Synthesis and Crystal Structure of (μ -Acetato)bis(μ -Alkoxo)dicobalt(II, III) Complex with an Unsymmetric Dinucleating Ligand

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The structure of the dinuclear Co(II, III) mixed-valence complex $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{tpdb})(\text{CH}_3\text{CO}_2)(\text{CH}_3\text{O})](\text{ClO}_4)_2 \cdot 0.75\text{CH}_3\text{OH} \cdot 0.25\text{CH}_3\text{CN}$ (**1**) was determined by X-ray crystallography, where tpdb is *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,4-diamino-2-butanolate. The compound crystallizes in the monoclinic space group, $P2_1/c$, with $a = 10.4372(4)$, $b = 27.8578(10)$, $c = 13.5496(5)$ Å, $\beta = 102.8116(10)$, $Z = 4$, $V = 3841.6(2)$ Å³. The $R1$ [$I > 2\sigma(I)$] and $wR2$ (all data) values are 0.0398 and 0.1035, respectively, for all 6799 independent reflections. The complex has a (μ -acetato)bis(μ -alkoxo)-dicobalt(II, III) core structure.

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The bimetallic active centers of metalloproteins exhibit versatile roles; model studies using simple dinuclear metal complexes are important in order to gain insight into the biological functions of such bimetallic cores.¹⁻⁵ The end-off type dinucleating ligands, having a phenolic and alcoholic oxygen as an endogenous bridge, have been used for modeling carboxylate-bridged bimetallic active sites of metalloproteins.¹⁻⁵ Previously, we reported on the synthesis and characterization of a peroxo complex, $[\text{Co}^{\text{III}}_2(\text{tpdb})(\text{O}_2)(\text{CH}_3\text{CO}_2)]^{2+}$,⁶ and a mixed-valence complex, $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{tpdb})(\text{C}_6\text{H}_5\text{CO}_2)]^{2+}$,⁷ having an unsymmetric dinucleating ligand with pyridyl groups (tpdb) as models for hemerythrin and purple acid phosphatase. In this paper, we report on the crystal structure of a dicobalt(II, III) mixed-valence complex, $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{tpdb})(\text{CH}_3\text{CO}_2)(\text{CH}_3\text{O})](\text{ClO}_4)_2 \cdot 0.75\text{CH}_3\text{OH} \cdot 0.25\text{CH}_3\text{CN}$ (**1**) (Fig. 1), which was obtained by an oxidative degradation of $[\text{Co}^{\text{II}}_2(\text{tpdb})(\text{CH}_3\text{CO}_2)]^{2+}$ in methanol/acetonitrile at ambient temperature under air.

A mixture of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.366 g, 1.0 mmol) and Htpdb (0.235 g, 0.5 mmol) in methanol/acetonitrile (3:1, 12 mL) was added to a methanol solution (5 mL) containing $\text{CH}_3\text{CO}_2\text{Na} \cdot 3\text{H}_2\text{O}$

(0.07 g, 0.5 mmol) and triethylamine (69 μL , 0.5 mmol) to give a dark-brown solution. Oxygen gas was bubbled for 5 min into the solution. The resulting dark-brown solution was allowed to stand for several weeks at ambient temperature under air to give single crystals of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{tpdb})(\text{CH}_3\text{CO}_2)(\text{CH}_3\text{O})](\text{ClO}_4)_2 \cdot 0.75\text{CH}_3\text{OH} \cdot 0.25\text{CH}_3\text{CN}$ (**1**) suitable for X-ray crystallography. Yield: 0.28 g, 63 % (Anal. Found: C, 41.20; H, 4.37; N, 9.28%. Calcd for $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{tpdb})(\text{CH}_3\text{CO}_2)(\text{CH}_3\text{O})](\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O} \cdot \text{C}_{31}\text{H}_{40}\text{Cl}_2\text{Co}_2\text{N}_6\text{O}_{13.5}$: C, 41.30; H, 4.47; N, 9.32%). It was picked up from the solution by a loop on a hand-made cold copper plate mounted inside a liquid N_2 Dewar vessel at -80°C ; the loop was mounted on the diffractometer. X-ray diffraction measurements were made on a Bruker D8 VENTURE diffractometer (Cu $K\alpha$ radiation) at 90 K. The structure was solved by a direct method (SHELXT)⁸ and expanded using a Fourier technique. The structure was refined by a full-matrix least-squares method by using SHELXL 2014⁹ (Yadokari-XG).¹⁰ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included using a riding model. For the disordered anion and solvent molecules, occupancy factors were refined using distance/ADP restraints. The crystal data are summarized in Table 1.

