Electronic Supplementary Information (ESI)

A single tripodal ligand stabilizing three different oxidation states (II, III, and IV) of manganese

Yukinari Sunatsuki,[a] Yukana Kishima,[a] Tamami Kobayashi,[a] Tomoka Yamaguchi,[a] Takayoshi Suzuki,[a] Masaaki Kojima,*[a] J. Krzystek[b] and Markku R. Sundberg[c]

[a] *Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530, Japan*

[b] *National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, USA*

[c] *Department of Chemistry, Laboratory of Inorganic Chemistry, POB 55, FIN-0014, University of Helsinki, Finland*

*E-mail: kojima@cc.okayama-u.ac.jp

Experimental Section

Caution! Perchlorate salts of metal complexes are potentially explosive. Only small quantities of material should be prepared and the samples should be handled with care.

Materials. All reagents and solvents used in the syntheses were of reagent grade and they were used without further purification. The triamine 1,1,1-tris(aminomethyl)ethane) hydrochloride (tame·3HCl) was prepared by the method of Fleischer et al.[1]

Synthesis of the H_3L ligand. To the tame·3HCl (0.113 g, 0.5 mmol) dissolved in water (20 mL) was added first a water solution (20 mL) of NaOH (0.06 g, 1.5 mmol) followed by a dichloromethane solution (40 mL) containing *o*-vanillin (0.228 g, 1.5 mmol). The mixture was stirred vigorously for two hours and transferred into a separating funnel. The dichloromethane layer was collected and dried. The solvent was removed to yield an orange-brown oil that used for preparation of the complexes. ^{1}H NMR (250 MHz, dimethyl sulfoxide–d_6): δ 1.16 (s, 3H, CH$_3$), 3.72 (s, 6H, CH$_2$), 3.90 (s, 9H, CH$_3$), 6.94 (t, $J = 8$ Hz, 3H, H5), 7.14 (d, $J = 8$ Hz, 3H, H4), 7.36 (d, $J = 8$ Hz, 3H, H6), 8.67 (s, 3H, HC=N), 13.79 (s, 3H, OH).

Synthesis of $NH_4[Mn^{II}L]\cdot2CH_3OH$ (1). The preparation was carried out in a glove box under a N$_2$ atmosphere. A methanol solution (3 mL) containing H$_3$L (0.129 g, 0.25 mmol) and NH$_4$CH$_3$CO$_2$ (0.025 g, 0.3 mmol) was added to Mn^{II}(CH$_3$CO$_2$)$_2$·4H$_2$O (0.031 g, 0.125 mmol). Triethylamine (76 µL, 0.5 mmol) was added to the mixture and the solution was left for two days to give red block crystals. Yield: 0.063 g (78%). Elemental analysis: Calcd for C$_{31}$H$_{42}$Mn$_1$N$_4$O$_8$: C, 56.96; H, 6.48; N, 8.57%. Found: C, 56.72; H, 6.26; N, 8.42%. IR (KBr pellet): $\nu_{C=N}$ (imine), 1615 cm^{-1}.

Synthesis of $[Mn^{III}L]$ (2). A methanol solution (50 mL) of Mn^{II}(CH$_3$CO$_2$)$_2$·4H$_2$O (0.124 g, 0.50 mmol) was added to a dichloromethane solution (50 mL) of H$_3$L (0.254 g, 0.50 mmol) and the mixture was stirred for 1 h in air. Water (10 mL) was added to the reaction mixture and organic solvents were removed using a rotary evaporator. The resulting precipitate was collected by suction filtration. Dark green prismatic crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the crude product. Yield: 0.11 g (38%). Elemental analysis: Calcd for C$_{29}$H$_{30}$Mn$_1$N$_3$O$_6$: C, 60.94; H, 5.29; N, 7.35%. Found: C, 60.65; H, 4.94; N, 7.32%. IR (KBr pellet): $\nu_{C=N}$ (imine), 1609 cm^{-1}.

