Supporting Information

Self-Assembled Heterometallic Complexes by Incorporation of Calcium or Strontium Ion into a Manganese(II) 12-Metallacrown-3 Framework Supported by a Tripodal Ligand with Pyridine-Carboxylate Motifs: Stability in their Manganese(III) Oxidized Form

Eric Gouré,[a] Bertrand Gerey,[a,b] Catalina Astudillo,[a] Jacques Pécaut[b] Selim Sirach,[a] Florian Molton,[a] Jérôme Fortage [a] and Marie-Noëlle Collomb [a,*]

[a] Univ. Grenoble Alpes, CNRS, DCM, 38000 Grenoble, France
[b] Univ. Grenoble Alpes, CEA, CNRS, IRIG, SyMMES, 38000 Grenoble, France

Table of Contents

1. General experimental details

The elemental analyses were carried out with a C, H, N analyzer (SCA, CNRS). Electrospray ionisation mass spectrometry (ESI-MS) were performed on a Bruker Esquire 3000 Plus ion trap spectrometer equipped with an electrospray ion source (ESI). The samples were analysed in either positive or negative mode ionization mode as well as in MS^2 by direct perfusion in the ESI-MS interface. The analyses were carried out in acetonitrile at a complex concentration of approximately 1 μmol L^{-1}. The infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrometer on powder samples in KBr pellets with a 2%w concentration. Powder X-band EPR spectra were recorded with a Bruker EMX, equipped with an ER-4192 ST Bruker cavity and an ER-4131 VT for the 100 K experiments. For experiments performed in glove box, the UV-Vis spectra were recorded with a MCS 501 UV-NIR (Carl Zeiss) spectrophotometer equipped with an automatic shutter. The light sources are halogen (CLH 500 20 W) and deuterium lamps (CLD 500) with optic fibers (041.002–UV SN 012105) with 1 mm and 1 cm path-length cells.

Elemental analysis, and mass spectrometry were performed within the ICMG Chemistry Nanobio Platform, Grenoble.

2. X-ray structure determination.

Single-crystal diffraction data were collected on an Oxford-Diffraction XCalibur S Kappa geometry diffractometer (MoKα radiation, graphite monochromator, λ 0.71073 Å). The CrysAlisPro program package (Agilent Technologies) was used for cell refinements and data reductions. For all complexes an absorption correction (CrysAlisPro) was applied to the data. The molecular structures were solved either by using the charge flipping method (Superflip)[2] or by intrinsic phasing method (ShelXT [3] and refined on F^2 by full matrix least-squares techniques using SHELXL[4] in OLEX2 software environment;[5] For all complexes, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were either found by Fourier transformation and refined with individual isotropic displacement parameters or they were placed at their calculated positions. A summary of X-ray data collection and structure refinement for all complexes is reported in Appendices tables A.1.1 to D.3.2.

3. Electrochemistry

The electrochemical measurements were run under argon atmosphere in a dry-glove box, at room temperature. Cyclic voltammetry measurements were performed using an EG&G Princeton Applied Research model 173 potentiostat/galvanostat equipped with a Princeton Applied Research model 175 universal programmer and a Princeton Applied Research model 179 digital coulometer equipped with a digital coulometer and a Sefram TGM 164 X-Y recorder. A standard one-compartment, three-electrode electrochemical cell was used. Experiments were performed in dry and argon degassed CH_3CN (Fisher, HPLC grade, 99.99%) with tetra-n-butylammonium perchlorate (Bu_4NClO_4 (Fluka, ≥ 99.0%), 0.1 M) as the supporting electrolyte. Potentials were referred to an $Ag/AgNO_3$ (0.01 M + Bu_4NClO_4 (0.1 M) in CH_3CN) reference electrode. The auxiliary electrode was a Pt wire, isolated from the solution by an ionic bridge. The working electrode was either a carbon vitreous disk (3 mm in diameter) or a Pt disk (5 mm in diameter), polished with 2 μm diamond paste (Mecaprex Presi). Measured potentials were calibrated through

the use of an internal ferrocene/ferricinium standard. Bulk electrolysis was conducted at ambient temperature using a sheet of reticulated vitreous carbon 45 ppi (Electrosynthesis Co.) three-dimensional meshes (1.0 cm x 0.7 cm x 0.4 cm), or a platinum plate (1.5 cm x 1.5 cm) as working electrode. For the three **Mn_3M** complexes, the exhaustive electrolyses were performed at a potential of +1.2 V. The solutions of the complexes are completely oxidized after 10-15 min when a sheet of reticulated VC 45 ppi and out 45 min when the platinum plate was used. Reference and auxiliary electrodes were the same as those used for cyclic voltammetry.

4. Crystallographic tables

Table S1. Crystallographic refinement data for complexes $[\{Mn(tpada)\}_3Mn](ClO_4)_2 \cdot 2CH_3CN$ (**Mn_3Mn**$(ClO_4)_2 \cdot 2CH_3CN$), $[\{Mn(tpada)\}_3Ca(OH_2)](PF_6)_2 \cdot 0.25CH_3CN \cdot 1.75CH_3CO_2C_2H_5$ (**Mn_3Ca**$(PF_6)_2 \cdot 0.25CH_3CN \cdot 1.75CH_3CO_2C_2H_5$) and $[\{Mn^{II}(tpada)\}_3Sr^{II}(OH_2)]_2(PF_6)_4 \cdot 2CH_3OH \cdot 1.5CH_3CO_2C_2H_5 \cdot 0.5H_2O$ (**$\{Mn_3Sr\}_2$**$(PF_6)_4 \cdot 2CH_3OH \cdot 1.5 CH_3CO_2C_2H_5 \cdot 0.5H_2O$)

	Mn_3Mn $(ClO_4)_2 \cdot 2CH_3CN$	**Mn_3Ca**$(PF_6)_2 \cdot 0.25CH_3CN \cdot 1.75CH_3CO_2C_2H_5$	**$\{Mn_3Sr\}_2$**$(PF_6)_4 \cdot 2CH_3OH \cdot 1.5CH_3CO_2C_2H_5 \cdot 0.5H_2O$
CCDC reference	2059901	2059902	2059903
Empirical formula	$C_{64}H_{54}Cl_2Mn_4N_{14}O_{20}$	$C_{67.50}H_{64.41}CaF_{12}Mn_3N_{12.25}O_{16.50}P_2$	$C_{128}H_{121}F_{24}Mn_6N_{24}O_{31.5}P_4Sr_2$
Formula weight	1629.87	1806.05	3584.24
Colour, shape	Light yellow, block	Light yellow, block	Light yellow, needle
Crystal size, mm	0.4325x0.3271x0.2097	0.392x0.259x0.055	0.3632x0.0719x0.0676
Crystal system	Orthorhombic	Monoclinic	Tetragonal
Space group	*P 2₁ 2₁ 2₁*	*P 2₁/a*	*I 4₁/a*
a, Å	12.2514(4)	17.365(2)	56.4175(14)
b, Å	21.3469(7)	25.185(2)	56.4175(14)
c, Å	25.8718(7)	18.697(6)	18.2195(7)
α, deg.	90	90	90
β, deg.	90	97.30(2)	90
γ, deg.	90	90	90
V, Å^3	6766.2(4)	8111(3)	57991(4)
Z	4	4	16
T, K	150(2)	149.95(10)	150(2)
ρ (calc), g/cm^3	1.600	1.477	1.642
μ, mm^{-1}	0.894	0.660	1.392
θ range, deg.	2.064 to 26.369	3.017 to 26.372	1.861 to 26.372
No.of rflcn measured/used	31008/13840	17975/17975	196168/29635
GooF	1.033	0.736	1.021
*R*1	0.0573	0.0846	0.0799
*wR*2	0.1135	0.1914	0.1854

Table S2. Selected Bond Lengths (Å) and Angles (deg) for the three {Mn(tpada)} units of **Mn_3Mn**$(ClO_4)_2$·$2CH_3CN$.

