FULL PAPER

Self-Assembly of Organodiphosphonate, Polyoxomolybdate and Diphenanthrolinecobalt(II) into Two Clusters and One Linear Polymer

Rui-Biao Fu,[a] Xin-Tao Wu,*[a] Sheng-Min Hu,[a] Jian-Jun Zhang,[a] Zhi-Yong Fu,[a] Wen-Xin Du,[a] and Sheng-Qing Xia[a]

[{Co(1,10-phen)$_2$}$_2${(Mo$_4$O$_{12}$)(O$_3$PCH$_2$CH$_2$PO$_3$)}·(H$_2$O)] (**1**), [{Co(1,10-phen)$_2$}$_2${(Mo$_4$O$_{12}$)(O$_3$PCH$_2$CH$_2$CH$_2$PO$_3$)}·(1.5H$_2$O)] (**2**) and [{Co(1,10-phen)$_2$(H$_2$O)$_2$}{Co(1,10-phen)$_2$(H$_2$O)}-{(Mo$_5$O$_{15}$)(O$_3$PCH$_2$CH$_2$CH$_2$CH$_2$PO$_3$)}·(6H$_2$O)] (**3**) were synthesized by self-assembly of H$_2$O$_3$P(CH$_2$)$_n$PO$_3$H$_2$ (n = 2–4), polyoxomolybdate and [Co(1,10-phen)$_2$]$^{2+}$ (1,10-phen = 1,10-phenanthroline) under hydrothermal conditions. Compounds **1** and **2** are novel heterometallic hexanuclear clusters, while compound **3** is a new linear polymer.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

Metal-organic units have been successfully introduced into organic-inorganic hybrid systems as charge-compensating motifs, structure-directing components and building blocks to synthesize many new compounds such as micropores.[1−13] In the molybdenum organodiphosphonate system three one-dimensional and two two-dimensional polymers have been produced by incorporating copper-phenanthroline, copper-2,2′-bipyridine and copper-tetra(2-pyridyl)pyrazine as metal-organic subunits.[14−15] In previous work we have successfully used [Co(1,10-phen)$_2$]$^{2+}$ as a metal-organic subunit to synthesize two one-dimensional polymers in the oxovanadium-organodiphosphonate systems.[16] But what the structures will be after self-assembling of different lengths of organodiphosphonate ligands, polyoxomolybdate and [Co(1,10-phen)$_2$]$^{2+}$ as metal-organic subunit together is still unknown. In this paper we report the synthesis and crystal structures of two novel clusters, [{Co(1,10-phen)$_2$}$_2${(Mo$_4$O$_{12}$)(O$_3$PCH$_2$CH$_2$PO$_3$)}·(H$_2$O)] (**1**) and [{Co(1,10-phen)$_2$}$_2${(Mo$_4$O$_{12}$)(O$_3$PCH$_2$CH$_2$-CH$_2$PO$_3$)}·(1.5H$_2$O)] (**2**), and one linear polymer, [{Co(1,10-phen)$_2$(H$_2$O)$_2$}{Co(1,10-phen)$_2$(H$_2$O)}-{(Mo$_5$O$_{15}$)(O$_3$PCH$_2$CH$_2$CH$_2$CH$_2$PO$_3$)}·(6H$_2$O)] (**3**).

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science,
Fuzhou, Fujian 350002, P. R. China
Fax: (internat.) + 86-591/371-4946
E-mail: wxt@ms.fjirsm.ac.cn

