

Rubidium dimolybdate, $\text{Rb}_2\text{Mo}_2\text{O}_7$, and caesium dimolybdate, $\text{Cs}_2\text{Mo}_2\text{O}_7$

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The crystal structures of dirubidium heptaoxodimolybdate, $\text{Rb}_2\text{Mo}_2\text{O}_7$, and dicaesium heptaoxodimolybdate, $\text{Cs}_2\text{Mo}_2\text{O}_7$, in the space groups $Ama2$ and $P2_1/c$, respectively, have been determined for the first time by single-crystal X-ray diffraction. The structures represent two novel structure types of monovalent ion dimolybdates, $A_2\text{Mo}_2\text{O}_7$ (A = alkaline elements, NH_4 , Ag or Tl). In the structure of $\text{Rb}_2\text{Mo}_2\text{O}_7$, Mo atoms are on a twofold axis, on a mirror plane and in a general position. One of the Rb atoms lies on a twofold axis, while three others are on mirror planes. Two O atoms attached to the Mo atom on a mirror plane are located on the same plane. Rubidium dimolybdate contains a new kind of infinite Mo–O chain formed from linked MoO_4 tetrahedra and MoO_6 octahedra alternating along the a axis, with two terminal MoO_4 tetrahedra sharing corners with each octahedron. The chains stack in the $[001]$ direction to form channels of an approximately square section filled by ten-coordinate Rb ions. Seven- and eight-coordinate Rb atoms are located between chains connected by a c translation. In the structure of $\text{Cs}_2\text{Mo}_2\text{O}_7$, all atoms are in general positions. The MoO_6 octahedra share opposite corners to form separate infinite chains running along the c axis and strengthened by bridging MoO_4 tetrahedra. The same Mo–O polyhedral chain occurs in the structure of $\text{Na}_2\text{Mo}_2\text{O}_7$. Eight- to eleven-coordinate Cs atoms fill the space between the chains. The atomic arrangement of caesium dimolybdate has an orthorhombic pseudosymmetry that suggests a possible phase transition $P2_1/c \rightarrow Pbca$ at elevated temperatures.

Comment

Dimolybdates of monovalent ions formed in the systems $A_2\text{MoO}_4\text{–MoO}_3$ (A = alkaline metals, NH_4 , Ag or Tl) have been known for a long time and are mainly used as good low-melting fluxes for the crystallization of many oxide materials. The structures of the dimolybdates studied to date, namely $\text{Na}_2\text{Mo}_2\text{O}_7$ (Lindqvist, 1950*a,b*; Seleborg, 1967), $\text{K}_2\text{Mo}_2\text{O}_7$ (Magarill & Klevtsova, 1971), $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ (Lindqvist, 1950*b*; Knopnadel *et al.*, 1974; Armour *et al.*, 1975) and

$\text{Ag}_2\text{Mo}_2\text{O}_7$ (Gatehouse & Leverett, 1976; Guo & Liu, 2005), contain infinite chains of MoO_6 octahedra and MoO_4 tetrahedra linked by corners or edges (Fig. 1). In contrast, in the structure of MgMo_2O_7 (Stadnicka *et al.*, 1977), there are separate dimolybdate ions, $\text{Mo}_2\text{O}_7^{2-}$, consisting of two MoO_4 tetrahedra sharing a corner. Although rubidium and caesium dimolybdates are well known in the literature (Spitsyn & Kuleshov, 1951; Salmon & Caillet, 1969; Hoekstra, 1973; Goel & Mehrotra, 1985, 1986; Bazarova *et al.*, 1990), their lattice dimensions and crystal structures have not previously been determined. The present crystal structure study of $\text{Rb}_2\text{Mo}_2\text{O}_7$, (I), and $\text{Cs}_2\text{Mo}_2\text{O}_7$, (II), closes a gap in the crystal chemistry of monovalent ion dimolybdates and confirms the compositions found chemically.

We have obtained single crystals of (I) and (II) in our study of complex molybdates. Powder diffraction patterns of the compounds were consistent with X-ray diffraction data for samples of $\text{Rb}_2\text{Mo}_2\text{O}_7$ (Goel & Mehrotra, 1986; PDF No. 40–955) and $\text{Cs}_2\text{Mo}_2\text{O}_7$ (Goel & Mehrotra, 1985; PDF No. 39–60) prepared by the thermal decomposition of molybdenum(VI) oxalate complexes, $A_2[\text{Mo}_2\text{O}_5(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ (A = Rb or Cs) and $\text{Cs}_2[\text{Mo}_2\text{O}_6(\text{C}_2\text{O}_4)] \cdot \text{H}_2\text{O}$. Both the cell parameters and the space groups of (I) and (II) indicate that these compounds are not isostructural with other monovalent cation dimolybdates. Our preliminary communication (Solodovnikova & Solodovnikov, 2002) on the synthesis and the crystal structure of (I) was presented at the All-Russian Scientific Conference devoted to the memory of Professor M. V. Mokhosoev (Ulan-Ude, Russia).

