Helical Water Chain

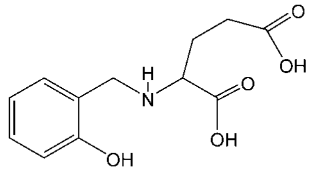
Helix inside a Helix: Encapsulation of Hydrogen-Bonded Water Molecules in a Staircase Coordination Polymer**

*Bellam Sreenivasulu and Jagadese J Vittal**

Inspired by the fascinating structural features of helices that exhibit cooperative self-assembly and recognition, as well as remarkable functions such as chemical transport and screening by membrane channels in biological systems, helicity has been successfully introduced into artificial systems by chemists working in the field of metallo-supramolecular chemistry.[1] As a result, today helical polymers are among the most explored and best investigated supramolecular architectures.[2] As hydrogen bonds and other noncovalent interactions are the main driving forces behind this self-assembly process, supramolecular chemistry is now in a phase of characterizing and understanding various hydrogen-bonded water clusters in the form of hexamers,[3,4] octamers,[5,6] decamers,[7] $(H_2O)_{15}(CH_3OH)_3$ clusters[8] and one-dimensional (1D) infinite water chains[9,10] in diverse environments of various crystal hosts. Zeolite-like 3D network structures with chiral channels filled with highly ordered water molecules are well known.[11]

At this juncture, 1D water chains are attracting a great deal of attention because of their vital role in the biological transport of water, protons, and ions.[12] It was recently found that transport of water or protons across the cell involves the assembly of highly mobile hydrogen-bonded water molecules into a single chain at the positively charged constricted pore of the membrane-channel protein aquaporin-1.[13] While 1D water chains play crucial roles in stabilizing the native conformation of biopolymers, such helical water chains are extremely rare in synthetic crystal hosts.[9,10] Here we report an interesting staircaselike helical coordination polymeric architecture of a Ni^{II} complex that hosts a 1D helical chain of lattice water molecules in a helical pore through hydrogen bonding.

The single-crystal X-ray structure of $[(H_2O)_2\subset\{Ni(Hsglu)(H_2O)_2\}]\cdot H_2O$ (**1**; H_3sglu = *N*-(2-hydroxybenzyl)-L-glutamic acid) was determined unambiguously.[14] Compound **1** crystallizes in the monoclinic system with two independent molecules in the asymmetric unit. Each Ni^{II} unit has octahedral geometry (Figure 1), and the $Hsglu^{2-}$ ligand is coordinated through the phenolic oxygen atom (Ni1−O1 2.089(4) Å, Ni2−O6 2.101(3) Å), secondary amine N atom (Ni1−N1 2.084(4) Å, Ni2−N2 2.082(4) Å), and carboxylate α-oxygen atom (Ni1−O2, 2.047(4) Å, Ni2−O7 2.042(4) Å) in a *fac* manner, along with two aqua ligands, and another carboxylate oxygen atom from the neighboring molecule. The intermolecular connectivity via the second carboxylate O atom generates a left-handed staircaselike coordination polymeric architecture with a pseudo-4_1 screw axis. In this helical staircase, the aqua ligands *trans* to phenolic oxygen atoms (i.e., O11 and O13) point into the tube, normal to the helical axis. The NH and OH protons form hydrogen bonds to the carboxylate oxygen atoms along the surface of the helical staircase, as shown in Figure 2; hydrogen-bond parameters are given in Table 1.



