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Two new manganese(III) complexes with salicylaldimine Schiff bases: Synthesis, structure, self-assembly and phenoxazinone synthase mimicking activity

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Abstract

Two new mononuclear manganese(III) complexes, $[Mn(L^1)_2]ClO_4$ (1) and $[Mn(L^2)(NCS)(H_2O)] \cdot DMSO$ (2), where $HL^1 = 3 \cdot (N, N-dimethylamino)$ propyliminomethyl-6ethoxyphenol, $H_2L^2 = N, N'$ -bis(3-ethoxysalicylidene) ethane-1,2-diamine have been prepared and characterized by elemental analysis, IR, UV–Vis spectroscopy and single crystal X-ray diffraction studies. Manganese(III) in each complex assumes distorted octahedral geometry. Supramolecular interactions in these complexes were explored. Both complexes show phenoxazinone synthase activity but presence of a solvent molecule in the coordination site of complex **2** makes it more efficient catalyst than complex **1**. Therefore these complexes may be used as functional models for copper(II) containing enzyme, phenoxazinone synthase.

Keywords: Manganese(III), Schiff base, X-Ray structure; Supramolecular interactions, Phenoxazinone synthase mimicking activity.

1. Introduction

Coordination chemistry of manganese with a diverse range of ligands has long been investigated as an area of considerable interest in inorganic biochemistry [1-4]. Manganese containing redox enzymes are omnipresent in nature and perform a number of vital functions [5-7]. A large number of Schiff base complexes of manganese(III) possess suitable biometric properties that can mimic the structural features of the active site in metalloenzymes, redox and non-redox proteins [8-9]. Many such complexes are also shown to have interesting catalytic [10-11] and magnetic properties [12-14]. There has been enhanced interest in the synthesis and characterization of such complexes for their biological importance [15-18], especially mimicking the oxygen-evolving compound (OEC) of photosystem II (PSII) [19-20]. They have also been reported for water oxidation to generate dioxygen [21-22] and have been used to artificially model PSII [23]. They have also been used to mimic several oxidase enzymes (which catalyze a kinetically unfavorable reaction of triplet molecular dioxygen to water in various biochemical pathways) [24-27]. It is very useful and promising area of research to develop more efficient, bio-inspired and environment friendly catalysts for in vitro oxidation reactions. One of such enzymes is phenoxazinone synthase, a multicopper oxidase enzyme, found naturally in the bacterium, Streptomyces antibioticus, which catalyzes the oxidative condensation of ortho aminophenol derivatives into phenoxazinone chromophore [28-30]. The latter is used clinically for the treatment of Wilm's tumor, gestational choriocarcinoma, and other tumors in which phenoxazinone chromophore is recognized to inhibit DNA-dependent RNA synthesis by intercalation to DNA [31-32].

Studies on the oxidation of o-aminophenol to phenoxazinone by molecular dioxygen in presence of some mono- and di-nuclear first row transition metal complexes as catalysts have

been reported by several groups [33-36]. The essential condition for a complex to have phenoxazinone synthase activity is the presence of labile sites on the metal centers. In the present work, we have prepared two manganese(III) Schiff base complexes with two different Schiff base ligands (one tridentate and one tetradentate). Both complexes have been characterized by spectral and elemental analysis. Single crystal X-ray diffraction analysis was used to confirm the structures of both complexes. Phenoxazinone synthase mimicking activities of both the complexes have been studied. The complex of the tetradentate Schiff base was found to be more active toward phenoxazinone synthase mimicking activity.

2. Experimental Section

All chemicals were of reagent grade and used as purchased from Sigma-Aldrich without further purification.

Caution??? Although no problems were encountered in this work, metal complexes containing organic ligands in the presence of perchlorates are potentially explosive. Only a small amount of the material should be prepared and it should be handled with care.

2.1. Preparations

2.1.1. Preparation of the ligand, 3-(N,N-dimethylamino)propyliminomethyl-6-ethoxyphenol (HL^{1})

The tridentate Schiff base ligand, HL^1 was prepared by refluxing 3-ethoxysalicylaldehyde (166 mg, 1 mmol) with N,N-dimethylpropane-1,3-diamine (0.13 ml, 1 mmol) in methanol (5 mL) for ca. 1 h. The solvent was evaporated under reduced pressure and the residue of the ligand was dissolved in acetonitrile. Solid ligand was obtained after 3 days and was used for the preparation of the complex **1**.

