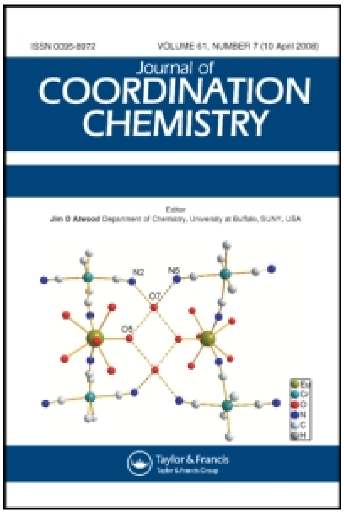

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and characterization of [Fe(μ-Cl)$_2$(phen)] <b> <i>n</i> and [Fe(H$_2$O)$_3$(phen)SO$_4$]

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To cite this Article Sui, Xina , Lu, Xiaoming , Feng, Junhe , Wang, Shuo and Li, Peizhou(2008) 'Synthesis and characterization of [Fe(μ-Cl)$_2$(phen)] <b> <i>n</i> and [Fe(H$_2$O)$_3$(phen)SO$_4$]', Journal of Coordination Chemistry, 61: 10, 1568 — 1574

To link to this Article: DOI: 10.1080/00958970701598985

URL: http://dx.doi.org/10.1080/00958970701598985

Journal of Coordination Chemistry
Vol. 61, No. 10, 20 May 2008, 1568–1574

Synthesis and characterization of $[Fe(\mu\text{-}Cl)_2(phen)]_n$ and $[Fe(H_2O)_3(phen)SO_4]$

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(*Received 12 March 2007; in final form 24 May 2007*)

$[Fe(\mu\text{-}Cl)_2(phen)]_n$ (**1**) and $[Fe(H_2O)_3(phen)SO_4]$ (**2**) have been synthesized and characterized by single crystal X-ray diffraction analysis, IR and UV spectra. Complex **1** crystallizes in monoclinic system with space group of $C2/c$ and **2** crystallizes in monoclinic system with space group of $P21/c$. The structure of **1** shows that each Fe(II) coordinates with one phen and four chlorides forming a distorted octahedral environment, and $[Fe(\mu\text{-}Cl)_2(phen)]$ as a repeating unit forms a one-dimensional chain. The structure of **2** shows that each Fe(II) coordinates with one SO_4^{2-}, one 1,10-phen and three H_2O molecules; the crystal architecture is stabilized by hydrogen bonds and π–π interactions.

Keywords: Iron; 1,10-Phenanthroline; 1D chain; π–π Stacking interaction

1. Introduction

Rational design and synthesis of coordination polymers with specific supramolecular architectures based on metal-organic coordination, hydrogen bonding as well as π–π stacking interactions remains a challenge; bridging ligands play a very important role in construction of supramolecular systems [1–5]. Iron has variable oxidation states and coordination preferences, making the structural chemistry of iron materials complex, but promising a wider range of materials [6]. 1,10-phenanthroline (1,10-phen) is a good N-donor ligand for π–π stacking interactions [7]. Complexes of iron(II) with 2,2′-bipyridine and 1,10-phenanthroline and their derivatives are of general interest to coordination chemists. In these compounds, octahedral iron(II) can be either low-spin ($S=0$) or high-spin ($S=2$); the $[Fe(bpy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ complexes are mostly low-spin, but their magnetochemical behavior depends on the counter-ion used, *e.g.* $[Fe(bpy)_3](BF_4)_2\cdot 2H_2O$ exhibits a thermally induced low-spin to high-spin crossover. Substitution of one 2,2′-bpy or 1,10-phen by a monodentate N-donor ligand can lead to compounds where transition from a low-spin to a high-spin state can be observed. The spin-crossover behavior, which can be either thermally or light induced, was intensively studied on the $[Fe(bpy)_2X_2]$ and $[Fe(phen)_2X_2]$ complexes, where $X = NCS^-$ or $NCSe^-$ [8].

