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The catalytic activities and magnetic behaviours of a μ_3 -chlorido TO1567A and a $\mu_{1,1,1}$ -azido bridged rare defective dicubane tetranuclear Mn(II) complexes

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Abstract

Reaction of Mn(II) salt with flexidentate Mannich base ligand, N,N'-dimethyl-N,N'-bis(2hydroxy-3-methoxy-5-methylbenzyl)ethylenediamine (H₂L) in presence of chloride or azide ions yielded two new tetranuclear complexes, $[Mn_4L_2(\mu_3-Cl)_2Cl_2]$ (1) and $[Mn_4L_2(\mu_{1,1}-L_2)]$ $N_3_2(N_3_2)$ (2). Single crystal X-ray structural analyses reveal that these two discrete tetranuclear Mn(II) complexes possess defective dicubane cores with two μ_3 -Cl (for 1) or two $\mu_{1,1,1}$ -N₃ bridges (for 2). One of the triply bridging groups is situated above and the other one below the plane of the four Mn(II) ions. In both complexes, all Mn(II) ions are in hexacoordinated distorted octahedral environment. Both complexes 1 and 2 exhibit catecholase like activity and phenoxazinone synthase-like activity under ambient condition. The turn over numbers (k_{cat}) for the aerobic oxidation of 3,5-di-tert-butylcatechol are 1492.4, 1431.2 h^{-1} and those of *o*-aminophenol are 2265.5, 2132.2 h^{-1} for complexes 1-2, respectively. Mass spectral analyses have been performed to get an idea about the probable mechanistic pathway for these catalytic reactions. Variable temperature magnetic susceptibility measurements of solid sample reveal that both the complexes are antiferromagnetically coupled. The coupling constants are calculated to be $J_1 = -0.19 \text{ cm}^{-1}$, $J_2 = -6.87 \text{ cm}^{-1}$ and $J_3 = -0.70 \text{ cm}^{-1}$ for 1 and $J_1 = 0.11$ cm⁻¹, $J_2 = -0.64$ cm⁻¹ and $J_3 = 0.11$ cm⁻¹ for **2** and these values are rationalized by DFT calculations.

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Introduction

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Multinuclear metal complexes are of continual interest of the chemists because their connectivity, structural variations, porosity and functionality make them promising materials for applications in the field of magnetism, gas storage and separation, sensors, drug delivery, and catalysis.¹⁻⁵ A common strategy for the synthesis of such multinuclear complexes is the self-assembly of the metal ions by suitable organic ligands and bridging anions. The structure and nuclearity of these types of complexes depend upon various factors such as charge, HSAB behavior, coordination number and geometry of metal ion, and denticity, flexibility, shape and size of ligands.⁶ The flexidentate Mannich base, N,N'-dimethyl-N,N'-bis(2hydroxy-3-methoxy-5methylbenzyl)ethylenediamine (H₂L) is an excellent polynucleating ligand and has been used to synthesize quite a few discrete homo- and heterometallic complexes of several metal ions.^{3c,7-8} The nuclearity of the complexes is found to be dependent on the metal ions. For example, complexes of Zn(II) and M(II)-Ln(III) [M = Ni, Zn, Co and Ln = Tb, Dy, Gd] are dinuclear, those of Cu(II) are trinuclear where as the complexes of Cd(II), Ni(II) and Co(II) are tetranuclear. To the best of our knowledge, with this flexidentate ligand, no complex of manganese in any of its oxidation states is reported till date.

Manganese is an important element for human health, metabolism, the antioxidant system and essential for photosynthetic oxygen evolution in photosystem II.⁹ In recent times, several groups are engaged in the specific design and synthesis of coordination complexes of manganese, mostly for their catalytic activities and versatile magnetic properties.¹⁰⁻¹¹ The NO donor ligands have been employed widely for the synthesis of such complexes. It has been observed that very often, during reaction, especially with N,O donor Schiff base ligands, the Mn(II) ion undergoes aerial oxidation to form complexes of single valence Mn(III), or Mn(IV) or mixed valence Mn(II/III) or Mn(III/IV). In recent years, these complexes have made a remarkable impact in the study of magnetic properties of polynucler metal complexes because of their spin-canted properties, slow relaxation of magnetization and SMM like behaviours.¹²⁻¹³ Moreover, it is well known that the complexes of manganese in its various oxidation states can act as efficient catalysts for bio-mimicking oxidase (e.g. catecholase, phenoxazinone synthase) and oxygenase (e.g. epoxidation) reactions. ¹⁴⁻¹⁵

In this paper, we report the synthesis, crystal structures, magnetic properties and catalytic oxidase activities of two tretranuclear Mn(II) complexes $[Mn_4L_2(\mu_3-Cl)_2Cl_2]$ (1) and $[Mn_4L_2(\mu_{1,1,1}-N_3)_2(N_3)_2]$ (2) derived from the Mannich base ligand, N,N'-dimethyl-N,N'-

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bis(2-hydroxy-3-methoxy-5-methylbenzyl)ethylenediamine (H₂L). Single crystal_{10.1} Single

Experimental

Starting materials

2-methoxy-4-methylphenol, *N*,*N*'-dimethylethylenediamine and formaldehyde were purchased from Sigma, India and were of reagent grade. They were used without further purification. The other reagents and solvents were of commercially available reagent quality, unless otherwise stated.

Caution! Azide salts of metal complexes derived from organic ligands are potentially explosive. Only a little amount of material should be synthesized and it should be handled with care.

Synthesis of ligand H₂L The Mannich base ligand H₂L was synthesized by following reported method.^{3c,7b,8b} 20 mmol of *N*,*N'*-dimethylethylenediamine (2.2 mL) was stirred with 40 mmol of formaldehyde (1.2 mL) in 40 mL methanol for 30 min. Then, 40 mmol of 2-methoxy-4-methylphenol (5 mL) was added to it and the resulting solution was refluxed for about 5 h. On cooling the resulting solution, white solid separated out. The solid product was filtered and washed with methanol.

