

Synthesis and Crystal Structure of a Novel Compound of $(C_2N_2H_8O_2) H_6V_{10}O_{28}$

Ju Tao LIU, Xiao Hong WANG, Jing Fu LIU*

Faculty of Chemistry, Northeast Normal University, Changchun 130024

Abstract: A novel vanadate decamer, involving all vanadium atoms present in +5 oxidation and one formhydroxamic acid dimer cation readical, has been synthesized. The single-crystal X-ray diffraction shows that the orange crystal is formed in the triclinic system, space group $P\bar{1}$, $a = 8.4960(17)$, $b = 10.447(2)$, $c = 11.299(2)$ Å, $\alpha = 68.82(3)^\circ$, $\beta = 87.35(3)^\circ$, $\gamma = 66.97(3)^\circ$. $V = 855.3(3)$ Å³, $Z = 8$, $R_1 = 0.0857$, $wR_2 = 0.2551$. X-ray crystallographic and packing in superlattice studies showed that the crystal structure was constructed by electrostatic attraction of O—H···O hydrogen bonds between formhydroxamic acid dimer cation and decavanadate polyanion. Formhydroxamic acid dimer is got through controlling the condition of the reaction using formhydroxamic acid.

Keywords: Formhydroxamic acid dimmer, decavanadate, synthesis, crystal structure.

Vanadium is a rare metal with exceptional properties. Both its cationic and anionic forms can interact with biomolecules, and its coordination chemistry plays a predominant role in these interactions. Among several biological functions of vanadium, many important therapeutic effects have been described, including hormonal, cardiovascular, anticarcinogenic, sugar lowering activities^{1,2}.

Because of the physiological relevance of vanadium, a better understanding of its complexation behavior with organic ligands is of vital interest. The interactions of this metal with nitrogen compounds like protein and amino acid *etc.* and its role in enzymatic reactions have been studied extensively.

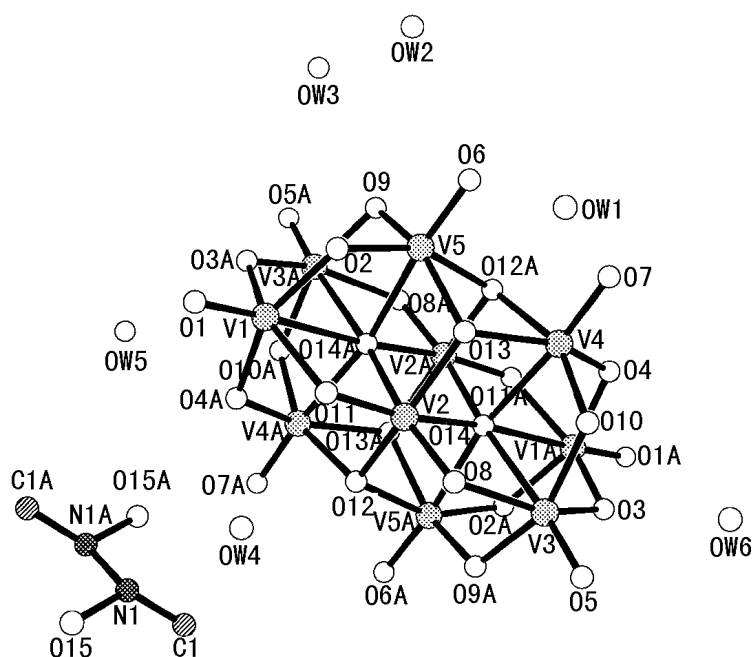
In spite of the importance of these interactions, but no information regarding the interaction between formhydroxamic acid dimer with any of these polyoxovanadates or other polyoxometalates at the molecular level is available now. The present study provides new information regarding the structure of the compound $(C_2N_2H_8O_2) H_6V_{10}O_{28}$, which is formed by the interaction between decavanadate and formhydroxamic acid dimer. The unambiguous structural characterization of the hydrogen bonding observed between formhydroxamic acid dimer and the decavanadate anion based on unequivocal location of the hydrogen-bonding formhydroxamic acid dimer involved clearly illustrates between polyoxometalates and formhydroxamic acid dimer³⁻⁵.

