**Supplementary Material**

Synthesis and characterization of a manganese(III) Schiff base complex and exploration of Br···Br interaction in the solid state structure of the complex

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**1. Experimental Section**

*1.1. Materials*

All starting materials and solvents were of reagent grade and used as purchased directly from commercial suppliers and were used without any further purification. The reactions and all manipulations of the samples were carried out under aerobic conditions.

***Caution!!!*** Although no problems were encountered in this work, metal complex containing organic ligand in the presence of perchlorate is potentially explosive. Only a small amount of the material should be prepared and it should be handled with care.

*1.2. Preparation of [MnL(CH3OH)(H2O)]ClO4*

A methanol solution (20 ml) of 2,2-dimethylpropane-1,3-diammine (0.12 mL, ~1 mmol) and 5-bromo-2-hydroxy-3-methoxybenzaldehyde (462 mg, ~2 mmol) was refluxed for *ca.* 1.5 h to prepare N2O2 donor tetradentate Schiff base ligand, H2L. A methanol solution (10 mL) of manganese(II) perchlorate hexahydrate (740 mg, ~2 mmol) was then directly added to the methanol solution of *H2L* and the resulting solution was refluxed further for 1 h. After that the resulting mixture was cooled to room temperature and immediately a small amount of side product was separated, which was subsequently filtered off. Dark brown single crystals of the complex, suitable for X-ray diffraction, were obtained after few days by slow evaporation of the solution in open atmosphere.

**Yield:** 525 mg (~72 %); based on manganese(III). Anal. Calc. for C22 H28Br2MnN2O10Cl (FW = 730.65): C, 36.17; H, 3.86; N, 3.83 %. Found: C, 36.3; H, 4.0; N, 3.7 %. FT-IR (KBr, cm-1): 1090 (υClO4); 1611, (υC=N); 2830-2970 (υC-H); 3420 (υO-H). UV-Vis, λmax (nm), [εmax (L mol-1 cm‑1)] (CH3CN), 240 (3.39 x 104), 294 (1.24 x 104), 410 (5.03 x 103), 540 (1.84 x 102). Magnetic moment = 4.98 μB.

*1.3. Physical measurements*

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin Elmer 240C elemental analyzer. IR spectrum in KBr (4500-500 cm-1) was recorded with a Perkin Elmer Spectrum Two spectrophotometer. Electronic spectrum in acetonitrile medium (800–200 nm) was recorded on a SHIMADZU UV-1700(E) Pharma Spec UV-Vis spectrophotometer. The magnetic susceptibility measurements were performed with a magnetic susceptibility balance made by Sherwood Scientific, Cambridge, UK at room temperature (300 K). The corrected magnetic susceptibility, χm, was calculated using the relation: χm = χmeas – χD. Diamagnetic susceptibilities, χD were calculated using Pascal’s constants [1]. Effective magnetic moments were calculated using the formula, μeff = 2.828(χm T)1/2, where χm was the corrected molar susceptibility. The instrument was calibrated using metallic nickel.

*1.4*. *X-ray crystallography*

Suitable single crystal of the complex was used for data collection using a ‘Bruker D8 QUEST area detector’ diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 273 K. The molecular structure was solved by direct method and refined by full-matrix least squares on *F2* using the SHELXL-2018/1 package [2]. Non hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms, attached to oxygen atom of methanol and water, were located by difference Fourier maps and were kept at fixed positions. Other hydrogen atoms were placed in their geometrically idealised positions and constrained to ride on the atoms to which they were attached. Multi-scan empirical absorption corrections were applied to the data using the program SADABS [3]. Crystallographic data and refinement details of the complex are given in Table S1. Selected bond lengths and of the complex are listed in Tables S2 (subunit A) and S4 (subunit B). Coordinate bond angles are listed in Tables S3 (subunit A) and S5 (subunit B).

