

Fig. 3. Projection of the lower half of the unit cell of $\text{Cs}_2\text{CuSi}_4\text{O}_{12}$ on (001). Cs is represented by the large open and filled circles. Si and Cu are shown as small and large dots, respectively, inside the tetrahedra.

slow convergence during attempted refinement. However, population parameters in the refined $P4_12_1$ model close to their ideal values (Table 2) suggest that the $P4_12_1$ distribution is correct. Independent of this possible ambiguity, the structure refinement clearly shows that copper is incorporated in the Si—O framework of the zeolite-like pollucite structure.

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Structure of $\text{NdMo}_8\text{O}_{14}$ Containing the New Mo_8 Cluster

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Abstract. Neodymium octamolybdate, $\text{NdMo}_8\text{O}_{14}$, $M_r = 1135.75$, orthorhombic, $Aba2$, $a = 9.209$ (3), $b = 10.008$ (2), $c = 11.143$ (4) Å, $V = 1026.9$ (6) Å³, $Z = 4$, $D_x = 7.346$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 143.0$ cm⁻¹, $F(000) = 2032$, $T = 295$ K, $R = 0.021$

for 1079 observed reflections. The title compound contains the new Mo_8 cluster based on a distorted octahedron capped by two additional Mo atoms. The Mo_8 clusters are connected by bridging oxygens and arranged in layers parallel to the bc plane. The

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Nd atoms located within the cluster layers are surrounded by 12 oxygens at distances ranging from 2.362 (8) to 3.139 (6) Å.

Introduction. Since the discovery of NaMo_4O_6 (Torardi & McCarley, 1979) built up from infinite chains of *trans*-edge-sharing Mo_6 octahedra, various reduced molybdenum oxides containing chain fragments have been synthesized. Thus chain-like clusters with two, four and five condensed Mo_6 octahedra have been isolated in LaMo_5O_8 ($|\text{Mo}_6|_2$) (Hibble, Cheetham, Bogle, Wakerley & Cox, 1988), $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$ ($|\text{Mo}_6|_4$ and $|\text{Mo}_6|_5$) (Mattausch, Simon & Peters, 1986) and $\text{In}_3\text{Mo}_{11}\text{O}_{17}$ ($|\text{Mo}_6|_5$) (Simon, Mertin, Mattausch & Gruehn, 1986). We present here the crystal structure of $\text{NdMo}_8\text{O}_{14}$ comprising the new Mo_8 cluster. The latter, based on an Mo_6 octahedron capped by two additional Mo atoms, constitutes a new type of fragmentation of the infinite chain.

Experimental. Single crystals were obtained by heating a stoichiometric mixture of Nd_2O_3 , MoO_2 and Mo in a sealed molybdenum crucible at about 2100 K for 15 min, cooling it at 50 K h^{-1} to 2000 K, then at 100 K h^{-1} to 1273 K and finally furnace cooling to room temperature.

A crystal with dimensions $0.08 \times 0.10 \times 0.14 \text{ mm}$ was selected for the intensity data collection carried out on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromatized $\text{Mo K}\alpha$ radiation. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with $12 \leq 2\theta \leq 27^\circ$. 1143 reflections were recorded in the range $2 \leq 2\theta \leq 60^\circ$ with $h: 0 \rightarrow 14$, $k: 0 \rightarrow 16$, $l: 0 \rightarrow 17$; ω - 2θ mode was used with scan width $\Delta\omega = (0.95 + 0.35\tan\theta)^\circ$ and counter aperture $\Delta l = (2 + 0.5\tan\theta) \text{ mm}$. Three orientation and three intensity control reflections were checked every 250 reflections and every hour, respectively, and showed no significant variation. Data were corrected for Lorentz-polarization, and an empirical absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to isotropically refined data. The minimum and maximum correction factors were 0.939 and 1.069. The structure was solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent difference Fourier synthesis. The function minimized in the least-squares program was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma^2(F_o) + 0.0004F_o^2 + 1]$ (Killean & Lawrence, 1969). The refinement of all atoms anisotropically and the extinction coefficient (106 variables) converged to $R = 0.021$, $wR = 0.029$, $S = 0.989$ for 1079 reflections with $F_o^2 > 3\sigma(F_o^2)$. The largest shift/e.s.d. was < 0.01 . Maximum and minimum electron density in final

