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Yamagata, Yamagata & Yamaguchi, 1986). In this communication, we report the synthesis and structural characterization of a benzyl complex, *trans*-[(Mo6Cl8)(C7H7)4{P(n-C4H9)3}2], (1), and an alkynyl complex, *trans*-[(Mo6Cl8)(C8H5)4{P(n-C5H11)3}2].-2C7H8, (2).

trans-[(Mo6Cl8)(C7H7)4{P(n-C4H9)3}2] and *trans*-[(Mo6Cl8)(C8H5)4{P(n-C5H11)3}2].-2C7H8

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Abstract

The title compounds, tetrabenzyl-$2\kappa C,3\kappa C,4\kappa C,5\kappa C$-octa-$\mu_3$-chloro-bis(tributylphosphine)-$1\kappa P,6\kappa P$-*octahedro*-hexamolybdenum($12Mo$—Mo), (1), and tetrakis(phenylethynyl)-$2\kappa C,3\kappa C,4\kappa C,5\kappa C$-octa-$\mu_3$-chloro-bis(tripentylphosphine)-$1\kappa P,6\kappa P$-*octahedro*-hexamolybdenum($12Mo$—Mo)-toluene (1/2), (2), containing octahedral Mo clusters with four σ-C ligands, were prepared by the reaction of *trans*-[(Mo6Cl8)Cl4(PR_3)2] with tribenzylaluminium and tris(phenylethynyl)aluminium, respectively, and their structures determined. The octahedral Mo6 cores of both compounds are on inversion centres and are almost regular. Average interatomic distances in the clusters for (1) are Mo—Mo$_{edge}$ 2.618, Mo···Mo$_{opposite}$ 3.703, Mo—Cl 2.477 and Mo—C 2.26 Å, and for (2) are Mo—Mo$_{edge}$ 2.626, Mo···Mo$_{opposite}$ 3.714 and Mo—C 2.13 Å.

Comment

Classic examples of molybdenum cluster complexes with the [Mo6Cl8]$^{4+}$ core are [Mo6Cl14]$^{2-}$ and [Mo6Cl8(H2O)6]$^{4+}$. The [Mo6Cl8]$^{4+}$ core can accept various kinds of ligands and recent examples are (CF3SO3)$^-$ (Johnston, Gaswick, Lonergan, Stern & Shriver, 1992) and [Mn(CO)2Cp]$^-$ (Johnston, Stern & Shriver, 1992). We have reported the preparation and structural analysis of the molybdenum cluster complexes *trans*-[(Mo6Cl8)Cl4(PR_3)2] (*R* = n-C3H7, n-C4H9, n-C5H11) and an alkyl derivative all-*trans*-[(Mo6Cl8)Cl2(C2H5)2{P(n-C4H9)3}2] (Saito, Nishida,

(1)

(2)
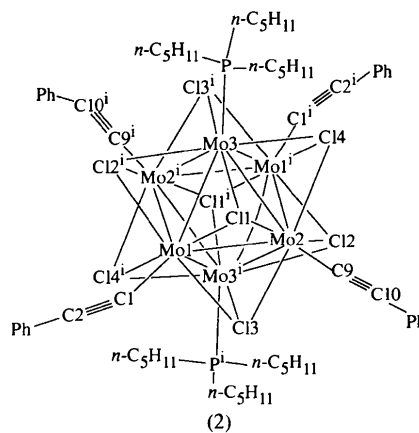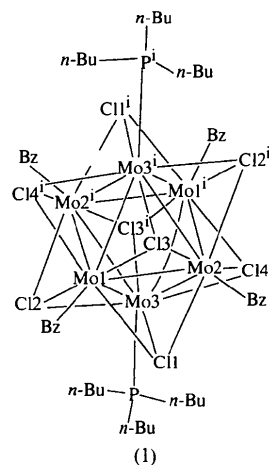
In both (1) and (2), the cluster units are at the crystallographic inversion centres and the shape of the Mo6 core is an almost perfect octahedron. The regular shape is consistent with the number of metal cluster electrons (24 e) of these cluster complexes. The molecular structures of (1) and (2) are shown in Figs. 1 and 2, respectively. Selected geometric parameters are listed in Tables 1 and 2.

