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Dimeric Dioxomolybdenum(VI) and Oxomolybdenum(V) Complexes with Citrate at Very Low pH and Neutral Conditions

Zhao-Hui Zhou,* Yuan-Fu Deng, Ze-Xing Cao, Rong-Hua Zhang, and Yuan L. Chow

State Key Laboratory for Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

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A novel dimeric dioxomolybdenum(VI) citrate complex, $K[(MoO_2)_2(OH)(H_2cit)_2]\cdot 4H_2O$ (**1**), with weak coordination of β-carboxylic acid groups and the first structural example of an oxomolybdenum(V) citrate complex, $(NH_4)_6[Mo_2O_4(cit)_2]\cdot 3H_2O$ (**2**) (H_4cit = citric acid), are isolated in a very acidic solution (pH 0.5–1.0) and neutral conditions (pH 7.0–8.0), respectively. Complex **1** displays strong double hydrogen bonds through β-carboxyl and β-carboxylic acid groups [2.621(9) Å]. Transformations of the dimeric molybdenum(VI) citrate show that protonation of a carboxyl group will weaken the coordination of molybdenum(VI) citrate. There are obvious dissociations of molybdenum(VI/V) citrate complexes based on ^{13}C NMR observations in solution.

Recent high-resolution X-ray crystallographic analysis of nitrogenase has revealed a previously unrecognized light atom that coordinated to six Fe atoms located in the center of *R*-homocitrate-$MoFe_7S_9X$ (X = light element such as N or O) (FeMoco).[1,2] Density-functional and electrostatics calculations have concluded that this light atom is most likely an N atom.[3−6] But very recent results from ENDOR and ESEEM observations strongly indicated that X is not an N.[6] The new discovery of the central atom makes the middle Fe atoms of FeMoco coordinately saturated. This strengthens the notion that the Mo atom directly participates in substrate binding and reduction.[7,8] It is proposed that homocitrate may facilitate the binding of dinitrogen through the ejection of the bound α-alkoxyl or α-carboxyl groups from the Mo atom[9−12] and the formation of intramolecular hydrogen bonding.[14] However, there is no direct evidence for the protonation of the coordinated carboxyl group prior to the process of ejection. As a part of our systematic study related to coordination chemistry of molybdate citrate,[15−17] herein we further report the interactions of molybdate and citric acid in a very acidic solution and neutral conditions that result in the isolation and characterization of a novel dinuclear molybdenum(VI) citrate complex, $K[(MoO_2)_2(OH)(H_2cit)_2]\cdot 4H_2O$ (**1**), and a molybdenum(V) citrate complex, $(NH_4)_6[Mo_2O_4(cit)_2]\cdot 3H_2O$ (**2**).[18,19]

The syntheses of dimeric molybdenum(VI) and molybdenum(V) citrate complexes and their transformations are shown in Scheme 1, which shows a pH-dependent reaction pattern. Noteworthy is the requirement of pH 0.5−1.0 and 7.0−8.0 in the preparations of compounds **1** and **2**, respectively. While there are a wealth of reports available concerning molybdenum citrate complexes,[15−17,20] none of these have been isolated in a very acidic solution.

Figures 1 and 2 show the anion structures of **1** and **2** from X-ray analysis, respectively.[21] Selected bond parameters are given in the captions. Figure 1 shows a remarkable feature

* To whom correspondence should be addressed. E-mail: zhzhou@xmu.edu.cn. Tel: +86-592-2184531. Fax: +86-592-2183047.

