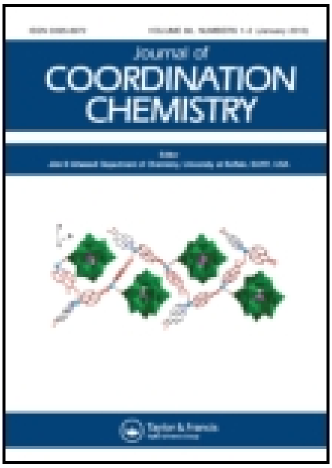
This article was downloaded by: [Institute Of Atmospheric Physics]
On: 09 December 2014, At: 15:16
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



CrossMark

Click for updates

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

An unexpected Mn^{2+} linked 1-D zigzag chain compound based on triethanolamine-functionalized hexamolybdoarsenate

Yanyan Yang[ab], Lin Xu[a], Fengyan Li[a], Guanggang Gao[a] & Xiaoshu Qu[b]

[a] Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun, PR China

[b] JiLin Institute of Chemical Technology, Jilin City, PR China

Accepted author version posted online: 01 Jul 2014.Published online: 25 Jul 2014.

To cite this article: Yanyan Yang, Lin Xu, Fengyan Li, Guanggang Gao & Xiaoshu Qu (2014) An unexpected Mn^{2+} linked 1-D zigzag chain compound based on triethanolamine-functionalized hexamolybdoarsenate, Journal of Coordination Chemistry, 67:13, 2249-2256, DOI: 10.1080/00958972.2014.939647

To link to this article: http://dx.doi.org/10.1080/00958972.2014.939647

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,

Journal of Coordination Chemistry, 2014
Vol. 67, No. 13, 2249–2256, http://dx.doi.org/10.1080/00958972.2014.939647

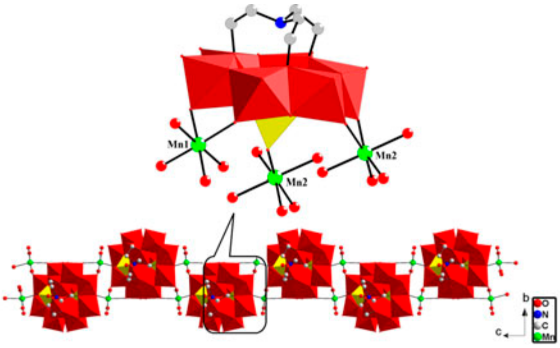
Taylor & Francis
Taylor & Francis Group

An unexpected Mn^{2+} linked 1-D zigzag chain compound based on triethanolamine-functionalized hexamolybdoarsenate

YANYAN YANG†‡, LIN XU*†, FENGYAN LI†, GUANGGANG GAO† and XIAOSHU QU‡

†Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun, PR China
‡JiLin Institute of Chemical Technology, Jilin City, PR China

(*Received 2 April 2014; accepted 9 June 2014*)



The first sample of triethanolamine-functionalized hexamolybdoarsenate $[(HOCH_2CH_2)_3NH]_n(H_3O)_n[\{Mn(H_2O)_2\}_{0.5}Mn(H_2O)_3\{HN(CH_2CH_2O)_3As^VMo_6O_{22}\}]_n{\cdot}3.25nH_2O$ (**1**) has been synthesized in aqueous solution and characterized by elemental analysis, IR spectroscopy, thermal gravimetric analysis, and single-crystal X-ray diffraction. X-ray analysis showed that a new kind of heteropolyanion $[HN(CH_2CH_2O)_3As^VMo_6O_{22}]^{5-}$ is linked by Mn^{2+} ions forming a zig-zag chain. The magnetic properties of **1** have been studied by measuring its magnetic susceptibility from 2.0 to 300.0 K, indicating the existence of antiferromagnetic interactions.

