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Triammonium hexahydroxidoctadeca-oxidohexamolybdogallate(III) heptahydrate

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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{Mo}-\text{O}) = 0.004$ Å; H-atom completeness 19%; R factor = 0.040; wR factor = 0.110; data-to-parameter ratio = 15.7.

The title compound, $(\text{NH}_4)_3[\text{GaMo}_6(\text{OH})_6\text{O}_{18}] \cdot 7\text{H}_2\text{O}$, contains two centrosymmetric GaMo_6 B-type Anderson cluster units consisting of central GaO_6 octahedra surrounded by a hexagonal assembly of MoO_6 edge-sharing octahedra. Like other B-type Anderson clusters, where the central Mo atom is substituted with a di- or trivalent metal ion, the central six μ_3 -oxido bridges are protonated. The average Ga—O bond length is 1.97 (1) Å, whereas the average Mo—O distances are 2.29 (2), 1.94 (1) and 1.709 (5) Å, respectively, for Mo—(μ_3 -OH), Mo—(μ_2 -O) and Mo=O bonds. In the crystal structure, the $\text{Ga}(\mu_3\text{-OH})_6\text{Mo}_6\text{O}_{18}^{3-}$ polyanionic clusters are surrounded by NH_4^+ cations and solvent water molecules, forming an extended network of hydrogen bonds.

Related literature

The gallium-substituted B-type Anderson cluster has been observed previously in solution and the solid state (Rollins & Earley, 1959; Kitazumi *et al.*, 2003), but crystal structures have not been reported. Anderson–Evans clusters are well known and many papers dealing with their preparation have been published (Anderson, 1937; Lorenzo-Luis & Gili, 2000; Lee *et al.*, 2001, and references therein). A similar planar core of seven metals is observed in the recently reported structure of $[\text{Ga}_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(\text{H}_2\text{O})_{24}](\text{NO}_3)_{15}$ (Rather *et al.*, 2005). Research into this structure led to isolation of the title compound.

Experimental

Crystal data

$(\text{NH}_4)_3[\text{GaMo}_6(\text{OH})_6\text{O}_{18}] \cdot 7\text{H}_2\text{O}$ $b = 10.9651$ (7) Å
 $M_r = 1215.65$ $c = 11.7599$ (8) Å
 Monoclinic, $P2_1/c$ $\beta = 100.2120$ (10)°
 $a = 22.7642$ (15) Å $V = 2888.9$ (3) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 3.56$ mm⁻¹

$T = 173$ (2) K
 $0.38 \times 0.20 \times 0.03$ mm

Data collection

Bruker SMART APEX CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1995)
 $T_{\text{min}} = 0.345$, $T_{\text{max}} = 0.901$

15163 measured reflections
 6225 independent reflections
 4471 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.110$
 $S = 1.17$
 6225 reflections
 397 parameters
 6 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 1.02$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.10$ e Å⁻³

Table 1

Selected bond lengths (Å).

| | | | |
|---------------------|-----------|-----------------------|-----------|
| Ga1—O3 | 1.953 (3) | Mo3—O6 | 1.949 (4) |
| Ga1—O1 | 1.954 (4) | Mo3—O3 | 2.252 (4) |
| Ga1—O2 | 1.972 (3) | Mo3—O1 ⁱ | 2.286 (4) |
| Ga2—O15 | 1.968 (3) | Mo4—O19 | 1.705 (4) |
| Ga2—O13 | 1.969 (3) | Mo4—O20 | 1.713 (4) |
| Ga2—O14 | 1.978 (3) | Mo4—O17 | 1.939 (3) |
| Mo1—O7 | 1.703 (4) | Mo4—O16 | 1.948 (3) |
| Mo1—O8 | 1.711 (4) | Mo4—O13 | 2.286 (3) |
| Mo1—O5 | 1.918 (4) | Mo4—O14 | 2.324 (3) |
| Mo1—O4 | 1.939 (4) | Mo5—O21 | 1.702 (4) |
| Mo1—O1 | 2.293 (4) | Mo5—O22 | 1.708 (3) |
| Mo1—O2 | 2.307 (4) | Mo5—O17 | 1.932 (4) |
| Mo2—O9 | 1.704 (4) | Mo5—O18 | 1.956 (3) |
| Mo2—O10 | 1.714 (4) | Mo5—O15 | 2.285 (3) |
| Mo2—O6 | 1.943 (4) | Mo5—O14 | 2.284 (3) |
| Mo2—O5 | 1.948 (4) | Mo6—O23 | 1.712 (3) |
| Mo2—O3 | 2.287 (4) | Mo6—O24 | 1.719 (4) |
| Mo2—O2 | 2.300 (3) | Mo6—O16 ⁱⁱ | 1.917 (4) |
| Mo3—O12 | 1.711 (4) | Mo6—O18 | 1.944 (4) |
| Mo3—O11 | 1.715 (4) | Mo6—O15 | 2.273 (3) |
| Mo3—O4 ⁱ | 1.918 (4) | Mo6—O13 ⁱⁱ | 2.290 (3) |

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

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|--|----------|--------------|--------------|----------------|
| O2—H2 ⁱⁱⁱ ···O10 ⁱⁱⁱ | 0.84 (2) | 2.00 (3) | 2.822 (5) | 166 (6) |
| O13—H13 ^{iv} ···O23 ^{iv} | 0.84 (2) | 1.86 (2) | 2.691 (5) | 173 (7) |
| O14—H14 ^v ···O22 ^v | 0.84 (2) | 1.98 (2) | 2.808 (5) | 168 (6) |
| O3—H3 ^{vi} ···O45 ^{vi} | 0.85 (2) | 1.76 (3) | 2.602 (5) | 169 (8) |
| O1—H1 ^{vii} ···O11 ^{vii} | 0.85 (2) | 1.87 (4) | 2.682 (5) | 159 (9) |
| O15—H15 ^{viii} ···O15 | 0.83 (2) | 1.87 (3) | 2.645 (5) | 155 (7) |

Symmetry codes: (iii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (vi) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (vii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$.

Table 3

Short contact geometry (Å).

| | | | |
|---------------------------|-----------|--------------------------|-----------|
| N1S···O24 ⁱⁱ | 2.911 (7) | O2S···O12 | 2.797 (6) |
| N1S···O6S ^{vi} | 2.784 (8) | O2S···O3S ^{xii} | 2.830 (7) |
| N2S···O16 | 2.779 (6) | O2S···O6S ^{ix} | 2.704 (7) |
| N2S···O21 ⁱⁱⁱ | 2.979 (6) | O3S···O9 | 3.016 (6) |
| N2S···O24 ^{vii} | 2.901 (6) | O3S···O19 | 3.034 (7) |
| N2S···O3S ^{viii} | 2.899 (7) | O3S···O5S ^{iv} | 2.917 (8) |
| N2S···O7S | 2.898 (7) | O4S···O3 ^{xiii} | 2.602 (5) |
| N3S···O5 ⁱ | 2.775 (6) | O4S···O6 | 2.773 (6) |
| N3S···O12 ^{xii} | 2.907 (7) | O4S···O6 ^{xii} | 2.934 (6) |
| N3S···O5S | 2.801 (8) | O5S···O8 | 2.782 (6) |
| N3S···O7S ^d | 3.030 (8) | O5S···O16 ^f | 3.083 (6) |
| O1S···O18 ^x | 2.794 (5) | O6S···O20 | 2.776 (6) |
| O1S···O18 ⁱⁱ | 2.905 (6) | O6S···O7S | 2.769 (7) |
| O2S···O4 ^{xi} | 2.718 (5) | O7S···O7 ^{xiv} | 2.973 (6) |

Symmetry codes (i): $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii): $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii): $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv): $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (v): $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (vi): $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (vii): $-x, y - \frac{1}{2}, -z + \frac{3}{2}$; (viii): $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ix): $1 - x, 1 - y, 1 - z$; (x): $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (xi): $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (xii): $-x + 1, -y, -z + 1$; (xiii): $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (xiv): $x, -y + \frac{3}{2}, z + \frac{1}{2}$

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2161).

