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Structural Studies of Molybdenum Amino-Acid Complexes: the Crystal and Molecular Structures of Hydrogendi(bis-π-cyclopentadienyl)-L-cysteinatomolybdenum(IV) Chloride, Hydrogendi(bis-π-cyclopentadienyl)-L-cysteinatomolybdenum(IV) Hexafluorophosphate, Bis-π-cyclopentadienylglycinatomolybdenum(IV) Chloride Monohydrate and Bis-π-cyclopentadienylsarcosinatomolybdenum(IV) Chloride Methanolate

BY C. K. PROUT, G. B. ALLISON,* L. T. J. DELBAERE† AND E. GORE‡

Chemical Crystallography Laboratory, South Parks Road, Oxford OX1 3QS, England

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The crystal and molecular structures of hydrogendi(bis-π-cyclopentadienyl)-L-cysteinatomolybdenum(IV) chloride (orthorhombic, $a=13\cdot23$, $b=15\cdot90$, $c=6\cdot26$ Å, space group $P2_12_12$, linear diffractometer data 1785 reflexions, $R=0\cdot038$), hydrogendi(bis-π-cyclopentadienyl)-L-cysteinatomolybdenum(IV) hexafluorophosphate (triclinic, $a=15\cdot94$, $b=7\cdot61$, $c=6\cdot19$ Å, $\alpha=95\cdot6$, $\beta=101\cdot8$, $\gamma=90\cdot1°$, space group $P1$, four-circle diffractometer data 2205 reflexions, $R=0\cdot119$), bis-π-cyclopentadienylglycinatomolybdenum(IV) chloride hydrate (monoclinic, $a=13\cdot68$, $b=16\cdot65$, $c=6\cdot00$ Å, $\gamma=105\cdot8°$, space group $P2_1/b$, visually estimated photographic data 1819 reflexions, $R=0\cdot109$) and bis-π-cyclopentadienylsarcosinatomolybdenum(IV) chloride methanolate (orthorhombic $a=13\cdot43$, $b=14\cdot05$, $c=7\cdot98$ Å, space group $P2_12_12_1$, linear diffractometer data 1140 reflexions, $R=0\cdot072$) have been determined by three-dimensional X-ray methods. In the bis-π-cyclopentadienylmolybdenum groups the rings are staggered in the sarcosine and cysteine chloride complexes but eclipsed in the glycine and cysteine hexafluorophosphate. The mean length of the normals to the rings from molybdenum is 1·98 Å and the mean angle between them is 133°. The cysteine chelates through nitrogen and sulphur (Mo–N 2·256, Mo–S 2·446 Å in the chloride) and the carboxylate groups are hydrogen bonded to form a typical acid carboxylate dimer (O–H···O 2·46 Å). The cysteine has different conformations in the PF_6^- and Cl^- complexes. In the glycine and sarcosine complexes the molybdenum is chelated through oxygen and nitrogen [Mo–N 2·24 (mean), Mo–O 2·10 Å (mean)].

Introduction

Molybdenum has been found in a number of enzyme systems, xanthine oxidase (Bray & Meriwether, 1966) aldehyde oxidase (Handler & Rajagoplan, 1964), nitrate reductase (Fewson & Nicholas, 1961) and nitrogenase (Nicholas, Wilson, Heinen, Palmer & Beinert, 1962), and e.s.r. studies suggest that the molybdenum atom is bound to cysteine (Bray & Meriwether, 1966; Handler & Rajagoplan, 1964; and Huang & Haight, 1969). These observations have stimulated work on the properties and structure of molybdenum amino-acid complexes. The structures of disodium di-μ-oxo-bis[oxocysteinatomolybdenum(V)] pentahydrate (Knox & Prout, 1969*a*), bis-μ-oxo-bis-(L-histidinato-oxo-molybdenum(V) trihydrate (Delbaere & Prout, 1971), di-μ-oxo-bis[oxo-(L-cysteinatoethylester)-molybdenum(V)] and di-μ-sulphido-bis[oxo-(L-cysteinato-methylester)molybdenum(V)] (Dew & Kay, 1971) have been reported, but there is little information about the molybdenum amino-acid complexes in other oxidation states. The bis-π-cyclopentadienyl compounds of the type $(\pi\text{-}C_5H_5)_2MoX_2$ provide an extensive series of compounds for the investigation of the chemistry of molybdenum(IV).

The crystal structures of bis-π-cyclopentadienylmolybdenum dihydride (Gerloch & Mason, 1965), bis-π-cyclopentadienylmolybdenum toluene-3,4-dithiol and bis-π-cyclopentadienyl(2-aminoethanethiolato)molybdenum iodide (Knox & Prout, 1969*a*, *c*), bis-π-cyclopentadienylmolybdenum benzene 1,2-dithiol (Kutoglu & Kopf, 1970) and $(\pi\text{-}C_5H_5)_2Mo(\mu\text{-}SBu^n)_2FeCl_2$ (Cameron & Prout, 1971) have been reported and show that the presence of the $(\pi\text{-}C_5H_5)_2Mo$ group has little effect on the behaviour of the ligand although the ligand X appears to affect the conformation of the $(\pi\text{-}C_5H_5)_2Mo$ group.

Now a group of bis-π-cyclopentadienylmolybdenum amino-acid complexes have been prepared and characterized by Gore & Green (1970), who kindly supplied us with the samples for X-ray work. For optically active amino acids the complexes were prepared from the L-form of the acid. In all the structures six complex

salts, $H[(\pi\text{-}C_5H_5)_2\overline{MoNH_2CH(CH_2S})COO]^+Cl_-$,

$H[(\pi\text{-}C_5H_5)_2\overline{MoNH_2CH(CH_2S})COO]^+PF_6^+$,

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* Present address: Division of Soils, C.S.I.R.O., Private Bag No. 1, Glen Osmond, South Australia 5064.

† Present address: Department of Biochemistry, University of Alberta, Edmonton 7, Alberta, Canada.

‡ Present address: Department of Chemistry, Ohio State University, Columbus, Ohio 43210, U.S.A.

$[(\pi\text{-}C_5H_5)_2\overline{MoNH_2CH_2COO}]^+Cl^-.H_2O$,

$[(\pi\text{-}C_5H_5)_2\overline{MoHN(CH_3)CH_2COO}]^+Cl^-$,

$[(\pi\text{-}C_5H_5)_2\overline{MoNH_2CH(CH_2CH(CH_3)_2)COO}]^+PF_6^-$ and $[(\pi\text{-}C_5H_5)_2Mo(\text{L-proline})]^+PF_6^-$ have been investigated. In this paper we report the structures of the first four of these. The L-leucine and L-proline complexes will be the subject of a later paper. The chloride salts refined easily, but the hexafluorophosphates have all presented unexpected difficulties.

Experimental and crystal data

In parentheses are the abbreviated name of the complex and the initials of the author responsible for the experimental work.

(*a*) Hydrogendi(bis-π-cyclopentadienyl)-L-cysteinatomolybdenum(IV) chloride (cysteine-Cl) (L.T.J.D.) $H[(\pi\text{-}C_5H_5)_2\overline{MoNH_2CH(CH_2S})COO]^+Cl^-$ $C_{26}H_{31}Mo_2N_2O_4S_2Cl$, $M=726\cdot7$, orthorhombic, $a=13\cdot23\pm0\cdot01$, $b=15\cdot90\pm0\cdot01$, $c=6\cdot26\pm0\cdot01$ Å, $U=1316\cdot8$ Å^3, space group $P2_12_12$ (D_2^3, No. 18), $D_m=1\cdot81$ g.cm^{-3} (by flotation), $D_c=1\cdot83$ g.cm^{-3} (for $Z=2$), $F(000)=732$, Mo $K\alpha$ radiation ($\lambda=0\cdot7107$), $\mu=12$ cm^{-1}.

A single crystal ($0\cdot16\times0\cdot24\times0\cdot64$ mm) of the compound with the forms {100} and {010} was mounted about the *c* axis. The intensities of 1785 reflexions with $I>3\sigma$ of the *hk*0–*hk*7 layers were recorded on a Hilger and Watts linear diffractometer by a moving-crystal stationary-counter method with Mo $K\alpha$ radiation and balanced filters. The total scan range was 2·5° with the peak scan twice each background scan. The Lorentz and polarization factors were applied but no absorption corrections were made.

The locations of the molybdenum and sulphur atoms and the chloride ion were determined from Patterson syntheses. The molybdenum and sulphur atoms were in the fourfold general positions whereas the chloride ions were in the twofold special positions $(0,0,z)$ and $(\frac{1}{2},\frac{1}{2},\bar{z})$ situated on diad axes. The positions of the carbon atoms were then determined by successive difference syntheses. The trial structure suggested a hydrogen bonded $[(\pi\text{-}C_5H_5)_2\overline{MoNH_2CH(CH_2S})COO]_2H^+$ cation with a crystallographic diad axis. Three cycles of full-matrix least-squares refinement of the scale factor, positional parameters and isotropic temperature factors led to a residual R of 0·072 ($R=||F_o|-|F_c||/|F_o|$). Three further cycles of least-squares refinement with anisotropic temperature factors reduced R to 0·042. Two matrix blocks, one for the refinement of the scale factor and anisotropic temperature factors and the other for the positional parameters were used. A difference synthesis gave the positions of all the hydrogen atoms except the one in the hydrogen bond between the carboxyl groups of the dimer. With these hydrogen atoms included in the structure factor calculation, the refinement of the parameters of all the non-hydrogen atoms lowered the residual R to 0·038. Each hydrogen atom was assigned the isotropic temperature factor obtained, after the isotropic temperature refinement, for the atom to which the hydrogen was bonded. The weighting scheme used was:

$$w=\{1+[(F_o-26\cdot8)/14\cdot6]^2\}^{-1}.$$

Convergence was achieved in the final cycle of refinement with the largest parameter shift 0·3 of its estimated standard deviation.

(*b*) Hydrogendi(bis-π-cyclopentadienyl)-L-cysteinatomolybdenum(IV) hexafluorophosphate (cysteine-PF$_6$) $H[(\pi\text{-}C_5H_5)_2\overline{MoNH_2CH(CH_2S})COO]_2^+PF_6^-$ (G.B.A.) $C_{26}H_3Mo_2N_2O_4S_2PF_6$, $M=836$, triclinic, $a=15\cdot94\pm0\cdot01$, $b=7\cdot61\pm0\cdot01$, $c=6\cdot19\pm0\cdot01$ Å; $\alpha=95\cdot6\pm0\cdot1$, $\beta=101\cdot8\pm0\cdot1$, $\gamma=90\cdot1\pm0\cdot1^\circ$, $D_m=1\cdot90$ g.cm^{-3} (by flotation), for $Z=1$, $D_c=1\cdot87$ g.cm^{-3}, Mo $K\alpha$ radiation, $\mu=12\cdot5$ cm^{-1}, piezoelectric; space group $P1$ (C_1, No. 1).

The intensities of 2205 independent reflexions with $I>3\sigma$ were obtained with a Hilger and Watts four-circle diffractometer from a crystal $0\cdot2\times0\cdot4\times1\cdot0$mm. using an ω–2θ scan. The intensities of the reflexions, which all came from the same hemispherical shell ($h_{\max}-\bar{h}_{\max}$, $k_{\max}-\bar{k}_{\max}$, $0-l_{\max}$), were corrected for Lorentz and polarization effects, but not for absorption or extinction.

The crystals, prepared from optically resolved L-cysteine, were piezoelectric. Therefore, they had to be non-centrosymmetric. However, the Patterson function was consistent with a pair of molybdenum atoms and a PF_6^- ion at inversion centres in $P\bar{1}$. Subsequent F_o and difference syntheses indicated locations for the π-cyclopentadienyl groups and the nitrogen and sulphur atoms in $P\bar{1}$ with the apparent inversion centres still present, but after these atoms were included in the structure factor calculation the difference synthesis in $P\bar{1}$ showed two sets of peaks for the carboxyl and α carbon atoms.

