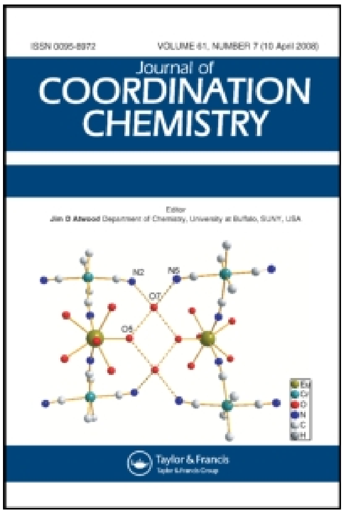

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A 4-fold interpenetrated metal-organic diamondoid framework: synthesis, crystal structure, and properties

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To cite this Article Meng, Lu-Yan , Wu, Jie , Li, Bao-Ding , Niu, Cao-Yuan , Wu, Ben-Lai and Zhang, Hong-Yun(2009) 'A 4-fold interpenetrated metal-organic diamondoid framework: synthesis, crystal structure, and properties', Journal of Coordination Chemistry, 62: 14, 2316 — 2323

To link to this Article: DOI: 10.1080/00958970902818216

URL: http://dx.doi.org/10.1080/00958970902818216

Journal of Coordination Chemistry
Vol. 62, No. 14, 20 July 2009, 2316–2323

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A 4-fold interpenetrated metal-organic diamondoid framework: synthesis, crystal structure, and properties

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(*Received 19 September 2008; in final form 18 November 2008*)

The coordination polymer, $[Cu_2(bpp)_4Cl_2]Cl_2$, was prepared by self-assembly of benzo[f][1,10]phenanthroline-6,7-dicarboxylic acid and bpp [bpp = 1,3-*bis*(4-pyridyl)propane] with $CuCl_2 \cdot 2H_2O$, and determined by X-ray crystallographic diffraction, IR spectrum, and thermal analysis. The complex features a 3-D 4-fold interpenetrated metal–organic framework with diamondoid topology. There are two sets of diamondoid frameworks independently constructed by bpp bridging the same copper centers, and the two sets of diamondoid frameworks interpenetrate one another to form an interesting 4-fold interpenetrating 3-D architecture.

Keywords: Copper(II) coordination polymer; Interpenetration structure; Diamondoid topology

1. Introduction

Design and synthesis of metal-organic coordination frameworks, especially with certain porous structures [1] through self-assembly reactions, have attracted much attention in coordination chemistry because of their potential applications for zeolite-like materials [2], molecular sieving [3], catalytic materials [4], molecular recognition [5], ion exchange [6], molecular absorption [7], gas storage [8], optical-electronic devices [9], etc. 1,3-*Bis*(4-pyridyl)propane (bpp), a rigid and flexible bidentate ligand, can assemble with transition metals to form coordination polymers with interesting structural topologies [10–13]. For example, the reaction of CuI with bpp generated a rare 3-D chiral triple-interpenetrated coordination polymer constructed from rigid tetrahedral Cu_4I_4 clusters bridged by bpp spacers [11]. Carlucci *et al.* [12, 13] made great contributions in this field. In addition, long spacer bpp has been selected as a bridging co-ligand and constructed a great number of coordination compounds with novel frameworks, such as interpenetration and porous structures, and potential properties, showing splendid effect upon structure topologies [14].

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970902818216

For this consideration, we have made use of rigid multipyridyl ligand benzo[f] [1,10]phenanthroline-6,7-dicarboxylic acid and bbp to assemble with transition metals in order to design and synthesize coordination polymers containing certain cavities. Unexpectedly, the coordination polymer of 1,3-*bis*(4-pyridyl)propane with $CuCl_2$ was obtained. To our surprise, there are two sets of diamondoid frameworks independently constructed by bpp bridging the same copper centers in the complex, and the two sets of diamondoid frameworks interpenetrate one another to form an interesting 4-fold interpenetrating 3-D architecture. Moreover, its IR, thermal analysis, and electrochemistry were also investigated.

2. Experimental

2.1. *Materials and physical measurements*

Reagents and solvents used were analytically pure grades. Benzo[f] [1,10]phenanthroline-6,7-dicarboxylic acid and 1,3-*bis*(4-pyridyl)propane were purchased from Shang Hai State-operated Chemical Company and used without purification. IR spectrum was recorded on a Nicolet IR-470 spectrometer in KBr pellets from 4000 to 400 cm^{-1}. Thermal analysis curve was scanned in the range of 30–800°C in air on a STA 409 PC thermal analyzer.

2.2. *Synthesis of $[Cu_2(bpp)_4Cl_2]Cl_2$*

To a solution of $CuCl_2 \cdot 2H_2O$ (0.0170 g, 0.1 mmol) in CH_3OH (15 mL) a solution of benzo[f] [1,10]phenanthroline-6,7-dicarboxylic acid (0.0318 g, 0.1 mmol) in DMF (5 mL) was added dropwise with vigorous stirring, and then a solution of bpp (0.0198 g, 0.1 mmol) in CH_3OH (5 mL) was slowly added dropwise with continuous stirring for 30 min. After filtration, the filtrate was allowed to evaporate undisturbed at ambient temperature. One week later, blue block crystals suitable for X-ray single crystal diffraction analysis were collected by filtering and washing with methanol and acetone, and dried in air in 32% yield. IR (KBr, cm^{-1}): 3061 w, 3026 m, 2927 m, 2856 w, 1613 s, 1556 w, 1503 m, 1429 m, 1384 m, 1223 m, 1070 m, 1024 m, 812 m, 519 m.

2.3. *X-ray structural determination*

Crystallographic data were collected at 291(2) K on a Bruker APEX-II area-detector diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å). The absorption correction was applied using SADABS. The structure was solved with direct methods and refined with full-matrix least-squares on F^2 using the SHELXTL program package [15]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restraints. The value of R_{int} is a bit greater due to weak diffraction caused by the small size of the crystal. Thus, we tuned the weighting details and utilized the reflections collected at the theta range from 2.35° to 25.00° to refine the structure parameters, and finally obtained the comparatively good results summarized in table 1. Selected bond lengths and angles are listed in table 2.

Table 1. Crystallographic data and structure refinement for complex.

Structural parameter	
Empirical formula	$C_{52}H_{56}Cl_4Cu_2N_8$
Formula weight	1061.93
Crystal system	Tetragonal
Space group	$I4_1/a$
Crystal size (mm)	0.217 × 0.062 × 0.054
Temperature (K)	291(2)
Units of cell dimensions (Å, °)	
a	17.3335(14)
b	17.3335(14)
c	40.872(7)
α	90
β	90
γ	90
V (Å^3)	12,280(2)
Z	8
D_{calcd} (g cm^{-3})	1.149
Reflections collected/unique	42,124/5123
Data/restraints/parameters	5123/0/296
R_1, wR_2 [$I > 2\sigma(I)$]	0.0915, 0.2027
Goodness-of-fit on F^2	1.144
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	1.231, −0.438

Table 2. Selected bond lengths (Å) and angles (°) for the polymer.

Cu1–N1	2.077(6)	Cu1–N1A	2.077(6)
Cu1–N2B	2.057(6)	Cu1–N2C	2.057(6)
Cu1–Cl1	2.6917(19)	Cu1–Cl1A	2.6917(19)
Cu2–N4	2.026(8)	Cu2–N4F	2.026(8)
Cu2–N3D	2.043(8)	Cu2–N3E	2.043(8)
N2C–Cu1–N2B	92.3(3)	N2C–Cu1–N1	176.9(3)
N2B–Cu1–N1	87.6(2)	N2C–Cu1–N1A	87.6(2)
N2B–Cu1–N1A	176.9(3)	N1–Cu1–N1A	92.6(3)
N2C–Cu1–Cl1A	88.60(18)	N2B–Cu1–Cl1A	91.13(18)
N1–Cu1–Cl1A	88.35(17)	N1A–Cu1–Cl1A	91.93(17)
N2C–Cu1–Cl1	91.13(18)	N2B–Cu1–Cl1	88.60(18)
N1–Cu1–Cl1	91.93(17)	N1A–Cu1–Cl1	88.35(17)
Cl1A–Cu1–Cl1	179.61(11)	N4–Cu2–N4F	90.9(5)
N4–Cu2–N3D	89.0(3)	N4–Cu2–N3E	176.1(4)
N4F–Cu2–N3D	176.1(4)	N4F–Cu2–N3E	89.0(3)
N3D–Cu2–N3E	91.3(4)		

Symmetry transformations used to generate equivalent atoms: A: $-x$, $-y+1/2$, z; B: $-y+1/4$, $x+3/4$, $z-1/4$; C: $y-1/4$, $-x-1/4$, $z-1/4$; D: $-y+3/4$, $x+1/4$, $z+1/4$; E: $y+1/4$, $-x+5/4$, $z+1/4$; F: $-x+1$, $-y+3/2$, z.

3. Results and discussion

3.1. *IR spectra*

In the IR spectrum of the complex, bands at 3061 and 3026 cm^{-1} are attributed to C–H stretching vibration of the pyridine ring, while bands at 2927 and 2856 cm^{-1} are assigned to C–H stretching vibration of asymmetric and symmetric motions of the methylene. The bands centered at 1613 and 1223 cm^{-1} are assigned to the C=N stretching vibration of pyridine and the C–C stretching vibration of methylene, respectively. Medium intensity bands appear in a range 1070–812 cm^{-1}, corresponding to C–H in-plane and out-of-plane deformation of the aromatic ring.

3.2. *Structural description of [$Cu_2(bpp)_4Cl_2$]Cl_2*

X-ray diffraction analysis displays that the complex crystallizes in a tetragonal space group $I4_1/a$. The asymmetric unit of the complex contains two crystallographically independent metal centers, Cu1 and Cu2 (figure 1). Cu1 is six-coordinate by four nitrogens from four independent bpp located in the equatorial plane and two chlorides at axial positions in a sharply distorted octahedral geometry. The Cu1–N bond distances range from 2.057(6) to 2.077(6) Å, markedly shorter than Cu1–Cl of 2.6917(19) Å. The coordination environment around Cu2 is different from that of Cu1, four-coordinate by four nitrogens from four distinct bpp to form a square coordination geometry, with mean deviation from the plane N3D–N3E–N4F–N4–Cu2 being 0.0547 Å and the deviation of N3D, N3E, N4F, and N4 from the plane being −0.0680, 0.0680, −0.0688, and 0.0688 Å, respectively. The dihedral angle between the planes N1–N1A–N2C–N2B–Cu1 and N3D–N3E–N4F–N4–Cu2 is 87.7°.

As usual, every rigid and flexible bidentate bpp in the complex is an exo-bidentate spacer, but only links with the same copper centers (Cu1 or Cu2) through pyridyl nitrogen atoms, and each Cu1 or Cu2 center is surrounded by four bpp bridges whose other binding sites sharply deviate from the equatorial plane. As a result, two sets of diamondoid frameworks are independently constructed by bpp bridging the Cu1 and Cu2, respectively. In the diamondoid frameworks, separation of adjacent Cu1···Cu1 or Cu2···Cu2 bridged by bpp is 13.399 Å, and the long spacers between coordination sites result in large cavities within the diamondoid cages (figure 2). However, the two sets of diamondoid frameworks interpenetrate one another to fill the void space, forming an interesting 4-fold interpenetrating 3-D architecture (figure 3).

Comparing with another 3-D 4-fold interpenetrated diamondoid framework of $CuCl_2$ and bpp reported [13], the two compounds show some comparability. Both have

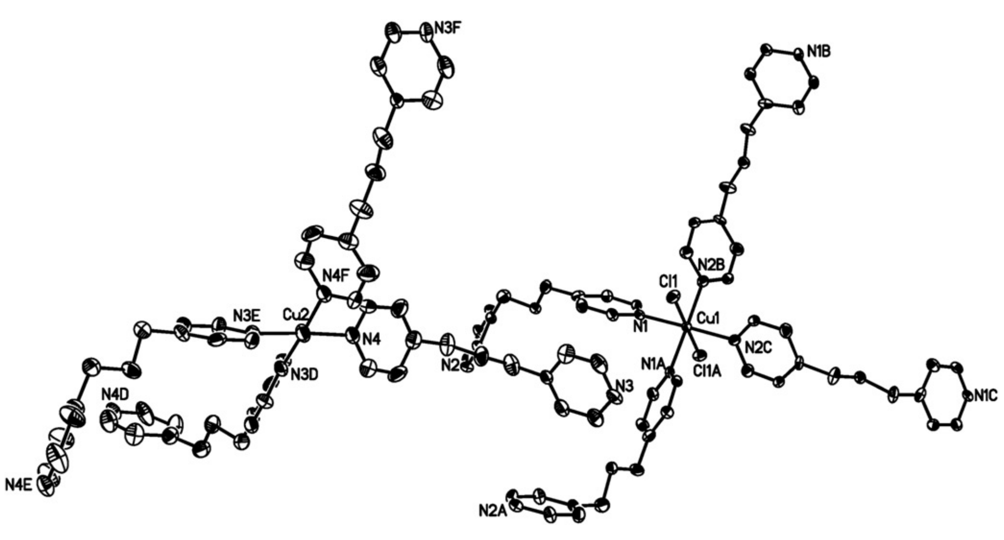

Figure 1. Coordination spheres around Cu1 and Cu2.

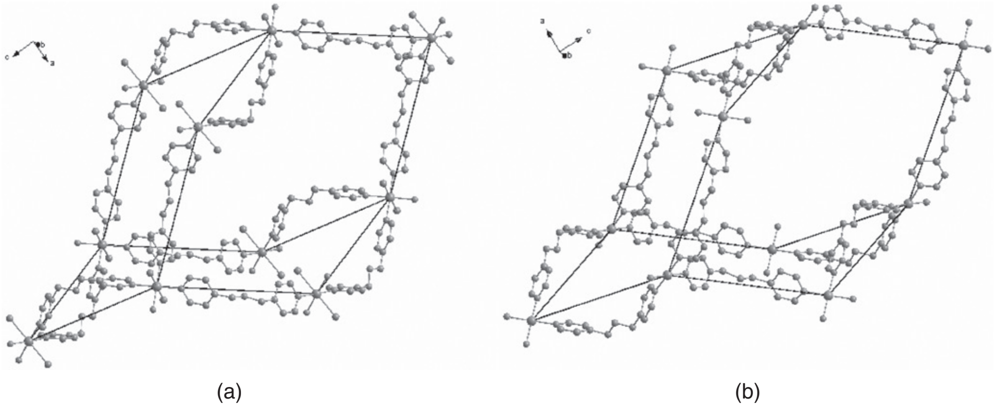

Figure 2. A diagram showing fourteen metal centers bridged by 18 bpp ligands to form each adamantane cage: (a) Cu1 adamantane cage and (b) Cu2 adamantane cage.

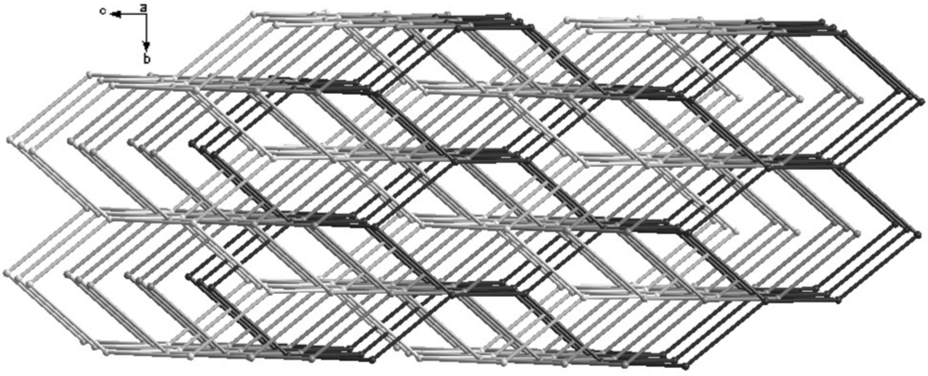

Figure 3. A diagram showing the 3-D 4-fold interpenetrated diamondoid framework of the complex.

3-D 4-fold interpenetrated diamondoid framework, but the coordination models of metal centers is different. For the title complex, apart from the six-coordinate octahedral geometry for Cu1 appearing in the reported case, the four-coordinate square geometry for Cu2 is also involved.

3.3. *Thermogravimetric analysis*

The DSC-TG curve of the coordination polymer (shown in figure 4) was scanned in the range 30–800°C on a STA 409 PC thermal analyzer under air with a flow rate of $30\,\mathrm{mL\,min^{-1}}$ and a heating rate of $10^{\circ}\mathrm{C\,min^{-1}}$. At 122°C the coordination polymer begins to decompose and the DSC curve has an endothermic peak at 131°C. Up to 200°C the weight loss is 13.85%, corresponding to the loss of four chlorides (Calcd 13.35%). The successive mass loss of 80.60% from 200 to 740°C accompanied by two

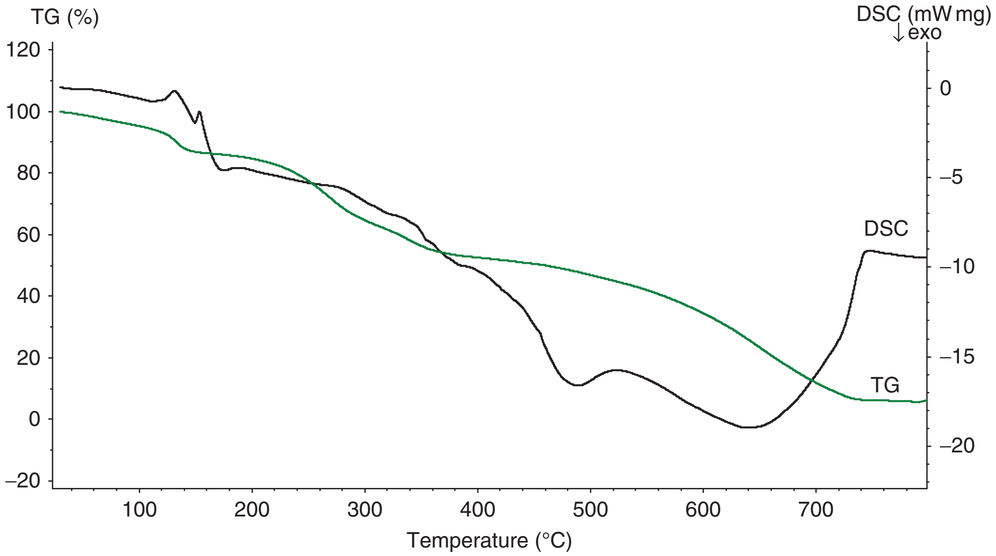

Figure 4. The DSC-TG curve of the coordination polymer.

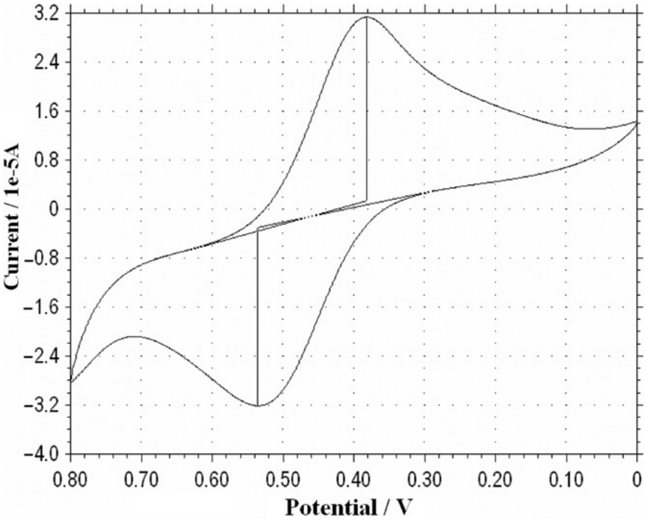

Figure 5. Cyclic voltammogram of the complex in 0.1 M TBAP at scan rate 100 mV s^{-1}.

exothermic peaks at 490 and 641C may be caused by the decomposition of bpp (Calcd 74.68%). The remains may be CuO.

3.4. *Electrochemistry property*

Electrochemistry of the complex was investigated using cyclic voltammetry performed on a CHI660B electrochemical analyzer with three electrodes, a Pt working electrode, a Pt auxiliary electrode, and a commercially available saturated calomel electrode as the reference electrode. A DMF solution of the complex (5×10^{-4} M) and the supporting electrolyte tetrabutylammonium perchlorate (0.1 M) as the electrolytic solution was examined under N_2. As shown in figure 5, the cyclic voltammetric curve of the complex shows a reversible oxidation potential (E_{pa}) at 0.536 V and reduction potential (E_{pc}) at 0.381 V at a scan rate of $100\,mV\,s^{-1}$, which is most likely attributed to Cu(II) $\rightleftharpoons$ Cu(I). $CuCl_2$ in DMF solution gives peaks with oxidation potential (E_{pa}) at 0.597 V and reduction potential (E_{pc}) at 0.331 V [16]. The oxidation potential of our complex shifts to lower potential and its reduction potential to higher potential, which may be due to the influence of bpp. The values of ΔE_p ($\Delta E_p = E_{pa} - E_{pc} = 0.155$ V) and I_{pa}/I_{pc} ($I_{pa}/I_{pc} = 2.921 \times 10^{-5}\,A/3.009 \times 10^{-5}\,A = 0.97 \approx 1$) indicate the reversible nature of the electrode process.

Supplementary material

X-ray crystallographic data in CIF format for the title compound have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 702735. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

Acknowledgments

We gratefully acknowledge financial support from the National Natural Science Foundation of China (20771094, 20671083) and the Science and Technology Key Task of Henan Province (0524270061).

References

[1] D.-X. Xue, Y.-Y. Lin, X.-N. Cheng, X.-M. Chen. *Cryst. Growth Des.*, **7**, 1332 (2007).

[2] (a) A.V. Nossov, D.V. Soldatov, J.A. Ripmeester. *J. Am. Chem. Soc.*, **123**, 3563 (2001). (b) D.M.L. Goodgame, D.A. Grachvogel, D.J. Williams. *Angew. Chem. Int. Engl.*, **38**, 153 (1999).

[3] (a) J.A.R. Navarro, E. Barea, A. Rodriguez-Dieguez, J.M. Salas, C.O. Ania, J.B. Parra, N. Masciocchi, S. Galli, A. Sironi. *J. Am. Chem. Soc.*, **130**, 3978 (2008). (b) J.W. Yoon, S.H. Jhung, Y.K. Hwang, S.M. Humphrey, P.T. Wood, J.S. Chang. *Adv. Mater. (Weinheim, Germany)*, **19**, 1830 (2007).

[4] (a) S.G. Baca, M.T. Reetz, R. Goddard, I.G. Filippova, Y.A. Simonov, M. Gdaniec, N. Gerbeleu. *Polyhedron*, **25**, 1215 (2006). (b) H. Han, S. Zhang, H. Hou, Y. Fan, Y. Zhu. *Eur. J. Inorg. Chem.*, 1594 (2006).

[5] (a) T.A. Zeidan, S.V. Kovalenko, M. Manoharan, R.J. Clark, I. Ghiviriga, I.V. Alabugin. *J. Am. Chem. Soc.*, **127**, 4270 (2005). (b) M. Vinodu, I. Goldberg., *Cryst. Eng. Comm.*, **5**, 490 (2003).

[6] (a) P. Wang, J.-P. Ma, Y.-B. Dong, R.-Q. Huang. *J. Am. Chem. Soc.*, **129**, 10620 (2007). (b) Q.-R. Fang, G.-S. Zhu, M. Xue, J.-Y. Sun, S.-L. Qiu. *Dalton Trans.*, **20**, 2399 (2006).