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Triammonium hexahydroxidooctadecaoxidohexamolybdogallate(III) heptahydrate

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Comment

Compounds containing Anderson-type clusters have been explored for applications as structural aesthetics, biologically active compounds, and catalysts (Rollins & Earley, 1959; Lorenzo-Luis & Gili, 2000). They have also been shown to act as building blocks for larger molecular assemblies, where they can be linked to form extended networks with pores and cavities (Lorenzo-Luis & Gili, 2000). The majority of Anderson clusters are based on $\text{Mo}_7\text{O}_{24}^{6-}$ or $\text{W}_7\text{O}_{24}^{6-}$ frameworks, and many structures have been synthesized with substitution of the central octahedron or variable bridging ligands (Lorenzo-Luis & Gili, 2000). Due to the similarity of the structure of the $\text{Mo}_7\text{O}_{24}^{6-}$ complex to the inner planar core of our recently reported flat- Ga_{13} metal-hydroxo cluster $[\text{Ga}_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(\text{H}_2\text{O})_{24}](\text{NO}_3)_{15}$ (Rather *et al.*, 2005), it was hypothesized that a mixed-metal Mo_7Ga_6 compound could be obtained by reaction of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ with six or more equivalents of $\text{Ga}(\text{NO}_3)_3$. Setting up the reaction in a similar manner to the synthesis of flat- Ga_{13} (dissolving starting materials in a $\text{MeOH}:\text{H}_2\text{O}$ mixture and adding *N*-nitroso-di-*n*-butylamine), single crystals of the gallium-substituted B-type Anderson cluster, $(\text{NH}_4)_3[\text{Ga}(\mu_3\text{-OH})_6\text{Mo}_6\text{O}_{18}]\cdot 7\text{H}_2\text{O}$, (I), were isolated and structurally characterized by X-ray crystallography.

Anderson-type polyanions were first described by Anderson (1937). The planar structure consisting of seven metals observed in that compound is also observed in the structure of (I), with average Ga—O bond lengths of 1.97 (1) Å. The average Mo—O distances are 2.29 (2), 1.94 (1) and 1.710 (5) Å, respectively, for Mo-(μ_3 -OH), Mo-(μ_2 -O) and Mo=O. There are six μ_3 -OH bridges, six μ_2 -oxo bridges, and twelve terminal oxo ligands for each of the two independent cluster anions (Figure 1).

Extensive literature reports have covered the different structural variants and chemistry of hexamolybdoaluminate(III) polyanions (Lorenzo-Luis & Gili, 2000). The synthesis reported herein also represents an alternative preparation of the Al-substituted structure, with no acid addition required (as is usually the case). Synthesis by this method also represents a far more benign method than that previously reported. The Ga-substituted B-type Anderson compound had been synthesized previously by adding a solution of Ga metal in concentrated HNO_3 to a solution of MoO_3 in aqueous NaOH . The mixture was heated overnight and rinsed several times with acetone, and vacuum dried overnight, affording product as the sodium salt. However, a crystal structure determination of the title compound has not been reported previously (Rollins & Earley, 1959; Kitazumi *et al.*, 2003).

Experimental

Commercial products $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ (Baker and Adamson) and $\text{Ga}(\text{NO}_3)_3$ (Strem) were used to obtain the title compound, (I). $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ (0.25 g, 0.2 mmol) and $\text{Ga}(\text{NO}_3)_3$ (0.7 g, 1.92 mmol) were dissolved in a 1:1 $\text{H}_2\text{O}/\text{MeOH}$ mixture (10 ml) in a 20 ml scintillation vial. The mixture was heated slightly, with some cloudiness remaining in the mixture. *N*-nitroso-di-*n*-butylamine (0.45 g, 0.5 ml, 2.8 mmol) was added, and was not initially miscible. Additional MeOH (~2 ml) brought most into solution, and the mixture was then filtered. The remaining solution was evaporated, and after 9 d clear,

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colorless crystals with block-like habit had formed around the outside edge of the vial. The crystals were isolated in 90% crude yield. Fewer equivalents of $\text{Ga}(\text{NO}_3)_3$ (relative to $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$) and no organic additive (H_2O as solvent only) have also been used successfully to produce crystals of (I).

Refinement

The H atoms of the μ_3 -oxo groups were found from difference Fourier maps and were refined with restraints; the value of 0.85 Å was used as a target for corresponding O—H distances in the refinement. The H atoms in the NH_4^+ cations and solvent water molecules were not found and thus were not taken into consideration. Positions of N atoms of the NH_4^+ cations *versus* positions of the solvent water molecules were found based on analysis of the network of H-bonds in the structure. The positions of two NH_4^+ cations found in the structure of (I) are close to positions of the K cations found in the structure of $\text{K}_3[\text{Co}(\mu_3\text{-OH})_6\text{Mo}_6\text{O}_{18}]\cdot 7\text{H}_2\text{O}$ (Lee *et al.*, 2001), but the position of the third one is different against the positions of the third K cation in the potassium compound. Both structures crystallize in the same space groups and exhibit similar lattice parameters of the unit cells. However, the β -angles in these structures are different ($100.212(1)^\circ$ in (I) *versus* $94.577(9)^\circ$ in $\text{K}_3[\text{Co}(\mu_3\text{-OH})_6\text{Mo}_6\text{O}_{18}]\cdot 7\text{H}_2\text{O}$) that indicates the packing in these structures seems to be different. The highest peak and the deepest hole observed in the final Fourier map are 0.96 and 0.87 Å away from atoms O1S and Mo6, respectively.

Figures

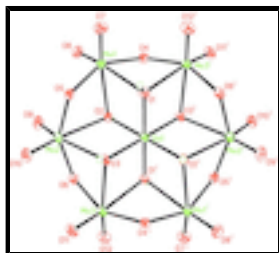


Fig. 1. One of the two symmetrically independent $\text{Ga}(\mu_3\text{-OH})_6\text{Mo}_6\text{O}_{18}^{-3}$ anions in the crystal structure of (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code (i): $1 - x, 1 - y, 1 - z$].

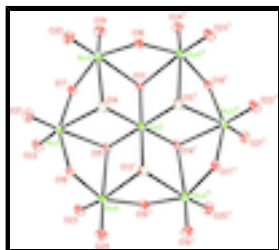


Fig. 2. The second polyanionic cluster, displayed at the same probability level than in Fig. 1. [Symmetry code: (ii) $-x, 1 - y, 1 - z$].

