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Key indicators

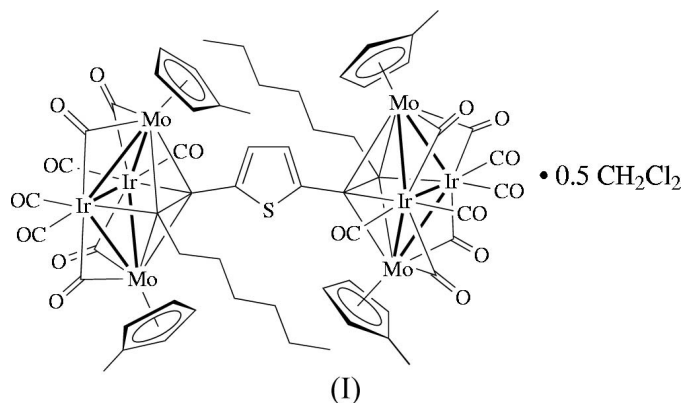
Single-crystal X-ray study
 $T = 473$ K
Mean $\sigma(\text{C}-\text{C}) = 0.011$ Å
Disorder in solvent or counterion
 R factor = 0.026
 wR factor = 0.034
Data-to-parameter ratio = 11.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>. **$[\mu_8-\eta^4-2,5\text{-Bis}(\text{oct-1-ynyl})\text{thiophene}]$ bis[octacarbonyl-
bis(η^5 -methylcyclopentadienyl)-*tetrahedro*-diiridium-
dimolybdenum] dichloromethane hemisolvate**The title compound, $[\text{Mo}_4\text{Ir}_4(\eta^5\text{-C}_6\text{H}_7)_4(\text{C}_{20}\text{H}_{28}\text{S})(\text{CO})_{16}] \cdot 0.5\text{CH}_2\text{Cl}_2$, is a mixed-metal dicluster compound in which the cluster modules are linked by a bridging 2,5-bis(oct-1-ynyl)thiophene ligand. The cluster units each have butterfly metal core geometries, with Mo atoms at the wing-tip sites and Ir atoms at the hinge positions.

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Comment

The alkyne chemistry of group 6-iridium mixed-metal clusters has attracted significant recent interest (Lucas *et al.*, 1997; Notaras *et al.*, 2001; Dalton *et al.*, 2004). The $\mu_4-\eta^2$ -coordination mode of the alkyne ligand at the $M_2\text{Ir}_2$ cluster cores ($M =$ group 6 metal) is very robust, and organic di- and triynes can be readily prepared; we have recently reported di- and tricluster compounds in which the individual clusters are linked by di- or triynes (Lucas, Notaras, Cifuentes & Humphrey, 2003; Lucas, Notaras, Petrie *et al.*, 2003; Notaras *et al.*, 2003). The title compound, (I), is an example of such a species, and it has now been structurally characterized.As expected, the alkyne units formally insert into the Mo–Mo bonds of the precursor tetrahedral cluster $\text{Mo}_2\text{Ir}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2$ to afford *closo*-octahedral $\text{Mo}_2\text{Ir}_2\text{C}_2$ cluster units bridged by a 2,5-disubstituted thiophenyl group (Fig. 1). The diyne ligand is $\mu_4-\eta^2$ -coordinated at each cluster, with the alkyne C–C bonds parallel to the Ir–Ir vectors, completing pseudo-octahedral $\text{Mo}_2\text{Ir}_2\text{C}_2$ units. The Mo atoms are each ligated by a methylcyclopentadienyl ligand, and the Ir atoms are each ligated by two terminal carbonyls, with the coordination completed by four bridging carbonyls, each of which lies across an Mo–Ir linkage. The $\text{Mo}_2\text{Ir}_2\text{C}_2$ core bond distances in (I) are essentially identical to those of the tungsten-containing analogue $[\text{W}_2\text{Ir}_2(\text{CO})_8(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]_2 \{\mu_8-\eta^4\text{-Me}(\text{CH}_2)_5\text{C}_2\text{-2-C}_4\text{H}_2\text{S-5-C}_2(\text{CH}_2)_5\text{Me}\}$

(Notaras *et al.*, 2003), with the exception of the Ir–Ir vectors, which are shorter in (I) [2.6960 (4) – 2.6963 (4) Å (*M* = Mo) versus 2.718 (1) – 2.7621 (9) Å (*M* = W)].

Experimental

The synthesis of (I) was carried out according to the procedure of Notaras *et al.* (2003). The crystal used in this study was grown by slow diffusion of a layer of methanol into a dichloromethane solution of (I) at 276 K.