Three non-bonding Mo···Mo distances between the opposite Mo atoms in the Mo6 core are 3.699 (3), 3.704 (3) and 3.705 (3) Å for (1), and 3.709 (2), 3.715 (2) and 3.718 (2) Å for (2). The averages of these distances are comparable in (1) and (2) (3.703 and 3.714 Å, respectively). The average Mo—Cl distances in (1) and (2) are also very similar to one another (2.477 and 2.474 Å, respectively). The Mo—C distances of (1), 2.239 (14) and 2.271 (15) Å, are similar
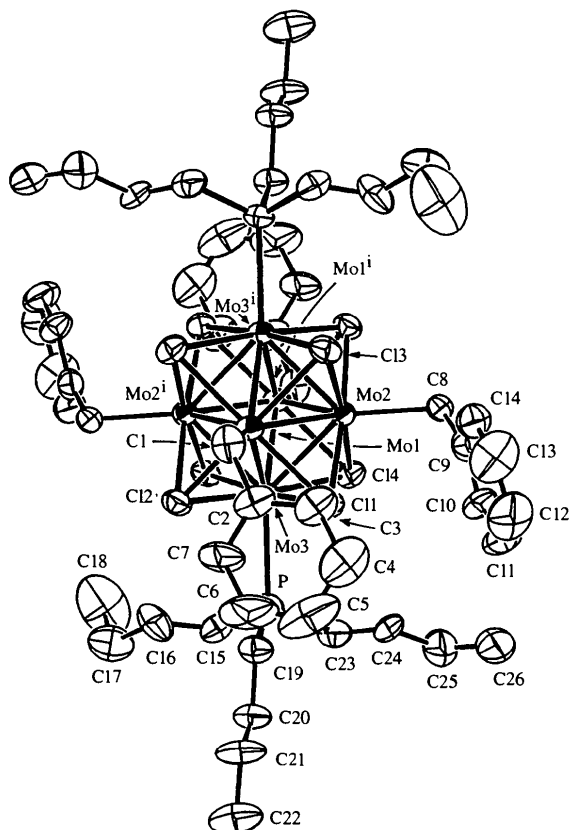
Fig. 1. View (ORTEPII; Johnson, 1976) of (1) showing the labelling of the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.
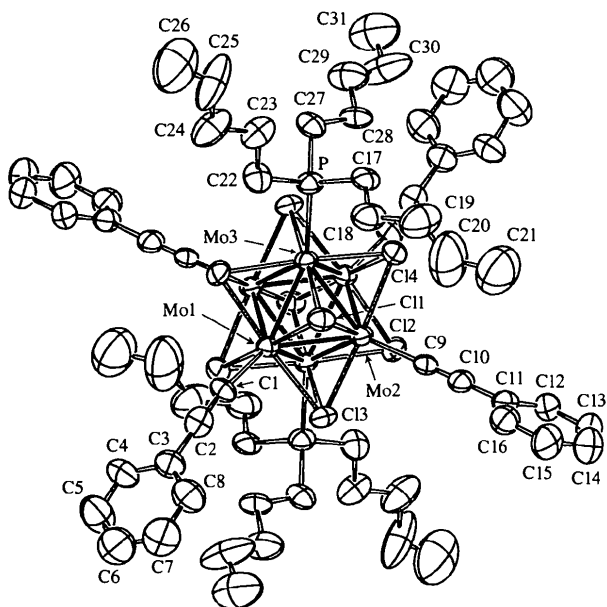

Fig. 2. View (ORTEPII; Johnson, 1976) of (2) showing the labelling of the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.

to those observed in the ethyl cluster complex trans-[(Mo₆Cl₈)Cl₂(C₂H₅)₂{P(n-C₄H₉)₃}₂] [2.21 (3) Å; Saito, Nishida, Yamagata, Yamagata & Yamaguchi, 1986]. The Mo—C distances of (2), 2.108 (12) and 2.161 (13) Å, are somewhat shorter than those of (1) and are similar to those in mononuclear alkynylmolybdenum complexes [2.18 (2) (Pombeiro, Hills, Hughes & Richards, 1990) and 2.093 (8) Å (Buang, Hughes, Kashef, Richards & Pombeiro, 1987)]. The C≡C triple-bond lengths in the alkynyl ligands are 1.193 (15) and 1.19 (2) Å, and are similar to the distance found in free acetylene of 1.2047 Å (Christensen, Eaton, Green & Thompson, 1956).