Yield 4.972g (64%). Anal. Calc. for $C_{22}H_{32}N_2O_4$ (388.5), Calculated C, 68.01; H, 8.30; N, 7.21; Found C, 68.18; H, 8.12; N, 7.34. IR: $v(O-H) = 3437 \text{ cm}^{-1}$, $v(C-O) = 1240 \text{ cm}^{-1}$. UV/vis: $\lambda max = 284 \text{ nm}$. ESI-MS (positive ion mode) calc. m/z 389.32, found 389.3 (100%, $[H_2L+H]^+$) (Fig. S1, ESI). ¹H NMR (300 MHz, DMSO-d6, ppm): δ 6.63 (s, 2H), δ 6.49 (s, 2H), δ 3.69 (s, 6H), δ 3.53 (s, 6H), δ 2.53 (s, 4H), δ 2.14 (s, 6H), δ 2.12 (s, 6H) (Fig. S2, ESI). **Synthesis of the complex, [Mn₄L₂(\mu_3-Cl)₂Cl₂] (1): 20 mL of methanolic solution containing ligand H₂L (1 mmol, 0.398 g) and MnCl₂·4H₂O (2 mmol, 0.396 g) was stirred at room**

temperature for 2 h. Then the reaction mixture was filtered and kept overnight. After 1_{33}^{View} Aricle Online days, crystalline compound of 1 was appeared then it was separated, washed with methanol and dried in a desiccator containing anhydrous CaCl₂. A portion of the compound was then dissolved in dichloromethane and layered with hexane. Finally, after a few days, needle-shaped crystals suitable for diffraction were formed.

Yield 0.369 g (65%). Anal. Calc. for $C_{44}H_{60}Cl_4Mn_4N_4O_8$ (1134.53). Calculated C, 46.58; H, 5.33; N, 4.94; Found C, 46.47; H, 5.41; N, 4.75. IR: $v(C-H) = 2862 \text{ cm}^{-1}$, $v(C-O/Phenolate) = 1251 \text{ cm}^{-1}$, $v(C-N) = 1157 \text{ cm}^{-1}$ (Fig. S3, ESI). UV/vis: $\lambda max = 353 \text{ nm}$. ESI-MS (positive ion mode) Calc. m/z 441.17, found 441.18 [Mn(L)], Calc. m/z 473.18, found 473.19 [Mn(L)CH₃OH]⁺ (Fig. S4, ESI).

Synthesis of the complex, $[Mn_4L_2(\mu_{1,1,1}-N_3)_2(N_3)_2]$ (2): Methanolic solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (2 mmol, 0.722 g) was added to 20 mL methanol solution of ligand H_2L (1 mmol, 0.398 g) in a beaker. Then the resulting solution was stirred for 1 h at room temperature. After that, a 1:1 methanol/water (v/v) solution of sodium azide (2 mmol, 0.130 g) was added drop wise to the reaction mixture. Crystalline compound of 2 was separated from filtrate on standing overnight. Diffraction quality single crystal was grown by direct diffusion of hexane into dichloromethane solution of the compound 2.

Yield 0.406 g (70%). Anal. Calc. for $C_{44}H_{60}Mn_4N_{16}O_8$ (1160.80), Calculated C, 45.53; H, 5.21; N, 19.31; Found C, 45.38; H, 5.09; N, 19.46. IR: $v(C-H) = 2859 \text{ cm}^{-1}$, $v(N_3^-) = 2079 \text{ cm}^{-1}$, $v(C-O/Phenolate) = 1261 \text{ cm}^{-1}$, $v(C-N) = 1158 \text{ cm}^{-1}$ (Fig. S5, ESI). UV/vis: $\lambda max = 354 \text{ nm}$. ESI-MS (positive ion mode) Calc. m/z 441.17, found 441.18 [Mn(L)], Calc. m/z 473.18, found 473.19 [Mn(L)CH_3OH]⁺ (Fig. S6, ESI).

Physical Measurements

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 2400 series II CHN analyzer. The FTIR spectra of the complexes were recorded using KBr pellets at ambient temperatures in the range 4000–400 cm⁻¹ on a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra in methanol solvent (650–200nm) were recorded in a Hitachi U-3501 spectrophotometer. The electrospray ionization mass spectrometry (ESI-MS positive) was collected with Xevo G2-S QTof (Waters) mass spectrometer, equipped with a Z-spray interface spectrometer. Temperature-dependent molar magnetic susceptibility of the Mn^{II}_4 complexes **1** and **2** were measured by superconducting quantum interference device vibrating

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sample magnetometer (SQUID-VSM, Quantum Design) with an applied magnetic field wappele Online 500 Oe throughout the temperature range 2–300 K for powdered samples. The susceptibility data were corrected by Pascal's diamagnetic contributions following the literature.¹⁶ Isothermal magnetizations measurements were performed at 2 K up to 5 Tesla for both the complexes.

Crystallographic data collection and refinement

Appropriate single crystals of complexes (1-2) were mounted on glass fibres without any protection. Intensity data were collected on a Bruker-AXS SMART APEX II CCD diffractometer equipped with a monochromatized Mo-K α ($\lambda = 0.71073$ Å) radiation source using the $\omega/2\theta$ scan technique at 298K. The crystals were placed at 60 mm from the CCD. Frames were measured with a counting time of 10 s. No decay from single crystal was observed during the data collection. The structures were solved with the SHELXS 2016/6,^{17a} SHELXL 2016/6,^{17b-c} PLATON 99¹⁸ structure solution program and the disorder treatment of two nitrogen atoms (N7 and N8) was carried out by using Olex2¹⁹ (for **2**). Non-hydrogen atoms were modelled anisotropically. The hydrogen atoms were calculated and isotropically fixed in the final refinement. Absorption corrections were carried out using the SADABS program.²⁰ In addition, the structures also contain solvent-accessible voids, which were smoothened using Olex2.¹⁹ Data collection, structure refinement parameters and crystallographic data for the complexes are given in Table 1.

 Table 1. Summary of X-ray crystallographic data for complexes 1-2.

Parameters	1	2
Composition	C ₄₄ H ₆₀ Cl ₄ Mn ₄ N ₄ O ₈	C ₄₄ H ₆₀ Mn ₄ N ₁₆ O8
Formula wt.	1134.52	1160.84
Crystal System	monoclinic	trigonal
Space group	$P2_1/n$	R3
a/Å	14.134(5)	32.5215(12)
b/Å	10.725(4)	32.5215(12)
c/Å	18.983(7)	14.0934(6)
a/deg	90	90
β/deg	100.235(7)	90
γ/deg	90	120
V/Å ³	2831.8(18)	12908.9(13)

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$ ho_{ m calc}/ m g~ m cm^{-3}$	1.331	1.344		
Temp/K	298	298		
λ (Mo K _a)/Å	0.71073	0.71073		
Z	2	9		
$F(000), \mu \text{ mm}^{-1}$	1168.0, 1.107	5400.0, 0.920		
$2\theta_{\rm max}/[^{\rm o}]$	50.486	52.78		
TotalReflectionsCollected, Unique	57421, 5085	40474, 5743		
$R1(F_0)$, GOF on F^2	0.1012, 1.04	0.0466, 1.04		
No. of parameters	289	340		
Largest diff. peak, Deepest hole, eÅ ⁻³	1.165, -0.757	0.845, -0.343		