2.1. 2. Preparation of the ligand, N,N'-bis(3-ethoxysalicylidene)ethane-1,2-diamine (H_2L^2)

The tetradentate Schiff base ligand, H_2L^2 was prepared by refluxing 3ethoxysalicylaldehyde (332 mg, 2 mmol) and ethane-1,2-diamine (0.1 ml, 1 mmol) in methanol (5 mL) for ca. 1 h. The solid ligand was isolated and dissolved in acetonitrile. Crystals of the ligand were obtained one week which were used for the preparation of the complex **2**.

2.1.3. Preparation of $[Mn(L^1)_2]ClO_4(1)$

A methanol solution of HL^1 and the methanol solution (5 mL) of manganese(II) perchlorate hexahydrate (185 mg, 0.5 mmol) was added to the resulting mixture was refluxed for ca. 1 h to give a brown solution. It was cooled and kept for slow evaporation in open atmosphere. Single crystals suitable for X-ray diffraction were obtained after three days.

Yield: 118 mg (42%). Anal. Calc. for C₂₈H₄₂MnN₄O₈Cl (FW = 663.05): C, 60.75; H, 7.65; N, 10.12%. Found: C, 60.6; H, 7.5; N, 10.3%. ESI-MS (positive ion mode, CH₃CN) *m/z*: 553.47 (100%, $[Mn(L^{1})_{2}]^{+}$). IR (KBr, cm⁻¹): 1119 (v_{ClO4}), 1609 (v_{C=N}). UV-Vis, λ_{max} (nm) [ε_{max} (L mol⁻¹ cm⁻¹)] (DMSO): 500 (0.83×10²), 292 (1.9×10³), 270 (2.1×10³). Magnetic moment = 5.13 μ_{B} .

2.1.4. Preparation of $[Mn(L^2)(NCS)(H_2O)]$ ·DMSO (2)

A methanol solution (5 mL) of manganese(II) perchlorate hexahydrate (370 mg, 1 mmol) was added to the methanol solution of H_2L^2 (1 mmol) and the resulting mixture was refluxed for ca. 1 h to give a deep brown solution. A methanol solution (5 mL) of sodium thiocyanate (80 mg, 1 mmol) was added in it and refluxed further for 1 h. DMSO was added in the mixture as solvent. It was kept for slow evaporation in open atmosphere. Single crystals suitable for X-ray diffraction were obtained after one week.

Yield: 462 mg (82%). Anal. Calc. for $C_{23}H_{30}MnN_3O_6S_2$ (FW = 563.56): C, 49.02; H, 5.37; N, 7.46%. Found: C, 49.0; H, 5.2; N, 7.6%. ESI-MS (positive ion mode, CH₃CN) *m/z*:

467.11 (100%, [Na(2-aminophenoxazine-3-one)(H₂O)]⁺), 409.12 (100%, [Mn(L²)]⁺). IR (KBr, cm⁻¹):1619 (v_{C=N}), 2063 (v_{SCN}), 3437 (v_{OH}), UV-Vis, λ_{max} (nm) [ϵ_{max} (L mol⁻¹ cm⁻¹)] (DMSO): 412 (4.58×10²), 324 (1.17×10³), 268 (1.55×10³). Magnetic moment = 5.14 μ_B .

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a PerkinElmer 240C elemental analyzer. IR spectra in KBr (4500-500 cm⁻¹) were recorded with a PerkinElmer Spectrum Two spectrophotometer. Electronic spectra (800-200 nm) were recorded on a PerkinElmer Lambda 35 UV-visible spectrophotometer. The magnetic susceptibility measurement was done with an EG & PAR vibrating sample magnetometer (model 155) at room temperature and diamagnetic corrections were performed using Pascal's constants [37]. Powder X-ray diffraction was performed on a Bruker D8 instrument with Cu K_a radiation ($\lambda = 1.548$ Å) generated at 40 kV and 40 mA. The powder XRD spectrum was recorded in a 20 range of 5–50° using 1D Lynxeye detector at ambient conditions. Electro-spray ionization mass spectra were recorded with Waters QTOF Micro YA263.