Experimental

All reactions were carried out in an atmosphere of nitrogen using Schlenk techniques. Tribenzylaluminium diethyl ether-ate and tris(phenylethynyl)aluminium diethyl etherate were prepared according to literature methods (Eisch & Bieder-mann, 1971; Demarne & Cadiot, 1968) and used without further purification. For (1), a toluene solution (10.8 ml) of [Al(CH₂Ph)₃].Et₂O (8.64 × 10⁻³ mmol) was added to a suspension of trans-[(Mo₆Cl₈)Cl₄{P(n-C₄H₉)₃}] (2.0 g, 1.42 × 10⁻³ mmol) in toluene (60 ml) and the mixture was stirred at room temperature for one day. The unreacted complex was removed by filtration. Removal of volatile materials from the filtrate in vacuo gave a deep-red oil. The residual oil was cooled at 253 K to yield orange crystals. The crude crystals were washed with ether (10 ml × 3); yield 0.47 g (20%). For the X-ray measurements, deep-orange–red crystals were prepared from a toluene solution at 257 K; yield 0.3 g (13%), m.p. 423 K (decomp.); IR: ν(Mo—C) 418 (s), ν(Mo—Cl) 348 (w) cm⁻¹. A crystal was sealed in a glass capillary for X-ray analysis. Compound (2) was obtained from the reaction of trans-[(Mo₆Cl₈)Cl₄{P(n-C₅H₁₁)₃}₂] (0.106 g, 7.14 × 10⁻⁵ mol) with [Al(CCPh)₃].Et₂O (0.357 g, 1.07 × 10⁻³ mol) by the same procedure as that described for (1); yield 24 mg (19%). For the X-ray analysis, orange crystals were obtained from a solution of toluene at 278 K; IR (KBr tablet): ν(C≡C) 2070 (s), ν(C≡C) 1590 (vs) cm⁻¹. The crystals for X-ray analysis were coated with silicone grease and sealed in glass capillaries in the presence of toluene.

Compound (1)

Crystal data

[(Mo₆Cl₈)(C₇H₇)₄-(C₁₂H₂₇P)₂]
$M_r = 1628.43$
Monoclinic
$P2_1/n$
$a = 10.033 (9)$ Å
$b = 20.540 (18)$ Å
$c = 15.464 (17)$ Å
$\beta = 94.14 (7)°$
$V = 3178 (5)$ Å³
$Z = 2$
$D_x = 1.702$ Mg m⁻³
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 59 reflections
$\theta = 8.86–12.21°$
$\mu = 1.567$ mm⁻¹
$T = 294 (1)$ K
Prism
$0.43 \times 0.10 \times 0.07$ mm
Deep-orange–red

Data collection

Rigaku AFC-4R diffractom- eter	2556 reflections with $F > 4\sigma(F)$
ω–2θ scans	$R_{int} = 0.05$
Absorption correction: empirical *via* ψ scan (North, Phillips & Mathews, 1968)	$\theta_{max} = 27.5°$ $h = -13 \to 13$ $k = 0 \to 26$ $l = 0 \to 20$
$T_{min} = 0.822$, $T_{max} = 0.894$	3 standard reflections
7721 measured reflections	every 100 reflections
7314 independent reflections	intensity decay: none

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.0$
$R = 0.0620$	$\Delta\rho_{max} = 0.977$ e Å^{-3}
$wR = 0.0452$	$\Delta\rho_{min} = -0.930$ e Å^{-3}
$S = 1.111$	Extinction correction: none
2556 reflections	Scattering factors from *Inter-*
307 parameters	*national Tables for X-ray*
H atoms not refined	*Crystallography* (Vol. IV)
$w = 1/\sigma^2(F)$	

