CHEMISTRY LETTERS, pp. 1253-1254, 1993.

Preparation and Structure of the Novel Dinuclear Vanadium(III) Complex Bridged by an Alkoxo Group and a Carboxylato Group

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The reaction of 1,3-diamino-2-propanol-*N*,*N*,*N*′,*N*′-tetraacetate (dpot) with VCl_3 followed by the addition of benzoic acid (Hbza) or hydroxybenzoic acid (Hhbza) has yielded the dinuclear vanadium(III) complex, $[V_2(dpot)(bza\ or\ hbza)(H_2O)_2]$, bridged by both a deprotonated alkoxo group of dpot and a carboxylato group of bza or hbza.

Vanadium(III) chemistry has been receiving a great deal of attention since 1911 when Henze1) discovered that the sea squirts or tunicates accumulate V(III) ion to a great extent in their blood cells. Despite the importance of the coordination chemistry of V(III) in elucidating the role of vanadium in the blood cells of tunicates, it is only recently that the V(III) complexes have been well characterized.

All complexes were prepared under an Ar atmosphere using standard Schlenk techniques. A suspension of H_5dpot (1.6 g, 5 mmol) in H_2O (30 cm^3) was neutralized with NaOH (1 g, 25 mmol). This solution was mixed with a solution of VCl_3 (1.6 g, 10 mmol) in H_2O (30 cm^3) followed by the addition of Hbza (0.6 g, 5 mmol) in methanol (30 cm^3) or *o*-, *m*-, or *p*-Hhbza (0.7 g, 5 mmol) in 1:2 methanol/water (30 cm^3). The reaction mixture was allowed to stand at 60 °C for a day. The deposited dark green crystals were collected by filtration. The yields were 75-99%. Anal: Found: C, 38.18; H, 3.89; N, 4.72%. Calcd for $[V_2(dpot)(bza)(H_2O)_2]\cdot H_2O$ ($C_{18}H_{24}N_2O_{14}V_2$): C, 38.36; H, 4.07; N, 4.72%. Found for *o*-hbza complex: C, 35.26; H, 3.80; N, 4.67%. Found for *m*-hbza complex, C, 35.86, H, 3.85, N, 4.71%. Found for *p*-hbza complex, C, 34.96; H, 3.68; N, 4.65%. Calcd for $[V_2(dpot)(hbza)(H_2O)_2]\cdot H_2O$ ($C_{18}H_{24}N_2O_{15}V_2$): C, 35.44; H, 3.96; N, 4.59%.

The *m*-hbza complex, $[V_2(dpot)(m\text{-}hbza)(H_2O)_2]$ (**1**), crystallized in an appropriate size with good quality and was subjected to an X-ray crystal structure analysis.2) The perspective view of **1** is shown in Fig. 1. The structure of **1** is very similar to that of the Fe(III) analogue.3) Two V(III) centers are bridged by a deprotanated alkoxo group of dpot and a carboxylato group of *m*-hbza.4) The alkoxo bridge angle is 131.3(1)° and is larger than those in bis(μ–alkoxo) complexes; 110.3° for $[V_2(dpot)_2]^{2-}$ 5,6) and 108° for $[V_2(hedtra)_2]^{2-}$ 7) (hedtra=*N*-hydroxyethyl-*N*,*N*′,*N*′-triacetate). Consequently, the V-V separation (3.593 Å) is longer than the corresponding ones in $[V_2(dpot)_2]^{2-}$ (3.343 Å) and $[V_2(hedtra)_2]^{2-}$ (3.296 Å). The geometry and dimensions in the carboxylato bridging moiety are similar to those in $[V_2L_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2]^{2+}$ (L=1,4,7-trimethyl-1,4,7-triazacyclononane).8)

