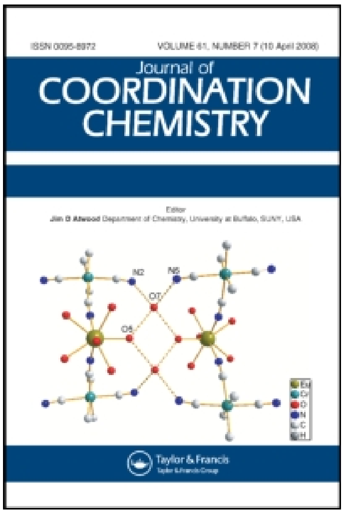

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Enforced 2D supramolecular structures within hydrogen-bonded molecular cocrystals

Shengli Huang[a]; Hongwei Hou[a]; Liwei Mi[a]; Yaoting Fan[a]
[a] Department of Chemistry, Zhengzhou University, Zhengzhou 450001, China

To cite this Article Huang, Shengli , Hou, Hongwei , Mi, Liwei and Fan, Yaoting(2009) 'Enforced 2D supramolecular structures within hydrogen-bonded molecular cocrystals', Journal of Coordination Chemistry, 62: 12, 1964 — 1971
To link to this Article: DOI: 10.1080/00958970902741269
URL: http://dx.doi.org/10.1080/00958970902741269

Journal of Coordination Chemistry
Vol. 62, No. 12, 20 June 2009, 1964–1971

Taylor & Francis
Taylor & Francis Group

Enforced 2D supramolecular structures within hydrogen-bonded molecular cocrystals

SHENGLI HUANG, HONGWEI HOU*, LIWEI MI and YAOTING FAN

Department of Chemistry, Zhengzhou University, Zhengzhou 450001, China

(*Received 22 August 2008; in final form 2 October 2008*)

Two new coordination polymers, $\{[Co(btmb)_2(H_2O)_2]\cdot(Fc(SO_3)_2)\}_n$ (**1**) and $\{[Cd(bbbm)(H_2O)_4]\cdot(p\text{-}FcC_6H_4SO_3)_2(CH_3OH)\}_n$ (**2**) (Fc = ferrocene; btmb = 1,4-bis(triazol-1-ylmethyl)-benzene); bbbm = 1,1′-(1,4-butanediyl)bis-1H-benzimidazole), were synthesized as cocrystals and characterized by single crystal X-ray diffraction, elemental analysis and IR spectrum. In **1**, two btmb molecules link Co(II) ions into one 1D double-stranded chain of loops, and these chains are bridged by $Fc(SO_3)_2^{2-}$ ligands through H-bonds, resulting in an infinite 2D sandwich-type network. In **2**, two adjacent Cd(II) ions are interconnected by bbbm to generate a 1D zigzag chain structure, and $p-FcC_6H_4SO_3^-$ squeezes like a wedge into the adjacent chains, further being assembled by O–H···O hydrogen bonds and π–π stacking interactions to form a 2D supramolecular network.

Keywords: Cocrystal; H-bond; Coordination polymer; Sulfonates; Electrochemistry

1. Introduction

Inorganic crystal engineering (ICE) is a hybrid discipline of supramolecular chemistry and material science for rational design of functional materials [1]. Optimizing a material via controlling its structure at the molecular level attracts an increasing number of scientists. However, the relationship between structure and functional property of solids still is in doubt [2]. Furthermore, how to precisely control a crystal's structure and geometry of the network is uncertain.

The nature of intermolecular forces responsible for packing in molecular crystals frustrates solid-state design, limiting the synthesis of inorganic crystal [3]. Indeed, slight modification of crystal packing forces can lead to a completely unanticipated solid-state structure [4]. This has prompted the study of weak intermolecular interactions existing in inorganic crystal [5]. They play an important role in self-assembly, recognition of aromatic compounds [6], forming of double-helical DNA structure [7] and semiconductor materials [8].

