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Structural Studies of Molybdenum–Amino Acid Complexes. The Crystal Structures of Bis-η-cyclopentadienyl-L-prolinatomolybdenum Hexafluorophosphate and Bis-η-cyclopentadienyl-L-leucinatomolybdenum Hexafluorophosphate

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The structures of the title compounds have been determined: (*a*) L-proline complex, monoclinic, $a = 9{\cdot}842$, $b = 9{\cdot}939$, $c = 8{\cdot}921$ Å, $\beta = 100{\cdot}22°$, space group $P2_1$, Mo $K\alpha$ radiation, Philips four-circle diffractometer data, 2919 reflexions, structure determined by Patterson methods and refined by least squares; final R 0·044; (*b*) leucine complex, monoclinic, $a = 6{\cdot}44$, $b = 10{\cdot}04$, $c = 30{\cdot}05$ Å, $\gamma = 94{\cdot}1°$, space group $P2_1/b$, Mo $K\alpha$ radiation, Hilger & Watts four-circle diffractometer data, 2135 reflexions, Patterson methods followed by least-squares refinement; final R 0·061. In each compound the $(\eta\text{-}C_5H_5)_2Mo$ moiety is chelated by the amino acid through O and N (proline Mo—O 2·108, Mo—N 2·255; leucine Mo—O 2·078, Mo—N 2·215 Å). The conformation of the $(\eta\text{-}C_5H_5)_2Mo$(prolinato) cation is consistent with the bulk of the prolinato ligand. In the leucine complex the shape and dimensions of the amino acid ligand are somewhat unsatisfactory possibly owing to disorder.

The presence of Mo in enzyme systems has promoted several crystallographic investigations of Mo–amino acid complexes. The bis-η-cyclopentadienyl compounds of the type $(\eta\text{-}C_5H_5)_2MoX_2$ provide a suitable system for the study of Mo^{IV} chemistry and previously we have reported the structures of compounds in which the bidentate chelating ligands X_2 were the amino acid anions of cysteine, sarcosine and glycine (Prout, Allison, Delbaere & Gore, 1972). It was demonstrated that Mo^{IV} complexed more readily with S than O and that the *N*-methyl substituent in sarcosine had little effect on the conformation of the complex. Here we report the structures of two further complexes, bis-η-cyclopentadienyl-L-prolinatomolybdenum(IV) hexafluorophosphate and bis-η-cyclopentadienylleucinatomolybdenum(IV) hexafluorophosphate–(?hydrate). The crystals were prepared by Dr M. L. H. Green and his co-workers.

(*a*) *Bis-η-cyclopentadienyl-*L*-prolinatomolybdenum hexafluorophosphate* (MoP)

$C_{15}H_{18}F_6MoNO_2P$, $M_r = 485{\cdot}22$, monoclinic, $a = 9{\cdot}842\,(3)$, $b = 9{\cdot}939\,(2)$, $c = 8{\cdot}921\,(2)$ Å, $\beta = 100{\cdot}22\,(4)°$, $U = 858{\cdot}8$ Å^3, $D_c = 1{\cdot}88$ g cm^{-3} for $Z = 2$. Space group $P2_1$, systematic extinctions $0k0$, $k = 2n + 1$. Mo $K\alpha$ radiation, graphite monochromator, $\mu = 8{\cdot}2$ cm^{-1}, crystal size $0{\cdot}18 \times 0{\cdot}06 \times 0{\cdot}70$ mm.

The cell dimensions were determined on a Philips PW 1100 diffractometer and refined by a least-squares fit over 25 reflexions. The intensities of a unique set of 3144 reflexions were measured in the range $\theta = 2$–$32°$ (total scan range 1·6°, scan rate 0·04° s^{-1}, ω–2θ scan mode) of which 225 with $I < \sigma(I)$ were discarded as unobserved. The variation in the absorption of X-rays by the crystal was investigated by ψ scans for 300 reflexions and it was found that any absorption correction would be negligible. The data reduction was carried out by the method of Davies & Gatehouse (1973).

The position of the Mo atom was determined from a Patterson synthesis and those of the remaining non-hydrogen atoms from successive F_o syntheses. The trial structure was refined by full-matrix least squares with unit weights, first with isotropic and then anisotropic temperature factors. The refinement converged at $R = 0{\cdot}044$ for observed reflexions; 0·048 for all reflexions. A difference map gave some indication of the positions of certain H atoms but it was decided to ignore them.

All calculations were carried out on the Honeywell 6030 computer of the Centro di Calcolo dell'Università di Pavia with programs developed locally. Scattering factors were taken from Hanson, Herman, Lea & Skillman (1964) and anomalous dispersion corrections from Cromer & Liberman (1970).

