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Three-dimensional five-connected coordination polymer $[M_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ with 4^46^6 topologies ($M = \text{Zn, Cu}$; hmt = hexamethylenetetramine)

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Abstract

Two novel three-dimensional five-connected coordination polymers $[M_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ with 4^46^6 topologies ($M = \text{Zn, Cu}$; hmt = hexamethylenetetramine) were synthesized and characterized by elemental analysis, crystal structure, IR, thermal gravimetric analyses. Both $[Zn_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ and $[Cu_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ all crystallize in the orthorhombic system, space group *Imm*2, and with $Z = 2$. Metal ions have all octahedral geometry coordinated by four oxygen atoms from three malonates, one oxygen atom from a water molecule and one nitrogen atom of hmt ligand. Each malonate binds a metal ion with its two oxygen atoms in a chelating mode and connects to adjacent two metal ions with another two oxygen atoms to form an infinite wavy layer. The layers are bridged by μ_2-hmt molecules to form a three-dimensional framework with channels. The magnetic susceptibility data show there is a weak antiferromagnetic exchange interaction in the complex $[Cu_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$.

Keywords: Crystal structure; Zinc; Copper; Magnetic properties; Coordination polymer; Hexamethylenetetramine

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1. Introduction

Crystal engineering and construction of coordination polymers with fascinating structural topologies have attracted great attention in recent years, due to their potential application in catalysis, separations, gas storage, and optoelectronics [1–3]. Self-assemble of multiconnected metal ions and organic bridging ligands (connectors) can give rise to new and varied topological types [4–9], but five-connected topologies remain rather rare [10–15]. Hexamethylenetetramine (hmt), a potential tetradentate ligand, has been used to assemble new supramolecular architectures with metal ions via various possible coordination modes, namely, involving one–four N atoms of hmt in coordination [8–9,16–21]. However, previous studies were mainly limited in using low-coordination metal ion Ag(I) as spacers to connect hmt [8,9], Hmt-based coordination polymers containing complex multidentate organic anions and high-coordination metal ions remain rather rare [19–21]. On the other hand, malonate, a possible tetradentate flexible ligand, has also been used to connect metal ions to form multidimensional compounds [22–27]. Considering the fact that anions may play an important role in the supramolecular architectures construction [8,9,21] and that the structural difference of flexible malonate from rigid anions such as NCS^-, SO_4^{2-}, and NO_3^-, it is possible to obtain a new topological architecture via the self-assembly of *d*-block transition metal ions, hmt and malonate ligand. We report herein two novel coordination polymer $[M_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ ($M =$ Zn,

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Cu) consisting of unusual five-connected metal nodes, with hmt and a flexible malonate ligand, forming a unique and unprecedented three-dimensional 4^46^6 topological architecture.

2. Experimental

All regents were used as supplied. Elemental analysis was performed on a Perkin–Elmer 2400 microanalysis instrument. IR absorption spectra (KBr pellet) were recorded on a Nicolet FTIR 170X spectrophotometer. The thermal gravimetric analyses (TG-DTA) were carried out under nitrogen with a Universal V3.4C differential thermal analyzer with a rate of 10 °C min^{-1}. Variable-temperature magnetic susceptibilities were determined on a Quantum Design SQUID magnetometer with a 2000 Oe magnetic field in the temperature range of 1.8–300 K. Diamagnetic corrections were made using Pascal' constants.

2.1. Synthesis of $[Zn_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ *(**1**)*

$ZnSO_4 \cdot 7H_2O$ (0.287 g, 1 mmol) was added to an aqueous solution (8 mL) containing malonic acid (0.105 g, 1 mmol) with stirring until all $ZnSO_4 \cdot 7H_2O$ was dissolved, then, 10 mL aqueous solution of hmt(0.140 g, 1 mmol) was carefully added to the above resultant solution. The resulting colorless solution was allowed to stand for several days at ambient temperature to obtain colorless crystals of $[Zn_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ (0.122 g, 48% yield). Anal.calcd for $C_{12}H_{20}N_4O_{10}$ Zn_2: C, 28.20; H, 3.91; N, 10.96; Found: C, 28.38; H, 3.82; N, 10.86. IR data (cm^{-1}, KBr pellet): 3181(s, br) (ν_{OH}), 2360(m), 1571(s) ($\nu_{a\ OCO}$), 1446(s) ($\nu_{s\ OCO}$), 1359(s) ($\nu_{s\ OCO}$), 1262(w), 1248(m), 1227(m), 1163(w), 1059(w), 1032(m), 994(s), 968(w), 947(w), 932(w), 841(w), 826(w), 803(m), 706(m), 684(w), 667(w), 617(m), 579(m), 485(w).

