Weak Antiferromagnetism in a μ-Alkoxo-μ-Pyrazolato-Bridged Dinuclear Vanadium(IV) Complex

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A vanadium(IV) complex with 2-hydroxy-*N*,*N′*-bis(1-methyl-3-hydroxy-3-phenyl-2-propen-1-ylidene)-1,3-propane-diamine (H_3L), $[(VO)_2(L)(pz)]$ (Hpz = pyrazole), was synthesized and characterized by measurements of the magnetic moment and the electronic spectra. The X-ray crystal structure analysis shows that the compound has a dinuclear structure with two square-pyramidal N_2O_3 coordination environments, which are bridged by the alkoxo and the pyrazolato groups. The antiferromagnetic interaction between the two metal atoms is fairly weak.

The structural chemistry of vanadium compounds has received much attention in the last three decades.[1,2] However, only a limited number of compounds have been synthesized and characterized by X-ray crystallography in the case of dinuclear vanadium(IV) complexes,[3] where an interesting magnetic interaction should be expected from such a dinuclear d^1–d^1 system. In this study, we synthesized a new dinuclear vanadium(IV) complex by using 1,3-bis(benzoylacetoneimine)-propan-2-ol (2-hydroxy-*N*,*N′*-bis(1-methyl-3-hydroxy-3-phenyl-2-propen-1-ylidene)-1,3-propanediamine, abbreviated as H_3L), which affords oligonuclear metal species as well as dinuclear metal complexes.[4–8] Herein, we describe the synthesis as well as structural and magnetic characterization of $[(VO)_2(L)(pz)]$ (Hpz = pyrazole) (**1**).

The treatment of H_3L with $[VO(acac)_2]$ (Hacac = 2,4-pentanedione) in a mixture of CH_2Cl_2 and CH_3CN containing pyrazole afforded black crystals of **1**. An X-ray crystallographic study revealed that the two vanadium atoms with terminal oxo groups, V1 and V2, are bridged by an alkoxo-oxygen (O3) of L and pyrazolato group, forming a distorted square-pyramidal environment for each metal center (Fig. 1). The V1–V2 separation is 3.446(1) and the V1–O3–V2 angle is 122.9(2)°. Similar structural features were found in analogous μ-alkoxo-μ-pyrazolato-bridged dinuclear complexes $[M_2(L')(pz)]$ (H_3L' = 1,3-bis(salicylideneamino)-2-propanol) [M = Cu: Cu–Cu 3.349 Å, Cu–O–Cu 121.7°; M = Ni: Ni–Ni 3.245(1) Å, Ni–O–Ni 125.4(2)°].[9,10] The terminal oxo-groups are in *syn*-positions with respect to each other. The short bond lengths of V1–O4 [1.584(3)] and V2–O5 [1.591(3)] indicate a considerable double-bond character, because is usual for oxovanadium complexes.[2] The double-bond character can be confirmed by the IR spectrum of **1**, where the V=O stretching band was observed at 994 cm^{-1}.[3,11,12] In the mean plane defined by the basal N_2O_2 atoms, V1 and V2 atoms are displaced towards the terminal oxygen by 0.62 and 0.61 Å, respectively. The dihedral angle between these two planes is 165.8°.

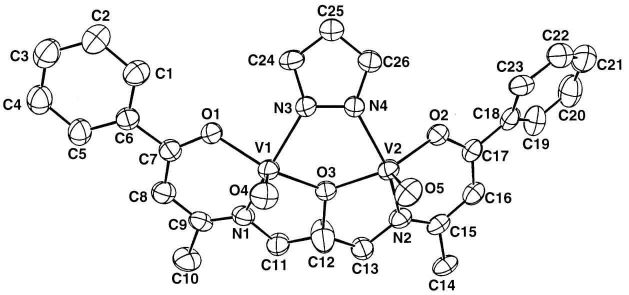

Fig. 1. Perspective view of the structure of **1**. Hydrogen atoms are omitted for clarity.

The diffuse reflectance spectrum of **1** shows bands at 324, 390sh, 526, 630, and 905 nm. The electronic spectrum of **1** in CH_2Cl_2 resembles the diffused reflectance spectrum. The electronic conductance measurement in CH_2Cl_2 confirms that **1** is essentially a non-electrolyte. These results show that the dinuclear structure is maintained in the solution. Judging from the transition energies and intensities, the former two bands in the near-ultraviolet region may be ascribed as being due to charge-transfer transitions, and the latter three bands in the visible region may be assigned to d–d transitions.

The magnetic moment of **1** is 2.46 B.M. per dinuclear molecule at room temperature, and slightly decreases upon lowering the temperature, reaching 1.82 B.M. at 4.5 K. The magnetic data can be well represented by the Bleaney–Bowers equation,

$$\chi_M = (2Ng^2\beta^2/kT)[3 + \exp(-2J/kT)]^{-1}, \qquad (1)$$

where $-2J$ is equal to the energy separation between the spin-singlet and the spin-triplet states; the other symbols have their usual meanings.[13] The best-fitting parameters are g = 2.00 and J = -2.3 cm^{-1}; the solid curve in Fig. 2 was calculated using these parameters. This result shows that there is a weak

