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Bis(isonicotinato)iron(II): a rare, neutral three-dimensional iron coordination polymer

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The reaction of iron(III) perchlorate with 4-pyridinecarbaldehyde under hydro(solvo)thermal conditions affords bis(isonicotinato)iron(II) 1, in which both pyridine and carboxylate groups coordinate to iron centers resulting in an unprecedented neutral, three-dimensional polymeric network with a carboxylate-bridged Fe–Fe infinite chain.

Coordination polymers with one-, two-, and three-dimensional infinite frameworks have been actively sought in recent years owing to their potential applications as magnetic materials,[1] zeolite analogues,[2] and catalysts.[3] Research effort in this area has so far been mostly focused on coordination polymers with either neutral donor ligands (*e.g.*, 4,4′-bipyridine)[4] or strictly anionic groups (*e.g.*, carboxylates).[5] Very little is known about coordination polymers with multifunctional ligands in which both neutral and anionic donor groups are present and can coordinate to metal centers potentially resulting in neutral polymeric structures. We report here the synthesis and characterization of bis(isonicotinato)iron(II), a rare, neutral three-dimensional iron coordination polymer. In this three-dimensional network, the isonicotinate group acts as a bifunctional ligand by coordinating to Fe(II) centers through both carboxylate and pyridine functional groups. Iron(II) coordination polymers are also of great interest because they can exhibit interesting spin crossover phenomena if the coordinating ligands have suitable ligand field strength.[6]

Bis(isonicotinato)iron(II) **1** was synthesized by a hydro(solvo)thermal reaction between $Fe(ClO_4)_3\cdot 6H_2O$ and 4-pyridinecarbaldehyde.† In this reaction, Fe(III) centers were reduced to Fe(II), while 4-pyridinecarbaldehyde was oxidized to isonicotinic acid. The presence of carboxylate groups in **1** was suggested by the strong peaks at 1611, 1552, and 1405 cm^{-1} (C=O stretching) in the infrared spectrum. Additionally, the IR spectrum indicated that no perchlorate group is present in **1**.

The three-dimensional polymeric structure of **1** was revealed by an X-ray single crystal diffraction study.‡ The coordination geometry around the Fe(II) center in **1** is a slightly distorted octahedron (Fig. 1). The Fe(II) center is bonded to four oxygen atoms from four different isonicotinate ligands, and to two pyridine nitrogen atoms from two isonicotinate moieties; these oxygen and nitrogen atoms are related by an inversion center lying at the Fe ion.[7] The four oxygen atoms bind to the Fe(II) center equatorially, while the two pyridine nitrogen atoms bind to the Fe(II) center in axial positions. All the Fe–O [2.074(1) and 2.142(1) Å] and Fe–N [2.198(2) Å] bond distances are normal. The bond angles around the Fe center range from 86.9(1) to 93.1(1)°, and deviate no more than 3.1° from those expected for an ideal octahedron. The iron center is bridged by four carboxylate groups to two adjacent iron centers to result in an infinite Fe–Fe chain along the crystallographic *a* axis (Fig. 1). Two adjacent iron centers in this infinite chain form an eight-membered ring with two bridging carboxylate groups. Each carboxylate group of the isonicotinate ligand bridges two iron centers in a *syn-anti* fashion.[8] Consequently, if the central carbon of the carboxylate group is omitted, the two iron and four oxygen atoms in the ring are not coplanar; they instead adopt a chair-like conformation (Fig. 1). The Fe–O_{syn} bond length of 2.074(1) Å is slightly shorter than the Fe–O_{anti} bond length of 2.142(1) Å, probably as a result of the higher basicity of the lone pair in the *syn* carboxylate oxygen.[8] This *syn-anti* carboxylate bridging structure is very rare, and the Fe–Fe distance of 4.954 Å in **1** is significantly longer than those of known diiron complexes with *syn-anti* carboxylate bridging groups; the previously reported longest Fe–Fe distance in a *syn-anti* carboxylate bridged diiron complex is 4.612(3) Å.[9] Although there are numerous transition metal carboxylate complexes in the literature, to our knowledge, such a doubly carboxylate-bridged, infinite chain with a *syn-anti* conformation has not been previously observed.

