

Three manganese complexes of anionic N₄-donor Schiff-base macrocycles: monomeric Mn(II) and Mn(III), and dimeric Mn(IV)

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Supporting information

Table S1. Crystal data and structure refinement for $[\text{Mn}^{\text{IV}}_2(\text{L}^{\text{Et}})_2(\text{O})_2](\text{ClO}_4)\cdot 3\text{DMF}$

Identification code	RS184	F(000)	2376
Empirical formula	$\text{C}_{45}\text{H}_{59}\text{N}_{11}\text{Mn}_2\text{O}_{13}\text{Cl}_2$	Crystal Size	$0.60 \times 0.10 \times 0.10 \text{ mm}^3$
Formula weight	$1142.81 \text{ g mol}^{-1}$	Theta range for data collection	2.18 to 26.41°
Temperature	$90(2) \text{ K}$	Index ranges	$-12 \leq h \leq 11$
Wavelength	0.71073 \AA		$-59 \leq k \leq 59$
Crystal system	Monoclinic		$-11 \leq l \leq 13$
Space group	$P2_1/n$	Reflections collected	43704
Unit cell dimensions	$a = 9.747(3) \text{ \AA}$	Independent reflections	10138 [$R_{\text{int}} = 0.0983$]
	$b = 47.881(15) \text{ \AA}$	Completeness to $\theta = 26.41^\circ$	99.6%
	$c = 10.883(3) \text{ \AA}$	Absorption correction	Semi-empirical from equivalents
	$\alpha = 90^\circ$	Max. and min. transmission	0.9339 and 0.6810
	$\beta = 102.771(19)^\circ$	Refinement method	Full-matrix least-squares on F^2
	$\gamma = 90^\circ$	Data / restraints / parameters	10138 / 0 / 706
Volume	$4953(3) \text{ \AA}^3$	Goodness-of-fit on F^2	1.027
Z	4	Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0599$, $wR_2 = 0.1230$
Density (calculated)	1.533 Mg/m^3	R indices (all data)	$R_1 = 0.1056$, $wR_2 = 0.1428$
Absorption coefficient	0.694 mm^{-1}	Largest diff. peak and hole	0.728 and $-0.504 \text{ e.\AA}^{-3}$

Table S2. Crystal data and refinement for $[\text{Mn}^{\text{III}}\text{L}^{\text{Pr}}(\text{NCS})_2]$ (two molecules in the asymmetric unit)

Identification code	RKW542	F(000)	2032
Empirical formula	$\text{C}_{22}\text{H}_{23}\text{N}_6\text{MnS}_2$	Crystal Size	$0.40 \times 0.06 \times 0.04 \text{ mm}^3$
Formula weight	$490.52 \text{ g mol}^{-1}$	Theta range for data collection	1.55 to 26.42°
Temperature	$91(2) \text{ K}$	Index ranges	$-16 \leq h \leq 12$
Wavelength	0.71073 \AA		$-16 \leq k \leq 16$
Crystal system	Monoclinic		$-33 \leq l \leq 32$
Space group	$P2_1/n$	Reflections collected	59916
Unit cell dimensions	$a = 13.529(2) \text{ \AA}$	Independent reflections	9558 [$R_{\text{int}} = 0.1684$]
	$b = 13.263(2) \text{ \AA}$	Completeness to $\theta = 26.42^\circ$	98.4%
	$c = 26.707(5) \text{ \AA}$	Absorption correction	Semi-empirical from equivalents
	$\alpha = 90^\circ$	Max. and min. transmission	0.9704 and 0.7517
	$\beta = 99.651(6)^\circ$	Refinement method	Full-matrix least-squares on F^2
	$\gamma = 90^\circ$	Data / restraints / parameters	9558 / 9 / 538
Volume	$4724.2(14) \text{ \AA}^3$	Goodness-of-fit on F^2	1.052
Z	8	Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1147$, $wR_2 = 0.3057$
Density (calculated)	1.379 Mg/m^3	R indices (all data)	$R_1 = 0.2310$, $wR_2 = 0.3759$
Absorption coefficient	0.757 mm^{-1}	Largest diff. peak and hole	1.395 and $-0.999 \text{ e.\AA}^{-3}$

