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Structural Characterization of a Dioxovanadium(V) Complex with 4,8-Dihydroxyquinoline-2-carboxylic Acid

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4,8-Dihydroxyquinoline-2-carboxylic acid (**1**) possessing quinoline-*N*, hydroxy-*O*, and carboxy-*O* donor functions was demonstrated to serve as a tridentate ligand in the complexation with NH_4VO_3, affording the *cis*-dioxovanadium(V) complex **2**. Each molecule of **2** was found to be packed in a hexagonal molecular arrangement through π–π interaction in the crystal packing, creating a channel cavity which was occupied by water molecules that form a one-dimensional water chain.

The biochemical roles of vanadium have gained growing interest from both biological and chemical perspectives.[1] Vanadium haloperoxidases, which are found in marine algae, catalyze the oxidation of halides with hydrogen peroxide to the corresponding hypohalous acids for halogenation of organic compounds.[1a,1d,2] A five-coordinated vanadium(V) moiety in a trigonal bipyramidal geometry[3] or a square pyramidal geometry in the case of the peroxo form,[4] in which the vanadium ion is bound by the protein through a histidine imidazole as well as having oxygen donors has been found as the vanadium active site. Vanadium haloperoxidases have raised much interest, and structural and/or functional models have been investigated extensively.[5] A tridentate ligand with an O_2N donor is thought to be a good candidate to mimic the dioxovanadium(V) intermediate species. 4,8-Dihydroxyquinoline-2-carboxylic acid, which has quinoline-*N*, hydroxy-*O*, and carboxy-*O* donor functions, is one of the products of tryptophan metabolism,[6] and the 4-hydroxy moiety is expected to participate in hydrogen bonding to construct supramolecular systems.[7] Yano et al. have utilized 3-hydroxypyridine-2-carboxylic acid as a ligand for oxovanadium(IV) complexes to design supramolecular architectures.[8] From these points of view, we focused on 4,8-dihydroxyquinoline-2-carboxylic acid as a functional ligand. We, herein, report the structural characterization of a vanadium(V) complex with 4,8-dihydroxyquinoline-2-carboxylic acid, which contains a tridentate *cis*-VO_2 structural unit.

Complexation of 4,8-dihydroxyquinoline-2-carboxylic acid (**1**) with NH_4VO_3 in water afforded dioxovanadium(V) complex **2** quantitatively. Dioxovanadium(V) complex **2** exhibited two sharp bands at 930 and 940 cm^{-1} in the IR spectrum, indicating the presence of *cis*-VO_2 structural unit.[5d,5m,5f]

X-ray crystallographic analysis was performed in order to clarify the structure and self-assembling properties. A suitable crystal for the single-crystal X-ray structure determination was obtained by recrystallization from water and acetone. The crystal structure of **2** supported the presence of a *cis*-VO_2 structural unit possessing the penta-coordinated geometry with two oxo ligands of tridentate ligand **1** (utilizing the quinoline-*N*, hydroxy-*O*, and carboxy-*O* donor functions), as depicted in Fig. 1.[9] The oxygen (O6) of one of the oxo ligands participates in hydrogen bonding with a water molecule, and the other oxo ligand (O5) is involved in hydrogen bonding with the ammonium counter ion (Fig. 1c), resulting in slightly longer V=O bonds (V1–O5, 1.637(4); V1–O6, 1.627(4) Å) than non-hydrogen bonded V=O bonds.[5f] The oxygen (O1) of the 4-hydroxy moiety also forms a hydrogen bond to a water molecule. The O5–V1–O6 angle (109.9(2)°) of the *cis*-VO_2 core is very close to other penta-coordinated vanadium(V) complexes containing the *cis*-VO_2 structural unit.[5f] The planar tridentate chelation of **1** was observed upon binding to vanadium to form two five-membered chelate rings with bite angles of 76.2(1)° (N1–V1–O2) and 75.2(1)° (N1–V1–O4). The V–O(carboxylate), V–N(pyridine), and V–O(hydroxide) bond lengths for the tridentate chelation are 1.995(2), 2.023(3), and 2.010(2) Å, respectively, which are slightly shorter than those of (4-hydroxypyridine-2,6-dicarboxylato)dioxovanadate(V)[5f] probably due to the accommodation of the VO_2 unit. The structural parameter τ ($=(\beta - \alpha)/60$, where α and β represent two basal angles ($\beta > \alpha$)) for the coordination geometry of the penta-coordinated complexes proposed by Addison, Reedijk, et al. is 0.43.[10] The parameters for ideal square pyramidal and trigonal bipyramidal geometries are $\tau = 0$ ($\alpha = \beta = 180°$) and $\tau = 1$ ($\alpha = 120°$ and $\beta = 180°$), respectively. The τ value of **2** indicates that the coordination geometry around the vanadium(V) ion is intermediate between square pyramid and trigonal bipyramid.

