

A novel oxo-centred, trinuclear iron nicotinato complex: Fe₃(O)(C₆NO₂H₅)₆(H₂O)₃·3H₂O·7Cl

Wentong Chen*

School of Chemistry and Chemical Engineering, Jiangxi Province Key Laboratory of Coordination Chemistry, Jingtangshan University, Ji'an, Jiangxi 343009, P. R. China

Hydrothermal reaction of FeCl₃ and nicotinic acid gave a novel, trinuclear metal-nicotinato complex Fe₃(O)(C₆NO₂H₅)₆(H₂O)₃·3H₂O·7Cl. An X-ray crystal structure analysis reveals that it features an isolated structure. The crystal belongs to the rhombohedral, space group *R*-3*c* with *a* = *b* = 19.9410(6) Å, *c* = 30.505(1) Å, *V* = 10504.9(6) Å³, *Z* = 6, C₃₆H₄₂Cl₇Fe₃N₆O₁₉, *M_r* = 1278.46, *D_c* = 1.213 g cm⁻³, *S* = 0.980, μ(MoKα) = 0.936 mm⁻¹, *F*(000) = 3894, *R* = 0.0694 and *wR*² = 0.1579. The iron atom has a slightly distorted octahedral geometry, coordinated by six oxygen atoms. All three octahedrons interconnect to each other *via* corner-sharing an oxygen atom, yielding an oxo-centred, trinuclear iron cluster. The [Fe₃(O)(C₆NO₂H₅)₆(H₂O)₃]⁷⁺ species, lattice water molecules and chloride ions are held together *via* hydrogen bonds to construct a three-dimensional (3-D) open framework, with a large void space (2803.9 Å³) corresponding to 26.7% of the unit-cell volume (10504.9 Å³).

Keywords: crystal structure, hydrothermal reaction, iron, nicotinic acid, supramolecular chemistry

Supramolecular chemistry is of great interest in the design of new solid materials because it takes advantage of self-assembly to synthesise new materials by virtue of weak cooperative interactions such as aromatic π–π stacking interactions, ion–ion interactions, hydrogen bonding, dipole–dipole interactions, and ion–dipole interactions to connect subunits together and many supramolecular materials have been prepared.^{1,2} Zeolitic materials with open framework have gained increasing attention in supramolecular chemistry due to their variable applications as molecular sieves, catalysts, biosensors, *etc.*³ Especially, organic and coordination zeolitic materials have gained much interest because they exhibit some specific functions that are not available with inorganic zeolitic materials. However, only a few zeolitic materials with 3-D open frameworks have been documented.⁴ Therefore, the design and preparation of such materials are still a challenge. We have been exploring methods to prepare new coordination zeolitic materials by hydrothermal reaction, which is a powerful technique in such syntheses. Furthermore, nicotinate anions are quite interesting tectons in constructing supramolecular and extended structures because they are unsymmetrical divergent ligands that can link two metal centres by coordinating to one metal centre with the nitrogen atom and, to the other one, with one or two carboxylato-oxygen atoms.⁵ We report here the hydrothermal synthesis and crystal structure of an oxo-centred, trinuclear, iron nicotinato-complex: Fe₃(O)(C₆NO₂H₅)₆(H₂O)₃·3H₂O·7Cl (**1**), which possesses a 3-D supramolecular open framework.

Experimental

All reactants of A.R. grade were obtained commercially and used without further purification.

Fe₃(O)(C₆NO₂H₅)₆(H₂O)₃·3H₂O·7Cl (1**):** Prepared by mixing FeCl₃ (1 mmol, 162.2 mg), nicotinic acid (2 mmol, 246.2 mg) and distilled water (10 mL) in a 23 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 10 days. After being slowly cooled to room temperature at 6 °C/h, yellow crystals suitable for X-ray analysis were obtained; yield 70%.

