Note Added in Proof. Since this paper was submitted for publication, two new 84-electron, bicapped tetrahedral metal cluster complexes have been reported: $H_2Ru_6(CO)_{17}$ (McCarthy, D. A.; Krause, J. A.; Shore, S. G. *J. Am. Chem. Soc.* **1990**, *112*, 8587) and $Pt_2Os_4(CO)_{12}(COD)_2$ (Adams, R. D.; Wu, W. *Organometallics* **1991**, *10*, 35).

Acknowledgment. K.H.W. thanks the Robert A. Welch Foundation and the National Science Foundation for support and Dr. Graham Palmer (Rice University) for providing the ESR spectra. T.A.A. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Robert A. Welch Foundation, and the National Science Foundation (for a grant of supercomputer time at the Pittsburgh Supercomputing Center). J.-Y.S. and J.-F.H. thank the CNRS for financial support.

Supplementary Material Available: Tables of atomic coordinates, anisotropic displacement parameters, full crystallographic data collection parameters, and bond angles and distances for [PPN][**2a**], [PPN]$_2$[**2a**], and [Cp_2Co][**2b**] and ORTEP diagrams for [PPN][**2a**] and [Cp_2Co][**2b**] (18 pages); listings of observed and calculated structure factors (52 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Faculty of Science,
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Preparation and Redox Chemistry of Novel Carbonato-Bridged Cobalt(II) Complexes with 1,4,8,11-Tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane and 1,4,8,11-Tetrakis(pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane

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Received June 1, 1990

Carbonato-bridged binuclear cobalt(II) complexes with 1,4,8,11-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec), $[Co_2CO_3(taec)](ClO_4)_2 \cdot 2H_2O$ (**1a**) and $[Co_2CO_3(taec)]X_2 \cdot NaX \cdot H_2O$ ($X = ClO_4$ (**1a′**) and BF_4 (**1b**)), and with 1,4,8,11-tetrakis(pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc), $[Co_2CO_3(tpmc)]X_2 \cdot 2H_2O$ ($X = ClO_4$ (**2a**) and BF_4 (**2b**)), were prepared and characterized by IR and electronic spectra, magnetic susceptibility and cyclic voltammetry. Complex **1a′** has been structurally characterized by X-ray crystallography. It crystallizes in the space group $P2_1/a$ with $a = 26.419$ (10) Å, $b = 12.774$ (5) Å, $c = 10.410$ (3) Å, $\beta = 90.51$ (4)°, $V = 3513$ Å^3, $Z = 4$ and $\rho_{calcd} = 1.72$ g/cm^3. The structure was refined by full-matrix least-square techniques to a final R factor of 0.068 and R_w factor of 0.057 for 3582 data with $|F_o| > 3.0\sigma(|F_o|)$. The complex can be described in terms of distorted-octahedral geometry. That is unique among the taec complexes in taking six-coordination owing to the special bridging structure of CO_3^{2-}. Cyclic voltammograms of the cobalt complexes were compared with five-coordinated cobalt complexes $[Co_2OH(taec)](ClO_4)_3$ (**1c**) and $[Co_2OH(tpmc)](ClO_4)_3$ (**2c**) and revealed that the six-coordinated structure lowered the redox potential for oxidation of cobalt(II) to cobalt(III). Air oxidation of **1a** and **1b** in aqueous solution produced a cobalt(III) complex that was detected by characteristic absorption at 364 and 532 nm. The spectral, magnetic, and elemental analysis data demonstrated that the oxidized product isolated was a mixed-valence $Co^{III}Co^{II}$ complex.

Introduction

In the series[1] of investigations on octaamine ligands 1,4,8,11-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec) and 1,4,8,11-tetrakis(pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc) Kida and co-workers reported that $[Co_2OH(taec)](ClO_4)_3$ (**1c**[2]) is usually stable against chemical and electrochemical oxidation. This was attributed to the steric hindrance of methylene groups[3] of the ligand for attaining six-coordination of cobalt. It was also shown that the chromium(II) oxidation state is stabilized in $Cr_2(taec)X_4$ (X = Cl, Br)[4] for the same reason. In the continuing efforts to obtain new complexes of taec and tpmc, $[Ni_2CO_3(taec)](ClO_4)_2$[5] was found to have distorted octahedral coordination caused by the novel bridging structure[6] of carbonate ion[7] as depicted in Figure 1.

Recently, we prepared a carbonato-bridged cobalt(II) complex with a tricyclic octaamine ligand derived from cyclam and partially reported the cyclic voltammetry of the complex.[17] The redox potential for the Co(II)/Co(III) process of the complex certainly decreased, compared with that of the hydroxo-bridged cobalt(II) complex of the tricyclic ligand. The cause of the stabilization of Co(III) state, however, was not investigated in detail, and isolation of the oxidized Co(III) complex was not attained.

Thus, in this study, we aimed to obtain six-coordinate cobalt(II) complexes with taec and tpmc, expecting them to undergo much more facile oxidation to cobalt(III).

Experimental Section

Safety Note. *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Preparations. $Co(ClO_4)_2 \cdot 6H_2O$ was prepared from basic cobalt(II) carbonate (Nacalai Tesque, reagent grade).[8a] $Co(BF_4)_2 \cdot 6H_2O$ was obtained in a manner similar to that used for the perchlorate except that aqueous HBF_4 was used instead of $HClO_4$. The ligands, taec[1a] and tpmc,[8b] were prepared by the literature methods.

