Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

All reagents were purchased and used without further purification.
UV-Vis spectrophotometry: Measurements were performed on a varian Cary 300 Bio UV-Vis spectrometer
Electrospray ionization mass spectrometry: Experiments were carried on a MicrOTOF-Q Bruker instrument using a source acceleration voltage of 3 kV and transfer capillary temperature (i.e. Dry heater on this particular instrument) of 140°C. About 1 pM solutions were injected without addition of charge carriers. Data was calibrated internally with ESI-L Low Concentration Tuning Mix (Agilent-Technologies).
Magnetism: The magnetic properties of **(1)** and **(2)** were studied on a SQUID Quantum Design MPMS 5 spectrometer using a microcrystalline samples placed in gelatin capsules. Experimental molar magnetic susceptibility ($\chi_m T$) measurements were performed in a temperature (T) range of 10 to 400 K in an applied constant magnetic field of 5000 Oe. Collected data were corrected from the contribution of the sample holder and from diamagnetic contributions deduced using Pascal's constant tables.
Gaz Chromatorgaphy: measurements were performed using a SHIMADZU GC-2014A equipped with a POROPAK Q 80/100 column (1/8") and a FID detector. The following conditions were used: vector gaz = N_2. $T_{injector}$ = 250°C. T_{oven} = 150°C. $T_{detector}$ = 250°C.
X-ray crystallography: Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and flashfrozen in a nitrogen-gas stream at 100 K. The temperature was maintained throughout the experiment to within an accuracy of ±1 K by means of a 700 series Cryostream cooling device. X-ray diffraction data were collected using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) and corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SIR-97[1] and refined against F^2 by full-matrix least-squares techniques using SHELXL-97[2] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed using the crystal structure crystallographic software package WINGX.[3] The crystal data collection and refinement parameters are given in Table S1.

Synthesis: In a 5 mL round bottom flask, ACC (11 mg, 0.11 mmol, 1 equiv.) and $N(n\text{-}Bu)_4OH \cdot 30\ H_2O$ (90 mg, 0.11 mmol, 1 equiv.) were stirred in water (1 mL) for 5 min. Water was then evaporated and the obtained ionic liquid was transferred into a glove box under argon. With the help of acetonitrile (2 mL) the ionic liquid was added to an acetonitrile (20 mL) solution of **(1)** (98.7 mg, 0.11 mmol, 1 equiv.) in a 200 mL round bottom flask. After addition of ether (150 mL) a solid formed, it was collected by filtration and wasted with 100 mL of ether. Recrystallization by slow ether diffusion in acetonitrile provided 20 mg (27 %) of crystalline **(2)**.

Reactivity studies with H_2O_2: 1 mM acetonitrile solutions of complex **(2)** or 1:1 mixture of iron(II) triflate and $N(n\text{-}Bu)_4ACC$ (blank) were placed in hermetically sealed tubes. The reactions were initiated by injection of 1 and up to 100 equiv. of concentrated H_2O_2 (30%) solutions through the septa of the seals (final concentration ranging from 1 to 100 mM). After one hour of reaction time at RT, gas from the headspace was analyzed by Gas Chromatography.

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1) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, J. Appl. Crystallogr., 1999, 32, 115-119.
2) G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112-122.
3) L. J. Farrugia, J. Appl. Crystallogr., 1999, 32, 837-838.

Cambridge Crystallographic Data Centre (CCDC) numbers 1029372-1029373 and the attached .CIF files contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the CCDC via http://www.ccdc.cam.ac.uk/Community/Requestastructure.

Table S1. Crystallographic data and structure refinement details for compounds (1) and (2).

