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The First Alternating Mn^{II}-Mn^{III} 1D Chain: Structure, Magnetic Properties and Catalytic Oxidase Activities

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Abstract

unprecedented one-dimensional mixed-valence chain An $[\{Mn^{III}(L)_2\}\{Mn^{II}(bpy)_2\}(ClO_4)(H_2O)_{0.5}]_{\infty}, (H_2L = N-salicylidene-L-alanine and bpy = 2,2'$ bipyridine) has been synthesized. The complex has been characterized by elemental analysis, IR spectroscopy, single-crystal X-ray diffraction analysis, and variable-temperature magnetic measurements. The structural analysis reveals that the $[Mn(bpy)_2]^{2+}$ unit is linked to the pendent carboxylate arm of the $[Mn^{III}(L)_2]^-$ unit to produce a unique syn-anti carboxylate bridged 1D coordination polymer. Variable-temperature (2-300 K) magnetic susceptibility measurements show the presence of antiferromagnetic interaction between the Mn^{III} and Mn^{II} centres with J =-0.98 (2) cm⁻¹. Using 3,5-di-tert-butylcatechol (3,5-DTBC) and o-aminophenol (OAPH) as the substrates, the catecholase-like activity and phenoxazinone synthase-like activity of the complex have been studied; the turnover numbers (k_{cat}) for these oxidase reactions have been calculated to be 126.9 and 738.0 h⁻¹ respectively.

Introduction

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The coordination chemistry of manganese with a diverse range of ligands has been an active field of research for decades.¹ This is not only because of their interesting magnetic properties ² but also due to their structural diversities,³⁻⁸ and presence of manganese in the active site of many enzymes that are involved in biological redox processes.⁹ In these regards, the mixed valance Mn-complexes deserve special mention for their fascinating single molecule magnet properties.² Moreover, besides catalytic activities of these mixed valence species for various chemical reactions,¹⁰ it has been found recently that these species have very high biological activities e.g. catalase-like activity, catecholase activity, DNA binding activity etc.⁹ Mixed-valence polymetallic clusters of manganese ions of different shapes and sizes, from simple triangles,³ cubes,⁴ and butterflies,⁵ to wheels,⁶ discs,⁷ rods,^{2c} supercubanes,⁸ are known. Moreover, coordination polymers based on manganese-clusters "node" and exo-bidentate linker

produces various zero dimensional (dumbbell shaped dimer),¹¹ one-dimensional (1D) (both linear and zigzag chains),¹² or and three-dimensional (3D) hexagonal-like motif.^{12c} Several approaches leading to the isolation of mixed valence manganese core are reported.¹³⁻¹⁵ The first one is based on $Mn^{II}(O_2CR)_2$ oxidation with oxygen^{13a} or $MnO_4^{-.13b}$ The second one involves reduction of $[Mn^{II}Mn^{III}_{2}O]^{6+}$ to $[Mn^{II}_{2}Mn^{III}O]^{5+}$ and further coupling of $[Mn^{II}_{2}Mn^{III}O]^{5+}$ resulting in the formation of the mixed valence core $[Mn^{II}_4M_2^{III}O_2]^{10+.14}$ The third method involves reductive fragmentation of [Mn₁₂O₁₂(O₂CCHCl₂)₁₆(H₂O)₄] to obtain mixed valence species,¹⁵ where, the average oxidation state of Mn ions changes from +3.33 in Mn₁₂ $[(Mn^{3+})_8(Mn^{4+})_4]$ to +2.33 in Mn₆ $[(Mn^{3+})_2(Mn^{4+})_4]$. The procedures for the synthesis of the synthesynthesynthesis of the synthesynthesis mentioned mixed valence complexes involve the use of some oxidising agents e.g. persulfate, permanganate, hydrogen peroxide, or dioxygen,¹³ or reducing agent *e.g.* tetrathiotetracene, triiodide, trichloroacetic acid,^{14,15b} so that the Mn ion of different oxidation states is produced *in* situ and the desired complex is separated from the solution depending upon the nature of the ligands. Therefore, it is obvious that all of these procedures are rather serendipitous. Till now, no synthetic route has been reported in which a designed mixed-valence complex is prepared by mixing pre-formed compounds of Mn ions in desired oxidation states and stoichiometric ratios. Such a procedure does not require in situ change of oxidation states of Mn and thus is expected to provide better control over the synthesis of targeted complex.