$Mn(1)\text{-}N(1)_{tert}$	2.426(5)	$Mn(2)\text{-}N(21)_{tert}$	2.439(6)	$Mn(3)\text{-}N(41)_{tert}$	2.437(6)
$Mn(1)\text{-}N(2)_{py}$	2.224(6)	$Mn(2)\text{-}N(22)_{py}$	2.264(6)	$Mn(3)\text{-}N(42)_{py}$	2.248(6)
$Mn(1)\text{-}N(3)_{py}$	2.210(5)	$Mn(2)\text{-}N(23)_{py}$	2.196(6)	$Mn(3)\text{-}N(43)_{py}$	2.188(6)
$Mn(1)\text{-}N(4)_{py}$	2.245(6)	$Mn(2)\text{-}N(24)_{py}$	2.270(6)	$Mn(3)\text{-}N(44)_{py}$	2.293(6)
$Mn(1)\text{-}O(1)_{COO^-}$	2.244(4)	$Mn(2)\text{-}O(21)_{COO^-}$	2.243(5)	$Mn(3)\text{-}O(41)_{COO^-}$	2.232(5)
$Mn(1)\text{-}O(3)_{COO^-}$	2.279(5)	$Mn(2)\text{-}O(23)_{COO^-}$	2.263(5)	$Mn(3)\text{-}O(43)_{COO^-}$	2.279(5)
$Mn(1)\text{-}O(42)_{\mu\text{-}COO^-}$	2.214(5)	$Mn(2)\text{-}O(2)_{\mu\text{-}COO^-}$	2.173(5)	$Mn(3)\text{-}O(22)_{\mu\text{-}COO^-}$	2.214(5)
N(3)-Mn(1)-O(42)	84.9(2)	O(2)-Mn(2)-N(23)	88.9(2)	N(43)-Mn(3)-O(22)	86.4(2)
N(3)-Mn(1)-N(2)	142.3(2)	O(2)-Mn(2)-O(21)	89.40(18)	N(43)-Mn(3)-O(41)	145.6(2)
O(42)-Mn(1)-N(2)	89.5(2)	N(23)-Mn(2)-O(21)	147.0(2)	O(22)-Mn(3)-O(41)	90.84(18)
N(3)-Mn(1)-O(1)	145.53(19)	O(2)-Mn(2)-O(23)	96.65(18)	N(43)-Mn(3)-N(42)	142.4(2)
O(42)-Mn(1)-O(1)	90.72(17)	N(23)-Mn(2)-O(23)	72.9(2)	O(22)-Mn(3)-N(42)	86.9(2)
N(2)-Mn(1)-O(1)	71.58(19)	O(21)-Mn(2)-O(23)	74.50(17)	O(41)-Mn(3)-N(42)	71.45(19)
N(3)-Mn(1)-N(4)	94.4(2)	O(2)-Mn(2)-N(22)	89.1(2)	N(43)-Mn(3)-O(43)	72.3(2)
O(42)-Mn(1)-N(4)	170.99(19)	N(23)-Mn(2)-N(22)	141.6(2)	O(22)-Mn(3)-O(43)	99.51(18)
N(2)-Mn(1)-N(4)	85.6(2)	O(21)-Mn(2)-N(22)	71.40(19)	O(41)-Mn(3)-O(43)	74.33(17)
O(1)-Mn(1)-N(4)	94.83(19)	O(23)-Mn(2)-N(22)	145.3(2)	N(42)-Mn(3)-O(43)	145.26(19)
N(3)-Mn(1)-O(3)	72.25(18)	O(2)-Mn(2)-N(24)	169.1(2)	N(43)-Mn(3)-N(44)	94.2(2)
O(42)-Mn(1)-O(3)	97.50(18)	N(23)-Mn(2)-N(24)	96.2(2)	O(22)-Mn(3)-N(44)	165.8(2)
N(2)-Mn(1)-O(3)	145.41(19)	O(21)-Mn(2)-N(24)	91.54(19)	O(41)-Mn(3)-N(44)	96.6(2)
O(1)-Mn(1)-O(3)	74.48(17)	O(23)-Mn(2)-N(24)	94.1(2)	N(42)-Mn(3)-N(44)	84.0(2)
N(4)-Mn(1)-O(3)	90.84(19)	N(22)-Mn(2)-N(24)	80.9(2)	O(43)-Mn(3)-N(44)	94.2(2)
N(3)-Mn(1)-N(1)	71.6(2)	O(2)-Mn(2)-N(21)	97.4(2)	N(43)-Mn(3)-N(41)	71.9(2)
O(42)-Mn(1)-N(1)	95.67(19)	N(23)-Mn(2)-N(21)	71.2(2)	O(22)-Mn(3)-N(41)	92.0(2)
N(2)-Mn(1)-N(1)	71.9(2)	O(21)-Mn(2)-N(21)	141.6(2)	O(41)-Mn(3)-N(41)	142.5(2)
O(1)-Mn(1)-N(1)	142.8(2)	O(23)-Mn(2)-N(21)	141.1(2)	N(42)-Mn(3)-N(41)	71.4(2)
N(4)-Mn(1)-N(1)	75.6(2)	N(22)-Mn(2)-N(21)	71.0(2)	O(43)-Mn(3)-N(41)	141.5(2)
O(3)-Mn(1)-N(1)	140.09(19)	N(24)-Mn(2)-N(21)	75.3(2)	N(44)-Mn(3)-N(41)	74.7(2)

Table S3. Selected Bond Lengths (Å) and Angles (deg) of the Mn^{2+} present in the central cavity of **Mn_3Mn**$(ClO_4)_2$·$2CH_3CN$.

Mn(4)-O(43)	2.117(5)	Mn(4)-O(1)	2.235(5)
Mn(4)-O(23)	2.138(5)	Mn(4)-O(41)	2.282(4)
Mn(4)-O(3)	2.158(5)	Mn(4)-O(21)	2.283(5)
O(43)-Mn(4)-O(23)	112.76(18)	O(3)-Mn(4)-O(41)	81.72(17)
O(43)-Mn(4)-O(3)	109.12(18)	O(1)-Mn(4)-O(41)	83.63(18)
O(23)-Mn(4)-O(3)	113.16(19)	O(43)-Mn(4)-O(21)	83.64(18)
O(43)-Mn(4)-O(1)	157.83(18)	O(23)-Mn(4)-O(21)	76.07(17)
O(23)-Mn(4)-O(1)	82.38(17)	O(3)-Mn(4)-O(21)	157.84(18)
O(3)-Mn(4)-O(1)	77.09(17)	O(1)-Mn(4)-O(21)	84.62(17)
O(43)-Mn(4)-O(41)	76.48(17)	O(41)-Mn(4)-O(21)	83.94(17)
O(23)-Mn(4)-O(41)	156.53(19)		

Table S4. Selected Bond Lengths (Å) and Angles (deg) for the three {Mn(tpada)} units of **Mn_3Ca**$(PF_6)_2$·0.25CH_3CN·1.75 $CH_3CO_2C_2H_5$.