2.2. Synthesis of $[Cu_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ *(**2**)*

$Cu(C_3H_2O_4) \cdot 2H_2O$ was synthesized according to the method described previously [23]. To an aqueous solution (30 mL) of $Cu(C_3H_2O_4) \cdot 2H_2O$ (0.202 g, 1 mmol), an ethanol solution (10 mL) of hmt (0.070 g, 0.5 mmol) was added. The resulting solution was filtered off, and the clear filtrate was allowed to stand for several days at ambient temperature to obtain green crystals of $[Cu_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ (0.142 g, 56% yield). Anal. calcd for $C_{12}H_{20}$ $Cu_2N_4O_{10}$: C, 28.20; H, 3.91; N, 10.96; Found: C, 28.38; H, 3.82; N, 10.86. IR data (cm^{-1}, KBr pellet): 3208(s, br) (ν_{OH}), 2350(w, br), 1577(s) ($\nu_{a\ OCO}$), 1463(w), 1433(s) ($\nu_{s\ OCO}$), 1391(w), 1339(s) ($\nu_{s\ OCO}$), 1250(w), 1227(m), 1163(w), 1061(w), 1033(m), 992(s), 948(w), 857(w), 844(w), 810(w), 776(w), 713(m), 683(m), 655(w), 637(w), 581(w), 502(w).

2.3. X-ray crystallography

Single-crystal X-ray diffraction measurement of **1** and **2** were carried out with a Bruker Smart Apex CCD area detector at 293 K. Intensities of reflections were measured using graphite-monochromatized Mo*K*α radiation ($\lambda = 0.71073$ Å) with the ω scans mode in the range of $2.97 < \theta < 25.95°$ (for **1**) and $2.63 < \theta < 26.98°$ (for **2**). The structures were solved by direct methods (SHELXS-97)[28] and refined by full-matrix least-squares methods on F^2 by the SHELXS-97 program package. Anisotropic thermal factors were assigned to all the non-hydrogen atoms. Hydrogen atoms were included in calculated position and refined with isotropic thermal parameters riding on the parent atoms. Crystallographic data and experimental details for structural analyses are summarized in Table 1, and the selected bond lengths (Å) and bond angles (°) are given in Table 2, respectively.

3. Results and discussion

3.1. Synthesis and general characterization

Complex $[Zn_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ **1** was obtained by slow evaporation of aqueous solution of $ZnSO_4 \cdot 7H_2O$, malonic acid and hmt in a molar ratio of 1:1:1; the green crystals of complex $[Cu_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ **2** were obtained by slow evaporation of EtOH–H_2O solution of $Cu(C_3H_2O_4) \cdot 2H_2O$ and hmt in a molar ratio of 2:1, but the powder of Cu complex

Table 1
Crystallographic data for complexes **1** and **2**

Empirical formula	$C_{12}H_{20}N_4O_{10}Zn_2$	$C_{12}H_{20}N_4O_{10}Cu_2$
Formular weight	511.06	507.4
T (K)	293(2)	293(2)
Space group	*Imm*2	*Imm*2
a (Å)	7.6130(11)	7.6236(11)
b (Å)	15.736(2)	15.488(3)
c (Å)	6.9581(10)	6.9565(10)
V (Å^3)	833.6(2)	821.4(2)
Z	2	2
λ (Å)	0.71073	0.71073
D_c (g cm^{-3})	2.036	2.052
μ (mm^{-1})	2.945	2.657
Total reflections	924	983
Independent reflections	913	943
R_1, wR_2[a]	0.0434, 0.1082	0.0404, 0.1264
Goodness-of-fit on F^2	1.358	1.071

