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Bidentate citrate with free terminal carboxyl groups, syntheses and characterization of citrato oxomolybdate(VI) and oxotungstate(VI), Δ/Λ-$Na_2[MO_2(H_2cit)_2]\cdot 3H_2O$ (M = Mo or W)

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The first example of monomeric bidentate citrato oxomolybdate(VI) and -tungstate(VI) have been prepared by cleavage of dimeric citrato molybdate and tungstate.

The FeMo-cofactor in nitrogenase, where dinitrogen is bound and transformed, is a $MoFe_7S_9$ cluster, and homocitrate is an integral part in the coordination sphere of molybdenum through vicinal carboxylate and alkoxide.[1] Alternatively polycarboxylic acid (*i.e.*, $MoFe_7S_9$: citrate) results in low nitrogen fixing ability, but is able to reduce C_2H_2 to C_2H_4.[2] It has been suggested that a possible function of the tricarboxylic acid in the biosynthesis of the cofactor of nitrogenase is to mobilize molybdenum from the appropriate storage enzyme. Molybdenum is believed to be taken up by organisms as MoO_4^{2-}, this would be essential for the assembly of the final cofactor cluster from an oxomolybdenum–homocitrate precursor.[3] While the precise role of homocitrate is poorly understood, the discovery and elucidation of the interactions between molybdenum and the tricarboxylic acid are of great importance.[4] Moreover, high valent molybdenum oxotransferases are enzymes that catalyze oxygen atom transfer from a substrate. In order to understand the chemistry and oxo-transfer properties of these enzymes, numerous dioxo-Mo(VI) complexes having a wide range of ligands have been prepared and structurally characterised.[5] Although a few molybdenum and tungsten complexes of citrate are known,[6,7] none of these meets the requirements for a satisfactory structural model, since they are binuclear or tetranuclear complexes and contain the citrate in a tridentate mode. Here we report closer structural models of the mononuclear precursors: $Na_2[MO_2(H_2cit)_2]\cdot 3H_2O$ (M = Mo **3** or W **4**) prepared from the cleavages of dimeric tridentate citrato molybdate(VI) and tungstate, which contain the correctly coordinated carboxylate–alkoxide moiety.

Dimeric citrato complexes $Na_4[Mo_2O_5(cit)_2]\cdot 4H_2O$ **1** and $Na_4[W_2O_5(cit)_2]\cdot 8H_2O$ **2** were prepared from the reactions of sodium molybdate or tungstate with citric acid (H_4cit) as described previously.[8] When **1** (4.8 g, 5 mmol) was added with an excess of citric acid (2.5 g, 12 mmol) and the solution heated at 60 °C for 4 h, $Na_2[MoO_2(H_2cit)_2]\cdot 3H_2O$ **3**† was obtained in 43% yield (2.6 g). Similarly, when **2** was reacted with an excess of citric acid, a 35% yield of $Na_2[WO_2(H_2cit)_2]\cdot 3H_2O$ **4**† was separated. Both complexes were characterised by single X-ray structure determination and were shown to be isomorphous.‡

Direct cleavage of dinuclear citrato complexes with excess citric acid results in the preparation of the title complexes, in which the pH values remain in the range of 3.5.[8] The crystal structures of **3** and **4** comprise discrete sodium cations, water molecules and dihydrocitrato dioxo molybdate or tungstate anions. Fig. 1 and Fig. 2 show plots of the anion structures of **3** and **4** respectively, which show one of the stereoisomers (Δ configuration) of each complex. Selected bond parameters are given in the captions. Both molybdenum and tungsten atoms are quasi-octahedrally coordinated by two *cis*-oxo groups and two citrate ligands. Each citrate ion acts as a bidentate ligand *via* its alkoxy and α-carboxyl groups, while the other two β-carboxylic acid groups remain uncomplexed. Bidentate coordination of citrate through its alkoxy and α-carboxyl group is rare. Complex $Na_2[MoO_2(H_2cit)_2]\cdot 3H_2O$ **3** represents the first example of a structurally characterised monomeric oxomolybdenum–citrate complex, which exhibits the bidentate coordination mode of the tricarboxylic acid to molybdenum. Such is the case in the related dinuclear citrato vanadate $K_2[VO_2(H_2cit)]_2\cdot 4H_2O$,[9] in which the citrate ligand is bidentate. There are two enantiomers of the two complexes, which results from the asymmetric octahedral coordination environment around molybdenum or tungsten. This is similar to that of FeMo-co, in

