

Rapid communication

Hydrothermal synthesis and crystal structure of a novel two-dimensional organic–inorganic hybrid copper molybdate with mixed organodiamine and dicarboxyl ligands[☆]

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Abstract

An unusual compound, $[\{\text{Cu}(2,2'\text{-bpy})\}_2(\text{tp})\text{Mo}_4\text{O}_{13}]$ (tp = terephthalate) **1**, has been hydrothermally synthesized and structurally characterized by the elemental analyses, IR spectrum, X-ray photoelectron spectrum, TG analyses and the single crystal X-ray diffraction. The structure of **1** exhibits a layered network built up from bimetallic one-dimensional ribbons bridged by dicarboxylate ligands. Compound **1** represents the first hybrid molybdates composed of mixed organodiamine and dicarboxylate ligands. Crystal data for compound **1**: triclinic, space group $P\bar{1}$, $a = 7.3748(15)$ Å, $b = 9.9692(2)$ Å, $c = 12.0692(2)$ Å, $\alpha = 69.223(3)^\circ$, $\beta = 76.123(3)^\circ$, $\gamma = 76.623(3)^\circ$; $V = 794.83(3)$ Å³; $Z = 1$, $R(\text{final}) = 0.0688$. The data were collected on a Rigaku R-Axis RAPID IP diffractometer at 293 K using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) and oscillation scans technique in the range $1.83^\circ < \theta < 27.48^\circ$.

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1. Introduction

The widespread contemporary interest in organic–inorganic hybrid compounds, which are expected to be endowed with enhanced or combined functionalization of both organic and inorganic substructures [1,2], has been focused on the richness of their structures and special properties in the fields of catalysis and materials science as well as in biology, magnetism, nonlinear optics and medicine [3,4]. Integration metal-organic complexes and molybdenum oxide moieties into a single structure characterized one fruitful subclass of organic–inorganic hybrid materials. Typically, the organic components may be introduced into the solid phases: (i) as a charge-compensating and space-filling constituent; (ii) as a ligand coordinated covalently to the molybdenum oxide scaffolding; and (iii) as a ligand

bound directly to a secondary metal center [5]. More recently, the rational design of organic–inorganic molybdenum oxide phases is achievable in defining their structures contributed to the increasing understanding of the methods to control the synergistic interaction between organic and inorganic chemical compositions [5]. During the studies of such kinds of solid materials, an astonishing variety of novel phases with discrete or polymeric structures have been isolated hydrothermally [6–23]. Till now, the polyanions in these solids are limited to $\{\text{Mo}_6\text{O}_{19}\}$ [10–12] (or $\{\text{Mo}_6\text{O}_n\text{N}_{19-n}\}$ [13–16]) and $\{\text{Mo}_8\text{O}_{26}\}$ [10,12,17–19] clusters. Hybrid solid-state materials based on tetramolybdate are rare [7,20,21]. Moreover, the organic molecules introduced into the reaction systems are mostly restricted to the organo-nitrogen ligands. Organic–inorganic hybrid molybdate containing carboxyl ligands are rarely reported. The possible reason is that the carboxyl-containing ligands possess more negative charges, and make it difficult to meet the charge balance with the polyanions [9,22]. Therefore, it remains a great challenge to incorporate carboxyl-containing ligands into the molybdate

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scaffolding. Furthermore, one promising goal to the design and synthesis of organic–inorganic hybrid materials is to introduce more than one type of organic molecule with distinctive linking manners and coordination preferences into the inorganic substructures in constructing organic–inorganic hybrid solids with remarkable structural features and attractive properties [22,23].

On the basis of the aforementioned points, a novel organic–inorganic hybrid compound, $[\{\text{Cu}(2,2'\text{-bpy})\}_2(\text{tp})\text{Mo}_4\text{O}_{13}]$ (tp = terephthalate) **1**, has been successfully isolated by the introduction of mixed nitrogen and oxygen donor ligands via hydrothermal technology. To the best of our knowledge, compound **1** represents the first hybrid molybdenum oxide skeleton combined with mixed organodiamine and dicarboxylate ligands into one phase.

