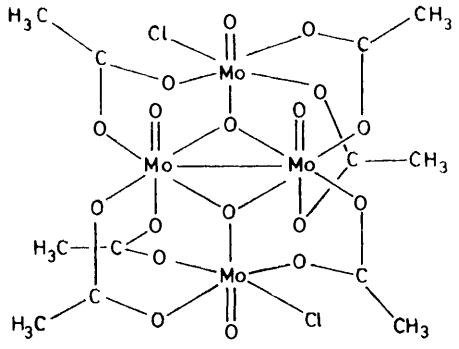
Notes

Preparation and Crystal Structure of Hexa-μ-acetato-dichlorodi-μ$_3$-oxo-tetraoxotetramolybdenum(v)–Acetic Anhydride (1/1) †

By **Boris Kamenar,* Branka Korpar-Čolig,** and **Maja Penavić,** Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, P.O. Box 153, 14001 Zagreb, Yugoslavia

Crystals of the title complex are monoclinic, with a = 14.992(5), b = 12.720(4), c = 17.536(6) Å, β = 101.46(2)° space group $C2/c$, and Z = 4. The intensities of 4 603 reflections collected on an automatic diffractometer have been used to solve and refine the structure to R 0.036. The tetranuclear complex molecule, which has four molybdenum atoms bridged through two oxo-groups and six bidentate acetato-ligands, is located on a two-fold axis. Two of the four molybdenum atoms have Mo–Mo 2.609 Å.

Up to now the structure of $[Mo_4Cl_4O_6(OC_3H_7)_6]$ has been the only known example of molybdenum complexes containing discrete tetranuclear species with two pairs of Mo–Mo bonds.[1] We report the synthesis and structure



of another type of tetranuclear complex $[\{Mo_2ClO_3(OCOCH_3)_3\}_2]\cdot(CH_3CO)_2O$ (1) in which only two of four molybdenum atoms are bonded together.

EXPERIMENTAL

The complex $[\{Mo_2ClO_3(OCOCH_3)_3\}_2]\cdot(CH_3CO)_2O$ was obtained by dissolving $MoCl_2O_2$ (5 g) in acetic anhydride (20 cm^3). The reaction mixture was warmed to 90 °C, filtered, and evaporated at 20 mmHg ‡ to 10 cm^3. The deep olive crystalline precipitate (*ca.* 4.5 g) obtained by cooling the solution in a refrigerator (5°C) was filtered off, washed with CCl_4, dried over Na[OH], and recrystallized from hot acetic anhydride (Found: C, 19.15; H, 2.45; Cl, 6.90; Mo, 38.05. Calc. for $C_{16}H_{24}Cl_2Mo_4O_{21}$: C, 19.1; H, 2.40; Cl, 7.05; Mo, 38.1%). The crystals were moderately stable in a dry atmosphere at room temperature. After long exposure to air solvent was gradually lost; on heating to 100 °C at 20 mmHg the weight loss was 10.76%, corresponding to a 1 : 1 mol ratio of tetrameric complex and acetic anhydride.

Crystal Data.—$C_6H_{24}Cl_2Mo_4O_{21}$, M = 886·9, Monoclinic, space group $C2/c$, a = 14.992(5), b = 12.720(4), c = 17.536(6) Å, β = 101.46(2)°, U = 3 277.4 Å^3, D_m = 2.11 (by flotation), Z = 4, D_c = 2.04 g cm^{-3}, $F(000)$ = 1 820, μ(Mo-K_α) = 17.1 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å.

Intensity data were collected on a Philips PW 1100 computer-controlled diffractometer (graphite-monochromatized Mo-K_α radiation) with the ω—2θ scan technique (scan width 1.60°, scan speed 0.04 ° s^{-1}) up to (sinθ)/λ = 0.75. Three standard reflections were measured after every 2 h, and their changes used to bring the reflections to a common scale. Because of crystal decomposition the intensity data were collected from three different crystals mounted in a capillary tube. The data were re-scaled, and corrected for Lorentz and polarization factors but not for absorption. A total of 4 732 reflections was measured, of which 4 603 having $I > 2\sigma(I)$ were used for the structure determination.

