Polish J. Chem., **75**, 1791–1796 (2001) **COMMUNICATION**

Synthesis and Structure of $[Ni(en)_2]_2H\{[Ni(en)_2][Mo^{V}_{4}Mo^{VI}_{4}V^{IV}_{8}O_{40}(V^{V}O_4)]\}\cdot 3H_2O$ with 1-D Extended Heteronuclear Chains

by Q.X. Zeng, J.Q. Xu[*], G.Y. Yang, X.B. Cui, Y.J. Song and Z.D. Zheng

Department of Chemistry, Jilin University, Changchun 130023, P. R. China

(Received March 28th, 2001; revised manuscript July 5th, 2001)

Polyoxometallates containing Keggin moieties have provoked significant interest in their new structure architectures and potential applications to catalysis, sorption, clathration, electrical conductivity, magnetism and photochemistry [1–8]. While extensive Keggin and transition metal substituted Keggin species have been reported, structural types about capped Keggin structures are very limited, and only mono- bi-, and tetra-capped Keggin derivatives are structurally known [9,10]. To date, there is only one known example of tetra-capped Keggin discrete clusters. Polymers of clusters with a diverse structure have been obtained by fusion of polyoxoanion subunits [11]. Here we report the 1-D cluster polymer consisting of polyanion $\{[Ni(en)_2]$-$[Mo^{V}_{4}Mo^{VI}_{4}V^{IV}_{8}O_{40}(V^{V}O_4)]\}^{5-}$ with tetra-capped Pseudo-Keggin structure mode as a cluster unit. At the center of the cage structure lie two half-occupied VO_4 tetrahedrons.

Compound $[Ni(en)_2]_2H\{[Ni(en)_2][Mo^{V}_{4}Mo^{VI}_{4}V^{IV}_{8}O_{40}(V^{V}O_4)]\}\cdot 3H_2O$ **1** was prepared hydrothermally from a mixture of MoO_3, V_2O_5, $Ni(OAc)_2$, en, $H_2C_2O_4\cdot 2H_2O$ and water in the molar ratio of 1.0:1.3:1.3:2.5:2.5:275 which was sealed in 30 cm^3 Teflon-lined reactor and was kept at 160°C for 72 h. To black prismatic crystal of **1** was obtained (*ca*. 35% based on Mo) along with a mixture of an unidentified brown powder. The IR spectrum of **1** exhibited intense bands at 970, 840, 720 and 675 cm^{-1}, attributed to ν(M=O), ν(M–O–M) (M = V or Mo).

The single-crystal X-ray structure analysis of the thin black prismatic crystal revealed that the title compound, as shown in Figure 1, consists of infinite chains of $[Ni(en)_2]_2H\{[Ni(en)_2][Mo^{V}_{4}Mo^{VI}_{4}V^{IV}_{8}O_{40}(V^{V}O_4)]\}\cdot 3H_2O$ clusters covalently linked through $[Ni(1)(en)_2]$ spacers, and isolated $[Ni(2)(en)_2]^{2+}$ cations, occupying the interchain regions and providing charge compensation. The final atomic coordinates, thermal parameters, and list of observed and calculated structure factors have been deposited as supplementary material at the Cambridge Crystallographic Data Center (CCDC 119244).

---

[*] Author to whom all correspondence should be addressed.

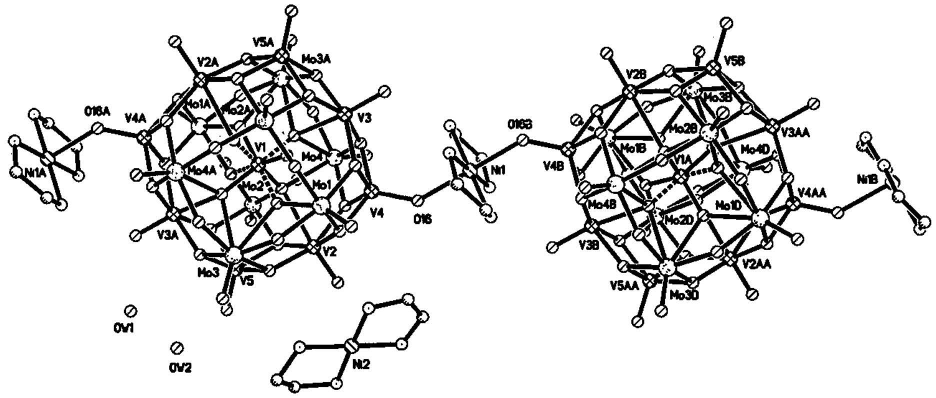

Figure 1. The structure of $[Ni(en)_2]_2H\{[Ni(en)_2][Mo^{V}_{4}Mo^{VI}_{4}V^{IV}_{8}O_{40}(VO_4)]\}\cdot 3H_2O$ (the O atoms of the central VO_4 group are disordered, have an occupancy of 0.5, two tetragonals have the same centre, the V–O bonds of one tetragonal indicated by dotted lines).

