

Data collection: *Diffractometer Control Software* (Enraf–Nonius, 1993). Cell refinement: *Diffractometer Control Software*. Data reduction: *REDU4* (Stoe & Cie, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLUTON93* (Spek, 1993). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1148). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hexaaquagallium Hexahydrogenhexamolybdocobaltate(III) Decahydrate[†]

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Abstract

The structure of hexaaquagallium(III) hexahydrogen-tetracosaoxocobalt(III)hexamolybdate decahydrate, $[\text{Ga}(\text{H}_2\text{O})_6][\text{Co}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 10\text{H}_2\text{O}$, includes a polyanion with the so-called Anderson structure, of general formula $\text{H}_6[\text{X}^{n+}\text{Mo}_6\text{O}_{24}]^{(6-n)-}$ (X is a heteroatom), where

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all the O atoms in the central XO_6 octahedron are protonated. The Ga^{3+} ion is coordinated by six water molecules and the Co^{3+} ion by six O atoms. Both ions are located at inversion centers.

Comment

The title compound was investigated as part of structural studies on polymolybdate salts. *B*-type Anderson structure heteropolyanions (Anderson, 1937), *i.e.* containing a heteroatom X of low oxidation state within a protonated polyanion such as $\text{H}_6[\text{X}^{n+}\text{Mo}_6\text{O}_{24}]^{(6-n)-}$, have been reported for heteroatoms Cr^{3+} (Perloff, 1970), Cu^{2+} (Ito, Ozeki, Ichida & Sasaki, 1989) and Co^{3+} (Nagano, Lee, Ichida & Sasaki, 1990).

The present polyanion, $[\text{Co}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$, containing Co^{3+} as the heteroatom but Ga^{3+} as the counter ion, is close to having $D_{3d}(\bar{3}m)$ symmetry. It consists of a ring of six distorted MoO_6 octahedra surrounding one Co atom; the six Mo atoms form an almost planar (r.m.s. deviation 0.003 Å) hexagon with an edge of approximately 3.36 Å. The O atoms in the anion can be divided into three groups, *Oc*, *Ob* and *Ot*, where *Ot* represents a terminal O atom bound to one Mo atom, *Ob* represents a bridging O atom bound to two Mo atoms and *Oc* represents a central O atom coordinated to both the Co atom and an Mo atom. The Mo—O distances are Mo—*Oc* 2.282 (4)–2.352 (4), Mo—*Ob* 1.944 (4)–1.971 (4) and Mo—*Or* 1.715 (5)–1.749 (4) Å. A similar trend has been found in $\text{Ba}_3[\text{Co}(\text{OH})_6\text{Mo}_6\text{O}_{18}]_2\cdot 20\text{H}_2\text{O}$ (Soriano-García, Panneerselvam & Holguín-Quiñones, 1996), $(\text{C}_{12}\text{H}_{24}\text{O}_6\text{K})_2\text{K}[\text{Co}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 12\text{H}_2\text{O}$ (Nagano, Lee, Ichida & Sasaki, 1990) and $\text{Na}_3[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]\cdot 8\text{H}_2\text{O}$ (Perloff, 1970).

The Co^{3+} and Ga^{3+} ions both have coordination number six. The Co^{3+} ion is coordinated to six *Oc* atoms at an average distance of 1.967 (4) Å. Of the 16

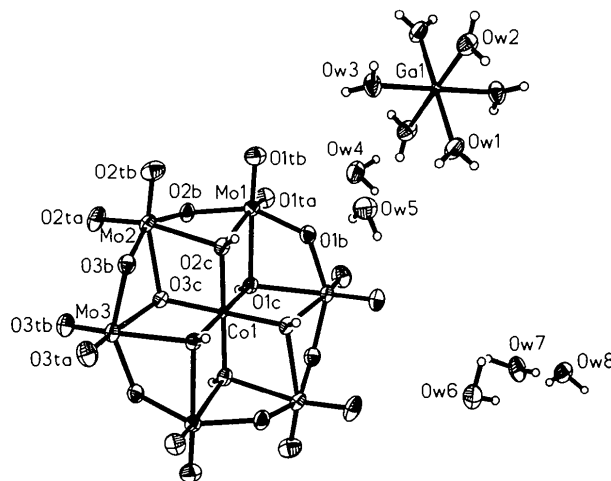


Fig. 1. The molecular structure of the title compound showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level.

