

N-heterocycle chelated oxomolybdenum(VI and V) complexes with bidentate citrate†

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A 1,10-phenanthroline (phen) chelated molybdenum(VI) citrate, $[(\text{MoO}_2)_2\text{O}(\text{H}_2\text{cit})(\text{phen})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**) (H_4cit = citric acid), is isolated from the reaction of citric acid, ammonium molybdate and phen in acidic media (pH 0.5–1.0). A citrato oxomolybdenum(V) complex, $[(\text{MoO})_2\text{O}(\text{H}_2\text{cit})_2(\text{bpy})_2]\cdot 4\text{H}_2\text{O}$ (**2**), is synthesized by the reduction of citrato molybdate with hydrazine hydrochloride in the presence of 2,2'-bipyridine (bpy), and a monomeric molybdenum(VI) citrate $[\text{MoO}_2(\text{H}_2\text{cit})(\text{bpy})]\cdot\text{H}_2\text{O}$ (**6**) is also isolated and characterized structurally. The citrate ligand in the three neutral compounds uses the α -alkoxy and α -carboxy groups to chelate as a bidentate leaving the two β -carboxylic acid groups free, that is different from the tridentate chelated mode in the citrato molybdate(VI and V) complexes. **1** and **2** in solution show obvious dissociation based on ^{13}C NMR studies.

Introduction

The undefined X atom in the bidentately coordinated R-homocitrato-MoFe₇S₉X cluster of FeMoco in nitrogenase has made the six central Fe atoms coordinately saturated,^{1–3} which is supported by the model compound synthesis of iron sulfur clusters with a similar core of Fe₈S₉ and Fe₈S₈N.⁴ Despite intensive research and knowledge of the macromolecular structures of the nitrogenase component proteins from several different sources, the precise location of dinitrogen coordination at FeMoco remains an open question.^{5–7} Moreover, it is proposed that homocitrate and molybdenum are inserted into the precursor of FeMoco in the final step.⁸ This stimulates our interests in the coordination chemistry of molybdenum complexes with homocitrate and citrate, both are homologous to hydroxy-tricarboxylate ligands.⁹ In our former studies on the molybdenum citrate system, we have attempted to show the reactivity of the Mo-tricarboxylate by isolating citrato molybdate under highly acidic conditions, where the coordinated β -carboxylic acid group remains protonated.¹⁰ The present results show that, with the aid of N-heterocycle ligands, two novel dinuclear bidentate citrate molybdenum(VI and V) complexes $[(\text{MoO}_2)_2\text{O}(\text{H}_2\text{cit})(\text{phen})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**), $[(\text{MoO})_2\text{O}(\text{H}_2\text{cit})_2(\text{bpy})_2]\cdot 4\text{H}_2\text{O}$ (**2**) and a monomeric citrate molybdenum(VI) $[\text{MoO}_2(\text{H}_2\text{cit})(\text{bpy})]\cdot\text{H}_2\text{O}$ (**6**) are prepared.

Experimental

Physical measurements

Infrared spectra were recorded as Nujol mulls between KBr plates on a Nicolet 360 FT-IR spectrometer. Elemental analyses

were performed with an EA 1100 elemental analyzer. Electronic spectra were recorded on a UV 2501 spectrophotometer with an integrating sphere for reflectance spectroscopy. ^1H and ^{13}C NMR spectra were recorded in DMSO solution at 298 K on a Bruker BIOSPIN AV400 spectrometer. ^1H and ^{13}C shifts are referenced to internal solvent resonances and reported relative to 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS). XRD patterns were recorded on a Philips X'Pert Pro Super X-ray diffractometer equipped with X'Celerator and Xe detection systems.

