mol) was added 2,6-bis(chloromethyl)-4-methylphenol (0.05 mol) with stirring in small portions during 1 h at −30 °C. The solution was stirred for 1 h at 0 °C and then dimethylformamide was removed under reduced pressure. The residue was dissolved in 200 cm^3 of hot methanol and after cooling, white powder was obtained.

Preparation of Complexes. For the preparation of the bpmp and the bpmep cobalt(II) complexes, all the manipulations were carried out under argon atmosphere.

$[Co_2L(CH_3COO)_2]ClO_4$ (L=bpmp, bpmep, bpep, or bbimp). The complexes were prepared by the same method as that of $[Co_2(bpmp)(CH_3COO)_2]ClO_4$.[5]

$[Co_2L(CH_3COO)](ClO_4)_2$ (L=bpmp or bpep). Sodium acetate (0.5 mmol) was mixed with a methanol solution (30 cm^3) containing HL (0.5 mmol) and $Co(ClO_4)_2\cdot 6H_2O$ (1 mmol). Pink crystals deposited were collected by filtration, washed with methanol, and dried *in vacuo*. The bpmp complex was air-sensitive and exposure to air caused a color change from pink to brown. The elemental analysis was carried out for the brown compound.

$[Co_2L(OH)](ClO_4)_2$ (L=bpmp or bbimp). The prepar-

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ation of the bpmp complex is exemplified. To a methanol solution (30 cm^3) containing Hbpmp (0.5 mmol) and $Co(ClO_4)_2 \cdot 6H_2O$ (1 mmol) was added a methanol solution (20 cm^3) of CH_3ONa (1 mmol) with stirring. The complex was obtained as green powder, which was filtered, washed with methanol, and dried *in vacuo*.

$[Co_2(bpmp)X_2]ClO_4$ (X=N_3^-, NCS$^-$, Cl$^-$, or Br$^-$). The complexes were prepared in a similar way. The typical procedure of the preparation is as follows. To a methanol solution (30 cm^3) of Hbpmp (0.5 mmol) and NaBr (1 mmol) was added a methanol solution (20 cm^3) of $Co(ClO_4)_2 \cdot 6H_2O$ (1 mmol). Violet crystals deposited were collected by filtration, washed with methanol, and dried *in vacuo*.

$[Co_2L(C_3H_3N_2)](ClO_4)_2$ (L=bpmp or bpmep). To a mixture of HL (0.5 mmol), $Co(ClO_4)_2 \cdot 6H_2O$ (1 mmol), and pyrazole (0.5 mmol) in hot ethanol was added dropwise a methanol solution (20 cm^3) of CH_3ONa (1 mmol) with stirring and then the solution was concentrated to 20 cm^3 under reduced pressure. Reddish brown powder deposited was collected by filtration, washed with cold ethanol, and dried *in vacuo*. The complexes were air-sensitive and exposure to air caused a color change from reddish brown to brown. The elemental analysis of the bpmp complex was carried out for the brown compound. For the bpmp complex, the elemetal analysis was carried out for the dioxygen complex (*vide infra*).

$[Co_2(bbimp)(OH_2)_2](ClO_4)_3$. Addition of Hbbimp (0.5 mmol) to 30 cm^3 of ethanol solution of $Co(ClO_4)_2 \cdot 6H_2O$ (1 mmol) gave violet crystals, which were filtered, washed with ethanol, and dried *in vacuo*.

$[Co_2(bbimp)(py)_2](ClO_4)_3 \cdot 2H_2O$. Addition of ethanol (50 cm^3) to a methanol solution (20 cm^3) containing Hbbimp (0.5 mmol), $Co(ClO_4)_2 \cdot 6H_2O$ (1 mmol), and 500 mg of pyridine afforded violet crystals, which were filtered, washd with ethanol, and dried *in vacuo*.

$[Co_2L(CH_3COO)(O_2)](ClO_4)_2$ (L=bpmp or bpmep). A brown methanol solution (100 cm^3) containing HL (0.5 mmol), $Co(ClO_4)_2 \cdot 6H_2O$ (1 mmol), and CH_3COONa (0.5 mmol) was left to stand overnight in air atmosphere. Brown crystals deposited were filtered, washed with ethanol, and dried.

$[Co_2(bpmp)(C_3H_3N_2)(O_2)](ClO_4)_2 \cdot 2H_2O$. To a methanol solution (50 cm^3) containing Hbpmp (0.5 mmol), $Co(ClO_4)_2 \cdot 6H_2O$ (1 mmol), and pyrazole (0.5 mmol) was added dropwise a methanol solution of CH_3ONa (1 mmol) with stirring. The resulting solution was exposed to air and allowed to stand overnight. The brown powder deposited was filtered, washed with ethanol, and dried.

$[Co_2(bpmp)(OH)(O_2)](BPh_4)_2 \cdot CH_3CN \cdot H_2O$. Sodium tetraphenylborate ($NaBPh_4$)(1.5 mmol) was added to an acetonitrile solution of $[Co_2(bpmp)(OH)](ClO_4)_2 \cdot 0.5H_2O$ (0.5 mmol) in air atmosphere. The resulting brown solution was allowed to stand overnight to give brown crystals, which were filtered, washed with methanol, and dired.