The structure was solved by direct methods with the use of MULTAN.[2] From the E map obtained, two molybdenum, one chlorine, and two terminal oxo-groups were located (R 0.26). From the next Fourier map the positions of all non-hydrogen atoms except those belonging to the solvent molecule were deduced (R 0.116). Further least-squares refinement with anisotropic temperature factors reduced R to 0.048. At this stage the acetic anhydride molecules in disordered positions about $\bar{1}$ were located by a difference-Fourier synthesis. Due to this disorder the peaks belonging to the methyl-carbon and carboxyl-oxygen atoms were not clearly resolved so that in the refinement they were both treated as carbon atoms. In the last cycles of the refinement the population within the acetic anhydride molecule was set at 0.5 for the bridging oxygen and 1.0 for all other atoms. The refinement converged at R 0.036. Unit weight was assumed for all observations. The values of atomic scattering factors were taken from ref. 3 with corrections for anomalous scattering according to ref. 4. Calculations were made on the UNIVAC 1110 computer of the University Computing Centre in Zagreb with the system of programs developed by Domenicano *et al.*[5] Final atomic co-ordinates are given in Table 1, while the thermal parameters with observed and calculated structure factors are listed in Supplementary Publication No. SUP 22918 (58 pp.).§

† 1,2;1,2;1,4;2,3;3,4;3,4-Hexa-μ-acetato-*OO'*-1,3-dichloro-1,2,-4; 2,3,4-di-μ$_3$-oxo-1,2,3,4-tetraoxo-*cyclo*-tetramolybdenum(v)-(*Mo*^{2}–*Mo*^{4})-acetic anhydride (1/1).

‡ Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

§ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

DISCUSSION

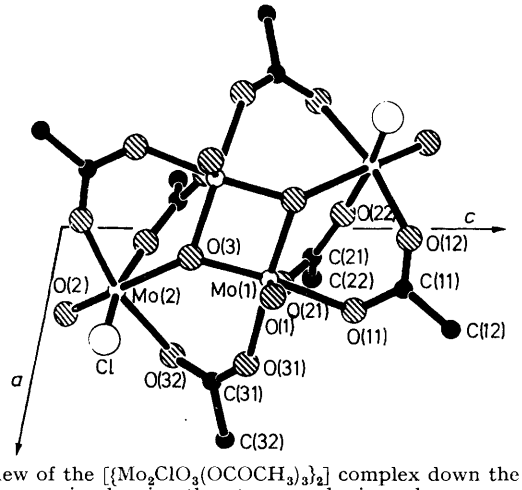
The structure of the tetranuclear complex is shown in the Figure; the bond distances and angles are given in Table 2. The molecule has a crystallographically imposed two-fold symmetry axis. Both molybdenum

TABLE 1

Atomic positions ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Mo(1)	786.6(2)	2 098.9(3)	2 978.8(2)
Mo(2)	1 005.0(2)	1 113.3(3)	947.9(2)
O(1)	949(3)	3 388(3)	3 058(2)
O(2)	1 402(2)	441(3)	273(2)
O(3)	449(2)	1 876(2)	1 853(2)
O(11)	1 283(2)	1 969(3)	4 192(2)
O(12)	107(2)	1 689(3)	4 765(2)
O(21)	861(2)	375(2)	3 149(2)
O(22)	−227(2)	−109(2)	3 787(2)
O(31)	2 112(2)	1 717(3)	2 891(2)
O(32)	1 994(2)	659(3)	1 857(2)
Cl	1 759(1)	2 690(1)	894(1)
C(11)	938(3)	1 895(4)	4 779(2)
C(12)	1 535(4)	2 065(5)	5 574(3)
C(21)	447(3)	−292(3)	3 463(3)
C(22)	769(4)	−1 420(4)	3 468(4)
C(31)	2 421(3)	1 032(4)	2 498(3)
C(32)	3 363(5)	613(8)	2 806(5)
C(111)	4 492(11)	302(13)	379(9)
C(112)	3 592(10)	86(13)	366(9)
C(113)	4 676(16)	929(17)	958(12)
O(111)	5 285(4)	439(12)	275(7)

