

Teller effect). It may also explain the absence of phase transitions in chromium bromine and iodine and in copper bromine boracites, where the transition-metal atoms seem to occupy stable positions between the halogen atoms. They find a

favourable symmetry environment needing no Jahn–Teller deformation.

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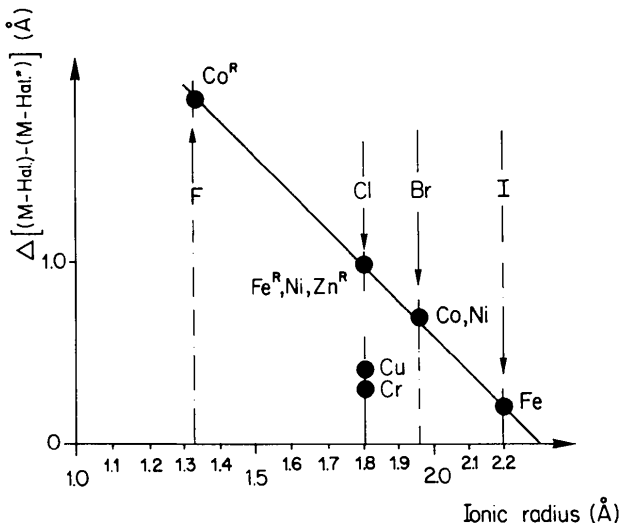


Fig. 1. Difference between the two metal–halogen distances of non-cubic boracites as a function of the halogen ionic radius. Superscript 'R' indicates values from a rhombohedral structure; other structures are orthorhombic. The parameter for Co–F was taken from the work of Berset, Depmeier, Boutellier & Schmid (1985); Zn–Cl from Mao, Mendoza-Alvarez, Depmeier, Kubel, Schmid & Yvon (1991); Ni–Cl and Co–Br from Kubel, Mao & Schmid (1992); Fe–Cl from Dowty & Clark (1973); Cu–Cl from Thornley, Nelmes & Kennedy (1976); Cr–Cl (at 100 K) from Mao, Kubel, Schmid & Yvon (1992); and Ni–Br from Abrahams, Bernstein & Svensson (1981).

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Structure of $Ce_{16}Mo_{21}O_{56}$ Containing Single Mo Atoms and Isolated Mo_{10} Clusters

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Abstract. $Ce_{16}Mo_{21}O_{56}$, $M_r = 5152.63$, monoclinic, $P2_1/c$, $a = 13.450$ (3), $b = 13.398$ (5), $c = 13.357$ (4) Å, $\beta = 99.92$ (1)°, $V = 2371.0$ (1.2) Å³, $Z = 2$, $D_x = 7.217$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 205.97$ cm⁻¹, $F(000) = 4516$, $T = 295$ K, $R = 0.034$ for 5277 observed reflections. The structure

displays MoO_6 octahedra and $|Mo_{10}O_{18}|O_8$ cluster units sharing O atoms to form the three-dimensional lattice. In the MoO_6 octahedra, the Mo–O distances range between 2.029 (7) and 2.051 (8) Å. The Mo–Mo distances within the two independent Mo_{10} clusters vary from 2.601 (1) to 2.842 (1) Å and the

Mo—O distances from 1.949 (8) to 2.164 (7) Å. The Mo₁₀ clusters as well as the single Mo atoms have no direct interactions between them. The Ce ions occupy irregular O sites with coordination numbers varying from 8 to 11.

