# Complexation between Molybdenum(VI) and Citrate: Structural Characterisation of a Tetrameric Complex, $K_4[(MoO_2)_4O_3(cit)_2]\cdot6H_2O$†

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The complex anion obtained by crystallisation from an aqueous solution of molybdate and citric acid ($H_3$cit) at pH *ca.* 3 is of the type (i), $[(MoO_2)_4O_3(cit)_2]^{4-}$, as determined by *X*-ray analysis of the salt $K_4[Mo_4O_{11}(cit)_2]\cdot6H_2O$. Principal dimensions [ranges or means; estimated standard deviation (e.s.d.) 0.005 Å] are: Mo=O 1.692—1.734; Mo–O(bridging) 1.886—1.948; Mo–O(hydroxy) 1.972(5); Mo–O(carboxylate) (unidentate) 2.185—2.318, (bridging) 2.296—2.333 Å. The crystals are triclinic, space group $P\bar{1}$, $a$ = 8.966(4), $b$ = 12.319(6), $c$ = 15.962(9) Å, $\alpha$ = 89.34(4), $\beta$ = 99.80(4), $\gamma$ = 107.04(4)°, $R$ = 0.041 for 4 399 observed $[I/\sigma(I) \geqslant 2.0]$ reflections. The complex is tetranuclear with the citrato-ligands co-ordinated through the deprotonated hydroxy group and the α-carboxy group to form five-membered chelate rings. One of the oxygens of the β-carboxylate groups bridges between two Mo atoms [Mo(1)–Mo(2) and Mo(3)–Mo(4)] whereas the other oxygen bridges between these dimers. The other β-carboxylate group is not co-ordinated to molybdenum but is protonated. The i.r. and Raman solid-state spectra are in agreement with this structure as well as a study in solution (Raman, $^1$H and $^{13}$C n.m.r. spectroscopy, molecular weight determination).

Hydroxypolycarboxylic acids might be expected to produce various types of anion complexes with molybdenum(VI). Citric acid (dianion, Hcit; trianion, cit) has been found to form two different compositional types, *viz.* with Mo:cit ratio 2:1 [type (i)] and 1:1 [type (ii)],[1–8] although early solution studies also suggested 7:3[9] and 1:2[10] complexes. These have not been confirmed in recent work. Salts of type (i) were obtained by Williams and co-workers[4] and formulated as $M_2[Mo_2O_5(OH)(H_2O)(cit)]\cdot0.5H_2O$, where M = $K^+$ or $NH_4^+$.

Formation of complexes of type (i) or (ii) is determined principally by the variation of pH: type (i) crystallises over the range pH 2—3, and type (ii) at 4—8.[7,8] Three main points are controversial concerning the molybdenum citrate complexes: (*a*) the composition of the complexes, (*b*) the type of bonding, and (*c*) the degree of aggregation of the central molybdenum part of the complex (mono-, bi-, tetra-meric, or some other form). In this paper, we report the properties of a complex of type (i) in the solid state and in aqueous solutions, as well as the first *X*-ray crystal structure of an oxomolybdenum(VI) citrate complex.

## Experimental

*Preparation and Spectroscopic Characterisation.*—The method used for preparation of $K_4[Mo_4O_{11}(cit)_2]\cdot6H_2O$ was essentially that of Williams and co-workers[4] with modification of the recrystallisation procedure. To obtain single crystals the salt was dissolved in water and ethanol was added dropwise up to the first precipitation. Then the mixture was stored for several days in a refrigerator (Found: C, 11.6; H, 1.9; $H_2O$, 8.3; $K_2O + MoO_3$, 63.5; Mo, 31.2. Calc. for $C_{12}H_{10}K_4Mo_4O_{25}\cdot6H_2O$: C, 12.0; H, 2.0; $H_2O$, 9.0; $K_2O + MoO_3$, 63.5; Mo, 31.9%). I.r. (Nujol): ν(CO) 1 720s, 1 660vs, 1 620vs (sh), 1 595vs, 1 560vs, 1 430s, and 1 410vs ; ν($MoO_2$) 950vs, 920vs, 900vs, 890vs (sh), 870m, 850m, 820m, and 800m; ν(Mo–O–Mo) 740vs (sh), 730vs, br, 690vs (sh), 650vs, and 620vs cm$^{-1}$. Raman: ν($MoO_2$) (solid) 940s, 910w, 880m, 850w, and 820vw; (aqueous solution) 935vs, p, 905w, dp, 897m, p, and 855w, dp cm$^{-1}$. N.m.r. ($D_2O$); $^1$H, δ 4.71(s) and 2.29(br q); $^{13}$C, δ$(CO_2)_\alpha$ 183.4, δ(CO) 84.5, δ($CH_2$) 43.8, and δ($CO_2$) 173.6 and 178.6 p.p.m.

