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Synthesis and Characterization of Copper(II), Nickel(II), and Cobalt(II) Binuclear Complexes with a New Tricyclic Octadentate Ligand, 1,5,8,12,15,19,22,26-Octaazatricyclo[17.9.2.2^{5,15}]dotriacontane (tcoa): Trapping of CO_2 in a Neutral Aqueous Solution

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A new tricyclic ligand, 1,5,8,12,15,19,22,26-octaazatricyclo[17.9.2.2^{5,15}]dotriacontane (tcoa) was prepared from 1,4,8,11-tetrakis(2-(tosylamino)ethyl)-1,4,8,11-tetraazacyclotetradecane and 1,3-propanediyl ditosylate by a cyclization reaction of 1:2 molar ratio, respectively. Eight copper(II), one nickel(II), and two cobalt(II) binuclear complexes of tcoa were prepared and characterized by elemental analyses, IR spectra, electronic absorption and reflectance spectra, magnetic susceptibility, and X-ray crystal analyses. $[Cu_2(tos)_2(tcoa)](ClO_4)_2\cdot 4H_2O$ (tos represents the tosylate ion) crystallizes in the triclinic system, space group $P1$, with $a = 11.811$ (3) Å, $b = 12.448$ (1) Å, $c = 9.994$ (2) Å, $\alpha = 106.23$ (1)°, $\beta = 113.45$ (1)°, and $\gamma = 76.98$ (1)°. $[Cu_2(tcoa)](ClO_4)_4\cdot H_2O$ reacted in aqueous solutions with various anions, F^-, Cl^-, Br^-, I^-, and N_3^-, to form anion-bridged complexes. $[Co_2OH(tcoa)]ClO_4)_3$ rapidly trapped CO_2 in an aqueous solution to form $[Co_2CO_3(tcoa)](ClO_4)_2\cdot 3H_2O$ quantitatively. $[Co_2CO_3(tcoa)](ClO_4)_2\cdot 3H_2O$ crystallizes in a monoclinic system, space group $P2_1/a$, with $a = 17.641$ (6) Å, $b = 17.139$ (6) Å, $c = 12.559$ (4) Å, and $\beta = 91.60$ (2)°.

Introduction

In previous papers we reported stable binuclear metal complexes with octadentate ligands, such as 1,4,8,11-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane[1] (taec) and 1,4,8,11-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane[2] (tpmc), which were prepared by attaching pendant groups at nitrogen sites of a tetraaza macrocycle. These complexes were classified into two groups depending on the presence (type 1 structure) or absence (type 2 structure) of bridging anions, as shown in Figure 1. They exhibit the following interesting behavior: (1) extraordinary large equilibrium constants[2d] for the formation of anion-bridged complexes (eq 1) compared to those

$$[Cu_2L]^{4+} + X^- \rightarrow [Cu_2XL]^{3+} \qquad (1)$$

$$L = \text{taec, tmpc; } X = F^-, Cl^-, Br^-, I^-, N_3^-, NO_2^-$$

for the formation of Cu–X complexes from simple aqueous Cu^{2+} and X^-; (2) unusually large stability of the cobalt(II) complexes against oxidation to the cobalt(III) state.[3] For the origins[4] of such unusual characteristics of the octaamine ligands, we have proposed some factors, but a definite conclusion has not been drawn yet. Thus, in this study, we have synthesized a new tricyclic octadentate ligand, 1,5,8,12,15,19,22,26-octaazatricyclo[17.9.2.2^{5,15}]dotriacontane (hereafter abbreviated as tcoa), and its metal complexes in hope of finding novel properties and also of providing more data to elucidate the characteristics of the taec and tpmc complexes.

Experimental Section

Materials. Dimethylformamide (DMF) was distilled after stirring with anhydrous BaO. 1,3-Bis((*p*-tolylsulfonyl)oxy)propane was prepared from 1,3-propanediol and toluenesulfonyl chloride in dry pyridine. *N*,*N′*,*N″*,*N‴*-Tetratosylated taec was prepared by the method previously reported.[1] The other synthetic reagents were purchased and used without further purification.

Syntheses. Tetratosyled tcoa. N,N′,N″,N‴-Tetratosylated taec (44.2 g, 45 mmol) was dissolved in dry DMF (80 mL) at 75 °C under a nitrogen atmosphere. To this solution was added sodium hydride (63.6% in oil, 6.9 g, 180 mmol), and the mixture was heated at 75–85 °C for 1 h. To the resulting pale orange solution was added dropwise with stirring 1,3-bis((*p*-tolylsulfonyl)oxy)propane (34.8 g, ca. 90 mmol) in DMF (250 mL) during 3 h at 95–100 °C. Stirring and heating were further continued for 4 h. The solution was concentrated to ca. 150 mL under vacuum, diluted with ethanol (300 mL), and kept in a refrigerator overnight. The crystals that resulted were collected by filtration and washed with ethanol, water, ethanol, and ether successively. Yield: 19 g, 40%.

In order to purify the product, the crude product was dissolved in DMF heated on a water bath. The solution was filtered, and the filtrate was diluted with methanol. The crystals that resulted were collected by filtration, washed with methanol, and dried under vacuum at 100 °C; mp 250 °C. Anal. Calcd for $C_{52}H_{76}N_8O_8S_4$: C, 58.39; H, 7.18; N, 19.48. Found: C, 58.22; H, 7.17; N, 10.64.

Hydrogen Bromide Salt of tcoa. Crude tetratosyled tcoa (19 g, 17.8 mmol) was refluxed with a 1:1 v/v mixture of 47% hydrobromic acid and acetic acid (800 mL) for 3 days. The reaction mixture was diluted with 1 L of water to give a clear solution, which was treated with activated charcol and filtered. The filtrate was evaporated to dryness under vacuum. To the residue was added ethanol, which was evaporated. Addition and evaporation of ethanol was repeated several times, and the resulting solid residue was triturated with ethanol and collected by filtration.

The crude product (23 g) was dissolved in the minimum amount of water heated on a water bath, and the mixture was filtered. Concentrated hydrobromic acid was added to the filtrate. The mixture was diluted with a large amount of ethanol and kept in a refrigerator overnight. The crystals resulted were collected by filtration and dried over calcium chloride. Yield: 11 g, 57%.