Introduction. In recent systematic surveys of the reduced ternary oxides of molybdenum with the rare earths by solid-state reactions, new compounds showing different Mo—Mo bonding interactions were obtained: La₄Mo₂O₁₁ (Gall & Gougeon, 1992), containing isolated Mo₂ dimers; Gd₅Mo₂O₁₂ (Torardi, Fecketter, McCarroll & Di Salvo, 1985), in which the Mo₂ pairs form infinite chains; REMo₈O₁₄ [RE = La, Ce, Pr, Nd and Sm (Leligny, Ledesert, Labbe, Raveau & McCarroll, 1990; Gougeon & McCarley, 1991)], comprising Mo₈ clusters; REMo₅O₈ [RE = La, Ce, Pr, Nd, Sm, Eu and Gd (Hibble, Cheetham, Bogle, Wakerley & Cox, 1988; Gougeon, Gall & Sergent, 1991)], containing chains of bioctahedral Mo₁₀ clusters; RE₄Mo₄O₁₁ [RE = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y (Gougeon, Gall & McCarley, 1991a)], characterized by infinite chains of *trans*-edge-shared Mo₆ octahedra; and RE₄Mo₁₈O₃₂ [RE = Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y (Gougeon, Gall & McCarley, 1991b)], which contains three kinds of infinite Mo chains: linear chains with alternate short and long Mo—Mo distances, chains of *trans*-edge-shared rhomboidal clusters and chains of *trans*-edge-shared octahedral Mo₆ clusters. Moreover, the existence of reduced Mo compounds with rare earths should also be noted, such as Nd₃MoO₇ (Czeskleba-Kerner, Cros & Tourne, 1981) and the pyrochlores RE₂Mo₂O₇ (Hubert, 1974) in which the Mo atoms have no direct interactions. We present here the crystal structure of Ce₁₆Mo₂₁O₅₆, the main feature of which is the occurrence of single Mo atoms and isolated bioctahedral Mo₁₀ clusters.

Experimental. Single crystals were obtained by heating a mixture of overall composition 'K₂Ce₂Mo₄O₁₁' (starting materials: K₂MoO₄, CeO₂, MoO₃ and Mo) in a sealed molybdenum crucible at about 1980 K for 48 h. The crucible was then cooled at a rate of 100 K h⁻¹ to 1300 K and finally furnace-cooled to room temperature. The absence of potassium in the crystals thus obtained was checked by qualitative microanalyses using a JEOL JSM-35 CF scanning electron microscope equipped with a Tracor energy-dispersive-type X-ray spectrometer.

An irregularly shaped crystal with dimensions 0.06 × 0.08 × 0.11 mm (density not measured) was selected for the intensity-data collection carried out on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo Kα radiation. Accurate cell parameters were obtained by a least-

Table 1. *Positional parameters and isotropic or equivalent isotropic thermal parameters (Å²)*

Isotropic thermal parameters are indicated by asterisks. For anisotropically refined atoms, $B_{eq} = (4/3)\sum_i \beta_{ij} a_i \cdot a_j$.

