

THE CRYSTAL STRUCTURE OF SOME DICARBONYL ALLYL  
DERIVATIVES OF SUBSTITUTED CARBONYLS OF MOLYBDENUM  
II. THE CRYSTAL STRUCTURE OF (ISOTHIOCYANATO)DICARBONYL-  
1,10-PHENANTHROLINE(2-METHYLALLYL)MOLYBDENUM  $\text{NCS}(\text{CO})_2-$   
 $(\text{C}_{12}\text{H}_8\text{N}_2)(\text{C}_4\text{H}_7)\text{Mo}$

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SUMMARY

The crystal structure and molecular configuration of the complex (isothiocyanato)dicarbonyl-1,10-phenanthroline(2-methylallyl)molybdenum,  $\text{NCS}(\text{CO})_2-(\text{C}_{12}\text{H}_8\text{N}_2)(\text{C}_4\text{H}_7)\text{Mo}$  have been determined from three dimensional data collected photographically at  $20^\circ$ . The unit cell is monoclinic, spacegroup  $P2_1/c$  with four formula units per cell of dimensions  $a = 8.034 \pm 0.004$ ,  $b = 13.406 \pm 0.001$ ,  $c = 17.869 \pm 0.009$  Å;  $\beta = 105^\circ 5' \pm 5'$ . The structure has been refined to  $R = 0.1135$  by the application of isotropic/anisotropic block-diagonal-approximation least-squares refinement using 3106 independent non-zero reflections.

The complex has essentially an octahedral arrangement of ligands. If it is viewed with the plane of the dicarbonyl ligands horizontal, the methallyl and isothiocyanato ligands lie axially, one on each side of the dicarbonyl plane. The phenanthroline ligand plane lies  $27.5^\circ$  below the horizontal, dipping away from the methallyl. The other interplanar angles are methallyl/dicarbonyl  $7.6^\circ$ ; phenanthroline/methallyl  $34.4^\circ$ .

The central allylic carbon atom is closer to the molybdenum, at  $2.274 \pm 0.012$  Å, than the two terminal ( $\text{CH}_2$  type) carbon atoms at  $2.320 \pm 0.012$  Å and  $2.350 \pm 0.012$  Å. The allylic  $\text{CH}_2-\text{C}-\text{CH}_2$  angle is  $111.5 \pm 1.1^\circ$  and the  $\text{C}-\text{CH}_2$  (mean) and  $\text{C}-\text{CH}_3$  bond lengths are  $1.428 \pm 0.017$  Å and  $1.491 \pm 0.017$  Å respectively. The methyl carbon atom is  $0.044$  Å out of the plane defined by the three  $\text{CH}_2-\text{C}-\text{CH}_2$  carbon atoms representing a distortion of less than  $2^\circ$ . The mean  $\text{Mo}-\text{C}$  (carbonyl) and  $\text{C}-\text{O}$  bond lengths are  $1.969 \pm 0.010$  Å and  $1.146 \pm 0.015$  Å, respectively. The thiocyanato ligand is in the iso-form, the  $\text{Mo}-\text{N}$  distance being  $2.146 \pm 0.009$  Å, with bond lengths  $\text{N}-\text{C}$  at  $1.168 \pm 0.014$  Å and  $\text{C}-\text{S}$  at  $1.613 \pm 0.012$  Å.

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INTRODUCTION

This complex is the second in a series of three, taken from those prepared by Hull and Stiddard<sup>1</sup>, studied to investigate the relative stereochemical positions of the various ligands present and to investigate the type of bonding present for the allyl and

thiocyanato ligands. The first structure determination<sup>2</sup>, of (isothiocyanato)dicarbonyl-2,2'-bipyridine- $\pi$ -allylmolybdenum (henceforth MCBAS), conclusively showed the thiocyanato ligand to be N-bonded and the allyl to be  $\pi$ -bonded. This second complex (isothiocyanato)dicarbonyl-1,10-phenanthroline-2-methylallylmolybdenum will henceforth be referred to as MC $\phi$ AS.

#### CRYSTAL DATA

As with MCBAS, very small crystals of MC $\phi$ AS, of approximately 0.05 mm in maximum dimension, were obtained from C. Hull of University College, London. Larger, more suitable crystals were recrystallised from a solution in dimethylformamide and these appeared as simple red parallelepipeda, with well formed [100], [010] and [001] faces, of sizes about  $0.2 \times 0.2 \times 0.3$  mm. One such crystal was reduced to a rough cylinder of mean diameter approximately  $0.09 \pm 0.01$  mm in an attempt to reduce absorption effects.

