The Crystal Structure of Dicarbonyl(η-cyclopentadienyl)(3-aminopropionyl)molybdenum(II)

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Abstract. $(\eta\text{-}C_5H_5)Mo(CO)_2(COCH_2CH_2NH_2)$, orthorhombic, $Pna2_1$, $a = 18 \cdot 932$ (35), $b = 8 \cdot 734$ (12), $c = 6 \cdot 472$ (18) Å, $D_m = 1 \cdot 79$, $D_c = 1 \cdot 81$ g cm^{-3}, $Z = 4$. The structure was determined from room-temperature counter data and refined by least-squares calculations to a final R of $0 \cdot 079$ for 799 observed reflections. Molecules are associated through intermolecular hydrogen bonds ($>C=O\cdots H-N$) with distances of $2 \cdot 090$ Å for $O\cdots H$, $1 \cdot 04$ Å for H–N, $3 \cdot 087$ Å for $O\cdots N$, and an $O\cdots H-N$ angle of $159°$.

Introduction. Crystals were supplied by Knoth (1973). Cell dimensions resulted from the least-squares refinement of the angles for seven reflections centered on the diffractometer. A needle crystal of dimensions $0 \cdot 007 \times 0 \cdot 006 \times 0 \cdot 039$ cm was mounted with its c axis parallel to the φ axis of a Picker automatic diffractometer for data collection. Intensities for 1038 reflections [799 with $F_o > \sigma(F_o)$] were measured by the θ–2θ scan technique at a scan rate of $1°$ min^{-1} using Zr-filtered Mo $K\alpha$ radiation ($0 \cdot 7107$ Å, $2\theta_{max} = 50°$). A symmetrical scan range of $1 \cdot 5°$ in 2θ was used plus the $K\alpha_1$–$K\alpha_2$ angle dispersion; backgrounds of 15 s were measured before and after each peak. No crystal decomposition was observed. Lorentz and polarization corrections were applied but no absorption correction [μ(Mo $K\alpha$) = $12 \cdot 0$ cm^{-1}].

Preliminary precession and Weissenberg films showed systematic absences of $0kl$ ($k+l = 2n+1$) and $h0l$ ($l = 2n+1$) indicative of space groups $Pna2_1$ and $Pnma$ (a, c, b, orientation). The correct space group is $Pna2_1$ as confirmed by the refinement. The structure was solved by Patterson and Fourier techniques and refined by full l-matrix least-squares calculations (Prewitt, 1965) minimizing $\sum w(|F_o| - |F_c|)^2$. Neutral-atom scattering factors were used (Hanson, Herman, Lea & Skillman, 1964); the molybdenum atom was corrected for the real and imaginary part of the anomalous scattering effect (*International Tables for X-ray Crystallography*, 1962).

The molybdenum, cyclopentadienyl, and terminal carbonyl atoms were given anisotropic thermal parameters in the refinement. The aminopropionyl ring was not refined anisotropically in the final refinements because we suspect there is a superposition of the conformation found with small contribution(s) from

(an)other conformation(s) which we have not accounted for. Intermediate anisotropic refinement of the aminopropionyl atoms showed these atoms to be quite anisotropic in some cases bordering of the non-positive-definite limit. Final electron density difference maps calculated parallel to MoC(3)N, based on isotropic aminopropionyl atoms, showed very broad peaks remaining, especially around C(4) and C(5); however, the largest was only $0 \cdot 5$ e Å^{-3}.

All members of the form were measured for 11 reflections which showed the largest calculated difference between $F(hkl)$ and $F(\bar{h},\bar{k},\bar{l})$ to determine the correct enantiomorph with respect to the polar c axis. Members of the form having the same anomalous dispersion factor were averaged. All differences greater than 1σ (8 out of 11) indicated the enantiomorph described here is the correct one. Although individual differences were not significant, the fact that all were in the same direction is significant; in any case, a separate refinement for the other enantiomorph was essentially equivalent with respect to all structural features.

