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# Synthesis, Structure, and Magnetic Property of a Dinuclear Vanadium(III) Complexes with *N*-Hydroxyethyliminodiacetate

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A vanadium(III) complex with *N*-hydroxyethyliminodiacetate (heida(3-)) was prepared. The X-ray crystallography has revealed that the compound is a dinuclear vanadium(III) complex, which contains a di-$\mu$-alkoxo bridge derived from the deprotonation of the hydroxyethyl group of the parent heida(2-) ligand. Each vanadium(III) center adopts a distorted octahedral structure. The temperature-dependent magnetic susceptibility measurement suggests that the electronic spin moments of the two vanadium(III) centers are antiferromagnetically coupled ($g = 1.98$ and $J = -36.9$ cm$^{-1}$).

The coordination stereochemistry of vanadium(III) complexes is known to be very flexible. In fact, vanadium(III) complexes with a variety of geometrical structures have been obtained using a tripodal tetradentate ligand with different functional groups. For example, nitrilotriacetate (nta) yields a heptacoordinate complex,[1] while the replacement of one acetate group of nta by a 2-pyridylmethyl group, i.e., *N*-(2-pyridylmethyl)iminodiacetate (pda), results in the formation of a hexacoordinate mononuclear complex as well as a $\mu$-oxo dinuclear complex.[2] *N*-Hydroxyethyliminodiacetate (heida(2-)) has a hydroxy group in the place of the pyridyl group of pda. The alkoxy group has a tendency to act as a bridging ligand accompanied by deprotonation, giving multinuclear vanadium(III) complexes.[3–6] It is, therefore, of interest to examine whether heida gives a hepta- or hexa-coordinate vanadium(III) complex, and also to see if the alkoxy group of heida acts as a bridging group. Here, we report on the synthesis, X-ray structure, and magnetic property of the vanadium(III)-heida(3-) complex (heida(3-): $(^{-}\mathrm{OOCCH_2})_2\mathrm{NCH_2CH_2O^-}$).

The treatment of $\mathrm{VCl_3}$ with *N*-hydroxyethyliminodiacetate in water under an anaerobic condition yielded a green crystalline vanadium(III)-heida(3-) complex (**1**), which was subjected to an X-ray crystal structure analysis. Figure 1 shows a perspective view of this complex; its selected bond distances and angles are listed in the figure caption. As expected, complex **1** has a dinuclear structure bridged by alkoxo groups formed by deprotonation of the hydroxyethyl functionality of the heida(2-) ligand, i.e., [V$_2$(heida(3-))$_2$(H$_2$O)$_2$]. Each vanadium(III) center is coordinated by six atoms, forming a distorted octahedron. Water oxygen (O6), in addition to the four atoms from its own heida(3-) ligand and one alkoxo oxygen from another heida-H ligand complete hexacoordination. A di-$\mu$-alkoxo bridge, as in **1**, has also been found in [V$_2$(hedta(4-))$_2$]$^{2-}$ (hedta(4-): $(^{-}\mathrm{OOCCH_2})_2\mathrm{NCH_2CH_2N(CH_2COO^-)CH_2CH_2O^-}$), though the vanadium(III) center in this complex adopts heptacoordination.[3] There is a center of symmetry in the middle of the V$_2$O$_2$ core. The V1–O5 distance is 1.991(1) Å, which is slightly longer than the V1–O5$^*$ distance (1.941(1) Å). The V1$\cdots$V1$^*$ separation is 3.0492(5) Å, and is shorter than the corresponding distance in [V$_2$(hedta(4-))$_2$]$^{2-}$ (3.296(1) Å). The V–O (alkoxo or carboxylato) and V–N (amine) distances are also shorter than the corresponding distances in [V$_2$(hedta(4-))$_2$]$^{2-}$, reflecting the difference in the coordination number. The meridional coordination of the iminodiacetate moiety of a heida(3-) ligand leads to a large distortion in the O1–V1–O3 axial angle (149.49(7)°), which is comparable to that found in [V$_2$(dpot)(hbza)(H$_2$O)$_2$] (151°) (dpot: 1,3-diamino-2-propanol-*N*,*N*,*N′*,*N′*-tetraacetate; hbza: hydroxybenzoate).[7]