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = \{\sum w(F_o^2-F_c^2)^2/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (deg) for complexes **1** and **2**

*Compound **1***			
Zn1–O1	2.098 (3)	Zn1–O1A	2.098 (3)
Zn1–O1W	2.131 (5)	Zn1–O2B	2.110 (3)
Zn–N1	2.206 (5)	Zn1–O2C	2.110 (3)
O1–Zn1–O1W	90.81 (14)	O1–Zn1–N1	95.37 (13)
O1W–Zn1–N1	171.61 (19)	O1A–Zn1–O1	85.02 (18)
O1–Zn1–O2B	86.13 (14)	O1–Zn1–O2C	171.14 (12)
O1A–Zn1–O2C	86.13 (14)	O2B–Zn1–O2C	102.71 (19)
O2B–Zn1–O1W	89.74 (12)	O2B–Zn1–N1	85.02 (12)
*Compound **2***			
Cu1–O1	2.137 (4)	Cu1–O1A	2.137 (4)
Cu1–O1W	1.988 (6)	Cu1–O2B	2.149 (5)
Cu1–N1	2.111 (6)	Cu–O2C	2.149 (5)
O1–Cu1–O1W	89.89 (16)	O1–Cu1–N1	95.32 (15)
O1–Cu1–O1A	85.55 (17)	O1–Cu1–O2B	85.00 (16)
O1–Cu1–O2C	170.53 (17)	O1W–Cu1–N1	172.9 (2)
O1W–Cu1–O2B	89.67 (14)	O2B–Cu1–N1	85.98 (13)
O1A–Cu1–O2B	170.53 (17)	O2B–Cu1–O2C	104.46 (16)

Symmetry codes A: 2−*x*, 2−*y*, *z*; B: 2−*x*, *y*, *z*; C: *x*, 2−*y*, *z*.

was only obtained by slow evaporation of aqueous solution of $CuCl_2 \cdot 4H_2O$, malonic acid and hmt in a molar ratio of 1:1:1 or 1:1:2. Complexes **1** and **2** showed similar IR spectra. The strong broad absorption band at the region 3200–3000 cm^{-1} corresponds to v (OH) of the coordination water molecules. 2350–2360 cm^{-1} band should attributed to the v (CH_2) of methylene groups in hmt molecules [18]. The strong peaks at ca. 1570 cm^{-1}, and ca. 1440, ca. 1350 $cm^{-1}$are the v_a (OCO), and v_s (OCO) stretching mode of malonate, respectively, while medium intensity absorption at ca. 710 cm^{-1} is the δ (OCO) bent vibration of malonate. The difference values of 220 and 130 cm^{-1} defined as the difference between v_a (OCO) and v_s (OCO) indicate that both bridging and chelating modes of the malonate are present [29] as proved by the X-ray crystal structure analysis of $[M_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n (M = \text{Zn,Cu})$.The thermogravimetric analyses (TG-DTA) of compounds **1** and **2** showed the occurrence of three consecutive processes, namely dehydration, ligand pyrolysis (or volatilization) and inorganic residue formation. The TG-DTA for **1** showed the complete loss of two water molecules at ca. 135 °C (found 8.0%; calcd. 7.04%). The dehydrated compound remained stable up to ca. 225 °C without any weight loss, then at a temperature range of 225–420 °C the pyrolysis (or volatilization) of both malonate and hmt ligands occurred leaving residual ZnO (remaining weight: found 32.50%; calcd. 2ZnO: $[Zn_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ 31.86%). The TG-DTA for compound **2** showed an initial weight loss of 8.50% from 110 to 130 °C corresponding to the removal of two lattice water molecules per formula unit (calcd. 7.09%), followed by another weight loss of 60.50% from 190 to 325 °C for elimination of the malonate and hmt ligands from the framework, the remaining residue was CuO (remaining weight: found 31.0%; calcd. 2CuO: 31.34%). Elemental analyses revealed the components of **1** and **2** to be $[M_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ ($M = $ Zn, Cu). Complexes **1** and **2** are very stable in air and can be preserved for a long time at room temperature, and the dehydrated compounds of Complexes **1** and **2** all get rehydrated on exposure to humid (RH~60%) atmosphere.

