Crystal Structure of a Hydrolyzed Product of the Cobalt(III) Complex with 1-(3,5-Dichlorosalicylideneamino)-3-amino-2-propanol

Masahiro MIKURIYA,^{*,†} Nagisa TSUCHIMOTO,^{*} Yoshiki KOYAMA,^{*} Ryoji MITSUHASHI,^{**} and Motohiro TSUBOI^{*}

^{*}Department of Applied Chemistry for Environment and Research Center for Coordination Molecule-based Devices, School of Biological and Environmental Sciences, Kwansei Gakuin University, 2-1 Gakuen, Sanda 669-1337, Japan

^{**}Institute of Liberal Arts and Science, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan

The crystal structure of a hydrolyzed product of the cobalt(III) complex with 1-(3,5-dichlorosalicylideneamino)-3-amino-2-propanol (H₂dcsalpr) was determined by the single-crystal X-ray diffraction method at 90 K. It crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.2242(15)$ Å, $b = 9.3391(16)$ Å, $c = 9.5525(16)$ Å, $\alpha = 75.574(3)^\circ$, $\beta = 85.550(3)^\circ$, $\gamma = 69.154(3)^\circ$, $V = 744.7(2)$ Å³, $D_x = 1.634$ g/cm³, and $Z = 1$. The $R1$ [$I > 2\sigma(I)$] and $wR2$ (all data) values are 0.0489 and 0.1093, respectively, for all 3319 independent reflections. The X-ray structure analysis revealed a centrosymmetric octahedral Co(III) complex with two hydrolyzed Schiff-base ligands, Hdcsalpr[−], in a *facial* mode, one chloride ion, two acetonitrile molecules, and two water molecules in the unit cell, which was formed from the reaction solution of cobalt(II) chloride hexahydrate with 1,3-bis(3,5-dichlorosalicylideneamino)-2-propanol in the presence of triethylamine in acetonitrile.

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Much interest has been attracted to the coordination chemistry of potential pentadentate Schiff-base ligands, 1,3-bis(salicylidene-amino)-2-propanol (H₃bsalpr) and its substituted derivatives, with two phenolato-oxygen, two imino-nitrogen, and one alcoholate-oxygen donor atoms, are of interest. In the crystals, these Schiff-base ligands have intramolecular hydrogen bonds between imino-nitrogen and phenolato-oxygen atoms and intermolecular hydrogen bonds between an alcohol-oxygen atom and a phenolato-oxygen atom of neighboring Schiff-base molecule.^{1–5} The reaction between these Schiff-base ligands and metal salts generates mononuclear copper(II),⁶ tetranuclear zinc(II)⁷ complexes with a tetradentate *O, N, N, O*-chelate, and dinuclear copper(II),⁸ nickel(II),⁹ manganese(III),^{10,11} and cobalt(III)¹², and tetranuclear manganese(II,III)^{13,14} complexes with a tridentate *O, N, O*-chelate. Aiming at extending these systems, we decided to prepare a cobalt complex with 1,3-bis(3,5-dichlorosalicylideneamino)-2-propanol (H₃bdcsalpr), which has not been reported so far. In this study, we performed a reaction between H₃bdcsalpr and cobalt(II) chloride hexahydrate in the presence of triethylamine in acetonitrile, and determined the crystal structure of the isolated complex, which has been found to be a new mononuclear cobalt(III) complex with hydrolyzed Schiff-base ligands, 1-(3,5-dichlorosalicylidene-amino)-3-amino-2-propanol (Hdcsalpr[−]), [Co(Hdcsalpr)₂]Cl·2CH₃CN·2H₂O (**1**), as depicted in Fig. 1, is different from the expected dinuclear cobalt complexes that we prepared before.¹²

A Schiff-base ligand, H₃bdcsalpr, was synthesized by a similar method to the previously reported one.⁵ 1,3-Diamino-2-propanol (0.703 g, 7.8 mmol) and 3,5-dichlorosalicylaldehyde (3.00 g, 15.7 mmol) were dissolved in methanol (70 cm³). The

solution was refluxed for 3 h, and then left at room temperature. The resulting yellow precipitate was filtered off, washed with methanol, and dried under a vacuum. Yield, 3.16 g (93%). IR (KBr, cm^{−1}): 3219 ($\nu(\text{OH})$), 3064 ($\nu(\text{CH}(\text{phenyl}))$), 2951 ($\nu_{\text{as}}\text{CH}_2$), 2872 ($\nu_{\text{s}}\text{CH}_2$), 1626($\nu\text{C}=\text{N}$).