Preparations of $[(\text{MoO}_2)_2\text{O}(\text{H}_2\text{cit})(\text{phen})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**)

A mixture of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.18 g, 0.14 mmol), citric acid monohydrate (0.66 g, 3.15 mmol), 1,10-phenanthroline monohydrate (0.10 g, 0.52 mmol) in aqueous ethanol solution (1:1 v/v) and a few drops of concentrated hydrochloric acid was heated at 100 °C for 3 h and then at 86 °C for 7.5 h and cooled to rt. The milky solution treated with hydrothermal condition changed to a light blue cloudy solution after one week at rt, product **1** was isolated as light yellow-brown spicules. 43% yield (0.145 g) based on molybdenum. C, N and H elemental analyses. Found (calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_{15}\text{Mo}_2$): C, 30.7 (31.1); H, 3.1 (2.9); N, 4.0 (4.0). IR (KBr, cm^{-1}): $\nu(\beta\text{-CO}_2\text{H})$ 1721; $\nu_{\text{as}}(\text{CO}_2)$ 1691_s, 1634_{as}; $\nu_s(\text{CO}_2)$ 1431_m, 1392_m, 1357_m; $\nu(\text{Mo}=\text{O})$ 944_s, 906_{vs}; $\nu_{\text{as}}(\text{Mo}-\text{O}-\text{Mo})$ 806_{vs}. ^1H NMR δ_{H} (400 MHz, DMSO- d_6): δ_{H} 9.498 (d, J 4.0 Hz, CH, 2H), 8.892 (d, J 8.0 Hz, CH, 2H), 8.450 (s, CH, 1H), 8.238 (s, CH, 1H), 8.150 (dd, J 8.0, 4.0 Hz, CH, 2H), 2.752 (d, J 16.8 Hz, CH₂, 2H), 2.576 (d, J 16.8 Hz, CH₂, 2H). ^{13}C NMR(DMSO- d_6): δ_{C} 178.9 ($\alpha\text{-CO}_2$), 171.0 ($\beta\text{-CO}_2$), 153.1, 141.8, 140.8, 129.5, 127.4, 126.4 (phen), 81.0 ($\equiv\text{CO}$), 43.3 ($=\text{CH}_2$) ppm.

Preparations of $[(\text{MoO})_2\text{O}(\text{H}_2\text{cit})_2(\text{bpy})_2]\cdot 4\text{H}_2\text{O}$ (**2**)

$\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ (0.24 g, 1.0 mmol), citric acid monohydrate (0.46 g, 2.2 mmol) and 2,2'-bipyridine (0.16 g, 1.01 mmol) were mixed in 100 ml aqueous ethanol solution (1:2 v/v). The reactants were dissolved by continuous stirring, then hydrazine

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dihydrochloride (0.44 g, 4.2 mmol) was added. The solution turned carmine. The pH value was adjusted to 3.0 and the solution turned dark red. The product **2** was isolated as dark violet after three days. 64% yield (0.319 g) based on molybdenum. C, N and H elemental analyses for $C_{32}H_{36}N_4O_{21}Mo_2$: found (calc.): C, 37.8 (38.2); N, 5.5 (5.6); H, 3.8 (3.6). IR (KBr): $\nu(\beta\text{-CO}_2\text{H})$ 1725_{vs}; $\nu_{as}(\text{CO}_2)$ 1644_{vs}; $\nu_s(\text{CO}_2)$ 1475_m, 1442_m, 1403_m; $\nu_s(\text{Mo=O})$ 949_s, 902_w; $\nu_{as}(\text{Mo-O-Mo})$ 851_m cm^{-1} . $^1\text{H NMR}$ δ_{H} (400 MHz, DMSO- d_6): δ_{H} 8.689 (d, J 4.8 Hz, CH, 2H), 8.387 (d, J 8.0 Hz, CH, 2H), 7.956 (t, J 15.2, 7.6 Hz, CH, 2H), 7.461 (t, J 12.4, 6.0 Hz, CH, 2H), 2.714 (dd, J 27.2, 15.4 Hz, CH_2 , 4H). $^{13}\text{C NMR}$ (DMSO- d_6): δ_{C} 180.9 ($\alpha\text{-CO}_2$), 173.1 ($\beta\text{-CO}_2$), 157.0, 151.2, 139.3, 126.1, 122.3 (bpy), 82.8 ($\equiv\text{C-O}$), 44.4 ($=\text{CH}_2$) ppm.