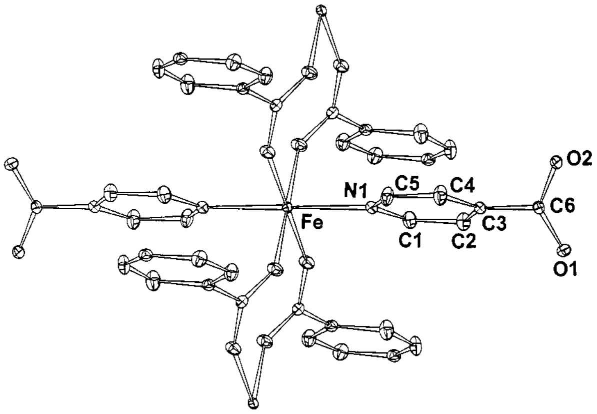

Fig. 1 An ORTEP[12] drawing showing the coordination geometry of the iron(II) center in **1** (30% probability). The asymmetric unit is labeled.

The most striking feature of **1** is, however, the connection of the doubly carboxylate-bridged, infinite Fe–Fe chain to the four adjacent Fe–Fe chains by isonicotinate groups to form a three-dimensional network (Fig. 2). The Fe–Fe chains are connected to each other along the (0 1 1) and (0 −1 1) planes. In the (0 1 1) planes, the Fe–Fe chain is connected to two neighboring Fe–Fe chains with the pyridine ends of the isonicotinate groups. In the (0 −1 1) planes, the Fe–Fe chain is connected to two other neighboring Fe–Fe chains with the carboxylate groups of the isonicotinate ligands. Therefore, **1** adopts a very regular three-dimensional network structure *via* coordination of iron centers to both pyridine and carboxylate functionalities of isonicotinate groups. A perspective view of **1** down the *a* axis is shown in Fig. 3. The centroid-to-centroid distance between adjacent pyridyl rings is rather long at 4.95 Å; there are thus no π–π interactions between the pyridyl rings. Compound **1** does not have any cavity accessible to solvent molecules. This represents the first example of a neutral transition metal isonicotinate with both pyridine and carboxylate functionalities coordinating to the metal centers.[10,11]

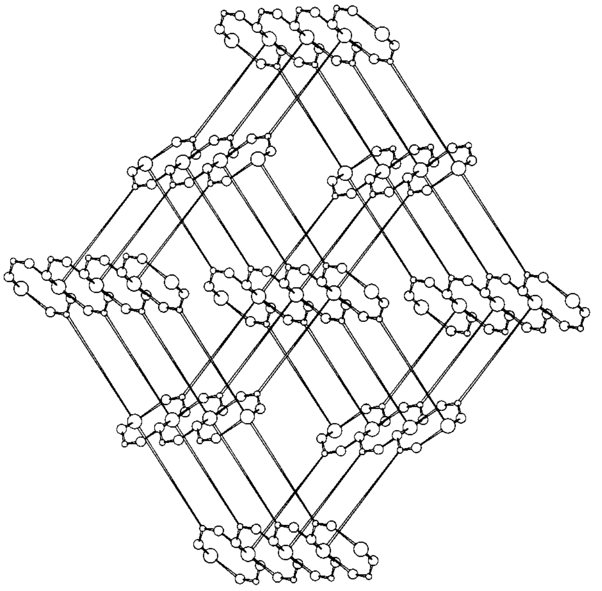

Fig. 2 Diagram illustrating the connectivity between different Fe chains doubly bridged by the carboxylate end of the isonicotinate group. For clarity, the pyridine ring of the isonicotinate group is represented with a straight line. The open circles with increasing sizes are C, O, and Fe, respectively.