* E-mail: sdjingfu@public.cc.jl.cn

Experimental

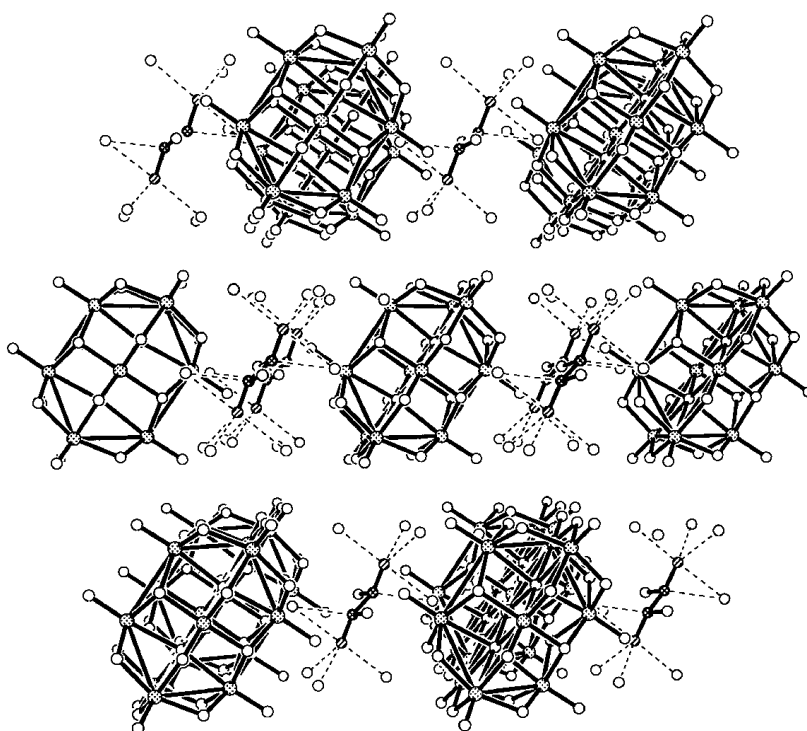
NaOH (6.0 g, 0.15 mol) in 50 mL of H₂O solution was stirred at room temperature. HCOOC₂H₅ (7.5 g, 0.1 mol), NH₂OH•HCl (7.0 g, 0.1 mol) and NaBH₄ (3.8 g, 0.1 mol) were added with stirring for 16 h, and then 2 mL 30% aqueous hydrogen peroxide was added dropwise to give a clear orange solution. The pH of this solution was adjusted to 6.5 - 7.0 with HCl (1:1), and then VOSO₄•3H₂O (11.0 g, 0.05 mol) in 30 mL of H₂O was added dropwise. The solution was stirred overnight and then kept for two months and brown crystals were collected. Elemental analysis (C, H and N) was performed on a Perkin-Elmer 2400 CHN Elemental analyzer. V was determined by a Leaman inductively coupled plasma (ICP) spectrometer. The elemental analysis found: C 2.04 %, H 2.28 %, N 2.39 %, V 43.94 % (Calcd. C 2.06 %, H 2.25 %, N 2.41 %, V 43.78 %).

