The First Example of μ-Oxo-bis(μ-carboxylato)dioxovanadium(IV,V) Complex

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A novel dinuclear oxovanadium(IV,V) complex, $[(VO)_2(O)(Ph_2CHCOO)_2(bpy)_2]NO_3 \cdot CH_3OH$ (**1**), has been prepared. X-Ray structural analysis has revealed that **1** has a μ-oxo-bis(μ-carboxylato)-bridged structure. Magnetic susceptibility data for **1** show the paramagnetic behavior which is attributable to the d^1-d^0 system.

Many transition metal complexes having a μ-oxo-bis(μ-carboxylato)dimetal core have been reported[1] as a structural motif in biology and inorganic chemistry. In our previous paper, we described both the magnetic properties and the crystal structure for a novel copper(II) analogue of the hemerythrin active center.[2] As a part of continuing projects in this study, we have prepared a novel dioxovanadium(IV,V) complex, $[(VO)_2(O)(Ph_2CHCOO)_2(bpy)_2]NO_3 \cdot CH_3OH$ (**1**), having the μ-oxo-bis(μ-carboxylato)dimetal core, where bpy is 2,2'-bipyridine and Ph_2CHCOO^- is diphenylacetato ion. To the best of our knowledge no dioxovanadium(IV,V) complexes with such a core are known.

The complex was obtained as follows. To a yellowish green solution of $[VOCl_2(bpy)(C_2H_5OH)]$[3] (0.34 g, 1 mmol) in 20 cm^3 of methanol, $AgNO_3$ (0.34 g, 2 mmol) was added. This mixture was stirred for 5 min with shutting off the light, and the resulting suspension was centrifuged and filtered off. To the filtrate a solution of $Ph_2CHCOOH$ (0.22 g, 1 mmol) in 5 cm^3 of acetonitrile was added under stirring, and the reaction mixture was adjusted to pH 5.1 with triethylamine. The solution was allowed to stand for a week at room temperature. Black crystals were collected by suction, washed with methanol, and dried in air (yield 0.143 g, 14.6 %).[4]

The crystal structure[5] of **1** is shown in Figure 1. This complex consists of a dioxovanadium core contains two hexa-coordinated vanadium ions linked by one oxo and two diphenylacetato bridges. The coordination environment around each vanadium ion is a distorted octahedral geometry with the equatorial plane comprised of two nitrogen atoms of a terminal ligand, one oxygen atom of the bridging oxide, and one oxygen atom of a bridging carboxylate. The axial sites are occupied by oxygen atoms of the oxovanadium group and of another bridging carboxylate. Each vanadium ion is deviated from the equatorial plane to O1 and O2 by 0.288 Å and 0.328 Å, respectively. The bond distances of V1–O1 (1.595(5) Å), V2–O2 (1.594(5) Å), V1–O3 (1.850(5) Å), and V2–O3 (1.821(5) Å) are comparable to the corresponding distances reported for dioxovanadium(IV,IV) and (IV,V) complexes.[6–9] Thus, we could not distinguish which vanadium ion is V(IV) or V(V) in the molecule. The bond distances of V–O (V1–O4 2.256(6) Å, V2–O7 2.236(5) Å) trans to each V=O are longer than those in the equatorial plane (1.821(5) Å ~ 1.963(5) Å), because of the trans influence of the V=O bond. The V–O–V bridging angle is 133.9(3) ° and the V...V separation is 3.379(2) Å. These bridging angle and the metal–metal distance fall in the range of those reported for μ-oxo-bis(μ-carboxylato)-bridged divanadium(III) complexes.[10,11]

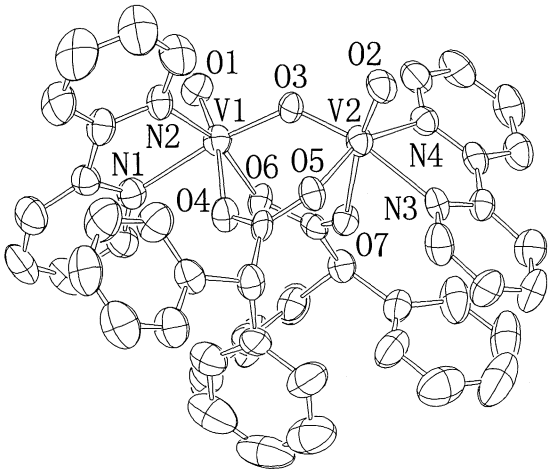

Figure 1. An ORTEP drawing for the complex cation of **1**. Selected bond distances (Å) and angles(°): V1–O1 1.595(5), V1–O3 1.850(5),V1–O4 2.256(6), V1–O6 1.963(5), V1–N1 2.138(6), V1–N2 2.109(6), V2–O2 1.594(5), V2–O3 1.821(5), V2–O5 1.953(5), V2–O7 2.236(5), V2–N3 2.166(7), V2–N4 2.131(6), V1...V2 3.379(2), O1–V1–O4 168.7(2), O2–V2–O7 170.4(2), O3–V2–N3 159.0(2), O6–V1–N2 161.9(2), O3–V1–N1 159.7(2), O5–V2–N4 156.4(2), V1–O3–V2 133.9(3).

