Fabrication of supramolecular frameworks by tuning the binding site of a tripodal ligand with d^{10} metal ions: Interplay of covalent and non-covalent interactions in solid-state structure

DEBAJYOTI GHOSHAL[a] and TAPAS KUMAR MAJI[b,]*

[a]Department of Chemistry, Jadavpur University, Jadavpur, Kolkata 700 032
[b]Molecular Materials Laboratory, Chemistry and Physics of Materials Unit,
Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064
e-mail: tmaji@jncasr.ac.in

Abstract. Two new coordination polymers of Zn(II) and Cd(II) have been synthesized using 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt), where it acts as a bi-bridging ligand. The compounds are characterized by IR spectroscopy, elemental analysis and single crystal X-ray diffraction studies. Compound $[Zn(tpt)(NO_3)_2(H_2O)_2]_n$ (**1**) and $[Cd(tpt)(NO_3)_2(H_2O)_2]_n$ (**2**) are isomorphous and show 1D coordination structure with almost octahedral metal center, which is extended to supramolecular 3D structure by cooperative weak interactions, like H-bonding, π–π and C–H…O interactions. Both the compounds reveal interplay of covalent and non-covalent interactions for fabricating supramolecular solid-state architecture.

Keywords. Zn(II)-complex; Cd(II)-complex; tpt bridge; H-bonding; supramolecular frameworks.

1. Introduction

In recent years there are incredible efforts in the field of designing metal–organic frameworks by covalent and non-covalent interactions,[1–6] which show not only magnificent structure but also exhibit brilliant functionalities like gas storage,[7,8] separation,[9,10] ion exchange[11,12] and heterogeneous catalysis.[13,14] The continuing challenge in this field is to tune the cooperative covalent and non-covalent interactions for designing the desired structure.[15–18] There are already established tool to control the covalent interactions;[1–5,7–12] one can modulate the ligand, can change the metal ion or even the counter anion. However, non-covalent forces like H-bonding and π–π interactions are important for the construction of solid-state architecture along with the directional covalent forces.[6,19–22] Due to the low energy association of such weak forces, which are less directional but cooperative. That is the beauty of the observation for experimentalist, which can help to attribute the whereabouts of weak interactions. Design and synthesis of metal-organic frameworks

of Zn(II) and Cd(II) are important due to their functionalities in molecular motors, bio-mimicking models, optoelectronic devices, catalytic activity and as anion exchanger.[23–26] The advantage of using these d^{10} systems as a node in such designed synthesis lies in their flexibility in co-ordination geometry.[24,25] Among the bridging ligands 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt) has been used efficiently to exploit its tridentate nature to design different type of coordination frameworks.[27–30] But in this present work, we used judicially the tpt ligand to the same ratio of metals so that it can bind only two metal to from 1 : 1 complex (scheme 1). This precedes us to observe the formation of the sinusoidal[31] 1D chains where no other secondary bridging ligand is present.
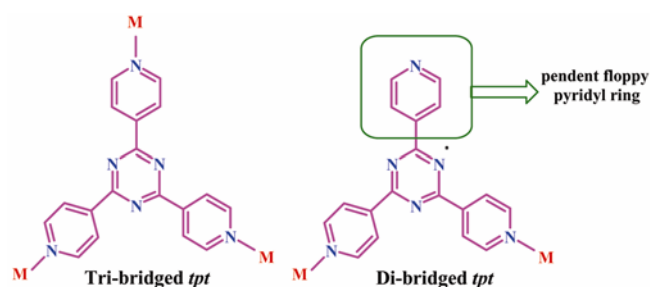
Scheme 1. Binding mode of tpt.

*For correspondence

Here we present the synthesis, characterization and single crystal X-ray structure of two supramolecular frameworks where tpt acts as a bi-bridging ligand. The pendent floppy pyridyl ring in all two cases is accessible for π–π stacking[32–35] which has an important influence on crystal packing to stabilize the supramolecular structures with other cooperative weak interactions, like H-bonding, π–π and C–H…O interactions.[36–38]

2. Experimental

2.1 *Materials*

The metal salts $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$ were obtained from the Sigma Aldrich Chemical Co. and 2,4,6-tri(4-pyridyl)-1,3,5-triazine was purchased from Tokyo Kasei Industrial Co. which were used as received. All other reagents and solvents employed were commercially available and used as supplied without further purification.

2.2 *Synthesis*

2.2a *Synthesis of [Zn(tpt)(NO₃)₂(H₂O)₂]ₙ* (**1**): Zn $(NO_3)_2 \cdot 6H_2O$ (0·25 mmol, 0·074 g) was dissolve in 10 ml methanol and 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt) (0·25 mmol, 0·078 g) was dissolved in 10 ml benzyl alcohol. 2 ml of 1 : 1 solvent mixture of methanol and benzyl alcohol is slowly and carefully layered on top of the benzyl alcohol solution (2 ml) of tpt in a glass-tube. On the top, methanolic solution (2 ml) of $Zn(NO_3)_2$ is also added carefully so that two reactant is separated by the 1 : 1 solvent mixture. Slow diffusion of the $Zn(NO_3)_2$ occurs betwen the solvent mixture and light yellow block type single crystals were grown at the junction of the two different solvents after two weeks. The crystals suitable for X-ray diffraction study were separated and washed with MeOH. Yield: 80%. Anal. Calcd. for $C_{18}H_{16}N_8O_8Zn$: C, 40·16; H, 2·97; N, 20·82. Found: C, 40·25; H, 3·04; N, 20·64%. IR (KBr cm^{-1}); 3560–3160 *br* ν(OH); 1435 ν_a (NO$_2$); 1375 ν_s (NO$_2$) and 1062 ν (NO).

2.2b *Synthesis of [Cd(tpt)(NO₃)₂(H₂O)₂]ₙ* (**2**): Compound **2** was synthesized adopting the similar procedure as for **1** using $Cd(NO_3)_2 \cdot 4H_2O$ (0·25 mmol, 0·077 g) instead of $Zn(NO_3)_2 \cdot 6H_2O$. Yield: 73%. Anal. Calcd. for $C_{18}H_{16}N_8O_8Cd$: C, 36·93; H, 2·76; N, 19·15. Found: C, 37·09; H, 2·59; N, 19·31%. IR

(KBr cm^{-1}); 3560–3160 *br* ν (OH); 1439 ν_a (NO$_2$); 1368 ν_s (NO$_2$) and 1060 ν (NO).

2.3 *Physical measurements*

Elemental analysis of carbon, hydrogen and nitrogen was carried out on a Perkin Elmer 2400 CHN–analyser. FTIR spectra were recorded using KBr pellets with a Bruker IFS 66v/S instrument in the range of 4000–400 cm^{-1}.

2.4 *X-ray crystallography*

In both the cases, a suitable single crystal was mounted on a glass fibre and coated with epoxy resin. X-ray data collection was carried out on a Rigaku Mercury diffractometer with graphite mono-chromated Mo-K$_\alpha$ radiation ($\lambda = 0.71069$ Å) and a CCD 2D detector. The size of the unit cell was calculated from the reflections collected on the setting angles of seven frames by changing 0·5° for each frame. Three different settings were used and were changed by 0·5° per frame and intensity data were collected with a scan width of 0·5°. Empirical absorption correction by using REQABA[39] was performed for both the complexes. The structures were solved by direct methods by using the SIR-92 program[40] and expanded by using Fourier techniques.[41] All calculations for **1** and **2**, were performed with the teXsan crystallographic software package from Molecular Structure Corp.[42] and PLATON.[43] In both cases hydrogen atoms could be located in the difference Fourier map and included in the final refinement. All the non-hydrogen atoms in both cases were refined anisotropically. Final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, isotropic thermal parameters for the hydrogen atoms. The crystallographic and structure refinement parameters for **1** and **2** are summarized in table 1. Selected bond lengths, angles, H-bonding parameters and π–π interactions of both complexes are reported in tables 2–3, tables S1 and S2 respectively.