Measurements. The electronic spectra of solutions and of solids were obtained with a Hitachi EPS-3T recording spectrophotometer and infrared spectra were recorded with a Hitachi 295 infrared spectrophotometer by means of KBr disks. Electrolytic conductivities at 25 °C on approximately 10^{-3} M (1 M=1 mol dm^{-3}) acetonitrile and methanol solutions were obtained using Yokogawa-Hawlett-Packard 4261 LCR meter. Magnetic susceptibilities were measured by Faraday method in a temperature range from liquid nitrogen temperature to room temperature. Magnetic moments were calculated by the expression, $\mu_{eff}=2.828\sqrt{\chi_a \times T}$, where χ_a is the magnetic susceptibility per one cobalt ion corrected for diamagnetism using Pascal's constants.

Oxygen Uptake Measurement. The equilibrium constants (K) for the reaction

$$[Co_2] + O_2 \rightleftharpoons [Co_2 \cdot O_2] \qquad (1)$$

were determined at 25 °C(±0.5) in acetonitrile or methanol using visible spectroscopy. In a typical measurement, 7×10^{-6} mol of $[Co_2(bpmp)(N_3)_2]^+$ was dissolved in 50 cm^3 of acetonitrile in a specially designed reaction cell equipped with a quartz cell (1 cm path length). The reaction cell was evacuated and filled with argon gas, and heated at 70 °C until almost colorless solution was obtained. Then the reaction cell was evacuated for a while. Subsequently, after temperature equilibration, various pressures of oxygen were added to the reaction cell, and the contents were stirred until the constant absorbance was obtained. In the case of $[Co_2(bpmp)(CH_3COO)]^{2+}$, $[Co_2(bpmp)(C_3H_3N_2)]^{2+}$, $[Co_2(bpmp)(OH)]^{2+}$, and $[Co_2(bpmp)(CH_3COO)_2]^+$, various pressures of argon gas containing known oxygen partial pressure were added. Equilibrium constants were calculated by the method of Collman *et al.*[8] using the following equation,

$$P_{O_2} = [Co_2]_T \cdot l \cdot \Delta\varepsilon \cdot P_{O_2}/(A-A_0) - K^{-1},$$

where P_{O_2} is the partial pressure of O_2, $[Co_2]_T$ is the total complex concentraton, l is the path length of the cell, A is the absorbance of the solution at the oxygen pressure P_{O_2} and A_0 is the absorbance of the solution in the absence of oxygen, $\Delta\varepsilon$ is the difference between molar extinction coefficients of the oxy and the deoxy complexes. A plot of P_{O_2} *vs.* $P_{O_2}/(A-A_0)$ should be a straight line with slope of $[Co_2]_T \cdot l \cdot \Delta\varepsilon$ (constant) and intercept of $-K^{-1}$. Straight lines were then computor fit and the equilibrium constants (K) were determined from the intercepts.

The slopes of the plots of $\log((A-A_0)/(A_\infty-A))$ *vs.* $\log(P_{O_2})$ were 1.0—1.2, indicating a 1:1 stoichiometry for the oxygenation reaction (1). In the cases where complete oxygenation was not obtained at O_2 pressure of *ca.* 700 Torr (1 Torr=133.322 Pa), the values of A_∞ were determined by extrapolating a plot of A *vs.* P_{O_2} to infinite pressure.[9]

In the case of $[Co_2(bpmp)(CH_3COO)]^{2+}$, $[Co_2(bpmp)(C_3H_3N_2)]^{2+}$, and $[Co_2(bpmp)(OH)]^{2+}$ the values for K could not be obtained because of very small amount of O_2 involved for those measurements and $P_{1/2}$ values are only roughly estimated numbers, where $P_{1/2}$ represents a partial oxygen pressure at which 50% of the complex is oxygenated.

Results and Discussion

Dinuclear Cobalt(II) Complexes. The magnetic moments of the dinuclear cobalt(II) complexes are given in Table 1 (4.1—4.8 BM, 1 BM=9.274×10^{-24} J T^{-1}). Those values indicate that all the complexes have the high-spin configuration.

The electronic spectral data of the dinuclear cobalt(II) complexes are summarized in Table 2 and the representative electronic spectra are shown in Fig. 2. The electronic spectra of the complexes indicate that $[Co_2L(CH_3COO)_2]^+$ (L=bpmp, bpmep, or bpep) are six-coordinate, whereas all the other complexes are five-coordinate.