Crystal data

[Mo₄Ir₄(C₆H₇)₄(C₂₀H₂₈S)·(CO)₁₆].0.5CH₂Cl₂
M_r = 2260.26
 Monoclinic, *P*2₁/*c*
a = 9.9141 (2) Å
b = 43.1674 (8) Å
c = 15.7682 (3) Å
 β = 104.6701 (5)°
V = 6528.3 (2) Å³
Z = 4

D_x = 2.300 Mg m⁻³
 Mo K α radiation
 Cell parameters from 138 312 reflections
 θ = 4.1–25.0°
 μ = 9.02 mm⁻¹
T = 473.2 K
 Block, red–brown
 0.18 × 0.11 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: by integration [Gaussian (Coppens, 1970) implemented in *maXus* (Mackay *et al.*, 1999)]
T_{min} = 0.315, *T_{max}* = 0.702
 73 643 measured reflections

11 612 independent reflections
 9300 reflections with *I* > 2 σ (*I*)
R_{int} = 0.057
 θ_{max} = 25.0°
h = –11 → 11
k = –50 → 51
l = –18 → 18

Refinement

Refinement on *F*²
R = 0.026
wR = 0.034
S = 1.00
 9300 reflections
 793 parameters

H-atom parameters constrained
w = 1/[$\sigma^2(F_o) + 0.0001|F_o|^2$]
 $(\Delta/\sigma)_{max}$ = 0.013
 $\Delta\rho_{max}$ = 1.63 e Å⁻³
 $\Delta\rho_{min}$ = –1.07 e Å⁻³

Table 1

Selected bond lengths (Å).

Ir11–Ir12	2.6963 (4)	Ir21–Ir22	2.6960 (4)
Ir11–Mo11	2.8027 (7)	Ir21–Mo21	2.8307 (6)
Ir11–Mo12	2.8223 (6)	Ir21–Mo22	2.8039 (6)
Ir12–Mo11	2.8386 (7)	Ir22–Mo21	2.8161 (6)
Ir12–Mo12	2.8054 (6)	Ir22–Mo22	2.8152 (6)

H atoms were placed in idealized positions [C–H = 0.95 Å and *U_{iso}*(H) = 1.2*U_{eq}*(C)], which were frequently recalculated. Residual electron density in the region of space adjacent to the cluster molecule was attributed to the dichloromethane solvent, which refined initially to an occupancy of *ca* 0.75. To circumvent a short contact between the C atoms of the solvent and its inversion image (2.74 Å), the occupancy was reduced to 0.5 as a more reasonable disorder model. Restraints were imposed on the bonding distances and angle of the disordered dichloromethane molecule. Atom C121, at the terminus of a hexyl chain and adjacent to the disordered solvent molecule, exhibits rather large anisotropy, although not sufficiently large to warrant modelling over multiple sites. The largest residual peaks were found close to the cluster core metal atoms.

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *DIRDIF92* *PATY* (Beurskens *et al.*, 1992); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1997); software used to prepare material for publication: *TEXSAN*.

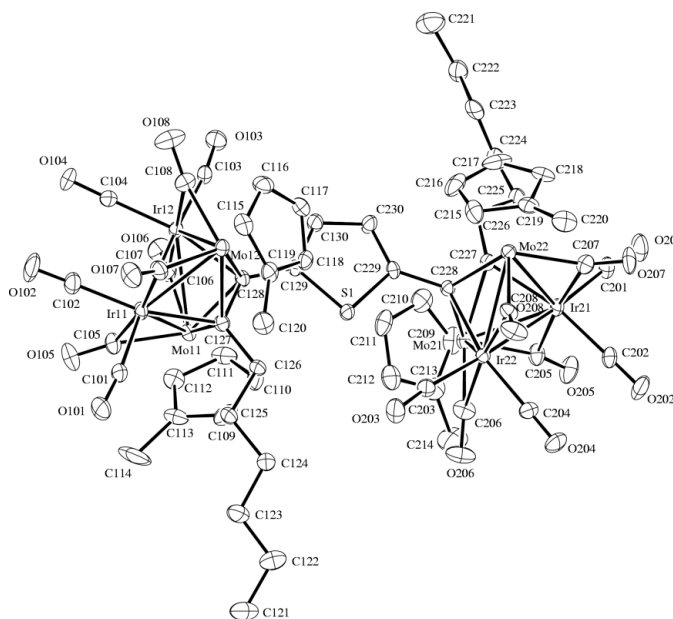


Figure 1

A view of (I), with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level. H atoms have been omitted for clarity.

al., 1992); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1997); software used to prepare material for publication: *TEXSAN*.

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