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Cycloheptatrienylmolybdenum Complexes. Part 3 [1]. Reaction of the Cation [Mo(acac)(H_2O)(η^7-C_7H_7)]$^+$ with Halide and Thiocyanate Anions; Molecular and Crystal Structure of [Mo(acac)(NCS)(η^7-C_7H_7)]

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The complex [Mo(acac)(H_2O)(η^7-C_7H_7)]BF_4 reacts with anionic nucleophiles to form neutral seventeen-electron paramagnetic compounds [Mo(acac)X(η^7-C_7H_7)] (X = Cl, Br, I or NCS). Crystals of the thiocyanic derivative are monoclinic, space group $P2_1/a$, *with* a = *12.762(2),* b = *12.634(4) and* c = *8.813(3)* Å, *β = 100.70(2)°; 2788 data ⩾ 1.0σ have been employed to solve and refine the structure to a conventional* R = *0.069. The molecule is almost identical with that of the cation [Mo(acac)(H_2O)(η^7-C_7H_7)]$^+$ with a non-linear N-bonded thiocyanate function replacing the water molecule at Mo–N 2.122(10)* Å.

Introduction

Earlier we reported [1] the complex [Mo(acac)(H_2O)(η^7-C_7H_7)]BF_4 (I), a useful precursor for the synthesis of other cycloheptatrienylmolybdenum species. In studies aimed at extending our knowledge [2–7] of reactions of nucleophiles with η^7-cycloheptatrienylmolybdenum complexes we herein report products obtained by treating the aquo complex with the anions Cl^-, Br^-, I^- and SCN^- [8].

Results and Discussion

Halide ions react with an acetone solution of (I) to give neutral complexes [Mo(acac)X(η^7-C_7H_7)] (II, X = Cl, Br or I) in high yield. These complexes have similar spectroscopic properties to the aquo cation [1] and presumably have a similar structure. Thus the i.r. spectra show bands from 1600–1500 cm^{-1} which can be assigned to the acetylacetonate ligand, and bands near 3050 and 800 cm^{-1} due to the η^7-C_7H_7 group. There is no evidence of a coordinated aquo group in the complexes. The ^{1}H n.m.r. spectra show broad peaks near τ 8.00 assignable to the methyl groups of the acetylacetonate ligand. The e.s.r. spectra show patterns very similar to that of (I) and have analogous g-values (~1.95), consistent with one unpaired electron.

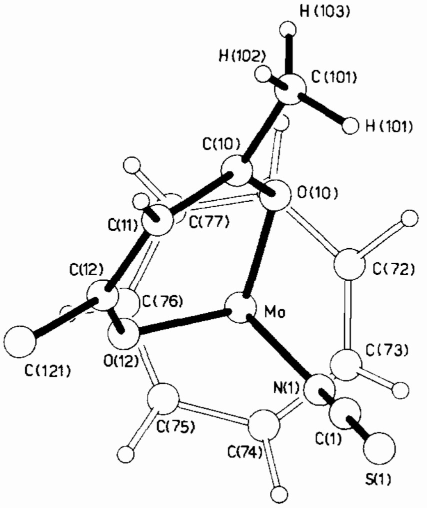

Figure 1. The molecule [Mo(acac)(NCS)(η^7-C_7H_7)] (III) in projection onto the C_7 ring.

Complex (I) also reacts with thiocyanate anion to afford the neutral complex [Mo(acac)(NCS)(η^7-C_7H_7)] (III). The i.r. spectrum of (III) shows a strong band at 2090 cm^{-1} which can be assigned to the coordinated NCS ligand. Other spectroscopic properties are analogous to those of the compounds (II). However, the ν_{max}(CN) at 2090 cm^{-1} can be assigned [9] to a complex where the NCS ligand is either nitrogen- or sulphur-bonded to the molybdenum atom and for this reason a single crystal X-ray diffraction study was carried out.

The molecular structure projected onto the plane defined by the carbon atoms of the η^7-ring is shown in Figure 1. In the solid state individual molecules possess slight asymmetry such that, for the view chosen, the central acetylacetonate carbon, C(11), lies to one side of the nearest cycloheptatriene atom, C(77). The molecular enantiomorph and atomic numbering scheme given in Figure 1 were selected to most closely resemble that already defined [1] for the cation of (I). Once again the ring hydrogens are numerically equivalent to their attendant carbon atoms.