water molecules present in the crystal, six are bonded to the Ga³⁺ ion, forming a regular octahedron. The mean Ga—O_w coordination length is 1.969 (4) Å. The remaining water molecules fill the empty space in the unit cell, forming a hydrogen-bond network (Table 3). The molecular packing, viewed down the *a* axis, is shown in Fig. 2. In the crystal, the polyanions and Ga(H₂O)₆ cations form alternate columns in the *a* direction. The columns are connected *via* O—H...O hydrogen bonds.

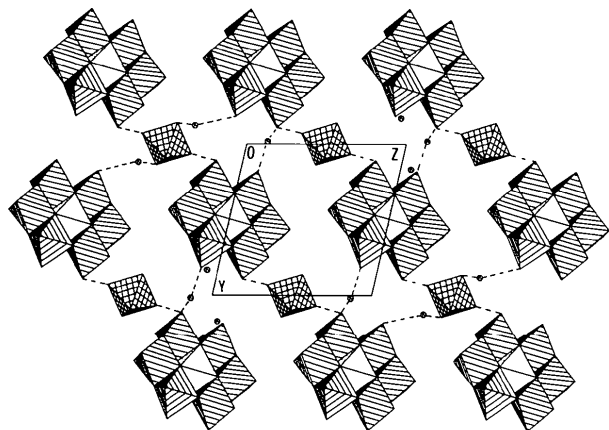


Fig. 2. A polyhedron drawing of the crystal packing. Hydrogen bonds are indicated by dashed lines.

Experimental

The compound was obtained by mixing hexamolybdocobaltic acid, H₃[Co(OH)₆Mo₆O₁₈], with an equivalent amount of gallium acetate. The aqueous solution was allowed to stand for three weeks. The precipitate that formed was filtered off, washed several times with cold water (276 K), then with ethanol and dried at room temperature. Green single crystals suitable for X-ray diffraction studies were obtained.

Crystal data

[Ga(H₂O)₆][Co(OH)₆Mo₆O₁₈].10H₂O

M_r = 1382.59

Triclinic

P $\bar{1}$

a = 6.891 (2) Å

b = 11.412 (6) Å

c = 11.780 (4) Å

α = 101.25 (4)°

β = 96.96 (1)°

γ = 102.06 (4)°

V = 875.8 (6) Å³

Z = 1

D_x = 2.622 Mg m⁻³

D_m = 2.638 Mg m⁻³

D_m measured by pycnometry

Data collection

Siemens P4 four-circle diffractometer

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 45 reflections

θ = 5.258–12.673°

μ = 3.418 mm⁻¹

T = 293 (2) K

Rhombohedral

0.24 × 0.22 × 0.22 mm

Green

2715 observed reflections
[*I* > 2σ(*I*)]

$\theta/2\theta$ scans

Absorption correction:

semi-empirical from 15

ψ scans (North, Phillips

Mathews, 1968)

