

Molybdenum(vi) Complexes with Malic Acid: their Inter-relationships, and the Crystal Structure of Caesium Bis[(S)-malato(2-)]-cis-dioxomolybdate(vi)-Water (1/1) †

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The complex anions obtainable in salts crystallising from aqueous solutions of molybdate and malic acid (H_3mal) are of the types (i) $[\text{MoO}_2(\text{Hmal})_2]^{2-}$, (ia) $[\text{MoO}_2(\text{mal})_2]^{4-}$, and (ii) $[\text{Mo}_4\text{O}_{11}(\text{mal})_2]^{4-}$. The formation of each type is dependent primarily upon the reactant ratio, $\text{M}^+ : \text{Mo} : \text{H}_3\text{mal}$. With the structure of the type (ii) anion already known, the structure of the (simpler) anion (i) was determined by X-ray analysis of its salt, $\text{Cs}_2[\text{MoO}_2(\text{Hmal})_2] \cdot \text{H}_2\text{O}$. The complex is mononuclear, with each malato-ligand co-ordinated through the deprotonated hydroxy group and the vicinal carboxy group to form a five-membered chelate ring. The second carboxylate group is not co-ordinated, but there is inter-anion H-bonding between the two carboxy functions. The structural features of class (i) and (ii) anions show the importance of ligand characteristics in determining the type of molybdenum-oxygen core which forms. Compositional and i.r. evidence relating to class (ia) indicates it to be derived from (i) through proton replacement.

As a hydroxy-dicarboxylic acid able to provide five- or six-membered chelate rings, malic acid (dianion Hmal; trianion mal) might be expected to produce various types of anion complexes with molybdenum(vi). In principle, both the molybdenum-malate ratio and the pH might influence the type of anion separating within a crystalline salt. A number of early solution studies¹ have suggested that at least five malato-molybdenum(vi) complexes exist in solution. The work of Darmois² was based on optical rotation measurements, and more recently Cadiot and Viostat³ have used a potentiometric method. Darmois' work led to recognition (though with sparsely reported analytical results) of crystalline salts of two different compositional types, viz. with Mo:malate ratios of 1:2 [type (i)] and 2:1 [type (ii)]. Salts of type (i) had probably been obtained earlier by Henderson *et al.*⁴

Using i.r. spectra to identify the crystalline phases we now confirm that (i) and (ii) do represent the two main classes of complexes obtainable in Cs^+ , NH_4^+ , $\text{NH}_2(\text{CH}_3)_2^+$, and $\text{N}(\text{CH}_3)_4^+$ salts. As reference compounds we used the title compound $\text{Cs}_2[\text{MoO}_2(\text{Hmal})_2] \cdot \text{H}_2\text{O}$ [type (i)] and $[\text{NH}_4]_4[\text{Mo}_4\text{O}_{11}(\text{mal})_2] \cdot 6\text{H}_2\text{O}$ [type (ii)]. It has been known since 1968 that the anion in the latter contains an MoOMo-OMoOMo chain with ligand bridges,⁵ but it remained to establish the structure of the class (i) anion. A determination of the structure of the caesium salt, which contains a mononuclear anion complex, provides the basis for the present report.

Formation of complexes of type (i) or (ii) was found to be determined principally by the availability of M^+ , Mo, and H_3mal in the requisite proportions (with M^+ from the reactant base). Any effect of pH variation is unimportant; type (i) crystallises over the pH range 1–5, and type (ii) at 2–6. There was no evidence of any crystalline phase of intermediate composition, although solution studies have suggested the existence of monomalato-complexes in which the ratio Mo:ligand is 1:1.^{6,7} Addition of HCl does not convert (ii) into (i), and so the equilibrium constant for any reaction such as