 ${}^{a}\mathbf{R}_{1} = \sum ||\mathbf{F}_{o}| - |\mathbf{F}_{c}|| / \sum |\mathbf{F}_{o}|, \ {}^{b}w\mathbf{R}_{2}(\mathbf{F}_{o}^{2}) = [\sum [w(\mathbf{F}_{o}^{2} - \mathbf{F}_{c}^{2})^{2} / \sum w \mathbf{F}_{o}^{4}]^{\frac{1}{2}}$

Computational Methodology

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The theoretical calculations based on broken symmetry DFT²¹ have been used to determine the coupling constants (*J*) of these complexes as proposed by Ruiz et al.²² Two different schemes for estimation of coupling constants have been employed viz. doped cluster approach (DCA) and the minimal cluster approach (MCA) and the detailed discussions about these methodological approaches will be found elsewhere.²³ All the coordinates of atoms were obtained from experimental X-ray structures and implemented in calculations without further optimization. The hybrid B3LYP functional²⁴ and widely employed Ahlrichs type triple zeta with polarization function def2-tzvp basis set^{25a} has been considered in all calculations as implemented in the ORCA package (version 3.0.3).^{25b} We have also incorporated zeroth-order regular approximation (ZORA) to describe scalar relativistic effects.^{26a} To speed up the calculations without hampering the desired accuracy, RIJCOSX approximation with auxiliary def2-TZVP/J coulomb fitting basis set^{26b} and tight SCF convergence criteria (Grid 4) have also been incorporated.

Catalytic Oxidation of 3,5-DTBC and o-aminophenol

To study the catecholase-like and phenoxazinone synthase-like activities of two complexes as a suitable catalyst towards the oxidation of 3,5-DTBC (3,5-di-tert-butylcatechol) and OAP (*o*-aminophenol), DCM/methanol solution of each complex was treated with 100 equiv. of 3,5-DTBC or OAP under aerobic conditions at room temperature. The reactions were followed spectrophotometrically by monitoring the increase in the absorbance maxima of the quinone band at 402 nm or phenoxazinone at 433 nm (time scan). To detect the formation of

hydrogen peroxide during the catalytic reaction, we followed the iodometric method of the catalytic reported earlier.^{5b}

Results and discussion

Syntheses

The Mannich base ligand (H₂L) was synthesised by the condensation of *N*,*N*² dimethylethylenediamine with formaldehyde and 2-methoxy-4-methylphenol in 1: 2: 2 molar ratios in methanol under reflux as described in the literature.^{3c,7b,8b} The ligand was characterized by IR, UV, Mass, NMR spectroscopy and used for the synthesis of two Mn(II) complexes. Crystalline compound of complex **1** was produced by the reaction of H₂L with MnCl₂·4H₂O in a 1:2 molar ratio in methanol solvent at ambient atmosphere whereas complex **2** was yielded from the reaction mixture of H₂L, Mn(ClO₄)₂·6H₂O and NaN₃ in 1:2:2 molar ratios under the same condition (Scheme 1). Single crystals of both complexes were grown by diffusion of hexane into dichloromethane solution of the compound. In both the complexes, two octadentate di-negative ligands (L²⁻) are coordinated to four Mn(II) ions along with two triply bridging chloride (in **1**) or azide (in **2**) ions forming the tetranuclear structures. All Mn(II) metal ions are hexa-coordinated in the complexes of NO donor Schiff base ligands, the Mn(II) ions do not undergo aerial oxidation to produce Mn(III) during synthesis.



Scheme 1. Syntheses of complexes 1-2.

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Infrared (IR) and UV–Vis spectroscopy

Complexes were characterized by the FT-IR spectroscopy. The important infrared bands are given in the experimental section. In the spectra of both complexes, a moderate band at 1256 cm⁻¹ indicates the presence of phenolic C–O bond.^{8b} The spectrum of complex **2** shows a strong and sharp peak at 2079 cm⁻¹ for the stretching vibrations of N_3^- ion.^{7b}

The electronic spectra of the complexes were recorded in methanol. The complexes (1 and 2) show two sharp absorption maxima at 353 nm and 354 nm respectively, attributed to ligand-to-metal charge transfer transitions.^{12b}

Description of crystal structures (1-2)

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Single crystal X-ray diffraction studies reveal that complex 1 crystallizes in monoclinic space group $P2_1/n$ whereas complex 2 crystallizes in trigonal space group $R\overline{3}$. Although there is symmetry difference in crystallographic cell settings, the molecular geometries of two complexes are very similar containing four Mn(II) ions arranged in a manner to form a centrosymmetric defective dicubane tetranuclear structure. ORTEP representations of the two complexes are shown in Figs. 1 and 2, respectively. Selected bond lengths and bond angles for the structures are given in Table S1, ESI. The asymmetric units of the complexes contain two Mn(II) ions, one deprotonated Mannich base ligand, and two chloride ions (one in μ_3 -Cl bridging and the other in terminal coordination mode in 1) or two azide ions (one $\mu_{1,1,1}$ bridging and one terminally coordinated azide ion in 2). In both structures, all four Mn(II) ions exit in distorted octahedral geometry. The equatorial plane around Mn1 is formed by O1, N2 and O3 atoms from the deprotonated Mannich base ligand L²⁻ and Cl1^a atom from the μ_3 bridging chlorido for 1 or N4 from $\mu_{1,1,1}$ bridging azido for 2. The axial positions are occupied by N1 from the ligand L2- and Cl1 from another bridging chlorido group for 1, or N4^a from another $\mu_{1,1,1}$ bridging azido group for 2. The other manganese atom Mn2 in the asymmetric unit is also hexa-coordinated by four oxygen atoms [O1^a, O2^a, O3 and O4] from two deprotonated Mannich base ligands and two Cl atoms [Cl1^a and Cl2] (for 1) or two N atoms [N3 and N4] from two azide groups (for 2). In both structures, the four coplanar Mn(II) ions occupy the four corners of a defective double cubane core. One of the two triply bridging groups (chloride and azide for 1 and 2, respectively) is situated above and the other below the plane of the four Mn(II) ions at the distances of 1.608(3) Å (for 1) and 1.190(3) Å (for 2). In both structures, the *cis* angles vary in the range 80.07(3)° to 102.19(1)° around 70.02(1)° to 111.70(2)° around Mn2. The distance between Mn1...Mn1^a are Mn1 and

3.552(2) Å, 3.504(7) Å and Mn1...Mn2 are 3.519(2) Å, 3.418(1) Å, for complexes 1.atig/c2bto1567A respectively. Among the bond distances, the Mn–O distances with the phenoxido groups are the shortest and the Mn–Cl distances are the longest.