Synthesis of [Mn^{IV}L]ClO$_4$ (3). A methanol solution (50 mL) of Mn^{II}(CH$_3$CO$_2$)$_2$·4H$_2$O (0.124 g, 0.50 mmol) was added to a dichloromethane solution (20 mL) of H$_3$L (0.26 g, 0.50 mmol) in a glove box under a N$_2$ atmosphere. NaClO$_4$·H$_2$O (0.070 g, 0.50 mmol) was added to the mixture. The solution was removed from the glove box and left in air. The color of the solution changed from yellow to deep green, and as the solvent evaporated dark green crystals slowly deposited. They were collected by filtration. Yield: 0.090 g (27%). Elemental analysis: Calcd for C$_{29}$H$_{30}$Cl$_1$Mn$_1$N$_3$O$_{10}$: C, 51.91; H, 4.50; N, 6.26%. Found: C, 51.80; H, 4.04; N, 6.21%. IR (KBr pellet): $\nu_{C=N}$ (imine), 1607 cm^{-1}, ν(ClO$_4$), 1076 cm^{-1}.

Synthesis of [Mn^{IV}L]PF$_6$ (3′). In a glove box under a N$_2$ atmosphere, a methanol solution (25 mL) of Mn^{II}(CH$_3$CO$_2$)$_2$·4H$_2$O (0.060 g, 0.25 mmol) was added to a dichloromethane solution (20 mL) of H$_3$L (0.13 g, 0.25 mmol). NaPF$_6$ (0.052 g, 0.31 mmol) was added. The solution was taken out of the glove box and left in air. The color of the solution changed from yellow to deep green, and dark green crystals which deposited in a few days were collected by filtration. Yield: 0.080 g (45%). Anal. Calcd for C$_{29}$H$_{30}$F$_6$Mn$_1$N$_3$O$_6$P$_1$: C, 48.61; H, 4.22; N, 5.86%. Found: C, 48.53; H, 3.95; N, 5.80%. IR (KBr pellet): ν(C=N$_{imine}$) 1607; ν(PF$_6$) 837 cm^{-1}.

Synthesis of [Mn^{III}LK(PF$_6$)] (4). A methanol solution (50 mL) of Mn^{II}(CH$_3$CO$_2$)$_2$·4H$_2$O (0.124 g, 0.50 mmol) was added to a dichloromethane solution (50 mL) of H$_3$L (0.26 g, 0.50 mmol). KPF$_6$ (0.101 g, 0.55 mmol) was added to the mixture to give a green solution. The solution was left undisturbed for a few days to give dark green plates. Yield: 0.283 g (75%). Elemental analysis: Calcd for C$_{29}$H$_{30}$F$_6$K$_1$Mn$_1$N$_3$O$_6$P$_1$: C, 46.09; H, 4.00; N, 5.56%. Found: C, 45.75; H, 3.85; N, 5.48%. IR (KBr pellet): $\nu_{C=N}$ (imine), 1616 cm^{-1}, ν(PF$_6$), 850 cm^{-1}.

Synthesis of [Mn^{III}LK(NO$_3$)] (5). A methanol solution (5 mL) of Mn^{II}(CH$_3$CO$_2$)$_2$·4H$_2$O (0.123 g, 0.5 mmol) was added to a methanol solution (10 mL) of H$_3$L (0.26 g, 0.5 mmol). To this, a solution of water (1 mL)–methanol (4 mL) containing KNO$_3$ (0.076 g, 0.75 mmol) was added, and the misture was left undisturbed to give deep green needles. Yield: 0.246 g (73%). Anal. Calcd for C$_{29}$H$_{30}$K$_1$Mn$_1$N$_4$O$_9$: C, 51.78; H, 4.50; N, 8.33%. Found: C, 51.71; H, 4.26; N, 8.28%. IR (KBr pellet): ν(C=N$_{imine}$) 1608; ν(NO$_3$) 1384, 1332 cm^{-1}.

