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Synthesis, structures and properties of two-dimensional honeycomb and stepwise networks from self-assembly of tripodal ligand 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene with metal salts †

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Received 28th February 2002, Accepted 5th August 2002
First published as an Advance Article on the web 16th September 2002

Three new coordination networks, $[Zn(L)_2](ClO_4)_2$ (**1**), $[Mn(L)_2](SO_4)\cdot 16H_2O$ (**2**) and $[Cd_3(L)_2(SO_4)_4(H_2O)_2(CH_3CH_2OH)_2][Cd(H_2O)_6]\cdot 2H_2O$ (**3**) were obtained by self-assembly of the corresponding metal salts with 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (L). Single crystal X-ray diffraction studies reveal that **1** and **2** have 2D honeycomb network structures in which each L ligand coordinates to three metal centers with the nitrogen atoms of imidazole group. When the ligand L reacts with $CdSO_4\cdot 2.7H_2O$, an interesting complex **3** with an unusual 2D stepwise structure involving the coordination of ethanol, water molecules, and sulfate anion, was obtained. Three distinct Cd centers reside in the complex **3**. One of them binds to six water molecules to form a $[Cd(H_2O)_6]^{2+}$ cation, and the other two are bridged by both L ligand and sulfate anion to give a 2D network. Furthermore, the complex **2** was found to have interesting properties of anion exchange and luminescence.

Introduction

The design and construction of supramolecular architectures is a rapidly developing area in the past years.[1–3] So far, considerable progress has been achieved in controlling the assembly and orientations of individual building blocks into structures with specific topologies and potentially interesting properties including ion/molecular recognition, selective guest inclusion, ion exchange *etc.*[4–7] Such progress makes possible the rational design and synthesis of one- (1D), two- (2D), or three-dimensional (3D) supramolecular frameworks including adamantoid,[8,9] cube,[10] ladder,[11] honeycomb,[12–15] and helical staircase.[16,17]

Two- or three-connecting ligands have been proved to be one of the most important ligands in construction of novel frameworks.[18–23] However most of these reported complexes are formed by assembly of the rigid ligands with metal ions, the reported flexible tripodal ligands with aromatic core in this field are relatively rare.[24–27] In the case of flexible ligands, the possible coordination modes are much more abundant than those of the rigid one due to the flexibility and low symmetry of the ligands since the flexible ligands can adopt different conformations according to the geometric needs of different metal ions.

We are currently interested in assembly and function of supramolecular frameworks containing flexible multidentate ligands.[26,27] Due to the presence of methylene group between the imidazole and benzene ring groups, 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (L) is a flexible divergent ligand. There are two different conformations (*cis*, *cis*, *cis* and *cis*, *trans*, *trans*) when L reacts with metal ions (Scheme 1) as demonstrated in the previous studies.[26,27] Now we extended our study to construct coordination polymeric materials using the L ligand. Here we reported the preparation, crystal structures and properties of three new coordination polymers of L with zinc(II), manganese(II) and cadmium(II) salts, namely $[Zn(L)_2](ClO_4)_2$ **1**, $[Mn(L)_2](SO_4)\cdot 16H_2O$ **2** and $[Cd_3(L)_2(SO_4)_4(H_2O)_2(CH_3CH_2OH)_2][Cd(H_2O)_6]\cdot 2H_2O$ **3**.

Experimental

All commercially available chemicals are of reagent grade and used as received without further purification. Ethanol was dried and purified by distillation before use. Samples for C, H and N analyses were dried in vacuum and the 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 IFS66V vacuum-type FTIR spectrophotometer by using KBr discs. Luminescence spectra were recorded on a Hitachi 850 fluorescence spectrophotometer at room temperature (25 °C).

Synthesis of $[Zn(L)_2](ClO_4)_2$ (1). The complex was synthesized by layering method. A solution of L (36.0 mg, 0.1 mmol) in ethanol (5 ml) was carefully placed on a solution of $Zn(ClO_4)_2\cdot 6H_2O$ (18.6 mg, 0.05 mmol) in water (5 ml). Colorless crystals **1** formed after several weeks. Yield: 43 mg, 87%. Calc. elem. anal. for $C_{42}H_{48}Cl_2N_{12}O_8Zn$: C 51.20; H 4.91; N 17.06. Found: C 51.31; H 5.00; N 17.07.

Synthesis of $[Mn(L)_2](SO_4)\cdot 16H_2O$ (2). The methanol (5 ml) solution of L (36.0 mg, 0.1 mmol) and water (5 ml) solution of $MnSO_4\cdot H_2O$ (8.5 mg, 0.05 mmol) was mixed and allowed to stand in air at room temperature for several days, colorless crystals suitable for X-ray diffraction were obtained. Yield: 34 mg, 58%. Calc. elem. anal. for $C_{42}H_{80}MnN_{12}O_{20}S$: C 43.48, H 6.95, N 14.49. Found: C 43.46, H 7.01, N 14.46.

