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ABSOLUTE CONFIGURATIONS OF ORGANOMETALLIC COMPOUNDS

V *. X-RAY STUDY OF $(-)_{578}$-$(\eta^5$-$C_5H_5)Mo(CO)_2SC(CH_3)NR'$ WITH $R' = (S)$-$CH(CH_3)(C_6H_5)$

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Summary

The structure and absolute configuration of the thioamido complex $(-)_{578}$-$(\eta^5$-$C_5H_5)Mo(CO)_2SC(CH_3)NR'$ with $R' = (S)CH(CH_3)(C_6H_5)$ have been determined by single-crystal X-ray diffraction. The substance crystallizes in the orthorhombic system; space group $P2_12_12_1$ with cell constants of $a = 8.314(1)$, $b = 9.020(1)$, and $c = 22.352(2)$ Å, and $Z = 4$ molecules/unit cell. The absolute configuration was determined using Bijvoet's method. Refinement of the data using the anomalous scattering contributions of Mo and S yields a final $R(F) = 0.036$ for 2715 independent reflections having $I > 3\sigma(I)$. The distorted square pyramidal coordination of the Mo atom is defined by two carbonyl carbons and the S and N atoms of the thioamido ligand occupying the four basal plane sites and the five carbons of the η^5-C_5H_5 ligand in the axial position. The Mo—ligand distances and most of the bond lengths and angles within the ligands are normal and compare closely with those of recent structure determinations. However, the distances and angles within the thioacetamide ligand show, distinctly, the effect of chelate binding to the Mo atom. In particular, the angles at the central thioacetamide carbon differ markedly from those of free thioacetamide and monodentate, S-bound metal thioacetamido complexes. The Mo atom is 1.041 Å above the plane formed by the four basal ligands. The conformation of the (S)-α-phenylethyl group with respect to the ligand plane, defined by the thio-

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* For part IV see ref. 1, also part IL of the series Optically active transition metal complexes (part XLVIII see ref. 2).

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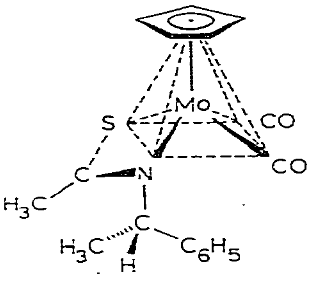
amido system and the Mo atom, is discussed. The configuration at the metal atom in the $(-)_{578}$-isomer of $(\eta^5\text{-}C_5H_5)Mo(CO)_2SC(CH_3)NR'$ is specified as (*S*).

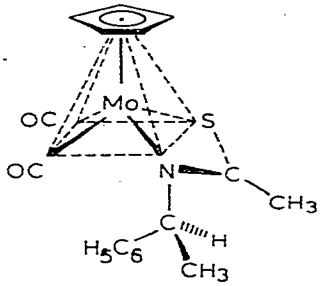
Introduction

A number of square-pyramidal organometallic complexes of the type $C_5H_5Mo(CO)_2LL'$, in which the metal is an asymmetric center, have been obtained in optically active form [3—5]. Determinations of the structure and absolute configuration have been carried out for $(+)_{578}$-$[C_5H_5Mo(CO)_2NN']PF_6$ [6,7] (NN' = Schiff base derived from pyridine carbaldehyde-2 and (*S*)-(—)-α-phenylethylamine) and $(-)_{578}$-$C_5H_5Mo(CO)_2[COCH(C_6H_5)CH(CH_3)NH(CH_3)]$ [8]. A new class of compounds in the series $C_5H_5Mo(CO)_2LL'$ is that in which the chelate ligand LL' is the bidentate (*S*,*N*)-thioamide system [9], which can be varied by changing in the thioamides SC(R)NHR' either group R at the carbon atom or group R' at the nitrogen atom.

In the reaction of $C_5H_5Mo(CO)_3Cl$ with $SC(CH_3)NHR'$, the thioacetamide derived from R' = (*S*)-(—)-α-phenylethylamine, a pair of neutral diastereoisomers Ia and Ib arise which differ only in the configuration at the Mo atom. Both isomers Ia and Ib show different ^1H NMR spectra. Isomer Ia can be obtained optically pure by fractional crystallisation [9]. Configurationally stable in the solid state and in solution at low temperatures, compounds Ia and Ib interconvert at 40°C in toluene solution by what seems to be an intramolecular metal centered rearrangement, probably taking place by a 180° rotation of the thioamido ligand with respect to the rest of the molecule [4,5,10]. In the equilibrium at 40°C, approached in toluene in a first order reaction with $\tau_{1/2} = 42$ min [9], the isomer ratio is Ia/Ib = 31/69. This isomer ratio represents a gauge of the optical induction which the asymmetric carbon atom in the amine part of the thioamide ligand exerts on the formation of the two different configurations at the Mo atom in the equilibrium [11].



(Ia)



(Ib)

An interesting feature is the extraordinarily varying degree of optical induction at the asymmetric Mo atom by the asymmetric center R' on equilibration. Depending on the substituents R and R', this optical induction ranges from 0 to 98% [5,9,10]. In order to establish the relationship between the optical induction and both, the absolute configuration at the metal center and the conformation of the (*S*)-α-phenylethyl group, we have determined by X-ray diffraction methods the structure and absolute configuration of $(-)_{578}$-$(\eta^5$-$C_5H_5)$Mo-$(CO)_2SC(CH_3)NR'$ with $R' = (S)$-α-phenylethyl.

Experimental

The details of the synthesis and physical properties of $(-)_{578}$-(C_5H_5)Mo-$(CO)_2SC(CH_3)NCH(CH_3)(C_6H_5)$ have been given elsewhere [9]. From a small quantity of crystalline material a clear, transparent fragment, more or less equidimensional, was chosen whose smallest and largest dimensions were approximately 0.3 and 0.4 mm, respectively. Preliminary cell parameters were determined directly on an Enraf-Nonius CAD-4 computer-controlled diffractometer using Mo-K_α radiation. The crystal belongs to the orthorhombic system and a check on the absences indicated that the space group is $P2_12_12_1$; this was subsequently verified with the absence of the total set of data and with the successful refinement using that space group. The subroutines used were SEARCH, INDEX, DETCELL and SCAN = —1 [12]. In order to obtain a strong set of reflections to define the orientation for data collection and for the refinement of the cell constants, the instrument was programmed to collect reflections of the type *hkl* and $hk\bar{l}$ which exceeded 400 counts above background in a prescan of approximately 5°/min and located in the range $36° \leqslant 2\theta \leqslant 50°$.