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701598985

In the past few years, some iron complexes involving 1,10-phen have been synthesized, e.g. [Fe(phen)Cl_3H_2O] [9], organically templated iron phosphate [Fe(phen)(HPO_4)(H_2PO_4) $\cdot$ 0.5H_2O] [6], molecule-assembled magnetic material NO-*trans*-Fe^{II}(miao)$_2$(phen) (miao = 1-methylimidazole-2-aldoximate) [10], coordination polymer *trans*-[Gd(o-phen)$_2$(H_2O)$_2$ (μ-CN)$_2$Fe(CN)$_4$]$_n$ $\cdot$ 2no-phen [11], iron(II) complex [Fe(phen)$_3$](ttcH$_2$)(ClO_4) $\cdot$ 2CH_3OH $\cdot$ 2H_2O [8] and heteropolytungstate K[Fe(phen)$_2$(H_2O)]$_2$[$PW_{12}O_{40}$] $\cdot$ 2H_2O etc. [12], but few iron complexes have chain-like structures. In this article, **1** was synthesized by reaction of iron(II) chloride with 1,10-phenanthroline and has an infinite 1D chain structure. We also present another new iron complex [Fe(II)(H_2O)$_3$(phen)SO_4] here.

2. Experimental

2.1. *Materials*

$FeCl_2 \cdot 4H_2O$, $FeSO_4 \cdot 7H_2O$, $Na_2C_2O_4 \cdot 2H_2O$ and 1,10-phenanthroline were of reagent grade and used as received from commercial sources without further purification. MoO_2(acac)$_2$ (acac = acetylacetone) was prepared according to the literature methods [13].

2.2. *Physical measurements*

IR spectra were recorded with KBr pellets on a Bruker EQUINOX 55 FT-spectrometer. Single-crystal structure determinations by X-ray diffraction were performed on a Bruker Smart CCD area detector with Mo-Kα radiation. The UV spectra was obtained on a TU-1221 spectrometer in the range 190–350 nm.

2.3. *Synthesis*

2.3.1. Synthesis of [Fe(*μ*-Cl)$_2$(phen)]$_n$. A mixture of 1,10-phen (0.099 g, 0.5 mmol), $FeCl_2 \cdot 4H_2O$ (0.099 g, 0.5 mmol) and 20 mL acetylacetone was stirred about 20 h at room temperature and then sealed in a 45 mL Teflon-lined autoclave and heated to 423 K for 20 h. After cooling the autoclave to room temperature for 48 h, red sheet crystals suitable for single crystal X-ray diffraction were obtained, filtered, washed several times with ether and dried in air. IR(KBr) 3051 cm^{-1}; 1624 cm^{-1}; 1582 cm^{-1}; 1515 cm^{-1}; 1424 cm^{-1}; 986 cm^{-1}; 727 cm^{-1}; 641 cm^{-1}; 527 cm^{-1}.

2.3.2. Synthesis of [Fe(H_2O)$_3$(phen)SO_4]. A mixture of MoO_2(acac)$_2$ (acac = acetylacetone) (0.160 g, 0.5 mmol), $Na_2C_2O_4 \cdot 2H_2O$ (0.201 g, 1.5 mmol), $FeSO_4 \cdot 7H_2O$ (0.139 g, 0.5 mmol), 1,10-phen (0.099 g, 0.5 mmol) and 30 ml mixed solvent ($V_{CH_3OH} : V_{H_2O} = 1:1$) was stirred about 20 h, and then the solution was filtered; the filtrate was transferred into a Teflon-steel autoclave inside a programmable electric furnace reactor heated at 423 K for 20 h. After cooling the autoclave to room temperature for 48 h, red prisms suitable for single crystal X-ray diffraction were

Table 1. Crystal data and structure refinement for $[Fe(\mu\text{-}Cl)_2(phen)]_n$ and $[Fe(H_2O)_3(phen)SO_4]$.

