Communication

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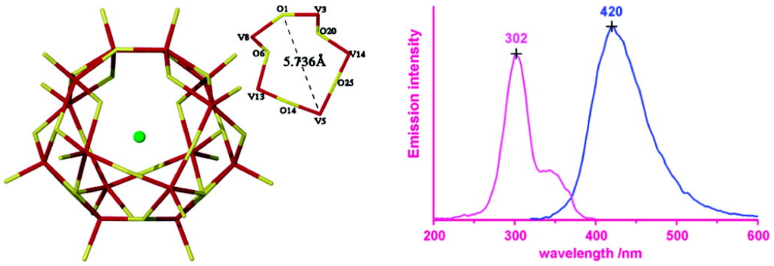

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A Basket Tetradecavanadate Cluster with Blue Luminescence

Lian Chen, Feilong Jiang, Zhengzhong Lin, Youfu Zhou, Chengyang Yue, and Maochun Hong*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, and Graduate School of the Chinese Academy of Sciences, Fujian, Fuzhou 350002, China

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Polyoxometalates have received long-lasting research interest because of their esthetically appealing structures and wide-ranging applications in catalysis, coatings, pigments, smart materials, luminescence, electrochemistry, biochemistry, and medicine.[1] In the large polyoxometalate family, polyoxovanadates, especially the mixed-valence clusters, form one of the most interesting subgroups due to their known abilities to catalyze redox reactions and to act as cathodes in lithium batteries.[2] Vanadate clusters in aqueous solutions have been studied extensively, and the reported structures include $(V_3O_9)^{3-}$, $(V_5O_{14})^{3-}$, $(V_8O_{14})^{4-}$, $(V_{12}O_{32})^{4-}$, $(V_{13}O_{34})^{3-}$, $(V_{15}O_{42})^{9-}$, and $(H_2V_{16}O_{39})^{7-}$.[3] Most of these clusters exhibit the closed sphere-like structures,[3] and only $(V_{12}O_{32})^{4-}$ has an open, bowl-shaped framework that can act as a host.[3d] Thus far, most polyoxovanadates have been synthesized in aqueous solution or under hydrothermal conditions, which may limit further research in this area. New synthetic routes, especially those in organic media with soluble vanadium precursors, are worth exploring, for they may lead to the assembly and construction of new vanadate clusters containing different compositions and frameworks.

In this communication, we report the first tetradecavanadate synthesized from organic solution. This mixed-valence vanadium compound displays an unprecedented half-open basket-shaped structure and gives an intense blue luminescent emission in solution.

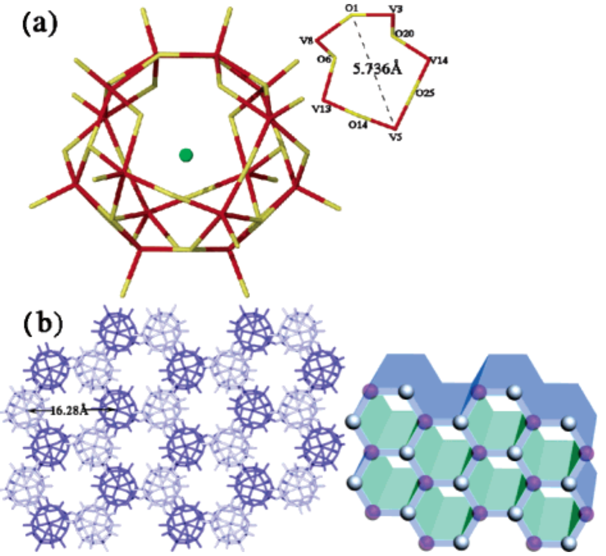

Figure 1. (a) Floral basket-shape tetradecavanadate cluster of **1** with large openings below the basket handle. (b) Clusters of **1** display the hexagonal close packing (left) and form infinite one-dimensional channels (right). The Et_4N^+ cations are omitted for clarity.

