Syntheses and Spectroscopic and Structural Characterization of Molybdenum(VI) Citrato Monomeric Raceme and Dimer, $K_4[MoO_3(cit)]\cdot 2H_2O$ and $K_4[(MoO_2)_2O(Hcit)_2]\cdot 4H_2O$

Zhao-Hui Zhou,* Hui-Lin Wan, and Khi-Rui Tsai

Department of Chemistry and State Key Laboratory for Physical Chemistry of Solid Surface,
Xiamen University, Xiamen, 361005, People's Republic of China

Received January 6, 1999

Investigation of the aqueous coordination chemistry for citrate and molybdenum(VI) resulted in the isolation of molybdenum(VI) citrato monomeric raceme and dimer $K_4[MoO_3(cit)]\cdot 2H_2O$ (**1**) and $K_4[(MoO_2)_2O(Hcit)_2]\cdot 4H_2O$ (**2**) (H_4cit = citric acid). Complex **1** can serve as the first structurally characterized monomeric citrato molybdate and may represent an early mobilized precursor in the biosynthesis of FeMo-co (FeMo-cofactor). The two complexes have been characterized by elemental analyses and IR and NMR spectroscopies. The IR and NMR spectra are consistent with a monomeric species or a monooxo-bridged dinuclear structure, as revealed by a single crystal X-ray diffraction study. Compound **1** is monoclinic space group $P2_1/c$ with $a = 7.225(1)$ Å, $b = 9.151(2)$ Å, $c = 22.727(2)$ Å, $\beta = 94.93(1)°$, $V = 1497.1(7)$ Å^3, and $Z = 4$. Full-matrix least-squares refinement resulted in residuals of $R = 0.027$ and $R_w = 0.032$. The molybdenum atom forms an octahedral coordination with three oxo groups and one tridentate citrate, in which the latter is coordinated through the alkoxy and vicinal carboxyl and much more weakly by one of the two terminal groups [2.411(3) Å]. Compound **2** is triclinic space group $P\bar{1}$ with $a = 8.2728(8)$ Å, $b = 8.9514(8)$ Å, $c = 10.0605(9)$ Å, $\alpha = 101.673(8)°$, $\beta = 100.672(7)°$, $\gamma = 112.938(7)°$, $V = 642.5(3)$ Å^3, and $Z = 1$. Full-matrix least-squares refinement resulted in residuals of $R = 0.033$ and $R_w = 0.039$. The complex anion contains a linear $(O_2Mo)O(MoO_2)$ core with the bridging oxo group lying at the center of inversion symmetry ($Mo{-}O_b{-}Mo$, 180°). Each citrate ligand is three-coordinated to one molybdenum atom through the deprotonated hydroxy, α-carboxyl, and one β-carboxyl group, making each metal atom six-coordinate.

Introduction

Recent single-crystal X-ray structural analysis of the nitrogenase proteins has revealed the structure of FeMo-co (FeMo-cofactor) as a cagelike $MoFe_7S_9$ homocitrate cluster,[1−9] in which the Mo is essentially octahedrally coordinated by three μ_3-S ligands, a histidine, and a bidentate homocitrate through the alkoxy and vicinal carboxyl groups, which may be termed an α-carboxyl group with reference to the alkoxy carbon atom as α-carbon atom. Early studies have shown that the mutant MoFe proteins lacking homocitrate, which may contain a Mo-bound citrate ligand to molybdenum as a replacement to homocitrate, prevented the enzyme from strong binding and efficient reduction of N_2 while acetylene and proton reduction remained at a high level.[10,11] Moreover, it has been suggested that a possible function of the tricarboxylic acid in the biosynthesis of the cofactor of nitrogenase is to mobilize molybdenum or vanadium from the appropriate storage enzyme. Molybdenum or vanadium is believed to be taken up by organisms as MoO_4^{2-} or VO_4^{3-}; this would be essential for the assembly of the final cofactor cluster from an oxomolybdenum− or oxovanadium−citrate precursor.[12−15] Tricarboxylic acid may play an early and essential role in the mobilization of the heterometal during cofactor biosynthesis, and the mobilized oxoheterometal tricarboxylic acid fragment must then undergo reduction, exchange oxo ligands for sulfide ligands, and merge with nif B-co.

While the precise role of homocitrate in both the biosynthesis of FeMo-co and the mechanism of dinitrogen reduction is still regarded as poorly understood,[16] the elucidation of the key role played by this tricarboxylic acid in nitrogenase catalysis has been pursued with great interest.[17] As part of our systematic study of the coordination chemistry of vanadium(V/IV) and molybdenum(VI) with hydroxycarboxylic acids, complexes formed from aqueous solutions of vanadate, vanadyl or molybdate, and citric acid (H_4cit) or its salt have been studied. We have first reported the preparations and structures of $K_2[VO_2(H_2cit)]_2\cdot 4H_2O$, $Na_2K_2[VO_2(Hcit)]_2\cdot 9H_2O$, $Na_2(NH_4)_4$-

---

* To whom correspondence should be addressed. E-mail: zhzhou@xmu.edu.cn.