(*b*) *Bis-η-cyclopentadienyl-*L*-leucinatomolybdenum hexafluorophosphate* (MoL)

$C_{16}H_{22}F_6MoNO_2P$, $M_r = 501{\cdot}27$, monoclinic, $a = 6{\cdot}44\,(1)$, $b = 10{\cdot}04\,(1)$ $c = 30{\cdot}05\,(3)$ Å, $\gamma = 94{\cdot}1\,(1)°$, $U = 1938$ Å^3, $D_c = 1{\cdot}72$ g cm^{-3} for $Z = 4$. Space group $P2_1/b$, systematic extinctions $hk0$, $k = 2n + 1$; $00l$, $l = 2n + 1$, $\mu = 8$ cm^{-1} for Mo $K\alpha$ radiation.

Systematic extinctions and preliminary cell dimensions were determined from Weissenberg and precession photographs. The cell dimensions were refined by least squares from Hilger & Watts four-circle diffractometer data. The intensities of 2135 reflexions with $I > 3\sigma(I)$ were measured with an ω–2θ scan procedure. Lorentz and polarization corrections were applied but not an absorption correction.

The compound was made from L-leucine but it appeared to possess a centrosymmetric space group. It was therefore assumed in the first instance that the L-leucine had racemized in the preparation. The Mo atom was found from an unsharpened Patterson synthesis and all non-hydrogen atoms except those of the isobutyl side chain of the amino acid were located from the Mo-phased F_o synthesis. The isobutyl group was found in the following F_o synthesis.

The trial structure was refined by least squares, first with a full matrix and isotropic temperature factors, then to convergence with anisotropic temperature factors and a two-block (one for positional parameters and one for thermal parameters and the scale factor) matrix. The refinement with weighting scheme $w = \{1 + [(|F_o| - 1275)/1683]^2\}^{-1}$ converged at $R = 0{\cdot}069$. The model resulting from this refinement had some unsatisfactory features. The α-C atom of the

Table 1. *Bis-η-cyclopentadienyl-*L*-prolinatomolybdenum hexafluorophosphate: fractional atomic coordinates and temperature factors*

Estimated standard deviations are given in parentheses. The anisotropic temperature factor T is given by: $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. All values are ×10⁴.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	2642 (0)	2326 (–)	4093 (0)	61 (3)	51 (3)	96 (5)	−6 (6)	15 (3)	4 (7)
P	6974 (2)	1294 (3)	328 (3)	101 (2)	124 (3)	148 (3)	−13 (2)	37 (2)	−35 (2)
F(1)	8154 (7)	2333 (12)	345 (10)	210 (9)	196 (9)	574 (21)	−78 (13)	171 (11)	−169 (18)
F(2)	5827 (10)	2384 (17)	20 (15)	284 (15)	307 (17)	879 (38)	167 (18)	198 (20)	71 (34)
F(3)	5881 (9)	119 (10)	361 (14)	261 (13)	256 (14)	683 (30)	−141 (12)	240 (17)	−137 (18)
F(4)	7012 (13)	1484 (13)	2022 (9)	635 (28)	492 (28)	195 (12)	−115 (24)	163 (16)	−125 (16)
F(5)	6882 (9)	978 (13)	−1381 (8)	330 (16)	467 (24)	207 (12)	−93 (17)	60 (11)	−82 (15)
F(6)	8080 (9)	106 (9)	624 (14)	211 (12)	201 (12)	703 (32)	73 (11)	−7 (16)	−47 (17)
C(11)	1218 (8)	1022 (12)	2378 (9)	114 (9)	213 (16)	111 (9)	−66 (10)	47 (8)	−81 (11)
C(12)	1512 (10)	2277 (17)	1616 (7)	209 (13)	190 (13)	85 (7)	101 (16)	−3 (8)	−23 (14)
C(13)	2926 (10)	2274 (18)	1545 (9)	213 (13)	162 (13)	138 (10)	−53 (18)	91 (10)	7 (16)
C(14)	3455 (10)	1013 (11)	2202 (10)	147 (11)	169 (13)	164 (13)	16 (10)	70 (10)	−29 (11)
C(15)	2462 (11)	303 (9)	2711 (9)	214 (14)	88 (8)	123 (11)	10 (9)	61 (10)	−13 (8)
C(21)	3460 (10)	4440 (8)	4813 (18)	111 (10)	52 (7)	466 (34)	−24 (7)	−28 (15)	−21 (13)
C(22)	3596 (10)	3594 (12)	6118 (11)	133 (11)	171 (14)	214 (16)	−86 (11)	32 (11)	−92 (13)
C(23)	4612 (7)	2589 (8)	5960 (10)	92 (7)	103 (12)	186 (12)	−31 (7)	−30 (7)	14 (8)
C(24)	5025 (8)	2833 (10)	4554 (13)	77 (7)	144 (12)	277 (20)	−36 (7)	4 (10)	−15 (12)
C(25)	4337 (9)	3941 (11)	3845 (13)	108 (10)	144 (13)	283 (20)	−64 (10)	−15 (11)	46 (13)
C(1)	−30 (6)	2758 (6)	5195 (7)	81 (6)	49 (4)	107 (8)	9 (4)	32 (5)	4 (5)
C(2)	346 (6)	1379 (6)	5885 (8)	90 (6)	46 (5)	140 (9)	9 (5)	41 (6)	21 (6)
C(3)	221 (12)	1291 (11)	7561 (10)	255 (19)	161 (14)	146 (13)	96 (14)	129 (13)	74 (11)
C(4)	1378 (10)	294 (8)	8180 (8)	198 (14)	89 (8)	101 (9)	6 (9)	44 (9)	22 (7)
C(5)	2557 (9)	685 (10)	7349 (9)	153 (10)	148 (12)	103 (10)	−2 (9)	−9 (8)	50 (9)
O(1)	809 (4)	3296 (4)	4412 (5)	87 (5)	50 (4)	146 (7)	7 (3)	38 (4)	21 (4)
O(2)	−1122 (6)	3295 (5)	5339 (7)	134 (7)	79 (5)	214 (10)	41 (5)	95 (7)	29 (6)
N	1776 (5)	989 (5)	5736 (5)	93 (5)	52 (4)	91 (6)	7 (4)	22 (5)	8 (4)