Fig. 1. ORTEP view of complex 1 with 30% ellipsoid probability.

It is worthy to mention that quite a few homo- and heterometallic multinuclear complexes of this Mannich base ligand are known.⁷⁻⁸Among the homometallic complexes, five are trinuclear Cu(II), three are dinuclear Zn(II), three are tetranuclear Cd(II) and four are Ni(II) complexes (two di- one tri- and one tetranuclear). In addition, seven heterometallic M(II)-Ln(III) (M = Co, Ni, Zn, and Ln = Tb, Dy, Gd] dinuclear complexes are reported. ⁷⁻⁸ There are also one tetranuclear and one hexanuclear Ni(II)-Na(I) complexes. The tetranuclear complexes are formed when the coordination number of metal ion is six or more and the metal:deprotonated ligand (L²⁻) ratio is 2:1. All these tetranuclear complexes of the two complexes are thus very similar to those of the reported tetranuclear complexes of this ligand. However, an interesting difference in the oxidation state of manganese is to be noted compared to the complexes of a very similar Schiff base ligand (condensation ligand of *o*-vanillin and ethylenediamine). The complexes of this Schiff base ligand with only manganese are mononuclear or dinuclear but when another metal ion is present,

heterometallic complexes of higher nuclearity are formed. It is to be noted that in all interface online complexes, Mn is in +3 oxidation state in contrast to the +2 state in the present complexes. Moreover, none of these reported complexes of this Schiff base ligand possesses tetranuclear structure.



Fig. 2. ORTEP view of complex **2** with 30% ellipsoid probability. (only one of the positions of the azide is shown).

A CSD search for triply chlorido bridged and triply azido bridged tetranuclear manganese complex containing any kind of N,O donor ligand reveals that there is no such triply chlorido bridged manganese complex like complex **1** but there are few triply azido bridged structures, nuclearity of which spans from four to eight. Among them, twenty complexes are tetranuclear and formed with N-donor ligands. But there is no example of both phenoxido and triply azido bridged manganese complex. So we can conclude that complex **2** is the first triply azido bridged tetranuclear defective dicubane structure with any kind of N,O donor ligands.

Catecholase Activity Study and Kinetics

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The catecholase activity of complexes **1** and **2** was determined using the substrate 3,5-di-tertbutylcatechol (3,5-DTBC) and was monitored spectrophotometrically by following the increase in absorbance of 3,5-di-tert-butylquinone (3,5-DTBQ) around 402 nm as reported earlier.^{5b,27-28} The catalytic reactivity study was performed in DCM/methanol solution

because of the low solubility of the complexes in methanol. Both the complexes statice Online Significant catalytic activity on the oxidation of 3,5-di-tert-butylcatechol. The oxidation reaction of 3,5-di-*tert*-butylcatechol to its corresponding *o*-quinone (3,5-DTBQ) is shown in Scheme 2.



Scheme 2. Catalytic Oxidation of 3,5-DTBC to 3,5-DTBQ in DCM/methanol.

For this purpose, 10×10^{-5} M DCM/methanol solution of each complex was treated with 100 eqv. methanolic solution of 3,5-DTBC under aerobic condition at room temperature. After addition of the substrate into the solution of manganese complex, the progress of the reaction was followed by recording the UV–Vis spectra of the mixture at 5 min time interval. The gradual increase of an absorption band around 402 nm in all cases indicates that these two complexes catalyze the aerobic oxidation of 3,5-DTBC to 3,5-DTBQ. The variation in absorption spectral behaviour of complex **2** during wavelength scan in the presence of 3,5-DTBC is depicted in Fig. 3. Similar plot for **1** is shown in Fig. S7, ESI.



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The kinetics for the oxidation of 3,5-DTBC to 3,5-DTBQ by complexes **1** and **2** were studied by the method of initial rates by monitoring the growth of the quinone band at 402 nm as a function of time. The rate constant for a particular complex substrate mixture was established from the $\log[A_{\alpha}/(A_{\alpha}-A_{t})]$ vs time plot. In all cases, a first-order kinetic dependence was noticed at low concentrations of 3,5-DTBC, whereas saturation kinetics was found at higher substrate concentrations. The observed reaction rates vs substrate concentration data were analyzed on the basis of the Michaelis–Menten approach of enzymatic kinetics to obtain the Lineweaver–Burk (double reciprocal) plot as well as the values of kinetic parameters K_M, V_{max} and k_{cat} . Both the curves of the observed rate vs [substrate] and the Lineweaver–Burk plot for complex **2** are shown in Fig 4. Similar plot for **1** is given in the Supporting Information (Fig. S8, ESI). The kinetic parameters for two complexes are listed in Table S2, ESI. The k_{cat} values are 1492.4 and 1431.2 h⁻¹ for complexes **1** and **2** respectively. The k_{cat} values obtained for complexes **1** and **2** are compared with other reported manganese complexes in Table S3, ESI.

Thus, these two tetranuclear Mn(II) complexes can be considered as a functional model of catecholase-like activity. Till date, catecholase-like activity of no tetranuclear Mn(II) complex have been studied. However, the k_{cat} values of these complexes are higher compared to those of reported manganese(II) complexes of other nuclearities but are less than most of the manganese complexes where the oxidation state of Mn is +III, +IV or mixed II/III.^{12d,14c,15a,29-32}



Fig. 4. Plot of the rate *vs* substrate concentration for complex **2**. Inset Shows Viet Agicle Online corresponding Lineweaver –Burk plot.

