Crystal and Molecular Structure of Tetrachlorotris(dimethylphenylphosphine)molybdenum(IV)–Ethanol †

By **Ljubica Manojlović-Muir,*** Chemistry Department, University of Glasgow, Glasgow G12 8QQ

The *X*-ray analysis of the title compound was based on 2 397 intensity data measured by diffractometer. The structure was solved by the heavy-atom method and refined by full-matrix least-squares to *R* 0.059. Crystals are monoclinic, with $a = 11.883(4)$, $b = 11.836(4)$, $c = 23.750(7)$ Å, $\beta = 104.61(2)°$, $Z = 4$, and space group $P2_1/c$.

The crystal structure is built of discrete molecular units of $[MoCl_4(PMe_2Ph)_3]$ and EtOH. The co-ordination geometry of the metal complex can be described as capped octahedral, with the $MoCl_3(PMe_2Ph)_3$ fragment adopting a *facial* configuration and the fourth chlorine ligand capping the triangular face formed by the phosphorus atoms. Metal–ligand bond lengths are: Mo–Cl(capping) 2.399(3), Mo–Cl(*trans* to P) 2.440(4)—2.454(4), and Mo–P 2.570(3)—2.579(4) Å.

THE molybdenum(IV) complex $[MoCl_4(EtCN)_2]$ reacts with an excess of alkaryl tertiary phosphines (L) in boiling ethanol to give air-stable diamagnetic oxo-complexes $[MoOCl_2L_3]$.[1] With dimethylphenylphosphine two forms were isolated: a blue and a green; on one occasion,[2] however, a mixture was obtained of green $[MoOCl_2(PMe_2Ph)_3]$ and a dark red solid gradually decomposing in air. By use of *X*-ray diffraction methods it has been shown that both forms of the PMe_2Ph oxo-complex,[3,4] as well as its PEt_2Ph analogue,[5] adopt an octahedral *cis-mer*-$[MoOCl_2L_3]$ configuration. To identify the dark red compound an *X*-ray crystal structure analysis of its solid has been carried out and the results, briefly reported earlier,[6] have shown that it can be formulated as $[MoCl_4(PMe_2Ph)_3]\cdot EtOH$.

This work is also of interest for further understanding of the stereochemistry of seven-co-ordinate complexes. Although the crystal structures of a number of such compounds have now been determined,[7,8] their ground-state geometry is still difficult to predict. The relative importance of various factors determining the type of co-ordination polyhedron, such as steric and electronic requirements of ligands, electronic configuration of the metal atom, and even crystal packing energy, is not yet well understood.

EXPERIMENTAL

Crystal Data.—$C_{24}H_{33}Cl_4MoP_3\cdot C_2H_6O$, $M = 698.3$. Monoclinic, $a = 11.883(4)$,‡ $b = 11.836(4)$, $c = 23.750(7)$ Å, $\beta = 104.61(2)°$, $U = 3\,232$ Å^3, $Z = 4$, $D_c = 1.435$ g cm^{-3}, $F(000) = 1\,432$. Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 8.9 cm^{-1}. Space group $P2_1/c$.

The crystal chosen for analysis had dimensions *ca.* $0.040 \times 0.010 \times 0.011$ cm and was coated with a non-crystalline polymer to prevent decomposition in air.

The space group and initial unit-cell parameters were determined from oscillation, Weissenberg, and precession photographs. Cell constants were later adjusted by a least-squares treatment of the setting angles of twelve reflexions centred manually on a Hilger and Watts Y 290 four-circle diffractometer controlled by a PDP 8 computer.

Intensity Measurements.—The intensities of all independent reflexions with θ(Mo-K_α) $\leqslant 23°$ were measured on Y 290 diffractometer, by use of zirconium-filtered molybdenum radiation in conjunction with a pulse-height analyser. The orientation of the crystal was such as to make *a* ‡ approximately coincident with the ϕ axis of the diffractometer. The θ—2θ scan technique was used, the scan step in 2θ and the counting time for each step being 0.02° and 1.5 s, respectively. Each reflexion was scanned through a 2θ range of 1.4° and the local background counted for 20 s at each end of the scan range. The intensities of two strong reflexions, monitored throughout, dropped by *ca.* 21% during data collection.