Anal. Calcd for $C_{24}H_{61}Br_7N_8O$ (tcoa·$7H_2O$): C, 27.79; H, 5.94; N, 10.81. Found: C, 27.52; H, 5.76; N, 10.61.

tcoa. The tcoa hydrogen bromide salt was freed from HBr by passing the aqueous solution of tcoa·7HBr·H_2O through a column of anionic exchange resin (Dowex 1×8) in OH^- form. The fractions above pH 8 were collected and evaporated to dryness, and the residues were dried in vacuo over P_2O_5. Oily residues were used without further purification.

Preparation of Metal Complexes of tcoa. $[Cu_2(tos)_2(tcoa)](ClO_4)_2\cdot 3H_2O$[14] (1a) (tos = Tosylate Ion). The crude tcoa hydrogen bromide salt obtained by the above procedure (530 mg) and copper perchlorate hexahydrate (365 mg, 1.0 mmol) were dissolved in water, and the pH of the solution was adjusted at ca. 5 with 5% aqueous NaOH. The solution was heated on a water bath for 1 h, and the insoluble material that resulted was removed by filtration. To the filtrate were added an excess of sodium

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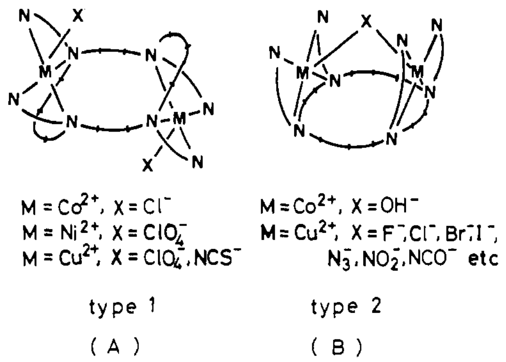

Figure 1. Coordination mode of taec and tpmc.

perchlorate and a small amount of methanol. The solution was allowed to stand for 24 h, and blue-violet crystals were formed. The crystals were recrystallized from water–methanol (1:1 v/v). Yield: 346 mg (21%). The presence of tosylate ion in the complex revealed that the starting material had contained a substantial amount of tosylate ion. Anal. Calcd for $C_{38}H_{72}Cl_2Cu_2N_8O_{17}S_2$: C, 38.84; H, 6.18; N, 9.54; Cu, 10.82. Found: C, 39.06; H, 6.03; N, 9.49; Cu, 10.91.

[Cu_2OH(tcoa)](ClO_4)$_3$·$2H_2O$ (1b). To a water solution of copper perchlorate hexahydrate (1 mmol, 370 mg) was added free tcoa (226 mg, 0.5 mmol), and the solution was heated on a water bath with stirring for 1 h. The brown precipitate that resulted was removed by filtration, and the filtrate was concentrated to 10 mL. An excess of sodium perchlorate was added to the concentrated solution to yield dark blue crystals. The crystals were collected by filtration and recrystallized from water. Yield: 350 mg (75%). Anal. Calcd for $C_{24}H_{57}Cl_3Cu_2N_8O_{15}$: C, 30.95; H, 6.18; 12.03; Cu, 13.65. Found: C, 30.52; H, 5.85; N, 11.77; Cu, 13.56.

[Cu_2(tcoa)](ClO_4)$_4$·H_2O (1c). An aqueous solution of tcoa was neutralized with 10% perchloric acid and adjusted around pH 7. The solution was mixed with an aqueous solution of copper perchlorate hexahydrate. Violet crystals were obtained. Yield: 363 mg (73%). Anal. Calcd for $C_{24}H_{54}Cl_4Cu_2N_8O_{17}$: C, 28.95; H, 5.48; N, 11.25; Cu, 12.76. Found: C, 28.71; H, 5.35; N, 11.04; Cu, 12.91.

[Cu_2X(tcoa)](ClO_4)$_3$·yH_2O (X = F, Cl, Br, I, N_3; y = 1, 3). To a methanol–water (1:2 v/v) solution of [Cu_2(tcoa)](ClO_4)$_4$·H_2O (249 mg, 0.25 mmol) was added 3 mL of a 0.1 M solution of NaX. The crystals that separated were recrystallized from methanol–water (5:1 v/v) and washed with ether.

[Cu_2F(tcoa)](ClO_4)$_3$·H_2O (1d). Fine blue crystals formed. Yield: 215 mg (94%). Anal. Calcd for $C_{24}H_{54}Cl_3Cu_2FN_8O_{13}$: C, 31.49; H, 5.96; N, 12.32; Cu, 13.89. Found: C, 31.67; H, 5.79; N, 12.24; Cu, 13.39.

[Cu_2Cl(tcoa)](ClO_4)$_3$·$3H_2O$ (1e). Fine violet crystals formed. Yield: 185 mg (76%). Anal. Calcd for $C_{24}H_{58}Cl_4Cu_2N_8O_{15}$: C, 29.78; H, 6.05; N, 11.58; Cu, 13.13. Found: C, 29.77; H, 5.77; N, 11.53; Cu, 13.25.

[Cu_2Br(tcoa)](ClO_4)$_3$·$3H_2O$ (1f). Blue needles formed. Yield: 162 mg (64%). Anal. Calcd for $C_{24}H_{58}BrCl_3Cu_2N_8O_{15}$: C, 28.48; H, 5.79; N, 11.07; Cu, 12.56. Found: C, 28.29; H, 5.45; N, 11.03; Cu, 12.40.

[Cu_2I(tcoa)](ClO_4)$_3$·H_2O (1g). Fine blue-green crystals formed. Yield: 127 mg (50%). Anal. Calcd for $C_{24}H_{54}Cl_3Cu_2IN_8O_{13}$: C, 28.17; H, 5.33; N, 10.95; Cu, 12.42. Found: C, 27.94; H, 5.24; N, 10.87; Cu, 12.59.

[Cu_2N_3(tcoa)](ClO_4)$_3$·CH_3OH (1h). A blue powder formed. Yield: 62 mg (52%). Anal. Calcd for $C_{25}H_{56}Cl_3Cu_2N_{11}O_{13}$: C, 31.53; H, 5.94; N, 16.18; Cu, 13.34. Found: C, 31.28; H, 5.90; N, 15.67; Cu, 13.47.