The most noteworthy structural feature is that each molecule of **2** is arranged in a hexagonal pattern in the crystal packing, in which two molecules of **2** are present in a face-to-face manner with an interplanar distance of ca. 3.6 Å between the quinoline moiety of **1** to form the π-stack dimer (Fig. 2). Interestingly, the hexagonal arrangement creates a channel cavity, which is occupied by water molecules to form a one-dimensional water chain. One-dimensional water chain structures are of interest from the view point of fundamental biological processes.[5j,11] Such a channel cavity for a one-dimensional water chain has not been observed in the case of the crystal structures of 4,8-dihydroxyquinoline-2-carboxylic acid,[7] and the nickel(II) complex with 8-hydroxyquinoline-2-carboxylic acids[12] although they contain water molecules.

In conclusion, 4,8-dihydroxyquinoline-2-carboxylic acid (**1**) was demonstrated to serve as a tridentate ligand possessing an

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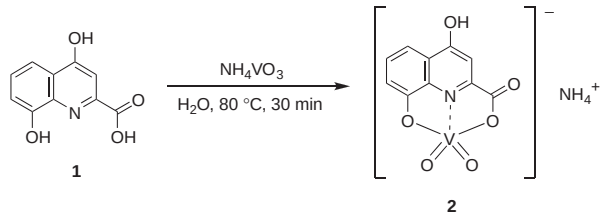

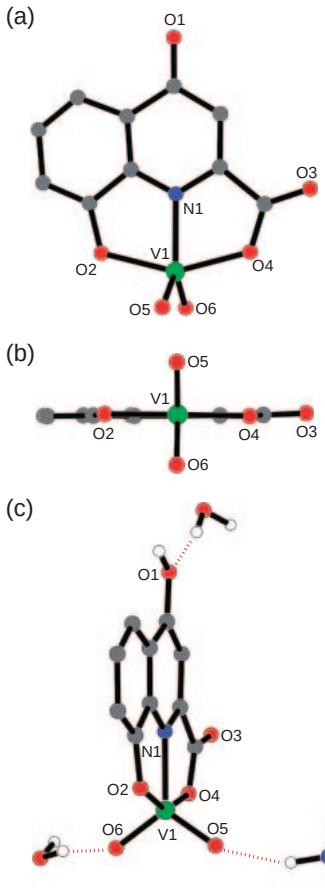

Fig. 1. (a) Top view and (b) side view of the molecular structure of **2** (Hydrogen atoms are omitted for clarity). (c) Hydrogen bonds in the molecular structure of **2** (Only hydrogen atoms bonded to heteroatoms are shown and broken lines represent hydrogen bonds).

O_2N donor set for complexating NH_4VO_3, affording the *cis*-dioxovanadium(V) complex **2**. The quinoline moiety of **1** was also found to control the molecular arrangement of the *cis*-dioxovanadium(V) complex **2** through π–π interaction in the crystal packing, creating a cavity in the channel for a one-dimensional water chain. Architectural control of self-assembly to construct well-organized structures with nano-dimensional cavities is an active current research area.[13] Studies on the application of the *cis*-dioxovanadium(V) complex for vanadium bromoperoxidase reactions are now in progress.

