

**(η^5 -Cyclopentadienyl)(*N,N*-dimethyl-
dithiocarbamato- κ^2 S,S')[η^4 -tetrakis-
(trifluoromethyl)cyclobutadienyl]-
molybdenum(IV)**

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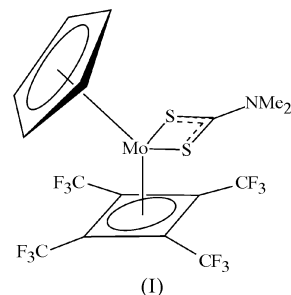
The title complex, [Mo(C₈F₁₂)(C₅H₅)(C₃H₆NS₂)], contains both a η^4 -C₄(CF₃)₄ cyclobutadienyl ligand with approximate C_{4v} local symmetry and a η^5 -C₅H₅ cyclopentadienyl ring. The centroids of the rings and the S atoms of a chelating dithiocarbamate ligand define the pseudo-tetrahedral coordination of the Mo atom. The Mo—C(cyclobutadienyl) bond lengths [2.189 (2)–2.211 (2) Å] are unusually short, probably reflecting strong electron withdrawal by the trifluoromethyl groups. The molecules straddle crystallographic mirror planes.

Comment

Complexes with η^4 -C₄R₄ cyclobutadienyl ligands are known for many transition metals. For example, nine structures containing the (η^4 -C₄R₄)Mo moiety occur in the Cambridge Structural Database (CSD; Version 5.25 of November 2003; Allen, 2002) (structural searches were carried out locally using the *QUEST* and *CONQUEST* search programs). In most of these compounds, R = Ph (CSD refcodes GICGUU10, LUJZOF, LUKBAU, LUJZUL, PABPMO, PCBMOC10 and TPCBMO), but an R = *p*-CH₃C₆H₄ complex (GIQTIJ) and a C₄Ph₃Me species (COXVIU) have also been characterized (see supplementary data for a list of references). We now describe the structure of the title compound, CpCbMo-(S₂CNMe₂), (I), where Cp = η^5 -C₅H₅ and Cb = η^4 -C₄(CF₃)₄. Compound (I) is the first structural example of a η^4 -C₄(CF₃)₄ complex of any transition metal.

Molecules of (I) have exact C_s symmetry; atoms Mo1, N1, C1, C3, C8–C11, F4 and F7 all lie on a crystallographic mirror plane in space group P2₁m (Fig. 1). The metal coordination is pseudo-tetrahedral, being defined by Cp—Mo—Cb and S—Mo—Sⁱ angles of 136.6 (2) and 70.0 (1)° (here Cp and Cb are the centroids of the C₅ and C₄ rings; symmetry code as in Table 1). The bonding in pseudo-tetrahedral CpCbMoL₂ species such as (I) has been reviewed by Curnow *et al.* (1993),

who argue that the Cb ligand is best considered as a dianionic C₄R₄²⁻ six-electron donor isoelectronic with Cp⁻, making (I) a d² Mo^{IV} complex. The metal lone pair in such complexes occupies a stereochemically active d_{z²}-like orbital, compressing the L—M—L angle. Thus, the Cl—Mo—Cl angle in Cp₂MoCl₂ (Prout *et al.*, 1974) is 82°, only 12° less acute than the S—Mo—Sⁱ angle in (I).



The Mo—S distance in (I) (Table 1) differs by only 0.002 (1) Å from the comparable mean of 2.472 Å in the isoelectronic Mo^{IV} cation [Mo(η^5 -In)₂(S₂CNET₂)]⁺ (In is indenyl; Drew *et al.*, 1998). The Mo—C(Cp) bond lengths are also unexceptional and the displacement of the Mo atom from the Cp plane [2.012 (1) Å] is close to the average of 2.008 (1) Å for all CpMo compounds in the CSD. However, (i) variations in Cp ring C—C distances and angles [1.338 (9)–1.391 (4) Å and 105.9 (4)–109.2 (2)°] and (ii) U_{eq} values of Cp ring C atoms nearly three times that of the Mo atom both suggest substantial libration, possibly even some disorder, of the ring about the Mo—Cp vector.

The Cb ligand deviates only slightly from C_{4v} symmetry. Thus, the ring C—C bond lengths differ by only 0.013 (4) Å. Atoms C7, C9 and C11 are displaced by 0.340 (2), 0.562 (4) and 0.504 (3) Å, respectively, to the opposite side of the C₄ ring plane from the Mo atom, probably to relieve intraligand repulsions. Rotation of the C7F₃ group from its ideal position by ca 8° is shown by F1—C7—C6—C8 and F1—C7—C6—C10 torsion angles of 84.1 (3) and –67.6 (3)°, respectively. The near equality of the U_{eq} values for the Mo and the Cb ring C atoms is consistent with the high barrier to libration about the

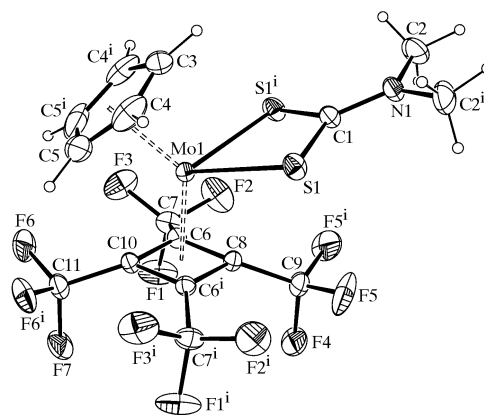


Figure 1

A view of the molecule of (I), showing 20% probability displacement ellipsoids. [Symmetry code: (i) $x, -y + \frac{1}{2}, z$.]