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(18) Potassium molybdate pentahydrate (1.64 g, 5 mmol) and citric acid monohydrate (1.50 g, 7 mmol) were dissolved in water (10 mL). The pH of the solution was adjusted to 1.0 by hydrochloric acid. The mixture was filtered and kept airtight in a refrigerator for 6 weeks. The colorless crystals deposited were washed with ethanol (95%) and dried in air; yield 0.76 g (40%). C and H elem anal. Found (calcd for $C_{12}H_{21}O_{23}K_1Mo_2$): C, 18.5 (18.8); H, 1.9 (2.1). IR (KBr, cm^{-1}): ν-(β-CO_2H) 1713_s; $\nu_{as}(CO_2)$ 1675_{vs}, 1649_{vs}; $\nu_s(CO_2)$ 1448_m, 1384_m, 1342_m; ν_s(Mo=O) 939_{vs}, 912_s; ν_{as}(Mo−O−Mo) 723. ^1H NMR (500 MHz, D_2O): δ_H 3.03 (d, J = 9.0 Hz, CH_2), 2.88 (d, J = 9.0 Hz, CH_2). ^{13}C NMR (D_2O): δ_C 186.0 [$(CO_2)_\alpha$], 175.7 [$(CO_2)_\beta$], 86.9 (≡CO), 45.4 (=CH_2).

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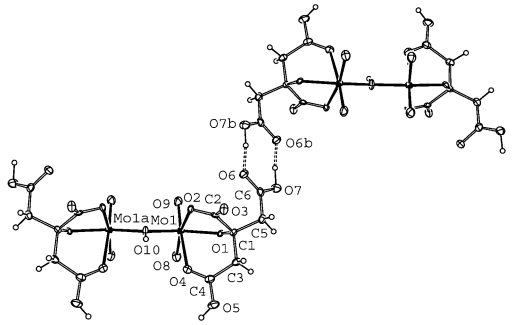


Figure 1. ORTEP plot of a $[(MoO_2)_2(OH)(H_2cit)_2]^-$ anion in **1** at the 30% probability level. Selected bond lengths (Å) and angles (deg): Mo1−O1 1.953(5), Mo1−O2 2.249(5), Mo1−O4 2.463(6), Mo1−O8 1.710(6), Mo1−O9 1.715(7), Mo1−O10 1.905(3), O7···H2···O6b 2.621(9); O8−Mo1−O9 104.3(3), Mo1−O10−Mo1a 133.3(5). *a* ($-x$, $^1/_2 + y$, $-z$); *b* (x, $^3/_2 - y$, z).

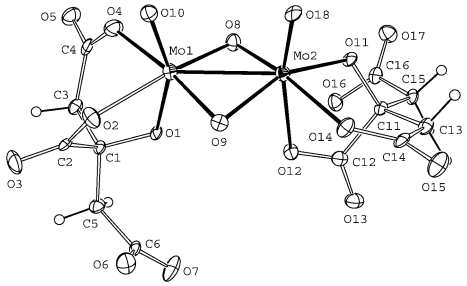
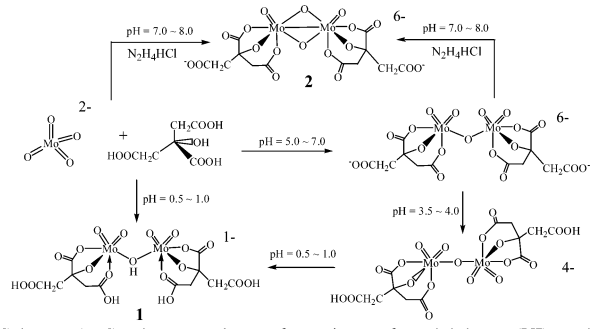


Figure 2. ORTEP plot of a $[(Mo_2O_4(cit)_2)^{6-}$ anion in **2** at the 30% probability level. Selected bond lengths (Å) and angles (deg): Mo1−O1 2.015(3), Mo1−O2 2.151(3), Mo1−O4 2.208(3), Mo1−O8 1.946(3), Mo1−O9 1.945(3), Mo1−O10 1.712(3), Mo2−O11 2.018(3), Mo2−O12 2.242(3), Mo2−O14 2.148(3), Mo2−O8 1.943(3), Mo2−O9 1.964(3), Mo2−O18 1.702(3), Mo1−Mo2 2.5861(5); Mo1−O8−Mo2, 83.4(1), Mo1−O9−Mo2 82.9(1).

