Electronic Supplementary Information

Synthetic, Structural, Spectroscopic and Theoretical Study of a Mn(III)-Cu(II) Dimer Containing a Jahn-Teller Compressed Mn ion

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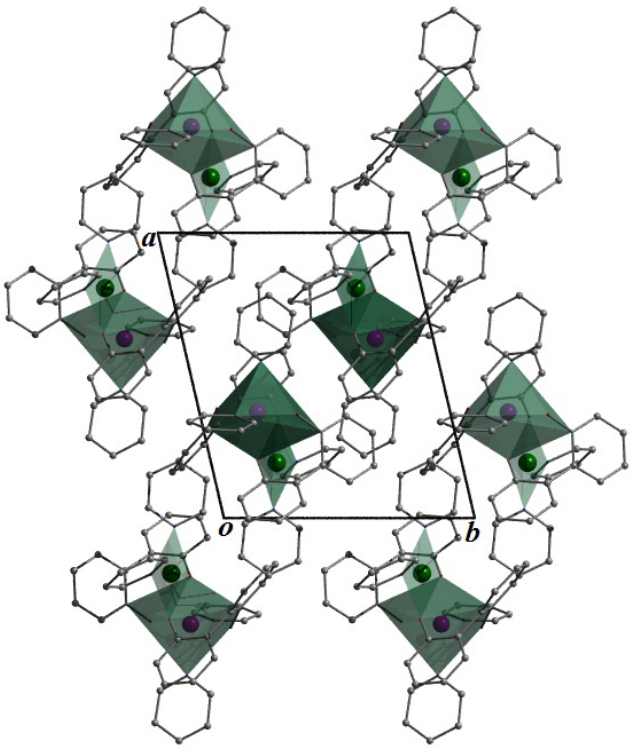

Figure S1: Packing diagram of **1** as viewed along the *c* direction of the unit cell. The EtOH solvents of crystallisation and ClO_4^- counter anions have been omitted for clarity.

Table S1 Crystal data for complex **1**

Parameters	**(1) at 150K**
Formula[a]	$C_{45}H_{40}N_4O_9CuMn$
M_W	934.77
Crystal System	Triclinic
Space group	P-1
a/Å	10.686(2)
b/Å	12.392(3)
c/Å	17.360(4)
α/°	97.99(3)
β/°	100.99(3)
γ/°	101.10(3)
V/Å^3	2177.2(8)
Z	2

T/K	150(2)
λ^b/Å	0.7107
D_c/g cm^{-3}	1.447
μ(Mo-Ka)/ mm^{-1}	0.901
Meas./indep.(R_{int}) refl.	7945 / 4906 (0.0553)
wR2 (all data)	0.1653
$R1^{d,e}$	0.0679
Goodness of fit on F^2	1.027

[a] Includes guest molecules. [b] Mo-Kα radiation, graphite monochromator. [c] $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2 / \Sigma w|F_o^2|^2]^{1/2}$. [d] For observed data. [e] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

Table S2 Pertinent Mn-L bond lengths observed in complex **1** when collected at 150 K and 250 K which highlight that no dynamic J-T effects are observed.

	(1) at 150K		**(1) at 250K**
Compressed bonds	**(Å)**	***Compressed bonds***	**(Å)**
Mn1-O2	1.880(4)	Mn1-O2	1.879(2)
Mn1-O4	1.871(3)	Mn1-O4	1.866(2)
Elongated bonds		***Elongated bonds***	
Mn1-O1	2.097(4)	Mn1-O1	2.089(2)
Mn1-O3	2.051(3)	Mn1-O3	2.050(2)
Mn1-N3	2.169(2)	Mn1-N3	2.175(3)
Mn1-N4	2.205(2)	Mn1-N4	2.201(3)

Table S3 Literature reported mononuclear Mn(III) complexes comprising compressed Jahn-Teller ions and their comparison with complex **1**. Ligand code: bpea = N,N-bis(2-pyridylmethyl)-ethylamine. Tolyl-terpy = 4'-(4-methylphenyl)-2,2':6',2''-terpyridine. Bpia = bis(picolyl)(N-methylimidazole-2yl)amine.