*Analytical Methods.*—Carbon, nitrogen, and hydrogen were determined by organic microanalysis (in the presence of $PbCrO_4$). Molybdenum was determined gravimetrically as $MoO_3$ using the method of Treadwell. The sum of oxides $MoO_3 + K_2O$ was determined gravimetrically after thermal decomposition of the sample. Water was determined by isothermal dehydration at 160 °C as well as by thermogravimetric analysis.

*Physical Measurements.*—I.r., Raman, and n.m.r. ($^1$H and $^{13}$C) spectra were recorded in a routine way. Thermogravimetric (t.g.) and differential thermal analysis (d.t.a.) analyses were performed under argon with a heating rate 5 °C min$^{-1}$ on a Mettler thermoanalyser. Potentiometric titrations were performed with a N-517 digital pH-meter (Mera Elwro, Poland) equipped with a S AgP-201W combined glass and reference electrode. The pH meter was standardised in the usual way.

The degree of association of the molybdenum citrate complex in aqueous solution was determined from the freezing point depression of water using a cryometer (Knauer, West Berlin).

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† Tetrapotassium di-$\mu_3$-citrato(3−)-tri-μ-oxo-tetrakis[dioxomolybdate(VI)] hexahydrate.

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

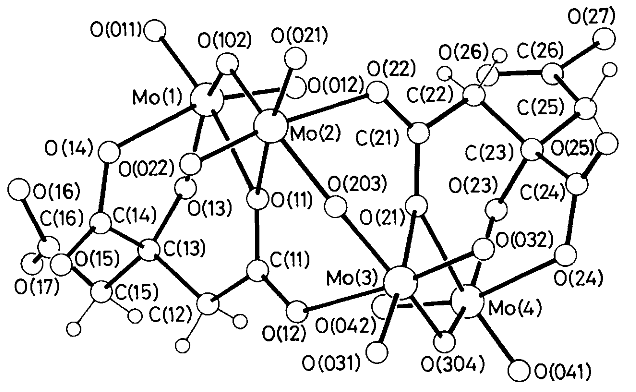

**Figure 1.** View of the $[(MoO_2)_4O_3(cit)_2]^{4-}$ ion showing the atomic numbering

Theoretical curves were calculated from equation (1) based on Debye–Hückel theory, where $\Delta T$ is the freezing point

$$\Delta T = -0.059|z^{+}z^{-}|(\Sigma_i \nu_i z_i^{2})^{\frac{1}{2}} \nu K_f m^{\frac{3}{2}} + \nu K_f m \qquad (1)$$

depression, $z^{+}$ and $z^{-}$ are the charges on the positive and negative ions, respectively, $\nu$ is the number of moles of ions per formula weight of the electrolyte ($\nu = \Sigma_i \nu_i$), $K_f$ is the molal freezing point depression of water, and $m$ is the molal concentration of the solute.