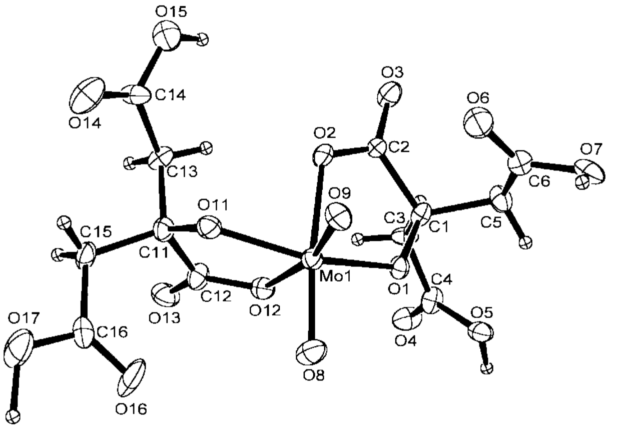

Fig. 1 Perspective view of the anion structure of $Na_2[MoO_2(H_2cit)_2]\cdot 3H_2O$ **3**, showing the 50% thermal ellipsoids. Bond lengths: Mo(1)–O(1) 1.953(6), Mo(1)–O(2) 2.190(7), Mo(1)–O(11) 1.960(7), Mo(1)–O(12) 2.247(6), Mo(1)–O(8) 1.703(8), Mo(1)–O(9) 1.704(6) Å. Bond angles: O(1)–Mo(1)–O(2) 75.1(3), O(11)–Mo(1)–O(12) 74.2(2), O(8)–Mo(1)–O(9) 103.3(3)°.

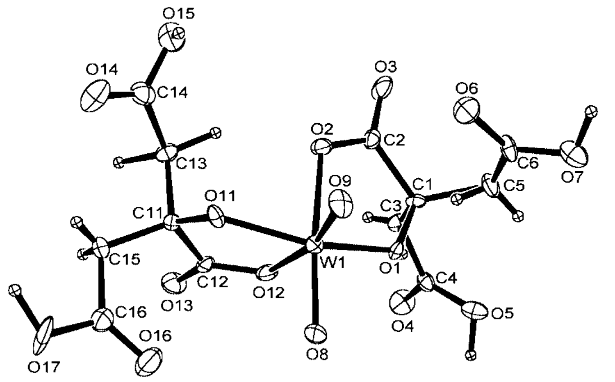

Fig. 2 Perspective view of the anion structure of $Na_2[WO_2(H_2cit)_2]\cdot 3H_2O$ **4**, showing the 50% thermal ellipsoids. Bond lengths: W(1)–O(1) 1.945(6), W(1)–O(2) 2.189(8), W(1)–O(11) 1.968(7), W(1)–O(12) 2.227(7), W(1)–O(8) 1.733(8), W(1)–O(9) 1.727(8) Å. Bond angles: O(1)–W(1)–O(2) 74.9(3), O(11)–W(1)–O(12) 74.3(3), O(8)–W(1)–O(9) 102.4(4)°.

which the octahedral coordination geometry for Mo is typically asymmetric.

