π-backbonding $[d\pi(Ru) \rightarrow \pi^*(azo)]$ power of the azo function is very considerable, making the net $(\sigma + \pi)$ bond order larger in Ru—N(azo) compared to Ru—N(py). The relatively longer N—N distance [1·28–1·31 Å, compared, for example, to 1·257 (2) and 1·254 (2) Å in the structure of 1-phenylazoacetaldehyde oxime (Roy & Sengupta, 1980)] is in full accord with the π-backbonding hypothesis. Certain chemical, electrochemical and spectroscopic data also indirectly suggested the presence of this kind of bonding (Krause & Krause, 1982; Goswami, Chakravarty & Chakravorty, 1983).

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Bis(*tert*-butylthio)bis(η^5-cyclopentadienyl)molybdenum(IV), $[Mo(C_5H_5)_2(C_4H_9S)_2]$

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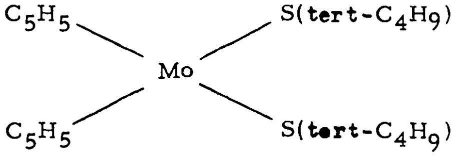
Abstract. $M_r = 404{\cdot}48$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}3424\ (8)$, $b = 13{\cdot}461\ (1)$, $c = 14{\cdot}884\ (1)$ Å, $V = 1871{\cdot}78$ Å^3, $Z = 4$, $D_x = 1{\cdot}43$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 77{\cdot}89$ cm^{-1}, $F(000) = 840$, $T = 298$ K. Final $R(F) = 0{\cdot}035$ for 1870 observed reflections. The Mo coordination is a distorted tetrahedron formed by the two S atoms of the *tert*-butylthio ligands and the ring normals to the cyclopentadienyl rings. These adopt an eclipsed orientation, giving the molecule an approximate C_{2v} symmetry. The Mo atom is at an average distance from the cyclopentadienyl rings of 2·006 (7) Å and the angle between the ring normals is 130·4 (3)°. The Mo—S bond lengths are 2·501 (1) and 2·491 (1) Å and the S—Mo—S bond angle is 71·1 (1)°.

Introduction. The structure analysis of (I) is a continuation of the investigation of complexes of the type $[M(\eta^5\text{-}C_5H_5)_2LL']$. The structure of the $[Ti(\eta^5\text{-}C_5H_5)_2(SCH_3)_2]$ complex was previously reported by Carrondo & Jeffrey (1983).



(I)

Experimental. $[Mo(\eta^5\text{-}C_5H_5)_2\{S(tert\text{-}C_4H_9)\}_2]$ prepared by Clementina Teixeira, Centro de Química Estrutural (Dias, Martinho Simões & Teixeira, 1981). D_m estimated by flotation but not measured. Laue symmetry and systematic absences consistent with $P2_12_12_1$, crystal $0{\cdot}28 \times 0{\cdot}13 \times 0{\cdot}067$ mm used to collect 1948 *hkl* intensities (range of *hkl*: *h* 0→11, *k* 0→16, *l* 0→17), 75 with $F_o < 3\sigma(F_o)$, θ–2θ scans, $\theta_{\max} = 66°$, CAD-4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Unit-cell parameters refined from 37 reflections, $40 < \theta < 48°$. $30\bar{3}$, 204, 040 used as standards, intensities showed no decay throughout data collection. Mo-atom position from

