C(4A)—N(4A)—O(4A)	124.8 (9)	C(4B)—N(4B)—O(4B)	119.8 (9)
C(4A)—N(4A)—Co(A)	112.7 (9)	C(4B)—N(4B)—Co(B)	116.7 (7)
O(4A)—N(4A)—Co(A)	122.3 (8)	O(4B)—N(4B)—Co(B)	123.1 (7)
C(9A)—N(5A)—Co(A)	120.7 (6)	C(9B)—N(5B)—Co(B)	119.2 (7)
N(1A)—C(1A)—C(2A)	113.8 (11)	N(1B)—C(1B)—C(2B)	115.8 (11)
N(1A)—C(1A)—C(5A)	125.4 (12)	N(1B)—C(1B)—C(5B)	123.0 (11)
C(2A)—C(1A)—C(5A)	120.4 (11)	C(2B)—C(1B)—C(5B)	121.2 (12)
N(2A)—C(2A)—C(1A)	110.8 (11)	N(2B)—C(2B)—C(1B)	108.8 (11)
N(2A)—C(2A)—C(6A)	122 (2)	N(2B)—C(2B)—C(6B)	124.7 (11)
C(1A)—C(2A)—C(6A)	126.7 (13)	C(1B)—C(2B)—C(6B)	126.5 (12)
N(3A)—C(3A)—C(7A)	127.5 (12)	N(3B)—C(3B)—C(7B)	121.4 (11)
N(3A)—C(3A)—C(4A)	107.5 (10)	N(3B)—C(3B)—C(4B)	114.3 (10)
C(7A)—C(3A)—C(4A)	123.8 (12)	C(7B)—C(3B)—C(4B)	124.2 (11)
N(4A)—C(4A)—C(8A)	119.4 (10)	N(4B)—C(4B)—C(8B)	126.3 (10)
N(4A)—C(4A)—C(3A)	117.1 (10)	N(4B)—C(4B)—C(3B)	112.4 (9)
C(8A)—C(4A)—C(3A)	122.7 (10)	C(8B)—C(4B)—C(3B)	121.1 (10)
C(10A)—C(9A)—C(14A)	119.3 (6)	C(10B)—C(9B)—C(14B)	122.6 (12)
C(10A)—C(9A)—N(5A)	119.5 (5)	C(10B)—C(9B)—N(5B)	116.6 (11)
C(14A)—C(9A)—N(5A)	121.3 (9)	C(14B)—C(9B)—N(5B)	120.6 (11)
C(11A)—C(10A)—C(9A)	118.2 (7)	C(11B)—C(10B)—C(9B)	114.7 (12)
C(10A)—C(11A)—C(12A)	122.3 (12)	C(10B)—C(11B)—C(12B)	125.3 (13)
C(13A)—C(12A)—C(11A)	118.3 (13)	C(13B)—C(12B)—C(11B)	117.6 (13)
C(12A)—C(13A)—C(14A)	119.3 (12)	C(12B)—C(13B)—C(14B)	121.0 (13)
C(13A)—C(14A)—C(9A)	122.2 (11)	C(13B)—C(14B)—C(9B)	118.6 (13)

The structure was solved by direct methods and refined by full-matrix least squares. A pseudo-orthorhombic cell exists with $a_o = 18.334$, $b_o = 35.425$, $c_o = 10.855$ Å [transformation matrix: (001/201/010)]; space group *Cmca*, but the Laue class was monoclinic and $R_{\rm int}$ for the orthorhombic cell was 0.317, so the determination and refinement were carried out using the monoclinic cell. Owing to the small size of the crystal, a low number of non-negative intensities were collected and the resolution was of low accuracy.

Data collection: Philips diffractometer software. Cell refinement: Philips diffractometer software. Data reduction: *CFEO* (Solans, 1978). Structure solution: *SHELXS*86 (Sheldrick, 1985). Structure refinement: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1976; Brueggemann & Schmid, 1990). Preparation of material for publication: *CIFTAB* (Sheldrick, 1994).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1144). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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***trans*-Tetracarbonylbis(tri-*tert*-butyl phosphite)molybdenum(0)**

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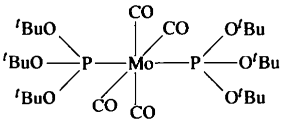
Abstract

The Mo atom in the title compound, $[Mo(CO)_4(C_{12}H_{27}O_3P)_2]$, lies on an inversion centre and has slightly distorted octahedral geometry, with principal dimensions Mo—P 2.4699 (7), Mo—C 2.027 (4), 2.031 (3) Å, P—Mo—P 180, *cis*-C—Mo—C 88.7 (2), C—Mo—P 86.12 (10) and 87.27 (9)°. The geometry about the P atom is distorted from tetrahedral, with Mo—P—O angles in the range 108.04 (9)–126.03 (10)° and reduced O—P—O angles in the range 96.71 (13)–106.09 (14)°. The average cone angle for the *tert*-butyl phosphite ligand is 156°.