The only systematically absent reflections on equi-inclination Weissenberg photographs were:

$$[h0l] \quad l = 2n + 1$$

$$[0k0] \quad k = 2n + 1$$

Thus the spacegroup was uniquely defined as  $P2_1/c$  (Number 14 in International Tables for X-ray Crystallography<sup>3</sup>-volume I).

One crystal only was used in this analysis and the following zones were collected:

(i). The  $(hNl)$  zones for  $N=0, 1, \dots, 11$ .

(ii). The  $(Nkl)$  zones for  $N=0, 1, 2, 3$ .

Both zones were collected using the equi-inclination Weissenberg technique.

All zones were collected using Ni-filtered Cu  $K\alpha$  radiation,  $\lambda(\bar{x}) = 1.54178 \text{ \AA}$  at 30 kV, 20 mA at a temperature of  $20^\circ$  in five-film packs. All data were measured visually by comparison with a calibrated wedge made from the chosen crystal.

The accurate cell parameters were obtained from the  $(h0l)$  and  $(0kl)$  zones using fine gold wire as a calibrating standard, Powell<sup>4</sup> and Graham<sup>5</sup>, as described previously<sup>2</sup>. The data used in this determination and the resulting cell parameters are as follows:

Cell constant for gold<sup>7</sup>  $a = 4.078504 \text{ \AA}$  at  $25^\circ$ ; copper radiation wavelengths<sup>3</sup>  $\lambda(\alpha_1) = 1.54051 \text{ \AA}$ ,  $\lambda(\alpha_2) = 1.54433 \text{ \AA}$  and  $\lambda(\beta) = 1.39217 \text{ \AA}$ ; coefficient of refraction<sup>3</sup>  $1.86 \times 10^{-4}$ ; coefficient of expansion  $1.41 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ ; accurate cell parameters  $a = 8.034 \pm 0.004 \text{ \AA}$ ,  $b = 13.406 \pm 0.001 \text{ \AA}$ ,  $c = 17.869 \pm 0.009 \text{ \AA}$  and  $\beta = 105^\circ 5' \pm 5'$ ; density  $D_{\text{obs.}} = 1.576 \pm 0.051 \text{ g}\cdot\text{cm}^{-3}$  and  $D_{\text{calcd.}} = 1.591 \pm 0.003 \text{ g}\cdot\text{cm}^{-3}$ ; formula units per cell  $Z = 4$  and linear absorption coefficients  $\mu_{\text{Mo}} = 8.5 \text{ cm}^{-1}$ ;  $\mu_{\text{Cu}} = 80.2 \text{ cm}^{-1}$ .

The density of the crystals were determined by the method of flotation in a bromoform/benzene mixture at  $20^\circ$ .

For the chosen crystal  $\mu \cdot R$  was calculated as 0.37 and 0.04 for Cu and Mo  $K\bar{\alpha}$  radiation respectively. However, Mo  $K\alpha$  radiation at the available operating voltages gives a large number of Laue streaks on Weissenberg zones. Consequently it was

decided to use Cu  $K\alpha$  radiation for which, allowing for the variation in  $R$  and  $\theta$ , the absorption coefficient  $A^*$  had extreme values of approximately 2.0 and 1.7. No absorption corrections were made.

The usual Lorentz, polarisation and spot-distortion corrections<sup>8</sup> were applied to the intensities and the ( $hNl$ ) layers of data were placed on an approximately absolute scale by the method of Wilson<sup>9</sup>, giving an overall isotropic  $B$  of  $2.61 \text{ \AA}^2$ . Individual layer scales were later refined in the least-squares routine. All data reduction was achieved on an Elliott 803B computer using programmes written by the authors and Mr. Powell. The ( $Nkl$ ) layers of data were scaled using reflections common with the ( $hNl$ ) layers and Sarma's programme based on the method of Hamilton, Rollett and Sparks<sup>14</sup>. Once scaled, the ( $Nkl$ ) data for  $k=12, 13 \dots 17$  were added to the ( $hNl$ ) data. However, all data for  $k=12, 13 \dots 17$  were given the same scale throughout the following refinement. Initially, 662 unobserved reflections were processed having been given  $1/3$  the lowest observed intensity<sup>10</sup> prior to data reduction. These were removed in the closing stages of refinement<sup>11</sup>.

#### THE STRUCTURE DETERMINATION

A three-dimensional Patterson synthesis, using Simmons' Fourier synthesis programme, gave the molybdenum and sulphur atomic sites and these were then used to phase the structure amplitudes for the first Fourier synthesis. In the phasing of these amplitudes, using the structure-factor programme written by Mair, both Mo and S were given isotropic thermal parameters of  $B=2.61 \text{ \AA}^2$ , all reflections were given unit weight<sup>11</sup>.