2. Experimental section

2.1. General procedures

All chemicals purchased were of reagent grade and used without further purification. The hydrothermal reactions were performed in 20 mL Teflon-lined stainless-steel vessels under autogenous pressure with a filling capacity approximately 60%. Water used in the reactions is distilled water. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Mo and Cu were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectrum was recorded in the range 400–4000 cm^{-1} on an Alpha Centaur FT/IR spectrophotometer using KBr pellets. X-ray photoelectron spectrum (XPS) analysis was performed on a VG ESCALAB MK II spectrometer with an $\text{MgK}\alpha$ (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during analysis. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^\circ\text{C min}^{-1}$.

2.2. Synthesis of $[\{\text{Cu}(2,2'\text{-bpy})\}_2(\text{tp})\text{Mo}_4\text{O}_{13}]$

Compound **1** was isolated as green blocks from the reaction of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, CuCl_2 , terephthalic acid, 2,2'-pyridine, HCl and H_2O in a molar ratio of 1:5:3:2:1:555 under autogenous pressure at 140°C for four days. After slow cooling to room temperature, the resulting crystals of **1** were collected as a major phase (60% yield on Mo) from the pale-yellow slurry, and then filtered off, washed with distilled water, and dried at ambient temperature. The green blocks were manually selected for structural determination and further characterization. Anal. Calc. for **2**: C, 28.14; H, 1.69; N,

4.69; Cu, 10.63; Mo, 32.11 (%). Found: C, 28.67; H, 1.61; N, 4.83; Cu, 10.92; Mo, 31.43 (%).

2.3. X-ray crystallography

The data were collected on a Rigaku R-AXIS RAPID IP diffractometer at 293 K using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and oscillation scans technique in the range $1.83^\circ < \theta < 27.48^\circ$. Empirical absorption correction was applied. A total of 3076 (2475 unique, $R_{\text{int}} = 0.0688$) reflections were measured. The structure was solved by direct methods using the program SHELXS-97 [24] and refined by full-matrix least-squares methods on F^2 using the SHELXL-97 [25] program package. All of the non-hydrogen atoms were refined anisotropically. Positions of the hydrogen atoms attached to carbon atoms were fixed at their ideal positions. Structure solution and refinement based on 2475 independent reflections with $[I > 2\sigma(I)]$ on 0 restraint and 250 parameters gave $R1$ (wR_2) = 0.0688 (0.1869). A summary of the crystallographic data and structural determination for compound **1** is provided in Table 1 (Table S1). Selected bond lengths and angles are listed in Table 3 (Table S2). Atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

3. Results and discussion

The X-ray diffraction analysis¹ reveals that the structure of **1** features a layered network constructed from bimetallic $[\{\text{Cu}(2,2'\text{-bpy})\}_2\text{Mo}_4\text{O}_{13}]^{2n+}$ ribbon connected by tp ligands. The basic building block of **1** is shown in Fig. 1. There is one crystallographically independent Cu atom and two Mo atoms in the asymmetric unit. The square–pyramidal coordination environment about Mo(1) atom is defined by a terminal oxygen atom and four bridging oxygen atoms with Mo–O bond lengths in the range 1.689–2.091 Å (Table S3). Mo(2) atom is coordinated by four bridging oxygen atoms with Mo–O bond length vary from 1.685 to 2.344 Å , three of them are linked with Mo atoms and the other linked with Cu, one terminal oxygen atom, and one carboxyl oxygen atom from the tp ligand to finish its octahedral coordination geometry. Cu(3) atom, residing in a distorted square–pyramidal coordination environment, is coordinated by two nitrogen atoms from a 2,2'-bpy with Cu–N distances of 2.005 and 2.015 Å , two bridging oxygen atoms from the molybdate cluster and a

¹Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 215191. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

Table 1
Crystal data and structure refinement for compound **1**

Empirical formula	C ₂₈ H ₂₀ Cu ₂ Mo ₄ N ₄ O ₁₇
Formula weight	1195.32
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	7.3748(15)
<i>b</i> (Å)	9.969(2)
<i>c</i> (Å)	12.069(2)
α (deg)	69.22(3)
β (deg)	76.12(3)
γ (deg)	76.62(3)
Volume (Å ³)	794.8(3)
<i>Z</i>	1
ρ_{calc} (g cm ⁻³)	2.497
Absorption coefficient (mm ⁻¹)	2.935
<i>F</i> (000)	578
Crystal size (mm)	0.480 × 0.274 × 0.173
θ Range for data collection (deg)	1.83–27.48
Limiting indices	−9 ≤ <i>h</i> ≤ 9, −12 ≤ <i>k</i> ≤ 12, −15 ≤ <i>l</i> ≤ 15
Reflections collected	3076
Independent reflections	2475 (<i>R</i> _{int} = 0.0688)
Data/restraints/parameters	2475/0/250
Goodness-of-fit on <i>F</i> ²	1.025
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ^a = 0.0688, <i>wR</i> ^b = 0.1869
Indices (all data)	<i>R</i> ^a = 0.0852, <i>wR</i> ^b = 0.1999