Compared with RCO_2^- and RPO_3^{2-}, RSO_3^- has been considered a poor ligand. Therefore, sulfonates as spacers for functional extended networks have been

---

*Corresponding author. Email: houhong@zzu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970902741269

limited [9]. Sulfonate in extended solids built up by cooperative coordination and other weak intermolecular interactions increase gradually [10]. Most transition metal sulfonates obtained from aqueous solution are aqua-metal sulfonate salts [11]. Using a subsidiary ligand, sulfonate anions can link chains composed of subsidiary ligand and metal ions through H-bonds and π–π stacking, particularly amenable for design of molecular cocrystals. Molecular cocrystals, a long known but little studied class of compounds, are of growing interest because of their relevance to pharmaceutical formulations [12], solid-state organic synthesis [13] and control of polymorphs [14]. We use $Fc(SO_3Na)_2$ and p-$FcC_6H_4SO_3Na$ as H-acceptors to obtain two inclusion compounds, $\{[Co(btmb)_2(H_2O)_2]\cdot(Fc(SO_3)_2)\}_n$ and $\{[Cd(bbbm)(H_2O)_4]\cdot(p\text{-}FcC_6H_4SO_3)_2(CH_3OH)\}_n$. Herein, we report their syntheses, crystal structures, and electrochemical properties.

2. Experimental

2.1. *Materials and apparatus*

All reagents were used as received without purification. Elemental analyses (carbon, hydrogen, and nitrogen) were carried out on a Carlo-Erba 1106 Elemental Analyzer. IR spectra were recorded on a Fourier Bruker Tensor-27 spectrophotometer with pressed KBr pellets from 400–4000 cm^{-1}.

2.2. *Synthesis of* $\{[Co(btmb)_2(H_2O)_2]\cdot(Fc(SO_3)_2)\}_n$ *(1)*

A methanol solution (3 mL) of btmb (48.0 mg, 0.2 mmol) was added to a methanol solution (3 mL) of $CoCl_2\cdot3H_2O$ (18.3 mg, 0.1 mmol), followed by dropwise addition of 3 mL H_2O solution of $Fc(SO_3Na)_2$ (33.4 mg, 0.1 mmol). Filtration gave a yellow solution, which was kept at room temperature in the dark for 2 weeks to afford the product as red crystals. Yield: 47%; Anal. Calcd for $\{[Co(btmb)_2(H_2O)_2]\cdot(Fc(SO_3)_2)\}_n$ (%): C, 44.41; H, 3.95; N, 18.28. Found: C, 44.05; H, 3.89; N, 18.36. IR data (KBr pellet, cm^{-1}): 3423(m), 3128(m), 1524(s), 1426(w), 1280(w), 1234(s), 1160(s), 1132(s), 1043(s), 1015(m), 887(w), 829(w), 732(m), 646(s).

2.3. *Synthesis of* $\{[Cd(bbbm)(H_2O)_4]\cdot(p\text{-}FcC_6H_4SO_3)_2(CH_3OH)\}_n$ *(2)*

A methanol solution (3 mL) of bbbm (29.1 mg, 0.1 mmol) was added to a methanol solution (3 mL) of $Cd(NO_3)_2\cdot(H_2O)_4$ (30.8 mg, 0.1 mmol), followed by dropwise addition of 3 mL H_2O solution of p-$FcC_6H_4SO_3Na$ (72.8 mg, 0.2 mmol). Filtration gave a yellow solution, which was kept at room temperature in the dark for 2 weeks to afford the product as red crystals. Yield: 41%; Anal. Calcd for $\{[Cd(bbbm)(H_2O)_4]\cdot(p\text{-}FcC_6H_4SO_3)_2(CH_3OH)\}_n$ (%): C, 51.51; H, 4.75; N, 4.71. Found: C, 51.39; H, 4.68; N, 4.79. IR data (KBr pellet, cm^{-1}): 3423(m), 3098(w), 2938(w), 1598(w), 1511(m), 1461(w), 1386(w), 1196(s), 1127(s), 1034(s), 1006(m), 831(m), 744(s), 634(s).

