Synthesis, Crystal Structure and Characterization of a 1D Polyoxometalate-based Compound: $\{[Pr(H_2O)_7][CrMo_6H_6O_{24}]\} \cdot 4H_2O$

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Z. Naturforsch. **2008**, *63b,* 799 – 803; received December 29, 2007

A novel polyoxometalated-based compound, $\{[Pr(H_2O)_7][CrMo_6H_6O_{24}]\}\cdot 4H_2O$, was prepared and characterized by elemental analysis, infrared and ultraviolet spectroscopy, TG measurement and single crystal X-ray diffraction. A chain-like coordination polymer is formed from a heteropolyanion $[CrMo_6H_6O_{24}]^{3-}$ as a building unit and $[Pr(H_2O)_7]^{3+}$ cations as linker. The chains are linked into an extensive three-dimensional supramolecular network through hydrogen bonding. The synthesis of **1** is accomplished only from pre-synthesized Anderson clusters, but not from simple starting materials.

Key words: Polyoxometalate, Lanthanide Cation, 1D Chain, Supramolecular

Introduction

Polyoxometalates (POMs), frequently referred to as molecular metal-oxygen cluster species, have an enormous structural variety and interesting electronic, optical, magnetic, and catalytic properties [1 – 4]. The class of POMs has been known for almost 200 years since the time of Berzelius. Modifying or linking discrete POMs clusters to build novel solid-state materials is of great interest not only from a structural point of view, but also because the as-synthesized materials may possess novel properties through synergistic effects [5]. However, the development of POM chemistry has largely depended on Keggin and related species which have tetrahedrally coordinated heteroatoms [6]. The progress with species of octahedrally coordinated heteroatoms, on the other hand, has been far slower. So the situation of this class of POMs has not changed much since 1983, and only a few new structures have been reported [7, 8]. Furthermore, the reaction chemistry of the species with octahedrally coordinated heteroatoms has largely been left unexplored, such as the Anderson-type POMs [9] which have an attractive planar structure. In addition, each Mo (or W) atom has two terminal oxygen atoms with high reactivity [10], which may facilitate the construction of novel hybrid compounds.

Recently, An *et al.* have reported some novel compounds based on $[Cr(OH)_6Mo_6O_{18}]^{3-}$ and lanthanide ions: $(C_6NO_2H_5)[(H_2O)_4(C_6NO_2H_5)Ln(CrMo_6H_6O_{24})]\cdot 4H_2O$ (*Ln* = La, Ce, Pr, and Nd) [11], $(C_6NO_2H_5)_2[Ln(H_2O)_5(CrMo_6H_6O_{24})]\cdot 0.5H_2O$ (*Ln* = Ce and La) [12], $(C_5H_9NO_2)[La(H_2O)_7CrMo_6H_6O_{24}]\cdot 11H_2O$ [13], $(C_6NO_2H_5)_2[(H_2O)_6DyCrMo_6H_6O_{24}]\cdot 4H_2O$ [14], $(C_6NO_2H_5)_2[La(H_2O)_7][CrMo_6H_6O_{24}]\cdot 10.5H_2O$ and $(C_6NO_2H_5)_2[Nd(H_2O)_5]$-$[CrMo_6H_6O_{24}]\cdot 10H_2O$ [15]. As a continuation of the design and syntheses of such compounds, we are also trying to construct novel extended structures based on the Anderson anion. Meanwhile, Lanthanide (*Ln*) cations were chosen as modification fragments or linkage groups in this work because of their fascinating coordination geometry and interesting structures along with special properties. In view of the high affinity of lanthanide ions for hard donor atoms, we attempted to link polyoxoanions to these ions to realize molecular assembly. Practicing this strategy, we report the syntheses of the compound $[Pr(H_2O)_7Cr(OH)_6Mo_6O_{18}]\cdot 4H_2O$ (**1**) which contains 1D chains running parallel to the crystallographic *b* axis.

Results and Discussion

Crystal structure description and discussion

The asymmetric unit of **1** contains one Anderson-type polyoxoanion $[Cr(OH)_6Mo_6O_{18}]^{3-}$ and $[Pr(H_2O)_7]^{3+}$ cations, as shown in Fig. 1. The anionic building block belongs to the *B*-type Anderson struc-

Table 1. Selected bond lengths (Å) and angles (deg) for **1**.

