Volume 34

Number 1

January 4, 1995

Inorganic Chemistry

Communications

A Novel Layered Mixed-Valence Vanadium Phenanthroline Complex: Hydrothermal Synthesis and Crystal Structure of $[V^{IV}V^{V}_2O_7(phen)]_n$

Chung-ying Duan,* Yu-peng Tian, Zhong-lin Lu, and Xiao-zeng You

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing, 210093 People's Republic of China

Xiao-ying Huang

State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002 People's Republic of China

Received May 6, 1994

Recent investigations of the coordination chemistry of polymetalated compounds with organic ligands revealed an extensive class of polyoxovanadium complexes,[1-4] but to our knowledge, polyoxovanadium complexes containing bidentate organic amines ligands are rare,[5] and no layered structures have been reported. This paper describes the hydrothermal synthesis and the layered structure of the mixed-valence vanadium complex $[V^{IV}V^{V}_2O_7(phen)]_n$.

A 0.182 g (10 mmol) sample of V_2O_5 and 0.198 g (10 mmol) of phenanthroline were placed in a 30 mL glass-lined autoclave. The filling was adjusted to 60% with distilled water, and the mixture was heated at 180 °C and autogeneous pressure for 2 days. After the reaction vessel was cooled to room temperature over a 12-h period, the blue-black prism crystals (0.12 g, 40% based on vanadium) were filtered off, washed several times with distilled water, and dried in air. Anal. Calc for $C_{12}H_8N_2V_3O_7$: C, 32.4; H, 1.8; N, 6.3. Found: C, 32.1; H, 2.0; N, 6.3.

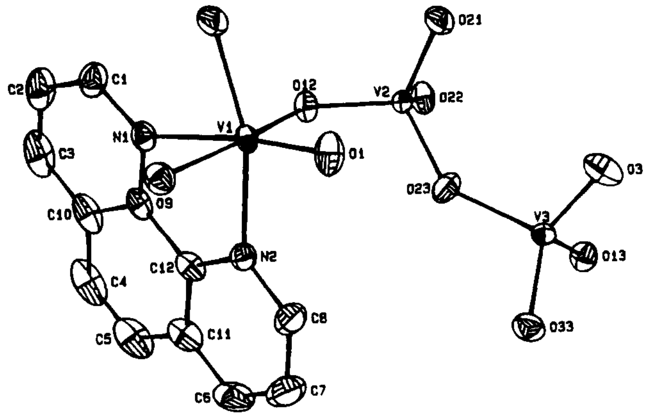

Figure 1. Molecular structure of $V^{IV}V^{V}_2O_7(phen)$. Important bond lengths (nm): V1−O1, 1.589(2); V1−O13, 1.955(2); V1−O21, 1.982(2); V1−O12, 2.059(2); V1−N1, 2.2772; V1−N2, 2.114(2); V2−O12, 1.660(2); V2−O21, 1.661(2); V2−O23, 1.735(2); V2−O22, 1.800(2); V3−O3, 1.597(2); V3−O13, 1.672(2); V3−O33, 1.7776(8); V3−O23, 1.815(2).

The atoms in the asymmetric unit and the numbering scheme are shown in Figure 1.[6] There are three chemically and crystallographically unique vanadium centers. The V1 site consists of a distorted octahedral center coordinated by two N atoms of phenanthroline, a terminal oxo, and three corner-sharing oxygens connected to the vanadium polyhedron. The V2 site consists of a distorted tetrahedral center coordinated by four corner-sharing oxygens connected to the vanadium polyhedron. The V3 site consists of a distorted tetrahedral center coordinated by a terminal oxo and three corner-sharing oxygens connected to the vanadium polyhedron. Bond valence calcula-

---

(1) Pope, M. T.; Miller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34.

(2) Klemperer, W. G.; Marquart, T. A.; Yaghi, O. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 49.

(3) Klean, M. I.; Chem, Q.; Hope, H.; Parkin, S.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 2929.

(4) Haushalter, R. C.; Wang, Z.; Thompson, M. E.; Zubieta, J.; O'Connor, C. J. *Inorg. Chem.* **1993**, *32*, 3966.

