# Synthesis and Structure of LaMo<sub>7.70</sub>O<sub>14</sub>, A Novel Compound Containing an Mo<sub>8</sub> Cluster

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Small single crystals having the composition LaMo<sub>7.70</sub>O<sub>14</sub> were prepared by fused salt electrolysis of a mixture of Na<sub>2</sub>MoO<sub>4</sub>, MoO<sub>3</sub>, and La<sub>2</sub>O<sub>3</sub>. The compound is orthorhombic with a = 11.1708(6), b = 9.98489(9), and c = 9.1960(7) Å. The structure was solved by X-ray diffraction methods in space group C2ca with R = 0.030 and  $R_W = 0.040$  for 1878 reflections. The dominant feature of the structure is a novel Mo<sub>8</sub> cluster formed by capping two faces of an Mo<sub>6</sub> octahedron which share an edge in common. In spite of its uniqueness, the structure can be described elegantly in terms of a hexagonal closest packing of oxygens. © 1990 Academic Press, Inc.

It is now well established that a rich and varied complex molybdenum oxide chemistry exists which is based upon the formation of strong metal-metal bonds. They include the digonal group which is found in  $MoO_2$  (1) and a variety of ternary compounds including  $La_2Mo_2O_7(2)$ ,  $Ln_5Mo_2O_{12}$  $(Ln = Y, Gd, Dy) (3, 4), and CrMoO_4 (5).$ Trigonal clusters are found in  $Zn_2Mo_3O_8(6)$ and related compounds (7-10), as well as  $Li_2MoO_3$  (11),  $La_3Mo_4SiO_{14}$  (12), and  $La_3$  $Mo_4Al_{1/3}Mo_{2/3}O_{14}$  (13), the latter two containing digonal groups as well. These clusters also condense to form hexagonal sheets of molybdenums in  $LiMoO_2$  (14). Tetranuclear rhomboidal clusters are the dominant feature in the hollandite-related phases  $Ba_{1.14}Mo_8O_{16}$  (15) and  $K_2Mo_8O_{16}$ (16) while  $Na_{2-x}Mo_2O_4$ -type phases (17–20)

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display these clusters in condensed form which result in infinite double chains of molybdenum.

Since the discovery by Torardi and Mc-Carley of infinite linear metal chains formed by trans edge sharing Mo<sub>6</sub> octahedra in Na  $Mo_4O_6$  (21) and  $Ba_{0.62}Mo_4O_6$  (15), a variety of related compounds have been found in which the basic unit of the infinite chain is maintained but their arrangement and crosslinking through oxygen is strongly dependent upon the oxidation state of molybdenum and the nature of the ternary ion. These include  $Zn_{1.25}Mo_4O_7$  (22),  $Mn_{1.15}$  $Mo_8O_{11}$  (17),  $Ca_{5,45}Mo_{18}O_{32}$  (18), and Zn  $Mo_8O_{10}$  (23). The formation of the trans edge sharing chain seems to require a molybdenum valence of less than three (17); however, zigzag chains involving a more complicated intercluster Mo bonding scheme have been reported for  $BaMo_6O_{10}$ (24).

Although oligomers containing two, four, and five Mo<sub>6</sub> trans edge sharing units are well established (25, 26) it is only recently that a discrete Mo<sub>6</sub> cluster was reported by Lindblom and Strandberg (27) in Ca<sub>16.5</sub> Mo<sub>13.5</sub>O<sub>40</sub> in spite of the fact that such discrete metal units are well established for several niobium oxides (28–32) and Sn<sub>10</sub>W<sub>16</sub>O<sub>46</sub> (33, 34).

In this paper we report on the existence of another type of cluster found in La  $Mo_{7.70}O_{14}$ . In particular, this compound contains quasi-discrete  $Mo_8$  units formed by capping two adjacent faces of an  $Mo_6$ octahedron with two other molybdenums, which because of partial occupancy of the face capping site may also exist as discrete  $Mo_6$  or  $Mo_7$  units.

