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Self-assembly of a one-dimensional iron(II) coordination polymer with *p*-phenylenebis(picolinaldimine)

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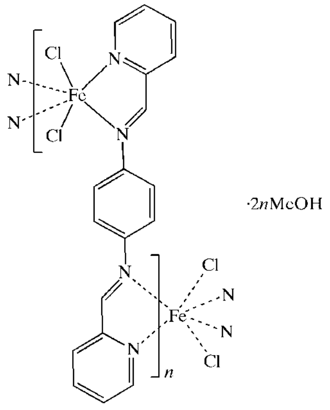
catena-Poly[[[dichloridoiron(II)]-μ-*N*,*N'*-bis(2-pyridylmethylene)benzene-1,4-diamine] methanol disolvate], $[FeCl_2(C_{18}H_{14}N_4)]\cdot 2CH_3OH$, forms a one-dimensional coordination polymer. The polymeric chains run parallel to the *c* axis. O—H$\cdots$Cl—Fe and C—H$\cdots$O hydrogen-bonding interactions with methanol solvent molecules stabilize the open supramolecular framework. Each Fe^{II} atom adopts an octahedral geometry coordinated by four N atoms from two *N*,*N'*-bis(2-pyridylmethylene)benzene-1,4-diamine ligands and completed by two *cis* Cl atoms. The compound has C_2 (and C_i) molecular symmetry, which is coincident with the crystallographic twofold symmetry at (0, *y*, $\frac{1}{4}$). The one-dimensional structure is propagated *via* the crystallographic inversion center located at the benzene ring centroid (0, $\frac{1}{2}$, 0).

Comment

A fundamental concept in inorganic supramolecular chemistry is the use of transition metal units (referred to as nodes) and polypyridyl molecules as bridging spacers to construct a vast array of multi-dimensional networks (Moulton & Zaworotko, 2001; Blake *et al.*, 1999; Balzani & Juris, 2001). Exploiting the different coordination geometries that transition metal complexes can adopt and varying the spacer unit are two ways to influence which molecular or network architecture may be observed. Fine tuning the stability and utility of these materials in applications such as molecular devices, sensors and catalysts can in part be accomplished through intra- and intermolecular interactions, such as π–π stacking, halogen bonding and hydrogen bonding (for example, Beatty, 2001; Braga *et al.*, 2005; Brammer, 2003).

The present work stems from our interest in developing complexes with interesting photophysical and photochemical properties. In one study, we investigated the binding properties of two pyridine-substituted ligands, namely 4,16-bis(picolinaldimine)bis[2.2]paracyclophane (bppc) and *p*-phenylenebis(picolinaldimine) (pbp) (Ball *et al.*, 2004). We describe here the self-assembly and structure of an iron(II) polypyridyl coordination polymer, (pbp)FeCl$_2$ as a methanol solvate, (I).



(I)

The molecular subunit (Fig. 1) forms the basis of the one-dimensional polymer shown in Fig. 2(*a*). The compound has C_2 molecular symmetry, which is coincident with the crystallographic twofold symmetry (0, *y*, $\frac{1}{4}$). The one-dimensional structure is propogated *via* the crystallographic inversion center located at the benzene ring centroid (0, $\frac{1}{2}$, 0). Each Fe^{II} atom adopts an octahedral geometry involving four coordinated N atoms from two pbp ligands and two *cis* Cl atoms. The pbp ligand is twisted; the mean plane of the pyridyl (py) ring is at a 49.08 (10)° angle to that of the benzene ring. Such twisting of the pbp backbone appears to be common (Shavaleev *et al.*, 2003; Wu *et al.*, 2006). The Fe—N$_{py}$ bond [2.177 (2) Å] is shorter than the Fe—N$_{imino}$ bond [2.257 (2) Å; Table 1], consistent with related iron–polypyridyl complexes (Small *et al.*, 1998; Britovsek *et al.*, 1999). Furthermore, the imino linkage, N2=C6, maintains double-bond character with a distance of 1.278 (4) Å [the distance in pbp is 1.273 (2) Å; Ball *et al.*, 2004]. Similarly, $[pbpZn(DMF)_2]_n(ClO_4)_{2n}\cdot nDMF$

