Inorg. Chem. **2006**, *45*, 8447−8451

Syntheses, Spectroscopies and Structures of Molybdenum(VI) Complexes with Homocitrate

Zhao-Hui Zhou,* Shu-Ya Hou, Ze-Xing Cao, Khi-Rui Tsai, and Yuan L. Chow

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

Received July 29, 2006

Initial investigations into the possible role of homocitric acid in iron molybdenum cofactor (FeMo-co) of nitrogenase lead us to isolate and characterize two tetrameric molybdate(VI) species. The complexes $K_2(NH_4)_2[(MoO_2)_4O_3(R,S\text{-Hhomocit})_2]\cdot 6H_2O$ (**1**) and $K_5[(MoO_2)_4O_3(R,S\text{-Hhomocit})_2]Cl\cdot 5H_2O$ (**2**) (homocitric acid = H_4homocit, $C_7H_{10}O_7$) are prepared from the reactions of acyclic homocitric acid and molybdates, which represent the first synthetic structural examples of molybdenum homocitrate complexes. The homocitrate ligand trapped by tetranuclear molybdate coordinates to the molybdenum(VI) atom through α-alkoxy and α-, β-carboxy groups. The physical properties, structural parameters, and their possible biological relevances are discussed.

Introduction

Homocitric acid, which exists in the γ-lactone form in solution,[1−10] is an integral part of iron molybdenum cofactor (FeMo-co) in nitrogenase.[11−13] While the precise role of homocitrate in the dinitrogen reduction pathway is poorly understood, the discovery and elucidation of the interactions between molybdenum and this tricarboxylic acid are needed in nitrogenase biochemistry.[14,15] Homocitrate is believed to be a key factor during biological nitrogen fixation as contrasted to the other alternative hydroxycarboxylates, such as citrate and malate, which greatly reduce the activities of the dinitrogen reduction.[16−18] The homocitrato entity in FeMo-co uses its oxygen atoms of α-alkoxy and α-carboxy groups to chelate the molybdenum atom, forming a giant cluster $MoFe_7S_9X$(S-cys)(N-His)(homocit).[19−27] It is proposed that homocitrate may form an intramolecular hydrogen bond with the imidazole group of histidine.[14,28] It may facilitate the binding of dinitrogen molecule through the dissociation