3.2. Description of crystal structures

The crystal structures of **1** and **2** are isostructural (Figs. 1 and 2 show the structure of **1**). The geometries around each metal center are all octahedral; the four oxygen atoms from three malonate define the equatorial positions, whereas one oxygen atom of water and one nitrogen atom of hmt ligand occupy the axial ones (Fig. 1). Selected bond lengths and angles are given in Table 2. The metal–oxygen bonds are in the range 2.098(3)–2.131(5) Å and 1.988(6)–2.149(5) Å for **1** and **2**, respectively, and the metal–nitrogen bonds are 2.206(5) and 2.111(6) Å for **1** and **2**, respectively. The bond angles around each metal center range from 85.02(12) to 171.61(19)° for **1** and from 85.00(16) to 172.9(2)° for **2**. Each malonate binds a metal ion with its two oxygen atoms in a chelating mode and binds adjacent two metal ions with its another two oxygen atoms, respectively, form an infinite wavy layer with cavities on *ac* plane (Fig. 2a). Hmt, as a μ_2-bridging ligand, connects the adjacent layers further to form a three-dimensional network with 2.47 × 5.20 Å for **1** and 2.17 × 5.19 Å for **2** effective channels along *c* direction (Fig. 2b). The three-dimensional structure exits as a five-connected body-centered tetragonal net (the nodes of the net are defined as $M(C_3H_2O_4)$ moieties), 1/5 of the links of which are hmt bridging molecules and 4/5 are bridging malonates (Zn–Zn 6.125 and 5.444 Å, Cu–Cu 5.930 and 5.470 Å, respectively). There are no solvent molecules in the channels, and coordinated water molecules are all linked with oxygen atoms of malonate by hydrogen bonds. Similar networks were found in the Co(II), Mn(II) analogues, $[Co_2(C_3H_2O_4)_2\ (\mu_2\text{-hmt})]_n \cdot 2H_2O$ [24],

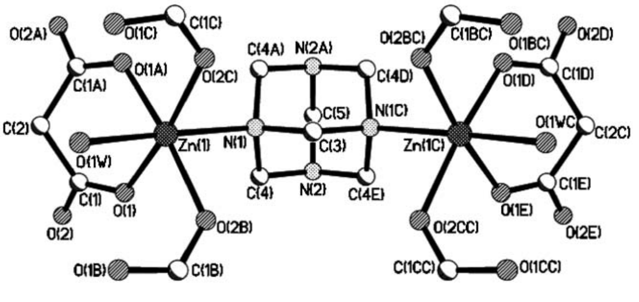

Fig. 1. The metal ion coordination environment in $[Zn_2(C_3H_2O_4)_2 (H_2O)_2(\mu_2\text{-hmt})]_n$ **1**.

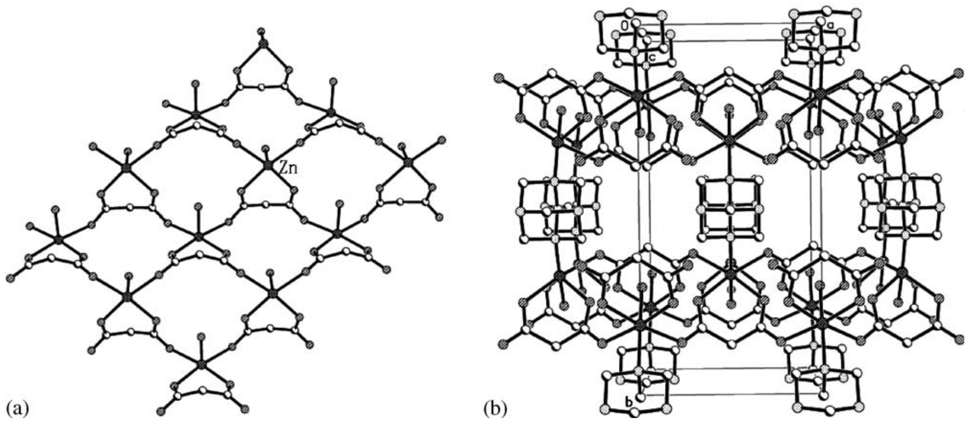

Fig. 2. Square grid coordination layer $[Zn_2(C_3H_2O_4)_2(H_2O)_2]_n$ in structure **1** (a). Three-dimensional network of **1** showing the channels along *c*-axis (b).