(1) Kim, J.; Rees, D. C. *Science* **1992**, *257*, 1677.
(2) Kim, J.; Rees, D. C. *Nature* **1992**, *360*, 553.
(3) Kim, J.; Wood, D.; Rees, D. C. *Biochemistry* **1993**, *32*, 7104.
(4) Chan, M. K.; Kim, J.; Rees, D. C. *Science* **1993**, *260*, 792.
(5) Rees, D. C.; Chan, M. K.; Kim, J. *Adv. Inorg. Chem.* **1993**, *40*, 89.
(6) Kim, J.; Rees, D. C. *Biochemistry* **1994**, *33*, 389.
(7) Bolin, J. T.; Ronco, A. E.; Mortenson, L. E.; Morgan, T. V.; Xuong, N. H. *Proc. Natl. Acad. Sci. U. S.A.* **1993**, *90*, 1078.
(8) Bolin, J. T.; Campobasso, N.; Muchmore, S. W.; Minor, W.; Morgan, T. V.; Mortenson, L. E. *New Horizons in Nitrogen Fixation*; Kluwer: Dordrecht, The Netherlands, 1993; p 83.
(9) Dean, D. R.; Bolin, J. T.; Zheng, L. *J. Bacteriol.* **1993**, *175*, 6737.
(10) Hoover, T. R.; Imperial, J.; Ludden, P. W.; Shah, V. K. *Biochemistry* **1989**, *28*, 2768.
(11) Burgess, B. K. *Chem. Rev.* **1990**, *90*, 1377.
(12) Shah, V. K.; Allen, J. R.; Spangler, N. J.; Ludden, P. W. *J. Biol. Chem.* **1994**, *269*, 1154.
(13) Hales, B. J. *Adv. Inorg. Biochem.* **1990**, 165.
(14) Wright, D. W.; Chang, R. T.; Mandal, S. K.; Armstrong, W. H.; Orme-Johnson, W. H.; Davis, W. H. *J. Bioinorg. Chem.* **1996**, *1*, 143.
(15) Müller, A.; Krahn, E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1071.
(16) Grönberg K. L. C.; Gormal, C. A.; Durrant, M. C.; Smith, B. E.; Henderson, R. A. *J. Am. Chem. Soc.* **1998**, *120*, 10613.
(17) Tsai, K. R.; Wan, H. L. *J. Cluster Sci.* **1995**, *6*, 485.

10.1021/ic990042s CCC: $19.00

$[VO_2(cit)]_2\cdot 6H_2O$, and $Na_4[VO(cit)]_2\cdot 6H_2O$.[18−21] The pH of the medium is the principal variable controlling complex formation and interconversion equilibria.[22,23] At high pH (>6) the anions of vanadium complex are vanadate(V), $[VO_2(cit)]_2^{6-}$, or vanadyl(IV) anion, $[VO(cit)]_2^{4-}$, while at lower pH three different dinuclear anions $[VO_2(H_2cit)]_2^{2-}$, $[VO_2(Hcit)]_2^{4-}$, or $[(VO)_2(cit)(Hcit)]^{3-}$ were observed.[18−26]

Complex formation between molybdate and citrate has been reported in different pH ranges by potentiometry, spectrophotometry, difference pulse polargraphy, and calorimetry.[27−32] The first well structurally characterized citrato molybdates with 2:1 ratios (Mo:cit) were reported as $[Me_3N(CH_2)_6NMe_3]_2[Mo_4O_{11}(cit)_2]\cdot 12H_2O$ and $K_4[Mo_4O_{11}(cit)_2]\cdot 6H_2O$.[33,34] Formation of the 1:1 complex was first obtained as $K_2[MoO_3(OH)(H_3cit)]\cdot 2H_2O$ and $K_3[MoO_4(H_3cit)]\cdot 2H_2O$,[35] later $K_4[(MoO_2)_2O(Hcit)_2]\cdot 5H_2O$, $K_6[(MoO_2)_2O(cit)_2]\cdot 7H_2O$, and $K_4[MoO_3(cit)H_2O]$ were obtained by precipitation from aqueous solution at pH 4−8.[36] In the neutral solution, the complex has been separated and structurally confirmed as a dimeric oxomolybdenum citrate as $K_2Na_4[(MoO_2)_2O(cit)_2]\cdot 5H_2O$ or $K_6[(MoO_2)_2O(cit)_2]\cdot 2H_2O$.[37,38] It is also shown that citric acid is the most effective eluent for the separation of W(VI) and Mo(VI) oxoanions.[39] In the use of eluents without alkoxy groups, W(VI) and Mo(VI) oxoanions were strongly retained, due to the formations of W(VI) and Mo(VI) polyanions. These complexes have been characterized by chemical analyses and various other methods and remained uncertain for their composition and the degree of aggregation. Moreover, the variety of possible functions exhibited by citrate in its interactions with molybdenum, a metal which plays an important role in different living plants and animal organisms,[40] prompted our further investigation of the coordination chemistry of molybdenum citrate complexes.

Experimental Section

Preparation of $K_4[MoO_3(cit)]\cdot 2H_2O$ (1). Potassium molybdate (20 mmol) prepared from the reaction of molybdenum trioxide and potassium hydroxide (82%) was added with an excess potassium dihydrogen citrate (K_2H_2cit, 30 mmol) from the reaction of citric acid and potassium hydroxide. The solution was stirred in a water bath at 80 °C for 4 h and filtered. An excess amount of ethanol was added until the solution turned cloudy. The mixture was kept refrigerated for several days, and the solid was collected and recrystallized from $H_2O-EtOH$ to give a white solid (5.1 g, 49%). Anal. Found: C, 13.3; H, 1.6. Calcd for $C_6H_8K_4MoO_{12}$: C, 13.7; H, 1.5. IR (KBr): ν_{asym} (C=O) $1603_{s,sh}$, $1575_{vs,b}$, ν_{sym} (C=O) $1425_{s,sh}$, 1398_{vs}, ν (Mo=O) 937_{w}, 897_{m}, 848_{s}, 826_{s}. ^1H NMR (500 MHz, D_2O; ppm): δ_H 2.666 (d, *J* 16.7 Hz, CH_2), 2.646 (d, *J* 14.9 Hz, CH_2), 2.543 (d, *J* 15.1 Hz, CH_2), 2.524 (d, *J* 16.6 Hz, CH_2). ^{13}C NMR (D_2O; ppm): δ_C 187.5 $(CO_2)_\alpha$, 179.6, 179.4 $(CO_2)_\beta$, 81.7 (≡CO), 46.4, 46.3 (=CH_2).

