Synthetic, Structural and Magnetic Implications of Introducing 2,2'-Dipyridylamide to Sodium-Ferrate Complexes

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Supporting Information

Experimental

General Conditions

All reactions were carried out under an inert dry argon atmosphere utilising standard Schlenk and glove-box techniques (MBraun, MB10 Compact, <0.5 ppm H_2O, O_2). NaHMDS and 2,2'-dipyridylamine were purchased from Sigma Aldrich and used as received. $Fe(HMDS)_2$ was prepared according to a modified literature procedure from Lappert *et al.*[1,2] Hexane was dried prior to synthesis by Grubbs column (PureSolv micro solvent purification system, Innovative Technologies) to remove any traces of moisture and dissolved oxygen and stored over 4 Å molecular sieves. Toluene and THF were used immediately after being freshly distilled over sodium benzophenone ketyl under nitrogen. Deuterated solvent C_6D_6 for NMR spectroscopy was stored over 4 Å molecular sieves in the glove-box prior to use. NMR spectroscopy samples for complexes **2**, **3** and **4** were prepared inside the inert argon atmosphere of the glove-box. ^1H (400.13 MHz) NMR spectra were recorded on either a Bruker AV400 or AV3 spectrometer using TopSpin (v2.1, Bruker Biospin, Karlsruhe) at 300 K. ^1H NMR spectra were referenced internally to the corresponding residual protio solvent peaks. Solution magnetic susceptibilities were determined by the Evans method at 300 K.[3,4] Elemental analyses were performed on a Perkin Elmer 2400 Series II CHNS/O Analyser. Single-crystal X-ray diffraction was performed on Oxford Diffraction Xcalibur and Gemini diffractometers at 123 K using Mo Kα ($\lambda = 0.71073$ Å) or Cu Kα radiation ($\lambda = 1.54178$ Å), respectively. The structures were solved by direct methods and refined on all unique F^2 values using the SHELXS[5] and SHELXL[6] package within either the WinGX[7] or ShelXle[8] GUIs.

Synthetic Procedures

[{NaFe(HMDS)$_3$}$_\infty$] (1)

Hexane solutions of complex **1** were prepared *in situ* according to the previously reported method.[2]

[{Fe(HMDS)(DPA)}$_2$] (2)

$Fe(HMDS)_2$ (0.754 g, 2 mmol) and DPA(H) (0.342 g, 2 mmol) were added to a Schlenk tube along with 20 mL of hexane. Upon stirring a brown solution with off-white precipitate was formed which was stirred at ambient temperature overnight. Addition of 8 mL of THF dissolved the precipitate and gave a black solution which was cooled to −30°C. This yielded orange plate-like crystals which were separated from solution and washed once with 3 mL of cold hexane (0.68 g, 88% yield).

^{1}H NMR (C_6D_6, 300 K) δ (ppm) = 47.15 [bs, DPA aryl C*H*'s, 2H], 25.00 [bs, DPA aryl C*H*'s, 2H], 21.27 [bs, DPA aryl C*H*'s, 2H], 17.01 [vbs, Si*Me*$_3$, 54H], −14.31 [bs, DPA aryl C*H*'s, 2H]

Anal. Calcd for $C_{32}H_{52}Fe_2N_8Si_4$: C 49.73, H 6.78, N 14.50 Found: C 49.94, H 6.78, N 14.80

[(THF)$_2$·NaFe(DPA)(HMDS)$_2$] (3)

To a 1 mmol hexane solution of **1**, 0.171 g of DPA(H) (1 mmol) was added via solid addition tube resulting in the immediate formation of sticky tan/brown solid residue at the base of the Schlenk tube in the green solution. After stirring overnight at ambient temperature this residue was a dark brown suspension in the green solution, addition of 2 mL of THF gave a black solution. Cooling to −30°C allowed for the isolation of orange plate-like crystals (0.43 g, 60%).

Complex **3** was also accessed via the addition of 0.0073 g (0.04 mmol) NaHMDS to a C_6D_6 solution of **2** (0.0155 g, 0.04 mmol) in a Young's NMR tube and refluxing for 90 minutes. A near identical very broad resonance (centred at 6.33 ppm) was observed in the ^{1}H NMR spectrum.