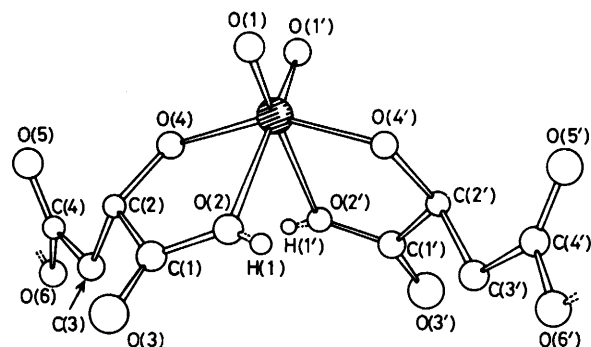
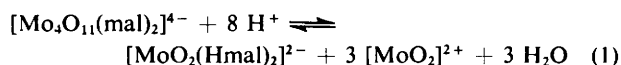


Figure 1. The anion $[\text{MoO}_2(\text{Hmal})_2]^{2-}$ in the salt $\text{Cs}_2[\text{MoO}_2(\text{Hmal})_2] \cdot \text{H}_2\text{O}$

(1), involving release of 'un-co-ordinated' molybdenum must be very small.



The only other class of anion found [type (ia)] was of composition $[\text{MoO}_2(\text{mal})_2]^{4-}$, obtained from solutions containing M^+ , Mo, and malate in the ratio 4:1:2 ($\text{M} = \text{Na}$ or Cs). This composition was also foreshadowed by the work of Darmois.^{2a,b} Compositional and i.r. evidence shows the anion in these salts to be related to type (i), but with replacement of the acidic proton on each ligand. A readily obtainable ammonium salt has the intermediate composition $[\text{NH}_4]_3[\text{MoO}_2\text{H}(\text{mal})_2] \cdot \text{H}_2\text{O}$, which may represent a link between the series (i) and (ia), but the structural role of the single acidic proton in this compound has not been established.

Crystal Structure of $\text{Cs}_2[\text{MoO}_2(\text{Hmal})_2] \cdot \text{H}_2\text{O}$.—The anion complex (Figure 1) comprises two doubly deprotonated malato-ligands co-ordinated with an MoO_2 cis-dioxo core [in which the terminal atoms O(1) and O(1') will be referred to as O₁]. Both ligands are in the S-configuration, corresponding to the use of L-malic acid in the preparation. Co-ordin-

† Supplementary data available (No. SUP 23584, 8 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1983, Issue 3, p. xvii.

