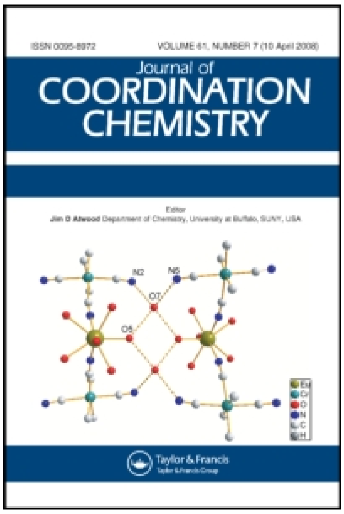
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A new α-keggin unit coordinated to two cobalt complex moieties $\{PMo^{VI}_{11}Mo^{V}O_{40}[Co(TATP)_2(H_2O)]_2\}\cdot 4H_2O$

Zhengbo Han[a]; Yongke He[a]; Yong Ma[a]; Zhenning Lou[a]
[a] School of Chemical Science and Engineering, Liaoning University, Shenyang 110036, P.R. China

To cite this Article Han, Zhengbo , He, Yongke , Ma, Yong and Lou, Zhenning(2007) 'A new α-keggin unit coordinated to two cobalt complex moieties $\{PMo^{VI}_{11}Mo^{V}O_{40}[Co(TATP)_2(H_2O)]_2\}\cdot 4H_2O$', Journal of Coordination Chemistry, 60: 10, 1029 — 1035

To link to this Article: DOI: 10.1080/00958970600990234

URL: http://dx.doi.org/10.1080/00958970600990234

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Coordination Chemistry
Vol. 60, No. 10, July 2007, 1029–1035

Taylor & Francis
Taylor & Francis Group

A new α-keggin unit coordinated to two cobalt complex moieties $\{PMo^{VI}_{11}Mo^{V}O_{40}[Co(TATP)_2(H_2O)]_2\} \cdot 4H_2O$

ZHENGBO HAN*, YONGKE HE, YONG MA and ZHENNING LOU

School of Chemical Science and Engineering, Liaoning University,
Shenyang 110036, P.R. China

(*Received 16 August 2006; in final form 5 September 2006*)

A new α-Keggin unit supported transition metal complex, $\{PMo^{VI}_{11}Mo^{V}O_{40}[Co(TATP)_2(H_20)]_2\} \cdot 4H_2O$ (**1**) (TATP = 1,4,8,9-tetranitrogen-trisphene), has been hydrothermally synthesized and characterized by single crystal X-ray diffraction. X-Ray analysis showed that the two $[Co(TATP)_2(H_2O)]$ units are covalently bonded to the α-Keggin unit $[PMo^{VI}_{11}Mo^{V}04o]^{4-}$ via the terminal oxygen atoms. **1** represents the α-Keggin type polyoxoanion coordinated with two transition metal complex moieties, which further acts as a neutral molecular unit to construct an interesting 3D supramolecualr framework.

Keywords: Polyoxometalates; Cobalt complex; Hydrothermal synthesis; Crystal structure

1. Introduction

The design and construction of inorganic–organic hybrid complexes has attracted much attention owing to their potential applications in functional materials [1–10]. An important advance in polyoxometalate chemistry is the decoration of polyoxoanions with various organic ligands or metal complexes [11–14]. In contrast to extensive reports on isopolyanions-supported transition metal complexes, only a few examples of Keggin- and Dawson-type heteropolyanion-supported transition metal complexes, such as $[Ni(2,2'\text{-bipy})]_{1\cdot5}[PW_{12}O_{40}Ni(2,2'\text{-bipy})_2(H_2O)] \cdot 0.5H_2O$, [15] $\{PW9V_3O_{40}[Ag(2,2'\text{-bipy})_2][Ag_{2-}(2,2'\text{-bipy})_3]\}$, [16] $\{Mo^{VI}_6Mo^{V}_2V^{IV}_8O_{40}(PO_4)[Co(Phen)_2(H_2O)]_2\}[Co_2(Phen)_2(OH)_2(H_2O)_4]_{1/2}$, [17] $[Zn(2,2'\text{-bipy})_3]_2[ZnW_{12}O_{40}Zn(2,2'\text{-bipy})_2] \cdot H_2O$, [18] are reported. Neutral frameworks in which heteropolyanions act as bidentate ligands coordinated to two transition metal complexes via the terminal oxygen atoms have not been reported. Herein we report on the hydrothermal synthesis and crystal structure of a α-Keggin unit coordinated to two cobalt complexes: $\{PMo^{VI}_{11}Mo^{V}O_{40}[Co(TATP)_2(H_2O)]_2\} \cdot 4H_2O$.