In the structure of (I), atoms Mo1, Mo2 and Mo3 are on a twofold axis, on a mirror plane and in a general position, respectively. Atom Mo1 possesses a distorted octahedral environment, whereas atoms Mo2 and Mo3 have tetrahedral coordinations. Rb atoms occupy special positions on twofold axes (Rb1) and mirror planes (Rb2, Rb3 and Rb4), and have coordination numbers of 8, 7, 10 and 10, respectively. The common arrangement of Mo and Rb atoms in the structure of (I) corresponds to cubic close packing somewhat compressed along the $[001]$ direction.

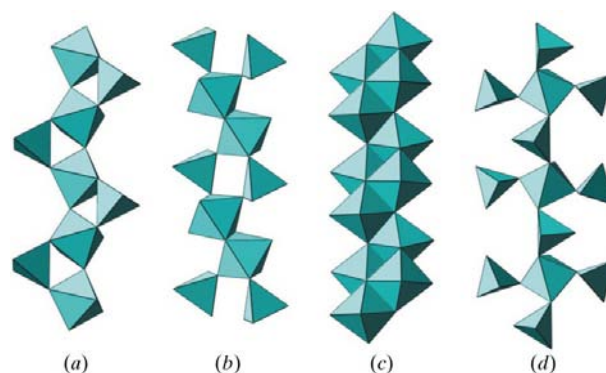


Figure 1
Polyhedral representations of the Mo–O chains in the structures of (a) $\text{Na}_2\text{Mo}_2\text{O}_7$ and $\text{Cs}_2\text{Mo}_2\text{O}_7$, (b) $\text{K}_2\text{Mo}_2\text{O}_7$ and $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$, (c) two forms of $\text{Ag}_2\text{Mo}_2\text{O}_7$ and (d) $\text{Rb}_2\text{Mo}_2\text{O}_7$.

The main and most original detail of the structure is an infinite polyhedral chain running along the *a* axis and formed of linked alternate Mo1O₄ octahedra and Mo2O₆ tetrahedra, with two terminal Mo3O₄ tetrahedra sharing the corners with each Mo1O₆ octahedron (Fig. 1*d*). The chain has a polar configuration, due to the bridging Mo2O₄ tetrahedra linked to four adjacent corners of the Mo1O₆ octahedron (Fig. 2*a*). The chains are stacked in the [001] direction in such a way that the projections of the terminal Mo3O₄ tetrahedra of adjacent chains connected by an *a* translation are superimposed. This results in the formation of channels of an approximately square section parallel to [001], each filled by Rb3 and Rb4 ions located on the mirror plane (Fig. 2*b*). Other Rb atoms are located between chains connected by a *c* translation and lie on twofold axes and mirror planes.

All atoms in the structure of (II) are in general positions. Atoms Mo1 and Mo3 have a distorted octahedral coordination and atoms Mo2 and Mo4 are tetrahedrally coordinated. MoO₆ octahedra share opposite corners to form separate infinite chains running along the *c* axis and strengthened by bridging MoO₄ tetrahedra. As in the structure of (I), the chains have polar configurations because of the MoO₄ tetrahedra attached to two adjacent corners of the MoO₆ octahedra (Fig. 3*a*). Each chain resembles the Mo–O polyhedral radical occurring in the structure of Na₂Mo₂O₇ (Fig. 1*a*). There are two symmetrically independent but topologically analogous chains involving Mo1O₆ octahedra and Mo2O₄ tetrahedra, and Mo3O₆ octahedra and Mo4O₄ tetrahedra, respectively (Fig. 3). Atoms Cs1, Cs2, Cs3 and Cs4 have coordination

numbers of 11, 9, 8, and 10, respectively, and occupy the space between the chains. Thus, our results have confirmed the previously stated assumption of a chain character for the structure of (II) (Gatehouse & Leverett, 1976).