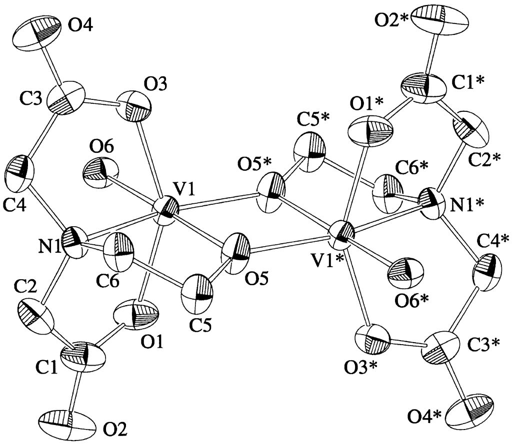

Fig. 1. Perspective view of [V$_2$(heida(3-))$_2$(H$_2$O)$_2$]. Selected bond distances (Å) and angles (°): V1–O1 1.947(1), V1–O3 1.974(1), V1–O5 1.991(1), V1–O5$^*$ 1.941(1), V1–O6 2.072(1), V1–N1 2.165(1), V1$\cdots$V1$^*$ 3.0492(5), O1–V1–O3 149.49(7), O1–V1–O5 94.25(6), O1–V1–O5$^*$ 104.38(7), O1–V1–O6 82.68(6), O1–V1–N1 79.87(6) O3–V1–O5 102.64(6), O3–V1–O5$^*$ 103.83(6), O3–V1–O6 82.56(5), O3–V1–N1 77.99(6), O5–V1–O5$^*$ 78.33(6), O5–V1–O6 173.67(5), O5–V1–N1 80.89(5), O6$^*$–V1–O6 97.01(6), O5$^*$–V1–N1 159.03(6), O6–V1–N1 103.91(6). The atoms marked with $^*$'s are expanded by symmetry operation ($-$x, $-$y, $-$z).

The diffuse reflectance spectrum of **1** exhibits bands at 383, 450 (sh), 525 (sh), and 633 nm. These bands became obscure in aqueous solution (420 (sh) and 620 (sh) nm), implying partial decomposition of **1** in water.

The magnetic susceptibility and the effective magnetic mo-

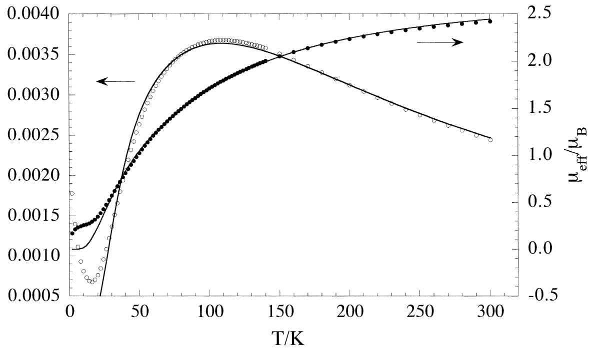

Fig. 2. Plot of the magnetic susceptibility and the effective magnetic moment against temperature.

ment of **1** in the range of 2–300 K are shown in Fig. 2. The magnetic moment is 2.42 B.M. (B.M. = $9.274 \times 10^{-24}$ J T$^{-1}$) per vanadium atom at 300 K, and decreases with decreasing temperature. Thus, the electronic spin moments of the two vanadium(III) centers are weakly antiferromagnetically coupled. The sharp increase in the susceptibility below 15 K would be due to the presence of traces of paramagnetic impurity. The temperature-dependent magnetic susceptibilities were analyzed based on the interaction of two d$^2$ ions, as described by the spin-Hamiltonian, $H = -2JS_1 \cdot S_2$ ($S_1 = S_2 = 1$). The best-fit parameters, $g = 1.98$ and $J = -36.9$ cm$^{-1}$, provide the solid line in Fig. 2, as calculated from the following equation:

$$\chi_A = (Ng^2\mu_B{}^2/kT)[5 + \exp(-4J/kT)]/ [5 + 3\exp(-4J/kT) + \exp(-6J/kT)].$$