The polyanion $\{Mo^{V}_{4}Mo^{VI}_{4}V^{IV}_{8}O_{40}(V^{V}O_4)\}^{7-}$ is based on the well know Pseudo-Keggin structure of $[XM_{12}O_{40}]^{n-}$ with four additional five-coordinated terminal {VO} units, which include V(4), V(5) and its symmetry-related partner V(4A) and V(5A). This tetracapped Pseudo-Keggin structure exhibits the common Pseudo-Keggin core, which consists of four internally edge-shared triads $\{Mo_2VO_{13}\}$ corner-shared to each other and disposed tetrahedrally around a central two-half occupied vanadium atom with T_d symmetry. Caps are formed through the ligation of oxygen atoms on the four opposite $\{Mo_2V_2O_4\}$ faces or pits to each {VO} units such that square pyramidal vanadium coordination environments are generated.

In the polyanion $\{Mo^{V}_{4}Mo^{VI}_{4}V^{IV}_{8}O_{40}(VO_4)\}^{7-}$, two VO_4 tetrahedra at the center with occupancy factor of O being 0.5 form an almost regular cube; distance range of V(1)–O are 1.622(14)–1.724(15) Å, and O–V(1)–O angles vary from 106.4(7)° to 112.1(7)°. The metal-oxygen bonds in MoO_6 octahedra are not equivalent. The variation of Mo–O bond lengths in MoO_6 octahedra can be well correlated to the coordination number of oxygen atoms; the longest Mo–O distances [2.387(15)–2.518(15) Å for μ_4-O], and the shortest Mo–O distance [1.648(8)–1.665(9) Å for terminal oxygen] are the typical values, while the Mo–O distances for μ_2-O and μ_3-O are between 1.858(9)–1.884(11) Å and 1.960(9)–2.006(8) Å, respectively. In the VO_6 octahedra, the metal to oxygen distances vary as follows: to terminal oxygen atom 1.608(8)–1.635(10) Å, to triply bridging oxygen, 1.966(10)–1.996(9) Å, and to μ_4-O, 2.405(15) Å and 2.408(14) Å. The capping V(5) and V(5A) atoms are all bound to five oxygen atoms, including one terminal (V–O, 1.635(10) Å), and four triply bridging (V–O, 1.938(8)

Å–1.952(9) Å) oxygen atoms. V(4) and V(4A) at the cap positions are all connected to four triply bridging oxygen atoms (V–O, 1.923(9)–1.946(8) Å) and one doubly bridging oxygen atom bonding spacer group $[Ni(1)(en)_2]$ (V–O, 1.633(8) Å). The Ni atom in the spacer group is coordinated to four N atoms from ethylene diamine ligands with Ni–N distances of 2.062(11) Å and 2.073(11) Å and two oxygen atoms bonded to cluster units $\{Mo_4Mo_4V_8O_{40}(VO_4)\}^{7-}$ with Ni–O distance of 2.152(8) Å, forming an almost regular coordination octahedron with N–Ni(1)–O bond angle range of 89.3(4)–90.7(4)°. The Ni–N distances of 1.842(19)–1.942(15) Å in compensation cation $[Ni(en)_2]^{2+}$ are obviously shorter than those in the spacer group, and this resulted probably from different coordination numbers of Ni atoms. There exist hydrogen bonds of distance range 2.979 Å to 3.210 Å between nitrogen atoms of spacer groups and terminal oxygen atoms of the cluster units (see Figure 2). Thus, the polymer chains of the clusters are linked to form a supramolecular network through the hydrogen bonds. The assignment of oxidation states for the vanadium and molybdenum atoms are confirmed by valence sum calculations [12], which give the values for Mo(1), Mo(2), Mo(3) and Mo(4) of 5.442, 5.523, 5.417 and 5.40, while the calculated valence sums for V(1), V(2), V(3), V(4) and V(5) are 5.307, 3.960, 3.970, 4.007 and 3.908, respectively. The average value of Mo(1)–Mo(4) and V(2)–V(5) are 5.446 and 3.961 respectively, consistently with the formula of **1**.