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

(1) Rodríguez, G. H.; Biellmann, J. F. *J. Org. Chem.* **1996**, *61*, 1822−1824.
(2) Ancliff, R. A.; Russell, A. T.; Sanderson, A. J. *Tetrahedron Asym.* **1997**, *8*, 3379−3382.
(3) Li, Z. C.; Xu, J. Q. *Molecules* **1998**, *3*, 31−34.
(4) Ma, G. X.; Palmer, D. R. J. *Tetrahedron Lett.* **2000**, *41*, 9209−9212.
(5) Paju, A.; Kanger, T.; Pehk, T.; Eek, M.; Lopp, M. *Tetrahedron* **2004**, *60*, 9081−9084.
(6) Tavassoli, A.; Duffy, J. E. S.; Young, D. W. *Tetrahedron Lett.* **2005**, *46*, 2093−2096.
(7) Xu, P. F.; Matsumoto, T.; Ohki, Y.; Tatsumi, K. *Tetrahedron Lett.* **2005**, *46*, 3815−3818.
(8) Huang, P. Q.; Li, Z. Y. *Tetrahedron Asym.* **2005**, *46*, 2093−2096.
(9) Jia, Y. H.; Palmer, D. R. J.; Quail, J. W. *Acta Crystallogr.* **2005**, *E61*, o4034−o4036.
(10) Tavassoli, A.; Duffy, J. E. S.; Young, D. W. *Org. Biomol. Chem.* **2006**, *4*, 569−580.
(11) Shah, V. K.; Brill, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 3249−3253.
(12) Hoover, T. R.; Robertson, A. D.; Cerny, R. L.; Hayes, R. N.; Imperial, J.; Shah, V. K.; Ludden, P. W. *Nature (London)* **1987**, *329*, 855−857.
(13) Hoover, T. R.; Imperial, J.; Ludden, P. W.; Shah, V. K. *Biochemistry* **1989**, *28*, 2768−2771.
(14) Grönberg, K. L. C.; Gormal, C. A.; Durrant, M. C.; Smith, B. E.; Henderson, R. A. *J. Am. Chem. Soc.* **1998**, *120*, 10613−10621.
(15) Burgess, B. K.; Lowe, D. J. *Chem. Rev.* **1996**, *96*, 2983−3011.
(16) Ludden, P. W.; Shah, V. K.; Roberts, G. P.; Homer, M.; Allen, R.; Paustian, T.; Roll, J.; Chatterjee, R.; Madden, M.; Allen, J. In *Molybdenm Enzymes, Cofactors and Model Systems*; Stiefel, E. I., Coucouvanis, D., Newton W. E., Eds.; American Chemical Society: Washington, DC, 1993; pp 196−215.
(17) Mayer, S. M.; Gormal, C. A.; Smith, B. E.; Lawson, D. M. *J. Biol. Chem.* **2002**, *277*, 35263−35266.
(18) Palmer, J. G.; Doemeny, P. A.; Schrauzer, G. N. *Z. Naturforsch.* **2001**, *56b*, 386-393.
(19) Kim, J.; Rees, D. C. *Science* **1992**, *257*, 1677−1682.
(20) Chan, M. K.; Kim, J.; Rees, D. C. *Science* **1993**, *260*, 792−794.
(21) Bolin, J. T.; Ronco, A. E.; Morgan, T. V.; Mortenson, L. E.; Xuong, N. H. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 1078−1082.
(22) Howard, J. B.; Rees, D. C. *Chem. Rev.* **1996**, *96*, 2965−2982.
(23) Peters, J. W.; Stowell, M. H. B.; Soltis, S. M.; Finnegan, M. G.; Johnson, M. K.; Rees, D. C. *Biochemistry* **1997**, *36*, 1181−1187.
(24) Schindelin, H.; Kisker, C.; Schlessman, J. L.; Howard, J. B.; Rees, D. C. *Nature (London)* **1997**, *387*, 370−376.
(25) Mayer, S. M.; Lawson, D. M.; Gormal, C. A.; Roe, S. M.; Smith, B. E. *J. Mol. Biol.* **1999**, *292*, 871−891.
(26) Einsle, O.; Tezcan, F. A.; Andrade, S. L. A.; Schmid, B.; Yoshida, M.; Howard, J. B.; Rees, D. C. *Science* **2002**, *297*, 1696−1700.
(27) Yang, T. C.; Maeser, N. K.; Laryukhin, M.; Lee, H. I.; Dean, D. R.; Seefeldt, L. C.; Hoffman, B. M. *J. Am. Chem. Soc.* **2005**, *127*, 12804−12805.

10.1021/ic061429f CCC: $33.50
Published on Web 09/07/2006

Table 1. ^{13}C NMR Spectral Data (in ppm) of Complexes **1** and **2** and Homocitrato γ-Lactone Acid[a]

compound	(≡CO)	$(CO_2)_\alpha$	$(CO_2)_\beta$	$(CO_2)_\gamma$	(=CH_2)
homocitrato γ-lactone acid	83.5	176.5	172.5	170.5	41.7, 31.9, 28.3
1	90.0(6.5)	186.5(10.0)	181.8(9.3)	180.7(10.2)	47.7(6.0), 37.1(5.2) 31.7(3.4)
2	90.2(6.7)	186.6(10.1)	182.0(9.5)	181.1(10.6)	47.8(6.1), 37.3(5.4), 31.9(3.6)

[a] $\Delta\delta$ values are given in brackets.

of either the bound α-carboxy or α-alkoxy group from the molybdenum atom.[29−34] In vitro biosynthesis experiments lacking homocitrate show no ^{99}Mo incorporation in any proteins other than the Mo-storage enzyme.[35]

However, the isolation of molybdenum homocitrate complexes in a crystalline form suitable for X-ray structural analysis has been proved to be difficult,[36] leaving the interaction between molybdate and homocitrate poorly understood and requiring further attention. Taking into consideration the syntheses of homocitrato lactone and homocitrato vanadate,[3,37] two yet undocumented tetrameric homocitrato molybdates(VI), $[(MoO_2)_4O_3(R,S\text{-Hhomocit})_2]^{4-}$, have been reported.

