



ACADEMIC
PRESS

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Solid State Chemistry 170 (2003) 232–236

JOURNAL OF
SOLID STATE
CHEMISTRY

http://elsevier.com/locate/jssc

$[\{(NiOH)_2Mo_{10}O_{36}(PO_4)Ti_2\}_n]^{5n-}$: a novel chainlike trimetal heteropolyanion based on pseudo-keggin fragments

Hong Zhang,^a Yangguang Li,^a Liying Duan,^a Yang Lan,^a Enbo Wang,^{a,b,*}
Changwen Hu,^a Yuangen Yao,^c Jiutong Chen,^c and Song Gao^d

^a Department of Chemistry, Institute of Polyoxometalate Chemistry, Northeast Normal University, Changchun, Jilin 130024, People's Republic of China

^b State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

^c Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People's Republic of China

^d State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

Received 17 May 2002; received in revised form 17 September 2002; accepted 25 September 2002

Abstract

A new mixed Mo/Ni/Ti heteropoly compound $[C_5H_5NH]_5[(NiOH)_2Mo_{10}O_{36}(PO_4)Ti_2]$ has been hydrothermally synthesized and structurally determined by the single-crystal X-ray diffraction. Black prismatic crystals crystallize in the monoclinic system, space group $P2(1)/n$, $a = 11.2075(2)$, $b = 37.8328(5)$, $c = 13.0888(1)$ Å, $\beta = 101.4580(10)^\circ$, $M = 2276.13$, $V = 5439.19(13)$ Å³, $Z = 4$. Data were collected on a Siemens SMART CCD diffractometer at 293(2) K in the range of $1.68 < \theta < 25.09^\circ$ using the ω -scan technique ($\lambda = 0.71073$ Å, $R(F) = 0.0872$ for 9621 reflections). The title compound contains a trimetal heteropolyanion polymer and “trans-titanium”-bridging pseudo-Keggin fragments linked to a chain.

© 2002 Elsevier Science (USA). All rights reserved.

Keywords: Pseudo-Keggin structure; Trimetal heteropolyanion; Chainlike; Single crystal

1. Introduction

A class of molecularly defined inorganic metal–oxygen clusters, polyoxometalates (POMs), possess intriguing structures and diverse properties and, therefore, are attracting increasing attention worldwide [1–4]. Their potential applications in functional materials have emerged in catalysis, photo-, electro-chromism and magnetism sciences [5–10]. Recently, there has been considerable interest in employing polyoxoanions as building blocks linked by inorganic metal bridges to form one- (1D), two- (2D) and three-dimensional (3D) framework materials [11–23]. The examples include $H_3Na_9[Fe_4(H_2O)_2(P_2W_{15}O_{56})_2] \cdot 62H_2O$ [4], $Cs_{0.5}[Ni(en)_2]_3[V_{18}O_{42}Cl] \cdot 2en \cdot 6H_2O$ [19], $[NaNi_2Mo_{12}O_{30}(PO_4)(HPO_4)_4(H_2PO_4)_3]^{7-}$ [16], $[(\beta_2-SiW_{11}MnO_{38}OH)_3]^{15-}$

[12], $[(CeSiW_{11}O_{39})(H_2O)_3]^{5-}$ [13], $Eu_2(H_2O)_{12}[(Mo_8O_{27}) \cdot 6H_2O]$ [12], $[Mo^VI_8V^IV_4O_{36}(V^VO_4)(V^VO)_2]^{7n-}$ [15], $[M_3V_{18}O_{42}(H_2O)_{12}(XO_4)] \cdot nH_2O$ ($M = Fe, Co, Zn, Mn, X = V, S, n = 24, 30$) [20–22] and $[(Co(H_2O)_4)_2(H_2W_{12}O_{42})]^{6n-}$ [18], in which the polyoxometalates as building blocks, were linked by the main group [4,16], d-block [15,18,19,20–23] or f-block [5,6] metal elements. To the best of our knowledge, all these extended polyoxoanions containing metal bridges are limited to two kinds of d-block transition metals in one polyanion system, and the extended polyoxometalates in which three types of d-block transitional metal ions coexist have not been found up to now. Here, we first report a novel polyoxometalate polymer, $[C_5H_5NH]_5n[(NiOH)_2Mo_{10}O_{36}(PO_4)Ti_2]_n$ **1**. It contains a pseudo-Keggin polymolybdophosphate cluster, which is substituted by two Ni atoms and linked via “trans-Ti” bridges to form a chain. Considering the special applications of transition metal-containing materials in catalysts for organic synthesis [24], such a trimetal heteropolyanion polymer is of particular importance to fundamental and practical researches.