T_{min} = 0.131, *T_{max}* =

0.195

3755 measured reflections

2980 independent reflections

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.0371

wR(*F*²) = 0.0995

S = 1.086

2980 reflections

221 parameters

H atoms included in

the structure-factor

calculations

w = 1/[σ²(*F_o*²) + (0.0455*P*)²

+ 5.7695*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

R_{int} = 0.019

θ_{\max} = 25°

h = -8 → 8

k = -13 → 13

l = -1 → 14

3 standard reflections

monitored every 97

reflections

intensity decay: 0.08%

(Δ/σ)_{max} = -0.018

$\Delta\rho_{\max}$ = 0.711 e Å⁻³

$\Delta\rho_{\min}$ = -0.936 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Co	1/2	1/2	0	0.0096 (2)
Ga	1/2	0	1/2	0.0215 (2)
Mo1	0.13028 (7)	0.33410 (5)	0.10480 (4)	0.0201 (2)
Mo2	0.16445 (7)	0.25757 (5)	-0.17807 (4)	0.0227 (2)
Mo3	0.52601 (8)	0.42752 (5)	-0.28861 (4)	0.0219 (2)
O1c	0.2922 (6)	0.5333 (4)	0.0974 (3)	0.0205 (9)
O1b	0.3555 (6)	0.3944 (4)	0.2343 (4)	0.0268 (9)
O11a	-0.0601 (7)	0.3891 (4)	0.1674 (4)	0.0308 (10)
O11b	0.0836 (7)	0.1808 (4)	0.1082 (4)	0.0348 (11)
O2c	0.3838 (6)	0.3268 (4)	-0.0024 (3)	0.0206 (9)
O2b	0.0157 (6)	0.3230 (4)	-0.0593 (4)	0.0259 (9)
O21a	-0.0027 (7)	0.2530 (5)	-0.3006 (4)	0.0398 (12)
O21b	0.1349 (7)	0.1071 (4)	-0.1660 (4)	0.0371 (11)
O3c	0.3201 (6)	0.4629 (4)	-0.1497 (3)	0.0194 (8)
O3b	0.4119 (6)	0.2711 (4)	-0.2478 (4)	0.0251 (9)
O31a	0.7106 (7)	0.3843 (5)	-0.3606 (4)	0.0379 (12)
O31b	0.3388 (7)	0.4339 (5)	-0.3962 (4)	0.0371 (11)
Ow1	0.7776 (6)	0.0937 (4)	0.5105 (4)	0.0329 (11)
Ow2	0.6042 (7)	-0.1382 (4)	0.5370 (4)	0.0313 (10)
Ow3	0.4904 (7)	-0.0676 (4)	0.3309 (4)	0.0297 (10)
Ow4	0.0157 (8)	0.3699 (5)	0.4133 (4)	0.0473 (13)
Ow5	0.6022 (8)	0.2638 (5)	0.3373 (5)	0.0434 (13)
Ow6	0.9885 (7)	0.8796 (5)	0.6511 (4)	0.0435 (13)
Ow7	0.6897 (8)	1.0180 (5)	0.8701 (4)	0.0440 (13)
Ow8	0.5886 (7)	1.1689 (5)	1.0680 (5)	0.0419 (12)

Table 2. Selected geometric parameters (Å, °)

Co—O3c	1.945 (4)	Mo2—O21a	1.719 (5)
Co—O2c	1.965 (4)	Mo2—O21b	1.723 (5)
Co—O1c	1.992 (4)	Mo2—O21b	1.956 (4)
Ga—Ow1	1.963 (4)	Mo2—O3b	1.971 (4)
Ga—Ow2	1.964 (5)	Mo2—O2c	2.302 (4)
Ga—Ow3	1.979 (4)	Mo2—O3c	2.304 (4)
Mo1—O11b	1.721 (5)	Mo3—O31a	1.715 (5)
Mo1—O11a	1.749 (4)	Mo3—O31b	1.719 (5)
Mo1—O1b	1.944 (4)	Mo3—O1b'	1.969 (5)
Mo1—O2b	1.967 (4)	Mo3—O3b	1.969 (4)
Mo1—O2c	2.282 (4)	Mo3—O3c	2.324 (4)
Mo1—O1c	2.336 (4)	Mo3—O1c'	2.352 (4)

O3c—Co—O2c ¹	96.6 (2)	Ow1—Ga—Ow2	89.3 (2)
O3c—Co—O2c	83.4 (2)	Ow1—Ga—Ow2 ²	90.7 (2)
O3c—Co—O1c	95.1 (2)	Ow1—Ga—Ow3 ¹	90.3 (2)
O2c—Co—O1c	84.3 (2)	Ow2—Ga—Ow3 ²	90.3 (2)
O3c—Co—O1c ⁴	84.9 (2)	Ow1—Ga—Ow3	89.7 (2)
O2c—Co—O1c ⁴	95.7 (2)	Ow2—Ga—Ow3	89.7 (2)