Mn(1)-O(42)	2.177(6)	Mn(2)-O(23)	2.168(5)	Mn(3)-O(22)	2.195(7)
Mn(1)-O(3)	2.209(5)	Mn(2)-O(2)	2.188(5)	Mn(3)-N(43)	2.222(6)
Mn(1)-N(3)	2.227(8)	Mn(2)-N(23)	2.219(7)	Mn(3)-N(44)	2.222(9)
Mn(1)-N(2)	2.255(7)	Mn(2)-N(22)	2.241(6)	Mn(3)-N(42)	2.240(7)
Mn(1)-N(4)	2.266(7)	Mn(2)-N(24)	2.292(7)	Mn(3)-O(43)	2.252(5)
Mn(1)-O(1)	2.277(6)	Mn(2)-O(21)	2.296(6)	Mn(3)-O(41)	2.262(5)
Mn(1)-N(1)	2.448(6)	Mn(2)-N(21)	2.464(8)	Mn(3)-N(41)	2.467(8)
Mn(1)-Ca(1)	3.6143(17)	Mn(2)-Ca(1)	3.663(2)	Mn(3)-Ca(1)	3.675(2)
O(42)-Mn(1)-O(3)	96.3(2)	O(23)-Mn(2)-O(2)	90.51(19)	O(22)-Mn(3)-N(43)	88.9(3)
O(42)-Mn(1)-N(3)	88.7(2)	O(23)-Mn(2)-N(23)	73.4(3)	O(22)-Mn(3)-N(44)	176.6(3)
O(3)-Mn(1)-N(3)	72.3(2)	O(2)-Mn(2)-N(23)	87.8(2)	N(43)-Mn(3)-N(44)	92.2(3)
O(42)-Mn(1)-N(2)	86.7(2)	O(23)-Mn(2)-N(22)	147.0(3)	O(22)-Mn(3)-N(42)	88.9(3)
O(3)-Mn(1)-N(2)	148.1(2)	O(2)-Mn(2)-N(22)	91.2(2)	N(43)-Mn(3)-N(42)	139.5(3)
N(3)-Mn(1)-N(2)	139.6(2)	N(23)-Mn(2)-N(22)	139.6(3)	N(44)-Mn(3)-N(42)	88.2(3)
O(42)-Mn(1)-N(4)	166.8(2)	O(23)-Mn(2)-N(24)	88.1(2)	O(22)-Mn(3)-O(43)	91.2(2)
O(3)-Mn(1)-N(4)	96.5(2)	O(2)-Mn(2)-N(24)	171.4(2)	N(43)-Mn(3)-O(43)	72.3(2)
N(3)-Mn(1)-N(4)	98.1(3)	N(23)-Mn(2)-N(24)	83.7(2)	N(44)-Mn(3)-O(43)	92.2(3)
N(2)-Mn(1)-N(4)	80.8(2)	N(22)-Mn(2)-N(24)	94.6(2)	N(42)-Mn(3)-O(43)	148.2(2)
O(42)-Mn(1)-O(1)	86.6(2)	O(23)-Mn(2)-O(21)	75.6(2)	O(22)-Mn(3)-O(41)	89.2(2)
O(3)-Mn(1)-O(1)	77.2(2)	O(2)-Mn(2)-O(21)	89.3(2)	N(43)-Mn(3)-O(41)	149.4(2)
N(3)-Mn(1)-O(1)	148.4(2)	N(23)-Mn(2)-O(21)	148.8(2)	N(44)-Mn(3)-O(41)	91.4(2)
N(2)-Mn(1)-O(1)	71.3(2)	N(22)-Mn(2)-O(21)	71.5(2)	N(42)-Mn(3)-O(41)	71.0(2)
N(4)-Mn(1)-O(1)	93.3(2)	N(24)-Mn(2)-O(21)	98.5(2)	O(43)-Mn(3)-O(41)	77.21(18)
O(42)-Mn(1)-N(1)	97.7(2)	O(23)-Mn(2)-N(21)	141.1(2)	O(22)-Mn(3)-N(41)	102.1(3)
O(3)-Mn(1)-N(1)	139.2(3)	O(2)-Mn(2)-N(21)	102.2(2)	N(43)-Mn(3)-N(41)	70.4(3)
N(3)-Mn(1)-N(1)	70.0(3)	N(23)-Mn(2)-N(21)	70.6(3)	N(44)-Mn(3)-N(41)	75.3(3)
N(2)-Mn(1)-N(1)	71.03(3)	N(22)-Mn(2)-N(21)	70.2(3)	N(42)-Mn(3)-N(41)	70.6(3)
N(4)-Mn(1)-N(1)	74.3(2)	N(24)-Mn(2)-N(21)	74.0(3)	O(43)-Mn(3)-N(41)	139.9(2)
O(1)-Mn(1)-N(1)	141.6(3)	O(21)-Mn(2)-N(21)	140.1(2)	O(41)-Mn(3)-N(41)	139.6(2)
O(42)-Mn(1)-Ca(1)	80.49(13)	O(23)-Mn(2)-Ca(1)	37.78(15)	O(22)-Mn(3)-Ca(1)	78.54(16)
O(3)-Mn(1)-Ca(1)	38.83(15)	O(2)-Mn(2)-Ca(1)	77.86(16)	N(43)-Mn(3)-Ca(1)	109.3(2)
N(3)-Mn(1)-Ca(1)	107.15(18)	N(23)-Mn(2)-Ca(1)	108.3(2)	N(44)-Mn(3)-Ca(1)	104.1(2)
N(2)-Mn(1)-Ca(1)	111.55(16)	N(22)-Mn(2)-Ca(1)	110.9(2)	N(42)-Mn(3)-Ca(1)	109.79(18)
N(4)-Mn(1)-Ca(1)	107.96(17)	N(24)-Mn(2)-Ca(1)	105.8(2)	O(43)-Mn(3)-Ca(1)	39.57(13)
O(1)-Mn(1)-Ca(1)	41.26(13)	O(21)-Mn(2)-Ca(1)	40.99(13)	O(41)-Mn(3)-Ca(1)	40.59(15)
N(1)-Mn(1)-Ca(1)	176.7(2)	N(21)-Mn(2)-Ca(1)	178.88(18)	N(41)-Mn(3)-Ca(1)	179.3(2)

Table S5. Selected Bond Lengths (Å) and Angles (deg) of the Ca^{2+} present in the central cavity for **Mn_3Ca**$(PF_6)_2 \cdot 0.25CH_3CN \cdot 1.75\ CH_3CO_2C_2H_5$.

Ca(1)-O(3)	2.346(5)	Ca(1)-O(1)	2.424(5)
Ca(1)-O(23)	2.359(6)	Ca(1)-O(21)	2.448(5)
Ca(1)-O(1CA)	2.376(5)	Ca(1)-O(41)	2.449(6)
Ca(1)-O(43)	2.412(5)		
O(3)-Ca(1)-O(23)	117.7(2)	O(23)-Ca(1)-O(21)	69.37(18)
O(3)-Ca(1)-O(1CA)	93.45(19)	O(1CA)-Ca(1)-O(21)	116.42(19)
O(23)-Ca(1)-O(1CA)	78.1(2)	O(43)-Ca(1)-O(21)	77.10(19)
O(3)-Ca(1)-O(43)	114.6(2)	O(1)-Ca(1)-O(21)	83.60(17)
O(23)-Ca(1)-O(43)	122.82(18)	O(3)-Ca(1)-O(41)	77.95(19)
O(1CA)-Ca(1)-O(43)	77.30(19)	O(23)-Ca(1)-O(41)	141.1 (2)
O(3)-Ca(1)-O(1)	71.83(19)	O(1CA)-Ca(1)-O(41)	139.2(2)
O(23)-Ca(1)-O(1)	73.90(18)	O(43)-Ca(1)-O(41)	70.82(18)
O(1CA)-Ca(1)-O(1)	136.6(2)	O(1)-Ca(1)-O(41)	78.80(19)
O(43)-Ca(1)-O(1)	146.10(18)	O(21)-Ca(1)-O(41)	80.7(2)
O(3)-Ca(1)-O(21)	150.00(18)		

Table S6. Selected Bond Lengths (Å) and Angles (deg) for the three {Mn(tpada)} units of **{Mn$_3$Sr}$_2$**$(PF_6)_4$·2CH_3OH·1.5$CH_3CO_2C_2H_5$·0.5H_2O in the first unit.