Table 1. *Selected geometric parameters (Å, °) for (1)*

Mo1—Mo1^i	3.705 (3)	Mo2—Cl3	2.492 (5)
Mo1—Mo2	2.612 (2)	Mo2—Cl4	2.485 (4)
Mo1—Mo2^i	2.623 (2)	Mo2—C8	2.239 (14)
Mo1—Mo3	2.618 (2)	Mo3—Mo3^i	3.704 (3)
Mo1—Mo3^i	2.621 (2)	Mo3—Cl1	2.464 (4)
Mo1—Cl1	2.472 (4)	Mo3—Cl2	2.480 (5)
Mo1—Cl2	2.463 (4)	Mo3—Cl3^i	2.495 (4)
Mo1—Cl3	2.477 (5)	Mo3—Cl4	2.478 (5)
Mo1—Cl4^i	2.474 (4)	Mo3—P	2.612 (5)
Mo1—Cl	2.271 (15)	P—Cl5	1.81 (2)
Mo2—Mo2^i	3.699 (3)	P—Cl9	1.83 (2)
Mo2—Mo3	2.617 (2)	P—C23	1.83 (2)
Mo2—Mo3^i	2.617 (2)	Cl—C2	1.48 (2)
Mo2—Cl1	2.465 (4)	C8—C9	1.50 (2)
Mo2—Cl2^i	2.480 (4)		
Mo1—Cl—C2	114.7 (10)	Mo2—C8—C9	115.0 (10)

Symmetry code: (i) $-x, -y, -z$.

Compound (2)

Crystal data

[(Mo$_6$Cl$_8$)(C$_8$H$_5$)$_4$- (C$_{15}$H$_{33}$P)$_2$].2C$_7$H$_8$	Mo $K\alpha$ radiation $\lambda = 0.71069$ Å
$M_r = 1936.86$	Cell parameters from 66
Monoclinic	reflections
$P2_1/n$	$\theta = 9.27$–$12.41°$
$a = 25.241$ (6) Å	$\mu = 1.213$ mm^{-1}
$b = 10.962$ (1) Å	$T = 294$ (1) K
$c = 15.180$ (2) Å	Prism
$\beta = 98.78$ (2)°	$0.70 \times 0.17 \times 0.07$ mm
$V = 4151$ (1) Å^3	Orange
$Z = 2$	
$D_x = 1.550$ Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-4R diffractom- eter	$R_{int} = 0.04$ $\theta_{max} = 27.5°$

ω–2θ scans	$h = -32 \to 32$
Absorption correction: none	$k = 0 \to 14$
9915 measured reflections	$l = 0 \to 19$
9550 independent reflections	3 standard reflections
3450 reflections with	every 50 reflections
$F > 4\sigma(F)$	intensity decay: none

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.0001$
$R = 0.0570$	$\Delta\rho_{max} = 0.99$ e Å^{-3}
$wR = 0.0451$	$\Delta\rho_{min} = -1.02$ e Å^{-3}
$S = 1.205$	Extinction correction: none
3450 reflections	Scattering factors from *Inter-*
359 parameters	*national Tables for X-ray*
H atoms not refined	*Crystallography* (Vol. IV)
$w = 1/\sigma^2(F)$	

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

Mo1—Mo1^i	3.718 (2)	Mo2—Cl2	2.485 (4)
Mo1—Mo2	2.628 (2)	Mo2—Cl3	2.461 (3)
Mo1—Mo2^i	2.624 (2)	Mo2—Cl4	2.478 (3)
Mo1—Mo3	2.639 (2)	Mo2—C9	2.161 (13)
Mo1—Mo3^i	2.617 (2)	Mo3—Mo3^i	3.715 (2)
Mo1—Cl1	2.472 (4)	Mo3—Cl1	2.468 (4)
Mo1—Cl2^i	2.472 (3)	Mo3—Cl2^i	2.465 (3)
Mo1—Cl3	2.484 (3)	Mo3—Cl3^i	2.474 (4)
Mo1—Cl4^i	2.480 (4)	Mo3—Cl4	2.468 (3)
Mo1—C1	2.108 (12)	Mo3—P	2.623 (4)
Mo2—Mo2^i	3.709 (2)	C1—C2	1.193 (15)
Mo2—Mo3	2.619 (2)	C2—C3	1.50 (2)
Mo2—Mo3^i	2.631 (2)	C9—C10	1.19 (2)
Mo2—Cl1	2.478 (4)	C10—C11	1.44 (2)
Mo1—C1—C2	166.7 (12)	Mo2—C9—C10	179.6 (11)
C1—C2—C3	176 (2)	C9—C10—C11	178 (2)

Symmetry code: (i) $1 - x, -y, 2 - z$.