*Crystal Structure Analysis.*—$K_4[(MoO_2)_4O_3(cit)_2]\cdot 6H_2O$, $M$ = 1 202.5, triclinic, space group $P\bar{1}$, $a$ = 8.966(4), $b$ = 12.319(6), $c$ = 15.962(9) Å, $\alpha$ = 89.34(4), $\beta$ = 99.80(4), $\gamma$ = 107.04(4)°, $U$ = 1 660(1) Å$^3$, $D_m$ = 2.35 g cm$^{-3}$, $Z$ = 2, $D_c$ = 2.41 g cm$^{-3}$, Mo-$K_\alpha$ radiation, $\lambda$ = 0.710 69 Å, $\mu$(Mo-$K_\alpha$) = 20.5 cm$^{-1}$, $T$ = 290 K, colourless plates.

Data were collected with a Syntex P2$_1$ four-circle diffractometer in $\omega$—2$\theta$ mode. Maximum 2$\theta$ was 50° with scan range ± 1.1° (2$\theta$) around the $K_{\alpha 1}$—$K_{\alpha 2}$ angles, scan speed 2—29° min$^{-1}$, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections, and showed about a 10% decrease during data collection. The data were rescaled to correct for this. Density was measured by flotation. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($20 < 2\theta < 22°$). Reflections were processed using profile analysis to give 5 872 unique reflections; 4 399 were considered observed [$I/\sigma(I) \geqslant 2.0$] and used in refinement; they were corrected for Lorentz, polarisation, and absorption effects, the last by the Gaussian method; maximum and minimum transmission factors were 0.93 and 0.80. Crystal dimensions were 0.04 × 0.09 × 0.20 mm. No systematic absences. The space group $P\bar{1}$ was assumed and confirmed by successful refinement. Heavy atoms were located by the Patterson interpretation section of SHELXTL and the light atoms then found on successive Fourier syntheses. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were given fixed isotropic thermal parameters, $U$ = 0.07 Å$^2$. Those defined by the molecular geometry were inserted at calculated positions and not refined; some water H atoms were included and refined, but three of the twelve and the protons on carboxylate O atoms O(16) and O(27) could not be located. Final refinement was on $F$ by least-squares methods using 499 parameters. The largest positive and negative peaks on a final Fourier difference synthesis were 0.9 e Å$^{-3}$. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g$ = 0.000 24 was used and shown to be satisfactory by a weight analysis. Final $R$ = 0.041, $R'$ = 0.040. Maximum shift/error in the final cycle 0.4. Computing with SHELXTL PLUS[11] on a DEC Microvax-II computer. Scattering factors in the analytical form and anomalous dispersion factors taken from ref. 12. Final atomic co-ordinates are given in Table 1, selected bond lengths and angles in Tables 2 and 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

## Results and Discussion

*Description of the Structure of* $K_4[(MoO_2)_4O_3(cit)_2]\cdot 6H_2O$.—The *X*-ray structural analysis has confirmed the composition of the complex as $K_4[(MoO_2)_4O_3(cit)_2]\cdot 6H_2O$ and established its structure. Although there have been *X*-ray crystal structure determinations of several hydroxypolycarboxylato-complexes of molybdenum(VI) this is the first citrato complex to be so characterised (apart from a peroxo complex, $K_2[MoO(O_2)_2(Hcit)]\cdot 3H_2O\cdot 0.5H_2O_2$ reported by Griffith and co-workers[13]). Figure 1 shows the structure of the $[(MoO_2)_4O_3(cit)_2]^{4-}$ anion.

Each of the Mo atoms is octahedrally co-ordinated; pairs of octahedra share an edge, and these pairs are linked by one vertex. The two citrate groups are each terdentate, from the central OH and the O atoms of two carboxylate groups. The fourth carboxylate is not co-ordinated. Charge balance, the Mo–O distances, and the C–O distances suggest that only this free carboxylate is protonated (see below).