Mn(1)-O(42)	2.136(6)	Mn(2)-O(2)	2.119(6)	Mn(3)-O(22)	2.152(6)
Mn(1)-O(3)	2.215(6)	Mn(2)-O(23)	2.208(5)	Mn(3)-O(43)	2.243(5)
Mn(1)-N(3)	2.253(7)	Mn(2)-O(21)	2.238(6)	Mn(3)-N(43)	2.261(8)
Mn(1)-N(4)	2.271(8)	Mn(2)-N(23)	2.251(8)	Mn(3)-N(42)	2.290(7)
Mn(1)-N(2)	2.283(8)	Mn(2)-N(22)	2.291(7)	Mn(3)-O(41)	2.298(6)
Mn(1)-O(1)	2.325(5)	Mn(2)-N(24)	2.331(7)	Mn(3)-N(44)	2.313(7)
Mn(1)-N(1)	2.472(7)	Mn(2)-N(21)	2.519(7)	Mn(3)-N(41)	2.479(7)
O(42)-Mn(1)-O(3)	96.1(2)	O(2)-Mn(2)-O(23)	103.3(2)	O(22)-Mn(3)-O(43)	98.8(2)
O(42)-Mn(1)-N(3)	91.8(3)	O(2)-Mn(2)-O(21)	92.0(2)	O(22)-Mn(3)-N(43)	85.6(3)
O(3)-Mn(1)-N(3)	71.4(2)	O(23)-Mn(2)-O(21)	79.0(2)	O(43)-Mn(3)-N(43)	71.3(2)
O(42)-Mn(1)-N(4)	169.1(3)	O(2)-Mn(2)-N(23)	94.7(3)	O(22)-Mn(3)-N(42)	84.5(2)
O(3)-Mn(1)-N(4)	94.4(3)	O(23)-Mn(2)-N(23)	72.3(2)	O(43)-Mn(3)-N(42)	151.3(2)
N(3)-Mn(1)-N(4)	88.9(3)	O(21)-Mn(2)-N(23)	151.3(2)	N(43)-Mn(3)-N(42)	137.4(3)
O(42)-Mn(1)-N(2)	91.1(3)	O(2)-Mn(2)-N(22)	90.9(3)	O(22)-Mn(3)-O(41)	90.5(2)
O(3)-Mn(1)-N(2)	148.4(2)	O(23)-Mn(2)-N(22)	147.8(2)	O(43)-Mn(3)-O(41)	80.79(19)
N(3)-Mn(1)-N(2)	139.3(3)	O(21)-Mn(2)-N(22)	71.6(2)	N(43)-Mn(3)-O(41)	150.8(2)
N(4)-Mn(1)-N(2)	81.3(3)	N(23)-Mn(2)-N(22)	135.9(3)	N(42)-Mn(3)-O(41)	70.6(2)
O(42)-Mn(1)-O(1)	93.9(2)	O(2)-Mn(2)-N(24)	166.5(2)	O(22)-Mn(3)-N(44)	159.1(2)
O(3)-Mn(1)-O(1)	78.57(19)	O(23)-Mn(2)-N(24)	90.0(2)	O(43)-Mn(3)-N(44)	102.0(2)
N(3)-Mn(1)-O(1)	149.8(2)	O(21)-Mn(2)-N(24)	88.8(2)	N(43)-Mn(3)-N(44)	102.6(3)
N(4)-Mn(1)-O(1)	90.9(3)	N(23)-Mn(2)-N(24)	91.0(3)	N(42)-Mn(3)-N(44)	76.5(2)
N(2)-Mn(1)-O(1)	70.2(2)	N(22)-Mn(2)-N(24)	76.6(3)	O(41)-Mn(3)-N(44)	91.2(2)
O(42)-Mn(1)-N(1)	95.6(3)	O(2)-Mn(2)-N(21)	97.0(2)	O(22)-Mn(3)-N(41)	90.9(2)
O(3)-Mn(1)-N(1)	138.9(2)	O(23)-Mn(2)-N(21)	136.5(2)	O(43)-Mn(3)-N(41)	137.9(2)
N(3)-Mn(1)-N(1)	69.1(3)	O(21)-Mn(2)-N(21)	138.7(2)	N(43)-Mn(3)-N(41)	68.8(3)
N(4)-Mn(1)-N(1)	74.5(3)	N(23)-Mn(2)-N(21)	68.0(3)	N(42)-Mn(3)-N(41)	70.1(3)
N(2)-Mn(1)-N(1)	70.2(3)	N(22)-Mn(2)-N(21)	68.0(3)	O(41)-Mn(3)-N(41)	140.4(2)
O(1)-Mn(1)-N(1)	139.4(2)	N(24)-Mn(2)-N(21)	73.9(3)	N(44)-Mn(3)-N(41)	74.7(2)

Table S7. Selected Bond Lengths (Å) and Angles (deg) for the three {Mn(tpada)} units of **{Mn^{II}_3Sr}$_2$**$(PF_6)_4$·$2CH_3OH$·1.5 $CH_3CO_2C_2H_5$·$0.5H_2O$ in the second unit.

Mn(4)-O(102)	2.152(6)	Mn(5)-O(62)	2.150(6)	Mn(6)-O(82)	2.101(6)
Mn(4)-O(63)	2.215(6)	Mn(5)-O(83)	2.218(5)	Mn(6)-O(103)	2.208(5)
Mn(4)-N(52)	2.253(8)	Mn(5)-N(84)	2.257(8)	Mn(6)-N(103)	2.226(7)
Mn(4)-N(63)	2.296(8)	Mn(5)-N(83)	2.264(7)	Mn(6)-O(101)	2.261(6)
Mn(4)-N(62)	2.295(8)	Mn(5)-N(82)	2.268(7)	Mn(6)-N(102)	2.303(7)
Mn(4)-O(61)	2.299(6)	Mn(5)-O(81)	2.296(6)	Mn(6)-N(104)	2.324(7)
Mn(4)-N(61)	2.501(8)	Mn(5)-N(81)	2.494(7)	Mn(6)-N(101)	2.485(7)
O(102)-Mn(4)-O(63)	99.8(2)	O(62)-Mn(5)-O(83)	91.7(2)	O(82)-Mn(6)-O(103)	105.1(2)
O(102)-Mn(4)-N(52)	85.5(3)	O(62)-Mn(5)-N(84)	174.2(3)	O(82)-Mn(6)-N(103)	95.6(3)
O(63)-Mn(4)-N(52)	71.5(3)	O(83)-Mn(5)-N(84)	93.0(2)	O(103)-Mn(6)-N(103)	72.6(2)
O(102)-Mn(4)-N(63)	154.5(3)	O(62)-Mn(5)-N(83)	95.8(3)	O(82)-Mn(6)-O(101)	91.7(2)
O(63)-Mn(4)-N(63)	105.8(3)	O(83)-Mn(5)-N(83)	71.7(2)	O(103)-Mn(6)-O(101)	79.0(2)
N(52)-Mn(4)-N(63)	103.0(3)	N(84)-Mn(5)-N(83)	82.5(3)	N(103)-Mn(6)-O(101)	151.5(2)
O(102)-Mn(4)-N(62)	81.1(3)	O(62)-Mn(5)-N(82)	86.9(3)	O(82)-Mn(6)-N(102)	85.5(2)
O(63)-Mn(4)-N(62)	150.7(3)	O(83)-Mn(5)-N(82)	149.8(2)	O(103)-Mn(6)-N(102)	147.8(2)
N(52)-Mn(4)-N(62)	137.4(3)	N(84)-Mn(5)-N(82)	90.7(3)	N(103)-Mn(6)-N(102)	137.7(3)
N(63)-Mn(4)-N(62)	76.4(3)	N(83)-Mn(5)-N(82)	138.5(3)	O(101)-Mn(6)-N(102)	70.2(2)
O(102)-Mn(4)-O(61)	90.7(2)	O(62)-Mn(5)-O(81)	92.5(2)	O(82)-Mn(6)-N(104)	161.8(2)
O(63)-Mn(4)-O(61)	80.1(2)	O(83)-Mn(5)-O(81)	78.9(2)	O(103)-Mn(6)-N(104)	92.7(2)
N(52)-Mn(4)-O(61)	150.1(3)	N(84)-Mn(5)-O(81)	91.7(2)	N(103)-Mn(6)-N(104)	93.4(3)
N(63)-Mn(4)-O(61)	93.1(3)	N(83)-Mn(5)-O(81)	149.5(2)	O(101)-Mn(6)-N(104)	88.0(2)
N(62)-Mn(4)-O(61)	70.6(2)	N(82)-Mn(5)-O(81)	71.1(2)	N(102)-Mn(6)-N(104)	77.2(2)
O(102)-Mn(4)-N(61)	88.0(3)	O(62)-Mn(5)-N(81)	99.6(2)	O(82)-Mn(6)-N(101)	93.8(2)
O(63)-Mn(4)-N(61)	138.8(3)	O(83)-Mn(5)-N(81)	140.8(2)	O(103)-Mn(6)-N(101)	138.8(2)
N(52)-Mn(4)-N(61)	68.9(3)	N(84)-Mn(5)-N(81)	74.6(3)	N(103)-Mn(6)-N(101)	69.4(2)
N(63)-Mn(4)-N(61)	73.3(3)	N(83)-Mn(5)-N(81)	69.9(2)	O(101)-Mn(6)-N(101)	137.6(2)
N(62)-Mn(4)-N(61)	70.4(3)	N(82)-Mn(5)-N(81)	68.7(2)	N(102)-Mn(6)-N(101)	68.4(2)
O(61)-Mn(4)-N(61)	140.7(3)	O(81)-Mn(5)-N(81)	137.2(2)	N(104)-Mn(6)-N(101)	74.6(2)

Table S8. Selected Bond Lengths (Å) and Angles (deg) of the Sr^{2+} present in the central cavity for **{Mn^{II}_3Sr}$_2$**$(PF_6)_4$·$2CH_3OH$·1.5 $CH_3CO_2C_2H_5$·$0.5H_2O$.