[Ni_2(tcoa)](ClO_4)$_4$ (2). This compound was obtained by a procedure similar to that for the copper analogue except for using nickel(II) perchlorate hexahydrate instead of copper perchlorate hexahydrate. An orange powder was obtained. Yield: 230 mg (47%). Anal. Calcd for $C_{24}H_{52}Cl_4N_8Ni_2O_{16}$: C, 29.78; H, 5.41; N, 11.58; Ni, 12.13. Found: C, 29.82; H, 5.72; N, 11.61; Ni, 12.06.

[Co_2OH(tcoa)](ClO_4)$_3$ (3a). This was obtained in a way similar to that for [Cu_2OH(tcoa)](ClO_4)$_3$·$2H_2O$, except for using cobalt(II) perchlorate hexahydrate instead of copper perchlorate hexahydrate. The crude product was recrystallized from acetonitrile–water (1:1 v/v). A purple precipitate was obtained. Yield: 62 mg (52%). Anal. Calcd for $C_{24}H_{53}Cl_3Co_2N_8O_{13}$: C, 32.53; H, 6.04; N, 12.65; Co, 13.30. Found: C, 32.27; H, 5.96; N, 12.57; Co, 13.34.

Table I. Crystal Data and Data Collection Details[a] of **1a** and **3b**

	1a	**3b**
compd	[Cu_2(tos)$_2$(tcoa)](ClO_4)$_2$·$4H_2O$	[Co_2CO_3(tcoa)](ClO_4)$_2$·$3H_2O$
formula	$C_{38}H_{74}Cl_2Cu_2N_8O_{18}S_2$	$C_{25}H_{58}Cl_2Co_2N_8O_{14}$
fw	596.60	883.567
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/a$
a/Å	11.811 (3)	17.641 (6)
b/Å	12.448 (1)	17.139 (6)
c/Å	9.994 (2)	12.559 (4)
α/deg	106.23 (1)	90.00
β/deg	113.45 (1)	91.60 (2)
γ/deg	76.98 (1)	90.00
V/Å^3	1283.4 (4)	3796.1
Z	1	4
D_x/g cm^{-3}	1.544	1.546
cryst size/mm	0.4 × 0.6 × 0.3	0.30 × 0.30 × 0.40
μ(Mo Kα)/cm^{-1}	10.87	10.83
scan mode	θ–2θ	θ–2θ
2θ range/deg	2.5–48	2.5–52
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
monochromator	Zr filter	graphite crystal
data collcd	$+h,\pm k,\pm l$	$+h,+k,\pm l$
no. of obsd reflcns with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	2923	5352
R/%	8.99	6.66
R_w/%	7.69	5.95
largest peak on D_3 Fourier/e Å^{-3}	1.1	0.8

[a] Common data: scan speed 6° min^{-1}; weighting scheme $1/[\sigma(F)]^2$; scan width $(1.2 + 0.35 \tan\theta)°$.

[Co_2CO_3(tcoa)](ClO_4)$_2$ (3b).[14] **Method 1.** A 300-mg amount of tcoa (0.663 mmol) was dissolved in 2 mL of water. To the solution were added cobalt(II) perchlorate hexahydrate (485 mg, 1.326 mmol) and Na_2CO_3 (70 mg, 0.663 mol) at 40 °C. After removal of a small amount of purple solid by filtration, the filtrate was concentrated. The fine crystals that resulted were collected by filtration and dried in vacuo. Yield: 212 mg (40%). The crude product was recrystallized from water. Anal. Calcd for $C_{25}H_{52}Cl_2Co_2N_8O_{11}$: C, 36.20; H, 6.32; N, 13.51; Co, 14.21. Found: C, 35.93; H, 6.30; N, 13.37; Co, 14.30.

Method 2. Carbon dioxide was bubbled into an aqueous solution of **3a** (60 mg, 6 mL) for 30 min. The solution was concentrated to dryness. To the residue was added 10 mL of methanol. The insoluble material was collected by filtration, washed with methanol, and dried over P_2O_5. Yield: 57%.

Measurements. Analytical data for carbon, hydrogen, and nitrogen were obtained at the Elemental Analysis Service Center, Kyushu University. Copper, nickel, and cobalt analyses were performed on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. Infrared spectra were measured with a JASCO IR Model 810 spectrometer on KBr disks, and electronic spectra were recorded with a Shimadzu Model MPS-2000 multipurpose spectrophotometer. Magnetic susceptibilities were measured by a Faraday balance designed in our laboratory. The instrument was equipped with a Cahn 2000 electrobalance and calibrated by the use of [Ni(en)$_3$]S_2O_3.[5] The diamagnetic corrections were made by Pascal's constants. Magnetic moments were calculated by the equation $\mu_{\text{eff}} = (8\chi_A T)^{1/2}$. Cyclic voltammograms of the cobalt complexes were obtained in acetonitrile solution containing NBu_4BF_4 (0.1 M) with an assembly composed of a Hokuto Denko HA501 potentiostat and an HB104 function generator. A glassy-carbon disk (diameter = 3 mm), a platinum plate, and a TOA saturated calomel electrode (SCE) were used as the working electrode, the counter electrode, and the reference electrode, respectively.

X-ray Crystal Structure Analysis. Single crystals of [Cu_2(tos)$_2$(tcoa)](ClO_4)$_2$·$4H_2O$ (**1a**) suitable for X-ray structural determination were obtained by slow evaporation of an aqueous solution of the complex at room temperature. Crystals of **1a** are blue-violet and stable under air. Single crystals of [Co_2CO_3(tcoa)](ClO_4)$_2$·$3H_2O$ (**3b**) suitable for X-ray structural determination were grown from an aqueous solution of [Co_2OH(tcoa)](ClO_4)$_3$ by exposing it to the open atmosphere. Crystals of **3b** are purple and stable under air. Diffraction data were obtained on a Rigaku Denki AFC-5 automated four-circle diffractometer with Zr-filtered Mo Kα radiation for **1a** and with graphite-monochromatized Mo Kα radiation for **3b** at room temperature. The diffraction data were corrected for Lorentz and polarization factors and used for the structure determination. Corrections for absorption and extinction effects were not made. Unit cell parameters were determined by 25 reflections (20° < 2θ < 30°). The details of the data collection and crystallographic data are summarized in Table I.