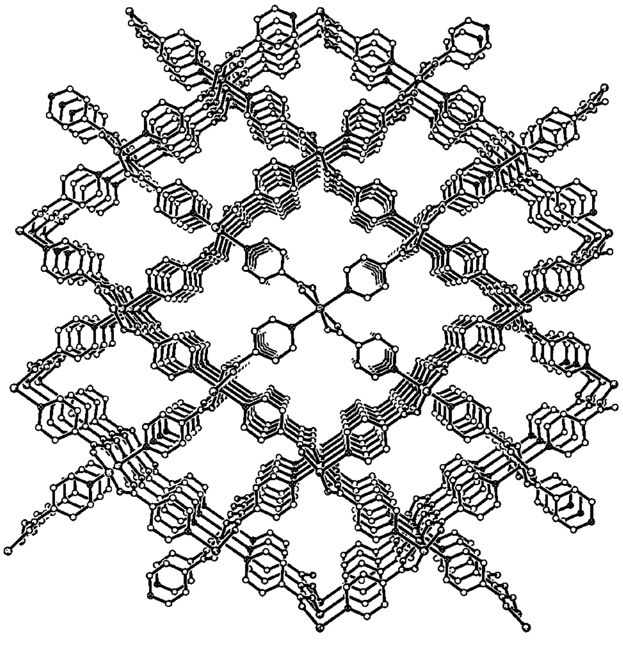

Fig. 3 A perspective view of **1** down the *a* axis. Open circles: carbon; hatched circles: nitrogen; dotted circles: oxygen and iron.

In summary, we have synthesized a rare, neutral three-dimensional iron coordination polymer using a hydro(solvo)-thermal method. Preliminary magnetic measurements indicate that **1** is low-spin up to 375 K. The synthesis of other coordination polymers with isonicotinate building blocks is currently under investigation.

Acknowledgements

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Notes and references

† Preparation of $Fe(C_7H_4NO_2)_2$: a heavy walled Pyrex tube containing a mixture of $Fe(ClO_4)_3 \cdot 6H_2O$ (0.18 g, 0.5 mmol) and 4-pyridinecarbaldehyde (0.14 mL, 1.5 mmol) in ethanol (0.3 mL) and H_2O (0.07 mL) was frozen and sealed under vacuum and placed inside an oven at 110 °C. Orange-red rodlike crystals were obtained after 24 hours of heating. Yield: 0.08 g (49.4%). IR (KBr, cm^{-1}): 1611 (vs), 1552 (s), 1405 (vs), 1217 (w), 1064 (w), 1018 (w), 875 (vw), 845 (w), 781 (m), 709 (w), 678 (m), 558 (vw).

‡ Crystal data for **1**: $C_{14}H_8N_2O_4Fe$, monoclinic, space group $P2_1/n$ (no. 14), $a = 4.9544(1)$, $b = 13.2443(2)$, $c = 10.4983(1)$ Å, $\beta = 101.586(1)°$, $V = 674.84(2)$ Å^3, $M = 300.05$, $F(000) = 304$, $Z = 2$, $D_c = 1.477$ g cm^{-3}, $T = 198(2)$ K, μ(Mo-Kα) = 11.3 cm^{-1}, λ(Mo-Kα) = 0.71073 Å. An orange crystal of approximate dimensions 0.60 × 0.08 × 0.04 mm was mounted on a SMART CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation. The crystal was twinned, and two distinct orientations were identified and integrated. The structure solution was carried out with non-overlapped reflections, while the refinement was by full-matrix least squares on F^2 with both non-overlapped and completely overlapped reflections. Final $R1$, $wR2$, and S are 0.057, 0.163, and 1.167 for 5981 reflections with $I > 2\sigma(I)$ out of 7105 unique reflections. CCDC reference number 186/1239. See http://www.rsc.org/suppdata/dt/1998/4089/ for crystallographic files in .cif format.

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