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Oxalato Complexes of the Trinuclear Aquo Ion of Molybdenum(IV), $[Mo_3O_4]^{4+}$

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Abstract

The preparations and X-ray crystallographic structure determinations of two compounds containing the complex oxalato anion of $Mo_3O_4^{4+}$, *viz.*, $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^-$, are reported. Compound **1**, $Cs_2[Mo_3O_4(C_2O_4)_3(H_2O)_3]\cdot 4H_2O\cdot \frac{1}{2}H_2C_2O_4$ forms monoclinic crystals (space group $P2_1/n$) with unit cell dimensions a = 12.082(2) Å, b = 16.764(3) Å, c = 12.529(2) Å, β = 91.31(2)° and Z = 4. Compound **2**, $Cs_3[Mo_3O_4(C_2O_4)_3(H_2O)_3]CF_3SO_3\cdot 3H_2O$, forms hexagonal crystals (space group $R3m$) with a = 12.955(1) Å, c = 14.738(2) Å and Z = 3. The $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$ ion has essentially the same dimensions in each case. In compound **1** no crystallographic symmetry is required while in **2** C_{3v} symmetry is imposed. Some important dimensions are the following, where we give first the mean value (averaged according to C_{3v} symmetry) for **1** and then the value for **2**: Mo–Mo, 2.486(1) Å. 2,491(1) Å; Mo–(μ_3-O), 2.019(6) Å, 2.01(1) Å; Mo–(μ_2-O), 1.921(4) Å, 1.908(7) Å; Mo–O(H_2O), 2.154(7) Å, 2.15(1) Å; Mo–O(oxalate), 2.091(4) Å, 2.102(8) Å; Mo–(μ_3-O)–Mo, 76.0(1)°, 76.6(6)°; Mo–(μ_2-O)–Mo, 80.6(1)°, 81.5(4)°.

Introduction

Less than a decade ago the known chemistry of molybdenum(IV) was minuscule, and the aqueous chemistry was particularly scant. Beginning in the middle 1970's an explosive growth of knowledge and activity has occurred and it is now recognized that this oxidation state of molybdenum has an extensive chemistry, much of which is unique in being based on metal atom clusters [1–22]. Molybdenum(IV), and to a lesser extent tungsten(IV), provide the only examples of extensive metal atom cluster chemistry in such a high oxidation state.

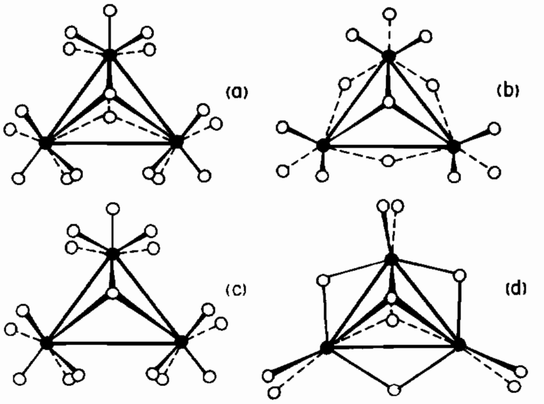

Fig. 1. Four of the most important types of trinuclear cluster structures known for Mo(IV) and W(IV). This paper is concerned with type (b) of which the Mo(IV) aquo ion and its complexes are the most important examples.

The predominent metal atom clusters of molybdenum(IV) and tungsten(IV) are equilateral triangular ones and four different types have been discovered so far. These are shown in Fig. 1. In this paper we are concerned with type (b), in which the triangle of metal atoms is capped on one side and has three edge bridging atoms on the other. In the case of the aquomolybdenum(IV) ion and its derivatives these four capping and bridging groups are all oxygen atoms.

