Weak reflections with $I < 10.0\sigma(I)$ were scanned a second time and the counts were accumulated to assure good counting statistics. The structure was solved by direct methods using *MITHRIL* (Gilmore, 1984) in the *TEXSAN* package (Molecular Structure Corporation, 1989). H atoms were placed in calculated positions (C—H = 1.08 Å).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, and a packing diagram have been deposited with the IUCr (Reference: AS1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(η⁵-indenyl)tetrakis(μ-iodo)dimolybdenum(*Mo—Mo*)

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Abstract

The title compound, $[Mo_2(I)_4(C_9H_7)_2]$, is synthesized by the reaction of $MoI_3(thf)_3$ (thf = tetrahydrofuran) and sodium indenyl, followed by the further reaction of an intermediate product with tetraphenylphospho-

nium iodide to form tetraphenylphosphonium indenyl-triiodomolybdate. The title compound forms from the latter compound by loss of tetraphenylphosphonium iodide. The product is a tetra-μ-iodo-bridged dinuclear molybdenum complex with two terminal indenyl ligands. The indenyl groups are η⁵-bonded to the Mo atoms. The molecule sits on a crystallographic inversion center and has non-crystallographic symmetry C_{2h}. The metal–metal distance is 2.720 (4) Å.

Comment

The title compound, (I), was obtained from an attempt to grow crystals of tetraphenylphosphonium indenyl-triiodomolybdate, whose structure at present remains unknown.

(I)
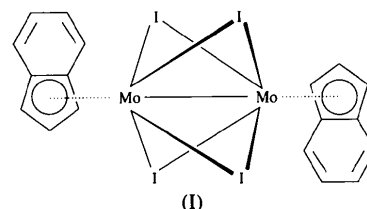
Although crystals of the title compound were found to be poorly formed and give only weak X-ray diffraction peaks with broad and irregular profiles, the structural analysis was carried out in order to identify the product and permit the synthetic program to move forward. Since techniques are now commonly available for carrying out analyses on problematic samples (Sheldrick, 1993), a meaningful refinement and useful analysis turned out to be possible.

The title compound crystallizes with one half-molecule per asymmetric unit. The molecule sits across a crystallographic inversion center. The indenyl groups occupy terminal positions and are η⁵-bonded to the Mo atoms through the five-membered rings of the indenyls, as can be seen in Fig. 1. The Mo—C distances lie in the range 2.18 (2)–2.41 (2) Å. The local twofold axis of the indenyl group bisects a projection of the planar $Mo_2(\mu$-I) systems. That is, if the molecule is viewed from end to end, the long axes of the indenyl groups are seen superposed with the bisector of opposite pairs of I—Mo—I bond angles. The overall symmetry of the dinuclear complex, including noncrystallographic symmetry, is thus C_{2h}. The mirror plane of the chemical point group runs longitudinally through the two indenyl ligands and bisects the I—Mo—I angles. Neighboring molecules form weak but energetically favorable packing interactions. Each terminal indenyl group of one molecule is related by a crystallographic inversion center to an indenyl group of another molecule, in such a way that the two groups are almost eclipsed. The interplanar distance is 3.41 (1) Å, which is almost identical to the stacking distance in graphite (Pauling, 1960). This indicates a weak van der Waals attraction, which is

the most prominent packing interaction in the crystal. The lack of stronger packing interactions helps explain the poor quality of the crystals. The Mo—Mo distance of 2.720 (4) Å is consistent with a net Mo—Mo single bond, which would be expected from electron counting.

Fig. 1. Structure of bis(η^5-indenyl)tetrakis(μ-iodo)dimolybdenum, showing non-H atoms as 50% displacement ellipsoids. The H atoms are represented as circles of fixed radii and are numbered according to the numbers of the parent C atoms.

Experimental

The title compound was prepared in a two-stage synthetic procedure. In the first step, MoI$_3$(thf)$_3$, and sodium indenyl, NaC$_9$H$_7$, were reacted in thf to yield Na[(C$_9$H$_7$)MoI$_3$]. The latter was further reacted with tetraphenylphosphonium iodide, PPh$_4$I, in a mixture of thf and dichloromethane to give PPh$_4$[(C$_9$H$_7$)MoI$_3$]. From a dichloromethane solution of this compound, crystals of the title compound were obtained by cooling to 253 K.

