A Heteropolyanion Containing Two Linked Mixed Mo/V Pentadecaoxometalate Clusters: Structure of $[Mo_{16}V_{14}O_{84}]^{14-}$

Yiping Zhang,[a,b] **Robert C. Haushalter,***[b] **Abraham Clearfield***[a]

[a] *Department of Chemistry, Texas A & M University, College Station, TX 77843*
[b] *NEC Research Institute, 4 Independence Way, Princeton, NJ 08540*

A novel thirty metal atom mixed Mo/V heteropolyanion has been hydrothermally synthesized and structurally characterized by single crystal X-ray diffraction.

There has been considerable current interest in the chemistry of polyoxometalates from both fundamental and practical points of view.[1,2]. Polyoxovanadates have been recently subjected to intensive study with many structurally characterized examples now known. Polyvanadate anions of $[V_{10}O_{28}]^{6-}$[3] and $[V_{12}O_{32}]^{4-}$[4] are among the well-known examples. Recently, tridecavanadate $[H_{12}V_{13}O_{40}]^{3-}$[5] and pentadecavanadate $[V_{15}O_{42}]^{9-}$[6] have been reported. The structure of pentadecavanadate, $[V_{15}O_{42}]^{9-}$, containing a central VO_4 unit, is based on the well known $\{XM_{12}O_{40}\}$ α-Keggin structure with two additional five-coordinate terminal VO^{3+} units capping the pits on either side of the Keggin unit which lie on the two-fold axis. Other closely related structures have also been reported for heteropolyvanadates. Examples include bicapped $\{PV_{14}\}$[7] and monocapped $\{PV_{13}\}$.[8] While the number of polyoxovanadates containing exclusively V^V continues to grow, the chemistry of reduced polyoxovanadates has also received recent attention.[9–15] In the course of our ongoing exploration of the use of

