Bull. Chem. Soc. Jpn. Vol. 81, No. 10, 1296–1298 (2008)

Preparation, Characterization, and Structures of Dinuclear Cobalt(III) Complexes Triply Bridged by Two μ-Hydroxo and One μ-Carbonato

Tomoharu Ama,* Toshiaki Yonemura, and Takahisa Yoshimura

Department of Material Science, Faculty of Science,
Kochi University, 2-5-1 Akebono-cho, Kochi 780-8520

Received April 22, 2008; E-mail: tomama@cc.kochi-u.ac.jp

Two $[Co_2(L)_2(\mu\text{-}CO_3)(\mu\text{-}OH)_2]$ complexes (L: *N*-methyliminodiacetato, or 1,4,7-triazacyclononane) were prepared and characterized. In each complex, the dihedral angle between $Co–O_{\mu\text{-}OH}–O'_{\mu\text{-}OH}$ and $Co'–O_{\mu\text{-}OH}–O'_{\mu\text{-}OH}$ planes was ca. 160° and the $\mu\text{-}CO_3{}^{2-}$ plane was perpendicular to each $Co–O_{\mu\text{-}OH}–\mu\text{-}O'_{\mu\text{-}OH}$ plane. ^{13}C NMR signals of $\mu\text{-}CO_3{}^{2-}$ in these complexes appeared at ca. 170 ppm.

As dinuclear cobalt(III) complexes containing $Co_2(\mu\text{-}CO_3)(\mu\text{-}OH)_2$ moieties are relevant to fixation reactions of atmospheric CO_2 and insertion reactions of CO_2 to metal–ligand bonds, many reports clarifying reaction mechanisms and stability of the complexes have been published.[1,2] Moreover, as μ-carbonato ligand can coordinate to cobalt(III) in modes similar to μ-carboxylato, of which complexes are related to some metalloenzymes, comparative investigations between μ-carbonato and μ-carboxylato complexes are of interest to bioinorganic chemists.[3–9] In spite of the continuing importance of cobalt(III)–μ-carbonato complex studies as mentioned above, there have been few reports of $[Co_2(L)_2(\mu\text{-}CO_3)(\mu\text{-}OH)_2]$ complexes of which structures have already been confirmed[8,10] except for ammine complexes.[11] This makes it necessary to report synthetic and structural studies of new cobalt(III) complexes containing $Co_2(\mu\text{-}CO_3)(\mu\text{-}OH)_2$ moieties.

In previous work, we reported that some $[Co_3(L)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]$ (L: tridentate) complexes which have incomplete cubane Co_3O_4 cores can be prepared by dehydroxo-condensation of $[Co(H_2O)_3(L)]$ complexes which were obtained by acid hydrolysis of $[Co(CO_3)(HCO_3)(L)]$ complexes.[12–15] However, when hydrolysis of the $[Co(CO_3)(HCO_3)(L)]$ complexes was insufficient and $[Co(HCO_3)(H_2O)_2(L)]$ complexes remained in solution, it was found that $[Co_2(L)_2(\mu\text{-}CO_3)(\mu\text{-}OH)_2]$ complexes can be prepared by basifying the hydrolyzed solutions to pH 8 at which decarboxylate–dehydrate dimerization reactions occur. In the present paper, we report the preparation, characterization, and structures of $Na_2[Co_2(mida)_2(\mu\text{-}CO_3)(\mu\text{-}OH)_2]\cdot 11H_2O$ (Na_2[complex ion **1**]$\cdot 11H_2O$; mida: *N*-methyliminodiacetato) and $[Co_2(tacn)_2(\mu\text{-}CO_3)(\mu\text{-}OH)_2]Cl_2\cdot 7H_2O$ ([complex ion **2**]$Cl_2\cdot 7H_2O$; tacn: 1,4,7-triazacyclononane).