Pr(1)–O(23)	2.630(7)	Mo(4)–O(23)	1.703(7)
Pr(1)–O(24)	2.470(7)	Mo(6)–O(29)	1.705(7)
Pr(1)–O(25)	2.498(7)	Cr(1)–O(2)	1.970(5)
Pr(1)–O(26)	2.572(8)	Cr(1)–O(3)	1.994(6)
Pr(1)–O(27)	2.487(7)	Cr(1)–O(7)	1.956(6)
Pr(1)–O(28)	2.524(9)	Cr(1)–O(8)	1.995(7)
Pr(1)–O(29)	2.570(7)	Cr(1)–O(13)	1.968(6)
Pr(1)–O(30)	2.403(8)	Cr(1)–O(14)	1.951(6)
Pr(1)–O(31)	2.512(10)		
O(7)–Cr(1)–O(2)	83.4(3)	O(7)–Cr(1)–O(8)	178.7(3)
O(7)–Cr(1)–O(13)	96.5(3)	O(13)–Cr(1)–O(2)	179.6 (3)

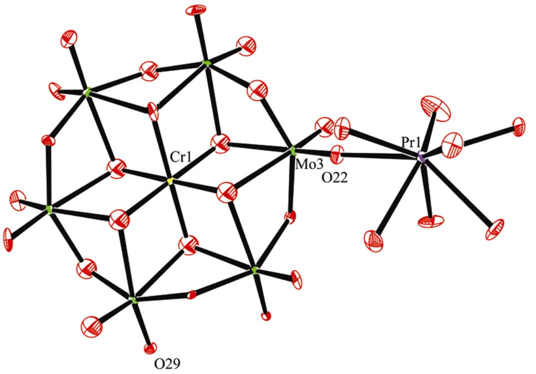

Fig. 1. Molecular structure of **1** in the solid state with partial atomic labeling (displacement ellipsoids are shown at the 50 % probability level).

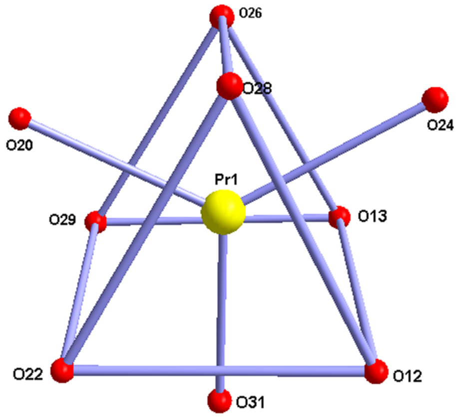

Fig. 2. Coordination environment around the Pr^{3+} ion in **1**.

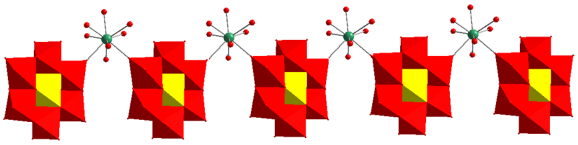

Fig. 3. View of the one-dimensional chains in **1**.

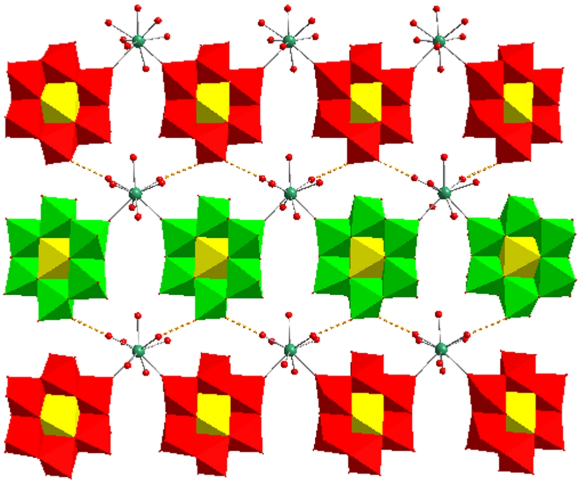

Fig. 4. View of the two-dimensional sheet of **1**.

ture, which consists of seven edge-sharing octahedra, six of which are $[MoO_6]$ octahedra, arranged hexagonally around the central $[Cr(OH)_6]$ octahedron. The Mo–O and the central Cr–O bond lengths lie in the ranges of 1.690(7) – 2.329(6) Å and 1.951(6) – 1.995(7) Å, respectively. The bond angles O–Cr–O_{cis} range from 83.4(3) to 96.5(3)°, and O–Cr–O_{trans} varies from 178.7(3) to 179.6(3)° (Table 1). All of the bond lengths and bond angles are within the normal ranges and are consistent with those described in the literature [11].

The crystallographically unique Pr^{3+} center is nine-coordinate (seven O atoms from water molecules, and the remaining two O atoms from two adjacent heteropolyanions). The coordination environment of the Pr^{3+} ion can be described as a tricapped trigonal prism in which O26, O30 and O31 occupy the three capping positions, and its side planes are composed of the groups [O24, O25, O27, O28], [O24, O28, O23, O29], and [O25, O27, O29, O23], respectively (Fig. 2). The average Pr–O bond length is 2.518 Å.