The integrated intensities, *I*, and their variances, $\sigma^2(I)$, were calculated from the peak and background counts, by relationships described earlier.[9] The empirical factor, *q*, was assigned a value of 0.05. The *I* and $\sigma(I)$ values were then corrected for Lorentz, polarisation, and crystal decomposition effects, but not for absorption. 2 397 Reflexions, having $I \geqslant 3\sigma(I)$, were used in the subsequent analysis.

Structure Analysis.—The position of the molybdenum atom was determined from a Patterson synthesis and those of the remaining non-hydrogen atoms from a subsequent difference synthesis.

The structure was refined by full-matrix least-squares. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$; the weights, *w*, were derived from the variances of F_o^2 as described

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† Reprints not available.

‡ Throughout the paper limits of error are estimated standard deviations derived either from the appropriate least-squares matrix, or in the case of average values from the range of individual measurements.

[1] A. V. Butcher and J. Chatt, *J. Chem. Soc.* (*A*), 1970, 2652.

[2] J. Chatt and J. R. Dilworth, personal communication.

[3] Lj. Manojlović-Muir, *J. Chem. Soc.* (*A*), 1971, 2796.

[4] Lj. Manojlović-Muir, K. W. Muir, and R. Walker, unpublished work.

[5] Lj. Manojlović-Muir and K. W. Muir, *J.C.S. Dalton*, 1972, 686.

[6] Lj. Manojlović-Muir, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 59.

[7] D. F. Lewis and S. J. Lippard, *Inorg. Chem.*, 1972, **11**, 621, and refs. therein.

[8] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1973, 2664, and refs. therein.

[9] Lj. Manojlović-Muir and K. W. Muir, *J.C.S. Dalton*, 1974, 2395.

previously.[3] Atomic scattering factors were taken from ref. 10, except those for molybdenum [11] and hydrogen.[12] Anomalous scattering of molybdenum, chlorine, and phosphorus atoms was accounted for, by use of $\Delta f'$ and $\Delta f''$ values from ref. 13.

TABLE 1

Final fractional co-ordinates and thermal parameters of atoms

Atom	x	y	z	$U_{\mathrm{iso}} \times 10^2$ Å^2	Atom	x	y	z	$U_{\mathrm{iso}} \times 10^2$ Å^2
Mo	0.201 23(8)	0.133 04(8)	0.158 41(5)	*	C(10)	0.153(1)	−0.013(1)	0.287 7(6)	6.7(4)
Cl(c)	0.346 1(2)	−0.005 0(2)	0.200 1(1)	*	C(11)	0.105(1)	−0.158(1)	0.184 1(5)	5.0(3)
Cl(2)	0.086 8(3)	0.248 9(3)	0.208 5(2)	*	C(12)	0.180(1)	−0.234(1)	0.217 3(6)	6.1(4)
Cl(3)	0.225 4(3)	0.306 0(3)	0.105 7(2)	*	C(13)	0.184(1)	−0.343(1)	0.197 8(7)	8.0(4)
Cl(4)	0.021 9(3)	0.098 6(3)	0.083 0(2)	*	C(14)	0.118(1)	−0.377(2)	0.149 2(7)	9.2(5)
P(1)	0.361 5(3)	0.241 4(3)	0.231 3(2)	*	C(15)	0.041(2)	−0.306(2)	0.114 2(8)	10.2(6)
P(2)	0.096 3(3)	−0.012 4(3)	0.207 8(2)	*	C(16)	0.034(1)	−0.193(1)	0.133 0(7)	8.0(4)
P(3)	0.273 8(3)	0.055 8(3)	0.072 3(1)	*	C(17)	0.201(1)	0.114(1)	0.000 0(6)	7.3(4)
O	−0.128(2)	0.351(2)	0.077(1)	31.4(1.3)	C(18)	0.255(1)	−0.097(1)	0.062 5(6)	7.5(4)
C(1)	0.501(1)	0.242(1)	0.210 1(6)	6.5(4)	C(19)	0.428(1)	0.080(1)	0.077 9(6)	6.0(4)
C(2)	0.338(1)	0.393(1)	0.240 4(6)	6.6(4)	C(20)	0.511(1)	0.000(1)	0.099 6(6)	7.0(4)
C(3)	0.398(1)	0.192(1)	0.306 1(6)	5.9(4)	C(21)	0.628(1)	0.024(1)	0.105 0(7)	8.4(5)
C(4)	0.322(1)	0.216(1)	0.341 3(7)	8.0(5)	C(22)	0.661(1)	0.126(1)	0.090 7(7)	8.5(4)
C(5)	0.346(2)	0.172(2)	0.398 2(8)	10.6(6)	C(23)	0.581(1)	0.208(1)	0.068 1(7)	8.8(5)
C(6)	0.444(2)	0.110(2)	0.419 4(9)	12.7(7)	C(24)	0.462(1)	0.184(1)	0.060 6(6)	6.9(4)
C(7)	0.515(2)	0.085(2)	0.387(1)	13.1(7)	C(25)	−0.109(4)	0.402(3)	0.031(2)	27.4(1.7)
C(8)	0.492(1)	0.123(1)	0.328 8(7)	8.8(5)	C(26)	−0.205(3)	0.471(3)	0.010(1)	20.8(1.2)
C(9)	−0.063(1)	0.009(1)	0.197 2(6)	7.0(4)					