Crystal data

[Mo$_2$(I)$_4$(C$_9$H$_7$)$_2$]
M_r = 929.77
Triclinic
$P\bar{1}$
a = 8.155 (13) Å
b = 8.546 (8) Å
c = 8.681 (11) Å
α = 102.47 (9)°
β = 117.42 (11)°
γ = 93.41 (11)°
V = 515.5 (12) Å^3
Z = 1
D_x = 2.995 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 16 reflections
θ = 10.0–14.8°
μ = 7.204 mm^{-1}
T = 291 (2) K
Poorly formed block
0.37 × 0.27 × 0.25 mm
Black

Data collection

Stoe Siemens AED four-circle diffractometer
ω–2θ scans
Absorption correction: empirical
T_{min} = 0.610, T_{max} = 1.000
1443 measured reflections
1356 independent reflections
994 observed reflections
[$I > 2\sigma(I)$]

R_{int} = 0.0242
θ_{max} = 22.49°
h = −8 → 7
k = −7 → 9
l = −7 → 9
1 standard reflection
frequency: 180 min
intensity decay: 15.6%

Refinement

Refinement on F^2
R = 0.0467
wR = 0.1010
S = 1.063
1356 reflections
109 parameters
H atoms treated as riding atoms, C—H 0.93 Å
$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 1.108 e Å^{-3}
$\Delta\rho_{min}$ = −1.039 e Å^{-3}
Extinction correction: none
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}
Mo1	−0.0410 (2)	0.1060 (2)	0.1130 (2)	0.0273 (4)
I1	−0.27753 (15)	0.03909 (14)	−0.26087 (15)	0.0443 (4)
I2	−0.19230 (15)	−0.22821 (13)	0.00659 (15)	0.0390 (4)
C1	−0.180 (2)	0.316 (2)	0.154 (2)	0.046 (5)
C2	−0.257 (2)	0.183 (2)	0.178 (2)	0.041 (4)
C3	−0.119 (3)	0.145 (2)	0.335 (2)	0.051 (5)
C4	0.044 (2)	0.271 (2)	0.407 (2)	0.042 (4)
C5	0.221 (3)	0.298 (2)	0.572 (2)	0.053 (5)
C6	0.345 (3)	0.435 (3)	0.614 (3)	0.068 (6)
C7	0.309 (3)	0.542 (2)	0.501 (3)	0.050 (5)
C8	0.148 (2)	0.513 (2)	0.346 (2)	0.039 (4)
C9	0.007 (2)	0.378 (2)	0.297 (2)	0.040 (4)

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

Mo1—C2	2.18 (2)	Mo1—Mo1^i	2.720 (4)
Mo1—C1	2.23 (2)	Mo1—I2^i	2.801 (4)
Mo1—C3	2.26 (2)	Mo1—I1	2.808 (5)
Mo1—C4	2.39 (2)	Mo1—I2	2.815 (4)
Mo1—C9	2.41 (2)	Mo1—I1^i	2.816 (5)
Mo1^i—Mo1—I2^i	61.29 (11)	Mo1^i—Mo1—I1^i	60.92 (13)
Mo1^i—Mo1—I1	61.24 (13)	I2^i—Mo1—I1^i	76.47 (12)
I2^i—Mo1—I1	76.66 (15)	I1—Mo1—I1^i	122.15 (11)
Mo1^i—Mo1—I2	60.77 (10)	I2—Mo1—I1^i	76.29 (14)
I2^i—Mo1—I2	122.05 (10)	Mo1—I1—Mo1^i	57.85 (11)
I1—Mo1—I2	76.38 (14)	Mo1^i—I2—Mo1	57.95 (10)

Symmetry code: (i) −x, −y, −z.

Normal data collection procedures were used. Data were scaled for an observed decay of *ca* 16% during data collection. Although the data were weak, and despite the poor peak shapes, the development and refinement of the structure proceeded routinely until the final refinement. Six of the seven H atoms were located initially in a difference map, and the remaining H atom, H8 (attached to C8 in Fig. 1), was placed at a calculated position. The positions of all H atoms were idealized after their initial placement. All H atoms were treated as riding atoms in the least-squares refinement. All non-H atoms were refined with anisotropic displacement parameters. C2 was restrained to isotropic-like behavior, *i.e.* six observational restraints were applied to the anisotropic displacement parameters so as to favor equality of the diagonal parameters and zero values for the off-diagonal elements. Each H atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent C atom. The final difference Fourier map showed higher than normal maximum peak and trough values, symptomatic of the quality of the crystal.