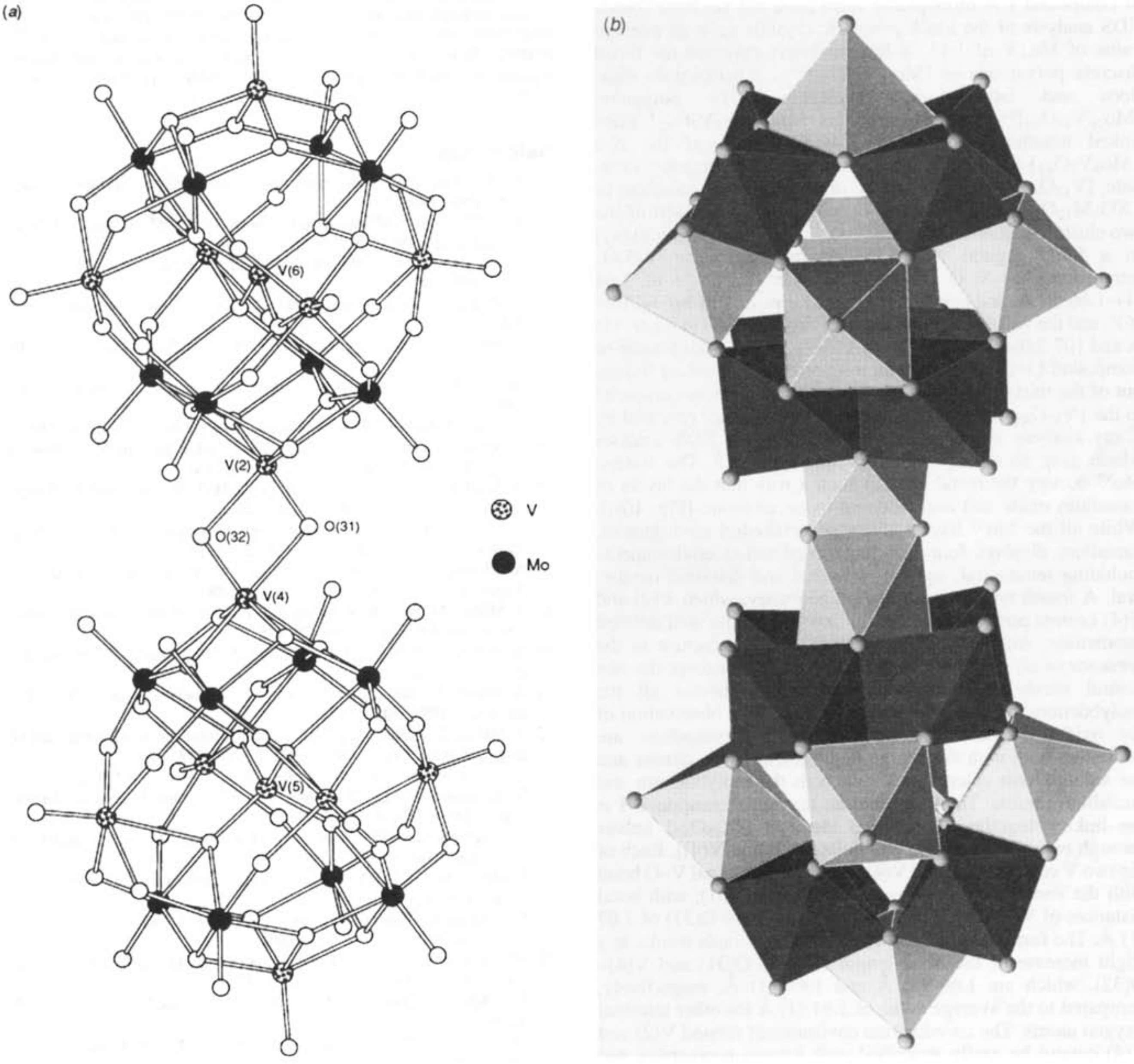

Fig. 1 (*a*) A ball and stick representation of the structure of the $[Mo_{16}V_{14}O_{84}]^{14-}$ polyanion. (*b*) A polyhedral representation of the structure of the $[Mo_{16}V_{14}O_{84}]^{14-}$ polyanion. The darker polyhedra represent Mo polyhedra.

hydrothermal techniques to prepare reduced polyoxomolybdates[16] and polyoxovanadates[17–18] of phosphates and phosphonates containing organic templates, we have isolated a series of 3-D supercage compounds of reduced polyvanadium phosphates containing fragments of known polyoxometalate structures.[19] While hydrothermal techniques have proven well suited for the preparation and crystal growth of the metal phosphates and phosphonate materials, this technique has also been successfully applied for the preparation of polyoxometalates.[20–23] Here we report the hydrothermal synthesis and single crystal investigation of a mixed Mo/V polyoxometalate, $(H_2NC_4H_8NH_2)_7[Mo^{VI}_{16}V^{IV}_{12}V^{V}_2O_{84}]\cdot nH_2O$ (*n ca.* 9) **1** which contains two $\{Mo_8V_7O_{42}\}$ units linked together by two V–O–V bonds.

Compound **1** was prepared as a minor product by a hydrothermal method. A mixture of $CsVO_3$, MoO_3, $H_2O_3PCH_3$, piperazine, 4,4′-dipyridyl hydrate and H_2O in the mole ratio of 1.31 : 1.0 : 2.52 : 2.22 : 1.24 : 782 was sealed in 23 cm^3 Teflon-lined reactor which was kept at 170 °C for 66 h. Black prismatic crystals of compound **1** were obtained (*ca.* 20% based on Mo) along with a mixture of an unidentified black powder and small plate-like crystals. The optimum conditions for the preparation of compound **1** in monophasic form have not yet been found. EDS analysis of the black prismatic crystals gave an average value of Mo : V of 1.15. X-Ray analysis† revealed the novel discrete polyanions of $[Mo_{16}V_{14}O_{84}]^{14-}$, piperazinium dications and lattice water molecules. The polyanion $[Mo_{16}V_{14}O_{84}]^{14-}$ (Fig. 1) contains two $\{Mo_8V_7O_{42}\}$ units linked together *via* two V–O bonds. Each of the two $\{Mo_8V_7O_{42}\}$ units is structurally similar to the pentadecavanadate, $[V_{15}O_{42}]^{9-}$, which is based on the α-Keggin structure of $\{XO_4M_{12}O_{36}\}$ with two *trans* capping VO units. Each of the two clusters contains a central V^{5+} [V(5) and V(6), respectively] in a fairly regular tetrahedral environment. The $V(5)O_4$ tetrahedron has V–O bond distances in the range of 1.64 (1)–1.66 (1) Å, and bond angles in the range of 106.7 (6)–115.4 (6)°, and the values for $V(6)O_4$ tetrahedron are 1.63 (1)–1.67 (1) Å and 107.2 (6)–114.0 (6)°, respectively. An unusual feature of compound **1** is the replacement, in an ordered fashion, of sixteen out of the thirty total metal sites by molybdenum as compared to the $\{V_{15}O_{42}\}$ structure. The number of Mo sites revealed by X-ray analysis is consistent with the result of EDS analysis which gave an average value of Mo : V of 1.15. The sixteen Mo^{VI} occupy the metal sites in such a way that the layers of vanadium oxide and molybdenum oxide alternate [Fig. 1(*b*)]. While all the Mo^{VI} have a distorted octahedral environment, vanadium displays four different coordination environments including tetrahedral, square pyramidal and distorted octahedral. A fourth type of coordination geometry, which V(2) and V(4) centres possess, does not fall into any of the well defined geometries. Another unusual feature of the structure is the presence of all vanadium in reduced form V^{IV} [except the two central tetrahedral ones which are V^{V}], whereas all the molybdenum are in the 6+ oxidation state. This observation of the oxidation states for molybdenum and vanadium are consistent both with the charge requirement of the cluster and the valance sum calculations[24] on both the molybdenum and vanadium centres. The most unusual feature of compound **1** is the linking together of the two identical $\{M_{15}O_{42}\}$ halves through two of the capping VO units [V(2) and V(4)]. Each of the two V centres, V(2) and V(4), forms an additional V–O bond with the vanadyl oxygen atoms, O(32) and O(31), with bond distances of V(2)–O(32) of 2.06 (1) Å and V(4)–O(31) of 2.07 (1) Å. The formation of these two additional bonds results in a slight increase of the bond length of V(2)–O(31) and V(4)–O(32), which are 1.66 (1) Å and 1.68 (1) Å, respectively, compared to the average value of 1.61 (1) Å for other terminal oxygen atoms. The coordination environment around V(2) and V(4) cannot be easily described with known geometries, but most closely resembles a distorted trigonal prism. To the best of our knowledge, this geometry has not been observed in other polyoxovanadates. The two V centres are separated by a distance of 2.879 (4) Å.

