Supporting information

Catalytic Disproportionation of *N*-Alkylhydroxylamines Bound to Pentacyanoferrates

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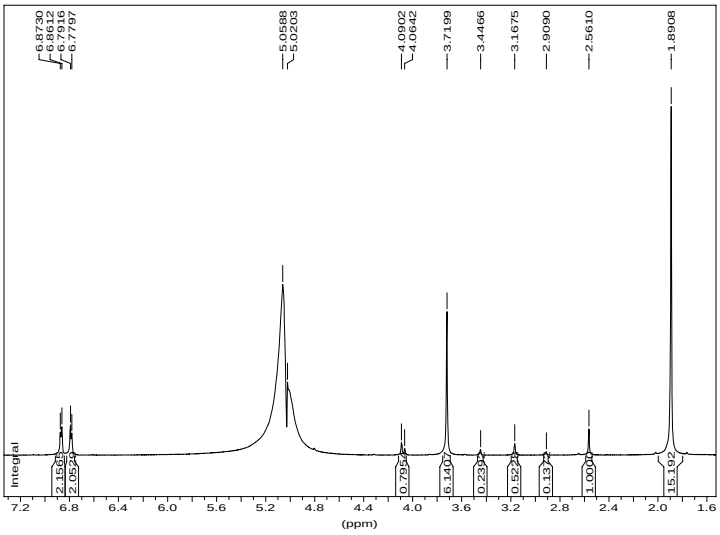

Figure 1. ^{1}H NMR spectrum of the solution of $[Fe(CN)_5H_2O]^{3-}$ 5 mM, MeHA 100 mM in D_2O, at room temperature, pH 7.1 (2.5 M phosphates), internal standard $NaCH_3CO_2$.

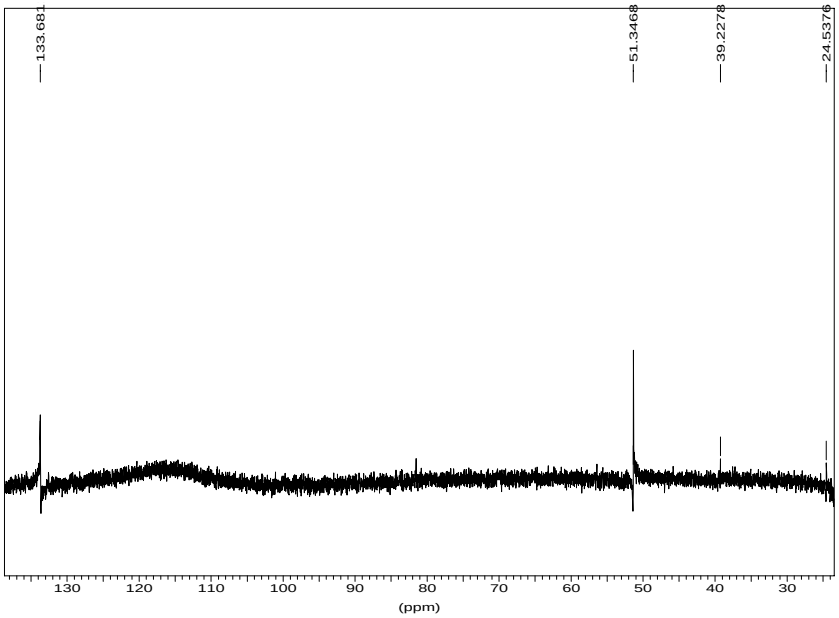

Figure 2. ^{13}C NMR spectrum of the solution of $[Fe(CN)_5H_2O]^{3-}$ 5 mM, MeHA 100 mM in D_2O, at room temperature, pH 7.1 (2.5 M phosphates), internal standard $NaCH_3CO_2$

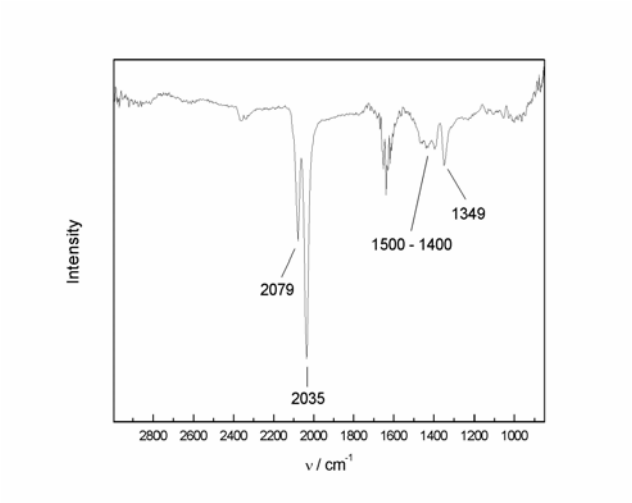

Figure 3. ATR spectrum of a reactive aqueous solution of $[Fe(CN)_5H_2O]^{3-}$ 0.1 M with [MeHA] 0.05 M, (pH ~ 4), at room temperature. A background of MeHA-solution has been substracted. Note the CN stretching of unreacted $[Fe(CN)_5H_2O]^{3-}$ at 2035 cm^{-1}. The CN stretching at 2079, CH bending at 1500-1400 and NO stretching at 1349 cm^{-1} correspond to the red complex.