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

	1	**2**
Chemical formula	$C_{36}H_{44}CoFeN_{12}O_{10}S_2$	$C_{52}H_{60}CdFe_2N_4O_{12}S_2$
Formula weight	983.73	1221.26
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$
Units of dimensions (Å, °)		
a	13.240(3)	9.673(1)
b	19.339(4)	8.9238(9)
c	8.7760(18)	31.595(3)
α	90.00	90.00
β	107.90(3)	93.25(2)
γ	90.00	90.00
V (Å^3)	2138.31	2722.88
Z	2	2
$F(000)$	1018	1256
D_c (mg m^{-3})	1.528	1.490
T (°C)	291(2)	291(2)
θ range (°)	1.62–24.99	2.41–25.50
Absorption coefficient (mm^{-1})	0.895	1.052
Goodness-of-fit on F^2	1.081	1.009
Final R indices	0.0707	0.0354
$[I > 2\sigma(I)]$	0.1836	0.0846
Largest differential peak and hole (e Å^{-3})	0.661, −0.550	0.481, −0.275

2.4. *X-ray diffraction determination*

Measurements of **1** and **2** were made on a Rigaku RAXIS-IV image plate area detector using graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). The data were collected at a temperature of 18 ± 1°C using the ω–2θ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. All calculations were performed using SHELXL-97 [15]. Crystal data and structure refinement are summarized in table 1. Selected bond lengths and angles of **1** and **2** are listed in tables 2 and 3.

3. Results and discussion

3.1. *X-ray crystallography of 1*

As shown in figure 1, complex **1** exhibits a petal-shaped geometry. The central Co(II) lies in a flatten octahedral coordination environment $[CoN_4O_2]$ formed by four nitrogens from four btmb groups and two H_2O molecules. The Co–N bonds range from 2.153 to 2.177 Å, and the Co–O distance is 2.090 Å. Four N atoms around Co(II) from four btmb bridging ligands are coplanar. O atoms of the $Fc(SO_3)_2^{2-}$ do not coordinate to Co(II) cations, but link with H of the H_2O coordinated to Co(II) cations.

The two-dimensional framework of **1** is depicted in figure 2 and based on $\{[Co(btmb)_2(H_2O)_2]\cdot(Fc(SO_3)_2)\}_n$ building blocks. Cobalt is at the center of the

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

1			
Co(1)–O(4)	2.090(4)	Co(1)–N(6)#3	2.177(4)
Co(1)–N(1)	2.153(4)	O(4)–Co(1)–N(1)	88.97(19)
O(4)#2–Co(1)–O(4)	180.000(1)	O(4)–Co(1)–N(1)#2	91.03(19)
N(1)–Co(1)–N(1)#2	180.000(1)	O(4)–Co(1)–N(6)#3	88.58(18)
N(1)–Co(1)–N(6)#3	86.72(18)	O(4)–Co(1)–N(6)#4	91.42(18)
N(1)–Co(1)–N(6)#4	93.28(18)	N(6)#3–Co(1)–N(6)#4	180.0
2			
Cd(1)–N(1)	2.3010(15)	Cd(1)–O(5)	2.3265(13)
Cd(1)–O(4)	2.3274(14)	N(1)–Cd(1)–N(1)#1	180.0
N(1)–Cd(1)–O(5)	89.33(5)	N(1)#1–Cd(1)–O(5)	90.67(5)
O(5)#1–Cd(1)–O(5)	180.0	N(1)–Cd(1)–O(4)	93.87(5)
O(5)#1–Cd(1)–O(4)	91.60(5)	O(5)–Cd(1)–O(4)	88.40(5)
N(1)–Cd(1)–O(4)#1	86.13(5)	O(4)–Cd(1)–O(4)#1	180.0

Symmetry transformations used to generate equivalent atoms: **1**: #1 $-x, -y+1, -z+1$; #2 $-x+1, -y+1, -z+2$; #3 $x+1, y, z$; #4 $-x, -y+1, -z+2$; #5 $x-1, y, z$. **2**: #1 $-x+1, -y+2, -z$; #2 $-x+2, -y+1, -z$.

Table 3. Hydrogen bond distances (Å) and angles (°) for **1** and **2**.

Complex	D–H···A	D–H	H···A	D···A	∠D–H···A
1	O4–H4F···O3	0.8406	1.8722	2.6907	164.187
2	O4–H2W···O1	0.817(7)	1.939(6)	2.741(2)	166.9(13)
	O5–H3W···O2	0.821(8)	1.917(8)	2.733(2)	172.6(12)
	O5–H4W···O3	0.823(7)	1.887(8)	2.705(2)	172.9(12)

octahedron and two adjacent Co(II) cations are bridged by two btmb, forming a double-stranded chain of loops extending along the crystallographic *b*-axis (figure 3). Each btmb adopts a trans–gauche conformation and the aromatic rings opposite are nearly parallel. Two adjacent chains are linked by $Fc(SO_3)_2^{2-}$, and the 1D chains transform to 2D networks through H-bonds. The interionic O–H···O hydrogen bond is 2.6907 Å.