The compound $[Et_4N]_5[V_{14}O_{36}Cl]$ (**1**) was obtained from the reaction of $VO_2(acac)$, Et_3N, and Et_4NCl in CH_3CN and was crystallized from DMF solution. We employed $VO_2(acac)$ as a soluble VO_2^+ source and the amine as a Lewis base to adjust the reaction conditions. The compound **1** is air-stable both in the solid state and in solution at room temperature. Single-crystal X-ray analysis[4] reveals that compound **1** is composed of a $\{V_{14}O_{36}\}$ cage, a chloride anion, and five Et_4N^+ cations. In the cage, the vanadium atoms are all five-coordinated with the VO_5 square pyramid coordination geometry and are divided into four groups according to their coordination with different bridging oxygen atoms (μ_2-oxygen or μ_3-oxygen atoms). These distorted VO_5 square pyramids constitute the novel half-open $\{V_{14}O_{36}\}$ shell configuration by sharing edges and vertexes through 10 μ_2-oxygen and 12 μ_3-oxygen atoms. Unlike most known polyoxovanadate clusters that exhibit closed sphere-like structures, this $\{V_{14}O_{36}\}$ shell contains two large openings at the surface, which makes it resemble a floral basket, as shown in Figure 1a. These two large openings below the handle of the basket both exhibit the irregular 10-membered rings consisting of V and O atoms. The longest distances between the diametrically opposed atoms in the two openings are 5.736 (Figure 1a) and 5.744 Å (not shown), respectively. The $\{V_{14}O_{36}\}$ shell is a highly irregular cage, whose only symmetry element is a 2-fold axis, which makes $\{V_{14}O_{36}\}$ a chiral cluster. The space group of the whole compound is noncentrosymmetric with the flack polarity parameter of 0.01(4). Encapsulated in the open cavity of $\{V_{14}O_{36}\}$ is a chloride anion, the average V$\cdots$Cl distance being 3.496 Å. Inclusion of an anionic guest into an anionic molecular oxide host has previously been observed in polyoxovanadate clusters with hollow structures.[5] These molecular oxides make closed cages, which prevent the guests from coming out of the host shells. However, the $V_{14}O_{36}$ shell in **1** has a half-open structure, which may offer a path for the guest to exchange with other ions. To our knowledge, these kinds of half-open basket polyoxovanadates, which can be viewed as intergradation from open bowl-like to closed cage structures, have never before been reported in polyoxometalate chemistry. Furthermore, the crystal packing of compound **1** is also interesting. As shown in Figure 1b, compound **1** can be described as a microstructured pseudohexagonal aggregate. Seen from the [001] axis, the $\{V_{14}O_{36}\}$ clusters display an {ABAB...}-type of close-packed layers forming hexagonal close packing (hcp). Every six clusters run along the 3-fold axis to form infinite one-dimensional channels, where the tetraethylammonium cations reside between the layers as well as inside the channels to counterbalance the negative charges of clusters and to stabilize the structure of **1**.[6] The diameter of the inside pseudohexagonal "pore" is about 9.831 Å, while the distance between the opposite central chloride anions of clusters in the channel is about 16.26 Å. As estimated by the PLATON program,[7] compound **1** has a large accessible void accounting for 64.7% of the crystal volume, which may be attributed to the large space between the mutually repulsive cluster anions.

The assignment of the oxidation states for the vanadium atoms is consistent with the electric charge and confirmed by bond valence sum calculations. The valence sums[8] ($\Sigma s = \exp\Sigma[(1.803 - d)/0.37]$, d = V$-$O distance in Å) for the 14 vanadium atoms are 4.33, 5.02,

10.1021/ja0422209 CCC: $30.25

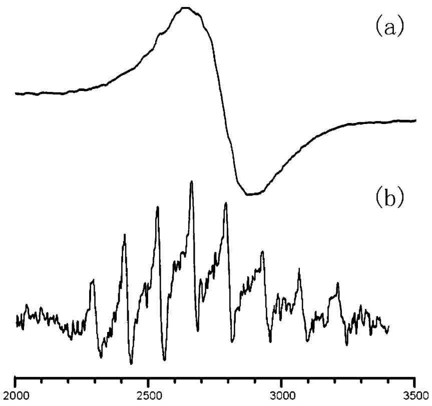

Figure 2. EPR spectra of compound **1**: (a) in solid state and (b) in aqueous solution.