## 3. Results and discussion

3.1 *Synthesis*

Compounds **1** and **2** have been synthesized by layer technique in a reaction tube using the same procedure.

Table 1. Crystal data and structure refinement parameters for **1** and **2**.

	1	2
Empirical formula	$C_{18}H_{16}N_8O_8Zn$	$C_{18}H_{16}N_8O_8Cd$
Formula weight	537·78	584·79
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$ (no. 15)	$C2/c$ (no. 15)
a (Å)	24·70(2)	24·83(3)
b (Å)	11·443(5)	11·453(7)
c (Å)	7·502(4)	7·644(5)
α (°)	90	90
β (°)	91·259(9)	91·90(2)
γ (°)	90	90
Volume (Å³)	2120(2)	2173(3)
Z	4	4
Temperature (K)	233	243
ρ_{calc} (g cm⁻³)	1·685	1·788
Absorption coefficient (mm⁻¹)	1·200	1·071
F (000)	1096	1168
θ_{max} for data collections (°)	31·1	30·6
λ (MoKα)(Å)	0·71070	0·71070
Reflection collected	10648	9439
Reflection [$I > 2\sigma(I)$]	2553	2341
R^a	0·0321	0·0270
$R_w{}^b$	0·0451	0·0378
Goodness-of-fit on F^2	1·08	0·92

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^b R_w = [\Sigma\{w(Fo2 - Fc2)2\}/\Sigma\{w(Fo2)2\}]1/2$.
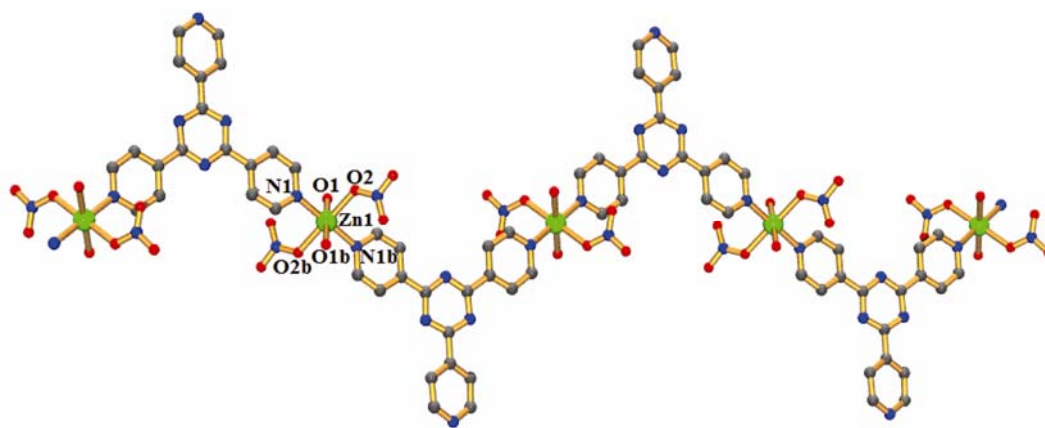
Figure 1. View of 1D coordination chain of $[Zn(tpt)(NO_3)_2(H_2O)_2]_n$ (**1**).

3.2 Structure description

3.2a *Structure description of [Zn(tpt)(NO₃)₂(H₂O)₂]ₙ* (**1**): The structure determination reveals that **1** consists of 1D coordination polymeric sinusoidal chain[31] bridged by the tpt ligand. A part of the chain with atom numbering scheme is given in figure 1. The coordination environment around each Zn(II) atom may be described as pseudo-octahedral with ZnN₂O₄ chromophore. Two nitrogen atoms (N1,

N1b; $b = 1/2 - x$, $3/2 - y$, $1 - z$) of the bridging tpt ligand and two oxygen atoms (O1, O1b) from symmetry related coordinated water molecules with four short bonds [Zn1–O1, 2·119(2) Å; Zn1–N1, 2·126(2) Å] are on the equatorial plane. The oxygen atoms (O2, O2b) from two pendant symmetry related nitrate anions having long bond distance [Zn1–O2, 2·173(2) Å] occupy the axial positions (table 2). Here, all the *transoid* angles are perfectly 180° and the slight distortion around Zn(II) is

Table 2. Selected bond lengths (Å) and angles(°) for **1**.