The first electron density distribution gave all the remaining atomic sites without difficulty and these were used in three cycles of refinement. All initial isotropic thermal parameters were set to  $2.61 \text{ \AA}^2$  and layer scale factors were not refined. After this refinement, in which  $\Sigma\omega\Delta^2 = \Sigma\omega|K \cdot F_o - F_c|^2$  was minimised, the residual given by  $R = \Sigma|K \cdot F_o - F_c| / \Sigma|K \cdot F_o|$  was 0.2379.

At this stage fast Fourier and structure-factor/least-squares programmes became available on the Crystal '69 system (Powell and Griffiths) for an I.C.L. 4130 computer, so all data were transferred to the new system.

Two cycles of refinement of  $x_n, y_n, z_n, B_n$  and scale factors for layers  $k=0, 1 \dots 11$  gave  $R=0.1798$  and mean  $\Sigma\omega\Delta^2=43$  absolute. All data for  $k > 11$  were given the same scale-factor which was also refined and unit weights were still employed for all reflections.

A difference Fourier synthesis at this stage gave clear indications of the anisotropic thermal motion of all atoms. Three cycles of full anisotropic refinement gave  $R=0.1479$  and mean  $\Sigma\omega\Delta^2=31$ . Reflections were given weights defined by  $\omega = [1 + \{(F_o - 52)/79\}^2]^{-1}$  and refinement of the layer-scale continued. An analysis of mean  $\Sigma\omega\Delta^2$  over ranges of  $|F_o|$  indicated the need for a change in weighting scheme. The next scheme chosen was  $\omega = |F_o|/20$  for  $|F_o| < 20$  and  $\omega = 20/|F_o|$  for  $|F_o| > 20$ . Three cycles of refinement using this did not improve the  $R$ -factor but did improve the weighting-scheme analysis. Another change, to  $\omega = |F_o|/10$  and  $10/|F_o|$ , was made to improve the analysis<sup>26</sup> still further. Also, at this stage the 662 unobserved reflections were removed<sup>11</sup> and three cycles of refinement gave  $R=0.1135$ .

Another difference Fourier synthesis was then plotted to investigate any

residual peaks and two main features were evident:

(i). Residual peaks of  $\pm 2e \text{ \AA}^{-3}$  were present around the Mo site similar to those found in MCBAS. There were still present after an undoubted reduction in absorption effects and were therefore thought to be most likely indicative of an electron density distribution around the molybdenum and neighbouring atoms being more complex<sup>13</sup> than the postulated ellipsoids.

(ii). In the presence of general background noise of less than  $0.4e \text{ \AA}^{-3}$  there were definite peaks of 0.6 to  $1.0e \text{ \AA}^{-3}$  within the range 1.0 to 1.2  $\text{\AA}$  of the CH carbon atoms of the 1,10-phenanthroline (Phen) ligand and the terminal methallyl carbons. An investigation of these peaks showed that those near the Phen carbons lay in the Phen plane and were all of peak height 0.6 to  $0.8e \text{ \AA}^{-3}$ . This indicates<sup>12</sup> hydrogen

TABLE 1

THE FINAL FRACTIONAL POSITIONAL PARAMETERS AND STANDARD DEVIATIONS ( $\times 10^4$ )

Atom	x	y	z
Mo	0.0240(0)	0.2651(0)	0.1103(0)
N(10)	-0.1261(11)	0.2929(7)	0.1914(5)
C(10)	-0.1623(13)	0.3131(8)	0.2487(7)
S	-0.2096(7)	0.3405(2)	0.3286(2)
C(1)	-0.1263(12)	0.1517(7)	0.0632(6)
O(1)	-0.2151(14)	0.0889(8)	0.0368(6)
C(2)	-0.1446(13)	0.3417(8)	0.0336(6)
O(2)	-0.2477(12)	0.3892(8)	-0.0101(6)
C(3)	0.1759(18)	0.1571(9)	0.0509(8)
C(4)	0.2543(17)	0.2554(9)	0.0588(7)
C(5)	0.1451(16)	0.3262(10)	0.0129(7)
C(6)	0.4266(16)	0.2798(11)	0.1111(8)
N(11)	0.1865(9)	0.1949(5)	0.2195(4)
C(11)	0.2621(12)	0.2609(6)	0.2743(5)
C(21)	0.3577(13)	0.2314(7)	0.3513(6)
C(31)	0.3589(16)	0.1319(9)	0.3675(7)
C(41)	0.2827(17)	0.0676(8)	0.3110(8)
C(51)	0.1977(14)	0.0976(8)	0.2393(7)
N(12)	0.1700(10)	0.3928(5)	0.1809(4)
C(12)	0.1555(14)	0.4873(8)	0.1599(6)
C(22)	0.2324(19)	0.5642(8)	0.2120(8)
C(32)	0.3149(20)	0.5403(9)	0.2875(8)
C(42)	0.3335(14)	0.4379(8)	0.3106(6)
C(52)	0.2555(13)	0.3650(7)	0.2542(6)
C(13)	0.4207(16)	0.4048(11)	0.3873(6)
C(23)	0.4309(14)	0.3061(10)	0.4060(6)
H(1)	0.084	0.513	0.103
H(2)	0.218	0.646	0.198
H(3)	0.372	0.602	0.330
H(4)	0.482	0.461	0.431
H(5)	0.500	0.288	0.465
H(6)	0.425	0.107	0.425
H(7)	0.284	0.012	0.327
H(8)	0.130	0.048	0.194

atoms of  $B < 6 \text{ \AA}^2$ . The peaks around the  $\text{CH}_2$  carbons in the allyl were less easily interpreted in that they were extended regions of height  $1.0e \text{ \AA}^{-3}$  and the  $\text{CH}_3$  peaks appeared as bulges on a toroid around the methyl carbon atom. The location of the methallyl hydrogen peak centres was not attempted.

A final structure-factor calculation was made including the Phen hydrogen positions ( $B = 2.61 \text{ \AA}^2$ ) gave  $R = 0.1135$  and mean  $\Sigma\omega\Delta^2 = 2.8$ .

The refinement was judged to be complete when the parameter shifts were less than 10% of the corresponding standard deviations in magnitude and when  $\Sigma\omega\Delta^2$  would reduce no further.

Tables 1 and 2 give the final positional and thermal parameters. Table 3 lists the root-mean-square thermal displacements,  $\bar{U}$ , and Table 4 gives the observed and calculated structure factors on an absolute scale.

#### THE MOLECULAR STRUCTURE

As may be seen from Fig. 1 this complex has an "octahedral" configuration similar to the MCBAS complex with the dicarbonyl and thiocyanato ligands occupying the same relative sites and with the 1,10-phenanthroline and methallyl ligand

TABLE 2

THE FINAL ANISOTROPIC THERMAL VIBRATIONS DEFINED BY  $T = \exp - 10^{-5} (h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})$

Atom	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$
Mo	189	30	14	4	8	3
N(10)	127	43	22	-7	30	0
C(10)	134	37	34	48	60	17
S	438	31	53	-3	221	-9
C(1)	108	37	23	-57	-28	5
O(1)	279	70	32	-83	-18	-4
C(2)	112	49	22	-25	-10	21
O(2)	174	86	49	60	-4	65
C(3)	223	53	39	-7	80	-27
C(4)	172	60	20	70	41	-14
C(5)	164	67	25	-4	48	0
C(6)	112	90	31	36	25	-30
N(11)	96	31	18	13	-5	9
C(11)	96	42	14	-12	21	-6
C(21)	107	43	21	-5	33	-7
C(31)	165	56	26	35	10	17
C(41)	190	41	38	35	4	21
C(51)	161	34	34	6	18	6
N(12)	141	29	17	-4	43	-2
C(12)	161	47	24	45	29	19
C(22)	255	40	42	-3	88	12
C(32)	267	39	44	-61	91	-32
C(42)	131	48	25	-18	40	-14
C(52)	118	38	22	8	66	-3
C(13)	146	91	13	-15	0	-28
C(23)	132	72	22	-44	29	-18

respectively replacing the 2,2'-bipyridyl (Bipy) and  $\pi$ -allyl ligands. The main difference between these two complexes lies in the angle between the dicarbonyl and the Phen (or Bipy) planes. In this complex the angle has been found to be  $27.5^\circ$  compared with only  $15.1^\circ$  for MCBAS.

The Phen ligand is given by the plane  $0.9546X - 0.0795Y - 0.2870Z + 0.8322 = 0$  where  $X, Y, Z$  are orthogonal axes defined by  $X = a \cdot x + c \cdot z \cos\beta$ ;  $Y = b \cdot y$  and  $Z = c \cdot z \cdot \sin\beta$ .

