

# A novel chiral coordination polymer with a two-dimensional undulated (6,4)-network: $[\text{Co}_4(2,2'\text{-bipy})_4(\text{H}_2\text{O})_2(\text{btec})_2]_n$ (btec = 1,2,4,5-benzenetetracarboxylate)<sup>†</sup>

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The novel coordination polymer  $[\text{Co}_4(2,2'\text{-bipy})_4(\text{H}_2\text{O})_2(\text{btec})_2]_n$  (btec = 1,2,4,5-benzenetetracarboxylate), **1**, has been hydrothermally synthesized. X-Ray diffraction experiments reveal that **1** exhibits an interesting two-dimensional (2D) chiral undulated (6,4)-network, which represents the first example of a 2D chiral coordination polymer containing two kinds of organic ligands. The value of the Flack parameter,  $x = 0.52(2)$ , shows that the crystal of **1** is an inversion twin containing approximately 50% of the right-handed and 50% of the left-handed crystal structure and the whole compound is a racemate. Variable temperature magnetic susceptibility indicates that antiferromagnetic interactions exist between metallic Co(II) centers in **1**.

Low dimensional coordination polymers, generally including one-dimensional (1D) chainlike and two-dimensional (2D) layerlike structures, have received much attention owing to their interesting structural features and unique electro-conductive, non-linear optical and magnetic properties, which are different from those of three-dimensional (3D) coordination polymers.<sup>1–7</sup> One of the attractive challenges in this field is the creation of chiral coordination frameworks as such systems may be exploited for applications in chiral synthesis and catalysis, second-order nonlinear optics, and in the pharmaceutical and biomedical industries.<sup>8–17</sup> Several approaches were previously reported for creating chiral polymeric coordination frameworks, including the introduction of chiral or achiral building blocks.<sup>13–16</sup> Among them, the use of octahedral metal (such as  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ ) complexes coordinated with chelating ligands has been considered as a promising one since these complexes, unlike the square-planar Pt or Pd complexes, possess inherently chiral centers.<sup>8,9</sup> Therefore, no enantiotropic organic ligands are required during the self-assembly of chiral polymers. Based on this method, a series of chiral molecular box-type polymers have been prepared by several groups.<sup>8,9</sup> Piguet *et al.* have reviewed the preparation of 1D chiral polymeric helices.<sup>18</sup> Furthermore, some 3D chiral coordination polymers have also been reported.<sup>10–14</sup> However, 2D chiral coordination polymers have rarely been observed so far.<sup>17</sup>

Taking advantage of the above synthetic method and the hydrothermal technique,<sup>19–21</sup> we have attempted to prepare new 2D chiral coordination polymers with octahedral metal ions and two kinds of organic ligands containing chelating moieties, that is, 1,2,4,5-benzenetetracarboxylic acid ( $\text{H}_4\text{btec}$ ) and 2,2'-bipyridine (2,2'-bipy). Although the preparation of

chiral coordination polymers *via* the self-assembly of metal ions with only one organic ligand has been studied,<sup>17</sup> the hydrothermal synthesis of chiral coordination polymers with two different organic ligands has so far been unexplored. It is well known that multi-dentate aromatic carboxylates are good candidates for the construction of 3D open frameworks due to their multiple bridging moieties and versatile coordination modes with transitional metal ions.<sup>12,22</sup> On the contrary, the chelate ligand 2,2'-bipy usually inhibits the expansion of the polymeric framework by the “passivation” of metal sites *via* the N donors of the organic groups.<sup>2,6</sup> Therefore, the appropriate combination of two such organic ligands with inherently chiral octahedral metal complexes could provide various possibilities for the construction of chiral polymers with low dimensional structures *via* self-assembly. Here, we report the hydrothermal synthesis and crystal structure of the novel chiral coordination polymer  $[\text{Co}_4(2,2'\text{-bipy})_4(\text{H}_2\text{O})_2(\text{btec})_2]_n$  (btec = 1,2,4,5-benzenetetracarboxylate), **1**, which exhibits an interesting 2D undulated (6,4)-network. To our knowledge, **1** represents the first example of a 2D chiral coordination polymer containing two kinds of organic ligands.

