Crystal structure of hexadecaneodymium henicosamolbydenum hexapentacontaoxide, $\text{Mo}_{21}\text{Nd}_{16}\text{O}_{56}$

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Fig. 1. Projection of the crystal structure of $\text{Nd}_{16}\text{Mo}_{21}\text{O}_{56}$ on the (a, c) plane. Nd atoms omitted for clarity.

Fig. 2. The numbering scheme in the $[\text{Mo}_{10}\text{O}_{18}]\text{O}_8$ cluster units. The first numbers correspond to cluster I and the second to cluster II (see text).

Source of material: Single crystals were obtained by heating a mixture of overall composition " $\text{K}_2\text{Nd}_2\text{Mo}_4\text{O}_{11}$ " (starting materials: K_2MoO_4 , Nd_2O_3 , MoO_3 and Mo) in a sealed molybdenum crucible at about 1980 K for 48 hours. The crucible was then cooled at a rate of 100 K/h down to 1300 K and finally furnace-cooled to room temperature. The absence of potassium in the crystals was checked by qualitative microanalyses using a JEOL JSM-35 CF scanning electron microscope equipped with a Tracor energy-dispersive-type X-ray spectrometer.

$\text{Nd}_{16}\text{Mo}_{21}\text{O}_{56}$ is isostructural with $\text{Ce}_{16}\text{Mo}_{21}\text{O}_{56}$ (see ref. 1). Its crystal structure is composed of MoO_6 octahedra and $[\text{Mo}_{10}\text{O}_{18}]\text{O}_8$ cluster units sharing O atoms with the Nd ions occupying irregular O sites. The $\text{Mo}(11)\text{O}_6$ octahedra are centered around inversion centers ($2d$ positions) and are only slightly distorted with Mo–O distances ranging between 2.030(9) Å and 2.050(9) Å [mean value 2.038 Å]. There are two crystallographically independent Mo_{10} clusters in $\text{Nd}_{16}\text{Mo}_{21}\text{O}_{56}$, both having crystallographic $\bar{1}$ symmetry. They can be viewed as resulting from the metal-edge condensation of two octahedral Mo_6 clusters. Each Mo_{10} cluster is surrounded by 26 oxygen atoms which are located above all free edges and corners. All of these oxygen atoms also participate to the environment of the Nd ions and some of them are shared with adjacent single Mo atoms. The Mo–Mo distances lie between 2.647(1) Å and 2.818(2) Å in the cluster I [Mo(1), Mo(2), Mo(3), Mo(4) and Mo(5)] and between 2.606(1) Å and 2.856(2) Å in the cluster II [Mo(6), Mo(7), Mo(8), Mo(9) and Mo(10)]. The average Mo–Mo distances are 2.730 Å and 2.722 Å for the clusters I and II, respectively. The shortest distance between Mo_{10} clusters is greater than 5 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 3.962(1) Å. 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 approximately square-pyramidal environment. The Mo–O distances range from 1.945(8) Å to 2.166(8) Å (mean value 2.048 Å) in the cluster I and from 1.953(9) Å to 2.130(9) Å (mean value 2.044 Å) in the cluster II. All the Nd ions are in a general position and occupy irregular oxygen sites within the Mo–O lattice. The coordination numbers of the Nd ions are 8 [Nd(6) and Nd(8)], 9 [Nd(2), Nd(5) and Nd(7)], 10 [Nd(1)] and 11 [Nd(3) and Nd(4)]. The Nd–O distances spread over a wide range [2.210(9) Å to 3.469(8) Å].

$\text{Mo}_{21}\text{Nd}_{16}\text{O}_{56}$, monoclinic, $P12/c1$ (No. 13), $a = 13.385(2)$ Å, $b = 13.368(1)$ Å, $c = 13.252(2)$ Å, $\beta = 100.38(1)^\circ$, $V = 2332.4$ Å³, $Z = 2$, $R(F) = 0.035$, $R_w(F^2) = 0.083$.

Table 1. Parameters used for the X-ray data collection

Crystal:	black, irregular, size 0.07 x 0.08 x 0.16 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	229.82 cm ⁻¹
Diffractometer:	Enraf-Nonius CAD4
Scan mode:	$\omega/2\theta$
$T_{\text{measurement}}$:	293 K
$2\theta_{\text{max}}$:	60°
$N(hkl)_{\text{unique}}$:	6779
Criterion for I_0 :	$I_0 > 2 \sigma(I_0)$
$N(\text{param})_{\text{refined}}$:	282
Program:	SHELXL-93

Table 2. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	U _{iso}
O(1)	4g	0.3296(6)	0.1007(7)	0.7641(6)	0.007(2)
O(2)	4g	0.3740(6)	0.9454(6)	0.2208(6)	0.006(2)
O(3)	4g	0.4615(7)	0.5710(7)	0.2627(7)	0.009(2)
O(4)	4g	0.4972(7)	0.2748(7)	0.2786(7)	0.008(2)
O(5)	4g	0.4649(6)	0.0816(7)	0.6180(6)	0.007(2)
O(6)	4g	0.3726(6)	0.2546(7)	0.4191(6)	0.007(2)
O(7)	4g	0.3315(7)	0.7056(7)	0.5643(7)	0.011(2)
O(8)	4g	0.4709(7)	0.7216(7)	0.4187(7)	0.009(2)
O(9)	4g	0.4534(7)	0.8701(7)	0.5569(7)	0.010(2)
O(10)	4g	0.3696(6)	0.3963(7)	0.5843(6)	0.006(2)
O(11)	4g	0.3261(6)	0.5619(6)	0.4015(6)	0.006(2)
O(12)	4g	0.2004(7)	0.5434(7)	0.5480(7)	0.008(2)
O(13)	4g	0.2072(7)	0.3915(7)	0.4182(7)	0.012(2)
O(14)	4g	0.0237(6)	0.1382(7)	0.2612(6)	0.007(2)