X-ray structure determination: A yellow single crystal with approximate dimensions of 0.24 × 0.17 × 0.16 mm was placed on the top of a glass fibre and mounted on an X-ray diffractometer. The intensity data were collected on a Rigaku Mercury CCD X-ray diffractometer equipped with a graphite monochromated Mo-*K*α radiation (λ = 0.071073 nm) by using an ω scan technique at 293 K. CrystalClear software was used for the data reduction and empirical absorption corrections.⁶ The structure was solved by direct methods with Siemens

SHELXTL™ Version 5 package of crystallographic software.⁷ The different Fourier maps based on these atomic positions yielded the other non-hydrogen atoms. The structure was refined by full-matrix least-squares refinement on *F*². All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were generated symmetrically, except for those of the lattice water molecules, which were allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but not refined. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths and bond angles are listed in Table 2.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 734863. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB1 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Results and discussion

The hydro(solvo)thermal method in the presence of organic components is a well known versatile technique in the syntheses of solid-state complexes with a variety of structural motifs. When superheated, water shows large differences from what is observed under normal conditions. The drastically lowered

Table 1 Summary of crystallographic data and structure analysis

Empirical formula	C ₃₆ H ₄₂ Cl ₇ Fe ₃ N ₆ O ₁₉
Formula weight	1278.46
X-ray	MoKα
Crystal system	Rhombohedral
Space group	<i>R</i> -3 <i>c</i>
Unit cell dimensions	<i>a</i> = <i>b</i> = 19.9410(6) Å <i>c</i> = 30.505(1) Å
<i>Z</i>	6
<i>V</i>	10504.9(6) Å ³
<i>D_x</i>	1.213 Mg m ⁻³
Absorption coefficient	0.936 mm ⁻¹
Crystal size	0.24 × 0.17 × 0.16 mm
No. of reflections collected/unique	20653/2502 [<i>R</i> _(int) = 0.0389]
Goodness-of-fit on <i>F</i> ²	0.980
Final <i>R</i> indices	<i>R</i> ¹ = 0.0694, <i>wR</i> ² = 0.1579
<i>R</i> indices (all data)	<i>R</i> ¹ = 0.0985, <i>wR</i> ² = 0.1696
Index ranges	–26 ≤ <i>h</i> ≤ 26, –26 ≤ <i>k</i> ≤ 26, –40 ≤ <i>l</i> ≤ 40
Measurement	Rigaku mercury CCD diffractometer
Monochromator	graphite
Structure determination	Siemens SHELXTL
(Δ/σ) _{max}	0

* Correspondent. E-mail: cwtqq@yahoo.com.cn

Table 2 Selected bond lengths and bond angles (Å, °)

Fe(1)–O(1)	1.9179(4)	O(1)–Fe(1)–O(2)	93.37(5)
Fe(1)–O(1W)	2.020(3)	O(3)#1–Fe(1)–O(2)	86.50(7)
Fe(1)–O(2)	2.032(2)	O(3)#2–Fe(1)–O(2)	92.96(7)
Fe(1)–O(2)#3	2.032(2)	O(1W)–Fe(1)–O(2)	86.63(5)
Fe(1)–O(3)#1	1.993(2)	O(1)–Fe(1)–O(2)#3	93.38(5)
Fe(1)–O(3)#2	1.993(2)	O(3)#1–Fe(1)–O(2)#3	92.96(7)
O(1)–Fe(1)–O(3)#1	94.55(5)	O(3)#2–Fe(1)–O(2)#3	86.50(7)
O(1)–Fe(1)–O(3)#2	94.56(5)	O(1W)–Fe(1)–O(2)#3	86.62(5)
O(3)#1–Fe(1)–O(3)#2	170.9(1)	O(2)–Fe(1)–O(2)#3	173.3(1)
O(1)–Fe(1)–O(1W)	180.0	Fe(1)–O(1)–Fe(1)#1	120.0
O(3)#1–Fe(1)–O(1W)	85.45(5)	Fe(1)–O(1)–Fe(1)#4	120.0
O(3)#2–Fe(1)–O(1W)	85.44(5)	Fe(1)#1–O(1)–Fe(1)#4	120.0

Symmetry codes: #1 $-x+y+1, -x, z$; #2 $y+2/3, x-2/3, -z-1/6$; #3 $x-y-1/3, -y-2/3, -z-1/6$; #4 $-y, x-y-1, z$.

viscosity, for example, increases the extraction of solids into solution and the diffusion rate of the reagents, as well as the rate of crystallisation. Moreover, different solubilities of the inorganic and organic ingredients are easily overcome.