^{1}H NMR (C_6D_6, 300 K) δ (ppm) = 6.39 [vbs], 4.97 [bs], 2.12 [bs] (meaningful integration and assignment of resonances not possible)

Anal. Calcd for $C_{26}H_{52}FeN_5NaOSi_4$ (loss of 1 THF): C 41.67, H 10.17, N 6.63 Found: C 41.24, H 9.99, N 7.16

Solution Magnetic Moment (C_6D_6, 300 K) = 4.93 μ_B

[{THF·NaFe(DPA)$_3$}$_\infty$] (4)

To a 1 mmol solution of **1** in hexane, 0.513 g of DPA(H) (3 mmol) was added via solid addition tube resulting in the immediate formation of sticky tan/brown solid residue at the base of the Schlenk tube in the green solution. After stirring overnight at ambient temperature there was a mustard coloured suspension in a dark brown solution. All volatiles were removed under vacuum and the mustard coloured solid residue was redissolved in 15 mL of toluene and 5 mL of THF. Cooling to −30°C allowed for the isolation of yellow plate-like crystals (0.49 g, 70% yield).

^{1}H NMR (C_6D_6, 300 K) δ (ppm) = meaningful integration and assignment of proton resonances not possible

Anal. Calcd for $C_{75}H_{72}Fe_2N_{18}Na_2O_2$ (2 monomer units + 1 eq. of co-crystallised toluene): C 63.65, H 5.13, N 17.82 Found: C 63.54, H 5.13, N 18.14

Solution Magnetic Moment (C_6D_6, 300 K) = 5.30 μ_B

NMR Spectra

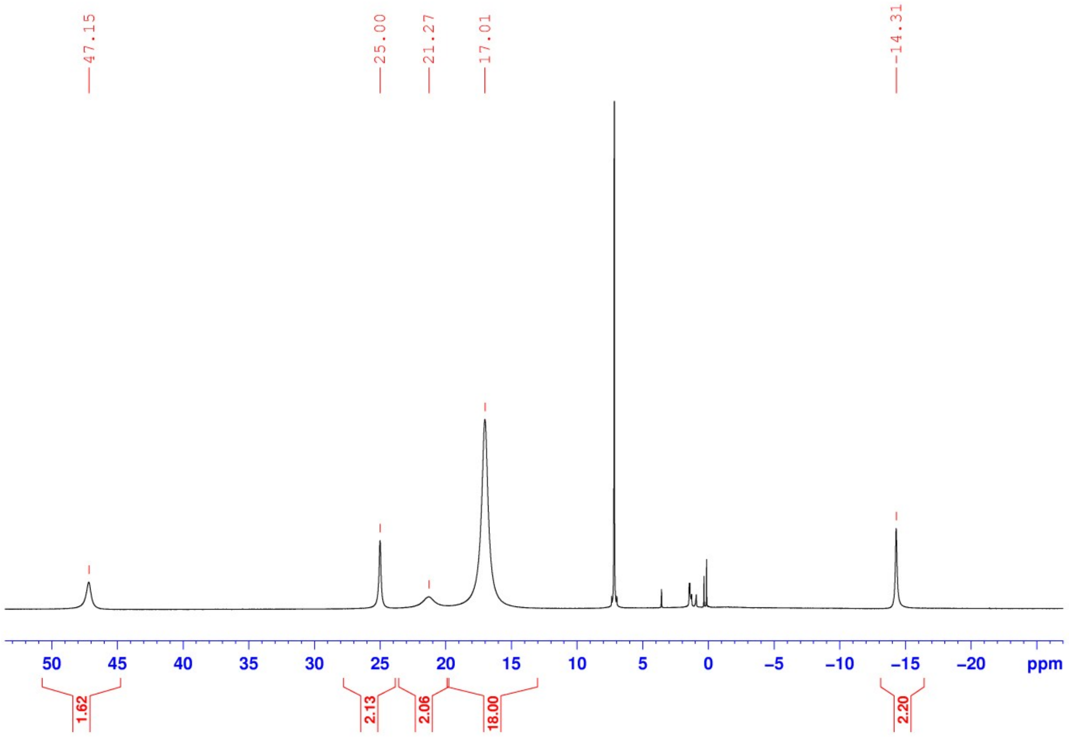

Fig. S1 ^{1}H NMR spectrum of **2** in C_6D_6

δ (^{1}H) / ppm	**Assignment**
47.15 (2H)	DPA aryl C*H*
25.00 (2H)	DPA aryl C*H*
21.27 (2H)	DPA aryl C*H*
17.01 (18H)	Si*Me*$_3$
−14.31 (2H)	DPA aryl C*H*