Prior to gathering an intensity set of data, an accurate determination of all the cell parameters was carried out by means of three sets of 15 reflections (maximum number the instrument can be programmed on each run) which were centered automatically by the diffractometer. The 45 reflections were then processed with the subroutine PARAM of the X-Ray '72 program [13] which only minimizes the error on 2θ during the least squares fit. A summary of the crystallographically important parameters for data collection and data processing is given in Table 1.

TABLE 1

CRYSTAL DATA

Unit cell dimensions were refined on the assumption the cell was triclinic in order to test the precision of our values.

Molecular formula	$C_{17}H_{17}NO_2SMo$
Molecular weight	395.33
Crystal shape	Irregular fragment
Crystal size	Largest dimension ~0.4 mm
Space group	$P2_12_12_1$
Unit cell data	$a = 8.314(1)$ Å
	$b = 9.020(1)$ Å
	$c = 22.352(2)$ Å
	$\alpha = 89.98(1)°$
	$\beta = 90.01(1)°$
	$\gamma = 90.02(2)°$
	$V = 1676.23$ Å^3
Density measured	1.56 gm/cm^3
Density calculated ($Z = 4$)	1.57 gm/cm^3
Radiation used for data collection	Mo-K_α = 0.71069 Å
Linear absorption coefficient	5.72 cm^{-1}
Number of independent reflections used in least squares refinement	2695

The data crystal was mounted, approximately, along the [1,0,1] direction. Therefore, in order to test experimentally the difference in intensity as a function of angle about the diffraction vector, three strong reflections of that type were measured, every 5°, over a range of 180°. The maximum deviation from the mean was much less than the square root of the intensity of any of the reflections in question. This was to be expected, given the size of the crystal, its dimensions and the magnitude of the absorption coefficient. Consequently, no effort was made to correct the data set for absorption prior to least-squares refinement. The details of data collection for this compound are identical with those of a parallel report [14] and need not be repeated here. The only changes from the parameters given in that report are as follows: (a) Only two standard reflections were used in this case (4,1,10 and $\bar{6},\bar{1},3$) and the standards were measured every 30 data points, (b) the interval of data collection ranged from $4° \leqslant 2\theta \leqslant 64°$. Of a total of 3327 reflections collected in that interval, only 2715 had intensities exceeding $3\sigma(I)$. These were corrected for Lorentz and polarization effects and used throughout the subseqeunt calculations, all of which were performed with the X-Ray '72 program [13].

Solution and refinement of the structure

A Patterson function was calculated using the 2715 independent data points measured and retained. Given the space group and the value of Z (= 4) we expected to find one Mo and one S atom amongst the most prominent vectors. The Mo was found to give the expected consistent set of vectors but the S was not totally unambiguous so the initial phasing was done with the Mo atom alone. The remaining atoms were easily found in subsequent Fourier maps and refinement of the scale factor, positional parameters of the atoms and their individual isotropic thermal parameters led to a discrepancy index:

$$R(F) = \sum|(F_o - kF_c)|/\sum|F_o| = 0.085$$

Conversion to anisotropic thermal parameters lowered this quantity to 0.056 and a difference Fourier map showed the positions of most of the hydrogen atom in the molecule. The positions of the remaining hydrogen atoms were computed and a structure factor calculation including all of the hydrogen atoms (B = 4.04 Å^2) gave an $R(F)$ factor of 0.054. Further anisotropic refinement of the heavy atoms and isotropic refinement of the hydrogens lowered the $R(F)$ factor to 0.045. The weighted discrepancy index, $R_w(F)$, at this point was

$$R_w(F) = [\sum w(F_o - kF_c)^2/\sum(wF_o)^2]^{1/2} = 0.055$$

The weighting scheme used is that described in the X-Ray '72 manual [13].

During the process of data collection on the substance immediately after the present one, we noticed, accidentally, that the diffractometer was inserting, in a random but seldom manner, an attenuator which was not needed for such a reflection. Furthermore, the instrument is programmed to make the decision during the pre-scan and, if an attenuator is needed, it is inserted before the start of the intensity scan. In the present case, the attenuator was inserted during the

TABLE 2

POSITIONAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x/a*	*y/b*	*z/c*
Mo	—0.17654(4)	0.23409(3)	0.15352(1)
S	—0.23575(14)	0.09957(11)	0.05750(5)
N	—0.1655(4)	0.3677(3)	0.0708(1)
C(1)	—0.4518(5)	0.1996(5)	0.1829(2)
C(2)	—0.4265(5)	0.3535(6)	0.1801(2)
C(3)	—0.2998(5)	0.3875(5)	0.2227(2)
C(4)	—0.2539(6)	0.2505(5)	0.2522(2)
C(5)	—0.3489(5)	0.1354(5)	0.2260(2)
C(6)	—0.1999(4)	0.2740(4)	0.0281(3)
C(7)	—0.2018(6)	0.2988(6)	—0.0377(2)
C(8)	—0.0356(7)	0.0622(5)	0.1604(2)
C(9)	0.0389(6)	0.3081(6)	0.1741(2)
C(10)	—0.1390(5)	0.5284(4)	0.0578(2)
C(11)	—0.2884(5)	0.6159(4)	0.0756(2)
C(12)	—0.4243(5)	0.6042(5)	0.0401(2)
C(13)	—0.5668(6)	0.6773(6)	0.0518(3)
C(14)	—0.5711(6)	0.7670(5)	0.1029(3)
C(15)	—0.4356(7)	0.7786(6)	0.1410(3)
C(16)	—0.2942(6)	0.7055(5)	0.1255(2)
C(17)	0.0159(6)	0.5823(6)	0.0872(3)
O(1)	0.0482(5)	—0.0392(5)	0.1629(3)
O(2)	0.1642(5)	0.3445(6)	0.1894(2)
H(1)	—0.518(6)	0.130(5)	0.149(2)
H(2)	—0.475(5)	0.426(4)	0.153(2)
H(3)	—0.282(7)	0.487(7)	0.229(3)
H(4)	—0.176(6)	0.237(5)	0.298(3)
H(5)	—0.310(6)	0.021(7)	0.229(3)
H(6)	—0.210(6)	0.203(5)	—0.067(2)
H(7)	—0.163(7)	0.377(6)	—0.057(3)
H(8)	—0.314(8)	0.324(9)	—0.054(3)
H(9)	0.102(7)	0.555(8)	0.060(3)
H(10)	0.002(9)	0.558(9)	0.135(4)
H(11)	0.032(6)	0.704(6)	0.078(2)
H(12)	—0.419(5)	0.574(7)	0.008(3)
H(13)	—0.671(5)	0.654(5)	0.019(2)
H(14)	—0.657(8)	0.826(9)	0.117(4)
H(15)	—0.469(7)	0.852(7)	0.165(3)
H(16)	—0.206(7)	0.686(6)	0.146(3)
H(17)	—0.143(5)	0.525(5)	0.015(2)

scan, most of the time *. This led us to examine the current data set for reflections which had (a) large discrepancies between observed and calculated values, (b) the intensities of such reflections would not, normally, be expected to require an attenuator. 24 such reflections were found (i.e., 0,2,0; 1,1,1; 0,1,1; 2,1,1; 1,0,2; 3,1,2; 1,1,2; 0,1,3; 0,0,4; 0,1,5; 0,0,6; 1,0,7; 1,0,8; 0,0,10; 1,0,11; 2,0,11; 1,0,12; 2,0,14; 1,0,15; 2,0,20; 1,0,21; 1,0,22; 2,0,23; 2,0,24) to meet