The Mo–O distances vary systematically. Mo=O is in the range 1.692(5)—1.734(5) Å, with all the shorter distances *trans* to the bidentate carboxylate oxygen atoms [O(11) and O(21)]. The Mo–O–Mo bridging distances range from 1.886(5) to 1.948(5); the longest distances are from the inner Mo atoms to the O atoms bridging to the terminal Mo atoms [Mo(2)–O(102) and Mo(3)–O(304)]. The Mo–O (hydroxy) distances are slightly longer [mean 1.972(5) Å], while those to the carboxylate O atoms are the longest of all, in the overall range 2.185—2.333(5) Å, with the bridging carboxylate O atoms forming the longest links. Overall the pattern of these distances suggests that each Mo atom is tending to achieve a uniform bond valence.[14] Similar anions are present in the ammonium tetramolybdates $[NH_4]_4[(MoO_2)_4O_3(mal)_2]\cdot 6H_2O$[15] and $[NH_4]_4[(MoO_2)_4O_3(mal)_2]\cdot H_2O$[16,17] obtained from malic acid ($H_3$mal) and ammonium molybdate, suggesting that this geometry is particularly favourable for terdentate ligands (or, as in the present case, quadridentate ligands with one free arm).

The conclusion that protonation (required for charge balance) has occurred at O(16) and O(27) (terminal $\beta$-carboxylic group) instead of O(13) and O(23) (hydroxyl group) can be drawn from the observed carbon–oxygen bond distances which are not equivalent (1.327 and 1.210 Å; 1.324 and 1.206 Å) as *e.g.* in $Na(H_2cit)$[18] or $LiNH_4(Hcit)\cdot 2H_2O$.[19] This formulation is supported by i.r. analysis (see below). The deprotonation of the co-ordinated hydroxo group but with the $\beta$-carboxylic group protonated appears unusual. However, co-ordination of $C_6H_6O_7^{2-}$ with loss of only the central carboxylate and the hydroxyl proton was also found in the case of $[MoO(O_2)_2(Hcit)]^{2-}$.[13] This deprotonation of the hydroxo group is likely to occur as part of the condensation process between $[MoO_2(OH)_4]^{2-}$ and $H_3$cit and seems to be typical for complexation of $Mo^{VI}$ with polycarboxylic hydroxy acids (see also ref. 20).

*T.G. and D.T.A. Analyses.*—The thermograms of polycrystalline and single crystal samples show that dehydration takes place in two separate steps. In the first which ends at 114 and 100 °C respectively the weight-loss measurements indicate that

