Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1047). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 3:1 Disordered Solid Solution of Di-μ-methoxo-O:O-bis[trimethoxooxomolybdenum(VI)] and Di-μ-methoxo-O:O-bis[chlorodimethoxooxomolybdenum(VI)]

WILLIAM CLEGG, MARK R. J. ELSEGOOD, R. JOHN ERRINGTON AND RIDLA BAKRI

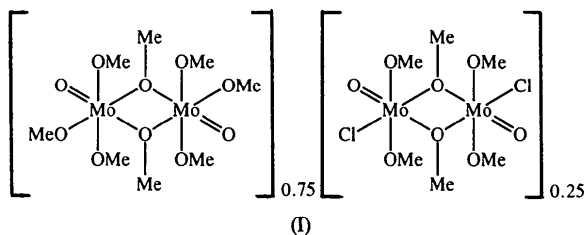*Department of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England. E-mail: w.clegg@ncl.ac.uk*

Abstract

The title structure, $[Mo_2(CH_3O)_8(O)_2]_{0.75}.[Mo_2Cl_2(CH_3O)_6(O)_2]_{0.25}$, contains two crystallographically independent centrosymmetric molecules, each of which has a major $[MoO(OMe)_4]_2$ disorder component and a minor $[MoOCl(OMe)_3]_2$ disorder component, with a *cis* arrangement of the chloro and oxo ligands. The oxo ligands lie in the equatorial plane of the metal atoms and bridging ligands. The methoxo bridges are markedly asymmetric as a consequence of the strong *trans* influence of the terminal oxo ligands compared with terminal methoxo ligands. Coordination of the Mo atoms is distorted octahedral.

Comment

As part of a wide ranging study of metal alkoxide complexes, which are soluble analogues of and precursors to metal oxides, we have been interested in oxoalkoxides, species intermediate between homoleptic alkoxides and oxides. For molybdenum and tungsten, neutral and anionic complexes have been crystallographically characterized containing two (Abbott, Cotton & Falvello, 1990; Clegg, Errington, Fraser & Richards, 1993), four (Kang, Liu, Shaikh, Nicholson & Zubieta, 1989), five (Chen, Ma, Liu & Zubieta, 1989), six (Chisholm, Folting, Huffman & Kirkpatrick, 1984) and eight (Liu & Zubieta, 1989) metal atoms and oxo–alkoxide stoichiometric ratios ranging from 5:4 to 16:1, the oxo ligands being in excess in most cases.

In addition to these, structures are known for a number of molybdenum and tungsten complexes with the simple empirical formula $[MO(OR)_4]$. Monomeric five-coordinate species are found for $[WO(OMe)_4]$ and $[WO(OEt)_4]$ (Kucheiko, Turova, Kozlova & Zhadanov, 1985), and for $[MoO\{OC(CF_3)_3\}_4]$ (Johnson, Taylor & Waugh, 1980) and $[WO(OC_6H_3{}^iPr-2,6)_4]$ (Gibson & McPartlin, 1996) with bulky substituents. Dimeric molecules with pairs of bridging alkoxide ligands giving octahedral coordination geometry are reported for $[MoO(OMe)_4]_2$ (Kessler, Mironov, Turova, Yanovsky & Struchkov, 1993), $[WO(OMe)_4]_2$ and $[WO(OC_6H_{11})_2]_2$ (Clegg, Errington, Kraxner & Redshaw, 1992). There is evidence from NMR measurements that many species of this kind are dynamic in solution, existing in both monomeric and dimeric forms (Clegg, Errington, Kraxner & Redshaw, 1992), and $[WO(OMe)_4]$ has been crystallographically characterized in both forms. The steric bulk of the alkoxide ligand substituents appears to be only one factor affecting the relative stability of the monomers and dimers.

