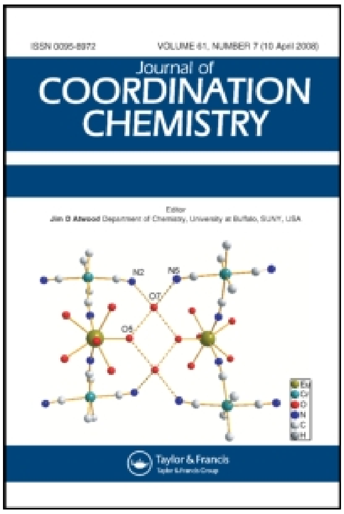

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Synthesis and crystal structure of $[Fe(phen)_3]L \cdot 2H_2L \cdot 4H_2O$ (H_2L = fumaric acid)

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Reaction of freshly precipitated $Fe_m(OH)_n(CO_3)_{3m-n/2} \cdot xH_2O$, fumaric acid ($H_2L$) and 1,10-phenanthroline (phen) in aqueous ethanol solution under ambient conditions yielded a new complex $[Fe(phen)_3]L \cdot 2H_2L \cdot 4H_2O$, which crystallizes in space group $P\bar{1}$ with $a = 12.126(1)$, $b = 12.493(2)$, $c = 17.014(2)$ Å, $\alpha = 77.26(1)$, $\beta = 89.786(8)$, $\gamma = 63.260(8)°$, $Z = 1$, $D_{calc} = 1.506\,g\,cm^{-3}$. The title compound consists of $[Fe(phen)_3]^{2+}$ complex cations, fumaric acid molecules, fumarate anions and hydrogen-bonded water molecules. Fe atoms are octahedrally coordinated by six nitrogen atoms of three phenanthroline ligands. The fumaric acid molecules, fumarate anions and water molecules build up a hydrogen-bonded anionic framework with the $[Fe(phen)_3]^{2+}$ complex cations in channels assembled into columnar chains through π–π stacking interactions. IR spectra and thermal analyses are discussed.

Keywords: Iron(II); Phenanthroline; Fumaric acid; Crystal structure; Thermal analysis; IR

1. Introduction

The design and construction of nanoporous supramolecular systems has recently become one of the most active research subjects in modern coordination and materials chemistry [1, 2]. It is well known that weak intermolecular, noncovalent interactions such as hydrogen bonds and aromatic (π–π) stacking interactions play important roles in supramolecular systems [3–5]. In particular, aromatic stacking interactions have been extensively reported to exist between heteroaromatic N-donor ligands such as 1,10-phenanthroline and 2,2-bipyridine. The past decade has witnessed an expansion of research on supramolecular architectures with specific topologies based on metal organic ligand coordination [6–8], and several rigid benzene di- and polycarboxylic acids have been used for the construction of metal organic frameworks [9, 10]. Aliphatic α,ω-dicarboxylate anions have also proved to be interesting bridging ligands because of their conformational flexibility and coordination versatility [11–13]. Previous research carried out by us and other groups has focused on divalent

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transition metals/heteroaromatic N-donor ligands/α,ω-dicarboxylic acids, resulting in two types of complex [14–27]. In one case, the metal atoms are coordinated only by the N-donor ligands to form complex cations while the dicarboxylate anions and lattice water molecules form hydrogen-bonded complex anions [14, 15]. In the other, the dicarboxylate anions and N-donor ligands coordinate to generate complex molecules [16–21] and polymers [22–27]. To the best of our knowledge, no work has been published on ternary systems consisting of Fe(II) ions, heteroaromatic N-donor ligands and α,ω-dicarboxylic acids. We report here the reaction of $Fe_m(OH)_n(CO_3)_{3m-n/2} \cdot xH_2O$, fumaric acid ($H_2L$) and 1,10-phenanthroline (phen) in aqueous ethanol under ambient conditions to produce a complex $[Fe(phen)_3]L \cdot 2H_2L \cdot 4H_2O$, composed of $[Fe(phen)_3]^{2+}$ cations, fumaric acid molecules, fumarate anions and hydrogen-bonded water molecules.

2. Experimental

2.1. *Physical measurements*

All chemicals of reagent grade were commercially available and used without further purification. Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 2400II CHNS/O instrument. IR spectra (KBr pellets) in the range 4000–400 cm^{-1} were recorded using a Shimadzu FTIR-8900 spectrophotometer. Thermal analyses (TG–DTA) were carried out on a Seiko Exstar6000 TG/DTA6300 analyzer in a dynamic dinitrogen atmosphere (flow rate: 100 cm^3 min^{-1}) with a heating rate of 10°C min^{-1}. Magnetic measurements were performed on polycrystalline samples with a Quantum Design MPMS-7 SQUID magnetometer with an applied field of 10 000 G.