	x	y	z	B_{iso}/B_{eq}
Ce(1)	0.36673 (4)	0.11915 (4)	0.27919 (4)	0.508 (9)
Ce(2)	0.14122 (4)	0.30375 (4)	0.27438 (4)	0.429 (9)
Ce(3)	0.32849 (4)	0.30971 (5)	0.07289 (4)	0.549 (9)
Ce(4)	0.10832 (4)	0.11063 (4)	0.05029 (4)	0.508 (9)
Ce(5)	0.64390 (4)	0.16581 (4)	0.64363 (4)	0.455 (9)
Ce(6)	0.84709 (4)	0.09661 (5)	0.13425 (4)	0.528 (9)
Ce(7)	0.12967 (4)	-0.16883 (4)	0.13818 (4)	0.428 (9)
Ce(8)	0.68169 (4)	0.12388 (5)	0.35409 (4)	0.535 (9)
Mo(1)	0.52337 (6)	-0.07504 (7)	0.21584 (6)	0.32 (1)
Mo(2)	0.51528 (6)	0.28934 (6)	0.42867 (6)	0.35 (1)
Mo(3)	0.35433 (6)	-0.05441 (6)	0.06243 (6)	0.30 (1)
Mo(4)	0.35216 (6)	0.08522 (7)	0.92249 (6)	0.32 (1)
Mo(5)	0.48478 (6)	-0.07318 (6)	-0.07708 (6)	0.28 (1)
Mo(6)	0.03950 (6)	-0.00542 (7)	0.28344 (6)	0.32 (1)
Mo(7)	0.19833 (6)	0.00798 (7)	0.42532 (6)	0.34 (1)
Mo(8)	0.93242 (6)	0.14665 (6)	0.55962 (6)	0.30 (1)
Mo(9)	0.04699 (6)	0.14339 (6)	0.42144 (6)	0.29 (1)
Mo(10)	0.91292 (6)	-0.01035 (6)	0.42363 (6)	0.27 (1)
Mo(11)	0.500	0.000	0.500	0.29 (2)
O(1)	0.3305 (60)	0.0910 (6)	0.7635 (5)	0.7 (1)*
O(2)	0.3731 (5)	0.9431 (5)	0.2202 (5)	0.4 (1)*
O(3)	0.4678 (5)	0.5737 (5)	0.2669 (5)	0.4 (1)*
O(4)	0.4942 (5)	0.2774 (5)	0.2767 (5)	0.5 (1)*
O(5)	0.4660 (6)	0.0767 (6)	0.6207 (5)	0.5 (1)
O(6)	0.3663 (6)	0.2605 (5)	0.4146 (5)	0.6 (1)
O(7)	0.3372 (6)	0.7082 (6)	0.5634 (5)	0.7 (1)*
O(8)	0.4821 (5)	0.7245 (5)	0.4223 (5)	0.5 (1)
O(9)	0.4615 (6)	0.8695 (6)	0.5603 (5)	0.7 (1)*
O(10)	0.3660 (5)	0.3987 (5)	0.5815 (5)	0.4 (1)*
O(11)	0.3310 (5)	0.5689	0.4034 (5)	0.5 (1)
O(12)	0.2021 (5)	0.5467 (6)	0.5482 (5)	0.6 (1)
O(13)	0.2052 (5)	0.4026 (6)	0.4146 (5)	0.8 (1)
O(14)	0.0259 (5)	0.1384 (5)	0.2639 (5)	0.5 (1)
O(15)	0.0437 (6)	0.8438 (5)	0.2842 (5)	0.6 (1)
O(16)	0.1121 (5)	0.4805 (5)	0.2290 (5)	0.4 (1)*
O(17)	0.1866 (6)	-0.0091 (6)	0.2759 (5)	0.6 (1)*
O(18)	0.0105 (6)	0.5085 (6)	0.6203 (5)	0.8 (1)
O(19)	0.1989 (5)	0.1570 (6)	0.4164 (5)	0.6 (1)
O(20)	0.2231 (6)	0.8630 (6)	0.4492 (5)	0.7 (1)*
O(21)	0.2396 (5)	0.0253 (5)	0.5767 (5)	0.4 (1)*
O(22)	0.3559 (5)	0.0162 (6)	0.4211 (5)	0.6 (1)*
O(23)	0.0890 (5)	0.1650 (6)	0.5783 (5)	0.5 (1)*
O(24)	0.1114 (5)	0.8579 (5)	0.5977 (5)	0.4 (1)*
O(25)	0.0736 (5)	0.7032 (5)	0.4547 (5)	0.5 (1)
O(26)	0.0435 (5)	0.2887 (5)	0.4067 (5)	0.4 (1)*
O(27)	0.2483 (6)	0.7748 (6)	0.7565 (6)	0.7 (1)
O(28)	0.2387 (6)	0.2927 (6)	0.6765 (5)	0.7 (1)

squares refinement of the setting angles of 25 reflections with $13 \leq 2\theta \leq 27^\circ$. The systematic absences ($h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$) indicated the space group to be $P2_1/c$ and this was confirmed by the structure solution. 7472 reflections were recorded in the range $2 \leq 2\theta \leq 60^\circ$ with $h \rightarrow 18$, $k \rightarrow 18$, $l \rightarrow 18$; $\omega - 2\theta$ mode was used with scan width $\Delta\omega = (1.00 + 0.35 \tan\theta)^\circ$ and counter aperture $\Delta l = (2 + 0.5 \tan\theta)$ mm. Three orientation and three intensity control reflections were checked every 250 reflections and every hour, respectively, and showed no systematic variations. 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 0.909 to 1.269. After averaging ($R_{int} = 0.023$), 6378 unique data were used to solve the structure with the aid of *MULTAN11/82* (Main, Fiske, Hull,

