# 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

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**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 |
| $\rho_{calc}$ 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 $\theta_{max}$/% | 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 |
| $\rho_{max}/\rho_{min}$, $eÅ^{-3}$ | 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)<br>98.71(6)<br>178.89(5)<br>89.14(6)<br>99.40(6)<br>81.38(6) |
| **O**$_X$–Mn(1)–**N**$_x$ | 85.78(6)<br>92.42(6)<br>166.60(6)<br>96.69(6)<br>97.53(6)<br>168.09(6)<br>93.11(6)<br>87.41(6) |
| **N**$_X$–Mn(1)–**N**$_Y$ | 78.99(6) |
| **O**$_X$–Mn(2)–**O**$_Y$ | 92.09(5)<br>97.18(5)<br>91.67(5)<br>87.22(5)<br>162.64(5)<br>92.46(6)<br>175.27(6)<br>89.50(6)<br>97.93(5)<br>89.92(6)<br>175.11(6)<br>96.52(5)<br>87.82(6)<br>77.73(5)<br>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) |

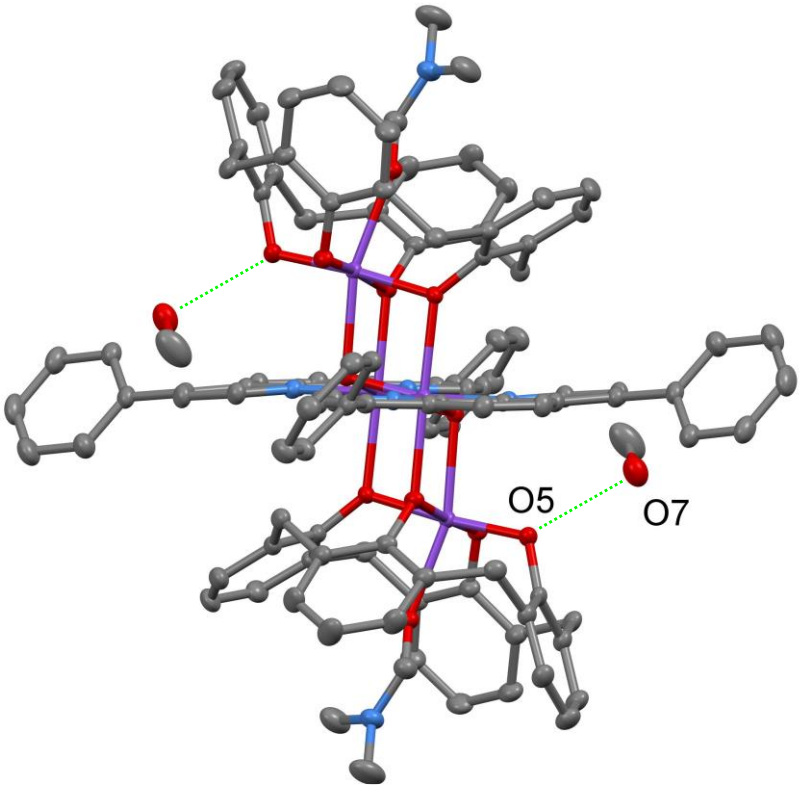


**Figure S1**. H-bonding between the solvate MeOH molecules with **$3_2$-$Mn_4$(bathophen)$_2$** cluster molecule within the crystal packing.

## References


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