TABLE I. Bond Lengths (Å) for Complex (III)^a.

Mo–C(71)	2.240 (9)	N(1)–C(1)	1.166 (14)
Mo–C(72)	2.246 (13)	C(1)–S(1)	1.599 (10)
Mo–C(73)	2.286 (11)		
Mo–C(74)	2.286 (11)	O(10)–C(10)	1.286 (11)
Mo–C(75)	2.263 (8)	C(10)–C(101)	1.502 (15)
Mo–C(76)	2.249 (10)	C(101)–H(101)	1.02 (15)
Mo–C(77)	2.298 (10)	C(101)–H(102)	0.82 (17)
Mo–N(1)	2.122 (10)	C(101)–H(103)	0.88 (17)
Mo–O(10)	2.086 (5)	C(10)–C(11)	1.376 (16)
Mo–O(12)	2.098 (7)	C(11)–H(11)	0.91 (9)
		C(11)–C(12)	1.394 (13)
C(71)–C(72)	1.411 (16)	C(12)–C(121)	1.497 (16)
C(72)–C(73)	1.378 (16)	C(12)–O(12)	1.269 (11)
C(73)–C(74)	1.401 (16)		
C(74)–C(75)	1.411 (16)	C(71)–H(71)	0.92 (6)
C(75)–C(76)	1.426 (15)	C(72)–H(72)	0.97 (8)
C(76)–C(77)	1.435 (15)	C(73)–H(73)	1.03 (14)
C(77)–C(71)	1.371 (15)	C(74)–H(74)	1.04 (10)
		C(75)–H(75)	0.99 (14)
		C(76)–H(76)	0.81 (9)
		C(77)–H(77)	1.07 (12)

^{a}Uncorrected for thermal effects.

Bond distances and inter-bond angles are given in Tables I and II, respectively. Several features of the molecular structure of (III) are shared by (I) and will, therefore, be mentioned only briefly. Thus, for the cycloheptatriene ring the C–C lengths {1.371(15) to 1.435(15) Å; mean 1.405(24)* Å} and C–C–C angles {123.9(9)–131.4(9)°; mean 128.6(28)°} compare favourably, and again define a regular heptagon, planar to within 0.01 Å. The molybdenum atom is situated 1.587 Å above the C_7 ring (in projection less than 0.02 Å from its centre) resulting in Mo–C distances from 2.240(9) to 2.298(10) Å [mean 2.267-(23) Å].

All internuclear separations and bond angles described by the [Mo(acac)] moiety agree well with their counterpart in (I). The Mo–O distances of 2.086(5) and 2.098(7) Å are complemented by an O····O bite of 2.795(9) Å.

The diffraction study clearly establishes that the thiocyanate function is N-bonded to the metal and tends to support our previous work [1], and that of Hackett and Jaouen [6] where attack by the anionic nucleophiles Cl^-, Br^- or I^- on $[Mo(CO)_3(\eta^7\text{-}C_7H_7)]\cdot BF_4$ occurs at the metal rather than at the η^7-cycloheptatrienyl ring, thus suggesting that the metal is the more electrophilic centre. In contrast, it has been reported [10] that methoxide attacks the ring in $[Mo(CO)_3(\eta^7\text{-}C_7H_7)]BF_4$ rather than the metal.

The distance Mo–N(1) [2.122(10) Å] is 3.4σ longer than the weighted mean of 2.088 Å in $[Mo(NCS)_6]^{3-}$ [11] and is consistent, therefore, with a formal oxidation state of +1 for the metal in the present molecule. Comparison with the corresponding distances of 2.117(7) and 2.146(9) Å, respectively, in $[Mo(NCS)(CO)_2(C_{10}H_8N_2)(\eta^3\text{-}C_3H_5)]$ [12] and $[Mo(NCS)(CO)_2(C_{12}H_8N_2)(\eta^3\text{-}C_4H_7)]$ [13] appears warranted, but is more hazardous since consideration of these molecules requires formal increase in both oxidation state and co-ordination number. Such changes, however, would vary the metal covalent

TABLE II. Bond Angles (°) for Complex (III)^a.