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)] \}^{1/2}.$$

Table 2
Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for **1**. *U*(eq) is defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Mo(1)	191(1)	9592(1)	1405(1)	23(1)
Mo(2)	−4172(1)	10129(1)	1321(1)	22(1)
Cu(3)	−6116(2)	7025(1)	2948(1)	26(1)
O(9)	1604(10)	9414(8)	−135(6)	23(2)
O(8)	−2240(10)	9819(8)	2321(6)	26(2)
O(7)	−4397(11)	6524(9)	1594(7)	34(2)
O(6)	−5595(11)	9003(9)	2495(6)	29(2)
O(5)	−5187(13)	11828(9)	1316(7)	35(2)
N(2)	−7449(14)	7077(10)	4592(8)	28(2)
O(4)	−2237(12)	7921(9)	1258(7)	33(2)
O(3)	1159(11)	10859(10)	1591(7)	33(2)
O(2)	1195(12)	7893(10)	2281(7)	36(2)
N(1)	−6452(15)	4924(11)	3722(8)	32(2)
O(1)	−5000	10000	0	31(2)
C(12)	−1331(16)	5905(12)	542(9)	26(2)
C(4)	−7922(19)	8278(14)	4947(11)	37(3)
C(5)	−7990(16)	5818(15)	5352(10)	34(3)
C(14)	−2776(16)	6879(11)	1161(9)	26(2)
C(13)	−1882(18)	4888(12)	204(10)	32(2)
C(7)	−7560(20)	3154(15)	5548(10)	39(3)
C(6)	−7322(16)	4549(13)	4889(9)	29(2)
C(11)	530(18)	6023(13)	331(11)	35(3)
C(1)	−9079(18)	5711(14)	6491(11)	35(3)
C(9)	−5980(20)	2418(14)	3850(12)	43(3)
C(10)	−5784(19)	3864(14)	3216(11)	39(3)
C(8)	−6900(20)	2070(15)	5026(11)	46(3)
C(3)	−8970(20)	8207(16)	6085(12)	48(3)
C(2)	−9548(19)	6950(14)	6848(10)	38(3)

carboxyl oxygen atom with a longer Cu–O distance of 2.192 Å and two shorter Cu–O distances of 1.954 and 1.955 Å.

The extension of the structure can be described as follows: two {MoO₅} square-pyramids and two {MoO₆} octahedra assemble together in a corner- and edge-sharing arrangement generating a tetranuclear molybdate cluster. The tetramolybdate clusters link to each other by sharing the terminal octahedral O atoms to form an infinite molybdenum oxide chain, which is engrafted by the square-pyramidal {Cu(2,2′-bpy)}²⁺ complexes via the terminal O atoms of {MoO₆} octahedra and {MoO₅} square pyramids (Fig. 2a). The tp ligands functioning in a bis-bidentate mode coordinated covalently to the Cu sites and octahedral Mo sites extending into a 2-D network (Figs. 2b and S2). It is also striking that there are extensive hydrogen-bond contacts (the average hydrogen-bonding distance is about 2.55 Å) and strong H–H interactions (the nearest distance of two parallel pyridine rings is about 3.50 Å) in the interlamellar regions of solid **1**, playing an important role in the stabilization of the structure (see Fig. 3) (Tables S4 and S5).

The {Mo₄O₁₈} cluster in **1** are quite distinct from the reported precursors: (i) the tetranuclear molybdenum cluster in [Ni(3,3′-bpy)₂]Mo₄O₁₄ consists of two

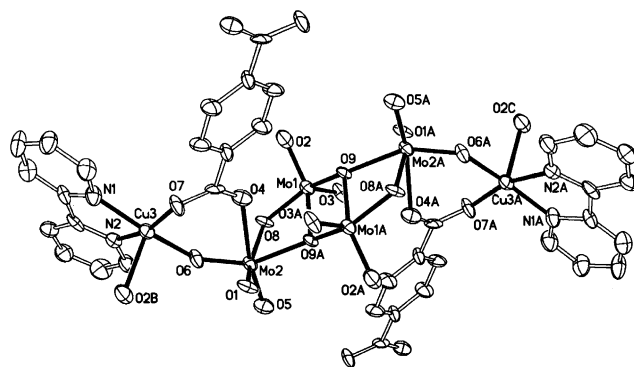


Fig. 1. ORTEP drawing of **1** showing the coordination environment around Cu and Mo with thermal ellipsoids at 50% probability.