Experimental Section

All experiments were carried out in the open air. All chemicals were analytical reagents and used without further purification.

Preparation of $K_2(NH_4)_2[(MoO_2)_4O_3(R,S\text{-Hhomocit})_2]\cdot 6H_2O$ (1) and $K_5[(MoO_2)_4O_3(R,S\text{-Hhomocit})_2]Cl\cdot 5H_2O$ (2). A prepared racemic homocitrato γ-lactone acid[3] (0.14 g, 0.7 mmol) was dissolved in a minimal amount of water. The pH value was adjusted by potassium hydroxide to 11 to generate the acyclic homocitrate as monitored with HPLC. After hydrolysis, ammonium paramolybdate (0.26 g, 0.2 mmol) was added in small portions over a few minutes. Upon cooling in an ice bath for 15 min, the pH value of the solution was adjusted to 2 to induce complex formation. The salts of chloride were filtrated with precipitation. Complex **1** was formed after sitting at room temperature for a few days. Yield: 0.49 g (56%). Found (calcd for $C_{14}H_{34}N_2O_{31}K_2Mo_4$): C, 14.0 (14.1); H, 3.0 (2.9). IR (KBr, cm^{-1}): $\nu_{as(COOH)}$ 1702_s, $\nu_{as(COO)}$ 1629_s, 1578_s; $\nu_{s(COO)}$ 1422_s, 1392_{vs}; $\nu_{s(Mo=O)}$ 926_s, 865_{vs} cm^{-1}.^1H NMR (500 MHz, D_2O): δ_H 2.937 (d, J = 18.0 Hz, CH_2), 2.860 (d, J = 18.5 Hz, CH_2), 2.511−2.478, 2.378−2.340, 2.169−2.123, 1.892−1.860 (m, CH_2).^{13}C NMR in D_2O: see Table 1.

The same procedure was applied to prepare complex **2**, and potassium molybdate (0.95 g, 4.0 mmol) was allowed to react with homocitric acid (0.48 g, 2.0 mmol). Yield 0.45 g (34%). Found (calcd for $C_{14}H_{24}O_{30}ClK_5Mo_4$): C, 12.6 (13.1); H, 2.0 (1.9). IR (KBr, cm^{-1}): $\nu_{as(COOH)}$ 1716_s, $\nu_{as(COO)}$ 1638_{vs}; $\nu_{s(COO)}$ 1422_s, 1401_{vs}; $\nu_{s(Mo=O)}$ 920_s, 892_{vs} cm^{-1}. ^1H NMR (500 MHz, D_2O): δ_H 2.81−2.99, 2.60−2.76, 2.32−2.42, 2.267, 2.12−2.24, 1.84−1.94 (CH_2). ^{13}C NMR in D_2O: see Table 1.

Table 2. Crystal Data and Structure Refinements for $K_2(NH_4)_2[(MoO_2)_4O_3(R,S\text{−Hhomo})_2]\cdot 6H_2O$ (**1**) and $K_5[(MoO_2)_4O_3(R,S\text{-Hhomo})_2]Cl\cdot 5H_2O$ (**2**)

empirical formula	$C_{14}H_{34}N_2O_{31}K_2Mo_4$	$C_{14}H_{24}O_{30}ClK_5Mo_4$
fw	1188.39	1287.04
temp (°C)	23	
radiation	Mo Kα (λ = 0.7107 Å)	
cryst color	colorless	
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
formula units/ unit cell	4	2
diffractometer	Smart Apex CCD	
crystal size (mm^3)	0.35 × 0.17 × 0.14	0.28 × 0.16 × 0.07
cell constants		
a (Å)	11.6965(5)	11.1529(4)
b (Å)	15.2089(6)	12.1790(4)
c (Å)	22.1252(9)	15.2720(5)
α (°)		86.640(1)
β (°)	101.424(1)	72.297(1)
γ (°)		67.387(1)
V ($Å^3$)	3857.9(3)	1820.2(1)
D_{calc} ($g\cdot cm^{-3}$)	2.046	2.348
abs coeff (mm^{-1})	1.589	2.096
F000	2344	1256
θ range (deg)	1.64−28.37	1.40−25.00
reflns collected/ unique	44 039/9215	17 542/6394
	[R(int) = 0.0837]	[R(int) = 0.1224]
data/restraints/params	9215/34/568	6394/17/523
GOF on F^2	0.959	1.029
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0436	R1 = 0.0375
	wR2 = 0.1398	wR2 = 0.0941
R indices (all data)[a]	R1 = 0.0481	R1 = 0.0416
	wR2 = 0.1434	wR2 = 0.0962
largest diff. peak and hole ($e\cdot Å^{-3}$)	1.413 and −2.147	1.310 and −0.776