$[M_2(\mathrm{mal})_2(4,4'\text{-bipy})(H_2O)_2]_n$ (M = Co, Mn; mal = malonate) [25], $[Zn_2(C_3H_2O_4)_2(H_2O)_2(C_4H_4N_2)]_n$ [26]. Besides, although complex **2** and compound **3** $[Cu_4(C_3H_2O_4)_4(\mathrm{hmt})]\cdot 7H_2O$ previously reported [24] have the same ligands, they have different structure. Copper atoms are five-coordinated with square pyramidal geometry in compound **3**, and compound **3** is a one-dimensional polymer. Copper atoms are also five-coordinated in the two-dimensional polymer $[Cu_2(\mathrm{mal})_2(H_2O)_2(4,4'\text{-bipy})]$[27] and the three-dimensional polymer $[Cu_2(\mathrm{mal})_2\,(C_4H_4N_2)]\cdot 2H_2O$ [26].

From the topological point of view, the shortest circuits formed around the metal connecting nodes are the same for structures **1** and **2** and include four 4-gons and six 6-gons, the topological type can be assigned by $4^4 6^6$ which were not predicated by Wells [30]. To our knowledge, there are only a few known five-connected nets with $4^4 6^6$ type, of which one has La(III) metal nodes [14], two have Ni (II) nodes and two have Co(II) nodes [15].

3.3. Magnetic property

Variable-temperature (1.8–300 K) magnetic susceptibility data were collected for a crystal sample of complex **2**. Global antiferromagnetic behavior is evident from the magnetic measurements as shown in Fig. 3. The χ_m values increase as the temperature decreases (Fig. 3) to reach a sharp maximum at 9 K and then decreasing on cooling 1.8 K. In compound **2**, there are two magnetic exchange pathways: (1) through bridging malonate, the metal–metal separation is 5.470 Å which could be responsible for the weak antiferromagnetic interaction, (2) through bridging hmt molecules, the metal–metal separation is 5.930 Å. The $\chi_m T$ value at room temperature is 0.866 $cm^3\,mol^{-1}$ K, which is slightly larger than the value expected for spin-only of two Cu(II) ions (0.827 $cm^3\,mol^{-1}$ K with $g = 2.10$). The $\chi_m T$ value is almost invariable up to 100 K (0.859 $cm^3\,mol^{-1}$ K) and gradually decreases from room temperature to 0.019 $cm^3\,mol^{-1}$ K at 1.8 K. This behavior is characteristic of an antiferromagnetic interaction in the whole temperature range.

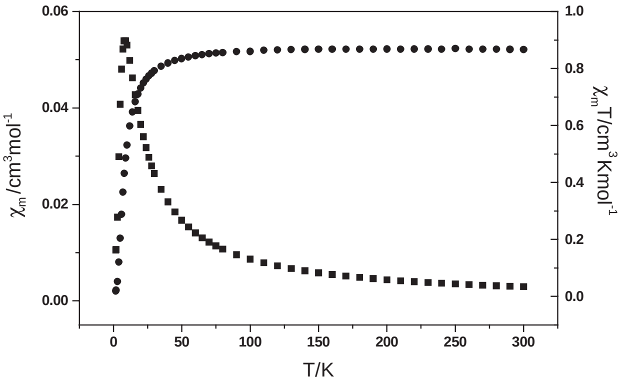

Fig. 3. Temperature dependence of χ_m (■) and χ_mT (●) vs. *T* for $[Cu_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$.