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* We were not doing background checks at the two ends of the scan; otherwise, the problem would have been evident from this comparison as soon as the trouble began. The trouble with the random insertion of the attenuator did not affect any of the standard reflections, either. It was accidentally noticed during the collection of data of the next crystal when a weak reflection, as noticed by the galvanometer needle of the ratemeter, was suddenly deemed strong enough to require an attenuator.

such criteria and omitting them from a structure factor calculation with no changes in the parameters lowered the $R(F)$ factor to 0.037. A software error was found by the Enraf-Nonius service engineer which was corrected and the original data crystal was remounted, oriented and checked for decay. The original parameters, including the standards, checked very well and the instrument was programmed [12] (using SCAN = −1) to collect the intensities of the two standards and of the 24 bad reflections. It was verfified that they were all badly measured since the intensity ratios of these 24 reflections to those of the standards were not only different, but their current values were close to the calculated values. Since it was considered unnecessary to have those 24 reflections and the amount of trouble needed to incorporate them into the main set and to refine them under a separate scale factor unwarranted, we eliminated them from the list using the "delete" option in the X-Ray '72 System (i.e., they are not entered in the refinement or entered in the data file, and so, they do not appear in the table of structure factors). Refinement of the structural parameters (heavy atoms anisotropic; hydrogen atoms with $B = 4.04$ Å^2) gave a $R(F)$ factor of 0.036 in one cycle and did not change with subsequent cycles of refinement. Throughout the processing of the data set, the scattering curves of Cromer and Mann [15] were used except for hydrogen atoms, for which the curve of Stewart et al. [16] was used. Corrections for the anomalous dispersion of Mo and S were made at the end of the refinement and during the calculations associated with the determination of the absolute configuration. For this correction, we used the values recommended by the International Tables for X-Ray Crystallography [17]. The final results are summarized in Tables 2, 3 and 4 which list the atomic coordi-

TABLE 3

THERMAL PARAMETERS (X 10^3) OF NON-HYDROGEN ATOMS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	31.4(2)	38.5(2)	32.2(2)	2.28(9)	−0.68(10)	−0.93(10)
S	53.8(6)	41.9(5)	41.6(5)	−1.9(4)	0.5(4)	−8.3(4)
N	30(1)	37(1)	40(2)	2(1)	1(1)	1(1)
C(1)	41(2)	56(2)	57(3)	−9(2)	0(2)	4(2)
C(2)	41(2)	55(2)	58(3)	5(2)	13(2)	3(2)
C(3)	42(2)	53(2)	50(2)	1(2)	12(17)	−11(17)
C(4)	49(2)	65(2)	32(2)	−4(2)	1(1)	−3(2)
C(5)	49(2)	55(2)	40(2)	−11(2)	8(2)	5(2)
C(6)	35(2)	47(2)	35(2)	0.7(1)	5(1)	−0.5(1)
C(7)	71(3)	75(3)	36(2)	−3(3)	8(2)	3(2)
C(8)	68(3)	60(2)	55(3)	22(2)	−14(2)	0.6(2)
C(9)	42(2)	71(3)	53(3)	2(2)	−1(2)	−5(2)
C(10)	38(2)	40(2)	50(2)	−5(1)	3(2)	4(2)
C(11)	35(2)	38(2)	51(2)	−6(1)	2(1)	6(2)
C(12)	44(2)	53(2)	56(3)	−2(2)	0.8(2)	6(2)
C(13)	49(3)	56(2)	71(3)	2(2)	0.6(2)	3(2)
C(14)	53(3)	45(2)	77(3)	6(2)	13(2)	3(2)
C(15)	65(3)	54(2)	73(3)	3(2)	12(2)	−21(2)
C(16)	47(2)	51(2)	69(3)	−3(2)	−3(2)	−12(2)
C(17)	44(2)	53(2)	101(5)	−12(2)	−3(3)	2(3)
O(1)	93(3)	83(3)	115(4)	48(3)	−21(3)	10(3)
O(2)	42(2)	123(4)	101(3)	−2(2)	−14(2)	−18(3)

TABLE 4

THERMAL PARAMETERS (X 10^3) OF THE HYDROGEN ATOMS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	U_{iso}	Atom	U_{iso}
H(1)	47(14)	H(10)	121(30)
H(2)	37(10)	H(11)	59(15)
H(3)	65(18)	H(12)	57(18)
H(4)	95(25)	H(13)	40(13)
H(5)	83(21)	H(14)	96(25)
H(6)	46(14)	H(15)	82(18)
H(7)	68(18)	H(16)	58(16)
H(8)	102(22)	H(17)	42(11)
H(9)	81(22)		

TABLE 5

BOND DISTANCES (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Mo—S	2.514(1)	C(1)—C(2)	1.406(7)	C(1)—H(1)	1.12(5)
Mo—N	2.209(3)	C(2)—C(3)	1.452(1)	C(2)—H(2)	0.97(4)
Mo—C(1)	2.402(5)	C(3)—C(4)	1.453(6)	C(3)—H(3)	0.92(6)
Mo—C(2)	2.415(5)	C(4)—C(5)	1.431(7)	C(4)—H(4)	1.22(6)
Mo—C(3)	2.314(5)	C(5)—C(1)	1.412(7)	C(5)—H(5)	1.09(7)
Mo—C(4)	2.303(4)	C(11)—C(12)	1.384(6)	C(7)—H(6)	1.08(5)
Mo—C(5)	2.339(5)	C(12)—C(13)	1.381(7)	C(7)—H(7)	0.89(6)
Mo—C(8)	1.949(5)	C(13)—C(14)	1.400(8)	C(7)—H(8)	1.02(7)
Mo—C(9)	1.966(5)	C(14)—C(15)	1.417(8)	C(17)—H(9)	0.96(7)
S—C(6)	1.731(4)	C(15)—C(16)	1.392(7)	C(17)—H(10)	1.09(10)
C(6)—N	1.306(5)	C(16)—C(11)	1.378(7)	C(17)—H(11)	1.12(6)
C(6)—C(7)	1.488(6)	C(8)—O(1)	1.151(7)	C(12)—H(12)	0.76(6)
N—C(10)	1.494(5)	C(9)—O(2)	1.144(7)	C(13)—H(13)	1.15(4)
C(10)—C(17)	1.526(7)			C(14)—H(14)	0.95(7)
C(10)—C(11)	1.525(5)			C(15)—H(15)	0.90(6)
				C(16)—H(16)	0.89(6)
				C(10)—H(17)	0.96(5)