In the course of our work, we prepared what appeared to be a second crystalline form of $[MoO(OMe)_4]$, previously shown to exist as a dimer (Kessler *et al.*, 1993). This was also found to be dimeric with alkoxide bridges, but initial refinement was unsatisfactory, with poor resolution and unacceptable geometry for one terminal alkoxide ligand in the asymmetric unit (half a dimer) of each of the two crystallographically independent molecules. Modelling of this as a disordered overlap of alkoxide and chloride ligands is successful, with no constraints or restraints necessary on the geometrical parameters. The disorder appears to be restricted to one pair of symmetry-related ligands in each molecule and is of unequal proportions in the two molecules. Molecule 1 contains only 15(2)% chloro ligands, while molecule 2 contains 34(3)%, giving an overall proportion of essentially 3:1 for the disorder, (I). The chloro ligands are due to incomplete substitution in the $[MoOCl_4]$ starting material. On purely X-ray crystallographic grounds, we are, of course, unable

to say whether the actual species present are just $[MoO(OMe)_4]_2$ and $[MoOCl(OMe)_3]_2$, or whether the disorder involves the $[Mo_2O_2Cl(OMe)_7]$ unsymmetrical dinuclear species in addition to, or even instead of, the symmetrical dichloro species.

(I)

Figs. 1 and 2 show the dimers with no and with two chloro ligands (based on molecules 1 and 2, respectively). Chemical microanalysis and proton NMR spectroscopy for the material as prepared indicate no significant quantities of the chloro species identified crystallographically as a minor product, which suggests that the crystal studied is not representative of the bulk. We note, however, that variable amounts of a less soluble darker orange material are often obtained in the reaction, depending on the precise reaction conditions and in particular on the time elapsed before sodium salts are separated from the reaction mixture. This minor product is likely to be a chloro complex and we are attempting to isolate and crystallize it for further study.

The geometry of the fully substituted alkoxide component is essentially identical to that of the orthorhombic $(P2_12_12_1)$ form reported previously (Kessler *et al.*, 1993). As for the other molybdenum and tungsten oxoalkoxide dimers, the alkoxide bridges are markedly asymmetric, with the longer Mo—O bond *trans* to oxo and the shorter bond *trans* to a terminal alkoxide ligand, demonstrating the strong *trans* influence of the oxo ligand; the oxo ligands are found in the equatorial plane of the dimer in every case. The geometry of the terminal equatorial alkoxide ligands in molecule 2 (O22 and C22) is somewhat anomalous, with unusually long Mo—O and short O—C bonds, but this is probably an artefact of the disorder and these parameters are rather imprecise.

The geometry associated with the chloro ligands (Mo—Cl bond length and O—Mo—Cl angles) in the minor disorder components is entirely consistent with that found in a dozen related structures (containing alkoxide and a *cis* arrangement of oxo and chloro ligands) drawn from the October 1995 release of the Cambridge Structural Database (Allen & Kennard, 1993), for which the mean Mo—Cl distance is 2.366 Å (range 2.300–2.472 Å) and the mean O=Mo—Cl angle is 99.8° (range 91.9–112.4°).

There are no notably short intermolecular contacts, the molecular surface consisting predominantly of methyl H atoms.
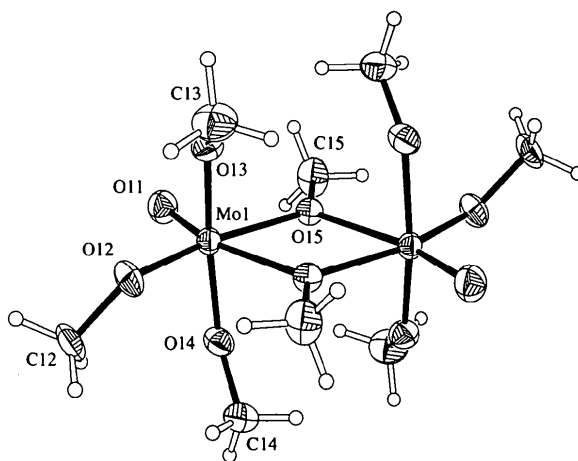