ESI-Mass Spectrometry Study

To get information about the complex-substrate intermediates and to show the probable mechanism for catecholase-like activity of complexes, we have recorded ESI-MS spectra of complexes 1 and 2 and a 1:10 mixture (v/v) solution of the complexes and 3,5-DTBCH₂ in DCM/methanol solution within 15 min of mixing. In the spectra of both the solutions, base peak is noticed at m/z = 441.18 (calcd. 441.17) which can be assigned to mononuclear species. In addition, another low intensity peak is observed at m/z 473.19 (calcd 473.18) for the species, $[MnL(CH_3OH)+H]^+$. After the addition of 3,5-DTBCH₂ into the solution of complexes 1 and 2, a drastic change is observed in the overall mass spectra. We focus here only on the spectrum of complex 2-substrate mixture to illustrate the probable mechanism (Figs. S9–S12, ESI). It shows a prominent peak at m/z 243.14 (calcd 243.13), which indicate the presence of species $[3,5-DTBQ+Na]^+$, the oxidized product of 3,5-DTBCH₂. The appearance of three new peaks at m/z 663.32 (calcd 663.31), 715.38 (calcd 715.37) and 716.36) assignable to $[(Mn^{III}L)(3,5-DTBCH)+H]^+,$ $[(Mn^{III}L)(3,5-$ 716.38 (calcd DTBSQ·)O₂+Na]⁺ and [(Mn^{III}L)(3,5-DTBSQ·)(OOH)+Na]⁺ species, respectively. These peaks are extremely significant from the mechanistic point of view as they clearly point out the formation of complex-substrate intermediates. Along with these, two other peaks are found at m/z = 701.27 (calcd.701.17) and m/z 460.27 (calc. 460.26) which can be assigned to the species [(Mn^{III}L)(3,5-DTBSQ)(H₂O)+Na]⁺ and [(Mn^{III}L)(H₂O)+H]⁺ respectively. We have also checked that no H₂O₂ is formed during this catalytic reaction.

Mechanistic insight

On the basis of ESI-Mass Spectrometry, we propose a probable mechanistic pathway for the oxidation of 3,5-*di-tert*-butylcatechol (substrate) using newly synthesized complex (**2**) as a catalyst (Scheme 3). We assume that our complexes catalyse the oxidation of 3,5-DTBCH₂ through a process as proposed earlier.^{5a} The tetranuclear complex $[Mn_4L_2(\mu_{1,1,1}-N_3)_2(N_3)_2]$ (**2**) dissociates in DCM/methanol solution to generate a catalytically active mononuclear species $[(Mn^{II}L)(CH_3OH)]$ (**A**). After the addition of 3,5-DTBCH₂ to the complex solution, it is deprotonated and coordinated to **A** *via* phenolic oxygen by replacing methanol solvent and hence intermediate $[(Mn^{III}L)(3,5-DTBCH)]$ (**B**) is generated. Then, the other hydroxyl group



Scheme 3. Proposed mechanism for the catalytic oxidation of 3,5-DTBC to 3,5-DTBQ by Complex 2

of 3,5-DTBC gets deprotonated and coordinates to manganese centre to produce **C**, $[(Mn^{III}L)(3,5-DTBC)]$. The species **C** is converted into its semiquinonate radical (**D**), $[(Mn^{III}L)(3,5-DTBSQ)O_2]$ with the reduction of Mn(III) to Mn(II). An oxygen molecule is then bonded with species (**D**) to result in the intermediate **E**, $[(Mn^{III}L)(3,5-DTBSQ)O_2]$. The species **E** takes up a proton to form **F** which on releasing a water molecule transforms into **G**. Finally, the Mn(III) in species **G** is reduced to Mn(II) regenerate the catalytically active

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species **H** with concomitant production of 3,5-DTBQ. oxygen is reduced to $H_2 O_{10.1039/C9DT01567A}$ product.

The X-ray crystal structure reveals that in both complexes all the Mn(II) ions exit in octahedral geometry and bridged with triply azido/chlorido groups. In solution, the mononuclear species is released (at least partly) with the coordinated solvent molecule to which 3,5-DTBC coordinate to form catalyst-substrate intermediate. Between complexes 1 and 2, the catecholase like activity of complex 1 is slightly higher than 2, presumably due to the fact that the catalytically active mononuclear complex is released more readily on breakage of μ_3 chlorido bridge than the corresponding azido bridge. It is also to be noted here that similar tetranuclear Co(II) complexes of this ligand do not show any catecholase like activity demonstrating that the complexes are better catalyst than the corresponding Co(II) complexes. To the best of our knowledge, the catecholase like activity of tetranuclear Mn(II) complex have yet not been studied as well as probable mechanistic pathway have not been established using mass spectral analysis.

Phenoxazinone synthase like activity

The phenoxazinone synthase-like activity for complexes **1** and **2** was performed by the catalytic oxidation of *o*-aminophenol (OAP) to aminophenoxazinone (APX) as reported previously.^{5b,27,32b} The oxidative dimerization reaction of OAP to APX is shown in Scheme 4. Before going to the details of kinetic investigation, the effectiveness of the complexes as suitable catalysts for the oxidation of *o*-aminophenol (substrate) in DCM/methanol under ambient condition was examined.



Scheme 4. Catalytic Oxidation of *o*-Aminophenol (OAP) to Phenoxazinone (APX) in DCM/methanol.

For this purpose, 5×10^{-5} M DCM/methanol solutions of each of the complexes **1** and **2** were treated with 100 equ. of OAP, and the growth of the UV–Vis absorption band of the phenoxazinone chromophore at 433 nm as a function of time was recorded, which indicates the catalytic oxidation of *o*-aminophenol to the corresponding aminophenoxazinone. A blank experiment without catalyst under similar condition was also performed where no significant

growth of the band around 433 nm was observed. In the presence of $substrate_{S9}^{Ver}A_{DT01567A}^{Article Online}$ aminophenol), the change in spectral behaviour of complex 2 is depicted in Fig. 5 and similar plot for 1 is shown in Fig. S13, ESI.



Fig. 5. Increase of the APX band at 433 nm after the addition OAP to a methanol solution with complex 2 (5 $\times 10^{-5}$ M). The spectra were recorded at 5 min intervals.

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Kinetic experiments were performed to estimate the extent of the catalytic activity of the complexes. The rate constant for the reaction was evaluated from the following relation $\log[A_{\alpha}/(A_{\alpha}-A_t)]$ vs time plot. In the reaction mixture of catalyst and substrate, a first-order kinetics was noticed at low concentrations of substrate (OAP), whereas saturation kinetics was observed at higher substrate concentrations. On the basis of the Michaelis–Menten approach of enzymatic kinetics, the observed reaction rates vs substrate concentrations data were analyzed to get the Lineweaver–Burk plot (double reciprocal) as well as the values of kinetic parameters K_M , V_{max} and k_{cat} . Both the curves of the observed rate vs [substrate] and the Lineweaver–Burk plot for complex **2** are given in Fig. 6. Similar plot for **1** is shown in the Supporting Information (Figs. S14, ESI). The kinetic parameters for two complexes are listed in Table S4, ESI. The k_{cat} values are 2265.5 and 2132.2 h⁻¹ for complexes **1-2** respectively. The k_{cat} values obtained for complexes **1** and **2** are compared with other reported manganese complexes in Table S5, ESI.

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Fig. 6. Plot of the rate vs substrate concentration for complex 2. Inset shows the corresponding Lineweaver–Burk plot.