amino acid anion had a near-planar configuration, the temperature factors of the isobutyl group were excessively large, the corresponding maxima in the F_o synthesis were diffuse, and the distance from the α-C atom to the first side-chain C atom, 1·36 Å, was almost as short as that to be expected for a double bond.

Further, the final difference map had an unexplained peak which was near the N of one cation and the non-coordinating O of another. When this was assumed to be a water molecule with a site occupancy of 0·36 the residual fell to 0·061. However, the $H_2O\cdots N$ and $H_2O\cdots O$ contacts were very short and there was little improvement in the dimensions of the amino acid ligand.

Investigation showed that the bulk sample had some optical activity although it appeared to contain only the one crystal form. It was considered possible that the crystals have a non-centrosymmetric space group (*e.g.* $P2_1$) and that the observed structure might represent an averaging following the introduction of a false symmetry centre which correctly relates a large fraction of the atoms [the anions and the $(C_5H_5)_2MoON$ moiety of the cation]. Numerous unsuccessful attempts were made to produce a better structure in a non-centrosymmetric space group. All calculations reported were carried out in Oxford on the 1906A computer. The initial work used the X-RAY 70 (Stewart, Kundell & Baldwin, 1970) series of programs and the later work, including refinement of non-centrosymmetric models, the Oxford *CRYSTALS* program suite with its extensive constrained-refinement facility. Scattering factors were taken from Cromer & Mann (1968) and corrections for the anomalous dispersion of Mo and P from Cromer & Liberman (1970). The final atom parameters are given in Tables 1 and 2.*

Results and discussion

The crystal structures of the two compounds are shown in Figs. 1 and 2 and their interatomic distances and interbond angles are in Tables 3 and 4. In each case the full variance–covariance matrix was used to calculate standard deviations.

In each compound the cation is formed by chelation of the bis-η-cyclopentadienylmolybdenum group by the O and N atoms of the amino acid.

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* A list of structure factors of the two compounds has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32058 (50 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Bis-η-cyclopentadienyl-*L*-leucinatomolybdenum hexafluorophosphate: fractional atomic coordinates* (x *and* y $\times 10^3$; z $\times 10^4$) *and temperature factors* ($\times 10^2$)

Estimated standard deviations of the last digit are given in parentheses. The anisotropic temperature factor T is given by:
$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