Synthesis of $[Cd_3(L)_2(SO_4)_4(H_2O)_2(CH_3CH_2OH)_2][Cd(H_2O)_6]\cdot 2H_2O$ (3). The complex was also synthesized by

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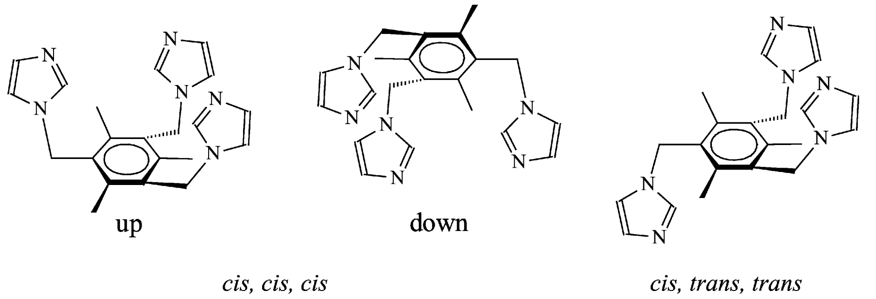
† Electronic supplementary information (ESI) available: hydrogen bond network indicated by dashed lines in **2** (Fig. S1), coordination environment of Cd2B (minor component) (Fig. S2), FT-IR spectra of anion exchange (Fig. S3) and excitation and emission spectra of **2** (Fig. S4). See http://www.rsc.org/suppdata/dt/b2/b202138b/

DOI: 10.1039/b202138b

Table 1 Crystallographic data for $[Zn(L)_2](ClO_4)_2$ (**1**), $[Mn(L)_2](SO_4)\cdot16H_2O$ (**2**) and $[Cd_3(L)_2(SO_4)_4(H_2O)_2(CH_3CH_2OH)_2][Cd(H_2O)_6]\cdot2H_2O$ (**3**)

Compounds	**1**	**2**	**3**
Formula	$C_{42}H_{48}Cl_2N_{12}O_8Zn$	$C_{42}H_{80}MnN_{12}O_{20}S$	$C_{46}H_{80}Cd_4N_{12}O_{28}S_4$
Formula weight	985.19	1160.18	1827.09
Crystal system	rhombohedral	monoclinic	triclinic
Space group	$R\bar{3}$	$C2/c$	$P\bar{1}$
a/Å	13.5818(8)	11.7906(2)	12.3739(13)
b/Å		20.4405(3)	14.5578(15)
c/Å		24.3496(8)	10.1860(10)
α/°	46.194(2)		95.632(3)
β/°		97.328(2)	110.726(7)
γ/°			69.367(3)
V/Å^3	1190.71(12)	5820.5(2)	1605.3(3)
Z	1	4	1
ρ(calc.)/g cm^{-3}	1.374	1.324	1.879
$F(000)$	512	2468	910
Crystal size/mm	0.2 × 0.2 × 0.1	0.3 × 0.3 × 0.1	0.4 × 0.3 × 0.3
Index ranges	$-17 \le h \le 17$ $-16 \le k \le 16$ $-15 \le l \le 15$	$-15 \le h \le 15$ $-26 \le k \le 24$ $-31 \le l \le 31$	$-15 \le h \le 16$ $-18 \le k \le 18$ $-13 \le l \le 12$
μ/cm^{-1}	6.91	3.42	15.30
Reflections collected	3599	11792	10861
Unique reflections	1833	6677	7053
R_{int}	0.0410	0.0394	0.0362
R [$I > 2\sigma(I)$]	$R = 0.0481$, $wR = 0.1071$ [a]	$R = 0.0676$, $wR = 0.1951$ [b]	$R = 0.0506$, $wR = 0.1441$ [c]
R(all data)	$R = 0.0818$, $wR = 0.1126$	$R = 0.1103$, $wR = 0.2082$	$R = 0.0600$, $wR = 0.1492$
Goodness of fit	0.979	1.078	1.103

[a] $w = 1/[\sigma^2(F_o)^2 + (0.0400P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. [b] $w = 1/[\sigma^2 (F_o)^2 + (0.0917P)^2 + 9.6231P]$, where $P = (F_o^2 + 2F_c^2)/3$. [c] $w = 1/[\sigma^2 (F_o)^2 + (0.0899P)^2 + 1.6579P]$, where $P = (F_o^2 + 2F_c^2)/3$.



Scheme 1

layering method. A solution of L (18.0 mg, 0.05 mmol) in ethanol (5 ml) was carefully layered over a solution of $CdSO_4\cdot2.7H_2O$ (25.7 mg, 0.1 mmol) in water (10 ml). Colorless crystals were isolated by filtration after several weeks. Yield: 32 mg, 70%. Calc. elem. anal. for $C_{46}H_{70}Cd_4N_{12}O_{28}S_4$: C 30.24; H 4.41; N 9.20. Found: C 30.38; H 4.49; N 9.14.

X-Ray crystal structure determination

The intensity data for **1**, **2** and **3** were collected on a Rigaku RAXIS-RAPID Imaging Plate diffractometer at 200 K, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods with SIR92,[28] and expanded using Fourier techniques.[29] All data were refined anisotropically by the full-matrix least-squares method for non-hydrogen atoms. The hydrogen atoms were generated geometrically. One cadmium atom, two sulfate anions, water molecules and the terminal methyl groups of coordinated ethanol are disordered in **3**. The atoms Cd2, O12, O13, O14 (s.o.f.: 0.70 and 0.30), O21, O22, O23, O24 (s.o.f.: 0.55 and 0.45), O31, O32, O33 (s.o.f.: 0.82 and 0.18), and C102 (s.o.f.: 0.56 and 0.44) are located with site occupancy factors (s.o.f.) given in the brackets. All calculations were carried out on SGI workstation using the teXsan crystallographic software package of the Molecular Structure Corporation.[30] Details of the crystal parameters, data collection and refinement for complexes **1**, **2** and **3** are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are given in Table 2.

CCDC reference numbers 180727–180729.

See http://www.rsc.org/suppdata/dt/b2/b202138b/ for crystallographic data in CIF or other electronic format.