Triammonium hexahydroxidoctadecaoxidohexamolybdogallate(III) heptahydrate

Crystal data

$(\text{NH}_4)_3[\text{GaMo}_6(\text{OH})_6\text{O}_{18}]\cdot 7\text{H}_2\text{O}$

$M_r = 1215.65$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 22.7642(15)$ Å

$F(000) = 2336$

$D_x = 2.795$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4958 reflections

$\theta = 2.6\text{--}27.0^\circ$

$b = 10.9651 (7) \text{ \AA}$
 $c = 11.7599 (8) \text{ \AA}$
 $\beta = 100.212 (1)^\circ$
 $V = 2888.9 (3) \text{ \AA}^3$
 $Z = 4$

$\mu = 3.56 \text{ mm}^{-1}$
 $T = 173 \text{ K}$
 Plate, colorless
 $0.38 \times 0.20 \times 0.03 \text{ mm}$

Data collection

Bruker SMART APEX CCD diffractometer
 Radiation source: fine-focus sealed tube graphite
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1995)
 $T_{\min} = 0.345$, $T_{\max} = 0.901$
 15163 measured reflections

6225 independent reflections
 4471 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$
 $\theta_{\max} = 27.0^\circ$, $\theta_{\min} = 0.9^\circ$
 $h = -29 \rightarrow 28$
 $k = -13 \rightarrow 12$
 $l = -15 \rightarrow 8$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.110$
 $S = 1.17$
 6225 reflections
 397 parameters
 6 restraints

Primary atom site location: structure-invariant direct methods
 Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 12.6663P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.02 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.10 \text{ e \AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|-------------|----------------------------------|
| Ga1 | 0.5000 | 0.5000 | 0.5000 | 0.01123 (17) |
| Ga2 | 0.0000 | 0.5000 | 0.5000 | 0.00902 (16) |
| Mo1 | 0.35141 (2) | 0.51841 (4) | 0.45196 (4) | 0.01479 (12) |
| Mo2 | 0.41872 (2) | 0.26668 (4) | 0.56993 (4) | 0.01458 (12) |
| Mo3 | 0.56707 (2) | 0.25263 (4) | 0.62097 (4) | 0.01402 (12) |

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| | | | | |
|-----|----------------|-------------|-------------|--------------|
| Mo4 | 0.149068 (19) | 0.48479 (4) | 0.54667 (4) | 0.01355 (12) |
| Mo5 | 0.079304 (19) | 0.73509 (4) | 0.42939 (4) | 0.01232 (11) |
| Mo6 | -0.069381 (19) | 0.74690 (4) | 0.37855 (4) | 0.01178 (11) |
| O1 | 0.43873 (16) | 0.6143 (3) | 0.5303 (3) | 0.0141 (7) |
| O2 | 0.43179 (15) | 0.4003 (3) | 0.4257 (3) | 0.0129 (7) |
| O3 | 0.49702 (16) | 0.3947 (3) | 0.6328 (3) | 0.0134 (7) |
| O4 | 0.37835 (15) | 0.6157 (3) | 0.3335 (3) | 0.0158 (8) |
| O5 | 0.37155 (16) | 0.4126 (3) | 0.5830 (3) | 0.0170 (8) |
| O6 | 0.49123 (16) | 0.1923 (3) | 0.5366 (3) | 0.0156 (7) |
| O7 | 0.31028 (18) | 0.6221 (4) | 0.5119 (3) | 0.0246 (9) |
| O8 | 0.30144 (17) | 0.4316 (4) | 0.3604 (3) | 0.0237 (9) |
| O9 | 0.36921 (17) | 0.1825 (4) | 0.4758 (3) | 0.0231 (9) |
| O10 | 0.41851 (18) | 0.2072 (4) | 0.7046 (3) | 0.0236 (9) |
| O11 | 0.56491 (18) | 0.1958 (4) | 0.7561 (3) | 0.0226 (9) |
| O12 | 0.61044 (18) | 0.1536 (4) | 0.5596 (3) | 0.0238 (9) |
| O13 | 0.06252 (15) | 0.3866 (3) | 0.4699 (3) | 0.0102 (7) |
| O14 | 0.06773 (16) | 0.6024 (3) | 0.5736 (3) | 0.0116 (7) |
| O15 | 0.00201 (15) | 0.6053 (3) | 0.3652 (3) | 0.0110 (7) |
| O16 | 0.12375 (16) | 0.3851 (3) | 0.6664 (3) | 0.0162 (8) |
| O17 | 0.12752 (16) | 0.5927 (3) | 0.4152 (3) | 0.0151 (7) |
| O18 | 0.00595 (15) | 0.8078 (3) | 0.4637 (3) | 0.0136 (7) |
| O19 | 0.19123 (17) | 0.3843 (4) | 0.4850 (3) | 0.0226 (9) |
| O20 | 0.19832 (17) | 0.5724 (4) | 0.6393 (3) | 0.0234 (9) |
| O21 | 0.12650 (17) | 0.8245 (4) | 0.5225 (3) | 0.0211 (8) |
| O22 | 0.07868 (17) | 0.7965 (3) | 0.2957 (3) | 0.0189 (8) |
| O23 | -0.06660 (17) | 0.8033 (3) | 0.2438 (3) | 0.0193 (8) |
| O24 | -0.11382 (17) | 0.8471 (3) | 0.4373 (3) | 0.0202 (8) |
| N1S | 0.1801 (2) | 0.5087 (5) | 0.2359 (5) | 0.0322 (12) |
| N2S | 0.1667 (2) | 0.4712 (5) | 0.8877 (4) | 0.0248 (11) |
| N3S | 0.3235 (3) | 0.0134 (5) | 0.2727 (5) | 0.0359 (14) |
| O1S | -0.0158 (3) | 0.5433 (4) | 0.1444 (4) | 0.0396 (13) |
| O2S | 0.6662 (2) | 0.0517 (4) | 0.3883 (4) | 0.0323 (10) |
| O3S | 0.2536 (2) | 0.1465 (5) | 0.5634 (4) | 0.0427 (12) |
| O4S | 0.4997 (3) | 0.0459 (5) | 0.3479 (4) | 0.063 (2) |
| O5S | 0.2479 (2) | 0.2149 (5) | 0.2729 (5) | 0.0456 (13) |
| O6S | 0.2500 (2) | 0.8016 (5) | 0.6761 (4) | 0.0430 (12) |
| O7S | 0.2491 (2) | 0.6706 (5) | 0.8771 (4) | 0.0446 (13) |
| H1 | 0.428 (4) | 0.643 (8) | 0.591 (5) | 0.07 (3)* |
| H2 | 0.434 (3) | 0.373 (6) | 0.360 (3) | 0.032 (19)* |
| H3 | 0.493 (4) | 0.416 (8) | 0.701 (3) | 0.06 (3)* |
| H13 | 0.062 (3) | 0.365 (6) | 0.401 (2) | 0.027 (18)* |
| H14 | 0.065 (3) | 0.634 (6) | 0.638 (3) | 0.027 (18)* |
| H15 | 0.003 (3) | 0.568 (5) | 0.304 (3) | 0.031 (19)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|------------|------------|------------|------------|
| Ga1 | 0.0137 (4) | 0.0111 (4) | 0.0095 (4) | 0.0004 (3) | 0.0037 (3) | 0.0004 (3) |