$[Co_2CO_3(taec)](ClO)_2 \cdot 2H_2O$ (1a). All procedures were carried out under an argon atmosphere in a Schlenk apparatus. To an aqueous solution (5 mL) containing taec (500 mg, 1.34 mmol) and Na_2CO_3 (144 mg, 1.34 mmol) was added $Co(ClO_4)_2 \cdot 6H_2O$ (1.008 g, 2.75 mmol) with stirring. The solution was stirred for 5 min. The resultant precipitates were removed by filtration, and the filtrate was concentrated to 2 mL. To the solution was added 5 mL of degassed ethanol, and the resultant solution was allowed to stand for 12 h. Purple crystals were formed, which were collected by filtration, washed with a small amount of cold water and dried in vacuo over P_2O_5. Yield: 530 mg (50.3%). **1a** could be recrystallized from water/ethanol to form microcrystals, but it was difficult to prepare crystals suitable for X-ray crystal structure analysis. Anal. Calcd for $C_{19}H_{48}N_8Cl_2O_{13}Co_2$: C, 29.05; H, 6.16; N, 14.26; Co, 15.01. Found: C, 29.32; H, 6.00; N, 14.29; Co, 14.23. IR (KBr pellet): 3440, 3250, 2860, 1560, 1460, 1330, 1150–1030, 990, 965, 900, 865, 840, 815, 755, 630 cm^{-1}. UV-vis (H_2O) λ_{max}, nm (ϵ): 504 (53), 552 (48).

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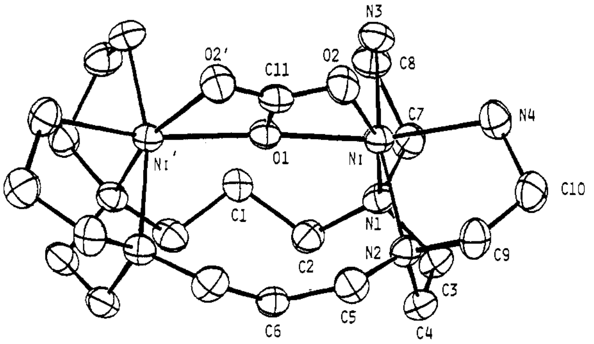

Figure 1. Structural drawing of $[Ni_2CO_3(taec)]^{2+}$.

$[Co_2CO_3(taec)](ClO_4)_2{\cdot}NaClO_4{\cdot}H_2O$ (1a′). Crystals suitable for X-ray structure analysis were obtained by recrystallizing **1a** from water containing an excess amount of sodium perchlorate; details are given in the X-ray crystal structure section. Anal. Calcd for $C_{19}H_{46}N_8Cl_3NaO_{16}Co_2$: C, 25.64; H, 5.21; N, 12.59; Co, 13.24. Found: C, 25.75; H, 5.15; N, 12.52; Co, 13.06. The electronic absorption spectrum of **1a′** was the same as that of **1a**. The IR spectrum of **1a′** was almost the same as that of **1a**, except for a small shift of the C–O stretching vibrations of the carbonate group. IR (KBr pellet): 3480, 3250, 3140, 2860, 1630, 1580, 1460, 1360, 1315, 1150–1030, 1000, 980, 900, 870, 830, 755, 620 cm^{-1}.

$[Co_2CO_3(taec)](BF_4)_2{\cdot}NaBF_4{\cdot}H_2O$ (1b) was prepared from taec (300 mg) by the same way as that used for **1a** except for the use of $Co(BF_4)_2{\cdot}6H_2O$ instead of $Co(ClO_4)_2{\cdot}6H_2O$. Yield: 353 mg (64.6%). Anal. Calcd for $C_{19}H_{46}N_8O_4B_3F_{12}NaCo_2$: C, 26.79; H, 5.44; N, 13.15; Co, 13.83. Found: C, 26.59; H, 5.33; N, 13.13; Co, 13.78. IR (KBr pellet): 3440, 3250, 3110, 2860, 1630, 1580, 1460, 1360, 1140–1000, 990, 900, 865, 830, 790, 755, 520 cm^{-1}. UV-vis (H_2O) λ_{max}, nm (ϵ): 506 (53), 544 (47).

$[Co_2CO_3(tpmc)](ClO_4)_2{\cdot}2H_2O$ (2a). Compound **2a** was obtained under open atmosphere by a method similar to that described above except for the use of tpmc (100 mg) instead of taec. Yield: 154 mg (96%). The product was recrystallized from acetonitrile/methanol (1:1, v/v). Anal. Calcd for $C_{35}H_{48}N_8O_{13}Cl_2Co_2$: C, 43.80, H, 4.84; N, 11.68; Co, 12.28. Found: C, 43.66; H, 4.78; N, 11.59; Co, 12.14. IR (KBr pellet): 3400, 2820, 1600, 1540, 1470, 1440, 1330, 1150–1030, 990, 840, 760, 630 cm^{-1}. UV-vis (H_2O) λ_{max}, nm (ϵ): 203 (25000), 261 (12000), 484 (33), 518 (40), 550 (32).

$[Co_2CO_3(tpmc)](BF_4)_2{\cdot}2H_2O$ (2b). Yield: 143 mg (90%). The product was recrystallized from acetonitrile/methanol (1:1, v/v). Anal. Calcd for $C_{35}H_{48}N_8O_4B_2F_8Co_2$: C, 45.59; H, 5.10; N, 11.82; Co, 12.43. Found: C, 45.32; H, 4.95; N, 11.99; Co, 12.56. IR (KBr pellet): 3400, 2820, 1600, 1540, 1470, 1440, 1330, 1160, 1050, 1020, 990, 840, 760, 625 cm^{-1}. UV-vis (H_2O) λ_{max}, nm (ϵ): 203 (25000), 264 (13000), 482 (33), 518 (40), 550 (32).