Molybdenum Co-ordination		*Acac Ligand*	
N(1)–Mo–O(10)	80.8 (3)	Mo–O(10)–C(10)	130.6 (6)
N(1)–Mo–O(12)	82.0 (3)	O(10)–C(10)–C(11)	123.4 (8)
O(10)–Mo–O(12)	83.8 (2)	O(10)–C(10)–C(101)	113.9 (10)
C(71)–Mo–C(72)	36.7 (4)	C(11)–C(10)–C(101)	122.6 (10)
C(72)–Mo–C(73)	35.4 (4)	C(10)–C(11)–C(12)	127.7 (9)
C(73)–Mo–C(74)	35.7 (4)	C(11)–C(12)–O(12)	122.6 (9)
C(74)–Mo–C(75)	36.1 (4)	C(11)–C(12)–C(121)	122.0 (9)
C(75)–Mo–C(76)	36.8 (4)	O(12)–C(12)–C(121)	115.4 (8)
C(76)–Mo–C(77)	36.8 (4)	C(12)–O(12)–Mo	131.3 (6)
C(77)–Mo–C(71)	35.1 (4)		
		Cycloheptatrienyl Ligand	
NCS Ligand		C(77)–C(71)–C(72)	131.0 (9)
Mo–N(1)–C(1)	157.1 (7)	C(71)–C(72)–C(73)	130.7 (11)
N(1)–C(1)–S(1)	178.9 (8)	C(72)–C(73)–C(74)	126.9 (11)
		C(73)–C(74)–C(75)	129.3 (10)
		C(74)–C(75)–C(76)	126.7 (9)
		C(75)–C(76)–C(77)	131.4 (9)
		C(76)–C(77)–C(71)	123.9 (9)

^{a}Hydrogen atom data is given in Appendix A.

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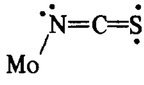
*σ_{mean} from $\sigma^2_{mean} = \{\sum_{i=1}^{N}(x_i - \bar{x})^2\}/(N - 1)$ where x_i is the ith and $\bar{x}$ the mean of N similar types.

radius in opposite senses and thus may have little net effect. The only other reported molybdenum N-thiocyanate structure is that of the anion $[Mo_2(\mu\text{-}O)_2(\mu\text{-}acac)(NCS)_4(O)_2]^{3-}$ [14]. Here the mean Mo–N separation of 2.136(9) Å appears long for Mo(V) and probably reflects their positions *trans* to Mo–O bonds of formal order 1.5.

In $[Mo(acac)(NCS)(\eta^7\text{-}C_7H_7)]$ the MoNCS sequence kinks [157.1(7)°] at N, towards the acetylacetonate ligand. Such a deviation from linearity is uncommon amongst N-co-ordinated thiocyanate ligands, although is by no means unknown [15] and, in the absence of any severe inter ligand forces, implies an important contribution from the resonance form:



One of the more interesting aspects of the molecular structures of the cation of (I) and of (III) is that in independently refining the cycloheptatriene H atoms, we find they reside on the same side of the C_7 plane as the co-ordinated metal atom. With tilt defined by the acute angle θ between the HC vector and C_7 plane, with θ positive for bending towards, and negative for bending away from the metal atom, mean values of θ are +9.4 and +10.8° for (I) and (III) respectively.

Hoffmann *et al.* [16] have optimized θ for a variety of $(CH)_n$ rings in the series of 12-electron fragments $M(CH)_n$, where M is a first series transition metal atom. They predict θ to be negative for $n = 3$ and 4, zero for $n = 5$, and positive for $n = 6$, 7 and 8, and interpret these results in terms of a re-orientation of the ring π-orbitals to maximise overlap with hybridised metal d orbitals. Our experiments provide the first confirmation of a positive θ for $n = 7$.

Finally, we note that although the precise location of hydrogen atoms *via* X-ray diffraction is subject to systematic error [17], the definition of a *directional* quantity such as tilt angle is not.

