Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

New girdle-like Mo$_{18}$ polyanions linked into chains

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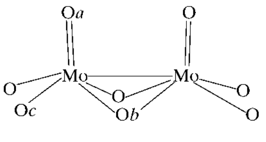
Received 2 July 2001
Accepted 15 October 2001
Online 23 January 2002

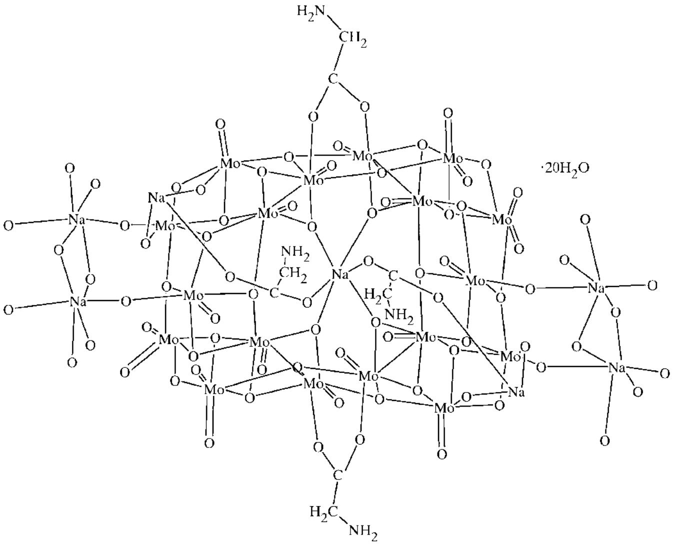
From the reduction of heptamolybdate, a polyoxomolybdate was obtained with the formula $[Na_6^+(H_2O)_{16}(NH_2CH_2COO)_2^-]^{4+}\cdot\{Na^+[H_9Mo_{10}^{VI}Mo_8^VO_{56}(NH_2CH_2COO)_2^-]^{5-}\}^{4-}\cdot 20H_2O$, *i.e.* heptasodium nonahydrogen tetracarbamate hexadecaaquahexapentacontaoxaoctadecamolybdate(V,VI) icosahydrate. The 18 Mo atoms are connected by bridging O atoms to form a centrosymmetric girdle-like structure, in which Mo^V–Mo^V units are found. An Na$^+$ cation occupies the central hole of the girdle, while four Na$^+$ cations are bonded to the O atoms on the girdle edge. The girdles are linked into a one-dimensional chain by the other Na$^+$ cations.

Comment

Polyoxometalates are molecular metal–oxygen clusters that are of fundamental and practical interest (Pope, 1983; Pope & Müller, 1994). One large branch are the polyoxomolybdates. Traditional high-nuclearity oxomolybdenum complexes contain Mo^{VI} centers only (iso- and heteropolymolybdates) or both Mo^V and Mo^{VI} centers with delocalized *d*-electrons (heteropoly blues) (Chae *et al.*, 1993). However, a new family of polyoxomolybdates whose Mo^V *d*-electrons are localized in Mo^V—Mo^V single bonds has emerged in recent years (Chae *et al.*, 1993; Müller *et al.*, 1998, 1999). Chae *et al.* (1993) concluded that all these compounds have $[Mo_2^VO_8]^{6-}$ units (see *Scheme* below).