Physical measurements. Elemental analyses were performed by Advance Science Research Center at Okayama University. ^{1}H NMR spectra were recorded at 250.13 MHz using a Bruker WM250 spectrometer and deuterated dimethyl sulfoxide was used as solvent. Chemical shifts

are given in ppm versus $SiMe_4$. Magnetic susceptibilities of the polycrystalline samples were measured using a Quantum Design MPMS XL5 SQUID susceptometer in the 1.9–350 K temperature range at 0.5 T. Diamagnetic corrections were applied using Pascal's constants.[2] HFEPR spectra were recorded using a spectrometer that differed from that described in Ref.[3] only by the use of a Virginia Diodes source operating at a base frequency of 12–14 GHz and multiplied by a cascade of multipliers. Infrared spectra were measured using a JASCO FT/IR-550 spectrophotometer. CV measurements were performed using a Fuso HECS 321B potential sweep unit with acetonitrile solutions containing $(n\text{-}Bu)_4NBF_4$ (0.1 M) as supporting electrolyte. The electrochemical cell was a three-electrode system consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag^+/Ag (Ag/0.01 M $AgNO_3$) reference electrode. As an external standard, the Fc^+/Fc (Fc = ferrocene) couple was observed at +0.085 V vs. Ag^+/Ag under the same conditions.

X-ray crystal structure analysis.

All measurements were carried out using a Rigaku R-AXIS RAPID II imaging plate area detector using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Numerical absorption corrections[4] were applied for all complexes. Structures were determined by direct methods (SHELX 97[5] or SIR2004[6]) and expanded using the Fourier technique and successive Fourier difference method with full-matrix least-squares refinement on F^2. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed at the ideal positions and refined using the riding model. All calculations were performed using the CrystalStructure 3.8 software package[7] except for refinement, which was performed using SHELX 97.[5]

Characterization and chemical identity.

Complexes **1**–**5** were characterized by X-ray diffraction, elemental analysis, FTIR spectroscopy, cyclic voltammetry, magnetic susceptibility measurements, HFEPR spectroscopy, and BVS calculations (vide infra). The homogeneity of the samples were checked by the elemental analyses and FTIR spectra. Although **1** is relatively unstable to air oxidation, we had no problem in handling the sample for physical measurements. All complexes are soluble in acetonitrile.

Crystallographic Data for 1–5.

1: Mo-Kα ($\lambda = 0.71073$ Å), $C_{31}H_{40}Mn_1N_4O_8$, $M_r = 651.62$, orthorhombic, space group $Pbca$, $a = 10.8867(10)$, $b = 25.958(2)$, $c = 22.332(2)$ Å, $V = 6310.8(9)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.376$ g cm^{-3}, $\mu = 4.739$ cm^{-1}, 90736 reflections collected, 7231 independent reflections, $2\theta_{max} = 55°$, $R_{int} = 0.044$, $R_1[I > 2.0\sigma(I)] = 0.0569$, wR(all data) $= 0.1756$, $T = 193$ K. CCDC 812372.

2: Mo-Kα ($\lambda = 0.71073$ Å), $C_{29}H_{30}Mn_1N_3O_6$, $M_r = 571.51$, monoclinic, space group $P2_1/c$, $a = 10.6650(8)$, $b = 15.9645(11)$, $c = 15.6061(9)$ Å, $\beta = 92.637(2)°$, $V = 2654.3(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.430$ g cm^{-3}, $\mu = 5.462$ cm^{-1}, 25633 reflections collected, 6046 independent reflections, $2\theta_{max} = 55°$, $R_{int} = 0.052$, $R_1[I > 2.0\sigma(I)] = 0.0375$, wR(all data) $= 0.0914$, $T = 193$ K. CCDC 812373.

