

Li Yu, Su-Zhi Li and Jing-Ping Wang*

Institute of Molecular and Crystal Engineering,
School of Chemistry and Chemical Engineering,
Henan University, Kaifeng 475001, People's
Republic of China

Correspondence e-mail: jpwang@henu.edu.cn

Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(r\text{-O}) = 0.003\text{ \AA}$
H-atom completeness 82%
 R factor = 0.036
 wR factor = 0.100
Data-to-parameter ratio = 12.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**[Na₃(H₂O)₁₁][CrMo₆O₂₄H₆]·2H₂O, with
an Anderson B-type heteropolyoxoanion**

The structural unit of the title compound, poly[[hexa- μ_2 -hydroxohexa- μ_3 -oxoundecaoxochromiumhexamolybdenum]- μ -oxo-[tetra- μ_2 -aquahehexaaquatrissodium]- μ -aqua], [CrMo₆-Na₃O₁₈(OH)₆(H₂O)₁₁]·2H₂O, consists of an Anderson B-type heteropolyoxoanion [CrMo₆O₂₄H₆]³⁻ with approximate D_{3h} point symmetry, an [Na₃(H₂O)₁₁]³⁺ cation chain and two water molecules of crystallization. The [CrMo₆O₂₄H₆]³⁻ anions are connected *via* Mo— μ -O—Na bonds to the [Na₃(H₂O)₁₁]³⁺ groups to form one-dimensional double chains extending parallel to the c axis.

Received 31 July 2006
Accepted 17 August 2006

Comment

Since Anderson-type heteropolyoxometalates were structurally confirmed by Evans (1948), these compounds have received increased attention because of their applications in homogeneous and heterogeneous catalysis (Hernandez-Perez *et al.*, 1994). In the present communication, we report a novel heteropolyoxometalate containing an Anderson B-type anion, *viz.* [Na₃(H₂O)₁₁][CrMo₆O₂₄H₆]·2H₂O, (I).

The structure of (I) is composed of an Anderson B-type heteropolyoxoanion [CrMo₆O₂₄H₆]³⁻ with approximate D_{3h} point symmetry, an [Na₃(H₂O)₁₁]³⁺ cation chain and two water molecules of crystallization (Fig. 1). Anderson-type heteropolyoxoanions can be divided into two groups according to the different valence and ionic radius of the central atom X , and the presence of protonated O atoms. The first type with general formula $[X^{n+}M_6O_{24}]^{(12-n)-}$ ($X = \text{Te}^{6+}, \text{I}^{7+}, \text{etc.}$, $M = \text{Mo}^{6+}, \text{W}^{6+}$) is described as an A-type polyanion, whereas the second type $[X^{n+}M_6O_{24}H_6]^{(6-n)-}$ ($X = \text{Cr}^{3+}, \text{Co}^{3+}, \text{etc.}$, $M = \text{Mo}^{6+}, \text{W}^{6+}$) is referred to as a B-type anion (Xiang *et al.*, 2002). Based on the bond valence model (Brown & Altermatt, 1985), the bond valence sums of atoms O19–O24 range from 1.12 to 1.27, suggesting that every O atom is additionally bonded to a proton which confirms that the anion of (I) belongs to the B-type.

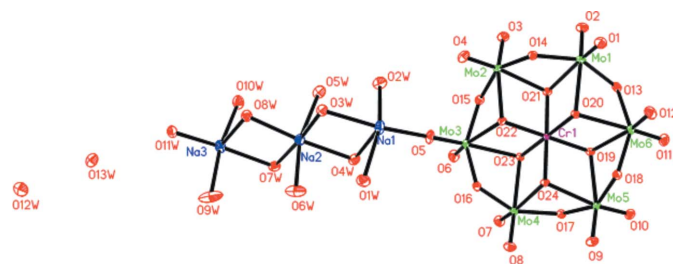


Figure 1

The asymmetric unit of the title compound drawn with displacement ellipsoids at the 30% probability level. All H atoms have been omitted for clarity.