* These atoms were assigned anisotropic temperature factors of the form $\exp(-2\pi^2 \times 10^{-4} \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i^* a_j^* h_i h_j)$, with U_{ij} parameters:

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	292(5)	348(5)	542(7)	15(5)	74(4)	24(6)
Cl(c)	331(15)	396(17)	595(20)	64(13)	100(13)	33(15)
Cl(2)	441(18)	501(20)	1 027(29)	60(16)	294(18)	−133(20)
Cl(3)	723(24)	501(20)	794(26)	−24(17)	143(19)	200(20)
Cl(4)	387(17)	774(26)	739(25)	−26(16)	−66(16)	50(20)
P(1)	369(18)	359(18)	700(24)	−27(14)	120(16)	−86(18)
P(2)	355(17)	418(20)	680(24)	−33(15)	167(16)	25(18)
P(3)	493(20)	670(24)	458(21)	−12(17)	130(16)	0(19)

Refinement of the scale factor and of the positional and isotropic thermal parameters of all non-hydrogen atoms in the metal complex led to R 0.116 and R' 0.146 [where $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$]. Allowance for anisotropic thermal vibrations of molybdenum, chlorine, and phosphorus atoms brought R to 0.079 and R' to 0.123. The subsequent difference map showed three peaks higher than background (1.7, 1.8, and 2.1 eÅ^{-3}), and their arrangement appeared compatible with the molecular geometry of ethanol. Hence, one oxygen and two carbon atoms were added to the list of atoms refined isotropically and R and R' decreased to 0.062 and 0.075, respectively. A low-angle difference synthesis, based on data with $\sin\theta/\lambda < 0.35$ Å^{-1}, revealed the positions of all phenyl group hydrogens. These hydrogen atoms were then included in the structure-factor calculations, but their parameters, deduced from the known stereochemistry of the benzene ring (C–H 1.08 Å), were not varied. Refinement converged at R 0.059 and R' 0.069.

In the last cycle of refinement all parameters shifted by $< 0.3\sigma$. The standard deviation of an observation of unit weight was 1.6. An analysis of the mean $w\Delta^2$ values as a bivariant function of $|F_o|$ and $\sin\theta/\lambda$ confirmed the adequacy of the applied weighting scheme. The function values in the final difference synthesis ranged from -0.50 to 0.59 eÅ^{-3}. Final atomic parameters are shown in Table 1, and the observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 21544 (10 pp., 1 microfiche).*

The computer programs used were C. K. Johnson's ORTEP and Atlas version of J. M. Stewart's '*X*-Ray '70 System.'

