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X-Ray Crystal Structure and Electrochemical Property of a Novel Monohydroxo-Bridged Binuclear Cobalt(II) Complex with *N,N′,N″,N‴*-Tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane

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Synopsis. The crystal structure of a binuclear cobalt(II) complex of *N,N′,N″,N‴*-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec), $[Co_2(taec)(OH)](ClO_4)_3$, was determined by the single-crystal X-ray diffraction method. The two cobalt ions are bridged by a single hydroxide ion in the cavity of taec. The cyclic voltammogram showed an irreversible profile with two anodic peaks at ca. 1.4 and 1.8 V vs. SCE.

In the previous paper, we reported the preparation of the μ-hydroxo-bridged cobalt(II) complexes with an octadentate ligand, *N,N′,N″,N‴*-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (abbreviated as taec), $[Co_2(taec)(OH)]X_3$ ($X=ClO_4$ and PF_6).[1] The taec ligand exclusively forms binuclear complexes where each metal ion is coordinated by two cyclam-ring nitrogens and two pendant amino nitrogens.[1–6] On the basis of infrared and electronic spectra and magnetic susceptibility data, we assumed that the two cobalt ions are bridged by only one hydroxide ion in the "cavity" of taec. Monohydroxo-bridged complexes are rare, although recently some examples have been reported for copper(II) complexes.[7] Interestingly these cobalt(II) complexes are inert toward aerobic or chemical oxidation. Attempts to obtain cobalt(III) species of taec were all unsuccessful. We assumed that the resistance to oxidation is due to the sterical difficulty in achieving six-coordination.[1] In this study, we have examined the electrochemical property and the X-ray crystal structure of $[Co_2(taec)(OH)](ClO_4)_3$ in order to confirm our assumption.

Experimental

The crystals were prepared as described in Ref. 1.

X-Ray Structure Determination. A Rigaku AFC-5

Table 1. Crystal Data and Data Collection Details

Complex	$[Co_2(taec)(OH)](ClO_4)_3$
Formula	$C_{18}H_{45}Cl_3Co_2N_8O_{13}$
Fw	805.82
Crystal system	Monoclinic
Space group	$P2_1/a$
a/Å	20.481(3)
b/Å	16.394(2)
c/Å	9.275(1)
β/°	91.23(1)
V/Å^3	3113.6(7)
Z	4
D_c/g cm^3	1.719
D_m/g cm^3	1.68
$F(000)$	1672
Radiation	Graphite-mnochromated Mo $K\alpha$ ($\lambda=0.71073$ Å)
Crystal size/mm	0.15×0.27×0.48
μ(Mo $K\alpha$)/cm^{-1}	13.9
Scan type	θ–2θ
Scan speed/° min^{-1}	3
Scan width/°	$1.1+0.5\tan\theta$
2θ range/°	1.5—55.0
Total number of observed reflections	7472
Number of unique reflections with $\lvert F_o\rvert>3\sigma(\lvert F_o\rvert)$	3123
Final number of variables	398
Final residuals	
R	0.046
R_w	0.052
Weighting scheme	$w=[\sigma_{\mathrm{count}}^2+(0.015\lvert F_o\rvert)^2]^{-1}$
Largest peak on final difference map	0.77 e Å^{-3} (near Cl(1))