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sharpened Patterson synthesis map, S- and C-atom positions from subsequent difference Fourier synthesis. Full-matrix least-squares refinement, isotropic temperature factors, gave $R = 0{\cdot}104$. Absorption corrections (transmission coefficients = 0·2837–0·6180), anisotropic refinement reduced R to 0·047 using *SHELX* (Sheldrick, 1976). H atoms included at positions calculated by *SHELX*, fixed trigonal planar angles (cyclopentadienyl) or tetrahedral angles (methyl), C—H distance 1·08 Å. Temperature factors fixed for six H atoms, remaining 22 refined isotropically, four different groups with same $U_{\rm iso}$. Weighting scheme, $w = K/[\sigma^2(F_o) + |g|F_o^2]$, refined to $K = 0{\cdot}8018$, $g = 0{\cdot}00202$. Three strong reflections (101, 012, 002) thought to be suffering from extinction removed from the data. Final refinement gave $R(F) = 0{\cdot}038$, $R_w(F) = 0{\cdot}058$; with omitted strong reflections, $R(F) = 0{\cdot}035$, $R_w(F) = 0{\cdot}050$. Final difference map with no peaks of magnitude greater than 0·37 e Å^{-3}, max. shift/error = 0·09. Atomic scattering factors for Mo, S, C from Doyle & Turner (1968), for H from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections (f', f'') for Mo from Cromer & Liberman (1970). Drawings made with *ORTEP*II (Johnson, 1976).

Discussion. Final atomic parameters for the non-H atoms are given in Table 1.*

The crystal structure of [Mo(η^5-C_5H_5)$_2${S(*tert*-C_4H_9)}$_2$] contains four discrete molecules of (I) with the conformation shown in Fig. 1 in space group $P2_12_12_1$. The metal atom is coordinated to two η^5-cyclopentadienyl rings and to the S atoms of two *tert*-butylthio ligands. The coordination geometry of the ring normals and the S atoms about the central Mo atom is a distorted tetrahedron. The projection onto the Mo,S(1),S(2) plane in Fig. 2 shows that the planar cyclopentadienyl rings have a nearly eclipsed orientation, giving the molecule an approximate C_{2v} symmetry.

The Mo atom is 2·014 (7) and 1·998 (7) Å from the best least-squares planes of the two cyclopentadienyl rings. The angle between the ring normals is 130·4 (3)°. The Mo—S bond lengths and the S—Mo—S angle are compared in Table 2 with the values observed in similar [Mo(η^5-C_5H_5)$_2LL'$] complexes. The Mo(η^5-C_5H_5)$_2$ moiety in this structure has the longest Mo—S bond length and the most acute S—Mo—S values hitherto reported.

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2)

E.s.d.'s given in parentheses refer to the least significant digit. The equivalent isotropic mean-square coefficient is

$$B_{\rm eq} = \tfrac{8}{3}\pi^2(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$B_{\rm eq}$
Mo	679·0 (4)	545·9 (3)	2428·3 (2)	2·95
S(1)	2100 (1)	2104 (1)	2632 (1)	4·23
S(2)	−297 (2)	1853 (1)	1414 (1)	3·70
C(11)	786 (10)	−623 (6)	1297 (6)	7·04
C(12)	1746 (9)	108 (5)	1040 (5)	6·05
C(13)	2834 (8)	151 (6)	1646 (6)	6·34
C(14)	2593 (10)	−559 (7)	2329 (6)	7·14
C(15)	1346 (13)	−1059 (7)	2091 (7)	7·82
C(21)	−387 (9)	1215 (5)	3722 (5)	5·40
C(22)	359 (9)	357 (6)	3949 (4)	5·96
C(23)	−369 (9)	−442 (4)	3496 (5)	5·34
C(24)	−1490 (9)	−24 (6)	2989 (5)	6·32
C(25)	−1513 (8)	991 (6)	3152 (5)	6·00
C(1)	3468 (7)	2159 (6)	3531 (5)	6·05
C(1*t*1)	4302 (11)	1188 (7)	3631 (8)	8·83
C(1*t*2)	4449 (13)	2994 (9)	3285 (9)	13·42
C(1*t*3)	2803 (15)	2392 (13)	4428 (6)	11·50
C(2)	−1702 (7)	1566 (6)	580 (5)	5·76
C(2*t*1)	−2178 (14)	2576 (9)	247 (7)	10·26
C(2*t*2)	−2932 (11)	986 (11)	949 (8)	12·59
C(2*t*3)	−1077 (13)	1045 (11)	−231 (6)	11·71