TABLE 6

ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

S—Mo—N	63.79(8)	C(2)—C(1)—C(5)	110.1(4)
S—Mo—C(8)	78.5(2)	C(1)—C(2)—C(3)	106.7(4)
S—Mo—C(9)	122.8(2)	C(2)—C(3)—C(4)	108.0(4)
N—Mo—C(9)	88.5(2)	C(3)—C(4)—C(5)	106.6(4)
N—Mo—C(8)	118.4(2)	C(4)—C(5)—C(1)	108.5(4)
C(8)—Mo—C(9)	72.8(2)	C(12)—C(11)—C(16)	118.7(4)
Mo—S—C(6)	81.5(2)	C(11)—C(12)—C(13)	123.7(5)
S—C(6)—C(7)	120.7(3)	C(12)—C(13)—C(14)	116.9(5)
S—C(6)—N	110.4(3)	C(13)—C(14)—C(15)	120.9(5)
C(7)—C(6)—N	128.8(4)	C(14)—C(15)—C(16)	119.1(5)
Mo—N—C(10)	134.3(2)	C(15)—C(16)—C(11)	120.6(5)
N—C(10)—C(11)	109.3(3)	Mo—C(8)—O(1)	178.2(5)
N—C(10)—C(17)	110.5(3)	Mo—C(9)—C(2)	175.2(5)
C(11)—C(10)—C(17)	114.2(4)		
C(10—C(11)—C(12)	118.4(4)		
C(10)—C(11)—C(16)	122.9(4)		

TABLE 7

LEAST SQUARES PLANES AND DISTANCES OF ATOMS FROM THE PLANE (Å) IN ORTHOGONAL Å SPACE

(a) Plane based on C(1), C(2), C(3), C(4), C(5)

$-0.6956x + 0.1449y + 0.7036z = 5.7534$

C(1)	−0.0023	C(2)	0.0081	C(3)	−0.0108
C(4)	0.0095	C(5)	−0.0046	Mo	−2.0118

(b) Plane based on C(11), C(12), C(13), C(14), C(15), C(16)

$-0.3091x - 0.7836y + 0.5390z = -2.7031$

C(11)	0.0022	C(12)	0.0071	C(13)	−0.0029
C(14)	−0.0100	C(15)	0.0189	C(16)	−0.0153

(c) Plane based on C(8), C(9), S, N

$-0.7898x + 0.1264y + 0.6002z = 2.4445$

C(8)	0.0125	C(9)	−0.0122	S	−0.0116
N	0.0112	Mo	1.0413		

(d) Plane based on S, N, C(6), Mo

$0.9702x - 0.2227y - 0.0960z = -2.2242$

S	−0.0007	C(10)	−0.0773
N(1)	−0.0012	C(6)	0.0013
C(7)	−0.0377	Mo	0.0006

(e) Plane based on S, N, C(6)

$0.9704x - 0.2229y - 0.0933z = -2.2221$

Mo	0.0070

(f) Equations of lines in orthogonal Å space [a]

(α) Line defined by C(10), C(17)

$L(1) = I = (-0.51186) + (0.84408)T$

$L(2) = J = (5.00910) + (0.31901)T$

$L(3) = K = (1.62000) + (0.43101)T$

(β) Line defined by C(10), C(11)

$L(1) = I = (-1.77700) + (0.09796)T$

$L(2) = J = (5.16060) - (0.51788)T$

$L(3) = K = (1.49060) - (0.26163)T$

(g) Angles between planes

Plane 1	Plane 2	Angle
(a)	(d)	39.22°
(b)	(d)	79.80°

(h) Angles between lines and planes

Line	Plane	Angle
(α)	(d)	45.05°
(β)	(d)	21.47°

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[a] See ref. 14 for definitions.

nates and the thermal parameters for the atoms. Bond lengths and angles are listed in Tables 5 and 6. The equations of least squares planes and the torsional angles are given in Tables 7 and 8. Table 7 also shows the deviations of relevant atoms from the least squares planes described. The stereo drawings (Figs. 1, 2, 3) were obtained with Johnson's ORTEP 2 [18] as locally implemented at the Houston computer center which includes the additional feature of an automatic-

TABLE 8

TORSIONAL ANGLES (°) [a]

Atoms				Angle
A	B	C	D	
C(8)	Mo	S	C	−129.76
C(8)	Mo	N	C(6)	58.62
C(6)	N	C(10)	C(17)	−130.91
C(6)	N	C(10)	C(11)	102.62
N	C(10)	C(11)	C(16)	106.59
N	C(10)	C(11)	C(12)	−73.19

[a] According to the IUPAC-IUP convention [19], i.e., in the fragment ABCD, + = clockwise rotation of bond AB about bond BC so as to eclipse CD with AB along the line of sight (BC).

ally chosen line of sight. This feature * allows for a view containing the minimum overlap of atoms possible along the line of sight of the viewer. A table of the structure factors, their estimated standard deviations and the values of the calculated structure factors is available **.