{MoO₆} octahedra and two {MoO₅} distorted trigonal bipyramids in an edge-sharing arrangement [7]; (ii) the {Mo₄O₁₄}^{4−} cluster in [Cu(terpy)Mo₂O₇] is constructed from four edge- and corner-sharing {MoO₅} distorted square pyramids [20]; and (iii) in the compound (C₂H₁₀N₂)[Mo₄O₁₂], the {Mo₄O₁₆} unit is composed of two Mo^{VI} and two Mo^V edge-sharing molybdenum

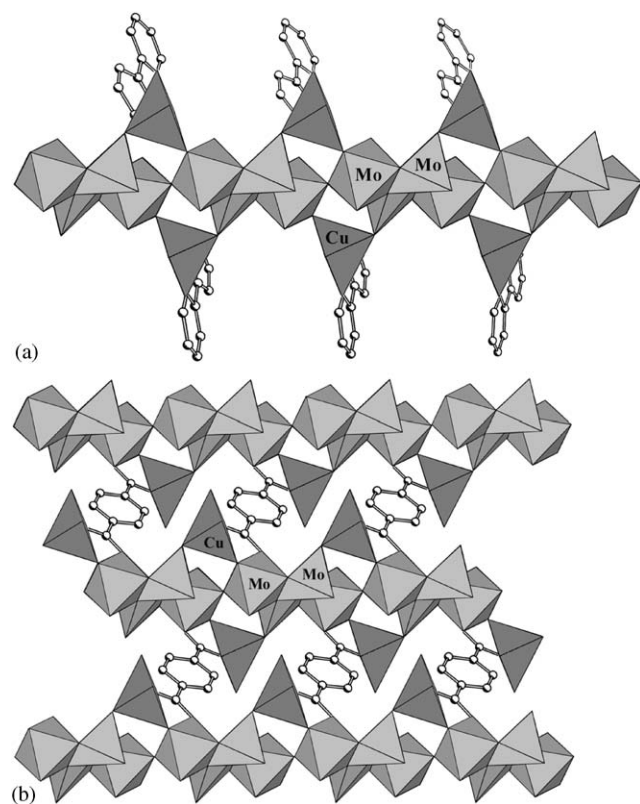


Fig. 2. (a) The polyhedral representation of individual 1-D ribbon in **1**. (b) Polyhedral representation of the 2-D network of compound **1**. For the sake of clarity, all the hydrogen atoms and the carbon atoms from the 2,2'-bpy ligands are omitted.

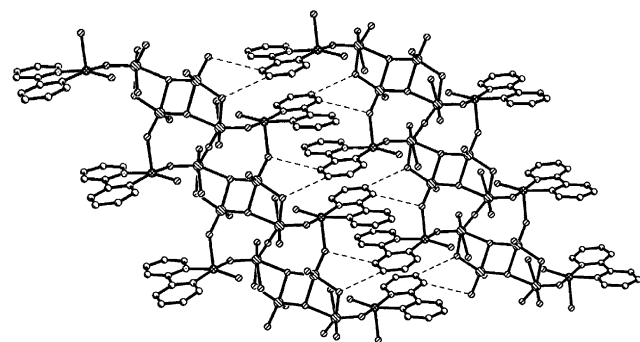


Fig. 3. The 3-D framework of **1**, exhibiting the linkage of hydrogen bonds and J1–J1 interactions.

octahedral [21]. This is mostly because the carboxyl-containing ligands introduced into the reaction systems coordinated directly to the Mo centers afforded additional oxygen donors leading to the formation of the unprecedented tetranuclear molybdate cluster. It can be proved that the tetranuclear oxide cluster is the same, if the carboxyl O atoms were removed, as the $\{\text{Mo}_4\text{O}_{14}\}$ cluster in $[\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7]$ [20]. It is also believed that the organic molecules, especially the carboxyl-containing components, play a critical role in the construction

of this unusual compound. The coordination environment around Cu and the connectivity of the molybdate cluster in **1** is similar to $[\text{Cu}(\text{terpy})\text{Mo}_2\text{O}_7]$. However, the distinctive feature of this compound is that the dicarboxylate ligands coordinated covalently to the bimetallic ribbon extending the structure into higher dimension via an infrequent linking mode.