	x	y	z	U_{11} or U_{iso}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	392·1 (1)	95·60 (8)	1526·9 (3)	4·16 (4)	4·57 (4)	7·37 (6)	0·43 (5)	−0·02 (5)	0·03 (3)
O(1)	650 (1)	66·5 (8)	1132 (3)	6·9 (5)	8·9 (6)	11·2 (7)	1·5 (5)	3·1 (5)	1·4 (4)
O(2)	804 (2)	−40 (1)	604 (4)	23 (1)	12·7 (9)	19 (1)	4·6 (8)	16 (1)	6·1 (9)
N(1)	278 (1)	−633 (8)	1057 (3)	10·2 (7)	5·3 (5)	5·6 (5)	−0·9 (4)	−0·01 (5)	−0·5 (4)
C(1)	652 (2)	−22 (1)	852 (5)	12 (1)	7·8 (8)	9 (1)	1·5 (7)	3·9 (9)	0·3 (8)
C(2)	466 (3)	−121 (1)	819 (5)	16 (2)	11 (1)	12 (1)	−5 (1)	6 (1)	−1 (1)
C(3)	434 (4)	−189 (2)	432 (8)	22 (2)	16 (2)	19 (2)	−11 (2)	−1 (2)	0 (2)
C(4)	262 (3)	−297 (2)	387 (6)	19 (2)	9 (1)	11 (1)	−1·1 (9)	−1 (1)	−2 (1)
C(5)	306 (4)	−432 (2)	568 (6)	26 (3)	13 (1)	12 (1)	4 (1)	3 (2)	5 (1)
C(6)	216 (4)	−320 (2)	−123 (6)	32 (3)	14 (2)	9 (1)	1 (1)	−4 (2)	−2 (2)
C(11)	304 (2)	232 (1)	973 (5)	12 (1)	5·5 (6)	12 (1)	2·0 (7)	−2·1 (9)	1·6 (7)
C(12)	458 (2)	309 (1)	1250 (5)	8·5 (8)	4·0 (5)	14 (1)	12 (7)	−0·6 (8)	−0·1 (5)
C(13)	372 (2)	326 (1)	1662 (6)	12 (1)	5·6 (7)	16 (2)	−1·2 (8)	2 (1)	1·6 (7)
C(14)	165 (2)	263 (1)	1670 (6)	11 (1)	7·4 (9)	19 (2)	0·6 (9)	3 (1)	5·1 (8)
C(15)	122 (2)	209 (1)	1250 (6)	6·4 (7)	6·2 (7)	20 (2)	1·0 (9)	−2·2 (9)	1·3 (6)
C(21)	355 (2)	98 (1)	2281 (4)	13 (1)	11 (1)	5·5 (7)	−1·1 (7)	0·2 (7)	0·7 (8)
C(22)	579 (2)	97 (2)	2172 (5)	10 (1)	15 (1)	9 (1)	0 (1)	−3·4 (9)	−2 (1)
C(23)	611 (2)	−25 (2)	1988 (5)	9·1 (9)	17 (2)	8 (1)	3 (1)	−1·9 (8)	5 (1)
C(24)	420 (2)	−99 (1)	1947 (4)	12 (1)	9·0 (9)	8·0 (9)	2·4 (7)	−1·5 (8)	4·0 (8)
C(25)	261 (2)	−25 (1)	2121 (4)	8·7 (8)	9·0 (8)	6·8 (8)	0·8 (6)	−1·1 (6)	0·4 (6)
P(1)	−100·2 (4)	119·5 (3)	3279 (1)	5·6 (1)	6·0 (2)	8·6 (2)	−0·0 (1)	−0·6 (1)	−0·1 (1)
F(1)	−343·7 (9)	129·7 (7)	3243 (3)	5·9 (4)	9·2 (5)	14·7 (6)	−0·3 (4)	−0·2 (4)	0·7 (3)
F(2)	145 (1)	114·0 (9)	3308 (3)	6·2 (4)	16·7 (8)	11·8 (6)	3·8 (5)	−1·1 (4)	−0·0 (4)
F(3)	−82 (1)	254·0 (8)	3556 (3)	13·1 (6)	9·4 (5)	12·0 (7)	−3·3 (5)	−1·0 (5)	−1·5 (4)
F(4)	−127 (1)	33·7 (8)	3712 (3)	11·3 (6)	12·7 (6)	10·7 (6)	4·2 (5)	−0·6 (5)	−2·6 (5)
F(5)	−121 (1)	−122 (7)	2987 (3)	12·4 (6)	7·7 (4)	14·3 (7)	−2·6 (5)	−2·3 (5)	2·7 (4)
F(6)	−70 (1)	207·0 (7)	2836 (2)	9·1 (5)	10·0 (5)	10·0 (5)	1·5 (4)	−1·5 (4)	−1·0 (4)
O(3)	9·9 (3)	41 (2)	283 (8)	9 (1)					

MoP crystals are built up from isolated anions and bis-η-cyclopentadienyl-L-prolinatomolybdenum cations linked into chains by hydrogen bonds between an amino hydrogen of one molecule and the non-coordination carbonyl O(2) of its neighbour along the twofold screw axis.

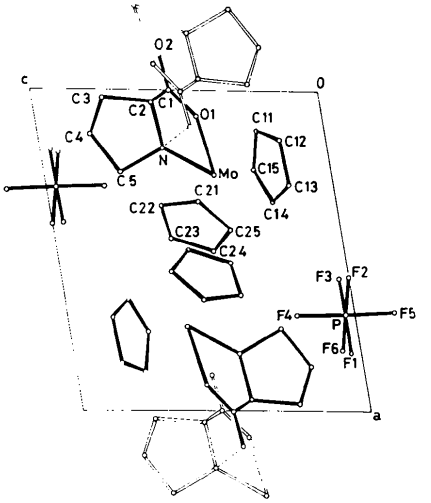

Fig. 1. The crystal structure of MoP projected down **b**.