### Experimental

### Synthesis

The crystals were synthesized by electrolysis of a melt obtained from a mixture of sodium molybdate, molybdenum (VI) oxide, and lanthanum oxide in a molar ratio of  $Na_2MoO_4: MoO_3: La_2O_3 = 3.50: 3.50: 1.00$ at 1080°C. The reactions were carried out in air using a charge of 35 g contained in a 25cm<sup>3</sup> McDanel 997 high density alumina crucible. Pt foil electrodes (1 cm<sup>2</sup>) were used with a current density of  $100 \text{ mA/cm}^2$ . The black crystals grow on the cathode in the form of intergrown tablets or plates, typically with a star-like twin morphology. The crystals could be separated from the matrix by alternate washes in hot 5% K<sub>2</sub>CO<sub>3</sub> solution and hot 2F HCl. Details of the electrolysis procedure are described elsewhere (35).

### Structure Determination

Although a semiquantitative chemical analysis indicated that Mo/La > 6, the crystal chemical formula  $LaMo_{7.70}O_{14}$  was determined by solving the structure. Oscil-

lation and Weissenberg photography were used to select a suitable monocrystal specimen and to establish possible space groups. Data for the structure determination was gathered using a CAD4 Enraf-Nonius diffractometer. The experimental data are summarized in Table I. 1878 reflections with  $I > 3\sigma(I)$  corrected for Lorentz polarization and absorption were used to refine the structure.

A Patterson synthesis showed the apparent symmetry of the space group *Cmca* because of fortuitous peak superpositions. Analysis in this space group allowed us to locate the lanthanum and three of the four molybdenum atoms.

However, the possibility of disorder or the lack of a center was indicated by the presence of a split peak in the difference Fourier map where the La had been placed as well as strong peaks of what appeared to correspond to additional molybdenum atoms which were unrealistically close to one another. Subsequently, the hypothesis of disorder was discarded since a successful refinement was achieved in the nonstandard, noncentrosymmetric space group C2ca. The trial positions of the heavy atoms were modified to accommodate the lower symmetry with the x coordinate of Mo(3) being fixed at zero to define the origin. After heavy atom position refinement using a full matrix least-squares routine, the oxygens were located from Fourier difference maps.

The refinement of all atomic parameters  $(x, y, z, \beta_{ij})$  assuming full site occupancies leads to a correct convergence with R = 0.036 and  $R_w = 0.048$ . However, the temperature factor  $B_{eq}$  of Mo(4) was 0.77 Å<sup>2</sup> which was about twice the size of  $B_{eq}$  values for the other Mo atoms. In this respect, it should be noted that Mo(4) is bonded to three other Mo atoms while Mo(4), Mo(2), and Mo(3) are linked to four, five, and five other Mo atoms, respectively. However, when a second refinement was carried out

TABLE	I
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EXPERIMENTAL DATA AND STRUCTURE REFINEMENT PARAMETERS FOR LaMo7 70014

Crystal shape and size	Sample bounded by $\{100\}$ $\{010\}$ $\{001\}$ $\{111\},$ and
	{111} forms 40 × 50 × 100 $\mu M^3$
Lattice parameters ( $T = 294$ K)	a = 11.1/08(6), b = 9.9848(9), c = 9.1960(7)  A $V = 1025.7 \text{ Å}^3$
Space group	C2ca (standard: Aba2, 41)
$D_{\rm c}, Z$	7.14 $gcm^{-3}$ , 4
Data collection technique	CAD4 Enraf-Nonius diffractometer
Scan mode	$\omega = 2/39$
Wavelength	$\lambda  \mathrm{Mo}  K \alpha  =  0.71069$
$(\sin \theta / \lambda) \max$	0.995
Number of measured reflections	2300 with $h_{\text{max}} = 22$ , $k_{\text{max}} = 19$ , $l_{\text{max}} = 18$ (+++ hkl octant)
Number of reflections with $I > 3\sigma(I)$	1878
Absorption correction	Based on the crystal morphology
Absorption coefficient	$\mu(Mo K\alpha) = 131 \text{ cm}^{-1}$
Extremal transmission factors	0.48, 0.31
Atomic scattering factors, $f'$ and $f''$	From SDP programs (36)
Weighting scheme	Killeau and Lawrence (37)
Secondary extinction coefficient	$g = 3.1(2)10^{-7} (38)$
$R, R_{\rm w}, {\rm GOF}$	0.030, 0.040, 0.97
$(\Delta/\sigma)$ max	10 <sup>-5</sup>