Schiff-base derived from amino acid and their metal complexes have drawn a great deal of attention due to their antibacterial and antifungal activity,¹⁶ but single crystal X-ray structure of the manganese Schiff-base complexes was not reported till date. It has been reported with the help of elemental analyses and physico-chemical studies that the Schiff bases of glycine/alanine with 2-hydroxynapthaldehyde readily produce complexes with Mn^{III} in which two ligands are coordinated to Mn^{III} and the complex species bears mono-negative charge. In an attempt to isolate and structurally characterize such a manganese Schiff-base unit using several cationic species, we finally became successful to get crystals of a bis-chelated Mn^{III} anionic unit derived from condensation of L-alanine and salicylaldehyde, with bis(2,2'-bipyridine)manganese(II) complex.

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Herein, we report the synthesis and X-ray single crystal structure analysis of this unique 1D helical chain of mixed-valent manganese complex $[\{Mn^{III}(L)_2\}\{Mn^{II}(bpy)_2\}(ClO_4)(H_2O)_{0.5}]_n,$ (1), $(H_2L = N$ -salicylidene-L-alanine and) obtained simply by mixing two precursor complexes i.e. $[Mn^{III}(L)_2]^-$ and $[Mn^{II}(bpy)_2(H_2O)(ClO_4)](ClO_4)](ClO_4)$ in methanol. This coordination polymer is formed by carboxylate bridge between the $[Mn^{III}(L)_2]^-$ and $[Mn^{II}(bpy)_2]^{2+}$ units. The synthetic procedure, architecture and stoichiometry of the compound are unprecedented among the plethora of reported $Mn^{II}Mn^{III}$ species. Variable-temperature magnetic susceptibility measurements show the presence of antiferromagnetic interactions between the carboxylate bridged Mn^{III} and Mn^{II} units. The compound exhibits appreciably high catecholase-like and phenoxazinone synthase-like activities which are also reported here along with probable mechanisms.

Experimental Section

Starting materials

Salicylaldehyde, LiOH, 2,2'-bipyridine and L-alanine were purchased from Spectrochem, India were reagent grade. They were used without further purification. and of $[Mn^{II}(bpy)_2(H_2O)(ClO_4)](ClO_4)$ was synthesized using procedure described previously.¹⁷ The other reagents and solvents were of commercially available reagent quality, unless otherwise DOI: 10.1039/C8NJ00414E stated.

Caution! Although not encountered during experiment, perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

Synthesis of the Schiff base ligand LiHL

Lithium salt of monocondensed Schiff base ligand N-salicylidene-L-alanine (LiHL) was prepared according to reported procedure.¹⁸ To a hot methanolic solution (30 mL) of LiOH (0.41 g, 10 mmol) and L-alanine (0.89 g, 10 mmol), salicylaldehyde (1.04 mL, 10 mmol) was added. The bright yellow solution was then refluxed for *ca*. 2 h and allowed to cool. The ligand solution thus produced was used directly for complex formation.

Synthesis of [{Mn^{III}(L)₂}{Mn^{III}(bpy)₂}(ClO₄)(H₂O)_{0.5}]_n, (1)

To the methanolic solution (10 mL) of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.361 g, 1 mmol), LiHL (2 mmol) and LiOH (2 mmol) in methanol (10 mL) was added. The solution was stirred for *ca*. 15-20 min and colour of the solution changed to intense brown. To this solution, 15 mL methanolic solution of $[Mn^{II}(bpy)_2(H_2O)(ClO_4)](ClO_4)$ (0.601 g, 1 mmol) was added. The entire mixture was stirred for *ca*. an hour. Dark brown coloured solid separated, that was further dissolved in methanol and layered with diethyl ether. Dark brown coloured block shaped single crystals suitable for X-ray diffraction was deposited on the wall of the tube after several days.