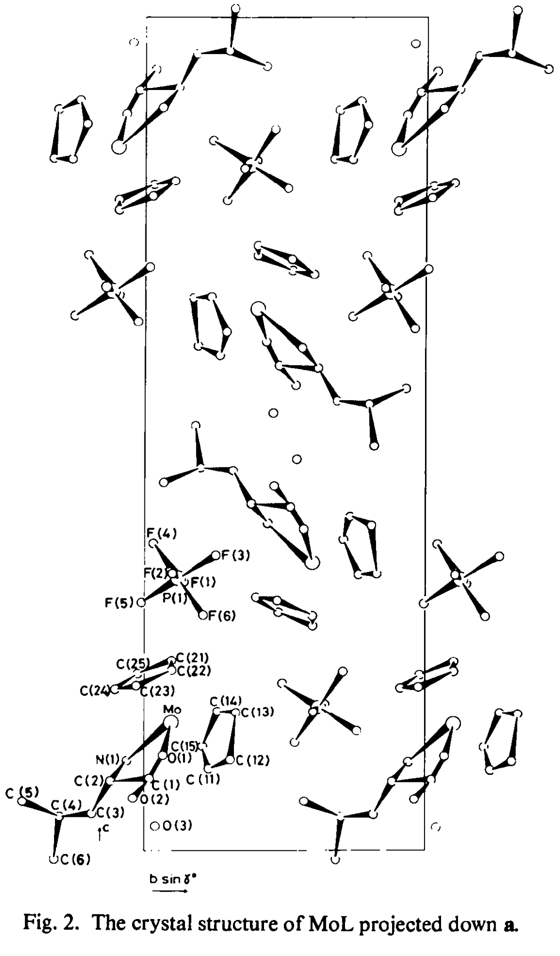

Fig. 2. The crystal structure of MoL projected down **a**.

The irregular shape of the proline leads to a deformed bis-η-cyclopentadienylmolybdenum entity, Fig. 3. In each cyclopentadienyl ring the C—C lengths are self consistent and the C temperature factors relatively low indicating a high degree of order. The normals to the cyclopentadienyl rings at the Mo atoms are equivalent in length {1·991 Å [C(11)–(15)] and 1·986 Å [C(21)–(25)]} and inclined at 135·6°. The five-membered ring of the proline is on the same side of the O—Mo—N plane as the cyclopentadienyl ring C(21)–(25). The O—Mo—N plane is inclined at 86·9° to the plane containing the normals to the cyclopentadienyl rings at the Mo atom in a sense which is consistent with the repulsion of the cyclopentadienyl ring C(21)–(25) by the proline ring. The line of intersection of the O(1)—Mo—N(1) plane and the plane containing normals to the cyclopentadienyl rings makes a greater angle, 69·8°, with the normal to C(11)–(15) than with the normal to C(21)–(25), 65·8°, consistent with repulsion between the five-membered ring of the proline group and the ring C(11)–(15) (Fig. 3). Further, this line of intersection makes a greater angle, 46·4°, with Mo—O(1) than with Mo—N(1), 29·2°. This represents a combination of repulsion effects twisting the proline as a whole away from the cyclopentadienyl rings and the bond-length asymmetry of the chelate rings.

In the proline ligand the interatomic distances and the interbond angles agree well with the values obtained for L-proline (Kaynshina & Vainshtein, 1965), but when the conformation of the ligand is compared with the proline system (see the dihedral angles about C—C$_\alpha$ in Table 5), significant differences are found. It has been found (Fridrichsons & Mathieson, 1962) that the proline ring is rather flexible and in this compound the conformation adopted appears to be that which max-

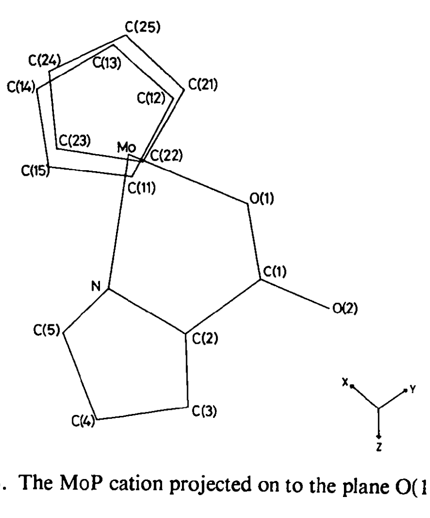

Fig. 3. The MoP cation projected on to the plane O(1)—Mo—N.

imizes the separation between H atoms at C(23) in the cyclopentadienyl ring, C(21)–(25), and the H of the proline C(5). In the proline ring, the group C(5), N(1), C(2), C(3) is planar and C(4) lies 0·6 Å out of the plane on the same side of the plane as C(1). This conformation requires that one H at each of C(5) and C(3) should lie almost in the C(5), N(1), C(2), C(3) plane and the other H at each of these atoms should be out of this plane on the opposite side to the cyclopentadienyl groups.

The crystal structure of MoL (Fig. 2) is much less well defined than that of MoP. The crystals are built up from bis-η-cyclopentadienylleucinatomolybdenum cations, which do not appear to be directly linked by hydrogen bonding, and hexafluorophosphate anions. There is a possible water-molecule site of low occupancy which may provide a hydrogen-bonded water bridge between the cations.

