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(Electronic Supplementary Information)

Hydrogen bond mediated intermolecular magnetic coupling in mononuclear high spin iron(III) Schiff base complexes: Synthesis, structure and magnetic study with theoretical insight

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Table: S1 Selected bond angles (°) in complexes **1** and **2**.

Atoms	1	2	Atoms	1	2
O1-Fe1-N1	93.57(9)	95.0(2)	N2-Fe1-N4	89.05(9)	97.2(2)
O1-Fe1-N2	163.15(9)	162.26(19)	N2-Fe1-N5	96.59(9)	–
O1-Fe1-N3	87.25(9)	85.8(2)	N3-Fe1-N4	91.56(9)	172.5(2)
O1-Fe1-N4	100.80(9)	98.1(2)	N3-Fe1-N5	175.36(9)	–
O1-Fe1-N5	97.38(9)	–	N4-Fe1-N5	88.01(10)	–
N1-Fe1-N2	78.02(9)	78.0(2)	Cl1-Fe1-O1	–	96.46(15)
N1-Fe1-N3	93.20(10)	90.8(2)	Cl1-Fe1-N1	–	167.29(19)
N1-Fe1-N4	165.06(9)	82.6(3)	Cl1-Fe1-N2	–	92.41(16)
N1-Fe1-N5	86.10(11)	–	Cl1-Fe1-N3	–	95.43(14)
N2-Fe1-N3	78.78(9)	78.03(18)	Cl1-Fe1-N4	–	90.5(2)

IR and UV-Vis spectra

The IR and electronic spectra of both complexes are in good agreement with their molecular structures. The IR spectra of both complexes exhibit strong bands at ~1580 cm^{-1}, corresponding to the azomethine (C=N) stretching vibrations.[1] In complex **1,** there is a bifurcated sharp band at 2075 cm^{-1} and 2042 cm^{-1} attributed to the two terminal thiocyanate groups.[2] Complex **2** shows a sharp band around 2040 cm^{-1}, due to the presence of the terminal azide ligand.[3] Both complexes show weak bands at ~3227 cm^{-1} due to the N-H stretching vibrations of the primary amine group and another weak bands at ~3134 cm^{-1}, corresponding to the N-H stretching vibrations of the secondary amine group.[4] In both cases, the C-H stretching vibrations appear in the range 2866-2944 cm^{-1}.[5] IR spectra of both complexes are shown in Fig. **S1**.

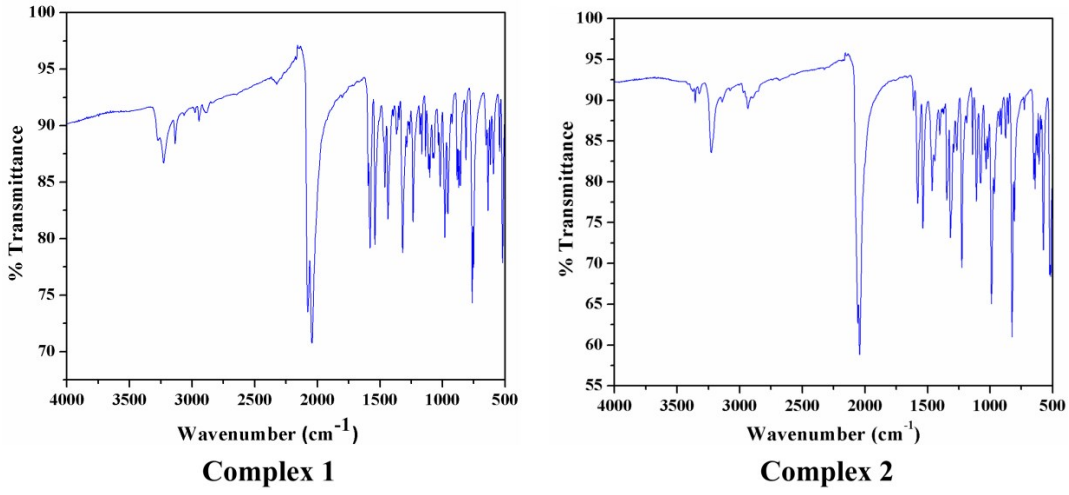

Fig. S1: IR spectra of complexes **1** (left) and **2** (right).

The colors of solid microcrystalline products of both complexes **1** and **2** are dark green and the colors of 10^{-4} M solutions of both complexes are light green. The electronic absorption

spectra of complexes **1** and **2** show similar features. The band (at 515 nm for **1** and 520 nm for **2**) in the electronic spectrum of each complex may be originated from d-d transition. The intensity of this band is weak as the d-d transitions in any d^5 iron(III) complex is forbidden by both Laporte and spin selection rules. A stronger band (at 330 nm in both complexes) may tentatively be assigned to a superposition of the amine-to-iron(III), azide to iron(II) and phenoxido-to-iron(III) charge transfer transitions.[6-9] For both complexes, bands around 230 and 270 nm may be assigned as intra-ligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively.[10] The band positions and intensities are comparable with those found in similar complexes.[6,7] UV-Vis spectra of both complexes are shown in Fig. **S2**.