---

*Corresponding author. Email: ceshzb@lnu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970600990234

2. Experimental

2.1. *Materials and methods*

The aromatic chelate ligand 1,4,8,9-tetranitrogen-trisphene (TATP) was synthesized according to the literature method; [19] all other reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the 4000–400 cm^{-1} range on a Nicolet 5DX spectrometer.

2.2. *Hydrothermal synthesis*

$\{PMo^{VI}{}_{11}Mo^{V}O_{40}[Co(TATP)_2(H_2O)]_2\}\cdot 4H_2O$ (1). A mixture of Na_2MoO_4 (0.40 g), $CoCl_2$(0.20 g), TATP (0.116 g) and H_2O (10 mL) was neutralized to pH = 4.0 with 30% H_3PO_3 and sealed in a 23 mL Teflon-lined reactor, which was heated to 180°C for six days. After cooling to room temperature, brown crystals of **1** were obtained in 20% yield. Anal. Cacld for $C_{56}H_{44}Co_2Mo_{12}N_{16}O_{46}P$ (%): C 22.59, H 1.49, N 7.53; found: C 22.22, H 1.31, N 7.72. IR (KBr, cm^{-1}): 3072 (m), 2985 (m), 1426 (m), 1318 (m), 1296 (m), 1245 (s), 1167 (m), 1128 (w), 1085(vs), 1014 (vs), 951(vs), 454(m).

2.3. *X-ray crystallography*

Crystallographic data of **1** were collected at room temperature with a Bruker SMART Apex CCD area-detector diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) and graphite monochromator using the ω-scan mode. Data reductions and absorption corrections were performed with SAINT and SADABS software, respectively. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL [20]. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically. Crystallographic data and experimental details for structural analysis are summarized in table 1. Selected bond lengths and angles are listed in table 2. The CCDC reference number is 6,11,407 for **1**. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int code +44(1223)336-033; Email: deposit@ccdc.cam.ac.uk].

3. Results and discussion

3.1. *IR spectrum*

IR spectrum of **1** exhibits an intense band at 951 cm^{-1} attributed to ν(Mo=O) and 1085, 1014 cm^{-1} attributed to ν(P–O), bands at 1426, 1318, 1296, 1245, 1167 cm^{-1} are attributed to characteristic vibrations of TATP ligands [21].

Table 1. Crystallographic data for **1**.

Empirical formula	$C_{56}H_{44}Co_2Mo_{12}N_{16}O_{46}P$
Formula weight	2977.18
Wavelength (Å)	0.70173
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	13.241(5)
b (Å)	14.222(5)
c (Å)	21.539(8)
β (°)	98.784(6)
V (Å^3)	4009(3)
Z	4
Dc (g cm^{-3})	2.467
μ (mm^{-1})	2.341
F(000)	2866
Crystal size (mm^3)	0.13 × 0.06 × 0.05
θ Range for data collection (°)	1.70–26.00
Reflections collected	28,859
Independent reflections (R_{int})	7838 (0.0568)
T (K)	293(2)
Data/restraints/parameters	7838/16/633
Final R indices [$I > 2\sigma$ (I)][a]	$R_1 = 0.0526$ $wR_2 = 0.1160$
R indices (all data)	$R_1 = 0.0752$ $wR_2 = 0.1275$
Largest diff. peak and hole (e Å^{-3})	2.794, −1.330

[a] $R1 = \sum \| F_o| - |F_C \| / \sum |F_o|$; $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