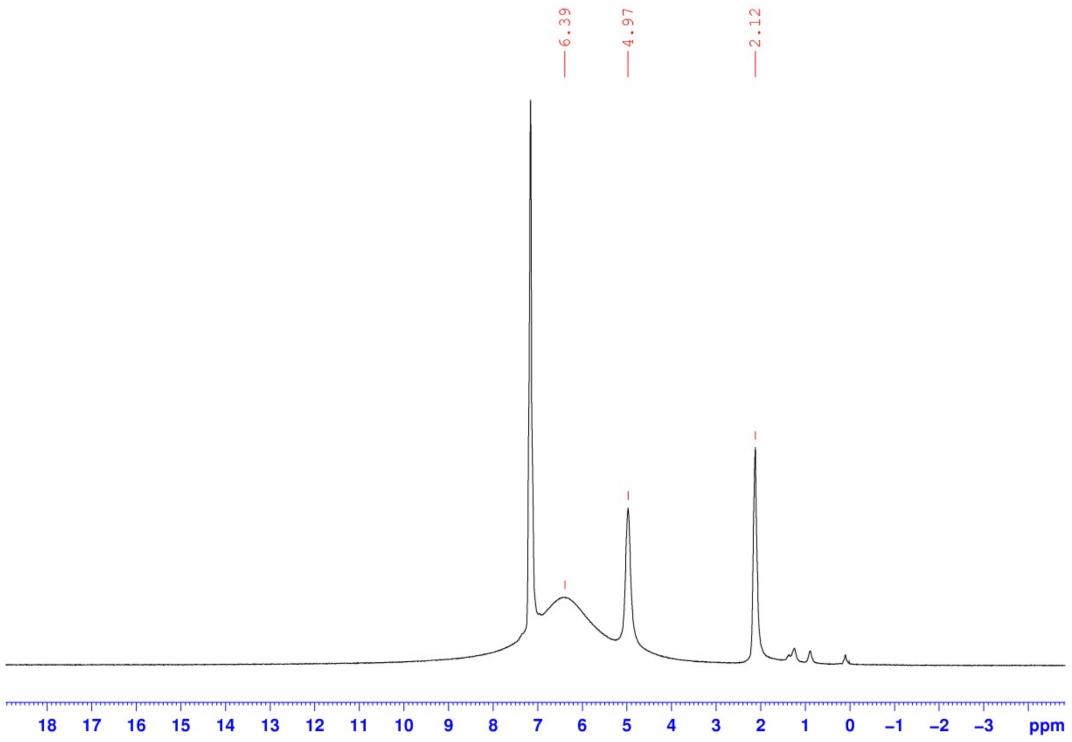

Fig. S2 ^{1}H NMR spectrum of **3** in C_6D_6

δ (^{1}H) / ppm	**Assignment**
6.39	Broad overlapping resonances preclude meaningful peak assignment and integration.
4.97	
2.12	

