Infinite octamolybdate chains cross-linked by
paramagnetic iron (II) centers

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Abstract: The paper presents a new polymeric polyoxomolybdate cluster with infinite octamolybdate chains cross-linked by iron (II) centers. The layer-type substance contains sodium cations sandwiched between the [Fe(H₂O)₄Mo₈O₂₇]⁻∞ layers. The structure was determined by single crystal X-ray diffraction analysis. Magnetic properties, due to the presence of paramagnetic iron (II) centers, are presented and discussed.
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1 Introduction

According to a widely used definition, polyoxometalates are the polyoxoanions of the early transition elements, mainly Mo, W and V, constructed of linked Moₙ units [1].

Over the past ten years, polyoxometalates underwent a spectacular development surpassing even the most optimistic expectations of the relatively few research groups focusing on this class of substances. The continuous diversification of polyoxometalates

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through the synthesis of an impressive number of new molecules, having interesting electronic structures, high symmetry, unexpected topologies, remarkable magnetic properties and numerous applications in different fields, is very impressive [2-5].

The great majority of polyoxometalate clusters are discrete/individual molecules, generated via condensation of the corresponding oxoanions. Sometimes the condensation process may, however, continue, yielding eventually infinite/polymeric molecules. These infinite clusters are molecular assemblies, generated through an inflationary multiplication of a discrete molecule in one, two or three dimensions, with the formation of chains (1D), layers (2D) or networks (3D) [6].

The largest group of extended polyoxometalate structures is based on octamolybdate units. Substances containing the \([\text{Mo}_8\text{O}_{26}]^{4-}\) octamolybdate anion precipitate from acidified aqueous solutions with \(Z=1.5\) (where \(Z\) is the \(\text{H}^+/{\text{MoO}}_4^{2-}\) molar ratio). The \(\alpha\)- and especially the \(\beta\)-isomer are most commonly crystallized [7-9]. A \(\gamma\)-[\(\text{Mo}_8\text{O}_{26}]^{4-}\) octamolybdate, proposed as an intermediate in the isomerisation process between the \(\alpha\)- and \(\beta\)-forms [10], was subsequently isolated and characterized [11]. Recently, two new isomers of the \([\text{Mo}_8\text{O}_{26}]^{4-}\) anion, namely \(\delta\)- and \(\epsilon\)-, have also been described [12, 13].

A new octamolybdate-type anion, formulated as \([\text{Mo}_8\text{O}_{27}]^{6-}\), was more recently obtained by acidifying aqueous molybdate solutions at a lower \(Z\) value (\(Z = 1.25\)). The new octamolybdate crystallizes as a polymeric anion in the \((\text{NH}_4)_8[\text{Mo}_8\text{O}_{27}].4\text{H}_2\text{O}\) substance [14]. The monomeric \([\text{Mo}_8\text{O}_{27}]^{6-}\) units adopt the basic structure of the \(\gamma\)-[\(\text{Mo}_8\text{O}_{26}]^{4-}\) isomer with two additional terminal positions. This leads to octahedral coordination for all metal centers, yielding 14 terminal and two bridging oxygen atoms, the latter linking the \([\text{Mo}_8\text{O}_{27}]^{6-}\) monomeric units.

The possibility of employing octamolybdates as ligands for metal linkers to form extended one- or two-dimensional structures has been demonstrated using hydrothermal methods to synthesize new and interesting composite networks, containing \(\alpha\) - or \(\beta\)-[\(\text{Mo}_8\text{O}_{26}]^{4-}\) units linked via amine-ligated transition metal ions [15, 16]. These results suggest that it should in principle be possible to synthesize similar first row transition metal-octamolybdate substances without large amine-ligands, which cause solubility problems in aqueous solutions. Using a versatile ligand such as the \([\text{Mo}_8\text{O}_{27}]^{6-}\) octamolybdate, which itself links to chain, would provide, under correct reaction conditions and with a suitable linking ion, ideal conditions for the formation of continuous layer-type substances.