## Experimental

### General methods

All chemicals purchased were of reagent grade and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Co was determined by a Leaman inductively coupled plasma (ICP) spectrometer. The FTIR spectrum was recorded in the range of 400–4000  $\text{cm}^{-1}$  on an Alpha Centaur FT/IR spectrophotometer using a KBr pellet. XPS analysis was performed on a VG ESCALAB MK II spectrometer with a Mg K $\alpha$  (1253.6 eV) achromatic X-ray source. The vacuum inside the

<sup>†</sup> Electronic supplementary information (ESI) available: packing diagram and XPS, IR and TG spectra of **1**. See <http://www.rsc.org/suppdata/nj/b2/b205718b/>

analysis chamber was maintained at  $6.2 \times 10^{-6}$  Pa during analysis. TG analysis was performed on a Perkin–Elmer TGA7 instrument in flowing  $N_2$  with a heating rate of  $10^\circ C\ min^{-1}$ . The variable temperature magnetic susceptibility was measured under 5000 Oe from 2 to 300 K (SQUID, Quantum Design).

### Hydrothermal synthesis

Compound **1** was synthesized from a reaction mixture of  $Co(OAc)_2 \cdot 4H_2O$  (0.5 mmol), 2,2'-bipy (0.5 mmol),  $H_4btec$  (0.25 mmol), NaOH (2 mmol) and  $H_2O$  (6 mL) in an 18 mL Teflon-lined autoclave under autogeneous pressure at  $180^\circ C$  for three days, followed by slow cooling ( $5^\circ C\ h^{-1}$ ) to room temperature. The product was washed with distilled water and air-dried at  $50^\circ C$ . The product was of high quality in the form of purple block crystals (yield: 90% based on Co). Elem. anal. found: C, 51.63; H, 2.81; N, 8.11; Co 16.96%; calcd. for  $C_{60}H_{40}Co_4N_8O_{18}$ : C, 51.59; H, 2.89; N, 8.02; Co, 16.88%. Selected FTIR data ( $cm^{-1}$ ): 1559(s), 1489(m), 1469(m), 1437(m), 1417(m), 1384(s), 1313(s), 1132(m), 1020(m), 940(w), 890(w), 855(m), 801(s), 763(s), 729(m), 655 (m), 587 (m), 540(s), 451 (s), 412 (s).

### X-Ray crystallographic determination

A purple crystal of **1** with dimensions of  $0.43 \times 0.38 \times 0.21$  mm was mounted inside a glass fiber capillary. Data were collected on a Rigaku R-Axis RAPID IP diffractometer with Mo-K $\alpha$  monochromated radiation ( $\lambda = 0.71073\ \text{\AA}$ ) at 293 K in the range of  $2.12 < \theta < 27.12^\circ$ . An empirical absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  with anisotropic displacement parameters for all non-hydrogen atoms.<sup>23</sup> Hydrogen atoms were located from a difference electron density map. The crystal data and structure refinement are summarized in Table 1. CCDC reference number 184022. See <http://www.rsc.org/suppdata/nj/b2/b205718b/> for crystallographic files in CIF or other electronic format.

## Results and discussion

### Description of the crystal structure

X-Ray diffraction experiments revealed that **1** crystallized in a chiral crystal structure in the orthorhombic space group  $C22_1$ . The fundamental unit is shown in Fig. 1. There is only one crystallographically unique Co center in the asymmetric

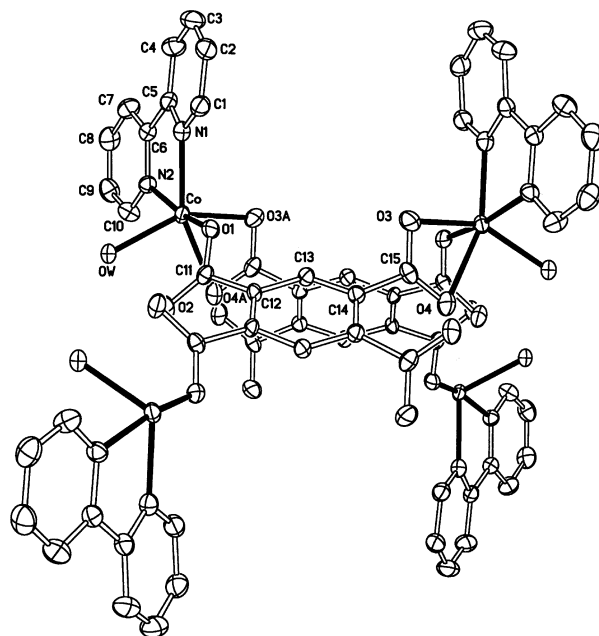
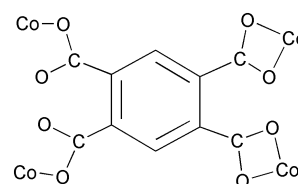