Caesium dimolybdate has a highly pseudosymmetrical structure, which is rather close to orthorhombic. For example, the β angle is practically equal to 90°, which explains the intensive pseudomerohedral twinning of the crystals. Moreover, two kinds of chains in the structure are connected to each other by additional pseudosymmetry elements, such as *b*-glide planes perpendicular to the *x* axis and *a*-glide planes perpendicular to the *z* axis (Fig. 3). The same pseudosymmetry elements connect atoms Cs1 and Cs3 with atoms Cs2 and Cs4, respectively. This implies that the monoclinic phase of (II) (space group *P*2₁/*c*) could transform to the orthorhombic form (space group *Pbca*) at elevated temperatures. Indeed, Hoekstra (1973) has observed a polymorphic transition in (II) at 668 K. A weak thermal effect of the transition would mean a distortive nature of the structural transformation, which agrees with our conclusion. The structural mechanism of the transition appears to be associated with slight shifts and rotations of the MoO₆ octahedra and MoO₄ tetrahedra in the Mo–O chains. If these considerations are correct, caesium dimolybdate could show ferroelastic or antiferroelectric properties at room temperature. Corresponding investigations of this compound will be conducted in the near future.

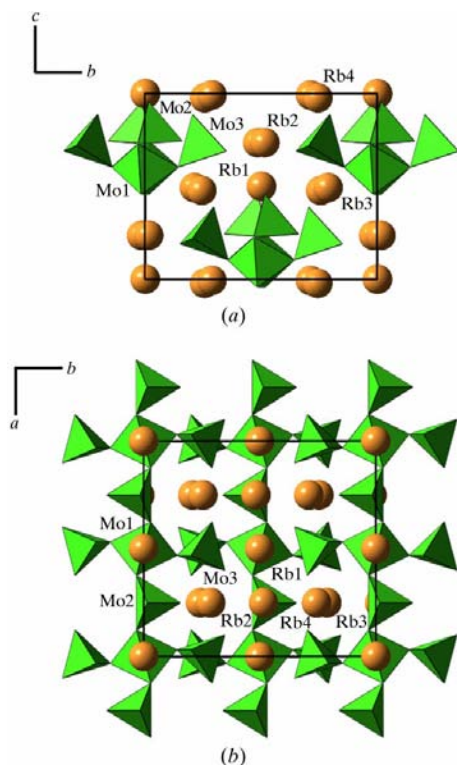


Figure 2 Projections of the Rb₂Mo₂O₇ structure on to (a) the (100) plane and (b) the (001) plane.

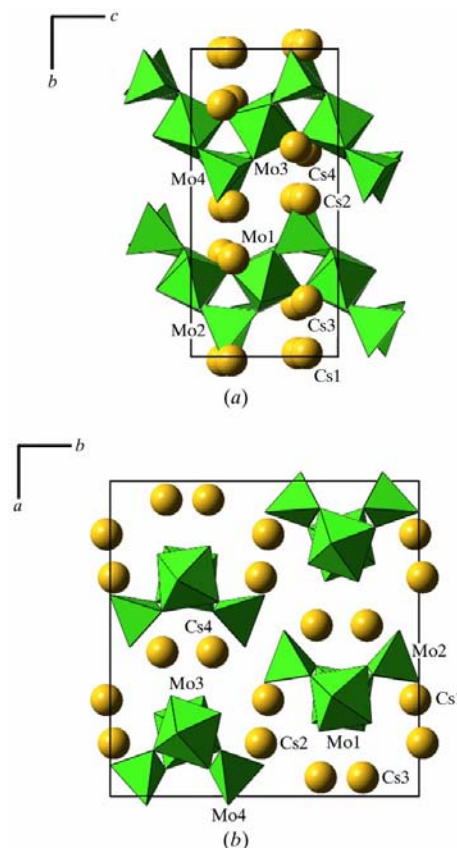


Figure 3 Projections of the Cs₂Mo₂O₇ structure on to (a) the (001) plane and (b) the (100) plane.

In conclusion, it is worth emphasizing that both title structures contain infinite polyhedral Mo–O chains formed by MoO₆ octahedra and MoO₄ tetrahedra sharing corners. Thus, our work completes the study of the structures of monovalent cation dimolybdates, confirming a common chain-like character of the series (Fig. 1).

Experimental

Due to their congruent melting at 763 (Salmon & Caillet, 1969) and 737 K (Hoekstra, 1973), respectively, crystals of (I) and (II) were grown from the melts of equimolar mixtures of A₂MoO₄ (A = Rb or Cs) and MoO₃. The mixtures were heated to 823 (A = Rb) and 693 K (A = Cs), held at that temperature for 24 h and then cooled to 703 (A = Rb) and 673 K (A = Cs), respectively, at a rate of 3 K h⁻¹. The crystals appeared as matted white fragments and colourless elongated plates, with maximum dimensions of 2 mm.