3.2. *X-ray crystallography of 2*

Different from **1**, single-crystal X-ray diffraction revealed that **2** is a 1D zigzag chain with molecular formula $\{[Cd(bbbm)(H_2O)_4]\cdot(p\text{-}FcC_6H_4SO_3)_2(CH_3OH)\}_n$. As illustrated in figure 4, each Cd(II) is octahedral with four H_2O's and two bbbm ligands. The Cd–O bond distances are in the range 2.3265–2.3274 Å and the Cd–N distance is 2.3010 Å. The bond angles around Cd(II) are between 86.13 and 93.8°.

In **2**, two adjacent Cd(II) cations are bridged by one bbbm forming a zigzag chain extending along the crystallographic *a* axis (figure 5). Adjacent chains are linked by *p*-$FcC_6H_4SO_3$ and the 1D chains transform to 2D networks through hydrogen bonds (figure 6). The interionic O–H···O hydrogen bonds are 2.705, 2.733, and 2.741 Å, respectively.

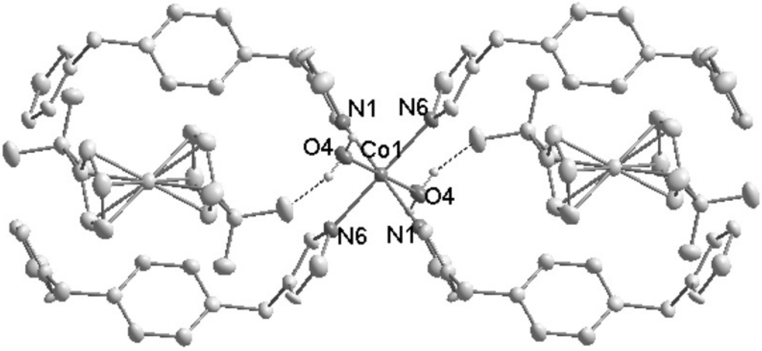

Figure 1. The coordination environment of Co(II) ion in **1** with thermal ellipsoids at 30% probability.

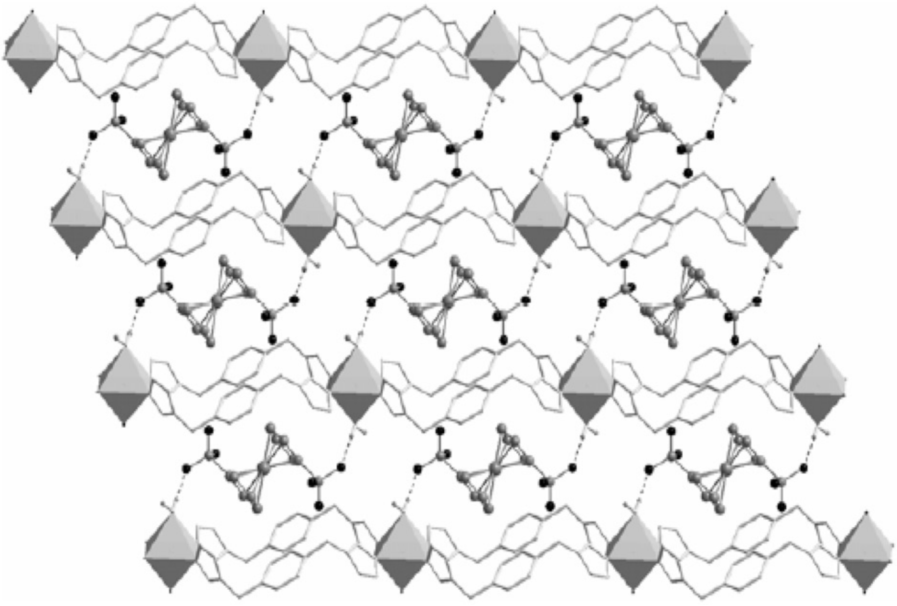

Figure 2. The 2D network viewed along *b*-axis in **1** (the dotted lines are H-bonds).