Results and Discussion

The crystal structure of **1** consists of a heterometallic hexanuclear Mo$_4$Co$_2$ cluster built up from an {Mo$_4$O$_{16}$} motif, {PCO$_3$} tetrahedrons and {CoN$_4$O$_2$} octahedrons (Figure 1a). Interestingly, the Mo atoms arrange themselves into a twisted zigzag line in the {Mo$_4$O$_{16}$} motif (Figure 1b), which is composed of four {MoO$_6$} octahedrons. {Mo1O$_6$} shares a face with {Mo2O$_6$} through the O8, O4 and O10 atoms. {Mo2O$_6$} and {Mo3O$_6$} are edge-shared through the O4 and O5 atoms. {Mo3O$_6$} shares a face with {Mo4O$_6$} through the O1, O5 and O6 atoms. Meanwhile {Mo1O$_6$} shares a corner with {Mo3O$_6$} through O4 atoms and {Mo2O$_6$} shares a corner with {Mo4O$_6$} thought O5 atoms. As a result, the Mo1−Mo2, Mo2−Mo3 and Mo3−Mo4 distances are 3.0729(10), 3.2033(10) and 3.0755(11) Å, respectively. The [Mo$_4$O$_{12}$(O$_3$PCH$_2$-CH$_2$PO$_3$)]$^{4−}$ anion is formed by the 1,2-ethylenediphosphonate ligand firmly chelating the Mo1 and Mo4 atoms [Mo1−O14 = 1.981(6), Mo1−O8 = 2.262(5), Mo4−O11 = 2.000(6) and Mo4−O6 = 2.321(5) Å] and linking to the middle two {MoO$_6$} octahedrons [Mo2−O8 = 2.260(6) and Mo3−O6 = 2.277(6) Å] (Figure 1c). Both Co^{II} atoms are in slightly distorted octahedral coordination geometries with four nitrogen atoms from two 1,10-phenanthroline ligands and two oxygen atoms. The {Co1N$_4$O$_2$} octahedron connects to the [Mo$_4$O$_{12}$(O$_3$PCH$_2$CH$_2$PO$_3$)]$^{4−}$ anion by sharing one oxygen atom with an {Mo2O$_6$} octahedron [Co1−O7 = 2.107(6) Å] and another oxygen atom with the {P1CO$_3$} tetrahedron [Co1−O18 = 2.048(6) Å] (Figure 1c). The {Co2N$_4$O$_2$} octahedron is attached to the [Mo$_4$O$_{12}$(O$_3$PCH$_2$CH$_2$PO$_3$)]$^{4−}$ anion through one oxygen atom of the {Mo3O$_6$} octahedron [Co2−O3 = 2.083(6) Å] and another oxygen atom of the {P2CO$_3$} tetrahedron [Co2−O17 = 2.067(6) Å] (Figure 1c). Consequently, each

(a)

(b)

(c)

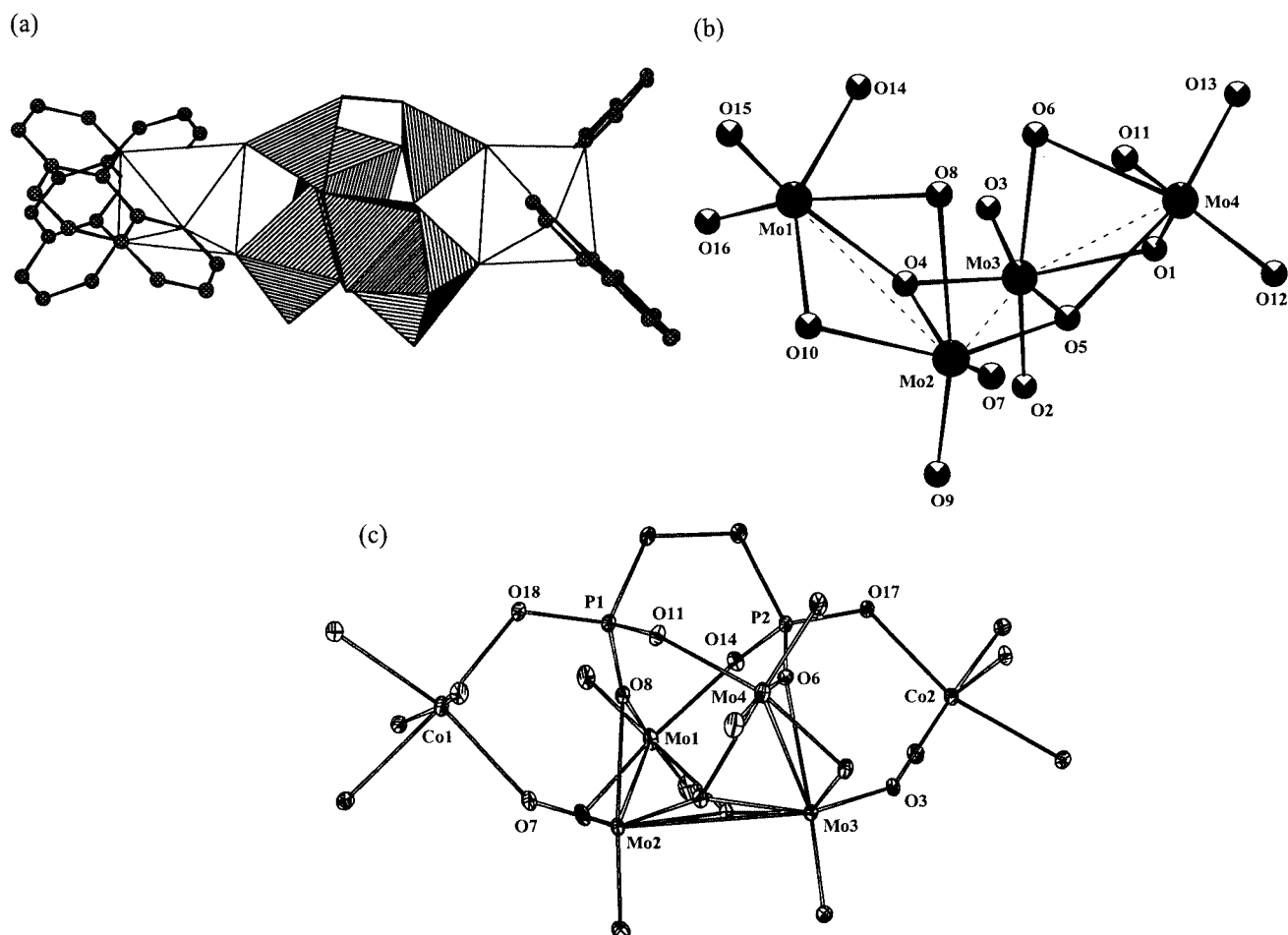Figure 1. (a) Polyhedron perspective of cluster of **1**; white octahedra: $\{CoN_4O_2\}$; black octahedra: $\{MoO_6\}$; black tetrahedra: $\{PCO_3\}$; hydrogen atoms are omitted for clarity; (b) perspective view of $\{Mo_4O_{16}\}$ motif of **1**; the dotted single lines represent the Mo-Mo bonds; (c) ORTEP view of **1** showing the coordination environments of cobalt, molybdenum and phosphorus (ellipsoids at 10% probability); free water molecules, hydrogen atoms and the carbon atoms of 1,10-phen ligands are omitted for clarity

$\{PO_3\}$ terminus of the 1,2-ethylenediphosphonate group links to one $\{CoN_4O_2\}$ and three different $\{MoO_6\}$ octahedra. The adjacent clusters interact each other through a strong π-π stacking of neighboring parallel 1,10-phen groups at a distance of 3.4−3.5 Å.[6,17,18]

The crystal structure of **2** is almost the same as that of **1** except for the 1,3-propylenediphosphonate ligand (Figure 2).
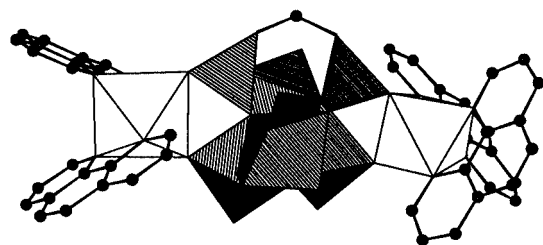

Figure 2. Polyhedron perspective of cluster of **2**; white octahedra: $\{CoN_4O_2\}$; black octahedra: $\{MoO_6\}$; black tetrahedra: $\{PCO_3\}$; hydrogen atoms are omitted for clarity

As expected, the structure of **3** is a linear polymer constructed from an $[Mo_5O_{15}(O_3PCH_2CH_2CH_2CH_2PO_3)]_n^{4n}$ anionic chain (Figure 3a) and $[Co(1,10\text{-phen})_2(H_2O)_2]^{2+}$ and $[Co(1,10\text{-phen})_2(H_2O)]^{2+}$ fragments (Figure 3b). In the anionic chain, the 1,4-butylenediphosphonate groups bridge the adjacent common $\{Mo_5O_{21}\}$ cyclic clusters.[14,15,19−24] Each $\{PO_3\}$ terminus only coordinates to five Mo^{VI} centers. This is obviously different from $[\{Cu(H_2O)_2(1,10\text{-phen})_2\}\{Cu(1,10\text{-phen})_2\}(Mo_5O_{15})\text{-}(O_3PCH_2CH_2CH_2PO_3)]\cdot2.5H_2O,[14]$ $[\{Cu(2,2'\text{-bipyridine})_2\}\text{-}\{Cu(2,2'\text{-bipyridine})(H_2O)\}(Mo_5O_{15})(O_3PCH_2CH_2\text{-}CH_2CH_2PO_3)]\cdot H_2O$ and $[\{Cu_2(\text{tetra}(2\text{-pyridyl})\text{pyprazine})\text{-}(H_2O)_2\}(Mo_5O_{15})(O_3PCH_2CH_2PO_3)]\cdot5.5H_2O.[15]$ Similar to compounds **1** and **2**, the Co^{II} atoms are also in slightly distorted octahedral coordination geometries with four nitrogen donors from two 1,10-phenanthroline ligands and two oxygen atoms. The $\{Co1N_4O_2\}$ moiety is linked to the anionic chain through an oxo group bridging to the $\{Mo1O_6\}$ octahedron [Co1−O7 = 2.063(5) Å]. While the $\{Co2N_4O_2\}$ octahedron interacts with the anionic chain through hydrogen bonds ($O_{24}\cdots O_{20} = 2.703$, $O_{23}\cdots O_{18} =$

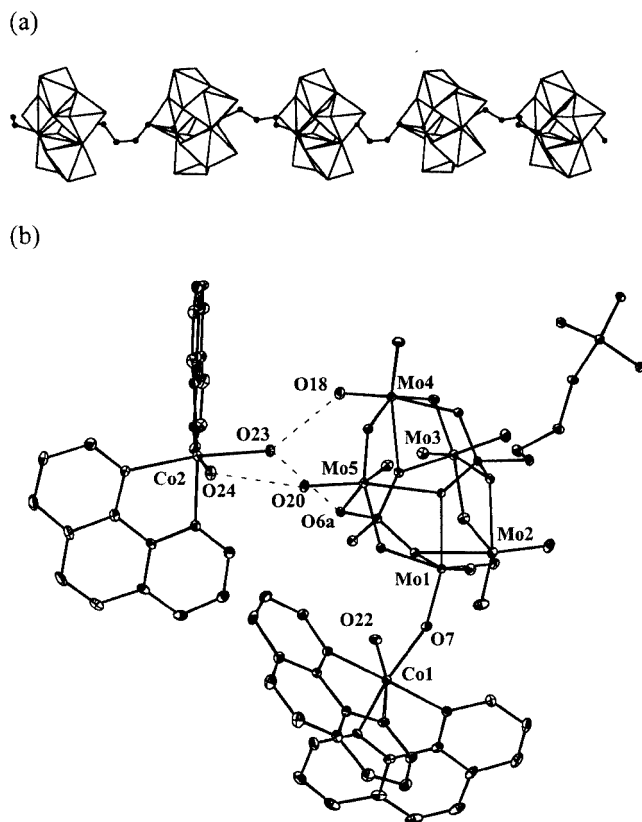R.-B. Fu, X.-T. Wu, S.-M. Hu, J.-J. Zhang, Z.-Y. Fu, W.-X. Du, S.-Q. Xia

(a)

(b)

Figure 3. (a) Perspective view of $[Mo_5O_{15}(O_3PCH_2-CH_2CH_2CH_2PO_3)]_n^{4n-}$ anionic chain of **3**; octahedra: {MoO_6}; black dots: P and C atoms; hydrogen atoms are omitted for clarity;(b) ORTEP view of **3** showing the coordination geometries of the cobalt, molybdenum and phosphorus atoms (ellipsoids at 10% probability); the dashed lines represent hydrogen bonds; free water molecules and hydrogen atoms are omitted for clarity; symmetry code *a*: $1/2 - x$, $-1/2 + y$, z.

2.829 and $O_{23}\cdots O_{6a} = 2.727$ Å). The adjacent chains interact thorough strong π-π stacking of neighboring parallel 1,10-phen groups at a distance of $3.2-3.6$ Å.[6,17,18]

Thermogravimetric analysis (TGA) studies were performed on polycrystalline samples under N_2 from room temperature to 1000 °C to study the stability of these compounds. The TGA data show an obvious weight loss starting at about 435 °C for these compounds.

In conclusion, two novel clusters and one linear polymer have been successfully self-assembled under almost identical hydrothermal conditions using $[Co(1,10\text{-phen})_2]^{2+}$ as the metal-organic subunit and organodiphosphonate ligands of different lengths. The structure of **3** differs from **1** and **2**, which may be mainly due to the increased length of the 1,4-butylenediphosphonate ligand.

Experimental Section

1,2-Ethylene-, 1,3-propylene- and 1,4-butylenediphosphonic acids were prepared according to the reported method.[25,26] Other chemicals were of reagent grade quality and obtained from commercial sources without further purification. Compounds **1**, **2** and **3** were synthesized in 25-mL, Teflon-lined, stainless steel vessels

under autogenous pressure with a filling capacity of about 40%. The reactants were stirred to homogeneity before heating. CHN analyses were performed with a Vario EL III element analyzer and UV-1100 spectrophotometer. Infrared spectra were obtained on a Nicolet Magna 750 FT-IR spectrometer.

Synthesis

Compound **1**, **2** and **3** were synthesized as red blocks in about 20% (0.1 g), 86.4% (0.357 g) and 40% (0.2 g) yields based on cobalt, respectively, at 180 °C for 48, 144 and 72 h, respectively. Hydrothermal reactions were performed as follows

For **1**: $Co(CH_3COO)_2\cdot4H_2O$ (0.1256 g, 0.5043 mmol), $Na_2MoO_4\cdot2H_2O$ (0.2408 g, 0.9952 mmol), MoO_3 (0.1446 g, 1.005 mmol), 1,10-phenanthroline·H_2O (0.1999 g, 1.008 mmol), $H_2O_3PCH_2CH_2PO_3H_2$ (0.1955 g, 1.029 mmol) and distilled water (10.0 mL, 555 mmol).

For **2**: $Co(CH_3COO)_2\cdot4H_2O$ (0.1254 g, 0.5035 mmol), $Na_2MoO_4\cdot2H_2O$ (0.2408 g, 0.9952 mmol), MoO_3 (0.1447 g, 1.005 mmol), 1,10-phenanthroline·H_2O (0.1996 g, 1.007 mmol), $H_2O_3PCH_2CH_2CH_2PO_3H_2$ (0.2010 g, 0.9850 mmol) and distilled water (10.0 mL, 555 mmol).

For **3**: $Co(CH_3COO)_2\cdot4H_2O$ (0.1253 g, 0.5031 mmol), $Na_2MoO_4\cdot2H_2O$ (0.2419 g, 0.9998 mmol), MoO_3 (0.1435 g, 0.9969 mmol), 1,10-phenanthroline·H_2O (0.1990 g, 1.004 mmol), $H_2O_3PCH_2CH_2CH_2CH_2PO_3H_2$ (0.2182 g, 1.001 mmol) and distilled water (10.0 mL, 555 mmol).

1: $C_{50}H_{38}Co_2Mo_4N_8O_{19}P_2$ (1618.5): calcd. C 37.11, H 2.37, N 6.92; found C 37.03, H 1.74, N 6.43. IR (KBr pellet): $\tilde{v}$ = 3500vs cm^{-1}, 3062m, 2904w, 1637w, 1624w, 1581m, 1514s, 1495m, 1423s, 1342w, 1300w, 1225w, 1117s, 1047vs, 982m, 924vs, 901s, 850s, 773m, 729s, 700s, 634s, 584s, 542w.