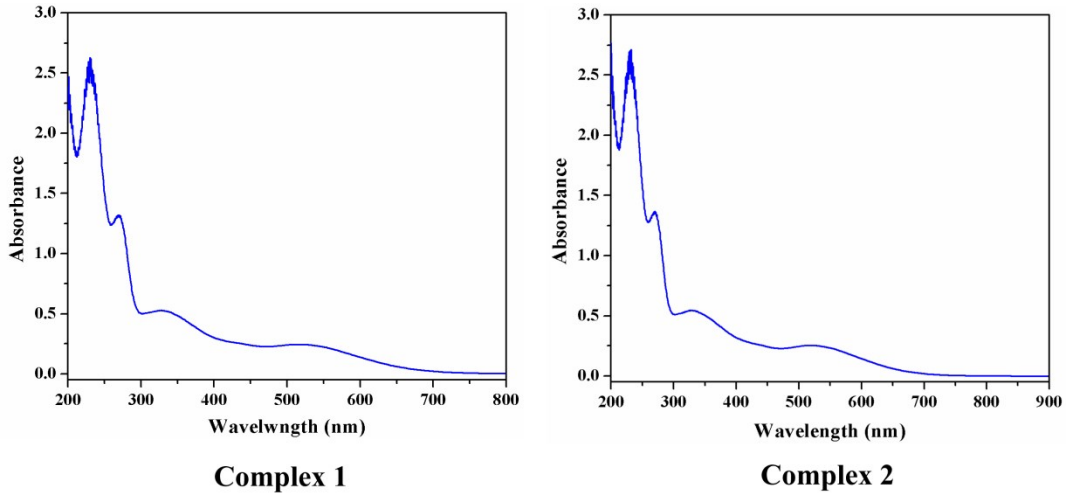

Fig. S2: UV-Vis spectra of complexes **1** (left) and **2** (right).

Curie-Weiss plots

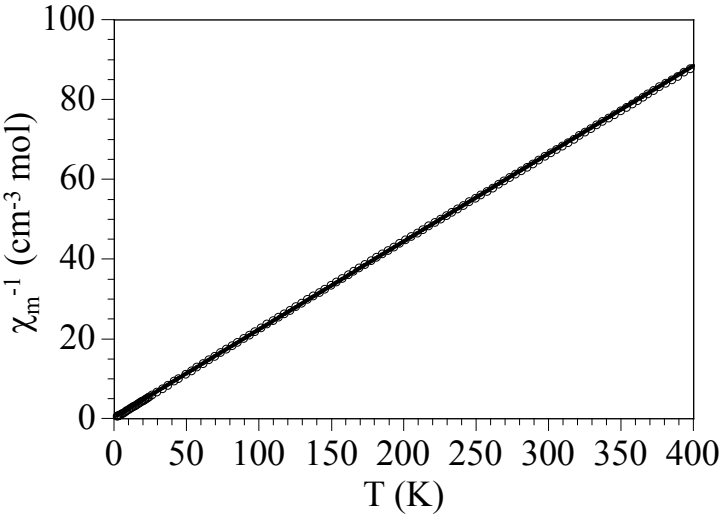

Fig. S3: Curie plot for complex **1**. Solid line is the best fit to the Curie-Weiss law with C = 4.54 cm^3 K mol^{-1} and θ = -1.61 K = -1.12 cm^{-1}.

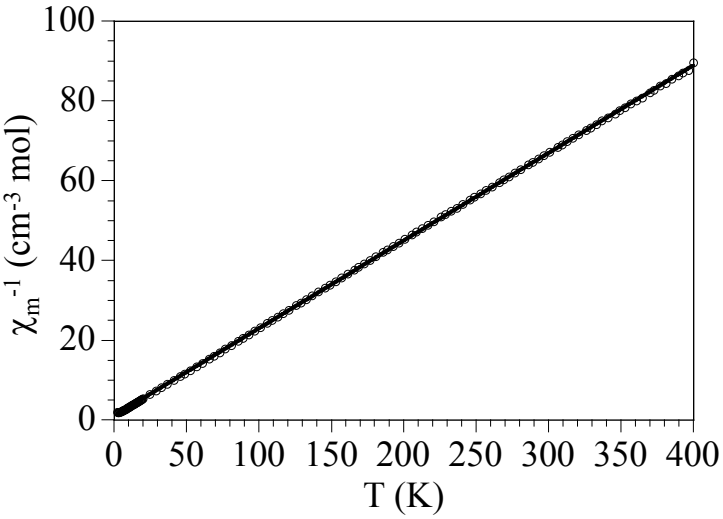

Fig. S4: Curie plot for complex **2**. Solid line is the best fit to the Curie-Weiss law with C = 4.55 cm^3 K mol^{-1} and θ = -4.73 K = -3.29 cm^{-1}.

Table S2: Ligands name of the following complexes mentioned in Table 5.