Fig. 1. The structure of the major component of molecule 1, with unique atom labels and 50% probability ellipsoids for non-H atoms.
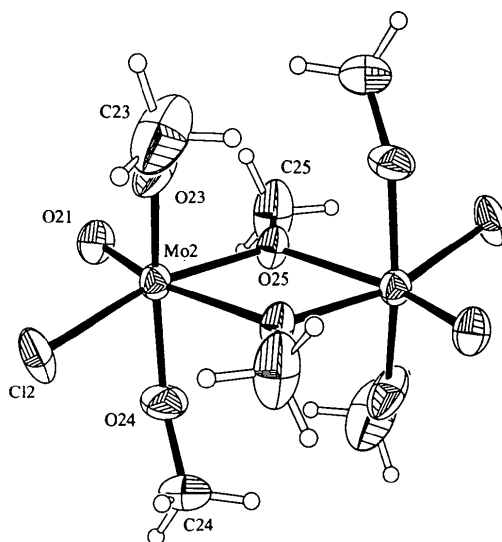

Fig. 2. The structure of the chloro component of molecule 2, with unique atom labels and 50% probability ellipsoids for non-H atoms.

Experimental

Crystal data

$[Mo_2(CH_3O)_8(O)_2]_{0.75}.-$	Mo $K\alpha$ radiation
$[Mo_2Cl_2(CH_3O)_6(O)_2]_{0.25}$	$\lambda = 0.71073$ Å

$M_r = 474.36$
Monoclinic
$P2_1/c$
$a = 11.798\,(3)$ Å
$b = 10.259\,(3)$ Å
$c = 13.326\,(4)$ Å
$\beta = 92.38\,(7)^\circ$
$V = 1611.5\,(8)$ Å^3
$Z = 4$
$D_x = 1.955$ Mg m^{-3}
D_m not measured

Cell parameters from 30
  reflections
$\theta = 10.57–12.52^\circ$
$\mu = 1.675$ mm^{-1}
$T = 160\,(2)$ K
Block
$0.34 \times 0.29 \times 0.23$ mm
Yellow

Data collection

Stoe–Siemens diffractometer
  with Cryostream cooler
  (Cosier & Glazer, 1986)
ω/θ scans with on-line
  profile fitting (Clegg,
  1981)
Absorption correction:
  empirical from ψ scans
  (*SHELXTL*; Sheldrick,
  1994)
$T_{min} = 0.267$, $T_{max} = 0.295$

4826 measured reflections
2711 independent reflections
2279 observed reflections
  $[I > 2\sigma(I)]$
$R_{int} = 0.0312$
$\theta_{max} = 24.97^\circ$
$h = -13 \rightarrow 13$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$
5 standard reflections
  frequency: 60 min
  intensity decay: 1.6%