| | | | | | | |
|-----|-------------|-------------|-------------|---------------|--------------|--------------|
| Ga2 | 0.0122 (4) | 0.0076 (4) | 0.0078 (4) | 0.0004 (3) | 0.0033 (3) | 0.0009 (3) |
| Mo1 | 0.0136 (2) | 0.0175 (3) | 0.0137 (2) | 0.00039 (17) | 0.00386 (17) | 0.00109 (18) |
| Mo2 | 0.0179 (2) | 0.0135 (2) | 0.0132 (2) | -0.00216 (17) | 0.00494 (17) | 0.00214 (17) |
| Mo3 | 0.0182 (2) | 0.0129 (2) | 0.0114 (2) | 0.00243 (17) | 0.00382 (17) | 0.00248 (17) |
| Mo4 | 0.0130 (2) | 0.0149 (2) | 0.0130 (2) | 0.00026 (16) | 0.00294 (17) | 0.00230 (17) |
| Mo5 | 0.0163 (2) | 0.0106 (2) | 0.0105 (2) | -0.00180 (16) | 0.00373 (17) | 0.00182 (16) |
| Mo6 | 0.0164 (2) | 0.0102 (2) | 0.0094 (2) | 0.00274 (16) | 0.00408 (16) | 0.00240 (16) |
| O1 | 0.0144 (19) | 0.018 (2) | 0.0103 (18) | 0.0022 (14) | 0.0039 (14) | 0.0003 (15) |
| O2 | 0.0146 (18) | 0.0135 (18) | 0.0107 (18) | -0.0024 (14) | 0.0026 (14) | 0.0000 (15) |
| O3 | 0.0168 (19) | 0.0130 (18) | 0.0111 (18) | 0.0005 (14) | 0.0045 (14) | 0.0018 (15) |
| O4 | 0.0149 (18) | 0.020 (2) | 0.0115 (17) | 0.0002 (15) | -0.0002 (14) | 0.0015 (15) |
| O5 | 0.0157 (19) | 0.019 (2) | 0.0188 (19) | -0.0008 (15) | 0.0090 (15) | 0.0015 (15) |
| O6 | 0.020 (2) | 0.0124 (18) | 0.0147 (18) | 0.0008 (14) | 0.0045 (14) | -0.0014 (15) |
| O7 | 0.024 (2) | 0.028 (2) | 0.023 (2) | 0.0061 (17) | 0.0100 (17) | 0.0019 (18) |
| O8 | 0.018 (2) | 0.026 (2) | 0.027 (2) | -0.0047 (16) | 0.0038 (16) | 0.0017 (18) |
| O9 | 0.024 (2) | 0.022 (2) | 0.023 (2) | -0.0078 (16) | 0.0037 (16) | -0.0005 (17) |
| O10 | 0.026 (2) | 0.023 (2) | 0.024 (2) | -0.0022 (17) | 0.0092 (17) | 0.0061 (17) |
| O11 | 0.028 (2) | 0.022 (2) | 0.0181 (19) | 0.0011 (17) | 0.0039 (16) | 0.0082 (17) |
| O12 | 0.029 (2) | 0.023 (2) | 0.020 (2) | 0.0043 (17) | 0.0072 (17) | -0.0003 (17) |
| O13 | 0.0146 (18) | 0.0108 (17) | 0.0059 (16) | 0.0017 (13) | 0.0037 (13) | -0.0002 (14) |
| O14 | 0.0200 (19) | 0.0109 (18) | 0.0046 (16) | -0.0005 (14) | 0.0037 (14) | -0.0001 (14) |
| O15 | 0.0197 (19) | 0.0091 (17) | 0.0050 (16) | 0.0009 (14) | 0.0042 (13) | -0.0008 (14) |
| O16 | 0.0175 (19) | 0.0160 (19) | 0.0148 (18) | 0.0015 (15) | 0.0025 (14) | 0.0037 (15) |
| O17 | 0.0184 (19) | 0.0167 (19) | 0.0113 (17) | 0.0001 (14) | 0.0058 (14) | 0.0023 (14) |
| O18 | 0.0173 (19) | 0.0097 (17) | 0.0140 (17) | -0.0011 (14) | 0.0037 (14) | -0.0001 (14) |
| O19 | 0.021 (2) | 0.025 (2) | 0.025 (2) | 0.0058 (16) | 0.0134 (16) | 0.0031 (17) |
| O20 | 0.022 (2) | 0.027 (2) | 0.019 (2) | -0.0062 (17) | -0.0009 (16) | 0.0002 (17) |
| O21 | 0.022 (2) | 0.020 (2) | 0.021 (2) | -0.0041 (16) | 0.0043 (16) | 0.0008 (16) |
| O22 | 0.029 (2) | 0.018 (2) | 0.0110 (18) | 0.0026 (16) | 0.0067 (15) | 0.0024 (15) |
| O23 | 0.028 (2) | 0.019 (2) | 0.0114 (18) | 0.0017 (16) | 0.0044 (15) | 0.0040 (15) |
| O24 | 0.023 (2) | 0.018 (2) | 0.022 (2) | 0.0041 (16) | 0.0089 (16) | -0.0009 (16) |
| N1S | 0.031 (3) | 0.041 (3) | 0.025 (3) | 0.000 (2) | 0.005 (2) | -0.007 (2) |
| N2S | 0.027 (3) | 0.029 (3) | 0.021 (2) | 0.001 (2) | 0.011 (2) | -0.005 (2) |
| N3S | 0.036 (3) | 0.042 (3) | 0.032 (3) | 0.006 (3) | 0.014 (3) | 0.016 (3) |
| O1S | 0.086 (4) | 0.019 (2) | 0.018 (2) | 0.004 (2) | 0.022 (2) | -0.0010 (18) |
| O2S | 0.034 (3) | 0.041 (3) | 0.021 (2) | 0.005 (2) | 0.0056 (18) | -0.001 (2) |
| O3S | 0.032 (3) | 0.051 (3) | 0.042 (3) | -0.005 (2) | -0.001 (2) | -0.002 (2) |
| O4S | 0.159 (7) | 0.021 (3) | 0.013 (2) | 0.008 (3) | 0.021 (3) | 0.0012 (19) |
| O5S | 0.038 (3) | 0.041 (3) | 0.057 (3) | -0.010 (2) | 0.008 (2) | -0.014 (3) |
| O6S | 0.044 (3) | 0.040 (3) | 0.044 (3) | -0.012 (2) | 0.007 (2) | -0.005 (2) |
| O7S | 0.053 (3) | 0.038 (3) | 0.038 (3) | -0.011 (2) | -0.004 (2) | -0.003 (2) |

Geometric parameters (Å, °)

| | | | |
|---------------------|-----------|---------------------|-----------|
| Ga1—O3 ⁱ | 1.953 (3) | Mo3—O6 | 1.949 (4) |
| Ga1—O3 | 1.953 (3) | Mo3—O3 | 2.252 (4) |
| Ga1—O1 ⁱ | 1.954 (4) | Mo3—O1 ⁱ | 2.286 (4) |
| Ga1—O1 | 1.954 (4) | Mo4—O19 | 1.705 (4) |