Table 1. *Positional parameters and equivalent isotropic thermal parameters*

$$B_{\text{eq}} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Mo(1)	0.11962 (5)	-0.07468 (5)	0.83996 (5)	0.275 (7)
Mo(2)	0.12050 (5)	0.16066 (5)	-0.03635 (5)	0.270 (6)
Mo(3)	0.12408 (5)	-0.08489 (5)	0.08359 (5)	0.315 (6)
Mo(4)	0.12494 (6)	0.66404 (5)	0.69606 (5)	0.295 (6)
O(1)	0.2422 (6)	0.3283 (5)	0.2045 (4)	0.62 (7)
O(2)	0.2473 (6)	0.0801 (4)	0.3346 (5)	0.57 (6)
O(3)	0.0127 (5)	0.2528 (5)	0.3336 (4)	0.47 (6)
O(4)	0.2339 (5)	0.3428 (5)	0.9579 (4)	0.46 (6)
O(5)	0.2668 (5)	0.0740 (4)	0.0785 (5)	0.52 (6)
O(6)	-0.0110 (5)	0.2632 (5)	0.0764 (4)	0.56 (6)
O(7)	0.0000	0.0000	0.7120 (6)	0.53 (9)
O(8)	0.0000	0.0000	0.2290 (6)	0.46 (9)
Nd	0.0000	0.0000	0.500	0.561 (6)

Table 2. *Selected bond distances (Å)*

Mo(1)—Mo(1)	2.662 (1)	Mo(2)—Mo(3)	2.727 (1)
Mo(1)—Mo(2)	2.729 (1)	Mo(2)—Mo(4)	2.590 (1)
Mo(1)—Mo(2)	2.744 (1)	Mo(3)—Mo(3)	2.848 (1)
Mo(1)—Mo(3)	2.717 (1)	Mo(3)—Mo(4)	2.789 (1)
Mo(1)—Mo(4)*	3.068 (1)	Mo(3)—Mo(4)	2.731 (1)
Mo(2)—Mo(3)	2.798 (1)	Mo(3)—Mo(4)*	3.637 (1)
Mo(1)—O(1)	2.120 (6)	Mo(3)—O(1)	2.022 (6)
Mo(1)—O(2)	1.976 (5)	Mo(3)—O(4)	2.048 (5)
Mo(1)—O(3)	1.988 (6)	Mo(3)—O(5)	2.064 (5)
Mo(1)—O(4)	2.057 (5)	Mo(3)—O(6)	2.068 (6)
Mo(1)—O(7)	1.951 (6)	Mo(3)—O(8)	2.157 (6)
Mo(2)—O(2)	2.050 (6)	Mo(4)—O(1)	1.969 (6)
Mo(2)—O(3)	2.087 (5)	Mo(4)—O(2)	2.087 (6)
Mo(2)—O(4)	2.101 (5)	Mo(4)—O(3)	2.051 (5)
Mo(2)—O(5)	2.050 (6)	Mo(4)—O(5)	2.058 (5)
Mo(2)—O(6)	2.025 (5)	Mo(4)—O(6)	2.081 (5)
		Mo(4)—O(8)	2.038 (1)
Nd—O(7)	2.362 (8)	Nd—O(8)	2×3.020 (7)
Nd—O(5)	2×2.434 (5)	Nd—O(2)	3.037 (6)
Nd—O(6)	2×2.520 (5)	Nd—O(3)	2×3.139 (6)
Nd—O(4)	2×2.708 (5)		

* Intercluster distance.