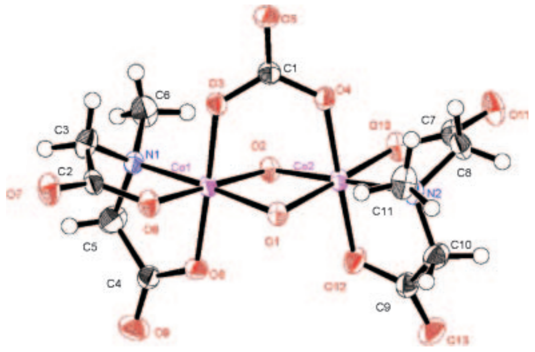

Figure 1. ORTEP drawing of $[Co_2(mida)_2(\mu\text{-}CO_3)(\mu\text{-}OH)_2]^-$ in Na_2[complex ion **1**]$\cdot 11H_2O$. Selected bond distances/Å are as follows: Co1–O1, 1.908(2); Co1–O2, 1.894(2); Co1–O3, 1.878(2); Co1–N1, 1.982(2); Co1–O6, 1.903(2); Co1–O8, 1.893(2); Co2–O1, 1.905(2); Co2–O2, 1.915(2); Co2–O4, 1.892(2); Co2–N2, 1.974(2); Co2–O10, 1.908(2); Co2–O12, 1.898(2); C1–O3, 1.309(4); C1–O4, 1.314(4); C1–O5, 1.258(4).

An ORTEP drawing of complex ion **1** is illustrated in Figure 1. The complex ion contains $Co_2(\mu\text{-}CO_3)(\mu\text{-}OH)_2$ and each cobalt atom is octahedrally surrounded by one $N_{nitrilo}$ and two $O_{carboxyl}$ atoms in the facially coordinated mida, two $O_{\mu\text{-}OH}$, and one $O_{\mu\text{-}carbonato}$. The trans position of each $O_{\mu\text{-}carbonato}$ is occupied by an $O_{carboxy}$. In complex ion **1**, $Co–N_{nitrilo}$ and $Co–O_{carboxy}$ distances are 1.978 and 1.901 Å (av.), respectively. The $Co–O_{\mu\text{-}carbonato}$ distances are 1.885 Å (av.), which are slightly shorter than the $Co–O_{\mu\text{-}carbonato}$ distances in $[Co_2(NH_3)_6(\mu\text{-}CO_3)(\mu\text{-}OH)_2]^+$ (1.906 Å (av.))[11] and the $Co–O_{\mu\text{-}acetato}$ distances in $[Co_2(bpy)_2(OAc)_2(\mu\text{-}OAc)(\mu\text{-}OH)_2]^+$ (1.916 Å (av.))[7] which bears $Co_2(\mu\text{-}OAc)(\mu\text{-}OH)_2$. The $Co–O_{\mu\text{-}OH}$ distances in complex ion **1** are 1.906 Å (av.). The $Co–O_{\mu\text{-}OH}–Co'$ and $O_{\mu\text{-}OH}–Co–O'_{\mu\text{-}OH}$ angles are 94.0 and 84.8°, respectively. These are comparable to the corresponding angles in $[Co_3(edma)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ (96.3 and 83.7°)[12] and $[Co_2(NH_3)_6(\mu\text{-}CO_3)(\mu\text{-}OH)_2]^+$ (94.5 and 82.6° (av.)).[11] In the three C–O bonds of the $\mu\text{-}CO_3{}^{2-}$, the $C1–O5_{uncoord}$ distance (1.258(4) Å) is shorter than the other two $C1–O_{coord}$ (C1–O3 and C1–O4) distances (1.312 Å (av.)) and has stronger double-bond character than the others. The $C1–O_{coord}$ distances in complex ion **1** are longer than the $C–O_{coord}$ distances of $\mu\text{-}OAc^-$ in $[Co_2(py)_4(OAc)_2(\mu\text{-}OAc)(\mu\text{-}OH)_2]^+$ (1.262 Å (av.)).[9]

The five atoms (Co1, O1, O2, O6, and N1) are almost coplanar and distances from the least-squares plane (basal plane 1) of each atom are less than 0.05 Å. The five atoms (Co2, O1, O2, O10, and N2) are almost coplanar (basal plane 2), as well. The dihedral angle between the basal plane 1 and 2 is 165.5°, which is related to the following order of nonbonding distances: $O3_{\mu\text{-}carbonato}–O4_{\mu\text{-}carbonato}$ (2.30 Å) < Co1–Co2 (2.79 Å) < $O8_{carboxy}–O12_{carboxy}$ (3.38 Å). The four atoms (O3, O4, O5, and C1) forming $\mu\text{-}CO_3{}^{2-}$ ion are also coplanar and the plane is almost perpendicular to both basal planes (85.1° (av.)).