At first, only two lanthanide-octamolybdate polymeric substances, formulated as \(\text{Sm}_2(\text{H}_2\text{O})_{12}[\text{Mo}_8\text{O}_{27}].6\text{H}_2\text{O}\) [17] and \(\text{Eu}_2(\text{H}_2\text{O})_{12}[\text{Mo}_8\text{O}_{27}].6\text{H}_2\text{O}\) [18] were reported. Each \([\text{Mo}_8\text{O}_{27}]^{6-}\) monomeric unit of a chain is supported by two hydrated \(\text{Sm}^{3+}\) or \(\text{Eu}^{3+}\) cations. Recently, two polymeric octamolybdates, which contain a first row transition metal, i.e. \(\text{Na}_4[\text{Mn}(\text{H}_2\text{O})_4\text{Mo}_8\text{O}_{27}].16\text{H}_2\text{O}\) and \(\text{Mn}_2[\text{Mn}(\text{H}_2\text{O})_4\text{Mo}_8\text{O}_{27}].22\text{H}_2\text{O}\), have also been reported [19].

Here we present the synthesis, investigation and characterization of a new polymeric polyoxometalate cluster resulted through the linkage of infinite octamolybdate chains by iron (II) centers. The new substance resembling to the above mentioned polymeric
clusters with manganese (II) centers, is also based on the $[\text{Mo}_8\text{O}_{27}]^{6-}$-type octamolybdate units.

## 2 Results and discussion

### 2.1 Synthetic aspects

The synthetic methodology is based on initially acidifying an aqueous Na$_2$MoO$_4$ · yH$_2$O solution to Z=1.25 (pH ≈ 3) to provide suitable conditions for the formation of the octamolybdate unit $[\text{Mo}_8\text{O}_{27}]^{6-}$. The subsequent addition of an excess of Fe$^{2+}$ ions and a high electrolyte concentration (NaCl) to control the solubility facilitated the precipitation of the crystals. Synthesis conditions were optimized such that single crystals of sufficient size for performing single crystal X-ray structure analysis were obtained. The yield can be improved significantly by increasing the Na$^+$ and Fe$^{2+}$ ions concentration, which consequently leads to an increase in the crystallization rate and a decrease in the crystal size.

### 2.2 Crystal structure analysis

Crystallographic data are summarized in Table 1. The chemical and thermogravimetric analysis suggested, initially, the Na$_4$[Fe(H$_2$O)$_4$Mo$_8$O$_{27}$]·16H$_2$O formula for the synthesized substance. But the fact that the substance is water insoluble indicated a more complex structure. Correspondingly, the single crystal X-ray structure analysis revealed that the new octamolybdate-based cluster has a layer-type structure, consisting of $[\text{Mo}_8\text{O}_{27}]^{6-}$ chains cross-linked by partially hydrated Fe$^{II}$ centers.

The basic/parent $[\text{Mo}_8\text{O}_{27}]^{6-}$ fragment comprises eight MoO$_6$ edge sharing octahedra. Two octahedra (Mo2) share edges with five other octahedra, four octahedra (Mo1, Mo4) share edges with three octahedra and two octahedra (Mo3) share edges with two octahedra. The $[\text{Mo}_8\text{O}_{27}]^{6-}$ fragments are linked through bridging $\mu_2-O$ atoms belonging to the Mo3–O9–Mo3 groups, forming $[\text{Mo}_8\text{O}_{27}]^{\infty}$ chains parallel to the crystallographic a axis. Each chain is cross-linked to an adjacent chain through Fe1–O13–Mo4 bridges, parallel to the c axis, while a $[\text{Fe(H}_2\text{O)}_4\text{Mo}_8\text{O}_{27}]^{\infty}$ layer in the ac plane is formed. The $[\text{Mo}_8\text{O}_{27}]^{6-}$ basic fragment and the $[\text{Fe(H}_2\text{O)}_4\text{Mo}_8\text{O}_{27}]^{4-}$ building block, which can be considered the formal monomer unit, are presented in Fig. 1.

The bridging Fe centers show a slightly distorted octahedral coordination geometry with the bond distances Fe–$(\mu_2-O)$=2.07 Å, Fe–OH$_2$ = 2.09–2.16 Å and the cis–O–Fe–O angles = 87.9–92.1$.^\circ$. The Fe centers form intra-layer parallelograms with dimensions identical to those of the parallelograms spanned by the crystallographic a and c axes. Thus, the Fe centers show intra-layer separation of 9.53 and 11.65 Å, which represents the side lengths of the parallelograms. The Fe centers also exhibit inter-layer separation (between two neighbored layers) of 9.85 Å (Fig. 2).

Interestingly, chains of Na$^+$ ions based on staggered groups of four Na centers ex-
tend parallel to the c axis between the layers. Five H2O ligands (Na–OH2 = 2.38–
2.42 Å) and one oxygen atom from a [Mo8O27]6− fragment (Na–O = 2.37–2.40 Å)
coordinate to each Na, which is also "connected" to an adjacent Na center via two
Na–(H2O)2–Na bridges and to one [Mo8O27]6− fragment via a Na–O–Mo bridge. This
results in additional cross-linking within and between the [Fe(H2O)4Mo8O27]∞ layers via
Mo–O–Na–(H2O)2–Na–O–Mo formal linkages (Fig. 3).