Table 2. Atomic Coordinates (×10^4) and Thermal Parameters

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
Co(1)	2765(1)	868(1)	7559(1)	2.2	N(5)	2891(3)	140(3)	5685(6)	3.6
Co(2)	1009(1)	1464(1)	7492(1)	2.3	N(6)	3060(3)	−60(3)	9017(6)	3.7
Cl(1)	1471(1)	−1239(1)	7525(2)	3.7	N(7)	448(3)	838(3)	9098(5)	3.5
Cl(2)	−1458(1)	152(1)	7415(2)	3.6	N(8)	446(3)	943(3)	5819(6)	3.8
Cl(3)	4718(1)	−559(1)	7489(2)	3.8	C(1)	3806(3)	2081(4)	7393(7)	3.1
O(1)	1819(2)	871(2)	7821(5)	3.5	C(2)	3488(3)	2336(4)	8783(7)	3.2
O(2)	1173(3)	−2022(3)	7537(5)	5.0	C(3)	2569(3)	1963(4)	10311(6)	2.9
O(3)	1510(5)	−904(5)	8896(7)	12.7	C(4)	2089(3)	2517(4)	9511(7)	2.7
O(4)	2103(3)	−1271(4)	7061(9)	11.1	C(5)	1411(3)	2492(4)	10097(7)	3.2
O(5)	1122(5)	−722(4)	6703(12)	17.1	C(6)	869(3)	3240(4)	8101(7)	3.4
O(6)	−1997(3)	704(3)	7413(7)	7.1	C(7)	665(3)	3099(4)	6588(7)	3.3
O(7)	−1532(3)	−329(4)	6157(6)	8.5	C(8)	1723(3)	2834(4)	5502(7)	3.6
O(8)	−1504(3)	−357(4)	8645(6)	7.7	C(9)	2232(3)	2179(4)	5165(7)	3.0
O(9)	−870(3)	571(5)	7427(7)	9.9	C(10)	2916(3)	2420(4)	5753(8)	4.0
O(10)	4841(6)	225(5)	7494(11)	18.3	C(11)	3641(3)	1256(5)	5196(7)	3.7
O(11)	5197(4)	−1095(7)	7189(10)	16.1	C(12)	3196(3)	628(4)	4533(7)	3.7
O(12)	4176(3)	−717(4)	6615(9)	10.8	C(13)	3533(3)	1103(4)	10263(7)	3.6
O(13)	4550(5)	−736(6)	8890(8)	13.4	C(14)	3229(3)	278(4)	10458(7)	3.8
N(1)	3312(2)	1737(3)	6358(5)	2.8	C(15)	245(3)	2291(4)	9579(7)	3.8
N(2)	3100(2)	1654(3)	9386(5)	2.5	C(16)	203(3)	1428(5)	10175(7)	4.0
N(3)	892(2)	2460(3)	8937(5)	2.5	C(17)	764(3)	2162(4)	4501(7)	4.1
N(4)	1081(2)	2477(3)	5862(5)	2.7	C(18)	214(3)	1569(5)	4773(8)	4.3

automated four-circle diffractometer was used for all measurements at 25±1 °C. Crystal data and details of the data collections are given in Table 1. Lattice constants were determined by least-squares refinement based on 50 reflections with $20° < 2\theta < 30°$. The intensity data were corrected for Lorentz-polarization effects and for absorption. The structure was solved by the direct method. Refinements were carried out by the block-diagonal least-squares method. Hydrogen atoms were inserted in their calculated positions and fixed at their positions. The final discrepancy factors, $R=\sum||F_o|-|F_c||/\sum|F_o|$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$ are listed in Table 1. The thermal parameters of the ClO_4^- ions are high probably due to the partial disorder. The hydrogen atom of the bridging hydroxide ion could not be located on a final difference Fourier map.

The atomic scattering factors for all the atoms and the anomalous dispersion corrections for all the nonhydrogen atoms were taken from Ref. 8. All the calculations were carried out on the HITAC M-680H computer at the Computer Center of the Institute for Molecular Science using a local version of the MULTAN 78,[9] UNICS-III,[10] and ORTEP[11] programs. Atomic coordinates and thermal parameters of nonhydrogen atoms are listed in Table 2. The anisotropic thermal parameters of nonhydrogen atoms, the atomic coordinates and thermal parameters of hydrogen atoms, and the F_o-F_c tables have been deposited at the Office of the Chemical Society of Japan as a Document No. 8812.

Physical Measurement. Cyclic voltammetric measurement was carried out by using a Hokuto Denko HA-501 potentiostat with a Hokuto Denko HF-201 function generator and a Yokogawa 3086-11 X-Y recorder. A three-electrode cell consisting of a glassy carbon electrode, a platinum-flug counter electrode, and a saturated caromel references electrode (SCE) was used.

Results and Discussion

The crystal consists of binuclear cations $[Co_2(taec)(OH)]^{3+}$ and perchlorate ions. A perspective view of $[Co_2(taec)(OH)]^{3+}$ is shown in Fig. 2. The coordination mode of taec is the same as that of $[Cu_2(taec)Y](ClO_4)_3$ (Y=F, Br, I, N_3, NCO, NO_2).[1,5,6] The two cobalt ions are bridged by a single hydroxide ion. The geometry around each cobalt ion can be described as a distorted square pyramid. The basal plane is formed by two nitrogens of the cyclam ring and two pendant amino nitrogens. The deviations of the basal atoms from the mean plane are within ±0.22 Å, and Co(1) and Co(2) are displaced by 0.66 and 0.69Å, respectively, from the mean planes toward the hydroxide ion. The Co(1)–Co(2) distance of 3.727(1) Å is significantly shorter than the Cu–Cu distances of $[Cu_2(taec)Y](ClO_4)_3$ (4.299(2)—4.841(3) Å).[1,5,6] This may be attributed to the fact that the cobalt ions are further apart from the basal planes than are the copper ions of

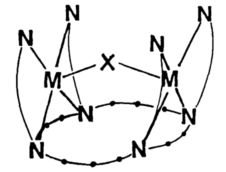

Fig. 1. Coordination mode of taec.