in which the metal atom site occupancies were allowed to vary, convergence was achieved at R = 0.030 and  $R_w = 0.040$ which showed all metal sites fully occupied except that of Mo(4) whose occupation factor was found to be 0.848(2). Using Hamilton's R factor test (39) the  $R_w$  decrease is deemed significant at the 0.005 level ( $R_{obs} =$ 1.20 vs R (1772, 0.005 = 1.002). The Rogers test (40) did not allow us to determine the crystal polarity. This failure is probably due to the large number of reflections unaffected by anomalous dispersion which is expected when a crystal structure displays pseudocentrosymmetric character. Nevertheless, the refinement of the two enantiomorphic configurations (x, y, z, and -x, y,z) leads to  $R_{\rm w}$  values of 0.040 and 0.042, respectively. This difference is significant at the 0.005 level when Hamilton's test is applied, even if only one-tenth of the reflections contain actual information on the crystal chirality (41). The atomic positions, temperature factors, and selected interatomic distances for the first enantiomorphic set are given in Tables II and III. The final electron density difference shows several small peaks, the highest being 4  $e/Å^3$ , which are located on or very near the heavy atoms.

## Description of the Structure and Discussion

The projection of the idealized structure along [001] is shown in Fig. 1. The structure can be described by considering either a close packing of oxygen and lanthanum atoms, or an assemblage of  $MoO_n$  polyhedra. The description that follows assumes complete occupancy for the Mo(4) site. The

Positional Parameters and Their Estimated Standard Deviations					
Atom	x	у	Z	<b>B</b> (Å <sup>2</sup> )	
Mo(1)	-0.12154(5)	0.07458(5)	0.37944(5)	0.396(5)	
Mo(2)	0.12254(5)	0.08311(5)	0.37586(6)	0.423(5)	
Mo(3)	0	-0.16009(5)	0.38115(5)	0.430(5)	
Mo(4)	0.23430(6)	-0.16269(7)	0.37616(7)	0.508(7)	
La	0.03038(7)	0	0	0.739(6)	
O(1)	0.2665(7)	0	1/2	1.0(1)	
O(2)	-0.0025(5)	-0.1569(5)	-0.2345(5)	0.58(5)	
O(3)	-0.1258(5)	-0.0815(4)	0.2456(7)	0.68(5)	
O(4)	0.1188(5)	-0.0779(5)	0.2355(6)	0.81(6)	
O(5)	-0.2548(4)	0.1703(5)	0.2580(6)	0.58(5)	
O(6)	0.1200(5)	0.2609(6)	0.4917(7)	1.08(7)	
O(7)	-0.1230(5)	0.2482(6)	0.4860(5)	0.62(6)	
O(8)	-0.2465(6)	0	1/2	0.52(8)	

TABLE II	
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*Note.* x coordinate of Mo(3) fixed to define the origin. All atoms refined anisotropically;  $B(Å^2)$  Beq. = 4/3  $\sum_i \sum_j (\beta^{ij} \mathbf{a}_i \cdot \mathbf{a}_j)$ .

#### TABLE III

### Selected Interatomic Distances (in A) for $LaMo_{7.70}O_{14}$ (e.s.d.'s in Parentheses)

2.671(1)	Mo(4)-O(1)	2.016(2)
2.728(1)	Mo(4)-O(3iii)	2.086(7)
2.724(1)	Mo(4)–O(4)	2.014(7)
2.708(1)	Mo(4)-O(5ii)	1.994(6)
2.823(1)	Mo(4)–O(6 <i>i</i> )	2.017(8)
2.731(1)	Mo(4)–O(7 <i>ii</i> )	2.086(6)
2.788(1)	La-O(1iii)	2.948(10)
2.718(1)	La-O(2)	2.690(5)×2
2.753(1)	La-O(3)	2.967(7)×2
2.618(1)	La-O(4)	2.504(7)×2
3.078(1) <sup>a</sup>	La-O(6iv)	2.590(7)×2
2.055(6)	La-O(7iv)	3.045(6)×2
1.987(6)	La-O(8iii)	2.491(7)
2.092(6)		
1.992(6)		
1.932(6)		
2.139(8)		
2.046(6)		
2.062(6)		
2.038(6)		
2.070(7)		
2.114(5)		
2.035(7)		
2.056(6)		
2.044(6)		
	2.671(1) 2.728(1) 2.724(1) 2.708(1) 2.823(1) 2.731(1) 2.731(1) 2.731(1) 2.753(1) 2.618(1) $3.078(1)^a$ 2.055(6) 1.987(6) 2.092(6) 1.992(6) 1.932(6) 2.139(8) 2.046(6) 2.062(6) 2.038(6) 2.070(7) 2.114(5) 2.035(7) 2.056(6) 2.044(6)	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Note. i: x, -y, -z; ii: 1/2 + x, 1/2 + y, z; iii: 1/2 + x, y, 1/2 - z; iv: x, 1/2 - y, 1/2 + z.