The literature on the red trinuclear aquomolybdenum(IV) ion is now fairly extensive [2–22]. After some early controversy and uncertainty about the

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nuclearity of the ion in solution [2–10], its trinuclear nature has become firmly established. The key developments that led to this were the observations by Bino, Cotton and Dori [11, 12] and by Murmann [15] that species precipitated from the aqueous solutions always contained the $Mo_3O_4^{4+}$ core surrounded by whatever ligands, *e.g.*, oxalate [12], EDTA [12] or SCN^- [15] were added, coupled with Murmann's observations [14] on the retention of ^{18}O by the ion in solution. Subsequent studies of crystalline products isolated from solution [16, 20] as well as kinetic [17, 18] and electrochemical studies [21] have given results consistent with the trinuclear structure. EXAFS data were at first thought to favor a dinuclear structure [13] but have more recently been shown to support the trinuclear structure [19].

The aquo ion can be formed in any of a number of comproportionation reactions in which Mo^{II} or Mo^{III} species are mixed with Mo^{V} or Mo^{VI} species in acid solution in ratios appropriate to obtain an average oxidation state of four. Such reactions seem to be essentially quantitative at equilibrium, but in many cases they proceed only slowly. Recently it has been shown [22] that reduction of an acid solution of molybdate with zinc leads promptly to the formation of the $Mo_3O_4^{4+}(aq)$ ion which can then be separated on a cation exchange column. This appears to be the handiest method available for preparing $Mo_3O_4^{4+}(aq)$ and its derivatives.

In this paper we wish to report in detail the preparation and structure determinations of two oxalato complexes of $Mo_3O_4^{4+}$. One of these is the compound previously reported in a preliminary communication [11], $Cs_2[Mo_3O_4(C_2O_4)_3(H_2O)_3]\cdot 4H_2O\cdot \frac{1}{2}H_2C_2O_4$ (1) and the other is a similar one that has not previously been mentioned in the literature, $Cs_3[Mo_3O_4(C_2O_4)_3(H_2O)_3]CF_3SO_3\cdot 3H_2O$ (2).

Experimental Procedures

Preparations

A solution of $Mo_3O_4^{4+}$ was prepared by the method of Ardon and Pernick [6]. The solution was poured onto a column of Dowex 50X X 2 cation exchange resin and the red band was eluted with a 0.5 M solution of oxalic acid. The red–purple eluate was then treated in two ways.

To obtain compound 1, about one mol of CsCl per gram-atom of molybdenum was added and this solution was set aside to evaporate slowly in air. Red–purple crystals of $Cs_2[Mo_3O_2(C_2O_4)_3(H_2O)_3]\cdot 4H_2O\cdot \frac{1}{2}H_2C_2O_4$, 1, were formed in about 80% yield over a period of 1–2 weeks.

To obtain compound 2, after the addition of CsCl, as above, a few drops of 1 M CF_3SO_3H were also added and the solution again set aside to undergo slow evaporation in the air. Crystals of red–purple $Cs_3[Mo_3O_4(C_2O_4)_3(H_2O)_3]CF_3SO_3\cdot 3H_2O$ formed during slow evaporation. Yields of about 80% can be obtained after several weeks.

X-ray Crystallography

Compound 1

The space group was established unambiguously from the systematic absences. The structure was solved by first using a Patterson map to locate the molybdenum atoms and then continuing with an alternating series of difference maps and least squares refinements until all nonhydrogen atoms were located. In addition to the four water oxygen atoms, O(50)–O(53), which are on general positions, a molecule of oxalic acid was found on the special ($\bar{1}$) position at ½, 0, ½; this consists of C(41), O(41) and O(42). That it is $H_2C_2O_4$ rather than $HC_2O_4^-$ or $C_2O_4^{2-}$ is, of course, an assumption, but it is in keeping with the ncessary stoichiometry for the trinuclear anion. All computing on this structure was done on a PDP 11/45 computer at the Molecular Structure Corporation, College Station, Texas, using the Enraf-Nonius structure determination package. Crystallographic parameters are given in Table I. The atomic coordinates are listed in Table II. The first 18 atoms in Table I were refined anisotropically and the remaining ones (19) isotropically. Tables of structure factors and thermal parameters are available as supplementary material.