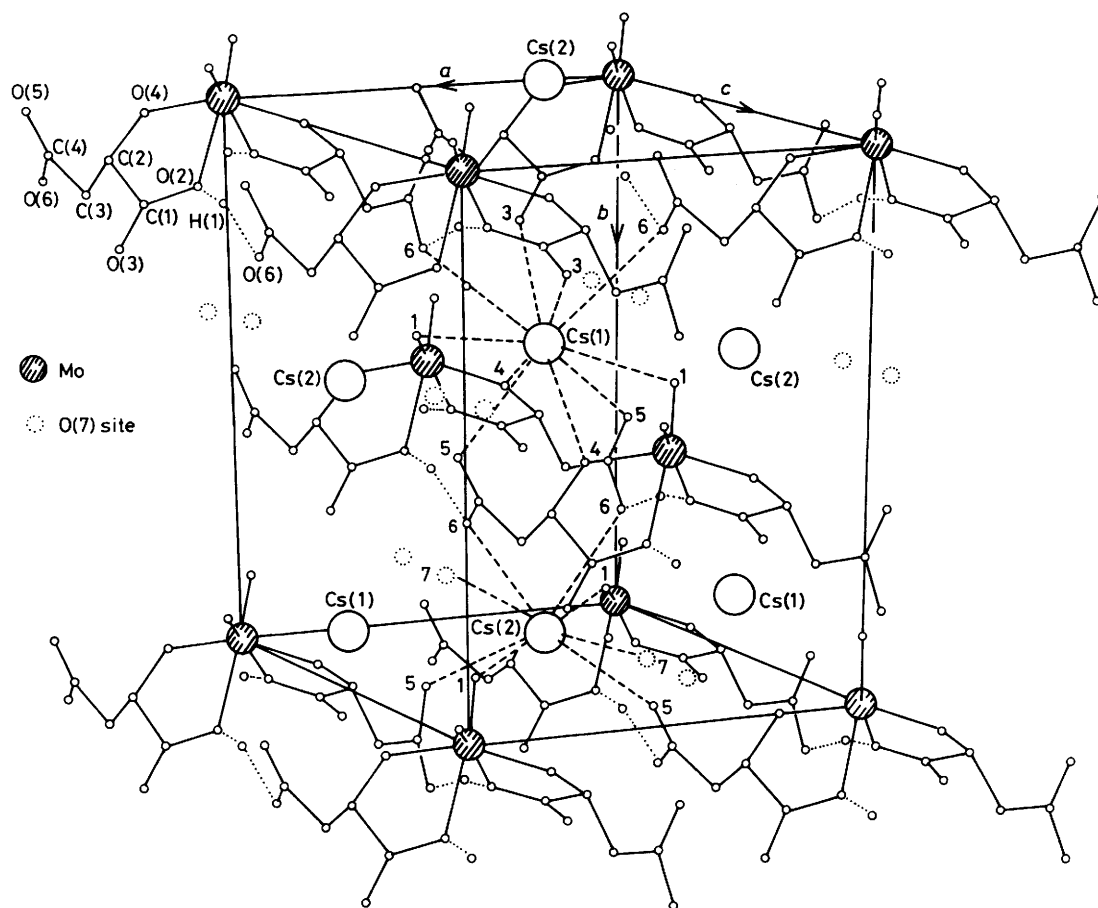


Figure 2. The unit cell of the salt $\text{Cs}_2[\text{MoO}_2(\text{Hmal})_2] \cdot \text{H}_2\text{O}$; dotted lines indicate the $\text{O}(2) \cdots \text{O}(6)$ inter-anion H-bonds which form chains parallel to the c axis; dashed lines from the caesium centres extend to the (numbered) oxygen atoms in their co-ordination spheres; the adjacent pairs of $\text{O}(7)$ sites are alternative positions available to *one* water molecule

ation occurs through $\text{O}(4)$ of the deprotonated hydroxy group and $\text{O}(2)$ of the vicinal carboxy group $\text{C}(1)\text{O}(2)\text{O}(3)$, which thus form a five-membered chelate ring. The second carboxy group $\text{C}(4)\text{O}(5)\text{O}(6)$ is not co-ordinated to molybdenum, but the complete structure (Figure 2) shows that there is a close (2.64 \AA) inter-anion $\text{O}(2) \cdots \text{O}(6)$ approach, indicating H-bonding between these two carboxy functions. While high residual electron density confirmed the presence of a proton, $\text{H}(1)$, in this region, and probably closer to $\text{O}(2)$ than to $\text{O}(6)$, the uncertainty in its peak position does not allow us to say with confidence which of these oxygen atoms remains formally protonated. Each anion complex develops four $\text{O}(2) \cdots \text{O}(6)$ hydrogen bonds which are used in pairs to link adjacent units. In consequence, the anion array consists of infinite chains parallel to the c axis (Figure 2). The Cs^+ ions fall in rows parallel to the b axis; they lie in cavities between the chains, with alternate ions in each of two different environments.

The co-ordination geometry around molybdenum (see Table 1) is consistent with the features usually observed for $[\text{MoO}_2\text{L}_2]$ complexes,^{8,9} where L is a singly deprotonated chelating oxo ligand. The $\text{Mo}-\text{O}$, bond length [$1.70(1) \text{ \AA}$] and the O_iMoO_i angle [$105.0(4)^\circ$] agree, within one e.s.d., with established values.^{10,11} The *trans* lengthening influence of the O_i atoms is in evidence (see later). Within the ligand, the $\text{C}-\text{O}$ bond lengths fall in the usual ranges, and the lengthening of $\text{C}(4)\text{O}(6)$ to 1.31 \AA , due to the $\text{O}(2) \cdots \text{H}(1) \cdots \text{O}(6)$ H-bonding is noteworthy.