In the heteropolyoxoanion, each metal atom is coordinated by six O atoms to form a distorted octahedron. The six different MoO₆ octahedra share edges with each other and are arranged around the central CrO₆ octahedron with which they likewise share edges (Fig. 1). According to the different manner of oxygen coordination, three kinds of O atoms exist in the heteropolyoxoanion: terminal atoms O_t (O1–O12) with bonds to one Mo atom, bridging atoms O_b (O13–O18) with bonds to two Mo atoms, and central atoms O_c (O19–O24) that have bonds to the central Cr atom and two Mo atoms.

Each of the three Na⁺ cations exhibits a distorted octahedral coordination (Fig. 1 and Table 1). Na1 is surrounded by four O atoms from four water molecules and two terminal O atoms from two parallel heteropolyoxoanions. The coordination environment around Na2 includes six O atoms from six water molecules, and Na3 is coordinated by five O atoms from five water molecules and a terminal O atom from another heteropolyoxoanion.

The [CrMo₆O₂₄H₆]³⁻ heteropolyoxoanions are connected via Mo–μ–O_t–Na bonds with the [Na₃(H₂O)₁₁]³⁺ triple octahedra to form one-dimensional double chains of the type [CC,AA,CC,AA] (C and A stand for cation and anion chain, respectively) extending parallel to the *c* axis (Fig. 2).

The geometry of the heteropolyoxoanion in (I) is very similar to that in the structure of the related compound Na₃[CrMo₆O₂₄H₆]·8H₂O (Perloff, 1970). Because of the lower water content of the latter, the coordination of the Na atoms and the connection of the single building blocks are different from those in (I).

Experimental

All reagents and solvents were used as obtained without further purification. Na₃[CrMo₆O₂₄H₆]·*n*H₂O was synthesized according to the procedure given by Perloff (1970). Na₃[CrMo₆O₂₄H₆]·*n*H₂O (3.8 g) was dissolved in water (10 ml) to which a methanol–water (20 ml) solution in a volume ratio of 5:3 was added. The pH of the resulting solution was adjusted to 3.5 with acetic acid. The resulting solution was filtered and slowly evaporated at ambient temperature. Pink crystals of (I) were collected after a few days.

Crystal data

| | |
|--|---|
| [CrMo ₆ Na ₃ O ₁₈ (OH) ₆ ·(H ₂ O) ₁₁]·2H ₂ O | $\gamma = 66.90 (3)^\circ$ |
| $M_r = 1320.87$ | $V = 1624.5 (6) \text{ \AA}^3$ |
| Triclinic, $P\bar{1}$ | $Z = 2$ |
| $a = 10.968 (2) \text{ \AA}$ | $D_x = 2.700 \text{ Mg m}^{-3}$ |
| $b = 11.686 (2) \text{ \AA}$ | Mo $K\alpha$ radiation |
| $c = 14.895 (3) \text{ \AA}$ | $\mu = 2.73 \text{ mm}^{-1}$ |
| $\alpha = 72.10 (3)^\circ$ | $T = 293 (2) \text{ K}$ |
| $\beta = 70.99 (3)^\circ$ | Block, pink |
| | $0.22 \times 0.18 \times 0.13 \text{ mm}$ |

Data collection

| | |
|---|--|
| Rigaku R-AXIS-IV CCD diffractometer | 5549 measured reflections |
| ω scans | 5549 independent reflections |
| Absorption correction: multi-scan (ABSCOR; Higashi, 1995) | 4842 reflections with $I > 2\sigma(I)$ |
| $T_{\min} = 0.585$, $T_{\max} = 0.718$ | $\theta_{\max} = 25.0^\circ$ |

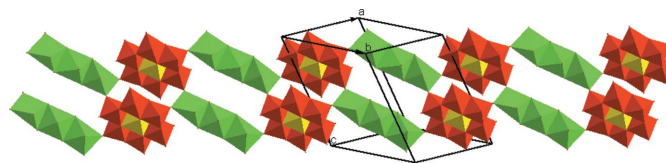


Figure 2

A polyhedral representation of the one-dimensional double chains extending along the *c* axis. Water molecules of crystallization and all H atoms have been omitted for clarity. Red: MoO₆ octahedra; yellow: CrO₆ octahedra; green: NaO₆ octahedra.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.100$
 $S = 1.11$
 5549 reflections
 433 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0611P)^2 + 2.0611P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.80 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.24 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths (Å).