A model for a hydrogen bonded dimeric cation essentially similar to that in Fig. 2 was set up with L-cysteine ligands. All atoms in the asymmetric unit had equivalent atoms related by inversion except O(1), O(2), C(2) and C(3) of one half of the dimer and O(3), O(4), C(4) and C(5) of the other half of the dimer. A system of this type on least-squares refinement gives an ill-conditioned normal matrix (Rae & Maslen, 1963), for which conditions of singularity are inherent on inversion, and the consequent parameter shifts may be wildly inaccurate. To try to preserve a chemically reasonable system, bond lengths were constrained by Waser's (1963) method as implemented by Ford (1970) and Rollett (1970) in those parts of the asymmetric unit related by the pseudo-inversion centre. Anisotropic temperature factors were given to all atoms except those of the cyclopentadienyl groups. The refinement was only partially successful and converged at $R = 11{\cdot}9\%$. The weighting scheme used was: $w = 20/F_o$ if $F_o > 20$, otherwise $w = 1$.

(*c*) Bis-π-cyclopentadienylglycinatomolybdenum(IV) chloride monohydrate (glycine-Cl)

$[(\pi\text{-}C_5H_5)_2\overline{\text{MoNH}_2\text{CH}_2\text{COO}}]^+Cl^-.H_2O$ (E.S.G.) $C_{12}H_{16}MoNO_3Cl$, $M = 353{\cdot}7$, monoclinic; $a = 13{\cdot}68 \pm 0{\cdot}02$, $b = 16{\cdot}65 \pm 0{\cdot}02$, $c = 6{\cdot}00 \pm 0{\cdot}02$ Å, $\gamma = 105{\cdot}8 \pm 0{\cdot}2$, space group $P2_1/b$ (C^5_{2h}, No. 14) $D_m = 1{\cdot}81$ g.cm^{-3}. (by flotation), $D_c = 1{\cdot}79$ g.cm^{-3} (for $Z = 4$), $F(000) = 712$. Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å), $\mu = 10$ cm^{-1}.

Equi-inclination Weissenberg photographs of the *hk*0 to *hk*5 layers of a single crystal of $[(\pi\text{-}C_5H_5)_2MoNH_2CH_2COO]Cl.H^2O$ rotating about the *c* axis were recorded by the multiple film technique. The unit-cell dimensions were obtained from calibrated zero-layer Weissenberg and precession photographs.

The position of the molybdenum atom was determined from a Patterson synthesis and those of the remaining non-hydrogen atoms in the structure from successive difference syntheses. The trial structure was refined by the full-matrix least-squares method. Isotropic temperature factors were initially assigned to all the non-hydrogen atoms but in the last stages of refinement the molybdenum atom and chloride ion were assigned anisotropic temperature parameters. The weighting scheme used was: $w = [1 - (|F_o| - 7/16)^2]^{-1}$. The final residual R is 0·106 for the 1819 observed reflexions.

(*d*) Bis-π-cyclopentadienylsarcosinatomolybdenum(IV) chloride methanolate (sarcosine-Cl)

$[(\pi\text{-}C_5H_5)_2\overline{\text{MoNH(CH}_3\text{)CH}_2\text{COO}}]^+Cl^-.CH_3OH$ (L.T.J.D.) $C_{14}H_{20}ClMoNO_3$, $M = 381{\cdot}7$, orthorhombic, $a = 13{\cdot}43 \pm 0{\cdot}01$, $b = 14{\cdot}05 \pm 0{\cdot}01$, $c = 7{\cdot}98 \pm 0{\cdot}01$ Å, $U = 1505$ Å^3, space group $P2_12_12_1$ (D^4_2, No. 19), $D_m = 1{\cdot}67$ g.cm^{-3} (by flotation), $D_c = 1{\cdot}68$ g.cm^{-3} (for $Z = 4$), $\mu = 10$ cm^{-1}, $F(000) = 776$ Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$), balanced filters.

A single crystal ($0{\cdot}25 \times 0{\cdot}15 \times 0{\cdot}75$ mm) of the compound, a rhombic prism of the form {110}, was mounted about the *c* axis. The intensities of 1140 independent reflexions with $I > 4\sigma$ of layers *hk*0 to *hk*8 were recorded with a Hilger and Watts linear diffractometer by a moving-crystal stationary-counter method. The Lorentz and polarization corrections were applied but not absorption or extinction corrections.

The location of the molybdenum atom was determined from a Patterson synthesis. Then the positions of the chloride ion, the light atoms of the cation and the solvent molecule, the presence of which was deduced from the unit-cell parameters, and the density were determined from successive F_{obs} and difference syntheses. The trial structure was refined by the least-squares method with three matrix blocks: one for the scale factor and U_{ii} anisotropic temperature parameters, the second for the U_{ij} temperature parameters, and the third for the space parameters. The weighting scheme was: $w = \{1 + [(|F_o| - 21)/21]^2\}^{-1}$. The refinement converged at $R = 0{\cdot}072$.

Calculations

All calculations were carried out on the Oxford University KDF9 computer with Rollett and Hodder's (unpublished) NOVTAPE system, Rollett and Ford's (unpublished) Algol system and ancillary programs made available by various members of our group.

In all calculations, the atomic scattering factors from *International Tables for X-ray Crystallography* (1962)

Table 1. *Hydrogendi(bis-π-cyclopentadienyl)*-L-*cysteinatomolybdenum(IV) chloride, fractional atomic coordinates and temperature factors*

Estimated standard deviations are given in parentheses. Coordinates are $\times 10^4$, thermal parameters $\times 10^3$. Here and in subsequent tables the anisotropic temperature factor T is given by:

$$T = \exp\,[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*) \times 10^{-3}].$$

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Mo	1252 (0)	2243 (0)	2049 (1)	11·6 (2)	15·7 (2)	23·6 (2)	−0·6 (4)	−2·6 (4)	2·4 (4)
Cl	0 (−)	0 (−)	5987 (5)	48 (2)	34 (1)	39 (2)	0 (−)	0 (−)	−48 (3)
S	2307 (1)	1545 (1)	−626 (3)	20·6 (8)	35·3 (9)	26·1 (9)	1 (1)	9 (1)	10 (1)
O(1)	3848 (4)	1021 (4)	4339 (11)	26 (3)	46 (3)	56 (4)	−37 (5)	−30 (6)	20 (5)
O(2)	4073 (4)	−28 (4)	2070 (12)	23 (2)	39 (3)	51 (3)	−23 (7)	−7 (5)	27 (4)
N	1806 (4)	1088 (3)	3785 (11)	17 (3)	15 (3)	31 (3)	4 (4)	4 (4)	5 (4)
C(1)	3534 (5)	507 (4)	3112 (14)	21 (3)	25 (3)	36 (4)	6 (6)	−7 (5)	4 (4)
C(2)	2391 (5)	430 (4)	2625 (11)	16 (3)	15 (3)	35 (4)	2 (4)	−7 (4)	6 (4)
C(3)	2172 (5)	467 (5)	288 (12)	25 (3)	30 (4)	29 (4)	−20 (5)	−12 (5)	19 (5)
C(11)	−70 (7)	2578 (6)	−209 (17)	29 (4)	44 (5)	51 (5)	21 (7)	−41 (7)	2 (6)
C(12)	57 (6)	1707 (6)	−487 (16)	18 (3)	51 (5)	49 (5)	−43 (8)	−18 (7)	14 (6)
C(13)	−106 (6)	1327 (5)	1518 (18)	21 (3)	34 (4)	71 (7)	1 (8)	−20 (7)	−12 (6)
C(14)	−365 (5)	1943 (7)	3009 (21)	10 (3)	65 (5)	61 (6)	8 (10)	9 (7)	−9 (6)
C(15)	−365 (5)	2716 (6)	1946 (16)	22 (3)	46 (4)	46 (5)	−33 (9)	−24 (6)	36 (6)
C(21)	1538 (6)	3703 (4)	2004 (18)	41 (4)	17 (3)	55 (5)	7 (7)	−24 (8)	−17 (5)
C(22)	1283 (7)	3478 (5)	4125 (15)	41 (4)	25 (4)	54 (5)	−37 (6)	8 (9)	2 (8)
C(23)	2005 (5)	2921 (5)	4912 (16)	62 (6)	21 (4)	41 (5)	−9 (6)	−24 (8)	−8 (6)
C(24)	2721 (5)	2781 (5)	3209 (16)	21 (3)	32 (4)	63 (6)	−17 (9)	−30 (6)	−16 (6)
C(25)	2429 (6)	3292 (5)	1511 (16)	37 (4)	28 (4)	52 (6)	3 (6)	15 (7)	−32 (6)

Table 1 (*cont.*)

All hydrogen parameters are given $\times 10^3$.

	x/a	y/b	z/c	U_{iso}
H(1)	211	125	480	22
H(2)	126	80	448	22
H(3)	219	−5	308	22
H(4)	160	16	−16	25
H(5)	258	19	−92	25
H(6)	17	308	−72	38
H(7)	13	147	−212	31
H(8)	8	69	212	37
H(9)	−66	188	440	43
H(10)	−60	323	220	35
H(11)	200	272	640	42
H(12)	85	383	460	39
H(13)	119	405	80	37
H(14)	266	344	0	37
H(15)	336	231	348	37

for neutral atoms, corrected for the real part of the the dispersion, were used.

Results

For each complex, copies of the observed structure amplitudes and structure factors calculated from the

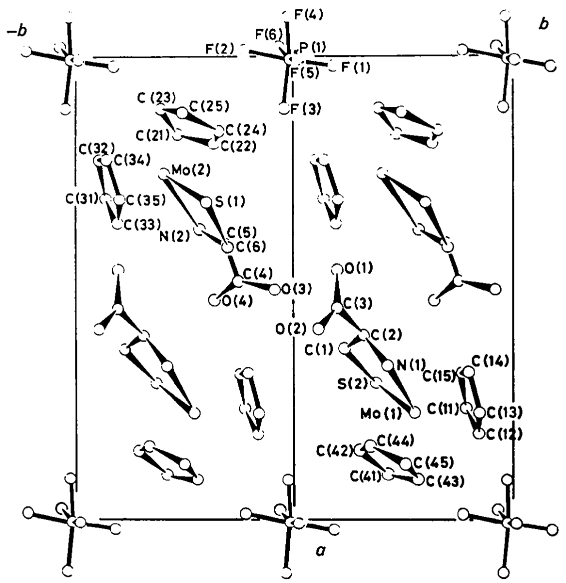

Fig. 2. Hydrogendi(bis-π-cyclopentadienyl)-L-cysteinatomolybdenum(IV) hexafluorophosphate: the crystal structure seen in projection down **c**.