2.3. X-ray crystallography

Suitable single crystals of both complexes were used for data collection using a 'Bruker SMART APEX II' diffractometer equipped with graphite-monochromated Mo K_{α} radiation (λ = 0.71073 Å) at 150 K. The molecular structures were solved by direct method and refined by fullmatrix least squares on F^2 using the SHELX-97 package [38-39]. Non hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached with oxygen atom of coordinated water molecule of complex **2** 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 [40]. Crystallographic data and refinement details of complexes are given in Table 1. Selected bond lengths and bond angles are listed in Tables 2 and 3 respectively.

2.4. Hirshfeld surface Analysis

Molecular Hirshfeld surfaces [41-43] and the associated 2D-fingerprint [44-46] plots were calculated using Crystal Explorer [47] which accepted a structure input file in CIF format. Bond lengths to hydrogen atoms were set to standard values. For each point on the Hirshfeld isosurface, two distances d_e , the distance from the point to the nearest nucleus external to the surface and d_i , the distance to the nearest nucleus internal to the surface, were defined. The normalized contact distance (d_{norm}) based on d_e and d_i was given by

$$\mathbf{d_{norm}} = \frac{(\mathbf{d_i} - \mathbf{r_i^{vdw}})}{\mathbf{r_i^{vwd}}} + \frac{(\mathbf{d_e} - \mathbf{r_e^{vdw}})}{\mathbf{r_e^{vwd}}}$$

Where r_i^{vdw} and r_e^{vdw} were the van der Waals radii of the atoms. The value of d_{norm} was negative or positive depending on intermolecular contacts, being shorter or longer than the van der Waals separations. The parameter d_{norm} displayed a surface with a red-white-blue colour scheme, where bright red spots highlighted shorter contacts, white areas represented contacts around the van der Waals separation, and blue regions were devoid of close contacts. For a given crystal structure and set of spherical atomic electron densities, the Hirshfeld surface was unique [48] and it was this property that suggested the possibility of gaining additional insight into the intermolecular interaction of molecular crystals. The 2D-fingerprint plot provides decomposition of Hirshfeld surfaces into contribution of different intermolecular interactions present in crystal structure. 2Dfingerprint plots of each Hirshfeld surface are shown as plots of d_i against d_e.

2.6. Catalytic oxidation of 2-aminophenol

 10^{-5} M solutions of the complexes in acetonitrile were treated with a 10^{-3} M solution of oaminophenol under aerobic conditions at 25° C. The reaction was followed spectrophotometrically by monitoring the increase in the absorbance maxima at ~433 nm. 10^{-5} M solutions of the complexes were mixed with at least 10 equivalents of substrate to maintain pseudo-first order conditions to determine the dependence of rate on the substrate concentration and various kinetic parameters. The rate of a reaction was derived from the initial rate method.



Scheme 1: Synthesis of complexes 1 and 2.

3. Results and discussion

3.1. Synthesis

Two Schiff base ligands HL^1 and H_2L^2 , were synthesized by condensation of 3ethoxysalicylaldehyde with N,N-dimethylpropane-1,3-diamine and ethane-1,2-diamine, respectively, following the literature method [49-50]. The IR and UV-Vis data of both ligands

are reported in literature [50-51]. The Schiff base ligand, HL^1 , was made to react with manganese(II) perchlorate hexahydrate in methanol to prepare the mononuclear manganese(III) complex, $[Mn(L^1)_2]ClO_4(1)$. Complex 2 ($[Mn(L^2)(NCS)(H_2O)] \cdot DMSO$), on the other hand, was synthesized by reacting H_2L^2 with the methanol solution of manganese(II) perchlorate hexahydrate in presence of pseudohalide thiocyanate. The formation of complexes 1 and 2 is shown in Scheme 1. In these two complexes manganese(II) get oxidized by the oxygen in the atmosphere to manganese(III) under the reaction conditions.

It is interesting to note here that the ligand H_2L^2 was used by a different group to prepare a very similar manganese(III) complex, $[Mn(L^2)(SCN)(H_2O)].[Mn(L^2)(H_2O)_2]ClO_4 \cdot CH_3CN$ [51]. The method of preparation of this complex is different from that of complex 2. Many other manganese(III) complexes, similar to complex 2, were also reported by various groups [52-53].