DISCUSSION

The crystal structure is built of discrete molecular units of $[MoCl_4(PMe_2Ph)_3]$ and EtOH. Molecular interactions are of the van der Waals type, as shown by a calculation of all intermolecular contacts <4.0 Å.

The molecular geometry of the solvent of crystallization, EtOH [represented by atoms O, C(25), and C(26) in Table 1], has been determined with relatively low accuracy: C(26)–C(25) 1.40(5), C(25)–O 1.33(6) Å, and C(26)–C(25)–O 105(4)°. The thermal motion of all three atoms is very high (Table 1) and may suggest either some degree of disorder or partial occupancy of the solvent molecule. However, attempts to alter the 1 : 1 ratio of the metal complex and the solvent have led to less satisfactory refinement.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

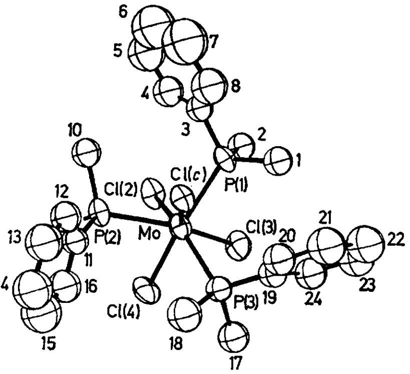
[10] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[11] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[12] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[13] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

The molecular structure of $[MoCl_4(PMe_2Ph)_3]$ (Figure) is closely similar to that of the tetrabromo-analogue[14] and it exhibits approximate C_{3v} symmetry. The co-ordination polyhedron around molybdenum can be described as a distorted capped octahedron, with the capped face formed by the three phosphorus atoms and the non-capped face formed by the chlorine atoms Cl(2), Cl(3), and Cl(4) [Cl(*f*)]; the fourth chlorine atom, Cl(*c*), occupies the unique capping position. Means of the interbond angles subtended at molybdenum are: Cl(*c*)–Mo–P 74.6, Cl(*c*)–Mo–Cl(*f*) 127.3, P–Mo–P 113.2, Cl(*f*)–Mo–Cl(*f*) 87.2, Cl(*f*)–Mo–P[*cis* to Cl(*f*)] 77.2, and Cl(*f*)–Mo–P[*trans* to Cl(*f*)] 158.1°. These angles are almost identical with the corresponding ones observed in the non-isomorphous solid of $[MoBr_4(PMe_2Ph)_3]$ (74.5, 127.4, 113.2, 86.9, 77.2, and 158.0°).[14] It thus appears that crystal packing forces are of relatively low importance in determining the co-ordination geometry of these complexes.



A view of the molecular geometry. For clarity, the carbon atoms are labelled only by the numbers they bear in Tables 1 and 2. The methyl group carbon C(9) is obscured by the phenyl group bonded to P(2)

Judging by the non-bonding intramolecular contacts (Table 2), the molecule of $[MoCl_4(PMe_2Ph)_3]$ is subject to a considerable strain due to ligand–ligand repulsions. However, while the Cl(*f*) ··· Cl(*f*) distances are only 0.21—0.26 Å shorter than the van der Waals diameter of chlorine, the respective Cl(*f*) ··· P and Cl(*c*) ··· P distances are as much as 0.53—0.61 and 0.68—0.70 Å shorter than the sum of the appropriate van der Waals radii. Some steric strain between the chlorine atoms and the methyl group substituents on the phosphorus atoms is also apparent. It seems, therefore, that in this highly crowded molecule the steric effects of the bulky PMe_2Ph ligands are balanced by the ligand charge repulsions between the *facial* chlorine atoms. The non-bonding intramolecular contacts are on the whole appreciably shorter than those observed in the *cis-mer*-$[MoOCl_2(PMe_2Ph)_3]$,[3] and this may account for the relatively lower stability of the tetrachloro compound in air.