Complex **1** was synthesised from the reaction of FeCl₃ and nicotinic acid by the hydrothermal method. X-ray diffraction analysis reveals that the structure of **1** is characterised by an isolated structure, based on the [Fe₃(O)(C₆NO₂H₅)₆(H₂O)₃]⁷⁺ species, lattice water molecules and chloride ions, as shown in Fig. 1. All the crystallographically-independent atoms except for Fe1, O1, O1W, O2W and Cl2 are in general positions. The iron atoms have a slightly distorted octahedral geometry, coordinating with six oxygen atoms. There is an oxo-centred triangular arrangement of three iron ions, forming a Fe₃O plane, as shown in Fig. 2. A crystallographic three-fold axis of symmetry exists in the Fe₃O plane. The triply-bridging oxygen atom O1 resides at a site of crystallographically symmetry-related centre, with the iron atoms and the nicotinato-ligands located on the crystallographic three-fold axes. The bond length of Fe1–O1_{triply bridging} is 1.9179(4) Å, comparable with those reported.^{8–10} The bond length of Fe1–O1W is 2.020(3) Å, comparable with those documented.^{11–12} The bond lengths of Fe–O_{nicotinato} range from 1.993(2) to 2.032(2) Å, comparable with those previously reported.¹³ The bond angle of Fe–O–Fe is 120°, exactly that of a regular triangle.

Bond valence calculations indicate that the iron atom is in the +3 oxidation state (Fe1: 3.163).¹⁴ There is no $\pi \dots \pi$ stacking interaction found between the pyridyl rings of the nicotinato-moieties in the title complex. However, some O–H...Cl, C–H...O and C–H...Cl hydrogen bondings interconnect the

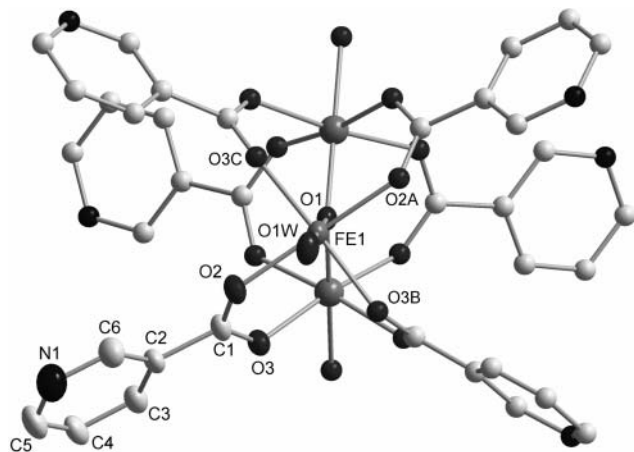


Fig. 1 ORTEP drawing of **1** with 30% thermal ellipsoids. Lattice water molecules, isolated chloride ions and hydrogen atoms were omitted for clarity. (Symmetry codes: A $-0.33333+x-y, -0.66667-y, -0.16667-z$; B $0.66667+y, -0.66667+x, -0.16667-z$; C $1-x+y, -x, z$).

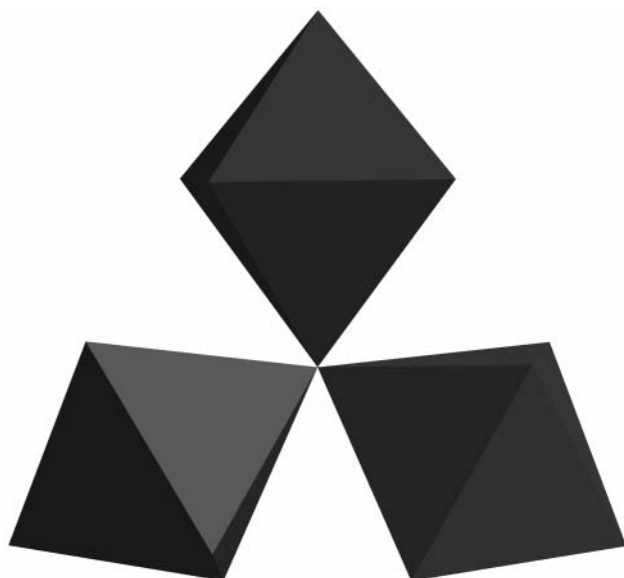


Fig. 2 Polyhedral perspective of **1** showing the oxo-centred, trinuclear iron cluster.