2.3 Magnetic data

The magnetic data indicates a paramagnetic behavior with a weak antiferromagnetic
exchange. The exchange interaction between the FeII metal centers is mediated via
Fe–(O–Mo)5–O–Fe and Fe–(O–Mo)3–O–Fe pathways.

χmolT shows temperature dependence, which is due both to weak antiferromagnetic
coupling and to zero-field splitting of the high spin FeII centers. The 25-fold ((2S + 1)
(2L + 1)) degenerated ground term 5D of the free Fe2+ ion is split in the octahedral
field into a 5E2g doublet and a 5T2g triplet ground state, which is furthermore split by
spin-orbit coupling into three states with J=1, J=2 and J=3. The energy differences
of these states are comparable to kT and are furthermore split by first- and second-order
Zeeman effects in an external field H.

By applying the Van Vleck equation to octahedral FeII complexes with 10 Dq< 13000
cm−1, χmolT equals to 3.97 emu K mol−1 at 300 K, which surpasses the spin-only value
of 3.0 emu K mol−1 for FeII. Typically, simple FeII complexes at room temperature show
χmolT values of 3.13–3.92 emu K mol−1 [8].

The diamagnetic correction, derived from measurements of various diamagnetic poly-
oxomolybdates, was found to be χdia = −315·10−6 emu mol−1.

For the investigated compound, at room temperature χmolT = 3.97 emu K mol−1 and
only significantly decreases below ca. 35 K (Fig. 4). Surprisingly, the typical temperature-
dependent features of an isolated octahedral FeII complex (a slight maximum of χmolT
around ca. 170 K) are not observed.

Interestingly, the approximately linear temperature dependence of χ−1mol resembles a
Curie-Weiss susceptibility term C/(T-Θ) with a Weiss temperature Θ = −1.9 K, indicating
the weak antiferromagnetic coupling (Fig. 5). The deviations of this form are mainly
due to the temperature dependence of the octahedral FeII complexes.

3 Experimental

3.1 Synthesis

40 mL of an aqueous Na2MoO4 · yH2O 0.5 mol dm−3 (20 mmol) solution was acidified
with 3.3 mL 25% HCl. 5.56 g (20 mmol) of FeSO4·H2O and 2.35 g (40 mmol) of NaCl
were subsequently added and the resulting brown-green solution was stored under argon.
The black purple crystals that precipitated after 14 days were filtered off, washed with
50 mL of water and dried under argon. Yield: 0.43 g (10.3 % based on Mo).

3.2 Investigation

The synthesized substance was initially characterized by elemental and thermogravimetric analysis. The chemical analysis was undertaken by OES-ICP with a BIRD 2070 spectrophotometer. Results: found (calculated for Na₄[Fe(H₂O)₄Mo₈O₂₇]·16H₂O) Na 5.51 (5.38); Fe 3.50 (3.27); Mo 45.30 (44.95); H₂O 20.86 (21.08).

Vibrational spectra were recorded on a Bruker FTIR IFS 66 with a Raman FRA 106 unit spectrophotometer (λₑ = 1064 nm). Characteristic spectroscopic data (ν(cm⁻¹)): a) IR (KBr pellet): 944s, 901s [υ(Mo=O)], 841m, 706m, 652sh, 557s.; b) Raman (KBr pellet, λₑ = 1064 nm): 961s, 891s [υ(Mo=O)], 815s; 537s; 467m.

For single crystal X-ray structure analysis (including bond valence sum calculations for determinations of the positions of the H atoms and identification of the Fe²⁺ centers), crystals were removed from the mother liquor and immediately cooled to 183(2) K on a Bruker AXS Smart diffractometer (three circle goniometers with 1 K CCD detector, Mo-Kα radiation, graphite monochromator). The structures were solved with the SHELXS-97 software and refined using the SHELXL-93 software.

Magnetic measurements were completed with a SQUID magnetometer in the temperature range of 3–300 K.

4 Conclusion

A new polymeric polyoxometalate cluster was synthesized. The crystal structure analysis has evidenced an interesting layer-type structure. The substance is made up of [Mo₈O₂₇]∞ chains, cross-linked by hydrated Fe²⁺ centers, thus forming [Fe(H₂O)₄Mo₈O₂₇]∞ layers. Eventually, the [Fe(H₂O)₄Mo₈O₂₇]∞ layers are linked by stacked Na centers.