3.2. Structure descriptions

3.2.1. $[Mn(L^{1})_{2}]ClO_{4}(1)$

Complex 1 crystallizes in the triclinic space group $P\overline{1}$. The X-ray structure determination reveals that in complex 1 there are two independent subunits (A and B). A perspective view of subunit A along with the selective atom numbering scheme is shown in Figure 1a. The perspective view and description of the structure of subunit B with selective atom numbering scheme is given in the Supplementary information.

The molecular structure of subunit A consists of a discrete mononuclear unit $[Mn(L^1)_2]ClO_4$. Manganese(III) center is in a six-coordinate octahedral environment, being bonded to two amine nitrogen atoms, N(1) and N(1)', two imine nitrogen atoms, N(2) and N(2)' and two phenoxo oxygen atoms, O(2) and O(2)' (Symmetry transformation: '= -x,-1-y,2-z), from two deprotonated Schiff base ligands $(L^1)^-$, which occupy facial positions (fac isomer). The six

membered ring, [Mn(1)–N(1)–C(17)–C(18)–C(19)–N(2)], has an intermediate conformation between chair and half chair, with puckering parameters q = 0.753(4) Å, $\theta = 163.6(4)^{\circ}$, $\phi = 166.5(12)^{\circ}$ [54-55]. The N(1)–Mn(1)–N(2) angle is 80.17(12)°. The Mn(1)–N_{imine} distance {2.026(3) Å} is shorter than the Mn(1)–N_{amine} distance {2.420(3) Å}.

The hydrogen atom, H(15b), attached with C(15), is involved in C–H··· π interaction with a symmetry related (1-x,-1-y,2-z) phenyl ring [C(21)-C(22)-C(23)-C(24)-C(25)-C(28)] to form a supramolecular chain (Figures 1b and 1c). Details of geometric features of C–H··· π interactions are given in Table 4.

3.2.2. $[Mn(L^2)(NCS)(H_2O)] \cdot DMSO(2)$

Complex **2** crystallizes in the triclinic space group $P\overline{1}$. The asymmetric unit consists of mononuclear [Mn(L²)(NCS)(H₂O)] unit and a solvent DMSO molecule. A perspective view of the complex with the selective atom numbering scheme is shown in Figure 2. Manganese(III) is coordinated by two imine nitrogen atoms, N(1) and N(2), and two phenolate oxygen atoms, O(1) and O(2), of the deprotonated tetradentate Schiff base ligand (L²)². Oxygen atom, O(3), of water molecule and nitrogen atom, N(3), of thiocyanate coordinate manganese(III) centre to complete a distorted octahedral geometry. The saturated five membered ring, [Mn(1)=N(1)=C(10)=C(11)=N(2)], twisted on C(10) and C(11) with puckering parameters q = 0.353(8) Å, $\varphi = 263.0(8)^{\circ}$ [54-55]. Coordinated water ligands of two symmetry related (ⁱ = 2x,2-y,1-z) mononuclear manganese(III) species, are connected through intermolecular hydrogen bonding interactions. The hydrogen atom, H(3A), attached with oxygen atoms, O(1)ⁱ and O(4)ⁱ. Similarly hydrogen atom, H(3B), attached with oxygen atom, O(3), form bifurcated hydrogen bonds with symmetry related (2-x,2-y,1-z) oxygen atoms, O(2)ⁱ and O(5)ⁱ. Similar type of

hydrogen bonding is shown by hydrogen atoms $H(3A)^i$ and $H(3B)^i$. Due to hydrogen bonding a well isolated supramolecular dimer has been created (Figure 2). Details of hydrogen bonding are given in Table 5.

The hydrogen atom, H(23A), attached with C(23), is involved in C–H··· π interaction with a symmetry related (2-x,2-y,2-z) phenyl ring [C(13)-C(14)-C(15)-C(16)-C(17)-C(18)] to form a supramolecular dimer as shown in Figure 3a. Details of geometric features of C–H··· π interactions are given in Table 4.