The X-ray crystallography of **1** reveals that the asymmetric unit contains a complex cation $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{tpdb})(\text{CH}_3\text{CO}_2)(\text{CH}_3\text{O})]^{2+}$, two ClO_4^- , and 0.75 methanol and 0.25 acetonitrile molecule (Fig. S1). An ORTEP drawing of the complex cation, $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{tpdb})(\text{CH}_3\text{CO}_2)(\text{CH}_3\text{O})]^{2+}$ of **1**, is shown in Fig. 2. Selected bond distances (Å) and angle ($^\circ$) are given in Table 2. The complex cation of **1** has distinct cobalt centers that are triply bridged by alkoxo oxygens of tpdb and methoxo, and acetate group as found for closely related dicobalt(II, III) mixed-valence complex $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{L})_2(\text{CH}_3\text{CO}_2)(\text{CH}_3\text{O})]^{2+}$ (**2**) ($\text{L} = N$ -methyl-*N,N*-bis(2-pyridylmethyl)amine).¹¹ The Co1–Co2 separation is 2.9918 Å, which is slightly longer than that of **2** (2.956 Å). Both of the cobalt atoms in **1** have a distorted octahedral structure with an N_3O_3 donor set, where three

Fig. 1 Chemical diagram of $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{tpdb})(\text{CH}_3\text{CO}_2)(\text{CH}_3\text{O})](\text{ClO}_4)_2 \cdot 0.75\text{CH}_3\text{OH} \cdot 0.25\text{CH}_3\text{CN}$ (**1**).

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Table 1 Crystal and experimental data

Chemical formula: $C_{32.25}H_{40.75}Cl_2Co_2N_{6.25}O_{12.75}$	
Formula weight = 908.72	
$T = 90\text{ K}$	
Crystal system: monoclinic	Space group: $P2_1/c$
$a = 10.4372(4)\text{ \AA}$	$b = 27.8578(10)\text{ \AA}$
$c = 13.5496(5)\text{ \AA}$	$\beta = 102.8116(10)^\circ$
$V = 3841.6(2)\text{ \AA}^3$	$Z = 4$
$D_x = 1.571\text{ g/cm}^3$	
Radiation: Cu $K\alpha$ ($\lambda = 1.54178\text{ \AA}$)	
$\mu(\text{Cu } K\alpha) = 8.659\text{ mm}^{-1}$	
$F(0\ 0\ 0) = 1872$	
Crystal size = $0.25 \times 0.16 \times 0.11\text{ mm}^3$	
No. of reflections collected = 71351	
No. of independent reflections = 6799	
θ range for data collection = 3.173 to 66.902°	
Data/Restraints/Parameters = 6799/185/595	
Goodness-of-fit on $F^2 = 1.039$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0398$, $wR2 = 0.1030$	
R indices (all data): $R1 = 0.0406$, $wR2 = 0.1035$	
$(\Delta/\sigma)_{\max} = 0.001$	
$(\Delta\rho)_{\max} = 0.484\text{ e \AA}^{-3}$ $(\Delta\rho)_{\min} = -0.449\text{ e \AA}^{-3}$	
Measurement: Bruker D8 VENTURE diffractometer	
Program system: Yadokari-XG	
Structure solving program: SHELXT	
Structure determination: SHELXL 2014	
Refinement: full-matrix least squares against F^2	
CCDC deposition number: CCDC 2039071

Fig. 2 ORTEP drawing of the complex cation, $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{tpdb})-(\text{CH}_3\text{CO}_2)(\text{CH}_3\text{O})]^{2+}$ of **1**, showing 50% probability ellipsoids. The hydrogen atoms are omitted for clarity.