**Table 1.** Atomic co-ordinates ( × $10^4$) of $K_4[(MoO_2)_4O_3(cit)_2]\cdot 6H_2O$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mo(1) | 1 640.5(7) | 3 052.0(5) | 1 801.6(4) |
| Mo(2) | −514.8(7) | 4 412.4(5) | 2 666.9(4) |
| Mo(3) | 2 148.9(7) | 7 114.0(5) | 3 603.5(4) |
| Mo(4) | 5 351.7(7) | 7 813.8(5) | 2 629.3(4) |
| K(1) | 0 | 5 000 | 5 000 |
| K(2) | 5 449(2) | 5 382(1) | 1 314(1) |
| K(3) | 0 | 0 | 0 |
| K(4) | 324(2) | −181(1) | 2 290(1) |
| K(5) | 9 020(2) | 1 351(2) | 4 202(1) |
| O(11) | 2 093(5) | 4 437(3) | 2 876(3) |
| O(12) | 3 319(6) | 5 700(4) | 3 947(3) |
| O(13) | 3 788(5) | 3 128(4) | 2 403(3) |
| O(14) | 1 235(5) | 2 071(4) | 2 934(3) |
| O(15) | 2 358(6) | 2 084(4) | 4 296(3) |
| O(16) | 3 771(6) | 732(4) | 2 918(3) |
| O(17) | 6 379(7) | 1 176(5) | 3 090(4) |
| O(21) | 2 696(5) | 6 686(4) | 2 304(3) |
| O(22) | 416(5) | 5 557(4) | 1 591(3) |
| O(23) | 4 993(5) | 7 581(4) | 1 385(3) |
| O(24) | 4 089(6) | 9 028(4) | 2 091(3) |
| O(25) | 2 221(6) | 9 156(4) | 1 017(3) |
| O(26) | 4 640(6) | 6 492(4) | −339(3) |
| O(27) | 4 871(7) | 7 878(5) | −1 255(3) |
| O(011) | 1 080(6) | 1 847(4) | 1 179(3) |
| O(012) | 2 393(5) | 4 115(4) | 1 132(3) |
| O(102) | −312(5) | 3 298(4) | 1 876(3) |
| O(021) | −2 353(5) | 4 467(4) | 2 243(3) |
| O(022) | −785(6) | 3 582(4) | 3 523(3) |
| O(203) | 359(5) | 5 823(4) | 3 303(3) |
| O(031) | 2 112(6) | 7 283(4) | 4 650(3) |
| O(032) | 1 363(6) | 8 114(4) | 3 125(3) |
| O(304) | 4 363(5) | 7 906(4) | 3 573(3) |
| O(041) | 7 093(6) | 8 856(4) | 2 871(3) |
| O(042) | 5 877(6) | 6 592(4) | 2 805(3) |
| C(11) | 3 201(8) | 4 846(6) | 3 515(4) |
| C(12) | 4 435(8) | 4 241(6) | 3 741(4) |
| C(13) | 3 988(8) | 3 040(5) | 3 302(4) |
| C(14) | 2 447(8) | 2 327(5) | 3 559(4) |
| C(15) | 5 316(8) | 2 516(6) | 3 610(5) |
| C(16) | 5 202(10) | 1 430(6) | 3 180(5) |
| C(21) | 1 725(8) | 6 294(6) | 1 606(4) |
| C(22) | 2 210(8) | 6 740(6) | 769(4) |
| C(23) | 3 668(8) | 7 809(6) | 872(4) |
| C(24) | 3 260(9) | 8 751(6) | 1 333(4) |
| C(25) | 4 085(9) | 8 227(6) | 16(4) |
| C(26) | 4 549(9) | 7 423(7) | −526(5) |
| O(001) | 8 024(7) | 6 233(6) | 607(4) |
| O(002) | −2 140(10) | 734(7) | 1 685(5) |
| O(003) | 1 800(11) | 3 526(9) | 5 548(6) |
| O(004) | 1 747(8) | 1 526(6) | −981(4) |
| O(005) | 3 628(12) | 287(8) | 5 211(6) |
| O(006) | 9 738(14) | 530(8) | 5 861(5) |

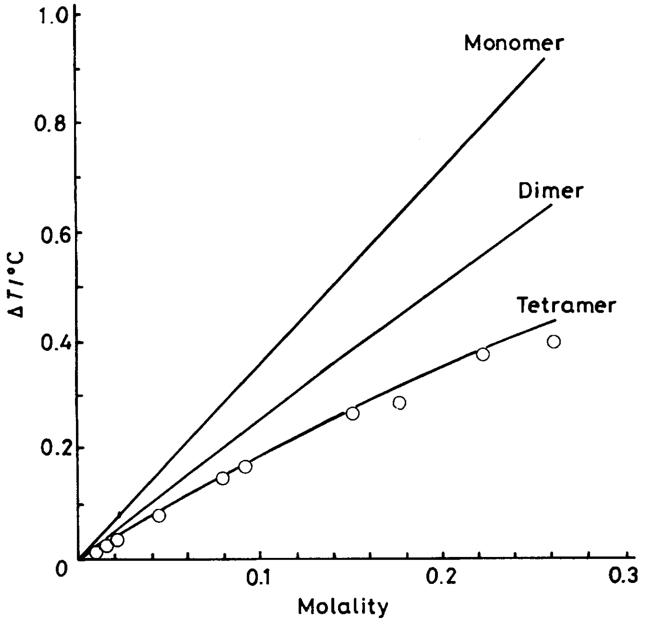

**Figure 2.** Freezing point depressions of solutions of $K_4[(MoO_2)_4O_3(cit)_2]$. The concentrations are based on the molecular weight of the monomer. The solid curves are theoretical curves based on the degrees of association indicated to the right [see equation (1)]

$4H_2O$ per mol of the complex are liberated. In the next step at 164 and 150 °C respectively the two strongly bonded water molecules are lost. At higher temperatures decomposition of the organic moiety occurs.