Table 2. Selected bond distances (Å)

Mo(1)—Mo(2)	2.637 (1)	Mo(6)—Mo(7)	2.606 (1)
Mo(1)—Mo(4)	2.702 (1)	Mo(6)—Mo(9)	2.706 (1)
Mo(1)—Mo(5)	2.706 (1)	Mo(6)—Mo(10)	2.740 (1)
Mo(1)—Mo(3)	2.800 (1)	Mo(6)—Mo(8)	2.801 (1)
Mo(2)—Mo(5)	2.706 (1)	Mo(7)—Mo(10)	2.711 (1)
Mo(2)—Mo(3)	2.720 (1)	Mo(7)—Mo(8)	2.747 (1)
Mo(2)—Mo(4)	2.754 (1)	Mo(7)—Mo(9)	2.721 (1)
Mo(3)—Mo(4)	2.641 (1)	Mo(8)—Mo(9)	2.601 (1)
Mo(3)—Mo(5)	2.738 (1)	Mo(8)—Mo(10)	2.748 (1)
Mo(3)—Mo(5)	2.782 (1)	Mo(8)—Mo(10)	2.762 (1)
Mo(4)—Mo(5)	2.746 (1)	Mo(9)—Mo(10)	2.714 (1)
Mo(4)—Mo(5)	2.772 (1)	Mo(9)—Mo(10)	2.741 (1)
Mo(5)—Mo(5)	2.822 (1)	Mo(10)—Mo(10)	2.842 (1)
Mo(1)—O(1)	1.949 (8)	Mo(6)—O(14)	1.950 (7)
Mo(1)—O(4)	1.995 (7)	Mo(6)—O(17)	1.999 (8)
Mo(1)—O(3)	2.007 (7)	Mo(6)—O(15)	2.020 (7)
Mo(1)—O(2)	2.047 (7)	Mo(6)—O(16)	2.025 (7)
Mo(1)—O(5)	2.164 (7)	Mo(6)—O(18)	2.147 (7)
Mo(2)—O(7)	1.969 (8)	Mo(7)—O(20)	1.987 (8)
Mo(2)—O(8)	1.993 (7)	Mo(7)—O(17)	1.988 (7)
Mo(2)—O(4)	2.007 (7)	Mo(7)—O(19)	2.000 (8)
Mo(2)—O(6)	2.018 (8)	Mo(7)—O(21)	2.016 (7)
Mo(2)—O(9)	2.152 (8)	Mo(7)—O(22)	2.133 (7)
Mo(3)—O(12)	2.026 (7)	Mo(8)—O(25)	2.021 (7)
Mo(3)—O(7)	2.074 (8)	Mo(8)—O(15)	2.059 (7)
Mo(3)—O(2)	2.079 (7)	Mo(8)—O(20)	2.078 (8)
Mo(3)—O(11)	2.102 (7)	Mo(8)—O(24)	2.084 (7)
Mo(3)—O(10)	2.104 (7)	Mo(8)—O(23)	2.093 (7)
Mo(4)—O(13)	1.967 (7)	Mo(9)—O(26)	1.956 (7)
Mo(4)—O(6)	2.081 (7)	Mo(9)—O(19)	2.064 (7)
Mo(4)—O(11)	2.094 (7)	Mo(9)—O(14)	2.076 (7)
Mo(4)—O(1)	2.095 (7)	Mo(9)—O(23)	2.094 (7)
Mo(4)—O(10)	2.110 (7)	Mo(9)—O(24)	2.102 (7)