Table S1. Crystal data and refinement details of the complex.

|  |  |
| --- | --- |
| Formula | C22 H27Br2MnN2O10Cl |
| Formula weight | 730.65 |
| Crystal system | Triclinic |
| Space group | *P* |
| a (Å) | 12.6199(10) |
| b (Å) | 14.1926(11) |
| c (Å) | 17.6694(14) |
| α (°) | 92.209(2) |
| β (°) | 92.686(2) |
| γ (°) | 115.688(2) |
| V (Å3) | 2842.7(4) |
| Z | 4 |
| *d*(calc) [g/cm3] | 1.707 |
| µ [mm-1] | 3.424 |
| F(000) | 1464 |
| Total reflections | 95687 |
| Unique reflections | 12479 |
| Observed data [I > 2 σ(I)] | 10292 |
| R(int) | 0.051 |
| R1, wR2 (all data) | 0.0606,0.1271 |
| R1, wR2 ([I > 2 σ(I)] | 0.0479,0.1188 |
| Residual electron density (eÅ-3) | 1.246, -0.965 |

Table S2. Selected bond lengths (Å) of the complex (subunit A).

|  |  |
| --- | --- |
| Mn(1)-O(3) | 2.230(2) |
| Mn(1)-O(4) | 2.312(3) |
| Mn(1)-N(1) | 1.996(3) |
| Mn(1)-N(2) | 2.015(3) |
| Mn(1)-O(1) | 1.882(3) |
| Mn(1)-O(2) | 1.889(2) |

Table S3. Selected bond angles (°) of the complex (subunit A).

|  |  |
| --- | --- |
| O(1)-Mn(1)-O(2) | 90.48(11) |
| O(1)-Mn(1)-O(3) | 91.35(10) |
| O(1)-Mn(1)-O(4) | 90.90(11) |
| O(1)-Mn(1)-N(1) | 90.46(13) |
| O(1)-Mn(1)-N(2) | 178.90(11) |
| O(2)-Mn(1)-O(3) | 92.42(10) |
| O(2)-Mn(1)-O(4) | 88.69(10) |
| O(2)-Mn(1)-N(1) | 175.64(11) |
| O(2)-Mn(1)-N(2) | 90.06(11) |
| O(3)-Mn(1)-O(4) | 177.49(10) |
| O(3)-Mn(1)-N(1) | 91.82(11) |
| O(3)-Mn(1)-N(2) | 87.67(10) |
| O(4)-Mn(1)-N(1) | 87.04(11) |
| O(4)-Mn(1)-N(2) | 90.07(11) |
| N(1)-Mn(1)-N(2) | 89.07(13) |

Table S4. Selected bond lengths (Å) of the complex (subunit B).

|  |  |
| --- | --- |
| Mn(2)-N(3) | 2.013(3) |
| Mn(2)-O(7) | 1.885(3) |
| Mn(2)-N(4) | 1.998(3) |
| Mn(2)-O(10) | 2.241(3) |
| Mn(2)-O(8) | 1.887(3) |
| Mn(2)-O(9) | 2.275(3) |

Table S5. Selected bond angles (°) of the complex (subunit B).

|  |  |
| --- | --- |
| O(7)-Mn(2)-N(3) | 90.65(13) |
| O(7)-Mn(2)-N(4) | 177.34(12) |
| O(8)-Mn(2)-O(9) | 89.51(12) |
| O(8)-Mn(2)-O(10) | 89.67(10) |
| O(8)-Mn(2)-N(3) | 174.22(11) |
| O(8)-Mn(2)-N(4) | 90.15(12) |
| O(9)-Mn(2)-O(10) | 176.78(12) |
| O(9)-Mn(2)-N(3) | 84.90(12) |
| O(9)-Mn(2)-N(4) | 91.06(12) |
| O(10)-Mn(2)-N(3) | 95.84(11) |
| O(10)-Mn(2)-N(4) | 85.83(10) |
| N(3)-Mn(2)-N(4) | 88.52(14) |
| O(7)-Mn(2)-O(8) | 90.92(11) |
| O(7)-Mn(2)-O(9) | 91.39(12) |
| O(7)-Mn(2)-O(10) | 91.74(11) |

Table S6. Hydrogen bond distances (Å) and angles (°) of the complex.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| D–H···A | D-H | H···A | D···A | ∠D-H···A |
| O(3)-H(3A)···O(1) a | 0.9000 | 2.3400 | 3.012(4) | 131.00 |
| O(3)-H(3A)···O(5) a | 0.9000 | 2.0200 | 2.840(4) | 152.00 |
| O(3)-H(3B)···O(2) a | 0.9500 | 2.1500 | 2.891(4) | 134.00 |
| O(3)-H(3B)···O(6) a | 0.9500 | 2.0600 | 2.917(3) | 149.00 |
| O(10)-H(10A)···O(7)b | 0.9000 | 2.3000 | 3.056(4) | 141.00 |
| O(10)-H(10A)···O(11)b | 0.9000 | 2.1000 | 2.898(4) | 146.00 |
| O(10)-H(10B)···O(8)b | 0.8000 | 2.2700 | 2.925(4) | 138.00 |
| O(10)-H(10B)···O(12)b | 0.8000 | 2.0800 | 2.804(4) | 149.00 |
| O(4)-H(4)···O(13) | 0.87(6) | 2.10(6) | 2.959(7) | 170(5) |
| O(9)-H(9)···O(19)c | 0.69(5) | 2.09(5) | 2.765(7) | 166(6) |

