DALTON
FULL PAPER

A new heterometalate anion $[GdMo_6(CH_3CHOCOO)_6O_{15}]^{3-}$ with a nine-coordinate gadolinium encapsulated at the center

Chuan-De Wu, Can-Zhong Lu,* Jia-Cheng Liu, Hong-Hui Zhuang and Jin-Shun Huang*

The State Key Laboratory of Structural Chemistry,
Fujian Institute of Research on the Structure of Matter, the Chinese Academy of Sciences,
Fuzhou, Fujian 350002, P. R. China. E-mail: czlu@ms.fjirsm.ac.cn

Received 30th March 2001, Accepted 11th September 2001
First published as an Advance Article on the web 15th October 2001

The reaction of an acetonitrile solution of ammonium molybdate with gadolinium chloride in the presence of lactic acid gives rise to the formation of a spherical cluster anion containing six Mo atoms with a Gd(III) encapsulated at the center, $[GdMo_6(CH_3CHOCOO)_6O_{15}]^{3-}$ **1**, which is further linked to a three-dimensional network by ammonium ions *via* hydrogen bonding. The magnetic properties of the complex have been studied by measuring its magnetic susceptibility at various temperatures in the 5–300 K range. The results are consistent with room temperature EPR data.

Introduction

Polyoxometalates are of a rich class of inorganic compounds with a remarkable degree of molecular and electronic tunability, which has attracted great attention from researchers in many fields, such as catalysis, materials science, medicine and magnetochemistry.[1–4] Although various preparative methods have been proposed in order to obtain such polynuclear complexes, a “rational” synthetic approach to new compounds is still one of the major challenges in polyoxometalate chemistry.

Since rare earth elements are known to be highly oxophilic and many oxoanions have oxygen-rich compositions, such as molybdates, tungstates and vanadates, we initiated a project to synthesise new polyoxometalates by reacting rare earth metal salts with conventional oxometalates in the presence of some chelating organic ligands. For example, such complexes of amino acids have been widely studied.[5–7] Lactic acid has two types of coordinating oxygen atoms and can act as a variously bridging ligand to form interesting complexes.[8] Furthermore, as a weak acid, it prevents the production of lanthanide oxometalate powder sediment and acidifies the reaction solution to prompt the formation of the polyoxometalate. Compared to the amino group of amino acids, the hydroxyl group in lactic acid is more favorable for the synthesis of the above-mentioned oxophilic heterometal complexes, however, studies on the complexes of lactic acid are far less common. Taking advantage of the properties of lactic acid as a ligand, the syntheses of heterometal complexes have been attempted. Here, we report one of our recent results, as embodied by the cluster anion $[GdMo_6(CH_3CHOCOO)_6O_{15}]^{3-}$ **1**.

Experimental

Materials and methods

All chemicals were of reagent grade and were used as received. Elemental analyses were performed with a Vario EL *III* CHNOS elemental analyzer. Infrared spectra were recorded on a FTS-40 spectrophotometer using pressed KBr pellets. The FT-Raman spectrum was measured on a Nicolet Raman 910 Fourier transform laser-Raman spectrometer, again using pressed KBr pellets, and EPR spectroscopy was performed on a Bruker ER 420 instrument. Variable temperature magnetic susceptibilities in the temperature range 5–300 K were measured on a model CF-1 superconducting extracting sample magnetometer with the powdered sample kept in the capsule for weighing.

Synthesis

A solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.9 g, 0.73 mmol) and $GdCl_3$ (0.6 g, 2.3 mmol) in 50 ml CH_3CN in the presence of lactic acid (8 ml) was stirred for about three hours, giving a light-brown reaction mixture, which was then filtered. Colorless crystals of the ammonium salt of **1**, formed after four days, were filtered off, washed with ethanol and diethyl ether, and finally dried in air. Yield: 0.96 g (72.5% based on Mo). Anal. calc. for the ammonium salt of **1**: C, 13.78; H, 2.31; N, 2.68%. Found: C, 13.95; H, 2.36; N, 2.62%. IR (solid KBr pellet, ν/cm^{-1}): 1662(vs), 1444(s), 1410(s), 1363(s), 1336(s), 1288(s), 1093(s), 1055(s), 951(s), 908(s), 872(m), 764(m), 690(vs), 615(s), 546(s), 486(m), 449(m). FT-Raman (solid, $\lambda = 1064$ nm, ν/cm^{-1}): 1444(m), 1295(m), 1093(m), 948(vs), 929(sh), 906(s), 871(m), 678(s), 622(m), 547(s), 489(w), 460(w), 397(s), 368(m) 254(s), 173(s).