supplementary materials

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|--|-------------|-----------------------|-------------|
| Ga1—O2 ⁱ | 1.972 (3) | Mo4—O20 | 1.713 (4) |
| Ga1—O2 | 1.972 (3) | Mo4—O17 | 1.939 (3) |
| Ga2—O15 ⁱⁱ | 1.968 (3) | Mo4—O16 | 1.948 (3) |
| Ga2—O15 | 1.968 (3) | Mo4—O13 | 2.286 (3) |
| Ga2—O13 ⁱⁱ | 1.969 (3) | Mo4—O14 | 2.324 (3) |
| Ga2—O13 | 1.969 (3) | Mo5—O21 | 1.702 (4) |
| Ga2—O14 | 1.978 (3) | Mo5—O22 | 1.708 (3) |
| Ga2—O14 ⁱⁱ | 1.978 (3) | Mo5—O17 | 1.932 (4) |
| Mo1—O7 | 1.703 (4) | Mo5—O18 | 1.956 (3) |
| Mo1—O8 | 1.711 (4) | Mo5—O15 | 2.285 (3) |
| Mo1—O5 | 1.918 (4) | Mo5—O14 | 2.284 (3) |
| Mo1—O4 | 1.939 (4) | Mo6—O23 | 1.712 (3) |
| Mo1—O1 | 2.293 (4) | Mo6—O24 | 1.719 (4) |
| Mo1—O2 | 2.307 (4) | Mo6—O16 ⁱⁱ | 1.917 (4) |
| Mo2—O9 | 1.704 (4) | Mo6—O18 | 1.944 (4) |
| Mo2—O10 | 1.714 (4) | Mo6—O15 | 2.273 (3) |
| Mo2—O6 | 1.943 (4) | Mo6—O13 ⁱⁱ | 2.290 (3) |
| Mo2—O5 | 1.948 (4) | O1—H1 | 0.85 (2) |
| Mo2—O3 | 2.287 (4) | O2—H2 | 0.84 (2) |
| Mo2—O2 | 2.300 (3) | O3—H3 | 0.85 (2) |
| Mo3—O12 | 1.711 (4) | O13—H13 | 0.84 (2) |
| Mo3—O11 | 1.715 (4) | O14—H14 | 0.84 (2) |
| Mo3—O4 ⁱ | 1.918 (4) | O15—H15 | 0.83 (2) |
| O3 ⁱ —Ga1—O3 | 180.0 | O19—Mo4—O13 | 92.19 (16) |
| O3 ⁱ —Ga1—O1 ⁱ | 96.11 (15) | O20—Mo4—O13 | 159.49 (16) |
| O3—Ga1—O1 ⁱ | 83.89 (15) | O17—Mo4—O13 | 83.94 (14) |
| O3 ⁱ —Ga1—O1 | 83.89 (15) | O16—Mo4—O13 | 71.12 (13) |
| O3—Ga1—O1 | 96.11 (15) | O19—Mo4—O14 | 159.82 (16) |
| O1 ⁱ —Ga1—O1 | 180.00 (14) | O20—Mo4—O14 | 92.85 (16) |
| O3 ⁱ —Ga1—O2 ⁱ | 83.70 (15) | O17—Mo4—O14 | 71.01 (13) |
| O3—Ga1—O2 ⁱ | 96.30 (15) | O16—Mo4—O14 | 82.43 (13) |
| O1 ⁱ —Ga1—O2 ⁱ | 84.55 (15) | O13—Mo4—O14 | 70.34 (12) |
| O1—Ga1—O2 ⁱ | 95.45 (15) | O21—Mo5—O22 | 105.42 (18) |
| O3 ⁱ —Ga1—O2 | 96.30 (15) | O21—Mo5—O17 | 102.56 (17) |
| O3—Ga1—O2 | 83.70 (15) | O22—Mo5—O17 | 98.72 (16) |
| O1 ⁱ —Ga1—O2 | 95.45 (15) | O21—Mo5—O18 | 95.58 (17) |
| O1—Ga1—O2 | 84.55 (15) | O22—Mo5—O18 | 99.26 (16) |
| O2 ⁱ —Ga1—O2 | 179.999 (1) | O17—Mo5—O18 | 149.97 (15) |
| O15 ⁱⁱ —Ga2—O15 | 180.0 | O21—Mo5—O15 | 158.85 (15) |
| O15 ⁱⁱ —Ga2—O13 ⁱⁱ | 96.04 (14) | O22—Mo5—O15 | 93.52 (16) |
| O15—Ga2—O13 ⁱⁱ | 83.96 (14) | O17—Mo5—O15 | 83.36 (14) |
| O15 ⁱⁱ —Ga2—O13 | 83.96 (14) | O18—Mo5—O15 | 71.71 (13) |
| O15—Ga2—O13 | 96.04 (14) | O21—Mo5—O14 | 91.86 (15) |
| O13 ⁱⁱ —Ga2—O13 | 180.0 | O22—Mo5—O14 | 161.99 (16) |

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| O15 ⁱⁱ —Ga2—O14 | 96.23 (14) | O17—Mo5—O14 | 72.03 (13) |
| O15—Ga2—O14 | 83.77 (14) | O18—Mo5—O14 | 83.77 (13) |
| O13 ⁱⁱ —Ga2—O14 | 95.44 (14) | O15—Mo5—O14 | 70.43 (12) |
| O13—Ga2—O14 | 84.56 (14) | O23—Mo6—O24 | 105.18 (18) |
| O15 ⁱⁱ —Ga2—O14 ⁱⁱ | 83.77 (14) | O23—Mo6—O16 ⁱⁱ | 98.37 (17) |
| O15—Ga2—O14 ⁱⁱ | 96.23 (14) | O24—Mo6—O16 ⁱⁱ | 101.31 (17) |
| O13 ⁱⁱ —Ga2—O14 ⁱⁱ | 84.56 (14) | O23—Mo6—O18 | 100.29 (17) |
| O13—Ga2—O14 ⁱⁱ | 95.45 (14) | O24—Mo6—O18 | 95.85 (17) |
| O14—Ga2—O14 ⁱⁱ | 180.0 | O16 ⁱⁱ —Mo6—O18 | 150.31 (15) |
| O7—Mo1—O8 | 106.2 (2) | O23—Mo6—O15 | 92.21 (15) |
| O7—Mo1—O5 | 98.15 (17) | O24—Mo6—O15 | 160.59 (15) |
| O8—Mo1—O5 | 101.91 (18) | O16 ⁱⁱ —Mo6—O15 | 84.25 (14) |
| O7—Mo1—O4 | 101.41 (17) | O18—Mo6—O15 | 72.17 (13) |
| O8—Mo1—O4 | 96.51 (17) | O23—Mo6—O13 ⁱⁱ | 160.43 (15) |
| O5—Mo1—O4 | 148.11 (15) | O24—Mo6—O13 ⁱⁱ | 93.42 (15) |
| O7—Mo1—O1 | 91.64 (17) | O16 ⁱⁱ —Mo6—O13 ⁱⁱ | 71.55 (13) |
| O8—Mo1—O1 | 160.15 (16) | O18—Mo6—O13 ⁱⁱ | 83.48 (13) |
| O5—Mo1—O1 | 83.59 (14) | O15—Mo6—O13 ⁱⁱ | 70.50 (12) |
| O4—Mo1—O1 | 70.98 (13) | Ga1—O1—Mo3 ⁱ | 102.26 (14) |
| O7—Mo1—O2 | 159.64 (17) | Ga1—O1—Mo1 | 103.21 (16) |
| O8—Mo1—O2 | 93.31 (16) | Mo3 ⁱ —O1—Mo1 | 93.09 (13) |
| O5—Mo1—O2 | 71.66 (13) | Ga1—O1—H1 | 135 (6) |
| O4—Mo1—O2 | 81.56 (14) | Mo3 ⁱ —O1—H1 | 115 (6) |
| O1—Mo1—O2 | 70.09 (13) | Mo1—O1—H1 | 99 (6) |
| O9—Mo2—O10 | 106.50 (19) | Ga1—O2—Mo2 | 102.79 (14) |
| O9—Mo2—O6 | 97.41 (17) | Ga1—O2—Mo1 | 102.15 (15) |
| O10—Mo2—O6 | 99.69 (17) | Mo2—O2—Mo1 | 92.85 (12) |
| O9—Mo2—O5 | 100.70 (18) | Ga1—O2—H2 | 116 (5) |
| O10—Mo2—O5 | 98.51 (17) | Mo2—O2—H2 | 119 (5) |
| O6—Mo2—O5 | 149.42 (15) | Mo1—O2—H2 | 120 (5) |
| O9—Mo2—O3 | 158.51 (16) | Ga1—O3—Mo3 | 103.53 (15) |
| O10—Mo2—O3 | 93.70 (16) | Ga1—O3—Mo2 | 103.88 (15) |
| O6—Mo2—O3 | 71.45 (14) | Mo3—O3—Mo2 | 94.30 (13) |
| O5—Mo2—O3 | 83.06 (14) | Ga1—O3—H3 | 128 (6) |
| O9—Mo2—O2 | 91.34 (16) | Mo3—O3—H3 | 116 (6) |
| O10—Mo2—O2 | 161.06 (17) | Mo2—O3—H3 | 106 (6) |
| O6—Mo2—O2 | 83.87 (14) | Mo3 ⁱ —O4—Mo1 | 119.01 (17) |
| O5—Mo2—O2 | 71.34 (14) | Mo1—O5—Mo2 | 119.36 (18) |
| O3—Mo2—O2 | 69.63 (12) | Mo2—O6—Mo3 | 117.54 (18) |
| O12—Mo3—O11 | 105.88 (19) | Ga2—O13—Mo4 | 103.36 (14) |
| O12—Mo3—O4 ⁱ | 101.65 (17) | Ga2—O13—Mo6 ⁱⁱ | 102.45 (13) |
| O11—Mo3—O4 ⁱ | 97.94 (17) | Mo4—O13—Mo6 ⁱⁱ | 93.37 (12) |
| O12—Mo3—O6 | 95.45 (17) | Ga2—O13—H13 | 117 (4) |
| O11—Mo3—O6 | 100.37 (17) | Mo4—O13—H13 | 113 (4) |
| O4 ⁱ —Mo3—O6 | 150.41 (15) | Mo6 ⁱⁱ —O13—H13 | 124 (5) |

