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CRYSTAL STRUCTURE OF [Bis(DIMETHYLFORMAMIDE) Bis(2,2'-PYRIDYL)QUINOLINE)IRON(II)]Bis-(TETRAPHENYLBORATE)

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Abstract

The goal of this research is to obtain single crystal and structural information of iron(II) complex with 2,(2'-pyridyl)quinoline(pq) ligands. The reaction of iron(II) salt with 2,(2'-pyridyl)quinoline ligand and sodium tetraphenylborate in the molar ratio of 1:3:2 in methanol-*N,N*-dimethylformamide(dmf) solution results in an iron(II) complex. The formula of the $[\text{Fe}(\text{pq})_2(\text{dmf})_2](\text{BPh}_4)_2$ complex has been obtained from the iron(II) and C, H, N contents. Single crystal of $[\text{Fe}(\text{pq})_2(\text{dmf})_2](\text{BPh}_4)_2$ suitable for X-ray investigation was obtained by evaporation of the complex solution in *N,N*-dimethylformamide at room temperature after 24 hours. This compound crystallizes in monoclinic system with *C2/c* space group, $a = 27.950(4)$, $b = 14.169(7)$, $c = 17.717(9)$ Å and $\beta = 105.669(11)^\circ$. The structure consist of iron(II) is chelated by two pq ligands through the N atoms and two dmf molecules in a six-coordination environment. The charge of the $[\text{Fe}(\text{pq})_2(\text{dmf})_2]^{2+}$ cation is balanced by two tetraphenylborate $(\text{BPh}_4)^-$ anions.

Keywords: crystal structure, distorted octahedral, $[\text{Fe}(\text{pq})_2(\text{dmf})_2](\text{BPh}_4)_2$

1. Introduction

Octahedral coordination compounds of transition metal ions with a d^4 to d^7 electronic configuration can be classified according to the ligand-field strength (LFS) into three groups; low-spin (LS) state (strong LFS), high-spin (HS) state (weak LFS), and thermal spin crossover between HS \leftrightarrow LS (intermediate LFS) [1].

The behaviour of spin crossover compounds is among the most striking and fascinating phenomena shown by relatively simple molecular species. Six-coordinate iron(II) ($3d^6$) spin crossover compounds are among the most investigated systems; they reversibly change from diamagnetic ($S = 0$) to paramagnetic ($S = 2$) spin states by thermal or pressure influences. The first iron(II) spin-crossover compound was reported by Baker and Bobonich in 1964 [2]. Since then there has been much interest in these materials due to their potential for applications such as information storage, molecular switches and visual displays [3-4].

While it is not possible to rationalize readily the great variety of ligand systems known to generate spin crossover behaviour in iron(II), sufficient strategy is recognized of the general features of such systems to

enable the fine-tuning of the field strength of model ligands so as to bring it into the crossover region [5]. Three strategies in particular are widely effective; the replacement of conjugated heterocyclic donor systems by aliphatic, the replacement of six-membered heterocycles by five membered, and the incorporation of substituents in the ligand structure. The position of substituent is adjacent to a donor atom, will de-stabilize the singlet state by hindering the close approach of the metal atom. This is illustrated by $[\text{Fe}(\text{mephen})_3]^{2+}$ (mephen = 2-methyl-1,10-phenanthroline) which is HS at room temperature but undergoes a transition to LS at low temperatures. In contrast, the unsubstituted $[\text{Fe}(\text{phen})_3]^{2+}$ is LS at all accessible temperatures. In other instances where the substituent is remote from the donor atom electronic effects may be operative and could be applied to stabilize either state. Introduction of a phenyl substituent adjacent to just one of the terminal *N*-donors ($L = 3$) has been shown to lead to either a HS or a LS complex in the solid state and to a temperature- and pressure-dependent spin equilibrium in solution. However, when phenyl or methyl substituents are present adjacent to both terminal donor atoms the $[\text{FeN}_6]^{2+}$ derivative is entirely HS.

Then, Onggo and co-worker [6] obtained two forms of $[\text{Fe}(\text{pq})_3][\text{ClO}_4]_2$ complexes, the first complex was isolated from acetone/benzene and the second complex readily isolable from warm ethanol when the pq ligand and $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were mixed in 5:1 mole ratio. The two complexes represent different crystal modifications are revealed by their X-ray powder diffraction profiles, which are quite distinct. This difference was also observed by their magnetic behaviours. The first complex is essentially high spin over the 89 – 300 K range and the other which shows an almost complete gradual spin crossover in that temperature range. No single crystal structure of the $[\text{Fe}(\text{pq})]^{2+}$ complex published by either Harris et al. or Onggo et al. have been reported. In the present study, crystals of $[\text{Fe}(\text{pq})_2(\text{dmf})_2](\text{BPh}_4)_2$, $\text{dmf} = N,N$ -dimethylformamide, $\text{BPh}_4 =$ tetraphenylborate were obtained by the use of voluminous anion, tetraphenylborate and dmf as solvent. Therefore X-ray investigation on the compound was carried out.