As shown in the Figure captions, the Mo–O and W–O distances in citrato molybdate **3** and tungstate **4** vary systematically. M=O bonds are 1.703(8) and 1.704(6) Å for Mo and 1.727(8) and 1.733(8) Å for W, indicating that they are double bonds. The resulting O=M=O angles, 103.3(3) and 102.4(4)° for **3** and **4**, respectively are considerably larger than the 90° regular octahedron value for *cis* groups. This is expected from the greater O···O repulsions between oxygens with short bonds to the metal atom. The Mo–O and W–O (alkoxy) bonds are slightly longer [1.953(6) and 1.960(7) Å for Mo and 1.945(6) and 1.968(7) Å for W], indicating the deprotonation of the hydroxyl group in the citrate anion, and those to the α-carboxyl are longer [2.190(7) and 2.247(6) Å for Mo and 2.189(8) and 2.227(7) Å for W]. This is compatible with the Mo–O (alkoxy) [1.996 and 2.035 Å] and Mo–O (α-carboxyl) bonds [2.167 and 2.206 Å] of coordinated homocitrate ligand in MoFe protein and its putative transition-state complex.[10] Therefore, compound **3** may be relevant to the assembly of NifV FeMo-co, in which molybdenum is coordinated by the citrate ion.

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Notes and references

† Selected spectroscopic data. For **3**. IR (KBr); ν_{as}(CO) 1733s, 1671s, 1636s, 1596s, ν_s(CO) 1406s, 1391s, 1360s, ν(MoO) 927s, 912s. δ_H (500 MHz, D_2O): 3.01 (d, 4H, *J* 14.1 Hz, CH_2), 2.98 (d, 4H, *J* 14.3 Hz, CH_2); δ_C (75 MHz, D_2O): 183.7 $(CO_2)_\alpha$, 174.0 $(CO_2)_\beta$, 85.8 (≡C–O); 43.5 (=CH_2). For **4**. IR (KBr); ν_{as}(CO) 1734s, 1671s, 1631s, 1607s, ν_s(CO) 1398s, 1391s, 1362s, ν(MoO) 914s, 904s. δ_H (500 MHz, D_2O): 3.01 (d, 4H, *J* 15.8 Hz, CH_2), 2.84 (d, 4H, *J* 15.8 Hz, CH_2); δ_C (75 MHz, D_2O): 184.5 $(CO_2)_\alpha$, 174.0, 173.9 $(CO_2)_\beta$, 85.7 (≡C–O); 43.5, 43.2 (=CH_2).

‡ Crystal data: for **3**: colorless crystal, $Na_2[MoO_2(H_2cit)_2]\cdot 3H_2O$, $C_{12}H_{18}O_{19}Mo_1Na_2$, $M = 608.19$, monoclinic, space group $P2_1/n$, $a = 7.6326(8)$, $b = 18.351(1)$, $c = 14.913(2)$ Å, $\beta = 103.15(1)°$, $V = 2031.5(7)$ Å^3, $Z = 4$, $D_c = 1.99$ g cm^{-3}, $F(000) = 1224$. Crystal dimensions: 0.05 × 0.05 × 0.08 mm, μ(Mo–Kα) = 7.64 cm^{-1}. $N = 4004$, N_o $[I > 3\sigma(I)] = 2439$, $R = 0.058$, $R_w = 0.072$.

For **4**: colorless crystal, $Na_2[WO_2(H_2cit)_2]\cdot 3H_2O$, $C_{12}H_{18}O_{19}W_1Na_2$, $M = 696.10$, monoclinic, space group $P2_1/n$, $a = 7.6329(8)$, $b = 18.318(3)$, $c = 14.860(2)$ Å, $\beta = 102.85(1)°$, $V = 2023.2(9)$ Å^3, $Z = 4$, $D_c = 2.29$ g cm^{-3}, $F(000) = 1352$. Crystal dimensions: 0.03 × 0.10 × 0.13 mm, μ(Mo-Kα) = 59.7 cm^{-1}. $N = 4918$, N_o $[I > 3\sigma(I)] = 3512$, $R = 0.046$, $R_w = 0.058$.

Unique diffractometer data sets were measured at *ca.* 296 K to $2\theta_{max} = 52°$ (CAD4 diffractometer, 2θ–θ scan mode, monochromatic Mo-Kα radiation, $\lambda = 0.71073$ Å), N independent reflections were obtained N_o being considered 'observed' and used in the full-matrix least squares refinements after Gaussian absorption correction. Anisotropic thermal parameters were included constrained at estimated values for **3** and **4**. CCDC reference number 186/1725.

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