Results and discussion

Crystal structure of 1

The compound crystallizes in space group $R\bar{3}$ and the asymmetric unit contains one-sixth of a molecule of $[Zn(L)_2](ClO_4)_2$. The same space group has been found in a cage-like complex $[Zn_3(tib)_2(OAc)_6]$ with analogous tripodal ligand 1,3,5-tris(imidazol-1-ylmethyl)benzene (tib) and zinc(II) acetate.[27a] A perspective view of the zinc(II) center of compound **1** is shown in Fig. 1a with atom numbering scheme, where Zn1 sits on the inversion threefold axis and the Cl1 and O1 atoms lie on the threefold axis. Each zinc(II) atom is coordinated by six N atoms of imidazole groups derived from six different L ligands. The coordination geometry of the Zn(II) center is octahedral with coordination angles (N–Zn–N) ranging between 89.58(9) to 180° and the Zn–N bond length of 2.186(5) Å (Table 2). The Zn–N distance is slightly longer than those of other reported zinc complexes,[31–33] to which the stereo hindrance of the six imidazole groups may contribute a great deal. For example, Zn–N bond lengths are 2.007(4), 2.012(4) and 1.993(4) Å in

Table 2 Selected bond distances (Å) and angles (°) for **1**, **2** and **3**[a]

$[Zn(L)_2](ClO_4)_2$ **1**			
Zn1–N12	2.186(5)	N12–Zn1–N12#1	89.58(9)
N12–Zn1–N12#2	90.42(9)	N12–Zn1–N12#3	180
$[Mn(L)_2](SO_4)\cdot 16H_2O$ **2**			
Mn1–N12	2.258(4)	Mn1–N32	2.293(3)
Mn1–N52	2.266(3)	N52–Mn1–N32	87.42(12).
N12–Mn1–N32	88.14(12)	N12–Mn1–N52	92.98(12)
N12–Mn1–N12#4	180	N52–Mn1–N52#4	180
N32–Mn1–N32#4	180	N12–Mn1–N52#4	87.02(12)
N12–Mn1–N32#4	91.86(12)	N52–Mn1–N32#4	92.58(12)
$[Cd_3(L)_2(SO_4)_4(H_2O)_2(CH_3CH_2OH)_2][Cd(H_2O)_6]\cdot 2H_2O$ **3**			
Cd1–N12	2.237(4)	Cd1–O11	2.337(4)
Cd1–O101	2.402(4)	Cd2–N32	2.217(4)
Cd2–O12	2.395(7)	Cd2–N52	2.233(4)
Cd2–O102	2.441(8)	Cd2–O21	2.244(9)
Cd2–O22#5	2.503(8)	Cd3–O32	2.304(3)
Cd3–O33	2.305(16)	Cd3–O31	2.318(15)
N12–Cd1–O11	88.83(15)	N12–Cd1–N12#6	180
N12–Cd1–O11#6	91.17(15)	N12–Cd1–O11#6	91.17(15)
O11–Cd1–O11#6	180	N12–Cd1–O101#6	95.02(15)
O11–Cd1–O101#6	89.42(16)	N12–Cd1–O101#6	95.02(15)
O11–Cd1–O101#6	89.42(16)	O101–Cd1–O101#6	180
N12–Cd1–O101	84.98(15)	O11–Cd1–O101	90.58(16)
N32–Cd2–N52	177.7(2)	N32–Cd2–O21	82.3(3)
N52–Cd2–O21	95.4(3)	N32–Cd2–O12	100.0(2)
N52–Cd2–O12	82.3(2)	O21–Cd2–O12	160.0(5)
N32–Cd2–O102	90.9(2)	N52–Cd2–O102	89.1(3)
O21–Cd2–O102	80.2(4)	O12–Cd2–O102	80.0(3)
N32–Cd2–O22#7	78.6(2)	N52–Cd2–O22#7	102.3(2)
O21–Cd2–O22#7	120.4(5)	O12–Cd2–O22#7	79.3(2)
O102–Cd2–O22#7	154.6(3)	O33–Cd3–O31	87.0(5)
O32–Cd3–O33	96.8(7)	O32–Cd3–O31	87.0(5)
O32–Cd3–O32#8	180	O32–Cd3–O33#8	83.2(7)
O33–Cd3–O33#8	180	O32–Cd3–O31#8	93.0(5)
O33–Cd3–O31#8	93.0(5)	O31–Cd3–O31#8	180

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-z, -x, -y$; (#2) z, x, y; (#3) $-x, -y, -z$; (#4) $-x+2, -y, -z+1$; (#5) $-x, -y+1, -z$; (#6) $-x+1, -y, -z+1$; (#7) $-x, -y+1, -z$; (#8) $-x+1, -y+1, -z+1$.