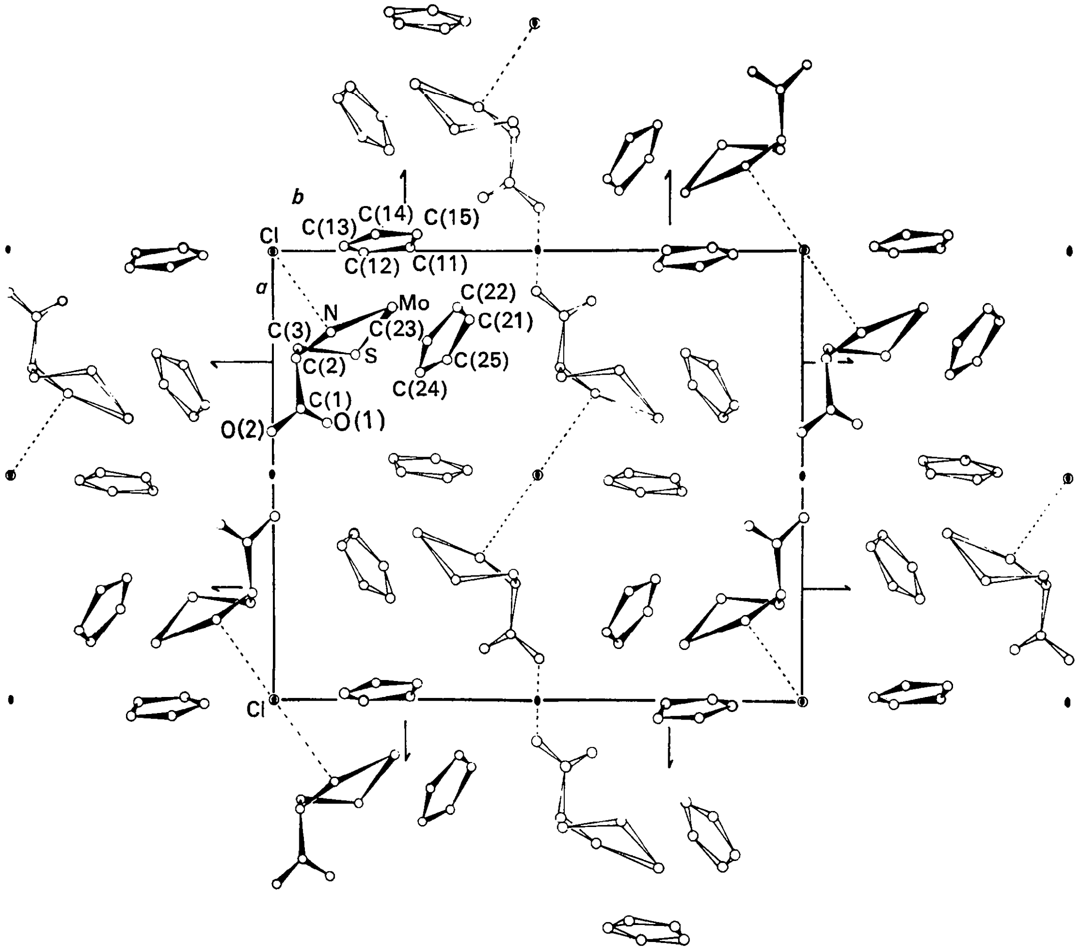

Fig. 1. Hydrogendi(bis-π-cyclopentadienyl)-L-cysteinatomolybdenum(IV) chloride: the crystal structure seen in projection down **c**.

Table 2. *Hydrogendi(bis-π-cyclopentadienyl)-*L-*cysteinatomolybdenum(IV) hexafluorophosphate, fractional atomic coordinates and temperature factors*

All parameters are × 10³. Standard deviations are in parentheses.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
P(1)	7 (1)	−12 (2)	−2 (2)	50 (4)	48 (4)	29 (3)	−18 (5)	17 (5)	−53 (6)
F(1)	22 (3)	182 (5)	−2 (5)	162 (32)	89 (25)	63 (21)	5 (39)	64 (42)	−56 (46)
F(2)	−14 (2)	−222 (3)	19 (5)	100 (18)	23 (10)	73 (19)	−18 (22)	29 (28)	−70 (22)
F(3)	113 (3)	−38 (8)	84 (6)	81 (26)	194 (49)	47 (21)	20 (50)	−34 (36)	−55 (59)
F(4)	−86 (2)	−23 (4)	−67 (5)	47 (14)	103 (20)	79 (20)	−22 (31)	68 (28)	−62 (28)
F(5)	7 (2)	17 (4)	269 (4)	104 (21)	89 (20)	34 (12)	−34 (25)	79 (26)	−65 (33)
F(6)	23 (2)	−66 (4)	−234 (4)	84 (18)	93 (22)	35 (13)	−16 (29)	3 (25)	−73 (34)
Mo(1)	770·5 (−)	552·4 (−)	333·6 (−)	23 (1)	51 (2)	18 (1)	2 (3)	4 (2)	−60 (3)
Mo(2)	252·5 (2)	−589·3 (3)	678·8 (4)	57 (2)	5 (1)	18 (1)	13 (2)	−7 (2)	−18 (2)
S(1)	315 (1)	−391 (1)	1016 (1)	36 (5)	70 (6)	13 (4)	−4 (8)	20 (7)	−81 (9)
S(2)	703 (1)	376 (1)	−10·6 (2)	96 (8)	26 (4)	16 (4)	8 (7)	−20 (9)	−41 (9)
O(1)	461 (2)	203 (6)	318 (6)	33 (15)	161 (37)	87 (24)	123 (50)	13 (30)	−9 (35)
O(2)	588 (2)	114 (3)	520 (4)	75 (17)	54 (14)	38 (12)	13 (20)	26 (23)	−71 (25)
C(1)	632 (3)	233 (7)	107 (5)	143 (39)	138 (39)	7 (14)	−57 (37)	33 (38)	−296 (72)
C(2)	596 (3)	319 (6)	261 (5)	80 (26)	106 (31)	18 (16)	−31 (37)	18 (33)	−182 (50)
C(3)	544 (2)	201 (4)	361 (4)	27 (16)	30 (16)	19 (13)	−3 (22)	10 (23)	−29 (26)
N(1)	668 (2)	427 (3)	440 (4)	64 (16)	9 (10)	14 (12)	−10 (18)	−48 (21)	−5 (20)
O(3)	505 (2)	−82 (4)	699 (5)	68 (18)	99 (22)	63 (17)	−25 (30)	85 (29)	−125 (33)
O(4)	527 (2)	−360 (4)	555 (5)	44 (15)	77 (20)	82 (21)	−32 (33)	35 (27)	−63 (28)
N(2)	371 (1)	−472 (4)	579 (4)	4 (9)	57 (16)	37 (15)	−37 (24)	32 (17)	−46 (18)
C(4)	486 (2)	−247 (4)	621 (6)	61 (30)	50 (23)	34 (18)	12 (34)	6 (39)	−59 (44)
C(5)	405 (3)	−310 (7)	698 (5)	76 (28)	117 (34)	11 (14)	−35 (37)	39 (34)	−51 (53)
C(6)	411 (3)	−298 (7)	960 (5)	87 (30)	117 (39)	11 (15)	8 (38)	18 (33)	−29 (52)

Table 2 (*cont.*)

	x/a	y/b	z/c	U_{iso}
C(11)	761 (2)	785 (5)	117 (5)	43 (7)
C(12)	812 (2)	844 (4)	323 (5)	35 (6)
C(13)	768 (3)	846 (7)	486 (5)	75 (12)
C(14)	681 (2)	804 (7)	383 (7)	76 (11)
C(15)	680 (2)	749 (5)	161 (6)	59 (9)
C(21)	166 (2)	−527 (4)	366 (5)	46 (8)
C(22)	188 (2)	−363 (4)	470 (5)	41 (8)
C(23)	113 (2)	−608 (4)	496 (5)	42 (7)
C(24)	160 (3)	−339 (4)	669 (6)	50 (10)
C(25)	121 (3)	−504 (5)	694 (6)	60 (11)
C(31)	307 (2)	−851 (4)	557 (4)	30 (6)
C(32)	224 (2)	−886 (4)	584 (5)	43 (7)
C(33)	359 (2)	−802 (5)	760 (5)	46 (7)
C(34)	226 (2)	−854 (5)	813 (5)	47 (8)
C(35)	308 (2)	−794 (5)	924 (5)	52 (9)
C(41)	903 (3)	428 (5)	293 (6)	54 (9)
C(42)	850 (3)	302 (5)	355 (7)	61 (11)
C(43)	912 (4)	569 (5)	463 (7)	81 (14)
C(44)	842 (4)	346 (7)	570 (8)	95 (19)
C(45)	880 (3)	510 (6)	640 (6)	74 (12)

final atomic parameters (Tables 1 to 4) have been deposited at the National Lending Library, England.*

Projections of the crystal structures are shown in Figs. 1 to 4. The bonded distances and interbond angles, certain dihedral angles and equations of important molecular planes are given in Tables 5 to 10 and Figs. 5 to 8.

Table 3. *Bis-π-cyclopentadienylglycinatomolybdenum(IV) chloride monohydrate, fractional atomic coordinates and temperature factors*

Estimated standard deviations in parentheses. All values × 10³.

	x/a	y/b	z/c	U_{iso}
Mo	271·3 (1)	579·5 (1)	334·0 (2)	*
Cl	173·6 (5)	336·5 (3)	−83 (1)	*
O(1)	353·8 (9)	552·9 (7)	605 (2)	47 (3)
O(2)	436 (1)	468·0 (8)	762 (3)	62 (3)
N	328 (1)	473·8 (8)	229 (2)	40 (3)
C(1)	383 (1)	484 (1)	608 (3)	46 (4)
C(2)	354 (2)	423 (1)	417 (4)	59 (5)
C(11)	139 (2)	503 (1)	565 (4)	65 (5)
C(12)	131 (2)	585 (1)	541 (4)	75 (6)
C(13)	110 (2)	598 (2)	321 (4)	73 (6)
C(14)	109 (2)	521 (2)	217 (5)	79 (6)
C(15)	131 (2)	465 (2)	374 (5)	77 (6)
C(21)	357 (2)	716 (2)	374 (5)	80 (7)
C(22)	289 (2)	710 (2)	191 (4)	78 (6)
C(23)	323 (2)	662 (2)	32 (5)	81 (6)
C(24)	405 (3)	648 (2)	102 (6)	105 (9)
C(25)	430 (2)	677 (2)	297 (5)	85 (7)
O(3)	64 (2)	221 (2)	−467 (4)	118 (7)

*

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Mo	27·4 (7)	35·3 (7)	35 (1)	−1 (1)	3·4 (9)	17·6 (9)
Cl	70 (3)	63 (3)	63 (3)	−15 (5)	−23 (5)	13 (5)

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* Supplementary Publication No. SUP 30011 (1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Bis-π-cyclopentadienylsarcosinatomolybdenum(IV) chloride methanolate, fractional atomic coordinates and temperature factors*

Estimated standard deviations in parentheses.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Mo	0·2855 (1)	0·2933 (1)	0·2186 (2)	0·0366 (7)	0·0226 (6)	0·0286 (7)	0·000 (1)	−0·003 (1)	−0·007 (1)
Cl	0·1549 (4)	0·0583 (3)	0·7748 (10)	0·057 (3)	0·042 (2)	0·064 (4)	−0·007 (6)	0·003 (6)	0·025 (4)
O(1)	0·2531 (10)	0·4358 (9)	0·1586 (19)	0·056 (7)	0·035 (6)	0·039 (8)	0·00 (1)	−0·06 (1)	−0·01 (1)
O(2)	0·2890 (12)	0·5895 (8)	0·1855 (20)	0·077 (9)	0·021 (5)	0·068 (11)	0·02 (1)	−0·04 (2)	0·01 (1)
N	0·355 (1)	0·383 (1)	0·418 (2)	0·039 (8)	0·029 (7)	0·041 (11)	−0·01 (1)	0·00 (1)	−0·01 (1)
C(1)	0·301 (1)	0·508 (1)	0·236 (3)	0·040 (9)	0·036 (8)	0·051 (13)	0·02 (2)	0·01 (2)	0·03 (1)
C(2)	0·377 (1)	0·480 (1)	0·361 (3)	0·039 (9)	0·037 (9)	0·029 (10)	0·00 (2)	0·03 (2)	−0·02 (2)
C(3)	0·438 (2)	0·344 (1)	0·523 (3)	0·053 (12)	0·041 (11)	0·060 (12)	0·02 (2)	−0·04 (2)	0·00 (2)
C(11)	0·154 (2)	0·187 (1)	0·195 (3)	0·069 (13)	0·050 (11)	0·025 (12)	−0·02 (2)	0·03 (2)	−0·02 (2)
C(12)	0·118 (1)	0·278 (2)	0·208 (3)	0·051 (10)	0·075 (13)	0·048 (13)	−0·01 (3)	0·02 (2)	−0·09 (2)
C(13)	0·144 (1)	0·309 (1)	0·369 (3)	0·037 (9)	0·051 (11)	0·038 (12)	−0·01 (2)	0·03 (2)	−0·03 (2)
C(14)	0·195 (1)	0·235 (1)	0·448 (3)	0·046 (11)	0·035 (9)	0·045 (13)	−0·01 (1)	0·01 (2)	−0·03 (1)
C(15)	0·202 (2)	0·158 (1)	0·335 (3)	0·060 (12)	0·043 (9)	0·045 (12)	0·05 (1)	−0·01 (2)	−0·05 (2)
C(21)	0·325 (2)	0·245 (2)	−0·046 (3)	0·050 (12)	0·087 (15)	0·047 (15)	−0·04 (2)	0·01 (2)	−0·02 (2)
C(22)	0·390 (2)	0·320 (1)	−0·010 (3)	0·064 (13)	0·030 (9)	0·052 (14)	−0·01 (2)	0·05 (2)	0·01 (2)
C(23)	0·448 (2)	0·295 (2)	0·128 (4)	0·051 (11)	0·048 (10)	0·084 (18)	−0·05 (3)	0·04 (2)	−0·04 (2)
C(24)	0·427 (1)	0·201 (2)	0·186 (3)	0·048 (9)	0·051 (10)	0·069 (16)	0·03 (2)	0·04 (2)	0·03 (2)
C(25)	0·351 (2)	0·170 (2)	0·066 (3)	0·085 (15)	0·041 (10)	0·044 (15)	0·01 (2)	0·05 (2)	0·03 (2)
O(3)	0·476 (2)	0·029 (2)	0·547 (5)	0·093 (15)	0·144 (19)	0·184 (34)	−0·11 (4)	0·03 (4)	−0·09 (3)
C(4)	0·417 (2)	0·062 (2)	0·653 (6)	0·094 (19)	0·050 (14)	0·154 (31)	−0·05 (4)	0·11 (4)	−0·01 (3)