All the oxygen atoms in the anion, except the (partially) protonated $\text{O}(2)$ (closest approach 3.93 \AA) can be seen as contributing to a Cs^+ co-ordination sphere (Table 2 and Figure 2). Pairs of $\text{O}(1)$, $\text{O}(3)$, $\text{O}(4)$, and $\text{O}(5)$ all lie within $3.0\text{--}3.3 \text{ \AA}$ of a Cs^+ ion. The atoms $\text{O}(6)$, the charge on which is reduced through the proximity of a proton, lie at greater distances [3.70 \AA from $\text{Cs}(1)$ and 3.45 \AA from $\text{Cs}(2)$]. The atoms $\text{O}(1)$, $\text{O}(5)$, and $\text{O}(6)$ provide bridging between $\text{Cs}(1)$ and $\text{Cs}(2)$. The $\text{Cs}(2)$ co-ordination sphere includes $\text{O}(7)$ of the single solvate water molecule. This single molecule is distributed between two sites, 1.50 \AA apart, related by a two-fold rotation axis, and there is probably additional disorder at each site, as evidenced by a high thermal parameter. However, the $\text{Cs}(2)-\text{O}(7)$ averaged distance, 3.30 \AA , is consistent with an electrostatic interaction.

Complete deprotonation of the hydroxy oxygen atom, $\text{O}(4)$, rather than $\text{O}(2)$ and $\text{O}(6)$ of the more acidic carboxy groups, was not expected. The capacity of molybdenum(vi) to promote proton release from hydroxylic groups is well known;^{8,9} but the association of the remaining acidic proton with the $\text{O}(2) \cdots \text{O}(6)$ pair seems likely to be a consequence of the role of this inter-carboxylate H-bonding in relation to the total crystal structure.

Comparison of Complexes.—For comparison, the structure of the type (ii) complex $[\text{Mo}_2\text{O}_{11}(\text{mal})_2]^{4-}$, as redrawn from the atomic co-ordinates in ref. 5, is shown in Figure 3. Unlike the present type (i) structure, the unusual *R*-configuration

Table 1. Bond lengths (Å) and angles (°) in $\text{Cs}_2[\text{MoO}_2(\text{Hmal})_2]\cdot\text{H}_2\text{O}$, with estimated standard deviations in parentheses

Bond lengths			
Mo-O(1)	1.708(9)	C(4)-O(6)	1.31(2)
Mo-O(2)	2.243(9)	C(1)-C(2)	1.57(2)
Mo-O(4)	1.939(8)	C(2)-C(3)	1.51(2)
C(1)-O(2)	1.28(2)	C(3)-C(4)	1.52(2)
C(1)-O(3)	1.19(2)	O(2)···O(6)	2.64(2)*
C(2)-O(4)	1.41(2)	O(2)-H(1)	1.3(2)
C(4)-O(5)	1.19(2)	O(6)-H(1)	1.5(2)
Bond angles			
O(1)-Mo-O(1')	104.5(6)	C(1)-C(2)-C(3)	108(1)
O(1)-Mo-O(2)	88.2(4)	C(1)-C(2)-O(4)	111(1)
O(1)-Mo-O(2')	164.6(5)	C(2)-C(3)-C(4)	113(1)
O(1)-Mo-O(4)	104.0(4)	C(2)-C(1)-O(2)	113(1)
O(1')-Mo-O(4)	92.9(4)	C(2)-C(1)-O(3)	119(1)
O(2)-Mo-O(2')	80.7(5)	C(3)-C(2)-O(4)	113(1)
O(2)-Mo-O(4)	75.4(3)	C(3)-C(4)-O(5)	124(2)
O(2)-Mo-O(4')	83.6(4)	C(3)-C(4)-O(6)	111(1)
O(4)-Mo-O(4')	152.3(4)	O(2)-C(1)-O(3)	128(2)
C(1)-O(2)-Mo	117.1(8)	O(5)-C(4)-O(6)	125(1)
C(2)-O(4)-Mo	123.4(6)	O(2)-H(1)-O(6)	140(12)

* Inter-anion H-bond.