Table 3 Hydrogen bonds data for complexes **1**, **2** and **3**

D–H ··· A	Distance of D ··· A/Å	Angle of D–H–A/°
$[Zn(L)_2](ClO_4)_2$ **1**		
C21–H ··· O2[a]	3.384(5)	163
$[Mn(L)_2](SO_4)\cdot 16H_2O$ **2**		
C32–H4 ··· O2[b]	3.230(5)	143
C52–H7 ··· O2	3.133(5)	159
C12–H1 ··· O2	3.421(5)	163
C51–H20 ··· O7	3.389(5)	138
O4–H25 ··· O5	2.782(5)	145
O5–H26 ··· O3	2.790(5)	162
O5–H27 ··· O6	2.829(5)	145
O6–H28 ··· O9[c]	2.893(6)	174
O8–H30 ··· O4	2.907(4)	170
O8–H31 ··· O1[c]	2.933(5)	178
O10–H32 ··· O8[d]	2.905(5)	164
O10–H33 ··· O5[d]	2.860(5)	117
$[Cd_3(L)_2(SO_4)_4(H_2O)_2(CH_3CH_2OH)_2][Cd(H_2O)_6]\cdot 2H_2O$ **3**		
O102–H25 ··· O41[e]	3.005(15)	151
C12–H1 ··· O14	3.279(6)	168
C32–H4 ··· O14	3.195(7)	145
C34–H6 ··· O32[f]	3.459(6)	168
C31–H13 ··· O101[f]	3.354(8)	134
C54–H9 ··· O(23)[g]	3.20(2)	147
C21–H18 ··· O101[f]	3.330(8)	144

Equivalent atoms generated by [a] $-x, 1-y, z$; [b] $2-x, -y, 1-z$; [c] $1+x, y, z$; [d] $-1+x, y, z$; [e] $-1+x, y, -1+z$; [f] $x, y, -1+z$; [g] $x, y, 1+z$.

complex $[ZnL'_{1.5}(H_2O)(SO_4)]\cdot 6H_2O$ [L′ = 1,1′-(1,4-butanediyl)-bis(imidazole)].[31] Each L connects three zinc(II) atoms, which form an equilateral triangle with a edge length (Zn ··· Zn separation) of 10.66 Å. Such coordination mode makes the compound a 2D network with honeycomb structure as shown in Fig. 1b, and a schematic drawing is shown in Fig. 1c. It is clear that all L ligands in the network have *cis*, *cis*, *cis* conformation with up- and down-orientations (see Scheme 1) alternatively. The distance between the two benzene ring planes of up- and down-orientations is 8.40 Å.

The packing diagram of complex **1** is illustrated in Fig. 1d. The perchlorate anions are located in the voids formed between two adjacent cationic layers, held there by one C–H ··· O hydrogen bond as tabulated in Table 3. In addition, benzene rings in one layer π-stacks face-to-face with those neighboring in the adjacent layer with a centroid-centroid distance of 3.71 Å.

Crystal structure of 2

The coordination environment around the manganese(II) center in complex **2** is shown in Fig. 2a, where the metal sits on the crystallographic inversion center and the S atom of the sulfate anion has crystallographically imposed 2-fold symmetry. Similar to **1**, Each manganese atom in **2** is coordinated by six imidazole nitrogen atoms from different L ligands. However, the complex **2** crystallized in monoclinic *C*2/*c* space group rather than rhombohedral $R\bar{3}$ space group as **1**. The local coordination environment around Mn(II) can be regarded as a slightly distorted octahedron with Mn–N bond distances ranging from 2.258(4) to 2.293(3) Å and N–Mn–N bond angles varying from 87.02(12) to 180° (Table 2), which are similar to those of other reported manganese(II) complexes.[34,35] An infinite 2D network structure based on honeycomb motifs is also formed in which the Mn(II) atoms serve as nodes (Fig. 2b). All the Mn atoms in the cationic layer are in one plane and the Mn ··· Mn distance of 11.80 Å is longer than the Zn ··· Zn separation of 10.66 Å in **1**. The distance of 8.90 Å between the two benzene ring planes with up- and down-orientations in **2** is also longer than the corresponding distance (8.40 Å) in **1**.

Similar crystal packing was found for **1** and **2** and a centroid-centroid distance of 3.55 Å between benzene rings of two adjacent layers indicates the presence of face-to-face π–π interactions in **2**. This framework creates open channels within each sheet as shown in Fig. 2c, which are filled with the lattice water molecules. Sulfate anions are located in the voids between two adjacent cationic layers and held there by three C–H ··· O (sulfate) hydrogen bonds (Fig. 2c and Table 3). The water molecules and sulfate anions are connected by hydrogen bonds crossed the channels and voids (Fig. S1 †).

Overall, it is similar for complexes **1** and **2** concerning the coordination mode and network structure. However, it is obvious that there are differences between these two complexes. First, they crystallize in different crystal systems as mentioned above, which was considered to be caused by different counter-ions of **1** and **2** since we found that $[Mn(L)_2](ClO_4)_2$ also has a $R\bar{3}$ space group ($a = b = c = 13.77$ Å, $\alpha = \beta = \gamma = 45.31°$) as same as **1**. Another important difference between **1** and **2** is the conformation of imidazole groups of L ligand. As exhibited in Fig. 1b and 2b, the dihedral angles between two of three imidazole groups of L ligand are from 60.6 to 67.9°, and the dihedral angles between each imidazole group and central benzene ring are 101.6, 80.6, 78.1°, respectively, in complex **2**. While in the case of complex **1**, three imidazole groups are essentially perpendicular each other with dihedral angle of 80.3°, and the dihedral angle between the imidazole group and central benzene ring is 62.0°. Such conformational difference determined the volume of open channel formed in each 2D honeycomb sheet in complex **1** or **2**, and therefore, the channels are occupied by water molecules in complex **2** and empty in complex **1** (Fig. 1d and 2c).