The polymeric octamolybdate-based cluster, which contains paramagnetic Fe²⁺ centers, also shows a weak antiferromagnetic coupling.

References

[1] M.T. Pope: *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, 1983.
[2] M.T. Pope and A. Müller (Eds.): *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Kluwer, Dordrecht, 1994.
[3] M.T. Pope and A. Müller (Eds.): *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*, Kluwer, Dordrecht, 2001.
[4] C.L. Hill (Ed.): Special Thematic Issue: “Polyoxometalates“, *Chem. Rev.*, Vol. 98, No. 1, (1998).
[5] L. Cronin, A. Müller and D. Fenske: “Nanosized inorganic clusters“, In: R.A. Meyers (Ed.): *Encyclopedia of Physical Science and Technology*, 3rd Ed., Vol. 10, Academic Press, New York, 2002, pp. 303–317.
[6] N. Hall: “Bringing inorganic chemistry to life”, Chem. Commun., (2003), pp. 803–806.

[7] I. Lindquist: “A crystal structure investigation of the paramolybdate ion”, Arkiv. Kemi., Vol. 2, (1950), pp. 325–341.

[8] V.W. Day, M.F. Fredrich, W.G. Klemperer and W. Shum: “Structural and dynamic stereochemistry of α-polyoxomolybdate (α-Mo₈O₄₋₆)”, J. Am. Chem. Soc., Vol. 99, (1977), pp. 952–953.

[9] M.T. Pope: “Molybdenum Oxygen Chemistry: Oxides, Oxo Complexes and Polyanions”, In: S.J. Lippard (Ed.): Progress in Inorganic Chemistry, Vol. 39, Wiley, New York, 1991, pp. 181–257.

[10] W.G. Klemperer and W. Shum: “Synthesis and interconversion of the isomeric α- and β-molybdate (Mo₈O₂₆⁴⁻)”, J. Am. Chem. Soc., Vol. 98, (1976), pp. 8291–8293.

[11] S. Dillinger: “Über die Bildung nanodimensionierter Polyoxometallate aus einfachen Basisfragmenten durch konservative Selbstorganisationsprozesse in wäßrigen Lösungen”, Ph.D. Thesis, University of Bielefeld, 1995.

[12] R. Xi, B. Wang, K. Isobe, K. Toriumi and Y. Ozawa: “Isolation and X-ray Crystal Structure of a New Octamolybdate: [(Rh(Cp*)(µ₂-SCH₃)$_3$][Mo$_8$O$_{26}$] 2CH₃CN (Cp* = η-C$_5$Me$_5$)”, Inorg. Chem., Vol. 33, (1994), pp. 833–836.

[13] P.J. Hagram, D. Hagram and J. Zubieta: “Perspectives in the Solid State Coordination Chemistry”, In: M.T. Pope and A. Müller (Eds.): Polyoxometalate Chemistry From Topology via Self-Assembly to Applications, Kluwer, Dordrecht, 2001, pp. 269–300.

[14] M.L. Niven, J.J. Cruywagen and J.B.B. Heyns: “The 1st observation of gamma-Octamolybdate – Synthesis, Crystal and Molecular-Structure of [Me$_3$N(CH$_2$)$_6$NMe$_3$]$_2$[Mo$_8$O$_{26}$] 2H$_2$O”, J. Chem. Soc., Dalton Trans., (1991), pp. 2007–2011.

[15] M. Inoue and T. Yamase: “Synthesis and Crystal Structures of β-Type Octamolybdates Coordinated by Chiral Lysines”, Bull. Chem. Soc. Jpn., Vol. 68, (1995), pp. 3055–3063.

[16] D. Hagrman, P.J. Zapf and J. Zubieta: “A two-dimensional network constructed from hexamolybdate, octamolybdate and [Cu$_3$(4,7-phen)$_3$]$^{3+}$clusters: [{Cu$_3$(4,7-phen)$_3$}]$_2$[Mo$_{14}$O$_{45}$]”, Chem. Commun., (1998), pp. 1283–1284.

[17] T. Yamase and H. Naruke: “X-Ray Structural Photoluminescence Spectroscopic Investigation of the Europium Octamolybdate Polymer Eu$_2$(H$_2$O)$_{12}$[Mo$_8$O$_{27}$]-6H$_2$O”, J. Chem. Soc., Dalton Trans., (1991), pp. 285–292.