[a] $R1 = \sum||F_o| - |F_c||/\sum(|F_o|)$, $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates using a Nicolet 360 FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded in D_2O on a Varian UNITY 500 NMR spectrometer or a Bruker AV400 NMR spectrometers using DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as an internal reference. Elemental analyses were performed using an EA 1110 element analyzer.

X-ray Structure Determination. Diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation at 296 K. The structures were solved by SHELXS-97 and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all of the non-hydrogen atoms. Hydrogen atoms were located from a difference Fourier map. All calculations were performed on a microcomputer using SHELXL-97 and SHELXS-97 programs.[38,39] Crystallographic data for homocitrato molybdates **1** and **2** are summarized in Table

(28) Tsai, K. R.; Wan, H. L. *J. Clust. Sci.* **1995**, *6*, 485−501.
(29) Leigh, G. J. *Science* **2003**, *301*, 55−56.
(30) Leigh, G. J. *Science* **1995**, *268*, 827−828.
(31) Holland, P. L. In *Comprehensive Coordination Chemistry II*; McCleverty J. A., Meyer T. J., Eds.; Elsevier Paragamon: New York, 2004; Vol. 8, (Que, L., Tolman, W. B., Eds.; pp 586−591.
(32) Durrant, M. C. *Biochemistry* **2002**, *41*, 13934−13945.
(33) Seefeldt, L. C.; Dance, I. G.; Dean, D. R. *Biochemistry* **2004**, *43*, 1401−1409.
(34) Zhou, Z. H.; Zhao, H.; Tsai, K. R. *J. Inorg. Biochem.* **2004**, *98*, 1795−1802.
(35) Allen, R. M.; Roll, J. T.; Rangaraj, P.; Shah, V. K.; Roberts, G. P.; Ludden, P. W. *J. Biol. Chem.* **1999**, *274*, 15869−15874.
(36) Li, D. M.; Xing, Y. H.; Li, Z. C.; Xu, J. Q.; Song, W. B.; Wang, T. G.; Yang, G. D.; Hu, N. H.; Jia, H. Q.; Zhang, H. M. *J. Inorg. Biochem.* **2005**, *99*, 1602−1610.
(37) Wright, D. W.; Chang, R. T.; Mandal, S. K.; Armstrong, W. H.; Orme-Johnson, W. H. *J. Biol. Inorg. Chem.* **1996**, *1*, 143−151.
(38) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **1** and **2**