*Corresponding author. Department of Chemistry, Institute of Polyoxometalate Chemistry, Northeast Normal University, Changchun, Jilin 130024, People's Republic of China. Fax: +86-431-568-4009.

E-mail address: wangbenbo@public.cc.jl.cn (E. Wang).

2. Experimental

2.1. General procedures

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Ni, Mo, P, and Ti were determined by a Leaman inductively coupled plasma (ICP) spectrometer. An IR spectrum was recorded in the range 400–4000 cm^{-1} on an Alpha Centaur FT/IR spectrophotometer using a KBr pellet. XPS analyses was performed on a VG ESCALAB MK spectrometer with a $\text{MgK}\alpha$ (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during the analysis.

2.2. Hydrothermal synthesis

Compound **1** was hydrothermally prepared from a mixture of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (0.242 g), Mo (0.096 g), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.237 g), TiCl_4 (0.190 g), pyridine (0.079 g) and H_2O in a mole ratio of 2.1:1.5:1.0:1.2:8:520 neutralized to pH = 6.0 with 50% phosphorous acid. The mixture solution was sealed in a 20 cm^3 Teflon-lined autoclave and heated at 160°C for 6 days. The black prismatic crystals of compound **1** were obtained (Yield: 43%, based on Mo). The IR spectrum of **1** exhibited several characteristic bands at 1091, 959, 913, 791, and 705 cm^{-1} ascribed to $\nu(\text{P}-\text{O})$, $\nu(\text{M}=\text{O})$ and $\nu(\text{M}-\text{O}-\text{M})$ ($\text{M} = \text{Ni}, \text{Mo}, \text{or Ti}$), respectively. The elemental analyses (ICP-AES method) for **1** showed the mole ratio of P:Mo:Ni:Ti to be 1.0:9.8:2.1:1.9.

Table 1
Crystallographic data and Structure Refinement for **1**

Empirical formula	$\text{C}_{25}\text{H}_{32}\text{Mo}_{10}\text{N}_5\text{Ni}_2\text{O}_{42}\text{PTi}_2$
Formula weight	2278.15
Crystal system	Monoclinic
Space group	$P2(1)/n$
a (Å)	11.2075(2)
b (Å)	37.8328(5)
c (Å)	13.0888(1)
α (°)	90
β (°)	101.4580(10)
γ (°)	90
V (Å ³)	5439.19(13)
Calculated density (g cm^{-3})	2.782
$F(000)$	4352
μ (mm^{-1})	3.312
Reflections collected	19 588
Independent reflections	9621 ($R_{\text{int}} = 0.0603$)
Goodness-of-fit on F^2	1.046
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0872$, $wR2 = 0.1754$
R indices (all data)	$R1 = 0.1533$, $wR2 = 0.1964$

2.3. X-ray crystallography

The structure of compound **1** was determined by the single-crystal X-ray diffraction. Crystallographic data are as follows: monoclinic, space group $P2(1)/n$, $a = 11.2075(2)$ Å, $b = 37.8328(5)$ Å, $c = 13.0888(1)$ Å, $\alpha = 90.00^\circ$, $\beta = 101.4580(10)^\circ$, $\gamma = 90.00^\circ$, $M = 2276.13$, $V = 5439.19(13)$ Å³, $Z = 4$ and calculated density $D_{\text{calc}} = 2.782$ g/cm^3 . A black prismatic crystal with the dimension of $0.60 \times 0.22 \times 0.20$ mm was