Table 5. *Hydrogen di(bis-π-cyclopentadienyl)-*L*-cysteinatomolybdenum(IV) chloride, interatomic distances and angles*

Estimated standard deviations in parentheses.

(*a*) Bond lengths and interbond angles

Mo—S	2·446 (2) Å	C(12)–C(11)–C(15)	107·6 (9)°
Mo—N	2·256 (7)	C(11)–C(12)–C(13)	107·1 (9)
Mo—C(11)	2·311 (11)	C(12)–C(13)–C(14)	109·4 (10)
Mo—C(12)	2·396 (10)	C(13)–C(14)–C(15)	107·4 (11)
Mo—C(13)	2·337 (11)	C(11)–C(15)–C(14)	108·4 (9)
Mo—C(14)	2·273 (13)		
Mo—C(15)	2·268 (10)	C(21)–C(22)	1·42 (2) Å
Mo—C(21)	2·353 (11)	C(21)–C(25)	1·38 (2)
Mo—C(22)	2·355 (10)	C(22)–C(23)	1·39 (1)
Mo—C(23)	2·317 (10)	C(23)–C(24)	1·44 (1)
Mo—C(24)	2·244 (8)	C(24)–C(25)	1·39 (1)
Mo—C(25)	2·307 (10)		
		C(21)–H(13)	1·0 Å
C(11)–C(12)	1·41 (2)	C(22)–H(12)	0·9
C(11)–C(15)	1·42 (1)	C(23)–H(11)	1·0
C(12)–C(13)	1·41 (2)	C(24)–H(15)	1·1
C(13)–C(14)	1·40 (2)	C(25)–H(14)	1·0
C(14)–C(15)	1·40 (2)	C(22)–C(21)–C(25)	107·0 (9)°
		C(21)–C(22)–C(23)	109·2 (9)
C(11)–H(6)	0·9	C(22)–C(23)–C(24)	106·7 (8)
C(12)–H(7)	1·1	C(23)–C(24)–C(25)	107·0 (8)
C(13)–H(8)	1·1	C(21)–C(25)–C(24)	110·0 (9)
C(14)–H(9)	1·0		
C(15)–H(10)	0·9		
Cysteine ligand			
S—C(3)	1·816 (8) Å	S—Mo—N	77·0 (2)°
C(2)—C(3)	1·49 (1)	Mo—N—C(2)	120·4 (5)
C(1)—C(2)	1·55 (1)	Mo—S—C(3)	99·0 (4)
C(2)—N	1·49 (1)	S—C(3)—C(2)	109·1 (5)
C(1)—O(1)	1·20 (1)	C(1)—C(2)—C(3)	112·3 (6)
C(1)—O(2)	1·29 (1)	C(3)–C(2)—N	110·4 (6)
O(2)···S	3·816 (8)	C(1)–C(2)—N	110·8 (6)
O(2)···N	3·65 (1)	C(2)–C(1)—O(1)	121·4 (8)
N····S	2·932 (7)	C(2)–C(1)—O(2)	112·9 (7)
C(2)–H(3)	0·9	O(1)–C(1)—O(2)	125·8 (9)
C(3) H(4)	0·9		
C(3)—H(5)	1·0		
N—H(1)	0·8		
N—H(2)	1·0		

Table 5 (*cont.*)

(*b*) Hydrogen bonds and close contacts

O(2)····O(2$^{\mathrm{i}}$)	2·455 Å	N·······O(1)	2·73 Å
C(1)—O(2)····O(2$^{\mathrm{i}}$)	122·0°	H(1)····O(1)	2·35
C(24)···O(1)	3·25 Å	N—H(1)···O(1)	110°
H(15)···O(1)	2·22	H(1)—N·····O(1)	54
C(24)—H(15)···O(1)	149°		
H(15)—C(24)···O(1)	20	S·······C(12)	2·99 Å
		S·······C(25)	3·09
N······Cl$^-$	3·23 Å	N······C(13)	2·93
H(2)····Cl$^-$	2·30	N······C(24)	2·97
N—H(2)····Cl$^-$	115°	N······C(23)	3·01
H(2)—N······Cl$^-$	4	C(15)···C(21)	2·97
		C(11)···C(21)	3·11
N······S$^{\mathrm{i}}$	3·63 Å	C(15)···C(22)	2·84
H(1)····S$^{\mathrm{ii}}$	2·91	H(6)····H(13)	2·26
N—H(1)····S$^{\mathrm{ii}}$	152°	H(10)···H(12)	2·61
H(1)—N······S$^{\mathrm{ii}}$	22		
C(2)—N······S$^{\mathrm{ii}}$	121		
Mo—N······S$^{\mathrm{ii}}$	111		

[i] Atom in Table 1 transformed by $(1-x, -y, z)$.

[ii] Atom in Table 1 transformed by $(x, y, 1+z)$.

Discussion

In the crystals of the cysteine complexes there are isolated anions and complex cations. In these cations the cysteine ligands chelate the bis-π-cyclopentadienylmolybdenum moieties through nitrogen and sulphur and they also form hydrogen bonds through the carboxylate oxygen atoms to give dimeric species typical of hydrogen carboxylates. In the crystals of the glycine and sarcosine complexes, the amino-acid ligands chelate the bis-π-cyclopentadienylmolybdenum groups through nitrogen and oxygen to give complex cations that are linked by hydrogen bonding to the anions and solvent of crystallization.

(i) The $(\pi\text{-}C_5H_5)_2Mo$ groups

In the crystals of the four complexes, there are five crystallographically independent bis-π-cyclopentadie-

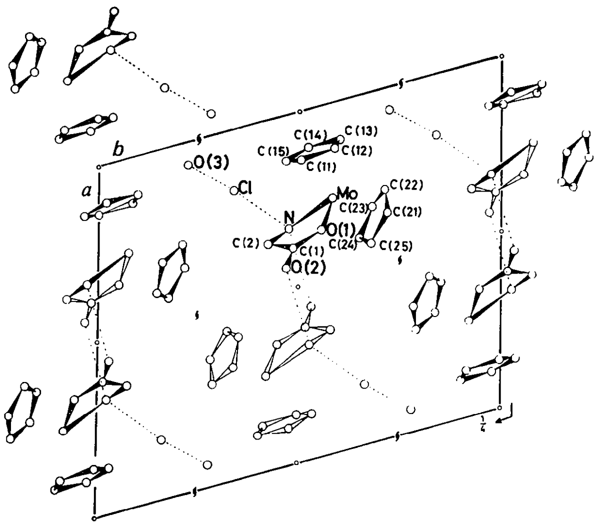

Fig. 3. Bis-π-cyclopentadienylglycinatomolybdenum(IV) chloride monohydrate: the crystal structure seen in projection down **c**.

nylmolybdenum groups (two in cysteine-PF_6). These groups are shown, projected onto the plane of the MoX_2 (X=O, N or S) group, in Fig 5(*a*–*e*). The π-cyclopentadienyl groups are planar within experimental error (Table 10) and the dimensions are essentially the same as those reported elsewhere by the Oxford group (Knox & Prout, 1969*a*, *b*); Cameron & Prout, 1972*a*, *b*) but differ from those found in the hydride $(\pi\text{-}C_5H_5)_2MoH_2$ by Gerloch & Mason (1965). In all cases the molybdenum atom was situated almost directly over the centroid of the π-cyclopentadienyl ring ring and the perpendicular distance from the molybdenum atom to the ring was found to be in the range 1·92–2·00 Å (Table 9). In contrast, the distance is 1·89 Å in the hydride. The point symmetry of the molybdenum atom approximates to C_{2v} with the plane of the ring normals approximately perpendicular to the MoX_2 (Table 9). The exact value of the angle appears to depend on the crystal packing. The angles between the normals to the π-cyclopentadienyl rings lie in the

Table 6. *Hydrogendi(bis-π-cyclopentadienyl)*-L-*cysteinatomolybdenum(IV) hexafluorophosphate, interatomic distances and interbond angles*

Standard deviations in parentheses.

(*a*) In the PF_6^- ion

P(1)—F(1)	1·50 (5) Å	F(1)—P(1)—F(6)	97 (2)°
P(1)—F(2)	1·66 (3)	F(2)—P(1)—F(3)	92 (2)
P(1)—F(3)	1·68 (7)	F(2)—P(1)—F(4)	91 (2)
P(1)—F(4)	1·49 (3)	F(2)—P(1)—F(5)	85 (2)
P(1)—F(5)	1·67 (4)	F(2)—P(1)—F(6)	89 (2)
P(1)—F(6)	1·53 (4)	F(3)—P(1)—F(4)	176 (2)
		F(3)—P(1)—F(5)	84 (2)
F(1)—P(1)—F(2)	174 (2)°	F(3)—P(1)—F(6)	85 (2)
F(1)—P(1)—F(3)	90 (3)	F(4)—P(1)—F(5)	93 (2)
F(1)—P(1)—F(4)	87 (2)	F(4)—P(1)—F(6)	98 (2)
F(1)—P(1)—F(5)	90 (2)	F(5)—P(1)—F(6)	167 (2)