Compound 2

The unit cell dimensions were derived by a least squares fitting to 25 centered reflections in the range 12–16° in θ. Lorentz and polarization corrections were applied but no absorption correction was deemed necessary. The direct methods program MULTAN was used to obtain positions of most of the atoms and refinement proceeded smoothly with use of anisotropic thermal vibration parameters for all nonhydrogen atoms except O(7), which is the oxygen atom of the uncoordinated water molecule. All crystallographic computing for this structure was done on a CYBER 74 computer employing the SHELX 1977 structure determination package. Since the space group *R3m* is non-centric, the mirror image of the structure initially refined (which gave R_1 = 0.046 and R_2 = 0.051) was then tested. It was found to be superior and is the one reported here.

TABLE I. Crystallographic Information.

Formula	1 $Cs_2Mo_3C_7H_{15}O_{25}$	2 $Cs_3Mo_3C_7H_{12}O_{25}F_3S$
Formula weight	1052.80	1271.74
Space group	$P2_1/n$	$R3m$
a, A	12.082(2)	12.955(1)
b, A	16.764(3)	–
c, A	12.529(2)	14.738(2)
β, degrees	91.31(2)	–
V, Å^3	2357(1)	2142(1)
Z	4	3
d_{calc}, g/cm^3	2.756	2.957
Crystal size, mm	0.10 × 0.15 × 0.15	0.15 × 0.15 × 0.20
μ(Mo-Kα), cm^{-1}	44.14	48.95
Data collection instrument	Syntex $P\bar{1}$	Phillips PW1100
Radiation (monochromated in incident beam)	Mo-Kα	Mo-Kα
Orientation reflections, number, range (2θ)	15 (20–30)	25 (24–32)
Temperature, °C	22°	22°
Scan method	$\theta-2\theta$	$\theta-2\theta$
Data col. range, 2θ, deg.	3–50	3–60
No. unique data, total	3699	815
With $F_o^2 > 3\sigma(F_o^2)$	2500	730
Number of parameters refined	239	75
R^a	0.041	0.039
R_w^b	0.061	0.044
Quality of fit indicator^c	1.37	1.12

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|)^2$.

TABLE II. Positional Parameters for Compound 1.

Atom	x	y	z	Atom	x	y	z
Cs(1)	0.34658(8)	0.33001(6)	0.96011(8)	O(13)	0.5514(8)	0.5156(6)	0.1229(8)
Cs(2)	0.53524(8)	0.06274(6)	0.19544(8)	O(14)	0.7229(8)	0.4983(6)	0.2730(7)
Mo(1)	0.65920(8)	0.28213(6)	0.12672(7)	O(23)	0.6343(7)	0.3684(5)	−0.3021(6)
Mo(2)	0.68025(8)	0.21362(6)	−0.04770(7)	O(24)	0.8417(8)	0.2929(6)	−0.3113(7)
Mo(3)	0.82863(8)	0.20301(6)	0.09210(7)	O(33)	1.1087(7)	0.3391(5)	0.1453(7)
O(1)	0.7756(6)	0.3016(4)	0.0156(5)	O(34)	1.1097(8)	0.2690(6)	−0.0599(8)
O(2)	0.5574(6)	0.2157(5)	0.0488(6)	O(41)	0.6188(11)	0.0247(9)	0.4296(11)
O(3)	0.7329(6)	0.2017(5)	0.2114(6)	O(42)	0.3927(11)	0.0276(8)	0.4069(10)
O(4)	0.7550(6)	0.1213(5)	0.0084(6)	O(50)	0.2994(9)	0.0487(7)	0.0631(8)
O(5)	0.5386(7)	0.2811(6)	0.2496(6)	O(51)	0.3732(8)	0.1415(6)	−0.1025(8)
O(6)	0.9170(7)	0.1079(6)	0.1716(7)	O(52)	0.3137(11)	0.4956(9)	0.1117(10)
O(7)	0.5817(7)	0.1305(5)	−0.1420(6)	O(53)	0.4012(15)	0.4394(11)	0.3127(14)
O(11)	0.7339(7)	0.3716(5)	0.2205(6)	C(11)	0.5973(10)	0.4508(8)	0.1326(10)
O(12)	0.5791(7)	0.3864(5)	0.0802(6)	C(12)	0.6941(11)	0.4414(8)	0.2173(10)
O(21)	0.6106(6)	0.3008(5)	−0.1492(6)	C(21)	0.6637(9)	0.3208(7)	−0.2319(9)
O(22)	0.7854(6)	0.2172(5)	−0.1780(6)	C(22)	0.7723(10)	0.2742(8)	−0.2443(9)
O(31)	0.9476(6)	0.2769(5)	0.1652(6)	C(31)	1.0368(10)	0.2519(8)	0.0040(10)
O(32)	0.9609(6)	0.2019(5)	−0.0120(6)	C(32)	1.0330(10)	0.2930(7)	0.1128(9)
				C(41)	0.4384(15)	0.0001(12)	0.4985(15)