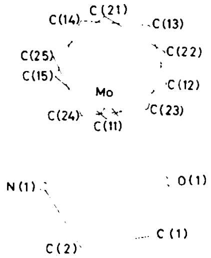

Fig. 4. The bis-η-cyclopentadienyl entity of MoL plotted on to the plane O(1)—Mo—N(1).

Table 3. *Bis-η-cyclopentadienyl-L-prolinatomolybdenum hexafluorophosphate: interatomic distances and interbond angles*

Standard deviations are given in parentheses.

(*a*) Bond lengths (Å) and interbond angles (°)

Mo—O(1)	2·108 (4)	P—F(1)	1·552 (8)	O(1)—C(1)—O(2)	122 (1)
Mo—N	2·255 (5)	P—F(2)	1·553 (11)	O(1)—C(1)—C(2)	117 (1)
Mo—C(11)	2·285 (7)	P—F(3)	1·592 (8)	O(2)—C(1)—C(2)	120 (1)
Mo—C(12)	2·290 (6)	P—F(4)	1·516 (7)	N—C(2)—C(1)	111 (1)
Mo—C(13)	2·339 (7)	P—F(5)	1·544 (7)	N—C(2)—C(3)	108 (1)
Mo—C(14)	2·381 (8)	P—F(6)	1·596 (8)	C(1)—C(2)—C(3)	113 (1)
Mo—C(15)	2·349 (8)			C(2)—C(3)—C(4)	102 (1)
Mo—C(21)	2·301 (8)	O(1)—Mo—N	75·6 (2)	C(3)—C(4)—C(5)	104 (1)
Mo—C(22)	2·265 (8)	Mo—O(1)—C(1)	121·9 (4)	C(4)—C(5)—N	102 (1)
Mo—C(23)	2·336 (7)	Mo—N—C(2)	112·1 (3)		
Mo—C(24)	2·362 (8)	Mo—N—C(5)	122·7 (4)	F(1)—P—F(2)	93·2 (7)
Mo—C(25)	2·354 (8)	C(2)—N—C(5)	107·0 (5)	F(1)—P—F(3)	174·3 (6)
				F(1)—P—F(4)	91·2 (5)
C(11)—C(12)	1·47 (2)	C(12)—C(11)—C(15)	107 (1)	F(1)—P—F(5)	93·3 (5)
C(12)—C(13)	1·40 (1)	C(11)—C(12)—C(13)	107 (1)	F(1)—P—F(6)	90·2 (5)
C(13)—C(14)	1·44 (2)	C(12)—C(13)—C(14)	106 (1)	F(2)—P—F(3)	92·5 (6)
C(14)—C(15)	1·35 (1)	C(13)—C(14)—C(15)	111 (1)	F(2)—P—F(4)	88·7 (7)
C(15)—C(11)	1·40 (1)	C(11)—C(15)—C(14)	108 (1)	F(2)—P—F(5)	93·0 (7)
C(21)—C(22)	1·42 (2)	C(22)—C(21)—C(25)	108 (1)	F(2)—P—F(6)	176·5 (7)
C(22)—C(23)	1·44 (1)	C(21)—C(22)—C(23)	107 (1)	F(3)—P—F(4)	88·3 (6)
C(23)—C(24)	1·41 (1)	C(22)—C(23)—C(24)	106 (1)	F(3)—P—F(5)	87·0 (6)
C(24)—C(25)	1·39 (1)	C(23)—C(24)—C(25)	110 (1)	F(3)—P—F(6)	84·0 (6)
C(25)—C(21)	1·41 (2)	C(21)—C(25)—C(24)	108 (1)	F(4)—P—F(5)	175·0 (7)
				F(4)—P—F(6)	91·8 (7)
C(1)—O(1)	1·29 (1)			F(5)—P—F(6)	86·1 (6)
C(1)—O(2)	1·23 (1)				
C(2)—N	1·49 (1)				
C(2)—C(1)	1·52 (1)				
C(2)—C(3)	1·52 (1)				
C(3)—C(4)	1·54 (1)				
C(4)—C(5)	1·53 (1)				
C(5)—N	1·54 (1)				

(*b*) Hydrogen bonds and close contacts (Å)

N···O(2)	2·88 (1)	(hydrogen bond)	C(13)···C(24)	3·13 (1)	C(22)···N	3·13 (1)
Mo···C(1)	2·996 (6)		C(13)···C(15)	2·81 (2)	C(22)···O(1)	2·90 (1)
Mo···C(2)	3·134 (6)		C(14)···C(24)	2·98 (1)	C(23)···N	3·19 (1)
C(11)···O(1)	2·97 (1)		C(15)···N	2·97 (1)	C(23)···C(5)	3·18 (1)
C(11)···N	2·95 (1)		C(15)···O(2)	3·09 (1)	C(25)···F(5)	3·07 (1)
C(12)···O(1)	2·89 (1)		C(21)···O(1)	2·81 (1)		