(*b*) In the $[(\pi\text{-}C_5H_5)_2MoSCH_2CH(NH_2)COO]_2H^+$ ion

Mo(1)-S(2)	2·45 (1) Å	C(31)—C(32)	1·39 (4) Å
Mo(1)-N(1)	2·14 (3)	C(31)—C(33)	1·38 (5)
Mo(1)-C(11)	2·31 (3)	C(32)—C(34)	1·41 (5)
Mo(1)-C(12)	2·33 (3)	C(33)—C(35)	1·42 (5)
Mo(1)-C(13)	2·35 (5)	C(34)—C(35)	1·41 (5)
Mo(1)-C(14)	2·42 (5)		
Mo(1)-C(15)	2·27 (4)	C(31)—C(33)—C(35)	108 (4)°
Mo(1)-C(41)	2·36 (4)	C(33)—C(35)—C(34)	106 (3)
Mo(1)-C(42)	2·29 (4)	C(35)—C(34)—C(32)	109 (3)
Mo(1)-C(43)	2·24 (6)	C(34)—C(32)—C(31)	106 (4)
Mo(1)-C(44)	2·38 (7)	C(32)—C(31)—C(33)	110 (4)
Mo(1)-C(45)	2·35 (5)		
Mo(2)-S(1)	2·48 (1)	S(2)—C(1)	1·86 (6) Å
Mo(2)-N(2)	2·32 (3)	C(1)—C(2)	1·33 (7)
Mo(2)-C(21)	2·23 (4)	C(2)—C(3)	1·48 (6)
Mo(2)-C(22)	2·38 (4)	C(2)—N(1)	1·59 (6)
Mo(2)-C(23)	2·28 (4)	C(3)—O(1)	1·30 (5)
Mo(2)-C(24)	2·41 (5)	C(3)—O(2)	1·32 (4)
Mo(2)-C(25)	2·21 (3)	O(2)—O(3)	2·47 (4) (hydrogen bond)
Mo(2)-C(31)	2·29 (3)		
Mo(2)-C(32)	2·29 (4)		
Mo(2)-C(33)	2·37 (4)	O(3)—C(4)	1·32 (4)
Mo(2)-C(34)	2·33 (4)	O(4)—C(4)	1·17 (5)
Mo(2)-C(35)	2·33 (3)	C(4)—C(5)	1·56 (6)
C(11)-C(12)	1·40 (5)	C(5)—N(2)	1·42 (6)
C(11)-C(15)	1·41 (5)	C(5)—C(6)	1·59 (7)
C(12)-C(13)	1·35 (6)	C(6)—S(1)	1·80 (6)
C(13)-C(14)	1·41 (7)		
C(14)-C(15)	1·39 (6)	N(1)—Mo(1)-S(2)	80 (1)°
		Mo(1)—S(2)—C(1)	98 (2)

Table 6 (*cont.*)

C(15) –C(11)–C(12)	105 (2)°	S(2)——C(1)——C(2)	114 (4)
C(11) –C(12)–C(13)	111 (3)	C(1)——C(2)——N(1)	109 (4)
C(12) –C(13)–C(14)	107 (4)	C(2)——N(1)——Mo(1)	119 (2)
C(13) –C(14)–C(15)	107 (4)	C(3)——C(2)——N(1)	113 (3)
C(14) –C(15)–C(11)	109 (4)	C(2)——C(3)——O(1)	122 (3)
		C(2)——C(3)——O(2)	115 (3)
C(41) –C(42)	1·41 (6) Å	O(1)——C(3)——O(2)	115 (3)
C(41) –C(43)	1·41 (7)	C(3)——O(2)···O(3)	117 (2)
C(42) –C(44)	1·38 (8)	O(2)····O(3)——O(4)	122 (3)
C(43) –C(45)	1·41 (7)	O(3)——C(4)——O(4)	132 (4)
C(44) –C(45)	1·38 (9)	O(4)——C(4)——C(5)	116 (4)
		O(3)——C(4)——C(5)	111 (4)
C(41) –C(43)–C(45)	108 (5)°	C(5)——C(6)——S(1)	109 (4)
C(43) –C(45)–C(44)	108 (5)	C(6)——S(1)——Mo(2)	106 (2)
C(45) –C(44)–C(42)	108 (5)	S(1)——Mo(2) –N(2)	78 (1)
C(44) –C(42)–C(41)	109 (4)	Mo(2)—N(2)——C(5)	116 (3)
C(42) –C(41)–C(43)	105 (4)		
		S(1)····C(24)	2·98 Å
C(21) –C(22)	1·36 (5) Å	S(1)····C(35)	3·03
C(21) –C(23)	1·45 (5)	S(2)····C(15)	2·98
C(22) –C(24)	1·40 (6)	S(2)····C(42)	3·00
C(23) –C(25)	1·37 (6)	N(1)····C(14)	2·93
C(24) –C(25)	1·43 (7)	N(1)····C(44)	2·74
		N(2)····C(22)	3·01
C(21) –C(23)–C(25)	107 (3)°	N(2)····C(33)	2·87
C(23) –C(25)–C(24)	108 (4)	C(12)···C(42)	2·74
C(25) –C(24)–C(22)	106 (4)	C(23)···C(32)	2·78
C(24) –C(22)–C(21)	110 (3)		
C(22) –C(21)–C(23)	107 (3)		

There are no intermolecular hydrogen bonds or very short contact distances.

range 130·9–133·9° (Table 9) for the Oxford work but in the hydride the angle is 145·9°. No regular pattern has been observed in the carbon–carbon bond length in the π-cyclopentadienyl rings of the amino acid complexes save that the more accurate the structure analysis, the more nearly equal are the observed bond lengths. In the hydride a pattern suggesting significant electron localization was found. We have concluded that the $(\pi\text{-C}_5\text{H}_5)\text{MoH}_2$ system is significantly different from the $(\pi\text{-C}_5\text{H}_5)\text{Mo}X_2$ systems we have examined and we believe that the differences might be attribut-

Table 7. *Bis-π-cyclopentadienylglycinatomolybdenum-(IV) chloride monohydrate, interatomic distances and angles*

Estimated standard deviations in parentheses.

(*a*) Bond lengths and interbond angles

Mo—O(1)	2·10 (1) Å	C(21)–C(22)	1·42 (4) Å
Mo—N	2·26 (1)	C(21)–C(25)	1·42 (4)
Mo—C(11)	2·36 (2)	C(22) C(23)	1·40 (4)
Mo—C(12)	2·30 (3)	C(23)–C(24)	1·28 (5)
Mo—C(13)	2·31 (3)	C(24)–C(25)	1·27 (5)
Mo—C(14)	2·28 (3)		
Mo—C(15)	2·32 (3)	C(22)–C(21)–C(25)	104 (2)°
Mo—C(21)	2·27 (3)	C(21)–C(22)–C(23)	105 (2)
Mo—C(22)	2·29 (3)	C(22)–C(23)–C(24)	109 (3)
Mo—C(23)	2·27 (3)	C(23)–C(24)–C(25)	113 (3)
Mo—C(24)	2·34 (4)	C(21)–C(25)–C(24)	109 (3)
Mo—C(25)	2·34 (3)		
		C(1)—O(1)	1·32 (2)°
C(11)–C(12)	1·41 (4)	C(1)—O(2)	1·24 (2)
C(11)–C(15)	1·30 (4)	C(1)—C(2)	1·51 (3)
C(12)–C(13)	1·38 (4)	C(2)—N	1·51 (3)
C(13)–C(14)	1·42 (4)		
C(14)–C(15)	1·42 (4)	O(1)—Mo—N	74·1 (5)°
		Mo—O(1)—C(1)	120 (1)
C(12)–C(11)–C(15)	111 (2)°	Mo—N——C(2)	115 (1)
C(11)–C(12)–C(13)	109 (2)		
C(12)–C(13)–C(14)	104 (2)	O(1)—C(1)—O(2)	121 (2)
C(13)–C(14)–C(15)	110 (2)	O(1)—C(1)—C(2)	119 (2)
C(11)–C(15)–C(14)	106 (2)	O(2)—C(1)—C(2)	119 (2)
		C(1)—C(2)—N	104 (2)

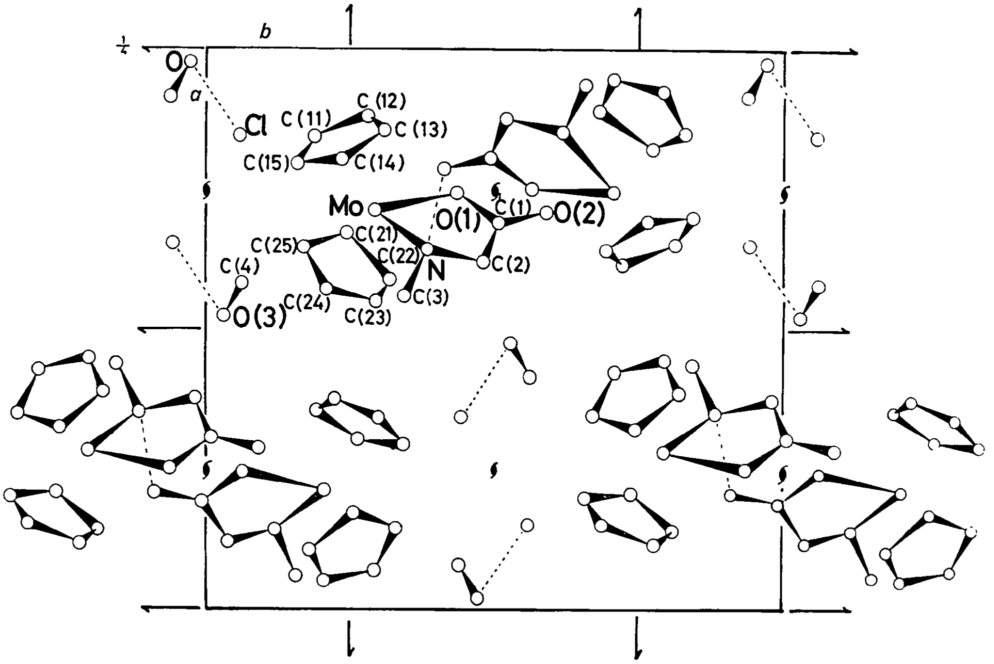

Fig. 4. Bis-π-cyclopentadienylsarcosinatomolybdenum(IV) chloride methanolate: the crystal structure seen in projection down **c**.

Table 7 (*cont.*)

(*b*) Hydrogen bonds and close contacts

N·····Cl	3·25 Å	N······O(2^{iii})	3·81 Å
Mo——N·····Cl	115°	Mo——N·····O(2^{iii})	123°
C(2)——N·····Cl	104	C(2)——N·····O(2^{iii})	118
		Cl$^-$·····N·····O(2^{iii})	72
O(3)···Cl	3·11		
O(3)···Cl$^{\mathrm{i}}$	3·21	C(13)···C(22)	2·76 Å
Cl$^-$····O(3)···Cl$^{\mathrm{i}}$	129°	N······C(15)	2·80
N·····O(2^{ii})	3·11	N······C(24)	2·91
		O(1)····C(11)	2·84
Mo——N·····O(2^{ii})	108°	O(1)····C(25)	2·75
C(2)——N·····O(2^{ii})	77	O(1)····C(21)	3·05
Cl$^-$····N·····O(2^{ii})	131		

Atom related to that in Table 3 by the following translations:– $^{\mathrm{i}}$ $-x, \frac{1}{2}-y, -\frac{1}{2}+z$; $^{\mathrm{ii}}$ $1-x, 1-y, 1+z$; $^{\mathrm{iii}}$ $x, y, -1+z$.

able to the small size and remarkable σ-donor properties of the hydrido ligands.