Refinement

Refinement on F^2
$R(F) = 0.0303$
$wR(F^2) = 0.0783$
$S = 1.122$
2709 reflections
210 parameters
H atoms riding (C—H
  0.98 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 4.4949P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.791$ e Å^{-3}
$\Delta\rho_{min} = -0.615$ e Å^{-3}
Extinction correction:
  SHELXTL
Extinction coefficient:
  0.0008 (2)
Atomic scattering factors
  from *International Tables
  for Crystallography* (1992,
  Vol. C, Tables 4.2.6.8 and
  6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Molecule 1				
Mo1	0.47793 (3)	0.12978 (3)	0.41507 (2)	0.02104 (13)
O11	0.3593 (3)	0.1708 (3)	0.3475 (2)	0.0345 (7)
Cl1†	0.6021 (19)	0.302 (2)	0.3792 (17)	0.054 (11)
O12‡	0.5896 (9)	0.2514 (7)	0.3796 (8)	0.031 (2)
C12‡	0.5903 (5)	0.3908 (11)	0.3916 (5)	0.037 (2)
O13	0.5437 (2)	0.0225 (3)	0.3201 (2)	0.0296 (6)
C13	0.6538 (4)	−0.0225 (3)	0.3013 (4)	0.0442 (12)
O14	0.4489 (2)	0.2337 (3)	0.5272 (2)	0.0298 (7)
C14	0.5124 (4)	0.2758 (5)	0.6133 (4)	0.0415 (11)
O15	0.4013 (2)	−0.0277 (3)	0.4782 (2)	0.0223 (6)
C15	0.2858 (4)	−0.0634 (5)	0.4551 (4)	0.0407 (12)
Molecule 2				
Mo2	−0.06440 (3)	0.13010 (3)	0.06119 (3)	0.02611 (13)
O21	−0.1823 (3)	0.1349 (3)	0.1270 (2)	0.0371 (7)
Cl2§	0.0093 (6)	0.3418 (7)	0.0818 (6)	0.046 (3)
O22¶	−0.0147 (10)	0.3144 (11)	0.0465 (11)	0.039 (2)
C22¶	0.0253 (9)	0.398 (2)	0.1127 (11)	0.047 (2)
O23	−0.1312 (3)	0.1723 (4)	−0.0631 (3)	0.0501 (9)
C23	−0.1040 (7)	0.2301 (8)	−0.1544 (5)	0.085 (3)
O24	0.0379 (3)	0.1025 (4)	0.1678 (3)	0.0519 (10)
C24	0.1554 (5)	0.1131 (8)	0.1889 (6)	0.084 (3)
O25	−0.0799 (2)	−0.0621 (3)	0.0308 (2)	0.0304 (7)
C25	−0.1672 (5)	−0.1404 (5)	0.0711 (6)	0.066 (2)

† Occupancy of 0.15(2).   ‡ Occupancy of 0.85(2).   § Occupancy of 0.34(3).   ¶ Occupancy of 0.66(3).

Table 2. *Selected geometric parameters (Å, °)*

Mo1—O11	1.686 (3)	Mo2—O21	1.675 (3)
Mo1—O13	1.870 (3)	Mo2—O24	1.848 (4)
Mo1—O14	1.878 (3)	Mo2—O23	1.856 (4)
Mo1—O12	1.889 (8)	Mo2—O22	1.992 (11)
Mo1—O15	2.049 (3)	Mo2—O25	2.020 (3)
Mo1—O15^i	2.232 (3)	Mo2—O25^{ii}	2.250 (3)
Mo1—Cl1	2.36 (2)	Mo2—Cl2	2.351 (6)
O15—Mo1—O15^i	69.45 (11)	O25—Mo2—O25^{ii}	69.67 (12)
Mo1—O15—Mo1^i	110.55 (11)	Mo2—O25—Mo2^{ii}	110.33 (12)

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $-x, -y, -z$.

H atoms were placed geometrically and refined with a riding model and with U_{iso} constrained to be $1.5U_{eq}$ of the carrier atom. Coordinates for the disordered methoxo and chloro groups in both molecules were freely refined and restraints (similarity and rigid-bond model) were applied to the anisotropic displacement parameters of these and the Mo atoms. The occupancy factors for the Cl atoms refined to 0.15 (2) in molecule 1 and 0.34 (3) in molecule 2, corresponding to an overall composition close to 3:1 for the two chemical components.

Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and local programs.

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The AsF6− Salt of a 1,2-Dithia-4-azolylium Cation with Sterically Demanding Substituents

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Abstract

The cation of the title compound, 3,5-bis(2-methylphenyl)-1,2,4-dithiazolylium hexafluoroarsenate(V), $C_{16}H_{14}NS_2^+.AsF_6^-$, has a central planar five-membered NCSSC ring with two *o*-tolyl substituents lying 29.11 (9)° out of this plane because of the steric hindrance of the methyl groups. The cation has a twofold rotation axis through the N atom and the midpoint of the S—S bond. Interionic interactions include short S···F and N···F contacts, but the cations are well separated with no S···S or N···S interactions.