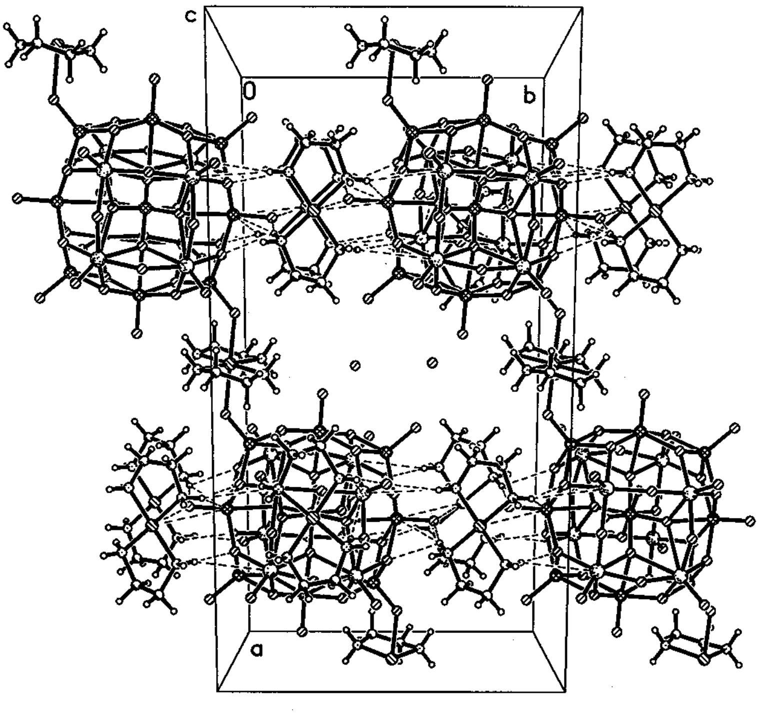

Figure 2. The unit cell of $[Ni(en)_2]_2H\{[Ni(en)_2][Mo^{V}_{4}Mo^{VI}_{4}V^{IV}_{8}O_{40}(VVO_4)]\}\cdot 3H_2O$. The hydrogen bonds indicated by dotted lines.

Table 1. Crystal data.

$C_{12}H_{55}Mo_8N_{12}Ni_3O_{47}V_9$	MoKα radiation
$Mr = 2521.79$	$\lambda = 0.71073$ Å
Monoclinic	
$C2/c$	
cell parameter from 50 Reflections	
$a = 26.260(5)$ Å	$\theta = 1.71–23.01°$
$b = 13.542(3)$ Å	$\mu = 3.551$ mm^{-1}
$c = 19.580(4)$ Å	T = 293(2) K
$\beta = 105.93(3)$ °	0.48 × 0.36 × 0.24 mm
$V = 6696(2)$ Å^3	Black cube
$Z = 4$	$F(000)$ 5012
$D_x = 2.502$ Mg/m^3	
Data collection	
Siemens P4 diffractometer	Rint = 0.0263
Absorption corrections:	$\theta_{max} = 23.01°$
ω Scans	$h = -27 \rightarrow 27$
Empirical *via* ψ Scans	$k = -1 \rightarrow 12$
(North *et al.*, 1968)	$l = -21 \rightarrow 21$
9828 Measured reflections	3 standard reflections
4338 reflections with	Every 97 reflections
$I > 2\sigma(I)$	
Refinement	
Refinement on F^2	$\Delta\ \rho_{max} = 1.800$ eÅ^{-3}
$R_1 = 0.0513$	$\Delta\ \rho_{max} = 1.040$ eÅ^{-3}
$wR_2 = 0.1579$	Extinction correction: none
$S = 1.098$	International Tables for
4338 reflections	Crystallography (Vol.C)
437 parameters	
H atoms: riding model	
$w = 1/[\sigma^2(Fo^2) + (0.0778P)^2 + 212.179P]$	
Where $P = (Fo^2 + 2Fc^2)/3$	