Preparation of $K_4[(MoO_2)_2O(Hcit)_2]\cdot 4H_2O$ (2). Potassium molybdate (20 mmol) prepared from the reaction of molybdenum trioxide and potassium hydroxide was added with an excess citric acid (22 mmol) and a small amount of potassium trihydrogen citrate (2 mmol). The solution was stirred in a water bath at 60 °C for 4 h. The mixture was filtered and added with an excess amount of ethanol. The solid formed was collected and recrystallized from $EtOH-H_2O$ to give a white solid. (3.6 g, 41%). Anal. Found: C, 16.0; H, 2.0. Calcd for $C_{12}H_{18}K_4Mo_2O_{23}$: C, 16.4; H, 2.1. IR (KBr): ν_{asym} (C=O) 1715_{s}, $1652_{vs,b}$, 1604_{s}, $1553_{s,b}$; ν_{sym} (C=O) 1440_{m}, 1426_{m}, 1404_{s}, 1346_{m}; ν (Mo=O) 933_{s}, $908_{s,sh}$, $895_{vs,b}$; $\nu_{as}(MoO_bMo)$, 785_{vs}; $\nu_s(MoO_bMo)$ 690_{s}. ^1H NMR (500 MHz, D_2O; ppm): δ_H 2.796 (d, 4H, *J* 16.9 Hz, CH_2), 2.590 (d, 4H, *J* 17.0 Hz, CH_2). ^{13}C NMR (D_2O; ppm): δ_C 185.3 $(CO_2)_\alpha$, 176.3 $(CO_2)_\beta$, 84.6 (≡CO), 43.6 (=CH_2).

Crystals of suitable quality for the subsequent X-ray diffraction studies were obtained as transparent prism or rhombhedral blocks by slow evaporation of the related solution of compounds **1** or **2** at room temperature. The resulting crystals were sealed in capillary to prevent loss of water molecules.

Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates using a Nicolet 740 FT-IR spectrometer. Elemental analyses were performed using EA 1106 elemental analyzers. ^1H NMR and ^{13}C NMR spectra were recorded on Varian UNITY 500 NMR and 300 NMR spectrometers, respectively, using DDS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as internal reference.

X-ray Data Collection, Structure Solution, and Refinement. Crystallographic data for the citratomolybdates **1** and **2** are summarized in Table 1. Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation at 296 K. A Lorentz−polarization factor, anisotropic decay, and empirical absorption corrections were applied. The structures were solved by heavy atom methods and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all the non-hydrogen atoms. H atoms were located from difference Fourier map and not refined. All calculations were performed on a 586 P/100 microcomputer using the MoLEN software package.[41] Selected atomic distances and bond angles are given in Table 2.

Results and Discussion

Preparation of the title compounds depends on pH control and the mole ratio of the reactants.[30,31] In this experiment the pH values in the reactions are controlled easily by citrate anions acting as both reactant and buffer agent. This is further supported by the preparation of deprotonated dimeric citrato molybdate.[37] The interconversion of the monomeric and dimeric oxocitrato molybdates is shown in Scheme 1. Transformation of mono-

---

(18) Zhou, Z. H.; Yan, W. B.; Wan, H. L.; Tsai, K. R.; Wang, J. Z.; Hu, S. Z. *J. Chem. Crystallogr.* **1995**, *25*, 807.

(19) Zhou, Z. H.; Wan, H. L.; Tsai, K. R. *Chin. Sci. Bull.* **1995**, *40*, 749.

(20) Zhou, Z. H.; Wan, H. L.; Hu, S. Z.; Tsai, K. R. *Inorg. Chim. Acta* **1995**, *237*, 193.

(21) Zhou, Z. H.; Zhang, H.; Jiang, Y. Q.; Lin, D. H.; Wan, H. L.; Tsai, K. R. *Trans. Met. Chem.* **1999**, *24*, 612.

(22) Ehde, P. M.; Anderson, I.; Petterson, L. *Acta Chem. Scand*. **1989**, *43*, 136.

(23) Kiss, T.; Buglyo, P.; Sanna, D.; Micera, G.; Decock, P.; Dewaele, D. *Inorg. Chim. Acta* **1995**, *239*, 145.

(24) Wright, D. W.; Humiston, P. A.; Orme-Johnson, W. H.; Davis, W. H. *Inorg. Chem*. **1995**, *34*, 4194.

(25) Burojevic, S.; Shweky, I.; Bino, A.; Summers, D. A.; Thompson, R. C. *Inorg. Chim. Acta* **1996**, *251*, 75.

(26) Murugesan, V.; Babu, V.; Sankaran, S. *Inorg. Chem*. **1998**, *37*, 1336.

(27) Creager, S. E.; Aikens, D. A.; Clark, H. M. *Electrochim. Acta* **1982**, *27*, 1307.