The crystal contains six molecules of water in the asymmetric unit. Four of these are co-ordinated to one $K^+$ ion, but the other two are multidentate, to two and three $K^+$ ions. This water co-ordination clearly correlates with the dehydration evidence. Three of the $K^+$ ions are eight-co-ordinate (approximately square antiprismatic), while K(3) and K(4) are respectively six-(octahedral) and nine-(tricapped trigonal prismatic) co-ordinate. The crystals contain numerous hydrogen bonds including two from the presumed carboxylate O–H atoms to co-ordinated O atoms in adjacent molecules.

*Molecular Weight Determination and Titrations.*—Comparison of experimental data points with calculated curves presented in Figure 2 clearly indicates that in aqueous solution the complex should be interpreted in terms of the tetramer found in the solid state.

Titration data with standardised sodium hydroxide revealed ten acidic protons per mol of tetramer. The loss of protons occurs in two steps with molar ratio 4:6, which suggests the reactions (2) and (3).

$$[(MoO_2)_4O_3(cit)_2]^{4-} + 4OH^- + 5H_2O \longrightarrow 2[MoO_2(OH)_4]^{2-} + 2[MoO_4(cit)H_3]^{2-} \quad (2)$$

$$[MoO_4(cit)H_3]^{2-} + 3OH^- \longrightarrow MoO_4{}^{2-} + cit^{3-} + 3H_2O \quad (3)$$

*Spectroscopic Characterisation.*—The i.r. and Raman spectra of the complex reflect its structural features as found by *X*-ray analysis. In the region between 1 800 and 1 400 $cm^{-1}$ we find clear evidence of the presence of a non-bonded and undissociated carboxylic group at 1 720 $cm^{-1}$.[21] The bands between 1 660 and 1 540 and between 1 440 and 1 390 $cm^{-1}$ corresponding to $\nu_{asym}$- and $\nu_{sym}$-($CO_2M$) (bound carboxyl group), respectively, are in accord with a chelate ring and bridging by the citrato ligand.[22,23]

In the region between 1 000 and 600 $cm^{-1}$ the complex shows several bands (eight i.r. and five Raman) which might result from the presence of *cis*-dioxo cores in five different environments. The low-frequency symmetric $MO_2$ stretching may be explained by intramolecular hydrogen bonding.[24]

The very strong i.r. band (with shoulders) at 730 $cm^{-1}$ can be assigned to $\nu_{asym}$ of two non-linear Mo–$O_b$–Mo bridges;[25]