The complexes, $[Co_2L(CH_3COO)_2]^+$, show two d-d bands at *ca.* 9000 and 21000 cm^{-1}, except for $[Co_2(bbimp)(CH_3COO)_2]^+$ (Table 2 and Fig. 2). The spectra are closely similar to that of octahedral hexaaquacobalt(II).[10] In these six-coordinate complexes, two acetate ions can coordinate to cobalt ions in two way, *viz.* as chelating ligands or as bridging ligands in syn-syn configuration.[11] An examination of a Dreiding model suggested that the two acetate ions function as

TABLE 1. ELEMENTAL ANALYSES AND MAGNETIC MOMENTS OF COMPLEXES AT ROOM TEMPERATURE

Complex	Found(Calcd)(%)			μ_{eff}/BM
	C	H	N	
$[Co_2(bpmp)(CH_3COO)_2]ClO_4$	51.10(51.37)	4.65(4.54)	9.42(9.71)	4.6
$[Co_2(bpmp)(CH_3COO)](ClO_4)_2$	45.15(45.52)	4.08(3.93)	8.85(9.10)	
$[Co_2(bpmp)(OH)](ClO_4)_2 \cdot 0.5H_2O$	45.54(45.43)	4.14(4.04)	9.44(9.63)	4.1
$[Co_2(bpmp)(N_3)_2]ClO_4 \cdot H_2O$	46.57(46.68)	4.00(4.15)	19.38(19.79)	4.2
$[Co_2(bpmp)(NCS)_2]ClO_4 \cdot H_2O$	47.67(47.71)	3.84(4.00)	12.48(12.71)	4.4
$[Co_2(bpmp)Br_2]ClO_4$	43.51(43.71)	3.65(3.67)	9.18(9.28)	4.3
$[Co_2(bpmp)Cl_2]ClO_4 \cdot 3H_2O$	45.51(45.46)	4.69(4.51)	9.29(9.64)	4.6
$[Co_2(bpmp)(CH_3COO)(O_2)](ClO_4)_2 \cdot 2H_2O$	43.04(43.18)	3.96(4.14)	8.55(8.63)	0.5
$[Co_2(bpmp)(C_3H_3N_2)(O_2)](ClO_4)_2 \cdot 2H_2O$	44.06(44.05)	3.89(4.11)	11.28(11.42)	0.7
$[Co_2(bpmp)(OH)(O_2)](Bph_4)_2 \cdot CH_3CN \cdot H_2O$	71.87(71.72)	5.60(5.73)	6.84(6.96)	0.2
$[Co_2(bpmep)(CH_3COO)_2]ClO_4 \cdot H_2O$	51.75(51.41)	5.22(4.98)	9.00(9.22)	4.7
$[Co_2(bpmep)(CH_3COO)(O_2)](ClO_4)_2 \cdot 2.5H_2O$	43.95(43.98)	4.41(4.49)	8.44(8.32)	
$[Co_2(bpmep)(C_3H_3N_2)](ClO_4)_2 \cdot 2H_2O$	46.61(46.69)	4.33(4.54)	11.19(11.46)	
$[Co_2(bpep)(CH_3COO)_2]ClO_4 \cdot H_2O$	52.20(52.43)	5.04(5.26)	8.92(8.95)	4.8
$[Co_2(bpep)(CH_3COO)](ClO_4)_2 \cdot 1.5H_2O$	47.35(47.38)	5.04(4.79)	8.27(8.50)	4.5
$[Co_2(bbimp)(CH_3COO)_2]BF_4 \cdot 3H_2O$	50.63(50.86)	4.47(4.65)	12.99(13.18)	4.2
$[Co_2(bbimp)(OH)](ClO_4)_2 \cdot 3H_2O$	45.90(45.87)	3.80(4.13)	13.14(13.05)	4.4
$[Co_2(bbimp)(OH_2)_2](ClO_4)_3$	43.09(43.27)	3.68(3.63)	12.27(12.31)	4.3
$[Co_2(bbimp)(py)_2](ClO_4)_3 \cdot 2H_2O$	47.08(47.26)	4.03(3.97)	12.84(12.97)	4.3