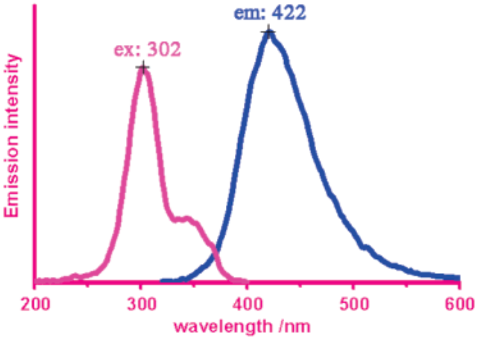

Figure 3. Luminescence excitation and emission spectra of compound **1** in aqueous solution at room temperature.

5.01, 4.95, 4.49, 5.07, 5.01, 4.37, 4.98, 5.03, 4.52, 4.96, 5.03, and 5.08. The average value of 4.85 is in good agreement with the expected bond valence of 4.86 calculated from the composition of $[Et_4N]_5[V_2^{IV}V_{12}^{V}O_{36}Cl]$. Although the vanadium atoms in **1** are in the mixed oxidation states, compound **1** gives a room temperature paramagnetic signal with $g = 1.9549$ in the solid state and exhibits an eight-line hyperfine structure (^{51}V, $I = 7/2$) with $g = 1.9566$ in aqueous solution (Figure 2). The eight-line spectrum suggests that the two V^{IV} atoms are indistinguishable in the half-open $\{V_{14}O_{36}\}$ shell through the C_2 symmetry operation. The broad, weak peaks may be attributed to small unresolved couplings to vanadium neighbors of the V^{V} sites.[9] The UV−vis spectrum of compound **1** (0.4 mM in H_2O) shows a broad absorption band ranging from 500 to 200 nm with three main shoulders at ca. 205, 258, and 314 nm, corresponding to oxide-to-vanadium charge transfer (LMCT).[1b,9,10] When the concentration is increased to 10 mM, a weak broad band appears around 900 nm, which is tentatively assigned to intervalence charge transfer (IVCT, $V^{4+} \rightarrow V^{5+}$).[9,10] With excitation at $\lambda = 302$ nm, this compound in aqueous solution produces intense blue luminescence, peaking at 422 nm (Figure 3). Since the excitation band of **1** is comparable with its LMCT absorption bands in UV−vis, it is likely that the origin of the emission involves an emissive state derived from an oxide-to-vanadium charge transition.[1b,9,10] Note that luminescence properties have rarely been reported for vanadium oxide clusters.

In summary, we have synthesized from organic media a blue luminescent tetradecavanadate complex with mixed-valence vanadium atoms. The results are significant not only for producing a novel type of polyoxovanadium cluster but also for further exploration of vanadate clusters through introducing new synthetic routes. On the basis of the mixed-valence and photophysical properties, the title compound could be active in photo-oxidation reactions and a potential photocatalyst,[11] which is worth further investigation.

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Supporting Information Available: X-ray crystallographic data in CIF format; complete ref 5a; bond lengths and angles; UV−vis absorption spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Katsoulis, D. E. *Chem. Rev.* **1998**, *98*, 359−387. (b) Yamase, T. *Chem. Rev.* **1998**, *98*, 307−325. (c) Sadakane, M.; Steckhan, E. *Chem. Rev.* **1998**, *98*, 219−237. (d) Rhule, J. T.; Hill, C. L.; Judd, D. A.; Schinazi, R. F. *Chem. Rev.* **1998**, *98*, 327−357. (e) Weber, R. S. *J. Phys. Chem.* **1994**, *98*, 2999−3005.