Crystal structure determination

The determination of the unit cell and the data collection for the ammonium salt of **1** were performed on a Siemens SMART CCD, and the data were collected using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K in the range $2.10 < \theta < 21.48°$, and were corrected with the SADABS program.[9] A total of 7392 data were collected, of which 798 ($R_{int} = 0.0660$) unique reflections were used. The structure was solved by direct methods using the program SHELXS-97[10] and refined by full-matrix least-squares methods with the SHELXL-97[11] program package. All atoms except hydrogen atoms were refined anisotropically. Crystallographic data are summarized in Table 1, and selected bond lengths and angles are listed in Table 2.

CCDC reference number 157032.

See http://www.rsc.org/suppdata/dt/b1/b102926f/ for crystallographic data in CIF or other electronic format.

DOI: 10.1039/b102926f

Table 1 Crystal data and structure refinement for $(NH_4)_3[GdMo_6(CH_3CHOCOO)_6O_{15}]$

Compound	$(NH_4)_3[GdMo_6(CH_3CHOCOO)_6O_{15}]$
Empirical formula	$C_{18}H_{36}GdMo_6N_3O_{33}$
Formula weight	1555.39
Crystal size	0.18 × 0.16 × 0.15 mm^3
Crystal color	Colorless
Crystal system	Trigonal
Space group	$R\bar{3}c$
a/Å	16.344(4)
c/Å	26.728(7)
V/Å^3	6183(3)
Z	6
Calculated density/Mg m^{-3}	2.506
$F(000)$	4470
μ/mm^{-1}	3.461
Reflections collected/unique	7392/798 [R(int) = 0.0660]
Parameters refined	95
Goodness-of-fit on F^2	0.846
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0302$, $wR2 = 0.0949$
R indices (all data)	$R1 = 0.0486$, $wR2 = 0.1107$
Max., Min. $\Delta\rho$/e Å^{-3}	0.759, −0.436

Table 2 Selected bond lengths [Å] and angles [°] for **1** [a]

Gd(1)–O(5)	2.38(1)	O(1)–Mo(1)–O(3)	100.0(3)
Gd(1)–O(6)	2.43(1)	O(2)–Mo(1)–O(3)	98.0(3)
Mo(1)–O(1)	1.69(1)	O(1)–Mo(1)–O(6)	98.5(3)
Mo(1)–O(2)	1.70(1)	O(2)–Mo(1)–O(6)	103.3(3)
Mo(1)–O(3)	1.92(1)	O(3)–Mo(1)–O(6)	147.2(3)
Mo(1)–O(6)	1.94(3)	O(1)–Mo(1)–O(5)	97.1(3)
Mo(1)–O(5)	2.19(1)	O(2)–Mo(1)–O(5)	157.9(3)
Mo(1)–O(4)^{i}	2.48(1)	O(3)–Mo(1)–O(5)	74.4(2)
O(1)–N(1)	2.81(1)	O(6)–Mo(1)–O(5)	76.6(3)
O(3)–C(1)	1.43(1)	O(1)–Mo(1)–O(4)^{i}	173.0(3)
O(4)–C(3)	1.20(1)	O(2)–Mo(1)–O(4)^{i}	82.3(3)
O(5)–C(3)	1.31(1)	O(3)–Mo(1)–O(4)^{i}	77.7(3)
O(5)^{i}–Gd(1)–O(5)	79.1(2)	O(6)–Mo(1)–O(4)^{i}	80.64(17)
O(5)–Gd(1)–O(5)^{iii}	129.0(3)	O(5)–Mo(1)–O(4)^{i}	75.9(2)
O(5)–Gd(1)–O(5)^{iv}	145.0(3)	Mo(1)–O(1)–N(1)	148.5(4)
O(5)–Gd(1)–O(5)^{v}	86.0(3)	C(1)–O(3)–Mo(1)	125.7(5)
O(5)–Gd(1)–O(6)^{i}	137.0(2)	C(3)–O(4)–Mo(1)^{ii}	132.6(6)
O(5)^{i}–Gd(1)–O(6)	72.5(1)	C(3)–O(5)–Mo(1)	116.7(6)
O(5)–Gd(1)–O(6)	64.5(1)	C(3)–O(5)–Gd(1)	136.5(6)
O(6)^{i}–Gd(1)–O(6)	120.0	Mo(1)–O(5)–Gd(1)	106.1(2)
O(5)^{ii}–Gd(1)–O(6)^{ii}	64.5(1)	Mo(1)–O(6)–Mo(1)^{iii}	134.6(5)
O(1)–Mo(1)–O(2)	104.7(4)	Mo(1)–O(6)–Gd(1)	112.7(2)

[a] Symmetry transformations used to generate equivalent atoms: i: $-y-1, x-y, z$; ii: $-x+y-1, -x-1, z$; iii: $y-1/3, x+1/3, -z+5/6$; iv: $-x-4/3, -x+y-2/3, -z+5/6$; v: $x-y-1/3, -y-2/3, -z+5/6$.