Preparations of $[\text{MoO}_2(\text{H}_2\text{cit})(\text{bpy})]\cdot\text{H}_2\text{O}$ (**6**)

A mixture of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.18 g, 0.14 mmol), citric acid monohydrate (0.64 g, 3.02 mmol), 2,2'-bipyridine (0.18 g, 1.14 mmol) in water and a few drops concentrated HCl was heated at 100 °C for 8 hours, then cooled to rt at 5 °C/h. The milky cloudy solution was turned to pink solution. The colorless crystal **6** was isolated from the white precipitate after one month. 5% yield (0.016 g) is based on bipyridine. C, N and H elemental analyses. Found (calcd for $C_{16}H_{16}N_2O_{10}Mo_1$): C, 38.7 (39.0); N, 5.6 (5.7); H, 3.2 (3.3). IR (KBr, cm^{-1}): $\nu(\beta\text{-CO}_2\text{H})$ 1748_s; $\nu_{as}(\text{CO}_2)$ 1658_s, 1603_{vs}; $\nu_s(\text{CO}_2)$ 1444_m, 1400_m, 1339_m; $\nu_s(\text{Mo=O})$ 937_s, 909_{vs}.

X-Ray structure determination

Crystals of **1**, **2** and **6** were measured on a Bruker Smart Apex CCD area detector diffractometer with graphite monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at $-50 \text{ }^\circ\text{C}$ for **1** and $23 \text{ }^\circ\text{C}$ for **2** and **6**. Data were corrected for absorption by using the SADABS program.¹¹ The structures were primarily solved by SHELXS in the WinGX program¹² and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all of the nonhydrogen atoms with SHELX-97.¹³ Hydrogen atoms were located from a difference Fourier map and refined isotropically.

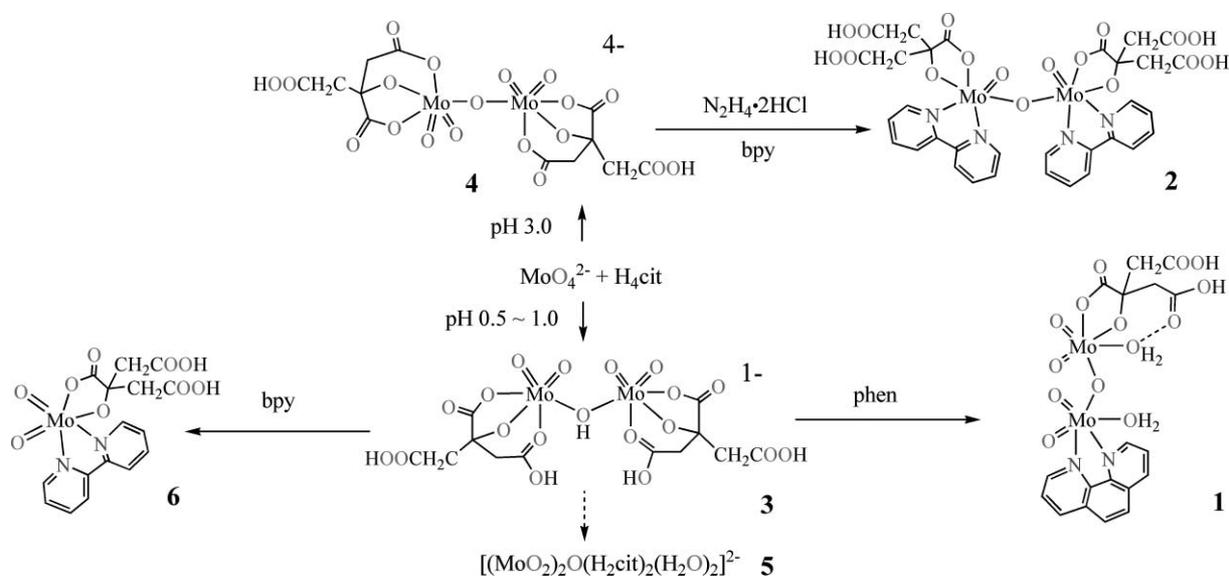
Crystal data for 1. $C_{18}H_{20}N_2O_{15}Mo_2$, $M = 696.24$, triclinic, space group $P\bar{1}$, $a = 7.6946(6)$, $b = 11.768(1)$, $c = 13.741(1) \text{ \AA}$, $\alpha = 87.550(2)$, $\beta = 76.478(1)$, $\gamma = 71.122(2)^\circ$, $V = 1143.9(2) \text{ \AA}^3$, $D_c = 2.021 \text{ g/cm}^3$, $Z = 2$, reflections collected/unique/observed = 7447/4873/3608, $R_{\text{int}} = 0.1152$, $R1 = 0.066$, $wR2 = 0.140$.