Compound	**1**	**2**
	CCDC 1029373	CCDC 1029372
Empirical Formula	$C_{20}\ H_{28}\ Fe\ N_6,\ 2(F_6\ Sb)$	$C_{20}\ H_{28}\ Fe\ N_5\ O_2,\ F_6\ Sb$
M_r	879.83	662.08
Crystal size, mm^3	0.17 x 0.12 x 0.03	0.08 x 0.07 x 0.04
Crystal system	monoclinic	monoclinic
Space group	$P\ 2_1/c$	$P\ 2_1/c$
a, Å	17.2217(6)	10.6202(3)
b, Å	20.1069(7)	20.6412(6)
c, Å	16.9451(6)	11.6374(3)
α, °	90	90
β, °	91.4780(10)	100.1960(10)
γ, °	90	90
Cell volume, Å^3	5865.7(4)	2510.79(12)
Z ; Z’	8 ; 2	4 ; 1
T, K	100(1)	100(1)
F_{000}	3408	1320
μ, mm^{-1}	2.416	1.725
θ range, °	1.56 – 33.82	1.95 – 30.63
Reflection collected	72 834	61 655
Reflections unique	21 292	7 528
R_{int}	0.0240	0.0485
GOF	1.021	1.068
Refl. obs. ($I>2\sigma(I)$)	17 682	6 041
Parameters	747	318
wR_2 (all data)	0.0751	0.0892
R value ($I>2\sigma(I)$)	0.0304	0.0368
Largest diff. peak and hole (e-.Å^{-3})	-1.516 ; 3.405	-1.336 ; 2.053

Table S2. Selected bond lengths and angles from the crystal structure of complex (2).

	Bond length (Å)		Angle (º)
Fe-N1	2.203(2)	O1-Fe-N1	79.89(8)
Fe-N2	2.232(2)	O1-Fe-N4	96.69(9)
Fe-N3	2.242(3)	O1-Fe-N3	103.04(9)
Fe-N4	2.203(2)	O1-Fe-N5	93.35(8)
Fe-N5	2.211(2)	N1-Fe-N4	96.08(9)
Fe-O1	2.0164(19)	N1-Fe-N2	97.74(8)
		N1-Fe-N5	93.18(8)

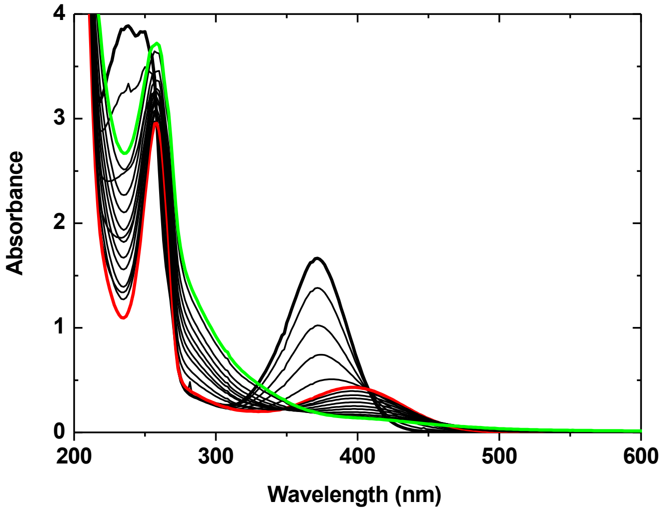

Figure S1. (A) UV-Visible monitoring of a 0,5 mM acetonitrile solution of complex $[Fe(BPMEN)(CH_3CN)_2](SbF_6)_2$ (1) (bold black line) upon successive additions of $N(n\text{-}Bu)_4ACC$ up to 3 equiv. (bold green line). The red line is obtained for the addition of 1 equiv. $N(n\text{-}Bu)_4ACC$.

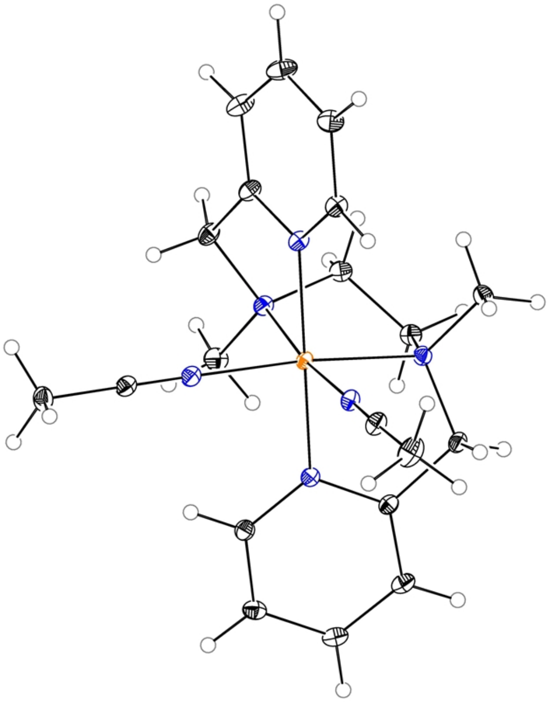

Figure S2. X-ray crystal structure of the $[Fe(BPMEN)(CH_3CN)_2](SbF_6)_2$ complex (1). Ellipsoids are drawn at the 30 % probability level. Counter ions are omitted for the sake of clarity.