[18] P.J. Zapf, C.J. Warren, R.C. Haushalter and J. Zubieta: “One- and two-dimensional organic-inorganic composite solids constructed from molybdenum oxide clusters and chains linked through {M(2,2'-bpy)}$^{2+}$ fragments (M = Co, Ni, Cu)”, Chem. Commun., (1997), pp. 1543–1546.

[19] A. Müller, A. Patrut, A. Nicoara, M. Koop, H. Bögge, A. Botar, P. Kögerler and M. Schmidtmann: “Cross-linking polymeric octamolybdate chains with paramagnetic manganese (II) centres”, Rev. Roum. Chim., Vol. 47, (2002), pp. 997–1003.

[20] A.F. Orchard: Magnetoochemistry, Oxford University Press, Oxford, 2003.
| Property                                      | Value                                      |
|----------------------------------------------|--------------------------------------------|
| Empirical formula                           | H40 O47 Na4 Fe Mo8                         |
| Formula weight                               | 1707.65                                    |
| Temperature                                  | 183(2) K                                   |
| Wavelength                                   | 0.71073 Å                                  |
| Crystal system                               | Triclinic                                   |
| Space group                                  | PT                                         |
| Unit cell dimensions                         |                                             |
| a = 9.535(3) Å                              | α = 103.927(5)°                           |
| b = 9.849(3) Å                              | β = 100.624(5)°                           |
| c = 11.653(4) Å                             | γ = 95.957(5)°                            |
| Volume                                       | 1031.3(5) Å³                              |
| Z                                            | 1                                          |
| Density (calculated)                         | 2.750 x 10³ kg m⁻³                        |
| Absorption coefficient                       | 2.861 mm⁻¹                                 |
| F(000)                                       | 822                                       |
| Crystal size                                 | 0.24 x 0.06 x 0.04 mm³                     |
| Theta range for data collection              | 1.84 to 27.07°                             |
| Index ranges                                 | -12<=h<=11, -10<=k<=12, -14<=l<=12         |
| Reflections collected                        | 5973                                      |
| Independent reflections                      | 4277 (R(int) = 0.0401)                     |
| Observed reflections (I>2σ(I))               | 3441                                      |
| Absorption correction                        | Semi-empirical from equivalents           |
| Max. and min. transmission                   | 0.4912 and 0.2907                         |
| Refinement method                            | Full-matrix least-squares on F²            |
| Data / restraints / parameters                | 4272 / 0 / 295                            |
| Goodness-of-fit on F²                         | 1.133                                     |
| Final R indices (I>2σ(I))                    | R1 = 0.0612, wR2 = 0.1499                 |
| R indices (all data)                         | R1 = 0.0714, wR2 = 0.1581                 |
| Largest diff. peak and hole                  | 2.962 and -3.059 e Å⁻³                   |

**Table 1** Crystal data and structure refinement for the Na₄[Fe(H₂O)₄]Mo₈O₂₇⁻·16H₂O polyoxometalate cluster with infinite chains.
Fig. 1 Ball-and-stick representation of the \([\text{Fe(H}_2\text{O)}_4\text{Mo}_8\text{O}_{27}]^{4-}\) building block of the \([\text{Fe(H}_2\text{O)}_4\text{Mo}_8\text{O}_{27}]_{\infty}\)-type layer cluster. \([\text{Mo}_8\text{O}_{27}]^{3-}\) fragments are linked to chains through Mo3–O9–Mo3 bridges while the chains are cross-linked through Fe1–O13–Mo4 bridges.
Fig. 2 Section of a $[\text{Fe(H}_2\text{O})_4\text{Mo}_8\text{O}_{27}]_\infty$ layer showing the $[\text{Mo}_8\text{O}_{27}]^{6-}$ fragments in polyhedral representation and the octahedral $\text{Fe}^{II}$ coordination sphere in ball-and-stick representation. The Fe centers form parallelograms in the $ac$ plane.
Fig. 3 Linking of two \([\text{Fe(H}_2\text{O)}_4\text{Mo}_8\text{O}_{27}]_\infty\) layers (shown as section of each 2×3 connected \([\text{Mo}_8\text{O}_{27}]^{6−}\) fragments in polyhedral representation) by stacked Na centers. One Na-6-Na-(μ-OH)_2-Na-O group is emphasized.
Fig. 4 The $\chi_{mol}T$ vs. $T$ curve.

Fig. 5 The $\chi_{mol}^{-1}$ vs. $T$ curve (with two scales).