Crystal data for 2. $C_{32}H_{36}N_4O_{21}Mo_2$, $M = 1004.53$, triclinic, space group $P\bar{1}$, $a = 10.306(3)$, $b = 13.089(5)$, $c = 16.049(9) \text{ \AA}$, $\alpha = 103.71(4)$, $\beta = 107.11(4)$, $\gamma = 94.48(3)^\circ$, $V = 1985(2) \text{ \AA}^3$, $D_c = 1.681 \text{ g/cm}^3$, $Z = 2$, reflections collected/unique/observed = 24574/12584/5116, $R_{\text{int}} = 0.0619$, $R = 0.055$, $wR2 = 0.125$.

Crystal data for 6. $C_{16}H_{16}N_2O_{10}Mo_1$, $M = 492.25$, monoclinic, space group $P 2_1/n$, $a = 14.688(1)$, $b = 7.7377(8)$, $c = 16.084(2) \text{ \AA}$, $\beta = 100.151(2)^\circ$, $V = 1799.3(3) \text{ \AA}^3$, $D_c = 1.817 \text{ g/cm}^3$, $Z = 4$, reflections collected/unique/observed = 10660/3167/2091, $R_{\text{int}} = 0.1278$, $R = 0.085$, $wR2 = 0.160$.

Results and discussion

The preparations of **1** and **2** are outlined in Scheme 1. The solution of Mo:H₄cit (1:1) was investigated by ^{13}C NMR spectra in the pH range of 0.5–4.0, showing that dimeric species, $\text{K}[(\text{MoO}_2)_2(\text{OH})(\text{H}_2\text{cit})_2]\cdot 4\text{H}_2\text{O}$ (**3**)¹⁰ and $\text{K}_4[(\text{MoO}_2)_2\text{O}(\text{Hcit})_2]\cdot 4\text{H}_2\text{O}$ (**4**),¹⁴ are in equilibrium with the free ligand: this led to the isolation of the three compounds. An attempt at synthesizing $\text{K}_2[(\text{MoO}_2)_2\text{O}(\text{H}_2\text{cit})_2(\text{H}_2\text{O})_2]$ (**5**) has been unsuccessful owing to the fact that **3** is a stable, hydrogen-bonded species and resists further solvation.¹⁰ It takes the assistance of strongly chelating 1,10-phenanthroline to displace the tridentate citrate with water to give neutral compound **1**, which is stabilized by the intramolecular hydrogen bonding of the coordinated water. Reduction of citrato molybdate **4** in the presence of 2,2'-bipyridine gives the dimeric bipyridine hydrogen citrato oxomolybdenum(V) $[(\text{MoO})_2\text{O}(\text{H}_2\text{cit})_2(\text{bpy})_2]\cdot 4\text{H}_2\text{O}$ (**2**) in 64% yield. When bipyridine is used instead of phen in the reaction of **3**, a mononuclear bipyridine citrato molybdate(VI), $[\text{MoO}_2(\text{H}_2\text{cit})(\text{bpy})]\cdot\text{H}_2\text{O}$ (**6**) has



Scheme 1 Synthesis and transformation of molybdenum(VI, V) citrate complexes in the presence of 1,10-phenanthroline and 2,2'-bipyridine.¹⁰

been isolated in a very low yield; this has not been reproduced at present.