Keywords: Hexamolybdoarsenate; Triethanolamine; Zig-zag chain; Manganese ions

1. Introduction

Polyoxometalates (POMs) are extremely versatile inorganic building blocks with potential applications in medicine, materials, and catalysis [1–8]. As a result, some POM-based

---

*Corresponding author. Email: linxu@nenu.edu.cn organic–inorganic hybrid materials containing hydroxymethyl have been prepared [9–12], and many reports show that they have the potential to activate dioxygen [13, 14] and to function as oxidation catalysts [15–17]. The bridging oxygens of POMs (Lindqvist-, Anderson-, Wells–Dawson-type) can be substituted with some tridentate ligands, such as tri(hydroxymethyl)aminomethane, and 2-acetamido-2-ethyl-1,3-propanediol. [18, 22]. However, most of the compounds were synthesized in organic solvents. We introduce some research on the modification of polymolybdates by organic groups in aqueous media, which may shed light on green chemistry functionalization of polyoxomolybdates [23]. Since triethanolamine has a similar geometry with tridentate ligands, some POMs based on triethanolamine (TEA) have been reported, such as $[Mn^{II}V^{IV}{}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]^{2+}$ cation [24], $(TEAH)_4\{Na_2[Mo_{36}O_{112}(H_2O)_{14}](TEAH)_2\}\cdot 28H_2O$, and $(TEAH)_6\{[Mo_{36}O_{112}(H_2O)_{14}](TEAH)_2\}\cdot 10H_2O$ [25], in which the TEA can coordinate to polyanions by some of the three primary alcohols of one TEA and stabilize them by hydrogen bonding interactions due to its excellent solubility and good coordination ability. Thus, our interest focused on the new combination of polyoxomolybdate and TEA in aqueous solution.

Here, we report the synthesis and crystal structure of a new compound, $[(HOCH_2CH_2)_3NH]_n(H_3O)_n[\{Mn(H_2O)_2\}_{0.5}Mn(H_2O)_3\{HN(CH_2CH_2O)_3As^VMo_6O_{22}\}]_n\cdot 3.25nH_2O$ (**1**). The single-crystal X-ray analysis [26] shows that the heteropolyanions are linked by metal ions in zig-zag chains, the first example that $[AsMo_6O_{25}]^{9-}$ is capped by TEA ligand through three sharing alkoxy oxygens.

2. Experimental

2.1. *Materials and physical measurements*

All reagents were purchased commercially and used without purification. Distilled water was used throughout. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Mo and As were determined by a Leaman inductively coupled plasma spectrometer. IR spectra were obtained on an Alpha Centaurt FT/IR spectrometer with KBr pellet from 400 to 4000 cm^{-1}. The thermal gravimetric (TG) analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}.

2.2. *Synthesis of 1*

Compound **1** was synthesized from the mixture of $Na_3AsO_4\cdot 12H_2O$ (0.424 g, 1 mM), $Na_2MoO_4\cdot 2H_2O$ (0.732 g, 3 mmol), and $(OHCH_2CH_2)_3N$ (1.80 g, 1.2 mmol) in H_2O (40 mL) and heated to 60 °C on a water bath. The pH of the solution was adjusted to 6.0 by addition of 1 M hydrochloric acid and then $MnSO_4$ (3 mL of 1 mol L^{-1} solution) was added. After adjusting the pH to 4 with 1 M hydrochloric acid, the mixture was refluxed at 60 °C for 2 h. The solution was cooled to room temperature and $(H_2NCNHNH_2)_2\cdot HNO_3$ (3 mL of 3 mol L^{-1} solution) was added into the stirred solution. After two weeks, yellow block crystals were formed by evaporation of the filtrate at room temperature. Elemental analysis (%): Calcd (found) for **1**: Mn 5.38 (5.41), As 4.89 (4.84), Mo 37.58 (37.36), C 9.41 (9.19), N 1.83 (1.86), H 3.06 (3.08).

Table 1. The crystal data and structure refinement for **1**.

Empirical formula	$H_{93}C_{24}N_4O_{72.5}Mn_3As_2Mo_{12}$
M	3063.92
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	34.375(3)
b/Å	12.3278(10)
c/Å	25.997(2)
α/°	90.00
β/°	130.3500(10)
V/Å^3	8396.1(12)
Z	4
D_c/Mg m^{-3}	2.515
μ/mm^{-1}	3.072
F(000)	8424
θ Range/°	1.55–26.05
Data/restraints/parameters	22,577/8297
R_{int}	0.0873
$R_1(I > 2\sigma(I))$	0.0510
wR_2	0.1102
Goodness-of-fit on F^2	0.924
$\Delta\rho_{\text{max, min}}$/e Å^{-3}	2.032, −1.230

Table 2. Selected bond lengths for **1**.