Table 2
Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for WEB-11. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
P	8748(3)	1113(1)	7867(3)	18(1)
Mo(1)	6158(1)	759(1)	6187(1)	36(1)
Mo(2)	6785(1)	562(1)	9006(1)	33(1)
Mo(3)	10433(1)	707(1)	6159(1)	31(1)
Mo(4)	11348(1)	1474(1)	9575(1)	38(1)
Mo(5)	11084(1)	514(1)	8994(1)	37(1)
Mo(6)	6440(1)	1712(1)	6748(1)	36(1)
Mo(7)	7088(1)	1522(1)	9573(1)	41(1)
Mo(8)	10693(1)	1660(1)	6735(1)	41(1)
Mo(9)	9384(2)	917(1)	10622(1)	50(1)
Mo(10)	8502(2)	170(1)	7329(1)	43(1)
Ni(1)	9033(2)	2052(1)	8415(2)	49(1)
Ni(2)	8119(2)	1296(1)	5111(2)	46(1)
Ti(1)	5030(3)	1166(1)	7903(3)	51(1)
Ti(2)	12458(3)	1056(1)	7858(3)	49(1)
O(1)	5774(11)	332(3)	9473(11)	54(4)
O(2)	10430(14)	1862(5)	9365(11)	92(6)
O(3)	7104(14)	365(5)	6379(10)	87(6)
O(4)	6891(16)	953(4)	5222(12)	80(5)
O(5)	8364(12)	−255(3)	7064(9)	47(3)
O(6)	5798(16)	700(4)	7622(10)	80(5)
O(7)	11676(14)	1519(5)	8116(10)	84(6)
O(8)	7567(14)	231(4)	8382(9)	76(5)
O(9)	7081(18)	1632(4)	5624(14)	100(7)
O(10)	8213(13)	1294(3)	10531(13)	83(6)
O(11)	9969(14)	2004(5)	7337(11)	93(6)
O(12)	11342(13)	538(5)	5424(12)	83(5)
O(13)	5610(16)	1231(4)	6581(11)	78(5)
O(14)	10421(14)	590(4)	10122(14)	81(5)
O(15)	6199(13)	1056(3)	9216(12)	74(5)
O(16)	9310(14)	925(4)	5211(13)	86(6)
O(17)	11896(14)	989(3)	9185(11)	68(5)
O(18)	6050(15)	1586(4)	8162(12)	78(5)
O(19)	9477(13)	334(3)	6358(10)	63(4)
O(20)	12269(12)	260(4)	9487(10)	56(4)
O(21)	9942(12)	198(3)	8380(10)	61(4)
O(22)	9133(13)	2459(3)	8654(12)	63(4)
O(23)	9463(15)	1603(4)	5620(13)	92(6)
O(24)	12640(11)	1611(3)	10272(10)	53(4)
O(25)	8027(13)	1887(4)	9371(10)	67(4)
O(26)	11281(15)	1165(3)	6530(10)	75(5)
O(27)	7564(12)	2025(4)	7351(10)	57(4)
O(28)	6166(12)	1695(4)	10317(12)	66(4)
O(29)	10581(15)	1274(4)	10502(12)	76(5)
O(30)	9671(15)	849(4)	11875(10)	68(4)
O(31)	5238(12)	1967(4)	6315(14)	81(5)

Table 2 (continued)