The metal–ligand bond lengths in $[MoCl_4(PMe_2Ph)_3]$, (I), can be compared with the corresponding ones in the isostructural species $[MoBr_4(PMe_2Ph)_3]$,[14] (II), and in the octahedral molybdenum(IV) complexes *cis-mer*-$[MoOCl_2(PMe_2Ph)_3]$,[3] (III), and *trans*-$[MoCl_2$(*N*-methyl-

TABLE 2

The molecular geometry of $[MoCl_4(PMe_2Ph)_3]$

(*a*) Bond lengths (Å)

Mo–Cl(*c*)	2.399(3)	C(4)–C(5)	1.41(3)
Mo–Cl(2)	2.440(4)	C(5)–C(6)	1.36(3)
Mo–Cl(3)	2.454(4)	C(6)–C(7)	1.32(4)
Mo–Cl(4)	2.447(3)	C(7)–C(8)	1.42(3)
Mo–P(1)	2.570(3)	C(8)–C(3)	1.39(2)
Mo–P(2)	2.575(4)	C(11)–C(12)	1.38(2)
Mo–P(3)	2.579(4)	C(12)–C(13)	1.37(2)
P(1)–C(1)	1.849(15)	C(13)–C(14)	1.28(2)
P(1)–C(2)	1.835(14)	C(14)–C(15)	1.36(2)
P(1)–C(3)	1.814(13)	C(15)–C(16)	1.42(3)
P(2)–C(9)	1.863(14)	C(16)–C(11)	1.36(2)
P(2)–C(10)	1.846(14)	C(19)–C(20)	1.37(2)
P(2)–C(11)	1.817(12)	C(20)–C(21)	1.39(2)
P(3)–C(17)	1.851(14)	C(21)–C(22)	1.34(2)
P(3)–C(18)	1.825(15)	C(22)–C(23)	1.37(2)
P(3)–C(19)	1.827(14)	C(23)–C(24)	1.41(2)
C(3)–C(4)	1.40(2)	C(24)–C(19)	1.39(2)

(*b*) Bond angles (°)

Cl(*c*)–Mo–Cl(2)	127.7(1)	C(10)–P(2)–C(11)	106.2(6)
Cl(*c*)–Mo–Cl(3)	127.9(1)	C(17)–P(3)–Mo	115.7(5)
Cl(*c*)–Mo–Cl(4)	126.2(1)	C(18)–P(3)–Mo	113.3(5)
Cl(*c*)–Mo–P(1)	74.3(1)	C(19)–P(3)–Mo	114.6(5)
Cl(*c*)–Mo–P(2)	74.7(1)	C(17)–P(3)–C(18)	103.7(6)
Cl(*c*)–Mo–P(3)	74.8(1)	C(17)–P(3)–C(19)	103.4(6)
Cl(2)–Mo–P(3)	157.6(1)	C(18)–P(3)–C(19)	104.8(7)
Cl(3)–Mo–P(2)	157.3(1)	P(1)–C(3)–C(4)	119(1)
Cl(4)–Mo–P(1)	159.5(1)	P(1)–C(3)–C(8)	123(1)
Cl(2)–Mo–P(1)	78.5(1)	C(8)–C(3)–C(4)	118(1)
Cl(2)–Mo–P(2)	76.2(1)	C(3)–C(4)–C(5)	120(1)
Cl(3)–Mo–P(1)	76.4(1)	C(4)–C(5)–C(6)	120(2)
Cl(3)–Mo–P(3)	77.6(1)	C(5)–C(6)–C(7)	121(2)
Cl(4)–Mo–P(2)	77.9(1)	C(6)–C(7)–C(8)	120(2)
Cl(4)–Mo–P(3)	76.4(1)	C(7)–C(8)–C(3)	121(2)
Cl(2)–Mo–Cl(3)	86.1(1)	P(2)–C(11)–C(12)	122(1)
Cl(2)–Mo–Cl(4)	87.8(1)	P(2)–C(11)–C(16)	120(1)
Cl(3)–Mo–Cl(4)	87.6(1)	C(16)–C(11)–C(12)	118(1)
P(1)–Mo–P(2)	112.9(1)	C(11)–C(12)–C(13)	120(1)
P(1)–Mo–P(3)	111.8(1)	C(12)–C(13)–C(14)	122(1)
P(2)–Mo–P(3)	114.9(1)	C(13)–C(14)–C(15)	121(2)
C(1)–P(1)–Mo	112.4(4)	C(14)–C(15)–C(16)	118(2)
C(2)–P(1)–Mo	117.3(4)	C(15)–C(16)–C(11)	120(1)
C(3)–P(1)–Mo	116.9(4)	P(3)–C(19)–C(20)	122(1)
C(1)–P(1)–C(2)	101.5(6)	P(3)–C(19)–C(24)	119(1)
C(1)–P(1)–C(3)	105.2(6)	C(24)–C(19)–C(20)	119(1)
C(2)–P(1)–C(3)	101.7(6)	C(19)–C(20)–C(21)	120(1)
C(9)–P(2)–Mo	116.1(5)	C(20)–C(21)–C(22)	121(1)
C(10)–P(2)–Mo	112.4(5)	C(21)–C(22)–C(23)	121(2)
C(11)–P(2)–Mo	114.9(5)	C(22)–C(23)–C(24)	119(2)
C(9)–P(2)–C(10)	103.4(6)	C(23)–C(24)–C(19)	120(1)
C(9)–P(2)–C(11)	102.7(6)		