Complex	CSD code/ CCDC no.	Ligands
$[Cu_2(L^a)_2]$	-	L^a= 2,2'-[(1,3-dimethyl-1,3-propanediylidene)dinitrilo]bis- ethanol
$[Cu_2(L^a)_2]$	HEAICU10	L^a= 2,2'-[(1,3-dimethyl-1,3-propanediylidene)dinitrilo]bis- ethanol
$[Cu_3(L^b)_2(C_6H_5COO)_2Cl]Cl$	DEPSAT	L^b= 2-(2-Hydroxyphenylmethylaminomethyl)pyridine
$[Cu_2(\mu_2\text{-}H_2O)(L^c)_2(H_2O)_2](ClO_4)_2{\cdot}2H_2O$	KEDNIR	L^c= 2-[1-[[2-(Dimethylamino)ethyl]imino]ethyl]phenol
$[Cu_2(L^d)_2(H_2O)_2(ClO_4)](ClO_4){\cdot}H_2O$	FUTCON	L^d= 2-((2-(Pyridin-2-yl)hydrazono)methyl)phenol
$[Cu(L^e)_2(H_2O)]$	BEYRAY	L^e= 2-Carboxypyrazine
$[Zn^{II}(H_2O)_6][Cu^{II}(L^f)_2(H_2O)_2]$	HULMOQ	L^f= malonic acid
$[Cu_2(L^g)_2(H_2O)_2]{\cdot}2H_2O$	MATLOJ	L^g= 2-di1H-2-imidazolylmethylmalonic acid
$[Cu(L^h)(H_2O)(NO_3)]$	NUQKOZ01	L^h= 2-(o-hydroxyphenyliminomethyl)pyridine

		N-oxide
$[Cu(L^i)_2(H_2O)_2]_n$	FAHNAE	L^i= 2-hydroxy-1,4-naphthoquinone
$[Cu(L^j)(H_2O)]\cdot 4H_2O$	SAGLAC	L^j= N-Salicylideneglycine
$[NiCl_2(L^k)_2]$	FUJQOQ	L^k= phenylenediamine
$[Cu(HL^l)(L^l)(H_2O)]_2NO_3$	AETCUB	[L^l= 2-amino-2-methylpropanol
$[Cu(HL^m)(L^m)]_2(NO_3)_2$	AETCUA	L^m= 2-aminoethanol
$[\{Cu(H_2L^n)\}\{Cu(Hsabhea)\}]BF_4$	ODALAG	L^n= N-salicylidene-2-(bis(2-hydroxyethyl)amino)ethylamine
$[\{Cu(H_2L^n)\}_2](BF_4)_2$	ODALEK	L^n= N-salicylidene-2-(bis(2-hydroxyethyl)amino)ethylamine
$[Cu(HL^o)(L^o)]PF_6$	MASQIJ	L^o= 2-pyridylmethanol
$[Cu(HL^p)(L^p)]BF_4\cdot 2H_2O$	YUKCOX	HL^p= N-t-butyl-N-2-pyridylhydroxylamine
$[Cu(L^q)_2(L^r)(H_2O)_2]$	BUQLIJ	L^q= 3- nitrobenzoate; L^r= nicotinamide
cis-$[Cu(L^s)_2(H_2O)_2]$	NEDPAO	L^s= 4-formyl-2-methoxyphenolato
trans-$[Cu(L^s)_2(H_2O)_2]\cdot H_2O$	PAXTUE	L^s= 4-formyl-2-methoxyphenolato
$[Ni_3(L^t)(CO_3)(H_2O)(py)_7]$	GIDNAK	L^t= 2,6-bis(5-(2-hydroxyphenyl)-pyrazol-3-yl)pyridine
$[\{Mn(bpy)H_2O)\}(L^u)_2(\mu\text{-}O)\{Mn(bpy)(ClO_4)\}]ClO_4$	AGOJOY	L^u= μ-2,6-dichlorobenzoato; bpy= bipyridine
$[\{Mn(bpy)H_2O)\}(L^u)_2(\mu\text{-}O)\{Mn(bpy)(NO_3)\}]NO_3$	AGOJUE	L^u= μ-2,6-dichlorobenzoato; bpy= bipyridine

$[Fe(L^{v})Cl(H_2O)]\cdot MeOH$	AZOXAO	L^{v}= 3,6,9,12-tetra-aza-1(2,6)-pyridinacyclotridecaphane-2,13-dione
$[(Ni(L^{w})_2)_3(Fe(CN)_6)_2]\cdot 7H_2O$	ROQCAB	L^{w}= Bis(1-pyrazolyl)methane
$\{[Mn(OH)(OAc)_2]\cdot AcOH\cdot H_2O\}_n$	HUWHOW	AcOH= acetic acid
$[FeL^{1}(NCS)_2]$	**2036380**	***HL*^{1}= 2-[1-[[2-[(2-aminoethyl)amino]ethyl]imino]ethyl]phenol and**
$[FeL^{2}(N_3)Cl]$	**2036381**	***HL*^{2}= 2-(-1-(2-(2-aminoethylamino)ethylimino)ethyl)-4-methylphenol**

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