The structures were solved by the standard heavy-atom method for **1a** and by direct methods (MULTAN) for **3b**. Several Fourier and dif-

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Table II. Fractional Positional Parameters (×10^4) and Thermal Parameters of Non-Hydrogen Atoms for $[Cu_2(tos)_2(tcoa)](ClO_4)_2 \cdot 4H_2O$[a]

atom	x	y	z
Cu	2419 (1)	1576 (1)	2036 (1)
Cl	1308 (3)	5861 (3)	3608 (4)
S	4004 (3)	−1068 (2)	2384 (3)
O1	3180 (7)	−176 (5)	1649 (8)
O2	3827 (9)	−1071 (7)	3755 (8)
O3	5321 (7)	−1036 (7)	2613 (9)
O4	662 (9)	6932 (7)	3595 (10)
O5	969 (10)	5297 (9)	4320 (12)
O6	2575 (9)	5951 (9)	4286 (12)
O7	1047 (11)	5237 (9)	2166 (12)
N1	1265 (8)	1618 (7)	−234 (9)
N2	820 (7)	1715 (6)	2388 (9)
N3	3242 (7)	1883 (6)	4302 (8)
N4	3722 (8)	2196 (7)	1713 (9)
C1	−38 (10)	2064 (8)	−192 (11)
C2	−28 (10)	2504 (8)	1388 (11)
C3	1021 (10)	2225 (9)	3983 (11)
C4	2318 (10)	1738 (9)	4883 (11)
C5	3662 (10)	3008 (8)	4938 (11)
C6	4580 (10)	3200 (9)	4353 (12)
C7	4019 (11)	3294 (9)	2725 (12)
C8	3181 (10)	2289 (9)	94 (11)
C9	1760 (10)	2559 (9)	−368 (12)
C10	1218 (10)	641 (8)	−1535 (10)
C11	947 (10)	−480 (8)	−1599 (11)
C12	−445 (10)	−526 (7)	−1895 (10)
C13	3603 (9)	−2352 (8)	1117 (11)
C14	3625 (10)	−2531 (9)	−325 (12)
C15	3274 (11)	−3518 (9)	−1327 (11)
C16	2910 (10)	−4337 (8)	−962 (11)
C17	2500 (14)	−5382 (10)	−2069 (13)
C18	2905 (11)	−4160 (8)	471 (12)
C19	3257 (11)	−3172 (8)	1504 (11)
OW1	6098 (8)	689 (6)	2240 (9)
OW2	2060 (9)	−1178 (7)	4893 (10)

[a] Values in parentheses are estimated standard deviations.

Table III. Selected Bond Distances (Å) and Angles (deg) of **1a**

Bond Distances			
(a) Macrocycle			
Cu···Cu	6.876 (3)	N3–C4	1.49 (2)
Cu–N1	2.140 (7)	N3–C5	1.47 (1)
Cu–N2	2.017 (9)	N4–C7	1.47 (1)
Cu–N3	2.038 (7)	N4–C8	1.51 (1)
Cu–N4	2.03 (1)	C1–C2	1.52 (1)
N1–C1	1.53 (1)	C3–C4	1.52 (1)
N1–C9	1.48 (2)	C4–C6	1.51 (2)
N1–C10	1.50 (1)	C6–C7	1.52 (2)
N2–C2	1.51 (1)	C8–C9	1.54 (2)
N2–C3	1.48 (1)	C10–C11	1.48 (2)
N2–C12	1.53 (1)	C11–C12	1.56 (2)
(b) Tosylate Ion			
Cu–O1	2.153 (6)	C13–C19	1.38 (2)
S–O1	1.455 (7)	C14–C15	1.38 (1)
S–O2	1.47 (1)	C15–C16	1.37 (2)
S–O3	1.488 (9)	C16–C17	1.48 (1)
S–C13	1.765 (9)	C16–C18	1.39 (2)
C13–C14	1.40 (2)	C18–C19	1.39 (1)
(c) Perchlorate Ion			
Cl–O4	1.380 (9)	Cl–O6	1.39 (1)
Cl–O5	1.34 (1)	Cl–O7	1.38 (1)
Bond Angles			
O1–Cu–N1	96.9 (3)	O1–Cu–N3	96.2 (3)
O1–Cu–N2	109.2 (3)	O1–Cu–N4	97.0 (3)

ference Fourier syntheses located all the non-hydrogen atoms. The non-hydrogen atoms were refined by isotropic and subsequently anisotropic thermal parameters with the use of block-diagonal least-squares methods. The hydrogen atoms bound to carbon atoms were introduced in their calculated positions. At the final stage, full-matrix least-squares methods for **1a** were carried out and block-diagonal least-squares methods for **3b** were carried out, where the hydrogen atoms of **1a** were not refined and the hydrogen atoms of **3b** were refined. In the both cases, the weighting scheme $1/[\sigma(F)]^2$ was adopted. The discrepancy factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The calculations were carried out on the FACOM-M 780 computer at the Computer Center of Kyushu University by using the UNICS III program system.[6] The atomic scattering factors were taken from the literature.[7] The final atomic coordinates of non-hydrogen atoms of **1a** and **3b** are given in Tables II and IV, respectively. Tables of observed and calculated structure factors, hydrogen positional and isotropic thermal parameters, anisotropic thermal parameters, and complete bond lengths and angles with their estimated standard deviations