Sr(1)-O(3)	2.534(5)	Sr(1)-Mn(1)	3.7572(15)	Sr(2)-O(83)	2.535(5)
Sr(1)-O(43)	2.595(5)	Sr(1)-Mn(3)	3.8484(14)	Sr(2)-O(63)	2.585(6)
Sr(1)-O(1)	2.598(5)	Sr(1)-Mn(2)	3.8566(14)	Sr(2)-O(81)	2.614(6)
Sr(1)-O(1SR)	2.612(5)			Sr(2)-O(4)	2.631(6)
Sr(1)-O(84)	2.624(5)			Sr(2)-O(61)	2.640(5)
Sr(1)-O(41)	2.637(5)			Sr(2)-O(103)	2.644(5)
Sr(1)-O(23)	2.641(5)	Sr(2)-Mn(5)	3.7967(14)	Sr(2)-O(2SR)	2.652(5)
Sr(1)-O(2SR)	2.754(5)	Sr(2)-Mn(4)	3.8609 (15)	Sr(2)-O(1SR)	2.683(5)
Sr(1)-O(21)	2.810(5)	Sr(2)-Mn(6)	3.8661(14)	Sr(2)-O(101)	2.860(6)
O(3)-Sr(1)-O(43)	129.88(18)	O(84)-Sr(1)-O(2SR)	103.91(16)	O(81)-Sr(2)-O(103)	84.39(17)
O(3)-Sr(1)-O(1)	68.15(17)	O(41)-Sr(1)-O(2SR)	79.35(16)	O(4)-Sr(2)-O(103)	70.00(17)
O(43)-Sr(1)-O(1)	134.96(17)	O(23)-Sr(1)-O(2SR)	136.46(17)	O(61)-Sr(2)-O(103)	130.82(17)
O(3)-Sr(1)-O(1SR)	108.34(17)	O(3)-Sr(1)-O(21)	130.58(17)	O(83)-Sr(2)-O(2SR)	110.63(17)
O(43)-Sr(1)-O(1SR)	77.92(16)	O(43)-Sr(1)-O(21)	69.88(17)	O(63)-Sr(2)-O(2SR)	78.07(17)
O(1)-Sr(1)-O(1SR)	141.93(18)	O(1)-Sr(1)-O(21)	69.93(17)	O(81)-Sr(2)-O(2SR)	143.93(18)
O(3)-Sr(1)-O(84)	70.86(18)	O(1SR)-Sr(1)-O(21)	120.76(16)	O(4)-Sr(2)-O(2SR)	67.11(17)
O(43)-Sr(1)-O(84)	144.94(17)	O(84)-Sr(1)-O(21)	121.67(17)	O(61)-Sr(2)-O(2SR)	138.09(18)
O(1)-Sr(1)-O(84)	75.77(18)	O(41)-Sr(1)-O(21)	69.46(16)	O(103)-Sr(2)-O(2SR)	73.40(16)
O(1SR)-Sr(1)-O(84)	67.86(17)	O(23)-Sr(1)-O(21)	62.43(16)	O(83)-Sr(2)-O(1SR)	73.12(17)
O(3)-Sr(1)-O(41)	77.96(17)	O(2SR)-Sr(1)-O(21)	133.20(16)	O(63)-Sr(2)-O(1SR)	64.87(17)
O(43)-Sr(1)-O(41)	68.44(17)			O(81)-Sr(2)-O(1SR)	137.70(17)
O(1)-Sr(1)-O(41)	79.11(18)	O(83)-Sr(2)-O(63)	128.54(18)	O(4)-Sr(2)-O(1SR)	104.22(17)
O(1SR)-Sr(1)-O(41)	138.61(17)	O(83)-Sr(2)-O(81)	67.66(17)	O(61)-Sr(2)-O(1SR)	78.11(17)
O(84)-Sr(1)-O(41)	145.43(18)	O(63)-Sr(2)-O(81)	132.88(18)	O(103)-Sr(2)-O(1SR)	136.97(16)
O(3)-Sr(1)-O(23)	135.10(18)	O(83)-Sr(2)-O(4)	72.55(18)	O(2SR)-Sr(2)-O(1SR)	65.71(16)
O(43)-Sr(1)-O(23)	94.79(18)	O(63)-Sr(2)-O(4)	144.61(18)	O(83)-Sr(2)-O(101)	130.10(17)
O(1)-Sr(1)-O(23)	84.05(17)	O(81)-Sr(2)-O(4)	78.83(18)	O(63)-Sr(2)-O(101)	67.37(17)
O(1SR)-Sr(1)-O(23)	72.71(16)	O(83)-Sr(2)-O(61)	76.13(18)	O(81)-Sr(2)-O(101)	70.99(17)
O(84)-Sr(1)-O(23)	68.45(17)	O(63)-Sr(2)-O(61)	67.52(18)	O(4)-Sr(2)-O(101)	124.72(17)
O(41)-Sr(1)-O(23)	131.87(17)	O(81)-Sr(2)-O(61)	77.76(18)	O(61)-Sr(2)-O(101)	68.83(17)
O(3)-Sr(1)-O(2SR)	71.65(17)	O(4)-Sr(2)-O(61)	146.19(18)	O(103)-Sr(2)-O(101)	62.04(16)
O(43)-Sr(1)-O(2SR)	66.53(17)	O(83)-Sr(2)-O(103)	136.73(18)	O(2SR)-Sr(2)-O(101)	119.22(16)
O(1)-Sr(1)-O(2SR)	137.39(17)	O(63)-Sr(2)-O(103)	94.71(18)	O(1SR)-Sr(2)-O(101)	129.30(16)
O(1SR)-Sr(1)-O(2SR)	65.22(16)				

Table S9. Selected intermetallic Mn···Mn and distances Mn···M (Å) and angles (°) for **Mn_3M.**

Mn_3Mn		**Mn_3Ca**	
Mn(1)···Mn(2)	5.5384(15)	Mn(1)···Mn(2)	5.723(2)
Mn(2)···Mn(3)	5.4935(16)	Mn(2)···Mn(3)	5.766(3)
Mn(3)···Mn(1)	5.4911(15)	Mn(3)···Mn(1)	5.6576(16)
Mn(1)···Mn(4)	3.4205(15)	Mn(1)···Ca(1)	3.6143(17)
Mn(2)···Mn(4)	3.4301(15)	Mn(2)···Ca(1)	3.663(2)
Mn(3)···Mn(4)	3.4045(15)	Mn(3)···Ca(1)	3.675(2)
Mn(3)-Mn(1)-Mn(2)	59.744(19)	Mn(3)-Mn(1)-Mn(2)	60.88(3)
Mn(1)-Mn(2)-Mn(3)	59.700(19)	Mn(1)-Mn(2)-Mn(3)	59.00(3)
Mn(2)-Mn(3)-Mn(1)	60.556(19)	Mn(2)-Mn(3)-Mn(1)	60.12(2)
$\{Mn_3Sr\}_2$			
Mn(1)···Mn(2)	5.7317(16)	Mn(4)···Mn(5)	5.8061(19)
Mn(2)···Mn(3)	5.5452(17)	Mn(5)···Mn(6)	5.7255(16)
Mn(3)···Mn(1)	5.7543(18)	Mn(6)···Mn(4)	5.5284(16)
Mn(1)···Sr(1)	3.7572(15)	Mn(4)···Sr(2)	3.8609(15)
Mn(2)···Sr(1)	3.8566(14)	Mn(5)···Sr(2)	3.7967(14)
Mn(3)···Sr(1)	3.8484(14)	Mn(6)···Sr(2)	3.8661(14)
Mn(3)-Mn(1)-Mn(2)	57.73(2)	Mn(6)-Mn(4)-Mn(5)	60.62(2)
Mn(1)-Mn(2)-Mn(3)	61.34(2)	Mn(4)-Mn(5)-Mn(6)	57.29(2)
Mn(2)-Mn(3)-Mn(1)	60.93(2)	Mn(5)-Mn(6)-Mn(4)	62.09(2)

Table S10. Averages Mn-ligand distances (Å) of the {Mn(tpada)} units for the **Mn_3M** complexes. The distances presented are average values calculated for equivalent positions around the different cations Mn^{2+}, n corresponding to the notation of the atoms in the equivalent positions.

Mn_3Mn		**Mn_3Ca**		**$\{Mn_3Sr\}_2$**	
Mn-N(n1)$_{tert}$	2.434(6)	Mn-N(n1)$_{tert}$	2.459(10)	Mn-N(n1)$_{tert}$	2.491(17)
Mn-N(n2)$_{py}$	2.245(16)	Mn-N(n2)$_{py}$	2.245(9)	Mn-N(n2)$_{py}$	2.289(12)
Mn-N(n3)$_{py}$	2.198(9)	Mn-N(n3)$_{py}$	2.222(4)	Mn-N(n3)$_{py}$	2.258(23)
Mn-N(n4)$_{py}$	2.269(20)	Mn-N(n4)$_{py}$	2.260(35)	Mn-N(n4)$_{py}$	2.291(35)
Mn-O(n1)$_{COO^-}$	2.240(5)	Mn-O(n1)$_{COO^-}$	2.278(17)	Mn-O(n1)$_{COO^-}$	2.286(31)
Mn-O(n3)$_{COO^-}$	2.274(8)	Mn-O(n3)$_{COO^-}$	2.210(42)	Mn-O(n3)$_{COO^-}$	2.218(13)
Mn-O(n2)$_{\mu\text{-}COO^-}$	2.200(19)	Mn-O(n2)$_{\mu\text{-}COO^-}$	2.209(46)	Mn-O(n2)$_{\mu\text{-}COO^-}$	2.135(21)

Table S11. Distances (Å) M-ligands for the central cations in the **Mn_3M** complexes.