	1	**2**		**1**	**2**
Mo(1)−O(1)$_{\alpha-\text{alkoxy}}$	1.929(4)	1.947(3)	Mo(1)−O(2)$_{\alpha-\text{carboxy}}$	2.194(4)	2.193(3)
Mo(1)−O(4)$_{\beta-\text{carboxy}}$	2.327(4)	2.312(3)	Mo(1)−O(8)	1.708(4)	1.701(3)
Mo(1)−O(9)	1.731(4)	1.701(3)	Mo(1)−O(10)	1.879(4)	1.920(3)
Mo(2)−O(4)$_{\beta-\text{carboxy}}$	2.288(4)	2.265(3)	Mo(2)−O(10)	1.950(4)	1.948(3)
Mo(2)−O(15)$_{\beta-\text{carboxy}}$	2.316(4)	2.332(3)	Mo(2)−O(18)	1.701(5)	1.718(3)
Mo(2)−O(19)	1.696(5)	1.701(3)	Mo(2)−O(20)	1.910(4)	1.897(3)
Mo(3)−O(5)$_{\beta-\text{carboxy}}$	2.318(4)	2.262(3)	Mo(3)−O(14)$_{\beta-\text{carboxy}}$	2.292(4)	2.313(3)
Mo(3)−O(20)	1.886(4)	1.929(3)	Mo(3)−O(21)	1.974(4)	1.928(3)
Mo(3)−O(22)	1.698(5)	1.694(3)	Mo(3)−O(23)	1.706(5)	1.706(3)
Mo(4)−O(11)$_{\alpha-\text{alkoxy}}$	1.955(4)	1.931(3)	Mo(4)−O(12) $_{\alpha-\text{carboxy}}$	2.181(4)	2.200(3)
Mo(4)−O(14)$_{\beta-\text{carboxy}}$	2.317(4)	2.296(3)	Mo(4)−O(21)	1.871(4)	1.903(3)
Mo(4)−O(24)	1.707(4)	1.691(3)	Mo(4)−O(25)	1.727(4)	1.728(3)
C(7)−O(6)	1.316(8)	1.34(1)	C(7)−O(7)	1.222(8)	1.20(1)
O(1)−Mo(1)−O(2)	74.7(2)	75.2(1)	O(1)−Mo(1)−O(4)	77.9(1)	77.6(1)
O(1)−Mo(1)−O(8)	106.8(2)	91.5(1)	O(1)−Mo(1)−O(9)	93.5(2)	106.9(2)
O(1)−Mo(1)−O(10)	145.8(2)	146.4(1)	O(2)−Mo(1)−O(4)	77.0(1)	76.5(1)
O(2)−Mo(1)−O(8)	92.2(2)	163.7(1)	O(2)−Mo(1)−O(9)	163.3(2)	89.1(2)
O(2)−Mo(1)−O(10)	83.6(2)	86.2(1)	O(4)−Mo(1)−O(8)	166.8(2)	91.7(1)
O(4)−Mo(1)−O(9)	89.1(2)	163.4(1)	O(4)−Mo(1)−O(10)	71.6(2)	70.9(1)
O(8)−Mo(1)−O(9)	102.7(2)	104.0(2)	O(8)−Mo(1)−O(10)	99.9(2)	100.6(2)
O(9)−Mo(1)−O(10)	101.0(2)	100.5(1)	O(4)−Mo(2)−O(10)	71.4(1)	71.5(1)
O(4)−Mo(2)−O(15)	78.8(1)	80.3(1)	O(4)−Mo(2)−O(18)	89.0(2)	163.0(1)
O(4)−Mo(2)−O(19)	164.3(2)	92.1(1)	O(4)−Mo(2)−O(20)	82.7(2)	82.8(1)
O(10)−Mo(2)−O(15)	77.8(2)	77.1(1)	O(10)−Mo(2)−O(18)	98.0(2)	98.8(1)
O(10)−Mo(2)−O(19)	98.8(2)	98.9(1)	O(10)−Mo(2)−O(20)	149.5(2)	148.9(1)
O(15)−Mo(2)−O(18)	167.9(2)	83.9(1)	O(15)−Mo(2)−O(19)	87.3(2)	172.1(1)
O(15)−Mo(2)−O(20)	81.6(2)	81.8(1)	O(18)−Mo(2)−O(19)	104.7(3)	103.5(2)
O(18)−Mo(2)−O(20)	97.4(2)	101.3(1)	O(19)−Mo(2)−O(20)	102.5(2)	99.2(1)
O(5)−Mo(3)−O(14)	79.3(1)	79.6(1)	O(5)−Mo(3)−O(20)	81.2(2)	81.6(1)
O(5)−Mo(3)−O(21)	76.5(2)	79.7(1)	O(5)−Mo(3)−O(22)	169.4(2)	88.4(1)
O(5)−Mo(3)−O(23)	86.4(2)	168.2(1)	O(14)−Mo(3)−O(20)	83.5(2)	83.3(1)
O(14)−Mo(3)−O(21)	70.7(1)	71.5(1)	O(14)−Mo(3)−O(22)	90.3(2)	166.5(1)
O(14)−Mo(3)−O(23)	163.7(2)	88.9(1)	O(20)−Mo(3)−O(21)	148.4(2)	150.9(1)
O(20)−Mo(3)−O(22)	99.6(2)	101.1(1)	O(20)−Mo(3)−O(23)	102.1(2)	94.7(1)
O(21)−Mo(3)−O(22)	98.5(2)	100.5(1)	O(21)−Mo(3)−O(23)	98.5(2)	99.1(1)
O(22)−Mo(3)−O(23)	103.6(2)	103.4(2)	O(11)−Mo(4)−O(12)	74.4(2)	75.0(1)
O(11)−Mo(4)−O(14)	77.2(1)	79.0 (1)	O(11)−Mo(4)−O(21)	146.2(2)	147.2(1)
O(11)−Mo(4)−O(24)	106.0(2)	104.7(1)	O(11)−Mo(4)−O(25)	90.4(2)	94.0(1)
O(12)−Mo(4)−O(14)	77.3(2)	76.6(1)	O(12)−Mo(4)−O(21)	86.0(2)	83.1 (1)
O(12)−Mo(4)−O(24)	90.0(2)	91.3(1)	O(12)−Mo(4)−O(25)	162.2(2)	163.3(1)
O(14)−Mo(4)−O(21)	71.7(2)	72.3 (1)	O(14)−Mo(4)−O(24)	165.7(2)	166.1(2)
O(14)−Mo(4)−O(25)	90.6(2)	89.2(1)	O(21)−Mo(4)−O(24)	101.1(2)	99.8(1)
O(21)−Mo(4)−O(25)	102.7(2)	101.1(1)	O(24)−Mo(4)−O(25)	103.2(2)	103.7(2)

