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).](image)

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. For both complexes, bands around 230 and 270 nm may be assigned as intra-ligand π→π* and n→π* transitions, respectively. The band positions and intensities are comparable with those found in similar complexes. 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 $\theta = -1.61$ 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 $\theta = -4.73$ K = -3.29 cm$^{-1}$.
**Table S2**: Ligands name of the following complexes mentioned in Table 5.

| Complex                                                | CSD code/CCDC no. | Ligands                                                                 |
|--------------------------------------------------------|-------------------|-------------------------------------------------------------------------|
| \([\text{Cu}_2(L^a)_2]\)                               | -                 | \(L^a = 2,2'-[[1,3\text{-dimethyl}-1,3\text{-propanediylidene}]\text{dinitrilo}]\text{bis-ethanol}\) |
| \([\text{Cu}_2(L^a)_2]\)                               | HEAICU10          | \(L^a = 2,2'[1,3\text{-dimethyl}-1,3\text{-propanediylidene}]\text{dinitrilo}]\text{bis-ethanol}\) |
| \([\text{Cu}_3(L^b)_2(C_6\text{H}_5\text{COO})_2\text{Cl}]\text{Cl}\) | DEPSAT            | \(L^b = 2\text{-}[2\text{-Hydroxyphenylmethylaminomethyl}]\text{pyridine}\) |
| \([\text{Cu}_2(\mu_2^-\text{H}_2\text{O})(L^c)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2\cdot2\text{H}_2\text{O}\) | KEDNIR            | \(L^c = 2\text{-}[1\text{-}[2\text{-}(\text{Dimethylamino})\text{ethyl}]\text{jimino}]\text{ethyl}]\text{phenol}\) |
| \([\text{Cu}_2(L^d)_2(\text{H}_2\text{O})_2(\text{ClO}_4)](\text{ClO}_4)\cdot\text{H}_2\text{O}\) | FUTCON            | \(L^d = 2\text{-}[2\text{-}(\text{Pyridin-2-yl})\text{hydrazono}]\text{methyl}]\text{phenol}\) |
| \([\text{Cu}(L^e)_2(\text{H}_2\text{O})]\)               | BEYRAY            | \(L^e = 2\text{-Carboxypyrazine}\)                                     |
| \([\text{Zn}^{II}(\text{H}_2\text{O})_6][\text{Cu}^{II}(L^f)_2(\text{H}_2\text{O})_2]\) | HULMOQ            | \(L^f = \text{malonic acid}\)                                        |
| \([\text{Cu}_2(L^g)_2(\text{H}_2\text{O})_2\cdot2\text{H}_2\text{O}\) | MATLOJ            | \(L^g = 2\text{-di1H-2-imidazolylmethylmalonic acid}\)                  |
| \([\text{Cu}(L^h)(\text{H}_2\text{O})(\text{NO}_3)]\) | NUQKOZ01          | \(L^h = 2\text{-}(\text{o-hydroxyphenyliminomethyl}]\text{pyridine}\)  |
| Complex | Formula | L | Notes |
|---------|---------|---|-------|
| [Cu(L)]₂(H₂O)₂ | FAHNAE | L= 2-hydroxy-1,4-naphthoquinone |
| [Cu(L)](H₂O)-4H₂O | SAGLAC | L= N-Salicylideneglycine |
| [NiCl₂(L)₂] | FUJQOQ | L= phenylenediamine |
| [Cu(HL)][(L')][H₂O]₂ | AETCUB | [L'= 2-amino-2-methylpropanol] |
| [Cu(HL)²](L²)₂(NO₃)₂ | AETCUA | L²= 2-aminoethanol |
| [[Cu(H₂L)²][Cu(Hsabhe)]][BF₄] | ODALAG | L²= N-salicylidene-2-(bis(2-hydroxyethyl)amino)ethylamine |
| [[Cu(H₂L)²][BF₄]₂ | ODALEK | L²= N-salicylidene-2-(bis(2-hydroxyethyl)amino)ethylamine |
| [Cu(HL)(L²)]PF₆ | MASQIJ | L²= 2-pyridylmethanol |
| [Cu(HL²)[L²]BF₄·2H₂O | YUKCOX | HL²= N-t-butyl-N-2-pyridylhydroxylamine |
| [Cu(HL²)(L²)](H₂O)₂ | BUQLIJ | L²= 3- nitrobenzoate; L²= nicotinamide |
| cis-[Cu(L²)₂(H₂O)₂] | NEDPAO | L²= 4-formyl-2-methoxyphenolato |
| trans-[Cu(L²)₂(H₂O)₂]·H₂O | PAXTUE | L²= 4-formyl-2-methoxyphenolato |
| [Ni₃(L²)(CO₃)(H₂O)(py)₇] | GIDNAK | L²= 2,6-bis(5-(2-hydroxyphenyl)pyrazol-3-yl)pyridine |
| [{Mn(bpy)H₂O}]²(μ-O)[Mn(bpy)(ClO₄)]ClO₄ | AGOJOY | L²= μ-2,6-dichlorobenzoato; bpy= bipyridine |
| [{Mn(bpy)H₂O}]²(μ-O)[Mn(bpy)(NO₃)]NO₃ | AGOJUE | L²= μ-2,6-dichlorobenzoato; bpy= bipyridine |
| Chemical Formula | Formula | Description |
|------------------|---------|-------------|
| [Fe(L\(^\nu\))Cl(H\(_2\)O)]·MeOH | AZOXAO | L\(^\nu\)= 3,6,9,12-tetra-aza-1(2,6)-pyridinacyclotricaphane-2,13-dione |
| [(Ni(L\(^w\))\(_2\)(Fe(CN)\(_6\))\(_2\)]·7H\(_2\)O | ROQCA B | L\(^w\)= Bis(1-pyrazolyl)methane |
| ([Mn(OH)(OAc)\(_2\)]·AcOH·H\(_2\)O\(_n\)) | HUWHOW | AcOH= acetic acid |
| [FeL\(^1\)(NCS)\(_2\)] | 2036380 | HL\(^1\)= 2-[1-[[2-[[2-(aminoethyl)amino]ethyl]iminato]ethyl]phenol |
| [FeL\(^2\)(N\(_3\))Cl] | 2036381 | HL\(^2\)= 2-[-1-(2-(2-aminoethylamino)ethyl)iminato]ethyl)-4-methylphenol |

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