P(1)–O(1)	1.522(5)	P(1)–O(3)	1.532(5)
P(1)–O(8)	1.538(5)	Mo(1)–O(1)	2.492(10)
Mo1)–O(7)	1.739(5)	Mo(1)–O(11)	1.892(8)
Mo(1)–O(13)	1.885(7)	Mo(1)–O(16)	1.804(8)
Mo(1)–O(22)	2.013(8)	Co(1)–O(21)	2.020(5)
Mo(2)–O(9)	1.737(4)	Mo(2)–O(12)	1.820(8)
Mo(2)–O(18)	1.821(9)	Mo(2)–O(19)	1.947(7)
Mo(2)–O(3)	2.501(10)	Mo(2)–O(16)#1	2.004(8)
Mo(3)–O(21)	1.745(4)	Mo(3)–O(20)	1.841(8)
Mo(3)–O(6)	1.847(10)	Mo(3)–O(13)	1.896(8)
Mo(3)–O(4)	1.958(10)	Mo(3)–O(8)	2.411(9)
Mo(3)–O(1)	2.444(10)	Mo(4)–O(14)	1.729(4)
Mo(4)–O(5)	1.864(10)	Mo(4)–O(11)#1	1.873(9)
Mo(4)–O(6)	1.965(10)	Mo(4)–O(12)	1.974(9)
Mo(4)–O(8)	2.493(9)	Mo(4)–O(2)	2.505(9)
Mo(5)–O(15)	1.739(4)	Mo(5)–O(22)	1.804(8)
Mo(5)–O(10)	1.835(7)	Mo(5)–O(20)	1.971(7)
Mo(5)–O(18)	1.996(8)	Mo(5)–O(3)	2.445(9)
Mo(5)–O(1)	2.487(10)	Mo(6)–O(17)	1.737(4)
Mo(6)–O(4)#1	1.842(10)	Mo(6)–O(19)	1.874(8)
Mo(6)–O(5)#1	1.930(10)	Mo(6)–O(10)	1.973(8)
Mo(6)–O(8)#1	2.461(9)	Mo(6)–O(3)	2.513(10)
O(1)#1–P(1)–O(1)	180.0(9)	O(1)–P(1)–O(3)#1	112.8(6)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+2$, $-y$, $-z$.