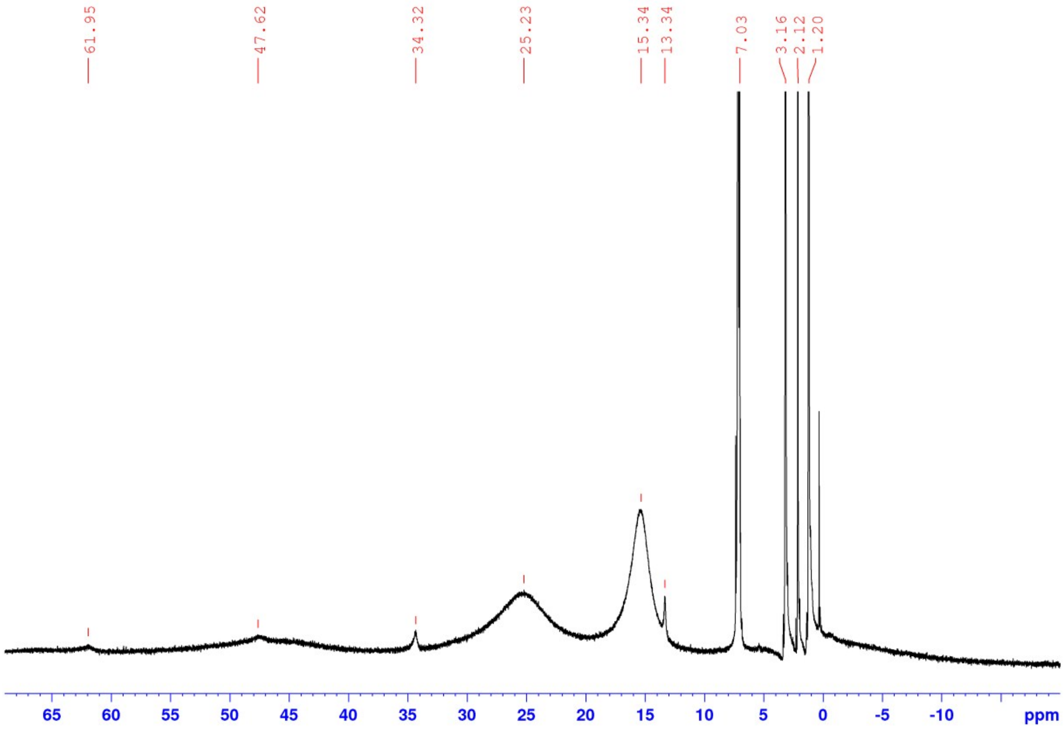

Fig. S3 ^{1}H NMR spectrum of **4** in C_6D_6

δ (^{1}H) / ppm	**Assignment**
61.95	Broad, overlapping and poorly resolved resonances preclude meaningful peak assignment and integration.
47.62	
34.32	
25.23	
15.34	
13.34	
7.03	Toluene CH (2,4,6)
3.16	THF CH_2 (2,5)
2.12	Toluene CH_3
1.20	THF CH_2 (3,4)

X-Ray Diffraction Data

All measurements were made with Oxford Diffraction CCD diffractometers and with monochromated radiation. Final models were refined to convergence on F^2 and against all unique reflections using SHELXL-2013.[6] A THF ligand and a $SiMe_3$ group of **3** and the toluene solvent molecule of **4** were modelled as disordered over two sites. Restraints were applied to the geometric and displacement parameters of these groups to ensure expected behaviour. Selected descriptors are given in Table S1 and full details are available in the submitted supplementary CIF files.

Table S1 Selected crystal parameters and refinement data.

Compound Label	**2**	**3**	**4**
CCDC Number	1538835	1538836	1538837
Chemical Identity	$C_{32}H_{52}Fe_2N_8Si_4$	$C_{30}H_{60}FeN_5NaO_2Si_4$	$C_{37.5}H_{36}FeN_9NaO$
Formula weight	772.87	714.03	707.59
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a Å	9.3817(2)	12.3817(2)	20.5102(10)
b Å	20.4274(4)	20.4492(4)	9.6402(4)
c Å	10.5678(2)	16.2656(3)	17.7307(7)
β °	104.402(2)	101.628(2)	99.067(4)
Volume $Å^3$	1961.61(7)	4033.86(13)	3462.0(3)
Z	2	4	4
Temperature K	123(2)	123(2)	123(2)
λ Å	0.71073	0.71073	1.54178
μ mm^{-1}	0.895	0.535	3.974
2θmax°	58.75	58.22	141.96
Refls. Collected	11789	33383	11902
Refls. Unique	4897	9918	6609
Reflns. Observed	3951	7690	3787
Rint	0.0279	0.0399	0.0757
No. Parameters	214	513	466
Goodness of Fit	1.035	1.031	0.990
$R[I>2\sigma(I)]$	0.0335	0.0384	0.0573
Rw2	0.0749	0.0880	0.1339

Magnetic Measurements

Variable-temperature magnetic susceptibility data was obtained with a Quantum Design MPMS5 SQUID magnetometer. Pascal's constants were used to estimate diamagnetic corrections to the molar paramagnetic susceptibility. X-Band (9.42 GHz) EPR spectra of powdered samples were determined on a Bruker ESP300E spectrometer, equipped with a liquid helium cryostat.

Bulk magnetisation properties were studied on powdered polycrystalline samples. Taking into account the extreme air and moisture sensitivity of the compounds, samples were prepared in a glovebox and immediately afterwards were stored in a Schlenk and transported to the SQUID. Gelatin capsules containing the samples were maintained under an inert atmosphere in a sealed compartment of a straw. During the whole process, the straw with the sample holder was removed from inert atmosphere between 20-45 s, just before being inserted to the SQUID. Results of SQUID measurements ($\chi_M T$ *vs* T and M *vs* H curves) were fitted using the program PHI (version 2.1.6).[9]

Studies of the temperature and frequency dependence of the alternate-current (AC) magnetic susceptibility were completed in the temperature range from 2 to 10 K using two frequencies (10 and 1000 Hz) under zero or 1000 Oe DC field and 4 Oe AC field.