Table IV. Fractional Positional Parameters (×10^4) and Thermal Parameters of Non-Hydrogen Atoms for $[Co_2(CO_3)tcoa](ClO_4)_2 \cdot 3H_2O$[a]

atom	x	y	z
Co1	1969 (1)	3165 (1)	4647 (1)
Co2	2585 (1)	4141 (1)	1730 (1)
OA	2398 (2)	3596 (3)	3204 (3)
OB	2856 (3)	4044 (3)	4727 (3)
OC	3162 (3)	4596 (3)	3172 (3)
CA	2833 (4)	4097 (4)	3725 (5)
N1	959 (3)	3921 (3)	4902 (4)
N2	1081 (3)	2347 (3)	4016 (4)
N3	2568 (3)	2103 (3)	4775 (5)
N4	1996 (3)	3222 (3)	6362 (4)
N5	1668 (3)	5013 (3)	1488 (4)
N6	1786 (3)	3424 (3)	707 (4)
N7	3353 (3)	3341 (3)	1101 (4)
N8	3202 (3)	5013 (3)	899 (4)
C1	279 (4)	3453 (4)	4567 (6)
C2	433 (4)	2586 (4)	4685 (5)
C3	1345 (5)	1556 (4)	4268 (7)
C4	1976 (5)	1502 (5)	4998 (8)
C5	3207 (4)	2047 (5)	5569 (6)
C6	2997 (4)	2251 (5)	6700 (6)
C7	2749 (4)	3072 (5)	6856 (5)
C8	1716 (4)	4014 (4)	6585 (5)
C9	948 (4)	4086 (4)	6067 (5)
C10	1090 (4)	4672 (4)	736 (5)
C11	1449 (4)	4049 (4)	39 (5)
C12	2258 (4)	2903 (4)	62 (5)
C13	3069 (4)	3186 (4)	12 (5)
C14	4174 (4)	3539 (4)	1186 (5)
C15	4395 (4)	4292 (4)	664 (6)
C16	4039 (4)	4994 (4)	1111 (5)
C17	2860 (4)	5750 (4)	1247 (5)
C18	2025 (4)	5706 (4)	971 (5)
C19	1019 (4)	4669 (4)	4310 (5)
C20	974 (4)	4591 (4)	3108 (5)
C21	1356 (4)	5263 (4)	2529 (5)
C22	801 (4)	2322 (5)	2875 (6)
C23	1417 (4)	2384 (4)	2032 (5)
C24	1174 (4)	2939 (4)	1157 (6)
Cl1	3659 (1)	1272 (1)	2318 (2)
Cl2	5192 (1)	2690 (1)	−1998 (2)
O1	4208 (5)	871 (7)	1950 (7)
O2	3401 (7)	878 (5)	3176 (7)
O3	3832 (4)	2001 (4)	2777 (6)
O4	3086 (4)	1396 (5)	1590 (6)
O5	5079 (6)	3082 (5)	−1125 (6)
O6	4787 (5)	2978 (8)	−2770 (7)
O7	5924 (4)	2721 (6)	−2242 (7)
O8	4962 (6)	1964 (5)	−1925 (9)
OW1	3092 (4)	5079 (4)	−1523 (4)
OW2	4635 (5)	4839 (9)	4027 (7)
OW3	4095 (7)	4681 (5)	−3040 (11)

[a] Values in parentheses are estimated standard deviations.

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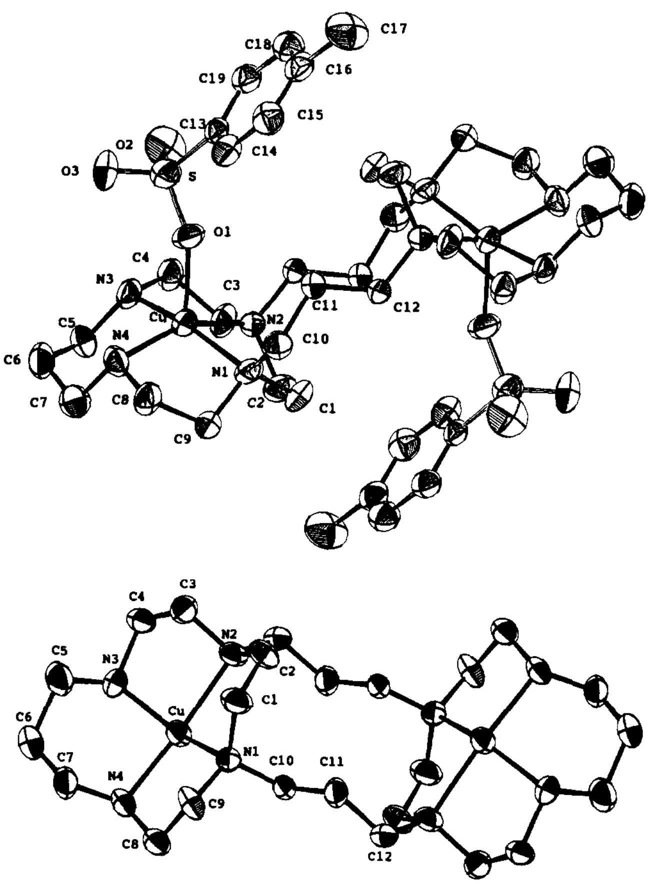


Figure 2. ORTEP diagram of the cation of $[Cu_2(tos)_2(tcoa)](ClO_4)_2{\cdot}4H_2O$ with 50% probability ellipsoids: (a, top) complete cation $[Cu_2(tos)_2(tcoa)]^{2+}$; (B, bottom) cation with tos^- groups omitted for clarity of view of the tricycle ligand structure.

are deposited as supplementary material.

Results and Discussion

Description of the Structures. 1a. The crystal consists of $[Cu_2(tos)_2(tcoa)]^{2+}$, ClO_4^-, and water molecules. An ORTEP diagram of the cation is shown in Figure 2. Selected interatomic distances and angles with their estimated standard deviations are given in Table III.

As required from crystallographic symmetry, the complex has an inversion center.

The coordination geometry of copper is a distorted square pyramid, where the basal plane is formed by two tertiary amine nitrogens and two secondary amine nitrogens and the apex is occupied by an oxygen of the tosylate ion. The tosylate ions are coordinated in an anti-fashion mode (Figure 2). The Cu–Cu distance of 6.876 (3) Å is significantly longer than those of $[Cu_2Br_2(tpmc)](ClO_4)_2$ (5.74 Å)[2a] and $[Cu_2(NCS)_2(taec)](ClO_4)_2{\cdot}H_2O$ (5.565 (1) Å).[1c] The conformation of the ligand may be regarded as type 1 of Figure 1. A 5,5,6,5-membered fused chelate ring is formed for each copper. The deviations of the basal nitrogen atoms from the mean plane are within ±0.12 Å. The copper atom is displaced by 0.34 Å from the mean plane toward the apex. The two coordination units are linked by the two $-(CH_2)_3-$ chains of the cyclam ring. It should be noted that tcoa has no possibility for linking two coordination units by $-(CH_2)_2-$ chains as was observed for $[Cu(taec)](ClO_4)_4$.[1a] Each of the two 13-membered macrocycles is dish-shaped, and the copper atom is at the outer side of the dish bottom so that the sixth coordination position of the metal center is blocked by the chelating groups.