3.3. *Electrochemistry*

The DMF solution differential pulse voltammograms of $Fc(SO_3Na)_2$, **1**, p-$FcC_6H_4SO_3Na$, **2**, and ferrocene are shown in 'Supplementary material'. These complexes show a single peak, assigned to the electron-transfer of the ferrocenyl moiety. Relative to ferrocene (0.464 V in DMF solution), the half-wave potentials ($E_{1/2}$) of the p-$FcC_6H_5SO_3Na$ (0.472 V) and **2** (0.496 V) are shifted to higher potential. Nevertheless, the half-wave potentials ($E_{1/2}$) of the $Fc(SO_3Na)_2$ (0.460 V) and **1** (0.460 V) are nearly equivalent to ferrocene. The electron-withdrawing ability of the sulfonate group should

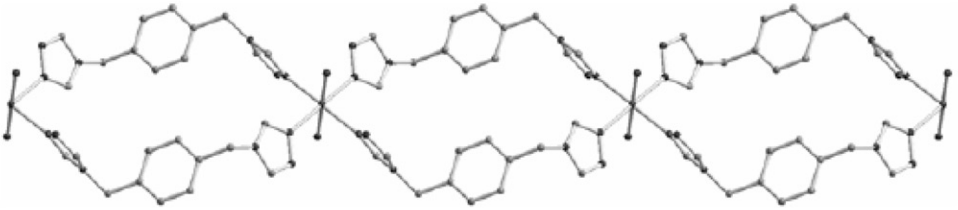

Figure 3. The 1D double-stranded chain of loops linked by btmb in **1**.

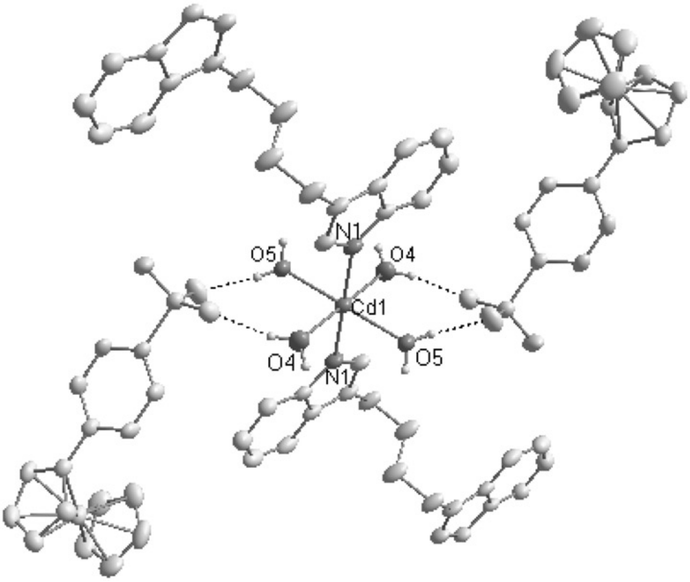

Figure 4. The coordination environment of Cd(II) ion in **2** with thermal ellipsoids at 30% probability.

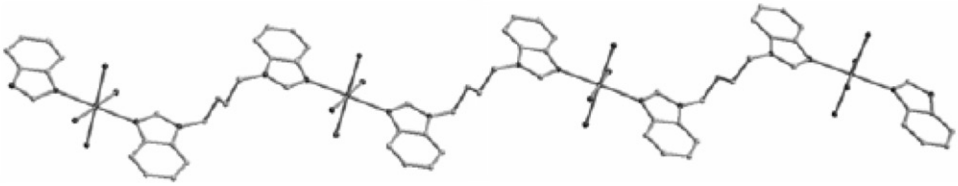

Figure 5. The 1D zigzag chain linked by bbbm in **2**.

be responsible for the increase of *p*-$FcC_6H_5SO_3Na$'s half-wave potential (0.012 V) and **2** (0.036 V). However, $Fc(SO_3Na)_2$ is centrosymmetric and sulfonate has little contribution to the half-wave potential. Compared with *p*-$FcC_6H_5SO_3Na$, **2** has a strong shift attributed to the influence of the central metal, consistent with the previous results of transition metal – ferrocenyl systems.