	x	y	z	U_{eq}
O(32)	8013(11)	620(3)	10125(11)	61(4)
O(33)	11440(13)	636(3)	7609(9)	60(4)
O(34)	4872(11)	610(3)	5466(11)	57(4)
O(35)	11725(11)	1883(3)	6248(11)	54(4)
O(36)	7841(11)	1377(3)	3899(9)	50(3)
O(37)	13840(20)	1428(6)	8093(18)	45(6)
O(38)	13710(20)	797(6)	7773(19)	45(6)
O(37')	13940(20)	1040(6)	8766(18)	38(6)
O(38')	3550(20)	1192(6)	6948(17)	37(6)
O(39)	9621(18)	1453(5)	8080(15)	24(5)
O(40)	8220(19)	1071(5)	8860(16)	30(5)
O(41)	7723(19)	1203(5)	6939(16)	30(5)
O(42)	9411(18)	792(5)	7671(15)	23(5)
O(39')	9332(17)	1154(5)	6868(15)	21(4)
O(40')	9740(19)	1015(5)	8822(16)	31(5)
O(41')	8060(20)	1444(6)	8027(17)	38(6)
O(42')	7906(19)	771(5)	7644(16)	33(5)
C(1)	6601(17)	52(5)	2154(18)	58(6)
C(2)	6216(17)	-91(6)	2999(18)	57(6)
C(3)	6787(18)	24(7)	3955(16)	65(7)
C(4)	7735(16)	263(6)	4142(17)	60(6)
C(5)	8100(20)	380(6)	3250(20)	70(7)
C(6)	7540(20)	286(6)	2219(19)	66(7)
C(7)	3680(20)	1652(6)	3950(30)	82(8)
C(8)	3420(20)	1455(8)	4764(17)	84(8)
C(9)	2640(20)	1203(6)	4596(18)	66(7)
C(10)	2080(20)	1119(6)	3630(30)	78(8)
C(11)	2290(30)	1301(9)	2780(20)	85(8)
C(12)	3090(30)	1562(9)	2970(20)	94(9)
C(13)	9810(20)	1930(6)	1646(19)	66(6)
C(14)	10670(30)	2201(7)	1840(20)	84(9)
C(15)	11220(30)	2312(7)	2750(40)	125(16)
C(16)	10910(30)	2149(10)	3630(20)	102(11)
C(17)	10090(20)	1887(7)	3550(20)	73(7)
C(18)	9560(20)	1788(7)	2540(30)	87(8)
C(19)	5200(20)	857(7)	2906(17)	70(7)
C(20)	4280(20)	619(7)	2671(19)	72(7)
C(21)	3760(20)	560(6)	1649(17)	64(6)
C(22)	4090(20)	756(7)	906(17)	76(8)
C(23)	4990(20)	988(7)	1115(19)	85(9)
C(24)	5560(20)	1041(7)	2110(20)	79(7)
C(25)	8230(30)	2740(12)	3230(30)	141(17)
C(26)	8990(40)	2843(8)	4040(40)	121(15)
C(27)	9060(40)	2661(12)	4990(40)	162(18)
C(28)	8230(30)	2424(12)	5090(40)	170(20)
C(29)	7390(30)	2339(8)	4230(40)	118(14)
C(30)	7300(40)	2509(14)	3220(50)	230(30)

mounted on a glass fiber. Data were collected on a Siemens SMART CCD diffractometer at 293(2) K in the range of $3.56 < 2\theta < 50.18^\circ$ by means of the ω -scan technique. A total of 19 588 reflections were collected and 9621 independent reflections ($R_{int} = 0.06$) were used, in which 5629 reflections were greater than $2\sigma(I)$. An empirical absorption correction was applied. The structure was solved by the direct method and refined by full-matrix least-squares method with the SHELXL-97 programs. Structure solution and refinement based on 9621 independent reflections and 779 parameters gave $R(R_w) = 0.0872$ (0.1754). Crystal data, details of the intensity measurements and data processing parameters are listed in Table 1. Atomic coordinates, isotropic displacement parameters, bond lengths, angles and anisotropic displacement parameters are deposited in supplementary information (Table 2).