(continued p. 187)

TABLE 3

THE R.M.S. THERMAL DISPLACEMENTS,  $\bar{U}$ , AND THE DIRECTION COSINES  $l, m, n$  WITH RESPECT TO THE REAL ORTHOGONAL AXES  $X, Y, Z$

Atom	$\bar{U}$	$l$	$m$	$n$	Atom	$\bar{U}$	$l$	$m$	$n$
Mo	0.1426	0.3362	-0.2289	0.9135	C(31)	0.1772	0.3813	-0.5139	0.7685
	0.1751	0.9203	0.0460	-0.3886		0.2520	0.2334	-0.5332	-0.8132
	0.1652	0.1827	-0.9751	-0.1259		0.2245	0.5964	-0.7269	-0.3405
S	0.3889	0.7868	-0.0223	0.6168	C(41)	0.2795	0.7186	-0.1009	-0.6880
	0.1613	0.2215	-0.9247	-0.3098		0.1708	0.3005	-0.8622	0.4078
	0.1935	0.5608	0.4358	-0.7039		0.2296	0.3877	0.6605	0.6429
C(1)	0.2546	0.7633	-0.4487	-0.4648	C(51)	0.2443	0.7347	-0.0563	-0.6760
	0.1144	0.6344	0.3977	0.6628		0.1751	0.0931	-0.9816	0.1666
	0.1858	0.1575	-0.7176	0.6784		0.2121	0.6555	0.2147	0.7239
O(1)	0.3372	0.8846	-0.3747	-0.2776	N(12)	0.2087	0.9050	-0.0625	0.4206
	0.1972	0.4215	0.4445	0.7904		0.1483	0.4107	-0.1324	-0.9021
	0.2405	0.2664	0.8659	-0.4245		0.1632	0.2656	0.8999	-0.3458
C(2)	0.1341	0.3542	-0.2783	0.8928	C(12)	0.1620	0.2375	-0.6285	0.7406
	0.2458	0.6079	-0.7018	-0.3713		0.2424	0.6967	0.6454	0.3131
	0.2012	0.4179	-0.6899	0.5910		0.2100	0.6877	-0.4089	-0.5999
O(2)	0.3448	0.2083	-0.6516	-0.7294	C(22)	0.2867	0.7786	0.0491	0.6256
	0.1712	0.5125	-0.5697	0.6425		0.1854	0.1585	0.9569	-0.2434
	0.2589	0.9852	0.0288	-0.1689		0.2336	0.5645	-0.3595	-0.7430
C(3)	0.1852	0.3240	-0.7427	-0.5859	C(32)	0.1531	0.0473	0.8524	0.5208
	0.2782	0.5517	-0.3590	0.7528		0.3000	0.7702	-0.3507	0.5327
	0.2387	0.5151	0.7746	-0.3669		0.2511	0.7985	0.0761	-0.5971
C(4)	0.2747	0.4682	0.6999	-0.5394	C(42)	0.2237	0.3518	-0.7878	0.5056
	0.1511	0.5419	-0.5269	-0.6546		0.1733	0.2560	-0.4556	-0.8526
	0.1935	0.6603	-0.5672	0.4923		0.1973	0.2026	-0.8158	-0.5417
C(5)	0.1848	0.4549	0.0219	-0.8903	C(52)	0.1282	0.7582	-0.1609	-0.6318
	0.2464	0.1029	-0.9941	0.0335		0.2135	0.6424	0.0356	0.7656
	0.2252	0.8853	0.1003	0.4540		0.1865	0.2254	-0.9367	0.2678
C(6)	0.3038	0.2549	0.9086	-0.3309	C(13)	0.2949	0.0400	0.9719	-0.2319
	0.1686	0.3505	-0.3771	-0.8573		0.1195	0.1407	0.2254	0.9641
	0.2070	0.2119	0.3326	0.9189		0.2233	0.9879	-0.0754	-0.1356
N(11)	0.2036	0.7678	-0.1101	-0.6310	C(23)	0.2676	0.2787	-0.9279	0.2473
	0.1368	0.4906	-0.5067	0.7089		0.1704	0.1421	0.3049	0.9417
	0.1710	0.0050	0.9709	0.2395		0.1966	0.8426	0.0729	-0.5335
C(11)	0.1984	0.2217	-0.9599	0.1714	N(10)	0.1825	0.2969	0.1205	-0.9473
	0.1396	0.1834	-0.1633	-0.9694		0.2022	0.6327	-0.7609	0.1438
	0.1665	0.8550	0.3293	0.4006		0.1928	0.7389	0.6230	0.2564
C(21)	0.2038	0.1321	-0.9028	0.4092	C(10)	0.1471	0.1535	-0.6956	0.7018
	0.1642	0.6003	-0.2567	-0.7575		0.2422	0.4619	0.4819	0.7445
	0.1821	0.7822	0.3529	0.5133		0.2020	0.7318	0.5732	-0.3686



