The cyclopentadienyl groups are planar and the C—C lengths and Mo—C contacts are consistent with those observed in other structures (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). The normals to the cyclopentadienyl rings are inclined at 133·6° to each other. The bis-η-cyclopentadienylmolybdenum group has an almost perfect staggered conformation (Fig. 4) and Mo—N(1) and Mo—O(1) are much more

Table 4. *Bis-η-cyclopentadienyl-*L*-leucinatomolybdenum hexafluorophosphate: interatomic distances and interbond angles with e.s.d.'s in parentheses*

(*a*) Bond lengths (Å) and interbond angles (°)

Mo(1)—O(1)	2·078 (7)	P(1)—F(1)	1·583 (7)	O(1)—C(1)—O(2)	124 (1)
Mo(1)—N(1)	2·215 (8)	P(1)—F(2)	1·587 (7)	O(1) C(1) C(2)	118 (1)
Mo(1)—C(11)	2·26 (1)	P(1)—F(3)	1·585 (8)	O(2)—C(1)—C(2)	117 (1)
Mo(1)—C(12)	2·31 (1)	P(1)—F(4)	1·565 (8)	N(1)—C(2)—C(1)	109 (1)
Mo(1)—C(13)	2·37 (1)	P(1)—F(5)	1·584 (7)	N(1)—C(2)—C(3)	119 (2)
Mo(1)—C(14)	2·34 (1)	P(1)—F(6)	1·599 (7)	C(1)—C(2)—C(3)	118 (2)
Mo(1)—C(15)	2·30 (1)			C(2)—C(3)—C(4)	121 (2)
Mo(1)—C(21)	2·28 (1)	O(1)—Mo(1)—N(1)	76·2 (3)	C(3)—C(4)—C(5)	116 (2)
Mo(1)—C(22)	2·28 (1)	Mo(1)—O(1)—C(1)	123·0 (9)	C(3)—C(4)—C(6)	108 (2)
Mo(1)—C(23)	2·37 (1)	Mo(1)—N(1)—C(2)	109·6 (8)	C(5)—C(4)—C(6)	105 (1)
Mo(1)—C(24)	2·35 (1)				
Mo(1)—C(25)	2·28 (1)				
		C(15)—C(11)—C(12)	105 (1)	F(1)—P(1)—F(2)	178·1 (4)
		C(11)—C(12)—C(13)	108 (1)	F(1)—P(1)—F(3)	89·8 (4)
C(11)—C(12)	1·47 (2)	C(12)—C(13)—C(14)	109 (1)	F(1)—P(1)—F(4)	91·4 (4)
C(12)—C(13)	1·37 (2)	C(13)—C(14)—C(15)	108 (1)	F(1)—P(1)—F(5)	89·5 (4)
C(13)—C(14)	1·44 (2)	C(14)—C(15)—C(11)	109 (1)	F(1)—P(1)—F(6)	89·3 (4)
C(14)—C(15)	1·39 (2)	C(25)—C(21)—C(22)	106 (1)	F(2)—P(1)—F(3)	89·2 (5)
C(15)—C(11)	1·44 (2)	C(21)—C(22)—C(23)	108 (1)	F(2)—P(1)—F(4)	90·2 (4)
C(21)—C(22)	1·48 (2)	C(22)—C(23)—C(24)	109 (1)	F(2)—P(1)—F(5)	91·4 (5)
C(22)—C(23)	1·37 (2)	C(23)—C(24)—C(25)	109 (1)	F(2)—P(1)—F(6)	89·1 (4)
C(23)—C(24)	1·40 (2)	C(24)—C(25)—C(21)	108 (1)	F(3)—P(1)—F(4)	91·7 (5)
C(24)—C(25)	1·42 (2)			F(3)—P(1)—F(5)	178·1 (5)
C(25)—C(21)	1·42 (2)			F(3)—P(1)—F(6)	88·4 (4)
				F(4)—P(1)—F(5)	90·1 (5)
O(1)—C(1)	1·22 (1)			F(4)—P(1)—F(6)	179·3 (4)
O(2)—C(1)	1·26 (2)			F(5)—P(1)—F(6)	89·8 (5)
N(1)—C(2)	1·55 (2)				
C(1)—C(2)	1·50 (2)				
C(2)—C(3)	1·36 (2)				
C(3)—C(4)	1·50 (2)				
C(4)—C(5)	1·50 (2)				
C(4)—C(6)	1·57 (2)				

(*b*) Hydrogen bonds and close contacts (Å)