The X-ray structure of **1** (Fig. 1) shows two *cis*-dioxo-Mo units oriented in a staggered *syn*-mode with respect to the oxo bridge, and both molybdenum atoms possessing six-coordinate, octahedral geometries. The citrate moiety coordinates to one molybdenum atom as a bidentate ligand *via* its α -alkoxy and α -carboxy groups leaving both β -carboxylic acid groups free to participate in intramolecular and intermolecular hydrogen bonding [O4...O1w 2.744(8), O7...O3a 2.604(9) Å; $a, -1 + x, y, z$]. The intramolecular hydrogen bond in FeMoco, when investigated theoretically using a model and quantum-mechanical computation, suggests that the long arm of *R*-homocitrate (γ -carboxy group) but not its free β -carboxy group is capable of undergoing intramolecular hydrogen bonding with the imidazole ligand on Mo.^{15,16}

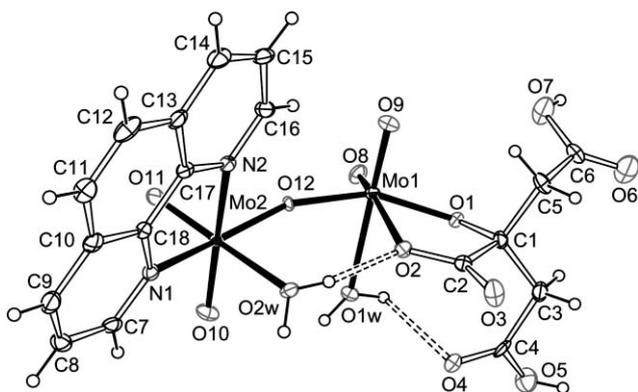


Fig. 1 The ORTEP plot of the molecular structure of $[(\text{MoO}_2)_2\text{O}(\text{H}_2\text{cit})(\text{phen})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**) at the 30% probability levels.

Selected bond distances (Å) and angles (°) of complexes **1**, **2** and **6** are shown in Table 1. The Mo–O distances in complex **1** vary systematically according to its bond types. The Mo=O distances ranged 1.667(6) to 1.710(5) Å are in agreement

Table 1 Selected bond distances (Å) and angles (°) for $[(\text{MoO}_2)_2\text{O}(\text{H}_2\text{cit})(\text{phen})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**), $[(\text{MoO}_2)_2\text{O}(\text{H}_2\text{cit})_2(\text{bpy})_2]\cdot 4\text{H}_2\text{O}$ (**2**) and $[\text{MoO}_2(\text{H}_2\text{cit})(\text{bpy})]\cdot\text{H}_2\text{O}$ (**6**)