Therefore, these tetranuclear Mn(II) complexes can also be considered as functional model for phenoxazinone synthase like activity. As can be found in Table S5, ESI, the k_{cat} values for complexes **1** and **2** are significantly higher than most of those reported for Mn(II), Mn(II), Mn(IV) or Mn(II/III) complexes.^{14b,29a,29c,32b,33} Therefore the complexes are not only the first examples of tetranuclear Mn(II) complexes exhibiting this phenoxazinone synthase like activity but the k_{cat} values of the complexes are one of the highest among the reported manganese complexes.

ESI-Mass Spectrometric Study

In order to establish the mechanistic pathway of phenoxazinone synthase-like activity and catalyst-substrate intermediate during the dimerization reaction of OAP, we have recorded ESI-MS spectra of two complexes and a 1:10 mixture (v/v) of the complex and OAP within 10 min of mixing in DCM/methanol solution.



Scheme 5. Proposed mechanism for catalytic oxidation of OAP by complex 2.

Here, we have focused only on the spectrum of complex **2**-substrate mixture. In the spectra of mixture of complex **2** and OAP, the base peak is found at m/z = 441.18 (calcd. 441.17) for the mononuclear species. In addition, two peaks are noticed at m/z 473.19 (calcd 473.18) and m/z 550.63 (calc. 550.64) which can be assigned to the species [MnL(CH₃OH)+H]⁺ and [MnL(OAP)+H]⁺, respectively. Along with these, another two low intensity peaks are observed at m/z = 603.13 (calcd 603.12) and 588.16 (calcd 588.15) which indicate the presence of the two complex-substrate intermediates [MnL(OAP)(O₂)+Na]⁺ and [MnL(OAP)(OH)+Na]⁺ respectively. There is also another important peak at m/z 589.16

(calcd 589.15) assignable to the presence of sodiated species $[MnL(OAP)(H_2O)+N_2]^{+VieWeitle Online}$ have also checked that H_2O_2 is not produced during this catalytic conversion.

Mechanistic insight

On the basis of ESI-Mass Spectrometry, here we propose a probable mechanistic pathway for the oxidation of o-aminophenol (Scheme 5). We presume that our Mn(II) complexes catalyse o-aminophenol oxidation through a process as proposed by Simándi et al.³⁴ In DCM/Methanol solution, the tetranuclear complex $[Mn_4L_2(\mu_{1,1}-N_3)_2(N_3)_2]$ (2) dissociates to mononuclear species, which is solvated with methanol to produce species (A), [MnL(CH₃OH)]. After addition of *o*-aminophenol to the complex-solution, OAP coordinates to species A via N atom of its amine group by replacing a methanol solvent and thus intermediate [Mn^{II}L(OAP)] (B) is generated. An O₂ molecule is then coordinated to species (**B**) to result the species $[(Mn^{III}L(OAP)(O_2)](C)]$. The intermediate species (**D**) is produced by exchanging proton of OAP with coordinated oxygen giving OAP free radical intermediate and further the peroxo linkage is dissociated to produce hydroxyl species (E) [(Mn^{III}L(OAP)(OH)]. Finally, [(Mn^{II}L(OAP)(OH₂)] (F) is produced by abstracting one proton from the solution. The active catalyst (A) in a catalytic cycle is reformulated with the release of OAP[•] and H₂O from the species (F). OAP[•] is oxidized to 2-benzoquinone monoimine (BQMI). The intermediate (BQMI) undergoes oxidative coupling with another OAP molecule to give final product phenoxazinone (APX) and oxygen is reduced to water as by-product. During this whole conversation 1.5O₂ is reduced and 3H₂O is produced as a byproduct.

Magnetic Properties

The recorded magnetic susceptibility data for the complexes **1** and **2** in the temperature range 300K to 2K are presented in Figs. 7 and 8 as the plot of $\chi_M T$ vs *T*. The $\chi_M T$ values at the room temperature region are 15.45 cm³ mol⁻¹ K and 17.14 cm³ mol⁻¹ K for the complexes **1** and **2**, respectively. These values are close to the expected value of 17.50 cm³ mol⁻¹ K considering four uncoupled Mn(II) species (g = 2.00, S = 5/2).

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Fig. 7. Plot of χT vs T for complex 1 in the temperature range of 2-300 K; the red line indicates fitting according to equation 1 in the text. The isothermal magnetization measurement at 2 K are shown in inset of the figure.

For both complexes, $\chi_M T$ values decrease on lowering the temperature suggesting a net antiferromagnetic coupling between the Mn(II) ions. The field variation isothermal magnetization measurements at 2 K are shown in inset of Figures 7 and 8. The molar magnetization values at 5T are much lower compared with the value for ideal non-interacting Mn(II) ions. This behaviour also suggests for the predominated antiferromagnetic interaction between Mn(II) centres in both the complexes.

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Fig. 8 Plot of χT vs T for complex 2 in the temperature range of 2-300 K; the red line indicates fitting according to equation 1 in the text. The isothermal magnetization measurement at 2 K are shown in inset of the figure.

Scheme 6 shows the possible exchange pathways between the metal centres in complexies Article Online and 2. The presence of centre of inversion as found in the crystal structure of the complexes implies that three possible exchange pathways are to be considered. The possible coupling parameters are J_1 ($J_{Mn1Mn3} = J_{Mn2Mn4} = J_1$), J_2 ($J_{Mn2Mn3} = J_2$) and J_3 ($J_{Mn1Mn2} = J_{Mn3Mn4} = J_3$). The HDVV Hamiltonian for these exchange schemes is represented as,

$$\mathbf{H} = -2J_1 \left[S_1 S_3 + S_2 S_4 \right] - 2J_2 S_2 S_3 - 2J_3 \left[S_1 S_2 + S_3 S_4 \right]$$
(1)

where $S_1 = S_2 = S_3 = S_4 = 5/2$.



Scheme 6. Schematic diagram of coupling scheme for complexes **1** and **2**. Corresponding Mn^{II}- Mn^{II} separation are given separately from crystallographic data.

The program PHI³⁵ was employed to fit the experimental data (300–2 K) by diagonalization of the Hamiltonian. To avoid over-parametrization, the *g* factor was fixed to 2.00 and Simplex fitting algorithm was used. An initial guess value was necessary to obtain the best fit and to obtain good initial guess values, a survey (survey keyword in PHI program) of data were done. The results from the DFT calculations (*vide infra*) were used as guide where (DFT value \pm 10) range for coupling constants were set for the survey.³⁶ A set of coupling constants which gives minimum residual value (see PHI user manual for details) were taken as an initial guess for the curve fitting. The corresponding values of J_1 , J_2 and J_3 are presented in Table 2.