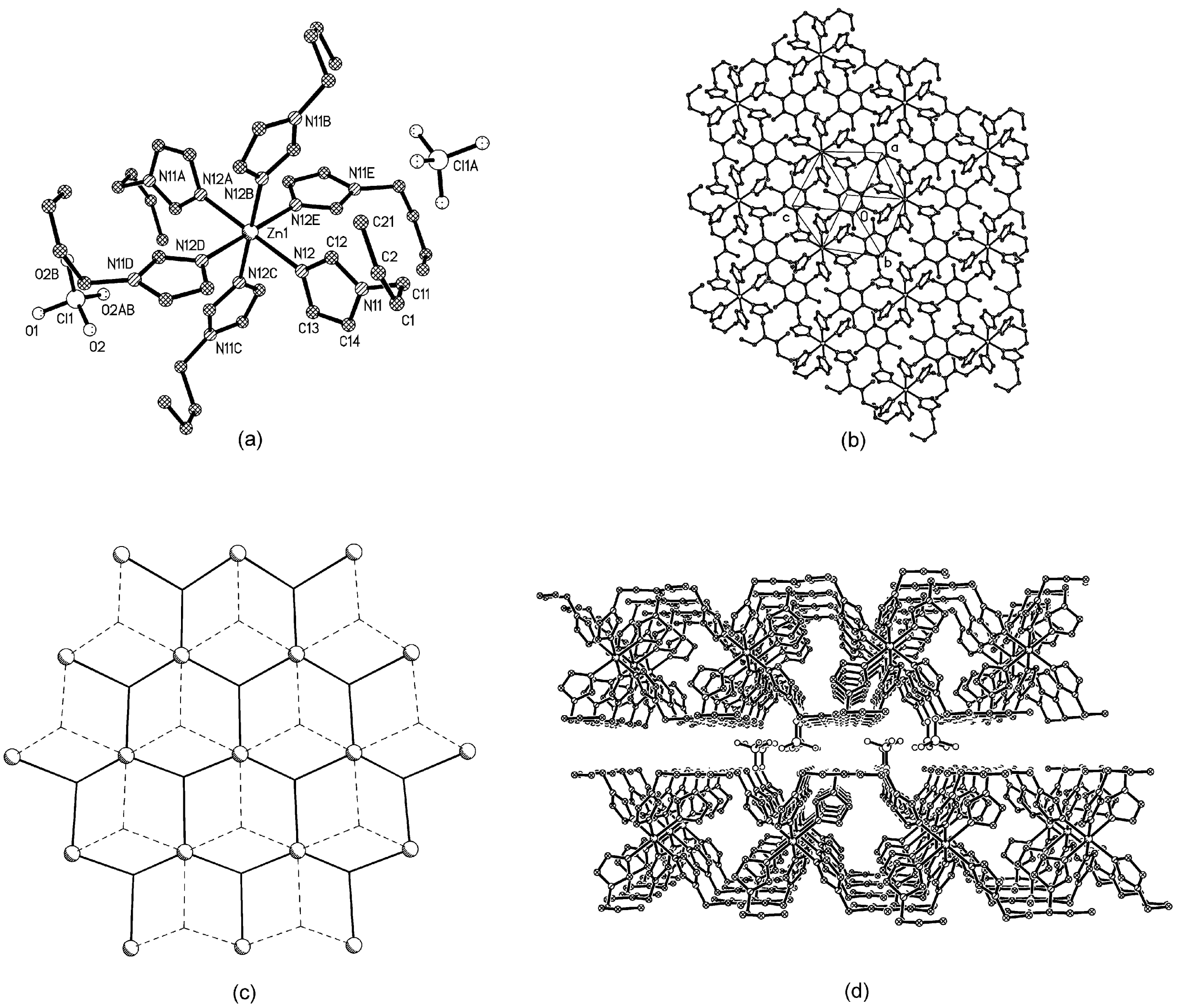


Fig. 1 (a) An ORTEP drawing of the local coordination of Zn in complex **1** with atom numbering scheme. (b) View of the 2D cationic layer with the honeycomb network. (c) Schematic drawing of 2D honeycomb network in which the L units are represented by three spokes radiating from a point and Zn centers by circles. The solid and dashed lines refer to L units above and below the plane formed by zinc atoms. (d) Crystal packing diagram for **1** with voids formed between two adjacent layers.

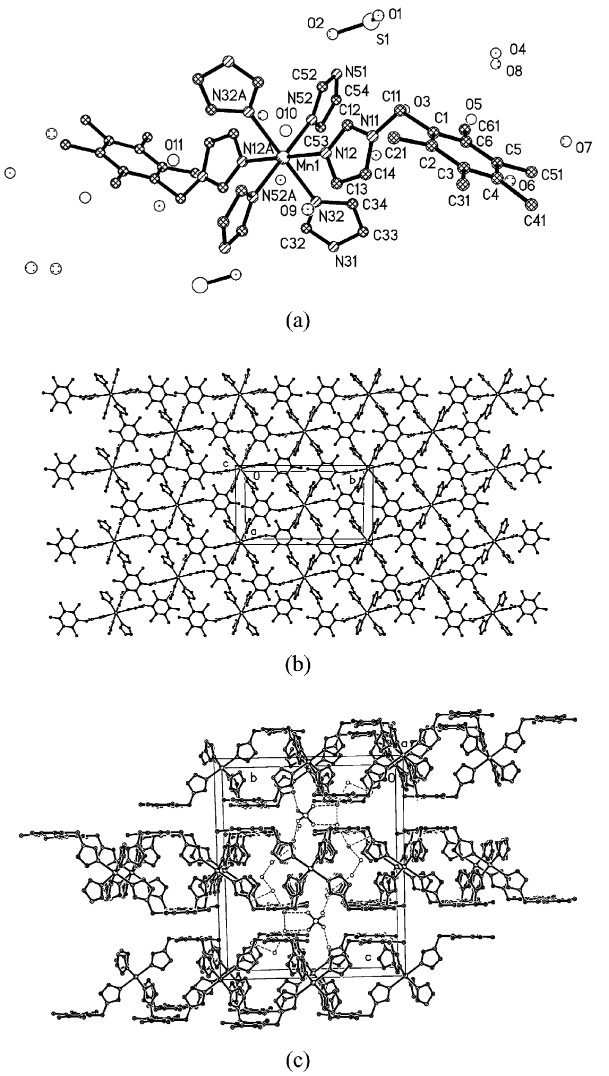
The 2D infinite network structures based on the honeycomb motif in complexes **1** and **2** are, to best of our knowledge, unprecedented. In the reported 2D polymers with honeycomb structures, rigid tripodal ligands, *e.g.*, 1,3,5-tricyanobenzene or benzene-1,3,5-tricarboxylate, enclosing an angle of 120° were used to link the linear metal centers.[12,14] In our case, the flexible L ligand with *cis*, *cis*, *cis* conformation linked three six-coordinated metal centers may direct the formation of the 2D honeycomb network.