The $\pi \cdots \pi$ stacking interaction occurs between the phenyl ring [C(3)-C(4)-C(5)-C(6)-C(7)-C(8)] and the symmetry related (2-x,2-y,1-z) phenyl ring [C(13)-C(14)-C(15)-C(16)-C(17)-C(18)] of neighbor molecule (Figure 3b). Details of geometric features of $\pi \cdots \pi$ stacking interactions are given in Table 6.

3.3. IR, electronic spectra and magnetic property

In the IR spectra of both complexes, distinct bands due to the azomethine (C=N) group within 1608–1619 cm⁻¹ region are customarily noticed [56]. Strong band at 1119 cm⁻¹ of **1** indicates the presence of perchlorate ion [57]. Complex **2** shows a strong and sharp band at 2063 cm⁻¹ due to presence of nitrogen bonded thiocyanate group [58].

The electronic absorption spectra of two complexes were recorded in DMSO. Absorption bands at 268-270 nm region are assigned to ligand to metal charge transfer (LMCT) bands from the phenolate oxygen $p_{\pi} \rightarrow d_{\pi^*}$ of metal orbital. Bands at 292-324 nm region is due to $n \rightarrow \pi^*$ transitions of (C=N). Appearance of absorption bands within the ranges of 412-501 nm is due to spin allowed d–d transition band. [59-61].

The room temperature magnetic susceptibility measurements show that both complexes have magnetic moments close to 5.1 μ_B . This value is expected for discrete, high-spin (S = 2), magnetically non-coupled manganese(III) complexes having four unpaired electrons [62-63].

3.4. Powder X-ray diffraction

The experimental PXRD patterns of the bulk products are in good agreement with the simulated XRD patterns from single crystal X-ray diffraction results, indicating consistency of the bulk samples (Figures S2a and S2b). The simulated patterns of the complexes were calculated from the single crystal structural data (Cif files) using the CCDC Mercury software.

3.5. Hirshfeld Surface analysis

The Hirshfeld surface analysis is a powerful method for gaining information about different intermolecular interactions, and to identify and quantify these interactions. Hirshfeld surfaces of two complexes, mapped over a 3D d_{norm} (range of -0.1 to 1.5 Å), shape index and curvedness, are illustrated in Figure 4. The surfaces are shown as transparent to allow visualization of the molecular moiety around which they are calculated. The intermolecular interactions listed in Table 4 are summarized effectively in the spots with the large circular depressions (deep red) visible on the d_{norm} surfaces indicative of hydrogen bonding contacts and other weak contacts. There are several bright red areas on d_{norm} of both complexes related to C–H… π interactions. 2D fingerprint plots of Hirshfeld surface for complexes and relative contributions of different interactions overlapping in the full fingerprint plots are shown in Figures 5 and 6, respectively. Complementary regions are visible in the fingerprint plots where one molecule acts as donor (d_e< d_i) and the other as an acceptor (d_e> d_i). The fingerprint plots can be decomposed to highlight particular atoms pair close contacts. For both complexes, the H…H interactions have the highest contribution (67.3% in 1 and 47.9% in 2) of the total

Hirshfeld surface. Despite the high share of this interaction, its role in the stabilization of structure is quite small in magnitude because this interaction is between the same species [64]. C···H/H···C close contacts, attributed to C-H··· π interactions, comprise 12.5% and 15.5% of the total surface for each molecule in **1** and **2**, respectively. The high proportion of C···H/H···C interactions and its appearing as bright red spots on d_{norm} surface of both complexes is indicating the importance of this interaction in structures of **1** and **2**. The proportion of O···H/H···O interactions comprise 25.5% and 17.6% of the Hirshfeld surfaces for complexes **1** and **2** respectively. Similarly the proportion of N···H/H···N interactions comprise 3.4% for complex **2**. The figure of 2D fingerprint plot of N···H/H···N interactions is given in Supplementary information (Figure S3). Complex **1** does not show any proportion of N···H/H···N interactions.

3.6. Phenoxazinone synthase like activity

To check the ability of the complexes to oxidize o-aminophenol to 2-aminophenoxazine-3-one (Phenoxazinone synthase mimicking activity), 10^{-3} M acetonitrile solution of oaminophenol were mixed separately with 10^{-5} M solution of each complex, and the spectra were recorded for 2 h and 5 min at room temperature. It was found that both complexes are showing phenoxazinone synthase mimicking activity. The time dependent spectral profiles of **1** and **2** are shown in Figures 7 and 8. The gradual increase of peak (characteristic of the phenoxazinone absorption) intensity at ~433 nm implies the catalytic conversation of o-aminophenol to 2aminophenoxazine-3-one in aerobic conditions. A blank experiment without catalyst under identical conditions does not show significant growth of the band at ~433 nm.