Results and discussion

Treatment of a stirred slurry of $GdCl_3$, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ and lactic acid in CH_3CN, gave rise to the ammonium salt of **1** as colorless crystals. The single-crystal X-ray diffraction study reveals that **1**, which crystallizes in the space group $R\bar{3}c$, is mainly built up from six $\{Mo(CH_3CHOCOO)O_{2.5}\}$ units and a nine-coordinate gadolinium atom in D_3 symmetry. The coordination environments around the Mo and Gd atoms in the complex are shown in Fig. 1 and a view of the molecular structure is shown in Fig. 2. Each lactic acid ligand in turn employs its carboxylate group and hydroxyl group to bridge three metal centers. The coordination environment for each molybdenum atom is a distorted octahedron and the angles involving the neighboring oxygen atoms range from 74.4(2) to 104.7(4)°. Each molybdenum atom is surrounded by six oxygen atoms: two carboxylate oxygen atoms, one of which coordinates to one molybdenum atom [Mo–O(4) = 2.476(7) Å], while another bridges one molybdenum atom [Mo–O(5) = 2.192(6) Å] and the central Gd atom [Gd–O(5) = 2.379(6) Å]; one hydroxyl oxygen atom, which only coordinates to one molybdenum atom [Mo–O(3) = 1.919(6)Å]; two terminal oxygen atoms [Mo–O(1) = 1.693(7) and Mo–O(2) = 1.701(7) Å]; one triply bridging oxygen atom, which links two neighboring molybdenum atoms [Mo–O(6) = 1.942(3) Å] and the central gadolinium atom [Gd–O(6) = 2.434(9) Å]. In the central nine-coordinate Gd atom, the Gd–O(5) bond [2.379(6) Å], of which the oxygen atom is from the carboxylate group, is slightly shorter than the Gd–μ_3-O(6) bond [2.434(9) Å]. Compared to those of previously reported compounds,[12] the overall Gd–O distances are significantly shorter, revealing a strong interaction between the Gd ion and the cavity.

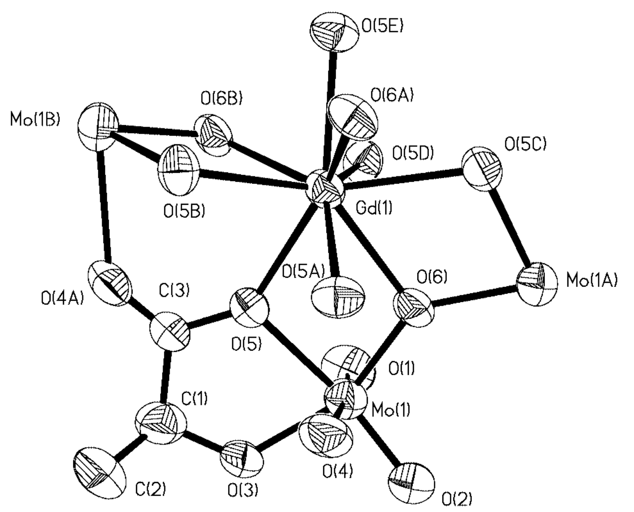

Fig. 1 Independent unit of compound **1**, showing the coordination environments around Mo, Gd atoms. Thermal ellipsoids drawn are at 50% probability and hydrogen atoms are omitted for clarity.

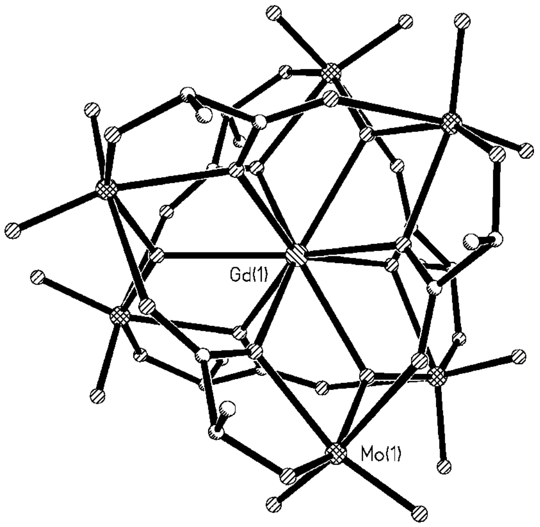

Fig. 2 A view of the molecular structure of **1** from the three-fold axis.