The (π-C_5H_5)$_2$Mo groups in the amino acid complexes, though similar in dimensions, differ in conformation (Fig. 5). Previously (Knox & Prout, 1969*b*) it was believed that the size of the ligands *X* would alone determine the conformation and angle of inclination of the π-cyclopentadienyl rings. Thus for the hydride this angle would have its smallest value, and it would increase with increasing size of *X*. Similarily, the eclipsed conformation was expected when *X* was small and staggered when *X* was larger. However, the angle of inclination and the conformation are independent of the nature of *X*. Indeed, for the cysteine complex the rings are staggered when the counter ion is chloride but eclipsed when it is hexafluorophosphate. There is in these amino-acid complexes no correlation between the carbon–carbon bond length in the π-cyclopentadienyl group and the molybdenum–carbon bond length. However, there is for a given π-cyclopentadienyl group a possible correlation between the molybdenum–carbon bond length and the position of the carbon atom relative to an approximate vertical mirror plane through the molybdenum atom (say, the plane through

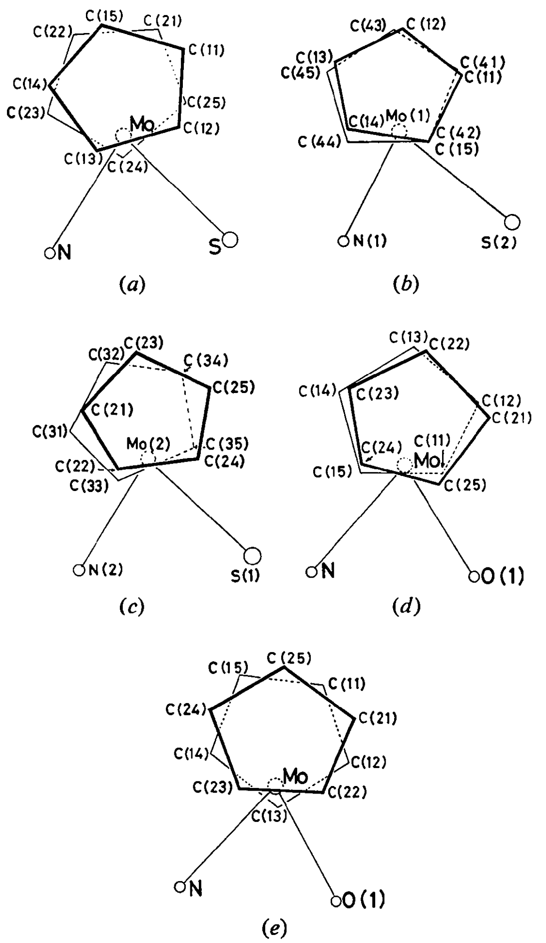

Fig. 5. View of the bis-π-cyclopentadienyl groups normal to the MoX_2 plane. (*a*) Hydrogendi(bis-π-cyclopentadienyl)-L-cysteinatomolybdenum(IV) chloride; (*b*) and (*c*) hydrogendi(bis-π-cyclopentadienyl)-L-cysteinatomolybdenum(IV) hexafluorophosphate; (*d*) bis-π-cyclopentadienylglycinatomolybdenum(IV) chloride hydrate; (*e*) bis-π-cyclopentadienylsarcosinatomolybdenum(IV) chloride methanolate.

Table 8. *Bis-π-cyclopentadienylsarcosinatomoylbdenum(IV) chloride methanolate, interatomic distances and angles*

Estimated standard deviations in parentheses.

(*a*) Bond lengths and interbond angles

Mo—O(1)	2·10 (2) Å	C(21)–C(22)	1·40 (4) Å
Mo—N	2·23 (2)	C(21)–C(25)	1·42 (4)
Mo—C(11)	2·32 (2)	C(22)–C(23)	1·39 (4)
Mo—C(12)	2·27 (3)	C(23)–C(24)	1·43 (4)
Mo—C(13)	2·26 (2)	C(24)–C(25)	1·46 (4)
Mo—C(14)	2·34 (2)	C(22)–C(21)–C(25)	106 (2)°
Mo—C(15)	2·40 (2)	C(21)–C(22)–C(23)	109 (2)
Mo—C(21)	2·28 (3)	C(22)–C(23)–C(24)	112 (2)
Mo—C(22)	2·33 (3)	C(23)–C(24)–C(25)	101 (2)
Mo—C(23)	2·30 (3)	C(21)–C(25)–C(24)	111 (2)
Mo—C(24)	2·31 (2)	C(1)—O(1)	1·34 (3) Å
Mo—C(25)	2·29 (3)	C(1)—O(2)	1·23 (3)
		C(1)—C(2)	1·48 (3)
C(11)–C(12)	1·37 (4)	C(2)—N	1·48 (3)
C(11)–C(15)	1·35 (3)	N——C(3)	1·51 (3)
C(12)–C(13)	1·40 (4)	O——Mo—N	73·4 (6)°
C(13)–C(14)	1·40 (3)	Mo—O(1)—C(1)	121 (1)
C(14)–C(15)	1·42 (3)	Mo—N——C(2)	113 (1)
		Mo—N——C(3)	120 (1)
C(12)–C(11)–C(15)	113 (2)°	O(1)—C(1)—O(2)	120 (2)
C(11)–C(12)–C(13)	106 (2)	O(1)—C(1)—C(2)	116 (2)
C(12)–C(13)–C(14)	108 (2)	O(2)—C(1)—C(2)	123 (2)
C(13)–C(14)–C(15)	108 (2)	C(1)—C(2)—N	108 (2)
C(11)–C(15)–C(14)	105 (2)	C(2)—N——C(3)	111 (2)

Solvent CH_3OH

C(4)—O(3)	1·25 (7) Å

(*b*) Hydrogen bonds and close contacts

O(3)···Cl$^{\mathrm{i}}$	3·05 Å	O(1)····C(13)	2·85 Å
C(4)——O(3)····Cl$^{\mathrm{i}}$	105°	O(1)····C(12)	2·90
N·····O(2^{ii})	2·91 Å	N······C(23)	2·90
C(2)——N······O(2^{ii})	104°	N······C(14)	2·99
C(3)——N······O(2^{ii})	98°	N······C(13)	3·04
Mo——N······O(2^{ii})	109	C(11)···C(25)	2·86
O(1)···C(22)	2·81 Å	C(15)···C(25)	2·94
		C(11)···C(21)	3·10

Atom related to that in Table 4 by the translations: $^{\mathrm{i}}$ $\frac{1}{2}-x, -y, -\frac{1}{2}+z$; $^{\mathrm{ii}}$ $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$.

Table 9. *Bis-π-cyclopentadienylmolybdenum groups*

I, perpendicular distance from the molybdenum atom to the plane of the π-cyclopentadienyl groups; II, the angle at the molybdenum between the normals to the π-cyclopentadienyl groups; III, the angle plane of the normals and the plane of the MoX_2 group.

Compound	I		II	III
$(\pi\text{-}C_5H_5)_2MoS_2C_6H_3CH_3$	1·999 Å	1·993 Å	132·5 °	88·8°
$(\pi\text{-}C_5H_5)_2MoS(CH_2)_2NH_2^+I^-$	1·976	2·002	130·9	88·8
$[(\pi\text{-}C_5H_5)_2MoNH_2CH(CH_2S)COO]_2H^+Cl^-$	1·981	1·980	133·7	88·6
$[(\pi\text{-}C_5H_5)_2MoNH_2CH(CH_2S)COO]_2H^+PF_6^-$	2·01	2·00	130	89
	1·96	1·99	133	86
$[(\pi\text{-}C_5H_5)_2MoNH(CH_3)CH_2COO]^+Cl^-\,.\,CH_3OH$	1·991	1·962	133·9	85·5
$[(\pi\text{-}C_5H_5)_2MoNH_2CH_2COO]^+Cl^-\,.\,H_2O$	1·993	1·986	132·2	84·3

Table 10. *π-Cyclopentadienyl planes*

Equation to plane followed by the distances of atoms from the plane.

(i) *Hydrogen dibis-π-cyclopentadienyl-*L*-cysteinatomolybdenum*(IV) *chloride*

(*a*) Cyclopentadienyl ring C(11) ~ C(15)

$$-0\cdot9651x-0\cdot1117y-0\cdot2367z-0\cdot3191=0$$

C(11)	−0·018 Å
C(12)	+0·015
C(13)	−0·006
C(14)	−0·005
C(15)	0·015

(*b*) π-Cyclopentadienyl ring C(21) ~ C(25)

$$0\cdot5412x+0\cdot7640y+0\cdot3513z-6\cdot0512=0$$

C(21)	0·011 Å
C(22)	0·001
C(23)	−0·012
C(24)	0·019
C(25)	−0·019

(*c*) Molybdenum–sulphur–nitrogen plane

$$-0\cdot7960x-0\cdot5106y-0\cdot3252z-3\cdot5560=0$$

(ii) *Hydrogen dibis-π-cyclopentadienyl-*L*-cysteinatomolybdenum*(IV) *hexafluorophosphate*

X, Y and Z refer to the right handed orthogonal axes a^*, b' and c when b' is on the same side of the a^*c plane as b.

(*a*) π-Cyclopentadienyl ring C(11) ~ C(15)

$$0\cdot199X-0\cdot968Y+0\cdot215Z+3\cdot193=0$$

C(11)	−0·019 Å
C(12)	−0·017
C(13)	−0·046
C(14)	−0·057
C(15)	0·048

(*b*) π-Cyclopentadienyl ring C(21) ~ C(25)

$$0\cdot782X-0\cdot435Y+0\cdot323Z-4\cdot487=0$$

C(21)	0·053 Å
C(22)	−0·009
C(23)	−0·078
C(24)	−0·039
C(25)	0·073

(*c*) π-Cyclopentadienyl ring C(31) ~ C(35)

$$0\cdot211X-0\cdot970Y+0\cdot178Z-7\cdot935=0$$

C(31)	0·013 Å
C(32)	−0·004
C(33)	0·024
C(34)	0·019
C(35)	−0·026

Table 10 (*cont.*)

(*d*) π-Cyclopentadienyl ring C(41) ~ C(45)

$$0\cdot799X-0\cdot472Y+0\cdot252Z-10\cdot33=0$$

C(41)	0·069 Å
C(42)	−0·056
C(43)	−0·057
C(44)	0·020
C(45)	0·024

(*e*) Molybdenum–sulphur–nitrogen planes

at Mo(1) $-0\cdot553X+0\cdot793Y+0\cdot219Z+2\cdot901=0$

at Mo(2) $0\cdot487X+0\cdot793Y-0\cdot340Z+6\cdot937=0$

(iii) *Bis-π-cyclopentadienylglycinatomolybdenum*(IV) *chloride hydrate*

X, Y and Z refer to the orthogonal set of axes a, b^* and c.

(*a*) π-Cyclopentadienyl ring C(11) ~ C(15)

$$-0\cdot9217X-0\cdot3461Y+0\cdot1715Z-1\cdot8767=0$$

C(11)	−0·029 Å
C(12)	0·020
C(13)	−0·004
C(14)	−0·012
C(15)	0·026

(*b*) π-Cyclopentadienyl ring C(21) ~ C(25)

$$-0\cdot3317X-0\cdot8566Y+0\cdot3951Z-9\cdot5124=0$$

C(21)	−0·022 Å
C(22)	0·027
C(23)	−0·024
C(24)	0·010
C(25)	0·009

(*c*) Nitrogen–oxygen O(1) plane

$$-0\cdot6828X-0\cdot6376Y+0\cdot3567Z-5\cdot9524=0$$

(iv) *Bis-π-cyclopentadienylsarcosinatomolybdenum*(IV) *chloride methanolate*

(*a*) π-Cyclopentadienyl ring C(11) ~ C(15)

$$-0\cdot8608x-0\cdot3621y+0\cdot3576z-2\cdot1781=0$$

C(11)	−0·004 Å
C(12)	0·002
C(13)	0·001
C(14)	−0·004
C(15)	0·005

(*b*) π-Cyclopentadienyl ring C(21) ~ C(25)

C(21)	0·034 Å
C(22)	−0·024
C(23)	0·005
C(24)	0·016
C(25)	−0·031

(*c*) Molybdenum–oxygen O(1)–nitrogen plane.

$$-0\cdot8427x-0\cdot0553y+0\cdot5355z-2\cdot5252=0.$$

C(13), Mo and C(25) in Fig. 5*d*). It appears that for any $(\pi\text{-}C_5H_5)_2Mo$ group, the carbon atom closest to the postulated mirror plane is nearer (2·27–2·28 Å mean)* to the molybdenum atom than the pair of carbon atoms bonded to it (2·29–2·30 Å mean) and significantly nearer (2·34–2·36 Å mean) than the second pair of carbon atoms. For the cysteine–Cl, glycine–Cl, sarcosine–Cl and others this is equally true if the carbon atom in the mirror plane is towards or away from the other ligands *X* and if the $(\pi\text{-}C_5H_5)_2Mo$ group is eclipsed or staggered (see Tables 5, 8 and 10). The agreement is not so good for the less accurate cysteine–PF_6 structure.