Yield: 0.780 g, 85.52%. Anal. calc. for C₄₀ H₃₅ Mn₂ N₆ O_{10.5} Cl: C, 52.62; H, 3.86; N, 9.20; % found: C, 53.07; H, 3.65; N, 9.16; %. IR (KBr pellet, cm⁻¹): v(C=N) 1602; v_{s+as}(COO⁻) 1401 and 1473; v(ClO₄⁻) 1095, v(O–H) 3419. UV/Vis: λ_{max} (nm) [ϵ_{max} (M⁻¹ cm⁻¹)] in (CH₃OH) = 895(160), 383(9530), 276(99000), 232(113000), 219(110600). HRMS (m/z, ESI⁺): found for [(2,2'-bipyridyl)(H)]⁺ = 157.07 (calc. 157.08), [Mn(2,2'-bipyridyl)₂]⁺² = 183.53 (calc. 183.53), [Mn(L)(CH₃OH)]⁺ = 279.00 (calc. 279.03), [Mn(L)(CH₃OH)₂(H₂O)]⁺ = 329.03 (calc. 329.07), [Mn(L)(ClO₄)Na(H₂O)₃]⁺ = 422.07 (calc. 422.97), [Mn(salicylate)₂(bpy)]K⁺= 493.11 (calc. 492.45), [Mn(salicylate)(bpy)(ClO₄)(H₂O)₃]Na⁺= 508.10 (calc. 508.00)

Physical measurements

Elemental analysis (C, H and N) of the complex were carried out using Perkin-Elmer 2400 series II CHN analyzer. IR spectra of the complex was recorded in KBr pellet (4000–500 cm⁻¹) using a Perkin-Elmer RXI FT-IR spectrophotometer. The UV-Vis spectrum (1000-240 nm) of the complex was recorded in spectroscopic grade methanol solution in a Hitachi U-3501 spectrophotometer. Powder X-ray diffraction patterns was recorded on a powder X-ray diffractometer (Model: X'Pert Powder, PANalytical) at 45 kV voltage and 40 mA current and calibrated with a standard silicon sample, using Ni-filtered Cu-K α ($\lambda = 0.15418$ nm) radiation. Thermogravimetric analysis (TGA) was carried out by Pyris6 TGA, The Netherlands in N2 atmosphere with flow and scanning rates of 20 mL min⁻¹ and 10 °C min⁻¹, respectively, within 30-800 °C. Electrospray ionization mass spectrometry (ESI-MS positive) ion mass spectra was acquired using a Xevo G2-S QTof (Waters) mass spectrometer, equipped with a Z-spray interface, over a mass range of 100-1200 Da, in a continuum mode. Aqueous sodium formate was used for Q-oa-Tof calibration. L-leucine was used as the external mass calibrant lock mass $[M+H]^+$ = 556.2771 Da. Solutions of compounds were injected at a flow rate of 5 µl/min. The magnetic properties of the 1D chain polymer was investigated with a Quantum Design superconducting quantum interference device vibrating sample magnetometer (SQUID-VSM). Powdered polycrystalline sample was used under a DC magnetic field and molar paramagnetic susceptibilities (χ_M) were measured under a constant magnetic field of 0.05T around 2 to 300 K temperature range. The susceptibility data was corrected by Pascal's diamagnetic contributions following the literature.¹⁹ Isothermal magnetization measurements were performed at 2 K up to 5 Tesla for the complex.

Crystallographic data collection and refinement

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Suitable X-ray quality single crystal of complex **1** was mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo-K α ($\lambda = 0.71073$ Å) radiation. Crystal was positioned at 60 mm from the CCD. 360 frames are measured with a counting time of 5s. Structure was solved using Patterson method by using the SHELXS 97.²⁰ Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atoms. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least squares refinement. Absorption corrections were carried out using the SADABS program.²¹ All calculations were carried out using SHELXS 14,²² SHELXL 14,²³ PLATON 99,²⁴ ORTEP-32²⁵ and WINGX 1.64.²⁶ Data collection, structure refinement parameters and crystallographic data for complex **1** is given in Table 1.