$[Co_2OH(tpmc)](ClO_4)_3{\cdot}H_2O$ (2c). To a suspension of tpmc (100 mg, 0.176 mmol) in water was added $Co(ClO_4)_2{\cdot}6H_2O$ (146 mg, 0.399 mmol) at 60 °C. After the suspension was stirred for 60 min, purple crystals were formed and collected by filtration. Yield: 160 mg (88%). The solid was recrystallized from acetonitrile–ethanol (1:1, v/v). Anal. Calcd for $C_{36}H_{48}N_9O_{13}Cl_3Co_2$: C, 41.45; H, 4.51; N, 11.76; Co, 11.00. Found: C, 41.51; H, 4.51; N, 11.53; Co, 11.17. IR (KBr pellet): 3450, 2880, 1610, 1480, 1440, 1300, 1150–1020, 980, 760, 620 cm^{-1}. UV-vis (CH_3CN) λ_{max}, nm (ϵ): 206 (26200), 264 (13000), 489 (60), 574 (80), 820 (15).

Air Oxidation of 1b. The pH of an aqueous solution of **1b** (300 mg) was adjusted with diluted HCl to about 6 and a small amount of active carbon (ca. $^1/_5$ of the amount of **1b**) was added. The solution was stirred with vigorous air-bubbling for 12 h. The reaction was monitored by measurements of electronic spectra. As the reaction proceeded, new absorption peaks appeared at 367 and 532 nm. After the reaction was over, active carbon was removed by filtration, and the filtrate was concentrated until a white precipitate appeared. This was removed by filtration, and the filtrate was concentrated in a rotary evaporator to yield an oily residue. Addition of acetonitrile (1.4 cm^3) gave purple microcrystals. The product was filtered, washed with acetonitrile, and dried in vacuo. Yield: 125 mg (41%). Anal. Calcd for $C_{19}H_{50}N_8O_6B_3F_{12}Co_2$: C, 26.38: H, 5.83; N, 12.92; Co, 13.45. Found: C, 26.13; H, 5.83; N, 12.95; Co, 13.62. IR (KBr pellet): 3450, 3200, 2950, 1640, 1460, 1280, 1100–1000, 995, 960, 830, 760 cm^{-1}. UV-vis (H_2O) λ_{max}, nm (ϵ): 367 (223), 532 (220).

Chemical Oxidation of 2a. To a saturated solution of **2a** (448 mg, 0.5 mmol) in acetonitrile was added dropwise 3% aqueous H_2O_2 at 0 °C with vigorous stirring. The color of the solution became dark. The solution was further stirred at 0 °C for 1 h, and filtered. An excess amount of sodium perchlorate (0.8 g) was added to the filtrate. After the solution was allowed to stand for 5 days, a brown precipitate was formed. This was collected by filtration, washed with ether, and dried over P_2O_5. Yield: 219 mg (39%). Anal. Calcd for $C_{35}H_{52}N_8O_{19}Cl_3Co_2$: C, 37.77; H, 4.71; N, 10.07; Co, 10.59. Found: C, 37.38; H, 4.34; N, 10.17; Co, 9.78.

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

compound	$[Co_2CO_3(taec)]$-$(ClO_4)_2{\cdot}NaClO_4{\cdot}H_2O$	D_x/g cm^{-3}	1.68
		cryst size/mm	0.2 × 0.2 × 0.15
formula	$C_{19}H_{46}Cl_3N_8$-$NaO_{16}Co_2$	μ(Mo Kα)/cm^{-1}	12.47
		scan mode	θ–2θ
fw	889.83	2θ range/deg	2.5–52
cryst syst	monoclinic	λ, Å (radiation)	0.71073 (Mo Kα)
space group	$P2_1/a$		
a/Å	26.419 (10)	monochromator	graphite
b/Å	12.774 (5)	data collcd	$\pm h,+k,+l$
c/Å	10.410 (3)	no. of obsd reflcns $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	3582
β/deg	90.51 (4)		
V/Å^3	3513		
Z	4	R/%	0.068
D_m/g cm^{-3}	1.72	R_w/%	0.057

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

Measurements. Analytical data for carbon, hydrogen, and nitrogen were obtained at the Elemental Analysis Service Center, Kyushu University. Cobalt analyses were performed with 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 multipurpose spectrophotometer Model MPS-2000. Magnetic susceptibilities were measured by the Faraday method. The apparatus was calibrated by the use of $[Ni(en)_3]S_2O_3$.[9] The diamagnetic corrections were made by Pascal's constants. Magnetic moments were calculated by the equation $\mu_{eff} = (8\chi_A T)^{1/2}$. Cyclic voltammograms were obtained in an aqueous KCl solution (0.1 M) and an 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) and a platinum plate were used as a working electrode and a counter electrode, respectively, and a TOA saturated calomel electrode (SCE) was used as the reference electrode with a 1% agar salt bridge (0.1 M KCl).

Iodometry of 3b. About 50 mg of **3b** and 100 equiv of potassium iodide were dissolved in water and the solution was acidified with ca. 0.5 mL of concentrated HCl. When the solution was heated with boiling water bath for 1 min, the color of the solution changed from purple to pale brown. After being cooled to room temperature, the pale brown solution was titrated with a $Na_2S_2O_3$ (1.16×10^{-2} M) solution, using starch as an indicator.