Figure 2 demonstrates the crystal packing, as seen along the *c* axis, looking towards the origin. There is only one intermolecular contact, 3.01(4) Å, between S(1) at x, y, z and H(75) at ½ – x, ½ – y, –z, less than the appropriate van der Waals' sum (3.20 Å). It may be assumed, therefore, that intermolecular forces have a minimal effect on the stereochemistry and molecular parameters adopted.

Experimental

I.r. spectra were recorded with a Perkin–Elmer 457 grating spectrophotometer using Nujol and hexachlorobutadiene mulls with KBr plates. ^1H N.m.r.

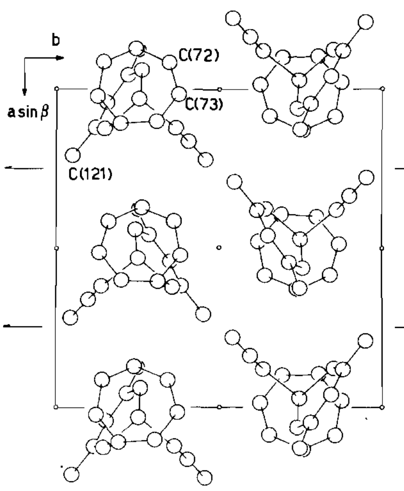


Figure 2. Packing diagram for complex (III). Hydrogen atoms have been omitted for clarity, and only sufficient symmetry elements to describe completely the packing are reproduced.

spectra were measured on a Varian HA100 spectrometer using $CDCl_3$ solutions. E.s.r. spectra were measured as described previously [1].

Molecular weights were determined from parent ions in the mass spectra, using an AEI MS902 instrument at 70 eV*. All reactions were carried out in an atmosphere of dry oxygen-free nitrogen.

Reactions of $[Mo(acac)(H_2O)(\eta^7\text{-}C_7H_7)]BF_4$ *(I)*

(a) With Et_4NCl

Complex (I) (0.2 g, 0.54 mmol) and Et_4NCl (0.5 g, 3.02 mmol) were refluxed in acetone (15 cm^3) for 1½ h. After filtration and taking the yellow filtrate to dryness, the residue was extracted with hot tetrahydrofuran. The extract was filtered, evaporated to give orange–yellow *crystals* (II, X = Cl) (0.13 g, 99%), from dichloromethane–diethyl ether at –23 °C, dec. ~169 °C [Found: C, 44.8; H, 5.1%. M, 323. $C_{12}H_{14}ClMoO_2$ requires: C, 44.8; H, 4.4%. M, 323 (^{35}Cl, ^{98}Mo)]. ^1H N.m.r.: τ, 8.70 br. I. r. ν_{max}: 3056m, 2991w, 2962w, 2923w, 2858w, 1572m, sh, 1568vs, 1537vs, 1524m, sh, 1429m, 1365s, 1357s, sh, 1284m, 1197w, 1186m, 1172w, 1105w, 1087w, 1063m, 1036m, 1025m, sh, 973m, 964m, 946m, 912m, 901w, 871w, 860m, 833vs, 809m, 680w, 667w, 587m, 493w and 452m cm^{-1}. E.s.r.: Central band (g, 1.959 ± 0.001) with four distinct satellites with another two partially obscured by the central band. $A_{iso(av)}$ 44 ± 2 Hz.

(b) With Me_4NBr

Complex (I) (0.2 g, 0.54 mmol) and Me_4NBr (0.7 g, 4.54 mmol) were refluxed (1 h) in acetone (15

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*1 eV ≈ 1.60 × 10^{-19} J.

TABLE III. Final Positional (Fractional, × 10^4; Mo × 10^5) and Anisotropic Thermal[a] (Å^2, ×10^3; Mo, S ×10^4) Parameters. of the Non-hydrogen Atoms in Compound (III).

