Electronic supplementary information

SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW RHOMBOID $\{Mn^{II}_2Mn^{III}_2\}$ CLUSTER BASED ON CALIX[4]ARENE AND BATHOPHENANTHROLINE LIGANDS

A. S. Ovsyannikov,*[a] I. V. Strelnikova,[a,b] A. A. Iova,[b] D. R. Islamov,[c]
P. V. Dorovatovskii,[d] S. E. Solovieva,[b] and I. S. Antipin[b]

[a] *Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, Tatarstan, 420088 Russia*
[b] *Kazan Federal University, ul. Kremlevskaya 18, Kazan, Tatarstan,420008 Russia*
[c] *Laboratory for Structural Analysis of Biomacromolecules, FRC Kazan Scientific Center, Russian Academy of Sciences, ul. Lobachevskogo 2/3, Kazan, Tatarstan,420111 Russia*
[d] *National Research Centre "Kurchatov Institute", pl. Akademika Kurchatova 1, Moscow, 123182 Russia*

Single crystal X-ray diffraction study

Diffraction data for single-crystals of **3_2-Mn_4(bathophen)$_2$** were collected at 100 K on a Belok/XSA beamline (λ = 0.745 Å, φ-scans) of the Kurchatov Synchrotron Radiation Source (Moscow, Russian Federation) [S1, S2]. Diffraction patterns were collected using Mardtb goniometer equipped with Rayonix SX165 2D positional sensitive CCD detector at 100 K. In total, 450 frames were collected with oscillation range of 1°. The data were indexed, integrated and scaled; absorption correction was applied using the XDS program package [S3]. The structures were solved by direct methods with software SHELXT [S4]. The structural model was investigated and refined by using Olex2 software [S5] by a full-matrix least-squares method on F^2 with anisotropic displacement. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and included in the refinement within the riding model with fixed isotropic displacement parameters Uiso(H) = 1.5Ueq(O), 1.2Ueq(N), and 1.2Ueq(C).

The crystallographic data and experimental details for **3_2-Mn_4(bathophen)$_2$** are presented in Table S1. CCDC 2383835 contains the supplementary crystallographic information for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

Table S1. Crystallographic data and structure refinement parameters for the coordination compound obtained

Compound name	**3_2-Mn_4(batophen)$_2$**
Empirical formula	$C_{110}H_{86}Mn_4N_6O_{12}$, $2(CH_4O)$
Formula weight, g·mol^{-1}	1967.69
Wavelength, Å	0.745
Temperature	100(1)
Crystal system	triclinic
Space group	*P-1*
a, *Å*	11.700(2)
b, *Å*	15.170(3)
c, *Å*	15.380(3)
α,°	108.65(3)
β,°	107.11(3)
γ,°	103.43(3)
V, Å^3	2305.8(10)
Z/Z′	1/0.5
ρ_{calc} g,cm^3	1.417

μ,cm^{-1}	0.684
F(000)	1020.0
Crystal size, mm^3	0.3 × 0.2 × 0.2
2θ range for data collection, °	5.076 ≤ 2θ ≤ 62.1
Index ranges	–16 ≤ h ≤ 16, –20 ≤ k ≤ 21, –21 ≤ l ≤ 21
Reflections collected/independ.	57179/12278
R_{int}	0.0385
Completeness to θ_{max}/%	95.7
Data/restraints/parameters	12278/0/617
Goodness-of-fit on F^2	1.031
Final R indexes [I > 2σ (I)] R_1/wR_2	0.0415/0.1056
Final R indexes [all data] R_1/wR_2	0.0470/0.1090
ρ_{max}/ρ_{min}, $eÅ^{-3}$	0.71/–0.54

Table S2. Coordination bond angles for Mn ions of **3_2-Mn_4(bathophen)$_2$** (°)

O_X–Mn(1)–**O_Y**	81.71(6) 98.71(6) 178.89(5) 89.14(6) 99.40(6) 81.38(6)
O_X–Mn(1)–**N_x**	85.78(6) 92.42(6) 166.60(6) 96.69(6) 97.53(6) 168.09(6) 93.11(6) 87.41(6)
N_X–Mn(1)–**N_Y**	78.99(6)
O_X–Mn(2)–**O_Y**	92.09(5) 97.18(5) 91.67(5) 87.22(5) 162.64(5) 92.46(6) 175.27(6) 89.50(6) 97.93(5) 89.92(6) 175.11(6) 96.52(5) 87.82(6) 77.73(5) 78.77(5)