3. Results and discussion

The X-ray analysis reveals that the crystal structure of **1** consists of a chainlike “trans-titanium”-bridging pseudo-Keggin type of $[(NiOH)_2Mo_{10}O_{36}(PO_4)Ti_2]_n^{5n-}$ polyanion (Fig. 1) and pyridinium cations. The building block unit of **1** (Fig. 2) could be described as follows. The cluster anion contains a central P^{5+} in an almost regular tetrahedral environment of oxygen atoms with P–O distances in the range 1.471(19)–1.61(2) Å and bond angles in the range 105.0(10)–112.3(10)°. Four oxygen atoms coordinated to P^{5+} were disordered (each position possession ratio: coordinated to P^{5+} 0.5). The two Mo atoms in the Keggin type of $\{Mo_{12}O_{36}(PO_4)\}$ species are replaced by two Ni atoms to result in a three-layered cluster structure, which are spanned by one $\{Mo_2Ni_2\}$ set and two $\{Mo_4\}$ sets. Within the middle layer, the distances of Mo–Mo, Ni–Mo and Ni–Ni are 5.08, 5.15, and 5.12 Å, respectively. The distance between adjacent layers is ca. 11.2 Å. The two $\{Mo_4\}$ layers consist of eight MoO_6 octahedra. In the $\{Mo_2Ni_2\}$ layer, there are two adjacent distorted NiO_5 square pyramids, accompanying with two distorted

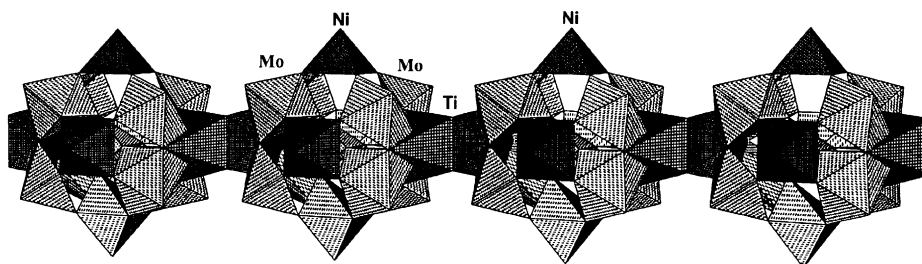


Fig. 1. The structure of the polymeric anion in compound **1**. The polyhedral representation of the chainlike structure of $[(NiOH)_2Mo_{10}O_{36}(PO_4)Ti_2]_n^{5n-}$.

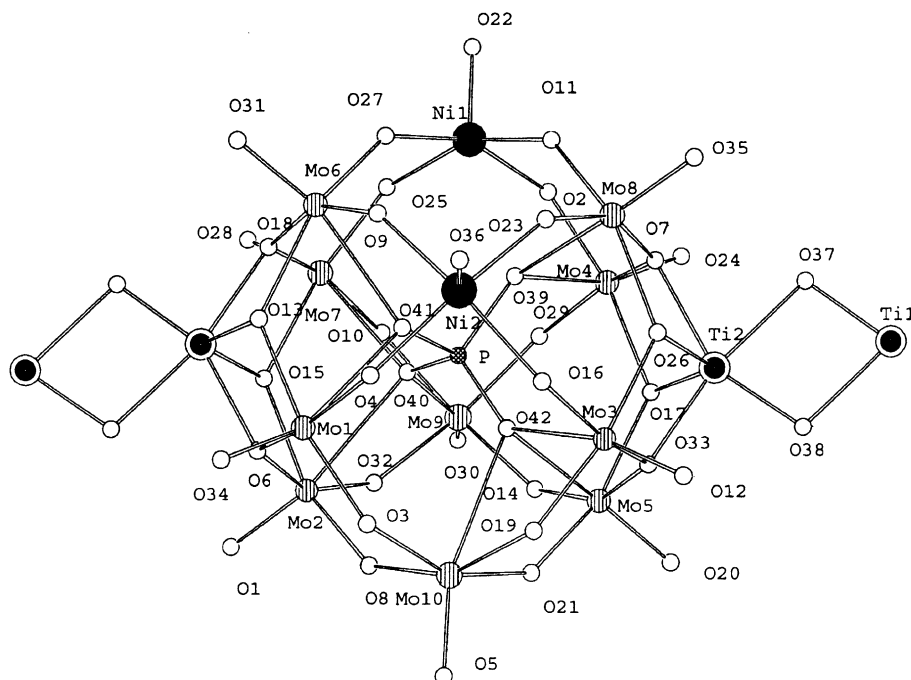


Fig. 2. Ball-and-stick representation of the pseudo-Keggin trimetal heteropolyanion $[(\text{NiOH})_2\text{Mo}_{10}\text{O}_{36}(\text{PO}_4)\text{Ti}_2]^{5-}$.