Mo(5)—O(8)	2.028 (7)	Mo(10)—O(16)	2.013 (7)
Mo(5)—O(11)	2.040 (7)	Mo(10)—O(21)	2.061 (7)
Mo(5)—O(10)	2.052 (7)	Mo(10)—O(23)	2.072 (7)
Mo(5)—O(3)	2.057 (7)	Mo(10)—O(24)	2.080 (7)
Mo(11)—O(5)	2.029 (7) × 2		
Mo(11)—O(9)	2.030 (8) × 2		
Mo(11)—O(22)	2.051 (8) × 2		
Ce(1)—O(28)	2.330 (8)	Ce(5)—O(8)	2.300 (7)
Ce(1)—O(22)	2.369 (7)	Ce(5)—O(27)	2.312 (7)
Ce(1)—O(3)	2.485 (7)	Ce(5)—O(2)	2.373 (7)
Ce(1)—O(2)	2.493 (7)	Ce(5)—O(20)	2.377 (7)
Ce(1)—O(6)	2.619 (7)	Ce(5)—O(22)	2.588 (7)
Ce(1)—O(10)	2.650 (7)	Ce(5)—O(5)	2.644 (7)
Ce(1)—O(4)	2.731 (7)	Ce(5)—O(9)	2.885 (8)
Ce(1)—O(9)	2.872 (8)	Ce(5)—O(4)	3.004 (7)
Ce(1)—O(17)	2.964 (8)	Ce(5)—O(17)	3.149 (8)
Ce(1)—O(19)	3.184 (7)	Ce(5)—O(7)	3.287 (7)
Ce(2)—O(13)	2.334 (8)	Ce(6)—O(25)	2.242 (7)
Ce(2)—O(26)	2.385 (7)	Ce(6)—O(16)	2.389 (7)
Ce(2)—O(28)	2.385 (7)	Ce(6)—O(11)	2.390 (7)
Ce(2)—O(16)	2.459 (7)	Ce(6)—O(12)	2.503 (7)
Ce(2)—O(15)	2.533 (8)	Ce(6)—O(18)	2.643 (8)
Ce(2)—O(23)	2.626 (7)	Ce(6)—O(27)	2.718 (8)
Ce(2)—O(14)	2.693 (7)	Ce(6)—O(13)	2.742 (8)
Ce(2)—O(19)	2.750 (7)	Ce(6)—O(14)	2.768 (7)
Ce(2)—O(1)	2.935 (8)		
Ce(3)—O(5)	2.396 (8)	Ce(7)—O(12)	2.340 (7)
Ce(3)—O(28)	2.415 (8)	Ce(7)—O(26)	2.372 (7)
Ce(3)—O(6)	2.446 (7)	Ce(7)—O(15)	2.439 (7)
Ce(3)—O(21)	2.517 (7)	Ce(7)—O(25)	2.480 (7)
Ce(3)—O(19)	2.520 (8)	Ce(7)—O(27)	2.488 (8)
Ce(3)—O(8)	2.782 (7)	Ce(7)—O(24)	2.594 (7)
Ce(3)—O(10)	2.837 (7)	Ce(7)—O(18)	2.667 (8)
Ce(3)—O(1)	2.868 (7)	Ce(7)—O(17)	2.841 (7)
Ce(3)—O(23)	3.153 (7)	Ce(7)—O(7)	3.167 (7)
Ce(3)—O(4)	3.237 (7)		
Ce(3)—O(23)	3.251 (7)		