The positional parameters for all non-H atoms were determined by direct methods (*SHELXS86*; Sheldrick, 1985). The refinements were carried out by full-matrix least-squares techniques (*ANYBLK*: Imoto, 1990). In compound (1), all non-H atoms were anisotropically refined. In compound (2), all non-H atoms were anisotropically refined except for the C atoms in the toluene molecule which were assumed to have the same isotropic displacement parameter and this was refined as one parameter. No reflections suitable for ψ-scan absorption corrections were found with $\chi > 85°$. The toluene molecule was refined as a rigid body with C—C$_{ring}$ = 1.394 Å and C$_{Ph}$—C$_{Me}$ = 1.505 Å. All H atoms were included as fixed contributions in idealized positions with C—H = 1.08 (sp^3-hybridized geometry) and 0.95 Å (sp^2-hybridized geometry). The H-atom displacement parameter (U_{iso}) was fixed at 0.09 Å^2 for those in the cluster molecule and at 0.18 Å^2 for those in the toluene molecule. The unusual appearance of some of the ellipsoids for (2), most notably for C14, appear to be a result of the large uncertainties in the cross terms of the displacement tensors. The F_o data were collected at the Research Centre for Protein Engineering Institute for Protein Research, Osaka University. All calculations were carried out on an NEC ACOS S3700 computer or an NEC EWS work station, at the Research Centre for Protein Engineering Institute for Protein Research, Osaka University.

For both compounds, data collection: *AFD* (Rigaku Corporation, 1985); cell refinement: *AFD*; data reduction: *AFD*; molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1022). Services for accessing these data are described at the back of the journal.

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A Dioxomolybdenum(VI) Complex with a New Enantiomerically Pure Tetrahydrosalen Ligand

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Abstract

The enantiomerically pure tetradentate ligand H₂L {2,2′-[*trans*-(*R,R*)-1,2-cyclohexanediylbis(*N*-methylaminomethyl)]diphenol} forms a neutral dioxomolyb-

denum(VI) complex, which was isolated as {2,2′-[*trans*-(*R,R*)-1,2-cyclohexanediylbis(*N*-methylaminomethyl)]-diphenolato-*O,N,N′,O′*}dioxomolybdenum(VI) trichloromethane solvate, [MoO₂(C₂₂H₂₈N₂O₂)].CHCl₃, and characterized by a single-crystal X-ray analysis. The coordination geometry around the metal is distorted octahedral. The two oxo O atoms are *cis* and the two phenolate O atoms are in (distorted) *trans* positions. The two N atoms are located approximately *trans* to the oxo O atoms and the Mo—N bonds are remarkably long.

Comment

Molybdenum is an essential element in many enzymes (Spiro, 1985) and plays an important role in industrial oxidation processes (Ullmann's Encyclopedia of Industrial Chemistry, 1993). Numerous Schiff-base complexes containing the MoO₂²⁺ unit have been prepared and studied (Morris, 1995, 1996). However, little is known about the corresponding tetrahydrosalen complexes (Rajan *et al.*, 1983). As part of our studies on the synthesis, characterization and catalytic potential of neutral six-coordinate salen-type Mo complexes, we report here the structure determination of the new chiral *cis*-dioxo-Mo^{VI} complex, (I).

(I)
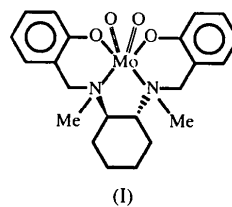
Complex (I) has a distorted octahedral geometry with approximate C₂ symmetry. The two oxo O atoms are *cis* with respect to one another and to the phenolate O atoms
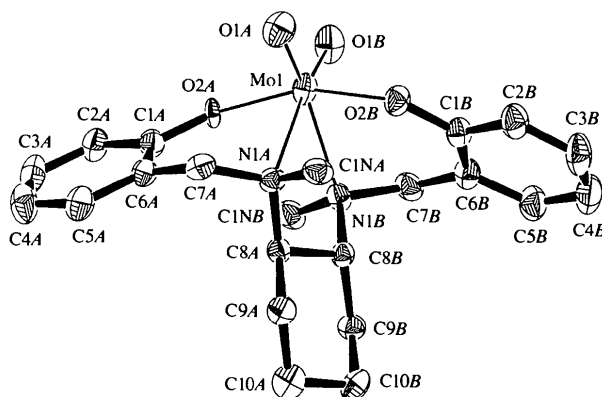

Fig. 1. *ORTEP* (Johnson, 1965) view of the title compound showing the labelling scheme for the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted.