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Synthesis and crystal structure of Mn(II) and Zn(II) complexes with 1,3,5-tris(carboxymethoxyl) benzene ligand

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Two complexes $(H_2bipy)[M_2(TB)_2(H_2O)_8] \cdot 5H_2O$ (M = Mn **1**, Zn **2**) (bipy = 4,4′-bipyridine, H_3TB = 1,3,5-tris(carboxymethoxyl)benzene) were synthesized by the reaction of the corresponding metal salt with ligand H_3TB and 4,4′-bipy in an aqueous methanol solution at room temperature, respectively. Their structures were determined by single crystal X-ray diffraction analysis. Both complexes **1** and **2** crystallize in the triclinic space group $P\bar{1}$ with the crystal parameters of **1**: $a = 9.725(12)$ Å, $b = 10.651(13)$ Å, $c = 10.882(13)$ Å, $\alpha = 91.72(2)^\circ$, $\beta = 96.41(2)^\circ$, $\gamma = 97.72(2)^\circ$, $V = 1109(2)$ Å^3, $Z = 1$ and **2**: $a = 9.610(10)$ Å, $b = 10.55(2)$ Å, $c = 10.83(2)$ Å, $\alpha = 91.60(4)^\circ$, $\beta = 95.32(2)^\circ$, $\gamma = 97.73(4)^\circ$, $V = 1082(3)$ Å^3, $Z = 1$. Complexes **1** and **2** have the same dinuclear structure, in which each metal atom is six coordinated with distorted octahedral geometry by two oxygen atoms from two different TB^{3-} ligands and four ones from four coordinated water molecules. The dinuclear units are further linked by hydrogen bonding and π–π interactions to form the three-dimensional framework structure.

KEY WORDS: Mn(II) complex; Zn(II) complex; crystal structure; carboxylate ligand; π–π interactions; hydrogen bonds.

Introduction

Studies on metal-organic frameworks (MOFs) are of great current interests, due to their novel structure, interesting properties and potential applications as new materials, for example, molecular magnets, catalysts, and so on.[1,2] In the building MOFs, it is important to design organic ligands and to choose suitable metal ion with definite coordination geometry. In addition to the coordination interactions, the results reported to now show that non-covalent interactions such as π–π and hydrogen bonding interactions are also very important in determining the structure and property of MOFs.[3–8] Therefore, organic ligands with aromatic moiety and hydrogen bonding ability are often used to react with varied metal salts to assembly into novel MOFs. Among the reported organic ligands, those containing benzenecarboxylates are an important family because they combine the principles of supramolecular chemistry along with favorable π–π and hydrogen bonding interactions, which may result in fascinating and interesting structures and properties.

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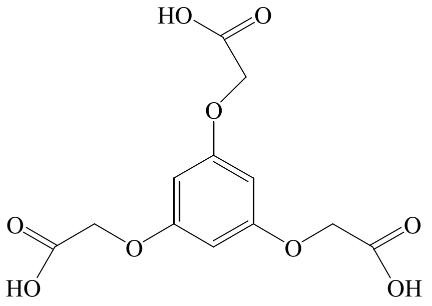

H$_3$TB

Scheme 1. Structure of ligand H$_3$TB.

We are interested in MOFs with flexible tripodal ligands with imidazole or carboxylate coordination moieties.[9,10] In this paper, we designed a new organic ligand containing benzene ring and carboxyl groups, namely 1,3,5-tris(carboxymethoxyl)benzene(H$_3$TB) (Scheme 1), and reactions with transition metal salts were carried out. Here we report the synthesis, structural characterization of coordination compounds $(H_2bipy)[Mn_2(TB)_2(H_2O)_8]\cdot 5H_2O$ (**1**) and $(H_2bipy)[Zn_2(TB)_2(H_2O)_8]\cdot 5H_2O$ (**2**) (bipy = 4,4′-bipyridine) obtained by reaction of ligand H$_3$TB with $Mn(ClO_4)_2\cdot 6H_2O$ and $ZnCl_2$ salts, respectively. The three-dimensional frameworks are sustained by non-covalent π–π interactions and hydrogen bonds.