**Table 2.** Selected bond lengths (Å)

| | | | |
|---|---|---|---|
| Mo(1)–O(11) | 2.333(5) | Mo(1)–O(13) | 1.976(5) |
| Mo(1)–O(14) | 2.185(5) | Mo(1)–O(011) | 1.695(5) |
| Mo(1)–O(012) | 1.734(5) | Mo(1)–O(102) | 1.886(5) |
| Mo(2)–O(22) | 2.318(5) | Mo(2)–O(11) | 2.296(5) |
| Mo(2)–O(021) | 1.692(5) | Mo(2)–O(102) | 1.942(5) |
| Mo(2)–O(203) | 1.907(4) | Mo(2)–O(022) | 1.705(5) |
| Mo(3)–O(12) | 2.300(5) | Mo(3)–O(21) | 2.312(5) |
| Mo(3)–O(203) | 1.896(4) | Mo(3)–O(031) | 1.693(5) |
| Mo(3)–O(032) | 1.703(6) | Mo(3)–O(304) | 1.948(4) |
| Mo(4)–O(23) | 1.968(5) | Mo(4)–O(21) | 2.351(4) |
| Mo(4)–O(304) | 1.894(5) | Mo(4)–O(24) | 2.211(5) |
| Mo(4)–O(042) | 1.711(6) | Mo(4)–O(041) | 1.693(4) |
| K(1)–O(203) | 2.918(5) | K(1)–O(022) | 2.814(5) |
| K(1)–O(003) | 2.805(12) | K(1)–O(031) | 3.002(5) |
| K(2)–O(23) | 2.862(6) | K(2)–O(13) | 3.360(5) |
| K(2)–O(012) | 2.695(5) | K(2)–O(26) | 3.034(6) |
| K(2)–O(001) | 2.673(7) | K(2)–O(042) | 2.733(5) |
| K(2)–O(26A) | 2.773(6) | K(2)–O(02A) | 2.761(6) |
| K(3)–O(004) | 2.736(7) | K(3)–O(011) | 2.800(5) |
| K(3)–O(25A) | 2.785(6) | K(4)–O(16) | 2.960(5) |
| K(4)–O(14) | 2.805(5) | K(4)–O(002) | 2.791(10) |
| K(4)–O(011) | 3.026(5) | K(4)–O(25A) | 3.117(7) |
| K(4)–O(03C) | 2.778(6) | K(4)–O(04A) | 3.088(6) |
| K(4)–O(00B) | 2.742(6) | K(4)–O(00D) | 2.985(9) |
| K(5)–O(17) | 2.661(6) | K(5)–O(006) | 2.862(9) |
| K(5)–O(15A) | 2.840(6) | K(5)–O(14A) | 3.021(6) |
| K(5)–O(03B) | 2.987(6) | K(5)–O(02B) | 2.911(5) |
| K(5)–O(00C) | 2.914(10) | K(5)–O(00E) | 2.859(13) |
| O(11)–C(11) | 1.286(7) | O(12)–C(11) | 1.234(9) |
| O(13)–C(13) | 1.422(8) | O(14)–C(14) | 1.310(7) |
| O(17)–C(16) | 1.215(12) | O(15)–C(14) | 1.221(8) |
| O(22)–C(21) | 1.253(7) | O(16)–C(16) | 1.319(8) |
| O(24)–C(24) | 1.299(8) | O(21)–C(21) | 1.292(7) |
| O(26)–C(26) | 1.204(10) | O(23)–C(23) | 1.421(9) |
| O(27)–C(26) | 1.324(9) | O(25)–C(24) | 1.216(10) |
| C(11)–C(12) | 1.500(11) | C(12)–C(13) | 1.556(9) |
| C(13)–C(14) | 1.524(9) | C(13)–C(15) | 1.524(11) |
| C(21)–C(22) | 1.522(9) | C(15)–C(16) | 1.480(11) |
| C(23)–C(24) | 1.544(11) | C(22)–C(23) | 1.546(9) |
| C(25)–C(26) | 1.512(12) | C(23)–C(25) | 1.523(10) |