D = donor; H = hydrogen; A = acceptor.   
Symmetry transformation: a = -x,1-y,-z, b = 1-x, 2-y,1-z, c= 1-x,1-y,1-z.

*1.5.* *Theoretical Methods*

The geometries of the complex included in this study were computed at the M06-2X/def2-TZVP level of theory using the crystallographic coordinates. For all calculations we have used the GAUSSIAN-09 program [4]. We have also used the Grimme’s dispersion [5] correction as implemented in GAUSSIAN-09 program since it is adequate for the evaluation of noncovalent interactions where dispersion effects are relevant like σ-hole interactions. The basis set superposition error for the calculation of interaction energies has been corrected using the counterpoise method [6]. The NCI plot [7] isosurfaces have been used to characterize noncovalent interactions. They correspond to both favorable and unfavorable interactions, as differentiated by the sign of the second density Hessian eigen value and defined by the isosurface color. The color scheme is a red-yellow-green-blue scale with red for ρ+cut (repulsive) and blue for ρ−cut (attractive).

*1.6. Hirshfeld surface analysis*

Hirshfeld surfaces [8-10] and the associated two-dimensional (2D) fingerprint plots [11‑13] were calculated using Crystal Explorer, [14] with bond lengths to hydrogen atoms set to standard values [15]. The more details could be found in many of our previous papers [16-18].

*1.7. Studies on catalytic decomposition of hydrogen peroxide*

Volumetric measurement of evolved dioxygen during the catalase-like function measurement experiment was carried out following the literature method [19-21]. A 50 ml three-necked round-bottom flask containing 10-3 M 5 mL DMF solution of the complex was placed in a water bath at 25 °C. One of the necks was connected to a burette and the other two were stoppered by a rubber septum. While the solution was stirring, hydrogen peroxide (30% v/v) was injected into it through the rubber septum using a microsyringe. Volumes of evolved dioxygen were measured for fixed time intervals volumetrically.

**2. Results and discussion**

*1.1. Structure description of [MnL(CH3OH)(H2O)]ClO4* *(subunit B)*

A perspective view of the complex (subunit B) along with selective atom-numbering scheme is shown in Figure S1. Single crystal X-ray diffraction experiments reveals that subunit B of the complex consists of a distinct mononuclear unit *[MnL(CH3OH)(H2O)]* together with a non-coordinated perchlorate anion. Selected bond lengths and angles of subunit B are listed in Tables S4 and S5, respectively.

The manganese(III) center Mn(2) has a six-coordinate distorted octahedral geometry in which two imine nitrogen atoms [N(3) and N(4)] and two phenoxo oxygen atoms [O(7) and O(8)] of a deprotonated Schiff base ligand, *L2−*, constitute the equatorial plane. On the other hand, the axial positions are coordinated by a water oxygen atom, O(9) and a methanol oxygen atom, O(10), furnishing a distorted octahedral coordination sphere around itself. The deviations of the coordinating oxygen atoms, O(7), O(8) and nitrogen atoms N(3), N(4) in the basal plane from the mean plane passing through them are 0.064(3), –0.076(2), –0.072(3) and 0.062(3) Å respectively. The deviation of manganese atom Mn(2) from the same plane is 0.0212(5) Å. The saturated six-membered chelate ring, R(2) [Mn(2)–N(3)–C(31)–C(32)–C(35)–N(4)] resembles a twist boat conformation with puckering parameters Q = 0.772(4) Å, θ = 89.4(3)°, ϕ = 278.2(3)°.

subunit 2.tif

Figure S1. ORTEP presentation of subunit B of the complex (ellipsoids are drawn at the 50% probability level) with selected atom-numbering scheme. Hydrogen atoms have been omitted for clarity.