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	3013 (5)[b]	2542 (5)	−173 (6)	316 (3)	317 (3)	260 (3)	28 (3)	84 (2)	−10 (3)
N(1)	1215 (8)	3671 (6)	−1146 (10)	74 (6)	41 (4)	46 (4)	−5 (4)	23 (4)	0 (3)
C(1)	1632 (7)	4054 (7)	−2083 (10)	35 (4)	38 (4)	47 (5)	−5 (3)	6 (3)	1 (3)
S(1)	2217 (4)	4590 (3)	−3341 (4)	1239 (29)	647 (18)	829 (21)	−183 (19)	691 (22)	29 (16)
O(10)	−603 (5)	2612 (6)	−2401 (6)	47 (3)	70 (4)	30 (2)	10 (3)	5 (2)	6 (3)
C(10)	−442 (8)	2197 (8)	−3670 (9)	50 (5)	67 (6)	29 (4)	−4 (4)	0 (3)	5 (4)
C(101)	−1243 (13)	2521 (15)	−5062 (12)	88 (9)	104 (10)	31 (4)	−33 (9)	−3 (5)	2 (7)
C(11)	423 (9)	1568 (10)	−3769 (11)	58 (6)	80 (7)	36 (4)	4 (5)	18 (4)	−7 (5)
C(12)	1211 (7)	1211 (7)	−2565 (10)	42 (4)	47 (4)	44 (4)	−8 (4)	24 (4)	−7 (4)
C(121)	2105 (11)	514 (9)	−2843 (15)	95 (9)	54 (6)	83 (8)	16 (6)	63 (7)	−8 (6)
O(12)	1242 (5)	1481 (5)	−1171 (7)	38 (3)	46 (3)	42 (3)	8 (2)	13 (3)	1 (3)
C(71)	−1287 (7)	2439 (9)	552 (10)	36 (4)	74 (6)	48 (4)	−29 (5)	17 (3)	−17 (5)
C(72)	−853 (11)	3449 (9)	968 (11)	90 (9)	65 (6)	34 (4)	36 (6)	30 (5)	8 (4)
C(73)	151 (8)	3741 (9)	1717 (11)	52 (5)	55 (5)	37 (5)	−3 (4)	−1 (4)	−16 (4)
C(74)	1004 (11)	3067 (9)	2288 (13)	72 (7)	51 (6)	55 (6)	−13 (5)	24 (5)	−8 (5)
C(75)	1065 (7)	1954 (9)	2201 (9)	36 (4)	72 (6)	20 (3)	10 (4)	−8 (3)	5 (4)
C(76)	225 (11)	1251 (7)	1560 (11)	102 (9)	32 (4)	38 (5)	8 (5)	36 (5)	8 (3)
C(77)	−852 (7)	1448 (8)	801 (11)	38 (4)	47 (5)	47 (5)	−9 (4)	10 (4)	−1 (4)

[a] Of the form exp $\{-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)\}$. [b] E.s.d. in parentheses throughout this paper.

cm^3). The mixture was filtered, the filtrate evaporated, and the resultant solid extracted with dichloromethane. Addition of diethyl ether and cooling to −23 °C afforded orange–yellow *crystals* (II, X = Br) (0.14 g, 70%), decomp. ~155 °C [Found: C, 38.6; H, 4.2%. M, 367. $C_{12}H_{14}BrMoO_2$ requires: C, 39.0; H, 3.8. M, 367 (^{79}Br, ^{98}Mo)]. ^{1}H N.m.r.: τ, 8.73 br. I.r. ν_{max}: 3051m, 2984w, 2962w, 2924m, 2856w, 1579m, sh, 1572s, sh, 1564vs, 1537vs, 1523m, sh, 1508m, sh, 1429m, 1387m, sh, 1367s, 1356s, sh, 1283s, 1199w, 1183m, 1172w, 1034m, 1025m, sh, 978m, sh, 973m, 970m, 964m, 945m, 910w, 902w, 871w, 858s, 832vs, 809s, 678w, 663w, 584s and 452m cm^{-1}. E.s.r.: Central band (g, 1.964 ± 0.001) and four distinct satellite signals, $A_{iso(av)}$ 44 ± 2 Hz.