4. Conclusion

In conclusion, self-assembly of hmt, flexible malonate ligand and six-coordination Zn(II) or Cu(II) ion constructs a five-connected three-dimensional coordination polymer with $4^4 6^6$ topological structure. To our knowledge, this is the first five-connected Zn(II), the third five-connected Cu(II) coordination polymer and the first characterized $4^4 6^6$ network. Our experimental results, and the fact that five-connected networks have not been found in analogous Ag-hmt-based coordination polymers [8,9], show that high-coordination-number Zn(II) and Cu(II) ions have their own role to play in constructing coordination networks. Antiferromagnetic exchange interaction exits between Cu(II) ions in the complex $[Cu_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$. The design and synthesis of novel topologies using hmt, other new flexible ligands and high-coordination-number metal centers, as well as studies on the properties of such compounds are currently under investigation.

5. Supplementary material

CCDC 239511 for $[Zn_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ (**1**) and CCDC 239512 for $[Cu_2(C_3H_2O_4)_2(H_2O)_2(\mu_2\text{-hmt})]_n$ (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.hmtl [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB21EZ, UK; fax; (internet) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]

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References

[1] T. Ezuhara, K. Endo, Y. Aoyama, J. Am. Chem. Soc. 121 (1999) 3279–3283;
L. Pan, M.B. Sander, X.Y. Huang, J. Li, M. Smith, E. Bittner, B. Bockrath, J.K. Johnson, J. Am. Chem. Soc. 126 (2004) 1308–1309;
M. Fujita, Y.J. Kwon, S. Washizu, K. Ogura., J. Am. Chem. Soc. 116 (1994) 1151–1152.

[2] M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, S. Kitagawa, Angew. Chem. Int. Ed. Engl. 36 (1997) 1725–1727;
T.M. Reineke, M. Eddaoudi, M. O'Keefe, O.M. Yaghi, Angew. Chem. Int. Ed. Engl. 38 (1999) 2590–2594.

[3] K.T. Holman, A.M. Pivovar, M.D. Ward, Science 294 (2001) 1907–1911.

[4] S.R. Batten, R. Robson, Angew. Chem. Int. Ed. Engl. 37 (1998) 1460–1494.

[5] H. Li, M. Eddaoudi, M. O'Keefe, O.M. Yaghi, Nature 402 (1999) 276–279.

[6] S–i. Noro, S. Kitagawa, M. Kondo, K. Seki, Angew. Chem. Int. Ed. Engl. 39 (2000) 2082–2084.

[7] B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629–1658
B. Rather, B. Moulton, R.D.B. Walsh, M.J. Zaworotko, Chem. Commun. (2002) 694–695.

[8] L. Carlucci, G. Ciani, D.M. Proserpio, A. Sironi, J. Am. Chem. Soc. 117 (1995) 12861–12862
L. Carlucci, G. Ciani, D.M.V. Gudenberg, D.M. Proserpio, A. Sironi, Chem. Commun. (1997) 631–632.;
L. Carlucci, G. Ciani, D.M. Proserpio, A. Sironi, Inorg. Chem. 36 (1997) 1736–1737;
L. Carlucci, G. Ciani, D.M. Proserpio, S. Rizzato, J. Solid State Chem. 152 (2000) 211–220.

[9] M.L. Tong, S.L. Zheng, X.M. Chen, Chem. Commun. (1999) 561–562.
S.L. Zheng, M.L. Tong, H.L. Zhu, Y. Fang, X.M. Chen, J. Chem. Soc., Dalton Trans. (2001) 2049–2053.
S.L. Zheng, M.L. Tong, X.L. Yu, X.M. Chen, J. Chem. Soc., Dalton Trans. (2001) 586–592.;
S.L. Zheng, M.L. Tong, R.W. Fu, X.M. Chen, Inorg. Chem. 40 (2001) 3562–3569;
S.L. Zheng, M.L. Tong, X.M. Chen, Chin. J. Inorg. Chem. 18 (2002) 17–23;
Q. Liu, X.Q. Sun, Y.Q. Zhu, B.L. Li, Z. Xu, H.B. Liu, K-B. Yu, Transition Met. Chem. 26 (2001) 369–371.

[10] L. Carlucci, G. Ciani, D.M. Prosperpio, A. Sironi, Angew. Chem. Int. Ed. Engl. 34 (1995) 1895–1898.