The ORTEP drawing of complex ion **2** is illustrated in Figure 2. The complex ion contains $Co_2(\mu\text{-}CO_3)(\mu\text{-}OH)_2$

Published on the web October 10, 2008; doi:10.1246/bcsj.81.1296

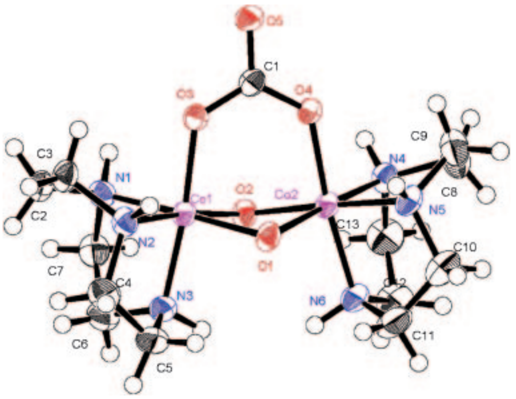

Figure 2. ORTEP drawing of $[Co_2(tacn)_2(\mu\text{-}CO_3)(\mu\text{-}OH)_2]^+$ in [complex ion **2**]$Cl_2 \cdot 7H_2O$. Selected bond distances/Å are as follows: Co1–O1, 1.926(2); Co1–O2, 1.916(2); Co1–O3, 1.926(2); Co1–N1, 1.938(2); Co1–N2, 1.942(2); Co1–N3, 1.931(3); Co2–O1, 1.918(2); Co2–O2, 1.916(2); Co2–O4, 1.907(2); Co2–N4, 1.937(2); Co2–N5, 1.926(2); Co2–N6, 1.933(2); C1–O3, 1.302(4); C1–O4, 1.286(4); C1–O5, 1.260(4).

moiety and two tacn coordinate to Co^{III} as facial tridentates. The $Co\text{–}O_{\mu\text{-carbonato}}$ distances are 1.917 Å (av.). The five atoms (Co1, O1, O2, N1, and N2) are almost coplanar (basal plane 1) and the five atoms (Co1, O1, O2, N4, and N5) are almost coplanar (basal plane 2), as well. The dihedral angle between basal plane 1 and 2 is 157.6° and the CO_3^{2-} plane is almost perpendicular to these basal planes (84.1° (av.)). The above-mentioned results are similar to those obtained for complex ion **1**.

The $Co\text{–}N_{imino}$ distances in complex ion **2** are 1.935 Å (av.) and slightly shorter than the $Co\text{–}N_{nitrilo}$ bonds in complex ion **1** (1.978 Å (av.)). The trans positions of $O_{\mu\text{-carbonato}}$ are occupied by $N3_{imino}$ and $N6_{imino}$ in complex ion **2**, while those are occupied by $O8_{\mu\text{-carboxy}}$ and $O12_{\mu\text{-carboxy}}$ in complex ion **1**. The nonbonding distances of the complex are as follows: $O3_{\mu\text{-carbonato}}\text{–}O4_{\mu\text{-carbonato}}$ (2.26 Å) < Co1–Co2 (2.82 Å) < $N3_{imino}\text{–}N6_{imino}$ (3.78 Å). The $N1_{imino}\text{–}N6_{imino}$ distance in complex ion **2** is much longer than the $O8_{carboxy}\text{–}O12_{carboxy}$ distance (3.38 Å) in complex ion **1**, while the other two nonbonding distances of complex ion **2** ($O3_{\mu\text{-carbonato}}\text{–}O4_{\mu\text{-carbonato}}$ and Co1–Co2) are comparable to those in complex ion **1**. The $N3_{imino}\text{–}N6_{imino}$ distance is also longer than $N_{imino}\text{–}N_{imino}$ the nonbonding distance (3.58 Å) observed in $[Co_3(dpa)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ in which large NH–HN repulsive interaction has been found.[12] These results shows that the NH–HN repulsive interaction is still serious in complex ion **2**.