 $^a$  This distance is that between two neighboring Mo\_8 groups, in the same (001) layer (see text).



FIG. 1. Projection of the idealized LaMo<sub>7.70</sub>O<sub>14</sub> structure along [001]. The oxygen layers with  $z \sim 0$ , 1/4, 1/2, 3/4 are indicated by A, B, A, and C, respectively. The La at  $z \sim 1/2$  and the Mo at  $z \sim 3/8$  and 5/8 have been omitted for purposes of clarity.

implications of its actual nonstoichiometry are discussed subsequently. One notes that the structure is indeed marked by a pseudosymmetry, in which all the oxygen, lanthanum, and molybdenum atoms, of types Mo(1), Mo(2), Mo(3), occupy positions close to those found in the higher symmetry Cmca group.

This structure can, in a first step, be described as derived from a hexagonal close packing of oxygen atoms, by replacing some oxygen atoms by lanthanum atoms, and creating some oxygen vacancies in an ordered way. A distorted pseudohexagonal lattice " $O_{56}La_4\Box_4$ " ( $\Box$  stands for the oxygen vacancies) can be generated from a pseudohexagonal cell defined by  $\overline{a}_h = \overline{a}/4$ ,  $\overline{b}_h = (2\overline{b} - \overline{a})/8$ , and  $\overline{c}_h = \overline{c}/2$  Å with  $a_h = 2.79$  Å,  $b_h = 2.86$  Å, yielding an average a parameter  $\langle a_h \rangle = 2.82$  Å. This value is nearly equal to the mean distance observed between the nearest neighbor's oxygen at-

oms ( $\langle 0-0 \rangle = 2.84$  Å; range 2.64 to 3.10 Å) and the value of the  $c_h/a_h$  ratio is very close to the ideal value of 1.6333. Through a period  $c = 2c_h$  the oxygen atoms (001) layers are stacked according to the sequence |ABAC|A... (Fig. 1). The B layers ( $z \sim 1/$ 4 level) and the C layers ( $z \sim 3/4$  level), which are fully occupied by oxygen, include the atoms of type O(2), O(3), O(4), and O(5): they can be formulated " $O_{16}$ "; these layers form a close packed array. The A layers ( $z \sim 0$  and 1/2) include the oxygen atoms of type O(1), O(6), O(7), and O(8). Within these slabs, 4 oxygen atoms out of 16 are missing in an ordered way, half of which are replaced by La atoms, yielding a layer having the composition " $O_{12}La_2\Box_2$ ." Each La atom is bound to 6 oxygen atoms of the same layer, 3 oxygen atoms of the lower layer, and 3 others of the upper layer. Because the La atoms are shifted slightly along [100] from the idealized positions (Fig. 1) a distorted LaO<sub>12</sub> icosahedron is obtained with the La-O distances ranging from 2.50 to 3.04 Å (Table III). In this pseudohexagonal close packing description, all the tetrahedral interstices are empty, while half of the octahedral interstices are filled by Mo atoms to form Mo<sub>8</sub> clusters (Fig. 1).