2. Experiment

Materials. The raw chemicals: $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ (sodium tetraphenylborate), CH_3OH (methanol), and $\text{HCON}(\text{CH}_3)_2$ (N,N -dimethylformamide = dmf) were used as commercially obtained without further purification. The $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{C}_{14}\text{H}_{10}\text{N}_2$ (2,2'-(pyridyl)quinoline = pq) have been prepared as described in the literature [6-8].

Synthesis of $[\text{Fe}(\text{pq})_2(\text{dmf})_2](\text{BPh}_4)_2$. A methanol solution (8 mL) of pq ligand (0.62 g, 3 mmol) was mixed in 3:1 mole ratio with a methanol solution (2 mL) of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.2 g, 1 mmol) under a nitrogen atmosphere. The red solution was obtained. A slight excess solution (10 mL) of $\text{Na}(\text{BPh}_4)$ (0.75 g, 2.2 mmol) in dmf was added to the red solution. The red crystals of $[\text{Fe}(\text{pq})_2(\text{dmf})_2](\text{BPh}_4)_2$ slowly deposited were filtered off, washed with methanol and dried over P_4O_{10} . Single crystals of $[\text{Fe}(\text{pq})_2(\text{dmf})_2](\text{BPh}_4)_2$ suitable for X-ray investigation were obtained by evaporation of the complex solution in N,N -dimethylformamide at room temperature after 24 hours.

X-ray diffraction measurements. Diffraction data was collected on a Bruker *SMART APEX* area-detector diffractometer at 295(2) K on a crystal of size 0.44 x 0.16 x 0.13 mm using the ω -scan technique over the range $2.0 < \theta < 26.0^\circ$ equipped with $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The intensity data was collected over the range $\theta = 2.0 - 26.0^\circ$ for 17469 independent reflections. Lorentz-polarization and absorption corrections were applied.

The structure was solved and refined by using *SHELXTL* system of programs [9]. The final R ($F^2 > 2\sigma(F^2)$) and R_w values were 0.068 and 0.151. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were treated by a mixture of independent and constrained refinement. The O1, C15, C38 and C39 atoms are disordered and were treated accordingly. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.055 P)^2 + 2.031P]$ where $P = (F_o^2 + F_c^2)/3$. The perspective view of the molecule was obtained using *ORTEP* [10].

3. Results and Discussion

Synthesis of $[\text{Fe}(\text{pq})_2(\text{dmf})_2](\text{BPh}_4)_2$. The reaction of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and pq in methanol and $\text{Na}[\text{BPh}_4]$ in dmf gave red solid product with 87% yield. The microelemental analysis data is agreement with the predicted formula, Found (%): Fe, 4.03; C, 77.98; H, 6.48 and N, 6.81; Calculated (%): Fe 4.46; C, 78.60; H, 5.95 and N, 6.71. Recrystallization from dmf afforded red crystals suitable for X-ray investigation. The magnetic susceptibility measurement of 5.3 BM at room temperature indicates that the $[\text{Fe}(\text{pq})_2(\text{dmf})_2](\text{BPh}_4)_2$ is paramagnetic with high-spin state of iron(II).

Crystal Structure of $[\text{Fe}(\text{pq})_2(\text{dmf})_2](\text{BPh}_4)_2$. The molecular structure of the compound with atomic numbering scheme is shown in Figure 1. Half of the complex molecule is symmetrically generated about the central Fe1 atom. The Fe1 atom is chelated by two pq ligands through the N atoms of the pyridyl and quinoline moieties and two dmf molecules in a six-coordination environment. The charge of the $[\text{Fe}(\text{pq})_2(\text{dmf})_2]^{2+}$ cation is balanced by two tetraphenylborate (BPh_4^-) anions. The compound crystallizes in monoclinic system with $C2/c$ space group, $a = 27.950(4)$, $b = 14.169(7)$, $c = 17.717(9) \text{ \AA}$ and $\beta = 105.669(11)^\circ$. Crystal data and structure refinement parameters are shown in Table 1.

The geometry of the Fe1 atom is a distorted octahedron with angle about Fe1 atom between $75.57-176.91^\circ$. The N1 atoms of the pyridyl moieties are *trans* to the O1 atoms of the dmf molecules. The two chelated pq planes are not exactly planar but verticle to each other. The Fe1-N2_{pyridyl} of 2.232(3) is longer than Fe1-N1_{quinoline}, 2.165(3) Å. The Fe1-O1 is 2.101(3) Å. The tetrafluoroborate anions maintain their tetrahedral geometry with angle about the boron atoms between $103.11(3) - 113.0(3)^\circ$. Other bond lengths and angles are in normal ranges (Table 2).