As(1)–O(12)	1.668(6)	Mo(1)–O(18)	1.686(7)
As(1)–O(21)	1.675(6)	Mo(1)–O(13)	1.750(7)
As(1)–O(11)	1.693(6)	Mo(1)–O(6)	1.925(6)
As(1)–O(9)	1.699(6)	Mo(1)–O(8)	1.949(6)
Mn(1)–O(13)	2.142(7)	Mo(1)–O(3)	2.190(6)
Mn(1)–O(16)	2.158(7)	Mo(1)–O(11)	2.238(6)
Mn(1)–O(25)	2.199(7)	Mo(2)–O(19)	1.707(7)
Mn(2)–O(15)	2.152(7)	Mo(2)–O(15)	1.755(6)
Mn(2)–O(29)	2.160(8)	Mo(2)–O(1)	1.908(6)
Mn(2)–O(17)	2.180(6)	Mo(2)–O(7)	1.929(6)
Mn(2)–O(30)	2.229(8)	Mo(2)–O(14)	2.154(6)
Mn(2)–O(22)	2.238(7)	Mo(2)–O(9)	2.273(6)
Mo(5)–O(10)	1.696(6)	Mo(3)–O(28)	1.704(8)
Mo(5)–O(17)	1.736(6)	Mo(3)–O(27)	1.725(7)
Mo(5)–O(6)	1.923(7)	Mo(3)–O(4)	1.908(6)
Mo(5)–O(1)	1.936(7)	Mo(3)–O(7)	1.960(7)
Mo(5)–O(3)	2.205(6)	Mo(3)–O(14)	2.213(6)
Mo(5)–O(9)	2.264(6)	Mo(3)–O(21)	2.295(7)
Mo(6)–O(24)	1.689(7)	Mo(4)–O(26)	1.697(7)
Mo(6)–O(23)	1.715(7)	Mo(4)–O(16)	1.735(7)
Mo(6)–O(4)	1.920(7)	Mo(4)–O(2)	1.915(6)
Mo(6)–O(2)	1.965(7)	Mo(4)–O(8)	1.943(6)
Mo(6)–O(5)	2.216(6)	Mo(4)–O(5)	2.183(7)
Mo(6)–O(21)	2.310(6)	Mo(4)–O(11)	2.260(6)

2.3. *Crystal structure determination*

The X-ray crystallographic data were collected at 273 K for **1** on a Bruker SMART CCD single-crystal diffractometer using Mo-Kα radiation (0.71073 Å). Direct methods were used to solve the structure and to locate the heavy atoms (SHELX97). Hydrogens were not included.

Table 3. Selected bond angles for **1**.