2.2. *Synthesis*

In a typical synthesis, the fresh brown precipitate obtained by addition of 3.0 cm^3 of 1 M Na_2CO_3 to a stirred aqueous solution of $FeCl_3 \cdot 6H_2O$ (0.270 g, 1.00 mmol) in 5 cm^3 of H_2O was added to 1,10-phenanthroline monohydrate (0.198 g, 1.00 mmol) and fumaric acid (0.115 g, 1.00 mmol) in 50 cm^3 of EtOH/H_2O (1 : 1 v/v). The mixture was stirred for ca 30 min, producing a red suspension. After filtration, the filtrate (pH = 3.84) was allowed to stand at room temperature. Red crystals were grown by slow evaporation over several days (yield >45% based on the initial $FeCl_3 \cdot 6H_2O$). Anal. Calcd for $C_{48}H_{42}FeN_6O_{16}$(%): C, 56.57; H, 4.12; N, 8.24. Found: C, 57.35; H, 4.29; N, 8.29. IR (cm^{-1}): 3396s (br), 3063m, 1697vs (sh), 1427vs (sh), 1255m, 1166w, 980w, 843s (sh), 725m (br: broad; sh: sharp).

2.3. *X-ray crystallography*

A suitable single crystal was carefully selected under a polarizing microscope, glued to a glass fiber, and mounted on a Bruker P4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) for cell determination and subsequent data collection. Lattice parameters were refined from 2θ values (10–25°) of 25 carefully centered reflections. Reflection intensities to $2\theta_{max} = 55°$ were collected at 293 K using the θ–2θ scan technique. On the basis of monitored reflections, no detectable decay occurred during data collection. Data were corrected for Lp and absorption effects.

Table 1. Crystal data and structure refinement details.

Compound	[Fe(phen)$_3$]L · 2H$_2$L · 4H$_2$O
Empirical formula	$C_{48}H_{42}FeN_6O_{16}$
Formula weight	1019.2
Description	Red plate
Crystal size (mm)	0.27 × 0.18 × 0.11
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	12.126(1)
b(Å)	12.493(2)
c(Å)	17.014(2)
α (°)	77.26(1)
β (°)	89.786(8)
γ (°)	63.260(8)
Volume (Å^3)	2231.59(65)
Z	1
D_{calc} (g cm^{-3})	1.507
F(000)	1048
μ (mm^{-1})	0.422
Absorption correction	Empirical
Min. and max transmission	0.157, 0.169
θ range (°)	1.88–27.50
Refinement method	Full-matrix least-squares on F^2
Reflections collected	11 635
Independent reflections (R_{int})	10 183 (0.0410)
Data/restraints/parameters	10 183/0/598
Goodness of fit on F^2	1.197
R_1, wR_2 [$I \geq 2\sigma(I)$]	0.0672, 0.1215
R_1, wR_2 (all data)	0.1336, 0.1507
Extinction coefficients	0.001(1)
A, B values in weighting scheme	0.0374, 1.4512
ρ_{max}, ρ_{min} (e Å^{-3})	1.036, −0.945

$wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$. $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ with $P = (F_o^2 - 2F_c^2)/3$.

SHELXS-97 and SHELXL-97 programs [28, 29] were used for structure solution and refinement. The structure was solved by direct methods. Subsequent difference Fourier syntheses enabled all nonhydrogen atoms to be located. After several cycles of refinement, all hydrogen atoms bonded to carbon atoms were geometrically generated while the water and hydroxyl hydrogen atoms were located from difference Fourier syntheses. Finally, all nonhydrogen atoms were refined with anisotropic displacement parameters by full-matrix least-squares techniques and hydrogen atoms with isotropic displacement parameters. Information concerning crystal data and the structure determination is summarized in table 1. Selected interatomic distances and bond angles are given in table 2.

3. Results and discussion

3.1. *Synthesis and characterization*

Under ambient conditions, reaction of fresh $Fe_m(OH)_n(CO_3)_{3m-n/2} \cdot xH_2O$ with fumaric acid and 1,10-phenanthroline yielded a diamagnetic Fe(II) complex, [Fe(phen)$_3$]L · 2H$_2$L · 4H$_2$O ($\chi_m = -590 \times 10^{-6}$ cm^3 mol^{-1}), indicating that the initial

Table 2. Selected interatomic distances (Å) and angles (°).