2. The large differential peaks and holes may be related to the heavy molybdenum atom. Selected bond distances and angles are given in Table 3.

Results and Discussions

^{13}C NMR chemical shifts observed on complex **2** are shown in Figure 1. This is a clear indication for the coordination of the α-alkoxy, α-carboxy, and β-carboxy groups in the complex. In comparison with free ligand under comparable conditions, the title complexes show generally large downfield shifts of the corresponding ^{13}C resonance as in Table 1. For example, both α- and β-carboxy carbons show large downfield shifts of $\Delta\delta$ 10.0, 9.3 ppm for **1** and 10.1, 9.5 ppm for **2**, respectively, in each case arising from the coordination. However, ^{13}C resonance shifts of γ-carboxylic acid in the open chain of complexes **1** and **2** cannot be compared directly with free homocitric acid. The later forms a five-membered ring lactone by γ-carboxy and α-hydroxy groups. The α-alkoxy carbons have somewhat small downfield shifts $\Delta\delta$ of 6.5 and 6.7 ppm for **1** and **2**, respectively. This is also related to the formation of lactone. Other peaks also showed downfield shifts in general for **1** and **2** and can be easily assigned to the remaining methylene carbons. The ^{13}C NMR spectra of the two complexes in solution show no obvious decomposition for 1 week. The tetrameric species are believed to be stable in solution.

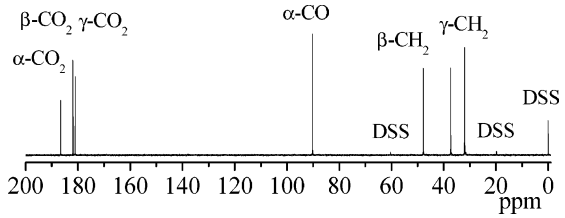

Figure 1. ^{13}C NMR spectra of molybdate(VI) $K_5[(MoO_2)_4O_3(R,S\text{-Hhomo})_2]Cl\cdot 5H_2O$ (**2**).

The FT-infared spectra of the two title complexes display the characteristic features of the coordinated homocitrato ligand and oxo groups. The antisymmetric stretching carboxy

(39) Sheldrick, G. M. *SHELXS-97 and SHELXL-97, Programs for Solution and Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.
(40) Alcock, N. W.; Dudek, M.; Gryboœ, R.; Hodorwicz, E.; Kanas, A.; Samotus, A. *J. Chem. Soc., Dalton. Trans.* **1990**, 707−711.
(41) Nassimbeni, L. R.; Niven, M. L.; Cruywagen, J. J.; Heyns, J. B. B. *J. Crystallogr. Spectrosc. Res.* **1987**, *17*, 373−382.