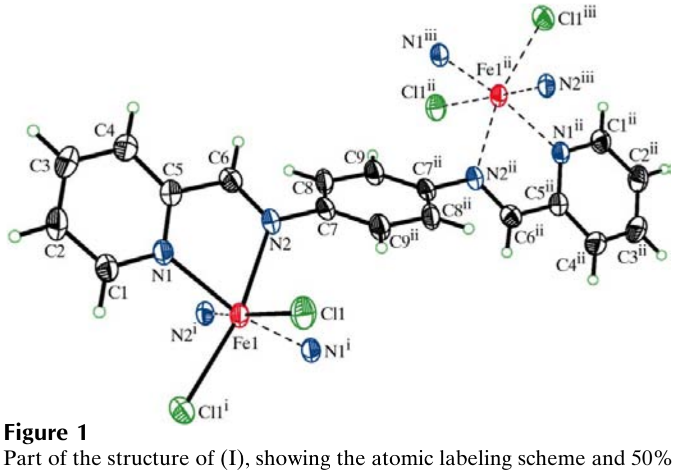


Figure 1
Part of the structure of (I), showing the atomic labeling scheme and 50% probability displacement ellipsoids. The disordered methanol solvent molecule is not shown. [Symmetry codes: (i) $-x, y, -z+\frac{1}{2}$; (ii) $-x, -y+1, -z$; (iii) $x, -y+1, -\frac{1}{2}+z$.]

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(DMF is dimethylformamide) is a one-dimensional zigzag coordination polymer with a six-coordinate Zn^{II} center (Yoshida *et al.*, 2000). The average Zn—N distances are 2.142 and 2.253 Å for the pyridyl and imine bonds, respectively. Self-assembly of $AgClO_4$ with pbp has been reported by Wu *et al.* (2006) to also form a one-dimensional polymeric array with Ag^I in a distorted tetrahedral environment. Although it appears that the pbp ligand promotes a polymeric extended bonding motif, this is not always the case. In the dinuclear complex $[\{(\eta^6\text{-}C_{10}H_{14})RuCl\}_2(\mu\text{-pbp})]BF_4$, the 'piano-stool' Ru–arene units are *trans* disposed with respect to the pbp ligand (Singh *et al.*, 2004).

Little interaction between the neighboring zigzag chains in (I) is observed. The chains are parallel with a separation of 8.2276 (11) Å (between planes drawn through the Fe atoms in a chain). As a result, a relatively open framework is adopted, with cavity sizes suitable for small guest molecule incorporation (Moulton & Zaworotko, 2001). The estimated void space occupied by the disordered methanol molecule is 98 Å^3 (Spek, 2003), with cavity dimensions of approximately 4.6 (1) × 8.7 (1) Å (between the *ortho* C atoms of the benzene group which face the interior of the cavity). Hydrogen bonds within our one-dimensional architecture primarily involve the methanol molecule residing in the cavity (Fig. 2*b*). The O—H···Cl—Fe interaction (see Table 2) is considered strong according to the classification of Aullón *et al.* (1998). A pair of C—H···O and C—H···Cl interactions lend stability to the overall extended structure.