Kinetics of the catecholase activity and phenoxazinone synthase-like activity

Like most of the catecholase activity studies of model complexes, 3,5-di-*tert*-butylcatechol (3,5-DTBC) was chosen as the substrate. The reaction was studied spectrophotometrically under aerobic condition in methanol solution by monitoring the increase in the absorption maxima of the quinone band at 400 nm as a function of time (time scan). To detect the formation of hydrogen peroxide during the catalytic reaction, reaction mixture was prepared as in the kinetic experiments.²⁷ After 1 h of reaction, the solution was acidified with H₂SO₄ until a pH of 2 was reached. In order to inhibit further oxidation, an equal volume of water was added, and the view Article Online formed quinone was extracted three times with dichloromethane. To the aqueous $^{DOI:10.1030/CBHJO00414E}$ a 10% solution of KI and three drops of 3% solution of ammonium molybdate were added. The formation of I_3^- was monitored spectrophotometrically due to development of the characteristic I_3^- band ($\lambda = 353$ nm, $\varepsilon = 26000$ M⁻¹ cm⁻¹).

The phenoxazinone synthase mimicking activity of complex **1** was performed by taking *o*-aminophenol as the substrate. The reaction was studied spectrophotometrically under aerobic condition in methanol solution by monitoring the increase in the absorption maxima of the phenoxazinone band at 420 nm as a function of time (time scan).

Results and discussions

Synthesis

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Coordination complexes of manganese and tridentate Schiff-base ligands derived from amino acid is not quite common.²⁹ Here, we have prepared the lithium salt (LiHL) of Schiff-base ligand (H_2L) by the condensation of alanine and salicylaldehyde according to the reported procedure.¹⁸ In open atmosphere, on reaction with LiHL, Mn^{II} is oxidized to Mn^{III} and in the resulted complex ([Mn^{III}(L)₂]⁻) six coordination sites of Mn^{III} are occupied by two binegative tridentate Schiff base ligands (L²⁻) (Scheme 1). One of the oxygen atoms of the carboxylato group remains as a pendent arm which is capable of coordination to another metal ion. On the other hand, the Mn^{II} precursor i.e. $[Mn(bpy)_2(H_2O)(ClO_4)]^+$ contains replaceable water molecule and perchlorate anion, coordinated to Mn^{II} centre. Thus, upon mixing of these two species, the uncoordinated oxygen atoms of the Schiff base from the Mn^{III} unit coordinates to the Mn^{II} centre by replacing water molecule and perchlorate anion to form the one-dimensional chain. The resemblance of the measured powder X-ray diffraction pattern of complex 1 to its simulated diffraction pattern (Fig. S1) indicates the purity of the complex. The TGA curve for complex 1 reveals that upon heating it starts to lose water at *ca*. 80 ^oC and becomes dehydrated at ca. 102 ^oC in a single step (Fig. S2). The observed weight loss (1.3%) corroborates the loss of half molecule water (calc. 0.9%). The compound does not show any colour change on water removal.



Scheme 1 Synthetic route to the complex 1

To the best of our knowledge, this type of synthetic strategy has been used for the first time here and the method results in an unprecedented alternating mixed-valence manganese (II/III) 1D chain (compound 1).

IR and UV-Vis spectra of the complex 1

The complex was initially characterized by elemental analysis and FT-IR spectroscopy. Due to the presence of azomethine group (CH=N), sharp band is found around 1602 cm⁻¹ for the complex. The carboxylate group of the Schiff base shows characteristic symmetric stretching at 1401 cm⁻¹ and antisymmetric stretching at 1473 cm⁻¹. The non-coordinated perchlorate gives sharp peaks around 1095 cm⁻¹. In addition, the appearance of a broad band at 3419 cm⁻¹ in the spectrum of **1** can be attributed to the presence of water molecule found in the interstitial site of the complex (Fig. S3).

UV-VIS-NIR spectroscopic study of the complex was done in the wave length region (200-1000) nm using spectroscopic grade methanol as a solvent. The complex shows broad peak corresponding to d-d transition at 895 nm. Besides, absorption peak at 383 nm is observed due to ligand to metal charge transfer and at 276, 232 and 219 nm due to intra-ligand charge transfer transitions (Fig. S4). The peak maxima along with the corresponding molar extinction coefficient values of the above three complexes are represented in Table S1in ESI.