Zn1–O1	2·119(2)	Zn1–O2	2·173(2)
Zn1–N1	2·126(2)	O1–Zn1–O2	82·86(4)
O1–Zn1–N1	92·99(5)	O1–Zn1–O1b	180·00
O1–Zn1–O2b	97·14(4)	O1–Zn1–N1	87·01(5)
O2–Zn1–N1	87·79(5)	N1–Zn1–N1b	180·00
O1b–Zn1–O2	97·14(4)	O2–Zn1–O2b	180·00
O2–Zn1–N1b	92·21(5)	O1b–Zn1–N1	87·01(5)
O2b–Zn1–N1	92·21(5)	O1b–Zn1–N1	92·99(5)

Symmetry code: $b = 1/2 – x, 3/2 – y, 1 – z$.
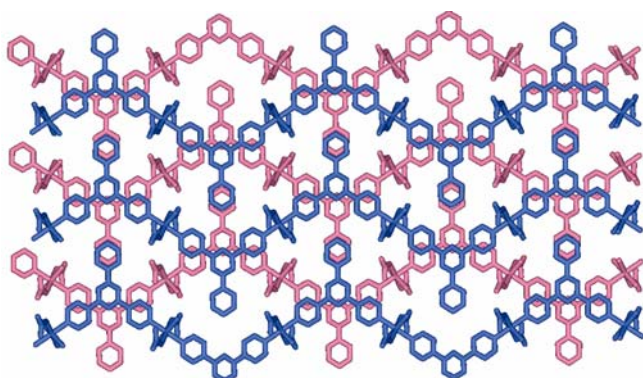
Figure 2. The stacking of the 2D undulated sheets with antiparallel fashion in **1** to facilitate the π-π interactions.
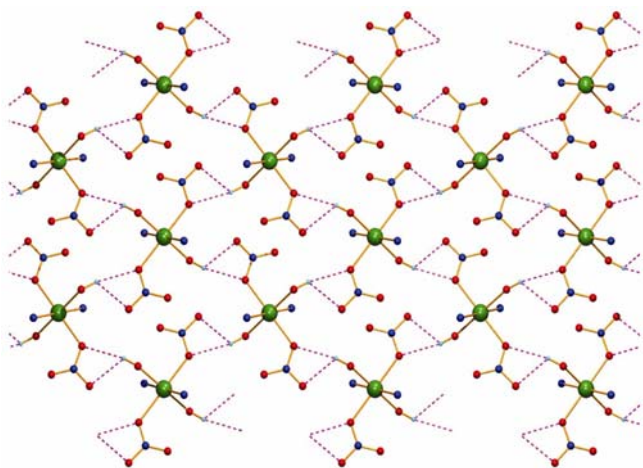
Figure 3. Inter-chain hydrogen bonding pattern in **1** (the tpt ligand has been omitted for clarity).

reflected by the observed *cisoid* angles, [82·86(4)–97·14(4)°]. The metal-to-metal separation in each 1D chain through tpt linkage is about 12·986(1) Å. The 1D chains stack in a similar fashion along crystallographic *a*-axis forming undulated 2D layer structure (pink sheet) (figures S1 and S2). A *c*-axis projection view of **1** clearly represents the packing