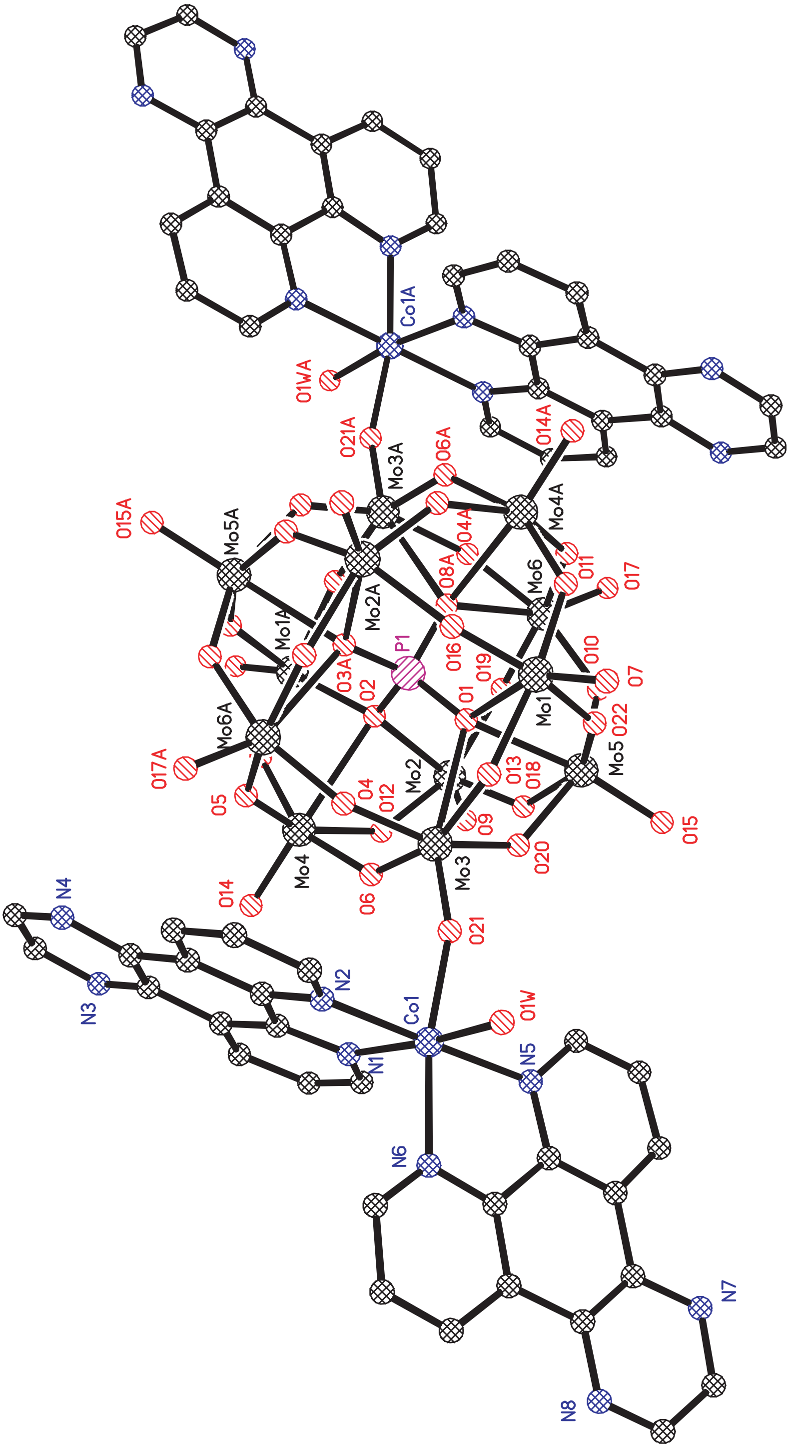


Figure 1. Molecular structure of **1**.

3.2. *Crystal structure*

X-ray diffraction analysis reveals **1** consists of two $[Co(TATP)_2(H_2O)]^{2+}$ units, one reduced $[PMo^{VI}{}_{11}Mo^{V}O_{40}]^{4-}$, and four lattice water molecules. As shown in figure 1, the heteropolyanion $[PMo^{VI}{}_{11}Mo^{V}O_{40}]^{4-}$ exhibits a α-Keggin structure, which is formed from twelve MoO_6 octahedra and one PO_4 tetrahedron. The P atom is located at the inversion center (10,000, 0, 0), which indicates that the central P atom is surrounded by a cube of eight oxygen atoms with each oxygen atom half-occupied. The P–O distances are in the range of 1.524(5)–1.536(5) Å, while the O–P–O angles vary from 107.5(6) to 112.8(6)°. Oxygen atoms in the $[PMo^{VI}{}_{11}Mo^{V}0_{40}]^{4-}$ anion can be divided into four groups according to their coordination number: O_t (terminal oxygen atoms connecting only one Mo atom), O_b (oxygen atoms located in the corner-sharing MoO_6 octahedrons between two Mo_3O_{13} units), O_c (oxygen atoms connecting edge-sharing MoO_6 octahedra in the same Mo_3O_{13} unit), O_a (oxygen atoms connecting the P heteroatom and Mo atoms). Relevant Mo–O distances can be grouped into three sets: Mo–O_t 1.729(5)–1.847(5), Mo–$O_{b/c}$ 1.864(4)–1.9974(5), Mo–O_a, 1.958(5)–2.526(5), while Mo–O–Mo bond angles in the range from 60.8(4) to 155.1(4)°. In comparison with other Keggin polyoxoanions, the unusual feature is that the reduced Keggin structural unit $[PMo^{VI}{}_{11}Mo^{V}O_{40}]^{4-}$ acts as a bidentate ligand towards Co^{2+}, to form a neutral transition metal complex. Two μ_2-oxygens, O(21) and its symmetry-related O(21A), links the Keggin unit and Co(1) atoms, the [Mo(3)–O(21) 1.749(4) Å, O(21)–Co(1) 2.016(5) Å, Co(1)–O(21)–Mo(3) 159.4(5)°, the Mo(3)–O(21) distance is longer than the other W–O_t bond lengths but shorter than W–$O_{b/c}$. The Co atom is coordinated by two TATP, one water molecule and one Keggin unit, with Co1–O(1W) 2.102(9) Å and Co1–N1 2.103(9) and Co1–N2 2.127(9) Å. There exists one Mo^{V} center in the Keggin unit of **1**, and the assignment of the oxidation state for the Mo atoms is consistent with the electric charge and confirmed by bond valence sum calculations [22]. The bond valence calculations, $S = \exp[-[(R - 1.908)/0.370]$ ($S =$ bond valence, $R =$ bond length), leads to S values for Mo(1), Mo(2), Mo(3), Mo(4), Mo(5) and Mo(6) of 5.803, 5.975, 6.067, 5.735, 5.958, 5.878, respectively. The average value for the calculated oxidation state of Mo is 5.909 (the expected average value for $Mo^{VI}{}_{11}Mo^{V}$is 5.916). The calculated results show one out of twelve Mo atoms in +5 oxidation state with one electron delocalized within the whole metal-oxide cluster, which is also consistent with the formula of **1**.