difference Fourier map was $+2.04$ and -2.24 e \AA^{-3} (both near the Nd atom), respectively; final value of g was 1.96×10^{-6} (Stout & Jensen, 1968). A refinement of the occupancy factors for the Nd and Mo sites confirmed that all of these sites are fully occupied. Scattering factors for neutral atoms and f' , f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed with the *SDP* (B. A. Frenz & Associates, Inc., 1982) programs on a PDP 11/60. Final atomic coordinates and B_{eq} are reported in Table 1 and selected interatomic distances in Table 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53417 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The main novel feature of $\text{NdMo}_8\text{O}_{14}$ is the Mo_8 cluster unit shown in Fig. 1 with its oxygen environment. Fig. 2(a) depicts the cluster arrangement within the unit cell. From Fig. 1, it is clear that this new cluster based on a distorted Mo_6 octahedron capped by two additional Mo atoms constitutes a fragment of the infinite chains observed in various reduced molybdenum oxides. In particular the short distance $\text{Mo}(2)\text{—Mo}(4)$ of 2.59 Å recalls the pairwise distortion occurring in $\text{ZnMo}_8\text{O}_{10}$ (Lii, 1985) and $\text{Gd}_4\text{Mo}_4\text{O}_{11}$ (Gougeon, Lii & McCarely, 1985) and leads to two different waist-waist bond distances as already observed in these latter compounds. Here they are respectively 2.662 and 2.848 Å for $\text{Mo}(1)\text{—Mo}(1)$ and $\text{Mo}(3)\text{—Mo}(3)$. The other Mo—Mo bond distances range between 2.717 and 2.798 Å and are on average shorter than those in the infinite chains (average 2.731 Å in $\text{NdMo}_8\text{O}_{14}$, ca 2.80 Å in NaMo_4O_6 and $\text{ZnMo}_8\text{O}_{10}$). The Mo atoms $\text{Mo}(1)$, $\text{Mo}(2)$ and $\text{Mo}(3)$ are bonded to four, five and six Mo atoms respectively and to five O atoms in an approximately square-pyramidal symmetry. The environment of $\text{Mo}(1)$ is similar to that of the metal atoms in compounds containing Mo_6X_{12} -type cluster units and that of $\text{Mo}(2)$ is similar to the apex Mo atoms of the infinite chains of edge-shared octahedral clusters. On the other hand, the environment of $\text{Mo}(3)$ as well as that of $\text{Mo}(4)$ is new. In particular, the capping $\text{Mo}(4)$ atom is bonded to three Mo atoms and to six O atoms forming a distorted octahedron. Each Mo_8 cluster is surrounded by 24 O atoms which are either linked only to one Mo_8 cluster [oxygen of type *i*: O(5), O(6), O(7) and O(8)], or shared with adjacent clusters [oxygen of *a-a* type: O(1) or *i-a* and *a-i* type: O(2), O(3) and O(4)], as reflected in the connective formula

$[\text{Mo}_8\text{O}_6^i\text{O}_{6/2}^{i-a}][\text{O}_{6/2}^{a-i}\text{O}_{6/3}^{a-a}]$. The oxygens O(5) and O(6) are bonded to three Mo atoms [$\text{Mo}(2)$, $\text{Mo}(3)$, $\text{Mo}(4)$] and one Nd atom. O(7) is bonded to two Mo atoms $\text{Mo}(1)$ and one Nd atom in a trigonal-planar arrangement. O(8) is surrounded by five atoms, one Nd and four Mo atoms in a 'butterfly' shape. Oxygen atoms O(1), O(2), O(3) and O(4) insure the cohesion between Mo_8 clusters and are linked simultaneously to Mo atoms of different clusters. Thus the oxygen atoms O(2), O(3), O(4) lie above octahedra edges but are also coordinated to one Mo atom of a neighboring cluster. Moreover, they participate in the environment of the Nd atoms. Finally, O(1) in a corner position is only linked to three Mo atoms of three different Mo_8 clusters. The Mo—O bond distances range from 1.951 (6) to 2.157 (6) Å with the shortest of these involving the oxygen atom O(7) bridging only one edge and the largest one, the oxygen O(8) which is linked to four Mo atoms. This interunit linkage through O atoms results in the Mo_8 clusters being arranged in layers parallel to the *bc* plane. The shortest Mo—Mo intercluster distance inside a layer is 3.068 (1) Å [$\text{Mo}(1)\text{—Mo}(4)$] and between layers 3.637 (1) Å [$\text{Mo}(3)\text{—Mo}(4)$].

Each Nd atom is surrounded by 12 O atoms of different Mo_8O_{24} cluster units. Eight of them form a strongly distorted cube and the others cap four faces

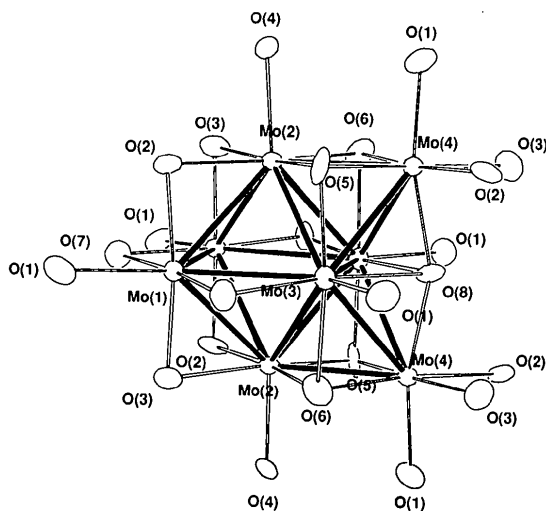


Fig. 1. The Mo_8 cluster and its oxygen environment.