(c) With KI

Compound (I) (0.2 g, 0.54 mmol) and KI (0.9 g, 5.1 mmol) were stirred (1 h) in acetone (20 cm^3) at room temperature. The mixture was taken to dryness and extracted with dichloromethane. Addition of diethyl ether precipitated an orange–yellow solid. Recrystallisation from dichloromethane–diethyl ether at −23 °C gave orange–brown *crystals* (II, X = I) (0.24 g, 97%), decomp. ~180 °C [Found: C, 34.6; H, 3.5%. M, 415. $C_{12}H_{14}IMoO_2$ requires: C, 34.9; H, 3.4%. M, 415 (^{98}Mo)]. ^{1}H N.m.r.: τ, 8.42 br. I.r. ν_{max}: 3046m, 2986w, 2967w, 2924w, 1580m, sh, 1575s, 1563m, sh, 1554vs, 1524vs, 1509s, sh, 1427s, sh, 1422s, 1360vs, 1351s, sh, 1282s, 1189m, 1182m, 1174m, 1113m, br, 1031m, 1017m, 974m, 965w, 944w, 907m, 898m, 870w, 848m, 823vs, 793s, 678w, 657w, 624w, 584m, 494w, 451m, and 428w cm^{-1}. E.s.r.: Central band (g, 1.968 ± 0.001) and four satellites with a further two partially obscured by the main band. $A_{iso(av)}$ 44 ± 2 Hz.

(d) With KSCN

Complex (I) (0.2 g, 0.54 mmol) and KSCN (0.5 g, 5.15 mmol) were refluxed in acetone (20 cm^3) for 3½ h. The bright yellow–brown solution was taken to dryness and extracted with water (20 cm^3) and dichloromethane (20 cm^3). The dichlormethane layer was evaporated and dried over calcium chloride, evaporated and the product re-crystallised from dichloromethane–light petroleum at −23 °C to give orange–yellow *crystals* of (III) (0.1 g, 57%), m.p. 197–198 °C [Found: C, 45.3; H, 4.0%. M, 346. $C_{13}H_{14}MoNO_2S$ requires: C, 45.4; H, 4.1%. M, 346 (^{98}Mo)]. ^{1}H N.m.r.: τ, 8.45. I.r. ν_{max}: 3056w, 2964w, 2922w, 2858w, 2090vs, 1580m, sh, 1574s, sh, 1564vs, 1534vs, 1525s, sh, 1510m, sh, 1432m, 1368vs, 1355s, 1286s, 1208w, 1036w, 971w, 946w, 898w, 846w, 819s, 588m, and 453m cm^{-1}. E.s.r.: Central band (g, 1.958 ± 0.001) and four satellite peaks with two partially hidden by the central band. $A_{iso(av.)}$ 44 ± 2 Hz.

X-ray Diffraction Study

Since (III) crystallises as such fragile plates, a single crystal, *ca.* 0.42 × 0.20 × 0.05 mm, was mounted in a 0.3 mm diameter Lindemann tube for easier handling.

TABLE IV. Hydrogen Atom Positional [a] and Isotropic Thermal[b] Parameters.

Atom	*x*	*y*	*z*	U_j, × 10^3
H(11)	50 (6)	138 (6)	−474 (10)	24 (19)
H(101)	−100 (11)	326 (12)	−531 (15)	75 (39)
H(102)	−117 (12)	225 (12)	−587(19)	85 (46)
H(103)	−190 (13)	232 (12)	−507 (17)	88 (47)
H(71)	−195 (6)	229 (5)	1 (8)	10 (15)
H(72)	−139 (6)	393 (6)	44 (9)	19 (17)
H(73)	44 (10)	450 (11)	181 (15)	78 (39)
H(74)	173 (8)	346 (8)	260 (11)	37 (24)
H(75)	182 (11)	174 (11)	253 (16)	83 (42)
H(76)	48 (7)	66 (7)	161 (9)	24 (19)
H(77)	−107 (9)	73 (10)	17 (13)	60 (32)

[a] Fractional co-ordinate, ×10^3. [b] Å^2, defined as $\exp\{-8\pi^2 U_j(\sin^2\theta)/\lambda^2\}$.

Oscillation and equi-inclination Weissenberg photographs (Cu-K_α radiation) revealed Laue symmetry $2/m$, and allowed approximate d spacings to be calculated. These were then used to facilitate setting on a Syntex $P2_1$ four-circle diffractometer in the usual manner [18].

In the centering routine 15 reflections, $12 < 2\theta < 27°$, were chosen (Mo-K_α radiation). For data collection the 2θ range was 2.9–60.0°, and reflections were scanned (θ–2θ) at rates which varied from 0.03367° s^{-1} to 0.48833° s^{-1} dependent on an initial 2s peak count in which 200 and 2000 were used as critical values.