Scheme 1. Syntheses and Transformations of Molybdenum(VI) and Molybdenum(V) Citrate Complexes[17]



of two *cis*-dioxo-Mo units in a syn configuration with respect to the hydroxyl bridge. However, the anion $[(MoO_2)_2O(Hcit)_2]^{4-}$ existing in a weak acidic solution shows the corresponding pair of *cis*-dioxo-Mo units in an anti configuration.[17] Each molybdenum atom is six-coordinate with an approximately octahedral geometry. The citrate ion coordinates to molybdenum as a tridentate ligand via the α-alkoxyl and α-carboxyl groups and one of the *β*-carboxylic acid groups, while the other *β*-carboxylic acid group remains free and participates in strong interactions of double hydrogen bonds, which results in the formation of a stable supramolecular entity. The polymeric O···O distance of 2.621(9) Å is comparable to that in acetic acid dimer (2.68 Å).[22] The tridentate coordination mode of the citrate ion in complex **1** through its α-alkoxyl and α-carboxyl groups and one of the *β*-carboxylic acid groups is unique, which is different from those of $(NH_4)_3[Ga(Hcit)_2]\cdot 4H_2O$,[23] $(NH_4)_4[M(Hcit)_2]\cdot xH_2O$ [M = Mn(II), Co(II), $x = 0$; M = Ni(II), $x = 2$],[24] $(NH_4)_5[M(cit)_2]\cdot 2H_2O$ [M = Mn(III), Fe, and Al].[24,25] The citrate ion in these compounds uses its α-hydroxyl (or α-alkoxyl), α-carboxyl, and deprotonated *β*-carboxyl groups to interact with the metal atom. Moreover, the angle of the Mo−O−Mo bridge [133.3(5)°] in complex **1** is different from that in $K_4[(MoO_2)_2O(Hcit)_2]\cdot 4H_2O$ (180°)[17] and is also smaller than those of the Mo−O−Mo bridges in $K_4Na_2[(MoO_2)_2O(cit)_2]\cdot 5H_2O$ [144.7(2)°],[15] $K_6[(MoO_2)_2O(cit)_2]\cdot 2H_2O$ [137.1(4)], and $K_6[(MoO_2)_2O(cit)_2]\cdot 5H_2O$ [153.8(2)],[20] which may be the effect of the protonation in the bridged oxygen atom.

The Mo−O distances in complexes **1** vary systematically according to its bond type. The Mo═O distances [1.710(6) and 1.715(7) Å] are in agreement with double bonds. The resulting angle of O8−Mo1−O9 is considerably larger than the regular octahedron value of 90° for cis groups; this is expected from the greater O···O repulsions between oxygens with short bonds to the metal atom. In comparison to the Mo−O distances in various molybdenum citrate complexes,[15−17,20] the Mo−O (α-alkoxyl) and Mo−O (α-carboxyl) distances observed in **1** are comparable with 1.953(5) and 2.249(5) Å, respectively. In contrast, the Mo−O (*β*-carboxylic acid) distance of complex **1** of 2.463(6) Å is longer than

(19) Triammonium citrate (3.65 g 15 mmol) and $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (1.77 g 1.4 mmol) were dissolved in 10 mL of water in a N_2 atmosphere. Hydrazine hydrochloride (0.52 g, 5 mmol) was added to give a red solution. The pH value of the solution was adjusted to 7.0 with the addition of ammonia hydroxide (20%). The resulting solution was stirred in a water bath at 40 °C for 6 h and filtered. Subsequently, the reaction mixture was kept refrigerated for several days. The brown crystals were collected and washed with 95% ethanol (2.58 g 69%). C, H, and N elem anal. Found (calcd for $C_{12}H_{38}O_{21}N_6Mo_2$): C, 18.3 (18.1); H, 4.9 (4.8); N, 10.3 (10.6). IR (KBr, cm^{-1}): $\nu_{as}(CO_2)$ 1638_s, 1578_{vs}; $\nu_s(CO_2)$ 1437_s, 1401_{vs}; ν_s(Mo═O) 925_s; ν_{as}(Mo−O−Mo) 728_m. ^{1}H NMR (500 MHz, D_2O): δ_H 2.668 (s, CH_2). ^{13}C NMR (D_2O): δ_C 189.3 [$(CO_2)_\alpha$], 181.9 [$(CO_2)_\beta$], 83.8 (≡CO), 49.1 (═CH_2). UV−vis: $\lambda_{max} = 300$ nm, $\epsilon = 6100$.

