COMMUNICATION

ChemComm
www.rsc.org/chemcomm

A novel left-handed double helicate constructed from L-tartrate bridged molybdenum(VI) and gadolinium(III) atoms†

Chuan-De Wu, Can-Zhong Lu,* Xiang Lin, Ding-Ming Wu, Shao-Fang Lu, 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 (in Cambridge, UK) 11th February 2003, Accepted 7th April 2003
First published as an Advance Article on the web 2nd May 2003

The one-dimensional double helicate, $[NH_4][Mo_2O_4Gd(H_2O)_6(L\text{-}C_4H_2O_6)_2]\cdot 4H_2O$ (1), which was synthesized by the reaction of $GdCl_3$, L-tartaric acid and ammonium molybdate in acidified water solution, is built up by two heft-handed single-helical chains, linked up further by eight-coordinated Gd^{III} pieces in an enantiopure left-handed double helical configuration, of which each helix is formed by L-tartrate bridged six-coordinated Mo^{VI} atoms.

The synthesis and characterization of novel hybrid materials have currently provoked significant temporary interest, owing to their enormous variety of intriguing structural topologies and their fascinating properties as well as great potential applications in many fields, such as, catalysis, material science, medicine and magnetochemistry.[1] Of particular interest is the crystal engineering of helical metal compounds.[2]

Molybdenum in its high oxidation states tends to form varied topological architectures, and also the higher coordination numbers of lanthanide ions and the inherent flexibility of their coordination geometries associated with their $4f^n$ electronic configurations providing distinct geometric biases might lead to form some unprecedented topological architectures.[3] So the combination of these two aspects of molybdenum oxides and lanthanide coordination fragments with their significant structural features might merge their merits to generate some interesting compounds with special properties. However, contrary to the fruitful production of hybrid materials coexisting of molybdenum oxides with transition-metal centers,[4] the combination of molybdates with lanthanide ions together remains relative rare.[5–7] Recently, Müller *et al*. reported a very interesting large supramolecular architecture including Eu^{III} cations.[5] In this communication, we report here the preparation, crystal structure and some physical properties of a novel enantiopure left-handed double helical coordination compound, $[NH_4][Mo_2O_4Gd(H_2O)_6(L\text{-}C_4H_2O_6)_2]\cdot 4H_2O$ (**1**).

A mixture of $GdCl_3$ (5.0 mmol), L-tartaric acid (10 mmol) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (1.46 mmol) in 120 ml water was adjusted to pH = 0.80 by 10% HCl. Colorless crystals of **1** were isolated in high yield after two weeks (97.9% yield, correct elemental analysis). The IR spectra of **1** exhibit broad bands at 1632–1066 cm^{-1}, assigned to the L-tartrate ligand, and at 912–723 cm^{-1} to the ν(Mo=O) or ν(Mo–O) streching vibrations. Similarly, the Raman band at 1594 cm^{-1} is for the ligand and at 940–796 cm^{-1} for ν(Mo=O) or ν(Mo–O–Mo), respectively.

The structure analysis‡ reveals that **1** is of an enantiopure left-handed double helicate. Each double helicate is built up from two L-tartrate bridging six-coordinated Mo left-handed single-helical chains that are further coupled up by eight-coordinated Gd^{III} pieces (Scheme 1 and Fig. 1). Each Mo^{VI} atom is six coordinated *via* two terminal oxygen atoms (Mo–O = 1.695(4)–1.701(4) Å), two hydroxyl oxygen atoms (Mo–O = 1.944(4)–1.946(4) Å) and two carboxylate oxygen atoms (Mo–O = 2.205(4)–2.227(4) Å) from two tartrate ligands. And then, the octahedral-coordinated Mo atoms are linked up *via* L-tartrate to form left-handed single-helical chains, which are intertwined themselves with a period of 18.661 Å running along the 6_5 axis. Such two helical chains are linked together in couple by eight-coordinated Gd^{III} atoms through coordinating to two carboxylate oxygen atoms of two tartrate on the outside of the helix to form a very interesting enantiopure left-handed double helicate. The coordination oxygen atoms around each Gd^{III} atom, which is in a slightly distorted eight-coordinated square-antiprismatic geometry, are of six aqua ligands (Gd–O = 2.372(5)–2.430(5) Å), two chelate carboxylate groups (Gd–O = 2.343(4) Å). It is very remarkable that such kind of arrangements of the tartrate, Mo and Gd atoms generate a very interesting nanotube along the 6_5 axis with the diameter of 5.495 Å (the shortest opposite O–O distance) (Fig. 2).

Finally, it should also be pointed out, the crystallization H_2O molecules and NH_4^+ cations, which occupy the channels and

Scheme 1 Scheme representation of the double helicate (blue and red ribbons represent the L-tartrate bridging six-coordinated Mo left-handed single-helical chains; green short sticks represent the eight coordinated Gd cations).