[11] S. R Batten, B.F. Hoskins, R. Robson, New. J. Chem. 22 (1998) 173–175.

[12] L. Pan, B.S. Finkel, X.Y. Huang, J. Li, Chem. Commun. (2001) 1064–1065.

[13] V.V. Ponomarova, V.V. Komarchuk, I. Boldog, A.N. Chernega, J. Sieler, K.V. Domasevitch, Chem. Commun. (2002) 436–437.

[14] D.L. Long, A.J. Champness, N.R. Wilson, C. Schröder, J. Am. Chem. Soc. 123 (2001) 3401–3402.

[15] X.H. Bu, W. Wang, J.R. Li, W. Chen, R.H. Zhang, Inorg. Chem. 41 (2002) 413–415.

[16] Q. Liu, X.Q. Sun, J-Z. Zou, Z. Xu, K-B. Yu, J. Coord. Chem. 55 (2002) 1021–1027;
Q. Liu, B.L. Li, X.Q. Sun, Z. Xu, K.B. Yu, Acta Crystallogr. Sect. E E57 (2001) m151–m153;
Q. Liu, H.T. Xi, X.Q. Sun, J.F. Zhu, Chin. J. Struct. Chem. 21 (2002) 355–358.

[17] L. Pan, N.W. Zheng, Y.G. Wu, W.J. Zheng, X.T. Wu, Inorg. Chim. Acta 303 (2000) 121–123;
T.C.W. Mak, Z. Kristallogr. 159 (1982) 247–254.

[18] Y. Zheng, J. Li, M. Nishiura, T. Imamoto, J. Mol. Struct. 520 (2000) 257–260.

[19] B. Moulton, J. Lu, M.J. Zaworotko, J. Am. Chem. Soc. 123 (2001) 9224–9225.

[20] S.R. Batten, B.F. Hoskins, R. Robson, Inorg. Chem. 37 (1998) 3432–3434.

[21] Q. Liu, B.L. Li, Z. Xu, X.Q. Sun, K-B. Yu, Transition Met. Chem. 27 (2002) 786–789;
Q. Liu, B.L. Li, Z. Xu, K-B. Yu, J. Coord. Chem. 56 (2003) 771–777.

[22] C. Ruiz-Pérez, J. Sanchiz, M. Hernández-Molina, F. Lloret, M. Julve, Inorg. Chim. Acta 298 (2000) 202–208;
F.S. Delgado, J. Sanchiz, C. Ruiz- Pérez, F. Lloret, M. Julve, Inorg. Chem. 42 (2003) 5938–5948;
Y. Rodriguez-martin, M. Hernandez-Molina, F.S. Delgado, C. Ruiz-Pérez, J. Sanchiz, F. Lloret, M. Julve, Cryst. Eng. Commun. 19 (2002) 440–446.

[23] J.M. Li, H.Q. Zeng, J.H. Chen, Q.M. Wang, X.T. Wu, Chem. Commun. (1997) 1213–1214.

[24] S. Konar, P.S. Mukherjee, M.G.B. Drew, J. Ribas, N.R. Chaudhuri, Inorg. Chem. 42 (2003) 2545–2552.

[25] T.K. Maji, S. Sain, G. Mostafa, T-H. Lu, J. Ribas, M. Mofort, N.R. Chaudhuri, Inorg. Chem. 42 (2003) 709–716;
P. Lightfoot, A. Sedden, J. Chem. Soc., Dalton Trans. (1999) 3549–3551.

[26] X. Zhang, C. Lu, Q. Zheng, S. Lu, W. Yang, J. Liu, H. Zhuang, Eur. J. Inorg. Chem. (2003) 1181–1185.

[27] Y. Rodriguez-Martin, C. Ruiz-Pérez, J. Sanchiz, F. Loret, M. Julve, Inorg. Chim. Acta 318 (2001) 159–165.

[28] G.M. Sheldrick, SHELEXTL-97, Program for X-ray Crystal Structure Determination, Göttingen University, Germany, 1997.

[29] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fourth ed, Wiley, New York, 1986.

[30] A.F. Wells, Further studies of three-dimensional nets, ACA, Monograph No. 8, 1979.