Experimental

Preparation of a Dioxovanadium(V) Complex 2. A mixture of 4,8-dihydroxyquinoline-2-carboxylic acid (**1**, 103 mg, 0.50 mmol) and NH_4VO_3 (58.8 mg, 0.50 mmol) in water (30 mL) was stirred at 80 °C for 30 min. After evaporation of the solvent, the dioxovanadium(V) complex **2** was isolated quantitatively as a yellow powder by reprecipitation from water and acetone. **2**: mp 168–171 °C (dec); IR (KBr) 940 (V=O), 925 (V=O) cm^{-1}; ^1H NMR (300 MHz, D_2O) δ 7.36 (t, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 6.96 (s, 1H), 6.79 (d, J = 8.0 Hz, 1H); ^{51}V NMR (104 MHz, D_2O) −505 ppm; ^{51}V NMR (104 MHz, CD_3OD) −499 ppm.

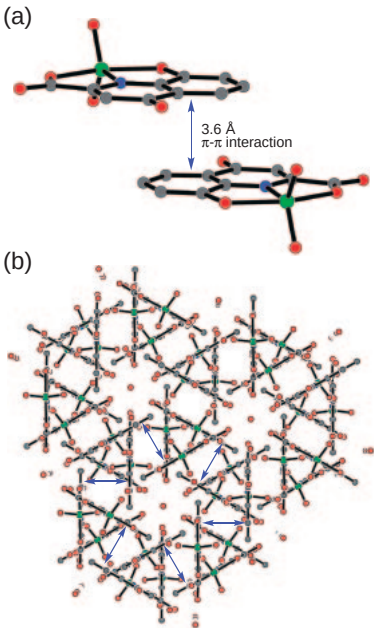

Fig. 2. (a) The π-stack dimer of **1**. (b) A layer containing a hexagonal arrangement in the crystal packing of **2**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **2**

Bond Lengths			
V1–N1	2.023(3)	N1–C9	1.347(4)
V1–O2	2.010(2)	C8–C9	1.408(4)
V1–O4	1.995(2)	C8–O2	1.356(4)
V1–O5	1.637(4)	C1–C10	1.510(4)
V1–O6	1.627(4)	C10–O3	1.230(4)
C1–N1	1.337(4)	C10–O4	1.296(4)
Bond Angles			
N1–V1–O2	76.2(1)	O5–V1–O6	109.9(2)
N1–V1–O4	75.2(1)	V1–O4–C10	121.8(2)
N1–V1–O5	124.6(2)	O4–C10–C1	112.6(3)
N1–V1–O6	125.5(2)	V1–N1–C1	120.9(2)
O2–V1–O4	151.4(1)	N1–C1–C10	109.4(3)
O2–V1–O5	96.7(1)	V1–O2–C8	117.9(2)
O2–V1–O6	97.6(1)	O2–C8–C9	114.4(3)
O4–V1–O5	99.6(1)	V1–N1–C9	118.9(2)
O4–V1–O6	98.7(1)	N1–C9–C8	112.6(3)

X-ray Structure Analysis. All measurements for **2** were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo Kα radiation. The structure of **2** was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and allowed to ride with the atoms to which each was bonded. Crystallographic details are given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with

the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-615743 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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9 Crystal data for **2**: $C_{10}H_9N_2O_6V_1 \cdot 3H_2O$, $M_r = 358.18$, trigonal, space group $R\bar{3}$ (#148), $a = 15.169(2)$ Å, $c = 31.840(3)$ Å, $V = 6345(1)$ Å^3, $Z = 18$, $T = 23.0\,^\circ$C, $D_{calcd} = 1.687\,g\,cm^{-3}$, $\mu(Mo\,K\alpha) = 7.53\,cm^{-1}$, Mo K$\alpha$ radiation ($\lambda = 0.71069$ Å), $R1 = 0.064$, $wR2 = 0.218$. CCDC-615743.

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