Complex	**g (x,y,z)**	**$D_{Mn(III)}$ (cm^{-1})**	**$E_{Mn(III)}$ (cm^{-1})**	**Determination method(s)**	**Reference**
[Mn(III)(bpea)$(N_3)_3$]	2.02(1), 1.98(1), 1.95(1)	+3.50(1)	+0.82(1)	HF-EPR	*J. Am. Chem. Soc*., 2003, 125, 12337
[Mn(III)(tolyl-terpy)$_2$]$(PF_6)_3$	2.09, 2.11, 1.95	+4.82†	+0.04	M vs. H, DFT	*Chem. Eur. J*., 2009, 15, 980.
[Mn(III)(bpia)(OAc)(OCH_3)](PF_6)	1.98(1), 1.952(6), 1.978(5)	+3.526(3)	+0.588(6)	INS, HF-EPR	*Inorg. Chem., 2008, 47, 439.*
1	1.97, 1.97, 1.98	+4.45* ($D_{cluster}$ = +6.27)	+0.41 (Es = ±0.51)	M vs H, HF-EPR	This work

† DFT analysis gave a DMn(III) value of +3.665 cm^{-1}.

* M vs H studies give a DMn(III) value of +4.95 cm^{-1}.

Table S4 DFT calculated D tensor on complex **1** with varying computational protocols.

Complexes	Method	D (cm^{-1})	E/D	g-tensor
With counter ion(MnCu)	B3LYP/TZVPPP	16.96	0.01	2.03
With counter ion(MnZn)	B3LYP/TZVPPP	1.75	0.3	1.99
Without counter ion(MnCu)	B3LYP/TZVPPP	12.47	0.02	2.03
Without counter ion(MnZn)	B3LYP/TZVPPP	1.78	0.3	1.99
Without counter ion(MnCu)	BP86/TZVPPP	2.35	0.06	1.98
Without counter ion(MnZn)	BP86/TZVPPP	1.94	0.06	1.99
Experimental MnCu	----------	6.27	0.09	----
Experimental Single ion	---------	4.78	0.08	1.98

Table S5 DFT calculated *J* values for **1** with <S**2> value.

Complex	Spin configuration	Energies	*J* value	<S**2> values
1	HS	-5769.99075	-83.7234265	8.8156
	BS	-5769.992657		4.7834
No counterion	HS	-5009.45679	-71.2361979	8.8134
	BS	-5009.458413		4.7751

Table S6 Overlap Integral Analysis on **1**

	Mn orbitals	**Cu orbital**
		($d_{x^2-y^2}$) 209
d_{xy}	212	-0.003
d_{xz}	213	0.009
d_{yz}	217	-0.023
$d_{x^2-y^2}$	220	-0.144
d_{z^2}	227	-0.007

X-Ray Diffraction details on the collection of 1

The structures of **1** was collected on an Xcalibur S single crystal diffractometer (Oxford Diffraction) using an enhanced Mo source. Each data reduction was carried out on the CrysAlisPro software package. The structures were solved by direct methods (SHELXS-97)[1] and refined by full matrix least squares using SHELXL-97.[2] SHELX operations were automated using the OSCAIL software package.[3] All non-hydrogen atoms (apart from the EtOH solvent of crystallisation) in **1** were modelled anisotropically while all hydrogen atoms in **1** were assigned to idealised positions. Despite many efforts, modelling of the EtOH solvent molecule gives rise to a short C-C bond (C50-C51) length presumably due to methyl group libration. In order to prove that this electron density was indeed due to an EtOH solvent molecule, a SQUEEZE analysis was carried out on a separate identical data set. The result (42 electrons per void = 2 x EtOH molecules per void), confirmed the presence of one EtOH molecule per $[CuMn(L)_2(py)_4]$ unit in **1**. This cif file is available on demand.

1. G. M. Sheldrick, *Acta. Crystallogr., Sect. A: Found. Crystallogr.,* 1990, **A46**, 467.
2. G. M. Sheldrick, SHELXL-97, A computer programme for crystal structure determination, University of Gottingen, 1997.
3. P. McArdle, P. Daly and D. Cunningham, *J. Appl. Crystallogr*., 2002, **35**, 378.