O(18)–Mo(1)–O(13)	103.0(3)	O(28)–Mo(3)–O(27)	103.8(4)	O(13)–Mn(1)–O(16)	85.7(2)
O(18)–Mo(1)–O(6)	102.8(3)	O(28)–Mo(3)–O(4)	100.8(3)	O(13)–Mn(1)–O(25)	86.4(3)
O(13)–Mo(1)–O(6)	97.3(3)	O(27)–Mo(3)–O(4)	101.0(3)	O(16)–Mn(1)–O(25)	89.5(3)
O(18)–Mo(1)–O(8)	98.2(3)	O(28)–Mo(3)–O(7)	103.0(3)	O(15)–Mn(2)–O(29)	162.2(3)
O(13)–Mo(1)–O(8)	99.0(3)	O(27)–Mo(3)–O(7)	92.7(3)	O(15)–Mn(2)–O(17)	83.3(2)
O(6)–Mo(1)–O(8)	149.7(3)	O(4)–Mo(3)–O(7)	148.7(3)	O(29)–Mn(2)–O(17)	93.6(3)
O(18)–Mo(1)–O(3)	89.4(3)	O(28)–Mo(3)–O(14)	87.6(3)	O(15)–Mn(2)–O(30)	80.1(3)
O(13)–Mo(1)–O(3)	166.1(3)	O(27)–Mo(3)–O(14)	162.7(3)	O(29)–Mn(2)–O(30)	82.7(3)
O(6)–Mo(1)–O(3)	73.6(3)	O(4)–Mo(3)–O(14)	89.4(3)	O(17)–Mn(2)–O(30)	96.1(3)
O(8)–Mo(1)–O(3)	85.1(3)	O(7)–Mo(3)–O(14)	71.7(2)	O(15)–Mn(2)–O(22)	103.6(3)
O(18)–Mo(1)–O(11)	166.3(3)	O(28)–Mo(3)–O(21)	167.0(3)	O(29)–Mn(2)–O(22)	93.1(3)
O(13)–Mo(1)–O(11)	87.5(3)	O(27)–Mo(3)–O(21)	88.4(3)	O(17)–Mn(2)–O(22)	79.6(2)
O(6)–Mo(1)–O(11)	84.2(2)	O(4)–Mo(3)–O(21)	72.1(3)	O(30)–Mn(2)–O(22)	173.8(3)
O(8)–Mo(1)—O(11)	71.2(2)	O(7)–Mo(3)–O(21)	80.4(3)	O(12)–As(1)–O(21)	112.5(3)
O(3)–Mo(1)–O(11)	81.2(2)	O(14)–Mo(3)–O(21)	81.6(2)	O(12)–As(1)–O(11)	107.6(3)
O(19)–Mo(2)–O(15)	102.3(3)	O(24)–Mo(6)–O(23)	104.8(4)	O(21)–As(1)–O(11)	109.5(3)
O(19)–Mo(2)–O(1)	100.7(3)	O(24)–Mo(6)–O(4)	99.6(3)	O(12)–As(1)–O(9)	110.5(3)
O(15)–Mo(2)–O(1)	99.8(3)	O(23)–Mo(6)–O(4)	101.2(3)	O(21)–As(1)–O(9)	108.4(3)
O(19)–Mo(2)–O(7)	102.5(3)	O(24)–Mo(6)–O(2)	102.2(3)	O(11)–As(1)–O(9)	108.2(3)
O(15)–Mo(2)–O(7)	94.4(3)	O(23)–Mo(6)–O(2)	94.7(3)	O(26)–Mo(4)–O(16)	102.9(3)
O(1)–Mo(2)–O(7)	149.4(3)	O(4)–Mo(6)–O(2)	148.7(3)	O(26)–Mo(4)–O(2)	104.4(3)
O(19)–Mo(2)–O(14)	92.4(3)	O(24)–Mo(6)–O(5)	89.2(3)	O(16)–Mo(4)–O(2)	94.6(3)
O(15)–Mo(2)–O(14)	162.9(3)	O(23)–Mo(6)–O(5)	162.9(3)	O(26)–Mo(4)–O(8)	98.4(3)
O(1)–Mo(2)–O(14)	85.8(2)	O(4)–Mo(6)–O(5)	85.8(3)	O(16)–Mo(4)–O(8)	98.2(3)
O(7)–Mo(2)–O(14)	73.7(3)	O(2)–Mo(6)–O(5)	72.3(2)	O(2)–Mo(4)–O(8)	150.5(3)
O(19)–Mo(2)–O(9)	170.1(3)	O(24)–Mo(6)–O(21)	166.5(3)	O(26)–Mo(4)–O(5)	89.2(3)
O(15)–Mo(2)–O(9)	85.4(3)	O(23)–Mo(6)–O(21)	87.3(3)	O(16)–Mo(4)–O(5)	165.3(3)
O(1)–Mo(2)–O(9)	71.6(2)	O(4)–Mo(6)–O(21)	71.6(2)	O(2)–Mo(4)–O(5)	74.0(3)
O(7)–Mo(2)–O(9)	82.8(2)	O(2)–Mo(6)–O(21)	82.5(2)	O(8)–Mo(4)–O(5)	88.1(3)
O(14)–Mo(2)–O(9)	81.1(2)	O(5)–Mo(6)–O(21)	80.1(2)	O(26)–Mo(4)–O(11)	165.2(3)
O(10)–Mo(5)–O(17)	102.9(3)	O(6)–Mo(5)–O(3)	73.3(2)	O(16)–Mo(4)–O(11)	89.0(3)
O(10)–Mo(5)–O(6)	102.0(3)	O(1)–Mo(5)–O(3)	88.4(2)	O(2)–Mo(4)–O(11)	83.1(2)
O(17)–Mo(5)–O(6)	96.3(3)	O(10)–Mo(5)–O(9)	165.8(3)	O(8)–Mo(4)–O(11)	70.8(2)
O(10)–Mo(5)–O(1)	101.7(3)	O(17)–Mo(5)–O(9)	90.5(2)	O(5)–Mo(4)–O(11)	80.5(2)
O(17)–Mo(5)–O(1)	97.6(3)	O(6)–Mo(5)–O(9)	81.0(2)	O(17)–Mo(5)–O(3)	167.2(3)
O(6)–Mo(5)–O(1)	149.0(3)	O(1)–Mo(5)–O(9)	71.4(2)	O(10)–Mo(5)–O(3)	86.8(3)

