Supporting Information

The syntheses, crystal structures, electrochemical and magnetic properties of tri-nuclear cyanide-bridged complexes [*cis*-$M^{II}(bpy)_2(CN)_2]_2Mn^{III}(salcy)(PF_6)$ (M = Fe, Ru, Os)

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Table S1 Detail of the Crystallographic Data Collection, Structural Determination and Refinement for Complexes **1-3**

	1	**2**	**3**
Chemical formula	$C_{64}H_{52}F_6Fe_2MnN_{14}O_2P$	$C_{69}H_{66}F_{12}MnN_{17}O_3P_2Ru_2$	$C_{73}H_{75}F_6MnN_{17}O_6Os_2P$
Formula weight	1360.80	1728.40	1866.81
Colour and Habit	Red prism	Yellow prism	Brown prism
Crystal Size / mm	0.36×0.29×0.10	0.26×0.10×0.07	0.20×0.10×0.05
T / K	123	123	123
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a / Å	15.566(12)	11.906(5)	11.835(5)
b / Å	23.082(17)	28.346(10)	28.365(10)
c / Å	22.534(18)	22.673(9)	22.093(9)
α / deg	90.00	90.00	90.00
β / deg	104.679(18)	96.952(10)	98.794(7)
γ / deg	90.00	90.00	90.00
V / Å^3	7832(10)	7596(5)	7330(5)
Z	4	4	4
D_{calc} / g cm^{-3}	1.154	1.511	1.692
μ / mm^{-1}	0.604	0.685	3.730
Completeness	96.6%	99.5%	99.8%

$F(000)$	2784	3496	3704
h, k, l, range	-18≤h≤18, -27≤k≤25, -26≤l≤26	-10≤h≤14, -33≤k≤33, -26≤l≤26	-14≤h≤12, -33≤k≤33, -25≤l≤26
θ range (deg)	2.07-25.00	2.04-25.00	2.10-25.00
Reflections measured	13329	13308	12879
Independent reflections	8113	10822	10329
R_{int}	0.0935	0.0544	0.0854
GOF	1.019	1.094	1.027
R_1, $_\omega R_2$ [$I>2\sigma(I)$]	0.1110, 0.3087	0.0850, 0.2166	0.0813, 0.1804
R_1, $_\omega R_2$ (all data)	0.1308, 0.3336	0.1012, 0.2297	0.0993, 0.1924

Table S2. Selected Bond Length (Å) and Bond Angle (°) for Complexes **1-3** (M = Fe, **1**; M = Ru, **2**; M = Os, **3**)

	1	**2**	**3**
M1-C1	1.917(7)	1.984(7)	1.991(11)
M1-C2	1.925(9)	2.003(8)	1.992(13)
M2-C43	1.898(6)	1.994(7)	1.998(12)
M2-C44	1.915(7)	2.010(8)	1.991(14)
M1-N3	2.000(5)	2.126(6)	2.109(8)
M1-N4	1.974(6)	2.063(6)	2.058(10)
M1-N5	2.000(8)	2.108(6)	2.094(11)
M1-N6	1.970(7)	2.067(6)	2.051(10)
M2-N11	2.016(5)	2.118(5)	2.132(9)
M2-N12	1.976(5)	2.081(6)	2.054(11)
M2-N13	2.003(5)	2.092(6)	2.110(9)
M2-N14	1.987(6)	2.062(6)	2.078(10)
Mn1-N1	2.286(5)	2.278(6)	2.275(10)
Mn1-N9	2.264(5)	2.288(5)	2.280(10)
Mn1-O1	1.897(5)	1.900(5)	1.890(8)
Mn1-O2	1.902(5)	1.892(5)	1.904(9)
Mn1-N7	2.007(5)	1.992(6)	1.996(9)
Mn1-N8	1.985(5)	1.982(6)	1.982(10)
C1≡N1	1.135(8)	1.166(9)	1.161(14)
C2≡N2	1.157(10)	1.168(10)	1.161(16)
C43≡N9	1.160(8)	1.161(8)	1.146(14)
C44≡N10	1.173(8)	1.153(10)	1.173(17)
C1-M1-C2	88.6(3)	88.5(3)	89.3(5)
C43-M2-C44	89.6(3)	88.0(3)	90.4(5)
N1≡C1-M1	177.9(6)	175.9(6)	176.9(10)
N2≡C2-M1	179.0(7)	178.0(7)	175.7(10)
N9≡C43-M2	177.0(5)	176.3(6)	176.0(11)
N10≡C44-M2	178.4(6)	177.0(6)	176.6(12)
C1≡N1-Mn1	141.6(5)	150.8(5)	149.2(9)

C43≡N9-Mn1	141.7(5)	149.3(5)	150.5(9)
O1-Mn1-O2	94.0(2)	93.0(2)	93.4(4)
N1-Mn1-N9	173.3(2)	170.4(2)	171.1(4)
M1···M2	9.95	7.94	7.93
Mn1···Mn2	12.77	12.15	11.71

Table S3. Data of Cyclic-Voltammetry, Cyanide Stretching Frequencies and Electronic Absorption Spectra for Complex **1-3** and Related Precursors.