It is worthwhile pointing out that extended intermolecular hydrogen bonds exist between the NH_4^+ cations and terminal oxygens of the molybdenum atoms, which connect each cluster to the nearest neighbors into three-dimensional framework (Fig. 3). Each $\{Mo(CH_3CHOCOO)O_{2.5}\}$ cluster unit has two terminal oxygen atoms that are involved in the intermolecular hydrogen bonding with ammonium cations. Most interestingly, NH_4^+ cations occupy the channels that are formed by three cluster anions, and each NH_4^+ involves multiple hydrogen bond interactions with its nearest neighbors' terminal oxygen atoms. The mean N–H···O contact is about 2.81 Å, which is well within the sum of the van der Waals radii (2.9 Å).

A six transition metal spherical cluster with a lanthanide cation encapsulated at the center, $\{Ni_6Sm\}$, has been reported,[5,6] however, for early transition metals, this hexanuclear polymolybdate cluster encapsulating a lanthanide cation is the first example. It is well known that polyoxometalate chemistry is

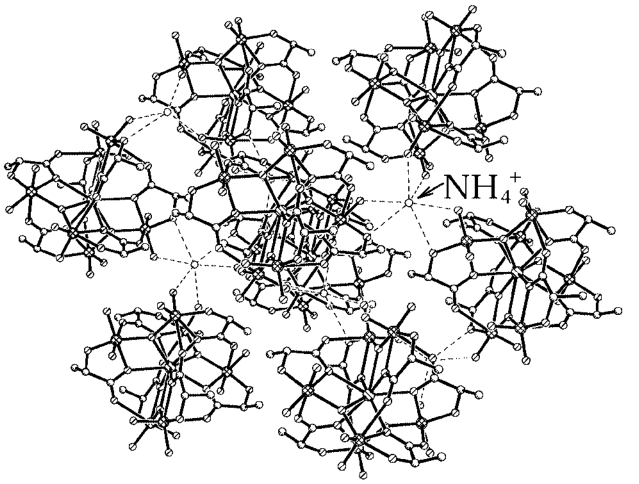

Fig. 3 Crystal packing of the ammonium salt of **1** showing the hydrogen bonding between the cluster anion and NH_4^+. For clarity, all the hydrogen atoms are omitted.

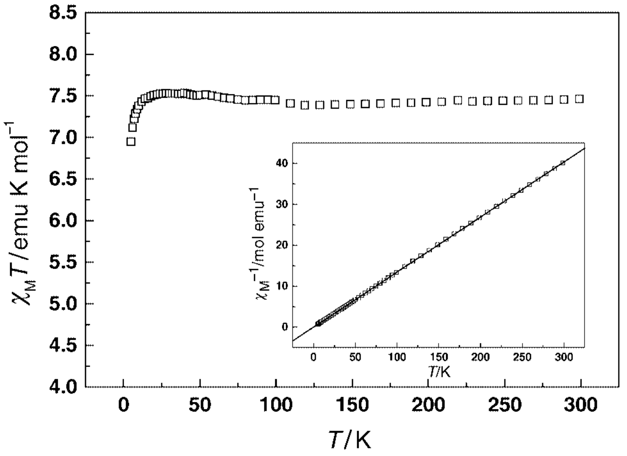

Fig. 4 Plot of $\chi_M T$ *vs.* temperature for the ammonium salt of **1**; the insert shows the inverse susceptibility with a linear regression based upon the Curie–Weiss law.

widely controlled by acid–base equilibria. Lactic acid, acts not only as a chelating organic ligand, but also as a weak acid to influence the equilibria and to prevent formation of powder sediment, which provides another synthetic route to systematically obtain novel and larger polyoxometalates with desirable properties.