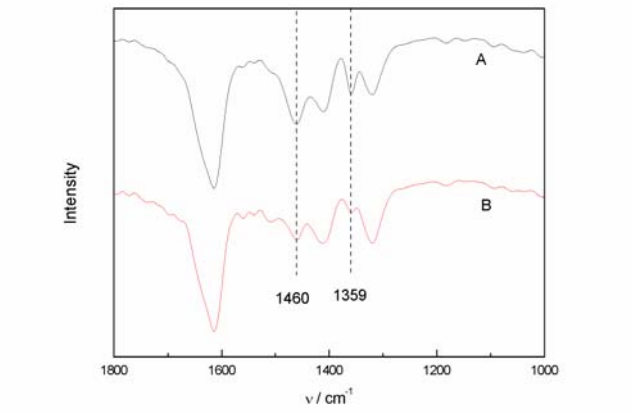

Figure 4. FTIR transmittance spectra of the red solid, KBr disk. CN stretching at 2090 (not showed), CH bending at 1460; NO stretching at 1359 cm^{-1}.

pH	$[Fe(CN)_5H_2O]^{3-}$, mM	$[HN(CH_3)OH]$, mM	k_{obs}, s^{-1}
5.9	0.18	9.2	0,12
6.05	0.14	13.5	0,24
6.05	0.12	27.0	0,50
6.1	0.053	1.0	0,014
6.1	0.116	5.9	0,089
7.12	0.07	3	0,11
7.12	0.27	3.8	0,13
7.12	0.137	1.5	0,036
7.12	0.12	1.1	0,036
7.12	0.16	2.1	0,056

Table 1. Pseudo-first order rate constants for the reaction of $[Fe(CN)_5H_2O]^{3-}$ with MeHA at different concentrations of reactants and pH´s. T = 25.0 ± 0.2 ºC, 20 mM phosphates and I = 1 M (NaCl).

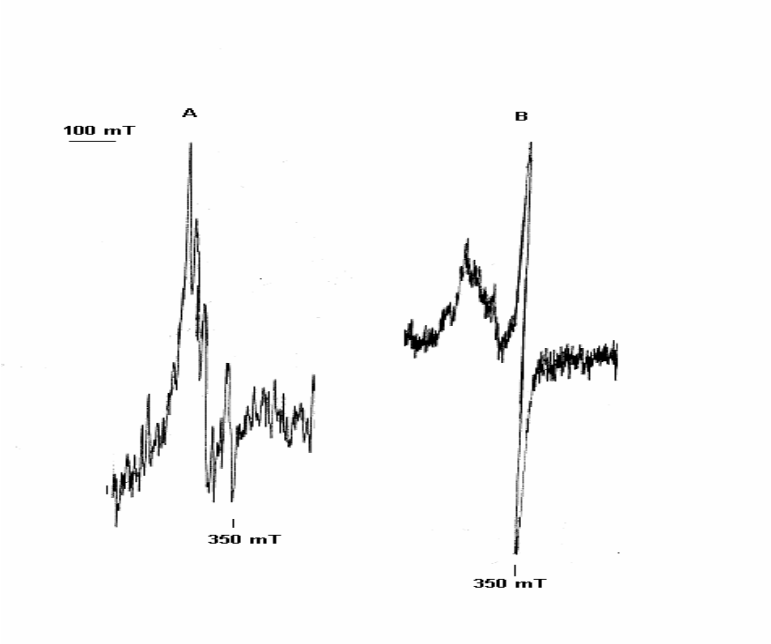

Figure 5. (A) Initial EPR spectrum of the red solid, obtained as a Zn-precipitate, for the reaction of $[Fe(CN)_5H_2O]^{3-}$ with MeHA, showing a triplet centered at 344 mT. (B) Final spectrum of the red solid, showing a singlet centered at 350 mT