An attractive manner of describing the metal atom cluster is to consider the arrangement of the  $MoO_n$  polyhedra. If one takes into consideration the oxygen vacancies with respect to the close packed array, two sorts of  $MoO_n$  polyhedra can be distinguished: (i) MoO<sub>5</sub> polyhedra which can also be described as MoO<sub>5</sub> octahedra, observed for Mo(1), Mo(2), and Mo(3) and (ii)  $MoO_6$ octahedra centered by Mo(4) atoms. In fact, the MoO<sub>5</sub> octahedra share their edges forming [Mo<sub>6</sub>O<sub>18</sub>] units which contain a slightly distorted Mo<sub>6</sub> octahedra with Mo-Mo distances between 2.67 and 2.82 Å. These [Mo<sub>6</sub>O<sub>18</sub>] units, whose pseudoternary axis is parallel to the c axis, share their edges with the MoO<sub>6</sub> octahedra asso-



FIG. 2. Stacking of the  $Mo_8O_{24}$  units in the (001) layers. The circles symbolize corners in which the oxygens are shared by the adjoining upper layer.

ciated with Mo(4) atoms to form infinite slabs  $[Mo_8O_{20}]$  parallel to (001) as shown in Fig. 2. In so doing the Mo(4) atoms cap two adjacent faces of the Mo<sub>6</sub> group to form a metal bonded Mo<sub>8</sub> cluster as shown in Fig. 3c. The vacancies in the closed packed oxygen lattice correspond to the centers of the Mo<sub>6</sub> units. The entire structure can then be described by the stacking along c of infinite  $[Mo_8O_{20}]$  layers in such a way that one layer shares the corners of its octahedra with those of the two adjacent [Mo<sub>8</sub>O<sub>20</sub>] layers; the latter are related to the first one through a "c" or "a" glide plane. These layers are connected to each other through strong O-Mo-O bonds in a fashion which results in large cavities where the lanthanum cations are located.

An examination of the Mo-O distances (Table III) for the various polyhedra shows that the MoO<sub>6</sub> octahedra, formed by the Mo(4) atoms which link the  $[Mo_6O_{18}]$  units to form the infinite Mo<sub>8</sub>O<sub>20</sub> slabs, are rather regular with Mo-O distances ranging from 1.99 to 2.09 Å. Further, the MoO<sub>5</sub> polyhedra, formed by Mo(2) and Mo(3), are characterized by a rather regular " $O_5$ " pyramid while the MoO<sub>5</sub> polyhedron, formed by Mo(1), is a somewhat less regular " $O_5$ " pyramid with the Mo-O distances ranging from 1.93 to 2.14 Å (Table III). The mean distances Mo-O observed in these polyhedra are 2.01 (Mo(1)), 2.07 (Mo(2)), 2.06 (Mo(3)), and 2.03 Å (Mo(4)). One also notes that the average Mo-Mo distance in the  $Mo_6$  unit of 2.73 Å is significantly longer than those formed between Mo(4) and the octahedral faces (2.697 Å), primarily as the result of the short (2.618 Å) Mo(3)–Mo(4) bond.

The calculation of the oxidation states of molybdenum from the bond length-bond strength formula of Brown and Wu (42) for the Mo-O bond,  $s = (1.882/d_{Mo-O})^{-6.0}$ , leads to the following results: 3.42 for Mo(1), 2.82 for Mo(2), 2.95 for Mo(3), and 3.76 for Mo(4). A similar calculation for La leads to s = 2.90, in excellent agreement with the expected value of 3. The summation of these assessed valences over the Mo atoms involved in the "average" Mo7.70 cluster is equal to 24.8, in excellent agreement with the value of 25 based on the stoichiometry, given the empirical nature of the calculation. The uneven valence distribution within the cluster is to be expected since the various molybdenums have differ-



FIG. 3. Isomeric forms of the bi-faced capped  $M_8$  octahedron.

ent metal-metal bonding requirements. We note with some resistance that an inverse relationship exists between the number of metal bonds formed by a given molybdenum and its calculated bond strength.

Bi-face capped octahedral clusters appear to be quite unusual. Certainly they are new to oxide systems. Of the three possible isomeric forms of the  $M_8$  cluster, the cis corner sharing form (Fig. 3b) has been observed in some carbonyl complexes of osmium such as  $Os_8(CO)_{22}$  and  $Os_8(CO)_{23}$  (43, 44) while the *trans* form (Fig. 3a) been found for Re<sub>8</sub>C(CO)<sub>24</sub> (45). To our knowledge, the cluster reported here for La  $Mo_{7.70}O_{14}$  is the first known example of the cis edge shared form. However, in this case one does not have isolated Mo<sub>8</sub>O<sub>24</sub> groups. Rather, strong Mo-O-Mo bonds are formed between the clusters in all directions.