To understand the extent of the catalytic efficiency, 10^{-5} M solutions of the complexes were treated with substrate (o-aminophenol) under pseudo-first order conditions. Time scan at the λ_{max} of 2-aminophenoxazine-3-one was carried out for a period of 125 min. The initial rate

was determined from the slope of the absorbance versus time plot. Rate saturation kinetics of both complexes is clearly indicated by initial rate of the reaction versus concentration of the substrate plot. This observation indicates that an intermediate complex substrate adduct is formed at a pre-equilibrium stage and that the irreversible substrate oxidation is the rate determining step of the catalytic cycle. This type of saturation rate dependency on the concentration of the substrate may be treated with the Michaelis-Menten model. This may also, upon linearization, give a double reciprocal Lineweaver-Burk plot which is used to analyze different parameters, viz. V_{max} (Maximum reaction velocity), K_M (Michaelis constant), and K_{cat} (Turnover number). The initial rate versus substrate concentration plot and Lineweaver-Burk plot for complexes 1 and 2 are shown in Figures 9 and 10, respectively. All kinetic parameters of both complexes are given in Table 7.

3.7. ESI-MS study

The electrospray ionization mass spectra (ESI-MS positive) are useful to know the nature of possible complex-substrate adduct. The ESI-MS positive spectra of both complexes are recorded in acetonitrile solution and the results are shown in Figures S4 and S5.

In the mass spectrum of **1**, the peak at m/z = 553.47 may be assigned to $[Mn(L^1)_2]^+$. Complex **2** exhibits peak at m/z = 409.12 corresponding to the presence of monopositive $[Mn(L^2)]^+$. In the mass spectra of complex **2** with o-aminophenol, peak at m/z = 467.11 may be assigned as $[Na(2-aminophenoxazine-3-one)_2(H_2O)]^+$ and indicates the formation of phenoxazinone from 2-aminophenol. The mass spectrum of the mixture of complex **2** with o-aminophenol is shows in Figure 11. Based on the above results a probable mechanism for oxidation of O-aminophenol has been proposed (Scheme 2).



Scheme 2: Probable mechanistic pathway for the formation of phenoxazinone.

4. Conclusion

Two new octahedral manganese(III) complexes with a Schiff base ligand have been prepared and characterized. X-ray crystal structure determination confirmed the structures of the complexes. In complex **1** Schiff base act as a tridentate ligand and form bis complex, whereas, in complex **2**, the dianionic tetradentate Schiff base and pseudohalide ligand occupy five coordinating sites and the remaining site is coordinated by water molecule. Both complexes are found to show phenoxazinone synthase mimicking activity but complex **2** is found to be more active. During the course of catalytic cycle, o-aminophenol has to coordinate the manganese(III) center by replacing any one coordinated ligand. Since water is a neutral molecule (and not at all bulky), it could be easily replaced by o-aminophenol and makes complex **2** more efficient catalyst than **1**.

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Appendix A. Supplementary data

CCDC 1461265 and 1461266 contain the supplementary crystallographic data for complexes **1** and **2** respectively. These data can be obtained free of charge via <u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>

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	1	2
Formula	$C_{28}H_{42}MnN_4O_4ClO_4$	C ₂₃ H ₃₀ MnN ₃ O ₆ S ₂
Formula Weight	653.05	563.56
Temperature (K)	150	150
Crystal System	Triclinic	Triclinic
Space group	$P\overline{1}$	ΡĪ
<i>a</i> (Å)	8.7492(6)	11.1318(7)
<i>b</i> (Å)	10.4830(7)	11.9760(4)
<i>c</i> (Å)	19.3978(13)	11.9946(4)
α (°)	75.538(4)	114.502(1)
β (°)	89.356(4)	107.042(2)
γ (°)	69.253(4)	95.745(2)
$V(Å^3)$	1605.2(2)	1345.26(1)
Z	2	2
d_{cal} (g cm ⁻³)	1.351	1.391
μ (mm ⁻¹)	0.546	0.687
F(000)	688	588
Total reflection	22534	20178
Unique Reflections	6199	5025
Observed data[I>2σ(I)]	4481	4258
R(int)	0.035	0.027
R1, wR2 (all data)	0.0825, 0.1808	0.0841, 0.2428
R1, wR2 [I>2 <i>o</i> (I)]	0.0594, 0.1648	0.0753, 0.2301

