



Preliminary communication / Communication

A novel two-dimensional framework solid composed of nanosized molybdenum-oxide molecules: synthesis and characterization of $[\{\text{Gd}(\text{H}_2\text{O})_5\}_4\{\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}\}]\cdot 34 \text{H}_2\text{O}$

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Received 15 September 2004; accepted 13 December 2005

Available online 14 July 2005

Abstract

Reaction of the ammonium salt of keplerate, $[\{\text{Mo}^{\text{VI}}\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4\text{CH}_3\text{COO}\}_{30}]^{42-}$ with $\text{Gd}(\text{NO}_3)_3$ leads to complex transformations with $[\{\text{Gd}(\text{H}_2\text{O})_5\}_4\{\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}\}]\cdot 34 \text{H}_2\text{O}$ (**1**) as final product. According to X-ray structural data it contains anions $[\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}]^{12-}$, cross-linked into a neutral 2D-framework by Gd^{3+} ions. **To cite this article:** *N.V. Izarova et al., C. R. Chimie 8 (2005).*

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Résumé

La réaction entre le keplerate d'ammonium $[\{\text{Mo}^{\text{VI}}\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4\text{CH}_3\text{COO}\}_{30}]^{42-}$ et le nitrate de gadolinium $\text{Gd}(\text{NO}_3)_3$ conduit à des transformations complexes, dont la résultante ultime est le composé $[\{\text{Gd}(\text{OH}_2)_5\}_4\{\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{OH}_2)_{16}\}]\cdot 34 \text{H}_2\text{O}$ (**1**). L'analyse structurale par diffraction des rayons X montre un réseau bidimensionnel construit à partir du fragment polyoxométallique $\{\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{OH}_2)_{16}\}$, interconnecté par les groupes $\{\text{Gd}(\text{OH}_2)_5\}$. **Pour citer cet article :** *N.V. Izarova et al., C. R. Chimie 8 (2005).*

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Keywords: Polyoxometalate; Molybdenum; Gadolinium; Coordination polymer; Crystal structure

Mots clés : Polyoxométallate ; Molbdène ; Gadolinium ; Polymère de coordination ; Structure cristalline

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1. Introduction

Giant polyoxometalates (POM) are relatively recent but increasingly fascinating object of study. Their peculiar topological, magnetic, optical and electric properties are being thoroughly investigated. One way of modifying their properties (and structure) is to alter self-assembly conditions, which give a specific giant POM molecule [1,2]. Another way to the structural and functional diversity involves using ‘pre-fabricated’ giant POM as macroligands toward heterometals. The heterometal can bring into the play its own specifics, such as magnetism. It also can exercise a structure-directing influence, facilitating the formation of even larger POM or polymeric frameworks. The oxophilic and paramagnetic lanthanide ions are especially well suited for this purpose [3–5]. One shall always keep in mind, however, that fragmentation and re-assembly of giant POM into different structures can also occur during these reactions. Here we report synthesis and structure of $[\{\text{Gd}(\text{H}_2\text{O})_5\}_4\{\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}\}] \cdot 34 \text{H}_2\text{O}$ (**1**), where the polyoxomolybdate fragments $\{\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}\}$ formed by a degradation of the keplerate, $[\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4\text{CH}_3\text{COO}\}_{30}]^{42-}$, are bound into a 2D-framework by $\{\text{Gd}(\text{H}_2\text{O})_5\}$ units.

2. Experimental section

2.1. Synthesis of **1**

To a stirred solution of $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.90 g, 2.08 mmol) in H_2O (60 ml), the NH_4^+ salt of $[\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4\text{CH}_3\text{COO}\}_{30}]^{42-}$ [6] (1.00 g, 0.036 mmol) was added. The resulting mixture was vigorously stirred in an open 100-ml Erlenmeyer flask (wide-necked) for 24 h. After acidification with HCl (1 M, 3 ml) and addition of NaCl (1.0 g), the stirred reaction mixture was heated to 90–95 °C and then filtered whilst still hot, and kept at 20 °C. After 1.5 months (from time to time separated amorphous solids were removed by filtration) light brown rhombic crystals of **1** were collected by filtration through a glass frit, washed twice with a little iced water, and dried in air. Yield: 0.221 g (23% based on molybdenum).