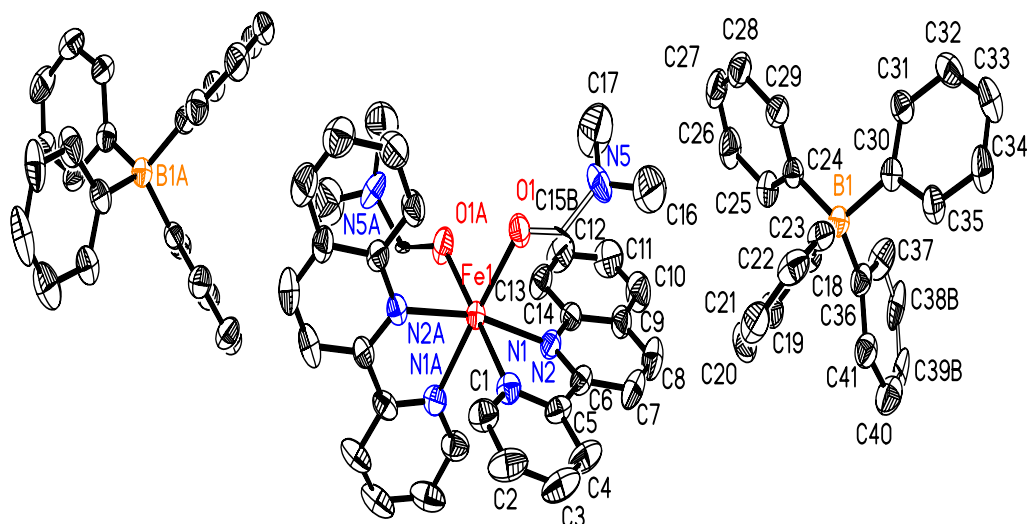


Figure 1. The Molecular Structure of $[\text{Fe}(\text{pq})_2(\text{dmf})_2](\text{BPh}_4)_2$ with 30% Probability Level Ellipsoid. Hydrogen Atoms are Omitted for Clarity and the Unlabelled Carbon Atoms Including B1A, N1A, N2A N5A are Symmetrically Generated

Table 1. Crystal Data and Structure Refinement

Crystal data	Structure refinement
Empirical formula	$\text{C}_{82}\text{H}_{74}\text{B}_2\text{FeN}_6\text{O}_2$
Formula weight	1253.0
Temperature (K)	273
Wavelength (\AA)	0.71073
Crystal system, space group	Monoclinic, $C2/c$
Unit cell dimensions	$a = 27.950(14)$ $b = 14.169(7)$ $c = 17.717(9)$ \AA $\beta = 105.669(11)^\circ$
V (\AA^3)	6756(6)
Z	4
ρ_{calc} (g cm^{-3})	1.232
Absorption coefficient (mm^{-1})	0.277
$F(000)$	2640
Crystal size (mm)	0.44 x 0.16 x 0.13
Theta range for data collection ($^\circ$)	1.62-25.24
Limiting indices	$-33 \leq h \leq 32$ $-13 \leq k \leq 16$ $-21 \leq l \leq 21$
Reflections collected / unique	17469/6104 [$R_{\text{int}} = 0.0690$]
Completeness to theta	25.24-99.7 $^\circ$
Data / restraints / parameters	6104/12/448
Goodness-of-fit on F^2	1.008
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.069$ $wR_2 = 0.124$
R indices (all data)	$R_1 = 0.151$ $wR_2 = 0.150$

Table 2. Selected Bond Lengths (Å) and Angles (°) of [Fe(pq)₂(dmf)₂](BPh₄)₂

Bond lengths (Å)			
O1-C15A	2.101(3)	C1-N1	1.333(4)
B1-C24	1.646(5)	B1-C30	1.641(5)
B1-C36	1.643(3)		
Bond and torsion angles (degree)			
O1-Fe1-O1A	87.65(10)	O1A-Fe1-N1	176.91(12)
O1-Fe1-N1	91.68(10)	O1-Fe1-N1	91.68(12)
N1-Fe1-N1A	89.15(16)	O1A-Fe1-N2	107.30(11)
O2-Fe1-N2	81.65(11)	N1-Fe1-N2	75.57(12)
N1A-Fe1-N2	95.68(12)	C24-B1-C30	111.80(9)
C24-B1-C36	113.00(3)	C30-B1-C36	103.10(3)
C24-B1-C23	104.50(3)	C36-B1-C23	111.80(3)
C36-B1-C23	112.90(3)	C14-N2-C6-C5	177.20(3)
N1-C5-C6-N2	-8.30(5)	C4-C5-C6-N2	172.30(3)

4. Conclusion

Single crystal of [Fe(pq)₂(dmf)₂](BPh₄)₂ complex has been grown out of evaporation of the complex solution in *N,N*-dimethylformamide at room temperature after 24 hours. This compound crystallize in monoclinic system with *C*2/*c* space group, *a* = 27.950(4), *b* = 14.169(7), *c* = 17.717(9) Å and β = 105.669(11)°. The structure consist of iron(II) is chelated by two pq ligands through the N atoms and two dmf molecules in a six-coordination environment. The charge of the [Fe(pq)₂(dmf)₂]²⁺ cation is balanced by two tetraphenylborate (BPh₄)⁻ anions.

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