Complex	**1**	**2**
Formula	$C_{12}H_8Cl_2FeN_2$	$C_{12}H_{14}FeN_2O_7S$
F_w	306.95	386.17
T (K)	273(2)	273(2)
Radiation (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P21/c$
a (Å)	17.3729(8)	11.9211(4)
b (Å)	10.3815(4)	10.0804(3)
c (Å)	6.9415(3)	13.7034(4)
β (°)	112.925(2)	111.612(2)
V (Å^3)	1153.06(9)	1530.96(8)
Z	4	4
Calcd density (g cm^{-3})	1.768	1.614
Goodness-of-fit on F^2	1.067	1.177
Crystal size (mm^3)	$0.48 \times 0.20 \times 0.12$	$0.19 \times 0.14 \times 0.12$
θ Range (°)	2.34 to 28.35	1.84 to 28.37
Reflections collected/unique	5015/1440	15034/3822
R_{int}	0.0317	0.0214
Final R_f and wR_{zd} indices	$R_1 = 0.0395$, $wR_2 = 0.1001$	$R_1 = 0.0311$, $wR_2 = 0.0934$
R_1 and wR_2 indices (all data)	$R_1 = 0.0609$, $wR_2 = 0.1085$	$R_1 = 0.0372$, $wR_2 = 0.0960$

obtained, filtered, washed several times with ether and dried in air. IR(KBr) 3051 cm^{-1}, 1622 cm^{-1}; 1516 cm^{-1}; 1427 cm^{-1}; 986 cm^{-1}; 729 cm^{-1}; 620 cm^{-1}.

2.4. *X-ray structure data collection and refinement*

A single crystal of the compounds was selected and mounted at the tip of a glass fiber. The data were collected on a Bruker APEX II CCD area detector device with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved by direct methods [14] and refined with the software package SHELXL-PLUS [15]. An absorption correction based on symmetry equivalent reflections was applied by using the SADABS program. The final refinement included atomic positions for all the atoms and anisotropic thermal parameters for all the non-hydrogen atoms. Full-matrix least-squares structure refinement against F^2 was carried out with the SHELXTL-PLUS package of programs. A summary of crystal data and structure refinement for the compounds is given in table 1. Selected bond lengths and angles are listed in tables 2 and 3.

3. Results and discussion

3.1. *IR spectra and UV spectra*

Infrared spectra were recorded using a Bruker EQUINOX 55 spectrometer over the range 4000 ~ 400 cm^{-1}. IR spectra of **1** shows absorptions at 3050, 1623, 1582, 1515, 1423 and 727 cm^{-1}, which correspond to the characteristic absorptions of 1,10-phenanthroline and a band at 527 cm^{-1}, which corresponds to the Fe–N

Table 2. Selected bond lengths (Å) and angles (°) for $[Fe(\mu\text{-}Cl)_2(phen)]_n$.

Fe(1)–Cl(1)	2.6476(6)	Fe(1)–N(1)	2.176(2)
Fe(1)–Cl(1A)	2.4180(7)		
N(1B)–Fe(1)–N(1)	75.70(12)	Cl(1A)–Fe(1)–Cl(1C)	100.28(4)
N(1)–Fe(1)–Cl(1A)	93.04(6)	N(1)–Fe(1)–Cl(1)	92.67(5)
N(1)–Fe(1)–Cl(1C)	163.57(6)	Cl(1C)–Fe(1)–Cl(1)	98.24(2)
N(1B)–Fe(1)–Cl(1)	84.71(5)	Cl(1)–Fe(1)–Cl(1B)	176.69(3)
Cl(1A)–Fe(1)–Cl(1)	83.90(2)	Fe(1A)–Cl(1)–Fe(1)	96.10(2)

Table 3. Selected bond lengths (Å) and angles (°) for $[Fe(H_2O)_3(phen)SO_4]$.