X-ray Crystal Structure Analysis

Single crystals of $[Co_2CO_3(taec)](ClO_4)_2{\cdot}NaClO_4{\cdot}H_2O$ (**1a′**) were grown by the slow diffusion technique whereby a deoxygenated aqueous solution of sodium perchlorate was layered onto an aqueous solution of the complex, **1a**, under Ar at room temperature. Purple rodlike crystals suitable for X-ray structure determination were obtained.

Diffraction data were obtained on a Rigaku Denki AFC-5 automated four-cycle diffractometer with graphite-monochromatized Mo Kα radiation 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 ($20° < 2\theta < 30°$). The details of the data collection and crystallographic data are summarized in Table I.

The structures were solved by the standard heavy-atom method. Several Fourier and difference 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 a block-diagonal least-squares method. The hydrogen atoms bound to carbon atoms were introduced in their calculated positions. The weighting scheme $1/\sigma(F^2)$ was adopted. The discrepancy factors are defined as $R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$ and $R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$. 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.[19] The atomic scattering factors were taken from the literature.[20]

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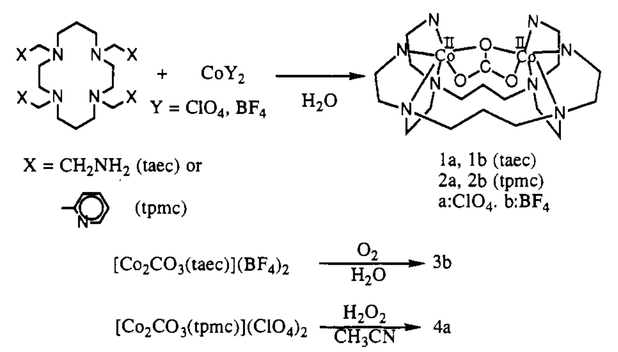
[9] Curtis, N. F. *J. Chem. Soc.* **1961**, 3147.

Scheme I



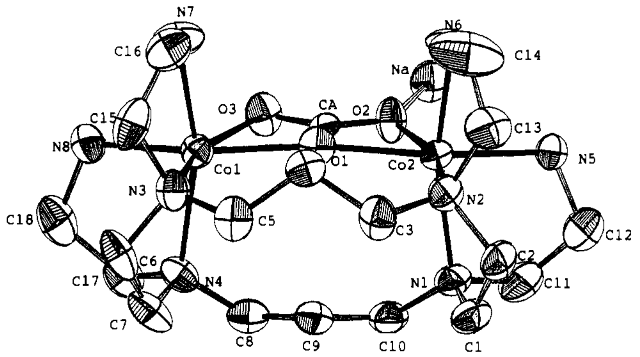


Figure 2. ORTEP diagram of the cation of [Co_2CO_3(taec)]$(ClO_4)_2$·$NaClO_4$·H_2O with 50% probability ellipsoids.

The final atomic coordinates of non-hydrogen atoms of the compound are given in Table II. A table of observed and calculated structure factors, a listing of atomic positional and anisotropic thermal parameters, and complete lists of bond lengths and angles with their estimated standard deviations are deposited as supplementary materials.

Results

The cobalt(II) complexes **1a**, **1a′**, **1b**, **2a**, and **2b** were prepared from a free ligand (taec or tpmc), sodium carbonate, and CoX_2·$6H_2O$ (X = ClO_4 or BF_4) in water. The transformations observed in this study are summarized in Scheme I. The spectroscopic, electrochemical, and magnetic properties of these complexes have been measured and are introduced at the appropriate places in the following sections and in Table IV and Figures 3–5.

Single crystals suitable for X-ray structure determination could be obtained only for **1a′**, whose results are presented in Tables I–III and Figure 2 and are discussed in the following section.

Discussion

X-ray Structural Analysis of 1a′. The crystal of **1a** consists of a discrete dinuclear complex cation, [Co_2CO_3(taec)]$^{2+}$, a sodium ion, three perchlorate ions, and a crystal water molecule. An ORTEP diagram is shown in Figure 2. The selected interatomic distances and angles with their estimated standard deviations are given in Table III.

As expected the two cobalt atoms are bridged by a carbonate ion in a way similar to that of [Ni_2CO_3(taec)]$(ClO_4)_2$·H_2O.[5] The coordination geometry of each cobalt atom can be described as a distorted octahedron formed by four nitrogens of taec and two oxygens from the carbonate ion.

The cobalt–cobalt distance is 4.213 (2) Å. The Co1–O1–Co2 bridge is nearly linear. The Co–O–Co angle (171.1 (3)°) is closer to the Ni–O–Ni angle (174.6 (5)°) of the corresponding nickel complex[5] rather than the Co–O–Co angle (167.1 (2)°) of the carbonato-bridged cobalt complex of tricyclic octaamine ligand (tcoa).[17]

Different from the nickel complex, in this complex, the two cobalt atoms are not equivalent because of the existence of the sodium ion located at the close proximity of the carbonate oxygen O2. The interatomic distance between Na and O2 is 2.270 (7) Å, which is significantly shorter than the sum of ionic radii of Na^+ and O^{2-} and even shorter than the shortest Na–O distance (2.30 A) observed in Na_2Co_3·H_2O.[18] These facts indicate the