Table 1. *Positional parameters given as fractions of lattice translations with estimated standard deviations in parentheses*

Values for C,H,N,O are $\times 10^4$, those for Mo $\times 10^5$.

	x	y	z
Mo	12148 (7)	18751 (16)	0
C(6)	500 (17)	3914 (35)	−1007 (44)
C(7)	1014 (12)	4480 (27)	604 (36)
C(8)	883 (13)	3787 (29)	2536 (39)
C(9)	327 (14)	2775 (27)	2207 (55)
C(10)	101 (11)	2809 (27)	135 (74)
C(1)	1003 (11)	−312 (23)	583 (30)
O(1)	839 (9)	−1517 (17)	830 (24)
C(2)	1133 (12)	903 (32)	−2685 (44)
O(2)	1083 (9)	334 (20)	−4300 (22)
C(3)	2159 (12)	2570 (24)	−1802 (41)
O(3)	2177 (8)	3260 (18)	−3397 (28)
C(4)	2860 (13)	2214 (24)	−637 (37)
C(5)	2757 (13)	2281 (28)	1597 (46)
N(1)	2128 (8)	1430 (19)	2167 (29)
H(6)	492	4214	−2470
H(7)	1395	5292	247
H(8)	1175	3875	3757
H(9)	66	2067	3277
H(10)	−265	2293	−576
H(41)	3008	1130	−1023
H(42)	3204	2954	−1200
H(51)	3236	1900	2193
H(52)	2750	3440	1936
H(N1)	2245	266	2091
H(N2)	1990	1670	3591

Table 2. *Final temperature factors and estimated standard deviations (in parentheses)*

Anisotropic temperature factors are given by the expression: $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

Anisotropic factors

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0·00165 (4)	0·00786 (18)	0·01555 (36)	0·00005 (11)	0·00099 (29)	0·00283 (62)
C(1)	0·0028 (7)	0·0084 (27)	0·0148 (76)	−0·0012 (11)	−0·0021 (15)	0·0046 (32)
C(2)	0·0018 (7)	0·0220 (49)	0·0312 (90)	0·0007 (16)	0·0010 (23)	0·0152 (60)
C(6)	0·0049 (12)	0·0186 (56)	0·0329 (98)	0·0064 (22)	0·0005 (30)	−0·0037 (64)
C(7)	0·0027 (8)	0·0158 (38)	0·0231 (83)	0·0054 (14)	0·0017 (17)	−0·0118 (72)
C(8)	0·0031 (8)	0·0167 (42)	0·0199 (74)	−0·0003 (16)	0·0029 (22)	−0·0030 (47)
C(9)	0·0033 (9)	0·0095 (42)	0·0425 (117)	0·0019 (14)	0·0031 (27)	−0·0106 (53)
C(10)	0·0029 (7)	0·0164 (42)	0·0346 (91)	−0·0003 (13)	−0·0012 (45)	−0·0077 (104)
O(1)	0·0045 (6)	0·0126 (25)	0·0273 (53)	−0·0027 (10)	−0·0028 (14)	0·0101 (28)
O(2)	0·0035 (6)	0·0217 (29)	0·0126 (46)	−0·0011 (10)	−0·0004 (12)	−0·0042 (26)

Table 2 (cont.)

Isotropic factors

	$B(\text{Å}^2)$		$B(\text{Å}^2)$
C(3)	2·85 (48)	H(9)	6·00
C(4)	3·92 (56)	H(10)	6·00
C(5)	4·20 (55)	H(41)	6·00
O(3)	4·66 (33)	H(42)	6·00
N(1)	3·07 (34)	H(51)	6·00
H(6)	6·00	H(52)	6·00
H(7)	6·00	H(N1)	6·00
H(8)	6·00	H(N2)	6·00

Hydrogen atom contributions were included in the final refinements in calculated positions based on regular geometries and N–H and C–H distances of 1·0 Å. The final R ($\sum||F_o|-|F_c||/\sum|F_o|$) for 799 reflections with $F>\sigma(F)$ was 0·079; the R_w {$[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$} was 0·069. For all data (1038 reflections) the R and R_w were 0·127 and 0·073, respectively.