The work at Texas A&M University was supported by the National Science Foundation under grant No. DMR-9107715 for which grateful acknowledgment is made.

Received, 21st March 1995; Com. 5/01795E

Footnote

† *Crystal Data* for **1**: Monoclinic, $P2_1/c$, a = 20.435 (6), b = 25.067 (7), c = 20.498 (7) Å, and β = 93.95 (3)°, V = 10 458 (4) Å^3, Z = 4. A black prismatic crystal with dimensions of 0.2 × 0.3 × 0.3 mm was mounted on a glass fibre. Data were collected on a Rigaku AFC7R four-circle diffractometer at 20 °C in the range of $5° < 2\theta < 50°$ using an ω scan technique. No decay of the crystal was observed throughout the data collection. A total of 14 226 reflections was collected of which 8353 reflections with $I_0 \geqslant 3\sigma(I_0)$ were used. An empirical absorption correction using the program of DIFABS was applied. The structure was solved by direct methods (MITHRIL) and refined using teXsan crystallographic software package of Molecular Structure Corporation. The metal atoms were refined anisotropically, and the remaining of non-hydrogen atoms refined isotropically. Structure solution and refinement based on 8353 reflections with $I_0 \geqslant 3\sigma(I_0)$ and 823 parameters gave $R(Rw)$ = 0.052 (0.059). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer Verlag, New York, 1983.

2 M. T. Pope and A. Müller, *Angew. Chem.*, 1991, **103**, 56; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34.

3 V. W. Day, W. G. Klemperer and D. J. Maltbie, *J. Am. Chem. Soc.*, 1987, **109**, 2991.

4 V. W. Day, W. G. Klemperer and O. M. Yaghi, *J. Am. Chem. Soc.*, 1989, **111**, 5959.

5 L. Pettersson, I. Andersson and O. W. Howarth, *Inorg. Chem.*, 1992, **31**, 4032.

6 D. Hou, K. S. Hagen and C. L. Hill, *J. Chem. Soc., Chem. Commun.*, 1993, 426.

7 R. Kato, A. Kobayashi and Y. Sasaki, *Inorg. Chem.*, 1982, **21**, 240.

8 A. Selling, I. Andersson, L. Pettersson, C. M. Schramm, S. L. Downey and J. H. Grate, *Inorg. Chem.*, 1994, **33**, 3141.

9 A. Müller, E. Kreickemeyer, M. Penk, H.-J. Walberg and H. Bögge, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1045.

10 A. Müller, M. Penk, E. Krickemeyer, H. Bögge and H.-J. Walberg, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1719.

11 A. Müller, E. Krickemeyer, M. Penk, V. Wittneben and J. Döring, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 88.

12 A. Müller, M. Penk, R. Rohlfing, E. Krickemeyer and J. Döring, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 926.

13 A. Müller, R. Rohlfing, J. Döring and M. Penk, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 588.

14 A. Müller, J. Döring, M. I. Khan and V. Wittneben, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 210.

15 A. Müller, E. Kreickemeyer, M. Penk, R. Rohlfing, A. Armatage and H. Bögge, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1674.

16 R. C. Haushalter and L. A. Mundi, *Chem. Mater.*, 1992, **4**, 31.

17 V. Soghomonian, Q. Chen, R. C. Haushalter and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 610.

18 V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta and C. J. O'Connor, *Science*, 1993, **259**, 1596.

19 L. Meyer, M. I. Khan, V. Soghomonian, J. Zubieta and R. C. Haushalter, manuscript in preparation.

20 M. I. Khan, Q. Chen, D. P. Goshorn, H. Hope, S. Parkin and J. Zubieta, *J. Am. Chem. Soc.*, 1992, **114**, 3341.

21 M. I. Khan, A. Müller, S. Dillinger, H. Bögge, Q. Chen and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1780.

22 M. I. Khan, Q. Chen, D. P. Goshorn and J. Zubieta, *Inorg. Chem.*, 1993, **32**, 672.

23 M. I. Khan, Q. Chen, H. Höpe, S. Parkin, C. J. O'Connor and J. Zubieta, *Inorg. Chem.*, 1993, **32**, 2929.

24 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B, Struct. Sci.*, 1985, **41**, 244.