Compound (I)

Crystal data

Rb ₂ Mo ₂ O ₇	Z = 8
<i>M_r</i> = 474.82	<i>D_x</i> = 4.036 Mg m ⁻³
Orthorhombic, <i>Ama</i> 2	Mo <i>Kα</i> radiation
<i>a</i> = 11.8887 (6) Å	<i>μ</i> = 15.57 mm ⁻¹
<i>b</i> = 12.8303 (6) Å	<i>T</i> = 293 (2) K
<i>c</i> = 10.2464 (4) Å	Fragment, colourless
<i>V</i> = 1562.94 (12) Å ³	0.06 × 0.06 × 0.06 mm

Data collection

Bruker–Nonius X8 APEX CCD area-detector diffractometer	4744 measured reflections
<i>φ</i> scans, frame data integration	1454 independent reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2004)	1416 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T_{min}</i> = 0.455, <i>T_{max}</i> = 0.455 (expected range = 0.393–0.393)	<i>R_{int}</i> = 0.022
	<i>θ_{max}</i> = 27.5°

Refinement

Refinement on <i>F</i> ²	<i>Δρ_{max}</i> = 0.70 e Å ⁻³
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.018	<i>Δρ_{min}</i> = -0.60 e Å ⁻³
<i>wR</i> (<i>F</i> ²) = 0.049	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
<i>S</i> = 1.15	Extinction coefficient: 0.00047 (5)
1454 reflections	Absolute structure: Flack (1983), with 456 Friedel pairs
110 parameters	Flack parameter: 0.019 (6)
<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0203 <i>P</i>) ²] where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3	
(<i>Δρ</i>) _{max} < 0.001	

Table 1

Selected bond lengths (Å) for (I).

Rb1–O8	2.888 (4)	Rb4–O6 ⁱⁱⁱ	3.074 (4)
Rb1–O7 ⁱ	2.995 (4)	Rb4–O7	3.109 (4)
Rb1–O5	3.0128 (10)	Rb4–O2	3.178 (3)
Rb1–O3	3.176 (4)	Rb4–O5 ^{vii}	3.482 (6)
Rb2–O7 ⁱⁱ	2.816 (4)	Rb4–O8 ⁱⁱⁱ	3.543 (4)
Rb2–O1	2.843 (4)	Mo1–O1	1.702 (4)
Rb2–O6 ⁱⁱⁱ	2.853 (4)	Mo1–O2	1.922 (3)
Rb2–O5 ^{iv}	2.871 (6)	Mo1–O3	2.288 (4)
Rb3–O6 ^v	2.964 (4)	Mo2–O4	1.723 (5)
Rb3–O8	3.003 (4)	Mo2–O5	1.738 (6)
Rb3–O1 ^{vi}	3.018 (4)	Mo2–O3	1.791 (4)
Rb3–O4	3.050 (6)	Mo3–O6	1.729 (4)
Rb3–O5	3.525 (6)	Mo3–O7	1.736 (4)
Rb3–O2 ^v	3.644 (3)	Mo3–O8	1.738 (4)
Rb4–O4	2.945 (6)	Mo3–O2	1.870 (3)

Symmetry codes: (i) *x*, *y* + ½, *z* + ½; (ii) *x*, *y* + ½, *z* – ½; (iii) –*x*, –*y* + ½, *z* – ½; (iv) *x*, *y*, *z* – 1; (v) –*x*, –*y* + ½, *z* + ½; (vi) *x*, *y* – ½, *z* + ½; (vii) *x*, *y* – ½, *z* – ½; (viii) –*x*, *y* – ½, *z* + ½; (ix) –*x* + 1, *y* – ½, *z* + ½; (x) *x*, *y*, *z* + 1.

Compound (II)

Crystal data

Cs ₂ Mo ₂ O ₇	Z = 8
<i>M_r</i> = 569.70	<i>D_x</i> = 4.435 Mg m ⁻³
Monoclinic, <i>P2₁/c</i>	Mo <i>Kα</i> radiation
<i>a</i> = 15.5580 (5) Å	<i>μ</i> = 11.34 mm ⁻¹
<i>b</i> = 15.1794 (5) Å	<i>T</i> = 293 (2) K
<i>c</i> = 7.2252 (2) Å	Fragment, colourless
<i>β</i> = 90.0059 (11)°	0.16 × 0.13 × 0.10 mm
<i>V</i> = 1706.31 (9) Å ³	

Data collection

Bruker–Nonius X8 APEX CCD area-detector diffractometer	21380 measured reflections
<i>φ</i> scans, frame data integration	8167 independent reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2004)	7405 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T_{min}</i> = 0.264, <i>T_{max}</i> = 0.397 (expected range = 0.214–0.322)	<i>R_{int}</i> = 0.028
	<i>θ_{max}</i> = 36.3°

Refinement

Refinement on <i>F</i> ²	(<i>Δρ</i>) _{max} = 0.001
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.028	<i>Δρ_{max}</i> = 1.52 e Å ⁻³
<i>wR</i> (<i>F</i> ²) = 0.058	<i>Δρ_{min}</i> = -1.48 e Å ⁻³
<i>S</i> = 1.07	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
8167 reflections	Extinction coefficient: 0.00018 (3)
201 parameters	
<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.009 <i>P</i>) ²] where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3	

Table 2

Selected bond lengths (Å) for (II).