(28) Pedrosa de Jesus, J. D.; Farropas, M. de D.; O′Brien, P.; Gillard, R. D.; Williams, P. A. *Trans. Met. Chem.* **1983**, *8*, 193.

(29) Bartusek, M.; Havel, J.; Matula, D. *Collect. Czech. Chem. Comm.* **1986**, *51*, 2702.

(30) Cruywagen, J. J.; Van de Water, R. F. *Polyhedron* **1986**, *5*, 521.

(31) Cruywagen, J. J.; Rohwer, E. A.; Wessels, G. F. S. *Polyhedron* **1995**, *14*, 3481.

(32) Martie, D. O.; Feliz, M. R.; Capparelli, A. L. *Z. Phys. Chem. (Leipzig)* **1989**, *270*, 951.

(33) Nassunbeni, L. R.; Niven, M. L.; Cruywagen, J. J.; Heyns, J. B. B. *J. Crystallogr. Spectrosc. Res*. **1987**, *17*, 373.

(34) Alcock, N. W.; Dudek, M.; Grybos, R.; Hodorowicz, E.; Kanas, A.; Samotus, A. *J. Chem. Soc., Dalton Trans*. **1990**, 707.

(35) Dudek, M.; Hodorowicz, E.; Kanas, A.; Samotus, A.; Sieklucka, B.; Szklarzewicz, J.; Beltowska-Lehman, E. *Proceedings of the 11th Conference on Coordination Chem*istry; Smolenice, Czechoslovakia, 1987; p 57.

(36) Samotus, A.; Kanas, A.; Dudek, M.; Grybos, R.; Hodorowicz, E. *Trans. Met. Chem*. **1991**, *16*, 495.

(37) Zhou, Z. H.; Wan, H. L.; Tsai, K. R. *Polyhedron* **1997**, *16*, 75.

(38) Xing, Y. H.; Xu, J. Q.; Sun, H. R.; Li. D. M.; Wang, R. Z.; Wang, T. G.; Bu, W. M.; Ye, L.; Yang, G. D.; Fan, Y. G. *Acta Crystallogr.* **1998**, *C54*, 1615.

(39) Maruo, M.; Hirayama, N.; Shiota, A.; Kuwamoto, T. *Anal. Sci.* **1992**, *8*, 511.

(40) *Molybdenum and Molybdenum-Containing Enzymes*; Coughlan, M. P., Ed.; Pergmon: New York, 1980.

(41) *MoLEN. An interactive Intelligent System for Crystal Analysis*; Enraf-Nonius: Delft, The Netherlands, 1990.

Table 1. Crystal Data Summaries of Intensity Data Collection and Structure Refinement for $K_4[MoO_3(cit)]\cdot 2H_2O$ (**1**) and $K_4[(MoO_2)_2O(Hcit)_2]\cdot 4H_2O$ (**2**)

	1	**2**
emp formula	$C_6H_8K_4MoO_{12}$	$C_{12}H_{18}K_4Mo_2O_{23}$
fw	524.47	878.55
cryst color, habit	colorless, prism	colorless, rhombic
cryst dimers (mm)	0.05 × 0.05 × 0.08	0.10 × 0.10 × 0.12
cryst syst	monoclinic	triclinic
no. of reflns used for unit cell determn (2θ range)	25 (15.0−17.0°)	25 (15.0−17.0°)
space group	$P2_1/c$	$P\bar{1}$
formula units/unit cell	4	1
cell constants:		
a (Å)	7.225(1)	8.2728(8)
b (Å)	9.151(2)	8.9514(8)
c (Å)	22.727(2)	10.0605(9)
α (deg)		101.673(8)
β (deg)	94.93(1)	100.672(7)
γ (deg)		112.938(7)
V (Å^3)	1497.1(7)	642.5(3)
D_{calc} (g/cm^3)	2.327	2.271
F_{000}	1032	434
μ(Mo Kα) (cm^{-1})	20.3	17.0
diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
radiation	Mo Kα ($\lambda = 0.7107$ Å)	Mo Kα ($\lambda = 0.7107$ Å)
temp	23°	23°
scan width	$0.37 + 0.35 \tan\theta$	$0.41 + 0.35 \tan\theta$
decay of standards (%)	±2	−2.0
no. of reflns measd	3172	2695
2θ range (deg)	$2 \leq 2\theta \leq 52$	$2 \leq 2\theta \leq 52$
Range of h, k, l	8, −11, ±28	10, ±11, ±12
no. of reflns obsd $[F_o \leq 3\sigma(F_o)]^a$	2564	2196
computer programs[b]	MoLEN	MoLEN
structure solution	MoLEN	MoLEN
no. of params varied	209	190
weight	$[\sigma(F_o)^2 + 0.0001(F_o)^2 + 1]^{-1}$	$[\sigma(F_o)^2 + 0.0001(F_o)^2 + 1]^{-1}$
GOF	0.86	0.75
$R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$	0.027	0.033
R_w	0.032	0.039
largest feature final diff. map (e$^-$ Å^{-3})	1.0	0.8

[a] Corrections: Lorentz−polarization. [b] Neutral scattering factors and anomalous dispersion corrections.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $K_4[MoO_3(cit)]\cdot 2H_2O$ (**1**) and $K_4[(MoO_2)_2O(Hcit)_2]\cdot 4H_2O$ (**2**)[a]