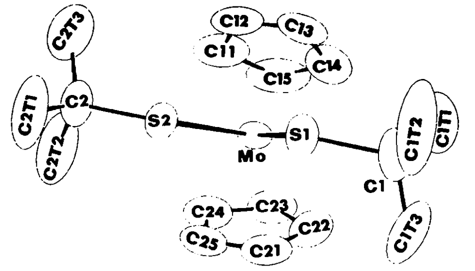

Fig. 1. Atomic notation and thermal ellipsoids for [Mo(η^5-C_5H_5)$_2${S(*tert*-C_4H_9)}$_2$].

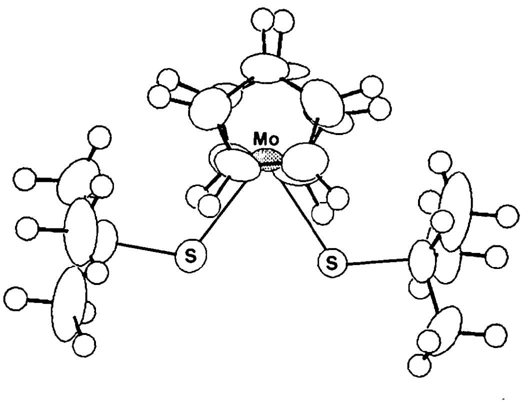

Fig. 2. View of the structure of [Mo(η^5-C_5H_5)$_2${S(*tert*-C_4H_9)}$_2$] showing the almost eclipsed orientation of the cyclopentadienyl rings.

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* Tables of selected bond lengths and angles, atomic coordinates of the H atoms, anisotropic thermal parameters for the non-H atoms, equations of some planes, and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39216 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Comparison of the* Mo *coordination geometry in various* $[\mathrm{Mo}(\eta^5\text{-C}_5\mathrm{H}_5)_2LL']$ *complexes*

	Mo—S (Å)	S—Mo—S (°)	Mo—Cp[a] (Å)	Cp—Mo—Cp[b] (°)	Reference
$[\mathrm{Mo}(\eta^5\text{-C}_5\mathrm{H}_5)_2\{\mathrm{S}(tert\text{-C}_4\mathrm{H}_9)\}_2]$	2·501 (1) 2·491 (1)	71·1 (1)	2·041 (7) 1·998 (7)	130·4 (3)	This work
$[\mathrm{Mo}(\eta^5\text{-C}_5\mathrm{H}_5)_2\mathrm{S}_4]$	2·450 2·456	88·2	1·997 2·002	134·2	Block & Allmann (1975)
$[\mathrm{Mo}(\eta^5\text{-C}_5\mathrm{H}_5)_2(\mathrm{S}_2\mathrm{C}_6\mathrm{H}_3\mathrm{CH}_3)]$	2·434 (5) 2·431 (5)	82·4 (2)	1·999 1·993	132·5	Knox & Prout (1969*a*)
$[\mathrm{Mo}(\eta^5\text{-C}_5\mathrm{H}_5)_2(\mathrm{S}_2\mathrm{C}_6\mathrm{H}_4)]$	2·437 (3) 2·437 (3)	81·9	2·01 2·02	138	Kutoglu & Kopf (1970)
$[\mathrm{Mo}(\eta^5\text{-C}_5\mathrm{H}_5)_2\{\mathrm{S}(\mathrm{CH}_2)_2\mathrm{NH}_2\}]\mathrm{I}$	2·438 (6)		1·976 2·002	130·9	Knox & Prout (1969*b*)
$\mathrm{H}[\mathrm{Mo}(\eta^5\text{-C}_5\mathrm{H}_5)_2\{\mathrm{NH}_2\mathrm{CH}(\mathrm{CH}_2\mathrm{S})\mathrm{COO}\}]_2\mathrm{Cl}$	2·446 (2)		1·981 1·980	133·7	Prout, Allison, Delbaere & Gore (1972)
$\mathrm{H}[\mathrm{Mo}(\eta^5\text{-C}_5\mathrm{H}_5)_2\{\mathrm{NH}_2\mathrm{CH}(\mathrm{CH}_2\mathrm{S})\mathrm{COO}\}]_2\mathrm{PF}_6$	2·47 (1)		2·01 2·00	130	Prout *et al.* (1972)