Mn_3Mn		**Mn_3Ca**		**$\{Mn_3Sr\}_2$**			
Mn(4)-O(1)	2.235(5)	Ca(1)-O(1)	2.424(5)	Sr(1)-O(1)	2.598(5)	Sr(2)-O(61)	2.640(5)
Mn(4)-O(3)	2.158(5)	Ca(1)-O(3)	2.346(5)	Sr(1)-O(3)	2.534(5)	Sr(2)-O(63)	2.585(6)
Mn(4)-O(21)	2.283(5)	Ca(1)-O(21)	2.448(5)	Sr(1)-O(21)	2.810(5)	Sr(2)-O(81)	2.614(6)
Mn(4)-O(23)	2.138(5)	Ca(1)-O(23)	2.359(6)	Sr(1)-O(23)	2.641(5)	Sr(2)-O(83)	2.535(5)
Mn(4)-O(41)	2.282(4)	Ca(1)-O(41)	2.449(6)	Sr(1)-O(41)	2.637(5)	Sr(2)-O(101)	2.860(6)
Mn(4)-O(43)	2.117(5)	Ca(1)-O(43)	2.412(5)	Sr(1)-O(43)	2.595(5)	Sr(2)-O(103)	2.644(5)
		Ca(1)-O(1CA)	2.386(5)	Sr(1)-O(1SR)	2.612(5)	Sr(2)-O(1SR)	2.683(5)
				Sr(1)-O(2SR)	2.754(5)	Sr(2)-O(2SR)	2.652(5)
				Sr(1)-O(84)	2.624(5)	Sr(2)-O(4)	2.631(6)

Table S12. Crystallographic refinement data for the complex $[Sr(tpada)(OH_2)]_4 \cdot 8CH_3CN \cdot 2H_2O$ (**Sr$_4$**$\cdot 8CH_3CN \cdot 2H_2O$).

Sr$_4$ $\cdot 8CH_3CN \cdot 2H_2O$	
CCDC reference	2059900
Empirical formula	$C_{24}H_{25}SrN_6O_{5.5}$
Formula weight	573.12
Colour, shape	Translucent colourless, octahedron
Crystal size, mm	0.299x0.237x0.177
Crystal system	Tetragonal
Space group	*I* $4_1/a$
a, Å	22.8544(2)
b, Å	22.8544(2)
c, Å	19.9770(4)
α, deg.	90
β, deg.	90
γ, deg.	90
V, Å^3	10434.5(3)
Z	16
T, K	150.05(10)
ρ (calc), g/cm^3	1.459
μ, mm^{-1}	2.114
θ range, deg.	3.186 to 30.504
No.of rflcn measured/used	125571/7971
GooF	1.044
*R*1	0.0483
*wR*2	0.0748

Table S13. Selected bond lengths (Å) and angles (deg) for **Sr_4**·$8CH_3CN$·$2H_2O$.

$Sr(1)\text{-}N(1)_{tert}$	2.9132(18)	$Sr(1)\text{-}O(1)_{COO^-}$	2.5708(16)
$Sr(1)\text{-}N(2)_{py}$	2.7327(19)	$Sr(1)\text{-}O(3)_{\mu\text{-}COO^-}$	2.5954(15)
$Sr(1)\text{-}N(3)_{py}$	2.7576(17)	$Sr(1)\text{-}O(3)\#1_{\mu\text{-}COO^-}$	2.7550(15)
$Sr(1)\text{-}N(4)_{py}$	2.753(2)	$Sr(1)\text{-}O(4)\#1_{\kappa\text{-}COO^-}$	2.6196(15)
		$Sr(1)\text{-}O(11)_{H_2O}$	2.5803(18)
O(11)-Sr(1)-O(1)	105.14(6)	O(3)#1-Sr(1)-O(4)#1	48.86(4)
O(3)-Sr(1)-O(1)	82.19(5)	O(3)#1-Sr(1)-N(2)	82.57(5)
O(3)-Sr(1)-O(11)	73.25(6)	O(3)#1-Sr(1)-N(4)	120.38(5)
O(4)#1-Sr(1)-O(1)	110.58(5)	N(3)-Sr(1)-O(1)	97.97(5)
O(4)#1-Sr(1)-O(11)	87.34(6)	N(3)-Sr(1)-O(11)	124.51(6)
O(4)#1-Sr(1)-O(3)	159.26(5)	N(3)-Sr(1)-O(3)	60.77(5)
N(2)-Sr(1)-O(1)	61.24(5)	N(3)-Sr(1)-O(4)#1	129.83(5)
N(2)-Sr(1)-O(11)	148.43(6)	N(3)-Sr(1)-N(2)	86.71(5)
N(2)-Sr(1)-O(3)	127.31(5)	N(3)-Sr(1)-N(4)	67.50(5)
N(2)-Sr(1)-O(4)#1	73.34(5)	N(3)-Sr(1)-N(3)#1	168.97(5)
N(4)-Sr(1)-O(1)	164.90(5)	N(1)-Sr(1)-O(1)	116.19(5)
N(4)-Sr(1)-O(11)	81.32(6)	N(1)-Sr(1)-O(11)	137.46(6)
N(4)-Sr(1)-O(3)	86.79(5)	N(1)-Sr(1)-O(3)	120.45(5)
N(4)-Sr(1)-O(4)#1	83.03(5)	N(1)-Sr(1)-O(4)#1	69.64(5)
N(4)-Sr(1)-N(2)	119.54(6)	N(1)-Sr(1)-N(2)	58.36(5)
O(3)#1-Sr(1)-O(1)	74.59(5)	N(1)-Sr(1)-N(4)	61.32 (5)
O(3)#1-Sr(1)-O(11)	66.01(6)	N(1)-Sr(1)-N(3)#1	114.74(5)
O(3)#1-Sr(1)-O(3)	124.81(6)	N(1)-Sr(1)-N(3)	60.79(5)

#1: y-3/4, -x+3/4, -z+3/4.

Table S14. Hydrogen bonds lengths (Å) and angles (deg) for **Sr_4**·$8CH_3CN$·$2H_2O$.

D-H…A	d(D-H)	d(H…A)	d(D…A)	< (DHA)
O(11)-H(11A)···O(1)#2	0.77(3)	2.06(3)	2.830(2)	173(3)
O(11)-H(11B)···O(1)#1	0.79(3)	2.41(3)	3.186(2)	167(3)
O(10)-H(10A)···O(2)#3	0.83(3)	1.95(3)	2.751(2)	164(4)

#1: y-3/4, -x+3/4, -z+3/4 ; #2: -y+3/4, x+3/4, -z+3/4 ; #3: x+1/2, y, -z+1/2.

