Electronic Supplementary Information for Dalton Transactions

Tuning of the charge in octahedral ferric complexes based on pyridoxal-N-substituted thiosemicarbazone ligands

Eddy W. Yemeli Tido[a], **Christophe Faulmann**[b], **Robby Roswanda**[a], **Auke Meetsma**[c] **and Petra J. van Koningsbruggen***[a]

[a]*Stratingh Institute for Chemistry and* [c]*Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.*
[b]*Laboratoire de Chimie de Coordination, LCC-CNRS UPR8241, 205 route de Narbonne, 31077 Toulouse – France*

Supplementary Information

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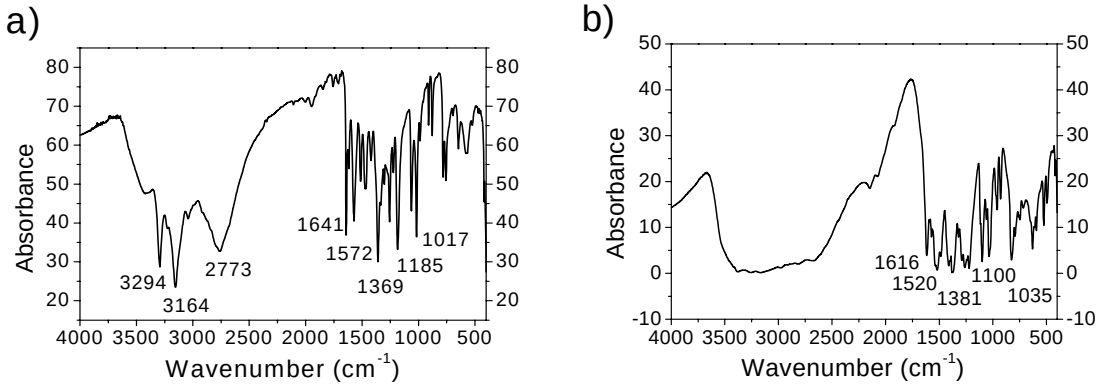

Fig. S1. KBr pellets IR spectra of: a) pyridoxalthiosemicarbazone hydrochloride (H_2thpy·HCl) and b) pyridoxalthiosemicarbazone monohydrate (H_2thpy·H_2O).

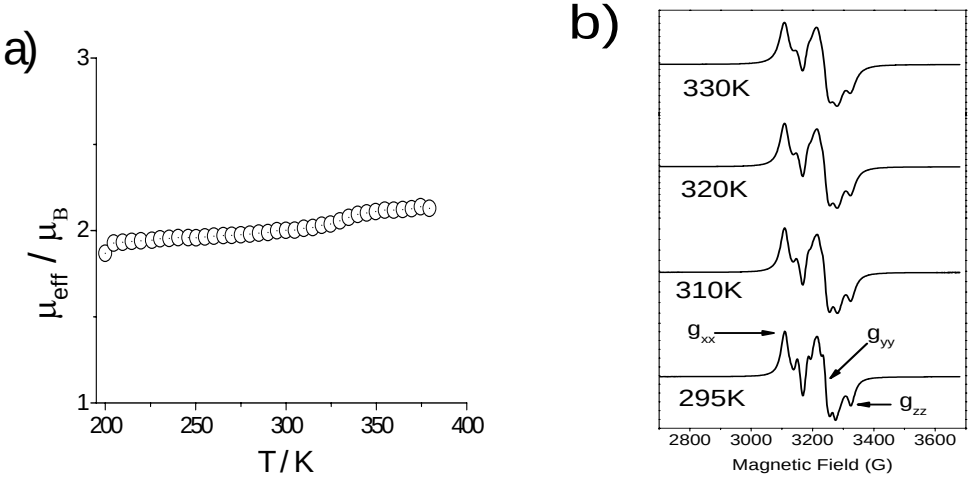

Fig. S2. a) μ_{eff} vs T plots. Sample was warmed from 2 to 400 K, at a rate of 5 K·min^{-1} and b) Temperature dependence X-band spectrum above RT with microwave frequency 9.515895 GHz. The Fe^{3+} spectrum consists of anisotropic g tensor with rhombic symetry at g_{xx} = 2.19, g_{yy} = 2.09 and g_{zz} = 2.04, for [Fe(Hthpy)$_2$](NO$_3$)·3H$_2$O.