TABLE 2. ABSORPTION SPECTRAL DATA

Complex	Absorption $^{a)}$ $\tilde{\nu}/10^3$ cm^{-1}					
$[Co_2(bpmp)(CH_3COO)_2]ClO_4$	$21.00^{b)}$	19.60^{s}	18.60^{s}		9.40	
$[Co_2(bpmp)(CH_3COO)](ClO_4)_2$	22.20	19.92	17.50		10.58	≈6.5
$[Co_2(bpmp)(OH)](ClO_4)_2 \cdot 0.5H_2O$	22.00	21.10	16.60	15.90^{s}	14.20^{s}	≈6.5
$[Co_2(bpmp)(N_3)_2]ClO_4 \cdot H_2O$	21.60	19.60	18.80^{s}	17.90	9.20	≈6.7
$[Co_2(bpmp)(NCS)_2]ClO_4 \cdot H_2O$	22.50	19.20	17.90		11.00	6.58
$[Co_2(bpmp)Br_2]ClO_4$	21.40	19.80	17.50	14.80^{s}	8.70	≈6.7
$[Co_2(bpmp)Cl_2]ClO_4 \cdot 3H_2O$	21.50	20.00^{s}	18.30^{s}	17.80	14.30	≈8.0—6.3$^{b)}$
$[Co_2(bpmp)(C_3H_3N_2)]^{2+}$	CT			17.50^{s}	10.50	≈6.0
$[Co_2(bpmep)(CH_3COO)_2]ClO_4 \cdot H_2O$	21.50^{s}	20.50	19.80^{s}	18.70^{s}	8.80	
$[Co_2(bpmep)(CH_3COO)]^{2+}$	CT	22.00^{s}			10.40	≈6.0
$[Co_2(bpmep)(C_3H_3N_2)](ClO_4)_2 \cdot 2H_2O$	21.70^{s}	19.80	18.90^{s}	11.40^{s}		≈7.4—5.9$^{b)}$
$[Co_2(bpep)(CH_3COO)_2]ClO_4 \cdot H_2O$	21.10^{s}	20.20	19.50^{s}	18.50^{s}	8.70	
$[Co_2(bpep)(CH_3COO)](ClO_4)_2 \cdot 1.5H_2O$	22.00^{s}	19.00	18.10	14.30^{s}	9.0	≈5.3
$[Co_2(bbimp)(CH_3COO)_2]BF_4 \cdot 3H_2O$	20.40^{s}	17.90		12.90		≈6.0
$[Co_2(bbimp)(OH)](ClO_4)_2 \cdot 3H_2O$	20.40	19.60	16.90	12.90		6.06
$[Co_2(bbimp)(OH_2)_2](ClO_4)_3$	20.40^{s}	18.50		13.70		6.20
$[Co_2(bbimp)(py)_2](ClO_4)_3 \cdot 2H_2O$	20.60^{s}	18.70		13.90		6.30

a): In acetonitrile. b): Broad band. s: Shoulder.

bridging ligands. Therefore, we assumed that the six-coordinate complexes possess the structure given in Fig. 3a, where two cobalt ions are linked by three bridging ligands, *viz.* two acetates and one phenolate.

In contrast to the above complexes, $[Co_2(bbimp)(CH_3COO)_2]^+$ shows several d-d bands in the visible and the near infrared regions (Fig. 2). In general, five-coordinate cobalt(II) complexes exhibit several d-d bands in 5000—25000 cm^{-1}.[12] Thus the electronic spectrum of the complex indicates the presence of a five-coordinate cobalt(II) chromophere. The two acetate ions in this complex, therefore, coordinate to cobalt ions as unidentate ligands. A possible structure of the complex is given in Fig. 3e. Of particular interest is that bbimp forms five-coordinate bis(acetato) complex, whereas the other dinucleating ligands form six-coordinate bis(acetato) complexes. Such structural change in the bbimp complex seems to be attributed to a steric requirement in the bbimp complex; a steric interaction between bulky benzimidazolyl groups and methyl groups of the acetate ions may enforce five-coordinate structure.

The electronic spectra of $[Co_2(bpmp)X_2]$ ($X = N_3^-$, NCS^-, Cl^-, or Br^-) show that the complexes have five-

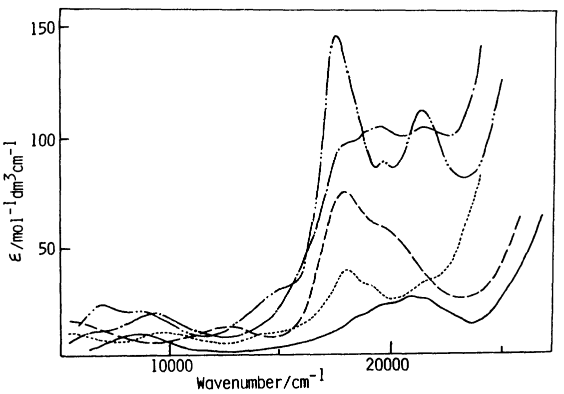

Fig. 2. Absorption spectra of $[Co_2(bpep)(CH_3COO)_2]^+$ (——), $[Co_2(bbimp)(CH_3COO)_2]^+$ (----), $[Co_2(bpep)(CH_3COO)]^{2+}$ (……), $[Co_2(bpmp)(N_3)_2]^+$ (—·—), and $[Co_2(bpmp)Br_2]^+$ (—··—) in acetonitrile.

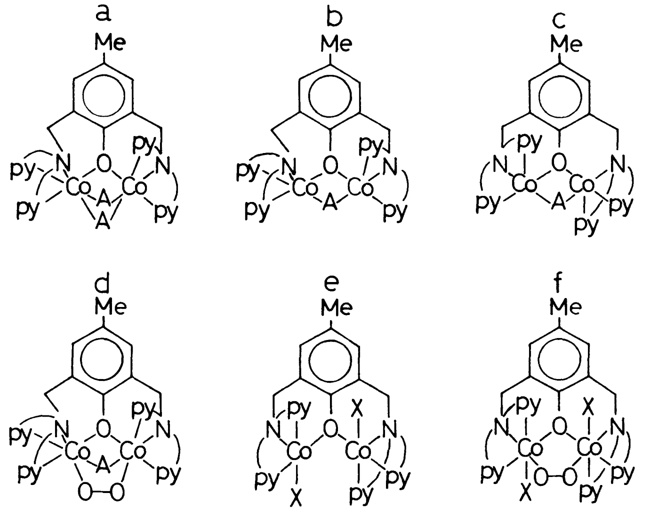

Fig. 3. Proposed structures of dinuclear complexes. A is CH_3COO^-, $C_3H_3N_2^-$, or OH^-, and X is N_3^-, NCS^-, Cl^-, or Br^-.