1			
Mo(1)–O(1)	1.941(4)	Mo(2)–O(10)	1.698(4)
Mo(1)–O(2)	2.209(5)	Mo(2)–O(11)	1.704(5)
Mo(1)–O(8)	1.710(5)	Mo(2)–O(12)	1.840(4)
Mo(1)–O(9)	1.695(5)	Mo(2)–O(2w)	2.286(5)
Mo(1)–O(12)	1.932(4)	Mo(2)–N(1)	2.210(6)
Mo(1)–O(1w)	2.307(5)	Mo(2)–N(2)	2.294(5)
Mo(1)–O(12)–Mo(2)	160.8(3)	O(1)–Mo(1)–O(2)	75.2(2)
2			
Mo(1)–O(1)	1.987(3)	Mo(2)–O(9)	1.888(3)
Mo(1)–O(2)	2.075(3)	Mo(2)–O(11)	1.976(3)
Mo(1)–O(8)	1.676(4)	Mo(2)–O(12)	2.077(3)
Mo(1)–O(9)	1.875(3)	Mo(2)–O(18)	1.686(3)
Mo(1)–N(1)	2.277(4)	Mo(2)–N(11)	2.257(4)
Mo(1)–N(2)	2.351(4)	Mo(2)–N(12)	2.342(4)
Mo(1)–O(9)–Mo(2)	169.9(2)	O(1)–Mo(1)–O(2)	78.3(1)
6			
Mo(1)–O(1)	1.907(6)	Mo(1)–O(9)	1.667(6)
Mo(1)–O(2)	2.144(6)	Mo(1)–N(1)	2.189(8)
Mo(1)–O(8)	2.351(4)	Mo(1)–N(2)	2.261(7)
O(1)–Mo(1)–O(2)	75.8(3)	O(8)–Mo(1)–O(9)	104.5(4)

with the double bond character. The Mo–O bridge is necessarily unsymmetrical exhibiting a shorter bond distance of Mo(2)–O(12) [1.840(4) Å] than that of Mo(1)–O(12) [1.932(4) Å] arising from the *trans*-effect of the phenanthroline ligand. The Mo–O (α -alkoxy) and Mo–O (α -carboxy) distances observed in **1** are 1.941(4) and 2.209(5) Å respectively, and the coordinated water molecules are longer [2.286(5) and 2.307(5) Å] than those coordinated in trinuclear molybdenum(IV) complexes such as $[\text{Mo}_3(\text{CH}_3\text{CO}_2)_3\text{Br}_3(\text{H}_2\text{O})_5(\text{CCH}_3)]\cdot\text{ClO}_4\cdot 4\text{H}_2\text{O}$ and $(\text{Ph}_4\text{P})_2[\text{Mo}_3(\mu_3\text{-S})(\mu_2\text{-S})_3(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_3]\cdot 11\text{H}_2\text{O}$ [2.211(9)_{av}, 2.15 – 2.22 Å].^{17,18} Thus insertion of a water molecule to form Mo–O_w bonds in **1** may be justifiable in view of the more weakly coordinated Mo–O _{β -carboxy} [2.463(6) Å] in **3**.¹⁰

As shown by the X-ray structure (Fig. 2), **2** is a dimeric bipyridine citrate molybdenum(V) complex consisting of a core of a *anti*-oxo-Mo entity with respect to the angled oxo-bridge with molybdenum in a distorted octahedral geometry. The Mo=O distances [1.676(4) and 1.686(3) Å] are in a shorter range compared to those of **1** and other dimeric citrate molybdenum(V, VI) complexes.^{10,14,19} The Mo(1)–O(9)–Mo(2) bridge [169.9(2)°] is bent and has approximately symmetric [1.875(3) and 1.888(3) Å] configuration. It is noteworthy that two coordinated bipyridine molecules are structurally non-equivalent [2.257(4) and 2.277(4); 2.342(4) and 2.351(4) Å] owing to the *trans* effect of the terminal oxo group.