Data collection: *DIF4* (Stoe & Cie, 1988a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1988b). Program(s) used to solve structure: *SHELXS90* (Sheldrick, 1990).

Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL93*.

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Bis(triphenylphosphine)iminium Tetrachlorooxomolybdenum(V) at 150 K

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Abstract

In the title compound $[C_{36}H_{30}NP_2]^+.[MoOCl_4]^-$, the anions reside in hydrophobic channels formed by the cations and, unlike other salts of this anion, the compound is stable with respect to atmospheric hydrolysis.

Comment

In order to obtain mixed Mo–Bi oxo complexes to serve as models for catalytic activity during the Sohio process for the oxidation of propene to acrolein (Grasselli & Burrington, 1981), the compound $PPN^+.Et_3NH^+.[Cl_2(O)Mo(\mu_2-O)_2(O)MoCl_2]^{2-}$ (Blake, Limberg, Parsons & Downs, 1995), where PPN^+ is $[N(PPh_3)_2]^+$, was treated with $BiCl_3$ in CH_2Cl_2. Green crystals, obtained as a by-product of this reaction, were shown to be $PPN^+.[MoOCl_4]^-$, (I), by chemical analysis and IR and NMR spectroscopy.

(I)
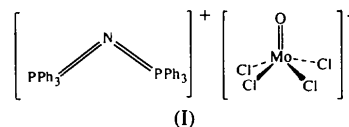
All known salts of the $[MoOCl_4]^-$ anion are unstable, both in non-aqueous solution and in the solid state, to the action of moist air and they readily take up one water molecule to give $[MoOCl_4(H_2O)]^-$ (*Gmelin Handbook of Inorganic Chemistry*, 1990). However, solid (I) proved to be completely stable in air, a fact which led us to investigate its structure in order to seek an explanation for this characteristic.

The structure of the $[MoOCl_4]^-$ anion in compound (I) (Fig. 1) is similar to those determined previously (*Gmelin Handbook of Inorganic Chemistry*, 1990) and most closely resembles that in $[AsPh_4]_2[MoOCl_4][MoOCl_4(CH_3CN)]$ (Weller, Müller, Weiher & Dehnicke, 1980). The strong Mo=O bond [1.646 (6) Å, bond order 2.5 (Schröder, 1975)] exerts a powerful *trans* influence which makes the formation of a trigonal-bipyramidal structure unfavourable and the $[MoOCl_4]^-$ anion universally adopts a square-pyramidal geometry. Repulsions between the closely bound O atom and the chloro ligands increase the O—Mo—Cl angles [109.6 (3), 108.4 (3), 101.8 (3) and 101.2 (3)° in compound (I)], which vary somewhat beyond the range (101–105°) defined as typical for oxo and nitrido complexes of the type $XMCl_4^-$ (X = N, O; M = Mo, Re, Ru, Os) (Dehnicke & Strähle, 1981). The metal atom lies 0.614 (2) Å from the mean plane of the four Cl atoms.

The distortion of the $[MoOCl_4]^-$ anion in (I) from C_{4v} symmetry is in contrast to the undistorted (though
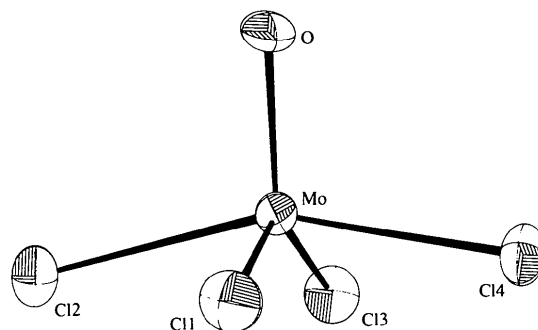

Fig. 1. The structure of the $[MoOCl_4]^-$ anion in compound (I). Displacement ellipsoids enclose 50% probability surfaces.