Crystal structure of 3

The structure of **3** is drastically different from that of **1** and **2**, although the cadmium(II) is usually also six-coordinate as zinc(II) and manganese(II), and **3** is prepared under the similar conditions as **1**. The asymmetric unit of **3** contains three distinct Cd centers, in which Cd1 and Cd3 lie on inversion centers (Fig. 3a). In addition to two molecules of L ligand, there are four sulfate anions, two water molecules and two ethanol molecules coordinated to three Cd ions to give a $[Cd_3(L)_2(SO_4)_4(H_2O)_2(CH_3CH_2OH)_2]^{2-}$ anion. Neglecting the interactions with the sulfates, each Cd1 and Cd2 is coordinated by two N atoms from two different L ligands with a trans angle of 180 (N12–Cd1–N12A) and 177.7(2)° (N32–Cd2–N52), respectively. Each L ligand in turn connects three cadmium atoms. It is noteworthy that the conformation of L in **3** is *cis*, *trans*, *trans* while that in **1** and **2** is *cis*, *cis*, *cis*. Such coordination mode and conformation of L ligand make the complex **3** an independent 1D stepwise chain as shown in Fig. 3b. These 1D chains were further linked by sulfate S2 bridges to generate a 2D network structure and the intra-chain Cd1 and Cd2 atoms are bridged by sulfate S1 (Fig. 3c). The distances between Cd1 and Cd2, and Cd2 and Cd2F are 6.19, and 4.51 Å, respectively.

The Cd1 center has a slightly distorted octahedral coordination geometry with bond angles ranging from 84.98(15) to 180° (Table 2). The Cd1 atom is coordinated by two imidazole N atoms from two different L ligands, two ethanol O atoms and two μ_2-bridged sulfate groups (Fig. 3c). There are two positions and two alternative coordination modes of Cd2. The major component (70% partial occupancy) shows six-coordination and is coordinated by two imidazole N atoms from L, three μ_2-bridged sulfate ions and one water molecule (Fig. 3c). While in the minor component (30% partial occupancy), the Cd2B is bound by two imidazole N atoms, one μ_2-bridged sulfate S1, and three O atom from sulfate S2 and has no bond to water molecule. The sulfate S1 coordinates to Cd1 and Cd2B in a monodentate manner and sulfate S2 coordinates to Cd2A and Cd2B in bidentate and μ-O bridging manner (see Fig. S2).

The Cd3 center binds to six water molecules to form a $[Cd(H_2O)_6]^{2+}$ cation (Fig. 3d) with Cd3–O distances of 2.304(3)–2.318(15) Å, which are comparable to those in related compounds.[36] The coordination geometry of Cd3 is also a slightly distorted octahedron with bond angles ranging from 83.2(7) to 180°. The $[Cd(H_2O)_6]^{2+}$ cations are located between



(a)

(b)

(c)

Fig. 2 (a) The coordination environment of Mn(II) in the complex **2** with atom numbering scheme and hydrogen atoms were omitted for clarity. (b) 2D honeycomb network of **2**. (c) Crystal packing diagram for **2** on *bc* plane with voids formed between two adjacent layers.

the adjacent 2D stepwise layers by hydrogen bonds (Table 3 and Fig. 3d). The 2D stepwise layers are linked through the C–H---O and O–H---O hydrogen bonding interactions to form a 3D structure.

Properties

The polymeric complexes **1** and **3** are insoluble in water and common organic solvents such as methanol, ethanol, acetonitrile, DMF, *etc.* Whereas the **2** has definite solubility in methanol, DMF and almost insoluble in water. In order to investigate the ion exchange property,[26] powder sample of **2** was suspended in an aqueous solution of $NaClO_4$ with stirring for one day at room temperature to allow anion exchange, then filtrated, washed with water and dried in vacuum to give a colorless powder. This procedure was repeated at least three times. The FT-IR spectrum (Fig. S3 †) of exchanged product showed characteristic bands at 1088 and 1109 cm^{-1} which are different from those of the original **2** (at 1087, 1114 and 1132 cm^{-1}), but almost same to those of above mentioned $[Mn(L)_2](ClO_4)_2$ (at 1086 and 1108 cm^{-1}). The results indicate that the anions of sulfate in the voids of network **2** can be exchanged by anions of perchlorate.