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(21) The room-temperature diffraction measurements for the crystal were recorded on a Bruker Apex CCD diffractometer fitted with Mo Kα radiation. Crystal data for **1**: $C_{12}H_{21}O_{23}KMo_2$, $M = 764.27$, monoclinic, space group $P2_1/m$, $a = 6.7618(5)$ Å, $b = 22.346(2)$ Å, $c = 8.5338(6)$ Å, $\beta = 109.077(1)°$, $V = 1218.6(2)$ Å^3, $D_c = 2.083$ g/cm^3, $Z = 2$, R1 = 0.078, wR2 = 0.152. Crystal data for **2**: $C_{12}H_{38}O_{21}N_6Mo_2$, $M = 794.36$, triclinic, space group $P\bar{1}$, $a = 9.6932(5)$ Å, $b = 10.6198(7)$ Å, $c = 15.1487(5)$ Å, $\alpha = 109.629(4)°$, $\beta = 99.707(3)°$, $\gamma = 73.106(5)°$, $V = 1401.0(1)$ Å^3, $D_c = 1.883$ g/cm^3, $Z = 2$, R1 = 0.039, wR2 = 0.960. The structure was solved by direct methods and refined by full-matrix least-squares procedures[32] with anisotropic thermal parameters for all of the non-hydrogen atoms.

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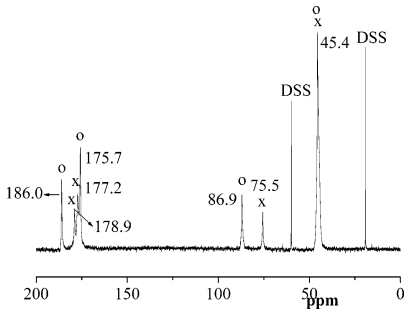

Figure 3. ^{13}C NMR spectra of $K[(MoO_2)_2(OH)(H_2cit)_2]\cdot 4H_2O$ (**1**) in D_2O 5 h after dissolution. Labels: (×) free citrate (H_3cit^-); (○) a coordinated molybdenum(VI) citrate complex.

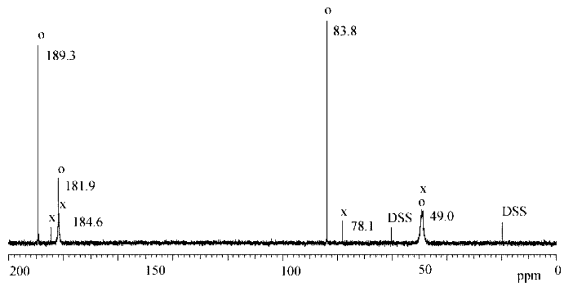

Figure 4. ^{13}C NMR spectra of $(NH_4)_6[Mo_2O_4(cit)_2]\cdot 3H_2O$ (**2**) in D_2O 5 h after dissolution. Labels: (×) free citrate ($Hcit^{3-}$); (○) a coordinated molybdenum(V) citrate complex.

that of its related deprotonted form $K_4[(MoO_2)_2O(Hcit)_2]\cdot 4H_2O$ [2.276(3) Å], indicating weak coordination to the molybdenum atom. This, in turn, implies that this weakly coordinated β-carboxylic acid group is easily replaced by another ligand, such as an imidazole group in histidine. This may result in the bidentate form of citrate to molybdenum-like protein-bound *nif*V$^-$ FeMo−cofactor,[26] using only α-alkoxyl and α-carboxyl groups for coordination.