In the ^{13}C spectrum of complex ion **1**, six signals are observed. These results suggest that the two coordinated mida are equivalent in complex ion **1** and the two CH_2COO^- moieties in a coordinated mida are non-equivalent in D_2O solution. In complex ion **2**, there are twelve CH_2 carbons in the facially two coordinated tacn's which appear as 4 peaks in the narrow chemical shift range of 49.79–50.12 ppm (49.79, 49.90(overlapped), 50.02(overlapped), and 50.12 ppm). We find ^{13}C NMR signals at ca. 170 ppm in neutral D_2O solutions for both complex ions (**1**: 169.09 and **2**: 168.66 ppm). As it is hard to assign these peaks to those arising from the facially coordinated mida and tacn, it is reasonable to assign them to the $\mu\text{-}CO_3^{2-}$. This assignment is supported by the protonation-shift on $\mu\text{-}CO_3$ in acidic solution: the ^{13}C NMR signal observed at 168.66 ppm in D_2O solution of complex ion **2** shifted to 165.32 ppm upon adding DCl to the D_2O solution.

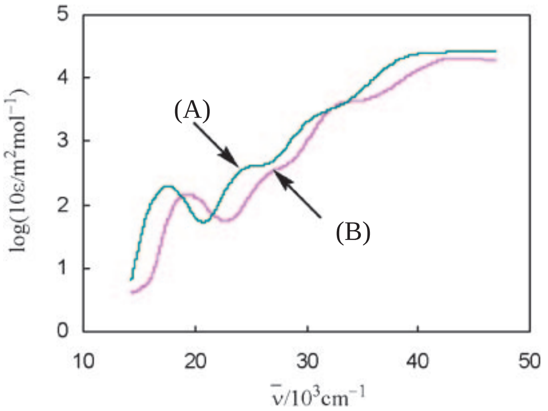

Figure 3. UV–vis absorption spectra of complex ion **1** and complex ion **2** in aqueous solutions. (A): complex ion **1**; and (B): complex ion **2**.

The absorption spectra of complex ion **1** and complex ion **2** in aqueous solution are illustrated in Figure 3. In complex ion **1**, the first absorption band (d–d transition band) appears in the region of $[Co(N)(O)_5]$ chromophores (at 17620 cm^{-1}) as a clear peak. On the other hand, the second absorption band appears as a shoulder (ca. 25000 cm^{-1}) beside a strong charge-transfer band arising from the $Co(\mu\text{-}OH)_2Co$ moiety (ca. 31000 cm^{-1}). The first absorption band of complex ion **2** appears at 19400 cm^{-1} corresponding to that of the $[Co(N)_3(O)_3]$ chromophore. Though the absorption spectrum of complex ion **2** is shifted to higher energy than that of complex ion **1**, the spectral pattern of complex ion **2** resembles that of complex ion **1**. The aqueous solutions of complexes ion **1** and complex ion **2** showed reversible absorption changes with pH: when the spectrum was measured at pH 3, the ε values decreased around at 250 nm compared with those at pH 6, and increased at around 220 nm (isosbestic points of complex ion **1**: 211.5, 242.5, and 313.5 nm; those of complex ion **2**: 206.5, 234.0, and 290.0 nm) (see Supporting Information). These seem to result from protonations of $\mu\text{-}CO_3$ as mentioned for the ^{13}C NMR spectra of the complexes.

In summary, we prepared two complexes containing $Co_2(\mu\text{-}CO_3)(\mu\text{-}OH)_2$ moiety and clarified the structural characteristics: in each complex, the dihedral angle between basal plane 1 and 2 was ca. 160° and the plane formed by the $\mu\text{-}CO_3^{2-}$ was almost perpendicular to both basal planes. The ^{13}C NMR signal of $\mu\text{-}CO_3^{2-}$ appears at ca. 170 ppm.