Fig. 1 ORTEP drawing of **1** showing the local coordination environment of Co(II) with thermal ellipsoids at 50% probability.

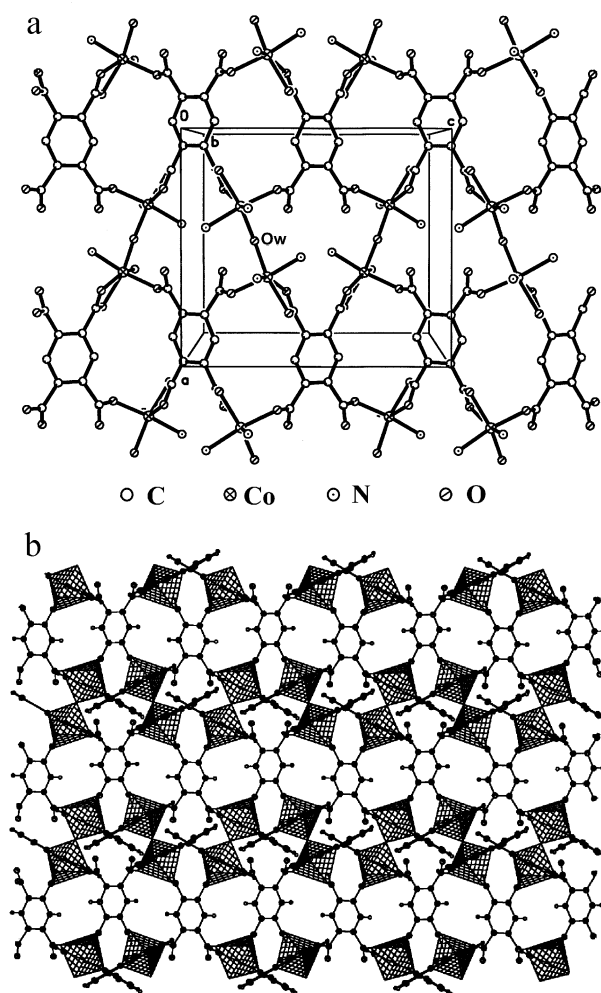
unit. The Co center coordinates to two nitrogen atoms of one 2,2'-bipy group, three oxygen atoms of two different carboxylate groups and one oxygen atom of a water molecule. Thus, all  $Co^{2+}$  centers display distorted octahedral coordination geometry. The four carboxylate groups of the btec ligand exhibit two kinds of coordination modes with the Co atoms, as shown in Scheme 1. That is, two of them adopt a *cis*-bidentate chelating mode, while the other two exhibit a monodentate bridging mode. Every two Co centers are linked by two bridging btec ligands to form a 1D ladder-like chain along the *a* axis. The adjacent ladder-like chains are connected together by sharing the water molecules coordinated to Co centers and exhibit a novel 2D (6,4)-network [as shown in Fig. 2(a)]. The water molecule (Ow) is located in a special position  $4b(0, y, 1/4)$  on a twofold axis with a Co–Ow bond length of  $2.148\ \text{\AA}$  and a Co–Ow–Co bond angle of  $120.7^\circ$ . The bond length and bond angle confirm that there exists an “aquo( $\mu$ - $H_2O$ )” bridge between the Co(II) centers.<sup>24</sup> To our knowledge, coordinated water molecules acting as bridging units, as in this case, have rarely been observed in coordination polymers.<sup>25</sup> The square 4-member ring is constructed by two Co centers and two btec ligands and the triangular 6-member ring contains four Co ions and two btec moieties, which are distributed alternately on the layer [as shown in Fig. 2(b)]. It is also noteworthy that the 2D undulated network of **1** is not a smooth plane but essentially an undulated layer as shown in Fig. 3. The dihedral angle between two aromatic ring planes of the btec ligands is *ca.*  $105.9^\circ$ . The most attractive structural feature of **1** is that the 2D undulated network possesses chirality. In the wavelike layer, there exists  $2_1$  helices that run through the aromatic ring planes of the btec units along the *c* axis and are parallel to each other. Furthermore, all the parallel helices lie along the same direction and exhibit the same