The structure of complex **2** can be described as syn dinuclear citratomolybdenum(V) linked by two bridged oxygen atoms. The other two oxygen atoms (O10 and O18) coordinate to Mo1 and Mo2, respectively, showing a syn configuration. Each molybdenum(V) atom exists in a *quasi*-octahedral geometry. The coordination sphere of the molybdenum(V) atom consists of one terminal oxygen atom, two bridged oxygen atoms, and three oxygen atoms from the α-alkoxyl and α-carboxyl groups and one of the β-carboxyl groups of a full deprotonated citrate ligand.

The average distance [2.017(3) Å] of Mo(V)−O (alkoxyl) in complex **2** is longer than those of molybdate(VI) citrate complexes. However, this is shorter than the strong reduced molybdenum in FeMo−co of citrato nitrogenase (2.253 Å) and Mo(0) citrate complex [2.230(2) Å].[20f,26] The interaction between Mo1 and Mo2 [2.5861(5) Å] suggests the existence of a weak metal−metal bond. The simple chemical transformation of molybdenum(VI) citrate and molybdenum(V) citrate in Scheme 1 suggests that the reductant-like iron-only *nif*B−cofactor might be required in the early stage during the biosynthesis of FeMo−co,[27,28] avoiding the strong coupling of the Mo−Mo bond without consideration of the complicated biosynthesis process in nature.[29] Note that the synthetic chemistry taking place in the solution does not necessarily reflect the biomolecular chemistry of the assembly of the FeMo−co in nitrogenase, where the metal ion rests in protein coordination cavities, often restricting the chances of Mo−Mo bond formation.

Owing to some dissociation, the ^{13}C NMR spectrum of the dimeric molybdenum(VI) citrate complex **1** shows additional small peaks (Figure 3), but the major peaks can be interpreted. In comparison with a free ligand under comparable conditions {KH_3cit ^{13}C NMR (D_2O): δ 179.5 [$(CO_2)_\alpha$], 175.6 [$(CO_2)_\beta$], 74.7 (≡CO), 44.6 (═CH_2)}, complex **1** shows generally downfield shifts of the corresponding ^{13}C NMR resonances. In particular, coordinated α-alkoxyl and α-carboxyl carbons show large downfield shifts $\Delta\delta$ of 11.5 and 7.2 ppm, which is a clear indication of the coordination of α-alkoxyl and α-carboxyl groups. However, the β-carboxyl carbons show smaller highfield shifts $\Delta\delta$ of 1.5 ppm. This indicates the weak bonding of the β-carboxylic acid group. Figure S2 in the Supporting Information illustrates the ^{13}C NMR spectrum of complex **1** taken after 3 months, which is similar to the pattern in Figure 3, despite the relatively broad peaks observed. The result reveals the presence of an equilibrium between complex **1**, free citrate (H_3cit^-), and oxomolybdenum species in different protonated forms such as $[HMoO_4]^-$ and $[MoO_2(OH)(OH_2)_3]^+$ at very low concentration ($<10^{-4}$ M),[30] which is supported by the protonation of a bridged oxo group in complex **1**. A similar pattern of ^{13}C NMR resonances was observed in the case of a mononuclear complex, $(NH_4)_5[Al(cit)_2]\cdot 2H_2O$.[25]

In complex **2**, there also exists some dissociation on dissolving in D_2O (Figure 4); the large low-field shift of some ^{13}C NMR resonances (in comparison with $Hcit^{3-}$ ions at the same pH) demonstrates that both the α-alkoxyl ($\Delta\delta$ of 5.8 ppm) and α-carboxyl ($\Delta\delta$ of 4.7 ppm) groups are coordinated. The fact that both β-carboxyl groups give only one ^{13}C NMR signal at 181.9 ppm leads us to think that the less strongly bonded β-carboxyl groups participate in coordination exchange when the solid complex is dissolved in D_2O. This result is in agreement with an earlier report.[31] The solution NMR spectra reflect a consistency between the solid and solution states, despite obvious dissociation of citratomolybdenum into a citrate anion in solution.

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Supporting Information Available: X-ray crystallographic files in CIF format and IR (Figure S1) and NMR (Figure S2) spectra. These materials are available free of charge via the Internet at http://pubs.acs.org.

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