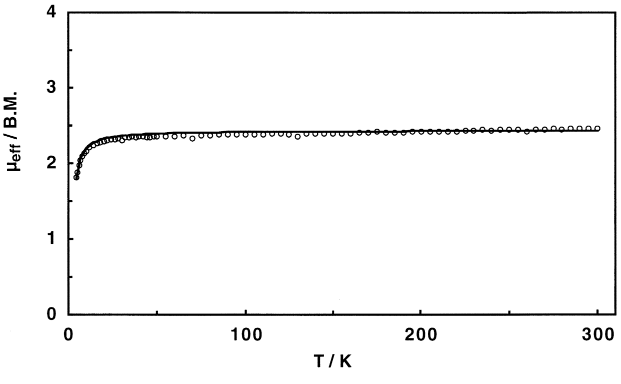

Fig. 2. Temperature dependence of effective magnetic moments (○) of **1**.

antiferromagnetic interaction between the two vanadium(IV) ions. This is in contrast to the case for the μ-alkoxo-μ-prazolato-bridged copper(II) complex, [$Cu_2(L')(pz)$], which shows a fairly strong antiferromagnetic interaction due to a superexchange through the μ-alkoxo-μ-prazolato-bridges of magnetic $d_{x^2-y^2}$ orbitals.[9] It is known that dinuclear oxovanadium(IV) complexes generally exhibit antiferromagnetic interaction between the two vanadium(IV) ions due to a direct overlap of the d_{xy} orbitals.[14] Thus, it can be expected that the magnitude of the antiferomagnetic interaction could rapidly decrease with increasing distance between the two metal centers. Moreover, any misdirecting of the d_{xy} orbitals due to the obtuse V–O–V may cause a small overlapping of the d_{xy} orbitals. In related phenoxo- or hydroxo-bridged dinuclear oxovanadium(IV) complexes, a fairly strong antiferromagnetic interaction was observed; the J values vary from -122 to -177 cm^{-1}, while the V–V separation lies between 2.965 and 3.077 Å.[3,15–17] In the present complex, the exogenous pyrazolato-bridge enforces the long metal-metal separation and the obtuse metal–O–metal angle, resulting in weak antiferromagnetism, which is rarely observed in dinuclear oxovanadium(IV) complexes. This is in line with Wieghardt et al's opinion accounting for the relatively weak antiferromagnetic property of their compound, although the $-J$ value of -114 cm^{-1} is not explicable, since the V–V distance of 4.075 Å is longer than that of **1**.[18]

Experimental

Synthesis of 1. H_3L (57 mg, 0.15 mmol), [$VO(acac)_2$] (Hacac = 2,4-pentanedione) (80 mg, 0.30 mmol), and pyrazole (20 mg, 0.30 mmol) were dissolved in a mixture of CH_2Cl_2 (2 cm^3) and CH_3CN (10 cm^3). The solution was kept at room temperature for several days. Black plates were deposited and collected by filtration and dried in vacuo over P_2O_5: Yield, 20 mg (23%). Found: C, 54.16; H, 4.56; N, 9.83%. Calcd for $C_{26}H_{26}N_4O_5V_2$: C, 54.18; H, 4.55; N, 9.72%. IR (KBr) ν(C=C) 1592 (s), 1569, ν(C=N) 1501 (s), ν(V=O) 994 (s) cm^{-1}. μ_{eff} (300 K) 2.46 B.M. λ_M (CH_2Cl_2) 0 $S mol^{-1} cm^2$. Electronic spectrum in CH_2Cl_2: λ_{max} (ε, $dm^3 mol^{-1} cm^{-1}$) 243 (16200), 355 (15700), 513 (57), 600 nm (51). Diffuse reflectance spectrum: 324, 390 sh, 526, 630, and 905 nm.

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out using a Perkin–Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JASCO Infrared Spectrometer Model IR700 in the 4000–400 cm^{-1} region. The electronic conductivities were measured on a Horiba conductivity meter (DS-14). The diffuse reflectance spectra and electronic absorption spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer (Model UV-3100). The magnetic susceptibilities were measured on a Quantum Design MPMS-5S SQUID susceptometer. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[19] The effective magnetic moments were calculated from the equation $\mu_{eff} = 2.828\sqrt{\chi_M T}$, where χ_M is the magnetic susceptibility per dinuclear molecule.

X-Ray Crystal Structure Analysis. The crystal was mounted on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo-$K\alpha$ radiation at 25 ± 1 °C. The unit-cell parameters were determined by a least-squares refinement based on 25 reflections with $20 \le 2\theta \le 30°$. Intensitiy data were corrected for Lorentz-polarization effects. An absorption correction was performed using the Ψ-scan method. The structures were solved by direct methods and refined by full-matrix least-squares methods using the weighting scheme $w = 1/[\sigma^2(|F_0|) + (0.02|F_0|)^2 + 1.0]$. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were inserted at their calculated positions and fixed at their positions. All of the calculations were carried out on a VAX station 4000 90A computer using a MolEN program package.[20]

Crystallographic data: for **1**; $C_{26}H_{26}N_4O_5V_2$, *F.W.* = 576.4, triclinic, space group $P\bar{1}$, $a = 11.452(3)$, $b = 13.673(4)$, $c = 9.936(3)$ Å, $\alpha = 95.04(2)$, $\beta = 113.30(1)$, $\gamma = 111.64(1)°$, $V = 1277.5(7)$ Å^3, $Z = 2$, $D_m = 1.50$, $D_c = 1.50$ g cm^{-3}, μ(Mo $K\alpha$) = 7.50 cm^{-1}, crystal dimensions 0.12 × 0.30 × 0.42 mm, 4004 reflections measured ($2\theta_{max} = 48°$), 3025 [$I \ge 3\sigma(I)$] used in the refinement, $R = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.041$, $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2} = 0.048$. The X-ray analysis data have been deposited as Document No. 74031 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have 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 157315.

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