3b. The crystal consists of a discrete dinuclear complex cation, $[Co_2CO_3(tcoa)]^{2+}$, perchlorate ion, and crystal water molecules. An ORTEP diagram is shown in Figure 3. Selected interatomic distances and angles with their estimated standard deviations are given in Table V.

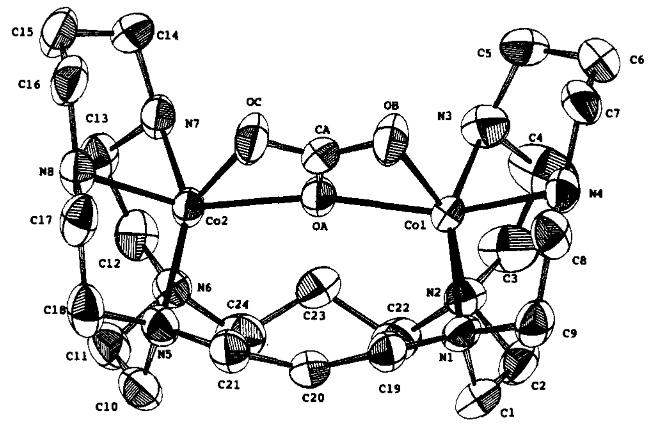
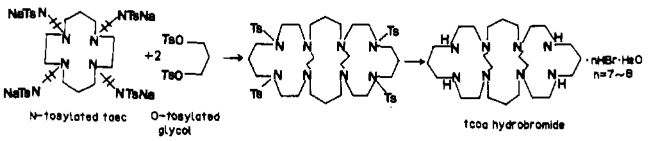


Figure 3. ORTEP diagram of the cation of $[Co_2CO_3(tcoa)](ClO_4){\cdot}3H_2O$ with 50% probability ellipsoids.

Scheme I



The two cobalt atoms are bridged by a carbonate ion in a way similar to that of $[Ni_2CO_3(taec)](ClO_4)_2{\cdot}H_2O$.[1e] The cobalt-cobalt distance is 4.198 (1) Å. The coordination geometry of each cobalt atom can be described as a distorted octahedron formed by four nitrogens of tcoa and two oxygens from the carbonate ion. Interestingly, all five-membered chelate rings adopt the envelope conformation, which is thermodynamically less favorable than the gauche conformation in the case of a single chelate ring. Similar conformations were also observed in some cobalt(III) and cobalt(II) complexes containing fused rings.[11,12] The Co1–OA–Co2 bridge is nearly linear, and the Co–O–Co angle (167.1 (2)°) is significantly larger than that of $[CoOH(taec)](ClO_4)_3$ (145.7 (2)°).[3]

Preparation of the Ligand and the Metal Complexes. For the synthesis of tcoa, several attempts of metal template reactions for ring closure on 1,4,8,11-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec)[1] were unsuccessful; the Richman and Atkins reaction[8] on N,N′,N″,N‴-tetratosylated taec and 1,3-propanediyl ditosylate, as shown in Scheme I.

The present metal complexes, **1a–c**, **2**, and **3a**, were prepared in aqueous solutions with a 2:1 metal/tcoa ratio, as described in the Experimental Section.

Copper complex **1c** reacted with anions, F^-, Cl^-, Br^-, I^-, and N_3^-, in an aqueous solution to form anion-containing copper complexes, **1d–h**, respectively. This behavior is similar to that observed in the case of copper complexes with taec and tpmc. Hence, the anion is most likely to be bound by both coppers in the tcoa complexes, as was demonstrated for the taec and tpmc complexes.[2c]

IR spectra of all the copper complexes showed strong bands corresponding to ν(N–H), $\nu(ClO_4^-)$, and $\delta(ClO_4^-)$ around 3450, 1100, and 620 cm^{-1}, respectively.[12] IR spectra of the anion-bridged complexes are similar to each other, suggesting similar structures.[10]

The hydroxo-bridged binuclear cobalt(II) complex, **3a**, trapped CO_2 rapidly in a neutral aqueous solution without a buffer system under CO_2 atmosphere and slowly in open air to give a carbonato-bridged complex, **3b**. IR spectra of **3b** showed the bands of coordinated carbonate ion[9] at 1565, 1460, and 1360 cm^{-1}.

The CO_2 trapping reaction was monitored by electronic spectra of an aqueous solution of **3a** (4×10^{-3} M). When carbon dioxide was bubbled through the solution, **3a** quantitatively changed into

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Table V. Bond Distances (Å) and Angles (deg) of **3b**