Table 2. Caesium-oxygen distances (Å) ^a in $\text{Cs}_2[\text{MoO}_2(\text{Hmal})_2]\cdot\text{H}_2\text{O}$

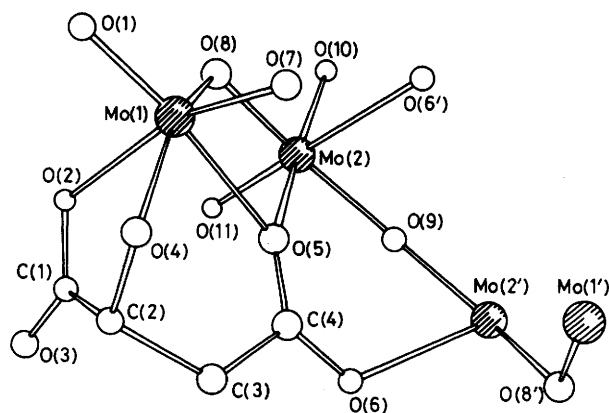
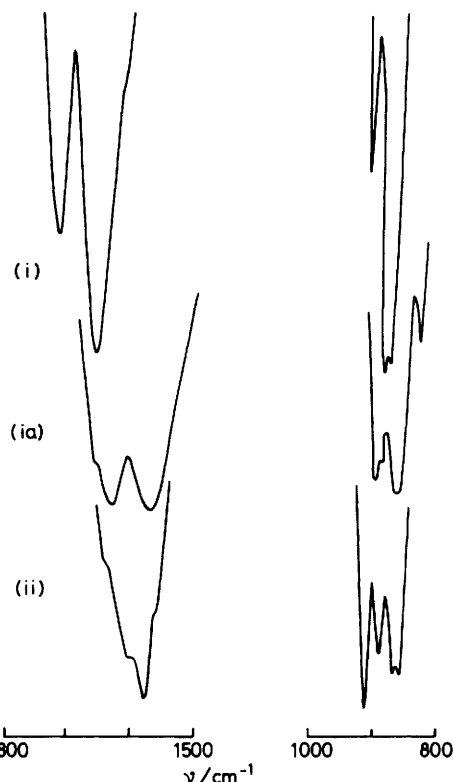
Cs(1)-O(3)	3.03 ^b	Cs(2)-O(5)	3.05 ^b
Cs(1)-O(5)	3.22 ^c	Cs(2)-O(1)	3.10 ^b
Cs(1)-O(4)	3.23 ^c	Cs(2)-O(7)	3.30 ^d
Cs(1)-O(1)	3.31 ^c	Cs(2)-O(6)	3.45 ^c
Cs(1)-O(6)	3.70 ^b	Cs(2)-O(2)	3.93 ^c

^a Distances less than 4.0 Å. ^b Inter-chain pair of oxygen atoms. ^c Intra-chain pair of oxygen atoms. ^d Distance to the disordered water molecule.

of the ligand is involved; but this still permits comparison of the connective features. In both cases the ligand forms a five-membered chelate ring and this must be seen as the primary feature of malate co-ordination. However, with the low ligand: Mo ratio there is now bridging co-ordination by the C(4)O(5)O(6) carboxylate as described in ref. 5. Bridging of the kind associated with the formation of a six-membered ring, as through the atom O(5), is not uncommon,^{9,12} but the O(6)-Mo(2') bond completes a distinctive ring system through carboxyl bridging across the Mo(2)O(9)Mo(2') segment of the chain. The match of the four ligand atoms O(2), O(4), O(5), and O(6) along the core-bridged chain seems specific to the particular ligand structure, and it is this co-ordination of the two malato-ligands, one from each end of the Mo_4O_{11} chain, which must promote development of this particular core.

In the complex anions of both types (i) and (ii) the carboxylate O(2) lies *trans* to an O_i atom, with Mo(1)-O(2) bond lengths 2.24 and 2.21 Å, respectively, but the alkoxy function, O(4), is *cis* to the O_i atoms, with Mo(1)-O(4) bond lengths 1.94 and 2.00 Å in the two compounds. The stronger bonding to O(4) arises presumably because this atom provides the more concentrated anion charge.