For EPR measurements, samples were stored in a Wilmad quartz EPR sample tube (4 mm thin wall, 25 cm long tube) which was closed in a glovebox with a tip-off manifold (4 mm).

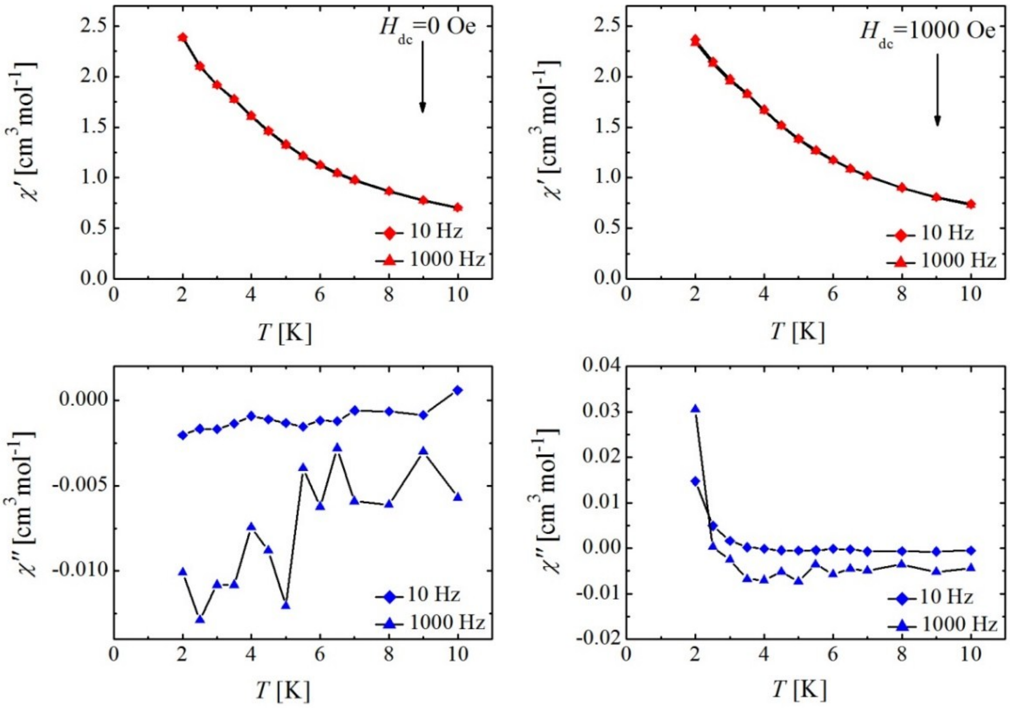

Fig. S4 AC studies of the compound **2**.