Elemental analysis for $\text{H}_{140}\text{Gd}_4\text{Mo}_{36}\text{N}_4\text{O}_{182}$ calculated (%): H 1.96; N 0.78; found (%): H 1.85; N 0.83.

IR (KBr pellet, cm^{-1}): 3517 (m); 3448 (m); 3364 (w); 3157 (w); 1617 (m); 1403 (m); 950 (m); 874 (s); 782 (m); 698 (m); 621 (s); 567 (s); 537 (s); 360 (m); 330 (m); 238 (m).

2.2. X-ray structure determination

The crystallographic data for **1** and structure refinement parameters data are listed in Table 1. The structure was solved by direct methods and refined by the full-matrix least-squares technique against P^2 with anisotropic displacement parameters for all atoms except for eight oxygen atoms of solvate water molecules. Two of such solvate water molecules were refined with half occupation. Hydrogen atoms were not defined. The SAINT [7] and SHELXTL-97 [8] program packages were used throughout the calculations.

Table 1
Crystallographic data and details of diffraction experiments for **1**.

| | |
|---|---|
| Empirical formula | $\text{H}_{140}\text{Gd}_4\text{Mo}_{36}\text{N}_4\text{O}_{182}$ |
| Formula weight | 7192.00 |
| Crystal system | Triclinic |
| Space group | <i>PT</i> |
| <i>a</i> (Å) | 13.5035 (14) |
| <i>b</i> (Å) | 16.2894 (17) |
| <i>c</i> (Å) | 18.905 (2) |
| α (°) | 77.376 (2) |
| β (°) | 80.336 (2) |
| γ (°) | 76.042 (2) |
| <i>V</i> (Å ³) | 3908.8 (7) |
| <i>Z</i> | 1 |
| <i>D</i> _{calc} (g cm ⁻³) | 3.055 |
| Temperature (K) | 120 (1) |
| Diffractometer | Bruker SMART 1000 with CCD area detector |
| Radiation | Mo K α ($\lambda = 0.71073$ Å) |
| $2\theta_{\text{max}}$ (°) | 55.60 |
| Range <i>h, k, l</i> | $-16 \leq h \leq 16, -20 \leq k \leq 19, -23 \leq l \leq 23$ |
| μ (mm ⁻¹) | 4.587 |
| Reflections measured | 34 353 |
| Unique reflns | 15 291 |
| <i>R</i> _{int} | 0.0859 |
| Observed ($F_0 > 4\sigma(F_0)$) | 6856 |
| Refined parameters | 987 |
| Restraints | 0 |
| <i>R</i> ₁ , <i>wR</i> ₂ ($I > 2\sigma(I)$) | <i>R</i> ₁ = 0.0781, <i>wR</i> ₂ = 0.1599 |
| <i>R</i> ₁ , <i>wR</i> ₂ (all data) | <i>R</i> ₁ = 0.1703, <i>wR</i> ₂ = 0.1848 |
| Goodness-of-fit on <i>F</i> ² | 1.012 |
| $(\Delta\rho)_{\text{max}}$ (e Å ⁻³) | 4.543 |
| $(\Delta\rho)_{\text{min}}$ (e Å ⁻³) | -4.027 |