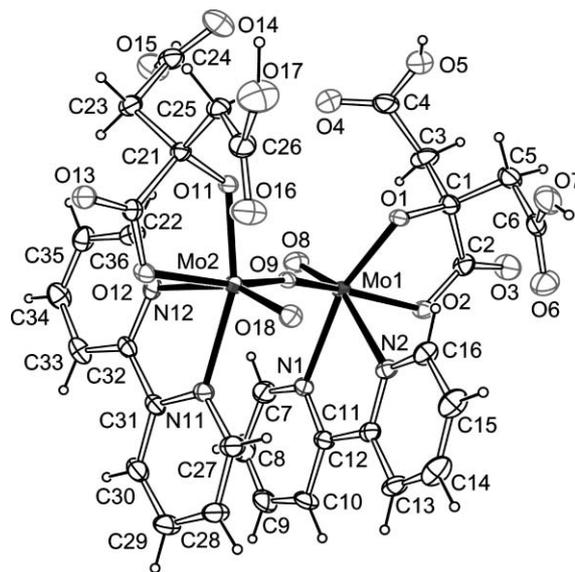


Fig. 2 The ORTEP plot of the molecular structure of $[(\text{MoO}_2)_2\text{O}(\text{H}_2\text{cit})_2(\text{bpy})_2]\cdot 4\text{H}_2\text{O}$ (**2**) at the 15% probability levels.

Complex **6** is a monomeric bipyridine citrate molybdenum(VI) complex as shown in Fig. 3, consisting of a core of a *cis*-dioxo-Mo entity in a distorted octahedral geometry. The Mo=O distances [1.667(6) and 1.670(7) Å] are in a shorter range compared to those of **1** and **2**. Both free β -carboxylic acid groups participate in hydrogen bonding with water molecule [O5a...O1w 2.67(1), O7b...O1w 2.61(1) Å; $a, 2 - x, -y, 2 - z; b, 1.5 - x, -0.5 - y, 1.5 - z$].

The citrate ligand in **2** and **6** coordinates bidentately through α -alkoxy and α -carboxy groups, leaving all the β -carboxylic acid groups free. In comparison to **1** and **6**, the reduced state of

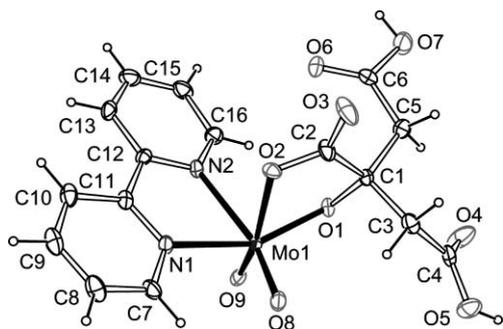


Fig. 3 The ORTEP plot of the molecular structure of $[\text{MoO}_2(\text{bpy})-(\text{H}_2\text{cit})]\cdot\text{H}_2\text{O}$ (**6**) at the 15% probability levels.

molybdate(V) in **2** results in longer Mo–O bond distances for α -alkoxy groups [1.941(4) and 1.907(6) Å for **1** and **6** respectively, 1.976(3) and 1.987(3) Å for **2**] and shorter Mo–O distances for α -carboxy groups [2.209(5) and 2.144(6) Å for **1** and **6** respectively, 2.075(3), 2.077(3) Å for **2**]; this situation is comparable to the coordination of FeMoco in nitrogenase (Av, 2.212, 2.162 Å; Kp-nifV, 2.253, 2.269 Å for α -alkoxy and α -carboxy groups).¹⁹

Complexes **1** and **2** are insoluble in water and ethanol but sparingly soluble in DMSO. ^{13}C NMR spectra in deuterated DMSO are shown in Fig. 4 and 5 with long time superposition. Two sets of signals are attributed to the coordinated and free citrate species: the chemical shifts for the latter free citrate are comparable with those for KH_3cit ion.

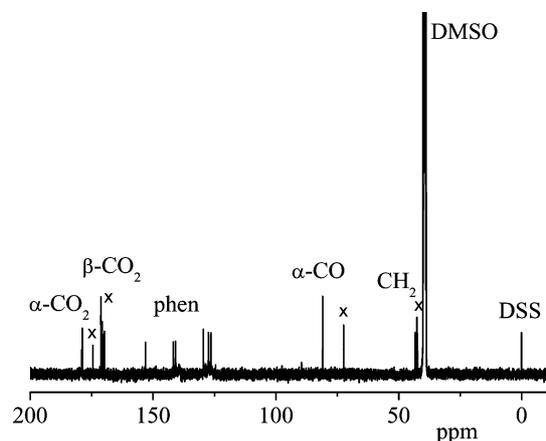


Fig. 4 The ^{13}C NMR spectrum of $[(\text{MoO}_2)_2\text{O}(\text{H}_2\text{cit})(\text{phen})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**) in $\text{DMSO}-d_6$. (x) denotes free citrate (H_3cit^-).