supplementary materials

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| O12—Mo3—O3 | 158.97 (16) | Ga2—O14—Mo5 | 102.74 (14) |
| O11—Mo3—O3 | 93.27 (16) | Ga2—O14—Mo4 | 101.74 (14) |
| O4 ⁱ —Mo3—O3 | 83.83 (14) | Mo5—O14—Mo4 | 93.04 (12) |
| O6—Mo3—O3 | 72.14 (14) | Ga2—O14—H14 | 117 (4) |
| O12—Mo3—O1 ⁱ | 92.00 (16) | Mo5—O14—H14 | 116 (5) |
| O11—Mo3—O1 ⁱ | 160.95 (16) | Mo4—O14—H14 | 122 (4) |
| O4 ⁱ —Mo3—O1 ⁱ | 71.47 (14) | Ga2—O15—Mo6 | 103.08 (14) |
| O6—Mo3—O1 ⁱ | 84.08 (14) | Ga2—O15—Mo5 | 103.06 (14) |
| O3—Mo3—O1 ⁱ | 70.29 (13) | Mo6—O15—Mo5 | 94.02 (13) |
| O19—Mo4—O20 | 106.2 (2) | Ga2—O15—H15 | 115 (5) |
| O19—Mo4—O17 | 97.87 (17) | Mo6—O15—H15 | 121 (5) |
| O20—Mo4—O17 | 102.08 (17) | Mo5—O15—H15 | 117 (5) |
| O19—Mo4—O16 | 101.89 (17) | Mo6 ⁱⁱ —O16—Mo4 | 118.93 (18) |
| O20—Mo4—O16 | 95.69 (17) | Mo5—O17—Mo4 | 119.45 (17) |
| O17—Mo4—O16 | 148.51 (15) | Mo6—O18—Mo5 | 117.47 (17) |
| O3 ⁱ —Ga1—O1—Mo3 ⁱ | 1.23 (15) | O15—Ga2—O13—Mo4 | 82.62 (15) |
| O3—Ga1—O1—Mo3 ⁱ | -178.77 (15) | O13 ⁱⁱ —Ga2—O13—Mo4 | 64 (8) |
| O2 ⁱ —Ga1—O1—Mo3 ⁱ | 84.27 (15) | O14—Ga2—O13—Mo4 | -0.50 (13) |
| O2—Ga1—O1—Mo3 ⁱ | -95.73 (15) | O14 ⁱⁱ —Ga2—O13—Mo4 | 179.50 (13) |
| O3 ⁱ —Ga1—O1—Mo1 | 97.41 (16) | O15 ⁱⁱ —Ga2—O13—Mo6 ⁱⁱ | -0.82 (14) |
| O3—Ga1—O1—Mo1 | -82.59 (16) | O15—Ga2—O13—Mo6 ⁱⁱ | 179.18 (14) |
| O2 ⁱ —Ga1—O1—Mo1 | -179.54 (14) | O14—Ga2—O13—Mo6 ⁱⁱ | 96.06 (15) |
| O2—Ga1—O1—Mo1 | 0.46 (14) | O14 ⁱⁱ —Ga2—O13—Mo6 ⁱⁱ | -83.94 (15) |
| O7—Mo1—O1—Ga1 | 170.39 (18) | O19—Mo4—O13—Ga2 | -169.21 (17) |
| O8—Mo1—O1—Ga1 | -35.1 (5) | O20—Mo4—O13—Ga2 | 36.9 (5) |
| O5—Mo1—O1—Ga1 | 72.37 (16) | O17—Mo4—O13—Ga2 | -71.52 (15) |
| O4—Mo1—O1—Ga1 | -88.10 (17) | O16—Mo4—O13—Ga2 | 88.98 (16) |
| O2—Mo1—O1—Ga1 | -0.41 (13) | O14—Mo4—O13—Ga2 | 0.45 (12) |
| O7—Mo1—O1—Mo3 ⁱ | -86.25 (16) | O19—Mo4—O13—Mo6 ⁱⁱ | 87.14 (16) |
| O8—Mo1—O1—Mo3 ⁱ | 68.3 (5) | O20—Mo4—O13—Mo6 ⁱⁱ | -66.7 (5) |
| O5—Mo1—O1—Mo3 ⁱ | 175.73 (15) | O17—Mo4—O13—Mo6 ⁱⁱ | -175.17 (14) |
| O4—Mo1—O1—Mo3 ⁱ | 15.26 (13) | O16—Mo4—O13—Mo6 ⁱⁱ | -14.67 (13) |
| O2—Mo1—O1—Mo3 ⁱ | 102.96 (14) | O14—Mo4—O13—Mo6 ⁱⁱ | -103.20 (13) |
| O3 ⁱ —Ga1—O2—Mo2 | -179.47 (14) | O15 ⁱⁱ —Ga2—O14—Mo5 | 179.66 (14) |
| O3—Ga1—O2—Mo2 | 0.53 (14) | O15—Ga2—O14—Mo5 | -0.34 (14) |
| O1 ⁱ —Ga1—O2—Mo2 | 83.75 (15) | O13 ⁱⁱ —Ga2—O14—Mo5 | -83.63 (15) |
| O1—Ga1—O2—Mo2 | -96.25 (15) | O13—Ga2—O14—Mo5 | 96.37 (15) |
| O3 ⁱ —Ga1—O2—Mo1 | -83.67 (15) | O15 ⁱⁱ —Ga2—O14—Mo4 | 83.78 (14) |
| O3—Ga1—O2—Mo1 | 96.33 (15) | O15—Ga2—O14—Mo4 | -96.22 (14) |
| O1 ⁱ —Ga1—O2—Mo1 | 179.55 (14) | O13 ⁱⁱ —Ga2—O14—Mo4 | -179.51 (13) |
| O1—Ga1—O2—Mo1 | -0.45 (14) | O13—Ga2—O14—Mo4 | 0.49 (13) |
| O9—Mo2—O2—Ga1 | -170.25 (18) | O14 ⁱⁱ —Ga2—O14—Mo4 | 130 (9) |
| O10—Mo2—O2—Ga1 | 29.1 (6) | O21—Mo5—O14—Ga2 | 168.49 (18) |
| O6—Mo2—O2—Ga1 | -72.94 (16) | O22—Mo5—O14—Ga2 | -27.7 (6) |