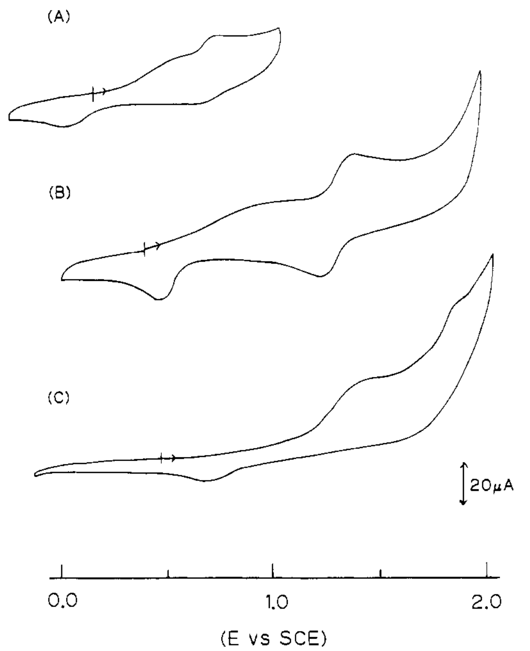


Figure 3. Cyclic voltammograms of **1a**, **2a**, and **2c** in CH_3CN containing 0.1 M of NBu_4BF_4 with a glassy-carbon electrode as a working electrode and a saturated calomel electrode as a reference electrode: (A) **1a**; (B) **2a**; (C) **2c**. Scan rate = 100 mV/s.

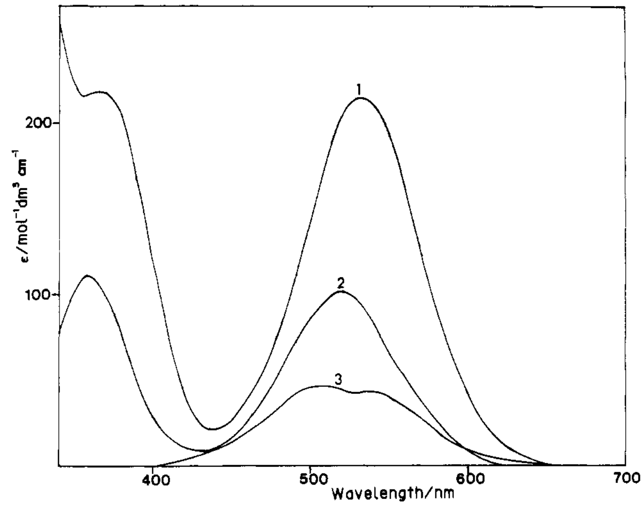


Figure 4. Electronic absorption spectra of cobalt complexes in H_2O: (1) [Co_2CO_3(taec)]$(BF_4)_3$·$3H_2O$ (mixed-valence complex); (2) [$CoCO_3(NH_3)_4$]NO_3; (3) [Co_2CO_3(taec)]$(BF_4)_2$.

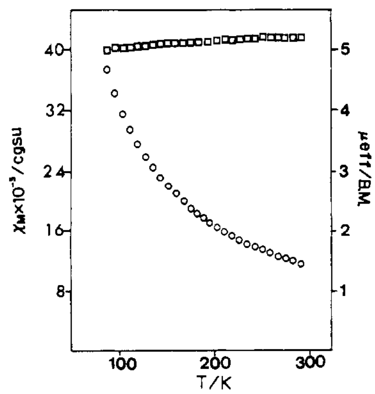


Figure 5. Temperature dependence of magnetic moment, μ_{eff} (□), and molecular magnetic susceptibility, χ_M (○), of [Co_2CO_3(taec)]$(BF_4)_3$·$3H_2O$.

Table II. Fractional Positional Parameters (×10⁴) and Thermal Parameters of Non-Hydrogen Atoms for $[Co_2CO_3(taec)](ClO_4)_2{\cdot}NaClO_4{\cdot}H_2O$[a]

atom	x	y	z	$B_{eq}/Å^2$
Co1	4268 (0)	2258 (1)	2876 (1)	2.57 (3)
Co2	3510 (0)	5160 (1)	2786 (1)	2.77 (3)
Cl1	4853 (1)	8211 (2)	3280 (2)	3.84 (7)
Cl2	7004 (1)	7010 (2)	2799 (2)	5.37 (9)
Cl3	3608 (1)	7445 (3)	6676 (3)	5.78 (9)
Na^+	5461 (1)	4025 (3)	4494 (4)	3.96 (11)
Ca	4324 (3)	4187 (7)	3424 (7)	2.59 (26)
O1	3917 (2)	3754 (5)	2960 (5)	2.95 (17)
O2	4698 (2)	3608 (5)	3614 (6)	3.48 (19)
O3	4298 (2)	5158 (5)	3631 (6)	3.68 (19)
O4	4550 (3)	8586 (6)	2249 (7)	6.43 (27)
O5	4971 (4)	9055 (6)	4066 (8)	9.95 (38)
O6	4611 (3)	7446 (7)	3995 (8)	9.38 (35)
O7	5290 (3)	7770 (10)	2812 (9)	13.05 (49)
O8	7284 (3)	7550 (7)	3717 (7)	9.22 (35)
O9	6575 (3)	6555 (8)	3319 (9)	9.95 (38)
O10	7323 (4)	6120 (8)	2443 (10)	12.55 (47)
O11	6892 (4)	7606 (9)	1758 (8)	11.73 (42)
O12	3447 (4)	7748 (10)	7807 (8)	14.83 (53)
O13	4037 (4)	6949 (11)	6761 (12)	19.57 (70)
O14	3252 (5)	7143 (14)	5970 (13)	23.48 (86)
O15	3684 (6)	8343 (11)	6011 (14)	20.34 (76)
N1	4542 (3)	2269 (6)	852 (6)	3.47 (23)
N2	3657 (3)	1261 (6)	2038 (7)	3.21 (23)
N3	2809 (3)	4579 (6)	1915 (7)	3.37 (23)
N4	3683 (3)	5583 (6)	768 (7)	3.09 (22)
N5	4922 (3)	1256 (6)	3090 (7)	3.40 (23)
N6	3954 (3)	1665 (6)	4648 (7)	3.94 (25)
N7	3092 (3)	4993 (7)	4546 (7)	4.47 (27)
N8	3427 (3)	6845 (6)	2922 (7)	3.94 (25)
C1	4207 (4)	1495 (8)	131 (9)	3.95 (31)
C2	3934 (4)	718 (7)	974 (9)	3.96 (31)
C3	3193 (4)	1729 (8)	1499 (9)	4.06 (32)
C4	2964 (3)	2644 (7)	2287 (8)	3.19 (28)
C5	2772 (3)	3516 (8)	1403 (9)	3.79 (31)
C6	2734 (4)	5319 (8)	817 (10)	4.37 (33)
C7	3200 (4)	5394 (8)	2 (9)	4.50 (33)
C8	4117 (4)	5021 (8)	183 (8)	3.73 (30)
C9	4049 (3)	3858 (7)	106 (8)	3.33 (29)
C10	4560 (4)	3325 (7)	252 (8)	3.73 (31)
C11	5080 (4)	1878 (9)	969 (10)	5.36 (38)
C12	5157 (4)	990 (9)	1854 (10)	5.35 (38)
C13	3554 (4)	481 (7)	3089 (9)	4.68 (34)
C14	3567 (5)	902 (10)	4357 (11)	7.96 (49)
C15	2408 (3)	4765 (8)	2919 (10)	4.76 (34)
C16	2601 (4)	4480 (9)	4225 (10)	5.43 (38)
C17	3820 (4)	6686 (7)	796 (9)	3.98 (32)
C18	3455 (4)	7329 (8)	1640 (10)	4.76 (34)
OW	4446 (3)	4463 (6)	6735 (8)	8.20 (32)

