# SHORT-FORMAT PAPERS

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# Structure of Triammonium Hexahydrogenhexamolybdorhodate(III) Hexahydrate

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**Abstract.** $(NH_4)_3[H_6RhMo_6O_{24}].6H_2O$, $M_r = 1230.79$, monoclinic, $P2_1/c$, $a = 11.435$ (3), $b = 11.017$ (2), $c = 11.789$ (2) Å, $\beta = 100.02$ (2)°, $V = 1462.6$ (6) Å$^3$, $Z = 2$, $D_m = 2.83$, $D_x = 2.79$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71069 Å, $\mu = 3.08$ mm$^{-1}$, $F(000) = 1176$, $T = 296$ K, final $R = 0.042$ for 2248 observed reflections with $|F_o| > 3.0\sigma(|F_o|)$. The $[H_6RhMo_6O_{24}]^{3-}$ polyanion, which has approximate $D_{3d}$ symmetry, is isostructural to $[H_6Cr^{III}Mo_6O_{24}]^{3-}$. The RhO$_6$ octahedron located on an inversion center is trigonally distorted with the Rh—O distances in the range 2.019 (5)–2.030 (5) Å. The Mo—O distances are in the range 1.701 (7)–2.298 (5) Å.

**Experimental.** Pale-yellow rhombic crystals were obtained from a mixed aqueous solution adjusted at pH 4 containing $RhCl_3.3H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ (Rh:Mo = 1:6). $D_m$ by flotation in $C_2H_4Br_2$–$CH_2I_2$. Crystal $0.11 \times 0.26 \times 0.28$ mm was mounted on an Enraf–Nonius CAD-4 diffractometer; graphite-monochromatized Mo $K\alpha$ radiation. Cell parameters were refined using $2\theta$ values of 25 reflections in the $\theta$ range 11.2–14.2°. 3632 intensities were collected in the $\theta$–$2\theta$ scan mode, $2\theta_{max} = 60°$, $-15 \le h \le 15, 0 \le k \le 15, 0 \le l \le 16$. Three standard reflections ($\overline{2}06$, $\overline{3}60$, $\overline{4}52$) were monitored every 2 h: no decay was observed. Numerical absorption correction was applied, transmission factors in range 1.17–1.44. No extinction corrections made. Positions of Rh and Mo atoms were located from Patterson functions. N and O atoms were found from difference Fourier syntheses. The number of NH$_4^+$ groups for two independent sites was 1.5, determined by elemental analysis, and the occupancies of N atoms were thus fixed at 0.75 each. Block-diagonal least-squares refinement was made on $F$. No H atoms were located. All atoms were anisotropically

Table 1. *Positional parameters ($\times 10^5$ for Rh and Mo; $\times 10^4$ for other atoms) and equivalent isotropic thermal parameters* (Å$^2$)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Rh | 0 | 0 | 0 | 1.14 (2) |
| Mo(1) | 29783 (6) | 1623 (7) | 4824 (6) | 1.86 (2) |
| Mo(2) | 13651 (7) | 24817 (6) | 12097 (6) | 1.67 (2) |
| Mo(3) | 16072 (7) | −23583 (6) | −6915 (6) | 1.74 (2) |
| O(1) | 1279 (5) | 1146 (5) | −312 (5) | 1.7 (1) |
| O(2) | 1386 (5) | −1034 (5) | 761 (5) | 1.5 (1) |
| O(3) | −72 (5) | 1102 (5) | 1356 (5) | 1.5 (1) |
| O(4) | 2443 (6) | 1152 (6) | 1650 (5) | 1.9 (1) |
| O(5) | 2563 (6) | −913 (6) | −824 (5) | 2.1 (1) |
| O(6) | −138 (6) | 3069 (5) | 350 (5) | 1.9 (1) |
| O(7) | 3817 (7) | 1164 (7) | −139 (6) | 2.9 (2) |
| O(8) | 3953 (7) | −689 (7) | 1414 (6) | 3.2 (2) |
| O(9) | 2244 (7) | 3469 (6) | 619 (6) | 2.7 (2) |
| O(10) | 1315 (7) | 3049 (6) | 2540 (6) | 2.8 (2) |
| O(11) | 1612 (7) | −2972 (6) | −2033 (6) | 2.8 (2) |
| O(12) | 2550 (7) | −3236 (6) | 241 (6) | 3.0 (2) |
| O(13) | 152 (14) | 4552 (7) | −1473 (8) | 7.0 (4) |
| O(14) | 5075 (13) | −2920 (12) | 2051 (13) | 8.6 (5) |
| O(15) | 5067 (16) | 3453 (14) | 895 (14) | 10.4 (6) |
| N(1)* | 3307 (9) | 4579 (11) | −1123 (7) | 2.4 (2) |
| N(2)* | 3528 (10) | −4828 (11) | 2297 (9) | 2.9 (3) |

* Occupancy of these atoms is 0.75.