coordinate structure. The molar conductivities of the complexes in acetonitrile are 134—139 Ω^{-1} cm^2 mol^{-1}, which are typical for 1 : 1 electrolytes in acetonitrile,[13] supporting the above formula, $[Co_2(bpmp)X_2]^+$. The structure of the complexes seem to be essentially identical to that of $[Co_2(bbimp)(CH_3COO)_2]^+$ (Fig. 3e), where the two cobalt(II) ions are bridged by only phenolate.

The electronic spectra of the mono(acetato), mono(pyrazolato), mono(hydroxo) complexes also revealed that all the complexes are five-coordinate. In these complexes, the acetate, pyrazolate, and hydroxide ions seem to function as bridging ligands as found in the dinuclear copper(II) complexes containing such ions.[14]

For those complexes, there are two possible structures shown in Fig. 3b and c. Judging from the reactivities of the mono(acetato) and mono(pyrazolato) complexes with molecular oxygen in the solid state (*vide infra*), the structure b seems to be preferable. On the other hand, the structure (c) seems to be preferable for the hydroxo complex (*vide infra*).

In general, the magnetic moments of six-coordinate complexes are larger than those of five-coordinate complexes because of an extensive contribution from an orbital angular momentum in $^4T_{1g}$ ground state in octahedral symmetry. Such tendency can be observed for the present complexes (Table 1).

Table 3. Magnetic data

Complex	μ_{eff} BM 82 K	μ_{eff} BM 291 K	θ K
$[Co_2(bpmp)(CH_3COO)_2]ClO_4$	4.37	4.61	−15
$[Co_2(bpmp)(OH)](ClO_4)_2 \cdot 0.5H_2O$	3.75	4.12	−27
$[Co_2(bpmp)(NCS)_2]ClO_4 \cdot H_2O$	3.73	4.37	−51
$[Co_2(bbimp)(OH_2)_2](ClO_4)_3$	3.73	4.28	−36
$[Co_2(bbimp)(OH)](ClO_4)_2 \cdot 3H_2O$	4.16	4.40	−12

The magnetic susceptibilities of the complexes listed in Table 3 were measured in the temperature range 80—300 K. The magnetic moment of the six-coordinate complex, $[Co_2(bpmp)(CH_3COO)_2]ClO_4$, decreases with temperature. However, this does not necessarily imply antiferromagnetic interaction between the cobalt(II) ions, since monomeric six-coordinate cobalt(II) complexes show such a decrease of magnetic moments because of an extensive contribution from an angular orbital momentum in $^4T_{1g}$ ground state in octahedral symmetry.[15] The magnetism of the complex obeys the Curie-Weiss law in the temperature range 80—300 K and the Weiss constant is −15 K. The Weiss constants of the monomeric cobalt(II) complexes have been shown to be in the range −10—−40 K.[15] Thus the magnetic interaction between the cobalt(II) ions must be negligibly small. The magnetisms of the five-coordinate complexes also obey the Curie-Weiss law. The Weiss constants are −10—−50 K. These values suggest that the antiferromagnetic interactions in the complexes are weak.

Oxygenation Reactions. Since all the oxygenated complexes showed intense brown color, the oxygenation can be easily followed spectrometrically. Brown color of the oxygenated complexes may be attributable to the charge transfer transitions from dioxygen and/or phenolic oxygen to the cobalt centers. The representative spectral change upon oxygenation is given in Fig. 4. The dioxygen complexes isolated are essentially diamagnetic (Table 1). The X-ray structure determination of $[Co_2(bpmp)(benzoato)(O_2)](BF_4)_2 \cdot 2H_2O$ has shown that the O-O bond distance is 1.43 Å and the two cobalt ions are bridged by three ligands, dioxygen, phenolate, and benzoate (see Fig. 3d). These observations suggest that the dioxygen complexes are of μ-peroxo type.