MoO_6 octahedra. All the distorted MoO_6 octahedra have the Mo–O bond distances in the range 1.628(13)–2.517(19) Å. The Ni–O bond distances for all the NiO_5 distorted square pyramids are in the range 1.572(12)–1.945(13) Å.

The coordination environments around two titanium centers (see Fig. 1) are not easily described with known geometries, but are very similar to a highly distorted octahedral coordination environment (each position possession ratio: coordinated to Ti^{4+} 0.5). Each of the two titanium centers, Ti(1) or Ti(2), forms two additional Ti–O bonds with the bridge oxygen atoms, O(37) and O(38), with bond distances 1.72(2) Å for Ti(1)–O(37) and 1.74(2) Å for Ti(2)–O(38). Compared to the average Ti–O bond length of 1.74 Å, those two additional bond lengths of 2.02(2) Å for Ti(1)–O(38) and 2.07(2) Å for Ti(2)–O(37) are slightly larger, suggesting that the highly geometric distortion of TiO_6 octahedron causes a weak Ti–O–Ti linkage between the Keggin-type clusters. These Keggin fragments are linked by both Ti(1)–O(37)–Ti(2) and Ti(1)–O(38)–Ti(2) bridges and form a one-dimensional chain along the *a*-axis, in which the two titanium centers between the Keggin-type clusters are separated by a distance of 2.902(5) Å.

In the unit cell of **1**, these chainlike trimetal heteropolyanions are parallel with each other and exhibit an interesting alternate arrangement of a normal chain and roll-over chain along the *b*-axis as shown in Fig. 3. The pyridine cations are distributed in the space formed by the polyanion chains.

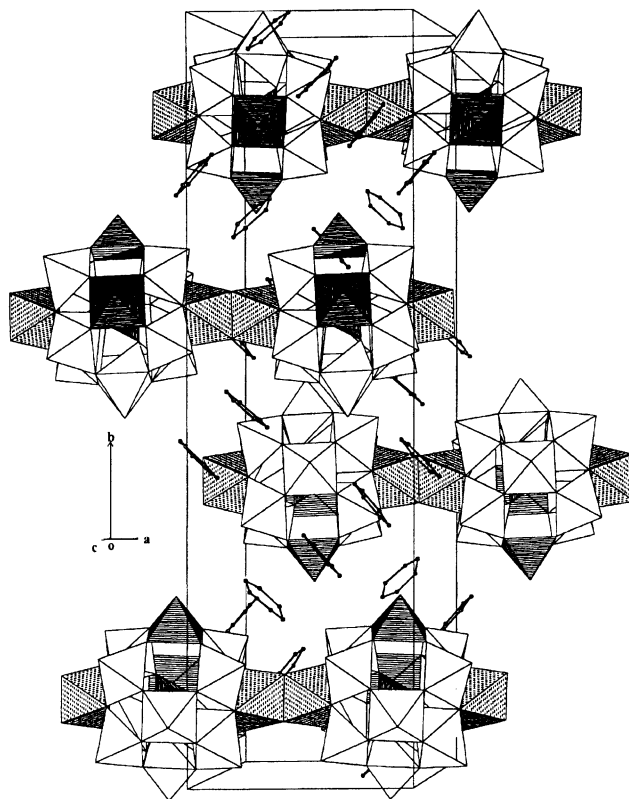


Fig. 3. The packing arrangement of **1** along the crystallographic *c*-axis.

The X-ray photoelectron spectra (XPS) for compound **1** were measured in order to identify the elemental composition and the valence state. The ratio

of the elements is determined to be P:Mo:Ni:Ti:O:C:N = 1:9.9:2.0:1.9:42.1:34.8:7.0, which was in agreement with the result of the elemental analysis. In addition, the oxidative states of metal atoms for **1** are also shown by the XPS. The measured Mo $3d_{5/2}$ binding energy (BE) of 228.7 eV suggests the assignation of all the Mo atoms in the +VI oxidation state. The oxidation states of Ni (II) and Ti (IV) atoms are reflected by their BE values of 854.6 eV for Ni $2p_{3/2}$ and 462.5 eV for Ti $2p_{3/2}$. These results are consistent with the valent sum calculations [25].