In contrast to the hepta-coordination in $[V_2(dpot)_2]^{2-}$, each V(III) center in **1** exhibits hexa-coordination which is completed by a tertiary amine nitrogen, two acetato oxygens, an alkoxo oxygen of dpot, a carboxylato oxygen of *m*-hbza, and an oxygen of water. This difference in coordination geometry would result from the expansion of the O9-V1(2)-O21(22) angle (93.4(1) and 93.7(1)°) of the bridging moiety due to the carboxylato bridge (69.7° for $[\mathrm{V_2(dpot)_2}]^{2-}$ 5,6)). Though the two V centers are crystallographically unequivalent, the geometry and dimensions around them are almost the same. The coordination bond distances of dpot in **1** are shorter than those found in $[\mathrm{V_2(dpot)_2}]^{2-}$ 5,6); $r_{av}(\mathrm{V\text{-}O_{carboxylato}})$, 1.959 vs 2.043 Å; $r_{av}(\mathrm{V\text{-}O_{alkoxo}})$, 1.973 vs 2.037 Å; $r_{av}(\mathrm{V\text{-}N})$, 2.153 vs. 2.309 Å., being consistent with the difference in the coordination number of the two complexes. The maximum deviation of the sum of the in-plane angles around the V(III) ion from 360° is 1.1°, indicating the high planarity of the vanadium center and four coordinating atoms.

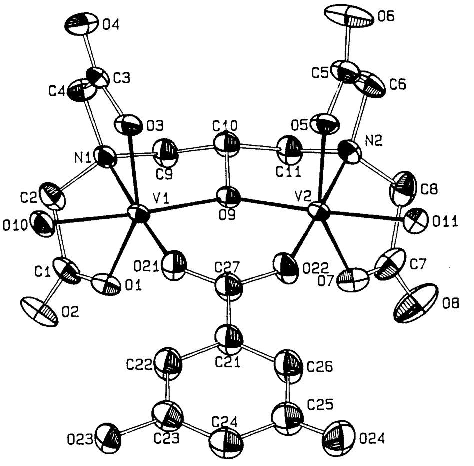

Fig. 1. Perspective view of **1**.

Interestingly, on each V(III) ion in **1**, the two carboxylato groups of dpot occupy trans position, while in $[\mathrm{V_2(dpot)_2}]^{2-}$ those are in a cis position. This trans coordination results in a fairly distorted octahedron which is displayed with the angles of 151.1(1)° and 151.6 (1)° for the O3-V1-O1 and O5-V2-O7 angles, respectively.

The IR, Raman, and electronic absorption spectral properties of the bza, *p*- and *o*-hbza complexes have shown that these complexes also have structures similar to that of the m-hbza complex **1**.

The fact that vanadium(III) forms a complex having a structure similar to that of the iron(III) analogue would give some implication to the puzzling role of vanadium(III) in biological systems.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 04640572) and financially supported by the Izumi Science and Technology Foundation.

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2) Crystal data for $[\mathrm{V_2(dpot)}(m\text{-hbza})(\mathrm{H_2O})_2]\cdot\mathrm{H_2O}$: M=610.28, triclinic, P1, a=6.770(2), b=10.268(2), c=16.191(4) Å, α=83.31(2), β=84.57(2), γ=80.27(2)°, V=1098.5(4) Å^3, Z=2, D_{calc}=1.84 gcm^{-3}, λ(Mo Kα)=0.71073 Å, F(000)=624, μ(Mo Kα)=9.1 cm^{-1}, room temperature, R(R_w)=0.044(0.050) for 3781 independent reflections with $|Fo| > 3\sigma|Fo|$ ($2\theta \leq 50°$). The data collection and the structure determination were performed by the same procedure described in a previous paper (K. Okamoto, J. Hidaka, M. Fukagawa, and K. Kanamori, *Acta Cryst.*, **C48**, 1025 (1992)). Selected bond distances (Å) and angles (°): V1-O1 1.972(3), V1-O3 1.956(3), V1-O9 1.975(3), V1-O10 2.094(3), V1-O21 1.976(3), V1-N1 2.145 (3), O1-V1-O9 101.0(1), O1-V1-O10 81.9(1), O1-V1-O21 101.7(1), O1-V1-N1 78.4(1), O3-V1-O9 95.8(1), O3-V1-O10 80.6(1), O3-V1-O21 100.7(1), O3-V1-N1 80.3(1), O9-V1-O21 93.4(1), O9-V1-N1 83.6(1), O10-V1-O21 88.5(1), O10-V1-N1 94.5, V1-O9-V2 131.3(1), V1-O21-C27 138.5(3), O9-V2-O22, 93.7(1).

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(Received May 13, 1993)