5. ESI mass spectra, electrochemical data and UV-Visible absorption and EPR spectra for Mn_3Mn, Mn_3Ca, $\{Mn_3Sr\}_2$

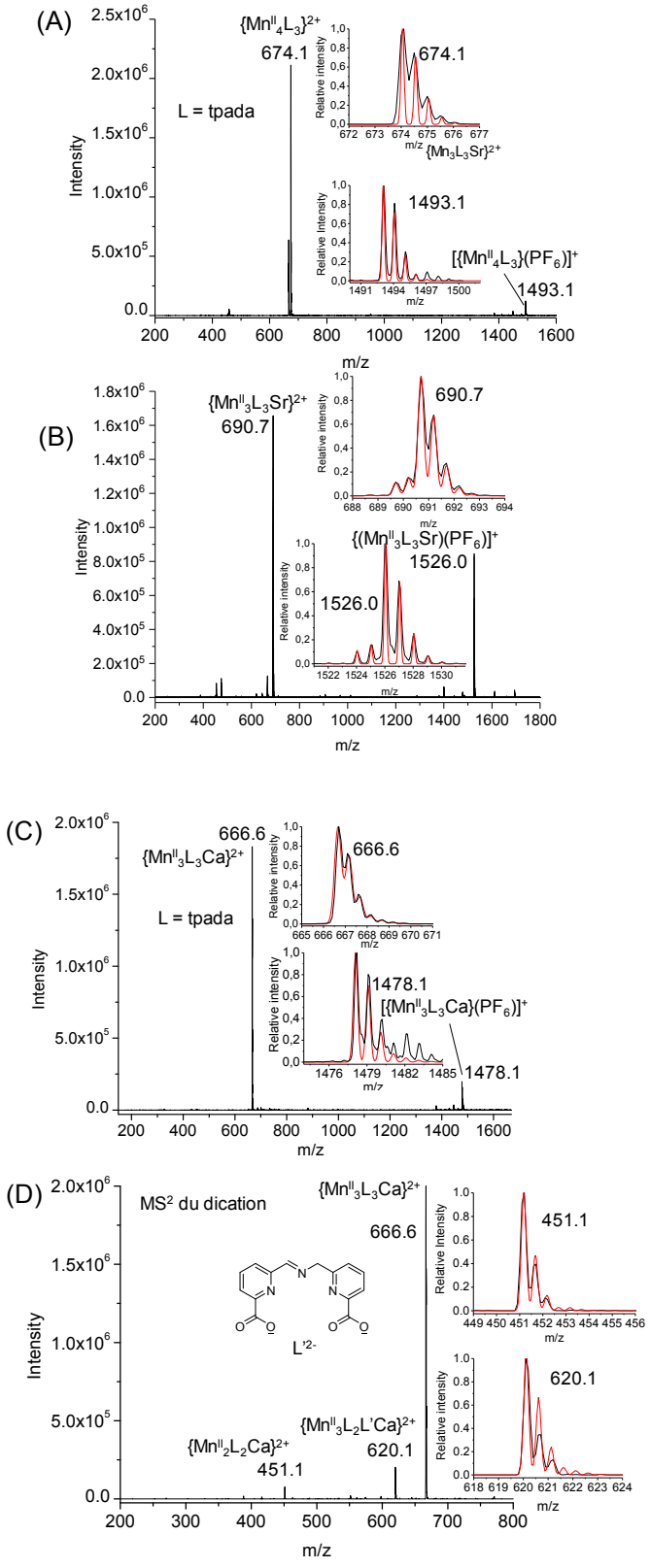

Figure S1. Positive ESI mass spectra of a 10^{-6} M solution in CH_3CN of **Mn_3Mn** (A), **$\{Mn_3Sr\}_2$** (B) and of **Mn_3Ca** (C) and MS^2 spectrum of the molecular mass present at 666.6 m/z with the enlargements of the dicationic isotopic masses at *m/z* 451.1 and 620.1 (D). The inserts reproduce the enlargements of the main isotopic massifs (in black) and the corresponding simulation (in red).

Table S15. Electrochemical potentials for **Mn_3M** complexes in acetonitrile under argon atmosphere, versus Ag/Ag^+ (0.01M $AgNO_3$ in CH_3CN, 0.1M $[Bu_4N]ClO_4$). Potentials can be converted to ferricinium/ferrocene (Fc^+/Fc^0) by subtracting 100 mV.

Complexes	Mn^{II}/Mn^{III} $E_{1/2}$ (V)	Ligand centered reduction processes $E_{1/2}$ (V)
Mn_3Mn	0.62 ; 0.74 ; 0.88	-2.00 ; -2.15 ; -2.27 ; -2.40 ; -2.50
Mn_3Ca	0.57 ; 0.70; 0.86	-2.06 ; -2.20 ; -2.30 ; -2.42 ; -2.56
$\{Mn_3Sr\}_2$	0.58 ; 0.75 ; 0.90	-2.12 ; -2.19 ; -2.30 ; -2.41 ; -2.52

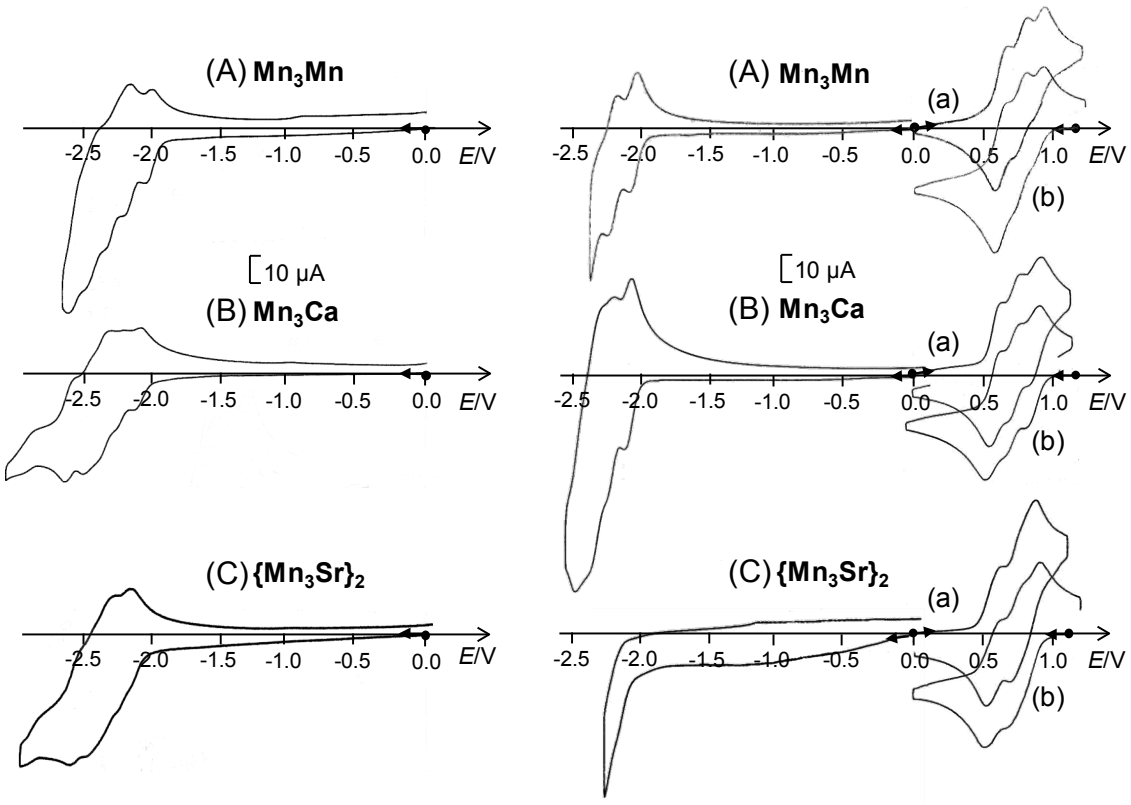

Figure S2. Cyclic voltammograms in CH_3CN, 0.1 M $[Bu_4N]ClO_4$ under argon atmosphere of (A) **Mn_3Mn** (0.64 mM), (B) **Mn_3Ca** (0.57 mM) and (C) **$\{Mn_3Sr\}_2$** (0.33 mM) at a scan rate of 100 mV s^{-1}: (left) initial solutions at a vitreous carbon electrode (diameter 0.3 mm), (right) at a platinum electrode (diameter 0.5 mm), (a) initial solutions and (b) after exhaustive oxidation at 1.20 V. Potentials are referenced to $Ag/AgNO_3$ (10 mM).

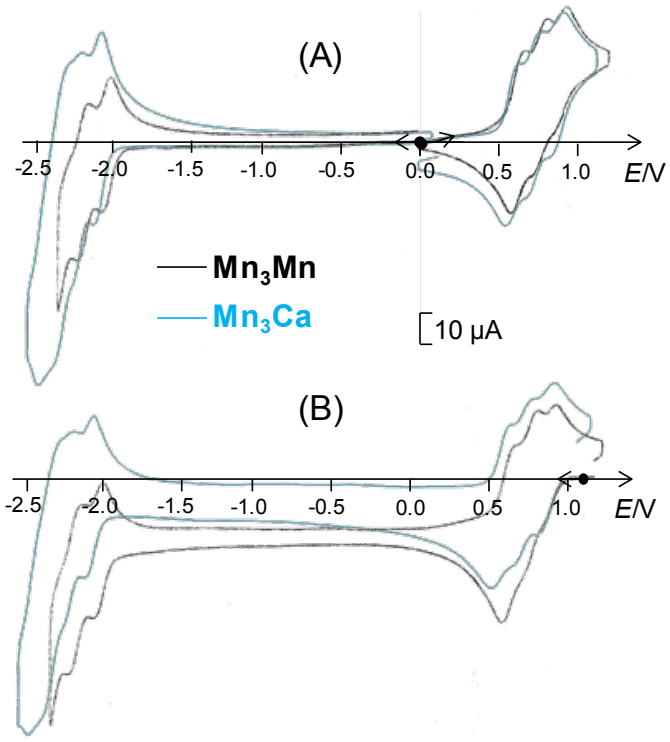

Figure S3. Cyclic voltammograms in CH_3CN, 0.1 M $[Bu_4N]ClO_4$ under argon atmosphere of **Mn_3Mn** (0.64 mM) and **Mn_3Ca** (0.57 mM) at a platinum electrode (diameter 0.5 mm), scan rate of 100 mV s^{-1}. (A) Initial solutions and (B) after exhaustive oxidation at 1.20 V. Potentials are referenced to $Ag/AgNO_3$ (10 mM).