| | | | |
|------------------------|-----------|---------|-----------|
| Na1–O2W | 2.359 (5) | Mo2–O3 | 1.708 (3) |
| Na1–O5 | 2.387 (4) | Mo2–O4 | 1.719 (4) |
| Na1–O3W | 2.392 (4) | Mo2–O15 | 1.903 (3) |
| Na1–O1 ⁱ | 2.412 (4) | Mo2–O14 | 1.956 (3) |
| Na1–O1W | 2.447 (5) | Mo2–O21 | 2.263 (3) |
| Na1–O4W | 2.508 (5) | Mo2–O22 | 2.302 (3) |
| Na1–O12 ⁱ | 2.905 (5) | Mo3–O6 | 1.685 (3) |
| Na2–O8W | 2.371 (4) | Mo3–O5 | 1.696 (4) |
| Na2–O4W | 2.385 (4) | Mo3–O16 | 1.934 (3) |
| Na2–O7W | 2.391 (4) | Mo3–O15 | 1.945 (3) |
| Na2–O5W | 2.412 (5) | Mo3–O23 | 2.301 (3) |
| Na2–O6W | 2.419 (5) | Mo3–O22 | 2.372 (3) |
| Na2–O3W | 2.425 (4) | Mo4–O7 | 1.695 (3) |
| Na3–O9W | 2.346 (5) | Mo4–O8 | 1.707 (4) |
| Na3–O10W ⁱⁱ | 2.395 (5) | Mo4–O16 | 1.919 (3) |
| Na3–O11W | 2.399 (4) | Mo4–O17 | 1.940 (3) |
| Na3–O7W | 2.429 (4) | Mo4–O23 | 2.289 (3) |
| Na3–O8W | 2.458 (4) | Mo4–O24 | 2.305 (3) |
| Na3–O7 ⁱⁱⁱ | 2.464 (4) | Mo5–O9 | 1.703 (4) |
| Cr1–O23 | 1.968 (3) | Mo5–O10 | 1.710 (3) |
| Cr1–O20 | 1.969 (3) | Mo5–O18 | 1.918 (3) |
| Cr1–O19 | 1.970 (3) | Mo5–O17 | 1.946 (3) |
| Cr1–O24 | 1.971 (3) | Mo5–O24 | 2.288 (3) |
| Cr1–O21 | 1.973 (3) | Mo5–O19 | 2.301 (3) |
| Cr1–O22 | 1.981 (3) | Mo6–O12 | 1.696 (4) |
| Mo1–O1 | 1.694 (4) | Mo6–O11 | 1.699 (4) |
| Mo1–O2 | 1.709 (4) | Mo6–O18 | 1.931 (3) |
| Mo1–O13 | 1.907 (3) | Mo6–O13 | 1.959 (3) |
| Mo1–O14 | 1.951 (3) | Mo6–O20 | 2.293 (3) |
| Mo1–O21 | 2.260 (3) | Mo6–O19 | 2.295 (3) |
| Mo1–O20 | 2.294 (3) | | |

Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x + 1, -y + 1, -z + 2$; (iii) $-x + 1, -y + 1, -z + 1$.

The H atoms of the water molecules were placed in calculated positions with an O–H distance of 0.85 Å. They were refined in the riding-model approximation with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{O})$. H atoms of the OH groups (O19–O24) could not be located or placed geometrically and were excluded from the refinement. The deepest hole in the final Fourier map is 0.93 Å from Mo1.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO* (Rigaku, 2002); data reduction: *Crystal-Structure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* (Farrugia,

1999); software used to prepare material for publication: *SHELXL97*.

Financial support from the Program for New Century Excellent Talents in University of Henan Province, the Institute of Education of Henan Province and the Natural Science Foundation of Henan Province is gratefully acknowledged.

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