of 2D sheets running in anti-parallel fashion (figure 2) facilitating the π–π interactions. Because of this arrangements the H atom (H7) of the coordinated water molecules of one chain are oriented to the co-ordinated nitrate anions of other antiparallel chain and facilitate bifurcated hydrogen bonding (table S1) with two O atoms (O2, O4) of the nitrate anion. By this H-bonding and π–π interactions the coordinated 1D chains extended to 3D supramolecular architecture. Figure 3 and figure S2 clearly indicates in the sheet structure O–H...O bonds generate two cyclic motifs R_4^4 (16), and R_1^2(4) in Etter's graph notation.[44,45] There are also C–H...O interactions other than classical H-bonding, between two O atoms of nitrate (O3, O4) and the C–H of tpt (C3–H3, C4–H4). The C–H...O interactions also act as a supporting tool to maintain the position of nitrate, which is the key factor for the formation of H-bonded supramolecular structure, as depicted in figure S3 and table S1. The zig–zag arrangement of the chains stitched together by the H-bonding and C–H...O interaction facilitates a nice orientation of the tripodal tpt ligand to form strong face-to-face π–π interaction between the rings of the tpt ligands (table S2, figure 2 and S3). It is interesting to note that the pendent pyridyl rings are oriented in face-to-face manner (dihedral angle 0° and slip angle 14.14°) and one ring is attached to the two adjacent rings by strong π–π interactions having the perpendicular distance between ring centroids about 3·815(3) Å (table S2).

3.2b *Structure description of [Cd(tpt)(NO₃)₂ (H₂O)₂]ₙ (2)*: X-ray single crystal structure determination of **2** reveals that it is isomorphous with **1** (figure S4). It also contains 1D coordination polymeric sinusoidal[31] chain connected by the tpt linker. Compound **2** only differs with **1** respect to the metal ion used. Here the Cd(II) is used instead of Zn(II), which results a little variation in the bond lengths

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Cd1–O1	2·311(3)	Cd1–O2	2·345(3)
Cd1–N1	2·314(3)	O1–Cd1–O2	78·79(6)
O1–Cd1–N1	95·39(5)	O1–Cd1–O1b	180·00
O1–Cd1–O2b	101·21(6)	O1–Cd1–N1b	84·61(5)
O2–Cd1–N1	87·23(6)	O1b–Cd1–O2	101·21(6)
O2–Cd1–O2b	180·00	O2–Cd1–N1b	92·77(6)
O1b–Cd1–N1	84·61(5)	O2b–Cd1–N1	92·77(6)
N1–Cd1–N1b	180·00	O1b–Cd1–O2b	78·79(6)

$b = 5/2 - x, 3/2 - y, 1 - z.$
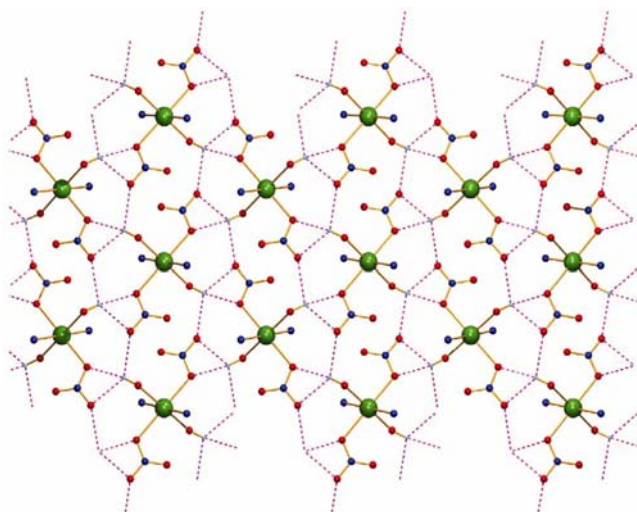
Figure 4. Inter-chain hydrogen bonding pattern in **2** (the *tpt* ligand has been omitted for clarity).

and bond angles (table 3) and obviously in metal-metal separation in the chains [Cd1–Cd1 distance is about 13·111(1) Å]. But due the change of metal atom in **2**, the supramolecular structure changed significantly. Like **1**, here also nitrate ions are oriented to form H-bonding between its O atom and the H atom of coordinated water molecules of the adjacent anti-parallel chains. Apart from these, the H atom (H7) of the coordinated water molecules also forms H-bonds to the nitrate oxygen of another adjacent chain to strengthen the H-bonded structure (figure 4; table S1). This trifurcated hydrogen bonding occurs here may be due to the bigger size of Cd(II) in comparison to Zn(II), which results the coordinated nitrate and water of the adjacent chains to come much closer than in case of **1**. In the 2D arrangements the O–H…O bonds generate three cyclic motifs R_2^2 (12), R_2^2 (6), and R_1^2 (4) in Etter's graph notation [44,45] (figure 4). The C–H…O interactions are also present which helps further stabilization of the supramolecular structure. Like **1**, here also the rings of tpt ligand undergo strong face-to-face π–π interactions, only differing in the parameter values (table S2). This

π–π interaction is also responsible here to form the overall 3D supramolecular entity, showing almost same packing view as that of **1**.