Experimental

Preparation of [Complex Ion 1]. To a suspension of 10 g of $KHCO_3$ in 10 cm^3 of water, a solution of 4.76 g of $CoCl_2 \cdot 6H_2O$ and 10 cm^3 of 30% H_2O_2 in 10 cm^3 of water was added dropwise with stirring at 0 °C ($K_3[Co(CO_3)_3]$ solution). After the $K_3[Co(CO_3)_3]$ solution was stirred for 15 min, 10 cm^3 of H_2O containing 5.17 g of H_2mida was added and then stirred for 1 h at room temperature. The solution was acidified to pH 1.0 with 30% $HClO_4$, stirred for 1 h, basified to pH 8.0 with 2 mol dm^{-3} KOH aqueous solution and then stirred for 1 h. Filtering off the insoluble white-brown precipitate, the filtrate was charged onto a QAE-Sephadex A-25 column (Cl^- form, ϕ4.7 cm × 90 cm). The column was swept with H_2O and the adsorbed band was developed with 0.2 mol dm^{-3} KCl solution. The eluate from the third blue-purple band was collected and concentrated to a small volume under reduced pressure, and then methanol was added to deposit KCl. The deposited KCl was removed by filtration. The potassium salt of complex ion **1** was obtained by standing the filtrate in a refrigerator. Yield: 76 mg. Anal. Found: C, 20.55; H, 3.70; N, 4.44%. Calcd for $C_{11}H_{24}N_2O_{17}K_2Co_2$: C, 20.25; H, 3.71; N, 4.30%. This potassium salt was converted to the sodium salt in the following manner to obtain a suitable single crystal for X-ray analysis. The aqueous solution of the potassium salt of complex ion **1** was poured onto an SP-Sephadex column (Na^+ form, 2 cm × 5 cm). The eluted solution with water was concentrated to a small volume and then methanol was added to deposit the sodium salt of complex ion **1**. The deposit was dissolved in an ethanol–water mixture (1:4). The single crystal used in the X-ray analysis was obtained by adding acetone to the ethanol–water solution.

Preparation of Complex Ion 2. To a $K_3[Co(CO_3)_3]$ solution prepared from 2.38 g of $CoCl_2 \cdot 6H_2O$, 10 cm^3 of H_2O containing 1.29 g of tacn was added and then stirred for 1 h at room temperature. After the solution was acidified to pH 1.0 with 30% $HClO_4$, it was basified to pH 8.0 with 2 mol dm^{-3} KOH aqueous solution and stirred for 1 h. Filtering off the insoluble materials, the filtrate was charged onto an SP-Sephadex C-25 column (K^+ form, ϕ4.7 cm × 90 cm). The column was swept with H_2O and the adsorbed band was developed with 0.2 mol dm^{-3} KCl solution. The eluate from the red band was collected and concentrated to a small volume under reduced pressure, and then methanol was added to deposit KCl. The deposited KCl was removed by filtration. The chloride of complex ion **2** (fine needles) was obtained by standing the filtrate in a refrigerator. Yield: 249 mg. Anal. Found: C, 24.77; H, 6.71; N, 13.39%. Calcd for $C_{13}H_{42}N_6O_{10}Cl_2Co_2$: C, 24.73; H, 6.71; N, 13.32%. The needle crystals dissolved in ethanol–water mixture (1:4). The single crystal used in the X-ray analysis was obtained by adding acetone to the ethanol–water (1:4) solution.

Measurements. UV–vis spectra of the complexes were measured in aqueous solution on a JASCO 670 Spectrometer and ^{13}C NMR spectra in D_2O solution were recorded on a JEOL LA-400 spectrometer using 1,4-dioxane (67.4 ppm) as an internal reference.

X-ray Crystallography. Each single crystal of Na_2[complex ion **1**]$\cdot 11H_2O$ and [complex ion **2**]$Cl_2 \cdot 7H_2O$ was mounted on a glass needle. All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated Mo Kα radiation. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The CH and NH hydrogen atoms were included but not refined.