Table 1: Crystal d	lata and refinement	details of complexes 1	and 2
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	1	2
Mn(1)-O(1)	_	1.880(4)
Mn(1)-O(2)	1.862(2)	1.881(4)
Mn(1)-O(3)	_	2.336(3)
Mn(1)-O(4)	_	
Mn(1)-N(1)	2.420(3)	1.978(5)
Mn(1)-N(2)	2.026(3)	1.975(5)
Mn(1)-N(3)	- 2	2.246(4)

Table 2: Selected bond lengths (Å) around manganese (III) for complexes 1 (subunit A) and 2

	1	2
O(1)-Mn(1)-O(2)	_	93.76(16)
O(1)-Mn(1)-O(3)	_	90.66(14)
O(1)-Mn(1)-N(1)	_	91.77(18)
O(1)-Mn(1)-N(2)	_	172.56(17)
O(1)-Mn(1)-N(3)	_	96.52(16)
O(2)-Mn(1)-O(3)	_	90.04(14)
O(2)-Mn(1)-N(1)	90.96(12)	172.91(19)
$O(2)-Mn(1)-N(1)^{a}$	89.05(12)	-
O(2)-Mn(1)-N(2)	89.15(12)	91.83(18)
$O(2)-Mn(1)-N(2)^{a}$	90.86(12)	_
O(2)-Mn(1)-N(3)		92.58(16)
O(3)-Mn(1)-N(1)		85.46(16)
O(3)-Mn(1)-N(2)	-	84.43(16)
O(3)-Mn(1)-N(3)	_	172.18(16)
N(1)-Mn(1)-N(2)	80.17(12)	82.3(2)
$N(1)-Mn(1)-N(2)^{a}$	99.83(12)	_
N(1)-Mn(1)-N(3)	_	91.20(18)
N(2)-Mn(1)-N(3)	_	88.12(18)

Table 3: Selected bond angles ($^{\circ}$) for complexes 1 (subunit A) and 2

Symmetry transformations: a = -x, -1-y, 2-z of subunit A of **1**.

Table 4: Geometric features (distances in Å and angles in °) of the C–H··· π interactions obtained for complexes **1** and **2**.

	X–H···Cg (Ring)	H···Cg (Å)	X–H···Cg (°)	X…Cg (Å)
1	$C(15)-H(15b)-Cg(5)^{c}$	2.83	162	3.753(5)
2	$C(23)-H(23A)\cdots Cg(5)^d$	2.89	143	3.697(12)
0				

Symmetry transformations: ^c = 1-x,-1-y,2-z; ^d = 2-x,2-y,2-z

Cg(5) = Centre of gravity of the ring [C(21)-C(22)-C(23)-C(24)-C(25)-C(28)] for 1 and Cg(5) = Centre of gravity of the ring [C(13)-C(14)-C(15)-C(16)-C(17)-C(18)] for 2.

Table 5: Hydrogen bond dista	nces (Å) and angle	s () for 2 .
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C

D–H…A	D-H	H···A	D····A	∠D-H…A
O(3)-H(3A)···O(1) ^e	0.85	2.34	2.34	131
$O(3)-H(3A)-O(4)^{e}$	0.85	2.21	2.24	160
$O(3)-H(3B)-O(2)^{e}$	0.84	2.21	2.21	141
O(3)-H(3B)····O(5) ^e	0.84	2.31	2.31	149

Symmetry transformation: e = 2-x, 2-y, 2-z D = donor; H = hydrogen; A = acceptor.

Table 6: Geometric features (distances in Å and angles in °) of the $\pi \cdots \pi$ stacking interactions obtained for **2**.