It is of interest to compare the $J$ value of **1** with those found in other dinuclear vanadium(III) complexes with a di-$\mu$-alkoxo bridge. Namely, the antiferromagnetic interaction of two vanadium(III) centers in **1** is larger than that in $[V_2(\mathrm{Hdpot})_2]^{2-}$ ($-14.5$ cm$^{-1}$)[8] and in $[V_2(\mathrm{hedta(4\text{-})})_2]^{2-}$ ($-8.6$ cm$^{-1}$),[3] and is comparable to that found in $[V_2(\mathrm{hpnbpda})_2]$ ($-35.2$ cm$^{-1}$) (hpnbpda: *N*,*N′*-bis(pyridylmethyl)-2-oxo-1,3-propanediamine-*N*,*N′*-diacetate).[6] Although the above three complexes have a heptacoordinate structure, the present complex has a hexacoordinate structure. The present result, thus, suggests that the magnetic interaction between two vanadium(III) centers greatly depends on the bridging mode,[6] though the coordination number does not appreciably affect it.

## Experimental

**Synthesis of 1.** All manipulations were carried out under an argon atmosphere using standard Schlenk techniques, or in a nitrogen-filled glove box. *N*-hydroxyethyliminodiacetic acid, H$_2$heida (0.71 g; 4 mmol) was neutralized by sodium carbonate (0.64 g; 6 mmol) in 40 cm$^3$ of water. To this solution was added a solution of VCl$_3$ (0.63 g, 4 mmol) in 20 cm$^3$ of water. Allowing the resulting brown solution to stand at 60 °C overnight afforded green crystals. Yield, 0.74 g (82%). Found: C, 29.70; H, 4.21; N, 5.68%. Calcd for $C_6H_{10}NO_6V$: C, 29.64; H, 4.15; N, 5.76%. IR (KBr) 1631 ($\nu_{as}$(COO)), 1374 cm$^{-1}$ ($\nu_s$(COO)).

**Measurements.** UV-vis spectra were measured using a JASCO Ubest 50 spectrophotometer. Infrared spectra were measured using a JASCO FT/IR-8000S. The magnetic susceptibility was measured by the extraction method using a MPMS-7 SQUID magnetometer.

**X-ray Structure Determination.** Intensity data were collected on a Rigaku AFC7S diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The unit-cell parameters were determined by a least-squares refinement using setting angles of 25 reflections in the range $29.4 < 2\theta < 29.9°$. The structure was solved by a direct method (SIR92 in TEXAN) and conventional difference Fourier techniques. The structure was refined by full-matrix least-squares techniques on $F$. All non-hydrogen atoms were refined anisotropically. The calculations were carried out on an INDIGO II computer using the crystallographic package TEXAN.[9] Crystallographic data for **1**: $C_6H_{10}NO_6V$, fw = 243.09, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.120(1)$, $b = 9.753(2)$, $c = 6.771(4)$ Å, $\alpha = 94.05(3)$, $\beta = 98.79(2)$, $\gamma = 102.90(1)°$, $V = 450.3(3)$ Å$^3$, $Z = 2$, $D_{calc} = 1.793$ g cm$^{-3}$, $\mu$(Mo $K\alpha$) = 11.05 cm$^{-1}$, crystal size $0.20 \times 0.30 \times 0.38$ mm, trans factors 0.85–1.00, 1919 observed reflections [$I > 1.5\sigma(I)$] used in the refinement, $R = 0.026$, $R_w = 0.048$, and GOF = 1.60. The X-ray analysis data have been deposited as Document No. 74062 at the Office of the Editor of Bull. Chem. Soc. Jpn. The data (CIF format) have also been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 170238.

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