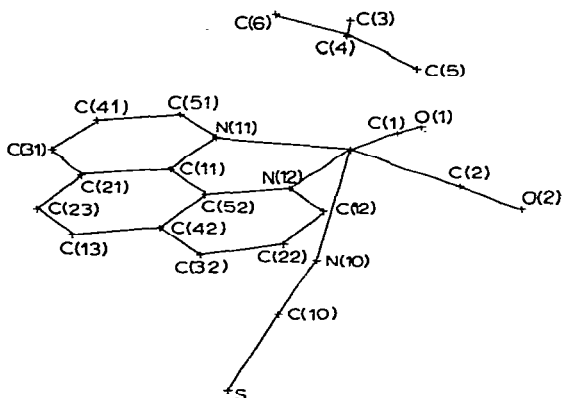


Fig. 1. The MCBAS molecular configuration and atomic designation.

The mean deviation of the Phen atoms from this plane is  $\pm 0.011$  Å and the molybdenum lies 0.3 Å out of the plane towards the thiocyanato ligand. The bond lengths have been found to be: C-N(mean)  $1.345 \pm 0.012$  Å and C-C in the range  $1.347 \pm 0.018$  Å to  $1.439 \pm 0.013$  Å. The interbond angles approach  $120^\circ$  being in the range  $116.2^\circ$  to  $122.7^\circ$ . These bonds and angles are in accordance with those previously reported for similar six-member heterocyclic molecules and ligands<sup>15-19,21</sup>. The planarity of each of the three rings was investigated but none of them was more than  $0.5^\circ$  from the best-fit plane for the full Phen ligand.

The four atoms of the dicarbonyl ligand-pair are also co-planar, the plane being given by  $0.7078X - 0.1327Y - 0.6918Z + 1.9483 = 0$ . The mean atom deviation is  $\pm 0.048$  Å and the molybdenum is 0.066 Å towards the thiocyanato ligand. The mean Mo-C and C≡O bond lengths at  $1.969 \pm 0.010$  Å and  $1.146 \pm 0.015$  Å respectively agree well with those obtained for MCBAS, Graham and Fenn<sup>2</sup>, and for other carbonyls referred to in the MCBAS paper. The Mo-C≡O angles have been found to be linear, the mean value being  $177.7 \pm 0.1^\circ$ .

TABLE 5

THE DISTANCES IN Å OF ATOMS FROM THE LEAST-SQUARES PLANES

Plane <sup>a</sup>	Atom	Distance	Atom	Distance
(I)	Mo	-1.994	C(6)	-0.044
(II)	Mo	-0.066		
	C(1)	-0.004	O(1)	0.003
	C(2)	0.004	O(2)	-0.003
(III)	Mo	-0.302		
	N(11)	-0.007	N(12)	-0.005
	C(11)	-0.012	C(12)	0.003
	C(21)	0.029	C(22)	0.022
	C(31)	-0.008	C(32)	-0.029
	C(41)	0.007	C(42)	0.005
	C(51)	-0.004	C(52)	0.015
	C(23)	-0.003	C(13)	0.011

<sup>a</sup> (I) Allylic carbon atoms; (II) dicarbonyl atoms; (III) 1,10-phenanthroline ligand.

The thiocyanato ligand is again in the iso-form and is linear,  $179.2 \pm 1.0^\circ$ . However the Mo-N(10)-C(10) angle has been found to be  $161.1 \pm 0.8^\circ$  in contrast to  $175.8 \pm 0.5^\circ$  for MCBAS. This bend is towards the Phen ligand in the plane containing C(4), C(6), Mo, N(10), C(10) and S. The bond lengths agree well with values obtained for MCBAS (Graham and Fenn<sup>2</sup>; Nardelli *et al.*<sup>19</sup>; Ferrari *et al.*<sup>20</sup>; Brown and Lingafelter<sup>21,22</sup> for other thiocyanates).