nitrogen atoms of tpdb are in a facial array. The oxidation states of the cobalt centers are clearly distinguished by comparing the Co–O and Co–N bond distances. The average Co1–O (2.08 Å) and Co1–N (2.12 Å) bond distances are comparable to the Co^{II}–O (2.07 Å) and Co^{II}–N (2.15 Å) bonds of the six-coordinate high-spin cobalt(II) center in **2**.¹¹ The average Co2–O (1.91 Å) and Co2–N (1.96 Å) bond distances are comparable to the Co^{III}–O (1.90 Å) and Co^{III}–N (1.96 Å) bonds of the six-coordinate low-spin cobalt(III) centers in **2** and $[\text{Co}^{\text{III}}_2(\text{tpdb})(\text{O}_2)-(\text{CH}_3\text{CO}_2)]^{2+}$.⁶ The average Co2–O (1.91 Å) and Co2–N (1.96 Å) bond distances are substantially shorter than the average Co1–O (2.08 Å) and Co1–N (2.12 Å) bond distances, indicating that the oxidation state of the Co1 is divalent and the Co2 is trivalent.

Table 2 Selected bond distances (Å) and angle (°)

Co1–O1	2.0182(18)	Co2–O1	1.9102(17)
Co1–O2	2.0636(19)	Co2–O3	1.9202(18)
Co1–O4	2.165 (2)	Co2–O4	1.906 (2)
Co1–N1	2.203 (2)	Co2–N4	1.968 (2)
Co1–N2	2.073 (3)	Co2–N5	1.960 (2)
Co1–N3	2.079 (2)	Co2–N6	1.950 (2)
Co1–Co2	2.9918(5)		
Co1–O1–Co2	99.17 (8)	Co1–O4–Co2	94.39 (8)

Thus, **1** can be described as a localized mixed-valence complex as similar to **2**.¹¹ The Co–O and Co–N bond length differences for the high-spin Co1 vs the low-spin Co2 center in **1** are 0.17 and 0.16 Å, respectively, which are similar to those observed for the dicobalt(II, III) mixed-valence complexes.^{11,12} The preferential occupation of Co^{II} and Co^{III} in two distinct coordination sites of tpdb can be interpreted in terms of the chelate ring size effect of the bridging skeleton. It is well known that the electron donor ability of the five-membered chelate ring is stronger than that of the six-coordinate chelate ring. Thus, the five-membered chelate ring site of tpdb prefers Co^{III} ion. A similar observation was made for a mixed-valence complex, $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{tpdb})(\text{C}_6\text{H}_5\text{CO}_2)_2]^{2+}$,⁷ where the Fe^{III} ion resides in the five-membered chelate ring site of tpdb.

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Supporting Information

A cif format file and Fig. S1. This material is available free of charge on the Web at <http://www.jsac.or.jp/xraystruct/>.

References

1. D. E. Fenton and H. Okawa, *Chem. Ber.*, **1997**, *130*, 433.
2. M. Suzuki, H. Furutachi, and H. Okawa, *Coord. Chem. Rev.*, **2000**, *200*, 105.
3. A. L. Gavrilova and B. Bosnich, *Chem. Rev.*, **2004**, *104*, 349.
4. E. Y. Tshuva and S. J. Lippard, *Chem. Rev.*, **2004**, *104*, 987.
5. A. J. Jasiewicz and L. Que Jr., *Chem. Rev.*, **2018**, *118*, 2554.
6. T. Kayatani, Y. Hayashi, M. Suzuki, and A. Uehara, *Bull. Chem. Soc. Jpn.*, **1994**, *67*, 2980.
7. M. Suzuki, S. Fujinami, T. Hibino, H. Hori, Y. Maeda, A. Uehara, and M. Suzuki, *Inorg. Chim. Acta*, **1998**, *283*, 124.
8. G. M. Sheldrick, *Acta Crystallogr.*, **2015**, *A71*, 3.
9. G. M. Sheldrick, *Acta Crystallogr.*, **2015**, *C71*, 3.
10. C. Kabuto, S. Akine, T. Nemoto, and E. Kwon, *J. Cryst. Soc. Jpn.*, **2009**, *51*, 218.
11. J. Luo, N. P. Rath, and L. M. Mirica, *Inorg. Chem.*, **2011**, *50*, 6152.
12. P. Chaudhuri, J. Querbach, K. Wiegardt, B. Nuber, and J. Weiss, *J. Chem. Soc. Dalton Trans.*, **1990**, 271.