In particular, the carbon atoms of coordinated α -alkoxy and α -carboxy groups show distinct downfield shifts $\Delta\delta$ of 4.3–4.6 and 8.6 ppm, respectively, which are a clear indication of the bidentate coordination. These are in agreement with the state of an equilibrium in spectral solution involving the dissociation of both α -carboxy and α -alkoxy groups. Further comparison of the ^{13}C NMR pattern of molybdate and citrate (1:1 molar ratio) in the pH range of 0.5–4.0 indicates that citrate molybdenum(VI) compounds **3** and **4** also show obvious dissociation in these acidic solutions. The XRD pattern of solid complex **1** is consistent in comparison with a theoretically simulated pattern. The solid species isolated in macroscale is the same as the sample for X-ray

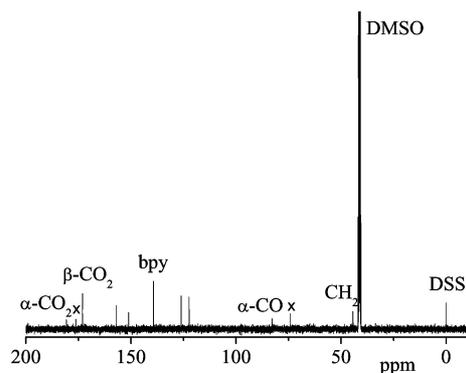


Fig. 5 The ^{13}C NMR spectrum of $[(\text{MoO})_2\text{O}(\text{H}_2\text{cit})_2(\text{bpy})_2]\cdot 4\text{H}_2\text{O}$ (**2**) in $\text{DMSO}-d_6$. (x) denotes free citrate (H_3cit^-).

structural analysis. This is supported by the theoretical simulation of XRD pattern shown in Fig. S4.†

Conclusion

There is sufficient evidence to show that the citrate group engages in tridentate coordination *via* the α -alkoxy, α -carboxy and β -carboxy groups in complexes $\text{K}[(\text{MoO}_2)_2(\text{OH})(\text{H}_2\text{cit})_2]\cdot 4\text{H}_2\text{O}$,¹⁰ $\text{K}_4[(\text{MoO}_2)_2\text{O}(\text{Hcit})_2]\cdot 4\text{H}_2\text{O}$,¹⁴ and $\text{K}_4\text{Na}_2[(\text{MoO}_2)_2\text{O}(\text{cit})_2]\cdot 5\text{H}_2\text{O}$.¹⁹ In fact, direct substitution of $\text{K}_4[(\text{MoO}_3(\text{cit}))\cdot 2\text{H}_2\text{O}]$ ¹⁴ in neutral conditions with a monodentate ligand has been largely unsuccessful because of the full dissociation of the citrate ligand. Even under highly acidic solutions, protonated species $[(\text{MoO}_2)_2(\text{OH})(\text{H}_2\text{cit})_2]^-$ (**4**)¹⁰ can form without any direct monodentate substitution. The present formation of symmetric and unsymmetric bidentate citrato molybdates **1**, **2** and **6** could be related to the assembly of homocitrato FeMoco in nitrogenase, that shows certain resemblance to a monodentate substitution of β -carboxy group with a coordinated water molecule. Although the structure and coordination of homocitrato molybdate precursor of FeMoco is unknown in the final process of biosynthesis.^{8,20,21} It is also noted that a large gap exists between the homocitrato molybdate in natural cofactor assembly and current model molecules, homocitrato and citrate, especially the very low pH required to induce bidentate coordination.

Acknowledgements

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