The i.r. spectra of the complexes (Figure 4) reflect these structural features and serve immediately to distinguish types (i) and (ii). In the $\nu(\text{Mo}-\text{O}_i)$ region, class (i) gives two narrowly separated strong bands, but class (ii) shows a broad band with four coalescing maxima, as would be expected from the presence of the *cis*-dioxo cores in two different environments

**Figure 3.** The anion $[\text{Mo}_4\text{O}_{11}(\text{mal})_2]^{4-}$, replotted from co-ordinates in ref. 5; one malato-ligand only is shown; its atom numbering corresponds with that in Figure 1; the perspective conceals the angularity (152°) at O(9)**Figure 4.** I.r. spectra of the caesium salts: type (i) $\text{Cs}_2[\text{MoO}_2(\text{Hmal})_2]\cdot\text{H}_2\text{O}$; (ia) $\text{Cs}_4[\text{MoO}_2(\text{mal})_2]\cdot 2.5\text{H}_2\text{O}$; (ii) $\text{Cs}_4[\text{Mo}_4\text{O}_{11}(\text{mal})_2]\cdot 7\text{H}_2\text{O}$

(Figure 3). The $\nu(\text{C}=\text{O})$ bands also differ. The Cs^+ , $\text{N}(\text{CH}_3)_4^+$, and $\text{NH}_2(\text{CH}_3)_2^+$ salts of class (i) show a narrow band at 1720 cm^{-1} attributable to $\nu_{\text{asym}}(\text{C}=\text{O})$ of the C(1)O(2)O(3) group when a large difference¹³ in the C(1)-O(2) and C(1)-O(3) bonds arises, as through linkage of O(2) to both Mo and H. Loss of the proton, as in both (ii) and (ia), displaces this band to lower frequency, so that the carboxylate absorptions fall entirely between 1660 and 1550 cm^{-1} . In the $\nu(\text{Mo}-\text{O}_i)$ region the class (ia) compounds show two strong bands characteristic of a *cis*-dioxo core.

Table 3. Elemental analyses (%) with calculated values in parentheses

Compound	C	H	N	Mo
$[\text{NH}_2(\text{CH}_3)_2]_2[\text{MoO}_2(\text{Hmal})_2]^a$	29.9 (29.8)	5.2 (5.0)	5.8 (5.8)	
$[\text{N}(\text{CH}_3)_4]_2[\text{MoO}_2(\text{Hmal})_2]^a$	35.5 (35.6)	6.1 (5.9)	5.3 (5.2)	17.9 (17.8)
$\text{Cs}_2[\text{MoO}_2(\text{Hmal})_2] \cdot \text{H}_2\text{O}^b$	14.2 (14.2)	1.4 (1.5)		14.1 (14.2)
$[\text{NH}_4]_4[\text{Mo}_4\text{O}_{11}(\text{mal})_2] \cdot 6\text{H}_2\text{O}^c$	10.2 (9.6)	3.4 (3.4)	5.6 (5.6)	
$[\text{N}(\text{CH}_3)_4]_4[\text{Mo}_4\text{O}_{11}(\text{mal})_2] \cdot 6\text{H}_2\text{O}^d$	23.0 (23.5)	4.9 (5.4)	4.6 (4.6)	
$\text{Cs}_4[\text{Mo}_4\text{O}_{11}(\text{mal})_2] \cdot 7\text{H}_2\text{O}^e$	6.8 (6.5)	1.6 (1.35)		26.3 ^f (26.0)
$[\text{NH}_4]_3[\text{MoO}_2\text{H}(\text{mal})_2] \cdot \text{H}_2\text{O}^{d,g}$	21.1 (20.7)	4.8 (4.5)	9.2 (9.1)	20.7 (20.7)
$\text{Cs}_4[\text{MoO}_2(\text{mal})_2] \cdot 2.5\text{H}_2\text{O}^h$	10.0 (9.8)	1.8 (1.15)		<i>i</i>