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|-----------------------------|--------------|--------------------------------|--------------|
| O5—Mo2—O2—Ga1 | 88.91 (17) | O17—Mo5—O14—Ga2 | -88.91 (17) |
| O3—Mo2—O2—Ga1 | -0.48 (13) | O18—Mo5—O14—Ga2 | 73.08 (16) |
| O9—Mo2—O2—Mo1 | 86.60 (17) | O15—Mo5—O14—Ga2 | 0.31 (12) |
| O10—Mo2—O2—Mo1 | -74.1 (5) | O21—Mo5—O14—Mo4 | -88.75 (16) |
| O6—Mo2—O2—Mo1 | -176.08 (14) | O22—Mo5—O14—Mo4 | 75.0 (5) |
| O5—Mo2—O2—Mo1 | -14.24 (13) | O17—Mo5—O14—Mo4 | 13.85 (13) |
| O3—Mo2—O2—Mo1 | -103.63 (14) | O18—Mo5—O14—Mo4 | 175.84 (14) |
| O7—Mo1—O2—Ga1 | -26.9 (5) | O15—Mo5—O14—Mo4 | 103.06 (14) |
| O8—Mo1—O2—Ga1 | 169.24 (17) | O19—Mo4—O14—Ga2 | 30.9 (5) |
| O5—Mo1—O2—Ga1 | -89.30 (17) | O20—Mo4—O14—Ga2 | -168.40 (17) |
| O4—Mo1—O2—Ga1 | 73.15 (16) | O17—Mo4—O14—Ga2 | 89.81 (16) |
| O1—Mo1—O2—Ga1 | 0.41 (12) | O16—Mo4—O14—Ga2 | -73.04 (15) |
| O7—Mo1—O2—Mo2 | 76.8 (5) | O13—Mo4—O14—Ga2 | -0.44 (12) |
| O8—Mo1—O2—Mo2 | -87.02 (16) | O19—Mo4—O14—Mo5 | -72.8 (5) |
| O5—Mo1—O2—Mo2 | 14.43 (13) | O20—Mo4—O14—Mo5 | 87.92 (16) |
| O4—Mo1—O2—Mo2 | 176.88 (14) | O17—Mo4—O14—Mo5 | -13.88 (13) |
| O1—Mo1—O2—Mo2 | 104.14 (14) | O16—Mo4—O14—Mo5 | -176.72 (14) |
| O1 ⁱ —Ga1—O3—Mo3 | 1.25 (15) | O13—Mo4—O14—Mo5 | -104.13 (13) |
| O1—Ga1—O3—Mo3 | -178.75 (15) | O13 ⁱⁱ —Ga2—O15—Mo6 | -0.83 (14) |
| O2 ⁱ —Ga1—O3—Mo3 | -82.55 (16) | O13—Ga2—O15—Mo6 | 179.18 (14) |
| O2—Ga1—O3—Mo3 | 97.45 (16) | O14—Ga2—O15—Mo6 | -97.00 (15) |
| O1 ⁱ —Ga1—O3—Mo2 | -96.74 (16) | O14 ⁱⁱ —Ga2—O15—Mo6 | 83.00 (15) |
| O1—Ga1—O3—Mo2 | 83.26 (16) | O13 ⁱⁱ —Ga2—O15—Mo5 | 96.51 (15) |
| O2 ⁱ —Ga1—O3—Mo2 | 179.46 (14) | O13—Ga2—O15—Mo5 | -83.49 (15) |
| O2—Ga1—O3—Mo2 | -0.54 (14) | O14—Ga2—O15—Mo5 | 0.34 (14) |
| O12—Mo3—O3—Ga1 | -35.2 (5) | O14 ⁱⁱ —Ga2—O15—Mo5 | -179.66 (14) |
| O11—Mo3—O3—Ga1 | 169.01 (18) | O23—Mo6—O15—Ga2 | -169.88 (18) |
| O4 ⁱ —Mo3—O3—Ga1 | 71.36 (16) | O24—Mo6—O15—Ga2 | 36.2 (5) |
| O6—Mo3—O3—Ga1 | -91.15 (17) | O16 ⁱⁱ —Mo6—O15—Ga2 | -71.69 (16) |
| O1 ⁱ —Mo3—O3—Ga1 | -1.13 (13) | O18—Mo6—O15—Ga2 | 90.02 (16) |
| O12—Mo3—O3—Mo2 | 70.2 (5) | O13 ⁱⁱ —Mo6—O15—Ga2 | 0.75 (13) |
| O11—Mo3—O3—Mo2 | -85.60 (17) | O23—Mo6—O15—Mo5 | 85.71 (16) |
| O4 ⁱ —Mo3—O3—Mo2 | 176.76 (14) | O24—Mo6—O15—Mo5 | -68.2 (5) |
| O6—Mo3—O3—Mo2 | 14.25 (13) | O16 ⁱⁱ —Mo6—O15—Mo5 | -176.10 (14) |
| O1 ⁱ —Mo3—O3—Mo2 | 104.27 (15) | O18—Mo6—O15—Mo5 | -14.39 (12) |
| O9—Mo2—O3—Ga1 | 29.5 (5) | O13 ⁱⁱ —Mo6—O15—Mo5 | -103.66 (14) |
| O10—Mo2—O3—Ga1 | -170.27 (18) | O21—Mo5—O15—Ga2 | -34.9 (5) |
| O6—Mo2—O3—Ga1 | 90.74 (17) | O22—Mo5—O15—Ga2 | 171.32 (17) |
| O5—Mo2—O3—Ga1 | -72.14 (16) | O17—Mo5—O15—Ga2 | 72.94 (16) |
| O2—Mo2—O3—Ga1 | 0.49 (13) | O18—Mo5—O15—Ga2 | -90.09 (16) |
| O9—Mo2—O3—Mo3 | -75.6 (5) | O14—Mo5—O15—Ga2 | -0.31 (12) |
| O10—Mo2—O3—Mo3 | 84.64 (17) | O21—Mo5—O15—Mo6 | 69.6 (5) |
| O6—Mo2—O3—Mo3 | -14.35 (13) | O22—Mo5—O15—Mo6 | -84.26 (15) |
| O5—Mo2—O3—Mo3 | -177.23 (14) | O17—Mo5—O15—Mo6 | 177.37 (13) |
| O2—Mo2—O3—Mo3 | -104.60 (14) | O18—Mo5—O15—Mo6 | 14.34 (12) |
| O7—Mo1—O4—Mo3 ⁱ | 66.8 (2) | O14—Mo5—O15—Mo6 | 104.12 (14) |

supplementary materials

| | | | |
|--------------------------------|-------------|--------------------------------|-------------|
| O8—Mo1—O4—Mo3 ⁱ | 174.9 (2) | O19—Mo4—O16—Mo6 ⁱⁱ | -68.1 (2) |
| O5—Mo1—O4—Mo3 ⁱ | -59.9 (4) | O20—Mo4—O16—Mo6 ⁱⁱ | -175.9 (2) |
| O1—Mo1—O4—Mo3 ⁱ | -20.98 (17) | O17—Mo4—O16—Mo6 ⁱⁱ | 59.7 (4) |
| O2—Mo1—O4—Mo3 ⁱ | -92.7 (2) | O13—Mo4—O16—Mo6 ⁱⁱ | 20.19 (17) |
| O7—Mo1—O5—Mo2 | 178.4 (2) | O14—Mo4—O16—Mo6 ⁱⁱ | 91.9 (2) |
| O8—Mo1—O5—Mo2 | 69.8 (2) | O21—Mo5—O17—Mo4 | 68.7 (2) |
| O4—Mo1—O5—Mo2 | -54.1 (4) | O22—Mo5—O17—Mo4 | 176.7 (2) |
| O1—Mo1—O5—Mo2 | -90.8 (2) | O18—Mo5—O17—Mo4 | -57.1 (4) |
| O2—Mo1—O5—Mo2 | -19.71 (18) | O15—Mo5—O17—Mo4 | -90.7 (2) |
| O9—Mo2—O5—Mo1 | -68.0 (2) | O14—Mo5—O17—Mo4 | -19.20 (18) |
| O10—Mo2—O5—Mo1 | -176.7 (2) | O19—Mo4—O17—Mo5 | -178.4 (2) |
| O6—Mo2—O5—Mo1 | 57.3 (4) | O20—Mo4—O17—Mo5 | -69.9 (2) |
| O3—Mo2—O5—Mo1 | 90.6 (2) | O16—Mo4—O17—Mo5 | 53.0 (4) |
| O2—Mo2—O5—Mo1 | 19.81 (18) | O13—Mo4—O17—Mo5 | 90.2 (2) |
| O9—Mo2—O6—Mo3 | 179.9 (2) | O14—Mo4—O17—Mo5 | 18.98 (17) |
| O10—Mo2—O6—Mo3 | -71.9 (2) | O23—Mo6—O18—Mo5 | -70.0 (2) |
| O5—Mo2—O6—Mo3 | 53.9 (4) | O24—Mo6—O18—Mo5 | -176.6 (2) |
| O3—Mo2—O6—Mo3 | 18.79 (17) | O16 ⁱⁱ —Mo6—O18—Mo5 | 58.1 (4) |
| O2—Mo2—O6—Mo3 | 89.33 (19) | O15—Mo6—O18—Mo5 | 19.05 (16) |
| O12—Mo3—O6—Mo2 | 178.4 (2) | O13 ⁱⁱ —Mo6—O18—Mo5 | 90.61 (18) |
| O11—Mo3—O6—Mo2 | 71.1 (2) | O21—Mo5—O18—Mo6 | 178.3 (2) |
| O4 ⁱ —Mo3—O6—Mo2 | -56.3 (4) | O22—Mo5—O18—Mo6 | 71.7 (2) |
| O3—Mo3—O6—Mo2 | -19.01 (17) | O17—Mo5—O18—Mo6 | -54.4 (4) |
| O1 ⁱ —Mo3—O6—Mo2 | -90.18 (19) | O15—Mo5—O18—Mo6 | -19.00 (16) |
| O15 ⁱⁱ —Ga2—O13—Mo4 | -97.38 (15) | O14—Mo5—O18—Mo6 | -90.41 (19) |