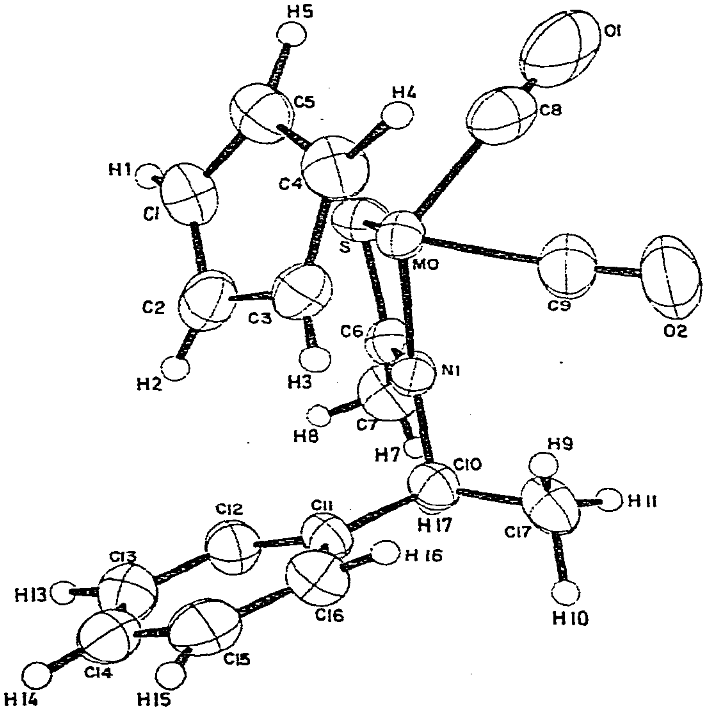

Fig. 1. A general view of Ia in its correct absolute configuration showing the labelling scheme used in the crystallographic study. The thermal ellipsoids are 50% probability envelopes for the heavy atoms and of convenient size for the hydrogen atoms. H(12) is obscured by C(12) and H(6) by other atoms.

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* We thank Dr. Raymnond E. Davis, University of Texas, Austin, for making his program available to us.

** A table of structure factors can be obtained from the authors.

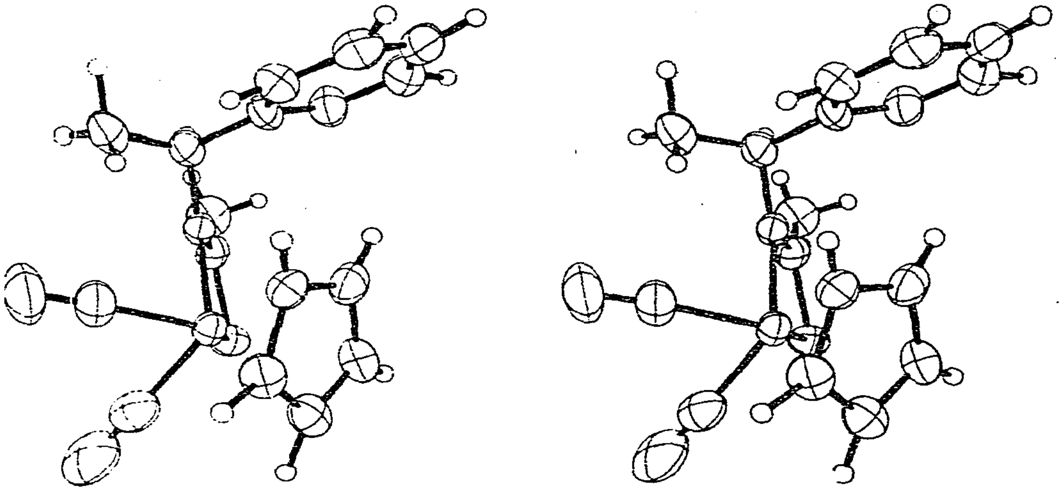


Fig. 2. A stereo pair of the molecular conformation of Ia in its correct absolute configuration. The ellipsoids are 50% probability envelopes.

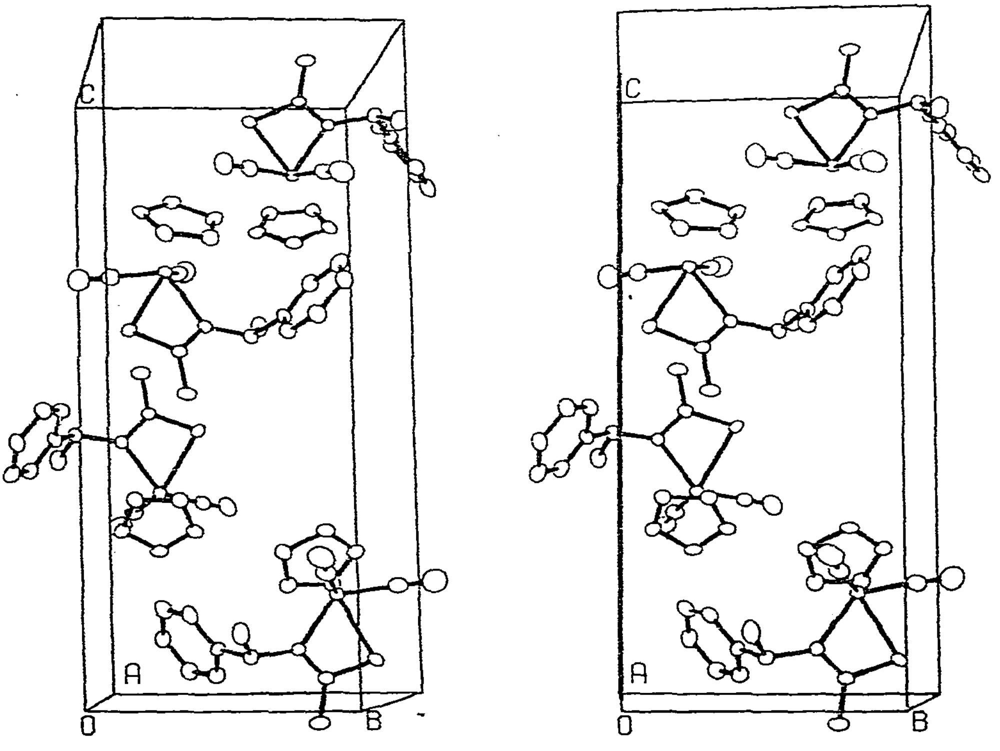


Fig. 3. A packing diagram in stereo showing the molecules Ia in their correct absolute configuration.