Mo(1)−O(1)	2.052(2)	Mo(1)−O(1)	1.958(3)
Mo(1)−O(2)	2.237(7)	Mo(1)−O(2)	2.210(3)
Mo(1)−O(3)	2.411(3)	Mo(1)−O(3)	2.276(3)
Mo(1)−O(8)	1.740(3)	Mo(1)−O(8)	1.703(3)
Mo(1)−O(9)	1.731(3)	Mo(1)−O(9)	1.714(5)
Mo(1)−O(10)	1.759(3)	Mo(1)−O(10)	1.8766(4)
O(1)−Mo(1)−O(2)	72.90(9)	O(1)−Mo(1)−O(3)	79.0(1)
O(1)−Mo(1)−O(3)	75.5(1)	O(1)−Mo(1)−O(8)	98.9(1)
O(1)−Mo(1)−O(8)	96.6(1)	O(1)−Mo(1)−O(9)	97.2(2)
O(1)−Mo(1)−O(9)	91.8(1)	O(1)−Mo(1)−O(10)	150.9(1)
O(1)−Mo(1)−O(10)	150.8(2)	O(2)−Mo(1)−O(3)	79.5(1)
O(2)−Mo(1)−O(3)	77.65(9)	O(2)−Mo(1)−O(8)	89.2(2)
O(2)−Mo(1)−O(8)	90.7(1)	O(2)−Mo(1)−O(9)	165.3(1)
O(2)−Mo(1)−O(9)	160.1(1)	O(2)−Mo(1)−O(10)	82.69(9)
O(2)−Mo(1)−O(10)	85.6(2)	O(3)−Mo(1)−O(8)	168.7(2)
O(3)−Mo(1)−O(8)	167.4(2)	O(3)−Mo(1)−O(9)	86.7(2)
O(3)−Mo(1)−O(9)	86.3(1)	O(3)−Mo(1)−O(10)	78.56(9)
O(3)−Mo(1)−O(10)	80.9(1)	O(8)−Mo(1)−O(9)	104.6(2)
O(8)−Mo(1)−O(9)	104.0(1)	O(8)−Mo(1)−O(10)	99.5(1)
O(8)−Mo(1)−O(10)	103.3(1)	O(9)−Mo(1)−O(10)	99.8(1)
O(9)−Mo(1)−O(10)	103.6(1)	Mo(1)−O(10)−Mo(1a)	180.000
O(1)−Mo(1)−O(2)	75.1(1)		

[a] (−x, −y, −z).

meric and dimeric oxocitrato molybdates can be accomplished by controlling the pH.

Previously the dominant mononuclear oxomolybdenum−citrate species in solution were formulated as $[MoO_4(H_2cit)]^{4-}$, $[MoO_3(cit)]^{4-}$, $[MoO_3(H_2cit)_2]^{4-}$, $[MoO_3(Hcit)]^{3-}$, $[MoO_2(cit)]^{2-}$, $[MoO_2(OH)(cit)]^{3-}$, and their protonated forms,[29−31] and the dinuclear oxomolybdenum−citrate species were in the compositions $[Mo_2O_5(cit)_2]^{6-}$, $[Mo_2O_5(cit)(H_2O)_3]^{2-}$, and their protonated forms. Furthermore, salts separated from the solution indicated monomeric forms, $K_2[MoO_3(OH)(H_3cit)]\cdot 2H_2O$, $K_3[MoO_4(H_3cit)]\cdot 2H_2O$, $K_4[MoO_3(cit)H_2O]$; their dinuclear forms, $K_4[(MoO_2)_2O(Hcit)_2]\cdot 5H_2O$, $K_6[(MoO_2)_2O(cit)_2]\cdot 7H_2O$; or their tetramer.[33−36] The precise distribution of the products for this reaction system is expected to be complex. Only 2:1 (Mo:cit) and 1:1 citrato molybdates have been structurally characterized as tetramer and dimer.[33,34,37] Complex $K_4[MoO_3(cit)]\cdot 2H_2O$ (**1**) represents a first example of a structurally characterized monomeric 1:1 molybdenum−citrate complex which exhibits the coordination of the polycarboxylic acid to the molybdenum, and the isolated hydroxy and water molecule are not involved in the coordination of the molybdenum site. Such is the case in the related peroxide adduct $K_2[MoO(O_2)_2(H_2cit)]\cdot {}^1/_2H_2O_2\cdot 3H_2O$,[42] in which two peroxo groups and the citrate ligand are bidentate.

The crystal structure of **1** comprises discrete potassium cations, water molecules, and citrato trioxo molybdate anions. As shown in Figure 1, each citrate ion acts as a tridentate ligand coordinated to the molybdenum atom via its alkoxy, α-carboxyl, and one β-carboxyl group, while the other β-carboxyl group remains uncomplexed. Tridentate coordination of citrate through

---

(42) Flangan, J.; Griffithe, W. P.; Skapski, A. C.; Wiggins, R. W. *Inorg. Chim. Acta* **1985**, *96*, L23.