Within this unit, the Mo^V—Mo^V bond distance lies in the range 2.5–2.7 Å, while the Mo^V—O bond distances are in the range 1.6–1.8 Å for O*a*, 1.9–2.0 Å for O*b* and 2.0–2.2 Å for O*c*. Frequently, but not always, a sixth oxygen ligand is weakly bonded to each Mo^V center *trans* to the O*a* ligand. From the reduction of heptamolybdate in an aqueous solution of glycine, we have synthesized several oxomolybdenum compounds containing $[Mo_2^VO_8]^{6-}$ units (Liu, Liu *et al.*, 2000), among which are the two interesting Mo$_{18}$ polyanions $[Ca_4^{2+}(H_2O)_{22}(NH_2CH_2COO^-)_2]^{6+}\cdot\{Ca^{2+}[Mo_{10}^{VI}Mo_8^VO_{52}(OH)_4(NH_3^+CH_2COO^-)_2]^{8-}\}^{6-}\cdot 20H_2O$, (II), and $[Ca_3^{2+}(H_2O)_{13}(NH_3^+CH_2COO^-)_3]^{6+}\cdot\{Ca^{2+}[Mo_{10}^{VI}Mo_8^VO_{52}(OH)_4(NH_3^+CH_2COO^-)_2]^{8-}\}^{6-}\cdot 19\ H_2O$, (III) (Liu, Wei *et al.*, 2000). We report here the structure of $[Na_6^+(H_2O)_{16}(NH_2CH_2COO^-)_2]^{4+}\cdot\{Na^+[H_9Mo_{10}^{VI}Mo_8^VO_{56}(NH_2CH_2COO^-)_2]^{5-}\}^{4-}\cdot 20H_2O$, (I) , a new member of this family.



(I)

Compound (I) has an Mo$_{18}$ centrosymmetric girdle-like structure (Fig. 1). The Mo–O framework of the polyanion is approximately the same as those of (II) and (III). Every Mo atom is coordinated by six O atoms and sits at the center of a distorted octahedron. Eight Mo–O octahedra share edges and vertices with each other to form an octagonal ring. Two octagonal rings, related by a symmetry center, overlap through 16 μ_3-O atoms to form a girdle with a slight gradient. Two Mo centers are situated on the outer edges of the girdle and connect to other Mo centers through four μ-O atoms. A characteristic of this complex is the existence of Mo—Mo single bonds between Mo1 and Mo2, and between Mo3 and Mo4, as well as between their symmetrically equivalents. The bond distances are in the range given by Chae *et al.* (1993). The bond-valence sums of these eight Mo atoms are calculated as 5 according to bond-valence theory (Brown, 1981). The coordination environment of these Mo^V centers is also the same as described by Chae *et al.* (1993), showing $[Mo_2^VO_{10}]^{10-}$ units which can be divided into $[Mo_2^VO_8]^{6-}$ units and weakly coordinated O atoms *trans* to the terminal O atoms. Two glycine molecules connect Mo1 and Mo4 of the other ring in a μ_2-bridging mode with their carboxyl group. The structural characteristics described above are similar to those of (II) and (III), and can be regarded as common characteristics of this series of compounds.

There are seven Na$^+$ cations in (I). One Na$^+$ (Na1) is located at the center of symmetry in the central hole of the girdle and is coordinated by six O atoms of the Mo^V centers. The other six are on the periphery. Na3 is captured by the terminal O atom (O21) of Mo7 and Na4 is captured by the terminal O

DOI: 10.1107/S0108270101017206

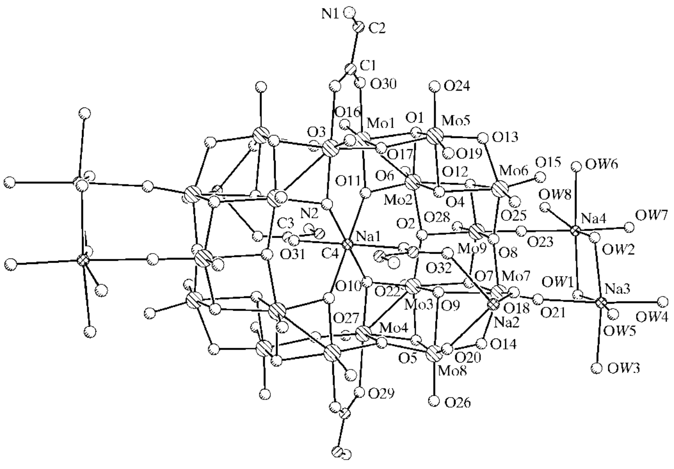


Figure 1

The structure of (I) with some water molecules and all H atoms omitted. Key: Mo (large hatched spheres), Na (crossed), O (shaded), C (small hatched) and N (stippled).