2: $C_{51}H_{41}Co_2Mo_4N_8O_{19.5}P_2$ (1641.5): calcd. C 37.32, H 2.52, N 6.83; found C 37.40, H 2.09, N 6.82. IR (KBr pellet): $\tilde{v}$ = 3500vs cm^{-1}, 3062m, 2893w, 1635w, 1624w, 1579m, 1512s, 1495m, 1452w, 1423s, 1342w, 1225w, 1188w, 1111s, 1049vs, 1028s, 987m, 922vs, 899vs, 860w, 847w, 771m, 727vs, 702vs, 629s, 586s, 567w, 523w.

3: $C_{52}H_{58}Co_2Mo_5N_8O_{30}P_2$ (1934.6): calcd. C 32.38, H 3.02, N 5.79; found C 32.21, H 1.68., N 5.74 IR (KBr pellet): $\tilde{v}$ = 3500vs cm^{-1}, 3064m, 2943w, 2899w, 2864w, 1624m, 1579m, 1518s, 1495m, 1427vs, 1344m, 1225w, 1188w, 1146m, 1111s, 1034s, 995m, 943vs, 908vs, 870vs, 762s, 727s, 661m, 590m, 563m, 503m.

X-ray Crystallography: X-ray data of single crystals were collected at a temperature of 293 ± 2 K on a Siemens SMART-CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data were reduced and absorption-corrected with the SMART and SADABS software packages, respectively. The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXTL-97.[27] All non-hydrogen atoms of the three compounds were treated anisotropically. H_1-H_{26} of **1**, all hydrogen atoms of **2** and H_1-H_{30} of **3** were treated geometrically. $H_{1a}-H_{10a}$ of **1** and $H_{1a}-H_{10a}$ of **3** were identified from the difference Fourier map and fixed with isotropic thermal parameters.

Crystal Data for 1: $C_{50}H_{38}Co_2Mo_4N_8O_{19}P_2$, M = 1618.44, triclinic, $P\bar{1}$, a = 12.2256(6), b = 12.9418(7), c = 18.9455(10) Å, α = 108.7050(10)°, β = 104.4880(10)°, γ = 96.2950(10)°, V = 2699.9(2) Å^3, Z = 2, $D_{calcd.}$ = 1.991 g cm^{-3}, T = 293(2) K, μ(Mo-K_α) = 1.645 mm^{-1}. Data were collected on a single crystal with dimensions 0.20 × 0.18 × 0.12 mm. 14204 reflections were measured in the range of $1.19 \le \theta \le 25.10$°, 9510 independent reflections

(R_{int} = 0.0385). Final R_1 = 0.0625 for 7201 observed reflections [$I > 2\sigma(I)$] and wR_2 = 0.1161.

Crystal Data for 2: $C_{51}H_{41}Co_2Mo_4N_8O_{19.5}P_2$, M = 1641.48, triclinic, $P\bar{1}$, a = 12.3372(3), b = 12.7558(3), c = 19.4102(5) Å, α = 108.3930(10)°, β = 102.7940(10)°, γ = 94.6870(10)°, V = 2788.41(12) Å^3, Z = 2, $D_{calcd.}$ = 1.955 g cm^{-3}, T = 293(2) K, μ(Mo-K_α) = 1.595 mm^{-1}. Data were collected on a single crystal with dimensions 0.54 × 0.54 × 0.50 mm. 14616 reflections were measured in the range of 1.15 ≤ θ ≤ 25.06°, 9773 independent reflections (R_{int} = 0.0173). Final R_1 = 0.0301 for 8837 observed reflections [$I > 2\sigma(I)$] and wR_2 = 0.0786.

Crystal Data for 3: $C_{52}H_{58}Co_2Mo_5N_8O_{30}P_2$, M = 1934.56, Orthorhombic, $Pbca$, a = 24.7212(4), b = 19.86320(10), c = 27.2651(2) Å, V = 13388.3(2) Å^3, Z = 8, $D_{calcd.}$ = 1.920 g cm^{-3}, T = 293(2) K, μ(Mo-K_α) = 1.530 mm^{-1}. Data were collected on a single crystal with dimensions 0.48 × 0.34 × 0.26 mm. 41605 reflections were measured in the range of 1.49 ≤ θ ≤ 25.06°, 11783 independent reflections (R_{int} = 0.0513). Final R_1 = 0.0482 for 8884 observed reflections [$I > 2\sigma(I)$] and wR_2 = 0.1117.