The good response of the manganese(II) $^4T_1(^4G)$ state to the change of ligand field strength, symmetry and the high sensitivity of luminescence techniques make the Mn^{2+} $[^4T_1(^4G) \longrightarrow {}^6A_1]$ emission attractive as a diagnostic tool for coordination characteristics of Mn(II).[37] However, Mn(II) complexes may emit photoluminescence at low temperature and their luminescent properties at room temperature are rarely reported.[34,38] The complex **2** in the methanol and DMF solution (1 : 1) shows photoluminescence with strong emission maxima at 381 and 398 nm and a weak one at 365 nm upon excitation at 344 nm (Fig. S4).

Conclusion

In summary, the present study provides evidence that the flexible tripodal ligands are useful for construction of novel coordination networks with metal salts. The flexible tripodal ligand 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (L) is capable of coordinating to metal centers with imidazolyl nitrogen atoms to result in novel 2D polymers with honeycomb and stepwise network structures. The L ligand in **1** or **2** is in the *cis*, *cis*, *cis* conformation while in **3** it is in the *cis*, *trans*, *trans* conformation. The combination of the *cis*, *cis*, *cis* conformation and potential of forming π–π interactions between the benzene rings of L units result in the layered structure. In complex **3**, the 2D stepwise structure is probably due to the *cis*, *trans*, *trans* conformation of L ligand. Furthermore the behaviors of sulfate anion in complexes **2** and **3** are different. The sulfate anions serve as bridging ligand in **3** and does not participate the coordination to metal atoms in **2**.

Acknowledgements

This work was supported by National Natural Science Foundation of China.

References

1 D. L. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975.
2 A. J. Blake, N. R. Brooks, N. R. Champness, M. Crew, L. R. Hanton, P. Hubberstey, S. Parsons and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1999, 2813.
3 M. Munakata, L. P. Wu and T. Kuroda-sowa, *Adv. Inorg. Chem.*, 1998, **46**, 173.
4 J. M. Jehn, *Pure Appl. Chem.*, 1994, **66**, 1961.
5 J. W. MacDonald and G. M. Whitesides, *Chem. Rev.*, 1994, **94**, 2383.
6 *Transitional Metals in Supramolecular Chemistry*, ed. L. Fabbrizzi and A. Poggi, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1994.
7 S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460.
8 A. J. Blake, N. R. Champness, S. S. M. Chung, W. S. Li and M. Schröder, *Chem. Commun.*, 1997, 1005.
9 L. R. MacGillivray, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1994, 1325.
10 B. F. Hoskins, R. Robson and D. A. Slizys, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2752.
11 M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 7287.
12 G. B. Gardner, D. Venkataraman, J. S. Moore and S. Lee, *Nature*, 1995, **374**, 792.
13 (*a*) K. Biradha and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1998, **120**, 6431; (*b*) C. Daiguebonne, Y. Gérault, O. Guillou, A. Lecerf, K. Boubekeur, P. Batail, M. Kahn and O. Kahn, *J. Alloy. Comp.*, 1998, **275–277**, 50.
14 H. J. Choi and M. P. Suh, *J. Am. Chem. Soc.*, 1998, **120**, 10622.
15 M. Mimura, T. Matsuo, Y. Motoda, N. Matsumoto, T. Nakashima and M. Kojima, *Chem. Lett.*, 1998, 691.
16 M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2327.
17 S. R. Batten, B. F. Hoskins and R. Robson, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 636.
18 S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.
19 O. M. Yaghi, H. Li and T. L. Groy, *J. Am. Chem. Soc.*, 1996, **118**, 9096.
20 D. M. L. Goodgame, D. A. Grachvogel and D. J. Williams, *Angew. Chem., Int. Ed.*, 1999, **38**, 153.
21 B. F. Abrahams, S. R. Batten, H. Hamit, B. F. Hoskins and R. Robson, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1690.
22 (*a*) M. Fujita, S. Nagao and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**,