Table 2. (Continued)

Atom	Site	x	y	z	U _{iso}
O(15)	4g	0.0415(6)	0.8426(6)	0.2839(6)	0.005(2)
O(16)	4g	0.1145(6)	0.4793(7)	0.2316(6)	0.007(2)
O(17)	4g	0.1839(6)	-0.0124(7)	0.2741(6)	0.007(2)
O(18)	4g	0.0059(7)	0.5087(7)	0.6183(7)	0.009(2)
O(19)	4g	0.1983(7)	0.1569(7)	0.4167(6)	0.008(2)
O(20)	4g	0.2235(7)	0.8622(7)	0.4484(7)	0.008(2)
O(21)	4g	0.2416(7)	0.0238(7)	0.5761(6)	0.008(2)
O(22)	4g	0.3559(7)	0.0184(7)	0.4181(7)	0.011(2)
O(23)	4g	0.0896(6)	0.1662(6)	0.5794(6)	0.005(2)
O(24)	4g	0.1138(6)	0.8573(6)	0.5986(6)	0.006(2)
O(25)	4g	0.0742(7)	0.7031(7)	0.4548(7)	0.009(2)
O(26)	4g	0.0398(6)	0.2888(7)	0.4058(6)	0.007(2)
O(27)	4g	0.2468(7)	0.7700(7)	0.7583(7)	0.012(2)
O(28)	4g	0.2380(6)	0.2952(6)	0.6769(6)	0.006(2)

Table 3. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Nd(1)	4g	0.37156(5)	0.12137(5)	0.27871(5)	0.0094(3)	0.0067(3)	0.0063(3)	0.0015(2)	0.0014(2)	0.0005(2)
Nd(2)	4g	0.14088(5)	0.30169(5)	0.27496(5)	0.0071(3)	0.0061(3)	0.0054(3)	0.0006(2)	0.0014(2)	-0.0001(2)
Nd(3)	4g	0.32351(5)	0.30974(5)	0.07379(5)	0.0100(3)	0.0073(3)	0.0077(3)	-0.0009(2)	0.0017(2)	0.0004(2)
Nd(4)	4g	0.10649(5)	0.11065(5)	0.04934(5)	0.0072(3)	0.0073(3)	0.0090(3)	-0.0002(2)	0.0028(2)	0.0012(2)
Nd(5)	4g	0.64523(5)	0.16196(5)	0.64452(5)	0.0064(3)	0.0064(3)	0.0061(3)	-0.0004(2)	0.0010(2)	0.0000(2)
Nd(6)	4g	0.84751(5)	0.09733(5)	0.13282(5)	0.0057(3)	0.0140(3)	0.0079(3)	-0.0014(2)	0.0001(2)	0.0044(2)
Nd(7)	4g	0.12939(5)	-0.16711(5)	0.13797(5)	0.0068(3)	0.0064(3)	0.0053(3)	-0.0002(2)	0.0013(2)	0.0003(2)
Nd(8)	4g	0.68532(5)	0.12906(5)	0.35552(5)	0.0068(3)	0.0076(3)	0.0074(3)	0.0007(2)	0.0016(2)	0.0013(2)
Mo(1)	4g	0.52467(7)	-0.07773(8)	0.21705(7)	0.0052(4)	0.0051(4)	0.0044(4)	0.0004(3)	0.0010(3)	0.0002(3)
Mo(2)	4g	0.52037(7)	0.28871(8)	0.43161(7)	0.0061(4)	0.0042(4)	0.0051(4)	-0.0002(3)	0.0017(3)	0.0005(3)
Mo(3)	4g	0.35312(7)	-0.05163(8)	0.06299(7)	0.0039(4)	0.0046(4)	0.0045(4)	-0.0004(3)	0.0002(3)	-0.0003(3)
Mo(4)	4g	0.35306(7)	0.09073(8)	0.92416(7)	0.0039(4)	0.0064(4)	0.0042(4)	0.0003(3)	0.0005(3)	0.0000(3)
Mo(5)	4g	0.48089(7)	-0.07166(8)	-0.07909(7)	0.0045(4)	0.0045(4)	0.0042(4)	-0.0002(3)	0.0010(3)	-0.0006(3)
Mo(6)	4g	0.03756(7)	-0.00622(8)	0.28169(7)	0.0045(4)	0.0048(4)	0.0045(4)	0.0002(3)	0.0003(3)	-0.0002(3)
Mo(7)	4g	0.19877(7)	0.00825(8)	0.42413(7)	0.0039(4)	0.0052(4)	0.0052(4)	0.0001(3)	0.0007(3)	0.0005(3)
Mo(8)	4g	0.93226(7)	0.14706(8)	0.55992(7)	0.0046(4)	0.0043(4)	0.0049(4)	0.0000(3)	0.0007(3)	0.0001(3)
Mo(9)	4g	0.04574(7)	0.14351(8)	0.42065(7)	0.0039(4)	0.0042(4)	0.0042(4)	0.0000(3)	0.0008(3)	-0.0001(3)
Mo(10)	4g	0.91133(7)	-0.01044(7)	0.42268(7)	0.0038(4)	0.0039(4)	0.0043(4)	0.0003(3)	0.0006(3)	-0.0003(3)
Mo(11)	2c	1/2	0	1/2	0.0042(6)	0.0042(6)	0.0037(5)	-0.0005(5)	0.0002(4)	-0.0001(5)

References

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