Single crystals of **1** were obtained as follows: H₃bdcsalpr (42.5 mg, 0.1 mmol) was dissolved in acetonitrile (3 mL). To this solution, cobalt(II) chloride hexahydrate (24.0 mg, 0.1 mmol) and six drops of triethylamine were added. The resulting brown solution was filtered after standing for several days to remove a small amount of white precipitate, and then the filtrate was left at room temperature for a further several days to give reddish-brown crystals. Yield, 5.7 mg (7.8% based on the metal salt). Reflectance spectra: λ_{max} 284, 422 ($^1A_{1g} \rightarrow ^1T_{2g}$), 550sh ($^1A_{1g} \rightarrow ^1T_{1g}$), 724 ($^1A_{1g} \rightarrow ^3T_{2g}$) nm.

X-ray diffraction data were collected on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo- $K\alpha$ radiation. Crystal data and details concerning the data collection are given in Table 1. The structure was solved by an

Fig. 1 Chemical structure of the title compound.

[†] To whom correspondence should be addressed.
E-mail: junpei@kwansei.ac.jp

Table 1 Crystal and experimental data

Chemical formula: $C_{24}H_{28}Cl_5CoN_6O_6$
Formula weight = 732.70
$T = 90$ K
Crystal system: triclinic
Space group: $P\bar{1}$
$a = 9.2242(15)$ Å $\alpha = 75.574(3)^\circ$
$b = 9.3391(16)$ Å $\beta = 85.550(3)^\circ$
$c = 9.5525(16)$ Å $\gamma = 69.154(3)^\circ$
$V = 744.7(2)$ Å ³
$Z = 1$
$D_x = 1.634$ g/cm ³
Radiation: Mo $K\alpha$ ($\lambda = 0.71073$ Å)
$\mu(\text{Mo } K\alpha) = 1.075$ mm ⁻¹
$F(0\ 0\ 0) = 374$
Crystal size = $0.32 \times 0.12 \times 0.10$ mm ³
No. of reflections collected = 4689
No. of independent reflections = 3319
θ range for data collection: 2.363 to 27.484°
Data/Restraints/Parameters = 3319/0/203
Goodness-of-fit on $F^2 = 0.953$
R indices [$I > 2\sigma(I)$]: $R1 = 0.0489$, $wR2 = 0.1023$
R indices (all data): $R1 = 0.0786$, $wR2 = 0.1093$
$(\Delta/\sigma)_{\text{max}} = 0.000$
$(\Delta\rho)_{\text{max}} = 0.665$ e Å ⁻³
$(\Delta\rho)_{\text{min}} = -0.452$ e Å ⁻³
Measurement: Bruker Smart APEX CCD diffractometer
Program system: SHELXTL
Structure determination: intrinsic phasing (SHELXT-2014/5)
Refinement: full matrix least-squares (SHELXL-2018/3)
CCDC deposition number: 2104534

intrinsic phasing method with SHELXT-2014, and refined by full-matrix least-squares methods with SHELXL-2018. The hydrogen atoms attached to the amino-nitrogen atom (N2) were located from the D-Fourier map, whereas the hydrogen atoms of the water-oxygen atom (O3) could not be found by the D-Fourier map; the other hydrogen atoms were inserted at their calculated positions, and fixed there. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre (Deposit number CCDC-2104534). Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.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).