Fe(1)–O(4)	2.0579(15)	Fe(1)–O(3)	2.1062(14)
Fe(1)–O(2)	2.1255(15)	Fe(1)–N(1)	2.1865(16)
Fe(1)–O(1)	2.1941(14)	Fe(1)–N(2)	2.2039(18)
O(4)–S(1)	1.4690(15)	S(1)–O(6)	1.4545(16)
S(1)–O(7)	1.4637(15)	S(1)–O(5)	1.4856(15)
O(4)–Fe(1)–O(3)	95.44(6)	O(4)–Fe(1)–O(2)	100.78(7)
O(3)–Fe(1)–O(2)	84.65(6)	O(4)–Fe(1)–N(1)	91.82(7)
O(3)–Fe(1)–N(1)	87.47(6)	O(2)–Fe(1)–N(1)	165.70(7)
O(4)–Fe(1)–O(1)	88.89(6)	O(3)–Fe(1)–O(1)	173.25(6)
O(2)–Fe(1)–O(1)	89.46(6)	N(1)–Fe(1)–O(1)	97.58(6)
O(4)–Fe(1)–N(2)	163.99(7)	O(2)–Fe(1)–N(2)	93.10(7)
O(3)–Fe(1)–N(2)	93.75(7)	O(1)–Fe(1)–N(2)	83.25(6)
N(1)–Fe(1)–N(2)	75.50(6)		

stretching vibrations. Comparing with free 1,10-phenanthroline, the stretching vibration of the ring in **1** blue-shift from 1696 and 1597 to 1623 and 1423 cm^{-1}, indicating coordination to iron.

IR spectra of **2** shows absorptions at 3051, 1626, 1516, 1422 and 728 cm^{-1}, which correspond to characteristic absorptions of 1,10-phenanthroline. The stretching vibration of 1,10-phenanthroline in **2** blue-shift from 1696 and 1597 to 1622 and 1426 cm^{-1}.

The UV spectra were measured in distilled water solutions. Complex **1** shows absorptions at 200, 223, 265 and 513 nm. Compared with free 1,10-phenanthroline, **1** shifts from 198, 221 and 264 nm to 200, 223 and 265 nm; there is no absorption at 513 nm in 1,10-phenanthroline.

The UV spectra of **2** in DMF shows absorptions at 206, 227, 272 and 515 nm. Absorptions at 206, 227 and 272 nm belong to the $\pi \rightarrow \pi^*$ transition of 1,10-phen. The red shift for **2** was caused by coordination of 1,10-phen ligand with iron.

3.2. *The crystal structure*

The structure of **1** has two μ_2-bridging chlorides linking two iron atoms, yielding an infinite 1D zigzag chain structure. The geometry of the monomeric units in **1** is shown in figure 1(a). Each Fe^{2+} is a distorted octahedron $\{FeCl_4N_2\}$, with two *cis*-nitrogen donors from one 1,10-phen and four chlorides as bridging ligands. In each octahedral $\{FeCl_4N_2\}$ unit, the Fe–N bonds are 2.176(2) Å. The Fe–Cl bonds range from 2.4180(7)–2.6476(6) Å. Taking into account the irregular bond angles (Cl–Fe–Cl angles