Cs1–O6 ⁱ	2.900 (3)	Cs4–O4 ⁱⁱⁱ	3.128 (4)
Cs1–O9 ⁱⁱ	2.985 (3)	Cs4–O5	3.169 (3)
Cs1–O2	3.140 (3)	Cs4–O8 ⁱ	3.197 (3)
Cs1–O3 ⁱⁱⁱ	3.149 (3)	Cs4–O8 ^{ix}	3.241 (3)
Cs1–O7	3.177 (4)	Cs4–O5 ⁱⁱⁱ	3.392 (3)
Cs1–O14	3.323 (4)	Cs4–O6 ^x	3.480 (4)
Cs1–O4 ⁱⁱⁱ	3.372 (3)	Cs4–O9 ^{ix}	3.608 (4)
Cs1–O8	3.408 (4)	Cs4–O3 ⁱⁱⁱ	3.620 (3)
Cs1–O5	3.508 (3)	Cs4–O6 ⁱ	3.677 (5)
Cs1–O11	3.539 (3)	Mo1–O1	1.706 (3)
Cs1–O1 ⁱⁱⁱ	3.697 (4)	Mo1–O2	1.724 (3)
Cs2–O13 ^{iv}	3.016 (3)	Mo1–O3	1.908 (3)
Cs2–O7	3.035 (4)	Mo1–O3 ⁱⁱⁱ	1.928 (3)
Cs2–O14 ^v	3.106 (4)	Mo1–O4	2.196 (3)
Cs2–O2	3.113 (3)	Mo1–O5	2.356 (3)
Cs2–O10 ^{vi}	3.150 (3)	Mo2–O6	1.729 (3)
Cs2–O9 ^{vi}	3.153 (3)	Mo2–O7	1.747 (3)
Cs2–O11	3.204 (3)	Mo2–O5	1.788 (3)
Cs2–O1 ^{vii}	3.270 (3)	Mo2–O4 ^{vii}	1.791 (3)
Cs2–O12 ^{vi}	3.449 (3)	Mo3–O8	1.706 (3)
Cs3–O14	2.960 (3)	Mo3–O9	1.718 (3)
Cs3–O13 ^{iv}	3.020 (3)	Mo3–O10	1.924 (3)
Cs3–O13 ^{viii}	3.182 (3)	Mo3–O10 ^{vi}	1.929 (3)
Cs3–O1 ⁱⁱⁱ	3.206 (4)	Mo3–O11	2.192 (3)
Cs3–O12 ^{viii}	3.296 (3)	Mo3–O12	2.434 (3)
Cs3–O12 ^{iv}	3.324 (3)	Mo4–O13	1.737 (3)
Cs3–O2	3.347 (3)	Mo4–O14	1.738 (3)
Cs3–O1	3.414 (4)	Mo4–O12 ⁱⁱ	1.778 (3)
Cs4–O7 ⁱ	3.007 (3)	Mo4–O11	1.788 (3)

Symmetry codes: (i) –*x* + 1, –*y* + 1, –*z* + 1; (ii) *x*, –*y* + ½, *z* + ½; (iii) *x*, –*y* + ½, *z* + ½; (iv) –*x*, –*y* + 1, –*z* + 1; (v) *x*, *y*, *z* – 1; (vi) *x*, –*y* + ½, *z* – ½; (vii) *x*, –*y* + ½, *z* – ½; (viii) –*x*, *y* – ½, *z* + ½; (ix) –*x* + 1, *y* – ½, *z* + ½; (x) *x*, *y*, *z* + 1.

The refinement of the structure of (II) was performed taking into account the pseudomeroheredral twinning of the crystal studied. The monoclinic cell of the single crystal can be transformed into a pseudo-orthorhombic cell with a twofold twin operation about the reciprocal *a** axis of the monoclinic cell. The twin fraction was refined to a value of 0.4946 (6).

For both compounds, data collection: *SMART* (Bruker, 2004); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *BS* (Ozawa & Kang, 2004); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3004). Services for accessing these data are described at the back of the journal.

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