Compound Method	J_1	(cm ⁻¹)	$J_2 ({\rm cm}^{-1})$	J_{3} (cm ⁻¹)			
obtained from DFT Calculations (see Scheme 6 for the J scheme)							
Table 2. List of Magnetic Coupling Constant from the Fits of $\chi_M T$ vs T Plots for 1 and 2 and those							

Compound	Method	J_1 (cm ⁻¹)	$J_2 ({ m cm}^{-1})$	J_{3} (cm ⁻¹)
1	Experimental	- 0.19	- 6.87	- 0.70

	Doped Cluster Ap	proach -	0.62	- 10.62	DOI: 19.1039/C9DT01567A
	(DCA)				
	The minimal	cluster -	0.55	- 8.90	- 1.13
	approach				
	(MCA)				
2	Experimental	0	0.11	-0.64	0.11
	Doped Cluster Ap	proach 0	0.31	- 0.33	0.28
	(DCA)				
	The minimal	cluster 0	0.31	- 0.24	0.28
	approach				
	(MCA)				

Theoretical Calculations.

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In order to further investigate the values of coupling constants, broken symmetry DFT formalism was employed. Calculations for multinuclear cluster having more than two coupled magnetic centres are not so straight forward as the dimeric compounds.²² Several methodologies have been proposed to estimate the coupling constants of multinuclear clusters. However, systematic comparisons of different approaches are rare.^{23a} In the present study, two different theoretical approaches *viz*. the 'Doped Cluster Approach' (DCA) and the Minimal Cluster Approach (MCA) were used to obtain the theoretical *J* values.

Doped cluster approach is a simplified technique for determination of coupling constants of polynuclear magnetic centres. In this methodology, BS calculations are performed on model clusters in which all the magnetic centres except two have been substituted with diamagnetic ions. In our present case, two of the four Mn^{II} centres were replaced by $Zn^{II} \{Mn_2Zn_2\}$ and the spin on one of the two remaining Mn ions were flipped, and broken symmetry SCF converged accordingly.

According to approximate spin projection technique proposed by Yamaguchi and coworkers,³⁷ the magnetic coupling constant (J) between a pair of metallic centres can be estimated from the relation,

$$\frac{\mathrm{E}_{\mathrm{HS}} - \mathrm{E}_{\mathrm{BS}}}{\langle \mathrm{S}_{\mathrm{HS}}^2 \rangle - \langle \mathrm{S}_{\mathrm{BS}}^2 \rangle} = -J \tag{2}$$

This relation is well behaved all over the full range from the weak to strong coupling limits.³⁸ The computed J values are presented in Table 2.

The minimal cluster approach has been also performed to obtain the theoretice online coupling constants. This methodology corresponds to the computations of the minimum number of BS (broken symmetry) determinants and the highest spin determinants on the whole cluster. The sufficient number of energy differences between the BS state and the HS (high spin) state equal to the number of independent magnetic coupling constants required by symmetry.

In our present case, both the Mn^{II}_4 clusters are centro-symmetric. According to Scheme 6, three BS states were sufficient to estimate the values of J_1 , J_2 and J_3 . However, we have calculated the energies of four BS states and HS states to estimate the very weak fourth J_{Mn1Mn4} (J_4 , not shown in Scheme 6) coupling parameter. Neglecting of the value of J_4 leads us to the following equations.

$$\frac{E_{HS} - E_{LS1}}{2S_1 S_2 + S_2} = -2J_1 - 2J_2 - 2J_3$$
(3)

$$\frac{E_{HS} - E_{LS2}}{2S_1 S_2 + S_2} = -2J_1 - 2J_3$$
⁽⁴⁾

$$\frac{E_{HS} - E_{LS3}}{2S_1S_2 + S_2} = -2J_2 - 4J_3$$
(5)

$$\frac{E_{HS} - E_{LS4}}{2S_1S_2 + S_2} = -2J_2 - 4J_1$$
(6)

In our case $S_1 = S_2 = 5/2$

Fig. 9 represents different spin conformations. One high spin conformations and four other spin flipped spin conformers have been considered for DFT treatment. Several parameters *viz.* energies of different spin conformers and their computed spin eigen values are presented in Table 3. The calculated coupling constants values with this approach are presented in Table 2. The spin density plots for **1** and **2** are shown in Figs. S17 and S18, ESI.

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Fig. 9. Different spin conformations considered for DFT analysis. Red arrow indicates flipped spin at those Mn centres.

Table 3. Parameters extracted from DFT calculation corresponding different spin

conformations.						
Compound	States	Determinants	Ms	<s<sup>2></s<sup>	<s<sup>2></s<sup>	SCF energy
				$= S_z^2 + S_{max}$	Computed	(hartree)
				Theoretical		
1	HS	(5/2)(5/2)(5/2)(5/2)>	10	110	110.017	-9035.912901
	LS1	(5/2)(5/2)(5/2)(5/2)>	5	35	34.994	-9035.914347
	LS2	(5/2)(5/2)(5/2)(5/2)>	5	35	35.00	-9035.913130
	LS3	$ (5/2)(5/2)(\overline{5/2})(\overline{5/2})\rangle$	0	10	9.9933	-9035.914427
	LS4	$ (\overline{5/2})(5/2)(\overline{5/2})(5/2)\rangle$	0	10	9.9944	-9035.914275
2	HS	(5/2)(5/2)(5/2)(5/2)>	10	110	110.0259	-7745.092020

LS1	(5/2)(5/2)(5/2)(5/2)>	5	35	35.0092	-7745.091972 View Article Online DOI: 10.1039/C9DT01567A
LS2	(5/2)(5/2)(5/2)(5/2)>	5	35	35.0153	-7745.091939
LS3	$ (5/2)(5/2)(\overline{5/2})(\overline{5/2})\rangle$	0	10	10.0091	-7745.091975
LS4	$ (\overline{5/2})(5/2)(\overline{5/2})(5/2)\rangle$	0	10	10.0091	-7745.091969

Structural Correlation

For complex 1, the theoretically estimated Mn···Mn coupling constants satisfactorily predict experimentally found *J* values. However, the theoretical method employed here slightly overestimates the values obtained from the experiment (Table 2). The manganese centres, connected through both oxo and chlorido bridge are weakly antiferromagnetically coupled and their *J* values are -0.19 cm⁻¹ and -0.70 cm⁻¹. Whereas, coupling between the manganese centres connected through double chlorido bridges are moderately antiferromagnetic as the experimental value of *J* is -6.87 cm⁻¹. Most of the previously reported dichlorido bridged Mn^{II} complexes were found either weakly ferromagnetic or weakly antiferromagnetic³⁹ with very small *J* values (*J* not larger than \pm 1). However exceptions are also found, where Mn^{II}-Mn^{II} couplings are moderately strong.⁴⁰ In our present complex, relatively stronger antiferromagnetic coupling can be explained from its structural point of view. The previously reported complexes reveal that the magnitude of antiferromagnetic coupling increases with the decrease of Mn···Mn distances (Fig. 10). The Mn···Mn distance in the present compound is rather short and thus the coupling is strong.^{39a,41}