Acknowledgments

This research was financially supported by the National Natural Science Foundation of China (20171010).

Supplementary materials

Crystallographic data of **1** have been deposited with the CCDC (12 Union Road, Cambridge CB2 1EZ, UK) and are available on request quoting the deposition numbers CCDC 169484.

References

- [1] M.T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, 1983.
- [2] M.T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl.* 103 (1991) 56–70.
- [3] M.T. Pope, A. Müller, *Polyoxometalates: from platonic solids to anti-retroviral activity*, Kluwer Academic Publishers, Dordrecht, Netherlands, 1994, pp. 1–26.
- [4] M.T. Pope, A. Müller, *Polyoxometalates: from platonic solids to anti-retroviral activity*; Kluwer Academic Publishers, Dordrecht, Netherlands, 1994, pp. 129–156.
- [5] C.L. Hill, *Chem. Rev.* 98 (1998) 1–389.
- [6] D.E. Katsoulis, *Chem. Rev.* 98 (1998) 359–388.
- [7] A. Müller, F. Peters, M.T. Pope, D. Gatteschi, *Chem. Rev.* 98 (1998) 239–271.
- [8] E. Coronado, C.J. Gómez-García, *Chem. Rev.* 98 (1998) 273–296.
- [9] L.H. Bi, E.B. Wang, J. Peng, R.D. Huang, L. Xu, C.W. Hu, *Inorg. Chem.* 39 (2000) 671–679.
- [10] C.W. Hu, Q.L. He, Y.H. Zhang, E.B. Wang, *J. Chem. Soc. Chem. Commun.* 2 (1996) 121–122.
- [11] X. Zhang, Q. Chen, D.C. Duncan, C.F. Campana, C.L. Hill, *Inorg. Chem.* 36 (1997) 4208–4215.
- [12] T. Yamase, H. Naruke, *J. Chem. Soc. Dalton Trans.* 2 (1991) 285–292.
- [13] M. Sadakane, M.H. Dickman, M.T. Pope, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 2914–2916.
- [14] V.N. Molchanov, I.V. Tatjanina, E.A. Torchenkova, *J. Chem. Soc. Chem. Commun.* 3 (1981) 93–94.
- [15] A. Müller, M. Koop, P. Schiffels, H. Bögge, *J. Chem. Soc. Chem. Commun.* 18 (1997) 1715–1716.
- [16] L. Xu, Y.Q. Sun, E.B. Wang, C.W. Hu, *New J. Chem.* 23 (1999) 1041–1044.
- [17] L. Xu, Y.Q. Sun, E.B. Wang, C.W. Hu, *J. Solid State Chem.* 146 (1999) 533–537.
- [18] C. Giménez-Saiz, J.R. Galán-Mascarós, S. Triki, E. Coronado, L. Ouahab, *Inorg. Chem.* 34 (1995) 524–526.
- [19] J.R.D. DeBord, J. Zubieta, *Inorg. Chim. Acta.* 256 (1997) 165–168.
- [20] M.I. Khan, E. Yohannes, R.J. Doedens, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 1292–1294.
- [21] M.I. Khan, E. Yohannes, D. Powell, *Chem. Commun.* 1 (1999) 23–24.
- [22] M.I. Khan, E. Yohannes, D. Powell, *Inorg. Chem.* 38 (1999) 212–213.
- [23] U. Kortz, S. Matta, *Inorg. Chem.* 4 (2001) 815–817.
- [24] M. Schneider, A. Baiker, *Catal. Rev. Sci. Eng.* 37 (1995) 515–556.
- [25] I.D. Brown, D. Altermatt, *Acta Crystallogr. B* 41 (1985) 244–247.