The X-ray structure analysis of **1** revealed that the unit cell consists of a centrosymmetric octahedral Co(III) complex cation with two hydrolyzed Schiff-base ligands, 1-(3,5-dichlorosalicylideneamino)-3-amino-2-propanol (Hdcsalapr), centered at the Co1 atom, $[\text{Co}(\text{Hdcsalapr})_2]^+$, one chloride ion (Cl3), two acetonitrile molecules, and two water molecules. The Co1 and Cl3 atoms are located at the crystallographic inversion centers. An ORTEP drawing of the $[\text{Co}(\text{Hdcsalapr})_2]^+$ complex cation is shown in Fig. 2. Selected bond distances and angles are given in Table 2. The Co1 atom is coordinated by two sets of the phenolate O1, imino N1, and amino N2 atoms of the Hdcsalapr ligand in a facial mode to achieve an octahedral geometry. The Co1-O1, Co1-N1, and Co1-N2 distances are 1.903(2), 1.924(3), 1.962(3) Å, respectively, being normal as Co(III)-O and N bond distances.¹⁵ The Hdcsalapr ligand forms two adjacent six-membered chelate rings with the Co1 atom, where the Co1-O1-C1-C6-C7-N1 ring forms a nearly planar configuration, whereas the Co1-N1-C8-C9-C10-N2 ring takes a chair conformation. In the crystal, the alcohol oxygen atom O2 is hydrogen-bonded to a water molecule (O3), which is further hydrogen-bonded by

Fig. 2 Complex cation, $[\text{Co}(\text{Hdcsalapr})_2]^+$, of the title compound. The thermal ellipsoids are shown at the 50% probability level.

Table 2 Selected bond distances (Å) and angles ($^\circ$)

Co1-O1	1.903(2)	N1-C7	1.285(4)
Co1-N1	1.924(3)	N1-C8	1.466(4)
Co1-N2	1.962(3)	N2-C10	1.497(4)
O1-Co1-O1 ⁱ	180.0	N1-Co1-N2	87.20(12)
O1-Co1-N1	90.75(10)	N1-Co1-N2 ⁱ	92.80(12)
O1-Co1-N1 ⁱ	89.25(10)	N1-Co1-N1 ⁱ	180.0
O1-Co1-N2	88.23(11)	N2-Co1-N2 ⁱ	180.0
O1-Co1-N2 ⁱ	91.77(11)		

Symmetry code: i (1-x, -y, 1-z).

Fig. 3 Packing diagram of the title compound, showing hydrogen bonds as dashed lines.

intermolecular hydrogen bonds with a chloride ion (Cl3) and an acetonitrile molecule (N3) [O2-H...O3 2.759 Å, O3-H...Cl3 3.211 Å, O3-H...N3 3.116 Å] (Fig. 3).

The diffused reflectance spectra of **1** (Fig. 4) are characteristic of octahedral low-spin cobalt(III), showing d-d bands in the visible region, being in harmony with the octahedral geometry of $[\text{Co}(\text{Hdcsalapr})_2]^+$. The spectra are similar to those of the dinuclear octahedral cobalt(III) complexes with 1,3-bis(3-nitrosalicylideneamino)-2-propanolato and 1,3-bis(5-nitrosalicylideneamino)-2-propanolato ligands.¹² The infrared spectra of H₃bdcslapr (Fig. 5) shows the absence of $\nu_{\text{as}}\text{NH}_2$ and $\nu_{\text{s}}\text{NH}_2$ bands expected to appear at ~ 3560 and ~ 3400 cm⁻¹, respectively,¹⁶ excluding the possibility of hydrolyzation of the Schiff-base ligand before the reaction with the metal ion. Therefore, the formation of a hydrolyzed Schiff-base in the

Fig. 4 Diffused reflectance spectra of the title compound.

Fig. 5 Infrared spectra of H₃bdcSalpr (KBr disk).

present complex may have occurred by a small amount of water molecules originated from metal salt and/or an acetonitrile solvent in the presence of triethylamine. A similar hydrolysis reaction and the degradation of Schiff-base molecules were observed in a few of metal complexes with Schiff-base ligands.^{10,17,18}

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