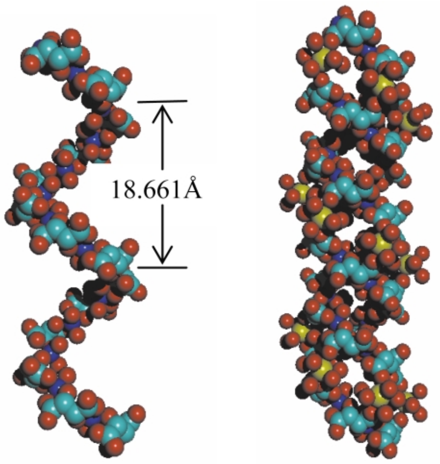

Fig. 1 Space-filling presentation: the left-handed single-helix (left) and the left-handed double helicate (Mo, Blue; C, Purple; O, Red; Gd, yellow).

---

† Electronic supplementary information (ESI) available: crystallographic data, TGA, powder X-ray patterns, ORTEP structure and molar susceptibility plot for compound **1**. See http://www.rsc.org/suppdata/cc/b3/b301542d/

DOI: 10.1039/b301542d

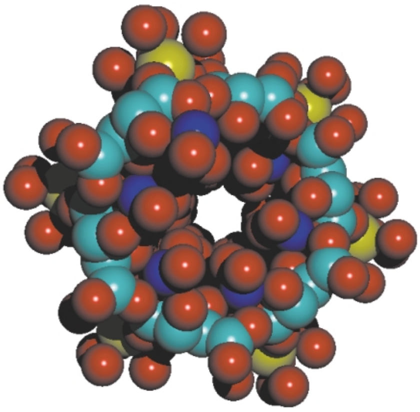

Fig. 2 Ball presentation of compound **1** to show the channel view for each double helix viewed down the 6_5 axis.

among adjacent double helices, connect the double helices to each other *via* complex hydrogen bonds between the coordination water molecules and the ligands into a three-dimensional framework (Fig. 3). The TGA performed on **1**, shows continuous weight loss above 30 °C and the curve has a discernible inflection point at approximately 220 °C. The observed weight loss (20.4%) is corresponding to the loss of four crystallization water molecules and six aqua ligands per formula unit (calcd. 19.9%). Above 220 °C, the product begins to decompose. A sample of **1** was heated at 70 °C under vacuum for 4 h and an XRPD was recorded for the remains. There is no sharp peak in its XRPD pattern. However, after being immersed in water for 12 h, this material reverted to the original compound, as confirmed by comparing the XRPD patterns. These results indicate that the crystallized H_2O and aqua ligands might play some important roles in the formation and stability of compound **1**.

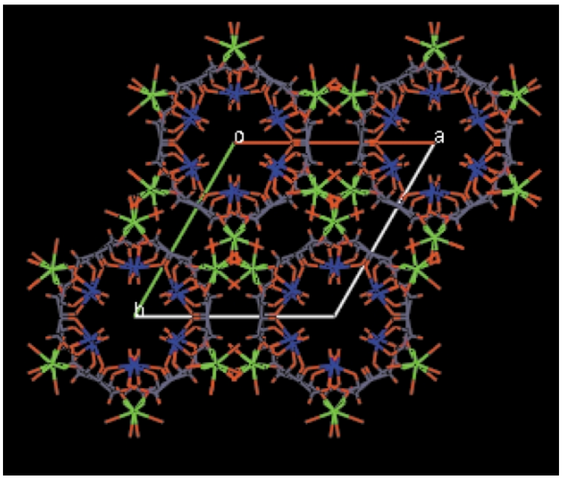

Fig. 3 The cell packing diagram of **1** viewed down the c axis (Mo, Blue; C, Deep gray; O, Red; Gd, Green).

The powder magnetic susceptibilities for **1** have also been studied. At 268 K, the $\chi_M T$ value is 7.14 emu K mol^{-1}, which increases slightly to a maximum of 7.80 emu K mol^{-1} when temperature was lowered to 30 K, and decreases to 6.97 emu K mol^{-1} at 4.2 K.

The experimental data were fitted to an isotropic chain model,[8] corrected by inter-chain coupling. The best fit suggest the intra-chain Gd–Gd interactions is of weak ferromagnetic (J = 0.168cm^{-1}), while weak antiferromagnetic interactions occur between adjacent chains (J' = 0.0335 cm^{-1}) with g = 1.90. The EPR spectra of polycrystalline **1** give g = 1.90 at rt and 1.88 at 77 K, which are comparable to the result from magnetic study. The low temperature magnetic behavior (30–4.2 K) might be due to a small zero-field splitting with the $^8S_{7/2}$ state.