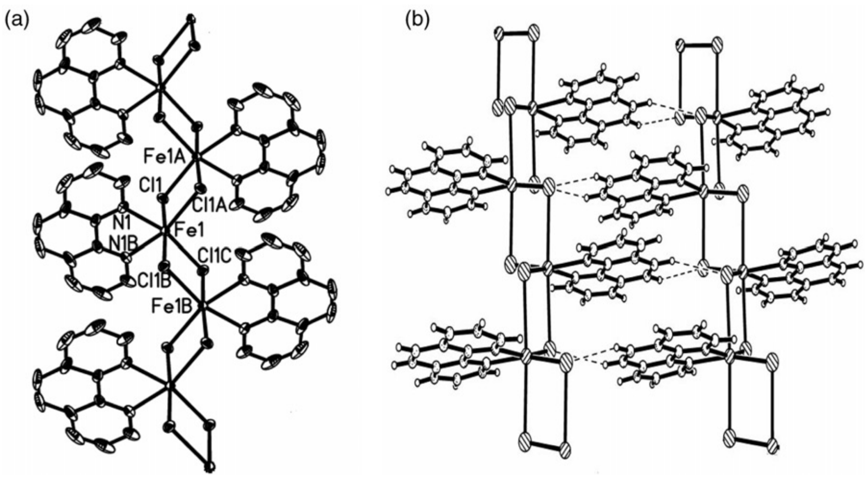

Figure 1. (a) ORTEP view of three monomeric units within a single chain of **1**; (b) the packing diagram of **1** down the b axis.

Table 4. H-bond parameters of **1**.

Donor–H···Acceptor	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
C(1)–H(1)···Cl(1)	0.93	2.81	3.409(4)	123
C(2)–H(2)···Cl(1)	0.93	2.80	3.679(4)	158
C(5)–H(5)···Cl(1)	0.93	2.81	3.692(3)	159

are in the range 83.90(2)–176.69(3)°, Cl–Fe–N angles are in the range 84.71(5)–163.57(6)°, N(1)–Fe–N(1B) angle is 75.70(12)°) and short Fe–N distances (2.176(2) Å), the geometry of each iron center in **1** is best described as a distorted octahedron.

The planar 1,10-phen molecules are nearly parallel to each other and perpendicular to the chain extension (figure 1b) along the c-axis, giving face to face π–π interactions between adjacent layers at 3.49 Å. Furthermore, hydrogen bonds also exist between Cl(1) and C(1)–H(1) (figure 1b) with the distance C(1)–H(1)···Cl(1) = 2.81 Å, Cl(1) and C(2)–H(2) with the distance C(2)–H(2)···Cl(1) = 2.80 Å, Cl(1) and C(5)–H(5) with the distance C(5)–H(5)···Cl(1) = 2.81 Å. Detailed information about the hydrogen bonding is summarized in table 4. We conclude that the hydrogen bonding and π–π stacking interactions of 1,10-phen groups play an important role in the stability of the whole structure of **1**.

The molecular structure of **2** is illustrated in figure 2(a). Central Fe coordinates with the ligands in pseudo-octahedral geometry, with one SO_4^{2-}, one 1,10-phen and three H_2O molecules. There are three O···H–O bonds among the SO_4^{2-} and three H_2O molecules, through the three terminal O atoms of SO_4^{2-} and three hydrogen atoms from three H_2O of two complexes (figure 2c). The average O···H distance is about 2.74 Å and even the angle O–H···O is about 160°. So the structure is stabilized by O–H···O bonds. Related H-bonds parameters are listed in table 5. The linkage of SO_4^{2-} through hydrogen bonds aligns **2** parallel into a two-dimensional structure (figure 2b). Organic–inorganic layers arrange alternately (figure 2c) and inter-molecular H-bonds link