Scheme 1 The two coordination modes of btec ligands.

Table 1 Crystal data and structure refinement of **1**

Molecular formula	$C_{60}H_{40}Co_4N_8O_{18}$
<i>M</i>	1396.72
<i>T</i> /K	293(2)
$\lambda$ /Å	0.71073
Space group	Orthorhombic
Crystal system	$C22_1$
<i>a</i> /Å	10.976(2)
<i>b</i> /Å	19.178(4)
<i>c</i> /Å	12.415(3)
<i>U</i> /Å <sup>3</sup>	2613.2(9)
<i>Z</i>	2
$\mu$ /mm <sup>−1</sup>	1.339
Reflections collected	8208
Independent reflections	2861
$R_1$ [ $I \geq 2\sigma(I)$ ]	0.0472
$wR_2$ [ $I \geq 2\sigma(I)$ ]	0.1191
$R_1$ (all data)	0.0501
$wR_2$ (all data)	0.1207

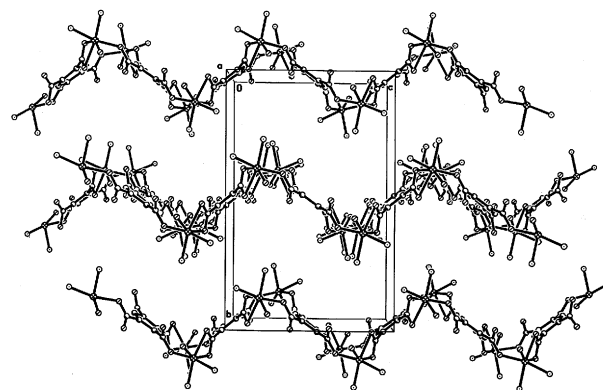


**Fig. 2** (a) The 2D (6,4)-network structure of **1** along the *b* axis; the carbon atoms of 2,2'-bipy and hydrogen atoms are omitted for clarity. (b) The polyhedron representation of the 2D layer of **1** along the *b* axis. Octahedra represent the octahedral Co(II) centers.

chirality. Therefore, the structure of **1** has overall chirality.<sup>14</sup> Fig. 4 illustrates this structural feature. According to the value of the Flack parameter,<sup>26</sup>  $x = 0.52(2)$ , the crystal of **1** is an inversion twin containing approximately 50% of the right-handed and 50% of the left-handed crystal structures. The whole compound is a racemate.

In the packing arrangement of **1** [Fig. S1, see Electronic supplementary information (ESI)], the adjacent 2D undulated layers are parallel with each other and construct a 3D framework *via*  $\pi$ - $\pi$  interactions between aromatic groups of the 2,2'-bipy ligands, which project perpendicularly beyond the wavelike layer. Both pyridine moieties of the 2,2'-bipy are not coplanar (interplane angle =  $6.0^\circ$ ). The  $\pi$ - $\pi$  stacking interactions occur between the N1, C1, C2, C3, C4, C5 pyridine moieties through a twofold axis parallel to *b* and show an interplanar distance of 3.39 Å and an interplanar angle of  $3.94^\circ$ . The  $\pi$ - $\pi$  interactions enhance the stability of the compound and lead to a higher dimensional structure with unusual triangular tunnels parallel to the *a* axis. Because no extra guest H<sub>2</sub>O molecules exist in the structure, the whole compound exhibits an interesting hollow host scaffolding.