Comment

As part of a continuing investigation of derivatives of 1,2-dithia-3,5-diazolyl (SSNCN) and 1,3-dithia-2,5-diazolyl (SNSCN) ring systems [see Rawson, Banister & Lavender (1995) for a general reference to this area], we have prepared and characterized a number of 1,3-dithia-2,5-diazolyl derivatives with *ortho*- and *meta*-substituted phenyl groups attached to the ring C atom (Banister, Hibbert, Aherne, Rawson, Clegg & Elsegood, 1996; Hibbert, 1993). The AsF6− salt of the 4-*o*-tolyl-1,3-dithia-2,5-diazolylium cation has been satisfactorily characterized by elemental analysis, IR spectroscopy and mass spectrometry (Hibbert, 1993), but in attempts to produce single crystals suitable for X-ray diffraction studies, further reaction with a small

excess of the starting material, *o*-tolyl cyanide, in solution in liquid SO_2 led to a very small amount of the title compound, (I).

(I)
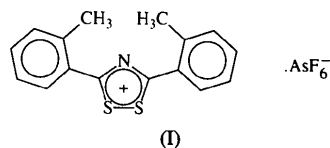
Both the cation and anion have crystallographic two-fold rotation symmetry (Fig. 1). The five-membered ring is essentially planar [r.m.s. deviation 0.012 (1) Å]. The steric bulk of the *o*-methyl groups on the aromatic substituents prevents coplanarity and full delocalization of the three rings; each of the planar six-membered rings [r.m.s. deviation 0.006 (2) Å] forms a dihedral angle of 29.11 (9)° with the central ring. This out-of-plane twist puts the C8 atom 2.873 (8) Å from the N atom and 4.20 (2) Å from the C8i atom [symmetry code: (i) $1 - x$, y, $\frac{1}{2} - z$]; coplanarity would significantly reduce these distances and give unacceptably short contacts for the methyl H atoms.
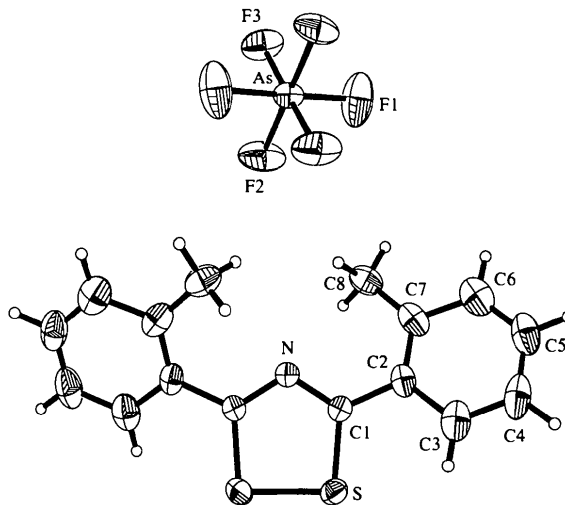

Fig. 1. The structure of the cation and anion of (I) with the atom labels (unique atoms) and 50% probability ellipsoids for non-H atoms.

The geometry of the *o*-tolyl substituent is unexceptional, with ring C—C bonds in the range 1.360 (6)–1.438 (5) Å and a C7—C8 distance of 1.473 (6) Å.

A search of the Cambridge Structural Database (Allen & Kennard, 1993) provided seven compounds containing the same central cationic ring system. The closest comparison is with the diphenyl derivative as its NP4S9− salt (Neels, Ziemer, Meisel & Leibnitz, 1986) and this has essentially the same ring geometry as the title compound. The hydrochloride (Hordvik & Sletten, 1966), hydrobromide (Peyronel, Pignedoli & Malavasi, 1982)