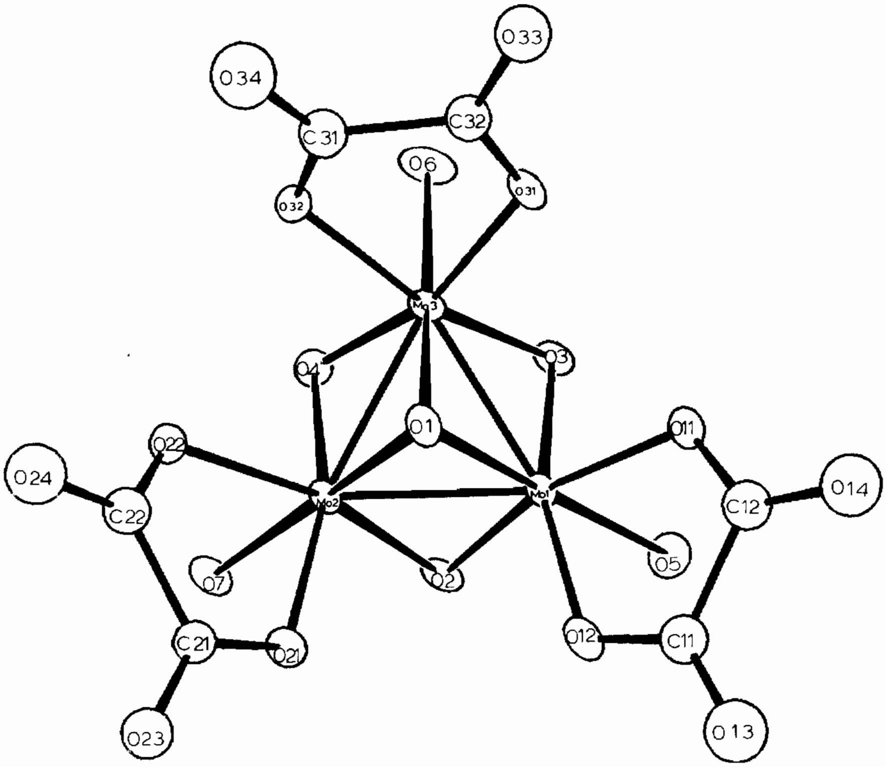

Fig. 2. The $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$ ion in compound **1** showing the atom labelling scheme.

TABLE III. Positional Parameters for Compound **2**.[a]

Atom	*x*	*y*	*z*
Mo	0.06410(5)	−0.06410(5)	−0.2500
Cs	−0.14456(8)	0.14456(8)	−0.5054(1)
S	0.00000	0.00000	−0.7770(9)
O(1)	0.00000	0.00000	−0.155(1)
O(2)	−0.0757(5)	0.0757(5)	−0.3221(8)
O(3)	0.1416(5)	−0.1416(5)	−0.3354(9)
O(4)	0.2623(8)	−0.0436(7)	−0.0255(5)
O(5)	0.2105(7)	−0.0143(7)	−0.1634(5)
O(6)	0.066(1)	−0.066(1)	−0.763(3)
C(1)	0.1935(9)	−0.0739(9)	−0.0900(8)
C(2)	0.00000	0.00000	−0.901(3)
F	−0.0541(9)	0.0541(9)	−0.931(1)
O(7)	0.1140(8)	−0.1140(8)	−0.570(1)