The valence sum calculations of the Co and O atoms are listed in Table 2. The bond valence calculations (Co, 1.82) suggest that all Co atoms are in the +2 oxidation state.<sup>27</sup> This result is also supported by the XPS measurement of the compound in the energy region of Co2p<sup>1/2</sup> and Co2p<sup>3/2</sup>. The XPS spectrum (as shown in Fig. S2, ESI) gives one peak at



**Fig. 3** The undulated network of **1** along the *a* axis; the carbon atoms of 2,2'-bipy and hydrogen atoms are omitted for clarity.

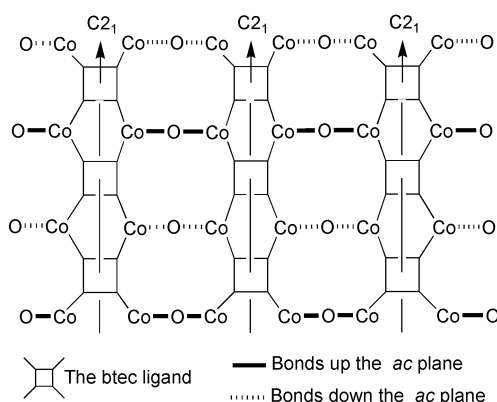
780.8 eV, attributable to Co<sup>2+</sup>.<sup>28</sup> The uncoordinated oxygen atom O(1) of the btec ligands and the bridging oxygen atom Ow have bond valence sums of 1.40 and 0.29, respectively. These values suggest that Ow is a coordinated water molecule, while O(1) is a deprotonated oxygen atom of the carboxylate group.<sup>25</sup> These results are consistent with the charge balance considerations and alkaline synthetic conditions used for compound **1**.

#### IR spectrum, thermal analysis and magnetic properties of compound **1**

The IR spectrum of compound **1** is shown in Fig. S3 (ESI) and the main absorption peaks are listed in Table 3. The absence of strong peaks around 1720 cm<sup>-1</sup> indicates that all carboxylic groups are deprotonated.<sup>29</sup> The values of  $\Delta\nu$  for **1** show that the carboxylate groups coordinate to the metal atoms in both monodentate (175 cm<sup>-1</sup>) and bidentate (52 cm<sup>-1</sup>) fashions,<sup>30</sup> which is consistent with the results of the X-ray analysis and valence sum calculations.

In the TG curve of compound **1** (see Fig. S4, ESI), there is only one weight loss of 78.11% in the temperature range 350–420 °C, corresponding to the concomitant release of coordinated water, btec and 2,2'-bipy ligands. The residue was CoO. The weight loss observed is in good agreement with the calculated value (78.54%).

The variable temperature magnetic susceptibility of **1** was measured from 2 to 300 K at 5000 Oe and are displayed in Fig. 5(a), plotted as the thermal variation of  $\chi_m$  and  $\chi_m T$ . The  $\chi_m T$  versus *T* plot shows a value of 10.32 emu K Oe<sup>-1</sup> mol<sup>-1</sup> at 300 K, and continuously decreases on cooling to a value of 2.13 emu K Oe<sup>-1</sup> mol<sup>-1</sup> at 2 K. The inverse susceptibility



**Fig. 4** Simplified schematic representation of the 2D chiral structure of **1** in the *ac* plane. The 2<sub>1</sub> helices are parallel with the *c* axis and run through the centers of the aromatic planes of the btec ligands.