[Fe₃(O)(C₆NO₂H₅)₆(H₂O)₃]⁷⁺ cations, lattice water molecules and chloride anions to yield a 3-D supramolecular open framework. Therefore, the hydrogen bondings and the electrostatic interactions between the [Fe₃(O)(C₆NO₂H₅)₆(H₂O)₃]⁷⁺ cations and the chloride anions contribute to the stabilisation of the crystal packing of **1** (Fig. 3). To our knowledge, complex **1** is the first oxo-centred, trinuclear iron nicotinato-complex, although many other oxo-centred, trinuclear iron complexes have been documented thus far.^{15,16}

A search from the CCDC shows that there are hundreds of nicotinato-complexes. However, among these compounds there are only two complexes containing iron metal.^{13,17} Therefore, complex **1** is only the third example consisting of both iron and nicotinato-moieties.

In conclusion, by using hydrothermal reactions of FeCl₃ and nicotinic acid, a novel complex that possesses a 3-D supramolecular open framework was obtained. It is the first example of an oxo-centred, trinuclear, iron-nicotinato complex. The scope for the syntheses of new coordination zeolitic materials with novel structures and properties appears to be very large, and further systematic experimental and theoretical investigations on this system are in progress.

We thank the financial support of the NSF of Jiangxi Province (200007GQH1685).

Received 22 May 2010; accepted 6 October 2010
 Paper 1000147 doi: 10.3184/030823410X12891378345819
 Published online: 23 December 2010