Fe–N1	1.987(3)	C37–O1	1.297(5)	C43–O7	1.251(5)
Fe–N2	1.980(3)	C37–O2	1.209(5)	C43–O8	1.274(5)
Fe–N3	1.988(3)	C39–O3	1.307(8)	C45–O9	1.250(2)
Fe–N4	1.988(3)	C39–O4	1.170(7)	C45–O10	1.260(2)
Fe–N5	1.976(3)	C41–O5	1.185(5)	C48–O11	1.229(7)
Fe–N6	1.979(3)	C41–O6	1.296(5)	C48–O12	1.273(2)

N1–Fe–N2	82.5(1)	N2–Fe–N6	92.2(1)
N1–Fe–N3	94.0(1)	N3–Fe–N4	82.3(1)
N1–Fe–N4	175.3(1)	N3–Fe–N5	97.8(1)
N1–Fe–N5	82.9(1)	N3–Fe–N6	173.5(1)
N1–Fe–N6	92.5(1)	N4–Fe–N5	90.4(1)
N2–Fe–N3	87.8(1)	N4–Fe–N6	91.2(1)
N2–Fe–N4	94.5(1)	N5–Fe–N6	82.7(1)
N2–Fe–N5	173.0(1)		

Hydrogen-bonding contacts

D–H···A	D–H	H···A	D···A	D–H···A
O1–H1A···O9	1.09	1.41	2.498	177
O3–H3A···O12	0.78	1.90	2.663	166
O6–H6A···O8	0.97	1.68	2.526	144
O7–H7A···O11	1.09	1.48	2.460	146
O13–H13A···O4$^{\#4}$	0.82	2.32	2.991	140
O13–H13B···O9$^{\#5}$	0.82	2.36	3.160	163
O14–H14A···O10$^{\#5}$	0.81	2.02	2.828	172
O14–H14B···O13	0.86	1.97	2.825	179
O15–H15A···O14$^{\#4}$	0.86	2.04	2.849	158
O15–H15B···O5	0.86	2.00	2.864	180
O16–H16A···O15	0.84	2.13	2.881	150
O16–H16B···O10$^{\#3}$	0.82	2.11	2.926	178

Symmetry codes: $\#3 = -x+1, -y+1, -z+1$; $\#4 = -x+1, -y+2, -z+1$, $\#5 = -x+2, -y+1, -z+1$.

Fe^{3+} is reduced to Fe^{2+}. IR spectra display a broad absorption centered at 3396 cm^{-1} due to lattice water. Strong sharp peaks at 1697 and 1427 cm^{-1} are assigned to the asymmetric and symmetric COO stretching vibrations, respectively [30]. Absorption bands at 1256, 1167, 979, 842 and 725 cm^{-1} are typical of coordinated phen [31, 32].

When heated from room temperature to 500°C, the complex decomposes in four steps. The initial weight loss of 6.87% between 106 and 184°C is very close to the calculated value of 7.1% for four H_2O molecules per formula unit, indicating complete dehydration. Over the range 190–280°C, the sample loses 38.81% weight in accordance with the liberation of three mols of phen (Calcd 39.1%). Upon further heating to 470°C, the additional weight loss of 31.85% corresponds to the calculated value of 33.07% for decomposition of fumaric acid. The residue (21.2%) at 500°C is a mixture of FeO carbon.

3.2. *Structure description*

The unit cell contains an $[Fe(phen)_3]^{2+}$ cation, four water molecules, four half-fumaric acid molecules centered at positions 1*a*, 1*d*, 1*f* and 1*h*, and one fumarate anion. The fumaric acid molecule centered at the 1*a* and 1*h* sites is disordered. As shown in figure 1, the Fe atom is octahedrally coordinated by six nitrogen atoms of three phen ligands, as expected. Fe–N distances average 1.983 Å (table 2), nearly identical to the