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 ×10^3) for title compound. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Mo(1)	2000(1)	3474(1)	1417(1)	24(1)
Mo(2)	2910(1)	4108(1)	–1207(1)	32(1)
Mo(3)	3365(1)	3703(1)	1528(1)	30(1)
Mo(4)	1538(1)	3885(1)	–1342(1)	33(1)
Ni(1)	0	5000	0	32(1)
Ni(2)	2613(1)	7302(2)	1602(1)	65(1)
V(1)	2500	2500	0	27(1)
V(2)	2410(1)	5144(2)	191(1)	23(1)
V(3)	1113(1)	2252(2)	–121(1)	28(1)
V(4)	1318(1)	4422(2)	60(1)	24(1)
V(5)	3531(1)	4808(2)	257(1)	36(1)
O(1)	2367(4)	6323(7)	268(5)	40(2)
O(2)	1113(4)	4523(8)	–1961(5)	46(3)
O(3)	3943(4)	5737(8)	360(6)	63(3)
O(4)	1969(3)	4671(7)	803(4)	34(2)
O(5)	491(3)	2162(7)	–187(5)	39(2)
O(6)	3088(3)	4851(7)	901(4)	36(2)
O(7)	1744(3)	4846(8)	–547(4)	44(2)
O(8)	3583(4)	3884(7)	485(5)	49(3)
O(9)	3524(8)	2378(8)	1741(8)	109(7)
O(10)	2175(4)	4152(13)	–1572(5)	97(6)
O(11)	3128(6)	2545(11)	574(8)	22(3)
O(12)	2863(3)	5055(9)	–462(4)	52(3)
O(13)	3813(5)	3683(8)	856(6)	67(4)
O(14)	2728(4)	3635(9)	1773(6)	71(4)
O(15)	3084(4)	4831(7)	–1794(5)	48(3)
O(16)	830(3)	5159(7)	79(5)	37(2)
O(17)	1339(4)	3265(7)	637(5)	45(2)
O(18)	1112(4)	3468(7)	–698(5)	50(3)
O(19)	3758(4)	4254(8)	2236(5)	50(3)
O(20)	1782(4)	3927(8)	2070(5)	53(3)
O(21)	2040(5)	2125(7)	1606(6)	81(4)
O(22)	2081(5)	2338(11)	488(8)	20(3)
O(23)	2604(6)	1414(11)	404(7)	23(4)
O(24)	2529(6)	3394(11)	561(8)	24(4)
N(1)	3075(8)	8281(12)	1407(8)	89(6)
N(2)	3225(7)	6533(11)	1932(8)	73(4)
N(3)	2009(8)	8044(14)	1252(13)	105(7)
N(4)	2139(6)	6336(11)	1835(7)	67(4)
N(5)	90(5)	5897(10)	876(6)	50(3)

Table 2 (continuation)

N(6)	165(5)	3893(9)	760(6)	46(3)
C(1)	3611(12)	7860(20)	1461(16)	125(10)
C(2)	3730(10)	7090(19)	2017(14)	104(8)
C(3)	1568(16)	7550(30)	1230(20)	170(15)
C(4)	1621(10)	6663(18)	1630(12)	94(7)
C(5)	131(11)	5273(18)	1506(9)	108(9)
C(6)	297(14)	4351(19)	1453(10)	142(13)
OW1	4976(12)	3810(40)	1832(17)	210(30)
OW2	4624(7)	4812(13)	2566(9)	119(6)

Acknowledgments

This work was supported by the National Science Foundation of China (29733090), the Research Funds for the Doctoral Program of Higher Education, and State Key Laboratory of Coordination Chemistry, Najing University.

REFERENCES

1. Pope M.T., *Herteropoly and Isopoly Oxometalates*. Springer-Verlag, Berlin,1983.
2. Pope M.T. and Müller A., *Angew Chem. Int. Ed. Engl.*, **30**, 34 (1991).
3. Pope M.T. and Müller A., *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*. Kluwer Academic Publishers, Dordrecht, The Netherlands, 1994.
4. Gatteschi D., Kahn O., Miller J.S. and Palacio F., *Magnetic Molecular Materials*, NATO ASI Ser. E, 198 (1991).
5. Bruce D.W. and O'Hare D., *Inorganic Materials*, Wiley, Chichester, 1992.
6. Petty M.C., Bryce M.R. and Bloor D., *Introduction to Molecular Electronics*, Edward Arnold, London, 1995.
7. Fujita M., Kwon Y.J., Sasahi O., Yamaguchi K. and Ogura K., *J. Am. Chem. Soc.*, **117**, 7287 (1995).
8. Masciocchi N., Cairati D., Carlucci L., Mezza G., Ciani G. and Sireni A., *J. Chem. Soc. Dalton Trans*, 2739 (1996).
9. Xu Y., Xu J.Q., Yang G.Y., Wang T.G., Xing Y., Lin Y.H. and Jia H.Q., *Polyhedron*, **17**, 2441 (1998).
10. Xu Y., Zhu H. G., Cai H. and You X.Z., *Chem. Commun.*, 787 (1999).
11. Hagrman D., Zapf P.J. and Zubieta J., *J. Chem. Soc. Chem. Commun.*, 1283 (1998).
12. Brown I.D. and Altermatt D., *Acta Cryst.*, **B41**, 244 (1985).