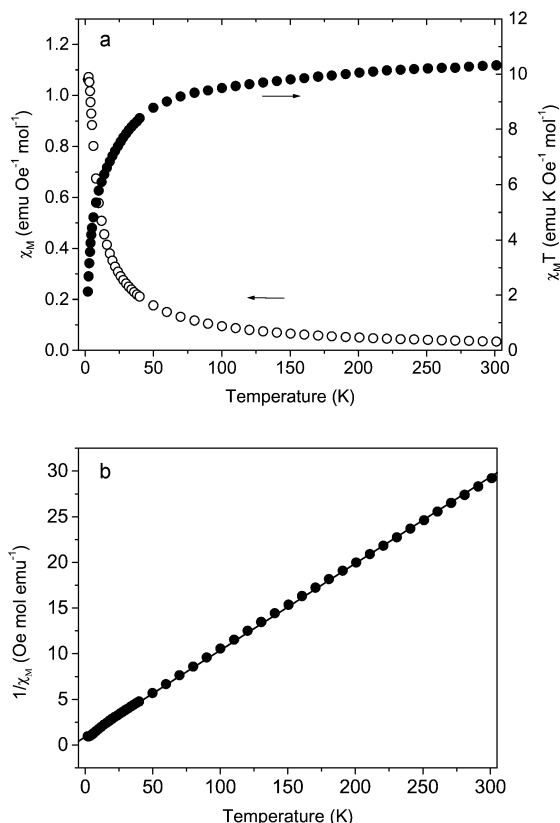
**Table 2** Valence sum calculations

Co–O(1)	2.009(3)	Co–O(3) <sup>a</sup>	2.087(3)
Co–N(1)	2.102(3)	Co–N(2)	2.105(3)
Co–Ow	2.1475(19)	Co–O(4) <sup>a</sup>	2.336(3)
$\sum S(\text{Co}) = 1.82$			
O(1)–C(11)	1.275(5)		
$\sum S[\text{O}(1)] = 1.40$			
Ow–Co	2.1475(19)		
$\sum S(\text{Ow}) = 0.29$			

<sup>a</sup>  $-x + 1$ ,  $y$ ,  $-z + 1/2$ .**Table 3** IR spectral data of compound **1**

Compound	$\nu_{\text{as}}(\text{COO})$	$\nu_{\text{s}}(\text{COO})$	$\Delta\nu^*$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{H}_2\text{O}}$
Na <sub>4</sub> betc	1515	1420	95			
<b>1</b>	1559	1384	175	451	412	3426
	1489	1437	52			

plot as a function of temperature [Fig. 5(b)] is linear, closely following the Curie–Weiss law with  $C = 10.54 \text{ emu K Oe}^{-1} \text{ mol}^{-1}$ , corresponding to about one  $S = 3/2$  spin per formula unit with  $g = 2.37$  for Co(II) centers. The effective magnetic moment per metal atom at 300 K,  $4.608 \mu_{\text{B}}$ , is in the range of experimentally observed values for high spin Co(II) ions. The Weiss temperature  $\theta = -9.39 \text{ K}$ , indicated that there exists predominantly antiferromagnetic interactions between metallic Co(II) centers. The magnetic behavior of compound **1** is different from that of related Co(II) coordination polymers containing carboxylate and hydroxyl ligands, which usually exhibit both antiferromagnetic interactions and weak ferromagnetic interactions.<sup>31,32</sup>

**Fig. 5** (a) Thermal variation of  $\chi_{\text{m}}$  and  $\chi_{\text{m}}T$  for compound **1**. (b) Thermal variation of  $\chi_{\text{m}}^{-1}$  for compound **1**.

## Conclusion

The successful preparation of **1** not only proves the utility of hydrothermal reactions in isolating novel organic-inorganic hybrid materials, but also further confirms that such coordination polymers can be designed and synthesized according to the inherent stereo and interactive information stored in the metal ions and organic ligands.<sup>22a</sup> Further research is on-going to prepare novel chiral polymeric frameworks and explore their valuable properties.