Nitrogens of triethanolamine cations were modeled as oxygens because nitrogens could not be distinguished from oxygens. As usual for POMs, the crystal of **1** shows large disorder of counterions and water molecules. The crystal data and structure refinement for **1** are listed in table 1 and selected bond lengths are listed in table 2. Selected bond angles for **1** are listed in table 3. Accordingly, the exact formula was determined by elemental analyses.

3. Results and discussion

3.1. *Description of the crystal structures*

The structure of the anion is shown in figure 1. The anion $[\{Mn(H_2O)_2\}_{0.5}Mn(H_2O)_3\{HN(CH_2CH_2O)_3AsMo_6O_{22}\}]^{2-}$ consists of six MoO_6 octahedra, which form a ring by edge-sharing and lie in a common plane, a $[(OCH_2CH_2)_3NH]^{2-}$ and an AsO_4 tetrahedron are attached to the ring from above and below, with their three oxygens shared with the ring. They can be regarded as capping both sides of the planar metal arrangement. The coordination geometry of the central As is regular, with a mean As–O distance of

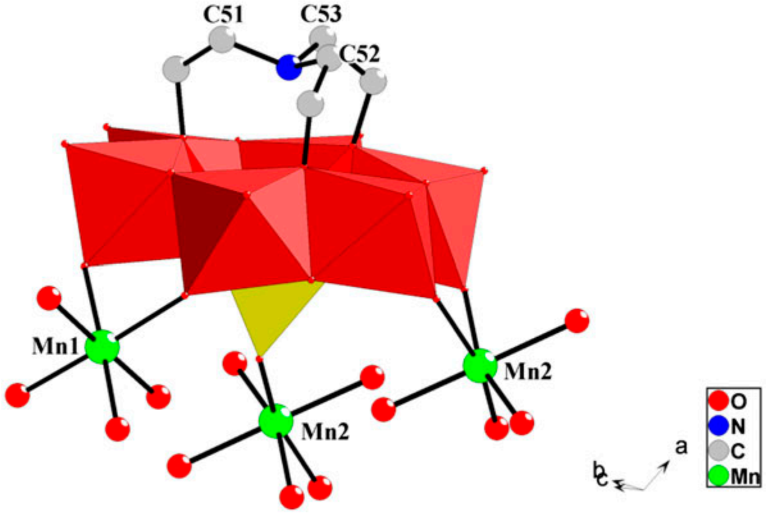


Figure 1. Combined polyhedral/ball-and-stick representation showing a part of the 1-D chain-like $[\{Mn(H_2O)_2\}_{0.5}Mn(H_2O)_3\{HN(CH_2CH_2O)_3AsMo_6O_{22}\}]^{2-}$ fragment.

1.684(6) Å and O–As–O bond angles of 107.6(3)–112.5(3)° in agreement with the $[As_2Mo_6O_{26}]^{6-}$ anion [26]. The TEA ligand grafted onto $[AsMo_6O_{25}]^{9-}$ represents cage geometry. The coordination geometry of the nitrogen is a tetrahedron, with nitrogen lying out of the plane defined by C(51), C(52), and C(53) by 0.466(5) Å towards $[AsMo_6O_{25}]^{9-}$. The C–O distances of TEA range from 1.410(16) to 1.440(15) Å within the normal limits [18–21].

In **1**, Mo–O distances are divided into five groups: (1) Mo–O_t (terminal oxygen), 1.686 (7)–1.725(7) Å; (2) molybdenum–oxygen linked to manganese, 1.735(7)–1.755(7) Å; (3) molybdenum–bridging oxygen, 1.908(6)–1.965(7) Å; (4) molybdenum–internal oxygen common to two molybdenum ions and an arsenic, 2.260(6)–2.295(6) Å, with longest oxygen–molybdenum bond lengths and in agreement with the $[As_2Mo_6O_{26}]^{6-}$ anion; and (5) molybdenum–internal oxygen common to two molybdenum ions and carbons 2.154 (6)–2.216(6) Å, which are slightly shorter than the Mo–O(bond to As atom) distance. The bond valance sum calculation suggests the average oxidation state +6.05 for Mo, +5.01 for As, −1.90 for O, and +2.04 for Mn.