Strong hydrogen bonding interactions among the coordinated water molecules, the lattice water molecules, the nitrogen atoms of TATP ligands and the terminal oxygen atoms of $[PMo^{VI}{}_{11}Mo^{V}O_{40}]^{4-}$ further consolidate the structure, and the detailed geometric data are listed in table 3. The hydrogen bonding and π–π packing

Table 3. Hydrogen-bonding geometric data (Å, °) in **1**.

D–H···A	D–H	H···A	D···A	∠D–H···A	Symmetry operations for A
O1W–H1WA···N7	0.85	2.349	2.974 (3)	131	$-x+3, -y+1, -z$
O1W–H1WB···017	0.85	2.232	3.017 (2)	153	$x+1/2, -y+1/2, z+1/2$
O2W–H2WA···O3W	0.85	2.282	2.862 (2)	126	$x-1/2, -y+1/2, z-1/2$
O2W–H2WB···O15	0.85	2.080	2.914 (3)	166	$-x+5/2, y-1/2, -z-1/2$
O3W–H3WA···O17	0.85	2.466	3.101 (2)	132	$x+1/2, -y+1/2, z+1/2$
O3W–H3WB···O2W	0.85	2.130	2.862 (3)	144	$x+1/2, -y+1/2, z+1/2$

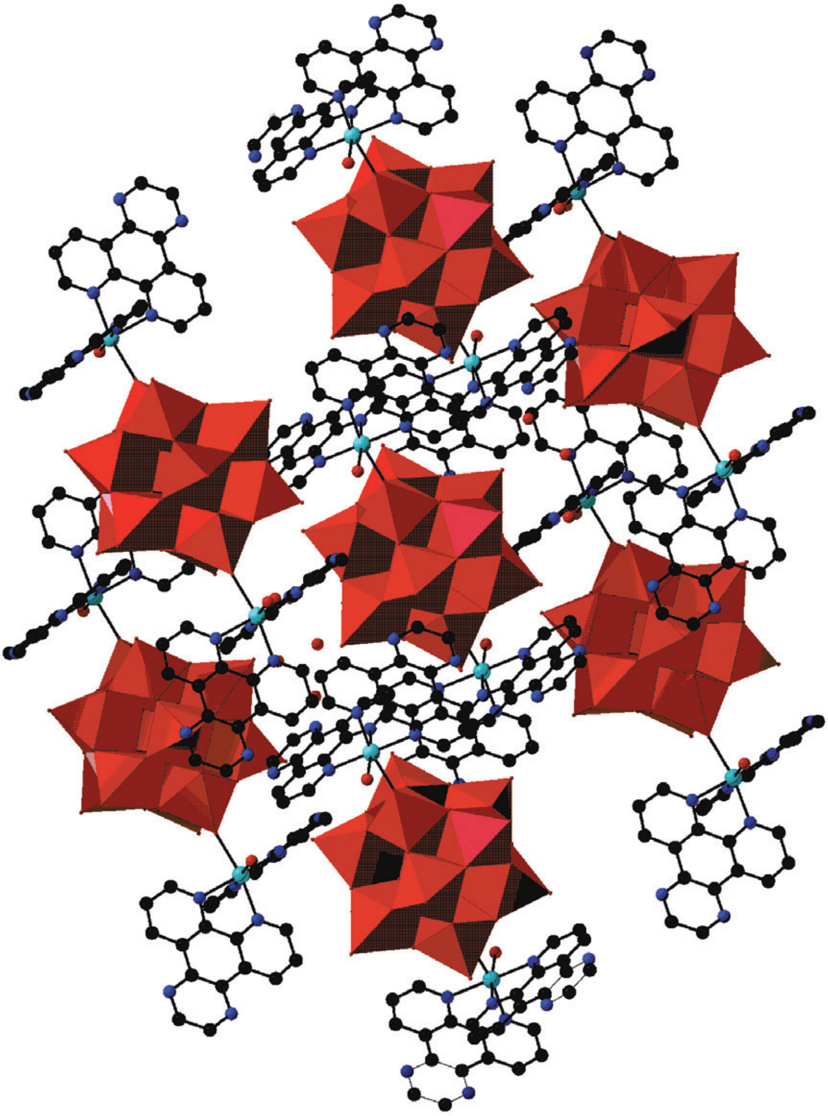


Figure 2. The packing arrangement of **1** viewed along the *c*-axis.

interactions link discrete neutral polyoxometalate derivatives to form an interesting 3D supramolecular framework (figure 2). The distance between aromatic groups is 3.601 Å.