Experimental

General

All commercially available chemicals are of reagent grade and used as received without further purification. Solvents were purified according to the standard methods. C, H and N elemental analyses were carried out on a Perkin-Elmer 240C elemental analyzer at the analysis center of Nanjing University. Infrared (IR) spectra were recorded on a Bruker Vector22 FT-IR spectrophotometer by using KBr discs. ^{1}H NMR spectral measurements were performed on the Bruker DRX-500 spectrometer.

Table 1. Crystal Data and Refinement Results for Complexes **1** and **2**

Complex	**1**	**2**
Empirical formula	$C_{34}H_{54}N_2Mn_2O_{31}$	$C_{34}H_{54}N_2Zn_2O_{31}$
Formula weight	1096.67	1117.53
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.725(12)	9.610(10)
b (Å)	10.651(13)	10.55(2)
c (Å)	10.882(13)	10.83(2)
α (°)	91.72(2)	91.60(4)
β (°)	96.41(2)	95.32(2)
γ (°)	97.72(2)	97.73(4)
V (Å^3)	1109(2)	1082(3)
Z	1	1
Crystal size (mm)	0.25 × 0.25 × 0.25	0.30 × 0.25 × 0.25
D_c (g cm^{-3})	1.642	1.714
μ (mm^{-1})	0.677	1.219
2θ max (°)	50.00	50.00
Reflns. collected	7127	6958
Independent reflns.	3728	3626
Obsd. reflns. ($I > 2\sigma(I)$)	3348	3396
Parameters refined	365	373
R_{int}	0.0532	0.0494
$T_{\max}/T_{\min}$	0.8489/0.8489	0.7504/0.7113
R ($I > 2\sigma(I)$)	0.0418	0.0351
wR_2 ($I > 2\sigma(I)$)	0.1148	0.0946
Goodness of fit	1.048	1.050
Residual electron density (eÅ^{-3})	0.524; −0.470	0.493; −0.567

Structure determinations

The data collections for complexes **1** and **2** were carried out on a Rigaku Saturn CCD area detector at 173 K, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). The structures were solved by direct method using SHELX-97[11] and refined by full-matrix least-squares methods anisotropically for non-hydrogen atoms. The hydrogen atoms except for those of water molecules were generated geometrically, while the ones of six water molecules were found in the differential Fourier map and located directly. However, the hydrogen atoms of uncoordinated water molecule

Table 2. Selected Bond Lengths [Å] and Angles [°] for Complexes **1** and **2**

1			
Mn1–O1	2.155(2)	Mn1–O10	2.191(3)
Mn1–O11	2.200(2)	Mn1–O12	2.229(2)
Mn1–O13	2.153(2)	Mn1–O4^a	2.187(2)
O1–Mn1–O10	92.32(10)	O1–Mn1–O11	95.72(10)
O1–Mn1–O12	173.05(6)	O1–Mn1–O13	91.47(10)
O10–Mn1–O11	171.95(6)	O10–Mn1–O12	82.17(10)
O10–Mn1–O13	90.38(9)	O11–Mn1–O12	89.85(10)
O11–Mn1–O13	89.01(9)	O12–Mn1–O13	92.78(10)
O1–Mn1–O4^a	85.05(10)	O10–Mn1–O4^a	87.36(9)
O11–Mn1–O4^a	93.73(9)	O12–Mn1–O4^a	90.47(10)
O13–Mn1–O4^a	175.76(6)		
2			
Zn1–O1	2.120(3)	Zn1–O10	2.104(3)
Zn1–O11	2.094(3)	Zn1–O12	2.141(3)
Zn1–O13	2.061(3)	Zn1–O4^b	2.070(3)
O1–Zn1–O10	91.60(11)	O1–Zn1–O11	88.66(10)
O1–Zn1–O12	91.60(13)	O1–Zn1–O13	176.56(6)
O10–Zn1–O11	172.04(7)	O10–Zn1–O12	89.01(13)
O10–Zn1–O13	90.66(11)	O11–Zn1–O12	83.03(13)
O11–Zn1–O13	89.46(10)	O12–Zn1–O13	91.03(13)
O1–Zn1–O4^b	83.55(13)	O10–Zn1–O4^b	94.22(13)
O11–Zn1–O4^b	93.71(13)	O12–Zn1–O4^b	174.23(6)
O13–Zn1–O4^b	93.70(13)		

Note. Symmetry transformation used to generate equivalent atoms:$^a 1 - x, 2 - y, 2 - z$;$^b 2 - x, 1 - y, 1 - z$.

at special position (O16) could not be found. Calculations were performed on a personal computer with the Siemens SHELXTL program package.[12] The crystal parameters, data collection and refinement results for the compounds are listed in Table 1. The selected bond lengths and bond angles are listed in Table 2.

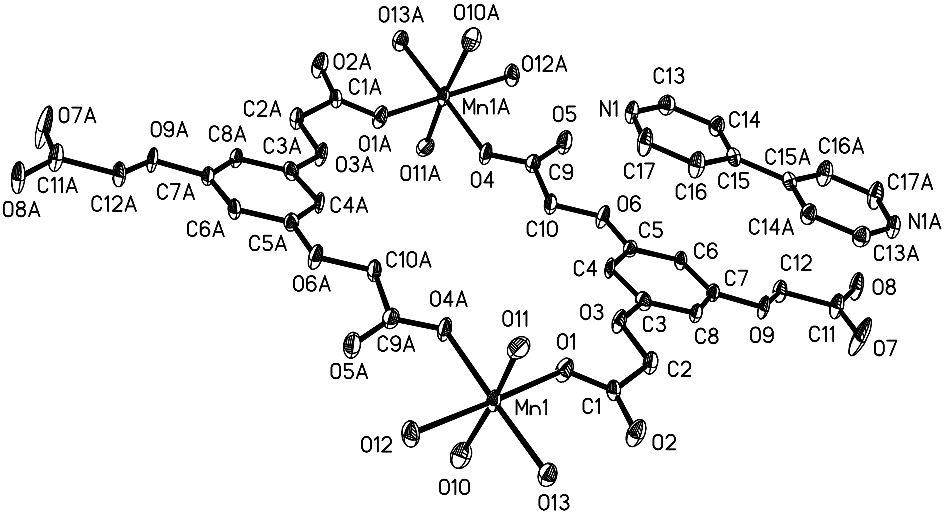

Fig. 1. The coordination environment of Mn (II) atom in **1** with thermal ellipsoids at 30% probability, the uncoordinated water molecules and hydrogen atoms are omitted for clarity.

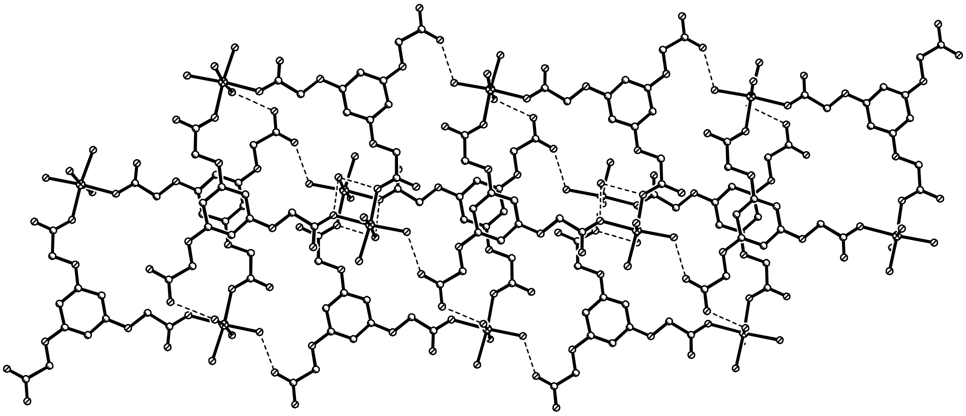

Fig. 2. Infinite 2D network structure of complex **1**, in which the hydrogen bonds are presented by dashed lines.

Synthesis of ligand 1,3,5-tris(carboxymethoxyl)benzene (H_3TB)

Ligand H_3TB was prepared by a similar method reported for the synthesis of α,α'-bis-(3,5-bis(phenylthiamethyl)phenyloxy)-α''-phthalimidomesitylene.[13] A mixture of chloroacetic acid (12.29 g, 130 mmol) and K_2CO_3 (9.67 g, 70 mmol) in DMF (30 mL) was stirred 1 h at room temperature. Then a mixture of phloroglucinol (4.5 g, 36 mmol) and K_2CO_3 (16.59 g, 120 mmol) in DMF (30 mL), which have been stirred for 1 h, was added. The mixture was further stirred 12 h at 74–78°C. After the evaporation of DMF under vacuum condition, the mixture was dissolved in water. Then concentrated sulfuric acid was added slowly to the aqueous solution until pH = 3 under ice bath condition. The product H_3TB was obtained by filtration, and washed by water till sulfate anions were removed completely, then dried in vacuum to give a pale yellow powder in 55% yield. Calcd. for $C_{12}H_{12}O_9$ (%): C, 48.01; H, 4.03; found (%): C, 48.10; H, 4.12. IR data (KBr pellet, cm^{-1}): 1722s, 1612s, 1540s, 1431m, 1261m, 1173s, 1093w, 811w.^1H NMR (500 MHz, D_2O): δ 6.18 (s, 3H); 4.78 (s, 6H).

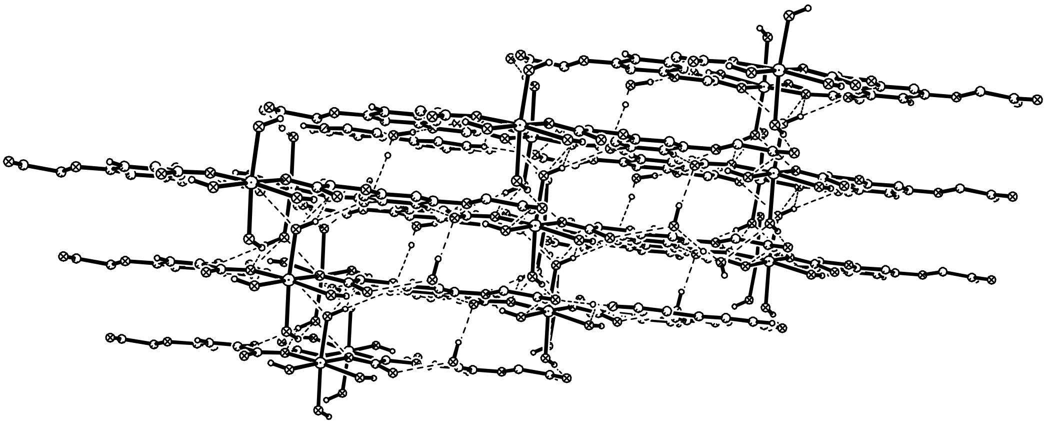

Fig. 3. Crystal packing diagram for complex **1** in which the hydrogen bonds are indicated by dashed lines.

Table 3. Bond Lengths and Angles of Hydrogen Bonding for Complexes **1**, **2**

D–H···A	D···A [Å]	D–H–A	D–H–A [°]
1			
O10–H14···O8[a]	2.754(4)	O10–H14–O8	167
O10–H14B···O14[a]	2.725(4)	O10–H14B–O3	176
O11–H15···O1[b]	2.848(4)	O11–H15–O9	133
O11–H15···O3[b]	3.025(4)	O12–H16–O6	152
O11–H15B···O4[c]	2.793(4)	O11–H15B–O4	158
O12–H16···O5[d]	2.727(4)	O12–H16–O5	170
O12–H16B···O8[e]	3.160(5)	O12–H16B–O8	174
O13–H17···–O2	2.694(4)	O13–H17–O2	157
O13–H17B···O7[f]	2.669(4)	O13–H17B–O7	164
O14–H18···O15[g]	2.695(4)	O14–H18–O15	162
O14–H19···O5[h]	2.905(4)	O14–H19–O5	154
O15–H20···O5[c]	2.794(4)	O15–H20–O5	164
O15–H20···O6[c]	3.093(5)	O15–H20–O5	127
O15–H21···O2[f]	2.786(4)	O15–H21–O2	175
N1–H22···O8[i]	2.747(4)	N1–H22–O8	171
C8–H5···O2[f]	3.503(5)	C8–H5–O2	177
C17–H13···O7[i]	3.100(5)	C17–H13–O7	127
C17–H13···O12[b]	3.055(5)	C17–H13···O12	127
2			
O10–H14···O1[j]	2.762(6)	O10–H14–O1	171
O10–H14B···O6[g]	3.012(6)	O10–H14B–O6	171
O11–H15···O8[i]	2.709(6)	O11–H15–O8	177
O11–H15B···O14[j]	2.720(6)	O11–H15B–O14	173
O12–H16···O8[k]	3.302(7)	O12–H16–O8	149
O12–H16B···O2	2.687(6)	O12–H16B–O2	169
O13–H17···O7[l]	2.646(6)	O13–H17–O7	162
O13–H17B···O5[m]	2.674(6)	O13–H17B–O5	150
O14–H18···O2[n]	2.919(6)	O14–H18–O2	153
O14–H18···O15[a]	3.172(7)	O14–H18–O15	135
O14–H19···O15[°]	2.689(6)	O14–H19–O15	166
O15–H20···O5[l]	2.796(6)	O15–H20–O5	174
O15–H21···O2[j]	2.783(6)	O15–H21–O2	162
O15–H21···O3[j]	3.085(6)	O15–H21–O3	128
N1–H22···O8[i]	2.710(6)	N1–H22–O8	176
C6–H4···O5[p]	3.454(7)	C6–H4–O5	178
C17–H13···O7[i]	3.068(7)	C17–H13–O7	128
C17–H13···O12[c]	3.059(7)	C17–H13–O12	130

Note. Symmetry transformation used to generate equivalent atoms:[a] $1-x, 1-y, 2-z$; [b] $2-x, 2-y, 2-z$; [c] $1+x, y, z$; [d] $1-x, 2-y, 2-z$; [e] $1+x, 1+y, 1+z$; [f] $2-x, 1-y, 2-z$; [g] $-1+x, y, z$; [h] $-x, 1-y, 1-z$; [i] $x, 1+y, z$; [j] $1-x, 1-y, 1-z$; [k] $1-x, -y, -z$; [l] $-1+x, 1+y, z$; [m] $2-x, 1-y, 1-z$; [n] $x, y, 1+z$; [°] $x, -1+y, z$; [p] $3-x, -y, 1-z$.

Synthesis of complex *$(H_2bipy)[Mn_2(TB)_2(H_2O)_8]\cdot 5H_2O$ (**1**)*

$Mn(ClO_4)_2\cdot 6H_2O$ (21.6 mg, 0.06 mmol), H_3TB (18 mg, 0.06 mmol), 4,4′-bipy (14 mg, 0.09 mmol) were added to 10 mL of CH_3OH and H_2O (*v*/*v* 1:1), and after being stirred at room temperature for 0.5 h, the clear solution was allowed to stand at room temperature for two weeks. Block yellow crystals were obtained in 41% yield. Elemental analysis calcd for $C_{34}H_{54}N_2Mn_2O_{31}$ (%): C, 37.24; H, 4.96; N, 2.55. Found (%): C, 37.41; H, 5.04; N, 2.68. IR data (KBr pellet, cm^{-1}): 1613bs, 1415m, 1326w, 1170m, 1078w, 808w.

Synthesis of complex *$(H_2bipy)[Zn_2(TB)_2(H_2O)_8] \cdot 5H_2O$ (**2**)*

Complex **2** was prepared by the same method as that of complex **1** except $Mn(ClO_4)_2 \cdot 6H_2O$ replaced by $ZnCl_2$ (8.2 mg, 0.06 mmol). Prism yellow crystals were isolated after four weeks in 35% yield. Elemental analysis calcd for $C_{34}H_{54}N_2Zn_2O_{31}$ (%): C, 36.54; H, 4.87; N, 2.51. Found (%): C, 37.06; H, 4.91; N, 2.61. IR data (KBr pellet, cm^{-1}): 1611bs, 1417m, 1325w, 1167m, 1072w, 810w.

Results and discussion

Single crystal X-ray analysis reveals that complexes **1** and **2** crystallize in the same space group with similar cell parameters as summarized in Table 1, and they are isomorphous and isostructural. Thus only the structure of **1** is described here in detail as an example. In complex **1**, the asymmetric unit consists of a Mn(II) atom, a ligand TB^{3-}, four coordinated and two and half uncoordinated water molecules, an half of protonated 4,4′-bipy, which acts as counterion. As shown in Fig. 1, each Mn(II) center is six coordinated by six oxygen atoms with a distorted octahedral geometry, four of which come from four H_2O molecules, while the other two are from two different TB^{3-} ligands. The Mn–O bond distances are in the range of 2.153(2) to 2.229(2) Å(Table 2), which are in agreement with those of the reported Mn–O bond lengths.[14] On the other hand, all carboxyl groups of the H_3TB ligand are completely deprotonated in **1** and **2**, which is confirmed by infrared spectral measurements since no strong band around 1722 cm^{-1} for –COOH of free H_3TB ligand was observed in **1** and **2**. The carboxyl group of the TB^{3-} ligand coordinates to the metal atom in the monodentate mode and each TB^{3-} ligand uses its two of three carboxyl groups to link two Mn(II) atoms, while the third one is free of coordination (Fig. 1). Therefore, two Mn(II) atoms are linked by two TB^{3-} ligands to give rise to a molecular $Mn_2(TB)_2$ metallocyclic ring.

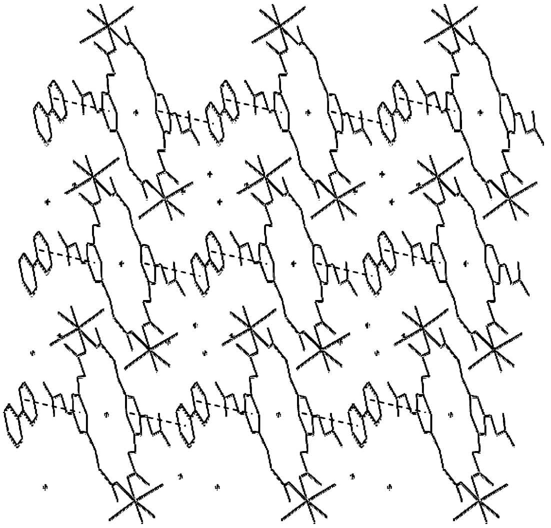

Fig. 4 Diagram for complex **1** with π–π interactions indicated by dashed lines.