In conclusion, by using a chiral organic ligand, L-tartrate, as a bridging ligand, a novel chiral left-handed double helicate has been prepared and characterized, whose framework structure contains tube formed by double helical chains.

This work was supported by the 973 Program of MOST (001CB108906), the National Natural Science Foundation (NSF) of China (90206040 and 20073048), the NSF of Fujian province (2002F015 and 2002J006) and the Chinese Academy of Sciences.

Notes and references

‡ Crystal data for **1**: $C_8H_{28}GdMo_2NO_{26}$, Mr = 903.44, space group $P6_522$, a = 15.298(1), c = 18.661(1) Å, V = 3782.2(1) Å^3, Z = 6, $D_{calc.}$ = 2.380 g cm^{-3}, μ = 3.692 mm^{-1}, $F(000)$ = 2634, the final $R1$ ($wR2$) = 0.0257 (0.0597) for 2038 reflections with $I > 2\sigma(I)$. The structure analysis and refinement were carried out using the **SHELXL-97** software package.[9] CCDC 203714. See http://www.rsc.org/suppdata/cc/b3/b301542d/ for crystallographic data in CIF or other electronic format.

1 *Chem. Rev.*, Polyoxometalates, Ed. C. L. Hill, 1998, , 98; M. T. Pope and A. Müller, *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994; M. T. Pope and A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34; M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, New York, 1983; O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 374; A. K. Cheetham, *Science*, 1994, **264**, 794 and references therein.

2 C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457; J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982; S. G. Telfer, B. Bocquet and A. F. Williams, *Inorg. Chem.*, 2001, **40**, 4818; E. C. Constable, M. J. Hannon and D. A. Tocher, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 230; L. J. Childs, N. W. Alcock and M. J. Hannon, *Angew. Chem., Int. Ed.*, 2001, **40**, 1097; J. Hamblin, A. Jackson, N. W. Alcock and M. J. Hannon, *J. Chem. Soc., Dalton Trans.*, 2002, 1635; L. J. Charbonniere, A. F. Williams, C. Piguet, G. Bernardinelli and E. Rivara-Minten, *Chem. Eur. J.*, 1998, **4**, 485; J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; J.-M. Lehn, A. Riganlt, J. Siegel, J. Harrowfield, B. Chevrier and D. Moras, *Proc. Natl. Acad. Sci. U. S. A.*, 1987, **84**, 2565; J.-M. Lehn and A. Riganlt, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1095; K. A. Hirsch, S. R. Wilson and J. S. Moore, *Chem. Commun.*, 1998, 13; O. Mamula, A. von. Zelewsky, T. Bark and G. Bernardinelli, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 2945.

3 D.-L. Long, A. J. Blake, N. R. Champness and M. Schröder, *Chem. Commun.*, 2000, 1369; D.-L. Long, A. J. Blake, N. R. Champness, C. Wilson and M. Schröder, *Angew. Chem., Int. Ed.*, 2001, **40**, 2444; L. Pan, E. B. Woodlock, X. Wang and C. Zheng, *Inorg. Chem.*, 2000, **39**, 4174; C.-D. Wu, C.-Z. Lu, W.-B. Yang, S.-F. Lu, H.-H. Zhuang and J.-S. Huang, *Eur. J. Inorg. Chem.*, 2002, 797.

4 P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638and reference therein.

5 L. Cronin, C. Beugholt, E. Krickemeyer, M. Schmidtmann, H. Bögge, P. Kögerler, T. K. K. Luong and A. Müller, *Angew. Chem., Int. Ed.*, 2002, **41**, 2805.

6 V. N. Molchanov, I. V. Tatjanina and E. A. Torchenkova, *J. Chem. Soc., Chem. Commun.*, 1981, 93; T. Yamase and H. Naruke, *J. Chem. Soc., Dalton Trans.*, 1991, 285; A. Kitamura, T. Ozeki and A. Yagasaki, *Inorg. Chem.*, 1997, **36** , 4275; M. Hashimoto, M. Takata and A. Yagasaki, *Inorg. Chem.*, 2000, **39**, 3712; Y. G. Kessler, N. Y. Turova, A. N. Panov, A. I. Yanovsky, A. P. Pisarevsky and Y. T. Struchkov, *Polyhedron*, 1996, **15**, 335; R. Villanneau, A. Proust, F. Robert and P. Gouzerh, *J. Chem. Soc., Dalton Trans.*, 1999, 421.

7 C.-D. Wu, C.-Z. Lu, J.-C. Liu, H.-H. Zhuang and J.-S. Huang, *J. Chem. Soc., Dalton Trans.*, 2001, 3202; C.-D. Wu, C.-Z. Lu, H.-H. Zhuang and J.-S. Huang, *J. Am. Chem. Soc.*, 2002, **124**, 3837.

8 M. E. Fisher, *Am. J. Phys.*, 1964, **32**, 343.

9 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.