Scheme 1. Syntheses and Transformation of Monomeric and Dimeric Citratomolybdates

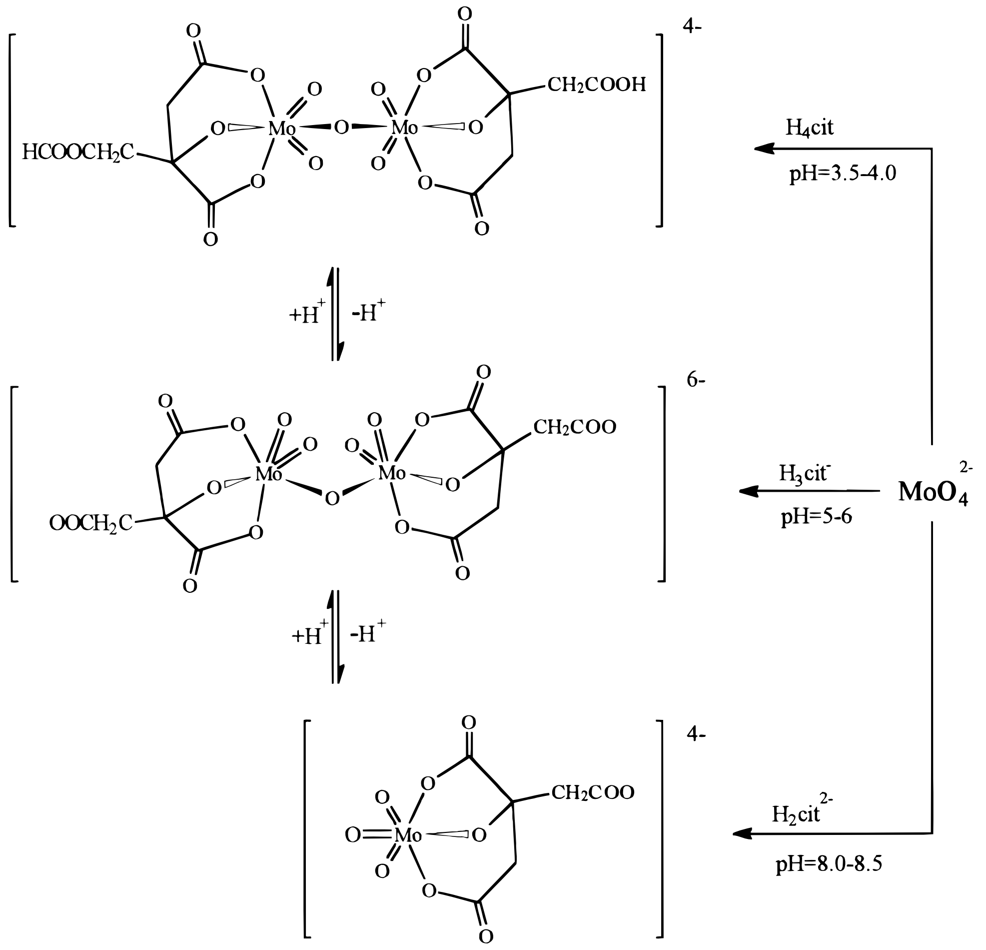
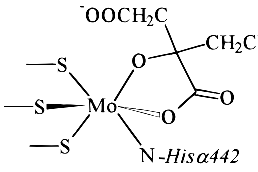


Chart 1. Schematic Representation of the First Coordination Sphere of Molybdenum in FeMo-cofactor[1]



its alkoxy or hydroxyl, α-carboxyl, and *β*-carboxyl group is a basic feature of mono- or dimeric citrate complexes. A similar type of coordination has also been seen in the mononuclear complexes of $(NH_4)_5Fe(C_6H_4O_7)_2{\cdot}4H_2O$, $(NH_4)_5Al(C_6H_4O_7)_2{\cdot}2H_2O$, and $(NH_4)_4[Ni(C_6H_5O_7)_2]{\cdot}2H_2O$.[43−45] There are two enantiomers of this complex, which resulted from the asymmetric coordination environment around molybdenum. This is similar to that of FeMo-co (Chart 1), in which the octahedral coordination geometry for Mo is typically asymmetrical. Attempts to resolve the enantiomers of **1** were unsuccessful.

As shown in Figure 2, the complex $K_4[(MoO_2)_2O(Hcit)_2]{\cdot}4H_2O$ (**2**) exists as a centrosymmetric dimer. Each citrate ion also acts as a tridentate ligand with the alkoxy, α-carboxyl, and one *β*-carboxyl oxygens coordinated to the molybdenum atom, and the other *β*-carboxyl group remains uncomplexed, as does its deprotonated form. The dimeric anion consists of a common oxobridged $[Mo_2O_5]^{2+}$ entity which is centrosymmetric. The angle of the Mo−O−Mo bridge is the same as that in $[(MoO_2)_2O(C_2O_4)_2(H_2O)_2]^{2-}$ (180°),[46] and is different from the angles of the Mo−O−Mo bridge [144.7(2) and 137.1(4)°] in

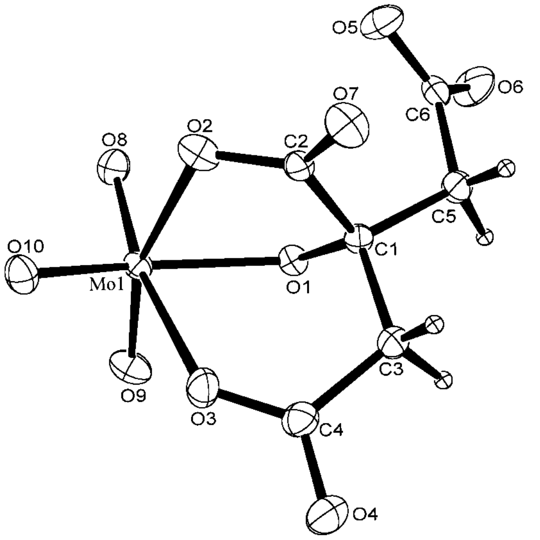


Figure 1. Perspective view of the anion structure of $K_4[MoO_3(cit)]{\cdot}2H_2O$. Thermal ellipsoids are drawn by ORTEP and represent 50% probability surfaces.