^a I.r. spectra show this compound to be anhydrous. ^b Water content established by X-ray structure determination. ^c Identity of present compound with that described in ref. 5, of known structure, was established through single-crystal X-ray photography. ^d Water content uncertain, since estimated from C, H analysis. ^e Water corresponding to weight loss (from different samples) under vacuum at 115 °C, 6.8 and 7.0 mol. ^f Caesium, 36.7 (36.0%). ^g It cannot be established whether the compound is identical with the ammonium salt mentioned in ref. 2(a), since no analysis was given. ^h Water corresponding to weight loss under vacuum at 150 °C, 2.4 mol. ⁱ Caesium, by atomic emission 52 ± 2 (55.0%).

The class (ia) anion, with its MoO_2 core, appears only at high pH (6), even though this in itself would be prejudicial to the formation of the parent $[\text{MoO}_2]^{2+}$ species.^{14,15} The appearance of the *cis*-dioxo core under these conditions is to be seen first as a consequence of the co-ordination and stoichiometry imposed by the deprotonated ligand. Then for the crystalline salts, with their high total ionic charges, lattice energy probably plays an important part in determining their stability.

Experimental

Preparations.—Examples of preparations are given. Crystalline compounds of types (i) and (ii) are obtainable by evaporation, but in a few cases, where solubility is high, addition of ethanol is advantageous. Type (ia) compounds are very soluble and crystallise only with difficulty from their highly viscous solutions. Elemental analyses are given in Table 3.

$\text{Cs}_2[\text{MoO}_2(\text{Hmal})_2] \cdot \text{H}_2\text{O}$. Using appropriate proportions, molybdenum trioxide was dissolved in a hot solution of caesium carbonate and L-malic acid. Clear crystals, suitable for X-ray analysis, formed on slow evaporation.

$[\text{N}(\text{CH}_3)_4]_2[\text{Mo}_4\text{O}_{11}(\text{mal})_2] \cdot 6\text{H}_2\text{O}$. Molybdenum trioxide (40 mmol) was dissolved in a hot solution of L-malic acid (20 mmol) and tetramethylammonium hydroxide pentahydrate (40 mmol) in water (18 cm³). After cooling, ethanol was added slowly to give a fine crystalline precipitate. This was washed with 50% ethanol, followed (in usual sequence) by ethanol, ether, and light petroleum.

$\text{Cs}_4[\text{MoO}_2(\text{mal})_2] \cdot 3\text{H}_2\text{O}$. Caesium carbonate (20 mmol), molybdenum trioxide (10 mmol) and L-malic acid (20 mmol) were dissolved in water (ca. 20 cm³), and the solution was allowed to evaporate until it became viscous. Sufficient ethanol was added, with stirring, to produce two layers. Clear crystals slowly separated from the aqueous layer, over several days. Residual mother-liquor was largely removed on filter paper and the hygroscopic crystals were washed quickly with 80% ethanol.

$[\text{NH}_4]_3[\text{MoO}_2\text{H}(\text{mal})_2] \cdot \text{H}_2\text{O}$. Ammonium molybdate (2.85 mmol) and L-malic acid (40 mmol) were dissolved in 5 mol dm⁻³ ammonia (12.6 cm³), to give the 4 : 1 : 2 molar ratio, as for type (ia). The solution (of pH 5.5) was allowed to evaporate

at room temperature to three-quarters volume, but there was loss of ammonia. Ethanol was added until two liquid layers separated. The crystals which formed overnight were dried between filter papers.

X-Ray Structure Determination.—Subject to the assumption, in the first place, that only the *S*-enantiomeric form of the ligand was present, the space group *C*2 was established from systematic absences and the Laue symmetry observed in a set of precession photographs. A prismatic crystal of volume 0.1 mm³ was used for intensity measurements. Intensities were recorded on a Hilger and Watts four-circle diffractometer with Zr-filtered Mo- K_α radiation ($\lambda = 0.7107 \text{ \AA}$) and the θ — 2θ scan technique. 1 578 Reflections were recorded at 298 K in the range $0 < 2\theta < 60^\circ$. Of these 1 019 had $I > 3\sigma(I)$ and were used in the analysis. The detailed procedures for data collection and assignment of errors were as described by Countryman and Penfold.¹⁶ Corrections for absorption and isotropic extinction were applied.