Description of the structure

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Complex 1 consists of repeating alternating mixed-valence Mn^{II} and Mn^{III} dimeric units, as shown in Fig. 1 together with the atomic numbering scheme for the metal coordination spheres. Selected bond lengths and angles are summarized in Table 2.



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Fig. 1 The ORTEP diagram of 1 with ellipsoids drawn at the 30% probability level (symmetry operation a = 1-x, 1/2+y, 1-z). The Hydrogen atoms and the anion were removed for picture clarity.

Within the asymmetric unit, both Mn^{III} [Mn(1)] and Mn^{II} [Mn(2)] ions are sixcoordinated with distorted octahedral geometry. The bis-chelated Mn^{III} centre [Mn(1)] is coordinated by two deprotonated Schiff base ligands via O(3), O(1), N(2), and N(1) atoms in the equatorial plane with Mn–O distances within the range of 1.955(5) - 2.054(4) Å, and with Mn–N distances within the range of 1.983(7)–1.986(6) Å and the axial positions are coordinated by O(2) and O(4) with corresponding bond distances of 1.974(6) and 2.100(5) Å, respectively. The oxygen atoms O(5) and $O(6)^{a}$ from the pendant carboxylate groups of the Schiff-base ligands are coordinated to Mn(2) with the bond distances of 2.116(4) and 2.113(5) Å, respectively. In addition to these, hexa-coordination around Mn^{II} centre [Mn(2)] is completed by nitrogen atoms (N(3), N(4), N(5) and N(6)) with Mn–N lengths within the 2.245(7) – 2.290(5)Å range from two chelating bpy moieties. Two bipyridine ligands which are cis in the metal precursor $[Mn(bpy)_2(H_2O)(ClO_4)]^+$, retains their *cis* position in complex **1.** The pyridine moieties of bpy are not in the same plane, rather makes an angle of 13.64° with respect to each other. The root mean squared deviation of the four basal donor atoms $\{O(3), O(1), N(2), and N(1)\}$ from their mean plane around Mn(1) is 0.058 Å where Mn(1) deviates from this mean plane by 0.090(9) Å in the direction of the phenoxido oxygen atom of the Schiff-base ligand. The root mean squared deviation of the four basal donor atoms $\{N(3), N(4), N(6), and O(5)\}$ from their mean plane around Mn(2) is 0.061 Å where Mn(2) deviates from this mean plane by 0.137(9) Å in the direction of the bridging axial carboxylato oxygen atom ($O(6)^a$). The oxygen atoms O(3) and O(4) of two bridging carboxylate groups are coordinated to Mn(1) in cis position and the other oxygen atoms of these carboxylate (O(5) and O(6)) coordinate to two different Mn^{II} ions. The oxidation states of the Mn ions of 1 were confirmed by inspection of the bond lengths, charge balance considerations, and bond valence sum (BVS) calculations (Table S2).²⁸ These syn-anti carboxylate bridged alternating units constitute the mixed-valence one-dimensional two-turn single-helical structure, whose helical handedness is left handed (Fig. 2).

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Fig. 2 Helical polymeric chain along crystallographic *c* axis (red = oxygen, grey = carbon, blue = nitrogen, violet = manganese).

It is to be noted here that, although transition metal complexes of Schiff-bases derived from amino acid ligands are well documented with several metal ions,^{16,30} it is very rare in Mn^{III} complexes.²⁹ To the best of our knowledge, complexes of Mn^{III} with H₂L (condensate of 2-hydroxynapthaldehyde and glycine/ L-alanine/ L-phenylalanine/ L- histidine/ L-threonine/ L-tryptophan/ L-asparagine/ L-aspartic acid/ L-glutamine/ L-glutamic acid) were isolated with Na+ cation and characterized by spectroscopic techniques, but X-ray single crystal structural analysis has not been performed yet for any of these species.²⁹ On the other hand, bis-chelated bpy complex of manganese(II) [Mn^{II}(bpy)₂(H₂O)(ClO₄)](ClO₄) was synthesised and structurally characterized.¹⁷ Using this as cationic species, we have succeeded to characterize the compound structurally and found the unprecedented alternating arrangement of Mn^{III}-Schiff base and Mn^{II}-bpy units linked by carboxylate ion in complex **1**.