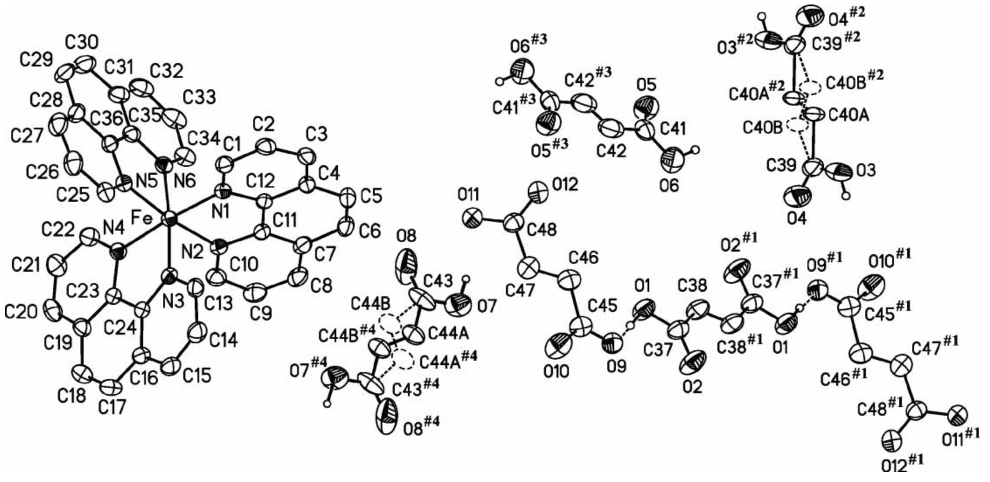

Figure 1. ORTEP view of the $[Fe(phen)_3]^{2+}$, fumaric acid molecules and fumarate anions with atom labels (displacement ellipsoids drawn at 35% probability). ($\#1 = -x + 1, -y, -z$; $\#2 = -x, -y + 2, -z$)

value of 1.977 Å observed in $[Fe(phen)_3](ttcH_2)(ClO_4) \cdot 2CH_3OH \cdot 2H_2O$ [33]. *Transoid* and *cisoid* N–Fe–N angles fall in the ranges 173.0–175.3 and 82.3–97.8°, respectively, indicating slight distortion of the octahedral coordination geometry. Both fumaric acid molecules and fumarate anions exhibit normal bond distances and angles [14, 15, 34].

Two distal carboxylate oxygen atoms O(9) and O(12) of the nondisordered fumarate anion are strongly hydrogen bonded in *anti* and *syn* fashion, respectively, to the carboxyl groups O(1)H and O(3)H of two fumaric acid molecules centered at 1*d* and 1*a* with $d(O \cdots O) = 2.498$, 2.663 Å (table 2), generating hydrogen-bonded zigzag chains. The fumaric acid molecule centered at the 1*f* site donates the carboxyl hydrogen atoms to the carboxylate O(8) atoms of the fumarate anions centered at 1*h* to form strong hydrogen bonds with $d(O \cdots O) = 2.526$ Å (table 2), resulting in hydrogen-bonded zigzag chains extending in the [010] direction. Both chains are interlinked through O(7)–H $\cdots$ O(11) hydrogen bonds into a 3D framework.

Lattice H_2O molecules participate in extensive hydrogen-bonding interactions (table 2). One water molecule [O(16)] forms hydrogen bonds to the carboxylate oxygen [O(10)] of one fumarate anion and to a water molecule [O(15)], which donates hydrogen atoms to oxygen [O(5)] of a fumaric acid molecule as well as to the third water oxygen [O(14)]. The latter [O(14)] is hydrogen bonded to [O(10)] of a fumarate anion and to the fourth water oxygen [O(13)]. The latter donates hydrogen atoms to O(4) of a disordered fumaric acid molecule and O(9) of the asymmetric fumarate anion.

Because of the extensive hydrogen-bonding interactions, the lattice water molecules, fumaric acid molecules and fumarate anions build up 3D hydrogen-bonded anionic framework with two different types of channels propagating in the [001] and $[1\bar{1}0]$ directions, respectively (figure 2).

The complex cations are located in channels parallel to [001] and arranged in such a way that the phen ligands involving N(1) and N(3) atoms of one cation are antiparallel to the symmetry-related partner of two neighboring cations. Mean interplanar distances are 3.31 Å between two adjacent phen ligands containing N(1) and 2.89 Å between two