In the polymeric chain, $[HN(CH_2CH_2O)_3AsMo_6O_{22}]^{5-}$ is a tridentate ligand coordinating to three manganese(II) ions through terminal oxygens (figure 2) of two adjacent MoO_6 octahedra and one AsO_4 tetrahedron, and two kinds of manganese ions exist according to the manner of oxygen coordination. Both manganese ions have distorted octahedral environment. One of the two manganese ions (Mn1) shares four bridging oxygen ligands with the two molybdenum ions of two $[HN(CH_2CH_2O)_3AsMo_6O_{22}]^{5-}$ units and two water molecules. The Mn2 is bound to three terminal oxygens from the AsO_4 tetrahedron of one $[HN(CH_2CH_2O)_3AsMo_6O_{22}]^{5-}$ and two MoO_6 octahedra of another $[HN(CH_2CH_2O)_3AsMo_6O_{22}]^{5-}$ unit.

3.2. *Magnetic properties*

The magnetic behavior of **1** from 300 to 2 K is shown as plots of the product $1/\chi_m$ *versus* T and $\chi_m T$ *versus* T in figure 3. The $1/\chi_m$ *versus* T plot for **1** displays Curie–Weiss behavior

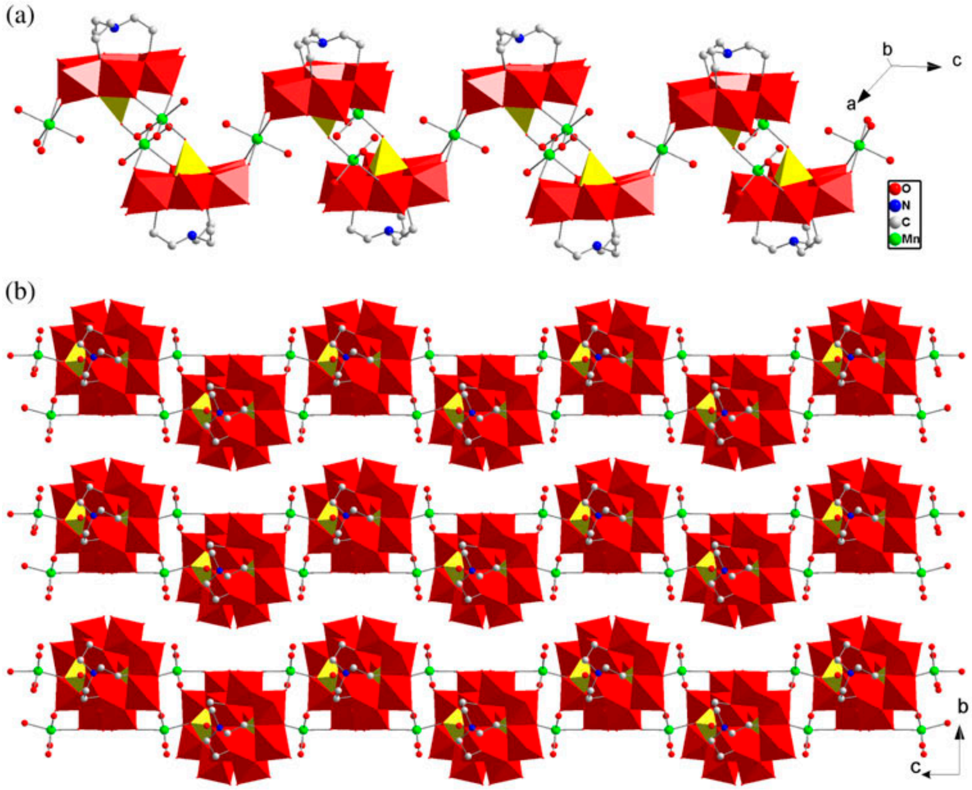


Figure 2. Combined polyhedral/ball-and-stick representation showing the 1-D "zig-zag" chain (a) and the chain viewed along the *a* axis (b). The cations and water molecules are omitted for clarity. The color code: MoO_6 (red), Mn (green) (see http://dx.doi.org/10.1080/00958972.2014.939647 for color version).