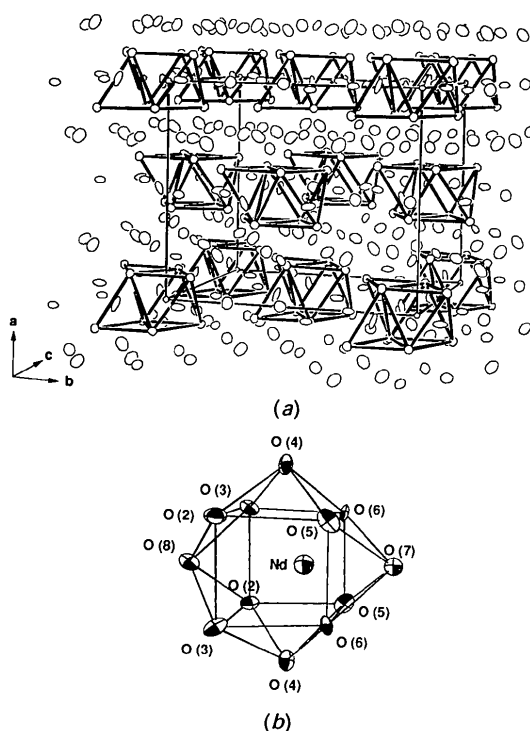


Fig. 2. (a) The arrangement of the Mo_8 clusters within the unit cell (only the Mo—Mo bonds have been drawn for clarity). (b) The oxygen environment about the Nd ion.

as shown in Fig. 2(b). From this drawing, we can also see that the Nd atom is slightly shifted away from the center of the pseudo cube towards the oxygen atom O(7). The Nd—O distances range between 2.362 (8) and 3.139 (6) Å within this distorted icosahedron.

Isostructural compounds are also formed with La, Ce, Pr, Sm and Gd as ternary element (Gougeon, Carlson & McCarley, 1989). Detailed studies of the magnetic and electrical properties of those metallic compounds will be published elsewhere.

Note added in proof. Since submission of this paper the structure of the related compound $\text{LaMo}_{7.7}\text{O}_{14}$ has appeared [Leligny, Ledesert, Labbé, Raveau & McCarroll (1990). *J. Solid State Chem.* **87**, 35–43].

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Structure Cristalline de $\text{K}_2\text{Th}(\text{MoO}_4)_3$

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Abstract. Dipotassium thorium trimolybdate, $\text{K}_2\text{Th}(\text{MoO}_4)_3$, $M_r = 790.05$, monoclinic, $C2/c$, $a = 17.649$ (2), $b = 12.143$ (2), $c = 5.3688$ (2) Å, $\beta = 105.756$ (5)°, $V = 1107$ (2) Å³, $Z = 4$, $D_x = 4.738$, $D_m = 4.75$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 179.16$ cm⁻¹, $F(000) = 1360$, room temperature. The structure was refined to $R = 0.025$ for 3516 independent reflections. The compound crystallizes in a scheelite-like structure with a one-dimensional ordering between K and Th atoms. The monoclinic unit cell is related to that of tetragonal CaWO_4 : $\mathbf{a} = \mathbf{a}_t$, $\mathbf{b} = \mathbf{c}_t$, $\mathbf{c} = -\mathbf{a}_t$.

Introduction. Dans le cadre d'une étude comparative des propriétés catalytiques de certains molybdates, nous avons voulu corrélérer leurs caractéristiques

structurales et leurs comportements chimiques. Parmi eux les molybdates $\text{K}_2\text{Th}(\text{MoO}_4)_3$ et $\text{K}_4\text{Th}(\text{MoO}_4)_4$ ont été indentifiés lors de travaux antérieurs (Bushuev, Trunov & Gizhinskii, 1975; Launay & Thoret, 1976) et présentés comme des composés de structures apparentées à celle de la scheelite. Nous présentons ici la structure de $\text{K}_2\text{Th}(\text{MoO}_4)_3$, isotype, d'après les diagrammes de diffraction X sur poudre, des molybdates $\text{K}_2M(\text{MoO}_4)_3$ ($M = \text{U}, \text{Pu}, \text{Np}$) et $\text{Rb}_2M(\text{MoO}_4)_3$ ($M = \text{Pu}, \text{Np}$) (Lee, 1976; Tabuteau & Pagès, 1980).

Partie expérimentale. Des monocristaux ont été obtenus après fusion vers 1028 K puis refroidissement lent (6 K h⁻¹) d'un mélange K_2MoO_4 – ThMo_2O_8 dans le rapport molaire 3/2; de couleur blanche, ils se présentent sous forme de prismes à base triangulaire, allongés selon [001]. Densité

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