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|----------|-------------|-------------|---------------|
| O2—H2 \cdots O10 ⁱⁱⁱ | 0.84 (2) | 2.00 (3) | 2.822 (5) | 166 (6) |
| O13—H13 \cdots O23 ^{iv} | 0.84 (2) | 1.86 (2) | 2.691 (5) | 173 (7) |
| O14—H14 \cdots O22 ^v | 0.84 (2) | 1.98 (2) | 2.808 (5) | 168 (6) |
| O3—H3 \cdots O4S ^{vi} | 0.85 (2) | 1.76 (3) | 2.602 (5) | 169 (8) |
| O1—H1 \cdots O11 ^{vii} | 0.85 (2) | 1.87 (4) | 2.682 (5) | 159 (9) |
| O15—H15 \cdots O1S | 0.83 (2) | 1.87 (3) | 2.645 (5) | 155 (7) |

Symmetry codes: (iii) $x, -y+1/2, z-1/2$; (iv) $-x, y-1/2, -z+1/2$; (v) $x, -y+3/2, z+1/2$; (vi) $x, -y+1/2, z+1/2$; (vii) $-x+1, y+1/2, -z+3/2$.

Table 3

Short contact geometry (\AA).

| | |
|---------------------------------|-----------|
| N1S \cdots O24 ⁱⁱ | 2.911 (7) |
| N1S \cdots O6S ^{vi} | 2.784 (8) |
| N2S \cdots O16 | 2.779 (6) |
| N2S \cdots O21 ⁱⁱⁱ | 2.979 (6) |

| | |
|---------------------------|-----------|
| N2S...O24 ^{vii} | 2.901 (6) |
| N2S...O3S ^{viii} | 2.899 (7) |
| N2S...O7S | 2.898 (7) |
| N3S...O5 ⁱ | 2.775 (6) |
| N3S...O12 ^{xii} | 2.907 (7) |
| N3S...O5S | 2.801 (8) |
| N3S...O7S ⁱ | 3.030 (8) |
| O1S...O18 ^x | 2.794 (5) |
| O1S...O18 ⁱⁱ | 2.905 (6) |
| O2S...O4 ^{xi} | 2.718 (5) |
| O2S...O12 | 2.797 (6) |
| O2S...O3S ^{xii} | 2.830 (7) |
| O2S...O6S ^{ix} | 2.704 (7) |
| O3S...O9 | 3.016 (6) |
| O3S...O19 | 3.034 (7) |
| O3S...O5S ^{iv} | 2.917 (8) |
| O4S...O3 ^{xiii} | 2.602 (5) |
| O4S...O6 | 2.773 (6) |
| O4S...O6 ^{xii} | 2.934 (6) |
| O5S...O8 | 2.782 (6) |
| O5S...O16 ⁱ | 3.083 (6) |
| O6S...O20 | 2.776 (6) |
| O6S...O7S | 2.769 (7) |
| O7S...O7 ^{xiv} | 2.973 (6) |

Symmetry codes (i): $x, -y+1/2, z-1/2$; (ii): $-x, y-1/2, -z+1/2$; (iii): $x, -y+3/2, z+1/2$; (iv): $x, -y+1/2, z+1/2$; (v): $-x+1, y+1/2, -z+3/2$; (vi): $x, -y+3/2, z-1/2$; (vii): $-x, y-1/2, -z+3/2$; (viii): $x, -y+1/2, z+1/2$; (ix): $1-x, 1-y, 1-z$; (x): $x, -y+3/2, z-1/2$; (xi): $-x+1, y-1/2, -z+1/2$; (xii): $-x+1, -y, -z+1$; (xiii): $x, -y+1/2, z-1/2$; (xiv): $x, -y+3/2, z+1/2$

Fig. 1

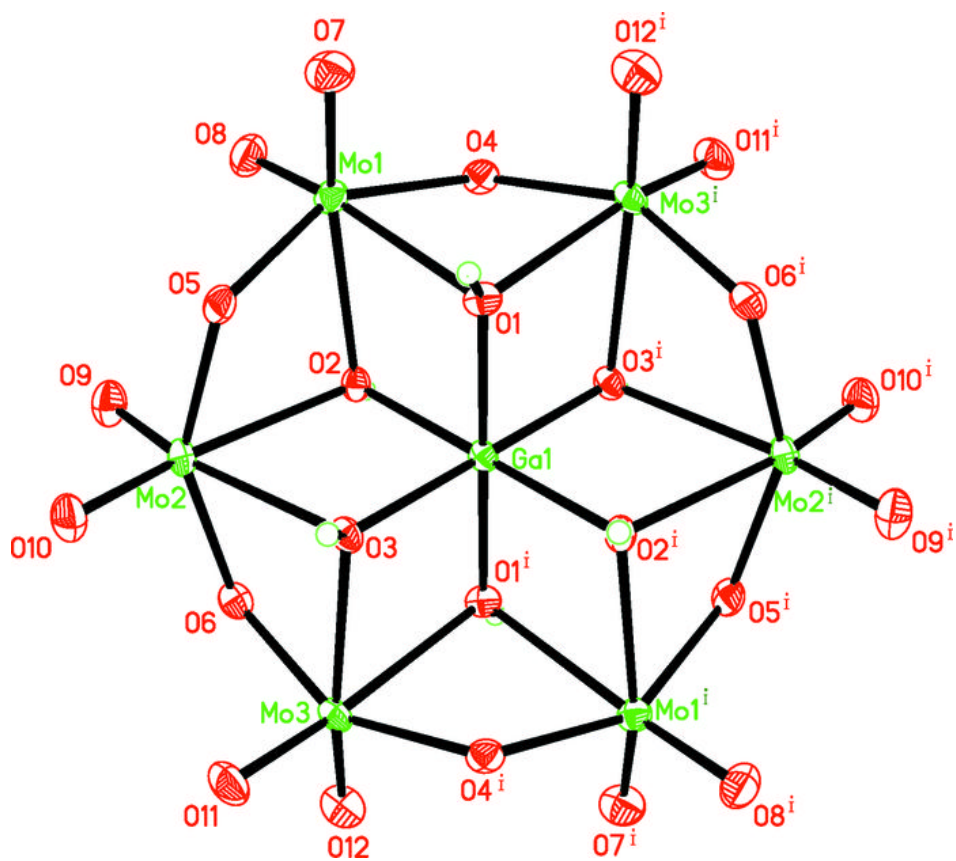


Fig. 2