Catecholase activity and kinetic studies

For detailed kinetic study, (1×10^{-4}) M solution of complex 1 was treated with 100 equivalents of 3,5-DTBC under aerobic condition in methanol solution because of the good solubility of the complex, the substrate, and the final product in this solvent.



Scheme 2 Catalytic oxidation of 3,5-DTBC to 3,5-DTBQ in methanol.

After addition of 3,5-DTBC, the increase of the absorption at ~400 nm, which is indicative of an oxidation from 3,5-DTBC to the corresponding quinone (3,5-DTBQ), indicated a considerable catecholase activity (Fig. 3).



Fig. 3 UV-Vis spectral scan for the oxidation of 3,5-DTBC (1.0×10^{-2}) M catalyzed by complex 1 (1×10^{-4}) M for up to ~1 h of reaction in dioxygen saturated methanol at 25 °C.

The kinetic study of the oxidation of 3,5-DTBC to 3,5-DTBQ by the complex was carried out by monitoring the growth of the absorbance at 400 nm by the initial rates method.

To determine the dependence of the rates on the substrate concentration and various kinetic parameters, solutions of complex were prepared with increasing concentrations of 3,5-DTBC (from 10 to 100 equivalents) under aerobic conditions at a complex concentration of (1.00 \times 10⁻⁴) M. A first order dependence was observed at low concentrations of the substrate, whereas saturation kinetics was found at higher concentrations of the substrate, as shown in Fig. 4.



Fig. 4 Plot of initial rates *versus* substrate concentration for the oxidation reaction of 3,5-DTBC catalyzed by complex **1**. Inset shows the Lineweaver–Burk plot.

The dependence on the substrate concentration indicates that a catalyst-substrate binding is the initial step in the catalytic mechanism. A treatment on the basis of Michaelis–Menten approach, originally developed for enzyme kinetics, was therefore applied and linearized by means of Lineweaver–Burk plot (double reciprocal) to calculate various kinetic parameters such as Michaelis–Menten constant ($K_{\rm M} = 3.60 \times 10^{-3}$ (Std. error = 1.04 x 10⁻⁴) M) and maximum initial rate ($V_{\text{max}} = 1.06 \text{ x } 10^{-4}$ (Std. error $1.08 \text{ x } 10^{-5}$) M min⁻¹). The turnover number of the complex ($k_{\text{cat}} = 126.9 \text{ h}^{-1}$) is calculated by dividing the V_{max} value by the complex concentration. It may be noted here that a blank experiment without catalyst (compound 1) does not show significant growth of the band at ~400 nm in an identical reaction condition (Fig. S7).

ESI-Mass spectrometric study

In order to investigate the probable complex-substrate intermediate, we have recorded the ESI-MS spectra of the complex 1 and 1/1 mixture (v/v) of complex 1 and substrate in methanolative within 5 minutes of mixing respectively. For the complex, the spectra shows three major peaks at m/z 279.00 (calc. 279.03), 329.03 (calc. 329.07) and 183.53 (calc. 183.53) corresponding to $[Mn^{III}(L)(CH_3OH)]^+$, $[Mn^{III}(L)(CH_3OH)_2(H_2O)]^+$ and $[Mn^{II}(bpy)_2]^{+2}$ species, respectively (Fig. S5). The nature of the ESI-MS spectra changed considerably after addition of 3,5-DTBC to the complex solution in the methanol (Fig. S13-S15). It shows two peaks at m/z = 247.00 (calc. 247.00) and m/z = 183.53 (calc. 183.53) (Fig. S13) which can be assigned to the constituent fragments of the complex i.e. $[Mn^{III}(L)]^+$ and $[Mn^{II}(bpy)_2]^{+2}$ respectively. Similar peaks have been observed in the mass spectrum of the complex. In addition, three new peaks are generated at m/z = 432.15 (calc. 432.15), 403.07 (calc. 403.07) (Fig. S14) and 404.07 (calc. 404.08) (Fig. S15), assignable to $[Mn^{II}(bpy)(3,5-DTBC)]^{+1}$, $[Mn^{III}(L)(bpy)]^{+}$ and $[Mn^{II}(L)(bpy)]H^{+}$ respectively. These peaks are highly significant to explain the substrate-catalyst intermediate and also the reduction of Mn^{III} centre during the catalytic conversion process. Another important peak is observed at m/z = 431.15 (calc. 431.15) (Fig. S14), which indicates the formation of the semiquinonate form of the intermediate [Mn^{II}(bpy)(3,5-DTBSQ[•])]⁺¹. The spectrum shows two peaks at m/z 243.13 (calc. 243.13) and 463.28 (calc. 463.28). The peaks can be assigned to [(3,5-DTBQ)Na]⁺, [(3,5-DTBQ)₂Na]⁺ respectively. These peaks indicate the catalytic oxidation of 3,5-DTBC to 3,5-DTBQ (Fig. S14).