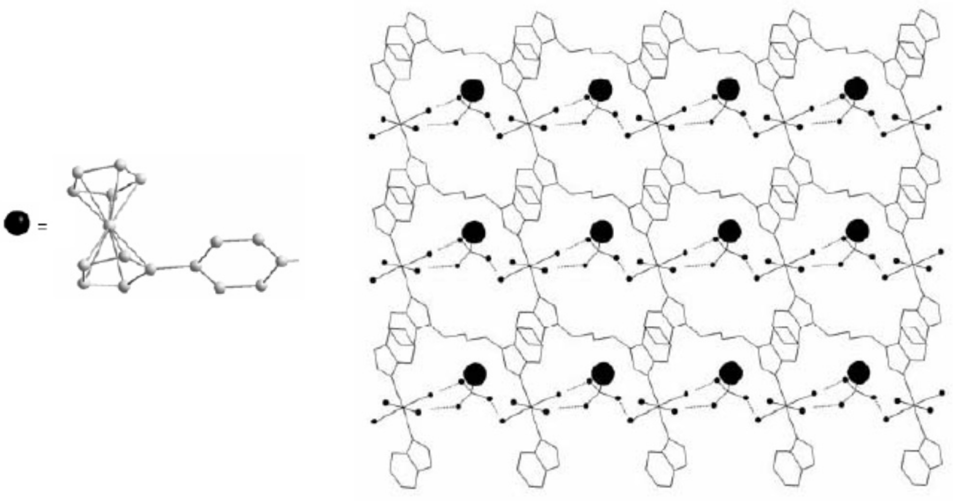

Figure 6. The 2D network viewed along *c*-axis in **2** (the dotted lines are H-bonds).

4. Conclusion

We report the synthesis and structures of two new inclusion compounds, $\{[Co(btmb)_2(H_2O)_2]\cdot(Fc(SO_3)_2)\}_n$ and $\{[Cd(bbbm)(H_2O)_4]\cdot(p\text{-}FcC_6H_4SO_3)_2(CH_3OH)\}_n$. Both contain a 1D chain which transforms to 2D networks through O–H $\cdots$ O bond. However, the connections are different. In **1**, each $-SO_3^-$ of $Fc(SO_3)_2^{2-}$ links two different chains, while in **2**, $-SO_3^-$ of $p\text{-}FcC_6H_4SO_3^-$ squeezes like a wedge into adjacent chains. The $-SO_3^-$ does not coordinate the metal but participates in X–H $\cdots$ O bonds (X = C, N, S, and O). The subsidiary ligand is a hard-template and H-bonds link for construction of the inclusion compound; the combined use of subsidiary ligand and weak intermolecular forces may offer a new method for design of functional materials.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 693977 and 693978 for **1** and **2**, respectively. Copies of this information may be obtained free of charge from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: 44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgment

This project is supported by National Nature Science Foundation of China (No. 20671082).

References

[1] D. Braga. *J. Chem. Soc., Dalton Trans.*, 3705 (2000).

[2] Y.F. Liu, J.C. Su, W.H. Li, J.G. Wu. *Inorg. Chem.*, **44**, 3890 (2005).

[3] (a) A. Gavezzottti. *Acc. Chem. Res.*, **27**, 309 (1994); (b) J.D. Dunitz, A. Gavezzotti. *Angew. Chem. Int. Ed.*, **44**, 1766 (2005).

[4] (a) J.D. Dunitz. *J. Chem. Soc., Chem. Commun.*, 545 (2003); (b) J.D. Dunitz, H.A. Scheraga. *Proc. Natl. Acad. Sci.*, **102**, 14309 (2004).

[5] (a) C.B. Aakeroy, A.M. Beatty. *Aust. J. Chem.*, **54**, 409 (2001); (b) B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001); (c) A.D. Burrows, C.W. Chan, M.M. Chowdhry, J.E. McGrady. *Chem. Soc. Rev.*, **24**, 329 (1995).

[6] C.A. Hunter, J.K. Sanders. *J. Am. Chem. Soc.*, **112**, 5525 (1990).

[7] C.A. Hunter. *J. Mol. Biol.*, **230**, 1025 (1993).

[8] A.N. Sokolov, T. Friscic, L.R. MacGillivray. *J. Am. Chem. Soc.*, **128**, 2806 (2006).