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

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1c—H1O _c ...O2b ¹	1.031	1.954	2.984 (5)	175.8
O2c—H2O _c ...Ow8 ⁱⁱ	0.889	1.820	2.700 (6)	169.8
O3c—H3O _c ...O1a ¹	0.807	1.920	2.723 (5)	173.5
Ow1—H1a...O2a ⁱⁱⁱ	0.743	1.923	2.646 (6)	164.5
Ow1—H1b...Ow6 ^{iv}	0.817	1.850	2.661 (7)	172.1
Ow2—H2a...Ow5 ^v	0.787	1.849	2.599 (7)	158.9
Ow2—H2b...Ow6 ^{vi}	0.841	1.975	2.769 (7)	157.0
Ow3—H3a...O3b ^{vii}	0.830	1.795	2.594 (6)	161.2
Ow3—H3b...Ow7 ^{viii}	0.881	1.922	2.751 (7)	156.3
Ow4—H4a...O3t ^{ix}	0.830	2.149	2.828 (6)	139.0
Ow5—H5a...O1b	0.801	2.022	2.801 (6)	164.3
Ow5—H5b...Ow4 ^x	0.848	2.089	2.811 (7)	142.8
Ow6—H6a...O2t ^{xi}	0.841	2.217	2.932 (6)	143.0
Ow6—H6b...Ow4 ^{xiii}	1.286	1.664	2.793 (7)	142.2
Ow7—H7a...O1t ^{xii}	0.831	2.373	3.043 (6)	138.2
Ow7—H7b...Ow3 ^{xiii}	1.113	2.215	2.751 (7)	106.8
Ow8—H8a...Ow7	1.043	1.916	2.866 (7)	149.8
Ow8—H8b...O1a ^{xi}	0.905	2.242	3.028 (6)	145.1

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $x, y-1, z-1$; (iii) $1+x, y, 1+z$; (iv) $2-x, 1-y, 1-z$; (v) $1-x, -y, 1-z$; (vi) $x, y-1, z$; (vii) $1-x, -y, -z$; (viii) $1-x, 1-y, 1-z$; (ix) $x, y, 1+z$; (x) $1+x, y, z$; (xi) $1+x, 1+y, 1+z$.

Data collection: P4 (Siemens, 1994a). Cell refinement: P4, XSCANS (Siemens, 1994b). Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL-Plus (Sheldrick, 1990). Software used to prepare material for publication: SHELXL93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1334). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[Os₅(μ-H)₂(CO)₁₆]: a Second Crystal Form

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Abstract

The title compound, hexadecacarbonyl- $1\kappa^3C, 2\kappa^3C, 3\kappa^3C, 4\kappa^4C, 5\kappa^5C$ -di- μ -hydrido- $1:2\kappa^2H; 1:3\kappa^2H$ -pentaosmium(8 Os—Os), has been crystallized in a different crystal form from that reported previously [Guy & Sheldrick (1978). *Acta Cryst.* **B34**, 1725–1727]. The form reported here has crystallographic mirror symmetry and the packing arrangement in the crystal exhibits a different relative orientation of the molecules from the earlier structure.

Comment

The title compound, (I), was first obtained by Eady, Johnson & Lewis (1973, 1977) from the vacuum pyrolysis of Os₃(CO)₁₂ in the presence of water. During our study of the reaction between Os₃(CO)₁₂ and Me₂GeH₂, we have also isolated compound (I) as a minor product. Crystallization from hot toluene gave brown, irregularly shaped crystals in the orthorhombic system.

In the earlier study by Guy & Sheldrick (1978), it was noted that the molecule has approximate C_s symmetry. In our particular sample, the mirror symmetry is crystallographically imposed, as the molecule sits on a mirror plane passing through Os1, Os3 and Os4 (Fig. 1). The molecular geometries and bond parameters are, however, otherwise identical within the e.s.d.'s reported for the earlier structure. Although the H atom was not located crystallographically, its position was calculated with the program HYDEX (Orpen, 1980) and it was included (but not refined) in the final cycles of refinement. The H atom was calculated to be bridging the longest Os—Os bonds (Os2—Os3 and Os2'—Os3). The closest intermolecular contacts in both the structure reported here and that reported by Guy & Sheldrick (1978) are quite similar; these involve O12 and O23 in