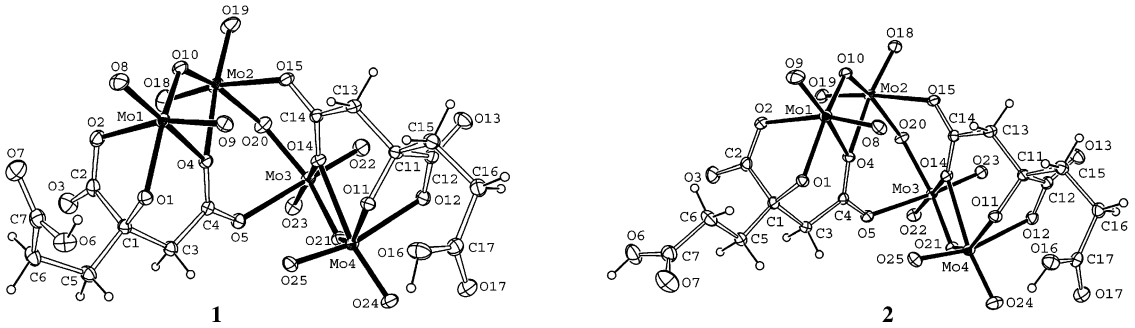

Figure 2. Perspective view of the anion structures of $K_2(NH_4)_2[(MoO_2)_4O_3(R,S\text{-Hhomo})_2]\cdot 6H_2O$ (**1**, left) and $K_5[(MoO_2)_4O_3(R,S\text{-Hhomo})_2]Cl\cdot 5H_2O$ (**2**, right) in $\Lambda_R\Lambda\Lambda\Lambda_R$ configurations.

Table 4. Mo−O Distances (Å) and Absolute Configuration Assignments in Homocitrato and Citrato Molybdates

complex	Mo−$O_{\alpha-\text{alkoxy}}$	Mo−$O_{\alpha-\text{carboxy}}$	Mo−$O_{\beta-\text{carboxy}}$	configuration assignments	ref
$K_2(NH_4)_2[(MoO_2)_4O_3(R,S\text{-Hhomocit})_2]\cdot 6H_2O$ (**1**)	1.929(4), 1.955(4)	2.194(4), 2.181(4)	$2.311_{av}(4)$, $2.309_{av}(4)$	$\Lambda_R\Lambda\Lambda\Lambda_R/\Delta_S\Delta\Delta\Delta_S$	this work
$K_5[(MoO_2)_4O_3(R,S\text{-Hhomocit})_2]Cl\cdot 5H_2O$ (**2**)	1.947(3) 1.931(3)	2.193(3), 2.200(3)	$2.280_{av}(3)$, $2.314_{av}(3)$		
$K_4[(MoO_2)_4O_3(Hcit)_2]\cdot 5H_2O$	1.976(5), 1.968(5)	2.185(5), 2.211(5)	$2.310_{av}(5)$, $2.357_{av}(5)$		[40]
$[Me_3N(CH_2)_6NMe_3]_2[(MoO_2)_4O_3(Hcit)_2]\cdot 12H_2O$	1.970(6)	2.217(6)	$2.328_{av}(5)$		[41]
$MoFe_7S_9X$(S-cys)(N-His)(homocit)					
Azotobacter vinelandii (*Av*1, 1992)	1.996	2.167		Δ_R	[19]
Clostridium pasturianum (*Cp*1)	2.035	2.206			[20]
Klebsiella pneumoniae (*Kp*1)	$2.35(2)_{re}$, $2.35(2)_{ox}$	$2.29(1)_{re}$, $2.29(2)_{ox}$			[25]
Azotobacter vinelandii (*Av*1, 2002)	2.212	2.162			[26]

vibrations of the two complexes all shift to lower values with respect to that of uncoordinated ligand. The bands at 1440−1390 cm^{-1} correspond to symmetric stretching vibrations, $\nu_{s(COO)}$, for the two compounds. The remaining ν(COOH) of γ-carboxylic acidic group appears at 1702 cm^{-1} for **1** and 1716 cm^{-1} for **2**. In the region around 900 cm^{-1}, both complexes show several bands that result from the presence of *cis*-dioxo molybdenum.