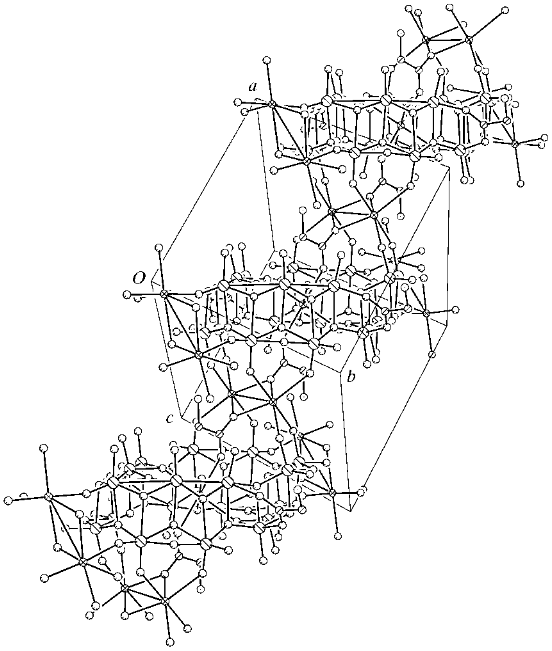


Figure 2

The linking of girdles into one-dimensional chains.

atom (O23) of Mo9. They stretch out of the girdle but are almost on the ring planes. Na3 and Na4 are connected by two μ_2-O atoms while coordinated by three water molecules each. Na2 sits above the ring plane and is coordinated by six O atoms, two (O18 and O20) from one polyanion, two (O19 and O25) from another polyanion, and two (O32 and its symmetrically equivalent) from the glycine molecules that also coordinate to Na1. The four terminal O atoms coordinate to one Na2 cation each, but O32 bridges two adjacent Na2 atoms in a μ_2 mode. Thus, there are two Na2 atoms cations between two polyanions and these Na^+ cations link the girdles into a one-dimensional chain (Fig. 2).

The position of Na1 in (I) is the same as that of Ca1 in (II) and (III). Generally speaking, Na2 occupies a similar position to Ca2, while Na3 and Na4 occupy similar positions to Ca3, but their number and coordination details are obviously different. However, the O atoms of the polyanion that coordinate to them are similar. O18 and O25, the O atoms above the ring planes, as well as O21 and O23, those stretching out of the girdle but almost on the ring planes, all take part in coordination to the Na^+ or Ca^{2+} cations. These terminal O atoms can be regarded as the active positions of the polyanions. The similarity of a girdle-like backbone and the active positions of these three compounds shows that they can be classified into a structural type with a formula $[Mo^{VI}_{10}Mo^{V}_{8}O_{56}(glycine)_2]^{14-}$. This type of structure, like the famous structural types of the Keggin and Dawson anions, can be modified by cations and organic acids while keeping the main structure unchanged.

There are ten water molecules not connected to metal ions per asymmetric unit. One of these waters of hydration is divided between two sites (O*W*14 and O*W*15, 1.54 Å apart), with occupancies that were fixed at 0.75 and 0.25, respectively, during refinement. No H atoms, except those of the methylene C atom of glycine, were included in the structure determination.

Experimental

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.70 g, 0.57 mmol), NH_2CH_2COOH (3.04 g, 40.5 mmol), NaCl (2.00 g, 34.2 mmol) and $N_2H_4\cdot H_2SO_4$ (0.20 g, 1.5 mmol) were added to water (60 ml, 3.3 mol) and the solution was stirred for 10 min whereupon a color change occurred from yellow to green. The solution was allowed to stand undisturbed for one day over which time the color changed to red. Red crystals were obtained after 14 d, together with a red precipitate. The crystals were carefully picked from the precipitate and washed quickly with cold water and dried in air at room temperature.