It is noteworthy that the $Mn_2(TB)_2$ metallocyclic rings are connected together through the O–H···O hydrogen bonding interactions between the coordinated water molecules and the oxygen atoms of the uncoordinated carboxyl groups of neighboring $Mn_2(TB)_2$ metallocyclic molecule to give extended two-dimensional (2D) network structure as illustrated in Fig. 2. Furthermore, there are N–H···O and C–H···O hydrogen bonds in complex **1**, which lead to the formation of three-dimensional (3D) structure (Fig. 3). The protonated 4,4′-bipy takes part in the formation of hydrogen bond N1–H22···O8 with N1–O8 distance of 2.747(4) Å in complex **1**. The hydrogen bonding data are summarized in Table 3. In addition, the π–π interactions also play important role in formation of the packing structure of complexes **1** and **2**. Face-to-face π–π interaction is observed in complex **1**. The distance between the centroids of the benzene ring of ligand TB^{3-} and the pyridine ring of the protonated 4,4′-bipy is 3.30 Å and the dihedral angle between these two aromatic rings is 2.4° (in complex **2**, the corresponding centroid-to-centroid distance is 3.26 Å, and the dihedral angle is 2.9°), which are comparable to the previously reported π–π interactions (Fig. 4).[15]

In summary, the complexes **1** and **2** were obtained by reactions of tricarboxylate ligand with metal salts. The dinuclear $M_2(TB)_2$ (M = Mn, Zn) metallocyclic molecules of complexes **1** and **2** are linked together through O–H···O, N–H···O, C–H···O hydrogen bonds and π–π interactions to generate three-dimensional framework.

Supplementary Material Crystallographic data (excluding structure factors) for the structures in this paper has been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 294381 and 294382. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223–336033 or e-mail: deposit@ccdc.cam.ac.uk).

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References

1. Boskovic, C.; Brechin, E.K.; Streib, W.E.; Folting, K.; Bollinger, J.C.; Hendrickson, D.N.; Christon, G. *J. Am. Chem. Soc.* **2002**, *124*, 3725.
2. Tsuchida, E.; Oyaizu, K. *Coord. Chem. Rev.* **2003**, *237*, 213.
3. Philp, D.; Stoddart, J.F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154.
4. Houk, K.N.; Menzer, S.; Newton, S.P.; Raymo, F.M.; Stoddart, J.F.; Williams, D.J. *J. Am. Chem. Soc.* **1999**, *121*, 1479.
5. Liu, Z.-H.; Duan, C.-Y.; Hu, J.; You, X.-Z. *Inorg. Chem.* **1999**, *38*, 1719.
6. Wang, Y.-Q.; Cao, R.; Bi, W.-H.; Li, X.; Li, X.-J.; Wang, Y.-L. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2309.
7. Kitagawa, S.; Uemura, K. *Chem. Soc. Rev.* **2005**, *34*, 109.
8. Hunter, C.A.; Sanders, J.K.M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.
9. Fan, J.; Zhu, H.-F.; Okamura, T.; Sun, W.-Y.; Tang, W.-X.; Ueyama, N. *Inorg. Chem.* **2003**, *42*, 158.
10. Zhang, Z.-H.; Shen, Z.-L.; Okamura, T.; Zhu, H.-F.; Sun, W.-Y.; Ueyama, N. *Cryst. Growth Des.* **2005**, *5*, 1191.
11. (a) Sheldrick, G.M. *SHELX97*, Program for Crystal Structure Determination, University of Göttingen, Germany, 1997. (b) Sheldrick, G.M. *SHELX97*, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
12. XSCANS, Version 2.1, Siemens Analytical X-ray Instruments, Madison, WI, 1994. SHELEXTL, Version 5.0, Siemens Industrial Automation, Analytical Instruments, Madison, WI, 1995.
13. Huck, W.T.S.; Prins, L.J.; Fokkens, R.H.; Nibbering, N.M.M.; van Veggel, F.C.J.M.; Reinhoudt, D.N. *J. Am. Chem. Soc.* **1998**, *120*, 6240.
14. Fan, J.; Gan, L.; Kawaguchi, H.; Sun, W.-Y.; Yu, K.-B.; Tang, W.-X. *Chem. Eur. J.* **2003**, *9*, 3965.
15. Barclay, T.M.; Cordes, A.W.; Mingie, J.R.; Oakley, R.T.; Preuss, K.E. *CrystEngComm.* **2000**, *2*, 89.