Table 2 (cont.)

Ce(4)—O(18)	2.362 (8)	Ce(8)—O(27)	2.322 (7)
Ce(4)—O(26)	2.384 (7)	Ce(8)—O(21)	2.374 (7)
Ce(4)—O(13)	2.415 (7)	Ce(8)—O(9)	2.404 (7)
Ce(4)—O(12)	2.459 (8)	Ce(8)—O(3)	2.447 (7)
Ce(4)—O(28)	2.564 (8)	Ce(8)—O(7)	2.537 (8)
Ce(4)—O(25)	2.733 (7)	Ce(8)—O(20)	2.723 (7)
Ce(4)—O(18)	2.892 (8)	Ce(8)—O(24)	2.757 (7)
Ce(4)—O(23)	3.046 (7)	Ce(8)—O(1)	3.271 (8)
Ce(4)—O(14)	3.255 (7)	Ce(8)—O(4)	3.280 (7)
Ce(4)—O(17)	3.416 (7)	Ce(8)—O(5)	3.393 (7)
Ce(4)—O(10)	3.421 (7)		

Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent difference Fourier syntheses. The function minimized in the least-squares program was $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/[\sigma^2(F_o^2) + (0.02F_o^2)^2]$. Anisotropic thermal parameters were used for all the Ce and Mo atoms and only one for some of the O atoms owing to their small contribution to the observed structure factors with respect to those of the La and Mo atoms. In the final cycle (347 variables including an extinction coefficient), convergence was achieved at $R = 0.034$, $wR = 0.035$, $S = 1.540$ for 5277 reflections with $F_o^2 > 2\sigma(F_o^2)$. The largest shift/e.s.d. was < 0.01 . Maximum and minimum electron densities in the final difference Fourier map were 2.25 and -0.94 e \AA^{-3} , respectively; the final value of g was 4.07×10^{-8} (Stout & Jensen, 1968). A refinement of the occupancy factors for the Ce and Mo sites confirmed that they 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 *MolEN* (Fair, 1989) programs on a Digital MicroVAX 3100. Final atomic coordinates and B_{eq} values are reported in Table 1 and selected interatomic distances in Table 2.* Fig. 1 shows the numbering scheme and Fig. 2 the arrangement of single Mo atoms and Mo₁₀ clusters within the unit cell.

Discussion. The structure of Ce₁₆Mo₂₁O₅₆ is composed of MoO₆ octahedra and |Mo₁₀O₁₈|O₈ cluster units sharing O atoms with the Ce ions occupying irregular O sites. The Mo(11)O₆ octahedra are centred around inversion centres [$2(d)$ positions] and are only slightly distorted. The Mo—O distances in the equatorial plane are 2.029 (7) [Mo(11)—O(5)] and 2.030 (8) Å [Mo(11)—O(9)] and the two *trans* Mo(11)—O(22) bonds are equal to 2.051 (8) Å [mean value 2.037 Å]. There are two crystallographically independent Mo₁₀ clusters in Ce₁₆Mo₂₁O₅₆, both

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55737 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1018]

having crystallographic $\bar{1}$ symmetry. Such groups were found before in the MMo_5O_8 series [$M = \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Ca, Sr, Sn}$ and Pb (Hibble *et al.*, 1988; Dronskowski & Simon, 1989; Gougeon, Potel & Sergent, 1990; Gougeon, Gall & Sergent, 1991)] and can be viewed as resulting from the metal–edge condensation of two octahedral Mo_6 clusters. However, while in the MMo_5O_8 compounds the Mo_{10} clusters are strongly linked through very short Mo–Mo intercluster bonds of about 2.7 Å to form infinite chains, in this new compound the shortest Mo–Mo intercluster distance is 5.423 (1) Å. In addition, they have no direct interactions with the single Mo(11) atoms, the shortest distance between Mo(11) atoms and Mo_{10} clusters being 3.991 (1) Å. Each Mo_{10} cluster is surrounded by 26 O atoms which are located above all free edges and corners. All of these O atoms also contribute to the environment of the Ce ions and some of them are shared with adjacent

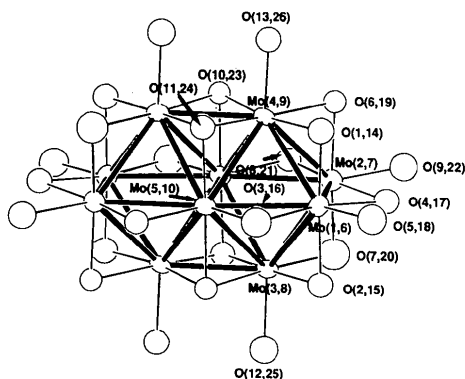


Fig. 1. Numbering scheme in the $[Mo_{10}O_{18}]O_8$ cluster units. The first numbers correspond to cluster (I) and the second to cluster (II) (see text).