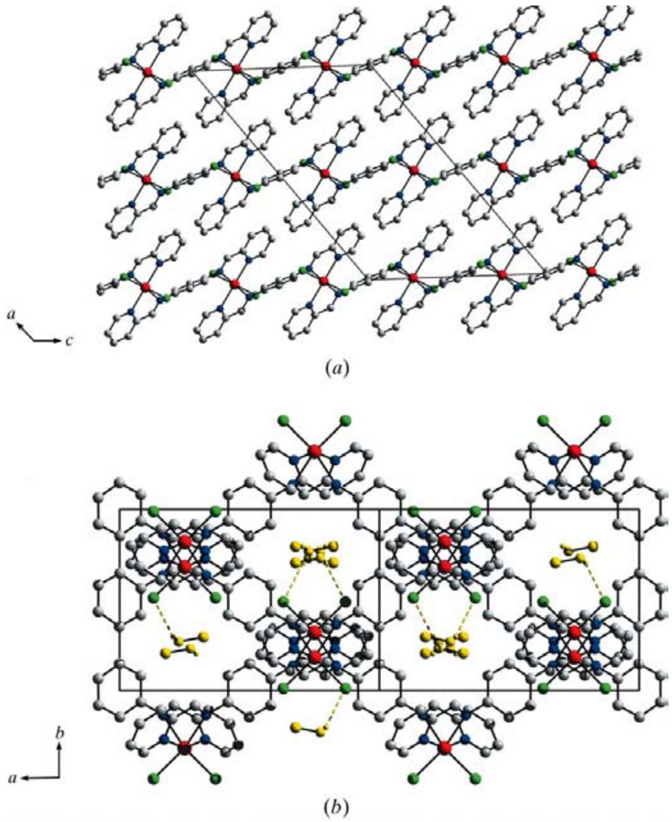

Figure 2
(*a*) The one-dimensional polymeric chain running parallel to the *c* axis. (*b*) Methanol solvent molecules (major conformer only, shown in yellow in the electronic version of the paper) fills the cavities; O—H···Cl—Fe interactions are shown as dashed lines and only the hydroxyl H atom of the methanol molecules are shown.

Experimental

The pbp ligand was prepared according to the method of Haga & Koizumi (1985). A bright-yellow solution of $FeCl_3\cdot 6H_2O$ (0.0371 g, 0.14 mmol) in methanol (5 ml) was layered over a pale-yellow solution of pbp (0.0207 g, 0.072 mmol) in dichloromethane (5 ml) in a test tube. The test tube was covered with Parafilm. After approximately a week, dark-red microcrystals of (I) suitable for X-ray analysis were formed.

Crystal data

$[FeCl_2(C_{18}H_{14}N_4)]\cdot 2CH_4O$
$M_r = 477.17$
Monoclinic, $C2/c$
$a = 20.646$ (3) Å
$b = 9.3893$ (13) Å
$c = 13.4869$ (19) Å
$\beta = 128.152$ (3)°
$V = 2055.9$ (5) Å^3
$Z = 4$
Synchrotron radiation
$\lambda = 0.77500$ Å
$\mu = 1.28$ mm^{-1}
$T = 173$ (2) K
0.04 × 0.03 × 0.01 mm

Data collection

Bruker Platinum 200 diffractometer
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{min} = 0.957$, $T_{max} = 0.987$
14014 measured reflections
2546 independent reflections
2096 reflections with $I > 2\sigma(I)$
$R_{int} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.126$
$S = 1.05$
2546 reflections
131 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.77$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—N1	2.177 (2)	Fe1—Cl1	2.4040 (8)
Fe1—N2	2.257 (2)		
$N1^i$—Fe1—N1	156.38 (13)	N1—Fe1—Cl1	100.57 (6)
N1—Fe1—$N2^i$	87.79 (8)	$N2^i$—Fe1—Cl1	167.39 (6)
N1—Fe1—N2	74.21 (8)	N2—Fe1—Cl1	91.87 (6)
$N2^i$—Fe1—N2	81.25 (12)	$Cl1^i$—Fe1—Cl1	96.73 (4)
N1—Fe1—$Cl1^i$	95.08 (6)		

Symmetry code: (i) $-x, y, -z+\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O10*A*—H10···Cl1	0.93	2.41	3.073 (6)	128
O10*B*—H10···Cl1	0.78	2.41	3.167 (15)	163
C1—H1···$Cl1^{iv}$	0.95	2.83	3.443 (3)	123
C6—H6···$O10B^v$	0.95	2.46	3.091 (16)	125

Symmetry codes: (iv) $-x, y, -z+\frac{1}{2}$; (v) $x, y+1, z$.

The methanol solvent molecule is disordered at the O atom. The C—O distances (C10—O10*A* and C10—O10*B*) were restrained to be similar. The refined occupancy of the major conformer is 71 (1)%. The O atoms were refined isotropically with the displacement parameters restrained to be equivalent. Hydroxy atom H10 was located directly from a difference map and its position was held fixed (AFIX 1) in subsequent refinements. The remaining H atoms were placed in calculated positions and treated with a riding model (aromatic C—H = 0.95 Å and methyl C—H = 0.98 Å). The isotropic displacement parameters for all H atoms were defined as aU_{eq} of the adjacent atom (a = 1.5 for hydroxy and a = 1.2 for all other H atoms).

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3097). Services for accessing these data are described at the back of the journal.

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