**Table 3.** Selected bond angles (°)

| | | | |
|---|---|---|---|
| O(11)–Mo(1)–O(13) | 77.4(2) | O(12)–Mo(3)–O(21) | 78.4(2) |
| O(11)–Mo(1)–O(14) | 76.3(2) | O(12)–Mo(3)–O(203) | 80.4(2) |
| O(11)–Mo(1)–O(011) | 166.8(2) | O(12)–Mo(3)–O(031) | 88.4(2) |
| O(11)–Mo(1)–O(012) | 89.1(2) | O(12)–Mo(3)–O(032) | 167.0(2) |
| O(11)–Mo(1)–O(102) | 72.0(2) | O(12)–Mo(3)–O(304) | 78.4(2) |
| O(13)–Mo(1)–O(14) | 75.7(2) | O(21)–Mo(3)–O(203) | 82.9(2) |
| O(13)–Mo(1)–O(011) | 104.2(2) | O(21)–Mo(3)–O(031) | 165.7(2) |
| O(13)–Mo(1)–O(012) | 91.8(2) | O(21)–Mo(3)–O(032) | 88.7(2) |
| O(13)–Mo(1)–O(102) | 146.3(2) | O(21)–Mo(3)–O(304) | 71.8(2) |
| O(14)–Mo(1)–O(011) | 91.2(2) | O(203)–Mo(3)–O(031) | 100.3(2) |
| O(14)–Mo(1)–O(012) | 162.4(2) | O(203)–Mo(3)–O(032) | 98.4(2) |
| O(14)–Mo(1)–O(102) | 83.8(2) | O(203)–Mo(3)–O(304) | 149.7(2) |
| O(011)–Mo(1)–O(012) | 103.9(2) | O(031)–Mo(3)–O(032) | 104.5(3) |
| O(011)–Mo(1)–O(102) | 102.6(2) | O(031)–Mo(3)–O(304) | 100.5(2) |
| O(012)–Mo(1)–O(102) | 101.2(2) | O(032)–Mo(3)–O(304) | 97.5(2) |
| | | | |
| O(11)–Mo(2)–O(22) | 78.7(2) | O(21)–Mo(4)–O(23) | 76.7(2) |
| O(11)–Mo(2)–O(102) | 71.9(2) | O(21)–Mo(4)–O(24) | 76.6(2) |
| O(11)–Mo(2)–O(021) | 164.6(2) | O(21)–Mo(4)–O(304) | 71.7(2) |
| O(11)–Mo(2)–O(022) | 89.6(2) | O(21)–Mo(4)–O(041) | 167.8(2) |
| O(11)–Mo(2)–O(203) | 82.3(2) | O(21)–Mo(4)–O(042) | 88.2(2) |
| O(22)–Mo(2)–O(102) | 78.7(2) | O(23)–Mo(4)–O(24) | 73.6(2) |
| O(22)–Mo(2)–O(021) | 87.9(2) | O(23)–Mo(4)–O(304) | 144.4(2) |
| O(22)–Mo(2)–O(022) | 167.7(2) | O(23)–Mo(4)–O(041) | 105.1(2) |
| O(22)–Mo(2)–O(203) | 81.2(2) | O(23)–Mo(4)–O(042) | 92.9(2) |
| O(102)–Mo(2)–O(021) | 99.2(2) | O(24)–Mo(4)–O(304) | 83.2(2) |
| O(102)–Mo(2)–O(022) | 98.9(2) | O(24)–Mo(4)–O(041) | 92.2(2) |
| O(102)–Mo(2)–O(203) | 149.9(2) | O(24)–Mo(4)–O(042) | 161.6(2) |
| O(021)–Mo(2)–O(022) | 104.4(2) | O(304)–Mo(4)–O(041) | 102.5(2) |
| O(021)–Mo(2)–O(203) | 102.1(2) | O(304)–Mo(4)–O(042) | 102.1(2) |
| O(022)–Mo(2)–O(203) | 96.2(2) | O(041)–Mo(4)–O(042) | 103.7(2) |
| | | Mo(2)–O(203)–Mo(3) | 146.5(3) |

the strong band at 620 cm$^{-1}$, also Raman active, probably corresponds to $\nu_{sym}$.[23] The strong i.r. band at 650 cm$^{-1}$ may be assigned to $\nu_{asym}$ of the more linear Mo–O$_b$–Mo group.

The profiles of the Raman spectra of the solid and concentrated aqueous solution (*ca.* 0.8 mol dm$^{-3}$) are very similar, which suggests that there is no structural change from solid to solution.

In the n.m.r. spectra the methylene protons of citric acid give rise to an AB quartet which shifts with pH.[26,27] Complexation with molybdenum(VI) leads to an asymmetric, partially superimposed AB signal (CH$_2$ environments are not equivalent). The large low shift of the $^{13}$C resonance (in comparison with citric acid) of the alcoholic (about 11 p.p.m.) and α-carboxylic (about 7 p.p.m.) groups shows clearly that the citric acid is co-ordinated through these two groups. Two main signals were obtained in the β-carboxylic region (173.6 and 178.6 p.p.m.), indicating that one of the two β-carboxyl groups bonds to molybdenum (shift about 5 p.p.m.) whereas the other does not participate in co-ordination. All these findings are in agreement with the view that the tetrameric structure of the anion is retained in aqueous solution.

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