Mo—Cb vector suggested by spectroscopic evidence (Davidson, 1987).

In other (η^4 -C₄R₄)Mo complexes the ring C—C bond lengths usually show little variation and their average value of 1.462 (2) Å agrees well with the individual values in (I). In contrast, the ring C—C bond lengths in C₄R₄ molecules indicate fixed double and single bonds (Irmgartinger *et al.*, 1988, and references therein).

The Mo—C(Cb) bond lengths in (I) vary slightly and are on average 0.08 Å shorter than the mean value of 2.284 (7) Å for other (η^4 -C₄R₄)Mo complexes (where R = Me, Ph, *etc.*). The displacement of the Mo atom from the Cb ring plane in (I) [1.944 (1) Å] is likewise less than the range of 1.995–2.074 Å found in other MoCb complexes.

Curnow *et al.* (1993) substantiate their view of Cb as a C₄R₄²⁻ dianionic ligand from extended Hückel molecular-orbital (EHMO) calculations, which show that in CpCbMoL₂ species much more charge is transferred from Mo to Cb than to Cp. Electron-withdrawing CF₃ substituents on the Cb C atoms might be expected to facilitate this transfer and thus to produce the very strong Mo—Cb π bonds found in (I).

Experimental

The preparation and spectroscopic characterization of (I) have been described by Davidson (1987).

Crystal data

[Mo(C ₈ F ₁₂)(C ₅ H ₅)(C ₃ H ₆ NS ₂)]	$D_x = 1.965 \text{ Mg m}^{-3}$
$M_r = 605.32$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/m$	Cell parameters from 25 reflections
$a = 8.918 (1) \text{ \AA}$	$\theta = 8.9\text{--}14.6^\circ$
$b = 12.185 (1) \text{ \AA}$	$\mu = 0.96 \text{ mm}^{-1}$
$c = 9.809 (2) \text{ \AA}$	$T = 295 \text{ K}$
$\beta = 106.28 (1)^\circ$	Prism, yellow
$V = 1023.2 (3) \text{ \AA}^3$	$0.54 \times 0.45 \times 0.28 \text{ mm}$
$Z = 2$	

Data collection

Enraf–Nonius CAD-4 diffractometer	2761 reflections with $I > 2\sigma(I)$
Non-profiled ω scans	$R_{\text{int}} = 0.020$
Absorption correction: Gaussian (ABSORB; Mallinson & Muir, 1985)	$\theta_{\text{max}} = 30.0^\circ$
$T_{\text{min}} = 0.730$, $T_{\text{max}} = 0.800$	$h = -12 \rightarrow 12$
5153 measured reflections	$k = 0 \rightarrow 17$
3025 independent reflections	$l = -13 \rightarrow 13$
	2 standard reflections
	frequency: 120 min
	intensity decay: 0%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.018P)^2 + 0.018P]$
$R[F^2 > 2\sigma(F^2)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.069$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
3025 reflections	$\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$
162 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.0188 (13)

Table 1

Selected geometric parameters (Å, °).

Mo1—C3	2.309 (3)	Mo1—S1	2.4697 (5)
Mo1—C4	2.324 (2)	C6—C10	1.448 (2)
Mo1—C5	2.324 (2)	C6—C8	1.461 (2)
Mo1—C6	2.198 (2)	C6—C7	1.476 (3)
Mo1—C8	2.189 (2)	C8—C9	1.480 (3)
Mo1—C10	2.211 (2)	C10—C11	1.490 (4)
C10—C6—C8	88.85 (13)	C6—C10—C6 ⁱ	91.67 (19)
C6—C8—C6 ⁱ	90.61 (18)		
C10—C6—C8—C6 ⁱ	−1.0 (2)		

Symmetry code: (i) $x, -y + \frac{1}{2}, z$.

The structure was solved by Patterson and Fourier methods. H atoms were located initially in difference maps. In the final refinement, the positions of the H atoms were determined by the HFIX instruction in SHELXL97 (Sheldrick, 1997) and they were then treated as riding on their parent C atoms [cyclopentadienyl C—H = 0.93 Å, methyl C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.3U_{\text{eq}}(\text{C})$]. A single parameter defining the orientation of the CH₃ group about the N—C bond was refined freely.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994); cell refinement: CAD-4 EXPRESS; data reduction: GX (Mallinson & Muir, 1985); program(s) used to solve structure: GX; program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1377). Services for accessing these data are described at the back of the journal.

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