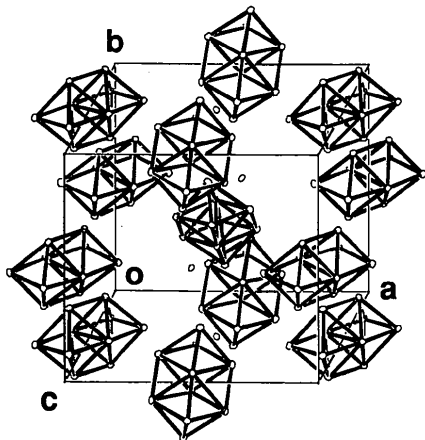


Fig. 2. The arrangement of the single Mo atoms (unconnected ellipsoids) and Mo_{10} clusters within the unit cell (O and Ce atoms have been omitted for clarity).

single Mo atoms. The Mo–Mo distances which lie between 2.637 (1) and 2.822 (1) Å in the cluster (I) [Mo(1), Mo(2), Mo(3), Mo(4) and Mo(5)] and between 2.601 (1) and 2.842 (1) Å in the cluster (II) [Mo(6), Mo(7), Mo(8), Mo(9) and Mo(10)] show some significant differences. Thus, in cluster (II) where the shortest distance between apical atoms occurs [Mo(8)—Mo(9)], the shared edge Mo(10)—Mo(10) and the ending edge Mo(6)—Mo(7) are longer and shorter, respectively, than the corresponding bonds in cluster (I) [Mo(5)—Mo(5) and Mo(1)—Mo(2), respectively]. This behaviour is quite similar to that observed in the infinite chains occurring in $Ho_4Mo_4O_{11}$ (Gougeon *et al.*, 1991a) and $ZnMo_8O_{10}$ (Lii, McCarley, Kim & Jacobson, 1986). The average Mo–Mo distances of 2.729 and 2.722 Å in clusters (I) and (II), respectively, are lower than those determined in the $M^{3+}Mo_5O_8$ (ca 2.75 Å) and $M^{2+}Mo_5O_8$ (ca 2.74 Å) ($M = \text{Ca, Sr}$ and Eu) compounds (Gall, 1990). With the exception of Mo(5) and Mo(10), which are shared by both octahedra constituting the Mo_{10} clusters and are surrounded by four O atoms, all the other Mo atoms are bonded to five O atoms in an approximately square-pyramidal environment. The Mo–O distances range from 1.949 (8) to 2.164 (7) Å (mean value 2.050 Å) in cluster (I) and from 1.950 (7) to 2.147 (7) Å in cluster (II) (mean value 2.047 Å). For the $M^{3+}Mo_5O_8$ and $M^{2+}Mo_5O_8$ compounds, the average Mo–O distances are about 2.076 and 2.063 Å, respectively.

All the Ce ions are in a general position and occupy irregular O-atom sites within the lattice. The coordination numbers of the Ce ions are 8 [Ce(6)], 9 [Ce(2) and Ce(7)], 10 [Ce(1), Ce(5) and Ce(8)] and 11 [Ce(3) and Ce(4)]. The Ce–O distances spread over a wide range [2.242 (7) to 3.421 (7) Å].