Crystal data. $\text{Cs}_2[\text{MoO}_2(\text{C}_4\text{H}_4\text{O}_5)_2] \cdot \text{H}_2\text{O}$ ($\text{C}_8\text{H}_{10}\text{Cs}_2\text{MoO}_{13}$), Monoclinic, space group *C*2, $M = 675.9$, $a = 9.141(7)$, $b = 13.222(8)$, $c = 7.994(5) \text{ \AA}$, $\beta = 119.1(1)^\circ$, $U = 844.3 \text{ \AA}^3$, $D_m = 2.66(4)$, $Z = 2$, $D_c = 2.66 \text{ g cm}^{-3}$, $\mu(\text{Mo}-K_\alpha) = 47.53 \text{ cm}^{-1}$.

Structure solution and refinement. A Patterson synthesis indicated that all heavy atoms lay in special positions and these were used for initial phasing. Subsequent electron-density syntheses revealed the light atom structure. For the least-squares refinement carbon-bonded H atoms were included at calculated positions (C—H 1.08 Å, H—C—H 109.5°); anisotropic temperature factors were used for Cs and Mo, and isotropic factors for the light atoms. A single temperature factor was assigned to all hydrogen atoms. This reduced *R* to 0.050. The difference map showed the presence of O(7) of the solvate water molecule at approximately half-occupancy in each of the two symmetry-related sites. The remaining (carboxy) hydrogen atom was also revealed at this stage in its inter-anion H-bonding position between O(2) and O(6). Refinement was continued with a half-weight contribution from O(7) at each of its two sites. This gave an unusually high temperature factor for the atom ($U_{11} = 0.14$), indicating further disorder, but this point was not examined

Table 4. Atomic co-ordinates ($\times 10^3$) for $\text{Cs}_2[\text{MoO}_2(\text{Hmal})_2]\cdot\text{H}_2\text{O}$, with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
Mo	500	500	000
Cs(1)	0	892.5(1)	500
Cs(2)	0	430.1(1)	500
O(1)	371(1)	421(1)	-181(2)
O(2)	337(1)	629(1)	-172(2)
O(3)	122(2)	723(2)	-208(3)
O(4)	372(1)	535(1)	126(1)
O(5)	209(2)	559(1)	378(2)
O(6)	307(2)	708(1)	509(2)
O(7)	509(5)	897(4)	913(5)
C(1)	227(2)	660(1)	-129(2)
C(2)	239(2)	606(1)	51(2)
H(2) ^a	127(2)	562(1)	13(2)
C(3)	256(2)	685(1)	195(2)
H(31) ^b	373(2)	724(1)	241(2)
H(32) ^b	154(2)	738(1)	127(2)
C(4)	256(2)	641(1)	371(2)
H(1)	377(20)	651(14)	-309(23)

^a E.s.d. values as for C(2). ^b E.s.d. values as for C(3).

further and refinement was completed with the temperature factor for O(7) fixed at 0.10.

The final R value was 0.0455, with the ligand in the S -enantiomeric form, as was used in the preparation. For the alternative configuration, R was slightly higher at 0.0465.* The function minimised was $\sum w||F_o| - |F_c||^2$ with the weights $w = 1.0/[\sigma^2(F) + 0.00250F^2]$. Scattering factors for Cs, Mo, C, and O were taken from Cromer and Mann,¹⁷ and those of H from Stewart *et al.*;¹⁸ anomalous dispersion corrections were made according to Cromer and Liberman.¹⁹ Atomic co-ordinates are given in Table 4.

* With respect to the enantiomeric form in the type (ii) anion,⁵ it is not stated which isomer of malic acid was used in the preparation, nor whether the ligand configuration in the crystal was tested.

Acknowledgements

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