3. Results and discussion

Light brown rhombic crystals of **1** are prepared from ammonium salt of keplerate, $[\{(\text{Mo}^{\text{VI}})\text{Mo}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4\text{CH}_3\text{COO}\}_{30}]^{42-}$ and $\text{Gd}(\text{NO}_3)_3$ in 23% yield by the synthetic procedure described in the Experimental Section. The compound has been characterized by elemental analysis, FT-IR spectroscopy and unambiguously by single-crystal X-ray diffraction technique. The compound **1** and $(\text{NH}_4)_{12}[\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}] \cdot 36 \text{H}_2\text{O}$ have similar FT-IR spectra showing only slight shifts in some band positions. The infrared spectra show characteristic absorption bands attributable to H_2O , $\nu(\text{Mo}-\text{O}_{\text{term}})$, $\nu(\text{Mo}-\mu_2-\text{O})$ and $\nu(\text{Mo}-\mu_3-\text{O})$ groups. The $\nu(\text{NO})$ vibrational frequency of 1617 cm^{-1} overlaps with $\delta(\text{HOH})$ and is typical for the linear $\{\text{MoNO}\}^{3+}$ moiety [9].

The structure of **1** was determined by X-ray diffraction from a single crystal, obtained directly in the synthesis. Main bond distances and angles are given in Table 2. The structure is a 2D neutral framework where the POM fragments $\{\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}\}$ [9,10] are united into layers by Gd^{3+} ions (Fig. 1). The POM anion is built of two large Mo_{17} subunits held together by two *cis*- MoO_2^{2+} groups. Within each subunit there are two $\text{Mo}(\text{NO})^{3+}$ groups with pentagonal–bipyramidal coordination, surrounded by five MoO_6 octahedra: three are derived from MoO_4^{4-} , and two from *cis*- MoO_2^{2+} . These six Mo atoms form a five-pointed star; two such stars are held together by two pairs of edge-sharing octahedra (*cis*- MoO_2^{2+} -type), and by one «inner» Mo atom with no terminal oxygen atoms, also octahedrally coordinated. Only terminal groups MoO_2^{2+} coordinate Gd^{3+} , and altogether 12 terminal oxygen

atoms of $[\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}]^{12-}$ participate in this bonding. If we designate the two octahedra, attached to the $\text{Mo}(\text{NO})^{3+}$ unit, as ‘coordinated’, type A; those in the dimer, holding two ‘stars’ together in each subunit, as «periferic», type B, and those holding two Mo_{17} subunits together, as ‘closing’, type C, we obtain the following pattern of the coordination polymer lattice building: in one direction (along *b* axis) we have ...type A– MoO_2^{2+} – Gd^{3+} –type C– MoO_2^{2+} ... regularity, while in the other direction (along *c* axis) this pattern is ...type A– MoO_2^{2+} – Gd^{3+} –type B– MoO_2^{2+} There are two unique gadolinium(III) atoms in the structure of **1**. Each Gd^{3+} ion is octacoordinated. Two neighboring A-type MoO_2^{2+} groups behave as bidentate ligands, while those of B- and C-types are monodentate. Thus the coordination polyhedron of each Gd is filled with three POM oxygen atoms, the rest being coordinated water.

Crystal packing of **1** consists of the adjusted neutral layers stacked in a *ABAB*... mode (Fig. 2). There are three types of solvent water molecules in **1**. Two water molecules are clathrated in the inner cavity of the POM. Some of them are placed inside the layer and others lay in the gap between adjacent layers. There is an extended network of hydrogen bonds involving water molecules and oxygen atoms of the cluster.

The structure of the title two-dimensional framework solid compound closely resembles that of recently published chain-like polymeric compounds $[\text{La}_2(\text{MoO})_2\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}] \cdot 68 \text{H}_2\text{O}$ (**2**) and $(\text{H}_3\text{O})_{12}\{[\text{Mo}_2\text{O}_5(\text{H}_2\text{O})_2][\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}]\} \cdot 44 \text{H}_2\text{O}$ (**3**) [11,12]. Compound **2** was prepared by directly from $[\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}]^{12-}$ and La^{3+} in the presence of hydroxylammonium chloride [11]. Two electrophilic MoO^{3+} groups in **2** are weakly coordi-