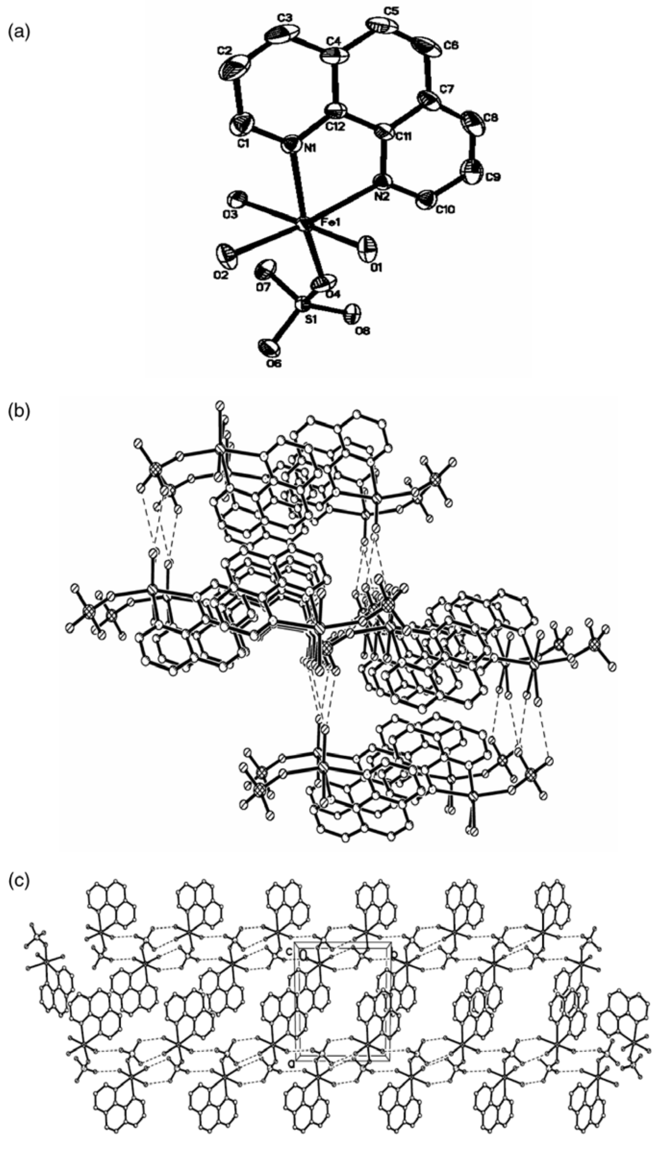

Figure 2. (a) The perspective views of **2**; (b) the packing diagram of **2** down the c axis; (c) the packing diagram of **2** down the a axis.

Table 5. H-bond parameters of **2**.

Donor–H ⋯ Acceptor	D–H (Å)	H ⋯ A (Å)	D ⋯ A (Å)	D–H ⋯ A (°)
O(3)–H(1) ⋯ O(6)	0.91(3)	1.84(3)	2.734(2)	166(2)
O(3)–H(2) ⋯ O(7)	0.82	1.93	2.704(2)	157
O(2)–H(3) ⋯ O(7)	0.83(3)	1.94(3)	2.761(2)	167(2)
O(2)–H(4) ⋯ O(8)	0.82	2.09	2.845(2)	153
O(1)–H(5) ⋯ O(7)	0.82	1.95	2.712(2)	154
O(1)–H(6) ⋯ O(8)	0.78(3)	1.95(3)	2.713(2)	166(3)

molecules within inorganic layers, while in organic layers, π–π interactions from aromatic rings connect adjacent inorganic layers to form a 3D structure.

4. Conclusion

Two lamellar iron complexes $[Fe(\mu\text{-}Cl)_2(phen)]_n$ and $[Fe(II)(H_2O)_3(phen)SO_4]$ have been synthesized by using solvothermal reaction and are structurally characterized. Complex **1** is a chloride-bridged, one-dimensional polymer and **2** is connected by intermolecular H-bonds and π–π interactions. In these compounds, the iron(II) ions are in a low-spin ($S = 0$) ground state with no signal in their EPR spectra.

Supplementary material

Crystallographic data in CIF format can be obtained free of charge from the Cambridge Crystallographic Data Center $[Fe(\mu\text{-}Cl)_2(phen)]_n$ CCDC 625095, $[Fe(H_2O)_3(phen)SO_4]$ CCDC 288732, Union Road, Cambridge CB2 1EZ UK (Fax: +44(0)1223-336066; Email: deposit@ccdc.cam.ac.uk).

Acknowledgements

We gratefully acknowledge the financial support of the Beijing Natural Science Foundation (20052007), which made this work possible.

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