CCDC-198179 (**1**), -198180 (**2**) and -198181 (**3**) contain the supplementary crystallographic data for this paper. 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: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[1] R. C. Finn, J. Zubieta, *J. Chem. Soc., Dalton Trans.* **2000**, 1821−1823.

[2] R. C. Finn, R. Lam, J. E. Greedan, J. Zubieta, *Inorg. Chem.* **2001**, *40*, 3745−3754.

[3] S. H. Feng, R. R. Xu, *Acc. Chem. Res.* **2001**, *34*, 239−247.

[4] Z. Shi, L. R. Zhang, G. S. Zhu, G. Y. Yang, J. Hua, H. Ping, S. H. Feng, *Chem. Mater.* **1999**, *11*, 3565−3570.

[5] J. Q. Xu, R. Z. Wang, G. Y. Yang, Y. H. Xing, D. M. Li, W. M. Bu, L. Ye, Y. G. Fan, H. Q. Jia, *Chem. Commun.* **1999**, 983−984.

[6] X. M. Zhang, M. L. Tong, X. M. Chen, *Chem. Commun.* **2000**, 1817−1818.

[7] S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1993**, *283*, 1148−1150.

[8] M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319−330.

[9] Z. Shi, S. H. Feng, L. R. Zhang, G. Y. Yang, J. Hua, *Chem. Mater.* **2000**, *12*, 2930−2935.

[10] Z. Y. Fu, X. T. Wu, J. C. Dai, L. M. Wu, C. P. Cui, S. M. Hu, *Chem. Commun.* **2001**, 1856−1857.

[11] C. Z. Lu, C. D. Wu, S. F. Lu, J. C. Liu, Q. J. Wu, H. H. Zhuang, J. S. Huang, *Chem. Commun.* **2002**, 152−153.

[12] H. L. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276−279.

[13] S. Y. Yang, L. S. Long, Y. B. Jiang, R. B. Huang, L. S. Zheng, *Chem. Mater.* **2002**, *14*, 3229−3231.

[14] R. C. Finn, J. Zubieta, *Inorg. Chem.* **2001**, *40*, 2467.

[15] R. C. Finn, E. Burkholder, J. Zubieta, *Chem. Commun.* **2001**, 1852−1853.

[16] F. B. Fu, S. M. Hu, Z. Y. Fu, J. J. Zhang, X. T. Wu, *New J. Chem.* **2003**, *27*, 230−232.

[17] S. B. Ferguson, E. M. Sanford, E. M. Seward, F. Diederich, *J. Am. Chem. Soc.* **1991**, *113*, 5410−5419.

[18] W. L. Jorgensen, D. L. Severance, *J. Am. Chem. Soc.* **1990**, *112*, 4768−4774.

[19] W. Kwak, M. T. Pope, T. F. Scully, *J. Am. Chem. Soc.* **1975**, *97*, 5735−5738.

[20] D. G. Lyxell, R. Strandberg, *Acta Crystallogr., Sect. C* **1988**, *44*, 1535−1538.

[21] M. P. Lowe, J. C. Lockhart, W. Clegg, K. A. Fraser, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 451−454.

[22] M. P. Lowe, J. C. Lockhart, G. A. Forsyth, W. Clegg, K. A. Fraser, *J. Chem. Soc., Dalton Trans.* **1995**, 145−152.

[23] Y. D. Chang, J. Zubieta, *Inorg. Chim. Acta* **1996**, *245*, 177−198.

[24] W. T. A. Harrison, L. L. Dussack, A. J. Jacobson, *Acta Crystallogr., Sect. C* **1997**, *53*, 856−859.

[25] A. K. Bhattacharya, G. Thyagarajan, *Chem. Rev.* **1981**, *81*, 415−430.

[26] K. Moedritzer, R. R. Irani, *J. Inorg. Nucl. Chem.* **1961**, *22*, 297−304.

[27] G. M. Sheldrick, SHELXT 97, *Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.

Received December 12, 2002