Determination of the absolute configuration of Ia

When refinement had converged, the molecular configuration was the mirror image of that given in Fig. 1, in which the numbering system employed in the crystallographic analysis is indicated. A check on the $F(hkl)$'s calculated for that absolute configuration and its enantiomer showed 21 reflections suitable

TABLE 9

DETERMINATION OF THE ABSOLUTE CONFIGURATION OF THE DIASTEREOISOMER WITH $[\alpha]^{20}_{578}$ — 470° IN TOLUENE SOLUTION

Reflection number	Indices	F(calc) (hkl)	F(calc) ($\bar{h}\bar{k}\bar{l}$)	Calc. F ratio [a]	Meas. F ratio [b]
1	1,4,1	44.91	45.98	0.98	1.02
2	1,2,1	62.40	59.85	1.04	0.97
3	3,1,1	17.63	16.49	1.07	0.94
4	7,1,1	48.15	46.77	1.03	0.98
5	5,1,2	73.84	72.83	1.01	0.98
6	4,1,2	22.29	20.58	1.08	0.93
7	2,1,2	32.50	31.23	1.04	0.98
8	7,2,2	54.66	55.89	0.98	1.01
9	4,4,2	26.67	25.70	1.04	0.97
10	2,7,2	19.22	18.27	1.05	0.95
11	5,6,3	19.79	21.00	0.94	1.05
12	4,6,3	33.88	34.97	0.97	1.04
13	6,2,3	18.09	16.66	1.08	0.92
14	4,2,3	95.03	93.71	1.01	0.98
15	2,2,3	70.79	69.59	1.02	0.99
16	1,1,2	25.56	23.69	1.08	0.95
17	2,1,4	107.86	106.47	1.01	0.98
18	2,2,4	68.52	66.60	1.03	0.97
19	3,2,4	7.73	9.00	0.86	1.19
20	6,2,4	41.91	42.93	0.98	1.01
21	1,1,4	5.17	4.15	1.25	0.76 [c]

[a] Calc. F(hkl)/Calc. F($\bar{h}\bar{k}\bar{l}$). [b] Ratio of experimentally measured F(hkl)/F($\bar{h}\bar{k}\bar{l}$). [c] This is the weakest reflection in the list and F(hkl) was measured with least precission but, clearly, its ratio to F($\bar{h}\bar{k}\bar{l}$) satisifes the test of being the smaller of the two by a wide margin.

for the Bijvoet test [20]. The diffractometer was programmed to measure each of the 21 pairs, four times each, and a summary of the results is given in Table 9. The measured values listed are averaged over the four independent measurements and the results, consistently, show that the correct absolute configuration of Ia is that shown in Fig. 1; i.e. the mirror image of that described by the coordinates in Table 2. The stereo pair shown in Fig. 2 and the packing diagram (Fig. 3) also depict the molecules of Ia in their correct absolute configuration. This result is in agreement with the fact that the optically active amine used in the synthesis was (*S*)—(—)-α-phenylethylamine. The absolute configuration shown in Figs. 1, 2, and 3 corresponds to isomer Ia with $[\alpha]^{20}_{578}$ — 470° and $[\alpha]^{20}_{365}$ + 7415° in toluene solution.

The proposed extension of the *R*,*S* system [21] to poly*hapto* ligands in organometallic compounds [22] gives as the priority sequence of ligands in Ia: $C_5H_5 > S > N > C(CO)$. Consequently, the absolute configuration at the Mo atom is (*S*), as shown in Figs. 1, 2, and 3. For a detailed discussion of the problems associated with the specification of configuration in square pyramidal complexes, see ref. 7.

Description of the molecular structure and discussion

As shown in Figs. 1—3, the molecule consists of a central Mo atom bound by a set of five ligands distributed in a distorted square-pyramidal arrangement. The

TABLE 10

COMPARISON OF MOLECULAR PARAMETERS WITH LITERATURE VALUES. DISTANCES IN Å AND ANGLES IN DEGREES

Compound		Mo—S	Mo—N	Mo—C(O)	Mo—C(Cp) [a]	S—C	C—N	S—Mo—X	Ref.
Ia	$(\eta^5\text{-}C_5H_5)Mo(CO)_2SC(CH_3)NR'$ R = (*S*)-α-phenylethyl	2.514(1)	2.209(3)	1.949(5) 1.966(5)	2.355(51)	1.731(4)	1.306(5)	63.79(8) [b]	This study
II	$(\eta^5\text{-}C_5H_5)_2Mo(S_2C_6H_3CH_3)$	2.434(5) 2.431(5)	—	—	2.337(47) 2.317(43)	1.777(16) 1.766(16)	—	83.9(4) [c]	23
III	$[(\eta^5\text{-}C_5H_5)_2Mo(S(CH_2)_2NH_2)]I$	2.438(6)	2.211(15)	—	2.307(65) 2.332(46)	1.823(25)	1.519(29)	78.4(4) [b]	24
IV	$Na_2Mo_2O_4(cyst)_2 \cdot 5H_2O$	2.490(6)	2.230(16)	—	—	1.865(24)	1.503(26)	80.7(4) [b]	25
V	$[C_{21}H_{19}MoN_2O_2]PF_6$	—	2.182(10) 2.258(11)	1.984(14) 1.988(14)	2.345(43)	—	1.270(16) 1.391(18) [e]	74.0(4) [d]	6,7
VI	$HB(pz)_3Mo(CO)_2NNC_6H_5$	—	2.231(5) 2.212(4) 2.210(4)	1.973(6) 2.020(6)	—	—	1.336	81.8(2)	26
VII	$Mo(S_2CC_6H_5)_4$	2.543(1) 2.475(1)	—	—	—	1.680(3) 1.679(4)	—	70.2(1) [c] 70.6(1) [c]	27
VIII	$Mo_2O_2(quin)_2(SCH_2CH_2O)$	2.484(2) 2.484(2)	2.201(6) 2.209(6)	—	—	— [f]	— [f]	76.8(2) [g] 75.5(2)	28
IX	$ONMo[S_2CN(t\text{-}Bu)_2]_3$	2.518(34) [h]	—	—	—	1.717(31) [h]	—	69(1) [i]	29

[a] Mean value and deviation *from* mean. Each ring is entered separately. [b] X = N. [c] X = S. [d] N—Mo—N angle. [e] Average of two values. [f] Not given. [g] O—Mo—N angle in the 8-hydroxyquinoline ligand; S *trans* to the 8-hydroxyquinoline nitrogen. [h] Mean of six independent values. [i] Mean of three independent values.

distortions are caused by the fact that the ligands are sufficiently dissimilar and the Mo ligand distances vary over a considerable range. For example, the Mo—S distance is 2.514(1) Å while the mean Mo—C(Cp), Mo—N, and Mo—C(CO) distances are, respectively, 2.355(51), 2.209(3), and 1.958(8) Å. The molecule is square-pyramidal around the Mo atom which can best be appreciated, looking at the stereo plot (Fig. 2), by the fact that the angles between the ring centroid and the ligand atoms of the basal plane are larger than 90°, and by the fact that the Mo atom is 1.041 Å above the plane defined by S, N, and the two carbonyl carbon atoms. This situation, then, is similar to that found for $[(\eta^5\text{-}C_5H_5)Mo(CO)_2NN']^+$ (NN' = the Schiff base of pyridine carbaldehyde-2 and (S)-(—)-α-phenylethylamine, described in detail elsewhere [6,7]. That Schiff base complex appears in Table 10 as compound V, and we note that the mean Mo—C(Cp) distance has not changed and that there has been a small, but distinct, change in the Mo—C(CO) distances in going from the Schiff base pair of nitrogens in V to the S,N pair in Ia. Interestingly, the C—Mo—C angle defined by the two carbonyl ligands remains the same in both cases, being 73.8(6)° for the Schiff base complex V, and 72.8(2)° for the thioacetamido complex Ia.