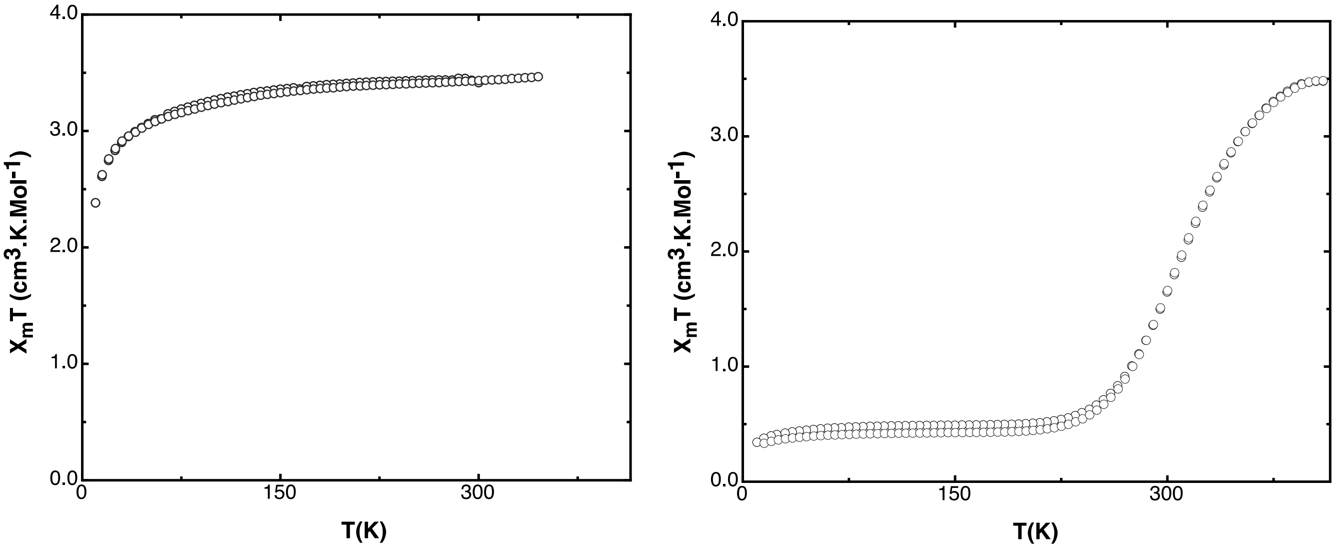

Figure S3. Plot of $\chi_m T$ *vs. T* obtained from the magnetization measurements collected from microcrystalline samples of complex (2) on the left and complex (1) on the right.

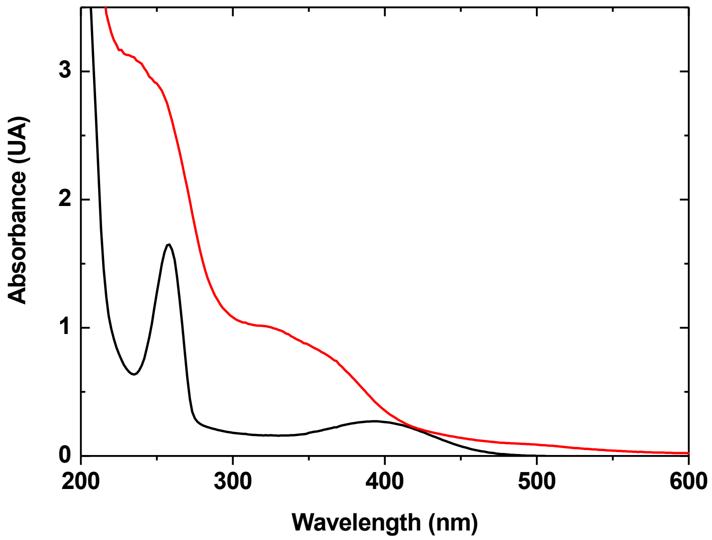

Figure S4. UV-visible spectra of a 0.25 mM solution of [Fe(BPMEN)ACC]SbF_6 complex (1) in CH_3CN before (black line) and after addition of 10 equivalent H_2O_2 (red line).