---

(43) Matzapetakis, M.; Raptopoulou, C. P.; Terzis, A.; Lakatos, A.; Kiss, T.; Salifoglou, A. *Inorg. Chem.* **1999**, *38*, 618.

(44) Matzapetakis, M.; Raptopoulou, C. P.; Tsohos, A.; Papaefthymiou, V.; Moon, N.; Salifoglou, A. *J. Am. Chem. Soc.* **1998**, *120*, 13266.

(45) Zhou, Z. H.; Lin, Y. J.; Zhang, H. B.; Lin, G. D.; Tsai, K. R. *J. Coord. Chem.* **1997**, *42*, 131.

(46) Cotton, F. A.; Morehause, S. M.; Wood, S. J. *Inorg. Chem.* **1964**, *3*, 1603.

Table 3. Relevant Infrared Data, ν/cm^{-1}, for Citrato Molybdates **1**−**4**, **1**, $K_4[MoO_3(cit)]\cdot 2H_2O$; **2**, $K_4[(MoO_2)_2O(Hcit)_2]\cdot 4H_2O$; **3**, $K_2Na_4[(MoO_2)_2O(cit)_2]\cdot 5H_2O$; **4**, $K_4[Mo_4O_{11}(cit)_2]\cdot 6H_2O$

	1	**2**	**3**	**4**
ν(OH)	3417_{vs}	3623_{s}, 3527_{s} 3423_{s}	3421	
$\nu(CH_2)$	2969_{m}	2960_{m}, 2921_{m}	2968_{m}, 2934_{m}	
ν(OH), carboxy		2717_{m}, 2604_{m} 2504_{m}		
ν_{as}(C═O)	$1603_{s,sh}$,$1575_{vs,b}$	1715_{s}, $1652_{vs,b}$, 1604_{s}, $1553_{s,b}$	1644_{vs}, 1588_{s}	1720_{s}, 1660_{vs}, $1620_{vs,sh}$, 1595_{vs}, 1560_{vs}
ν_{s}(C═O)	$1425_{s,\ sh}$, 1398_{vs}	1440_{m}, 1426_{m}, 1404_{s}, 1346_{m}	1398_{vs}	1430_{s}, 1410_{vs}
ν(Mo═O)	937_{w}, 897_{m}, 848_{s}, 826_{s}	933_{s}, $908_{s,sh}$, $895_{vs,b}$	950_{s}, 902_{s}	950_{vs}, 920_{vs}, 900_{vs}, $890_{vs,sh}$, 870_{m}, 850_{m}, 820_{m}, 800_{m}
$\nu_{as}(Mo{-}O_b{-}Mo)$		785_{vs}	780_{s}	$740_{vs,\ sh}$, $730_{vs,br}$
$\nu_{s}(Mo{-}O_b{-}Mo)$		690_{s}	715_{s}	$690_{vs,sh}$, 650_{vs}, 620_{vs}
ref	this work	this work	37	34

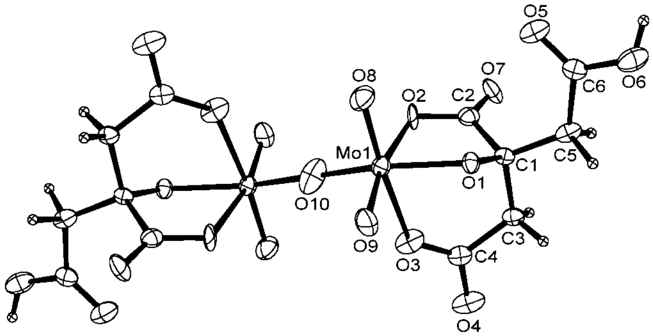


Figure 2. Perspective view of the anion structure of $K_4[(MoO_2)_2O(Hcit)_2]\cdot 4H_2O$. Thermal ellipsoids are drawn by ORTEP and represent 50% probability surfaces.

deprotonated citratomolybdate.[37,38] The two terminal oxo groups are in a *cis*-configuration. Each molybdenum atom is six-coordinate with approximately octahedral geometry. The terminal and bridging oxo groups adopt a *fac*-stereochemistry. The *trans* positions are occupied by a tridentate citrate.

As shown in Table 2, the Mo−O distances in citrato molybdates vary systematically. Mo═O is in the range 1.703(3)−1.759(3) Å, indicating that they are double bonds. The resulting O═Mo═O angles, 104.0(1), 103.3(1), 103.6(1), and 104.6(2)°, 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(10)−Mo bridging distance is 1.8766(4) Å. The Mo−O(alkoxy) bonds are slightly longer [2.052(2) and 1.958(3) Å], indicating the deprotonation of the hydroxyl group, and those to the α-carboxyl are longer [2.237(2) and 2.210(5) Å]. 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.[2,47]

The longest Mo−O(β-carboxyl) distances [2.411(3) Å] of monomer **1** show weak coordination of the β-carboxyl group to Mo(VI). This is much longer than those of dimeric **2** [2.276(3) Å], full deprotonated dimeric **3** [2.264(3) Å (a)], and tetrameric citratomolybdate **4** [2.318(5) Å (av)]. The significantly longer β-carboxylate−Mo distance is notable. In protein-bound FeMo-cofactor, only the alkoxy and α-carboxyl sites of homocitrate are coordinated to molybdenum. It suggests that coordinated β-carboxylate is probably much easier to replace by another ligand like histidine imidazole to form bidentate−citrato−Mo in FeMo-co biosynthesis.