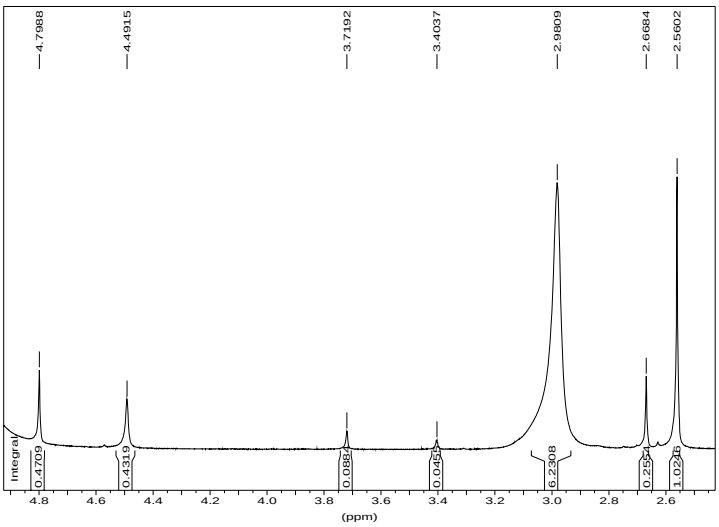

Figure 6. ^{1}H NMR spectrum of the solution of $[Fe^{II}(CN)_5H_2O]^{3-}$: 5 mM, Me_2HA 100 mM in D_2O, at room temperature, pH 7.1 (2.5 M phosphates), internal standard $NaCH_3CO_2$.

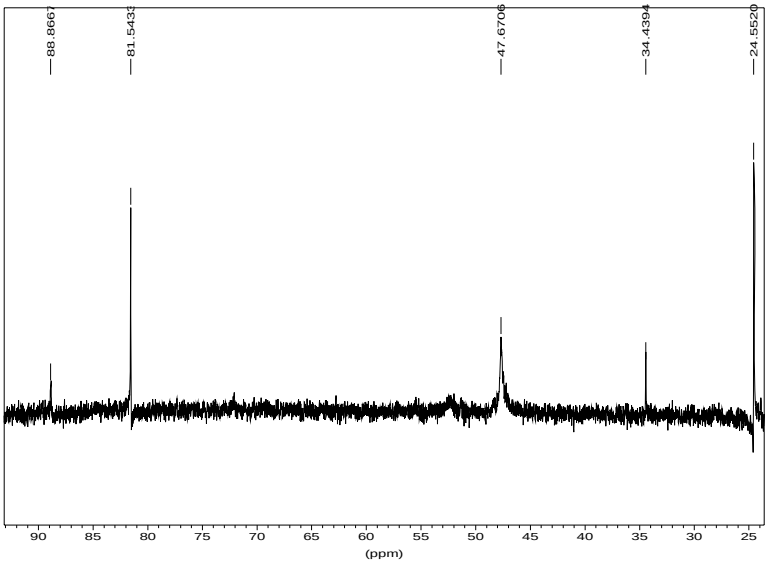

Figure 7. ^{13}C NMR spectrum of the solution of $[Fe(CN)_5H_2O]^{3-}$ 5 mM, Me_2HA 100 mM in D_2O, at room temperature, pH 7.1 (2.5 M phosphates), internal standard $NaCH_3CO_2$

pH	$[Fe(CN)_5H_2O]^{3-}$, mM	$[(CH_3)_2NOH]$, mM	k_{obs}, s^{-1}
6.05	0.12	1.54	0,00492
6.05	0.16	10.8	0,0327
6.05	0.053	38.0	0,125
6.05	0.12	9.8	0,0356
6.05	0.19	19.8	0,0693
6.05	0.07	5.1	0,0178
6.1	0.18	24.7	0,0752
6.1	0.16	12.0	0.0389
7.05	0.054	28.3	0.125
7.05	0.19	12.5	0.057
7.1	0.11	1.18	0.0046

Table 2. Pseudo-first order rate constants for the reaction of $[Fe(CN)_5H_2O]^{3-}$ with Me_2HA at different concentrations of reactants and pH´s, T = 25.0 ± 0.2 ºC, 20 mM phosphates and I = 1 M (NaCl).

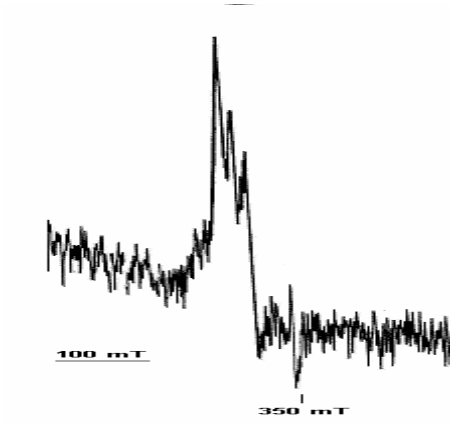

Figure 8. EPR spectrum of the solid obtained as a Zn-precipitate, for the reaction of $[Fe(CN)_5H_2O]^{3-}$ with Me_2HA, showing a triplet centered at 343 mT.