3: Mo-Kα ($\lambda = 0.71073$ Å), $C_{29}H_{30}Cl_1Mn_1N_3O_{10}$, $M_r = 670.96$, monoclinic, space group $P2_1/n$, $a = 13.8339(8)$, $b = 15.3790(13)$, $c = 14.4240(10)$ Å, $\beta = 109.2237(19)°$, $V = 2897.6(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.538$ g cm^{-3}, $\mu = 6.117$ cm^{-1}, 28037 reflections collected, 6604 independent reflections, $2\theta_{max} = 55°$, $R_{int} = 0.034$, $R_1[I > 2.0\sigma(I)] = 0.0336$, wR(all data) $= 0.0901$, $T = 193$ K. CCDC 812374.

3′: Mo$_{K\alpha}$ ($\lambda = 0.71073$ Å), $C_{29}H_{30}F_6Mn_1N_3O_6P_1$, $M_r = 716.47$, monoclinic, space group $P2_1/n$, $a = 13.7229(10)$, $b = 15.9755(11)$, $c = 14.5327(10)$ Å, $\beta = 108.966(2)°$, $V = 3013.0(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.579$ g cm^{-3}, $\mu = 5.766$ cm^{-1}, 47216 reflections collected, 6871 independent reflections, $2\theta_{max} = 55°$, $R_{int} = 0.045$, $R_1[I > 2.0\sigma(I)] = 0.0450$, wR(all data) $= 0.1323$, $T = 193$ K. CCDC 812375.

4: Mo-Kα ($\lambda = 0.71073$ Å), $C_{29}H_{30}F_6K_1Mn_1N_3O_6P_1$, $M_r = 755.57$, monoclinic, space group $P2_1/c$, $a = 13.0303(11)$, $b = 15.8880(12)$, $c = 15.6809(12)$ Å, $\beta = 92.234(3)°$, $V = 3243.9(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.547$ g cm^{-3}, $\mu = 6.652$ cm^{-1}, 29502 reflections collected, 7358 independent reflections, $2\theta_{max} = 55°$, $R_{int} = 0.070$, $R_1[I > 2.0\sigma(I)] = 0.0712$, wR(all data) $= 0.1808$, $T = 193$ K. CCDC 812376.

5: Mo-Kα ($\lambda = 0.71073$ Å), $C_{29}H_{30}K_1Mn_1N_4O_9$, $M_r = 672.61$, monoclinic, space group $P2_1/c$, $a = 11.4584(3)$, $b = 15.9260(8)$, $c = 16.0765(4)$ Å, $\beta = 94.5337(8)°$, $V = 2924.56(18)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.527$ g cm^{-3}, $\mu = 6.556$ cm^{-1}, 28111 reflections collected, 6704 independent reflections, $2\theta_{max} = 55°$, $R_{int} = 0.041$, $R_1[I > 2.0\sigma(I)] = 0.0380$, wR(all data) $= 0.1069$, $T = 180$ K. CCDC 812377.

Table S1. Selected bond lengths (Å) of $NH_4[Mn^{II}L]\cdot 2CH_3OH$ (**1**), $[Mn^{III}L]$ (**2**), $[Mn^{IV}L]ClO_4$ (**3**), and $[Mn^{IV}L]PF_6$ (**3′**)

	1	**2**	**3**	**3′**
Mn(1)–O(1)	2.1490(18)	2.0596(13)	1.8588(10)	1.856(2)
Mn(1)–O(2)	2.117(2)	1.9230(13)	1.8482(14)	1.8606(16)
Mn(1)–O(3)	2.111(2)	1.8820(12)	1.8638(10)	1.8665(14)
Mn(1)–N(1)	2.259(2)	2.0947(16)	1.9935(12)	2.0026(19)
Mn(1)–N(2)	2.243(2)	2.0152(15)	1.9954(14)	2.0020(18)
Mn(1)–N(3)	2.264(2)	2.1982(16)	1.9820(15)	1.992(2)

Table S2. Selected bond lengths (Å) of $[Mn^{III}LK(PF_6)]$ (**4**)