(ii) *The amino-acid ligands*

In each compound the bis-π-cyclopentadienylmolybdenum group is chelated by an amino acid and forms a Mo–N bond. The lengths of these bonds in the three more accurate analyses and in the 2-aminoethanethiol complex (Knox & Prout, 1969*c*) lie in the region 2·21 to 2·26 Å, but for those in the less accurate cysteine PF_6 analysis the corresponding lengths are 2·14 and 2·32 Å. In the Mo(V) complexes $Na_2Mo_2O_4$ $(cysteine)_2.2H_2O$ (Knox & Prout, 1969*a*), $Na_2Mo_2O_4$ $(histidine)_2.H_2O$ (Delbaere & Prout, 1971) and MoO_2 (cysteine ethyl ester) (Drew & Kay, 1971), the Mo–N bond lengths were also in the 2·21–2·26 Å region. The Mo–S bonds in the cysteine complexes (2·446 in cysteine–Cl and 2·45 and 2·48 Å in cysteine–PF_6) are not significantly different from those observed in the molybdenum(V) complexes bis-π-cyclopentadienyl(toluene-3,4-dithiolato)molybdenum (2·434 and 2·431 Å) (Knox & Prout, 1969*b*), bis-π-cyclopentadienyl)molybdenum iron(II)dichloride (Cameron & Prout, 1972*a*), but significantly shorter than the Mo(V)–S bond (2·490 Å) in the oxomolybdenum(V) cysteine complex (Knox & Prout, 1969*c*). The Mo–O bond in glycine–Cl and sarcosine–Cl are identical in length (2·10 and 2·10 Å), and in very good agreement with 2·11 and 2·15 Å Mo–O (oxalato) bonds in the Mo(VI) complex $BaMo_2O_4(C_2O_4)_2(H_2O)_2$ (Cotton & Morehouse, 1965). The *X*–Mo–*X* angles, cysteine–Cl 77·0°, cysteine–PF_6 80 and 78°, glycine–Cl 74·1° and sarcosine–Cl 73·4° are less than those found in the complexes with sulphur or chlorine ligands (Green, Green & Prout, 1972) but comparable to the angle of 75·7° found in $(\pi\text{-}C_5H_5)_2Mo(OH)NH_2CH_3^+$ (Prout, Critchley & Forder, 1972). The bite of the amino-acid ligand chelating through N and O provides the correct bond lengths and angles at the molybdenum without any observable distortion of the ligand. In both cysteine complexes the carboxylate groups are linked by a short hydrogen bond, in cysteine–PF_6 one 2·47 Å long across the pseudo inversion centre and the other in cysteine–Cl, 2·46 Å long across a crystallographic diad axis. These hydrogen bonds are similar to those found in many acid salts (Speakman, 1967; Sime, Speakman & Parthasarathy, 1970; Kroon, Kanters & Peerdeman, 1971). In the cysteine–Cl the hydrogen atom is indicated in the final difference map by two peaks of 0·2 e.Å^{-3} separated by about 1 Å and 0·3 Å above the line joining O(2) and O(2′). In contrast, the other hydrogen atoms in the structure, located at $R=0\cdot042$, had well resolved peaks with heights of 0·3–0·8 e.Å^{-3}. According to the Nakamoto–Margoshes–Rundle curve (Pimentel & McClellan, 1960; Currie, Speakman & Curry, 1967), for O–H···O hydrogen bonds studied by neutron diffraction, O–H bond length increases as the O···O distance decreases, and Hamilton & Ibers (1968) state that for O···O distances less than 2·5 Å the hydrogen atom may be symmetrically located between the oxygen atoms. However, in the case of potassium hydrogen succinate, X-ray diffraction studies (McAdam, 1969) have shown that the electron density of the hydrogen atom in a short O···H···O bond may be considered as two separate maxima, whereas the neutron diffraction studies on the same crystal modification of this compound (Currie & Speakman, 1970) indicated that the proton of the hydrogen atom is located midway between the two oxygen atoms. Kroon *et al.* (1971) found that the electron density of the hydrogen atom in one if the two short O···H···O bonds in potassium hydrogen *meso*-tartrate dihydrate appeared as two well resolved maxima acentric with respect to the O···O axis so that the C–O–H angle is 123° while the C–O···O angle is 129°. In the molybdenum cysteine dimer in cysteine–Cl observed electron density of the hydrogen atom is in accordance with previous observation and may represent a true phenomenon, but the position of the proton remains undetermined.

The bond lengths and interbond angles found for the cysteine ligand in cysteine–Cl are in good agreement with those obtained for $Na_2Mo_2O_4[NH_2CH(CH_2S)COO]\ 5H_2O$ by Knox & Prout (1969*a*) and for L-cysteine by Harding & Long (1968). In one of the two molecules in the asymmetric unit of L-cysteine, the nitrogen and sulphur atoms are *cis* with respect to the C_α–C_β bond and in the other they are *trans*. The former has the same conformation as those in cysteine–Cl and $Na_2Mo_2O_4[NH_2CH(CH_2S)COO]\ 5H_2O$, but the conformation of the cysteine in cysteine–PF_6 differs from these and the second type of molecule in L-cysteine. In cysteine–PF_6 the sulphur and nitrogen atoms are *cis* with respect to the C_α–C_β bond but hydrogen and carboxyl sites on C_α are interchanged relative to those in cysteine in cysteine–Cl (see Figs. 1, 2 and 6). With respect to a hypothetical (2-aminoethanethiolato)molybdenum five-membered chelate ring, the carboxylate group at C_α is axial in cysteine–Cl and $(Na_2Mo_2O_4[NH_2CH(CH_2S)COO].5H_2O)$, and equatorial in cysteine–PF_6. In cysteine–PF_6 the carboxylate groups are far away from the metal, and the metal

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* The average value varies in this range with the number of the examples included and the relative weighting given the accuracy of particular analyses.

atom might reasonably be thought of as in an equilibrium position relative to the C_β–C_α–N plane [Fig. 6(*a*), (*b*)]. The cysteine conformation found in cysteine–Cl brings the carboxylate oxygen atom closer to the molybdenum. The molybdenum atom is, however, coordinately saturated and is repelled away from the oxygen towards the C_β–C_α–N plane [Fig. 6(*c*)]. However, in $Na_2Mo_2O_4[NH_2CH(CH_2S)COO].5H_2O$ the cysteine acts as a tridentate ligand and the molybdenum is attracted towards the carboxylate oxygen atom and away from the C_β–C_α–N plane. In the three complexes there is little apparent strain and distorsion in the skeleton of the ligand measured in terms of the interbond angles. In Fig. 7 the various forms of the cysteine ligand are shown schematically projected down the C_α–C (carboxylate) bond. In one of the cysteine ligands in cysteine–PF_6, in cysteine–Cl and in the *cis* form of free cysteine [Fig. 7(*b*), (*c*) and (*e*)] the amino group is nearly coplanar with the carboxylate. In the other ligand in cysteine–PF_6, in $Na_2Mo_2[NH_2CH(CH_2S)COO]_2.5H_2O$ in the *trans* form of free cysteine [Fig. 7(*a*), (*d*) and (*f*)] the amino group is 30–40° out of the carboxylate plane. For cysteine–PF_6 in Fig. 7(*a*) and (*b*) the O–C–O system is not linear in projection. No significance is attached to this as it results from the inaccuracy of the positions of C(2) and C(5) which are more nearly planar than is chemically reasonable.

In the glycine–Cl the dimensions and dihedral angles [Fig. 8(*a*) and (*b*)] are like those of an α-glycine (Leung & Marsh, 1958) indicating that the dimensions and conformation are not significantly affected upon chelation to molybdenum.

The sarcosine ligand does not appear to have been described except as sarcosine hydrochloride, the structure of which was determined by Bhattacharyya, Mazumdar & Saha (1968). The dimensions of the sarcosine ligand are not significantly different from those of the sarcosine cation in the hydrochloride. The dihedral angles are given for the ligand and the cation in Fig. 8(*c*) and (*d*).

(iii) *Intermolecular hydrogen bonding*

In the cysteine–Cl (Fig. 1) the cysteine dimers are held together by the strong O–H···O hydrogen bonds parallel to the *a* axis. A further strong hydrogen bond exists between N–H(2)···Cl^-, as evidenced by the N···Cl^- distance of 3·23 Å, the H···Cl^- distance of 2·30 Å and the N–H···Cl^- angle of 175°. The other hydrogen atom bonded to nitrogen [H(1)] forms a weak hydrogen bond with the sulphur atom of the molecule in the above unit cell. The N···S $(x, y, z+1)$ distance of 3·63 Å is larger than the range of 3·23–3·52 Å found by Srivinasan & Chacko (1967) for N···S hydrogen bonds, but it is less than the 3·7 Å limit which they estimate for the N–H···S system. The H···S distance is 2·91 Å and the angle N–H···S is 152° (angle H–N···S, 22°). The N···O(1) distance is 2·73 Å, but the H(1)···O(1) distance is 2·35 Å and the N–H···O(1) angle is 110° [angle H–N···O(1), 54°] suggesting that no intermolecular hydrogen bond is formed between these atoms. There is also a close intramolecular contact of 3·25 Å between C(24) and O(1), with H(15)···O(1) at 2·22 Å and the C(24)–H(15)···O(1) angle at 149° [angle H(15)–C(24)···O(1)

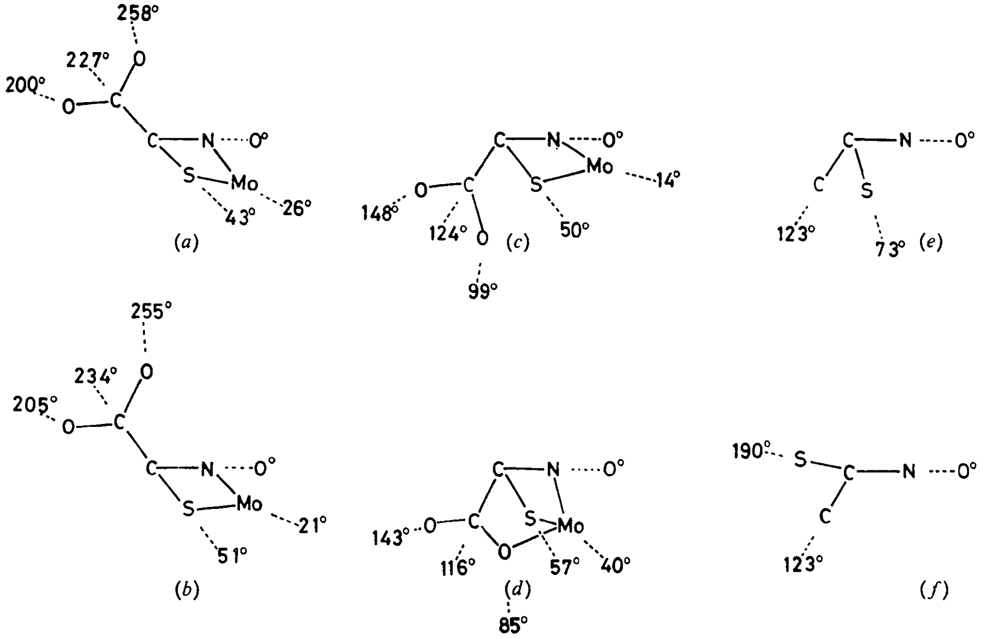

Fig. 6. Schematic views, showing dihedral angles of cysteinato ligand cysteine looking down the C_α–C_β bond: (*a*) and (*b*) hydrogen di(bis-π-cyclopentadienyl)-L-cysteinatomolybdenum (IV) hexafluorophosphate at Mo(1) and Mo(2); (*c*) hydrogendi(bis-π-cyclopentadienyl)-L-cysteinatomolybdenum (IV) chloride; (*d*) di-μ-oxobis(oxocysteinato-molybdenum(V) anion; (*e*) cysteine (*cis* conformer); (*f*) cysteine (*trans* conformer).

is 20°], which is within the range for possible C–H···O hydrogen bonds (Sutor, 1963). The crystal structure may be described in terms of an infinite network of strong hydrogen bonded chains parallel to the *a* axis. These chains are interconnected by weak hydrogen bonds between nitrogen and sulphur atoms forming sheets perpendicular to the *b* axis.