Compound	*P* / V	ν_{CN} (cm^{-1})	λ_{max}, nm(ε, $dm^3\ mol^{-1}\ cm^{-1}$)
cis-$Fe(bpy)_2(CN)_2{\cdot}3H_2O$	0.46	2069, 2079	382 (6252), 581 (6204)
cis-$Ru(bpy)_2(CN)_2{\cdot}2H_2O$	0.86	2062,2078	346 (9428),483 (10385)
cis-$Os(bpy)_2(CN)_2{\cdot}2H_2O$	0.47	2040, 2057	336 (11870), 372 (11569), 445 (10667), 496 (13074), 650 (3370)
$[Mn(salcy)](ClO_4){\cdot}2H_2O$	—	—	406 (3915), 475 (1387)
1	-0.41, 0.75	2090, 2098	382 (10397), 569 (8962), 610 (8023)
2	-0.42, 0.77	2051, 2071	335 (17276), 473 (13322), 493 (13120)
3	-0.13, 0.35	2031, 2059	341 (19103), 379 (17118), 407 (15893), 510 (14401), 672 (3647)

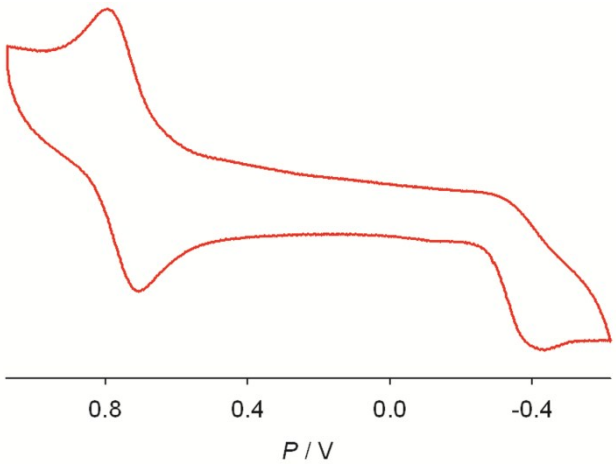

Figure S1. Cyclic voltammogram of complex **1** in CH_3CN containing 0.1 M $(Bu_4N)(PF_6)$ electrolyte. Scan rate was 100 mV/s.

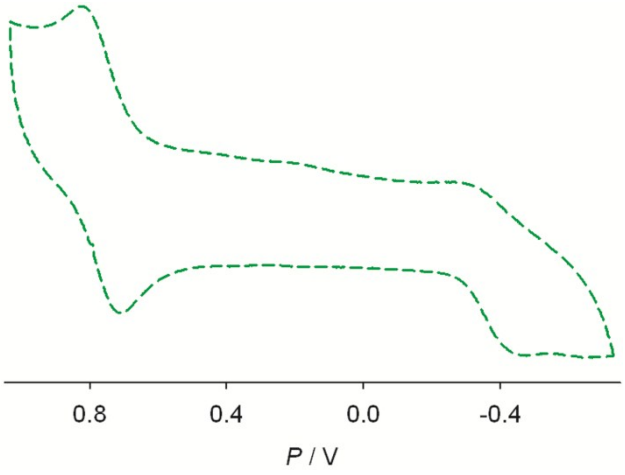

Figure S2. Cyclic voltammogram of complex **2** in CH_3CN containing 0.1 M $(Bu_4N)(PF_6)$ electrolyte. Scan rate was 100 mV/s.

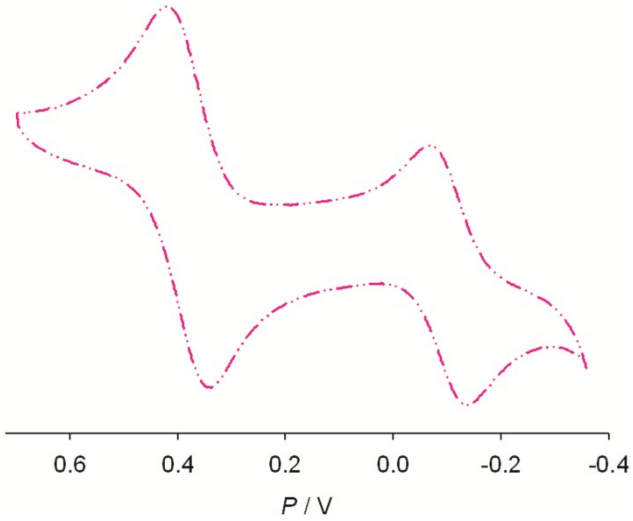

Figure S3. Cyclic voltammogram of complex **3** in CH_3CN containing 0.1 M $(Bu_4N)(PF_6)$ electrolyte. Scan rate was 100 mV/s.

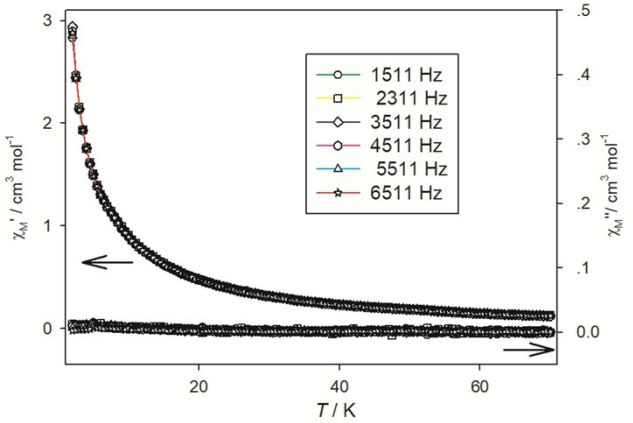

Figure S4. Temperature dependence of the in-phase and out-of-phase ac susceptibility for **2** in zero dc and 3 Oe ac applied field