The weak antiferromagnetic interaction between other two Mn^{II}-Mn^{II} couplings associated with mixed μ -oxo and μ -chlorido bridge (J_1 and J_3) can also be correlated with the structure⁴². The μ_2 -O bridges are expected to mediate antiferromagnetic couplings, as the corresponding Mn–O–Mn angles are large (109.99°,112.49°) and are within the range for antiferromagnetic interaction.⁴³ These bridging angles and the Mn···Mn separations (3.49Å, 3.51Å) would suggest a greater value of coupling constants²¹. However, the additional chlorido bridge can affect the exchange interaction and the weak antiferromagnetic exchange (-0.19 cm⁻¹, -0.70 cm⁻¹) might be due to the complementarity effect of μ -oxo pathway and μ chlorido pathway.⁴⁴

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Fig. 10. Plot of J vs. Mn···Mn distances for earlier reported dichloride bridged complexes listed in Table S6, ESI. Solid red circle represents complex **1**.

The experimental coupling constants (J_1 , J_2 and J_3) for complex **2** along with its theoretically estimated values using DFT methods are presented in Table 2. The antiferromagnetic and ferromagnetic nature of different Mn^{II}-Mn^{II} coupling pathways were predicted well by theoretical methods and the prediction of values were close to the experimental results. For the complex **2**, the J_2 coupling corresponds to coupling between two Mn^{II} centres connected through double azido bridge in end-on fashion and the coupling is found to be weakly antiferromagnetic with $J_2 = -0.64$ cm⁻¹. On the other hand, other two coupling (J_1 and are J_3) occurring through mixed end-on azido and oxo bridges are experimentally found to be weakly ferromagnetic (experimental values were found equal, J_1 = 0.11cm⁻¹ and $J_3 = 0.11$ cm⁻¹).

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The reported complexes containing double end-on azido bridge between Mn^{II} centres are depicted in Table S7 with their structural parameters and coupling constant values.^{45,46} The coupling are generally ferromagnetic. However, in our present case, complex **2** shows antiferromagnetic coupling although the Mn^{II}-Mn^{II} centres are connected through end-on double azido bridge. The unusual nature of coupling is not surprising if its structural parameters are considered. Generally, end on azido bridge, bound to Ni(II), Cu(II) and Mn(II) centres are known to interact ferromagnetically and this issue has been studied theoretically by Ruiz et al by use of hybrid density functional (DFT) methods.⁴⁷ It has been shown that the calculated coupling constants (*J*) follow parabollic dependence on Mn^{II}-N-Mn^{II} angles (θ) and attains maximum ferromagnetic value at $\theta \sim 114^{\circ}$; the crossover from ferro- to antiferromagnetism is predicted at $\theta \sim 98^{\circ.47}$ Later, Karmakar et al.^{45a} suggested that the experimental *J* values follow a linear relationship with θ following the equation $J = 0.64\theta$ -

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64.5 (*J* and θ are presented in cm⁻¹ and degree respectively). This relation predicts that the online of complex **2** is 98.37° and the Mn^{II}-Mn^{II} coupling is found to be weak antiferromagnetic (experimental value -0.64 cm⁻¹) as is expected from these theoretical calculations.

The other two Mn^{II}-Mn^{II} couplings associated with mixed oxo and azido bridges are found to be weakly ferromagnetic (experimental values are $J_1 = 0.11$ and $J_3 = 0.11$). The oxo bridging angles are 107.31° and 107.60° and the end-on azido bridging angles are 94.10° and 95.44° for J_1 and J_3 pathways, respectively. Both the individual bridging angles suggest antiferromagnetic pathway, however, complementary competitive effect of azido and oxo bridging seems to provide weak ferromagnetism.⁴⁵

Conclusions

In the present work, we reacted the polynucleating Mannich base ligand, N,N'-dimethyl-N,N'bis(2-hydroxy-3-methoxy-5methylbenzyl)ethylenediamine with Mn(II) and obtained two isostructural tetranuclear Mn(II) complexes (1 and 2) with a defective dicubane core. Two triply bridging groups, a necessary feature for such defective dicubane structure, are μ_3 chloride for complex 1 and $\mu_{1,1,1}$ azide for complex 2. The distinctive feature of the complexes is that these are the first examples of tetranuclear Mn-complexes of any N,O donor ligand, in which all the Mn ions are in +2 oxidation state with a defective dicubane core. Both the complexes show quite high catecholase and phenoxazinone synthase-like activity. Interstingly, the catechol oxidation reaction takes place with the formation of H_2O as by-product instead of H₂O₂, formation of which is a common feature of the synthesised model complexes of various metal ions. Magnetic susceptibility measurements reveal that both the complexes show weak antiferromagnetic interactions for 1 and 2, respectively $(J_1 = 0.19 \text{ cm}^{-1}$, $J_2 = -6.87 \text{ cm}^{-1}$ and $J_3 = -0.70 \text{ cm}^{-1}$ for **1** and $J_1 = 0.11 \text{ cm}^{-1}$, $J_2 = -0.64 \text{ cm}^{-1}$ and $J_3 = -0.70 \text{ cm}^{-1}$ for **1** and $J_4 = -0.11 \text{ cm}^{-1}$. = 0.11 cm⁻¹ for 2). These values are in accordance with the magnetostructural correlations of previously reported Mn(II) complexes. The coupling constants are rationalized from the structural parameters of the bridges, metal-metal distances and considering both the delocalization and polarization phenomena by DFT calculation.

Supporting Information

CCDC reference numbers are 1909672-1909673 for complexes 1-2, respectively, contain supplementary crystallographic data for this paper. These data can be obtained free of charge

from the Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_requesticite_Online</u> UV, IR, mass spectra, table of bond parameters of complexes **1–2**, catalytic activity parameter and K_{cat} values of complexes as well as the magnetization and DFT figures of complexes **1–2**.

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A triply-chlorido and a triply-azido bridged defective dicubane tetranuclear Mn(II) complexes of polynucleating Mannich base ligand show significant catecholase and phenoxazinone synthase like activities and are antiferromagnetically coupled which is rationalized by DFT calculation.