(2) (a) Gaspar, A. R.; Evtuguin, D. V.; Neto, C. P. *Ind. Eng. Chem. Res.* **2004**, *43*, 7754−7761. (b) Bose, A.; He, P.; Liu, C.; Ellman, B. D.; Twieg, R. J.; Huang, S. D. *J. Am. Chem. Soc.* **2002**, *124*, 4−5.

(3) (a) Hamilton, E. E.; Fanwick, P. E.; Wilker, J. J. *J. Am. Chem. Soc.* **2002**, *124*, 78−82. (b) Day, V. W.; Klemperer, W. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1989**, *111*, 4518−4519. (c) Hegetschweiler, K.; Morgenstern, B.; Zubieta, J.; Hagrman, P. J.; Lima, N.; Sessoli, R.; Totti, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 3436−3439. (d) Day, V. W.; Klemperer, W. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1989**, *111*, 5959−5961. (e) Hou, D.; Hagen, K. S.; Hill, C. L. *J. Am. Chem. Soc.* **1992**, *114*, 5864−5866. (f) Hou, D.; Hagen, K. S.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1993**, 426−428. (g) Lin, B. Z.; Liu, S. X. *Chem. Commun.* **2002**, 2126−2127.

(4) Crystal data for $[Et_4N]_5[V_{14}O_{36}Cl]$: $M_r = 1975.86$, orthorhombic, space group $Pca2_1$, $a = 24.315(6)$, $b = 13.850(4)$, and $c = 21.742(6)$, $V = 7322(3)$, $Z = 4$, $F(000) = 4008$, $Dc = 1.792$, $R = 0.0781$, $wR = 0.1824$, and $S = 1.072$ for 9364 reflections with $I > 2\sigma(I)$.

(5) (a) Müller, A. et al. *Inorg. Chem.* **1997**, *36*, 5239−5250. (b) Müller, A.; Krickemeyer, E.; Penk, M.; Rohlfing, R.; Armatage, A.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1674−1677. (c) Khan, M. I.; Yohannes, E.; Doedens, R. J. *Inorg. Chem.* **2003**, *42*, 3125−3129.

(6) (a) Özkar, S.; Finke, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 5796−5810. (b) Aiken, J. D., III; Finke, R. G. *J. Am. Chem. Soc.* **1999**, *121*, 8803−8810.

(7) Spek, L. A. *PLATON*, Multipurpose Crystallographic Tool. Utrecht University: Utrecht, The Netherlands, 1999.

(8) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr. Sect. B* **1991**, *47*, 192−197.

(9) (a) Chen, Q.; Goshorn, D. P.; Scholes, C. P.; Tan, X. L.; Zubieta, J. *J. Am. Chem. Soc.* **1992**, *114*, 4667−4681. (b) Codd, R.; Hambley, T. W.; Lay, P. A. *Inorg. Chem.* **1995**, *34*, 877−882. (c) Mondal, A.; Sarkar, S.; Chopra, D.; Guru Row, T. N.; Pramanik, K.; Rajak, K. K. *Inorg. Chem.* **2005**, *44*, 703−708.

(10) (a) Chen, Q.; Hill, C. L. *Inorg. Chem.* **1996**, *35*, 2403−2405. (b) Williamson, M. M.; Bouchard, D. A.; Hill, C. L. *Inorg. Chem.* **1987**, *26*, 1436−1441. (c) Müller, A.; Meyer, J.; Bögge, H.; Stammler, A.; Botar, A. *Chem.—Eur. J.* **1998**, *4*, 1388−1397.

(11) (a) Troupis, A.; Hiskia, A.; Papaconstantinou, E. *Environ. Sci. Technol.* **2002**, *36*, 5355−5362. (b) Jaynes, S. B.; Hill, C. L. *J. Am. Chem. Soc.* **1995**, *117*, 4704−4705. (c) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34−38.

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