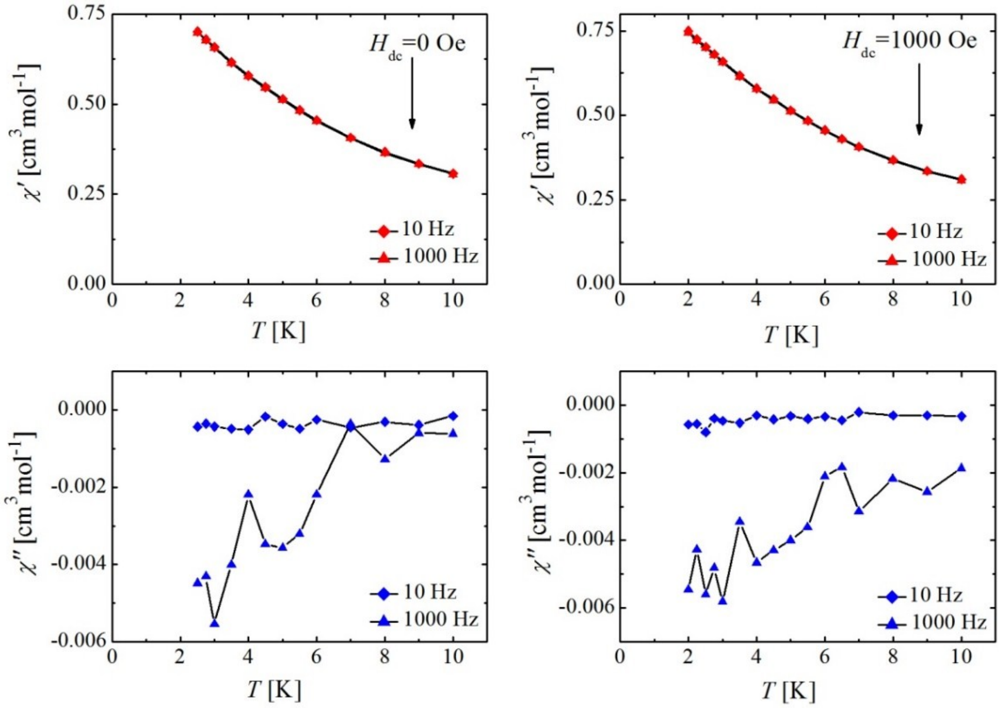

Fig. S5 AC studies of the compound **3**.

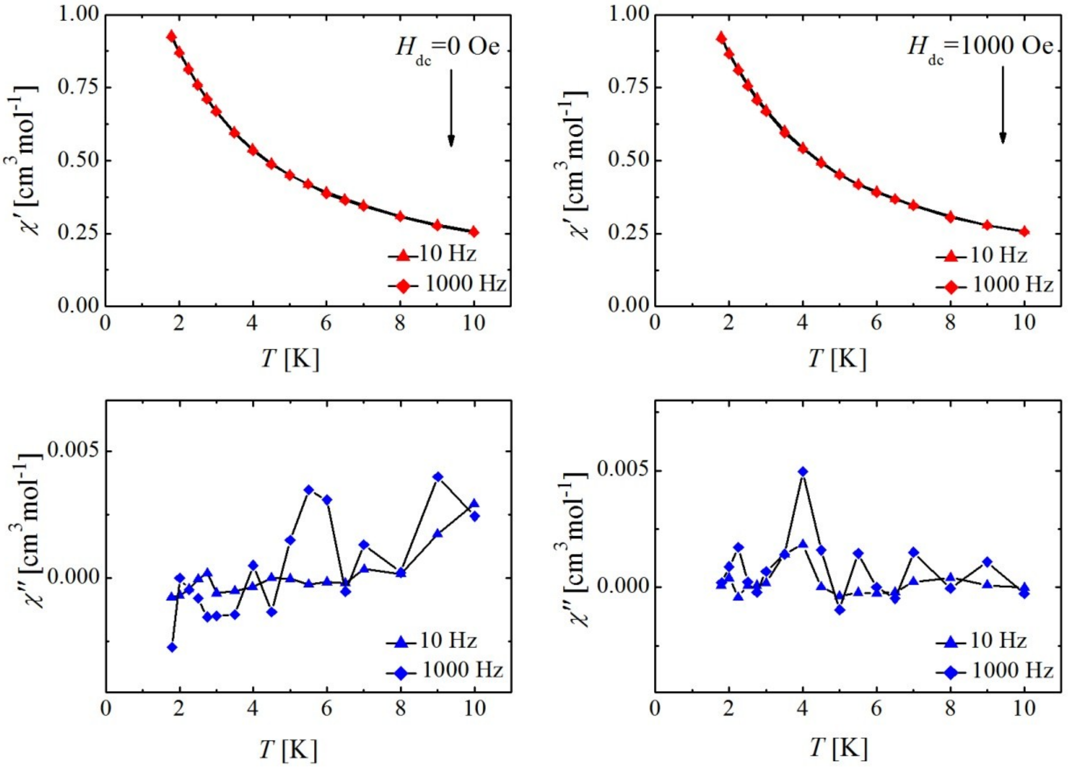

Fig. S6 AC studies of the compound **4**.

References

1 R. A. Andersen, K. Faegri, J. C. Green, A. Haaland, M. F. Lappert, W. P. Leung and K. Rypdal, *Inorg. Chem.*, 1988, **27**, 1782–1786.

2 L. C. H. Maddock, T. Cadenbach, A. R. Kennedy, I. Borilovic, G. Aromí and E. Hevia, *Inorg. Chem.*, 2015, **54**, 9201–9210.

3 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

4 E. M. Schubert, *J. Chem. Educ.*, 1992, **69**, 62.

5 G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.*, 2008, **64**, 112–22.

6 G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 3–8.

7 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.

8 C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.*, 2011, **44**, 1281–1284.

9 N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini and K. S. Murray, *J. Comput. Chem.*, 2013, **34**, 1164–1175.