Comment

The title compound, $[Mo(CO)_4\{P(O^tBu)_3\}_2]$, (1), was synthesized during our investigations of numerous $[Mo(CO)_{6-n}(PY_3)_n]$ (n = 1–3) complexes by ^{95}Mo

NMR spectroscopy (Alyea & Song, 1995*a*,*b*; Song, 1994). The effects of changes in the P substituent (*Y*) and the degree of carbonyl substitution have previously been studied by the X-ray analyses of *cis*-[Mo(CO)$_4${P(C$_6$H$_4$-F-*p*)$_3$}$_2$] (Alyea, Ferguson, Gallagher & Song, 1994), *cis*-[Mo(CO)$_4${P(OPh)$_3$}$_2$] (2) (Alyea, Ferguson & Zwikker, 1994) and *fac*-[Mo(CO)$_3${P(OPh)$_3$}$_3$] (Alyea, Ferguson & Song, 1995). A search of the October 1994 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1993) revealed the absence of any other *trans*-Mo(CO)$_4$P$_2$ fragments involving phosphite ligands. There were only three examples with *trans*-Mo(CO)$_4$P$_2$ systems having phosphine ligands, namely, *trans*-[Mo(CO)$_4${P(Ph)$_2$F}{P(Ph)$_2$(NH$_2$)}] (Bradley, Wong, Gabe & Lee, 1986), *trans*-[Mo(CO)$_4${P(Ph)$_2$(NHMe)}$_2$] (Gray & Zhang, 1993) and *trans*-[Mo(CO)$_4${(Ph)$_2$P-(CH$_2$)$_6$P(Ph)$_2$}$_2$Mo(CO)$_4$]] (Ueng & Hwang, 1991). Accordingly, we decided to examine the structural consequences and the effect on the ^{95}Mo NMR chemical shift of forming a disubstituted Mo complex with a bulkier phosphite, namely, P(O^{t}Bu)$_3$.



(1)

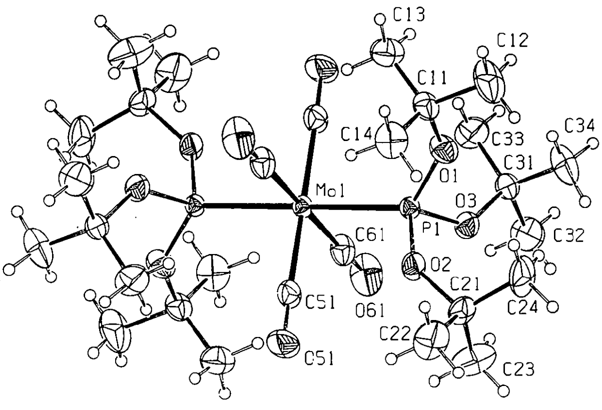


Fig. 1. A view of compound (1) with the numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

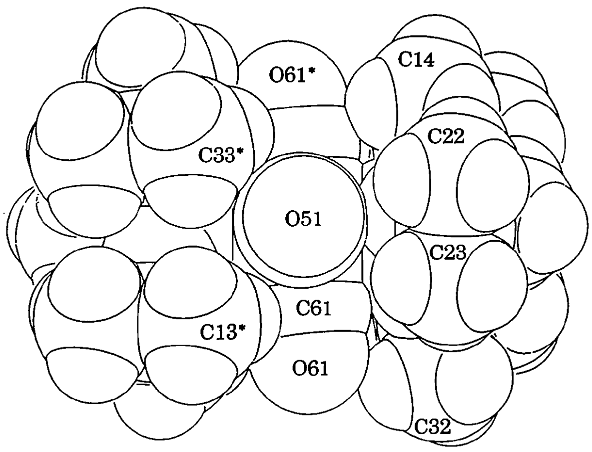


Fig. 2. A space-filling view of compound (1). Starred atoms (*) are at the equivalent position $-x$, $-y$, $-z$.