atoms in the asymmetric unit are octahedrally co-ordinated and are linked together by oxo-groups and acetato-ligands. The octahedra about Mo(1) and its symmetrically related Mo(1′) share a common edge and have common corners with the octahedra about Mo(2) and Mo(2′). Mo(1) and Mo(2) have different environments: Mo(1) is formally seven-co-ordinated being



View of the $[\{Mo_2ClO_3(OCOCH_3)_3\}_2]$ complex down the *b* axis, showing the atom-numbering scheme

bonded to Mo(1′), three acetato-oxygen atoms, and three oxo-oxygen atoms, two of which are bridging and one terminal; Mo(2) is also bonded to three acetato-oxygen atoms, but only to two oxo-oxygen atoms, one bridging and one terminal, and to one chlorine atom. Although the Mo(1)–Mo(1′) bond has little effect on the geometry around Mo(1), the angles at Mo(1) (75.9—105.0°) and those at Mo(2) (81.6—99.8°) indicate that the octahedron about Mo(1) is more distorted, most probably due to the metal–metal bond. The Mo(1)–Mo(1′) distance of 2.609 Å is almost exactly the same as that considered as a Mo–Mo single bond.[6] The central Mo_2O_2 core [Mo(1) and O(3), Mo(1′) and O(3′)] is folded at an angle of 155.4° along a line connecting two bridging oxygen atoms.

The O(3) oxo-oxygen atom bridging three molybdenum atoms has two short Mo–O bonds [Mo(1′)–O(3) 1.953 and Mo(1)–O(3) 1.959 Å], and one significantly longer bond [Mo(2)–O(3) 2.164 Å]. Apart from these,

TABLE 2

Molecular geometry of $[\{Mo_2ClO_3(OCOCH_3)_3\}_2]\cdot(CH_3CO)_2O$

(*a*) Distances (Å)

Mo(1)–Mo(1′)	2.609 3(3)	Mo(2)–O(32)	2.033(3)
Mo(1) · · · Mo(2)	4.101 5(3)		
Mo(1)–O(1)	1.659(3)	Mo(2)–Cl	2.312(2)
Mo(1)–O(3)	1.959(3)	O(11)–C(11)	1.245(6)
Mo(1)–O(3′)	1.953(3)	O(12)–C(11)	1.268(6)
Mo(1)–O(11)	2.166(3)	C(11)–C(12)	1.514(6)
Mo(1)–O(21)	2.213(3)	O(21)–C(21)	1.242(6)
Mo(1)–O(31)	2.081(3)	O(22)–C(21)	1.276(6)
Mo(2)–O(2)	1.663(4)	C(21)–C(22)	1.513(7)
Mo(2)–O(3)	2.164(3)	O(31)–C(31)	1.256(7)
Mo(2)–O(12′)	2.013(3)	O(32)–C(32)	1.269(6)
Mo(2)–O(22′)	2.051(3)	C(31)–C(32)	1.505(9)

(*b*) Bond angles (°)