In conclusion, we have synthesized a neutral α-Keggin heteropolyoxoanion-supported cobalt complex $\{PMo^{VI}{}_{11}Mo^{V}O_{40}[Co(TATP)_2(H_2O)]_2\} \cdot 4H_20$ at hydrothermal conditions. The synthesis of this complex confirms that two terminal oxygen atoms of heteropolyoxoanion act as a bidentate ligand to link transition metal complex moieties.

Acknowledgments

This work was granted financial support from the Program for Liaoning Excellent Talents in University (RC-05-11).

References

[1] M.T. Pope, A. Müller. *Polyoxometalates: from Platonic Solids to Antiretroviral Activity*, Kluwer, Dordrecht, (1994).
[2] M.T. Pope, T. Yamase. *Polyoxomtalte Chemistry for Nanocomposite Design*, Kluwer, Dordrecht, (2002).
[3] L.C.W. Baker, D.C. Glick. *Chem. Rev.*, **98**, 3 (1998).
[4] Y.P. Jeannin. *Chem. Rev.*, **98**, 51 (1998).
[5] G. Centi. *Catal. Today*, **16**, 5 (1993).
[6] P. Gouzerh, A. Proust. *Chem. Rev.*, **98**, 77 (1998).
[7] N. Mizuno, M. Misono. *Chem. Rev.*, **98**, 199 (1998).
[8] A. Müller, F. Peters, M.T. Pope, D. Gatteschi. *Chem. Rev.*, **98**, 239 (1998).
[9] E. Coronado, C.J. Gómez-García. *Chem. Rev.*, **98**, 273 (1998).
[10] V. Soghomonian, Q. Chen, R.C. Hausgalter, J. Zubieta. *Science*, **259**, 1596 (1993).
[11] S. Reinoso, P. Votiroa, L. Lezama, A. Luque, J.M. Gutiérrez-Zorrilla. *Inorg. Chem.*, **42**, 3709 (2003).
[12] X.M. Zhang, M.L. Tong, X.M. Chen. *Chem. Commun.*, 1817 (2000).
[13] Y.G. Wei, B.B. Xu, C.L. Barnes, Z.H. Peng. *J. Am. Chem. Soc.*, **123**, 4083 (2001).
[14] L. Xu, M. Lu, B.B. Xu, Y.G. Wei, Z.H. Peng, D.R. Powell. *Angew. Chem. Int. Ed.*, **41**, 4129 (2002).
[15] Y. Xu, J.Q. Xu, K.L. Zhang, Y. Zhang, X.Z. You. *Chem. Commun.*, 153 (2000).
[16] G.Y. Luan, Y.G. Li, S.T. Wang, E.B. Wang, Z.B. Han, C.W. Hu, N.H. Hu, H.Q. Jia. *Daltan, Trans*, 233 (2003).
[17] C.M. Liu, D.Q. Zhang, D.B. Zhu. *Crystal Growth Design*, **3**, 363 (2003).
[18] J.Y. Niu, Z.L. Wang, J.P. Wang. *Inorg. Chem. Commun.*, **6**, 1272 (2003).
[19] J.G. Collins, A.D. Sleeman, J.R. Aldrich-Wright, I. Greguric, T.W. Hambley. *Inorg. Chem.*, **37**, 3133 (1998).
[20] (a) G.M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997; (b) G. M. Sheldrick, SHELXS97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997; (c) G.M. Sheldrick, *Acta Crystallogr.*, *Sec. A*, 1990, **46**, 467.
[21] Z.B. Han, X.N. Cheng, X.M. Chen. *Crystal Growth Design*, **5**, 695 (2005).
[22] I.D. Brown, D. Altermatt. *Acta Crystallogr. Sec. B*, **41**, 244 (1985).