The presence of nonstoichiometry in the Mo<sub>8</sub> cluster is most interesting and unexpected. The vacant sites appear to be distributed at random as no satellite reflections are seen in the diffraction spectrum. Two plausible descriptions exist for the 85% occupancy of the face capping Mo(4) site: (i) 85 out of 100 sites are fully occupied and 15  $Mo_6$  clusters are formed and (ii) 70 out of 100 sites are fully occupied and 30 randomly distributed Mo<sub>7</sub> clusters exist. The first model is attractive in that the local symmetry of the C2ca space group is maintained. However, the presence of Mo<sub>6</sub> clusters seems unlikely from an electronic point of view. Removal of 2 Mo(4) atoms with an average valence of +3.76 yields an Mo<sub>6</sub> cluster which would have an average of 18.5 d electrons associated with it. Howtheoretical studies. which ever. are strongly supported by experimental evidence, show that such  $M_6X_{18}$  groups are stable only for between 13 and 16 skeletal electrons (25, 26, 28-34, 46-48). Unfortunately, for Ca<sub>16.5</sub>Mo<sub>13.5</sub>O<sub>40</sub>, the only compound with a well-defined Mo<sub>6</sub>O<sub>18</sub> cluster,

an accurate assignment of a valence for the cluster is not possible due to the presence of a second molybdenum whose stoichiometry and valence are uncertain. However, an electron count of 16 or less for the cluster is certainly not precluded.

From this perspective the combination of Mo<sub>7</sub> and Mo<sub>8</sub> clusters seems more plausible. While nothing concrete can be said about the optimum electron count in the metal skeleton of the Mo<sub>8</sub> cluster observed here, one does note that in general, as the number of d electrons/clustering atom increases, the complexity of the cluster tends to increase. Thus, as mentioned previously one finds 13–16 electrons per  $M_6 X_{18}$  group or 2.17-2.67 electrons/atom in the metal skeleton. This increases to 2.75 electrons/ Mo in LaMo<sub>7.70</sub>O<sub>14</sub>, 2.87 electrons/Mo for fully stoichiometric LaMo<sub>8</sub>O<sub>14</sub>, 3.40 electrons/Mo in LaMo<sub>5</sub>O<sub>8</sub>, which contains  $Mo_{10}$ clusters (26), and 3.20-3.65 electrons/Mo found for several compounds containing infinite trans edge sharing chains of Mo6 octahedra (17). It may be that a combination of  $Mo_7$  and  $Mo_8$  clusters is the best way of accommodating the 21.2 d electrons found for  $LaMo_{7,70}O_{14}$ .

To date we have not succeeded in growing single crystal specimens of a size suitable for electrical or magnetic measurements, although qualitative two probe measurements on large, twinned intergrowths yield a resistivity of the order of 1  $\Omega$ -cm. A conductivity mechanism based on  $\pi$ -like bands derived from overlap of metal d and oxygen p orbitals, which extend in three dimensions, appears possible. However, the possibility of quasi-low dimensional electronic behavior exists also. Within a given layer the distance between Mo(1) and Mo(4) on adjacent clusters is only 3.079 Å. Although considerably longer than the value found for a Mo-Mo single bond, it is much shorter than the critical Mo-Mo distance approximately of 3.72 Å, estimated by using Goodenough's as

method (49), which is necessary to achieve d-d orbital in overlap in the (001) plane. On the other hand Mo-Mo interactions between adjacent (001) layers are considerably longer, ranging from 3.65 to 3.82 Å.

Work is now in progress to prepare larger single crystals suitable for oriented measurements of the electrical and magnetic properties in order to test these hypotheses. We note finally that the compound is extremely stable chemically; e.g., it appears to be unaffected by hot 3F HCl or  $H_2SO_4$  and it is only slowly attacked by hot 3F HNO<sub>3</sub>. Given this remarkable stability, one might expect that this elusive Mo<sub>8</sub> cluster might be stabilized by a variety of large cations other than lanthanum and this possibility is also being explored.

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