[a] Values in parentheses are estimated standard deviations.

Table III. Selected Bond Distances and Angles for **1a′**

Bond Distances (Å)			
(a) Bridging Part			
Co···Co	4.213 (2)		
Co1–O1	2.126 (6)	O1–CA	1.29 (1)
Co1–O2	2.199 (6)	O2–CA	1.24 (1)
Co2–O1	2.100 (6)	O3–CA	1.26 (1)
Co2–O3	2.253 (6)	Na–O2	2.270 (7)
(b) Macrocycle			
Co1–N1	2.234 (7)	N4–C7	1.51 (1)
Co1–N2	2.227 (7)	N4–C8	1.48 (6)
Co1–N5	2.161 (7)	N4–C17	1.45 (1)
Co1–N6	2.165 (7)	N5–C12	1.47 (1)
Co2–N3	2.185 (7)	N6–C14	1.44 (1)
Co2–N4	2.168 (7)	N7–C16	1.48 (1)
Co2–N7	2.158 (7)	N8–C18	1.47 (1)
Co2–N8	2.168 (7)	C1–C2	1.51 (1)
N1–C1	1.52 (1)	C3–C4	1.55 (1)
N1–C10	1.48 (1)	C4–C5	1.52 (1)
N1–C11	1.51 (1)	C6–C7	1.50 (1)
N2–C2	1.50 (1)	C8–C9	1.49 (1)
N2–C3	1.47 (1)	C9–C10	1.51 (1)
N2–C13	1.50 (1)	C11–C12	1.47 (1)
N3–C5	1.46 (1)	C13–C14	1.42 (1)
N3–C6	1.49 (1)	C15–C16	1.49 (1)
N3–C15	1.51 (1)	C17–C18	1.45 (1)
(c) Perchlorate Ions			
Cl1–O4	1.416 (7)	Cl2–O10	1.46 (1)
Cl1–O5	1.386 (8)	Cl2–O11	1.354 (9)
Cl1–O6	1.387 (9)	Cl3–O12	1.313 (9)
Cl1–O7	1.37 (1)	Cl3–O13	1.30 (1)
Cl2–O8	1.386 (9)	Cl3–O14	1.24 (1)
Cl2–O9	1.388 (9)	Cl3–O15	1.45 (1)
Bond Angles (deg)			
(a) Bridging Carbonate			
Co1–O1–Co2	171.1 (3)	O1–Co1–O2	60.3 (2)
Co1–O1–CA	92.1 (4)	O1–Co2–O3	59.6 (2)
Co1–O2–CA	90.2 (5)	O1–CA–O2	117.3 (7)
Co1–O2–Na	141.1 (3)	O1–CA–O3	115.8 (7)
Co2–O1–CA	95.1 (5)	O2–CA–O3	126.8 (7)
Co2–O3–CA	89.2 (5)	Na–O2–CA	128.5 (5)
(b) Coordination Sphere of Co1			
O1–Co1–N1	100.2 (2)	Co1–N2–C2	101.3 (5)
O1–Co1–N5	151.2 (2)	Co1–N1–C13	103.2 (5)
O2–Co1–N1	98.8 (2)	Co1–N5–C12	112.9 (5)
O2–Co1–N2	162.8 (2)	Co1–N6–C14	109.4 (6)
N1–Co1–N2	82.7 (2)	C1–N1–C11	111.6 (7)
N1–Co1–N5	80.4 (2)	C2–N2–C13	108.8 (6)
N1–Co1–N6	159.2 (3)	N1–C1–C2	114.7 (7)
N2–Co1–N5	106.0 (2)	N1–C11–C12	115.3 (8)
N2–Co1–N6	81.5 (2)	N2–C2–C1	111.2 (7)
N5–Co1–N6	90.9 (2)	N2–C13–C14	114.7 (8)
Co1–N1–C1	105.5 (5)	N5–C12–C11	108.1 (8)
Co1–N1–C11	103.6 (5)	N6–C14–C13	117.4 (9)
(c) Coordination Sphere of Co2			
O1–Co2–N3	100.1 (2)	Co2–N4–C7	106.1 (5)
O1–Co2–N8	153.5 (2)	Co2–N4–C17	105.6 (5)
O3–Co2–N4	99.8 (2)	Co2–N7–C16	107.7 (5)
O3–Co2–N3	159.8 (2)	Co2–N8–C17	110.5 (5)
N3–Co2–N4	82.6 (2)	N3–C6–C7	111.6 (7)
N3–Co2–N7	83.1 (2)	N3–C15–C16	110.7 (7)
N3–Co2–N8	106.1 (2)	N4–C7–C6	113.7 (7)
N4–Co2–N7	159.8 (2)	N4–C17–C18	111.6 (7)
N4–Co2–N8	80.9 (2)	N7–C16–C15	112.7 (8)
N7–Co2–N8	89.4 (2)	N8–C18–C17	109.1 (7)
Co2–N3–C15	104.7 (5)	C6–N3–C15	109.9 (7)
Co2–N3–C6	101.9 (5)	C7–N4–C17	117.4 (9)
(d) Bridging Trimethylene Chains			
Co1–N1–C10	114.4 (5)	N2–C3–C4	115.5 (7)
Co1–N2–C3	121.0 (5)	N3–C5–C4	115.9 (7)
Co2–N3–C5	121.3 (5)	N4–C8–C9	114.0 (7)
Co2–N4–C8	115.8 (5)	C3–C4–C5	111.0 (7)
N1–C10–C9	114.6 (7)	C8–C9–C10	109.4 (7)
(e) Perchlorate Ions			
O4–Cl1–O5	107.8 (5)	O9–Cl2–O10	104.3 (6)
O4–Cl1–O6	112.6 (5)	O9–Cl2–O11	112.0 (5)
O4–Cl1–O7	109.8 (5)	O10–Cl2–O11	110.8 (6)
O5–Cl1–O6	109.4 (5)	O12–Cl3–O13	111.7 (7)
O5–Cl1–O7	110.1 (6)	O12–Cl3–O14	111.7 (7)
O6–Cl1–O7	107.6 (6)	O12–Cl3–O15	102.6 (8)
O8–Cl2–O9	111.8 (5)	O13–Cl3–O14	122.6 (9)
O8–Cl2–O10	104.8 (6)	O13–Cl3–O15	109.3 (8)
O8–Cl2–O11	112.4 (6)	O14–Cl3–O15	95.3 (9)