			Bond Distances				
			(a) Bridging Part				
Co···Co	4.198 (2)	Co2–OC	2.196 (4)	Co1–OB	2.173 (5)	OB–CA	1.261 (7)
Co1–OA	2.117 (4)	OA–CA	1.313 (8)	Co2–OA	2.108 (4)	OC–CA	1.254 (8)
			(b) Macrocycle				
Co1–N1	2.234 (5)	N6–C11	1.475 (9)	N2–C2	1.496 (9)	C8–C9	1.49 (1)
Co1–N2	2.231 (5)	N6–C12	1.478 (9)	N2–C3	1.464 (9)	C10–C11	1.53 (1)
Co1–N3	2.108 (6)	N6–C24	1.487 (9)	N2–C22	1.503 (9)	C12–C13	1.51 (1)
Co1–N4	2.154 (5)	N7–C13	1.467 (8)	N3–C4	1.50 (1)	C14–C15	1.50 (1)
Co2–N5	2.217 (5)	N7–C14	1.489 (9)	N3–C5	1.488 (9)	C15–C16	1.47 (1)
Co2–N6	2.246 (5)	N8–C16	1.493 (9)	N4–C7	1.472 (9)	C17–C18	1.50 (1)
Co2–N7	2.097 (5)	N8–C17	1.471 (9)	N4–C8	1.475 (9)	C19–C20	1.516 (9)
Co2–N8	2.138 (6)	C1–C2	1.52 (1)	N5–C10	1.491 (8)	C20–C21	1.53 (1)
N1–C1	1.495 (9)	C3–C4	1.42 (1)	N5–C18	1.500 (9)	C22–C23	1.54 (1)
N1–C9	1.491 (8)	C5–C6	1.52 (1)	N5–C21	1.495 (8)	C23–C24	1.51 (1)
N1–C19	1.487 (8)	C6–C7	1.49 (1)				
			(c) Perchlorate Ions				
Cl1–O1	1.28 (1)	Cl2–O5	1.305 (8)	Cl1–O3	1.404 (7)	Cl2–O7	1.338 (8)
Cl1–O2	1.360 (9)	Cl2–O6	1.29 (1)	Cl1–O4	1.361 (7)	Cl2–O8	1.312 (9)
			Bond Angles				
			(a) Bridging Carbonate				
Co1–OA–Co2	167.2 (2)	OA–Co2–OC	60.9 (2)	Co2–OA–CA	92.5 (3)	OA–CA–OC	116.4 (5)
Co1–OA–CA	91.2 (3)	OA–CA–OB	116.9 (6)	OA–Co1–OB	61.5 (2)	OB–CA–OC	126.7 (6)
			(b) Coordination Sphere of Co1				
OA–Co1–N4	147.3 (2)	Co1–N4–C8	103.5 (4)	Co1–N1–C1	106.6 (4)	N4–C8–C9	107.3 (5)
OB–Co1–N2	161.7 (2)	C1–N1–C9	110.2 (5)	Co1–N1–C9	106.4 (4)	C1–C2–N2	110.5 (6)
N1–Co1–N2	82.0 (2)	C2–N2–C3	112.0 (6)	Co1–N2–C2	99.7 (4)	C3–C4–N3	111.7 (7)
N1–Co1–N3	152.9 (2)	C4–N3–C5	110.4 (6)	Co1–N2–C3	106.8 (4)	C5–C6–C7	115.0 (6)
N1–Co1–N4	80.0 (2)	C7–N4–C8	112.5 (5)	Co1–N3–C4	104.9 (5)	C6–C7–N4	111.9 (6)
N2–Co1–N3	80.2 (2)	N1–C1–C2	111.0 (5)	Co1–N3–C5	118.4 (4)	C8–C9–N1	112.1 (5)
N2–Co1–N4	112.3 (2)	N2–C3–C4	115.9 (7)	Co1–N4–C7	114.1 (4)		
N3–Co1–N4	88.1 (2)	N3–C5–C6	114.3 (6)				
			(c) Coordination Sphere of Co2				
OA–Co2–N8	146.4 (2)	Co2–N8–C17	103.7 (4)	Co2–N5–C10	107.9 (4)	N7–C14–C15	115.3 (6)
OC–Co2–N6	159.2 (2)	C10–N5–C18	108.9 (5)	Co2–N5–C18	106.2 (4)	C12–C13–N7	108.5 (5)
N5–Co2–N6	81.2 (2)	N5–C10–C11	110.4 (6)	Co2–N6–C11	99.5 (4)	C16–N8–C17	112.2 (5)
N5–Co2–N8	80.8 (2)	C17–C18–N5	111.1 (5)	Co2–N6–C12	106.8 (4)	N8–C17–C18	107.1 (5)
N5–Co2–N7	149.9 (2)	C11–N6–C12	110.5 (5)	Co2–N7–C13	105.2 (4)	C15–C16–N8	112.3 (6)
N6–Co2–N7	80.1 (2)	N6–C12–C13	112.1 (6)	Co2–N7–C14	117.5 (4)	C14–C15–C16	114.6 (6)
N6–Co2–N8	115.0 (2)	C10–C11–N6	110.4 (5)	Co2–N8–C16	114.3 (4)		
N7–Co2–N8	86.0 (2)	C13–N7–C14	114.5 (5)				
			(d) Bridging Trimethylene Chains				
Co1–N1–C19	111.1 (4)	C19–C20–C21	113.3 (5)	Co2–N6–C24	122.6 (4)	C22–C23–C24	110.6 (6)
Co1–N2–C22	124.5 (4)	C20–C21–N5	112.2 (5)	N1–C19–C20	114.8 (5)	C23–C24–N6	115.8 (6)
Co2–N5–C21	111.0 (4)	N2–C22–C23	115.6 (6)				
			(e) Perchlorate ions				
O1–Cl1–O2	106.9 (6)	O5–Cl2–O6	109.9 (7)	O2–Cl1–O3	101.0 (5)	O6–Cl2–O7	109.3 (6)
O1–Cl1–O3	117.8 (6)	O5–Cl2–O7	110.1 (6)	O2–Cl1–O4	110.5 (5)	O6–Cl2–O8	104.5 (8)
O1–Cl1–O4	113.3 (5)	O5–Cl2–O8	112.0 (6)	O3–Cl1–O4	106.6 (5)	O7–Cl2–O8	110.9 (7)

3b in 30 s and the pH of the solution decreased to ca. 4. The pH decrease should be due to the deprotonation of bridging hydroxide ion of **3a** upon the addition of carbon dioxide to the Co–OH–Co site.

Electronic Spectra of the Complexes. Both electronic absorption and reflectance spectra of the all copper(II) complexes have broad bands corresponding to d–d transitions in the range 540–690 nm (Table VI). The extinction coefficients of the bands are very large compared with those of the d–d bands of common copper complexes, suggesting a considerably large distorsion from a centrosymmetric structure around each copper ion.

The d–d transition band of $[Cu_2(tcoa)](ClO_4)_4$ (**1c**) is located at much shorter wavelengths than those of the other tcoa complexes reported here in either absorption or reflectance spectra (see Table VI). The reflectance band of **1c** at 540 nm shifted to 577 nm when the compound was dissolved in water. This may be due to the partial formation of an aquated or hydroxo-bridged complex in aqueous solution. In contrast to this, when **1b** was dissolved in water, a blue shift of 40 nm was observed. These data suggest that there is an equilibrium between **1b** and **1c** in aqueous solution.