	4		
Mn(1)–O(1)	1.994(2)	Mn(1)–N(1)	2.019(3)
Mn(1)–O(2)	2.019(2)	Mn(1)–N(2)	2.162(3)
Mn(1)–O(3)	1.893(2)	Mn(1)–N(3)	2.106(3)
K(1)–O(1)	2.757(2)	K(1)–O(4)	2.866(3)
K(1)–O(2)	2.727(2)	K(1)–O(5)	2.840(3)
K(1)–O(3)	3.007(2)	K(1)-O(6)	2.749(2)
K(1)–F(1)	2.742(3)	K(1)–F(2)	2.864(4)
K(1)–F(3)	3.050(6)		

Table S3. Selected bond lengths (Å) of $[Mn^{III}LK(NO_3)]$ (**5**)

|	**5**		
Mn(1)–O(1)	1.8991(14)	Mn(1)–N(1)	2.0205(17)
Mn(1)–O(2)	1.9387(14)	Mn(1)–N(2)	2.2177(19)
Mn(1)–O(3)	2.0609(14)	Mn(1)–N(3)	2.0569(17)
K(1)–O(1)	2.8426(14)	K(1)–O(4)	2.7568(15)
K(1)–O(2)	2.8026(14)	K(1)–O(5)	2.8186(16)
K(1)–O(3)	2.7479(14)	K(1)–O(6)	2.8974(19)
K(1)–O(7)	2.771(2)	K(1)–O(8)	2.7885(19)

Table S4. Bond valence sum (BVS) calculations[8–11]