4. Conclusion

On the basis of equimolecular combination of tpt with d^{10} metal salts, here we have constructed two supramolecular entities, where the tpt ligand binds metal centre in bi-bridging coordination modes. From the foregoing discussion, we have demonstrated how in solid-state structures, the floppy bipyridyl ring of tpt is responsible for the face-to-face orientation to form the π–π interactions. Apart from π–π interactions in **1** and **2** the H-bonding also present to stabilize the overall supramolecular structure. Although the coordination structures are almost same, interestingly the H-bonding pattern is different in two cases. This may be due to the size of the metal ion, which may be attributed as a tool in the direction of supramolecular crystal engineering. The C–H…O interactions also present in all two compounds for further stabilization of the structures. In a nutshell, these discussions provoke us to question on the energetic hierarchy of the weak forces. Is the operation of different supramolecular forces are energy driven or acts in co-operative manner?

Supplementary data

Tables of X-ray crystallographic data in CIF format for the structures reported in this paper have been

deposited to the Cambridge Crystallographic Data Centre, CCDC numbers are 743919 (**1**) and 743920 (**2**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: C44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk web: http://www. ccdc. cam.ac.uk/deposit]. Supplementary figures and tables can be found in website (www.ias.ernet.in/ chemsci).

References

1. Rao C N R, Natarajan S and Vaidhyanathan R 2004 *Angew. Chem. Int. Ed.* **43** 1466
2. Kitagawa S, Kitaura R and Noro S-I 2004 *Angew. Chem. Int. Ed.* **43** 2334
3. Férey G 2008 *Chem. Soc. Rev.* **37** 191
4. Maji T K and Kitagawa S 2007 *Pure Appl. Chem.* **79** 2155
5. Férey G 2009 *Dalton Trans.* 4400
6. Desiraju G R 1996 *Acc. Chem. Res.* 441
7. Lin X, Jia J, Zhao X, Thomas K M, Blake A J, Walker G S, Champness N R, Hubberstey P and Schröder M 2006 *Angew. Chem. Int. Ed.* **45** 7358
8. Ma S, Sun D, Simmons J M, Collier C D, Yuan D and Zhou H-C 2007 *J. Am. Chem. Soc.* **130** 1012
9. Bradshaw D, Prior T J, Cussen E J, Claridge J B and Rosseinsky M J 2004 *J. Am. Chem. Soc.* **126** 6106
10. Pan L, Adams K M, Hernandez H E, Wang X, Zheng C, Hattori Y and Kaneko K 2003 *J. Am. Chem. Soc.* **125** 3062
11. Maji T K, Matsuda R and Kitagawa S 2007 *Nat. Mater.* **6** 142
12. Khlobystov A N, Champness N R, Roberts C. J, Tendler S J B, Thompson C and Schröder M 2002 *Cryst. Eng. Comm.* **4** 426
13. Seo S, Whang D, Lee H, Jun S L, Oh J, Jeon Y J and Kim K 2000 *Nature* **404** 982
14. Wu C-D, Hu A, Zhang L and Lin W 2005 *J. Am. Chem. Soc.* **127** 8940
15. Eddaoudi M, Moler B D, Li H, Chen B, Reineke M T, O'Keeffe M and Yaghi O M 2001 *Acc. Chem. Res.* **34** 319
16. Desiraju G R 2005 *Chem. Commun.* 2995