The intensities of three check reflections (024, $6\bar{3}\bar{2}$ and $\bar{2}42$) were re-recorded once every batch of 24 but showed [19] no significant variation over the *ca.* 150 h X-ray exposure. Of 4114 independent reflections examined 2788 had $I \geqslant 1.0\sigma$ and were retained for structure solution and refinement. *Crystal Data*: $C_{13}H_{14}MoNO_2S$, M = 344.26, Monoclinic, space group $P2_1/a$, a = 12.762(2), b = 12.634(4), c = 8.813(3) Å, β = 100.70(2)°, U = 1396.1(6) Å^3, D_C = 1.637, Z = 4, D_M = 1.61, $F(000)$ = 660, μ(Mo-K_α) = 9.9 cm^{-1}, T ≅ 298 °K.

Data were corrected for Lorentz and polarisation, but not for absorption effects, and the position of the metal atom easily deduced from a three dimensional Patterson. Thereafter atoms were located from electron density difference syntheses computed after full-matrix least-squares refinement. For hydrogen atoms, fine grid Fouriers sampled at 0.01 of each axial length, and produced using only those 1189 data with $\sin\theta/\lambda \leqslant 0.5$ were employed. Even so no unambiguous location of the three methyl hydrogens of C(12) could be made, and these atoms remained absent.

Weights were applied to F_o moduli according to $w^{-1} = xy$, with $x = 0.27/\sin\theta$ if $\sin\theta < 0.27$; $x = 1$ if $\sin\theta \geqslant 0.27$; and $y = F_o/45$ if $F_o > 45$; $y = 1$ if $F_o \leqslant 45$.

In the final stages all non-hydrogen atoms were assigned anisotropic temperature factors whilst the hydrogens were refined isotropically. At convergence R was 0.069, R' 0.070, with a data: variable ratio better than 13.4:1. An ultimate difference Fourier (0.3 Å resolution, all data) showed a maximum residue of 1.14 e Å^{-3} close to the molybdenum atom.

Atomic scattering factors for neutral atoms were those of ref. [20] (Mo), ref. [21] (N, C, S. O) and ref. [22] (H), with appropriate correction [23] for the effects of anomalous dispersion.

Tables III and IV list the derived atomic parameters. Appendix A contains bond angles involving H atoms, and B summarises least-squares planes' data. A table of structure factors is available from the Editor. Computer programs employed were as detailed previously [1].

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References

1. M. Green, H. P. Kirsch, F. G. A. Stone and A. J. Welch, *J. Chem. Soc. Dalton,* 1755 (1977).
2. A. Salzer, *Inorg. Chim. Acta, 17,* 221 (1976).
3. G. Deganello, T. Boschi, L. Toniolo and G. Albertin, *Inorg. Chim. Acta, 10,* L3 (1974).
4. E. E. Isaacs and W. A. G. Graham, *J. Organometal. Chem., 90,* 319 (1975).
5. K. M. Al-Kathumi and L. A. P. Kane-Maguire, *J. Chem. Soc. Dalton,* 1683 (1973).
6. P. Hackett and G. Jaouen, *Inorg. Chim. Acta, 12,* L19 (1975).
7. D. A. Sweigart, M. Gower and L. A. P. Kane-Maguire, *J. Organometal. Chem., 108,* C15 (1976).
8. M. Bochmann, M. Cooke, M. Green, H. P. Kirsch, F. G. A. Stone and A. J. Welch, *Chem. Comm.,* 381 (1976).
9. A. H. Norbury, *Advan. Inorg. and Radiochem., 17,* 231 (1975).
10. K. M. Al-Kathumi and L. A. P. Kane-Maguire, *J. Organometal. Chem., 102,* C4 (1975).
11. J. R. Knox and K. Eriks, *Inorg. Chem., 7,* 84 (1968).
12. A. J. Graham and R. H. Fenn, *J. Organometal. Chem., 17,* 405 (1969).
13. A. J. Graham and R. H. Fenn, *J. Organometal. Chem., 25,* 173 (1970).
14. T. Glowiak, M. Sabat, H. Sabat and M. F. Rudolf, *Chem. Comm.,* 712 (1975).
15. See, for example, T. Takeuchi and Y. Saito, *Bull. Chem. Soc. Jap., 30,* 319 (1957); N. A. Bailey and E. D. McKenzie, *J. Chem. Soc. Dalton,* 1566 (1972); C. A. Ghilardi and A. B. Orlandini, *J. Chem. Soc. Dalton,* 1698 (1972).
16. M. Elian, M. M. L. Chen, D. M. P. Mingos and R. Hoffmann, *Inorg. Chem., 15,* 1148 (1976).
17. M. R. Churchill, *Inorg. Chem., 12,* 1213 (1973).
18. A. G. Modinos and P. Woodward, *J. Chem. Soc. Dalton,* 2065 (1974).