Table 2
Selected bond distances (Å) and angles (°) in **1**

| Bond type | Distance (Å) | Angle | Value (°) |
|---------------------------------------|-----------------------|--------------------------------------|---|
| Gd–O | 2.333(16)–2.49 (2) | $\text{Mo}-\mu_4-\text{O}-\text{Mo}$ | 95.65 (1)–102.16 (1) 144.76 (1)–146.67 (1) |
| Mo– O_{term} | 1.662 (17)–1.932 (13) | $\text{Mo}-\mu_2-\text{O}-\text{Mo}$ | 88.50 (1)–121.25 (1) |
| Mo– $\text{O}_{\text{H}_2\text{O}}$ | 2.214 (15)–2.535 (3) | $\text{Mo}-\mu_3-\text{O}-\text{Mo}$ | 150.81 (1)–159.06 (1) |
| Mo– $\mu_2-\text{O}$ | 1.731 (13)–2.398 (13) | $\text{Mo}-\mu_2-\text{O}-\text{Gd}$ | 91.22 (1)–111.34 (1) 133.53 (1)–144.76 (1) |
| Mo– $\mu_3-\text{O}$ | 1.880 (12)–2.275 (12) | | 152.40 (1)–153.40 (1) 166.30 (1) |
| Mo– $\mu_4-\text{O}$ | 2.087 (13)–2.296 (12) | | |
| Mo–N | 1.663 (16)–2.371 (15) | | |
| N–O | 1.22 (2)–1.22 (3) | | |
| Mo– O_{Gd} Chto eto?? | 1.688 (14)–1.757 (15) | | |

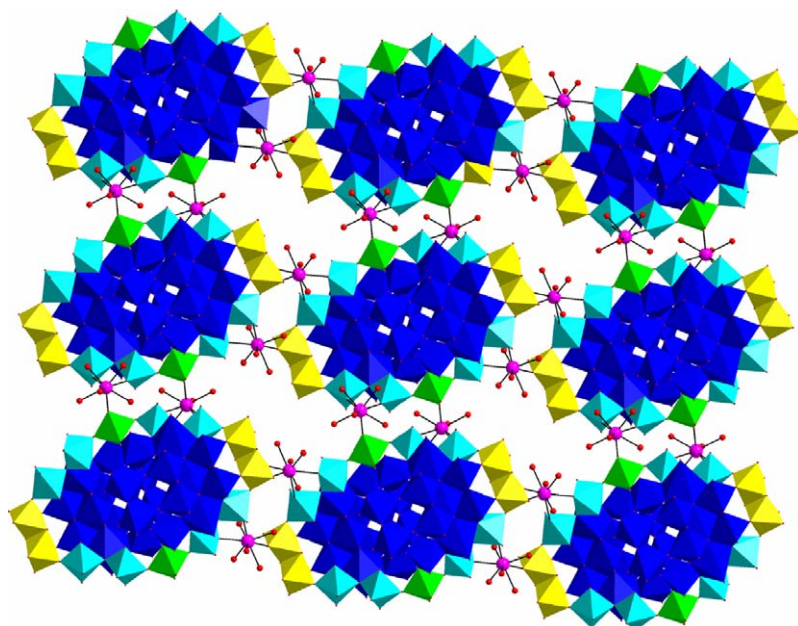


Fig. 1. Connectivity pattern in the crystal structure of compound **1** (view along a axis) distinguishing between the building units or constituents: $\{\text{Gd}(\text{H}_2\text{O})_3\}$ fragments in ball-and-stick (Gd-purple; O-red) and $\{\text{Mo}_{36}\}$ fragments in polyhedra (cyan-type A octahedra; yellow-type B octahedra; green-type C octahedra; blue-the rest of polyhedra) representation. Only one layer is shown. Crystallization water molecules are omitted for clarity.

nated by type A cis-MoO_2^{2+} . Chain-building is through type A- MoO_2^{2+} - La^{3+} (CN 9)-type C- MoO_2^{2+} interactions. In **3** the same $[\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}]^{12-}$ repeating units are connected by bridging $\{\text{Mo}_2\text{O}_4(\mu\text{-O})(\text{H}_2\text{O})_2\}$ groups coordinated to A-type MoO_2^{2+} groups only (type A- MoO_2^{2+} - $\{\text{Mo-O-Mo}\}$ -type A- MoO_2^{2+} connectivity) [12]. Again, as in **1**, two neighboring A-type MoO_2^{2+} groups behave as bidentate ligands. The different connectivity types of the $\{\text{Mo}_{36}(\text{NO})_4\}$ unit in **1–3** indicate that the same cluster unit can be assembled in various ways and give products of different dimensionality if adopting different linkage centers.