Table S3. CShM deviation values calculated by *SHAPE* program for Mn atoms in **3_2-Mn_4(bathophen)$_2$**

Complex name	Mn	HP-6	PPY-6	OC-6	TPR-6	JPPY-6
3_2-Mn_4(dmf)$_4$	Mn(1)	29.386	24.558	1.319	13.669	27.791
	Mn(2)	31.288	26.303	1.329	14.137	29.970

Label	Symmetry	Shape
HP-6	D_{6h}	Hexagon
PPY-6	C_{5v}	Pentagonal pyramid
OC-6	O_h	Octahedron
TPR-6	D_{3h}	Trigonal prism
JPPY-6	C_{5v}	Johnson pentagonal pyramid (J2)

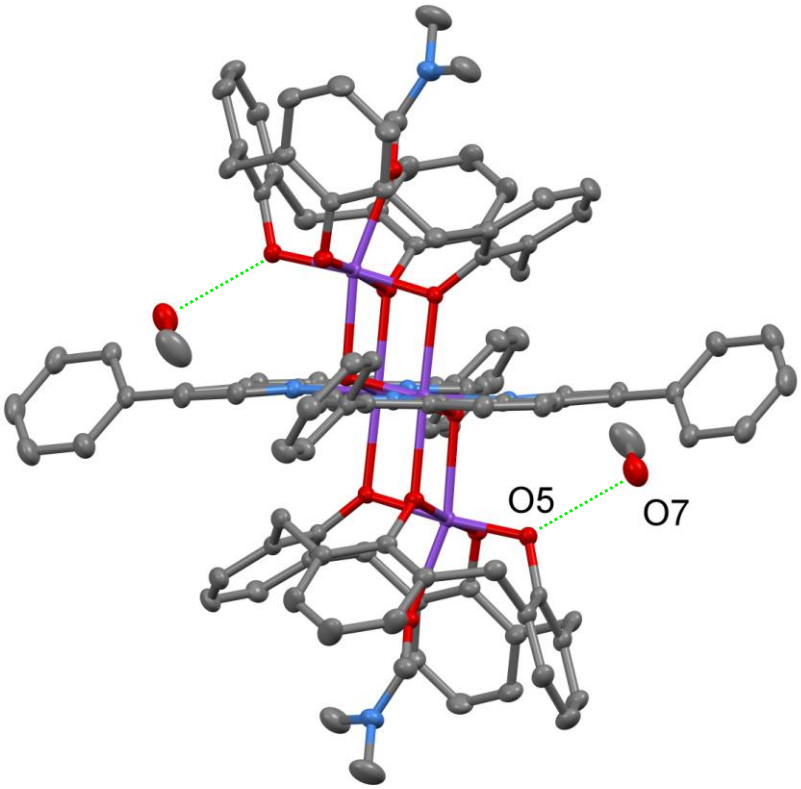

Figure S1. H-bonding between the solvate MeOH molecules with **3_2-Mn_4(bathophen)$_2$** cluster molecule within the crystal packing.

References

S1. V. A. Lazarenko, P. V. Dorovatovskii, Y. V. Zubavichus, A. S. Burlov, Y. V. Koshchienko, V. G. Vlasenko, V. N. Khrustalev, *Crystals*, **2017**, *7*, 325. DOI: 10.3390/cryst7110325

S2. R. D. Svetogorov, P. V. Dorovatovskii, V. A. Lazarenko, *Cryst. Res. Technol.*, **2020**, *55*, 1900184. DOI: 10.1002/crat.201900184

S3. W. Kabsch, *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, **2010**, *D66*, 125–132. DOI: 10.1107/S0907444909047337

S4. G. M. Sheldrick, *Acta Crystallogr. A: Found. Adv.*, **2015**, *71*, 3–8. DOI: 10.1107/S2053273314026370

S5. O. V. Dolomanov, L. J. Bourhis, R.J. Gildea, J. A. K. Howard, H. J. Puschmann, *J. Appl. Crystallogr.*, **2009**, *42*, 339–341. DOI: 10.1107/S0021889808042726