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## References

- 1 C. T. Chen and K. S. Suslick, *Coord. Chem. Rev.*, 1993, **128**, 293.
- 2 X. M. Zhang, M. L. Tong and X. M. Chen, *Angew. Chem., Int. Ed.*, 2002, **41**, 1029.
- 3 A. Caneschi, D. Gatteschi, N. Lalioti, C. Angregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini and M. A. Navak, *Angew. Chem., Int. Ed.*, 2001, **40**, 1760.
- 4 X. H. Bu, W. Chen, S. L. Lu, R. H. Zhang, D. Z. Liao, W. M. Bu, M. Shionoya, F. Brisse and J. Ribas, *Angew. Chem., Int. Ed.*, 2001, **40**, 3201.
- 5 A. Kamiyama, T. Noguchi, T. Kajiwarra and T. Ito, *Angew. Chem., Int. Ed.*, 2000, **39**, 3130.
- 6 Y. G. Li, E. B. Wang, H. Zhang, G. L. Luan and C. W. Hu, *J. Solid State Chem.*, 2002, **163**, 10.
- 7 (a) W. S. You, E. B. Wang and L. Xu, *Acta Crystallogr., Sect. C*, 2000, **56**, 289; (b) L. Xu, E. B. Wang, C. W. Hu and R. D. Huang, *Transition Met. Chem.*, 2001, **26**, 563.
- 8 X. H. Bu, H. Morishita, K. Tanaka, K. Biradha, S. Furusho and M. Shionoya, *Chem. Commun.*, 2000, 971.
- 9 Y. S. Zhang, S. N. Wang, G. D. Enright and S. R. Breeze, *J. Am. Chem. Soc.*, 1998, **120**, 9398 and references therein.
- 10 L. Carlucci, G. Ciani, P. Macchi and D. M. Proserpio, *Chem. Commun.*, 1998, 1837.
- 11 L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *Chem. Commun.*, 2000, 1319.
- 12 C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.*, 1998, 31.
- 13 R. G. Yiong, J. L. Zuo, X. Z. You, B. F. Abrahams, Z. P. Bai, C. M. Che and H. K. Fun, *Chem. Commun.*, 2000, 2061.
- 14 A. J. Blake, N. R. Champness, P. A. Cooke and J. E. B. Nicolson, *Chem. Commun.*, 2000, 665 and references therein.
- 15 Z. F. Chen, J. Zhang, R. G. Xiong and X. Z. You, *Inorg. Chem. Commun.*, 2000, **3**, 493.
- 16 P. Stang, B. Olenyuk, D. C. Muddiman and R. D. Smith, *Organometallics*, 1997, **16**, 3094.
- 17 W. B. Lin, O. R. Evans, R. G. Xiong and Z. Y. Wang, *J. Am. Chem. Soc.*, 1998, **120**, 13272.
- 18 C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005.
- 19 L. Xu, Y. Q. Sun, E. B. Wang, E. H. Shen, Z. R. Liu, C. W. Hu, Y. Xing, Y. H. Lin and H. Q. Jia, *New J. Chem.*, 1999, **23**, 1041.
- 20 P. J. Hargman and J. Zubietta, *Inorg. Chem.*, 2000, **39**, 3252.
- 21 S. H. Feng and R. R. Xu, *Acc. Chem. Res.*, 2001, **34**, 239.
- 22 (a) R. Cao, D. F. Sun, Y. C. Liang, M. C. Hong, K. Tatsumi and Q. Shi, *Inorg. Chem.*, 2002, **41**, 2087 and references therein; (b) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and L. D. Williams, *Science*, 1999, **283**, 1148.
- 23 (a) G. M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997; (b) G. M. Sheldrick, SHELXS97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.
- 24 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Waaston and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1–S83.
- 25 R. K. Chiang, C. C. Huang and C. S. Wur, *Inorg. Chem.*, 2001, **40**, 3237.
- 26 (a) H. D. Flack and G. Bernardinelli, *Acta Crystallogr., Sect. A*, 1999, **55**, 909; (b) H. D. Flack and G. Bernardinelli, *J. Appl. Crystallogr.*, 2000, **33**, 1143.
- 27 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244.

- 28 T. J. Chuang, C. R. Brundle and D. W. Rice, *Surf. Sci.*, 1976, **59**, 413.
- 29 Q. Shi, R. Cao, D. F. Sun, M. C. Hong and Y. C. Liang, *Polyhedron*, 2001, **20**, 3287.
- 30 (a) Y. Y. Wang, Q. Shi, Q. Z. Shi, Y. C. Gao and Z. Y. Zhou, *Polyhedron*, 1999, **18**, 2009; (b) W. Brzyska and J. Kowalewicz, *Zesz. Nauk. Politech. Slask. Chem.*, 1981, **677**, 141.
- 31 (a) C. Livage, C. Egger, M. Nogus and G. Férey, *J. Mater. Chem.*, 1998, **8**, 2743; (b) C. Livage, C. Egger and G. Férey, *Chem. Mater.*, 1999, **11**, 1546; (c) R. K. Chiang, C. C. Huang and C. S. Wur, *Inorg. Chem.*, 2001, **40**, 3237.
- 32 C. W. Hu, L. Xu and E. B. Wang, *Chin. Sci. Bull.*, 1998, **43**, 1234.