These Pr^{3+} cations link the $[Cr(OH)_6Mo_6O_{18}]^{3-}$ building blocks *via* the atoms O23 and O29 (the terminal oxygen atoms of Mo4 and Mo6, respectively) to form 1D zig-zag polymer chains running along the *b* axis (Fig. 3). Thus the Anderson-type polyoxoanions and $[Pr(H_2O)_7]^{3+}$ cations alternate in the crystal forming a ACAC chain mode.

Therefore, $[Cr(OH)_6Mo_6O_{18}]^{3-}$ anions and Pr^{3+} cations can be considered as 2-connected sites if the H_2O molecules coordinated to them are neglected.

These 1D chains are further connected by water molecules to form a 2D layer *via* hydrogen bonds, as shown in Fig. 4. These layers are further intercon-

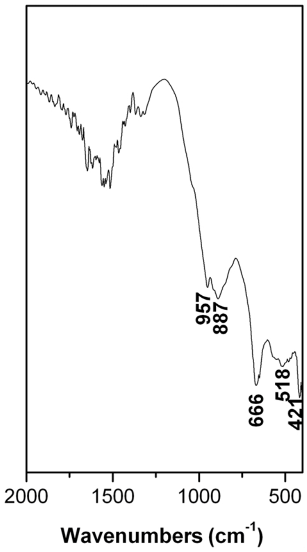

Fig. 5. The IR spectrum of **1**.

nected with each other *via* extensive hydrogen bonds to form a 3D framework. The representative hydrogen bonds are O6–O17 2.805, O6–O24 2.884, O26–O20 2.857, O30–O21 2.622, and O22–O7 2.764 Å. Obviously, these strong hydrogen-bonding interactions play an important role in the formation of the 3D supramolecular framework.

The bond valence sum calculations [16] indicate that the Cr and Pr atoms are in the +3 oxidation state, and all Mo atoms are in the +6 oxidation state. These results are consistent with the charge balance considerations.

FT-IR spectroscopy

In the IR spectrum of **1** (Fig. 5), the bands at 957, 887, 666, 518 cm^{-1} are attributed to ν_{as}(Mo–Od), ν_{as}(Mo–Ob–Mo), ν_{as}(Mo–Oc) and δ(W–Ob–W) of the $[Cr(OH)_6Mo_6O_{18}]^{3-}$ polyoxoanion. The absorption peak at 421 cm^{-1} is attributed to ν(Pr–O).

UV spectrum

The UV spectrum of $Na_3[Cr(OH)_6Mo_6O_{18}]$ was measured in water (Fig. 6). The first energy absorption band (198 nm) with low intensity is assigned to the charge transfer absorption Ot→W; the other absorption band (218 nm) is strong and assigned to the charge transfer absorption Ob→W. In terms of the UV spectrum of **1**, the first absorption band is similar to that of $Na_3[Cr(OH)_6Mo_6O_{18}]$, but the second absorption band is shifted to a higher wavelength (249 nm). This suggests that compound **1** may not be dissociated in dilute solution.

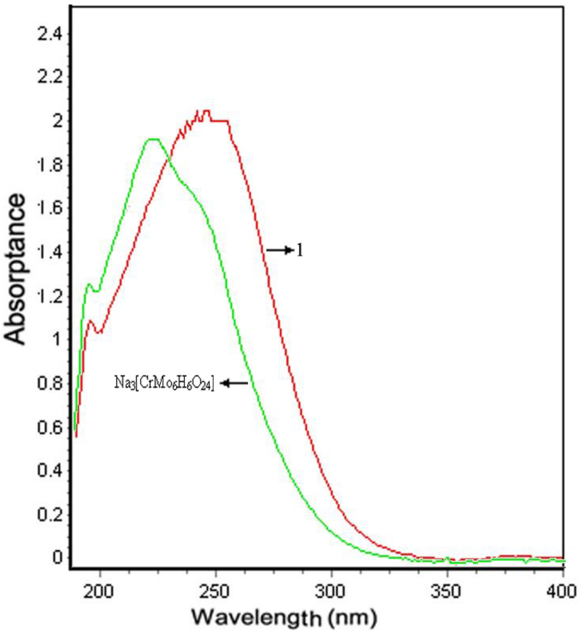

Fig. 6. The UV spectrum of **1**.

Thermogravimetric measurement

TG measurements of **1** were carried out under N_2. Guest and coordinated water molecules are released between 35 to 193 °C with a weight loss of 14.97 % (calcd. 14.59 %). The weight remains unchanged between 193 to 281 °C indicating that the framework of **1** is stable in this temperature range. Subsequently, the framework starts to collapse $>$ 281 °C.