The title molecule (Fig. 1) has the Mo atom on an inversion centre, which requires the compound to be the *trans* isomer with the P—Mo—P angle equal to 180°. The Mo atom has a slightly distorted octahedral coordination environment in the solid state. Although consideration of *trans* influences might have led us to predict a shorter Mo—P bond in (1) compared with *cis*-[Mo(CO)$_4${P(OPh)$_3$}$_2$], (2), the Mo—P bond distance in (1) [2.4699 (7) Å] is longer than the average Mo—P bond distance in (2) [2.442 (2) Å]. The Mo—P bond elongation in (1) can be attributed to the severe steric hindrance in the molecule (see below). As a result of this steric effect the ^{95}Mo NMR chemical shift is significantly downfield (-1626 p.p.m.) as compared with a normal δ(^{95}Mo) value for a *trans* species with a small non-bulky phosphite, *e.g.* -1859 p.p.m. for *trans*-[Mo(CO)$_4${P(OMe)$_3$}$_2$] (Song, 1994).

One consequence of the steric bulk of the *trans*-phosphite ligands, illustrated in the space-filling diagram (Fig. 2), is distortion of the Mo coordination geometry from octahedral, with the unique C—Mo—P angles [86.12 (10) and 87.27 (9)°] distorted from 90° and the Mo—C—O angles [177.8 (3) and 178.5 (3)°] being non-linear. Applying the 'ligand profile' concept (Ferguson, Roberts, Alyea & Khan, 1978) to calculate semi-cone angles (θ/2) for the phosphite substituents, values of 67, 82 and 85° are derived. The resultant average cone angle (θ) is thus 156°, as compared with the maximum cone angle of 172° given by the Tolman method using CPK models (Tolman, 1977). For comparison, the Tolman cone angle θ for P(OMe)$_3$ is only 107°.

Distortion of the tetrahedral geometry at the P atom of compound (1) is shown by variation in the Mo—P—O angles [108.04 (9)–126.03 (10)°] and the reduced O—P—O angles [96.71 (13)–106.09 (14)°]. In the case of (2), the Mo—P—O and O—P—O angles have ranges of 112.5 (1)–121.9 (1) and 96.9 (2)–104.4 (2)°, respectively. Relief from intramolecular overcrowding in (1) is also achieved by distortions in the O—C—C angles [102.3 (3)–112.7 (3)°]. By contrast, the C—C—C angles appear to be relatively unaffected, with a range of 108.8 (3)–113.5 (3)°. The smallest Mo—P—O angle [108.04 (9)°] leads to the greatest outward folding of the —O^{t}Bu substituent, wherein the van der Waals contact of methyl group C23 defines the semi-cone angle ($\theta/2$) value of 67°. The largest Mo—P—O angle [126.03 (10)°] corresponds to the greatest inward folding, with methyl group C13 giving a semi-cone angle ($\theta/2$) value of 85°.

Other bond distances and angles in (1) are normal [*e.g.* mean P—O 1.593 (10), mean O—C(^{t}Bu) 1.463 (4) and mean C—C 1.506 (11) Å]. Intermolecular contacts are of the van der Waals type.

Experimental

To a clear solution of 0.15 g of tetracarbonyl(norbornadiene)molybdenum, $[Mo(CO)_4(NBD)]$, in 5 ml of methylene chloride was added 0.8 ml of $P(O^tBu)_3$ ligand (Mark & Van Wazer, 1964). The mixture was refluxed for 2 h. ^{95}Mo NMR and IR spectra *in situ* indicated the formation of an $[Mo(CO)_4L_2]$ complex [$\delta(^{95}Mo) = -1626$ p.p.m., a poorly resolved triplet with $^1J(Mo—P) = 216$ Hz and $W_{1/2} = 283$ Hz; ν_{CO} (cm^{-1}): 1904 (*sh*), 1988 (*s*)]. Slow evaporation of the solvent yielded colourless needle crystals which were recrystallized from methylene chloride.

