

$[\{\text{Mo}^{\text{VI}}_8\text{V}^{\text{IV}}_4\text{O}_{36}(\text{VVO}_4)(\text{V}^{\text{IV}}\text{O})_2\}_n]^{7n-}$: capped α -Keggin fragments linked to a chain

Achim Müller,* Michael Koop, Peter Schiffels and Hartmut Bögge

Fakultät für Chemie der Universität, D-33501 Bielefeld, Germany

The synthesis and single-crystal X-ray structure analysis of the unusual Mo/V polyoxometalate compound $\text{Na}_{0.5}\text{K}_{6.5}[\text{Mo}^{\text{VI}}_8\text{V}^{\text{IV}}_4\text{O}_{36}(\text{VVO}_4)(\text{V}^{\text{IV}}\text{O})_2] \cdot 12.5\text{H}_2\text{O}$ which contains capped α -Keggin fragments linked to a chain is reported; this chain is an interesting object for magnetochemists and can be considered to consist of an assembly of electron storage units.

Despite their ability to act as ligands, polyoxometalate clusters are generally reported as discrete entities, for instance as Keggin type anions or their derivatives.^{1,2} Very few examples are known where polymers are built up (like chains) for instance by linking anionic polyoxometalate ligands with transition-metal centres^{3–5} as in the case of $[\{(\text{Co}^{\text{II}}(\text{H}_2\text{O})_4)_2(\text{H}_2\text{W}_{12}\text{O}_{42})\}_n]^{6n-}$. Only one compound has been reported in which a derivative of a lacunary $\{\text{W}_{11}\}$ type species (that means with an integrated low-valent metal atom) was linked to a chain,⁶ but until now, no corresponding compound has been isolated in which chains are built up by a classical polyanion containing metal centres from only group 5 and 6. Here we report the synthesis and single-crystal X-ray structure analysis of the blue-violet mixed valent polyoxometalate compound $\text{Na}_{0.5}\text{K}_{6.5}[\text{Mo}^{\text{VI}}_8\text{V}^{\text{IV}}_4\text{O}_{36}(\text{VVO}_4)(\text{V}^{\text{IV}}\text{O})_2] \cdot 12.5\text{H}_2\text{O}$ **1** containing capped, reduced α -Keggin type fragments which are linked to a chain.

Compound **1** was prepared by heating a solution of VOCl_2 (10 mmol), $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (20 mmol) and KCl (93.9 mmol) in 60 ml degassed water (pH 6.2) for 5 days at 45–50 °C in an argon atmosphere. Blue-violet crystals of **1** which precipitated from the solution at 45 °C (46% yield based on Mo) were filtered and characterized by a single-crystal X-ray structure analysis (including bond valence sum calculations),[†] vibrational spectra,[‡] and redox titrations for the determination of the number of V^{IV} centres. Compound **1** rapidly decomposes in solution in the presence of air, whereby a yellow colour is observed.

The crystal structure of **1** shows the abundance of chains built up by 'trans-vanadium' capped α -Keggin type $\{\text{Mo}^{\text{VI}}_8\text{V}^{\text{IV}}_4\text{O}_{36}(\text{VVO}_4)(\text{V}^{\text{IV}}\text{O})_2\}$ units [Fig. 1(a)]. These are structurally similar to the two $\{\text{Mo}_8\text{V}_7\text{O}_{42}\}$ units which build up the discrete $[\text{Mo}^{\text{VI}}_{16}\text{V}^{\text{IV}}_{12}\text{V}^{\text{V}}_2\text{O}_{84}]^{14-}$ anion.⁷ The structure of the basic (anionic) unit of **1** [Fig. 1(b)] can be described as follows: four Mo^{VI} centres of an α -Keggin type $[\text{Mo}^{\text{VI}}_{12}\text{O}_{36}(\text{VVO}_4)]^{3-}$ species are replaced by V^{IV} centres resulting in a 'layered' type structure formed by the different metal atoms. The corresponding three layers are spanned by one $\{\text{V}_5\}$ set and two $\{\text{Mo}_4\}$ type sets, the latter being separated by 4.8 Å [Fig. 1(a)]. The $\text{V}^{\text{IV}} \cdots \text{V}^{\text{IV}}$ distance between atoms within each layer is 5.1 Å and ca. 11 Å between layers in adjoining units. Therefore the compound is interesting for the study of exchange interactions by the magnetochemist. The rhombicuboctahedron spanned by 24 μ_3 -O atoms of the Keggin unit is capped at two parallel (100) planes by 2 $\{\text{V}^{\text{IV}}\}$ $[\text{V}(3)]$ groups (for details of the relevant topology see ref. 8). If all of the six equivalent planes were capped, a unit with a similar structure to the $\{\text{V}_{12}\text{O}_{36}(\text{VO}_4)(\text{VO})_6\}$ type species⁹ would result. Whereas the Mo^{VI} and V^{IV} centres Mo(1), Mo(2) and V(1) have, as expected, rather regular octahedral coordination environments, the two V(3) centres [Fig. 1(b)] possess a highly distorted octahedral

coordination environment, bordering on the distorted trigonal-prismatic geometry described for the above mentioned discrete $[\text{Mo}^{\text{VI}}_{16}\text{V}^{\text{IV}}_{12}\text{V}^{\text{V}}_2\text{O}_{84}]^{14-}$ anion.⁷ The Keggin fragments are linked by $\text{V}(3)\text{--O}(11)\text{--V}(3)$ bridges forming chains along the *c* axis [$\text{V}(3)\text{--O}(11)$ 1.88(1) Å; separation of adjacent V(3) centres 2.81(1) Å].