In the IR spectra of compound **1**, the vibration modes for $\nu(\text{Mo}=\text{O})$ and $\nu(\text{Mo}-\text{O}-\text{Mo})$ are observed at 965, 950, 889, 856, 836, 772, and 714 cm^{-1} . The characteristic absorption bands of organic ligands occur in the range $1600\text{--}1380\text{ cm}^{-1}$ (Fig. S1). The XPS measurements of compound **1** in the energy regions of $\text{Cu}2p_{1/2}$ and $\text{Cu}2p_{3/2}$ show one peak at 934.3 eV , attributable to Cu^{2+} [26,27], in the energy region of $\text{Mo}3d_{3/2}$ and $\text{Mo}3d_{5/2}$ give two peaks (the higher is at 232.0 eV), attributed to Mo^{6+} [28] (see Fig. S3). The results are in good accordance with the valence sum calculations for Mo^{6+} and Cu^{2+} and also confirm the structure analysis.

The TG curve of compound **1** exhibits two steps of weight losses, as shown in Fig. S4. The first weight loss is 8.75% from 320°C to 370°C , which is assigned to the loss of tp ligands (calculated value 8.38%); the second is 25.66% from 380°C to 580°C , attributable to the loss of 2,2'-bpy ligands (calculated value 26.13%). The whole weight loss in the temperature range $300\text{--}600^\circ\text{C}$ is 34.41%, which is in good agreement with the calculated value 34.51%.

In this work, a new inorganic–organic hybrid copper molybdate with organodiamine and dicarboxyl ligands has been reported. The compound displays a unique 2-D network constructed from bimetallic ribbons covalently bonded with 2,2'-bpy and tp ligands. The successful

Table 3
Selected bond lengths (\AA) and angles ($^\circ$) for compound **1**^a

Mo(1)–O(3)	1.689(8)	Mo(1)–O(9)	1.946(6)
Mo(1)–O(2)	1.749(9)	Mo(1)–O(9)#1	2.091(7)
Mo(1)–O(8)	1.878(7)	Mo(1)–Mo(2)	3.1578(15)
Mo(2)–O(5)	1.685(8)	Mo(2)–O(8)	1.985(7)
Mo(2)–O(6)	1.753(7)	Mo(2)–O(9)#1	2.116(7)
Mo(2)–O(1)	1.8918(9)	Mo(2)–O(4)	2.344(8)
Cu(3)–O(7)	1.954(7)	Cu(3)–N(1)	2.015(10)
Cu(3)–O(6)	1.955(8)	Cu(3)–O(2)#2	2.192(9)
Cu(3)–N(2)	2.005(9)	O(9)–Mo(1)#1	2.091(7)
O(3)–Mo(1)–O(2)	107.3(4)	O(8)–Mo(1)–O(9)#1	75.3(3)
O(3)–Mo(1)–O(9)	102.9(3)	O(2)–Mo(1)–Mo(2)	118.3(3)
O(8)–Mo(1)–O(9)	144.6(3)	O(9)–Mo(1)–Mo(2)	108.4(2)
O(5)–Mo(2)–O(1)	101.5(3)	O(6)–Mo(2)–O(9)#1	153.8(3)
O(6)–Mo(2)–O(1)	99.0(2)	O(1)–Mo(2)–O(9)#1	86.57(19)
O(6)–Mo(2)–O(8)	93.1(3)	O(5)–Mo(2)–O(4)	169.5(4)
O(1)–Mo(2)–O(8)	153.3(2)	O(6)–Mo(2)–O(4)	83.7(3)
O(9)#1–Mo(2)–O(4)	71.5(3)	O(1)–Mo(2)–Mo(1)	120.42(5)
O(7)–Cu(3)–O(6)	96.6(3)	O(6)–Cu(3)–N(2)	91.6(3)
O(7)–Cu(3)–O(2)#2	103.2(3)	N(1)–Cu(3)–O(2)#2	98.8(4)

^aSymmetry transformations used to generate equivalent atoms: #1 $-x, -y + 2, -z$ #2 $x - 1, y, z$.

preparation of **1** indicates the introduction of mixed organic ligands is an optional route for the preparation of novel high-dimensional inorganic–organic hybrid polyoxometalates with unique structures and remarkable properties. Future research may focus on the attempting to explore the effects of transition metal-organic fragments on the reaction systems.