(5) Huan, G.; Johnson, J. W.; Jacobson, A. J.; Merola, J. S. *J. Solid State Chem.* **1991**, *91*, 385.

(6) Crystal data: $C_{12}H_8N_2V_3O_7$, $M_r = 445.03$, monoclinic, space group $P2_1/c$, $a = 0.9594(4)$ nm, $b = 1.0063(2)$ nm, $c = 1.5012(2)$ nm, $\beta = 98.83(3)°$, $V = 1.4323(77)$ nm^3, $Z = 4$, $D_c = 2.06$ g cm^{-3}, An Enraf-Nonius CAD4 diffractometer with Mo Kα radiation ($\lambda = 0.710\,69$ Å) and a graphite monochromator was used to collect 3491 diffraction maxima ($2 < 2\theta < 53.9°$) from a blue-black prism crystal of dimensions 0.40 × 0.45 × 0.20 mm^3 at 296 K. Of these, 3301 were unique and 2774 observed [$I > 3\sigma(I)$]. No absorption correction was applied to the data ($\mu = 18.96$ cm^{-1}). The structure was solved by direct methods and refined by full-matrix least-squares procedures with $R = 0.034$, $R_w = 0.044$ ($w = \sigma^{-2}(F)$).

0020-1669/95/1334-0001$09.00/0

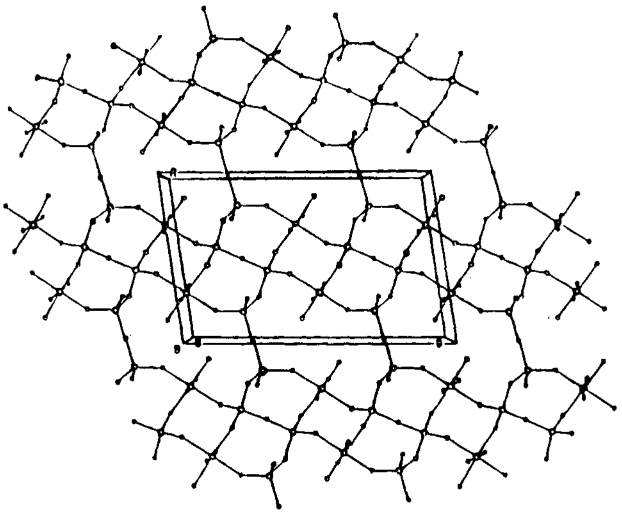

Figure 2. Unit cell contents viewed along the *b* axis: O, vanadium atom; ∘, oxygen atom; •, nitrogen atom.

tion by the Pauling principle[7] and the empirical formal derived by Brown and Altermatt[8,9] confirm that the sum of the formal oxidation states for the three vanadium atoms in one structure unit is 14. The result indicates that there is only one isolated V^{IV} species in the formula unit. The magnetic susceptibility data support this assignment, with an average magnetic moment of 2.16 μ_B at room temperature. Variable-temperature solid magnetic susceptibility studies show that the data approach Curie–Weiss behavior at high temperature with a paramagnetic Curie temperature $\Theta = -78.5$ K, indicating a strong antiferromagnetic exchange.

As shown in Figure 2, which is an illustration of the unit cell contents viewed along the *b* axis, the structure consists of infinite chains of V_3O_7(phen) units. Two adjacent infinite chains are held together by the V1–O–V2 and V2–O–V2 bonds through the bridged oxygen atoms O12, O21, and O22, to form a double-chain infinite ribbon along the *c* axis. All the ribbons are parallel to each other along the *c* axis, adjacent ribbons being held together by the V3–O33–V3 bond through the two corner-sharing VO_4 tetrahedra to form a network, thus forming the layered structure.

Acknowledgment. This work was supported by the National Nature Science Foundation of China and a grant for the Key Research Project from the State Science and Technology Commission of China.

Supplementary Material Available: Tables of structure determination data, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and atom deviations from the least-squares plane (7 pages). Ordering information is given on any current masthead page.

IC940502B

---

(7) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(8) Brown, I. D.; Wu, K. K. *Acta Crystallogr., Sect. B* **1976**, *32*, 1957.

(9) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244.