Figure 1 ORTEP drawing of the compound



The structure of the compound was determined by single crystal X-ray diffraction. **Figure 1** and **2** showed the molecular and crystal structure of the compound, respectively. Crystallographic data: C_{0.25}H_{3.25}N_{0.25}O_{4.5}V_{1.25}, M = 145.46, triclinic, P $\bar{1}$, a = 8.4960 (17), b = 10.447 (2), c = 11.299 (2) Å, β = 87.35 (3)°, V = 855.3 (3) Å³, Z = 8, D_{calc} = 2.100 g cm⁻³, λ (Mo-K α) = 0.71073 Å, F(000) = 536. An orange crystal with dimensions of 0.150×0.145×0.105 mm³ was mounted inside a glass fiber capillary. Data were collected on a Siemens P4 four-circle diffractometer at 293 K in the range of 1.94 < θ < 27.48° using the ω -scan technique. A total of 3749 (3749 independent, R_{int} = 0.044553) reflections were measured. Empirical absorption correction (ψ scan) was applied. The structure was

Figure 2 View of crystal packing of the compound along a axis for clarity, $[C_2H_8N_2O_2]$ and $V_{10}O_{28}^{6-}$ units are omitted.



solved by the direct method and refined by the Full-matrix least squares on F^2 using the SHELXL-93 software. All of the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located from difference Fourier maps. The structure solution and refinement based on 3749 independent reflections with $I > 2\sigma(I)$ and 253 parameters gave $R1$ ($wR2$) = 0.0857 (0.2551).

Results and Discussion

The data of elemental analysis are in accordance with the chemical formula. The single crystal X-ray analysis reveals that the compound consists of $[V_{10}O_{28}]^{6-}$ and $[C_2H_8N_2O_2]$. The observation of the interactions between the decavanadate anion and the associated $[C_2H_8N_2O_2]$ unit are the most interesting aspects of this structure. The hydrogen bonding interaction between N and O indicates the presence of the doubly bridging oxygen atom. Our unambiguous location of hydrogen oxygen bonds in the present structure is thus in accordance with both experimental and theoretical predictions regarding the basicity of oxygen sites on the decavanadate⁷⁻¹⁰. Other studies have reported interactions between cations and the oxygen atoms of the decavanadate anion. Very weak hydrogen bonding interactions between N atom and single and doubly coordinated oxygen atoms in decavanadate anion have also been observed¹¹⁻¹³. The H bonds observed in the formhydroxamic acid dimer in generating those H bonds that are most favorable^{1,2}.

Acknowledgments

We thank the National Natural Science Foundation of China for financial support (No. 20171011).

References

1. K. Elvingson, A. González Baró, L. Pettersson, *Inorg. Chem.*, **1996**, 35, 3388.
2. D. Crans, Comments *Inorg. Chem.*, **1994**, 16, 1.
3. M. M. Williamson, D. A. Bouchard, C. L. Hill, *Inorg. Chem.*, **1987**, 26, 1436.
4. D. Crans, M. Tahir, O. Anderson, M. Miller, *Inorg. Chem.*, **1994**, 33, 5586.
5. E. E. Hamilton, P. E. Fanwick, J. J. Wilker, *J. Am. Chem. Soc.*, **2002**, 124, 78.
6. Y. G. Li, E. B. Wang, S. T. Wang, *et al.*, *J. Mol. Struct.*, **2002**, 606, 175.
7. G. C. McClellan, A. L. Eds, W. H. Freeman. *CA*. **1960**, 225.
8. W. G. Klemperer, W. Shun. *J. Am. Chem. Soc.*, **1977**, 99, 3544
9. J. Y. Kempf, M. M. Rohmer, J. M. Poblet, C. Bo, M. Benard. *J. Am. Chem. Soc.*, **1992**, 114, 1136.
10. V. W. Day, W. G. Klemperer, D. J. Maltbie. *J. Am. Chem. Soc.*, **1987**, 109, 2991.
11. A. G. Swallow, F. R. Ahmed, *et al.*, *Acta Crystallogr.*, **1966**, 21, 397.
12. P. A. Durif, M. T. Averbuch-Pouchot. *Acta Crystallogr. Sect. B: Struct. Sci.*, **1980**, 36, 680.
13. X. Wang, H. X. Liu, X. X. Xu, X. Z. You. *Polyhedron*, **1993**, 12, 77.

Received 2 June, 2003