[a] E.s.d.s in the least significant digits are shown in parentheses.,

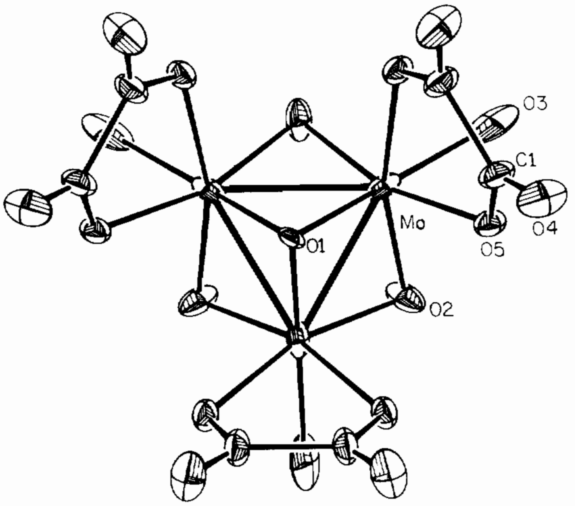

Fig. 3. The $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$ ion in compound **2** showing the atom labelling scheme. All unlabelled atoms are related to those labelled by the symmetry operations of group C_{3v}.

Results and Discussion

In each compound, as would be expected, the same trinuclear anion $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$ is present. In **1** no crystallographic symmetry is imposed whereas in **2** the anion resides in an environment of *3m* (C_{3v}) symmetry, which is, of course, the highest idealized symmetry that the anion is intrinsically capable of having. Drawings of the anions, giving the atomic numbering schemes are given in Figs. 2 and 3.

To compare the dimensions of the anions in the two compounds, it is appropriate to average those found in **1** according to C_{3v} symmetry. In Table

TABLE IV. Bond Lengths, Å.

Compound 1		Compound 2	
Mo(1)–Mo(2)	2.487(1)		
Mo(1)–Mo(3)	2.486(1)		
Mo(2)–Mo(3)	2.484(1)		
Mean Mo–Mo	2.486[1]	Mo–Mo	2.491(1)
Mo(1)–O(1)	2.028(6)		
Mo(2)–O(1)	2.022(6)		
Mo(3)–O(1)	2.008(7)		
Mean Mo–O(1)	2.019[6]	Mo–O(1)	2.01(1)
Mo(1)–O(2)	1.911(7)		
Mo(1)–O(3)	1.921(7)		
Mo(2)–O(2)	1.937(7)		
Mo(2)–O(4)	1.917(7)		
Mo(3)–O(3)	1.911(7)		
Mo(3)–O(4)	1.930(7)		
Mean Mo–(μ_2-O)	1.921[4]	Mo–(μ_2-O)	1.908(7)
Mo(1)–O(5)	2.144(7)		
Mo(2)–O(6)	2.151(8)		
Mo(3)–O(7)	2.166(7)		
Mean Mo–O(H_2O)	2.154[7]	Mo–O(H_2O)	2.15(1)
Mo(1)–O(11)	2.096(7)		
Mo(1)–O(12)	2.075(7)		
Mo(2)–O(21)	2.101(7)		
Mo(2)–O(22)	2.092(6)		
Mo(3)–O(31)	2.092(7)		
Mo(3)–O(32)	2.087(6)		
Mean Mo–O(ox)	2.091[4]	Mo–O(ox)	2.102(8)
C(11)–O(12)	1.28(1)		
C(12)–O(11)	1.26(1)		
C(21)–O(21)	1.28(1)		
C(22)–O(22)	1.27(1)		
C(31)–O(32)	1.25(1)		
C(32)–O(31)	1.26(1)		
Mean C–O	1.27[1]	Mo–O(5)	1.28(1)
C(11)–O(13)	1.22(1)		
C(12)–O(14)	1.23(1)		
C(21)–O(23)	1.23(1)		
C(22)–O(24)	1.24(1)		
C(31)–O(34)	1.24(1)		
C(32)–O(33)	1.26(1)		
Mean C–O	1.23[1]	Mo–O(4)	1.22(1)
C(11)–C(12)	1.57(1)		
C(21)–C(22)	1.53(1)		
C(31)–C(32)	1.54(1)		
Mean C–C	1.55[1]	C(1)–C(1)′	1.55(1)
		C(2)–F	1.29(2)
		C(2)–S	1.83(5)
		O(6)–S	1.50(1)

TABLE V. Averaged[a] Bond Angles in 1 and Selected Bond Angles in 2, Deg.