The potential of terminal cis-MoO_2^{2+} groups in POM as ligands for building coordination polymers was recognized some time ago. The rare-earth ions are efficient linkers here, as shows recent preparation of 1D chain polymer $[\text{La}(\text{H}_2\text{O})_7\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 4 \text{H}_2\text{O}$ [13], or $(\text{NH}_4)_6[\text{Gd}_2\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{22}] \cdot 50 \text{H}_2\text{O}$ [14].

The formation of a nitroso-POM, $[\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}]^{12-}$, from the keplerate in the presence of Gd(III) nitrate is somewhat unexpected. We think that the $\text{Mo}(\text{NO})^{3+}$ forms in the slow reaction between NO_3^- and Mo(V), present in the keplerate as $\text{Mo}_2\text{O}_4^{2+}$ units. Traditional way to $[\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}]^{12-}$ is to

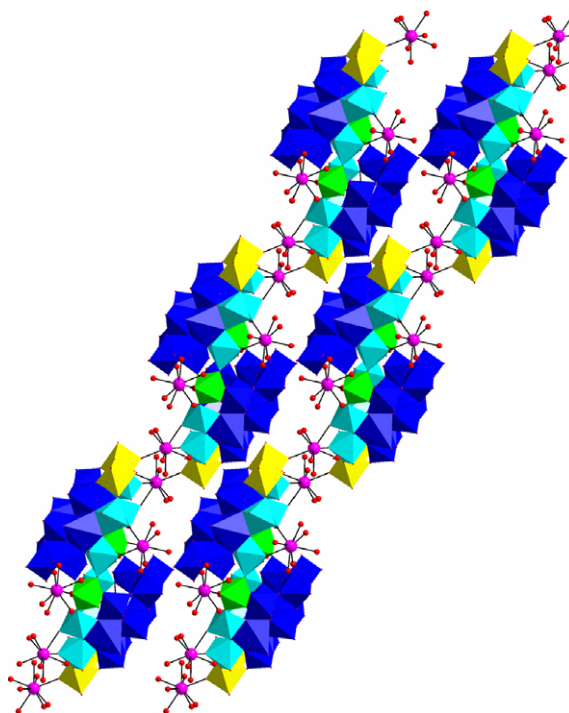


Fig. 2. Two neighbor layers (view along b axis) in the crystal structure of **1**. Crystallization water molecules are omitted for clarity. For color legend, see Fig. 1.

reduce molybdate with hydroxylammonium [9–12]. Another type of keplerate degradation was observed in the presence of Ni^{2+} , by a selective excision of $\text{Mo}_2\text{O}_4^{2+}$ moieties and their assembly into an ϵ -Kegging type structure $[\text{Mo}^{\text{V}}_{12}\text{O}_{30}(\mu_2\text{-OH})_{10}\text{H}_2\{\text{Ni}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$, together with four attached Ni^{2+} ions [15].

4. Supplementary materials

The supplementary material has been sent to the Fachinformationzentrum Karlsruhe, Abt. PROKA, 76344 Eggenstein-Leopoldshafen, Germany, as supplementary material No. 391260 (CIF) and can be obtained by contacting the FIZ (e-mail: crysdata@fiz-karlsruhe.de or www: <http://www.fiz-karlsruhe.de/fiz/products/icsdcsde.html>).

Acknowledgments

This work was supported by the Russian Foundation for Basic Research, grant No. 02-03-32604 and INTAS, grant no. 01-2346. N.V.I. thanks Haldor Topsoe A/S for a fellowship. M.N.S. is thankful to the Russian Science Support Foundation for a grant.

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