17. Ghosh A K, Ghoshal D, Zangrando E, Ribas J and Ray Chaudhuri N 2005 *Inorg. Chem.* **44** 1786
18. Ghoshal D, Ghosh A K, Ribas J, Zangrando E, Mostafa G, Maji T K and Ray Chaudhuri N 2005 *Cryst. Growth Des.* **5** 941
19. Caulder D L and Raymond K N 1999 *Acc. Chem. Res.* **32** 982
20. Beatty A M 2008 *Coord. Chem. Rev.* **246** 131
21. Ghoshal D, Maji T K, Mostafa G, Sain S, Lu T-H, Ribas J, Zangrando E and Ray Chaudhuri N 2004 *Dalton Trans.* 1687
22. Ghoshal D, Ghosh A K, Ribas J, Mostafa G and Ray Chaudhuri N 2005 *Cryst. Eng. Commun.* **7** 616
23. Kim H, Samsonenko D G, Das S, Kim G-H, Lee H-S, Dybtsev D N, Berdonosova E A and Kim K 2009 *Chem. Asian J.* **4** 886
24. Mirica L M, Ottenwaelder X and Stack T D P 2004 *Chem. Rev.* **104** 1013
25. Aboelella N W, Reynolds A M and Tolman W M 2004 *Science* **304** 836
26. Maji T K, Mostafa G, Sain S, Prasad J S and Ray Chaudhuri N 2001 *Cryst. Eng. Commun.* **3** 37
27. Batten S R, Hoskins B F, Moubaraki B, Murray K S and Robson R 2000 *Chem. Commun.* 1095
28. Abrahams B F, Batten S R, Grannas M J, Hamit H, Hoskins B F and Robson R 1999 *Angew. Chem. Int. Ed.* **38** 1475
29. Batten S R, Hoskins B F and Robson R 1995 *J. Am. Chem. Soc.* **117** 5385
30. Biradha K and Fujita M 2002 *Angew. Chem. Int. Ed.* **41** 3392
31. Ghoshal D, Maji T K, Mostafa G, Lu T-H and Ray Chaudhuri N 2003 *Cryst. Growth Des.* **3** 9
32. Hunter C A 1994 *Chem. Soc. Rev.* **23** 101
33. Janiak C 2000 *J. Chem. Soc. Dalton Trans.* 3885
34. Paul R L, Couchman S M, Jeffery J C, McCleverty J A, Reeves Z R and Ward M D 2000 *J. Chem. Soc. Dalton Trans.* 845
35. Britten J F, Clements O P, Cordes A W, Haddon R C, Oackley R T and Richardson J F 2001 *Inorg. Chem.* **40** 6820
36. Desiraju G R 1996 In *The crystals as a supra-molecular entity* (ed.) J M Lehn (John Wiley & Sons: Chester, UK) Vol. 2
37. Desiraju G R 1995 *Angew. Chem. Int. Ed. Engl.* **34** 2311
38. Desiraju G R and Steiner T 1999 In *The weak hydrogen bond in structural chemistry and biology* (Oxford University Press: Oxford)
39. Jacobson R A REQABA Empirical Absorption Correction Ver. 1.1-03101998, Molecular Structure Corp., The Woodlands, TX (1996–1998)
40. Altomare A, Burla M C, Camalli M, Cascarano G L, Giacovazzo C, Guagliardi A, Moliterni A G G, Polidori G and Spagna R 1999 *J. Appl. Crystallogr.* **32** 115
41. Beurskens P T, Admiraal G, Beurskens G, Bosman W P, deGelder R, Israel R and Smits J M M 1994 *The DIRDIF-94 program system; technical report of the crystallography laboratory* (University of Nijmegen: Nijmegen, The Netherlands)
42. TeXsan Crystal Structure Analysis Package; Molecular Structure Corp.: The Woodlands, TX (2000)
43. Spek A L PLATON molecular geometry program. *J. Appl. Crystallogr.* **36** 7
44. Etter M C 1991 *J. Phys. Chem.* 4601
45. Etter M C, MacDonald J C and Bernstein 1990 *J. Acta Cryst.* **B46** 256