It is believed molybdenum is taken up by organisms as MoO_4^{2-}, and a possible function of the tricarboxylic acid in the biosynthesis of the cofactor of nitrogenase is to mobilize molybdenum from the appropriate storage enzyme. Such structural changes would be essential for the assembly of the final cofactor cluster from an oxomolybdenum−homocitrate precursor.[12−14] Therefore, compound **1** may represent a close relevant form as a possible biomimetic precursor for the biosynthesis of FeMo-co, as well as a physiologically relevant form of metabolized molybdenum(VI) utilized in the assembly of FeMo-co.

The ^{1}H NMR spectrum of dimeric citrato molybdate **2** gives a sharp AB quartet for methylene protons of the coordinated citrate ligand, and the ^{1}H magnetic equivalence of the methylene groups gives only one unshifted ^{13}C NMR signal compared with KH_3cit at the same pH (3.4). [KH_3cit. ^{13}C NMR (D_2O; ppm): δ_C 177.6 $(CO_2)_\alpha$, 174.0 $(CO_2)_\beta$, 73.6 (≡CO), 43.0 ($=CH_2$). K_3-Hcit. ^{13}C NMR (D_2O; ppm): δ_C 182.2 $(CO_2)_\alpha$, 178.6 $(CO_2)_\beta$, 75.6 (≡CO), 45.4 ($=CH_2$).] This is similar to the NMR spectra of its deprotonated form $K_2Na_4[(MoO_2)_2O(cit)_2]\cdot 5H_2O$ and a dimeric citrato tungstate $Na_6[(WO_2)_2O(cit)_2]\cdot 11H_2O$.[37,48] The large low-field shift of some ^{13}C resonances in comparison with KH_3cit ions shows that both alkoxy (about δ 11) and α-carboxyl (about δ 8) groups are coordinated.

In the monomer form, the ^{1}H NMR spectrum of **1** shows two groups of sharp AB quartets in a 1:1 ratio, and the ^{13}C NMR signals of β-carboxyl and methylene groups are doubled. The large low-field shift of some ^{13}C resonances of **1** in comparison with K_3Hcit ions (see ^{13}C NMR data given earlier and ref 49) at the same pH (7.5) clearly shows that both alkoxy (about δ 6) and α-carboxyl (about δ 5) groups are coordinated, while β-carboxyl groups gives only a small shift ($\Delta\delta$ 1 ppm) of ^{13}C NMR signals, indicating that the bonding to molybdenum is weak.

The frequencies and assignments of selected IR absorption bands are given in Table 3. In the region between 1800 and 1400 cm^{-1} compound **2** gives a typical band of a nonbonded and undissociated carboxylic acid group at 1715 cm^{-1}. The bands between 1660 and 1540 cm^{-1} and between 1440 and 1340 cm^{-1} correspond to a bound carboxyl group ν_{asym} and ν_{sym} (CO_2M), respectively; this is in accord with a chelate ring and bridging by the citrato ligand. Loss of the proton in compounds **1** and **3** and the absence of a citrate bridge as in **1**−**3** reduce the number of bands and displace them to lower frequencies.

In the region between 1000 and 600 cm^{-1}, the complexes show several bands which might result from the presence of *cis*-dioxo cores in two different environments. The low-frequency symmetric MoO_2 stretching may be explained by intramolecular hydrogen bonding and the coordination with

---

(47) Schinderlin, H.; Kisker, H. C.; Schlessman, J. L.; Howard, J. B.; Rees, D. C. *Nature* **1997**, *387*, 370.

(48) Llopis, E.; Ramírez, J. A.; Doménech, A.; Cervilla, A. *J. Chem. Soc., Dalton Trans.* **1993**, 1121.

(49) Loewenstein, A.; Roberts, J. D. *J. Chem. Soc.* **1960**, *82*, 2705.

potassium cation. The band positions 890 and 840 cm^{-1} of an assumed *fac*-trioxo core were found to be like the other complexes with the MoO_3 core.[50] The strong IR band around 700 cm^{-1} observed only for the dimers or tetramer is attibuted to the $Mo-O_b-Mo$ bridges. Evidently, the β-carboxyl group of the citrate ion carries a proton in the structure of **2**; this is not only shown by the visibility of hydrogen atom in difference maps but also by the difference between the C−O distances of terminal carboxylate [O(5)−C(6), 1.203(6) Å; O(6)−C(6), 1.322(6) Å], as well as from the consideration of charge balance. The conclusion that full deprotonation of monomer **1** occurs can be drawn from the observed carbon−oxygen bond distances of β-carboxyl groups, which are equivalent [1.259(5), 1.251(5) Å]. This is further supported by IR bands found at $1603_{s,sh}$, $1575_{vs,b}$ and $1425_{s,sh}$, 1398_{vs} cm^{-1} corresponding to ν_{as} and ν_s (CO_2M) (bound carboxyl group), and the absence of IR bands between 1740 and 1700 cm^{-1}, indicating the presence of fully deprotonated carboxyl groups.

Acknowledgment. We thank the referee for his critical review. Financial support by the National Science Foundation of China (Grants 29503021 and 29933040) is gratefully acknowledged.

Supporting Information Available: Tables of X-ray crystal structure refinement data, positional and thermal parameters for $K_4[MoO_3(cit)]\cdot 2H_2O$ and $K_4[(MoO_2)_2O(Hcit)_2]\cdot 4H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990042S

---

(50) Stiefel, E. I. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: London, 1987, Vol. 3, p 1380.