Electronic Supplementary Information

Valence Directed Binding Mode of [2x2] Iron Grids of Unsymmetric Picolinic Hydrazine Based Ligand

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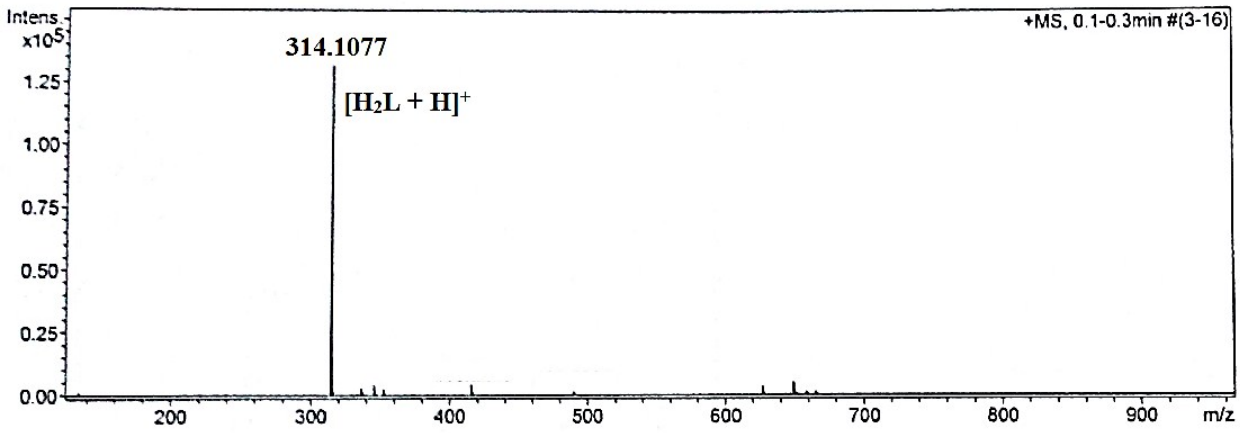

Fig. S1 ESI-MS spectrum of H_2L.

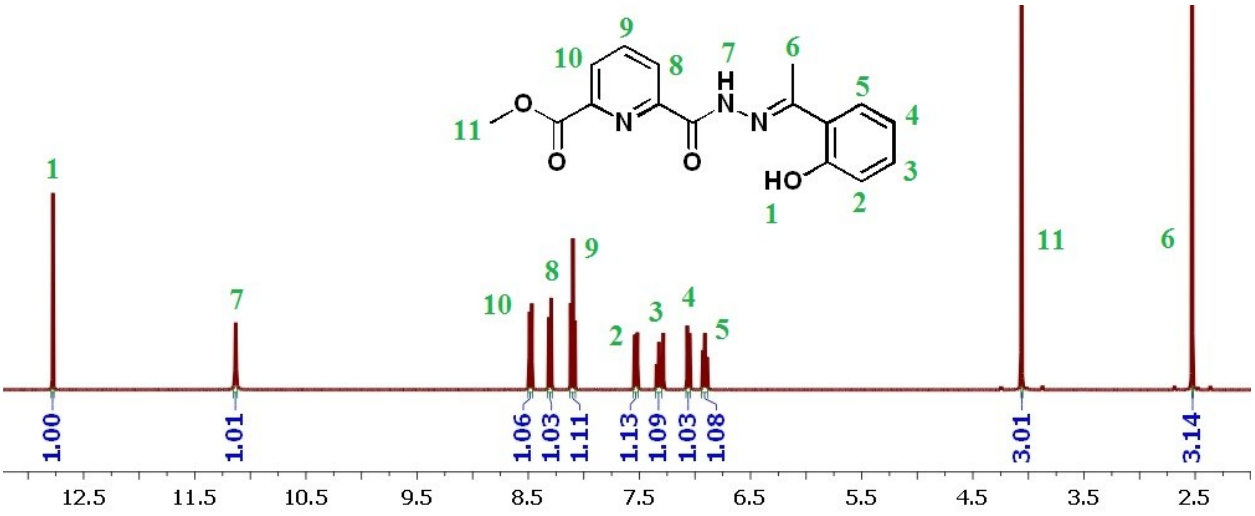

Fig. S2 ^{1}H NMR spectrum of H_2L in $CDCl_3$.