Two hydrogen atoms, H(10A) and H(10B), of a water molecule attached with Mn(2) in subunit 2 form bifurcated hydrogen bonds with the oxygen atoms of Schiff base ligand. Hydrogen atom, H(10A), forms symmetry (b = 1-x, 2-y,1-z) related hydrogen bonds with a phenoxy oxygen, O(7) and a methoxy oxygen, O(11). Similarly hydrogen atom, H(10B), form symmetry (b = 1-x, 2‑y, 1‑z) related hydrogen bonds with a phenoxy oxygen, O(8) and a methoxy oxygen, O(12). Hydrogen atom, H(9), attached with O(9) of a methanol forms symmetry (c = 1-x, 1-y,1-z) related hydrogen bond with the oxygen atom, O(19), of a perchlorate ion. The hydrogen bonding interactions are shown in Figure S2. Details of geometric features of hydrogen bonding interactions are given in Table S6.

sub b bonding.tif

Figure S2. Hydrogen bonding interactions in the complex (sub unit B). Only the relevant atoms have been shown for clarity.

*2.2. Hirshfeld surface analysis*

Hirshfeld surfaces of the complex, mapped over dnorm, shape index and curvedness, have been illustrated in Figure S3. The surfaces are shown as transparent to allow visualization of the molecular moiety around which they are calculated. The dominant interactions between O···H/H···O and Br···H/H···Br can be seen in the Hirshfeld surfaces as red spots on the *d*norm surface in Figure S3. Additional visible spots of light colour correspond to mainly C···H/H···C and H···H contacts have been also observed in the Hirshfeld surfaces signifying weaker and longer interaction. In addition, two dimensional fingerprint plots (Figure S4) represent the difference between the intermolecular interaction patterns and the relative contributions (in percentage) for the major intermolecular interactions associated with the complex. The intermolecular interactions appear as distinct spikes in two dimensional fingerprint plots (Figure S4). In the 2D fingerprint plots, complementary regions are also visible where one molecule acts as a donor (*d*e > *d*i) and the other as an acceptor (*d*e < *d*i).

**hirshfld2.tif**

Figure S3. Hirshfeld surfaces mapped with dnorm (left), shape index (middle) and curvedness (right) of the complex.

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Figure S4. Two dimensional fingerprint plots of the complex: Resolved into H···H (top left), H∙∙∙C/C∙∙∙H (top right), H∙∙∙O/O∙∙∙H (bottom left) and H∙∙∙Br/Br∙∙∙H (bottom right) contacts contributed to the total Hirshfeld Surface area of the complex.

*2.3. Spectral analysis of the complex*

The IR and electronic spectra of the complex are in well agreement with its crystal structure. The IR and electronic spectra of the complex are depicted in Figures S5 and S6, respectively. Infrared spectra provide enough information to identify the way of bonding of the ligands to the metal centres. In the IR spectrum of the complex, distinct band due to the azomethine (C=N) group at 1611 cm-1 is customarily noticed [22]. Strong absorption band at *ca.* 1090 cm-1 indicates the presence of non-coordinated perchlorate anion in the complex [23, 24]. Bands in the range of 2970–2830 cm-1 due to alkyl C–H bond stretching vibrations are typically noticed in IR spectra of the complex [25, 26]. Broad absorption bands centered at around 3420 cm-1 due to O–H stretching vibrations of the coordinated water molecule, are observed in IR spectra of all complexes [27-29].

Electronic spectrum of the complex consists of four major regions of absorptions. Intense absorption band in the high energy region of 240 and 294 nm may be assigned as intra-ligand n→π\* and π→π\* transitions, respectively involving the aromatic rings [30-32]. Strong and broad absorption band at 410 nm may be attributed to the ligand to metal charge transfer (LMCT) transitions from the phenolate oxygen pπ→dπ\* of metal orbital [30-32]. The complex shows an absorption shoulder at 540 nm for the manganese(III) based d-d transition [33, 34].

The formulation of the complex as manganese(III) complex is supported by the room temperature solid state magnetic moments close to ~4.98 μB. This value is suggestive of magnetically non-coupled high spin manganese(III) complexes (d4, S = 2) [30-32].

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Figure S5. Infrared spectrum of the complex.

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Figure S6. Electronic spectrum of the complex in acetonitrile medium.

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Figure S7. Turnover number {[Evolved O2]/[Catalyst]) vs time plot in the different initial amount of H2O2 in DMF medium at 25 °C.

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