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References

- [1] L.C.W. Baker, D.C. Glick, *Chem. Rev.* 98 (1998) 3.
- [2] X.-Y. Huang, J. Li, H.-X. Fu, *J. Am. Chem. Soc.* 122 (2000) 8789.
- [3] C.L. Hill, C.M. Prosser-McCartha, *Coord. Chem. Rev.* 143 (1995) 407.
- [4] C.L. Hill (guest ed.), Special issue on Polyoxometalates: *Chem. Rev.* 1 (1998) and references therein.
- [5] P.J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem. Int. Ed.* 38 (1999) 2638.
- [6] Y. Xu, J.J. Lu, N.K. Goh, *J. Mater. Chem.* 9 (1999) 1599.
- [7] R. L. LaDuca Jr., M. Desciak, M. Laskoski, R.S. Rarig Jr., J. Zubieta, *J. Chem. Soc., Dalton Trans.* (2000) 2255.
- [8] C.D. Wu, C.Z. Lu, H.H. Zhuang, J.S. Huang, *J. Am. Chem. Soc.* 124 (2002) 3836.
- [9] M. Yuan, Y.G. Li, E.B. Wang, C.G. Tian, L. Wang, C.W. Hu, N.H. Hu, H.Q. Jia, *Inorg. Chem.* 42 (2003) 3670.
- [10] D. Hagrman, P. Hagrman, J. Zubieta, *Inorg. Chim. Acta* 300–302 (2000) 212.
- [11] X.L. Wang, Y.Q. Guo, Y.G. Li, E.B. Wang, C.W. Hu, N.H. Hu, *Inorg. Chem.* 42 (2003) 4135.
- [12] D. Hagrman, P.J. Zapf, J. Zubieta, *Chem. Commun.* (1998) 1283.
- [13] H. Kwen, V.G. Young Jr., E.A. Maatta, *Angew. Chem. Int. Ed.* 38 (1999) 145.
- [14] A.R. Moore, H. Kwen, A.M. Beatty, E.A. Maatta, *Chem. Commun.* (2000) 1793.
- [15] J. Spandl, C. Daniel, I. Brüdgam, H. Hartl, *Angew. Chem. Int. Ed.* 42 (2003) 1163.
- [16] L. Xu, M. Lu, B.B. Xu, Y.G. Wei, Z.H. Peng, D.R. Powell, *Angew. Chem. Int. Ed.* 41 (2002) 4129.
- [17] J.Q. Xu, R.Z. Wang, G.Y. Wang, Y.H. Xing, D.M. Li, M.H. Bu, L. Ye, Y.G. Fan, Y. Xing, Y.H. Lin, H.Q. Jia, *Chem. Commun.* (1999) 983.
- [18] X.J. Wang, B.S. Kang, C.Y. Su, K.B. Yu, H.X. Zhang, Z.N. Chen, *Polyhedron* 18 (1999) 3371.
- [19] P.J. Zapf, C.J. Warren, R.C. Haushalter, J. Zubieta, *Chem. Commun.* (1997) 1543.
- [20] P.J. Hagrman, J. Zubieta, *Inorg. Chem.* 39 (2000) 5218.
- [21] N. Guillou, G. Ferey, M.S. Whittingham, *J. Mater. Chem.* 8 (1998) 2277.
- [22] J. Tao, X.M. Zhang, M.L. Tong, X.M. Chen, *J. Chem. Soc., Dalton Trans.* (2001) 770.
- [23] C.M. Liu, D.Q. Zhang, M. Xiong, D.B. Zhu, *Chem. Commun.* (2002) 1416.
- [24] G.M. Sheldrick, SHELXTL 97, Program for Crystal Structure Solution, University of Göttingen, 1997.
- [25] G.M. Sheldrick, SHELXTL 97, Program for Crystal Structure Refinement, University of Göttingen, 1997.
- [26] L. Beyer, R. Kimse, J. Stach, R. Szargan, E. Hoyer, *Z. Anorg. Allg. Chem.* 476 (1981) 7.
- [27] V.I. Nefedov, M.N. Firsov, I.S. Shaplygin, *J. Electron Spectrosc. Relat. Phenom.* 26 (1982) 65.
- [28] S.O. Grim, L.J. Matienzo, *Inorg. Chem.* 14 (1975) 1014.