TABLE 6

## INTERATOMIC DISTANCES AND BOND ANGLES

Bond lengths (Å) and standard deviations ( $\times 10^3$ )		Bond angles and standard deviations ( $\times 10^3$ )	
Mo-C(1)	1.987(10)	C(1)-Mo-C(2)	82.6(4)
Mo-C(2)	1.950(10)	N(1)-Mo-N(12)	74.7(3)
Mo-C(3)	2.320(13)	C(1)-Mo-N(10)	91.9(4)
Mo-C(4)	2.274(13)	C(2)-Mo-N(10)	88.5(4)
Mo-C(5)	2.350(12)	N(11)-Mo-N(10)	77.8(3)
Mo-N(10)	2.146(9)	N(12)-Mo-N(10)	77.5(3)
Mo-N(11)	2.252(8)		
Mo-N(12)	2.255(8)	Mo-N(11)-C(11)	114.0(6)
		Mo-N(12)-C(52)	113.0(6)
N(11)-C(11)	1.343(12)	N(11)-C(11)-C(21)	122.8(8)
C(11)-C(21)	1.446(13)	C(11)-C(21)-C(31)	116.2(9)
C(21)-C(31)	1.365(16)	C(21)-C(31)-C(41)	119.3(11)
C(31)-C(41)	1.348(18)	C(31)-C(41)-C(51)	122.7(11)
C(41)-C(51)	1.347(18)	C(41)-C(51)-N(11)	121.4(10)
C(51)-N(11)	1.349(13)	C(51)-N(11)-C(11)	117.3(8)
N(12)-C(12)	1.317(13)	N(12)-C(12)-C(22)	121.7(10)
C(12)-C(22)	1.419(17)	C(12)-C(22)-C(32)	119.3(11)
C(22)-C(32)	1.378(20)	C(22)-C(32)-C(42)	119.6(11)
C(32)-C(42)	1.430(16)	C(32)-C(42)-C(52)	117.3(10)
C(42)-C(52)	1.427(14)	C(42)-C(52)-N(12)	120.9(8)
C(52)-N(12)	1.370(12)	C(52)-N(12)-C(12)	121.0(8)
C(13)-C(42)	1.437(15)	N(11)-C(11)-C(52)	118.5(8)
C(13)-C(23)	1.362(20)	N(12)-C(52)-C(11)	118.6(8)
C(23)-C(21)	1.416(16)	C(42)-C(52)-C(11)	120.5(9)
C(11)-C(52)	1.413(16)	C(52)-C(11)-C(21)	118.6(8)
C(3)-C(4)	1.452(18)	C(11)-C(21)-C(23)	119.1(9)
C(4)-C(5)	1.404(17)	C(21)-C(23)-C(13)	122.0(10)
C(4)-C(6)	1.491(18)	C(23)-C(13)-C(42)	121.1(11)
		C(13)-C(42)-C(52)	118.5(10)
C(1)-O(1)	1.1251(5)		
C(2)-O(2)	1.168(15)	Mo-C(1)-O(1)	178.1(10)
N(10)-C(10)	1.168(14)	Mo-C(2)-O(2)	177.4(10)
C(10)-S	1.613(12)	Mo-N(10)-C(10)	161.0(8)
		N(10)-C(10)-S	179.2(10)
H(1)-C(12)	1.08		
H(2)-C(22)	1.12	C(3)-C(4)-C(5)	111.6(11)
H(3)-C(32)	1.13		
H(4)-C(13)	1.11		
H(5)-C(23)	1.09		
H(6)-C(31)	1.08		
H(7)-C(41)	1.10		
H(8)-C(51)	1.08		



TABLE 7

INTERMOLECULAR DISTANCES; CLOSEST APPROACHES FOR OUTER ATOMS<sup>a</sup>

Atoms	Distance (Å)	Atoms	Distance (Å)
<i>Bonds including hydrogens (s.d. × 10<sup>2</sup>)</i>			
H(1)-O(2) (g)	2.71(15)	H(5)-C(4) (a)	2.96(15)
H(2)-S (e)	2.65(15)	H(5)-C(6) (a)	2.96(16)
H(2)-C(10) (e)	2.52(15)	S-H(8) (e)	2.90(15)
H(3)-C(6) (c)	2.92(14)	O(1)-H(4) (f)	2.74(14)
H(3)-O(1) (e)	2.98(14)	O(1)-H(5) (f)	2.84(16)
H(4)-H(4) (b)	2.61(21)	N(10)-H(7) (e)	2.89(15)
H(4)-O(1) (e)	2.91(15)	C(10)-H(7) (e)	2.75(15)
<i>Other bonds (s.d. × 10<sup>3</sup>)</i>			
S-C(13) (d)	3.505(13)	C(22)-C(10) (e)	3.486(16)
S-C(23) (d)	3.542(12)	C(22)-O(2) (g)	3.695(18)
O(1)-C(13) (f)	3.412(16)	C(32)-O(1) (e)	3.497(18)
O(1)-C(23) (f)	3.475(16)	C(13)-O(1) (e)	3.439(17)
C(2)-C(31) (f)	3.355(16)	C(23)-C(4) (a)	3.488(17)
O(2)-C(12) (g)	3.389(15)	N(10)-C(6) (d)	3.511(15)
C(3)-C(5) (a)	3.513(17)	C(10)-C(6) (d)	3.596(17)

<sup>a</sup> The coordinates of those atoms marked a-g are related to those in Table 1 by: (a)  $x, \frac{1}{2}-y, \frac{1}{2}+z$ ; (b)  $1-x, 1-y, 1-z$ ; (c)  $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (d)  $x-1, y, z$ ; (e)  $-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (f)  $x-1, y, z-1$ ; (g)  $x-1, \frac{1}{2}-y, z-\frac{1}{2}$ .