Table VI. Electronic Spectra [λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})] and Magnetic Moments at Room Temperature (μ_B)

	λ_{max} (ϵ)		
	in aq soln	reflectance	μ_B/metal
1a	630 (561)	634	2.03
1b	650 (279)	690	1.84
1c	577 (367)	540	1.80
1d	590 (423)	600	1.76
1e	603 (440)	582	1.84
1f	604 (520)	620	1.79
1g	648 (607)	630	1.75
1h	607 (500)	610	1.98
2	458 (132), 617 (sh)	325, 469	diamag
3a	480 (sh), 550 (91), 800 (20)	482, 552, 800	4.02
3b	480 (sh), 518 (36), 550 (sh), 670 (8)	480, 520, 550, 670	4.20

The halogeno- and azido-bridged copper complexes showed smaller band shifts than **1c** upon dissolution in water. Such shifts should be closely related to the stability of the bridged structure in water.

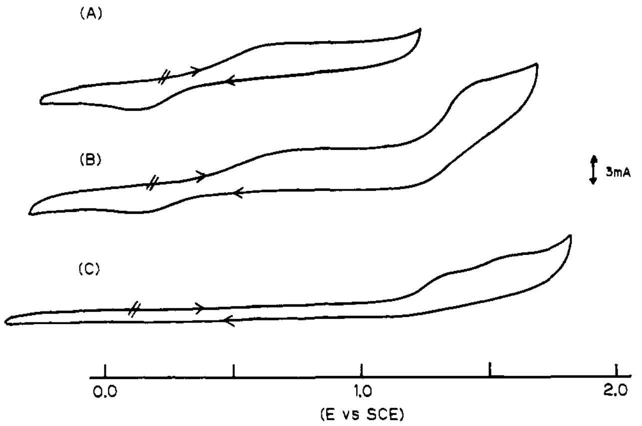

Figure 4. Cyclic voltammograms of **3a** and **3b** in acetonitrile containing 0.1 N n-Bu_4NBF_4 as supporting electrolyte with a glassy-carbon, platinum-plate, and saturated calomel electrode as a working electrode, a counter electrode, and a reference electrode, respectively: (A) **3b**, scan rate 100 mV/s and scan range -0.26 to 1.24 V; (B) **3b**, scan rate 100 mV/s and scan range -0.30 to 1.70 V; (C) **3a**, scan rate 100 mV/s and scan range -0.37 to 1.83 V.

Reflectance spectrum of the orange compound, **2**, showed a distinct band at 469 nm, and its aqueous solution was yellowish orange, giving an absorption at 458 nm and a shoulder at 617 nm.

Reflectance and absorption spectra of **3a** showed similar d–d bands (see Table VI), and the same was observed for **3b**, suggesting the maintenance of the bridging structure on dissolution in water. The absorption spectra of **3a** and **3b** were similar to those of the corresponding cobalt complexes[4] of taec and tpmc. Absorption coefficients of the d–d bands of **3a** are 2–3 times larger than those of **3b** due to the lower symmetry of **3a**, which may adopt a five-coordinate structure bridged by hydroxo ion.

Magnetic Properties of the Complexes. Effective magnetic moments of the all copper(II) complexes are in the range 1.75–2.08 μ_B/Cu at room temperature, suggesting that very weak or practically no magnetic interaction operates between two copper ions.

The nickel complex, **2**, is essentially diamagnetic, hence is assumed to adopt an essentially square-planar coordination.

The magnetic moment of **3b** was 4.20 μ_B/Co at room temperature. The temperature dependence of the magnetic susceptibility of **3b** was simulated by the Van Vleck equation based on the Heisenberg model ($H = -2JS_1S_2$).[13] The best-fit value of $-2J$ was determined at 35.1 cm^{-1} by least-squares calculation. This is much larger than the value (20 cm^{-1}) of the taec analogue, $[Co_2CO_3(taec)](ClO_4)_2$.[4] This may be attributed to the large Co–O–Co angle (167.1°).

Cyclic Voltammograms of the Cobalt Complexes. Cyclic voltammograms of **3a** and **3b** are shown in Figure 4. The cyclic voltammogram of **3b** in CH_3CN (0.1 M n-Bu_4NBF_4) at a glassy-carbon working electrode shows two redox couples (at 0.13 and 0.75 V, and 1.20 and 1.44 V vs SCE). The first anodic peak of **3b** is lower by 0.60 V than that of **3a**, and the second peak of **3b** is lower by 0.16 V than that of **3a**. The decrease of the redox potentials of the carbonate-bridged complex compared with those of the hydroxo-bridged cobalt complex was already investigated for other carbonato-bridged cobalt complexes,[4] $[Co_2CO_3(taec)]^{2+}$, and $[Co_2CO_3(tpmc)]^{2+}$ and was explained by stabilization of cobalt(III) state because of the six-coordinate structure of the carbonato-bridged complexes. In the case of **3b**, the low redox potentials are also reasonably explained by the six-coordinate structure. The potential difference (ca. 0.7 V) between the first and the second anodic peaks of **3b** is much larger than those of the carbonato-bridged taec and tpmc complexes (0.21 V for $[Co_2CO_3(taec)]^{2+}$ and 0.38 V for $[Co_2CO_3(tpmc)]^{2+}$).

Supplementary Material Available: Tables of hydrogen positional and isotropic thermal parameters, anisotropic thermal parameters, and complete bond lengths and angles (9 pages); tables of observed and calculated structure factors (39 pages). Ordering information is given on any current masthead page.

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(14) The number of crystal water molecules of **1a** and **3b** were determined by X-ray structure analysis to be 4 and 3, respectively, but elemental analysis data showed that 3 water molecules were contained in **1a** and no water molecule was contained in **3b**. The number of crystal water molecules depends on the degree of the dryness of the sample. Before measurement of elemental analysis, the product was dried in vacuo over P_2O_5, but before X-ray analysis, the crystal was not dried. Thus, except in the Experimental Section, 4 for **1a** and 3 for **3b** are adopted as the number of crystal water molecules throughout this paper.