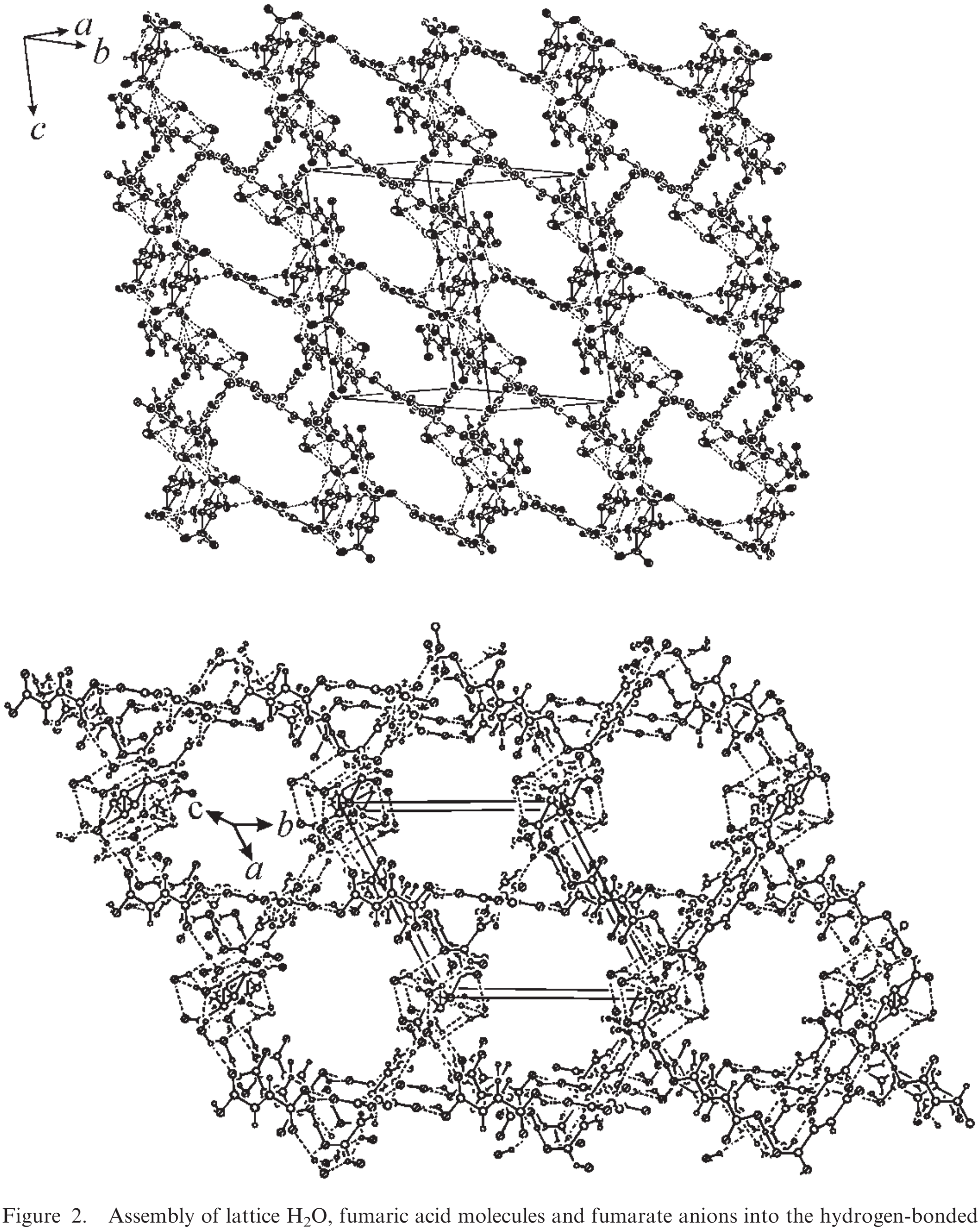

Figure 2. Assembly of lattice H_2O, fumaric acid molecules and fumarate anions into the hydrogen-bonded 3D framework.

adjacent phen ligands containing N(3), indicating significant π–π stacking interactions [35]. The stacking interactions are responsible for the assembly of the complex cations into chains, with the phen ligands containing N(5) atoms orientated outwards on both sides (figure 3). The groove of one chain is occupied by phen ligands containing N(5) atoms of neighboring chains and the cavities between adjacent antiparallel phen ligands are filled by fumaric acid molecules centered at the 1*d* sites.

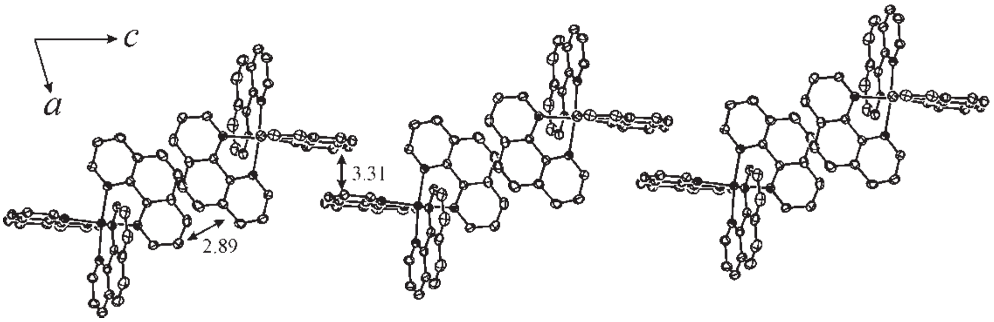

Figure 3. Assembly of the $[Fe(phen)_3]^{2+}$ cations due to π–π stacking interactions.

Supplementary data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 258136. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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