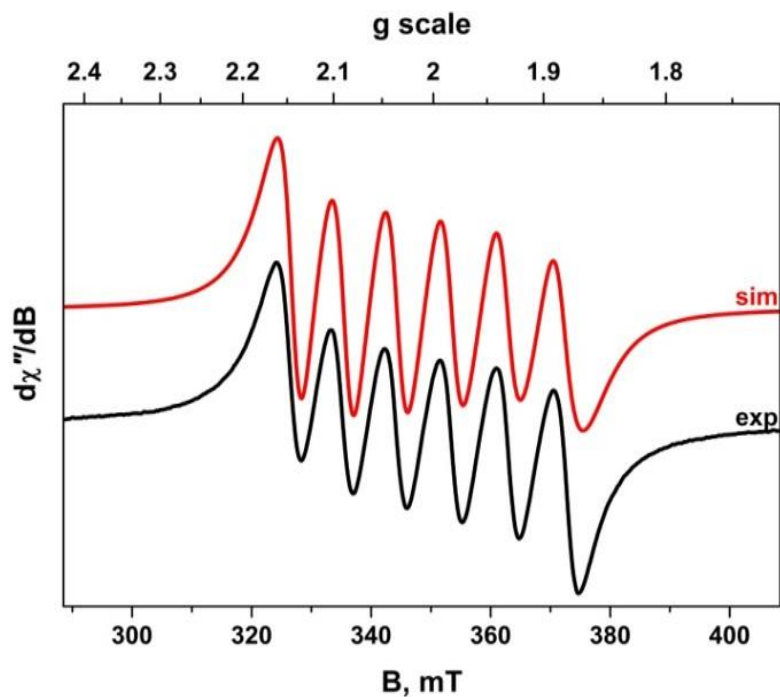


Figure S1. X-band EPR spectrum of $\text{Mn}^{\text{II}}\text{L}^{\text{Et}}(\text{NCS})(\text{H}_2\text{O})$ recorded in $\text{CH}_2\text{Cl}_2/\text{DMF}$ at 293 K (experimental conditions: frequency, 9.8083 GHz; power, 2.0 mW; modulation, 0.3 mT). Experimental data are represented by the black line; simulation is depicted by the red trace: $g_{\text{iso}} = 2.0026$; $A_{\text{iso}}\{^{55}\text{Mn}\} = 89 \times 10^{-4} \text{ cm}^{-1}$.

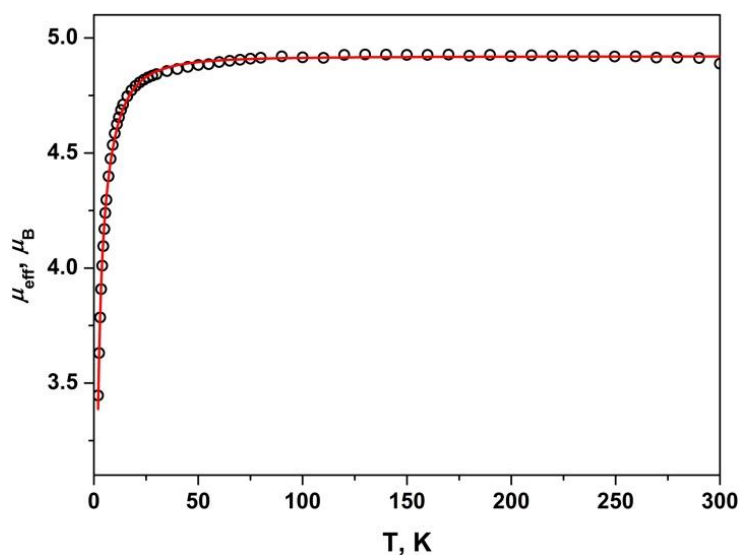


Figure S2. Temperature dependence of the magnetic moment, $\mu_{\text{eff}}, \mu_{\text{B}}$, of a powder sample of $[\text{Mn}^{\text{III}}\text{L}^{\text{Pr}}(\text{NCS})_2]$ (1 T external field). The open circles represent experimental data; solid line is a best fit, giving parameters $g = 2.008$; $D = -6.5 \text{ cm}^{-1}$; $E/D = 0.03$, for $S = 2$.

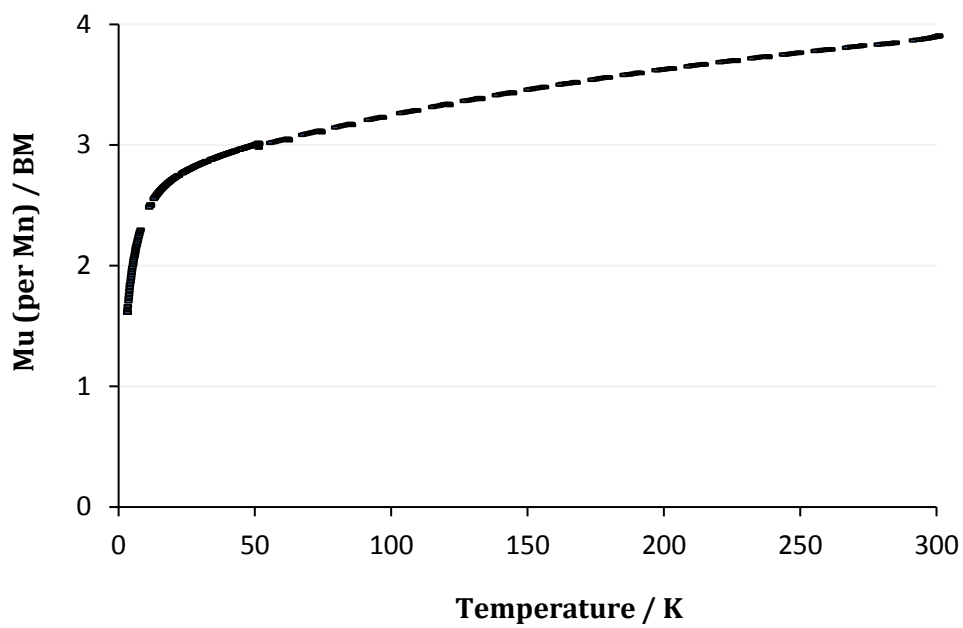


Figure S3. Plot of magnetic moment versus temperature for $[\text{Mn}^{\text{IV}}_2\text{L}^{\text{Et}_2}(\text{O})_2](\text{ClO}_4)_2 \cdot 3\text{DMF}$.