The ORTEP plots of the anions of complexes **1** and **2** are shown in Figure 2. The crystal structure of **1** comprises potassium cations, ammonium cations, lattice water molecules, and the tetrameric homocitrato molybdate(VI) anion. Each Mo atom contains a *cis*-dioxo-MoO_2 unit and exists in an approximately octahedral geometry. The two homocitrate ligands coordinate in a similar fashion with the molybdenum center. One homocitrate ligand coordinates to Mo1 with O1 of α-alkoxy, O2 of α-carboxy, and O4 of β-carboxy groups, as well as Mo2 and Mo3 with O4 and O5 of the β-carboxy group, respectively, leaving the γ-carboxylic acidic group free. The charge balance and the difference of C−O distances suggest that this γ-carboxy group is protonated. Thus, homocitrates act as tridentate ligands in this complex.

The structure analyses of complex **2** reveal that it has a similar anion with **1** except for the conformation of the pendant $CH_2CH_2CO_2$ arm of homocitrate. The latter is sufficiently long and flexible that its γ-carboxy group can orient differently in the two complexes. In complex **1**, the γ-carboxy group (C7) curls back toward the α-carboxy group (C2). However, it keeps away from α-carboxy group in complex **2**. The difference of the conformation may be caused by the cationic partners.

It is useful to examine some bond distances in Table 4 to evaluate the Mo−O bond strength. The α- and β-carboxy oxygen atoms of homocitrate orient opposite to the *cis*-dioxo molybdenum core in both complexes. Two sets of Mo−O (β-carboxy) distances in the two homocitrate complexes are averaged to give 2.311(4) and 2.309(4) Å for **1** and 2.280(3) and 2.314(3) Å for **2**. These figures are longer than the Mo−O (α-carboxy) bond distances of >2.20 Å in both complexes. That might arise from the strong trans influence of the dioxo groups. As shown in Table 3, the Mo−O (α-alkoxy) distances are shorter, implying the deprotonation of α-hydroxy group in homocitrate. The bond strength of Mo−O in homocitrate to molybdenum is in the order of α-alkoxy > α-carboxy > β-carboxy > γ-carboxy groups. The strong coordination of α-alkoxy and α-carboxy groups to molybdenum has been found in protein-bound FeMo-co.[25,26]

For comparison, some related Mo−O bond distances and absolute configurations of citrato and homocitrato molybdates are listed in Table 4. In tetranuclear citrato molybdates, the bond distances of α-alkoxy to molybdenum are shorter than those of α-carboxy group to molybdenum of complexes **1** and **2**. However, the difference of Mo−O (α-carboxy) and Mo−O (β-carboxy) distances is smaller, which demonstrates a β-carboxy group has comparable coordination ability. In this point, this implies the possible substitution of imidazole group by β-carboxy group of homocitrate in NMF extraction of the cofactor of nitrogenase.[14]

The reaction of a racemic mixture of homocitrate or citrate results in the isolation of racemic mixture of Λ- and Δ-complexes. The chiral configuration of molybdenum center in wild-type FeMo-co is Δ, which might be induced by the coordination of the chiral *R*-homocitrate. However, recent crystallographic structural analysis shows that (FeMo-co)* from a *nifV* mutant of *Klebsiella pneumoniae*, although achiral citrate acts as the ligand to the molybdenum, also possesses the same molybdenum configuration with the wild-

type FeMo-co. This is the further manifestation that the asymmetric coordination environment can induce chiral effects in the biosynthesis of FeMo-co.

Acknowledgment. Financially support by the Ministry of Science and Technology (001CB108906) and the National Science Foundation of China (20571061, 20021002, 20423002) is gratefully acknowledged. We thank the reviewers for their very constructive suggestions to update the paper.

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

IC061429F