19 A. G. Modinos, DRSYN, a Fortran program for data analysis.
20 D. T. Cromer and J. T. Waber, *Acta Cryst., 18,* 104 (1965).
21 D. T. Cromer and J. B. Mann, *Acta Cryst., A24,* 321 (1968).
22 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42,* 2175 (1965).
23 "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham (1974).

APPENDIX A. Bond Angles (°) Involving Hydrogen Atoms in $[\mathrm{Mo(acac)(NCS)}(\eta^7\text{-}\mathrm{C_7H_7})]$.

H(11)–C(11)–C(10)	116 (5)	H(72)–C(72)–C(73)	125 (5)
H(11)–C(11)–C(12)	116 (5)	H(73)–C(73)–C(72)	126 (7)
C(10)–C(101)–H(101)	104 (7)	H(73)–C(73)–C(74)	107 (7)
C(10)–C(101)–H(102)	115 (10)	H(74)–C(74)–C(73)	114 (5)
C(10)–C(101)–H(103)	116 (9)	H(74)–C(74)–C(75)	116 (5)
H(101)–C(101)–H(102)	96 (14)	H(75)–C(75)–C(74)	109 (8)
H(101)–C(101)–H(103)	126 (13)	H(75)–C(75)–C(76)	124 (8)
H(102)–C(101)–H(103)	98 (14)	H(76)–C(76)–C(75)	107 (6)
H(71)–C(71)–C(77)	102 (4)	H(76)–C(76)–C(77)	122 (6)
H(71)–C(71)–C(72)	127 (4)	H(77)–C(77)–C(76)	103 (6)
H(72)–C(72)–C(71)	104 (5)	H(77)–C(77)–C(71)	129 (6)

APPENDIX B. Least-squares Planes Data for $[\mathrm{Mo(acac)(NCS)}(\eta^7\text{-}\mathrm{C_7H_7})]$.

1. *Plane defined by atoms C(71)–C(77)*
Equation: $-6.056x - 0.737y + 8.382z = 1.072$, Å in which x, y and z are non-orthogonalised atomic fractional co-ordinates.

Deviations, Å

C(71)	−0.010	C(76)	+0.006	H(74)	−0.20
C(72)	+0.001	C(77)	+0.008	H(75)	−0.18
C(73)	0.000	H(71)	−0.05	H(76)	−0.06
C(74)	+0.011	H(72)	−0.15	H(77)	−0.33
C(75)	−0.016	H(73)	−0.16	Mo	−1.587

2. *Plane defined by atoms Mo, O(10, 12), C(10, 11, 12, 101, 121)*
Equation: $7.566x + 9.970y - 2.355z = 2.746$

Deviations, Å

Mo	+0.057	O(12)	−0.054
O(10)	−0.032	C(101)	+0.019
C(10)	−0.025	C(121)	+0.029
C(11)	+0.025	H(11)	+0.12
C(12)	−0.019		

The acute angle between these planes is 62.1°

3. *Line defined by MoN(1)C(1)S(1)*

The above atoms are co-linear to within 0.22 Å, the significant kink (*ca.* 157°) being at N (see Table II and Discussion)

To demonstrate the comparison of the present structure with that of the aquo cation (Reference 1, Appendix C) we have calculated the angles between the current planes (1) and (2) and the N(1) Mo vector to be 55.9° and 61.9° respectively.