Crystal data for Na_2[complex ion **1**]$\cdot 11H_2O$: $C_{11}H_{38}N_2O_{24}Na_2Co_2$, fw 746.27, orthorhombic, space group *Pbca* (#61), $a = 21.12(4)$ Å, $b = 19.533(5)$ Å, $c = 13.802(3)$ Å, $V = 5693(12)$ Å^3, $Z = 8$, $D_{calcd} = 1.74$ g cm^{-3}, crystal dimensions 0.4 × 0.4 × 0.15 mm^3. Total reflections (Mo Kα) radiation, (ω scan technique, $2\theta_{max} = 55.0°$): unique diffraction with $I > 0\sigma$: 6521. Final R and R_w values based on F^2 were 0.077 and 0.144, respectively.

Crystal data for [complex ion **2**]$Cl_2 \cdot 7H_2O$: $C_{13}H_{45}N_6O_{12}Co_2Cl_2$, fw 666.30, monoclinic, space group $C2/c$ (#15), $a = 28.410(6)$ Å, $b = 8.585(2)$ Å, $c = 22.907(4)$ Å, $\beta = 100.113(15)°$, $V = 5500.4(20)$ Å^3, $Z = 8$, $D_{calcd} = 1.61$ g cm^{-3}, crystal dimensions 0.5 × 0.3 × 0.2 mm^3. Total reflections (Mo Kα) radiation, (ω scan technique, $2\theta_{max} = 55.0°$): unique diffraction with $I > 0\sigma$: 6298. Final R and R_w values based on F^2 were 0.064 and 0.135, respectively.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-687261 and -687262 for Na_2[complex ion **1**]$\cdot 11H_2O$ and [complex ion **2**]$Cl_2 \cdot 7H_2O$ respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retriving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information

Bond angles of Na_2[complex ion **1**]$\cdot 11H_2O$ (Table S1) and [complex ion **2**]$Cl_2 \cdot 7H_2O$ (Table S2), and absorption spectral changes of complex ion **1** (Figure S1A) and complex ion **2** (Figure S1B) with pH change. These materials are available free of charge on the web at http://www.csj.jp/jounals/bcsj/.

References

1 P. C. Junk, J. W. Steed, *Polyhedron* **1999**, *18*, 3593.

2 G. G. Sadler, T. P. Dasgupta, *Inorg. Chem.* **1987**, *26*, 3254.

3 U. P. Singh, P. Babbar, K. Sharma, *Inorg. Chim. Acta* **2005**, *358*, 271.

4 W. T. Lowther, D. A. McMillen, A. M. Orville, B. W. Matthews, *Proc. Natl. Acad. Sci. U.S.A.* **1998**, *95*, 12153.

5 V. B. Romakh, B. Therrien, G. Labat, H. Stoekli-Evans, G. B. Shul'pin, G. Süss-Fink, *Inorg. Chim. Acta* **2006**, *359*, 3297.

6 P. Chaudhuri, J. Querbach, K. Wieghardt, B. Nuber, J. Weiss, *J. Chem. Soc., Dalton Trans.* **1990**, 271.

7 K. Dimitrou, K. Folting, W. E. Streib, G. Christou, *J. Am. Chem. Soc.* **1993**, *115*, 6432.

8 N. Kitajima, S. Hikichi, M. Tanaka, Y. Moro-oka, *J. Am. Chem. Soc.* **1993**, *115*, 5496.

9 C. E. Sumner, Jr., *Inorg. Chem.* **1988**, *27*, 1320.

10 I. Murase, G. Vučkovič, M. Kodera, H. Harada, N. Matsumoto, S. Kida, *Inorg. Chem.* **1991**, *30*, 728.

11 P. C. Junk, J. W. Steed, *Polyhedron* **1999**, *18*, 3593.

12 T. Ama, Md. M. Rashid, T. Yonemura, H. Kawaguchi, T. Yasui, *Coord. Chem. Rev.* **2000**, *198*, 101.

13 T. Ama, Md. M. Rashid, A. K. Sarker, H. Miyakawa, T. Yonemura, H. Kawaguchi, T. Yasui, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2327.

14 T. Ama, T. Yonemura, M. Yamaguchi, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1063.

15 T. Ama, K. Okamoto, T. Yonemura, H. Kawaguchi, Y. Ogasawara, T. Yasui, *Chem. Lett.* **1997**, 29.