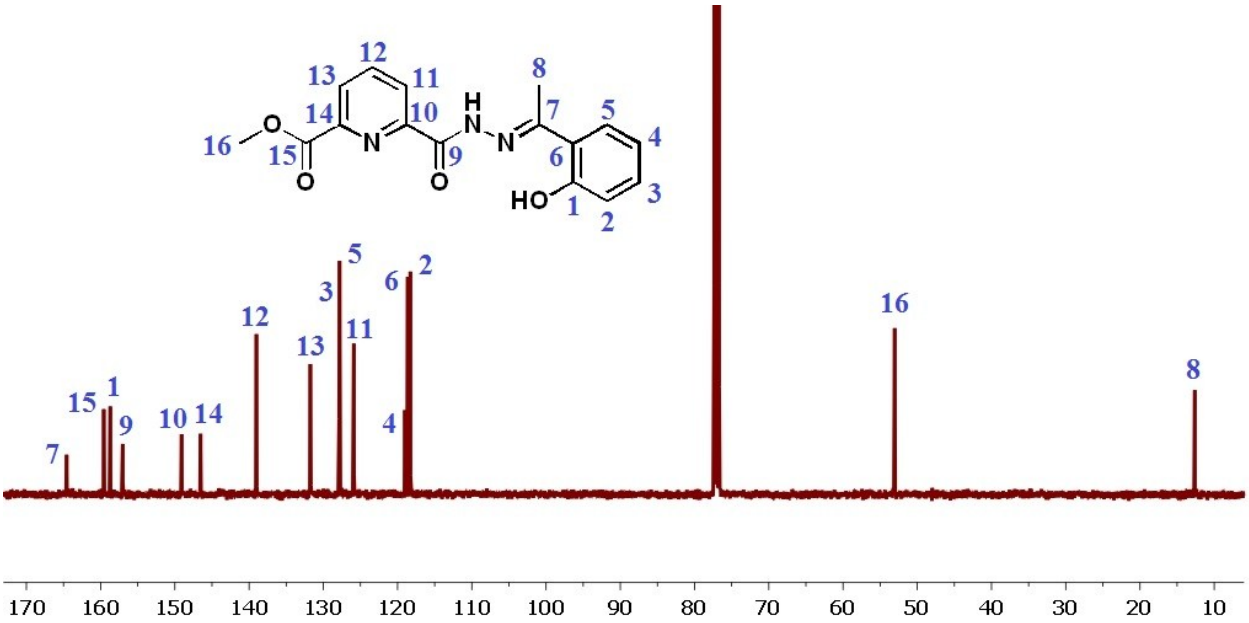

Fig. S3 ^{13}C NMR spectrum of H_2L in $CDCl_3$.

Redox properties

The electrochemical studies for $Fe(III)_4$ grid complex **1** could not be done because of its insolubility in any non-aqueous/aqueous solvent. Further the electrochemical studies were done on mixed-valent tertranuclear grid complex **2.** One irreversible oxidative response at +1.16 V can be seen in cyclic voltammogram (Fig. S4) though it is not very well defined peak. It seems that the redox potential for Fe(III/II) couple in this complex is very negative and hence small amount of Oxygen present in glove box might be the culprit to oxidize Fe(II) partially to Fe(III) in order to give the mixed valent tetra iron grid complex even though the reaction was done in inert atmosphere glove box and Fe(II) salt was used for the synthesis.

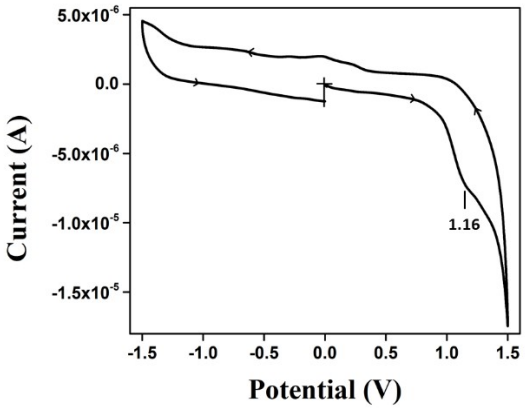

Fig. S4 Cyclic voltammogram (100 mV/s) of a 1.02 mM solution of complex **2** at a glassy carbon electrode in DMF (0.1 M TBAP). Indicated potential (in V) are vs Ag/Ag+ electrode.

Table S1 Selected Bond Distances (Å) and Angles (deg) for complexes **1** and **2**.

$[Fe^{III}_4(L')_4]$ (1)		$[[Fe^{II}_2Fe^{III}_2(L)_4](BF_4)_2 \cdot 2CH_3CN$ (2)	
Fe(1)-O(1)	1.863(4)	Fe(1)-O(1)	1.877(3)
Fe(1)-O(3)	2.009(4)	Fe(1)-O(5)	1.901(3)
Fe(1)-O(2)	2.038(3)	Fe(1)-O(2)	2.070(3)
Fe(1)-N(3)	2.085(5)	Fe(1)-O(6)	2.086(3)
Fe(1)-N(1)	2.099(4)	Fe(1)-N(1)	2.130(4)
Fe(1)-O(2)#1	2.191(3)	Fe(1)-N(4)	2.126(4)
		Fe(2)-N(6)	2.071(4)
		Fe(2)-N(9)	2.074(4)
		Fe(2)-O(6)	2.121(3)
		Fe(2)-O(7)	2.279(4)
		Fe(2)-O(10)	2.104(3)
		Fe(2)-O(11)	2.262(4)
		Fe(3)-O(9)	1.888(4)
		Fe(3)-O(10)	2.078(3)
		Fe(3)-O(13)	1.887(4)

	Fe(3)-O(14) 2.070(3)
	Fe(3)-N(7) 2.139(4)
	Fe(3)-N(10) 2.149(4)
	Fe(4)-N(3) 2.058(4)
	Fe(4)-N(12) 2.058(4)
	Fe(4)-O(2) 2.065(3)
	Fe(4)-O(3) 2.223(3)
	Fe(4)-O(14) 2.116(3)
	Fe(4)-O(15) 2.289(4)
Fe(1)-Fe(1)#2 3.837(5)	Fe(1)-Fe(2) 3.835(5)
	Fe(2)-Fe(3) 3.793(4)
	Fe(3)-Fe(4) 3.801(3)
	Fe(4)-Fe(1) 3.740(4)
Fe(1)-O(2)-Fe(1)#2 130.20(15)	Fe(1)-O(6)-Fe(2) 131.48(15)
	Fe(3)-O(10)-Fe(2) 130.21(16)
	Fe(3)-O(14)-Fe(4) 130.49(16)
	Fe(4)-O(2)-Fe(1) 129.52(15)