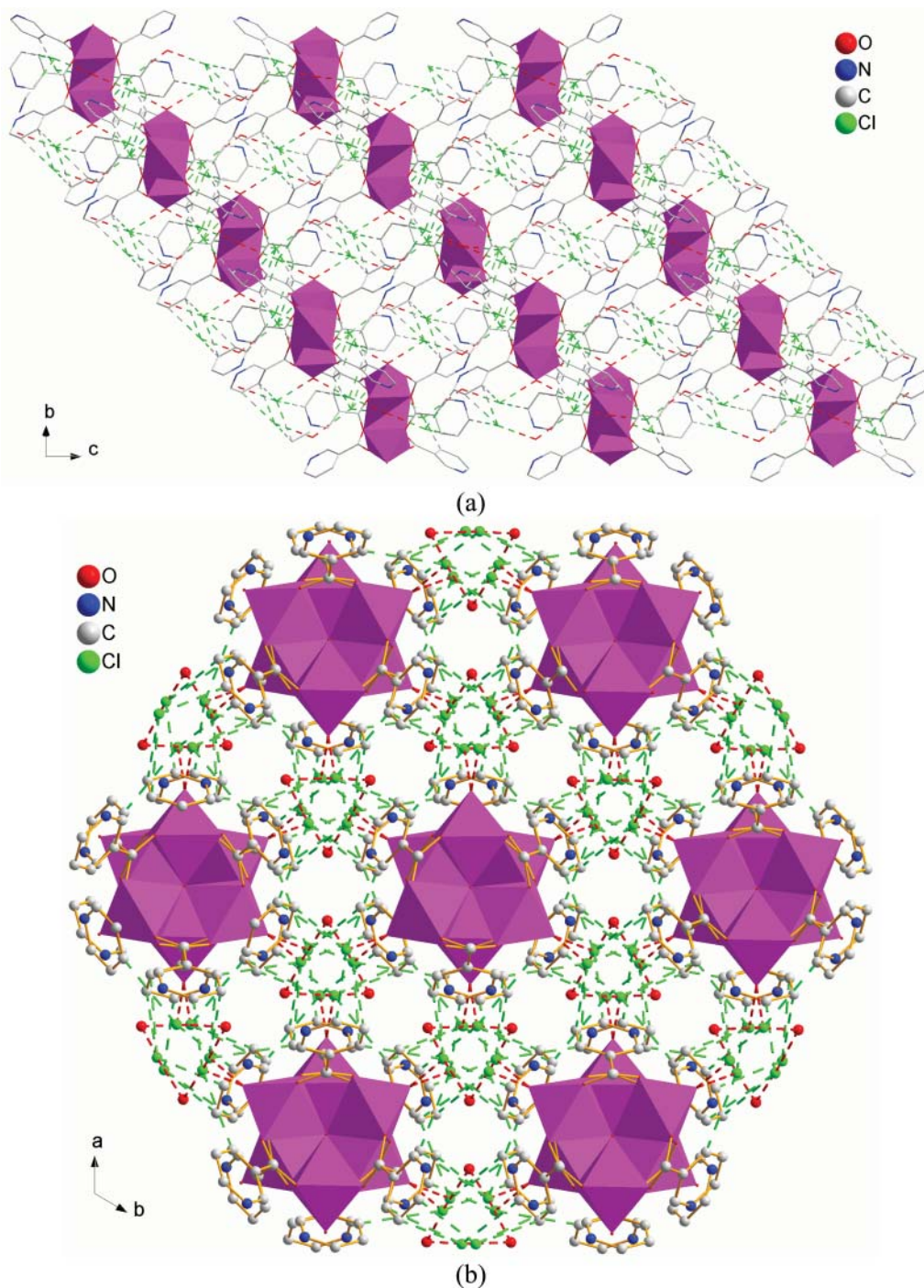


Fig. 3 Packing diagram of **1**: (a) viewed down along the *a* axis; (b) viewed down along the *c* axis. The dashed lines representing hydrogen bonds [D–H, H...A, D...A, <(DHA)] (Å, °): O1W–H1WA...Cl1 [0.82, 2.43, 2.995(2), 127], O2W–H2WA...Cl1 [0.960(8), 2.537(1), 3.269(1), 133.1(6)], C3–H3A...O3 [0.93, 2.40, 2.729(3), 101], C3–H3A...Cl1 [0.93, 2.74, 3.624(3), 160], and C5–H5A...Cl1 [0.93, 2.69, 3.506(3), 147].

References

- B.H. Ye, M.L. Tong and X.M. Chen, *Coord. Chem. Rev.*, 2005, **249**, 545.
- T.D. Hamilton and L.R. MacGillivray, *Cryst. Growth Des.*, 2004, **4**, 419.
- C.C. Freyhardt, M. Tsapatsis, R.F. Lobo, K.J. Balkus and M.E. Davis, *Nature*, 1996, **381**, 295.
- O.M. Yaghi, G. Li and H. Li, *Nature*, 1995, **378**, 703.
- M.E. Chapman, P. Ayyappan, B.M. Foxman, G.T. Yee and W. Lin, *Cryst. Growth Des.*, 2001, **1**, 159.
- Rigaku, CrystalClear Version 1.35, Rigaku Corporation 2002.
- Siemens, SHELXTL™ Version 5 Reference Manual, Siemens Energy & Automation Inc., Madison, Wisconsin, USA 1994.
- H.G. Jang, K. Kaji, M. Sorai, R.J. Wittebort, S.J. Geib, A.L. Rheingold and D.N. Hendrickson, *Inorg. Chem.*, 1990, **29**, 3547.
- T. Nakamoto, M. Hanaya, M. Katada, K. Endo, S. Kitagawa and H. Sano, *Inorg. Chem.*, 1997, **36**, 4347.
- R. Celenligil-Cetin, R.J. Staples and P. Stavropoulos, *Inorg. Chem.*, 2000, **39**, 5838.
- Y. Cui, Y.M. Wang, Y. Zheng, W.B. Zhou, L.J. He, S.H. Cai, B. Chen and L.N. Zhang, *Chinese J. Struct. Chem.*, 1999, **18**, 51.
- N.V. Izarova, M.N. Sokolov, A.V. Virovets, J.G. Latas and V.P. Fedin, *Zh. Strukt. Khim.*, 2005, **46**, 147.
- S.W. Ng, *Acta Crystallogr., Sect. E*, 2008, **64**, 'm728'.
- I.D. Brown and D. Altermat, *Acta Crystallogr. B.*, 1985, **41**, 244.
- W. Hibbs, P.J. van Koningsbruggen, A.M. Arif, W.W. Shum and J.S. Miller, *Inorg. Chem.*, 2003, **42**, 5645.
- H.A. Burkill, N. Robertson, R. Vilar, A.J.P. White and D.J. Williams, *Inorg. Chem.*, 2005, **44**, 3337.
- Y. Liang, W. Li and B.-J. Guo, *Acta Crystallogr., Sect. E*, 2005, **61**, 'm1782'.