By using the bond-length–bond-strength formula (Brown & Wu, 1976) for the Mo–O and Ce–O bonds $\{s = [d(\text{Mo–O})/1.882]^{-6.0}$ and $s = [d(\text{Ce–O})/2.160]^{-6.5}\}$, an assignment of oxidation states to the Mo and Ce atoms has been made. The valence of each independent Mo atom was determined as follows: Mo(1) + 3.21, Mo(2) + 3.23, Mo(3) + 2.76, Mo(4) + 2.85, Mo(5) + 2.42, Mo(6) + 3.23, Mo(7) + 3.25, Mo(8) + 2.84, Mo(9) + 2.95, Mo(10) + 2.34 and Mo(11) + 3.71. From these values we can deduce average Mo oxidation states of +2.90 and +2.92 in clusters (I) and (II), respectively. The value of +3.71 for the isolated Mo(11) indicates tetravalent molybdenum, although a mixture of Mo^{3+} and Mo^{4+} is also plausible. This underestimation of the oxidation state can be compared with that observed in some reduced oxoniobates for the Nb^{5+} atoms when they are connected *via* O atoms to Nb_6O_{12} cluster units (Hibble, Cheetham, Köhler & Simon, 1989). The calculated valence of the molybdenum in

$\text{Ce}_{16}\text{Mo}_{21}\text{O}_{56}$ is +2.95 which is close to that based on the stoichiometry, +3.05, when considering all the Ce ions as trivalent. Bond-valence sums of the Ce—O bonds are 3.09, 3.30, 2.93, 2.97, 3.38, 3.11, 3.20 and 3.07 for Ce(1), Ce(2), Ce(3), Ce(4), Ce(5), Ce(6), Ce(7) and Ce(8), respectively. It is interesting to note that for the total valence sum $\sum_s(\text{Mo—O}) + \sum_s(\text{Ce—O})$, we obtain a value of 112.05 per formula unit, which is in very good agreement with the theoretical value of 112 based on the 56 O atoms.

Isostructural compounds are also formed with La, Pr and Nd.

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Structure of $[\text{Ru}_2\text{Cl}_4(\text{Me}_2\text{SO})_5]$

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Abstract. *def*-Tri- μ -chloro-*a*-chloro-*bcghi*-pentakis-(dimethyl sulfoxide-*S*)diruthenium(II), $[\text{Ru}_2\text{Cl}_4(\text{C}_2\text{H}_5\text{OS})_5]$, $M_r = 734.62$, monoclinic, $P2_1/n$, $a = 11.085$ (1), $b = 15.647$ (1), $c = 15.167$ (2) Å, $\beta = 109.94$ (1)°, $V = 2472.9$ (5) Å³, $Z = 4$, $D_x = 1.973$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 20.6$ cm⁻¹, $F(000) = 1464$, $T = 294$ K, $R = 0.023$, $wR = 0.032$ for 5581 unique observed reflections. The structure is characterized by a triple chloro-bridged diruthenium core [Ru...Ru distance 3.236 (1) Å] with five terminal S-bonded dimethyl sulfoxide ligands. Three are bonded to Ru1 in a *fac* arrangement, and two are *cis* bonded to Ru2. The distorted octahedral coordination of both metal atoms is completed by Cl ligands.

Introduction. As part of a general study on halide (*X*) dimethyl sulfoxide (Me_2SO , dmsO) ruthenium

complexes (Alessio, Balducci, Calligaris, Costa, Attia & Mestroni, 1991), we prepared the title complex and determined its crystal structure, in order to verify the spectroscopically proposed structure (Heath, Lindsay & Stephenson, 1982) and obtain further structural data on $\text{RuX}_x(\text{dmsO})_y$ complexes.

Experimental. Crystals of $[\text{Ru}_2\text{Cl}_4(\text{dmsO})_5]$, suitable for X-ray analysis, were directly obtained from the reaction when 0.25 g of *cis*- $\text{RuCl}_2(\text{dmsO})_4$ (0.5 mmol) was partially dissolved in 15 ml of methanol. This mixture was stirred for 8 h at room temperature and then filtered over fine filter paper to remove a small amount of unreacted starting material (checked by NMR). Orange-red crystals of the product formed from the deep yellow solution within a week, upon addition of 3 ml of diethyl ether. They were filtered off, washed with cold methanol and diethyl ether and