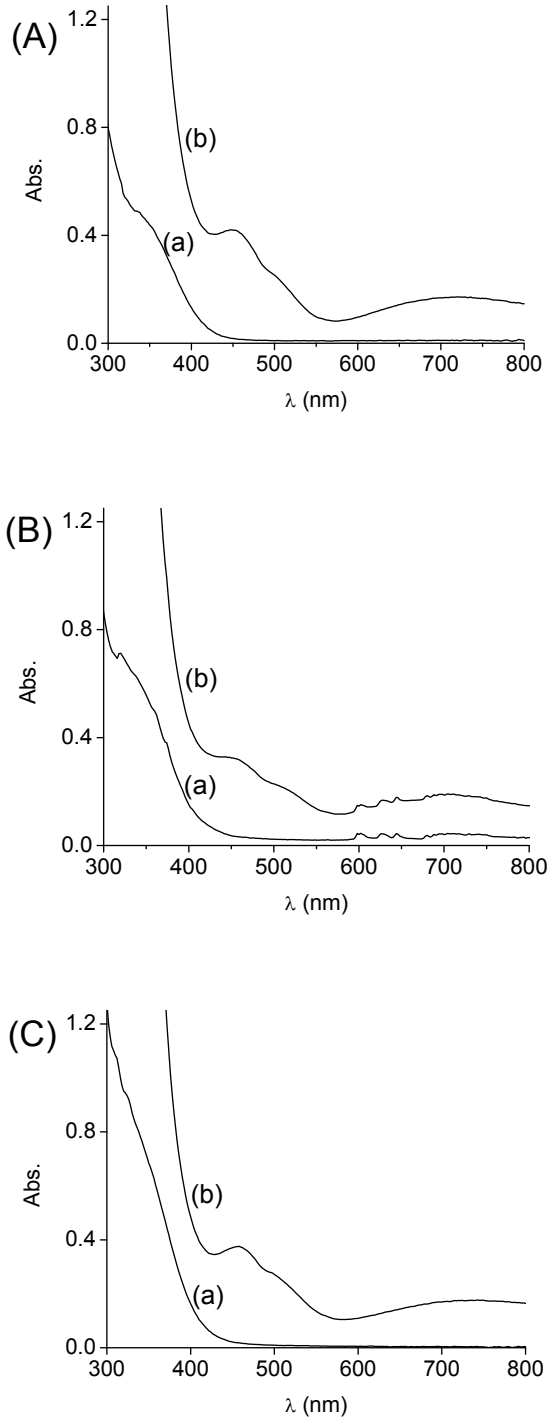

Figure S4. UV-Visible absorption spectra of solutions of (A) **Mn_3Mn** (0.64 mM), (B) **Mn_3Ca** (0.57 mM) and (C) **$\{Mn_3Sr\}_2$** (0.33 mM) in CH_3CN, 0.1 M $[Bu_4N]ClO_4$: (a) initial state and (b) after exhaustive electrolysis at +1.2 V (generation of **$Mn^{III}{}_3Mn^{II}$**, **$Mn^{III}{}_3Ca$** and **$Mn^{III}{}_3Sr$**). Optical path of 1 cm.

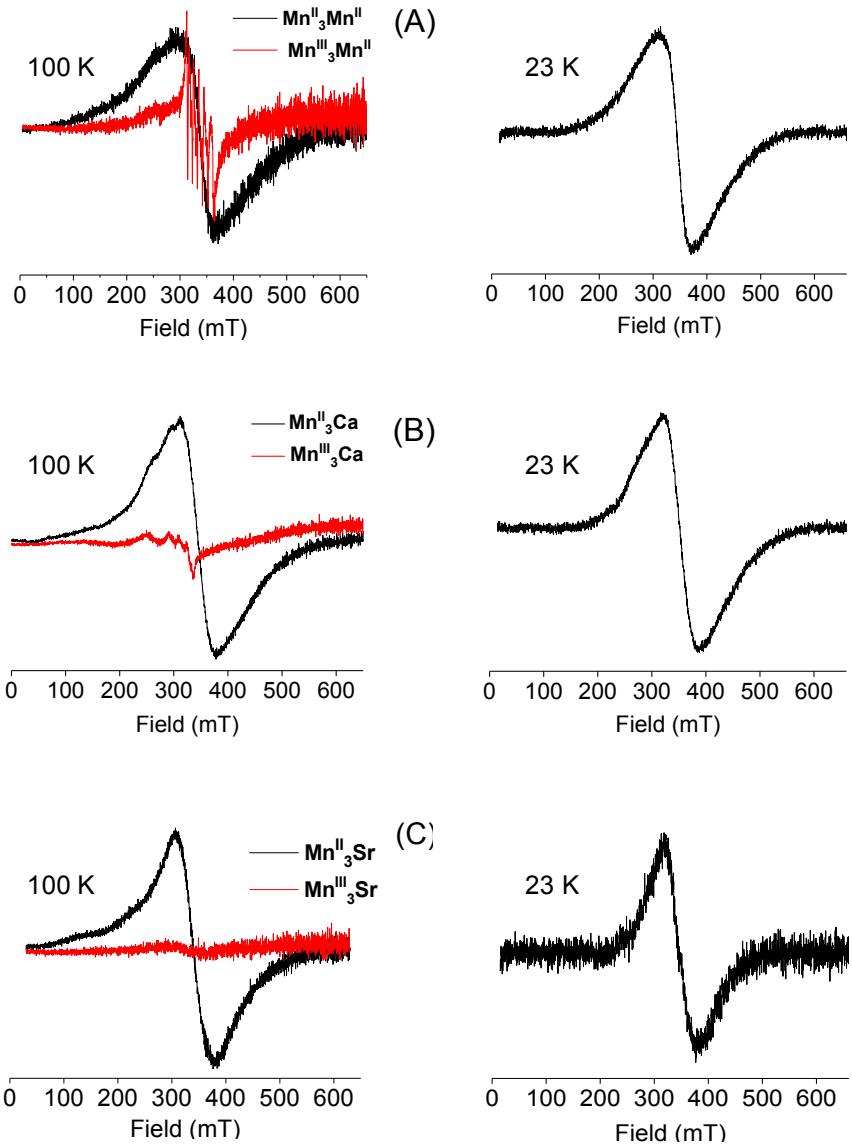

Figure S5. X-band EPR spectra for the complexes (A) **Mn_3Mn**, (B) **Mn_3Ca** and (C) **$\{Mn^{II}_3Sr\}_2$** in CH_3CN, 0.1 M $[Bu_4N]ClO_4$ before at 100 K and 23 K (black) and after exhaustive electrolysis at +1.2 V (generation of **$Mn^{III}_3Mn^{II}$**, **Mn^{III}_3Ca** and **Mn^{III}_3Sr**) at 100 K (red).

References

1. Gerey, B.; Gennari, M.; Goure, E.; Pecaut, J.; Blackman, A.; Pantazis, D. A.; Neese, F.; Molton, F.; Fortage, J.; Duboc, C.; Collomb, M.-N., Calcium and heterometallic manganese-calcium complexes supported by tripodal pyridine-carboxylate ligands: structural, EPR and theoretical investigations. *Dalton Trans.* **2015,** *44* (28), 12757-12770.
2. Palatinus, L.; Chapuis, G., SUPERFLIP– a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *J. Appl. Cryst.* **2007,** *40* (4), 786-790.
3. Sheldrick, G., SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallographica Section A* **2015,** *71* (1), 3-8.
4. Sheldrick, G., Crystal structure refinement with SHELXL. *Acta Crystallographica Section C* **2015,** *71* (1), 3-8.
5. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009,** *42* (2), 339-341.