O(3)···O(3)^{i}	2·25 (5)	C(11)···N(1)	2·97 (1)	C(14)···C(21)	2·81 (2)
N(1)···O(3)	2·83 (2)	C(11)···O(1)	2·91 (1)	C(15)···N(1)	3·04 (2)
O(2)···O(3)^{ii}	2·23 (3)	C(11)···O(3)	3·06 (3)	C(22)···O(1)	3·18 (2)
O(2)···O(3)^{iii}	2·74 (3)	C(12)···O(2)	2·83 (1)	C(23)···O(1)	2·74 (2)
Mo(1)···C(5)	3·100 (13)	C(13)···C(21)	2·95 (2)	C(24)···N(1)	2·86 (2)
Mo(1)···C(6)	2·927 (12)	C(13)···C(22)	3·14 (2)	C(25)···N(1)	3·22 (2)

O(3)^{i}, O(3)^{ii} and O(3)^{iii} are related to O(3) in Table 2 by the transformations $\bar{x}, \bar{y}, \bar{z}$; $1+x, y, z$; $1-x, \bar{y}, \bar{z}$.

Table 5. *Dihedral angles* (°) *of the prolinato ligand and* L*-proline looking down the* C(*carboxylate*)—C$_{\alpha}$ *bond*

Prolinato ligand		L-Proline	
C(1)C(2)O(1)^C(1)C(2)Mo	0		
C(1)C(2)O(1)^C(1)C(2)N	10	C(1)C(2)O(1)^C(1)C(2)N	−7
C(1)C(2)O(1)^C(1)C(2)C(5)	49	C(1)C(2)O(1)^C(1)C(2)C(5)	31
C(1)C(2)O(1)^C(1)C(2)C(4)	98	C(1)C(2)O(1)^C(1)C(2)C(4)	68
C(1)C(2)O(1)^C(1)C(2)C(3)	138	C(1)C(2)O(1)^C(1)C(2)C(3)	109
C(1)C(2)O(1)^C(1)C(2)O(2)	183	C(1)C(2)O(1)^C(1)C(2)O(2)	177

Table 6. *Torsion angles* (°) *of the leucinato ligand and* L-*leucine* (*in hydrobromide and hydroiodide*)

The dihedral angle about the bond *J–K* is defined as the angle by which the bond *K–L* is rotated from the *IJK* plane. It is positive when on looking from *IJ* to *KL* the rotation is clockwise.

I	*J*	*K*	*L*	Leucinato ligand	L-Leucine (hydrobromide)	L-Leucine (hydroiodide)
O(1)	C(1)	C(2)	N(1)	17·7	−13·3	−15·2
O(1)	C(1)	C(2)	C(3)	158·5	101·8	102·7
O(2)	C(1)	C(2)	N(1)	166·3	169·7	172·8
O(2)	C(1)	C(2)	C(3)	−25·5	−75·2	−69·4
C(1)	C(2)	C(3)	C(4)	174·9	73·4	71·9
N(1)	C(2)	C(3)	C(4)	−48·3	−172·4	−172·4
C(2)	C(3)	C(4)	C(5)	−81·0	65·0	56·6
C(2)	C(3)	C(4)	C(6)	160·3	−178·6	−175·5

symmetrically placed with respect to the $(\eta\text{-}C_5H_5)_2Mo$ moiety than in the proline complex. The N—Mo—O plane is inclined at 89·7° to the plane containing the normals to the η-cyclopentadienyl rings. The line of intersection of the plane containing the ring normals and the O(1)—Mo—N(1) plane makes a greater angle, 68·2°, with the normal to the C(11)—(15) ring than with the normal to the C(21)—(25) ring, 65·4 °. Further, this line of intersection makes angles of 40·3 and 36·0° with Mo—O(1) and Mo—N(1).

In the leucine ligand C(2) and the side chain are ill defined as stated above. Torsion angles are given in Table 6. The side chain at C(2) is equatorial with respect to the chelate ring so that the ligand as a whole is fairly flat. The torsion angles about C(1)—C(2) are given in Table 6 together with those from some similar leucine systems.

The Mo—N lengths, 2·215 Å in MoL and 2·255 Å in MoP, are in good agreement with those in other Mo^{IV} amino acid complexes [2·26 Å average, except molybdenum cysteine hexafluorophosphate, 2·14 Å, where pseudosymmetry problems were encountered (Prout *et al.*, 1972)]. Similarly the Mo—O bonds, 2·078 Å in MoL and 2·108 Å in MoP, agree almost exactly with the values for the glycine and sarcosine complexes, both 2·10 Å. The N(1)—Mo—O(1) angles are 76·2, 75·6, 73·4 and 74·1° in the leucine, proline, sarcosine and glycine complexes respectively. It appears therefore that the coordination of Mo by an α-amino acid with only amino-nitrogen and carboxylate-oxygen ligand sites is virtually unaffected by the presence of substituents on either the N atom or the α-C atom or both. Further the bis-η-cyclopentadienyl moiety will undergo considerable distortion to accommodate an awkwardly shaped ligand like L-proline.

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