[7] (a) A. Cingolani, S. Galli, N. Masciocchi, L. Pandolfo, C. Pettinari, A. Sironi. *J. Am. Chem. Soc.*, **127**, 6144 (2005). (b) J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim. *Nature*, **404**, 982 (2000).

[8] (a) M. Oh, C.A. Mirkin. *Nature*, **438**, 651 (2005). (b) S. Hermes, M.K. Schroeter, R. Schmid, L. Khodeir, M. Muhler, A. Tissler, R.W. Fischer, R.A. Fischer. *Angew. Chem. Int. Ed.*, **44**, 6237 (2005).

[9] (a) S. Zang, Y. Su, Y. Li, Z. Ni, Q. Meng. *Inorg. Chem.*, **45**, 174 (2006). (b) L. Wang, M. Yang, G. Li, Z. Shi, S. Feng. *Inorg. Chem.*, **45**, 2474 (2006).

[10] (a) J.-Q. Liu, Y.-Y. Wang, P. Liu, W.-P. Wu, Y.-P. Wu, X.-R. Zeng, F. Zhong, Q.-Z. Shi. *Inorg. Chem. Commun.*, **10**, 343 (2007). (b) M.J. Plater, M.R.St J. Foreman, J.M.S. Skakle. *Cryst. Eng.*, **4**, 293 (2001). (c) P.-X. Yin, J. Zhang, J.-K. Cheng, Z.-J. Li, Y.-G. Yao. *Inorg. Chem. Commun.*, **9**, 541 (2006). (d) C.V.K. Sharma, R.J. Diaz, A.J. Hessheimer, A. Clearfield. *Cryst. Eng.*, **3**, 201 (2000). (e) Y.-Y. Niu, Y.-L. Song, N. Zhang, H.-W. Hou, D.-J. Che, Y.-T. Fan, Y. Zhu, C.Y. Duan. *Eur. J. Inorg. Chem.*, 2259 (2006).

[11] S. Hu, M.-L. Tong. *Dalton Trans.*, **7**, 1165 (2005).

[12] (a) L. Carlucci, G. Ciani, D.M. Proserpio, S. Rizzato. *CrystEngComm*, **4**, 121 (2002). (b) L. Carlucci, G. Ciani, M. Moret, D.M. Proserpio, S. Rizzato. *Angew. Chem. Int. Ed.*, **39**, 1506 (2000).

[13] L. Carlucci, G. Ciani, M. Moret, D.M. Proserpio, S. Rizzato. *Chem. Mater.*, **14**, 12 (2002).

[14] (a) G.-H. Wang, Z.-G. Li, H.-Q. Jia, N.-H. Hu, J.-W. Xu. *Cryst. Growth Des.*, **8**, 1932 (2008). (b) Y.-W. Hu, G.-H. Li, X.-M. Liu, B. Hu, M.-H. Bi, L. Gao, Z. Shi, S.-H. Feng. *CrystEngComm*, **10**, 888 (2008). (c) P.-K. Chen, Y.-X. Che, L. Xue, J.-M. Zheng. *Cryst. Growth Des.*, **6**, 2517 (2006). (d) J.-H. Luo, M.-C. Hong, R.-H. Wang, R. Cao, L. Han, Z.-Z. Lin. *Eur. J. Inorg. Chem.*, 2705 (2003). (e) X.-J. Li, R. Cao, D.-F. Sun, W.-H. Bi, Y.-Q. Wang, X. Li, M.-C. Hong. *Cryst. Growth Des.*, **4**, 775 (2004). (f) X.-L. Wang, G.-C. Liu, B.-K. Chen, Y.-F. Bi, H.-Y. Lin. *J. Coord. Chem.*, **61**, 1635 (2008).

[15] G.M. Sheldrick. Bruker *SHELSTL-PC*, University of Göttingen, Göttingen, Germany (1997).

[16] X. Zhou, X. Meng, W. Cheng, H. Hou, M. Tang, Y. Fan. *Inorg. Chim. Acta*, **360**, 3467 (2007).