[9] (a) B.J. Gunderman, P.J. Squattrito. *Inorg. Chem.*, **34**, 2399 (1995); (b) B.J. Gunderman, P.J. Squattrito. *Inorg. Chem.*, **33**, 2924 (1994); (c) J.S. Haynes, J.R. Sams, R.C. Thompson. *Can. J. Chem.*, **59**, 669 (1981); (d) A.L. Arduini, M. Garnett, R.C. Thompson, T.C.T. Wong. *Can. J. Chem.*, **53**, 3812 (1975); (e) J. Cai, C.H. Chen, C.Z. Liao, J.H. Yao, X.P. Hu, X.M. Chen. *J. Chem. Soc., Dalton Trans.*, 1137 (2001); (f) A.J. Shubnell, E.J. Kosnic, P.J. Squattrito. *Inorg. Chim. Acta*, **216**, 101 (1994); (g) E.J. Kosnic, E.L. McClymont, R.A. Hodder, P.J. Squattrito. *Inorg. Chim. Acta*, **201**, 143 (1992); (h) M.A. Leopard, P.J. Squattrito, S.N. Dubey. *Acta Crystallogr., Sect. C*, **55**, 35 (1999); (i) B.J. Gunderman, S.N. Dubey, P.J. Squattrito. *Acta Crystallogr., Sect. C*, **53**, 17 (1997).

[10] (a) K.T. Holman, A.M. Pivovar, J.A. Swift, M.D. Ward. *Acc. Chem. Res.*, **34**, 107 (2001); (b) A.M. Pivovar, K.T. Holman, M.D. Ward. *Chem. Mater.*, **13**, 3018 (2001); (c) V.A. Russell, M.C. Etter, M.D. Ward. *J. Am. Chem. Soc.*, **116**, 1941 (1994).

[11] (a) E.J. Kosnic, E.L. McClymont, R.A. Hodder, P.J. Squattrito. *Inorg. Chim. Acta*, **201**, 143 (1992); (b) A.J. Shubnell, E.J. Kosnic, P.J. Squattrito. *Inorg. Chim. Acta*, **216**, 101 (1994); (c) B.J. Gunderman, L.D. Kabell, P.J. Squattrito, S.N. Dubey. *Inorg. Chim. Acta*, **258**, 237 (1997); (d) C.H. Chen, D.L. An, S. Gao, Z.B. Zhu, L.H. Huo, H. Zhao. *Acta Crystallogr., Sect. E*, **60**, m11 (2004).

[12] (a) O. Almarsson, M.J. Zaworotko. *J. Chem. Soc., Chem. Commun.*, 1889 (2004); (b) P. Vishweshwar, J.A. McMahon, J.A. Bis, M.J. Zaworotko. *J. Pharm. Sci.*, **95**, 499 (2006); (c) S.L. Childs, L.J. Chyall, J.T. Dunlap, V.N. Smolenskaya, B.C. Stahly, G.P. Stahly. *J. Am. Chem. Soc.*, **126**, 13335 (2004); (d) A.V. Trask, W.D.S. Motherwell, W. Jones. *Cryst. Growth Des.*, **5**, 1013 (2005).

[13] (a) M.C. Etter, G.M. Frankenbach, J. Bernstein. *Tetrahedron Lett.*, **30**, 3617 (1989); (b) X. Gao, L.R. MacGillivray. *Angew. Chem. Int. Ed.*, **43**, 232 (2004); (c) X. Quyang, J.W. Lauher, F.W. Fowler. *J. Am. Chem. Soc.*, **125**, 12400 (2003); (d) T. Caronna, R. Liantonio, T.A. Logothetis, P. Metrangolo, T. Pilati, G. Resnati. *J. Am. Chem. Soc.*, **126**, 4500 (2004).

[14] P. Vishweshwar, J.F. McMahon, M.L. Peterson, M.B. Hickey, M.J. Zaworotko. *J. Chem. Soc., Chem. Commun.*, 4601 (2005).

[15] (a) G.M. Sheldrick. *SHELXS 97, Program for the Solution of Crystal Structures* (1997); (b) G.M. Sheldrick. *SHELXL 97Program for the Refinement of Crystal Structures* (1997).