$Cg(Ring I) \cdots Cg(Ring J)$	Cg···Cg(Å)	α (°)	$Cg(I) \cdots Perp(Å)$	Cg(J)…Perp (Å)
$Cg(4)\cdots Cg(5)^{f}$	3.653(3)	2.2(3)	-3.369(2)	-3.388(2)
Symmetry transformation: ^f =	= 2-x,2-y,1-z.			

 α = Dihedral angle between ring I and ring J. Cg(I)…Perp = Perpendicular distance of Cg(I) on ring J. Cg(J)…Perp = Perpendicular distance of Cg(J) on ring I. Cg(4) = Centre of gravity of the ring [C(3)-C(4)-C(5)-C(6)-C(7)-C(8)] and Cg(5) = Centre of gravity of the ring [C(13)-C(14)-C(15)-C(16)-C(17)-C(18)] for **2**.

Complex	V_{\max} (M min ⁻¹)	$K_{\rm M}({ m M})$	$K_{\rm cat}$ (h ⁻¹)
1	1.064 x10 ⁻⁵	2.2 x 10 ⁻³	60
2	5.135 x 10 ⁻⁵	6.8x 10 ⁻³	308.13
PCC			

Table 7: Kinetic parameters of Phenoxazinone synthase like activity at 25°C in CH₃CN.



Figure 1: (a) Perspective view of **1** with selective atom numbering scheme. Symmetry transformation ^a=-x,-1-y,2-z. (b) Highlighted C-H… π interactions and (c) 1D array of **1** via C-H… π interactions. Selected atoms have been omitted for clarity.



Figure 2: Perspective view of **2** with the supramolecular dimeric structure which generated through intermolecular hydrogen bonding interactions. Symmetry transformation $^{i} = 2-x, 2-y, 2-z$. Only the relevant atoms are labeled. Ethyl groups attached to oxygen atoms have been omitted for clarity.

ACCE



Figure 3: Supramolecular dimer in **2**, (**a**) generated through C–H··· π interactions and (**b**) generated through π ··· π interactions. Selected atoms have been omitted for clarity.

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Figure 4: Hirshfeld surfaces mapped with d_{norm} (top), shape index (middle) and curvedness (bottom). d_{norm} displayed a surface with a red-white-blue colour scheme, where bright red spots highlighted shorter contacts, white areas represented contacts around the van der Waals separation, and blue regions were devoid of close contacts.





Figure 6: Relative contributions to the Hirshfeld surface area for the various intermolecular contacts in two complexes.



Figure 7: The spectral profile showing the growth of 2-aminophenoxazine-3-one at ~433 nm upon addition of 10^{-3} M o-aminophenol to a solution containing complex **1** (10^{-5} M) in CH₃CN.



Figure 8: The spectral profile showing the growth of 2-aminophenoxazine-3-one at ~433 nm upon addition of 10^{-3} M o-aminophenol to a solution containing complex **2** (10^{-5} M) in CH₃CN.



Figure 9: Plot of Initial rate vs. substrate concentration plot for the oxidation of o-aminophenol catalyzed by **1** in CH₃CN. Inset shows the Lineweaver–Burk plot.



Figure 10: Plot of Initial rate vs. substrate concentration plot for the oxidation of o-aminophenol catalyzed by **2** in CH₃CN. Inset shows the Lineweaver–Burk plot.



Figure 11: Electrospray ionization mass spectrum (ESI-MS positive) of a 1:50 mixture of Complex **2** and o-aminophenol in acetonitrile solution recorded after 5 min of mixing.

Rock

Two new manganese(III) complexes with salicylaldimine Schiff bases: Synthesis, structure, self-assembly and phenoxazinone synthase mimicking activity Nandita Sarkar, Mithun Das, Shouvik Chattopadhyay*

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Tow new mononuclear manganese(III) complexes with a Schiff base ligand have been synthesized and characterized. Both complexes show Phenoxazinone synthase mimicking activity.

Two new manganese(III) complexes with salicylaldimine Schiff bases: Synthesis, structure, self-assembly and phenoxazinone synthase mimicking activity

Nandita Sarkar, Mithun Das, Shouvik Chattopadhyay*

Research Highlights

- Synthesis and characterisation of two new manganese(III) Schiff base complexes
- Molecular structures on the basis of X-ray crystallography
- Supramolecular interactions

• Phenoxazinone synthase mimicking activity.