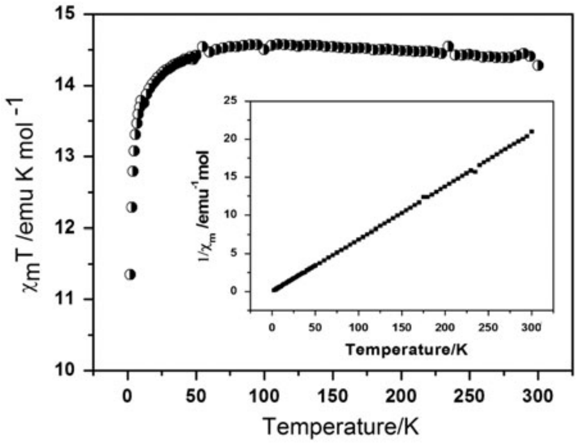


Figure 3. Temperature dependence of the $1/\chi_m$ product and $\chi_m T$ product for **1**. Magnetic measurements: MPMS-XL5 SQUID magnetometer (T range: 2–300 K; applied field: 0.1 T; diamagnetic corrections: estimated from Pascal's constants).

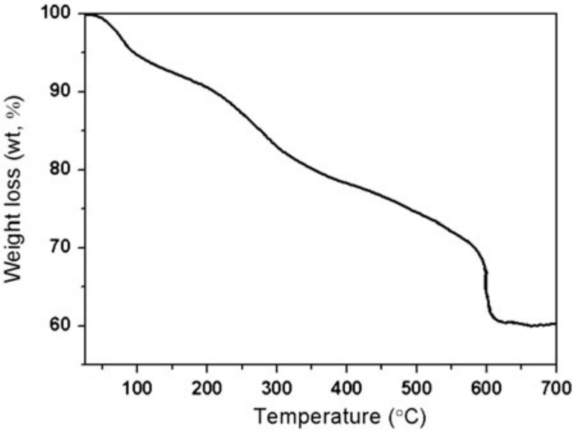


Figure 4. TGA curve of **1**.

from 300 to 2 K; the best linear fit of $\chi_m^{-1}(T)$ data above 40 K yields $C = 7.35$ cm^3 K mol^{-1} and $\theta = -0.61881$ K. The χ_mT value of **1** at 300 K is ca. 14.3 cm^3 K mol^{-1} (10.74 μB); this value is close to the sum (14.28 cm^3 K mol^{-1}, $g = 2.0$) of theoretical values for three $S = 5/2$ (13.14 cm^3 K mol^{-1}, $g = 2.0$) and for three $S = 1/2$ (1.14 cm^3 K mol^{-1}, $g = 2.0$). The temperature dependence of χ_mT shows a slight decrease from 14.3 to 14.5 emu K mol^{-1} between 300 and 60 K. These results suggest the presence of an interchain antiferromagnetic interaction. The magnetic interaction between the Mn(II) ions separated by polyanion can be enhanced through the antiferromagnetic interaction between the Mn(II) spin and the Mo(VI) spin.

3.3. *IR spectrum*

In the IR spectrum of **1**, bands at 931, 893, 840, 811, and 692 cm^{-1} are due to the ν(As–O$_a$), ν(Mo–O$_t$), ν(Mo–O$_c$), and ν(Mo–O$_b$) of the $[AsMo_6O_{26}]^{6-}$ fragment. The bands at 1617, 1457, and 1379 are attributed to characteristic vibrations of $[(HOCH_2CH_2)_3NH]^+$ groups.

3.4. *Thermogravimetric analysis*

The TG curve of **1** exhibits four steps of weight loss from 25 to 700 °C (figure 4). The first weight loss of 4.78% in the temperature range 25–95 °C corresponds to the release of 4.25 crystalline waters. The second stage, which occurs from 95 to 351 °C, is attributed to the loss of one organic molecule and four waters; the observed weight loss (14.81%) is in agreement with the calculated value (14.50%). The third stage loss of 9.72% from 351 to 575 °C corresponds to the release of one organic molecule (9.8% theoretical loss). The fourth step occurs at 575 °C, corresponding to the anion decomposition.

4. Conclusion

We report the first example of triethanolamine ligands grafted onto a $[AsMo_6O_{25}]^{9-}$ fragment in aqueous solution. The heteropolyanions are further linked by metal ions forming zig-zag chains. A new approach was demonstrated to realize the functionalization of hexamolybdoarsenate by triethanolamine ligand, which acts as both a cation and a ligand in aqueous solution.