The final set of atomic coordinates and their standard deviations are listed in Table 1. The final thermal parameters are given in Table 2.*

Discussion. The crystal structure consists of the packing of molecules which are associated through intermolecular hydrogen bonds to form infinite chains through the crystal. The molecular structure illustrating the labeling system used here is shown in Fig. 1. As the figure shows, the molecule exists as the Mo–NH$_2$ tautomer rather than the Mo–CH$_2$ tautomer; this assignment was our primary reason for the structure determination.

This assignment was made crystallographically by interchanging the assignment of N and C(4) corresponding to the other possible tautomer; the isotropic B for the real N atom went to 1·48 Å^2 while B for C(4) went to 5·73 Å^2. Pertinent interatomic distances and angles are listed in Table 3. These data are in the range of values found for related compounds particularly (η-C$_5$H$_5$)Mo(CO) complexes of which there are

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30765 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CN1 1NZ, England.

numerous examples. The Mo–N distance of 2·26 (2) Å can be compared with the 2·21–2·26 Å values found in molybdenum amino-acid complexes (Prout, Allison, Delbaere & Gore, 1972). We could not find any Mo–C(acyl) distances for comparison.

Table 3. *Interatomic distances* (Å) *and angles* (°)

E.s.d.'s are in parentheses. CNT is the C$_5$H$_5$ ring centroid.

Mo–N(1)	2·26 (2)	C(1)—O(1)	1·11 (3)
Mo–C(3)	2·22 (2)	C(2)—O(2)	1·16 (3)
		Average:	1·14 (3)
Mo–C(1)	1·99 (2)	C(3)—O(3)	1·20 (3)
Mo–C(2)	1·94 (3)	C(3)—C(4)	1·56 (3)
Average:	1·96 (3)		
Mo–C(6)	2·33 (3)	C(6)—C(7)	1·51 (4)
Mo–C(7)	2·34 (2)	C(7)—C(8)	1·41 (4)
Mo–C(8)	2·42 (3)	C(8)—C(9)	1·39 (4)
Mo–C(9)	2·34 (3)	C(9)—C(10)	1·41 (6)
Mo–C(10)	2·26 (2)	C(10)–C(6)	1·43 (4)
Average:	2·34 (3)	Average:	1·43 (2)
N(1)–C(5)	1·45 (3)		
C(4)–C(5)	1·46 (4)		

C(1)–Mo –CNT	121·7 (1·0)	Mo —N(1)—C(5)	112·5 (1·4)
C(2)–Mo –CNT	122·1 (1·1)	Mo—C(3)—O(3)	127·9 (1·8)
C(3)–Mo –CNT	116·6 (1·0)	Mo—C(3)—C(4)	112·2 (1·6)
N(1)–Mo –CNT	114·7 (1·0)	Mo—C(1)—O(1)	174·8 (1·8)
C(1)–Mo –C(3)	121·7 (0·8)		
C(1)–Mo –C(2)	74·5 (1·0)	Mo—C(2)—O(2)	179·4 (2·4)
C(1)–Mo –N(1)	82·6 (0·7)	C(6)—C(7)—C(8)	111·0 (2·1)
C(2)–Mo –C(3)	73·3 (1·0)	C(7)—C(8)—C(9)	105·7 (2·3)
C(2)–Mo –N(1)	122·8 (0·9)	C(8)—C(9)—C(10)	111·2 (2·7)
C(3)–Mo –N(1)	75·9 (0·8)	C(9)—C(10)—C(6)	110·3 (3·0)
C(3)–C(4)–C(5)	110·9 (2·1)	C(10)—C(6)—C(7)	101·8 (2·5)
C(4)–C(5)–N(1)	110·0 (2·1)	Average:	108·0 (1·8)
C(4)–C(3)–O(3)	119·6 (2·0)		