H_3sglu

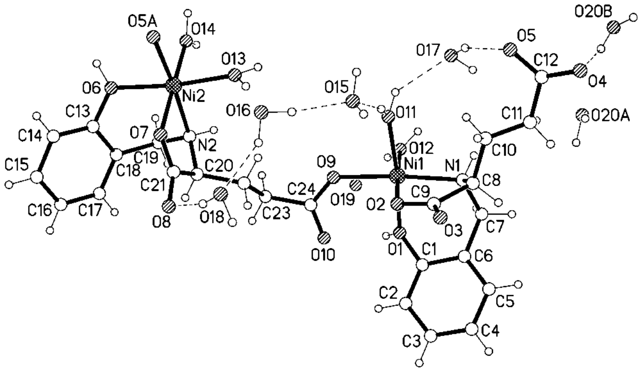


Figure 1. A view of the coordination environments at the two Ni^{II} centers in **1**. Selected bond lengths [Å]: Ni1-O(12) 2.043(4), Ni1-O2 2.047(4), Ni1-O(11) 2.051(4), Ni1-O(9) 2.059(3), Ni1-N1 2.084(4), Ni1-O1 2.089(4), Ni2-O(14) 2.039(4), Ni2-O(7) 2.042(4), Ni2-O(5) ($-x+1$, $y-\frac{1}{2}$, $-z+1$) 2.048(4), Ni2-O(13) 2.070(3) Ni2-N2 2.082(4), Ni2-O6 2.101(3).

The square-shaped chiral channel has dimensions of 7.654×7.529 Å (based on Ni···Ni distances; Figure 3). Of the six lattice water molecules present in the asymmetric unit, four are inside the helical pore, and two outside. Two of the former water molecules (O15 and O16, Figure 1) are hydrogen-bonded to produce a 1D helical polymer with a pseudo-4_1 screw axis. This helical water chain, as the pole of the helical staircase, supports and stabilizes its orientation by maintaining hydrogen bonding to aqua ligands. The other two water molecules (O17 and O18) propagate hydrogen bonding with both the helical water chain and the aqua ligands, and their hydrogen bonding tendency appears to have facilitated the positioning and orientation of the water molecules forming the helical chain.

The total solvent volume in the lattice, including that occupied by the helical-chain and lattice water molecules, is 405.1 $Å^3$ (22.7% of the unit cell).[14] All the tubular coordi-

---

[*] B. Sreenivasulu, Prof. J. J. Vittal
Department of Chemistry
National University of Singapore
Science Drive 3, Singapore 117543 (Singapore)
Fax: (+65) 6779-1691
E-mail: chmjjv@nus.edu.sg

[**] We thank the National University of Singapore for financial support (Grant No. R143-000-153-112).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200460516

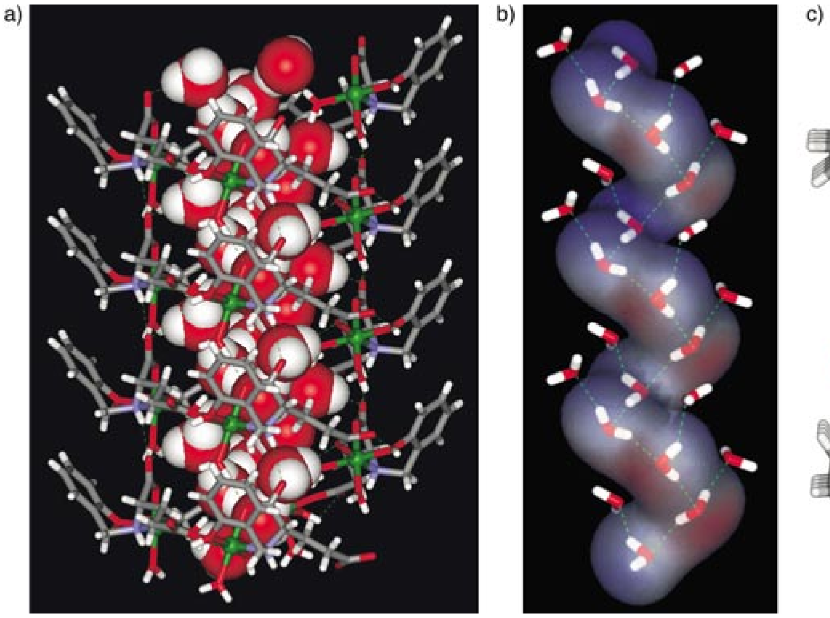


Figure 2. a) Hydrogen-bonded helical water chain inside the staircase coordination polymer in **1.** b) Hydrogen-bonded helical water stream in the channel. c) Top view of the staircase polymer filled with the helical water stream.