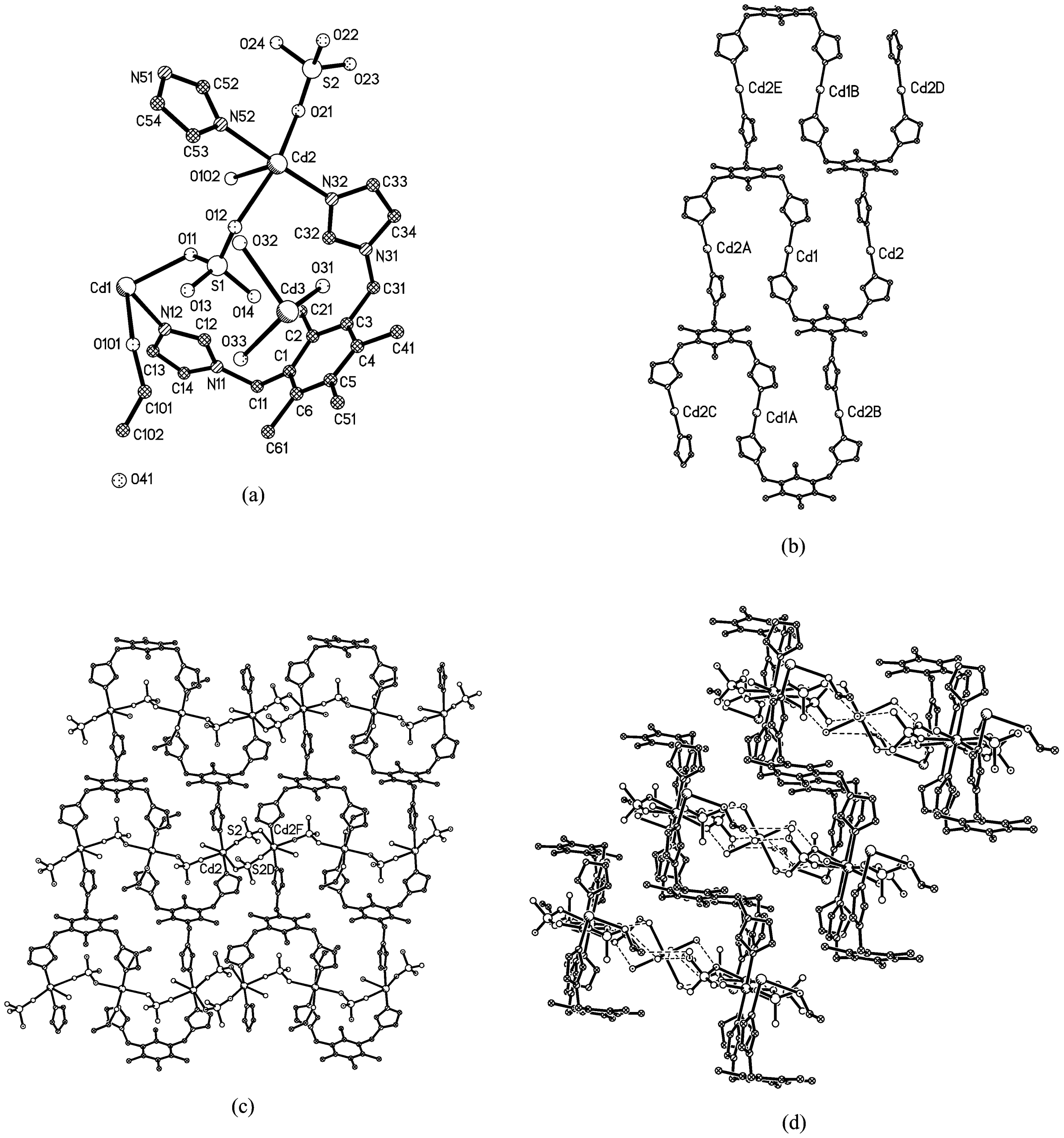


Fig. 3 (a) Coordination environments of three Cd centers in **3**. (b) A view of the stepwise 1D chain in which the sulfate anions were omitted for clarity. (c) 2D network formed by bridging of sulfate anions in complex **3**. (d) 3D structure of **3** linked by $[Cd(H_2O)_6]^{2+}$ cations through hydrogen bonds indicated by dashed lines.

1649; (*b*) N. Takeda, K. Umemoto, K. Yamaguchi and M. Fujita, *Nature*, 1999, **398**, 794.

23 (*a*) M. Kondo, M. Shimamura, S. Noro, S. Minakoshi, A. Asami, K. Seki and S. Kitagawa, *Chem. Mater.*, 2000, **12**, 1288; (*b*) M. Kondo, T. Okubo, A. Asami, S. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka and K. Seki, *Angew. Chem., Int. Ed.*, 1999, **38**, 140; (*c*) S. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem., Int. Ed.*, 2000, **39**, 2082.

24 M. Hong, Y. Zhao, W. Su, R. Cao, M. Fujita, Z. Zhou and A. S. C. Chan, *Angew. Chem., Int. Ed.*, 2000, **39**, 2468.

25 C. M. Hartshorn and P. J. Steel, *Chem. Commun.*, 1997, 541.

26 (*a*) W. Y. Sun, J. Fan, T.-a. Okamura, J. Xie, K. B. Yu and N. Ueyama, *Chem. Eur. J.*, 2001, **7**, 2557; (*b*) B. Sui, J. Fan, T.-a. Okamura, W. Y. Sun and N. Ueyama, *New J. Chem.*, 2001, **25**, 1379.

27 (*a*) H. K. Liu, W. Y. Sun, D. J. Ma, K. B. Yu and W. X. Tang, *Chem. Commun.*, 2000, 591; (*b*) H. K. Liu, W. Y. Sun, W. X. Tang, T. Yamamoto and N. Ueyama, *Inorg. Chem.*, 1999, **38**, 6313; (*c*) H. K. Liu, W. Y. Sun, H. L. Zhu, K. B. Yu and W. X. Tang, *Inorg. Chem. Acta*, 1999, **295**, 129.

28 SIR92: A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Cryst.*, 1994, **27**, 435.

29 DIRDIF94: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, The DIRFID-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.

30 teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation, 1999.

31 J. F. Ma, J. F. Liu, Y. Xing, H. Q. Jia and Y. H. Liu, *J. Chem. Soc., Dalton Trans.*, 2000, 2403.

32 R. W. Gable, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1990, 1677.

33 L. Carlucci, G. Ciani, D. M . Proserpio and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1997, 1801.

34 B. L. Fei, W. Y. Sun, Y. A. Zhang, K. B. Yu and W. X. Tang, *J. Chem. Soc., Dalton. Trans.*, 2000, 2345.

35 L. Ballester, I. Baxter, P. C. M. Duncan, D. M. L. Goodgame, D. A. Grachvogel and D. J. Williams, *Polyhedron*, 1998, **17**, 3613.

36 H. Ohtaki, M. Maeda and S. Ito, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2217.

37 H. O. N. Reid, I. A. Kahwa, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1999, 1565.

38 N. S. Fender, F. R. Fronczek, V. John, I. A. Kahwa and G. L. McPherson, *Inorg. Chem.*, 1997, **36**, 5539.