	1	2	Δ(esd)[b]
Mo–(μ_3-O)–Mo	76.0[1]	76.6(6)	0.6(6)
Mo–(μ_2-O)–Mo	80.6[1]	81.5(4)	0.9(4)
O(ox)–Mo–O(ox)	75.4[1]	74.4(4)	1.0(4)
(μ_2-O)–Mo–(μ_2-O)	98.5[4]	100.9(4)	2.4(6)
(μ_3-O)–Mo–O(H_2O)	169.8[7]	171.6(5)	1.8(9)
(μ_3-O)–Mo–O(ox)	87.4[6]	86.8(4)	0.6(7)
(μ_3-O)–Mo–(μ_2-O)	100.6[2]	99.7(3)	0.9(4)
O(H_2O)–Mo–O(ox)	84.6[3]	86.5(4)	1.9(5)
O(H_2O)–Mo–(μ_2-O)	85.9[3]	85.6(4)	0.3(5)
(μ_2-O)–Mo–O(ox)	165.0[8]	164.5(4)	0.5(9)
(μ_2-O)–Mo–O(ox)′	92.2[9]	91.8(4)	0.4(9)
F–S–C		110(2)	
F–C–F		109(2)	
C–S–O		98(1)	
O–S–O		118(1)	

[a] Averaged according to C_{3v} symmetry. [b] Δ(esd) is the difference between the mean value in 1 and the value in 2, and the e.s.d. of that difference.

IV some individual distances in 1 are given in groups and the mean values are compared with those for 2. This gives some idea of the variability of those within a given class as a result of the lack of symmetry in the environment. In Table V we have listed only the average values of some important angles in 1 for comparison with the corresponding ones in 2. Throughout, the agreement between the distances and angles in the two compounds is excellent. Only in a very few cases is the discrepancy, Δ, greater than three times its estimated standard deviation.

Also given in Tables IV and V are dimensions of the $CF_3SO_3^-$ ion in 2. In both 1 and 2 the water molecules not forming a part of the cluster anion are involved in coordination to the Cs^+ ions and in networks of hydrogen bonds. In the latter we find no unusual features and no further discussion seems necessary.

The Mo–Mo–Mo angles in the cluster in 1 are 59.93(3)°, 60.01(3)° and 60.06(3)°, which give an average value of 60.00°, as they must, while in 2 the value is exactly 60° by symmetry.

The Mo–Mo bond lengths in these two compounds, 2.486[1] Å in 1 and 2.491(1) Å in 2, are slightly shorter than those found in other complexes of the $Mo_3O_4^{4+}$ ion, viz., 2.51[1] Å in the EDTA complex [12], 2.518(5) Å in the $[Mo_3O_4(SCN)_8(H_2O)]^{4-}$ ion [15], 2.505(?) Å in the $[Mo_3O_4F_9]^{5-}$ ion [16], and 2.495[6] Å in a methyliminodiacetate complex [20].

Most of the angles listed in Table V are pertinent to the question of how closely the overall structure can be viewed as a fusion of three octahedra so that one vertex is shared by all three, with a set of three shared edges radiating from this vertex. It can be seen that while this is a valid way to regard this structure, there are appreciable distortions of the octahedra. Thus the angles that would ideally be 180° are 164.5° to 171.6° and the angles that ideally should be 90° range from 74.4° to 100.9°. There is a definite and reasonable pattern to the deviations. All of them are conducive to the close approach of the metal atoms to each other leading to the formation of Mo–Mo bonds. Thus, all of the angles between *cis* Mo–O bonds directed inwards are expanded and lie in the range 91.8° to 100.9° while those that look outwards are contracted and lie in the range 74.4° to 87.4°.

Acknowledgement

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Supplementary Material Available

Tables of structure factors for both compounds, complete tables of bond distances and angles in **1** and tables of thermal vibration parameters for **1** and **2** (22 pages). Copies are available on request from F.A.C.

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