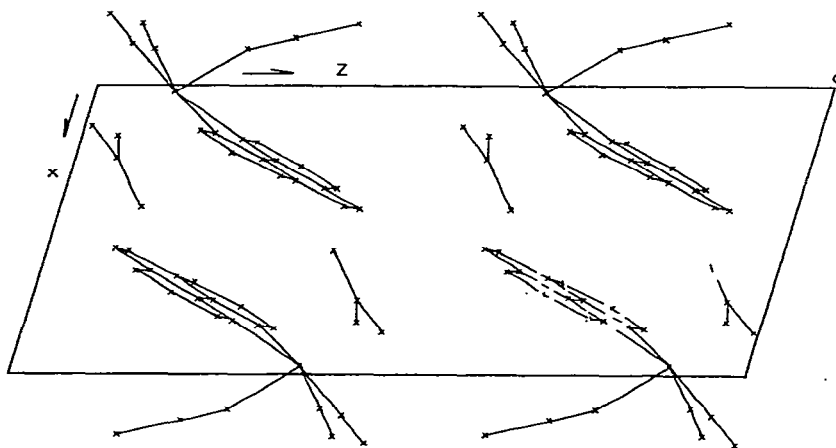


Fig. 2. The 010 projection omitting the overlap of the molecules in neighbouring unit-cells.

The methallyl ligand is defined by the plane through the atoms C(3), C(4) and C(5) and is given by  $0.6191X - 0.2005Y - 0.7593Z + 0.3614 = 0$ . It has an identical orientation, with respect to the other ligands, to the  $\pi$ -allyl in MCBAS. The angle made with the dicarbonyl is close to that in the MCBAS case, being  $7.6^\circ$  ( $8.3^\circ$ ). The methyl carbon is not significantly out of the plane being only  $0.043 \text{ \AA}$  towards the molybdenum. This corresponds to an angular distortion of less than  $2^\circ$  and contrasts

greatly with the  $9.5^\circ$  reported for  $(\pi\text{-CH}_2\text{MeCH}_2)\text{Ni}(\text{Diphos})\text{Br}$ , Churchill and O'Brien<sup>23</sup>, and  $12^\circ$  for bis(2-methylallyl)nickel, Uttech and Dietrich<sup>24</sup>. Within the ligand the C-CH<sub>2</sub> bonds agree well with the MCBAS values, having a mean of  $1.428 \pm 0.017 \text{ \AA}$ , and the C-CH<sub>3</sub> bond is  $1.491 \pm 0.018 \text{ \AA}$  compared with  $1.49 \text{ \AA}$  for bis(2-methylallyl)nickel<sup>24</sup>. The H<sub>2</sub>C-C-CH<sub>2</sub> angle is  $111.5 \pm 1.1^\circ$ ;  $115.7 \pm 1.1^\circ$  for MCBAS. The central carbon atom is again closer to the molybdenum atom, at  $2.274 \pm 0.013 \text{ \AA}$ , than the terminal CH<sub>2</sub> carbons at  $2.320 \pm 0.013 \text{ \AA}$  and  $2.350 \pm 0.012 \text{ \AA}$ .

A full list of bond lengths and angles is given in Table 6. Differences in equivalent bond lengths and angles are not claimed to be significant in view of the lack of knowledge concerning the effects of thermal motion, Busing and Levy<sup>25</sup>. The packing of molecules will also have some effect on the bonds and angles. The closest approaches are indicated by reference to Table 7 and to Fig. 2 which shows the 010 projection which was plotted using a programme written by Cross.

#### *The programmes used from the Crystal '69 system*

1. *PABLO*. This is a block-diagonal structure-factor/least-squares programme in which up to 90 atoms, fully anisotropic, and 20 layer scale factors may be refined. Several weighting schemes are available and an analysis of the scheme is output. Individual fudge factors may be applied to the variables to speed up convergence.

2. *POFOUR*. This is a fast general purpose Fourier synthesis programme using the Beevers-Lipson method of summation for space-groups 1 to 74<sup>3</sup>, excluding *Fdd2* and *Fddd*.

3. *PADI*. This is a molecular geometry programme calculating variances, covariances, mean-square thermal displacements, intra- and intermolecular bond lengths and angles, least-squares best-fit planes defined by up to 20 atoms and molecular projections onto any plane.

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