Supplementary material

CCDC 635807 contains the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk).

Funding

The authors are thankful for the financial support from the Natural Science Foundation of China [grant number 21001021] and [grant number 21273031] and from the Department of Science and Technology of Jilin Province [grant number 201201105], [grant number 20110345], [grant number 20130521024JH], and [grant number 201215171].

References

[1] M. Misono. *Catal. Rev. Sci. Eng.*, **29**, 269 (1987).
[2] J.T. Rhule, C.L. Hill. *Chem. Rev.*, **98**, 27 (1998).
[3] L. Ouahab. *Chem. Mater.*, **9**, 1909 (1997).
[4] M.T. Pope, A. Müller. *Angew. Chem. Int. Ed. Engl.*, **30**, 34 (1991).
[5] M.T. Pope. *Heteropoly and Isopolyoxometalates*, Springer, Berlin (1983).
[6] M.T. Pope, A. Müller. *Polyoxometalates: From Platonic Solid to Anti-Retro Viral Activity*, Kluwer, Dordrecht (1994).
[7] C.L. Hill. *Chem. Rev.*, **98**, 1 (1998).
[8] A.M. Khenkin, R. Neumann. *J. Am. Chem. Soc.*, **124**, 4198 (2002).
[9] Q. Chen, D.P. Goshorn, C.P. Scholes, X.L. Tan, J. Zubieta. *J. Am. Chem. Soc.*, **114**, 4667 (1992).
[10] Y. Hou, C.L. Hill. *J. Am. Chem. Soc.*, **115**, 11823 (1993).
[11] D.C. Crans, F. Jiang, J. Chen, O.P. Anderson, M.M. Miller. *Inorg. Chem.*, **36**, 1038 (1997).
[12] D.C. Crans, I. Boukhobza. *J. Am. Chem. Soc.*, **120**, 8069 (1998).
[13] R. Neumann, M. Dahan. *Nature*, **388**, 353 (1997).
[14] R. Neumann, M. Dahan. *J. Am. Chem. Soc.*, **120**, 11969 (1998).
[15] G.J. Chen, Y. Zhou, Z.Y. Long, X.C. Wang, J. Li, J. Wang. *ACS Appl. Mater. Interfaces*, **6**, 4438 (2014).
[16] G. Raj, C. Swalus, A. Guillet, M. Devillers, B. Nysten, E.M. Gaigneaux. *Langmuir*, **29**, 4388 (2013).
[17] A.M. Khenkin, I. Efremenko, J.M.L. Martin, R. Neumann. *J. Am. Chem. Soc.*, **135**, 19304 (2013).
[18] M.P. Santoni, A.K. Pal, G.S. Hanan, A. Proust, B. Hasenknopf. *Inorg. Chem.*, **50**, 6737 (2011).
[19] B. Hasenknopf, R. Delmont, P. Herson, P. Gouzerh. *Eur. J. Inorg. Chem.*, **2002**, 1081 (2002).
[20] C.M. Liu, Y.H. Huang, D.Q. Zhang, S. Gao, F.C. Jiang, J.Y. Zhang, D.B. Zhu. *Cryst. Growth Des.*, **5**, 1531 (2005).
[21] C.P. Pradeep, M.F. Misdrahi, F.Y. Li, J. Zhang, L. Xu, D.L. Long, T.B. Liu, L. Cronin. *Angew. Chem. Int. Ed.*, **48**, 8309 (2009).
[22] M.H. Rosnes, C. Musumeci, C.P. Pradeep, J.S. Mathieson, D.-L. Long, Y.F. Song, B. Pignataro, R. Cogdell, L. Cronin. *J. Am. Chem. Soc.*, **132**, 15490 (2010).
[23] F.Y. Li, L. Xu. *Dalton Trans.*, 4024 (2011).
[24] M.I. Khan, S. Tabussum, R.J. Doedens. *Chem. Commun.*, **2003**, 532 (2003).
[25] D.L. Long, C. Streb, P. Kögerler, L. Cronin. *J. Cluster Sci.*, **17**, 257 (2006).
[26] B. Hedman. *Acta Crystallogr.*, **B36**, 2241 (1980).