Table 2. *Selected bond distances* (Å) *and bond angles* (°)

| | | | |
|---|---|---|---|
| Mo(1)—O(1) | 2.279 (6) | Mo(2)—O(10) | 1.698 (7) |
| Mo(1)—O(2) | 2.317 (6) | Mo(3)—O(2) | 2.298 (6) |
| Mo(1)—O(4) | 1.937 (6) | Mo(3)—O(3$^i$) | 2.265 (6) |
| Mo(1)—O(5) | 1.936 (6) | Mo(3)—O(5) | 1.953 (6) |
| Mo(1)—O(7) | 1.708 (8) | Mo(3)—O(6$^i$) | 1.958 (7) |
| Mo(1)—O(8) | 1.704 (7) | Mo(3)—O(11) | 1.721 (7) |
| Mo(2)—O(1) | 2.309 (6) | Mo(3)—O(12) | 1.701 (7) |
| Mo(2)—O(3) | 2.267 (6) | Rh—O(1) | 2.013 (6) |
| Mo(2)—O(4) | 1.927 (6) | Rh—O(2) | 2.029 (5) |
| Mo(2)—O(6) | 1.948 (6) | Rh—O(3) | 2.021 (6) |
| Mo(2)—O(9) | 1.709 (8) | | |
| | | | |
| O(1)—Rh—O(2) | 84.1 (2) | O(1)—Rh—O(3$^i$) | 95.8 (2) |
| O(1)—Rh—O(3) | 84.2 (2) | O(2)—Rh—O(3) | 97.1 (2) |
| O(2)—Rh—O(3$^i$) | 82.9 (2) | O(1)—Rh—O(2$^i$) | 95.9 (2) |

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

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refined; final $R = 0.042$, $wR = 0.059$ and $S = 1.41$ were obtained for 2248 unique reflections ($R_{int} = 0.044$) with $|F_o| > 3\sigma(|F_o|)$; weighting scheme $w^{-1} = [\sigma^2(F_o) + (0.035|F_o|)^2]$; $(\Delta/\sigma)_{max} < 0.01$; $-1.0 \le \Delta\rho \le 3.0$ e Å$^{-3}$. Scattering factors with anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed by using the *UNICSIII* program (Sakurai & Kobayashi, 1979) on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science. Final atomic parameters are listed in Table 1* and selected bond distances and angles are in Table 2. Fig. 1 shows an *ORTEP* (Johnson, 1976) view of the discrete polyanion.

**Related literature.** Bond distances within some $X$Mo$_6$O$_{24}$ type polymolybdates incorporating transition metals are as follows: for $[H_6CrMo_6O_{24}]^{3-}$, Cr—O and Mo—O are in the ranges 1·968 (3)– 1·986 (3) and 1·695 (3)–2·347 (3) Å, respectively (Perloff, 1970); for $[PtMo_6O_{24}]^{5-}$, Pt—O and Mo—O are in the ranges 1·99–2·04 and 1·68–2·34 Å, respectively (Lee & Sasaki, 1984); for [H$_6$Cu-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53530 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
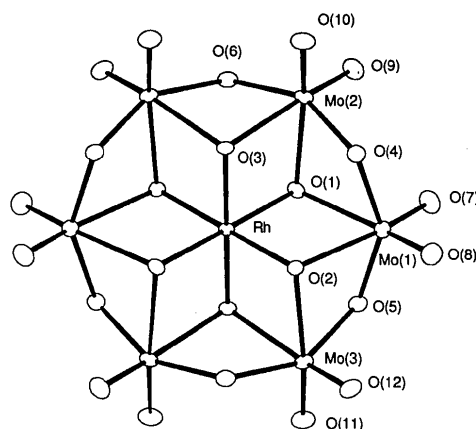


Fig. 1. *ORTEP* drawing of the discrete polyanion with 50% thermal probability level.

Mo$_6$O$_{24}]^{4-}$, Cu—O and Mo—O are in the ranges 2·02 (1) − 2·12 (1), and 1·70 (1)–2·25 (1) Å, respectively (Ito, Ozeki, Ichida, Miyamae & Sasaki, 1989).

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# Structure of Caesium Selenate

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**Abstract.** Cs$_2$SeO$_4$, $M_r = 408.77$, orthorhombic, *Pnam*, $a = 8.3777$ (8), $b = 11.276$ (2), $c = 6.434$ (2) Å, $V = 607.8$ (2) Å$^3$, $Z = 4$, $D_x = 4.46$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 185.06$ cm$^{-1}$, $F(000) = 704$, $T = 293$ K, $R = 0.048$, 3348 observed reflections. Average values of the Se—O and Cs—O distances are 1·637 (4) and 3·387 (3) Å, respectively [range 3·038 (5)–3·872 (6) Å with 9 and 11 coordination of caesium by oxygen].

**Experimental.** Single crystals of Cs$_2$SeO$_4$ were grown isothermally at 310 K from an aqueous solution (pH = 4·5), which contained the stoichiometric molar ratio of CsOH and H$_2$SeO$_4$. The colourless crystals obtained were of good optical quality.

A prismatic crystal of dimensions 0·31 × 0·15 × 0·15 mm was used to collect intensities with an Enraf–Nonius CAD-4 four-circle diffractometer, using graphite-monochromated Mo $K\alpha$ radiation. A