The six-coordinate complex, $[Co_2(bpmp)(CH_3COO)_2]ClO_4$, was stable on exposure to air in the solid state, whereas the complex underwent oxygenation in methanol. The molar conductivity of the complex in methanol gradually increased by bubbling O_2 (90 → 150 Ω^{-1} cm^2 mol^{-1}), indicating the formation of a 2 : 1 electrolyte upon oxygenation.[13] The addition of sodium perchlorate in methanol solution in air atmosphere afforded brown crystals, $[Co_2(bpmp)(CH_3COO)(O_2)]$-

TABLE 4. EQUILIBRIUM CONSTANTS FOR THE REACTION $[Co_2]+O_2 \rightleftharpoons [Co_2{\cdot}O_2]^{a)}$ AT 20 °C

Complex 7×10^{-6} mol	Solvent	$\log(K/\mathrm{Torr}^{-1})$	$P_{1/2}$/Torr
$[Co_2(bpmp)(CH_3COO)_2]^+$	CH_3OH	$-0.8 \pm 0.1^{b)}$	6
$[Co_2(bpmp)(CH_3COO)]^{2+}$	CH_3CN		$\approx 0.1^{c)}$
$[Co_2(bpmp)(C_3H_3N_2)]^{2+}$	CH_3CN		$\approx 0.1^{c)}$
$[Co_2(bpmp)(N_3)_2]^+$	CH_3CN	-1.70 ± 0.02	50
$[Co_2(bpmep)(CH_3COO)]^{2+}$	CH_3CN	-1.39 ± 0.03	24

a): Standard state of 1 Torr. b): For the reaction, $[Co_2(bpmp)(CH_3COO)_2]^+ + O_2 \rightleftharpoons [Co_2(bpmp)(CH_3COO)(O_2)]^{2+} + CH_3COO^-$, K is calculated by the following equation, $K=[Co_2{\cdot}O_2]/[Co_2]{\cdot}P_{O_2}$, where the concentration of the acetate ion dissociated is omitted. c): Only roughly estimated number.

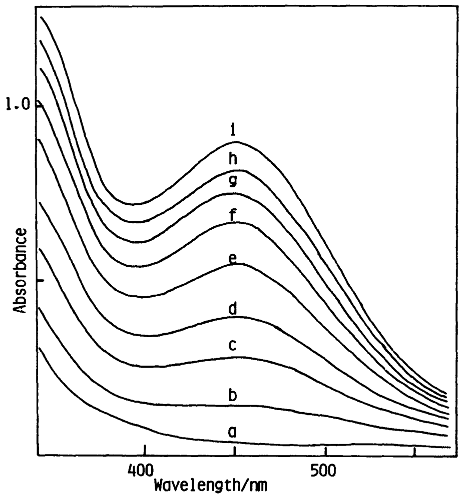

Fig. 4. Spectral change as a function of oxygen pressure for the reversible oxygenation of $[Co_2(bpmp)(N_3)_2]^+$ in acetonitrile at 20 °C. Spectra of a—i are at partial pressure of oxygen: 0, 6, 19, 32, 60, 104, 172, 284, and 692 Torr, respectively.

$(ClO_4)_2{\cdot}2H_2O$, the structure of which is given in Fig. 3d. It is noteworthy that no oxygenation was observed in acetonitrile and dichloromethane. In addition, the oxygenation in a methanol solution was suppressed by the addition of sodium acetate. Those observations suggest that the oxygenation proceeds *via* the five-coordinate complex, $[Co_2(bpmp)(CH_3COO)]^{2+}$, and the dissociation of the acetate ion from $[Co_2(bpmp)(CH_3COO)_2]^+$ is suppressed in acetonitrile and dichloromethane. Therefore, it is likely that the oxygenation of the complex proceeds as follows,

$$[Co_2(bpmp)(CH_3COO)_2]^+ \rightleftharpoons [Co_2(bpmp)(CH_3COO)]^{2+} + CH_3COO^-$$

$$[Co_2(bpmp)(CH_3COO)]^{2+} + O_2 \rightleftharpoons [Co_2(bpmp)(CH_3COO)(O_2)]^{2+}.$$

$P_{1/2}$ for the complex is 6 Torr in methanol at 20 °C and may be controlled by the addition of sodium acetate. $[Co_2(bpmep)(CH_3COO)_2]^+$ also reacted reversibly with molecular oxygen in methanol. However, the oxygen affinity is too low to determine $P_{1/2}$ at 20 °C. For $[Co_2(bpep)(CH_3COO)_2]^+$, no oxygenation was observed in methanol even at −40 °C.

In contrast to the above six-coordinate complex with bpmp, the five-coordinate complex, $[Co_2(bpmp)(CH_3COO)]^{2+}(ClO_4)_2$, is air-sensitive in the solid state. Finely powdered compound gradually changed its color from pink to brown in the presence of O_2. The magnetic moment of the pink compound gradually decreased from 4.3 to 1.4 BM with color change at room temperature in air atmosphere. The pink compound also showed an infrared spectral change (Fig. 5). The brown compound resulted on exposure to air for 24 h shows a spectrum almost identical to that of $[Co_2(bpmp)(CH_3COO)(O_2)](ClO_4)_2{\cdot}2H_2O$. Heating the brown compound at *ca.* 140 °C *in vacuo* regenerated pink compound. Thus $[Co_2(bpmp)(CH_3COO)](ClO_4)_2$ reacts reversibly with molecular oxygen in the solid state. Such reversible O_2 binding in the solid state suggests that the coordination sites of the two cobalt ions should be close enough to bind O_2 in μ-peroxo fashion without extensive rearrangement of the structure. A possible structure of the five-coordinate complex is sketched in Fig. 3b.