(*a*) Mo—ring-normals' lengths.
(*b*) Angle between the ring normals at the Mo atom.

A theoretical molecular-orbital-model calculation for bent $[M\mathrm{Cp}_2L_n]$ complexes (Lauher & Hoffmann, 1976) predicts an L—M—L angle of ~78° for d^n complexes when $n = 2$. Experimental values of 76–82° in d^2 complexes are reported by Prout, Cameron, Forder, Critchley, Denton & Rees (1974). The observed value of 71·1 (1)° in (I) is comparable to the values observed in binuclear complexes where the ligands L are bridging two metal atoms as in $[\{\mathrm{Mo}(\eta^5\text{-C}_5\mathrm{H}_5)_2(\mathrm{SCH}_3)_2\}_2\mathrm{Ni}](\mathrm{BF}_4)_2$ where S—Mo—S = 70·3 (1)° (Prout, Critchley & Rees, 1974), and $[\mathrm{Mo}(\eta^5\text{-C}_5\mathrm{H}_5)_2\{\mathrm{S}(n\text{-Bu})\}_2\mathrm{FeCl}_2]$ where S—Mo—S = 72·6 (1)° (Cameron & Prout, 1972).

The longer than usual Mo—S bonds and more acute S—Mo—S angle in (I) are qualitatively consistent with steric effects arising from the large $\mathrm{S}(tert\text{-C}_4\mathrm{H}_9)$ ligands, which will tend to increase the Mo—S distance. Similarly, limitations on the available van der Waals space between the cyclopentadienyl rings and the $\mathrm{S}(tert\text{-C}_4\mathrm{H}_9)$ ligands will force a smaller angle at the Mo atom.

The cyclopentadienyl C atoms are coplanar with a maximum deviation from the best least-squares planes of 0·018 (5) Å for Cp_1 and 0·016 (5) Å for Cp_2 and r.m.s deviations of 0·013 (5) Å for Cp_1 and 0·011 (5) Å for Cp_2. The details of these planes have been deposited.* The angle between the plane defined by the ring normals and Mo,S(1),S(2) is 90·6 (2)°, which is normal for this type of complex (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). The intermolecular contacts are normal, with two exceptions: S(2)···H(23) $(1 - x, -\tfrac{1}{2} + y, \tfrac{1}{2} - z) = 2{\cdot}62\ (5)$ Å, and S(2)···H(15) $(1 - x, -\tfrac{1}{2} + y, \tfrac{1}{2} - z) = 2{\cdot}66\ (5)$ Å.

The Mo—C distances range from 2·291 (6) Å for Mo—C(23) to 2·390 (7) Å for Mo—C(25), with a mean value of 2·344 Å. The C—C values in the cyclopentadienyl rings range from 1·359 (11) Å for C(12)—C(13) to 1·440 (10) Å for C(22)—C(23), with a mean value of 1·40 Å. The C—C values in the *tert*-butyl groups range from 1·494 (12) Å for C(2)—C(2*t*2) to 1·528 (11) Å for C(1)—C(1*t*1), with a mean value of 1·509 Å. The S(1)—C(1) and S(2)—C(2) bond lengths are 1·851 (7) and 1·846 (6) Å respectively. Details of these bond lengths and the values for the bond angles have been deposited.*

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* See previous footnote.

* See deposition footnote.

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