Crystal data

$[Na_6(H_2O)_{16}(NH_2CH_2COO)_2]\cdot\{Na[H_9Mo^{VI}_{10}Mo^{V}_{8}O_{56}(NH_2CH_2COO)_2]\}\cdot 20H_2O$
$M_r = 3737.75$
Triclinic, $P\overline{1}$
$a = 11.913$ (2) Å
$b = 15.027$ (3) Å
$c = 15.466$ (3) Å
$\alpha = 114.37$ (3)°
$\beta = 99.00$ (3)°
$\gamma = 99.17$ (3)°
$V = 2412.6$ (8) Å^3
$Z = 1$
$D_x = 2.573$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 5.0$–11.2°
$\mu = 2.42$ mm^{-1}
$T = 293$ (2) K
Sheet, red–brown
0.40 × 0.25 × 0.05 mm

Data collection

Rigaku AFC-6*S* diffractometer
2θ scans
Absorption correction: ψ scan (Coppens *et al.*, 1965)
$T_{min} = 0.494$, $T_{max} = 0.886$
8848 measured reflections
8499 independent reflections
6755 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 25°$
$h = -14 \rightarrow 13$
$k = 0 \rightarrow 17$
$l = -18 \rightarrow 16$
3 standard reflections every 400 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.179$
$S = 1.08$
8499 reflections
592 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1074P)^2 + 22.8082P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 2.36$ e Å^{-3}
$\Delta\rho_{min} = -2.03$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00063 (17)

Table 1
Selected interatomic distances (Å).

Mo1—O16	1.691 (7)	Mo5—O6	1.927 (6)
Mo1—O11	1.954 (6)	Mo5—O13	1.942 (7)
Mo1—O1	1.967 (6)	Mo5—O4	2.205 (6)
Mo1—O3	2.050 (7)	Mo5—O1	2.320 (7)
Mo1—O30	2.173 (7)	Mo6—O15	1.702 (7)
Mo1—O6	2.182 (7)	Mo6—O25	1.717 (8)
Mo1—Mo2	2.6033 (13)	Mo6—O8	1.936 (7)
Mo2—O17	1.687 (8)	Mo6—O13	1.949 (7)
Mo2—O11	1.943 (7)	Mo6—O4	2.209 (6)
Mo2—O2	2.001 (6)	Mo6—O12	2.264 (7)
Mo2—O1	2.006 (7)	Mo7—O21	1.700 (7)
Mo2—O12	2.134 (7)	Mo7—O18	1.701 (8)
Mo2—O4	2.305 (6)	Mo7—O14	1.937 (7)
Mo2—Mo9	3.2038 (15)	Mo7—O8	1.973 (7)
Mo3—O22	1.687 (8)	Mo7—O9	2.211 (6)
Mo3—O10	1.920 (7)	Mo7—O7	2.291 (7)
Mo3—O2	1.960 (6)	Mo8—O20	1.711 (8)
Mo3—O5	2.028 (7)	Mo8—O26	1.719 (8)
Mo3—O7	2.101 (6)	Mo8—O3$^{\rm i}$	1.922 (7)
Mo3—O9	2.301 (7)	Mo8—O14	1.938 (7)
Mo3—Mo4	2.5974 (18)	Mo8—O9	2.236 (6)
Mo4—O27	1.703 (8)	Mo8—O5	2.333 (7)
Mo4—O10	1.943 (6)	Mo9—O23	1.710 (8)
Mo4—O5	1.971 (7)	Mo9—O28	1.725 (8)
Mo4—O6$^{\rm i}$	2.059 (7)	Mo9—O12	1.960 (6)
Mo4—O29	2.169 (6)	Mo9—O7	1.969 (7)
Mo4—O3$^{\rm i}$	2.191 (6)	Mo9—O2	2.228 (7)
Mo5—O19	1.701 (8)	Mo9—O8	2.250 (7)
Mo5—O24	1.728 (8)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1990); software used to prepare material for publication: *SHELXL*97.

This work was supported by the National Natural Science Foundation of China (projects No. 29733080 and 29871003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1340). Services for accessing these data are described at the back of the journal.

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