Since the lanthanide family, in particular gadolinium complexes, exhibit ferromagnetic coupling ranging from 0.5 to 10 cm^{-1},[13] study of the magnetochemistry of the title anion salt might be very valuable. The variation of the molar magnetic susceptibility χ_M was investigated for the ammonium salt of **1** in the temperature range from 5.0 to 300 K in a 10 kG applied field. As shown in Fig. 4, the magnitude of the product $\chi_M T$ is almost constant at about 7.5 emu K mol^{-1} from 300 to 12.0 K, but below this temperature it decreases rapidly from 7.43 to 6.95 emu K mol^{-1}, with decreasing temperature from 12.0 to 5.0 K. Also shown is the χ_M^{-1} *versus* T plot (insert in Fig. 4), all data closely follow the Curie–Weiss law with $C = 7.69$ emu K mol^{-1} and $\theta = 0.12$ K, indicating weak ferromagnetic behavior and the magnetic data are consistent with the expected values for a $S = 7/2$ ground state. As shown in Fig. 5, the powder EPR spectrum of the ammonium salt of **1** at 293 K was interpreted from the fine structure Hamiltonian $\boldsymbol{H}_{FS} = \boldsymbol{D}\boldsymbol{S}_z^2$, in which zero-field splitting is assumed to be axial, with the parameter D.[14] The spectrum exhibits the expected seven transitions around 1188, 1854, 2521, 3188, 3854, 4521 and 5188 G, which correspond to $g = 2.1635$ and $|D| = 3.35 \times 10^{-2}$ cm^{-1}. This result clearly demonstrates the presence of zero-field splitting, and is consistent with the results of the study of the magnetic properties.

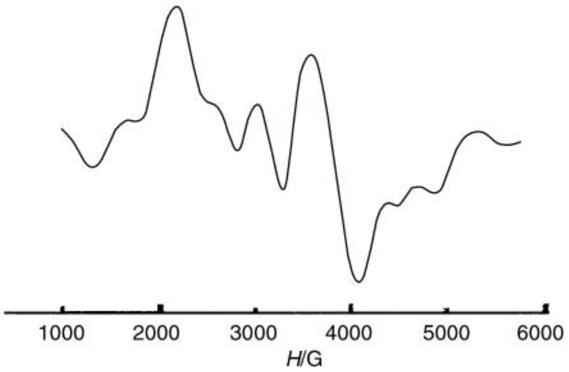

Fig. 5 EPR spectrum of the ammonium salt of **1** in the solid state at room temperature.

Acknowledgements

We gratefully thank the State Education Ministry, the State Personal Ministry, NSFC (20073048) and the Chinese Academy of Sciences for financial support.

References

1 *Polyoxometalates*, ed. C. L. Hill, *Chem. Rev.*, 1998, **98**.
2 M. T. Pope and A. Müller, *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1994.
3 M. T. Pope and A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34.
4 M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, New York, 1983.
5 Y. Yukawa, S. Igarashi, A. Yamano and S. Sato, *Chem. Commun.*, 1997, 711 and references therein.
6 S. Igarashi, Y. Hoshino, Y. Masuda and Y. Yukawa, *Inorg. Chem.*, 2000, **39**, 2509.
7 J. Chin, S. S. Lee, K. J. Lee, S. Park and D. H. Kim, *Nature*, 1999, **401**, 254 and references therein.
8 (*a*) M. Kojima, F. MD Akhter, K. Nakajima and Y. Yoshikawa, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2889; (*b*) S. M. Saadeh, M. S. Lah and V. L. Pecoraro, *Inorg. Chem.*, 1991, **30**, 8; (*c*) P. Liu and M. C. Hong, *Chin. J. Struct. Chem.*, 1992, **11**, 44; (*d*) T. Lis, *Acta Crystallogr., Sect. B*, 1982, **38**, 937; (*e*) K. D. Singh, S. C. Jain, T. D. Sakore and A. B. Biswas, *Acta Crystallogr., Sect. B*, 1975, **31**, 990; (*f*) M. Ahlgrén, V. Turpeinen and R. Hämäcäinen, *Acta Chem. Scand., Ser. A*, 1982, **36**, 841; (*g*) E. Bang, J. Eriksen, L. Mønsted and M. Mønsted, *Acta Chem. Scand., Ser. A*, 1994, **48**, 12.
9 G. M. Sheldrick, SADABS, Absorption Correction Program, University of Göttingen, Germany, 1996.
10 G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997.
11 G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
12 J. P. Costes, F. Dahan, A. Dupuis and J. P. Laurent, *Inorg. Chem.*, 2000, **39**, 169 and references therein.
13 A. Caneschi, A. Dei, D. Gatteschi, L. Sorace and K. Vostrikova, *Angew. Chem., Int. Ed.*, 2000, **39**, 246 and references therein.
14 M. Andruh, E. Bakalbassis, O. Kahn, J. C. Trombe and P. Porcher, *Inorg. Chem.*, 1993, **32**, 1616.