Table 10 was prepared in order to compare our current results with literature values. As can be seen from the extreme variety of substances listed in that table, there are not too many suitable compounds to compare ours with. There are large numbers of $(\eta^5\text{-}C_5H_5)Mo$ derivatives and we have already shown [7] that the geometry of this fragment is largely invariant to changes in ligands elsewhere in the molecule. The results quoted in Table 10 merely go to confirm this result. Also, it is true that, in general, there is enough vibrational motion in the C_5H_5 rings of these molecules to render comparisons impossible since the positions of the carbons are not always equally defined, as can be seen from the large values of the deivations from the mean values quoted in Table 10 and from even more extensive data given in refs 1 and 7. As expected, the C_5H_5 ring is planar (Table 7) and the difficulties we refer to here are associated with the locations of the carbon atoms in that plane [1,7]. The non-hydrogen atoms of the thioacetamide ligand (i.e., S, C(6), N, C(7)) and the Mo atom lie in the same plane, with the terminal methyl carbon C(7) only 0.04 Å out of the mean plane and towards the C_5H_5 ring. As can be seen from Table 6, the CO ligands are straight, the Mo—C—O angles being 178.2(5) and 175.2(5)°.

If we consider the Mo—S distances listed in Table 10 the following pattern emerges for most of the examples given: when the ligand angle, S—Mo—N or S—Mo—S, opens up and the S—C(ligand) distance is long, there is a short Mo—S distance. Compounds Ia, II, III and IV fall in this category. Compound VIII seems to do so, as well, but we cannot be sure since the authors of that report did not give S—C distances and coordinates were not available either. Judging from the fact that the sulfur is connected by a single bond to an aliphatic carbon, by the angle at Mo and the Mo—S distance, we believe the rest of the molecular parameters should resemble those in IV. Compound VII does not conform with this generalization since one of its Mo—S bonds is long and the other one short, compared with Ia. We believe, however, that this phenomenon us due to crowding of the 8 S atoms around the Mo atom causing long and short Mo—S distances to occur, as was noted in a related case of octacoordination [30]. It is interesting to observe that, in spite of the very drastic difference in the nature of Ia and

TABLE 11

A COMPARISON OF BONDING PARAMETERS IN THE THIOACETAMIDE LIGAND. DISTANCES IN Å AND ANGLES IN DEGREES

Compound		Nature of bonding	C—S	C—N	C—C	S—C—N	S—C—C	N—C—C	Ref.
Ia	$(\eta^5\text{-}C_5H_5)Mo(CO)_2SC(CH_3)NR'$ R' = (*S*)-α-phenylethyl	MoSCN bidentate	1.731(4)	1.306(5)	1.488(6)	110.4(3)	120.7(3)	128.8(4)	This study
X	Free thioacetamide [a]	—	1.700(8)	1.324(11)	1.497(11)	119.6(7)	121.7(6)	118.6(7)	31
			1.716(8)	1.323(23)	1.490(11)	121.7(6)	121.5(6)	116.7(7)	
XI	*trans*-Ni(thioacet)$_4$Cl$_2$ [b]	Ni—S monodentate	1.679(4)	1.307(6)	1.502(6)	123.4(7)	119.7(4)	117.0(4)	32

[a] Two independent molecules in the asymmetric unit. [b] Four independent ligands in the asymmetric unit; quantities listed are mean values.

IX, an angle at Mo of about the same magnitude and a similar S—C distance leads to similar Mo—S lengths.

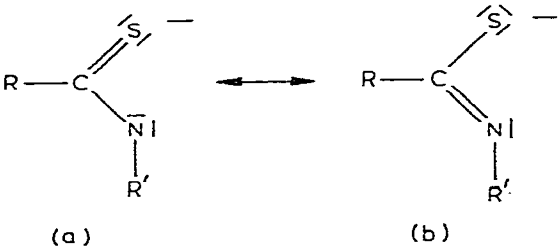
The behaviour of the Mo—N distances is somewhat more complex since no clear pattern is obvious from the examples cited. For instance, in comparing Mo—S vs. Mo—N distances in Ia and IV one is tempted to say that, since a decrease of the Mo—S distance in IV is accompanied by an increase in the Mo—N distance, this should be a sensible behaviour. The results for III are not very encouraging in that regard and those for VIII, if anything, are in the opposite direction. Attempts to compare Mo—N vs. Mo—C(CO) and efforts to look for *trans* effects are equally unrewarding. For example, the carbonyl Mo—C distances in VI are longer than those in Ia; however, the Mo—N distances are about the same in both. Furthermore, the longer Mo—C(CO) distance is associated with the longer Mo—N(*trans*) bond in VI, as is also the case in V. Therefore, since the examples of Table 10 are of such wide chemical variety and there are so many variables (i.e., changes in formal charge, coordination number, etc.), at this stage no further correlations will be attempted.

In the present structural study we found no unusual intermolecular contacts. The shortest contact is O(1)—H(4) (2.44 Å) between different molecules which is longer than the sum of Van der Waal's radii.

The effect of metal binding upon the thioamide ligand

It has been noted [32] that all previously available structural studies [32—34] of metal-complexed thioamides contain metal—sulfur bonds, only. Our compound Ia, therefore, is the first example of a structurally characterized bidentate thioamide derivative. As a result of this observation it seemed desirable to compare the bonding parameters of the free thioacetamide X [31] with those of a metal—sulfur bound species and with our bidentate ligand. Table 11 lists those results. We chose the most recent example of a monodentate thioamide complex, *trans*-dichlorotetrakis(thioacetamide)nickel(II) [32], however, the results found by Nardelli et al. [33] and by Amma et al. [34] are statistically the same as those given in the nickel complex XI.

The C—S bond in XI decreases markedly upon complexation by sulfur only while in the bidentate ligand in Ia the C—S distance has increased, on the average, by 0.023 Å (2.5 σ) compared with the free thioacetamide X. At the same time there is a significant difference in the C—N distance between Ia and X which, together with the C—S result, seems to indicate that resonance form (b) becomes more important on bidentate binding to Mo.