existence of a coordination bond between the Na and O2 atoms. Interestingly, contrary to our expectation, the Co2–O2 (2.199 (6) Å) and O2–CA (1.24 (1) Å) distances are both shorter than the distances Co2–O3 (2.253 (6) Å) and O1–CA (1.29 (1) Å), respectively. At present, we have no theory that gives an explanation of this fact.

The bond lengths Co(II)–O and Co(II)–N found in this study are in general close to those of the carbonato-bridged cobalt(II) complex of tcoa[17] and longer by ca. 0.2 Å (average) than those of bis(μ-hyrdoxo)(μ-carbonato-*O′,O″*)bis[triamminecobalt(III)] sulfate.[7b]

IR and Electronic Spectra of Cobalt(II) Complexes. The IR spectrum of **1b** was the same as that of **1a′**, except for the peaks of the counteranion. This suggests that **1a′** and **1b** take essentially the same structure.

The absorption spectra of **1a**, **1a′**, and **1b** in an aqueous solution were identical, indicating that those complexes take the same structure in the aqueous solution. Since d–d transitions are Laporte forbidden, intensities of d–d bands of octahedral complexes are much lower than those of lower symmetry complexes such as square-pyramidal and tetrahedral ones.[10] The absorption

Table IV. Cyclic Voltammogram Data for the Cobalt Complexes[a]

complex	redox peak[b] E_{a1}	E_{c1}	E_{a2}	E_{c2}
1a	0.55	0.05	0.76	0.68
1b	0.55	0.05	0.76	0.68
1c[c]	1.4	*d*	1.8	*d*
2a	1.00	0.36	1.38	1.20
2b	1.00	0.36	1.38	1.20
2c	1.40	0.70	1.87	*d*

[a] In CH_3CN containing $(n\text{-}C_4H_9)_4NBF_4$. [b] Anode peak, E_{a1}, E_{a2}; cathode peak, E_{c1}, E_{c2} (V vs SCE). [c] Reference 2. [d] No peak.

intensities of d–d bands of the present carbonato-bridged complexes, **1a**, **1a′**, **1b**, **2a**, and **2b**, are lower than those of the hydroxo-bridged complexes, **1c** and **2c**, being consistent with the view that the present carbonato-bridged complexes keep the six-coordination structure in an aqueous solution.