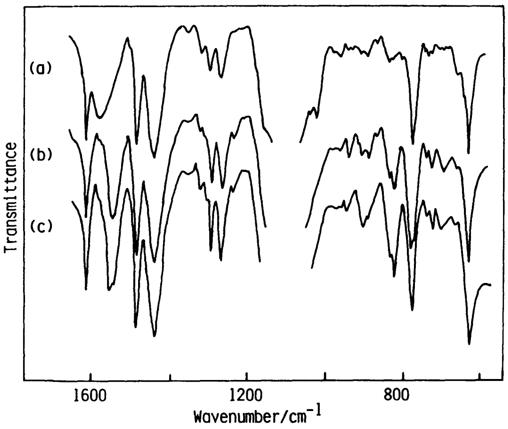

Fig. 5. Infrared spectra of $[Co_2(bpmp)(CH_3COO)](ClO_4)_2$ (a and b), and $[Co_2(bpmp)(CH_3COO)(O_2)](ClO_4)_2{\cdot}2H_2O$(c). a, freshly prepared; b, after 24 h.

The complex also underwent reversible oxygenation in acetonitrile. The deoxygenation by bubbling of argon gas was extremely slow at room temperature, whereas it was much accelerated by heating a solution at about 70 °C. No decomposition was observed after ten oxygenation-deoxygenation cycles. The $P_{1/2}$ of the complex is ≈0.1 Torr at 20 °C in acetonitrile. The dioxygen complex with bpmep, $[Co_2(bpmep)(CH_3COO)(O_2)](ClO_4)_2{\cdot}2H_2O$, also underwent reversible

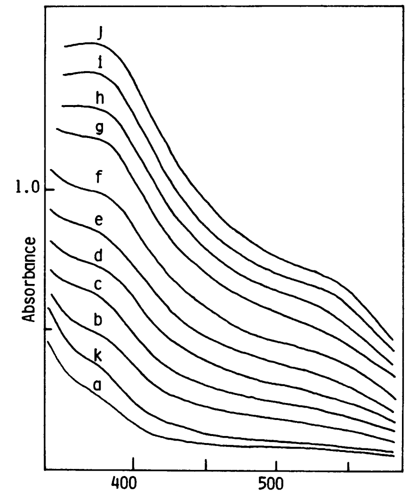

Fig. 6. Spectral change as a function of oxygen pressure for the oxygenation of $[Co_2(bpmep)(C_3H_3N_2)]^{2+}$ in acetonitrile at 20 °C. The spectra of a—j are at partial pressure of oxygen: 0, 10, 22, 42, 74, 119, 201, 301, 483, and 655 Torr, respectively. The spectrum k is at 0 Torr O_2 after oxygenation-deoxygenation cycle.

deoxygenation-oxygenations in acetonitrile. The $P_{1/2}$ is 25 Torr at 20 °C, which is considerably larger than that of the corresponding bpmp complex. In contrast to the above complexes, $[Co_2(bpep)(CH_3COO)]^{2+}$ did not react with molecular oxygen even at −40 °C in acetonitrile.

The pyrazolato-bridged complexes with bpmp and bpmep were also air-sensitive in the solid state. Reddish brown compounds turned brown upon exposure to air. For the bpmep complex, heating the brown compound at 140 °C regenerated the reddish brown compound, whereas the bpmp complex decomposed without the color change to reddish brown by heating. However, the reversible O_2 binding was observed for the bpmp complex in acetonitrile. The $P_{1/2}$ is $\approx$0.1 Torr at 20 °C, which is comparable to that of the mono(acetato) complex, with bpmp. On the other hand, for the bpmep complex, the oxygenation was not completely reversible in acetonitrile at 20 °C (Fig. 6) and a plot of P_{O_2} *vs.* $P_{O_2}/(A-A_0)$ did not give a straight line. Under such conditions, the $P_{1/2}$ was roughly estimated as $\approx$80 Torr.

In contrast to the above five-coordinate acetato- and pyrazolato-bridged complexes, $[Co_2(bpmp)(OH)](ClO_4)_2 \cdot 0.5H_2O$ was stable on exposure to air in the solid state. The complex reacted with molecular oxygen in acetonitrile to give brown solution and heating the brown solution at about 70 °C under argon atmosphere regenerated green solution. The addition of sodium tetraphenylborate to an acetonitrile solution in air atmosphere afforded brown crystals, $[Co_2(bpmp)(OH)(O_2)](BPh_4)_2 \cdot CH_3CN \cdot H_2O$. A possible structure of the oxygenated complex is given in Fig. 3d, which is essentially identical to those of the corresponding acetato and pyrazolato complexes.

An attempt to determine the $P_{1/2}$ was made in acetonitrile at 20 °C. The oxygenation was very slow as compared with those of the acetato and pyrazolato complexes at low oxygen pressure (0.2 Torr) and some decomposition was observed during the measurement. Under such conditions, the $P_{1/2}$ was roughly estimated as smaller than 0.2 Torr which is comparable to those of the acetato and pyrazolato complexes with bpmp.