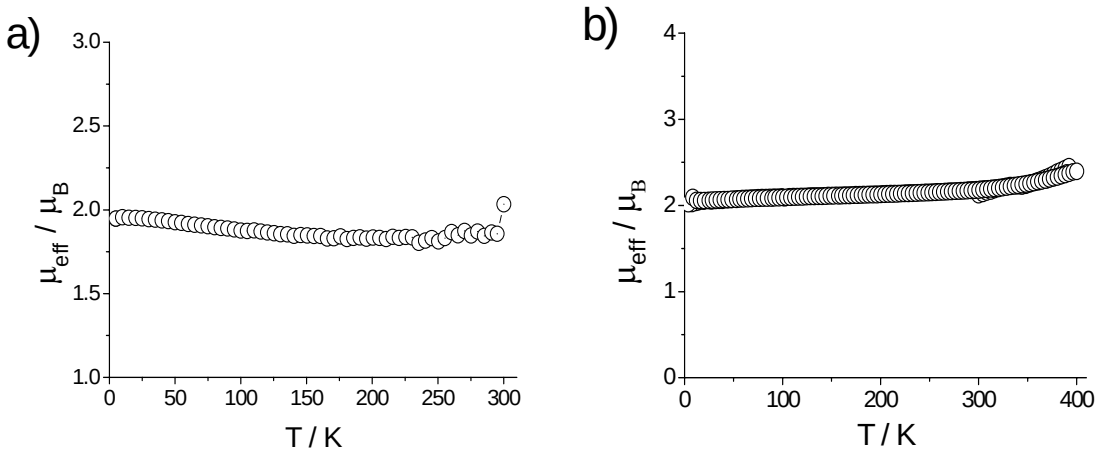

Fig. S3. μ_{eff} vs T plots for: a) $[Fe(Hthpy)_2](SO_4)_{0.5}\cdot 3.5H_2O$, sample was warmed from 5 to 300 K, at a rate of 5 K·min^{-1} and b) $[Fe(H_2mthpy)_2](CH_3C_6H_4SO_3)_3\cdot CH_3CH_2OH$, sample was warmed from 2 to 400 K and then cooled from 400 to 300 K, at a rate of 2 K·min^{-1}.

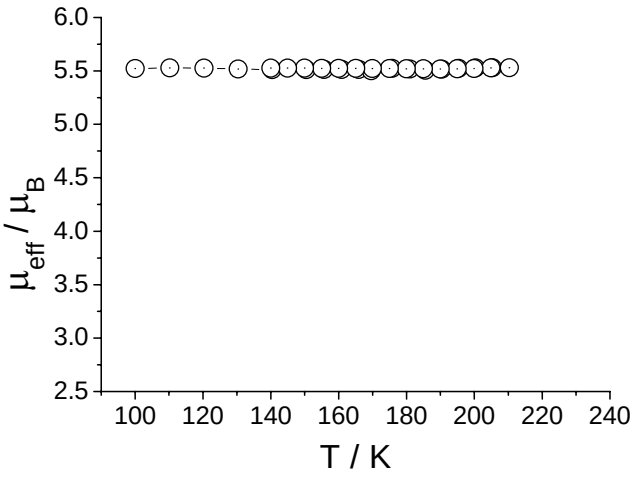

Fig. S4. The magnetic behaviour of [Fe(Hethpy)(ethpy)] in the form of μ_{eff} vs T plots. The sample was warmed from 100 to 210 K in the first run. Subsequently, the μ_{eff} was measured upon lowering the sample temperature from 210 to 140 K at a rate of 5 K·min^{-1}.