Conclusion

In summary, we have synthesized and characterized a novel compound which contains a chain-like extended structure based on an Anderson-type polyanion and hydrated lanthanide cationic linkers. The construction of this compound from well-defined discrete building blocks illustrates further opportunites to synthesize new classes of 1D inorganic solid materials.

Experimental Section

General methods and materials

IR spectra were obtained on an Alpha Centaur FT/IR spectrometer with KBr pellets in the 400–4000 cm^{-1} region. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. Elemental analyses (Mo, Pr, Cr) were carried out with a Leaman inductively coupled plasma (ICP) spectrometer. UV spectra were recorded on a 756 CRT UV/Vis spectrophotometer. $Na_3[CrMo_6H_6O_{24}]\cdot 8H_2O$ was prepared according to the literature [17] and its purity confirmed by IR spectroscopy. $Pr(NO_3)_3\cdot 6H_2O$ was prepared by addition of concentrated HNO_3 to Pr_2O_3 (99.9 %) and evaporation of the solvent to dryness. All the other reagents were used as purchased without further purification.

Synthesis

*$[Pr(H_2O)_7Cr(OH)_6Mo_6O_{18}]\cdot 4H_2O$ (**1**)*

15 mL of an aqueous solution containing 0.1231 g (0.1 mmol) of $Na_3[CrMo_6H_6O_{24}]\cdot 8H_2O$ was heated at approximately 60 °C for 5 min, followed by the addition of 5 mL of an aqueous solution containing 0.0889 g $Pr(NO_3)_3\cdot 6H_2O$ (0.2 mmol) with stirring. The pH of the solution was adjusted to 2.7 with dilute HNO_3 solution. The mixture was filtered, and the filtrate was allowed to evaporate at r. t. The pink block-shaped crystals of **1** were obtained within six days (yield: *ca.* 58 % based on Mo). Anal. for $[Pr(H_2O)_7Cr(OH)_6Mo_6O_{18}]\cdot 4H_2O$: calcd. Mo 42.43, Pr 10.39, Cr 3.83; found Mo 42.19, Pr 10.21, Cr 3.86.

Interestingly, when using $Cr(NO)_3\cdot 9H_2O$ and Na_2MoO_4 instead of $Na_3[CrMo_6H_6O_{24}]\cdot 8H_2O$, the production of **1** failed, confirming that the pre-synthesized Anderson clusters are essential as precursors for the synthesis of **1**.

X-Ray data collection and structure determination

The data of **1** were collected on a Bruker Smart CCD diffractometer equipped with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 293 K. An empirical absorption correction was applied. The structure was solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELX-97 software [18]. Most non-H atoms were refined with anisotropic displacement parameters, but some of the O atoms had to be refined isotropically, and 13 restraints were applied. The H atoms were only partially included into the structure factor calculations.

Table 2. Crystal and structure refinement data for **1**.

Empirical formula	$CrH_{28}Mo_6O_{35}Pr$
M_r	1356.77
Color, habit	pink, block
Cryst. size, mm^3	$0.13 \times 0.10 \times 0.03$
Crystal system	orthorhombic
Space group	$Pca2_1$
a, Å	11.828(15)
b, Å	10.966(16)
c, Å	22.545(3)
V, Å^3	2924.2(7)
Z	4
D_{calcd}, g cm^{-3}	3.08
F(000), e	2572
Temperature K	293 (2)
Radiation; wavelength, Å	MoK_α, λ = 0.71073
Absorption coeff. μ, mm^{-1}	4.60
Absorption correction	empirical
h, k, l ranges	$-14 \le h \le 14$, $-13 \le k \le 13$, $-27 \le l \le 19$
θ range for data collection, deg	1.81 – 26.05
Measured/independ. refl./ R_{int}	15413/4254/0.047
Refl. with $I \ge 2\sigma(I)$	3874
Data/restraints/ref. parameters	4254/13/307
Goodness-of-fit on F^2	1.106
Flack parameter	0.33(4)
Final $R1/wR2$ indices $[I \ge 2\sigma(I)]$	0.068/0.176
Final $R1/wR2$ indices^{a,b} (all data)	0.073/0.180
Largest diff. peak/hole, e Å^{-3}	7.8/−1.7

^{a} $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; ^{b} $wR2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$ with $w = 1/[\sigma^2(F_o^2)+(0.0993P)^2+103.2874P]$ where $P = (F_o^2+2F_c^2)/3$.

As the compound crystallizes in the orthorhombic non-centrosymmetric space group $Pca2_1$, tests were undertaken to ascertain this space group. Both, reduced-cell calculations as well as tests for higher symmetry of the parameter set, as incorporated in the program PLATON [19], did not reveal any higher symmetry, however. A summary of the crystallographic data and structure determination details for **1** is provided in Table 2.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-418918.

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