There are two possible structures for $[Co_2(bpmp)(OH)]^{2+}$ as shown in Fig. 3b and c. The structure (b) is essentially identical to those of the acetato and pyrazolato complexes and the oxygen binding sites are close to each other. Therefore, the complex having the structure (b) would be expected to react with molecular oxygen in the solid state. On the other hand, for the structure (c), an extensive rearrangement of the structure is necessary for O_2 binding. Since the complex did not react with molecular oxygen in the solid state and the oxygenation was extremely slow as compared with those of the acetato and pyrazolato complexes in acetonitrile, the structure (c) seems to be plausible.

The complexes, $[Co_2(bpmp)X_2]^+$ ($X=N_3^-$ or NCS^-), reversibly reacted with molecular oxygen in acetonitrile. However, the oxygenated complexes could not be isolated. Conductivity measurement of the azido complex showed that the oxygenated complex is a 1:1 electrolyte in acetonitrile (135 Ω^{-1} cm^2 mol^{-1}) and can be formulated as $[Co_2(bpmp)(N_3)_2(O_2)]^+$. A possible structure is given in Fig. 3f. The $P_{1/2}$ of the complex is 50 Torr at 20 °C, whereas that of the isothiocyanato complex could not be determined because of its low oxygen affinity. The chloro and bromo complexes did not react with molecular oxygen even at −40 °C. Thus, in a series of $[Co_2(bpmp)X_2]^+$, the order of the oxygen affinity is $N_3^- > NCS^- > Cl^-$, Br^-. This order reflects the differences in the electron donor abilities of the unidentate ligands to the cobalt centers; the stronger the electron donor ability of the ligand, the greater the amount of the electron density on the cobalt centers, and the greater the oxygen affinity.

The oxygen affinities of the complexes studied are highly dependent on the nature of the dinucleating ligand. The order of the oxygen affinities for changes in the dinucleating ligands is bpmp>bpmep>bpep. The order can be explained by considering the effect of the chelate ring size of the dinucleating ligand. Martell *et al.*[16)] demonstrated that, in a series of the cobalt(II) complexes with various quinquedentate ligands, the nitrogen donor atoms in the six-membered chelate rings are weaker electron donors than those in the corresponding five-membered chelate rings. This is also the case for the present complexes. In addition, it is likely that the observed differences in the oxygen affinities of the present complexes are also attributed to the steric requirement of the dinucleating ligand. The oxygen binding sites of the two cobalt ions must be held in suitable positions for the O_2 binding in μ-peroxo fashion and such a steric requirement which is governed by the nature of the dinucleating ligand would be also responsible to the stability of the dioxygen complex.

Martell *et al.*[17)] also suggested that the total basicities of the ligands are important in determining whether a cobalt(II) complex will form a dioxygen adduct, and the presence of three aliphatic nitrogen donors is sufficient but not necessary for dioxygen adduct formation. It should be noted that all the bbimp complexes (even [Co_2(bbimp)(py)$_2$]$^{3+}$ which has N_4O donor set for each cobalt ion) did not react with molecular oxygen even at −40 °C. Although the total basicities of Hbbimp and Hbpmp are not known, it is reasonable to assume that the total basicity of Hbbimp is larger than that of Hbpmp, because benzimidazole (pK_a=5.4) is stronger base than pyridine (pK_a=5.2). Stynes *et al.*[18] demonstrated that in 1 : 1 dioxygen adduct formation of LCoP (P=protoporphyrin IX dimethyl ester and L=various bases), pyridine is a better base than benzimidazole. In the above system, therefore, the lower oxygen affinity of the benzimidazole complex is ascribed not to the electronic effect but to the steric effect between benzimidazole and the porphyrine ring, which prevents close approach of benzimidazole to the cobalt center. It is likely that no reactivity of the bbimp complexes with molecular oxygen is also due to such a steric effect of benzimidazolyl groups.

It is interesting that the oxygen affinities of [$Co_2L(C_3H_3N_2)$]$^{2+}$ are comparable to or smaller than those of [$Co_2L(CH_3COO)$]$^{2+}$ (L=bpmp or bpmep). It is well known that the nitrogen donors tend to promote oxygenation, whereas the oxygen donors such as carboxylates tend to retard the dioxygen adduct formation.[17] Pyrazolate is a moderately strong base (pK_a's of the following equilibria, pyrazolium $\rightleftharpoons$ pyrazole+H^+ and pyrazole $\rightleftharpoons$ pyrazolate+H^+, are 2.5 and 14.2, respectively)[19] and therefore pyrazolate must be a more effective σ donor than acetate. However,the observed oxygen affinities of the pyrazolato complexes seem to be much weaker than those expected from the above general concept and the basicity argument. It is possible that pyrazolate plays a role as a strong π acceptor and/or pyrazolate-bridge prevents optimum binding of O_2 in μ-peroxo fashion.

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