Magnetic Properties of Cobalt(II) Complexes. Magnetic moments of **1a** and **2a** are 4.19 and 4.20 μ_B per cobalt ion at room temperature, respectively. These values are slightly larger than the spin-only value (3.87 μ_B) for $S = {}^3/_2$ and fall at the lower limit of the range of μ_{eff} value (4.2-5.2 μ_B)[11] for octahedral high-spin cobalt(II) complexes. The temperature dependence of the magnetic susceptibility of **1a** over the temperature range 80–300 K indicated the operation of an antiferromagnetic interaction between two cobalt(II) ions. The J value is evaluated at 20 cm^{-1} as a fitting parameter of the Van Vleck equation based on the Heisenberg model ($H = -2JS_1S_2$).[12]

Electrochemical Oxidation. All the redox waves of the present cobalt complexes are irreversible. Each of the two couples of anodic and cathodic peaks (see Table IV and Figure 3) may be assigned to a redox reaction at metal centers, since an anodic reaction due to the ligand oxidation was observed as an abrupt increase of the current at a higher potential than at 2 V. The constant potential electrolyses of **1a** and **2a** at 0.55 and 1.0 V vs SCE needed 0.95 and 0.98 equiv of current/mol, respectively, to reveal that the redox steps corresponded to one-electron oxidation. Therefore, the first anodic peak can be assigned to one-electron oxidation from $Co^{II}Co^{II}$ to $Co^{III}Co^{II}$ and the second one from $Co^{III}Co^{II}$ to $Co^{III}Co^{III}$.

As already reported,[2] the five-coordinate complex **1c** was shown to be very stable against oxidation based on its high redox potential, 1.4 and 1.8 V vs SCE in acetonitrile. A similar behavior is also observed in this study for the tpmc derivative **2c**, whose anodic peaks were 1.4 and 1.9 V vs SCE in acetonitrile. In the previous paper, such a large stability of the cobalt(II) state was attributed to the persistency of five-coordination due to the steric requirement.[2] However, this view has not yet been verified, since no six-coordinate cobalt complex with taec or tpmc to be compared with has been found. In the present study, the synthesis of **1a** and **1b** has made it possible to compare the redox properties of **1c** with those of **1a** and **1b**. The first and second anodic potentials of **1a** and **1b** are lower by 0.85 and 1.04 V, respectively, than those of **1c**. This is the first example showing the difference in the redox potential between five- and six-coordinate cobalt complexes.[13,14]

Thus, we have confirmed our previously reported view that the unusually large stability of the cobalt(II) complexes of taec and tpmc toward the oxidation to cobalt(III) stems from the five-coordination enforced by the ligands.

Chemical Oxidation. Air oxidation of **1a** and **1b** proceeded at room temperature in the presence of active carbon in a slightly acidic aqueous solution. The tpmc complexes **2a** and **2b** were inert against the air oxidation, but were oxidized with hydrogen peroxide in acetonitrile. The oxidation conditions are described in the Experimental Section. The facile oxidation of **1a** and **1b** compared with **2a** and **2b** is consistent with the lower oxidation potentials of **1a** and **1b**, by 450–620 mV, than those of **2a** and **2b**.

The air oxidation of **1a** and **1b** was monitored by the electronic absorption spectra of the solution. The new absorption peaks at 367 and 532 nm appeared as the reaction proceeded. The oxidized product, **3b**, was isolated as microcrystals and characterized by elemental analysis, IR and electronic spectra, magnetic measurements, and iodometry. The solubilities of **3a** and **3b** are different from those of **1a** and **1b**; i.e., the former compounds are very soluble in water but hardly soluble in acetonitrile, while the latter compounds are moderately soluble in water and in acetonitrile. The elemental analysis of **3b** agreed with the calculated value for the Co^{III}/Co^{II} mixed-valence complex $[Co_2CO_3(taec)](BF_4)_3\cdot 3H_2O$, within 0.2% error. The facts that the electronic absorption spectrum of **3b**, as shown in Figure 4, is similar to that of the (carbonato)tetraamminecobalt(III) complex[15] and the absorption coefficients at 367 and 532 nm are about five times larger than those of **1b** strongly suggest the formation of cobalt(III) species. The IR spectrum of **3b** showed three peaks at 1640, 1460, and 1280 cm^{-1}, characteristic of coordinated carbonate ion,[16] and the C=O stretching vibrational peak at 1640 cm^{-1}, shifted to high-energy side by 80 cm^{-1} compared to that of **1b**. The temperature dependence of the magnetic susceptibility of **3b** was measured over the temperature range 80–300 K (see Figure 5), indicating that there is no strong magnetic interaction. The effective magnetic moment, 5.10 μ_B/molecule at room temperature, falls in the range of the μ_{eff} values (4.2–5.2 μ_B) for high-spin octahedral cobalt(II) complexes. The oxidation equivalent obtained by iodometry was 1.05 equiv/mol. Thus, all experimental results consistently demonstrated that the oxidation occurred at a metal center and yielded a mixed-valence complex consisting of a low-spin Co(III) and a high-spin Co(II).

The purple powder, **4a**, obtained as the oxidized product of **2a** was supposed to be a $Co^{III}Co^{II}$ mixed-valence complex from its elemental analysis. However, the effective magnetic moment, 5.71 μ_B, of **4a** per molecule at room temperature is significantly larger than the μ_{eff} value (4.2-5.2 μ_B)[11] for common mononuclear octahedral high-spin cobalt(II) complexes. This is not consistent with the assumption of a high-spin Co(II) and low-spin Co(III) mixed-valence complex. Some impurity might be contained in the sample. Unfortunately, the electronic absorption spectrum of **4a** was not available due to its insolubility in any solvent. Further efforts seem to be necessary to obtain a pure compound for the oxidation product of **2a**.

Supplementary Material Available: Tables of complete bond distances and angles, atomic parameters, and anisotropic thermal parameters (4 pages); a table of structure factors (17 pages). Ordering information is given on any current masthead page.

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