| Complex	BVS	Assigned Oxidation State
$NH_4[Mn^{II}L] \cdot 2CH_3OH$ (**1**)	2.13	+2
$[Mn^{III}L]$ (**2**)	3.17	+3
$[Mn^{IV}L]ClO_4$ (**3**)	4.15	+4
$[Mn^{IV}L]PF_6$ (**3′**)	4.08	+4
$[Mn^{III}LK(PF_6)]$ (**4**)	3.11	+3
$[Mn^{III}LK(NO_3)]$ (**5**)	3.04	+3
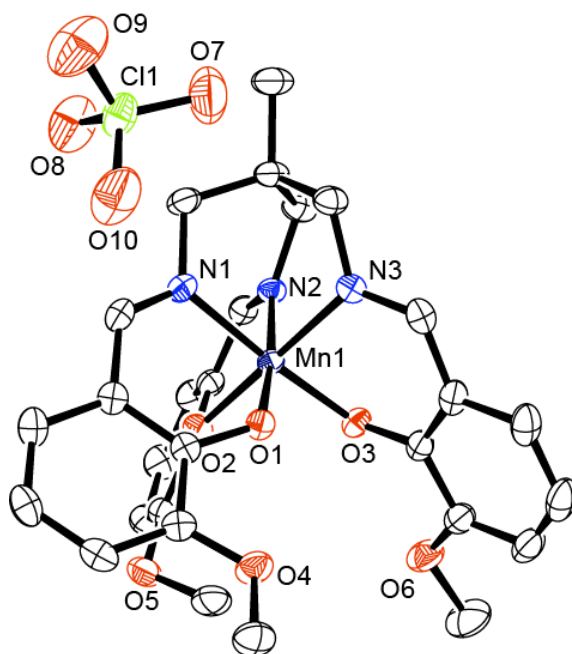
Fig. S1 Molecular structure of [Mn^{IV}L]ClO$_4$ (**3**).
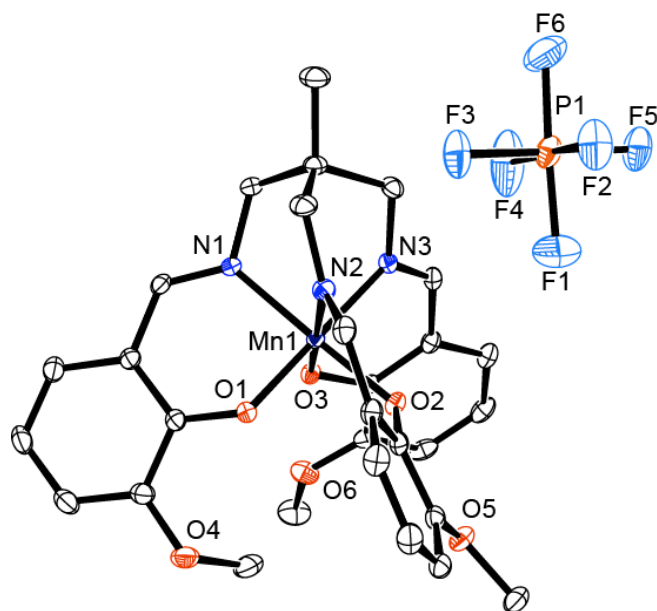
Fig. S2 Molecular structure of [Mn^{IV}L]PF$_6$ (**3′**).
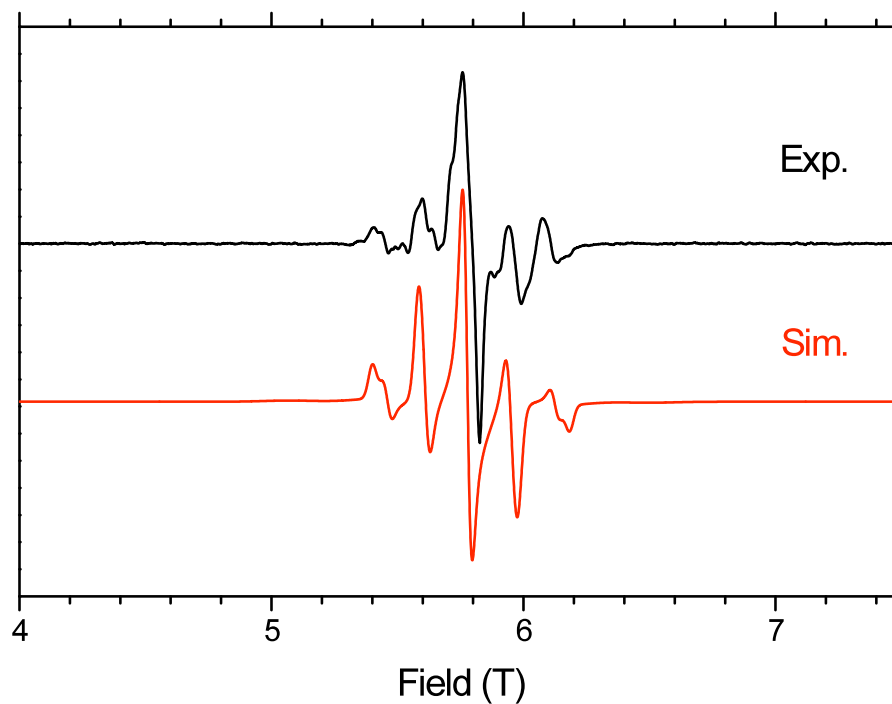
Fig. S3 Experimental (black trace) and simulated (red trace) HFEPR spectrum of NH$_4$[Mn^{II}L]·2CH$_3$OH (**1**) "as is" at 288 K and 162 GHz. The red trace was simulated using the following spin Hamiltonian parameters: $S = 5/2$, $D = 0.168$ cm^{-1}, $E = 0.005$ cm^{-1}, $g_{iso} = 2.00$. Given the small D value, and high temperature, no sign determination for D was possible. Lowering the temperature lead to serious artifacts in the spectra due to incomplete powder averaging.
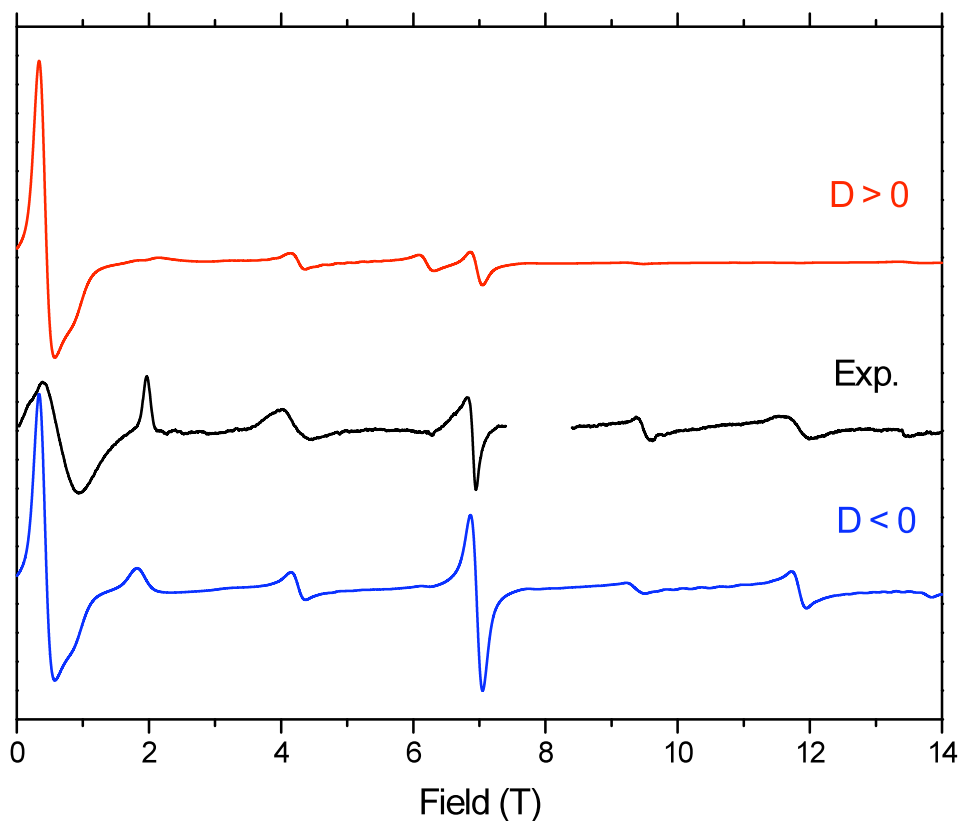