Crystal data

$[Mo(CO)_4(C_{12}H_{27}O_3P)_2]$
$M_r = 708.59$
Monoclinic
$P2_1/n$
$a = 9.2634 (10)$ Å
$b = 13.9834 (14)$ Å
$c = 14.2332 (12)$ Å
$\beta = 90.701 (11)°$
$V = 1843.5 (3)$ Å^3
$Z = 2$
$D_x = 1.277$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 11.5–19.5°$
$\mu = 0.488$ mm^{-1}
$T = 294 (1)$ K
Needle
0.40 × 0.28 × 0.28 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.835$, $T_{max} = 0.886$
4221 measured reflections
3985 independent reflections

2920 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.014$
$\theta_{max} = 26.9°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0388$
$wR(F^2) = 0.1059$
$S = 1.034$
3985 reflections
188 parameters
H atoms riding with C—H = 0.96 Å
$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2 + 0.5082P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$

$\Delta\rho_{max} = 0.838$ e Å^{-3}
$\Delta\rho_{min} = -0.299$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0020 (6)
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)*

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

	x	y	z	U_{eq}
Mo1	0	0	0	0.03407 (12)
P1	0.06456 (8)	0.11753 (5)	0.12305 (5)	0.0343 (2)
O1	0.0654 (3)	0.2309 (2)	0.1112 (2)	0.0630 (6)
O2	−0.0304 (3)	0.0960 (2)	0.21205 (14)	0.0586 (6)
O3	0.2232 (2)	0.1083 (2)	0.1687 (2)	0.0554 (6)
O51	−0.1722 (4)	−0.1109 (2)	0.1573 (2)	0.0933 (10)
O61	0.2804 (4)	−0.1106 (2)	0.0674 (3)	0.1005 (11)
C11	−0.0407 (4)	0.3015 (2)	0.0778 (3)	0.0558 (8)
C12	0.0125 (6)	0.3927 (3)	0.1220 (4)	0.108 (2)
C13	−0.0290 (5)	0.3046 (3)	−0.0280 (3)	0.0802 (12)
C14	−0.1917 (5)	0.2793 (3)	0.1093 (3)	0.0838 (13)
C21	−0.0137 (4)	0.1040 (3)	0.3137 (2)	0.0573 (9)
C22	−0.1683 (5)	0.0945 (4)	0.3469 (3)	0.103 (2)
C23	0.0789 (7)	0.0238 (4)	0.3489 (4)	0.116 (2)
C24	0.0490 (6)	0.1991 (4)	0.3417 (3)	0.096 (2)
C31	0.3638 (3)	0.1479 (2)	0.1433 (2)	0.0519 (8)
C32	0.4706 (5)	0.0756 (4)	0.1842 (4)	0.0939 (15)
C33	0.3824 (4)	0.1532 (4)	0.0399 (3)	0.0873 (14)
C34	0.3857 (5)	0.2421 (3)	0.1921 (4)	0.094 (2)
C51	−0.1118 (4)	−0.0715 (3)	0.0998 (2)	0.0551 (8)
C61	0.1799 (4)	−0.0718 (2)	0.0415 (3)	0.0578 (9)

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

Mo1—P1	2.4699 (7)	O1—C11	1.467 (4)
Mo1—C51	2.031 (3)	O2—C21	1.458 (4)
Mo1—C61	2.027 (4)	O3—C31	1.465 (4)
P1—O1	1.595 (2)	O51—C51	1.138 (4)
P1—O2	1.580 (2)	O61—C61	1.135 (4)
P1—O3	1.604 (2)		
P1—Mo1—C51	87.27 (9)	O1—C11—C12	102.8 (3)
P1—Mo1—C61	86.12 (10)	O1—C11—C13	106.6 (3)
C51—Mo1—C61	88.7 (2)	O1—C11—C14	112.7 (3)
Mo1—P1—O1	126.03 (10)	O2—C21—C22	102.3 (3)
Mo1—P1—O2	108.04 (9)	O2—C21—C23	109.2 (3)
Mo1—P1—O3	116.52 (9)	O2—C21—C24	111.5 (3)
O1—P1—O2	106.09 (14)	O3—C31—C32	103.3 (3)
O1—P1—O3	96.71 (13)	O3—C31—C33	112.2 (3)
O2—P1—O3	100.14 (12)	O3—C31—C34	109.4 (3)
P1—O1—C11	134.3 (2)	Mo1—C51—O51	178.5 (3)
P1—O2—C21	136.7 (2)	Mo1—C61—O61	177.8 (3)
P1—O3—C31	133.0 (2)		