O(1)–Mo(1)–O(3)	103.4(1)	O(3)–Mo(2)–O(12′)	84.2(1)
O(1)–Mo(1)–O(3′)	105.0(2)	O(3)–Mo(2)–O(22′)	81.6(1)
O(1)–Mo(1)–O(11)	88.7(1)	O(3)–Mo(2)–O(32)	83.1(1)
O(1)–Mo(1)–O(31)	91.0(1)	O(3)–Mo(2)–Cl	84.5(1)
O(3)–Mo(1)–O(3′)	93.9(1)	O(12′)–Mo(2)–O(22′)	88.8(1)
O(3)–Mo(1)–O(21)	89.3(1)	O(12′)–Mo(2)–Cl	90.6(1)
O(3)–Mo(1)–O(31)	87.2(1)	O(22′)–Mo(2)–O(32)	83.7(1)
O(3′)–Mo(1)–O(11)	89.5(1)	O(32)–Mo(2)–Cl	84.5(1)
O(3′)–Mo(1)–O(21)	81.9(1)	O(11)–C(11)–O(12)	124.6(4)
O(11)–Mo(1)–O(21)	77.8(1)	O(11)–C(11)–C(12)	118.9(4)
O(11)–Mo(1)–O(31)	91.0(1)	O(12)–C(11)–C(12)	116.5(4)
O(21)–Mo(1)–O(31)	75.9(1)	O(21)–C(21)–O(22)	125.6(4)
Mo(1)–O(3)–Mo(1′)	83.7(1)	O(21)–C(21)–C(22)	117.6(5)
O(2)–Mo(2)–O(12′)	96.6(2)	O(22)–C(21)–C(22)	116.8(4)
O(2)–Mo(2)–O(22′)	94.1(1)	O(31)–C(31)–O(32)	124.7(4)
O(2)–Mo(2)–O(32)	95.9(2)	O(31)–C(31)–C(32)	118.1(5)
O(2)–Mo(2)–Cl	99.8(1)	O(32)–C(31)–C(32)	117.2(6)

Primed atoms are related to unprimed atoms by a two-fold symmetry axis.

Mo(1) and Mo(2) are additionally bonded to one terminal oxo-oxygen atom at 1.659 and 1.663 Å, respectively. The acetates function as bidentate ligands, the molybdenum–acetato-oxygen bond lengths varying (2.013—2.213 Å) according to their positions in the structure (*i.e. cis* or *trans* to the oxo-oxygen atoms). The Mo(2)–Cl bond length is 2.312 Å. The distances and angles in the acetato-ligands are within the expected values.

The crystal structure was found to contain a statistically disordered solvate molecule of acetic anhydride. Consequently, this part of the structure has been determined with relatively low accuracy.

Magnetic measurements at 294 K gave a magnetic moment of 2.35 B.M. for the tetrameric unit, or 0.59 B.M. per molybdenum atom. This value is lower than expected for a molybdenum(v) complex, but is consistent with the structure and can be explained in terms of

coupling through the bridging oxo-oxygen atoms and/or as a direct spin–spin interaction.

The i.r. spectra are consistent with the structure; bands at 980vs and 890w cm^{-1} were assigned to $\nu(Mo{-}O_t)$ and at 758s cm^{-1} to $\nu(Mo{-}O_b)$,[7] while those at 1 570 and at 1 400—1 450 cm^{-1} (broad) were attributed to $\nu_{asym}(CO_2)$ and to $\nu_{sym}(CO_2)$ respectively.[8] Sharp absorption maxima at 1 838s, 1 780w, and 1 715m cm^{-1} assigned as stretching frequencies, $\nu(C{=}O)$, and that at 1 120 cm^{-1}, assigned as $\nu(C{-}O{-}C)$, indicated the presence of acetic anhydride as a solvate molecule in the crystal structure.

Studies of related systems with formato-, propionato-, and benzoato-ligands are in progress.

We thank Professor D. Grdenić for his interest during this research, and the Foundation for Scientific Research of the S.R. Croatia, Zagreb, for support.

[0/229 *Received*, 8*th February*, 1980]

REFERENCES

[1] J. A. Beaver and M. G. B. Drew, *J.C.S. Dalton*, 1973, 1376.
[2] J. P. Declerq, G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1973, **A29**, 231.
[3] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1968, vol. 3, p. 202.
[4] T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.
[5] A. Domenicano, R. Spagna, and A. Vaciago, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1969, **47**, 331.
[6] F. A. Cotton, *Inorg. Chem.*, 1965, **4**, 334; *J. Less-Common Metals*, 1977, **54**, 3.
[7] C. G. Baraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3552; P. C. H. Mitchell, *Quart. Rev.*, 1966, **20**, 103.
[8] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1954, p. 152.