The formation of **1** is facilitated by the direct use of a solution containing VO^{2+} ions. The relevant reaction using V^{V} centres under similar reaction conditions at pH 4–6.5 yields the discrete $[\text{Mo}^{\text{VI}}_6\text{V}^{\text{V}}_2\text{O}_{26}(\text{H}_2\text{O})_{16}]^{6-}$ anion.^{10,11} In a previous investigation of the $\text{V}^{\text{IV}}/\text{Mo}^{\text{VI}}$ system^{12,13} it was erroneously proposed that such solutions with relative concentration $\text{Mo}^{\text{VI}}/\text{V}^{\text{IV}} = 2$ yielded the salts $\text{K}_4\text{H}_2[\text{V}_2\text{Mo}_4\text{O}_{19}] \cdot 9\text{H}_2\text{O}$ at pH 4.5 and $\text{K}_2\text{H}_4[\text{V}_2\text{Mo}_4\text{O}_{19}]$ at pH 3, whereby the authors assumed that these would contain Lindquist type anions. One can envisage the formation of the obtained chains *via* the initial formation of highly nucleophilic species such as $\{\text{Mo}^{\text{VI}}_8\text{V}^{\text{IV}}_4\text{O}_{36}(\text{VVO}_4)\}^{11-}$ {whose structure may be analogous to the discrete $[\text{Mo}^{\text{VI}}_8\text{V}^{\text{IV}}_4\text{O}_{40}(\text{VO}_4)]^{7-}$ anions¹⁴} and the subsequent interception of these by the VO^{2+} nucleophiles present in solution. This deliberation corresponds to our general procedure to generate growth of species by increasing their negative charge and consequently their nucleophilicity, a procedure which facilitates the generation of increasingly larger molecular systems. In the

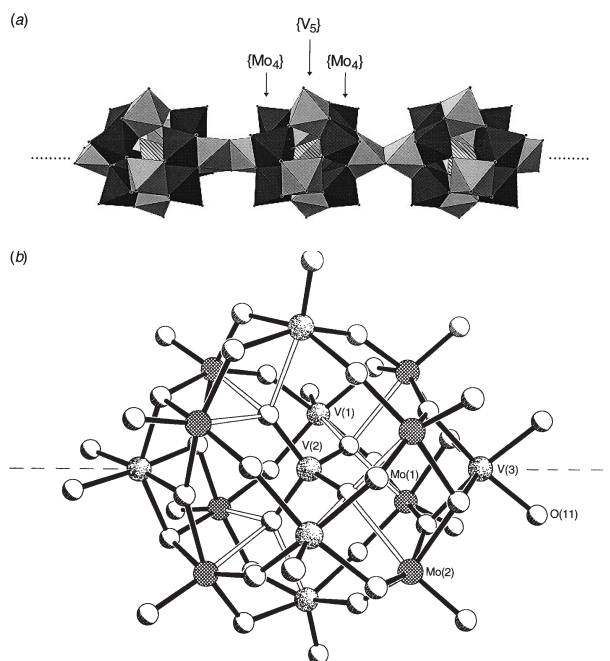


Fig. 1 The structure of the polymeric anion in crystals of **1**: (a) polyhedral representation (darker polyhedra represent $\text{Mo}^{\text{VI}}\text{O}_6$ octahedra, hatched ones the VVO_4 tetrahedra). The Mo^{VI} and V^{IV} atoms of the relevant polyhedra span $\{\text{Mo}^{\text{VI}}_4\}$ and $\{\text{V}^{\text{IV}}_4\}$ layers. (b) Ball-and-stick representation of the capped α -Keggin type unit with stoichiometry $\{\text{Mo}^{\text{VI}}_8\text{V}^{\text{IV}}_4\text{O}_{36}(\text{VVO}_4)(\text{V}^{\text{IV}}\text{O})_2\}$; V atoms dotted, Mo atoms cross hatched; $\text{V}(2)\text{--O}$ 1.71(1) Å, $\text{V}(3)\text{--O}(11)$ 1.88(1) Å, $\text{V}(3)\cdots\text{V}(3')$ 2.81(1) Å; $\text{O}(11)\text{--V}(3)\text{--O}(11)$ 83.0(5)°.

present case, the increased nucleophilicity results from the simple replacement of metal centres with a high oxidation state (Mo^{VI}) by those with a lower one (V^{IV}). Groups containing the V^{IV} centres are directly added to the reaction medium which is in contrast to an earlier investigation¹⁵ where a solution containing Mo^{VI} and V^{V} centres was treated with a reducing agent, thus resulting in the reduction of the V^{V} , but also some of the Mo^{VI} . Additionally, it is important to note that in the present case, linking *via* $\text{V}^{\text{IV}}\text{--O--V}^{\text{IV}}$ bonds is preferred to linking *via* $\text{Mo}^{\text{VI}}\text{--O--Mo}^{\text{VI}}$ bonds as a consequence of the expected higher basicity of the O atom in M–O bonds containing M centres in lower oxidation states.