Examination of the structure with the *SOLV* option in *PLATON* (Spek, 1994*a*) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD-4/PC Software* (Enraf–Nonius 1992). Cell refinement: *SET*4 and *CELDIM* (Enraf–Nonius 1992). Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94, *ORTEP*II (Johnson, 1976) in *PLATON* (Spek, 1994*a*) and *PLUTON* (Spek, 1994*b*). Software used to prepare material for publication: *NRCVAX*94 and *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1022). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Novel Octanuclear Mixed-Metal Cluster: $Na_2[Cr_{0.5}Fe_{0.5}Mo_3O_4(O_2CEt)_8]_2$

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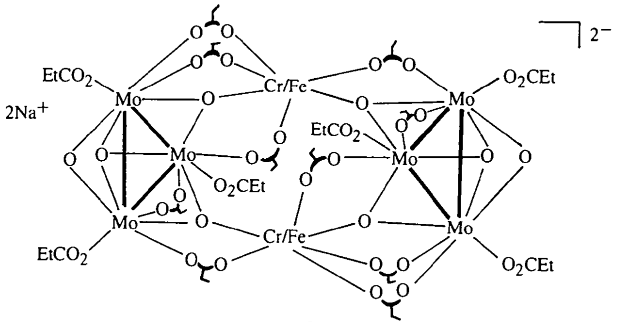
Abstract

The structure of disodium bis[μ-oxo-tri-μ_3-oxo-pentakis(μ-propionato-κO:$\kappa O'$)tris(propionato-κO)-0.5-chromium-0.5-irontrimolybdenum](3 *Mo—Mo*), $Na_2[Cr_{0.5}Fe_{0.5}Mo_3O_4(C_3H_5O_2)_8]_2$, consists of a centrosymmetric cluster anion, $[(EtCO_2)_8Mo_3O_4CrFeO_4Mo_3(O_2CEt)_8]^{2-}$, in which two Mo_3O_4 units are joined by the Fe and Cr atoms to complete a circular $[Mo_3O_4CrFeO_4Mo_3]^{14+}$ species. Each Na atom is coordinated to five O atoms to form a trigonal bipyramid with an average Na—O distance of 2.32 (2) Å. The anions are connected by Na cations to form a one-dimensional infinite chain structure.

Comment

Triangular trinuclear cluster species with an $[M_3O_4]^{4+}$ core (M = Mo, W) have been studied extensively (Mardon & Pernick, 1973; Murmann & Shelton, 1980). The sandwich-cubane type $[Mo_3S_4M'S_4Mo_3]$ and double-cubane type $[M_3S_4M'M'S_4M_3]$ species have been investigated by Shibahara, Akashi, Yamasaki & Hashimoto (1991), and Wolff, Berg, Hodgson, Frankel & Holm (1979). Here, we report a novel insoluble octanuclear mixed-metal cluster with a circular $[Mo_3O_4CrFeO_4Mo_3]^{14+}$ cation.

The black crystals of title compound, (I), were obtained from the redox reaction of $Na_2MoO_4.2H_2O$ with $Cr(CO)_6$ and $Fe(CO)_5$ in propionic anhydride. The crystals are very stable in air and difficult to dissolve in water, general organic solvents and acids.



(I)

The X-ray structure study indicates that Cr and Fe atoms are disordered in the crystal lattice. The structure of $Na_2[MMo_3O_4(O_2CEt)_8]_2$ (M = 0.5Cr + 0.5Fe) consists of an octanuclear centrosymmetric anion $[(EtCo_2)_8Mo_3O_4MMO_4Mo_3(O_2CEt)_8]^{2-}$, where the two $[Mo_3O_4(O_2CEt)_8]^{4-}$ units are joined by two M atoms through four μ_3-O (from μ_2-O atoms in both the Mo_3 units) and eight bridging $EtCO_2$ groups as shown in Fig. 1.

Each M atom is coordinated by six O atoms, two from μ_3-O atoms and four from propionate bridges. They complete regular octahedral coordination. The average M—μ_3-O bond length of 1.980 (9) Å is significantly longer than the Fe—μ_3-O length of 1.905 (5) Å found in the related cation $[Fe_3O(O_2CR)_6L_3]^+$ (Blake & Fraser, 1975) or the Cr—μ_3-O length of 1.89 Å in $[Cr_3O(O_2CR)_6L_3]^+$ (Chang & Jeffrey, 1970), as a result of the Fe_3O or Cr_3O four-centre *d–p–d* π-bonding found in the latter two.