The intermolecular hydrogen bonding involving the amine donor and acyl oxygen acceptor is characterized as follows.

$$\text{N} \xrightarrow{\overset{3\cdot087}{\underset{1\cdot04 \quad\quad 2\cdot09}{\text{H}}} \underset{159°}{} \text{O}}$$

The hydrogen atom position involved here was not refined. These data are in agreement with the data found in organic hydrogen-bonding situations between

similar donors and acceptors; the N$\cdots$O distance here is on the long side of the observed range (Donohue, 1968). Fig. 2 shows the hydrogen-bonding network; the donor–acceptor arrangement is proof that our tautomer assignment based on thermal parameters is correct. Other intermolecular distances are normal.

The cyclopentadienyl ring is planar ($-0.6513X + 0.7210Y + 0.2367Z - 1.678 = 0$) with a maximum carbon atom deviation of 0.016 Å. The Mo atom is 2.00 Å out of the C_5H_5 plane, right on the value frequently found for Mo to C_5H_5 planes (for leading references see Prout, Allison, Delbaere & Gore, 1972; Cotton & Rusholme, 1972).

Individual cyclopentadienyl carbon atoms are very anisotropic, consistent with the usual large librational motion associated with these rings (Wheatley, 1967). The conformation of the aminopropionyl ring is similar to that frequently found in chelate rings, as in the diamines for example. The C(4) atom is 0.13 Å on one side of the MoC(3)N plane while C(5) is 0.46 Å on the other side. The fact that there are probably small amounts of other conformations present (see above) is not surprising in view of the conformations observed for metal-chelated ethylenediamine (Gollogly & Hawkins, 1969) and dimethylphosphinoethane (Meakin, Guggenberger & Tebbe, 1974) rings.

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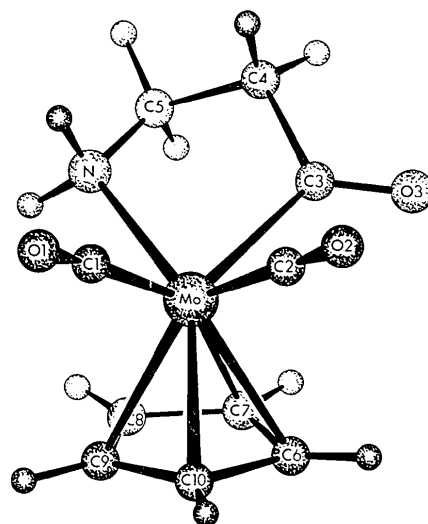PREWITT, C. T. (1965). Personal communication. State Univ. of New York, Stony Brook, Long Island, New York.

Fig. 1. Molecular structure of
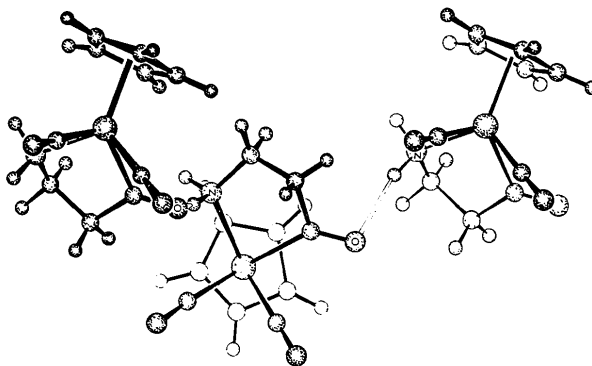
$(\eta\text{-}C_5H_5)Mo(CO)_2(COCH_2CH_2NH_2)$.

Fig. 2. Hydrogen bonding in

$(\eta\text{-}C_5H_5)Mo(CO)_2(COCH_2CH_2NH_2)$.

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