Whereas the electron density at the C—S bond is diminished the non-bonded electron density from N is drawn towards the carbon atom to increase the bond order between those two atoms. It is notable that a major rearrangement of bond angles at the thioamide carbon takes place at the same time: In the free thioacetamide and in the S-bound metal complexes all three angles about the central carbon are close to 120°. However, in our case, one angle (S—C—C = 120.7(3)° does not change from that value while the other two change markedly, i.e., S—C—N to 110.4(3)° and N—C—C to 128.8(4)°, the mean of these two values being nearly 120°. This phenomenon of having a trigonal carbon atom with one normal angle while one contracts and the other expands as a result of electronic shifts caused by metal binding has already been noticed by us [1] and by Churchill and Chang [35] in related systems.

Stereochemical considerations

Plane d of Table 7, defined by S, N, C(6), and Mo is referred to as the ligand plane. With small deviations this plane also contains C(7) and C(10). Although small, the deviation of C(10) (—0.077 Å) is towards the C_5H_5 ring as was the case for the (*S*)-α-phenylethyl substituent with respect to its ligand plane in $(+)_{578}$-$[C_5H_5Mo(CO)_2NN']PF_6$ (NN' = Schiff base derived from pyridine carbaldehyde-2 and (*S*)-α-phenylethylamine [7]. Two major sources for different conform ations within the molecule can be envisaged in Ia: first, the conformers that arise from rotation of the (*S*)-α-phenylethyl group around the N—C(10) bond; second, the conformers that arise from rotation of the phenyl ring around the C(10)—C(11) vector. The last quantity can be defined as the torsional angle of the C(11)—C(12) vector with respect to the N—C(10) vector about the C(10)—C(11) bond. As the chiral carbon atom C(10) attempts to rotate around the N—C(10) bond its substituents, the large phenyl ring, the middle size methyl group, and the small substituent H(17) [36—38], give rise to different degrees of crowding with adjacent groups. After describing the angular arrangement of the vectors between C(10) and its substituents with respect to the ligand plane and the closest contacts between these substituents and adjacent intramolecular fragments, we shall discuss how rotation, around N—C(10), of the entire (*S*)-α-phenylethyl group affects the intramolecular contacts.

The conformation found in the crystal

The phenyl ring projects towards the cyclopentadienyl ring, and the angle between the vector from the asymmetric carbon atom C(10) to the phenyl ring carbon C(11) with the ligand plane is 102.62° (Fig. 1) while the torsional angle of the phenyl ring, as defined above, is —73.19°, using the IUPAC notation [19]. The vector C(10)—C(17), from the asymmetric carbon atom to the methyl group, forms a torsional angle of —130.91° with the vector N—C(6). Thus, the methyl group points to the side opposite of the cyclopentadienyl ring. The hydrogen atom H(17), bonded to the asymmetric carbon atom C(10) defines a C(10)—H(17) vector which is almost in the ligand plane. There are no intramolecular contacts for the conformation of Ia found in the crystal, which are shorter than normal packing contacts *. The distances between C_5H_5 hydrogens

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* Normal packing contacts are in the range of 2.20 to 2.40 Å [39].

and all other atoms exceed 2.50 Å and the orientation of the phenyl plane is such as to avoid short contacts with adjacent groups. Whereas in the conformation found in the structure determination the closest contacts between the phenyl ring *ortho*-hydrogens H(12) and H(16) with H(17), H(9), H(10), H(11) and H(6), H(7), H(8) are larger than 2.3 Å, rotation around the C(10)—C(11) vector produces, in unfavourable situations, contacts as short as 1 Å.

Other conformations the molecule can aquire

In fluid media molecule Ia could prefer conformations different from that found in the crystal studied and which arise by rotation of the (*S*)-α-phenylethyl group around the N—C(10) bond: Clockwise rotation by about 120° brings the methyl group C(17) into the ligand plane, in which case the methyl carbon atoms C(17) and C(7) would come as close as 2.7 Å and which would cause severe steric interaction of their hydrogen atoms. On anti-clockwise rotation by about 120° the phenyl carbon atoms C(11) and C(14) are coplanar with the ligand plane. If the phenyl ring is normal to the ligand plane the distance of the methyl carbon atom C(7) to the phenyl plane is only 2.7 Å and the interaction of the methyl hydrogens H(6), H(7), H(8) with the π-cloud of the aromatic system would be unacceptable. Rotation of the phenyl plane around the bond C(10)—C(11) would make the interatomic contacts C(12)/H(12), C(16)/H(16) on the one hand and C(7)/H(6), H(7), H(8) on the other hand even worse. Also, a conformation in which, on a projection along the ligand plane, the methyl carbon atom C(7) bisects the angle between the big substituent (phenyl) abd the middle size substituent (methyl), at the asymmetric center C(10), would suffer from steric crowding. However, all the conformations in which H(17) is either in the ligand plane, pointing away from the Mo atom, or at angles of up to ±30 to 40° with respect to the ligand plane seem to be conformations with no intramolecular short contacts.

In the Introduction, the two possible diastereoisomers for the thioacetamido complexes Ia and Ib abd their equilibrium ratio, 69/31, were discussed. On the basis of the present structure determination there are no obvious reasons why diastereoisomer Ia dominates the equilibrium mixture over Ib. Model considerations show that for diastereoisomer Ib conformations with no bad intramolecular contacts can also be found. In the recent structure determination of $(+)_{578}$-$[C_5H_5Mo(CO)_2NN']PF_6$, NN′ = Schiff base derived from pyridine carbaldehyde-2 and (*S*)-(—)-α-phenylethylamine [7], we found a delicate balance of reasonable to unacceptable conformations as the (*S*)-α-phenylethyl group rotates with respect to the ligand plane. Even in the best conformation, distances shorter than packing constants cannot be avoided. This is due, at least in part, to the different chelate ring size in the Schiff base complex compared to the thioamido complex Ia. Because of the five-membered ring in the Schiff base derivative, the distance of the asymmetric carbon atom to the Mo atom is only 3.2 Å, whereas in the four-membered chelate ring of the thioamido complex Ia the distance from the Mo atom to the asymmetric carbon atom C(10) is 3.4 Å. The increase in the distance between the metal atom and the asymmetric carbon, attached to it via the nitrogen atom, is responsible for the fact that in the thioamido complex Ia the methyl and phenyl substitutents at atom C(10) are much farther away from the C_5H_5 ring and the CO groups than are comparable groups in the Schiff base complex. The dominant feature for the conformation of Ia seems to be the repulsion of the methyl group C(17), H(6), H(7), H(8) with the phenyl and methyl substituents at the asymmetric carbon atom C(10).

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