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Footnotes and References

* E-mail: amueller@cheops.chemie.uni-bielefeld.de

† *Crystal data* for **1**: $\text{H}_{25}\text{K}_{6.5}\text{Mo}_8\text{Na}_{0.5}\text{O}_{54.5}\text{V}_7$, $M = 2286.95 \text{ g mol}^{-1}$, tetragonal, space group $I4/m$, $a = 14.941(2)$, $c = 22.124(5) \text{ \AA}$, $U = 4938.8(15) \text{ \AA}^3$, $D_c = 3.076 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 3.89 \text{ mm}^{-1}$, $Z = 4$, $T = 198 \text{ K}$, $R = 0.052$ for 1428 reflections with $I_0 \geq 2\sigma(I_0)$, crystal dimensions: $0.1 \times 0.1 \times 0.2 \text{ mm}$; Siemens R3m/V diffractometer (Mo-K α , graphite monochromator). A total of 2503 reflections were collected ($4 < 2\theta < 50^\circ$). The structure was solved by direct methods¹⁶ and refined¹⁶ by full-matrix least-squares techniques. In the asymmetric unit two under-occupied sodium positions were found each at a distance of *ca.* 1.8 \AA from two (also underoccupied) potassium positions. The occupancy factors of the disordered atoms were refined in agreement with the above given formula. Ψ -scan reflections for an empirical absorption correction were collected. As the absorption correction showed no significant effect, however, the uncorrected data were used in the final refinement process. The bond valence sum calculations indicate, as expected, the presence of only Mo^{VI}

and V^{IV} centres in the shell, as well as one central V^{V} atom. CCDC 182/547.

‡ *Characteristic spectroscopic data* for **1**: IR, ν/cm^{-1} (KBr pellet prepared under argon, $1100\text{--}400 \text{ cm}^{-1}$): $\nu(\text{V=O})/\nu(\text{Mo=O})$ 976m, 952m; $\nu_{\text{as}}(\text{M--O--M}')$; M, M' = Mo, V) 848s, 815m, 754m; Raman ($\lambda_e = 1064 \text{ nm}$): $\nu(\text{V=O})/\nu(\text{Mo=O})$ 989w, 817s; VIS–NIR, λ_{max} (KBr pellet): *ca.* 575 nm.

- 1 M. Pope and A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34.
- 2 M. Pope, *Heteropoly and Isopoly Oxometalates, Inorganic Chemistry Concepts*, Springer, Berlin, 1983, vol. 8.
- 3 V. Molchanov, I. Tatjanina and E. Torchenkova, *J. Chem. Soc., Chem. Commun.*, 1981, 93.
- 4 T. Yamase and H. Naruke, *J. Chem. Soc. Dalton Trans.*, 1991, 285.
- 5 C. Giménez-Saiz, J. Galán-Mascarós, S. Triki, E. Coronado and L. Ouahab, *Inorg. Chem.*, 1995, **34**, 524.
- 6 J. Galán-Mascarós, C. Giménez-Saiz, S. Triki, C. Gómez-García, E. Coronado and L. Ouahab, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1460.
- 7 Y. Zhang, R. Haushalter and A. Clearfield, *J. Chem. Soc., Chem. Commun.*, 1995, 1149.
- 8 A. Müller, M. Penk and J. Döring, *Inorg. Chem.*, 1991, **30**, 4935.
- 9 A. Müller, J. Döring, H. Bögge and E. Krickemeyer, *Chimia*, 1988, **42**, 300.
- 10 A. Björnberg, *Acta Crystallogr., Sect. B*, 1979, **35**, 1995.
- 11 A. Bekturov, A. Il'yasova and A. Amirbekova, *Zh. Neorg. Khim.*, 1970, **15**, 2781; *Russ. J. Inorg. Chem.*, 1970, **15**, 1446.
- 12 D. Labonnette and S. Ostrowetsky, *C. R. Acad. Sci. Ser. C*, 1976, **282**, 341.
- 13 D. Labonnette, *J. Chem. Res.*, 1979, (S) 252; (M) 2801.
- 14 A. Björnberg, *Acta Crystallogr., Sect. B*, 1980, **36**, 1530.
- 15 E. Krickemeyer, S. Dillinger, T. Heitkamp and K. Janiak, unpublished work.
- 16 SHELXS-86 and SHELXS-93, Programs for crystal structure solution and refinement, respectively, G. M. Sheldrick, University of Göttingen.

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