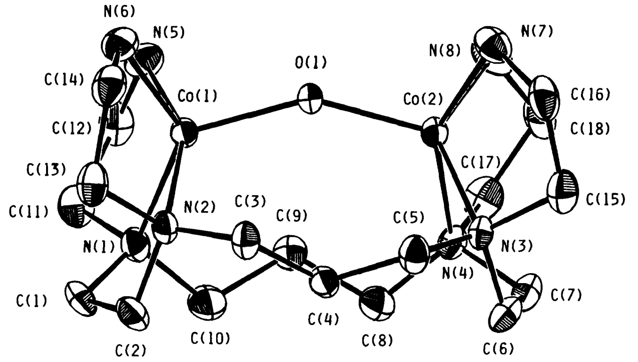

Fig. 2. ORTEP diagram of $[Co_2(taec)(OH)]^{3+}$.

Table 3. Selected Interatomic Distances (l/Å) and Bond Angles (ϕ/°)

Co(1)-Co(2)	3.727(1)	Co(2)-O(1)	1.942(4)
Co(1)-O(1)	1.958(4)	Co(2)-N(3)	2.128(5)
Co(1)-N(1)	2.139(5)	Co(2)-N(4)	2.252(5)
Co(1)-N(2)	2.226(5)	Co(2)-N(7)	2.161(5)
Co(1)-N(5)	2.128(5)	Co(2)-N(8)	2.096(5)
Co(1)-N(6)	2.115(5)		
Co(1)-O(1)-Co(2)	145.7(2)	N(3)-Co(2)-N(4)	82.4(2)
N(1)-Co(1)-N(2)	81.6(2)	N(3)-Co(2)-N(7)	82.1(2)
N(1)-Co(1)-N(5)	82.8(2)	N(4)-Co(2)-N(8)	81.2(2)
N(2)-Co(1)-N(6)	81.4(2)	N(7)-Co(2)-N(8)	91.4(2)
N(5)-Co(1)-N(6)	94.7(2)	O(1)-Co(2)-N(3)	113.1(2)
O(1)-Co(1)-N(1)	126.4(2)	O(1)-Co(2)-N(4)	114.0(2)
O(1)-Co(1)-N(2)	101.2(2)	O(1)-Co(2)-N(7)	96.8(2)
O(1)-Co(1)-N(5)	103.9(2)	O(1)-Co(2)-N(8)	111.5(2)
O(1)-Co(1)-N(6)	101.1(2)		

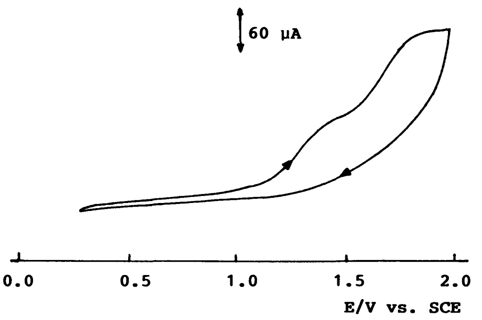

Fig. 3. Cyclic voltammogram of $[Co_2(taec)(OH)](ClO_4)_3$ (1/2 mM) (1 M=1 mol dm^{-3}) in acetonitrile containing 0.1 M $(C_2H_5)_4NBF_4$. The scan rate is 100 mV s^{-1}.

$[Cu_2(taec)Y](ClO_4)_3$ (0.37—0.48 Å).[1,5,6] In this structure, the sixth coordination site of the cobalt ion is blocked by the methylene groups of taec. Thus, the result also consists with our previous assumption that the strong resistivity to the oxidation from Co(II) to Co(III) in these complexes arises mainly from prohibition against six-coodination which stabilizes Co(III) oxidation state characteristically.[1]

Cyclic voltammetric measurements were carried out with a glassy carbon electrode in acetonitrile solution. The cyclic voltammogram showed an irreversible profile with two anodic peaks at ca. 1.4 and 1.8 V vs. SCE (Fig. 3). The remarkable high oxidation potentials agree with the fact that the chemical oxidation of the cobalt(II) of this complex is very difficult. The complex was oxidized electrolytically at ca. 1.4 V vs. SCE in acetonitrile solution. The solution turned from purple to reddish orange yielding an amorphous precipitate at the anode. Attempts to obtain a cobalt(III) complex were unsuccessful. The degradation of ligand seemed to take place with the oxidation.

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