Table S1 Geometry of selected intra- and intermolecular hydrogen bonds (Å,°) for **1**, **2** and **4**. Standard deviations in the last decimal place are given in parentheses.

D–H---A	D–H (Å)	H---A (Å)	D---A (Å)	D–H---A (°)
		Compound **1**		
O7–H31---O9	0.59(19)	2.36(18)	2.900(19)	153(19)
O11–H35---O7	1.09(14)	1.52(13)	2.491(15)	145(12)
N2–H22---O5[b]	0.70(9)	2.14(8)	2.783(10)	154(9)
N4–H24'---O7[c]	0.74(8)	2.27(8)	2.967(12)	159(8)
O7–H31---O5[b]	0.82(12)	1.97(12)	2.783(11)	170(14)
O9–H33---O2[d]	1.2(2)	2.09(18)	2.753(18)	113(12)
O11–H35'---S1[e]	0.87(16)	2.40(17)	3.253(14)	166(12)
N6A–H61---O6[f]	0.88(3)	2.12	2.816(15)	136
		Compound **2**		
O4–H24---O5[g]	0.82(3)	2.19(3)	2.9903(18)	166(2)
N2–H32---O6[h]	0.90(2)	1.90(2)	2.7980(17)	175.2(18)
N6–H36---O5[i]	0.82(2)	2.08(2)	2.8819(19)	167(2)
O2–H22---O9[i]	0.83(2)	1.91(2)	2.7357(18)	172(2)
O9–H29---O10[j]	0.77(2)	2.01(2)	2.7750(18)	173(2)
O8–H28'---O6[k]	0.84(3)	1.95(3)	2.7815(18)	171(2)
N6–H36---O7[i]	0.82(2)	2.50(2)	3.1477(18)	137.3(18)
O9– H29'---S2[l]	0.83(3)	2.52(2)	3.3216(13)	165(2)
O10–H211---S1[m]	0.82(3)	2.56(3)	3.3626(13)	166(2)
		Compound **4**		
N1–H1---O36[c]	0.83(5)	1.95(5)	2.769(6)	176(6)
N4–H24---O37[n]	0.88	2.11	2.990(7)	174
N8–H28---O31[p]	0.88	2.08	2.950(6)	170
O33–H33---N3[b]	0.84(4)	2.12(5)	2.941(7)	165(5)
O33–H33'--O34[b]	0.84(3)	2.33(2)	3.129(8)	158(4)
O34–H34---O33[b]	0.84(4)	2.57(3)	3.129(8)	125(5)
O35–H35---N7[f]	0.84(3)	2.08(4)	2.861(6)	154(5)
O35–H35'---O38[f]	0.84(4)	1.92(4)	2.745(6)	168(4)
O38–H38'--O32[c]	0.84(4)	1.92(4)	2.754(7)	170(5)
O36–H36'---N5[c]	0.84(5)	1.85(5)	2.670(6)	168(5)

O37–H37---O35[c]	0.84(4)	1.95(4)	2.786(6)	172(4)

Atoms marked with a letter are generated by the symmetry operations: b = -x, y, 1/2-z; c = 1/2-x, -1/2+y, 1/2-z; d = x,1-y,1/2+z; e = -1/2+x, 1/2+y, z; f = 1/2-x, 1/2+y, 1/2-z; g = x, 1/2-y, -1/2+z; h = 1-x, 1-y, -z; i = 1+x, 1/2-y, -1/2+z; j = 1-x, -y, 1-z; k = 1-x, -1/2+y, 1/2-z; l = x, 1/2-y, 1/2+z; m = -1+x, y, z; n = 1/2-x, 1/2-y, -z; p = x, -y, -1/2+z.