(*c*) Selected intramolecular contacts (Å)

Cl(2) ··· Cl(3)	3.340(6)	P(3) ··· Cl(4)	3.108(5)
Cl(2) ··· Cl(4)	3.388(5)	Cl(*c*) ··· C(1)	3.43(1)
Cl(3) ··· Cl(4)	3.392(5)	Cl(*c*) ··· C(10)	3.47(2)
Cl(*c*) ··· P(1)	3.003(4)	Cl(*c*) ··· C(18)	3.35(1)
Cl(*c*) ··· P(2)	3.021(4)	Cl(2) ··· C(2)	3.36(1)
Cl(*c*) ··· P(3)	3.025(5)	Cl(2) ··· C(9)	3.33(1)
P(1) ··· Cl(2)	3.172(4)	Cl(3) ··· C(2)	3.31(1)
P(1) ··· Cl(3)	3.109(5)	Cl(3) ··· C(17)	3.34(2)
P(2) ··· Cl(2)	3.095(5)	Cl(4) ··· C(9)	3.30(2)
P(2) ··· Cl(4)	3.157(5)	Cl(4) ··· C(17)	3.25(2)
P(3) ··· Cl(3)	3.156(5)		

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[14] M. G. B. Drew, J. D. Wilkins, and A. P. Walters, *J.C.S. Chem. Comm.*, 1972, 1278.

salicylaldiminato)$_2$],[15] (IV). The Mo–P bond lengths in (I) [mean 2.575(3) Å] and (II) [2.580(7) Å] are equivalent, while the Mo–Cl(*f*) [mean 2.447(4) Å] and Mo–Br(*f*) [2.560(5) Å] distances reflect the difference in the covalent radii of chlorine and bromine (0.99 and 1.14 Å). In (I) and (II) the Mo–P bonds are *ca.* 0.08 Å longer than the Mo–P(*trans* to Cl) bond in (III) [2.500(3) Å], and this lengthening might be due to steric effects in the crowded seven-co-ordinate complexes. The Mo–Cl(*c*) distance in (I) [2.399(3) Å] is approximately the same as the Mo–Cl(*trans* to Cl) distance in (IV) [2.388(2) Å], whereas the mean Mo–Cl(*f*) distance is *ca.* 0.05 Å longer and may indicate an appreciable *trans*-influence of the PMe$_2$Ph ligands. In (III), where the Mo–P(*trans* to Cl) bond is somewhat shorter and presumably stronger than the corresponding bonds in (I), the Mo–Cl(*trans* to P) bond [2.464(3) Å] is *ca.* 0.08 Å longer than the Mo–Cl-(*trans* to Cl) bond in (IV).

The geometry of the phosphine ligands (Table 2) reveals no unexpected features.

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