The magnetic susceptibility data for **1** show essentially paramagnetic behavior attributed to the d^1-d^0 system, though the magnetic moment per unit dimer of 1.74 B.M. at room temperature slightly decrease to 1.65 B.M. at 81.2 K. Oxovanadium(IV) compounds have usually a five- or six-coordination environment, and in either case the strong axial ligand field quenches the angular momentum effectively. The magnetic moments for magnetically diluted oxovanadium(IV) compounds are close to 1.73 B.M. at all temperatures following the Curie law. Therefore, the slight decrease of the magnetic moment for **1** may be caused by the existence of very small amounts of antiferromagnetic impurities such a dioxovanadium(IV,IV) species.

X-Band ESR spectrum of **1** was recorded as a polycrystalline sample or in dichloromethane solution at room temperature. The polycrystalline spectrum showed a broad unresolved signal at around 335 mT in the range of 60–560 mT. On the other hand, the spectrum in dichloromethane solution consists of 15 lines (Figure 2) corresponding to the interaction of the unpaired electron with both ^{51}V ($I = {}^7/_2$) nuclei. The values of the isotropic hyperfine constant (A_{iso}) and the g factor (g_{iso}) are 47×10^{-4} cm^{-1} and 1.99, respectively. This spectral feature is

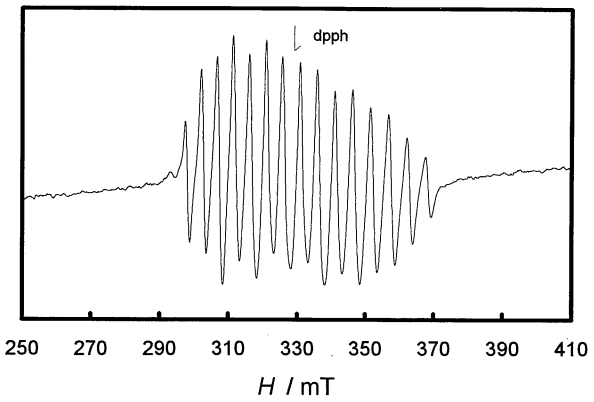

Figure 2. X-Band ESR spectrum of **1** in dichloromethane solution at room temperature.

quite similar to those for the mixed valence complexes containing the dinuclear $V_2O_3^{3+}$ core.[7]

The reflectance spectrum of **1** displays four bands at 21800 cm^{-1}, 17900 cm^{-1}, 14800 cm^{-1}, and 10100 cm^{-1} in the visible and near infrared region. The former three bands can be assigned to the d-d transitions of $^2B_2 \rightarrow {}^2A_1$, $^2B_2 \rightarrow {}^2B_1$, and $^2B_2 \rightarrow {}^2E$, respectively.[12] The band at 10100 cm^{-1} is assignable to the intervalence band ($V^{IV} \rightarrow V^V$) as found for $Na[V_2O_3(S\text{-peida})_2]\cdot NaClO_4\cdot H_2O$ (9400 cm^{-1})[8] and $H[V_2O_3(pmida)_2]\cdot 4H_2O$ (10500 cm^{-1}).[9]

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3 The $[VOCl_2(bpy)(C_2H_5OH)]$ complex was prepared according to the method of M. Köppen[10] by the reaction of VCl_3 with bpy.

4 Anal. Found: C, 59.87; H, 4.19; N, 7.10; V, 10.29%. Calcd for $C_{49}H_{42}N_5O_{11}V_2$: C, 60.13; H, 4.33; N, 7.16; V, 10.41%.

5 Crystal data for **1**: $C_{49}H_{42}N_5O_{11}V_2$, monoclinic, $P2_1/n$(#14), a = 9.145(5) Å, b = 15.338(7) Å, c = 32.422(6) Å, β = 93.90(4)°, V = 4537(3) Å^3, Z = 4, D = 1.433 g cm^{-3}, 2θ (max) = 55.0°, R = 0.063, R_w = 0.062.

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