Fig. S4 Experimental (black trace) and simulated (colored traces) HFEPR spectrum of [Mn^{III}L] (**2**) pressed into a pellet with *n*-eicosane at 10 K and 224 GHz. A *g* = 2 impurity resonance was removed from the experimental spectrum. Simulations used the following spin Hamiltonian parameters: $S = 2$, $|D| = 4.53$ cm^{-1}, $|E| = 0.795$ cm^{-1}, $g_{iso} = 2.00$. Red trace: positive *D*; blue trace: negative D.

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References

1   E. B. Fleischer, A. E. Gebala, A. Levey and P. A. Tasker, *J. Org. Chem.*, 1971, **36**, 3042.

2   O. Kahn, *Molecular Magnetism*. VCH: Weinheim, 1993.

3   A. K. Hassan, L. A. Pardi, J. Krzystek, A. Sienkiewicz, P. Goy, M. Rohrer and L.-C. Brunel, *J. Magn. Reson.,* 2000, **142**, 300.

4   T. Higashi, Rigaku Corporation, Tokyo, Japan, 1999.

5   G. M. Sheldrick, *SHELX97*, University of Göttingen, Germany, 1997.

6   M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Cystallogr.*, 2005, **38**, 381.

7   CrystalStructure 3.8; Crystal Structure Analysis Package, Rigaku and Rigaku Americas, The Woodlands, TX, USA, 2001–2007.

8   I. D. Brown and D. Altermatt, *Acta Crystallogr.*, 1985, **B41**, 244.

9   W. Liu and H. H. Thorp, *Inorg. Chem.*, 1993, **32**, 4102.

10 V. S. Urusov, *Acta Crystallogr.*, 1995, **B51**, 641.

11 G. P. Palenik, *Inorg. Chem.*, 2003, **42**, 2725.