nation polymers are aligned along the *b* axis, and two more water molecules (O19 and disordered O20) occupy the empty space in the lattice outside the helical channels. The TG analysis of **1** revealed weight loss in the temperature range 26–232 °C. The total weight loss observed (21.6 %) agrees with the calculated value (22.5 %) for the loss of five water molecules per Ni atom. The single crystal crumbles on removal of water and on cooling to −50 °C.[15] The structure is not expected to be robust when dehydrated, because these coordination polymers are not supported by strong non-covalent interactions (Figure 3).

In contrast to **1**, in the crystal structure of [Cu(Hsglu)-(H_2O)]·H_2O (**2**)[16] the connectivity of the neighboring carboxylate oxygen atoms with Cu^{II} centers results in a 1D zigzag coordination polymer (Figure 4).

As in the majority of the supramolecular syntheses, self-assembly of metal ions and ligands resulted in the formation of single-, double-, triple-, and quadruple-stranded helical structures.[2] However, a helical chain inside a helical structure is very rare. Recently a hydrogen-bonded helical supramolecular host was found to be anchored by hydrogen bonding to alternate water molecules in a single-stranded, both right- and left-handed, helical chain of water molecules.[17] However, the structure of **1** has a hydrogen-bonded helix inside a helical 1D coordination polymer. This highly ordered helical stream of water molecules inside another helical polymer is striking and is a unique structural feature among existing porous helical structures[2c,18–20] and other patterns of water structures observed in diverse environments of inorganic[5,7] and organic hosts[3,4,9] and 2D supramolecular $(H_2O)_{12}$ rings.[21] Whereas designing chiral materials from achiral molecular compounds is a promising theme in materials science, using simple and available chiral precursors as an alternative is another practical approach. The structure of **1** exemplifies the feasibility of such an approach.[22]

In conclusion, the structure of the left-handed helical coordination polymer **1**

Table 1: Relevant hydrogen-bonding parameters in compound **1**.[a]

D−H⋯A	D−H [Å]	H⋯A [Å]	D⋯A [Å]	∡D−H⋯A [°]	Symmetry equivalent operators
O1−H1[b]⋯O10	0.93	2.14	2.484(5)	100	
N1−H1A[b]⋯O3	0.91	2.08	2.953(6)	161	$x, y+1, z$
N2−H2[b]⋯O8	0.91	2.06	2.937(6)	161	$x, y+1, z$
O6−H6[b]⋯O4	0.93	1.98	2.453(9)	109	$x-1, y-{}^{1}/_{2}, z$-1
O11−H11C⋯O15	0.89(3)	1.84(3)	2.713(6)	165(3)	
O11−H11D⋯O17	0.89(2)	2.10(3)	2.801(6)	135(4)	
O12−H12A⋯O2	0.89(2)	1.87(2)	2.745(5)	167(3)	$x, y+1, z$
O12−H12B⋯O19	0.90(3)	1.83(3)	2.695(9)	160(1)	
O13−H13A⋯O18	0.89(2)	2.03(3)	2.774(5)	141(4)	$x, y+1, z$
O13−H13B⋯O16	0.89(2)	1.84(2)	2.724(6)	172(2)	
O14−H14A⋯O20B	0.09(3)	2.35(5)	2.803(15)	111(3)	$x-1, y-{}^{1}/_{2}, z$-1
O14−H14B⋯O7	0.90(3)	1.99(4)	2.773(6)	145(5)	$x, y+1, z$
O15−H15A⋯O16	0.90(3)	1.92(4)	2.772(7)	158(4)	$x-1, y+{}^{1}/_{2}, z-1$
O15−H15B⋯O17	0.89(4)	1.86(4)	2.727(7)	163(5)	$x, y-1, z$
O16−H16A⋯O15	0.90(4)	1.88(4)	2.767(7)	169(4)	
O16−H16B⋯O18	0.90(5)	1.93(5)	2.732(7)	148(5)	
O17−H17A⋯O5	0.89(4)	2.26(4)	3.120(6)	162(4)	
O17−H17A⋯O13	0.89(4)	2.35(3)	2.943(6)	124(3)	$x-1, y+{}^{1}/_{2}, z-1$
O17−H17B⋯O3	0.90(4)	1.99(4)	2.842(6)	157(4)	$x, y+1, z$
O18−H18A⋯O8	0.90(3)	1.86(3)	2.729(6)	164(4)	
O18−H18B⋯O9	0.89(4)	2.11(4)	2.996(6)	161(3)	$x, y-1, z$
O18−H18B⋯O11	0.89(4)	2.49(4)	3.011(5)	118(3)	$x, y-1, z$
O20B−H20C⋯O4	0.90(4)	2.26(3)	3.035(15)	145(4)	

[a] A = acceptor, D = donor. [b] The hydrogen atoms have been placed in the calculated positions.

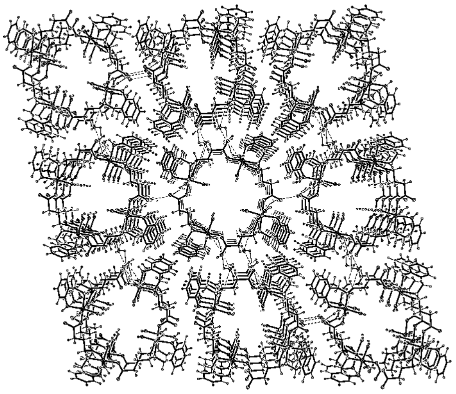


Figure 3. Packing of the staircase polymer viewed along the *b* axis. The water molecules in the channels are omitted for clarity.

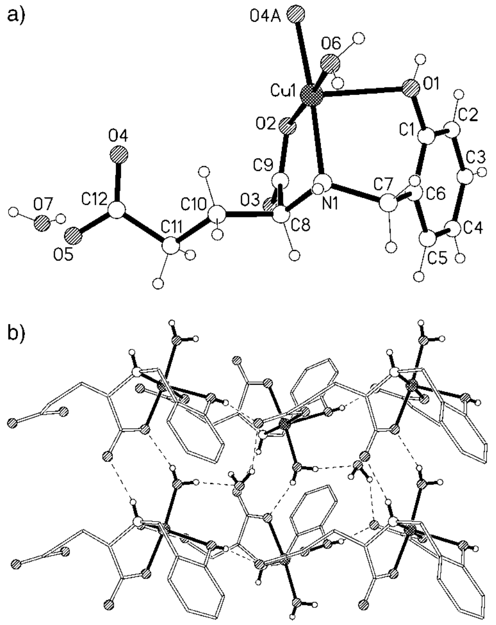


Figure 4. a) A view showing the coordination environment of Cu^{II} in **2**. Selected bond lengths [Å]: Cu1-O4 1.921(1), Cu1-O6 1.964(2), Cu1-O2 1.969(1), Cu1-N1 1.978(2), Cu1-O1 2.345(2). b) A portion of the 2D sheets formed by hydrogen bonding between the zigzag coordination polymer.

encapsulating a hydrogen-bonded helical stream of water molecules exhibits novel cooperative assembly and recognition of water molecules in the inorganic crystal host. These results exemplify the maxim that the structural constraints acting on the orientation of water by its surroundings and vice versa can be very significant. The captivating structure of **1**, in which a helical chain of water molecules supports a helical coordination polymer staircase, suggests another fascinating model for the water chains in membrane aquaporin proteins for the transport of water or protons, and it appears to be extremely rare among metal coordination polymers till now.[23] The 1D zigzag coordination polymeric structure containing the same ligand in **2** demonstrates that the overall topology depends on the nature of the metal and the coordination geometry at the metal centers.

Experimental Section

H_3sglu: Salicylaldehyde (0.57 g, 4.7 mmol) was added to a solution of L-glutamic acid (0.69 g, 4.7 mmol) and NaOH (0.37 g, 9.4 mmol) in MeOH/H_2O (v/v (1:1), 20 mL), and the resulting yellow solution was stirred for 30 min and cooled in an ice bath prior to reduction with a slight excess of $NaBH_4$ (0.19 g, 5.1 mmol). The yellow color disappeared immediately, and stirring was continued for a further 20 min. The pH of the mixture was adjusted to 5–6 by adding acetic acid, and it was to stirred for a further 45 min. The solvent from the resulting clear solution was completely removed on a rotary evaporator. The sticky mass was treated with EtOH (25 mL). The white product was collected by filtration, washed with EtOH and Et_2O, and dried under vacuum. Yield: 0.85 g (71 %). M.p. 247–248 °C (decomp). Elemental analysis (%) calcd for $C_{12}H_{15}NO_5$: C 56.9, H 5.9, N 5.5; found: C 56.4, H 5.8, N 5.6. ^1H NMR (300 MHz, D_2O): $\delta =$ 6.78–7.27 (m, 4H, ArH), 3.92–4.12 (m, $J_{AB} = 13.2$ Hz, 2H, CH_2), 3.36–3.55 (t, $J = 6.42$ Hz, 1H, CH), 2.24–2.30 (t, $J = 8.4$ Hz, 2H, CH_2), 2.0–2.02 ppm (m, $J = 6.4$ Hz, 2H, CH_2). IR (KBr): $\tilde{\nu} = 3460$ (OH), 2960 (NH), 1573, 1388 (COO^-), 1276 cm^{-1} (phenolic CO).

1: A clear solution of H_3sglu (0.25 g, 1 mmol) in water (2.5 mL) was allowed to diffuse slowly into a clear solution of nickel nitrate hexahydrate (0.29 g, 1 mmol) in water (2.5 mL). Greenish rodlike crystals suitable for X-ray diffraction studies were obtained after one week from the solution on slow evaporation. Yield: 0.28 g (70 %). Elemental analysis (%) calcd for $C_{12}H_{23}NNiO_{10}$: C 36.0, H 5.8, N 3.5; found: C 36.2, H 5.6, N 3.7. IR (KBr): $\tilde{\nu} = 3368$ (OH), 2746 (NH), 1623, 1348 (COO^-), 1253 cm^{-1} (phenolic CO). UV/Vis (Nujol): $\lambda_{max} =$ 385 (CT), 737 nm (d–d). TGA: weight loss (%) calcd for 5 H_2O: 22.5; found: 21.6.

2: A clear solution of H_3sglu (0.25 g, 1 mmol) in water (2.5 mL) was allowed to diffuse slowly into a clear solution of copper nitrate trihydrate (0.24 g, 1 mmol) in water (2.5 mL). Dark blue blocks suitable for single-crystal X-ray diffraction studies were obtained after 1 d. Yield: 0.26 g (74 %). Elemental analysis (%) calcd for $C_{12}H_{17}CuNO_7$: C 41.0, H 4.9, N 4.0; found: C 40.7, H 4.8, N 4.2. IR (KBr): $\tilde{\nu} = 3429$ (OH); 3118 (NH); 1650, 1429 (COO^-), 1262 cm^{-1} (phenolic CO). UV/Vis (Nujol): $\lambda_{max} = 285$ (CT), 613 nm (d–d). TGA: weight loss calcd for 2 H_2O: 10.4; found: 10.8.

Received: April 30, 2004
Revised: July 8, 2004

Keywords: coordination polymers · host–guest systems · hydrogen bonds · nickel · supramolecular chemistry

---

[1] a) J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinhein, **1995**; b) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457; c) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005; d) M. J. Hannon, L. J. Childs, *Supramol. Chem.* **2004**, *16*, 7.

[2] a) O. Mamula, A. von Zelewsky, T. Bark, G. Bernardinelli, *Angew. Chem.* **1999**, *111*, 3129; *Angew. Chem. Int. Ed.* **1999**, *38*, 2945; b) C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton, A. H. White, *Angew. Chem.* **1998**, *110*, 970; *Angew. Chem. Int. Ed.* **1998**, *37*, 920; c) D. A. McMorran, P. J. Steel, *Angew. Chem.* **1998**, *110*, 3295; *Angew. Chem. Int. Ed.* **1998**, *37*, 3295; d) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, *Chem. Eur. J.* **1999**, *5*, 1862; e) M. J. Hannon, C. L. Painting, N. W. Alcock, *Chem. Commun.* **1999**, 2023.

[3] J. N. Moorthy, R. Natarajan, P. Venugopalan, *Angew. Chem.* **2002**, *114*, 3567; *Angew. Chem. Int. Ed.* **2002**, *41*, 3417.

[4] R. Custelcean, C. Afloroaei, M. Vlassa, M. Polverejan, *Angew. Chem.* **2000**, *112*, 3224; *Angew. Chem. Int. Ed.* **2000**, *39*, 3094.

[5] W. B. Blanton, S. W. Gordon-Wylie, G. R. Clark, K. K. Jordon, J. T. Wood, U. Geiser, T. J. Collins, J. *Am. Chem. Soc.* **1999**, *121*, 3551.

[6] J. T. Atwood, L. J. Barbour, T. J. Ness, C. L. Ratson, P. L. Ratson, *J. Am. Chem. Soc.* **2001**, *123*, 7192.

[7] a) L. J. Barbour, W. G. Orr, J. L. Atwood, *Nature* **1998**, *393*, 671; b) L. J. Barbour, W. G. Orr, J. L. Atwood, *Chem. Commun.* **2000**, 859.

[8] K. Raghuraman, K. K. Katti, L. J. Barbour, N. Pillarsetty, C. L. Barnes, K. V. Katti, *J. Am. Chem. Soc.* **2003**, *125*, 6955.

[9] a) L. Infantes, J. Chisholm, S. Motherwell, *CrystEngComm* **2003**, *5*, 480; b) L. Infantes, S. Motherwell, *CrystEngComm* **2002**, *4*, 454.

[10] a) L. E. Cheruzel, M. S. Pometun, M. R. Cecil, M. S. Mashuta, R. J. Wittebort, R. M. Buchanan, *Angew. Chem.* **2003**, *115*, 5610; *Angew. Chem. Int. Ed.* **2003**, *42*, 5452; b) S. Pal, N. B. Sankaran, A. Samanta, *Angew. Chem.* **2003**, *115*, 1783; *Angew. Chem. Int. Ed.* **2003**, *42*, 1741.

[11] See, for example, a) B. Zhao, P. Cheng, X. Chen, C. Cheng, W. Shi, D. Liao, S. Yan, Z. Jiang, *J. Am. Chem. Soc.* **2004**, *126*, 3012; b) Y. B. Dong, X. Zhao, B. Tang, H. Y. Wang, R. Q. Huang, M. D. Smith, H. C. zur Loye, *Chem. Commun.* **2004**, 220; c) W. Runde, A. C. Bean, B. L. Scott, *Chem. Commun.* **2003**, 1848.

[12] a) R. Ludwig, *Angew. Chem.* **2001**, *113*, 1856; *Angew. Chem. Int. Ed.* **2001**, *40*, 1808; b) D. Konozo, M. Yasui, L. S. King, P. Agre, *J. Clin. Invest.* **2002**, *109*, 1395; c) B. Roux, R. MacKinnon, *Science* **1999**, *285*, 100; d) U. Buck, F. Huisken, *J. Am. Chem. Soc.* **2000**, *100*, 3863.

[13] K. Mitsuoka, K. Murata, T. Walz, T. Hirai, P. Agre, J. B. Heymann, A. Engel, Y. Fujiyoshi, *J. Struct. Biol.* **1999**, *128*, 34.

[14] Crystal data of **1**: $C_{12}H_{23}NNiO_{10}$, monoclinic, space group $P2_1$, $a = 17.135(1)$, $b = 6.1945(4)$, $c = 17.160(1)$ Å, $\beta = 101.220(2)°$, $V = 1786.6(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.487\ g\,cm^{-3}$. In the final least-squares refinement cycles on $|F|^2$, the model converged at $R_1 = 0.0500$, $wR_2 = 0.1191$, and GOF = 1.050 for 5179 reflections with $F_o > 4\sigma(F_o)$ and 485 parameters. The Flack parameter was refined to −0.004(16); A. L. Spek, *Acta Crystallogr. A* **1990**, *46*, C34.

[15] Several initial attempts to collect the X-ray data at low temperature failed due to this phenomenon.

[16] Crystal data of **2**: $C_{12}H_{17}CuNO_7$, monoclinic, space group $P2_1$, $a = 5.9362(2)$, $b = 10.1204(4)$, $c = 11.9417(4)$ Å, $\beta = 94.377(1)°$, $V = 715.33(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.629\ g\,cm^{-3}$. In the final least-squares refinement cycles on $|F|^2$, the model converged at $R_1 = 0.0288$, $wR_2 = 0.0763$, and GOF = 1.053 for 2844 reflections with $F_o > 4\sigma(F_o)$ and 209 parameters. Data for **1** and **2** were collected on a Bruker APEX diffractometer equipped with a CCD detector and graphite-monochromated $Mo_{K\alpha}$ radiation from a sealed tube (2.4 kW) at 296(2) K. Absorption corrections were made with the program SADABS,[24] and the crystallographic package SHELXTL[25] was used for all calculations. CCDC-236742 (**1**) and CCDC-236743 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[17] A. Mukherjee, M. K. Saha, M. Nethaji, A. R. Chakravarty, *Chem. Commun.* **2004**, 716.

[18] C. D. Wu, C. Z. Lu, X. Lin, D. M. Wu, S. F. Lu, H. H. Zhuang, J. S. Huang, *Chem. Commun.* **2003**, 1284.

[19] A. L. Pickering, G. Seeber, D. L. Long, L. Cronin, *Chem. Commun.* **2004**, 136.

[20] C. D. Wu, C. Z. Lu, S. F. Lu, H. H. Zhuang, J. S. Huang, *Dalton Trans.* **2003**, 3192.

[21] B. Q. Ma, H. L. Sun, S. Gao, *Angew. Chem.* **2004**, *116*, 1398; Angew. *Chem. Int. Ed.* **2004**, *43*, 1374.

[22] B. Moulton, M. J. Zaworotko in *Crystal Engineering: From Molecules and Crystals to Materials* (Eds.: D. Braga, F. Grepioni, A. G. Orpen), Kluwer, Dordrecht, **1999**, p. 311.

[23] a) C. Schmuck, *Angew. Chem.* **2003**, *115*, 2552; *Angew. Chem. Int. Ed.* **2003**, *42*, 2448; b) A. E. Rowan, R. J. M. Nolte, *Angew. Chem.* **1998**, *110*, 65; *Angew. Chem. Int. Ed.* **1998**, *37*, 63.

[24] G. M. Sheldrick, SADABS, Software for empirical absorption corrections, University of Göttingen, Germany, **2000**.

[25] SHELXTL Reference Manual, Version 5.1, Bruker AXS, Analytical X-Ray Systems, Inc., Madison, WI, USA, **1997**.