Crystals of cysteine–PF_6 have no intermolecular hydrogen bonds.

In the glycine complex, interatomic distances suggest that there is a strong hydrogen bond between the amino group of the glycine residue and the chloride ion, N···Cl, 3·25 Å, similar to that found in cysteine–Cl, and that the other hydrogen atom bonded to nitrogen forms a possible bifurcated hydrogen bond between two crystallographically equivalent oxygen atoms [Table 2, N···O(2″) 3·11 Å; N···O(2‴) 3·18 Å]. The water molecule forms a strong hydrogen bond to the chloride ion (3·11 Å) and there is a weak interaction (3·21 Å) of the second hydrogen atom of the water with another chloride ion.

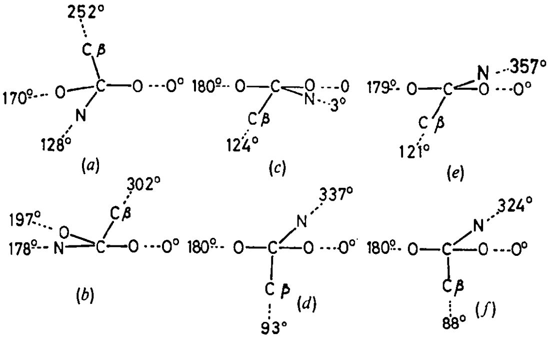

Fig. 7. Schematic views, showing dihedral angles of cysteinato ligands and cysteine looking down the C_α–C(carboxylate) bond: (*a*) and (*b*) hydrogendi(bis-π-cyclopentadienyl)-L-cysteinatomolybdenum(IV) hexafluorophosphate at Mo(1) and Mo(2); (*c*) hydrogendi(bis-π-cyclopentadienyl)-L-cysteinatomolybdenum(IV) chloride; (*d*) di-μ-oxobis(oxocysteinato-molybdenum(V) anion; (*e*) cysteine (*cis* conformer); (*f*) cysteine (*trans* conformer).

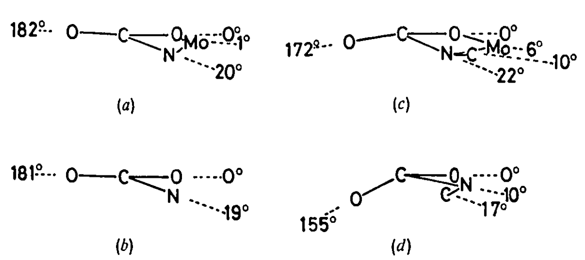

Fig. 8. Schematic views showing dihedral angles of glycine and sarcosine ligands and anions looking down the C_α–C(carboxylate) bond: (*a*) bis-π-cyclopentadienylglycinatomolybdenum(IV) chloride hydrate; (*b*) glycine hydrochloride; (*c*) bis-π-cyclopentadienylsarcosinatomolybdenum(IV) chloride methanolate; (*d*) sarcosine hydrochloride.

The crystal of sarcosine–Cl is built up from chloride anions, complex cations and isolated molecules of methanol of solvation (Fig. 4). The methanol of solvation lies in a cavity in the structure, and is not well defined. The oxygen atom O(3) and the carbon atom C(4) were distinguishable because (*a*) the methanol was located from a difference synthesis where the peak assigned to O(3) was larger than that assigned to C(4), (*b*) refinement with the oxygen and carbon atoms interchanged lead to anomalous temperature factors and (*c*) the 3·05 Å Cl···O(3) contact may correspond to a hydroxyl group–chloride ion hydrogen bond but is too short for a chloride ion–methyl group van der Waals contact. There is a hydrogen bond N···O(2), 2·91 Å, linking into chains complexes related by the two-fold screw axis (Fig. 4).

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References

Bray, R. C. & Meriwether, L. S. (1966). *Nature, Lond.* **212**, 467.

Bhattacharyya, S. C., Mazumdar, S. K. & Saha, N. N. (1967). *Indian J. Phys.* **41**, 850.

Cameron, T. S. & Prout, C. K. (1971). *Chem. Commun.* p. 161.

Cameron, T. S. & Prout, C. K. (1972*a*). *Acta Cryst.* **B28**, 453.

Cameron, T. S. & Prout, C. K. (1972*b*). *J. Chem. Soc.* In the press.

Cotton, F. A. & Morehouse, S. M. (1965). *Inorg. Chem.* **4**, 1377.

Currie, M. & Speakman, J. C. (1970). *J. Chem. Soc.* (*A*), p. 1923.

Currie, M., Speakman, J. C. & Curry, N. A. (1967). *J. Chem. Soc.* (*A*), p. 1862.

Delbaere, L. T. J. & Prout, C. K. (1971). *Chem. Commun.* p. 162.

Drew, M. G. B. & Kay, A. (1971). *J. Chem. Soc.* (*A*), pp. 1846, 1851.

Fewson, C. A. & Nicholas, D. J. D. (1961). *Biochim. Biophys. Acta*, **49**, 335.

Ford, G. (1970). D. Phil. Thesis, Oxford.

Gerloch, M. & Mason, R. (1965). *J. Chem. Soc.* p. 296.

Gore, E. S. & Green M. L. H. (1970). *J. Chem. Soc.* (*A*), p. 2315

Green, J. C., Green, M. C. H. & Prout, C. K. (1972). *Chem. Commun.* p. 421.

Hamilton, W. C. & Ibers, J. A. (1968). *Hydrogen Bonding in Solids*, p. 52. New York: Benjamin.

Handler, P. & Rajagoplan, K. V. (1964). *J. Biol. Chem.* **239**, 2027.

Harding, M. M. & Long, H. A. (1968). *Acta Cryst.* **B24**, 1096.

Huang, T. J. & Haight, G. P. (1969). *Chem. Commun.* p. 985.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–203, 211. Birmingham: Kynoch Press.

KNOX, J. R. & PROUT, C. K. (1969*a*). *Acta Cryst.* B**25**, 1857.
KNOX, J. R. & PROUT, C. K. (1969*b*). *Acta Cryst.* B**25**, 2013.
KNOX, J. R. & PROUT, C. K. (1969*c*). *Acta Cryst.* B**25**, 2482.
KROON, J. KANTERS, J. A. & PEERDEMAN, A. F. (1971). *Nature, Lond.* **229**, 120.
KUTOGLU, A. & KOPF, H. (1970). *J. Organometal. Chem.* **25**, 455.
LEUNG, Y. C. & MARSH, R. E. (1968). *Acta Cryst.* **11**, 17.
MCADAM, A. (1969). Ph. D. Thesis, Glasgow.
NICHOLAS, D. J. D., WILSON, P. W., HEINEN, W., PALMER, G. & BEINERT, H. (1962). *Nature, Lond.* **196**, 433.
PIMENTEL, G. C. & MCCLELLAN, A. L. (1960). *The Hydrogen Bond*, p. 259. San Francisco: Freeman.
PROUT, C. K., CRITCHLEY, S. R. & FORDER, R. A. (1972). Unpublished work.
RAE, A. I. M. & MASLEN, E. N. (1963). *Acta Cryst.* **16**, 703.
ROLLETT, J. S. (1970). In *Crystallographic Computing*, pp. 167–181. Copenhagen: Munksgaard.
SIME, J. G., SPEAKMAN, J. C. & PARTHASARATHY, R. (1970). *J. Chem. Soc.* (*A*), p. 1919.
SPEAKMAN, J. C. (1967). *Chem. Commun.* p. 32.
SRINIVASAN, R. & CHACKO, K. K. (1967). In *Conformation of Biopolymers*. Vol. 2, pp. 607–615. Edited by C. N. RAMACHANDRAN. London & New York: Academic Press
SUTOR, D. J. (1963). *J. Chem. Soc.* p. 1105.
WASER, J. (1963). *Acta Cryst.* **16**, 1091.

Acta Cryst. (1972). B**28**, 3056

The Crystal Structure of $CaKAsO_4.8H_2O$

BY BRIAN DICKENS AND WALTER E. BROWN*

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, *U.S.A.*

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$CaKAsO_4.8H_2O$ crystallizes in the orthorhombic unit cell $a=7{\cdot}146$ (1), $b=11{\cdot}696$ (2), $c=7{\cdot}100$ (2) Å at 25°C with cell contents of 2[$CaKAsO_4.8H_2O$]. The density calculated from the X-ray data is 2·027 g.cm^{-3}; that calculated from the refractive indices is 2·10 g.cm^{-3}. The structure has been refined to $R_w=0{\cdot}037$, $R=0{\cdot}043$ in space group $Cm2m$, using 1023 observed reflections measured on an automated diffractometer and corrected for absorption. Allowance was made for anomalous dispersion and secondary isotropic extinction. All ions in $CaKAsO_4.8H_2O$ are completely hydrated. Ca coordinates to eight water oxygen atoms with Ca···O distances in the range 2·460 (5) to 2·490 (3) Å. K coordinates to eight water oxygen atoms with K···O distances ranging from 2·756 (3) to 2·960 (7) Å. The coordination polyhedron of Ca shares one face of four water molecules and two edges with neighboring coordination polyhedra of K. Each oxygen atom of the AsO_4 ion is the acceptor in hydrogen bonds from four water molecules and forms no bonds with the cations. The two crystallographically different As–O distances in the AsO_4^{3-} ion are 1·682 (4) and 1·684 (4) Å when uncorrected for thermal motion, and 1·690 and 1·692 Å with the riding model correction. The structure of $CaKAsO_4.8H_2O$ is related to that of $MgNH_4PO_4.6H_2O$, struvite. This structural type may be common to several calcium phosphates and related compounds.

Introduction

In crystallization, nucleation is an important step which could conceivably control the identities and forms of materials that grow to macroscopic sizes. For various reasons (Dickens & Brown, 1970), studies of hydrates may give valuable clues to the existence of possible precursors or nuclei of crystallization in aqueous environments. In the formation of inorganic deposits *in vivo*, hydration of ions is likely to play a significant role, and the formation of ion pairs or higher complexes may be important. We found in our study of $CaCO_3.6H_2O$ (Dickens & Brown, 1970) that in the crystal structure, the Ca^{2+} and CO_3^{2-} ions are all in [Ca^{2+}, CO_3^{2-}]° ion pairs which are completely surrounded by water molecules. To examine the hydration of Ca and the possible retention in the solid state of ion complexes involving XO_4 ions, in this case AsO_4^{3-}, we have determined the crystal structure of $CaKAsO_4.8H_2O$.

Data collection and structure refinement

$CaKAsO_4.8H_2O$ was prepared by mixing 20 cm^3 of 0·1 M.l^{-1} $CaCl_2$ solution, 25 cm^3 1·0 M.l^{-1} tripotassium citrate solution and 10 cm^3 3·0 M.l^{-1} KOH solution at 0°C and then adding 10 cm^3 0·2 M.l^{-1} K_2HAsO_4 solution. The resultant mixture was kept at 0°C; precipitation of $CaKAsO_4.8H_2O$ began after about two hours. This procedure is an adaptation of that given for $CaNH_4PO_4.7H_2O$ by Lehr, Brown, Frazier, Smith & Thrasher (1967).

The crystal used in the data collection was a rectangular plate with dimensions 0·06 × 0·10 × 0·12

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* Director, American Dental Association Research Unit at the National Bureau of Standards, Washington, D. C. 20234, U.S.A.