Mechanistic insight

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It has been shown with mechanistic studies with copper-based model complexes that there can be two possible mechanisms for the oxidation of 3,5-DTBC to 3,5-DTBQ. One occurs through the formation of a dicopper(II) catecholate intermediate where the dicopper(II) species oxidizes the catecholic substrate to its respective quinone and itself reduces to a dicopper(I) species. This dicopper(I) species further react with an oxygen molecule to generate a peroxo dicopper(II) adduct, which then oxidizes a second molecule of the catechol substrate to quinone; water is formed as a byproduct through this four-electron-reduction process.^{27b} The second mechanism involves the formation of an organic radical intermediate such as copper(I) semiquinone.³¹ Its subsequent reaction with an oxygen molecule may result in the two-electron reduction of two oxygens, leading to the further oxidation of the copper(I) ion and release of the quinone molecule, with hydrogen peroxide as a byproduct.³² Now, a number of studies of the possible mechanisms of the catechol oxidation reaction catalyzed by nickel(II), cobalt(II/III), manganese(II/III/IV), and zinc(II) complexes with the formation of hydrogen peroxide have been

reported.³³ To understand the mechanism of the present catalysis by this complex, we have checked whether any H_2O_2 has been formed as a side product. Iodometric method has been followed in order to estimate H_2O_2 both qualitatively as well as quantatively by monitoring the I_3^- band (~353 nm) by UV–Vis spectroscopy.²⁷ It has been found that generation of H_2O_2 gradually increases with time during addition of the complex to 3,5-DTBC and after addition of the complex to 3,5-DTBC. The plot showing the increase of the absorption band at 353 nm due to generation of hydrogen peroxide is shown in Fig. S9 in ESI. Along with it, plot of absorption maxima at different time interval is shown in Fig. S10 in ESI.

On basis of ESI-mass spectra as well as UV-Vis study we propose a possible mechanism^{14E} here. The complex in methanol, gets dissociated into its two constituent fragments $[Mn^{II}(L)]^+$ (A) and $[Mn^{II}(bpy)_2]^{+2}$ (B) respectively. The doubly charged species (B) reacts with the incoming 3,5-DTBC molecule at first to generate $[Mn^{II}(bpy)(3,5-DTBC^{-})]^{+1}$ (D) in which, one of the phenolic hydroxyl group of 3,5-DTBC is deprotonated and coordinated to the Mn^{II} centre. The substituted bpy ligand is then coordinated to Mn^{III} centre to form $[Mn^{III}(L)(bpy)]^+$ (C). In the next step, the species (D) releases a hydrogen to convert to its radical semiquinonate form $[Mn^{II}(bpy)(3,5-DTBSQ^{-})]^{+1}$ (F) with subsequent reduction of Mn^{III} in (C) to Mn^{II} to form (E). Finally, in presence of dissolved oxygen, the organic semiquinolate radical is converted to the quinone moiety 3,5-DTBQ and gets eliminated from the Mn^{II} centre along with immediate oxidation of the metal centre in (E). Thus, the catalytic precursors (A) and (B) are regenerated at the end of reaction and is used for next catalytic cycle.

We have checked whether one of our synthetic precursor $Mn(bpy)_2^{2^+}$ is also active in the present catalysis reaction. In order to do so, we have monitored spectrophotometrically the increase of characteristic band at 400 nm in the identical condition like that of the complex **1** (Fig. S8). However, no significant increase of the quinine band at 400 nm after 30 minutes is observed. This clearly validates the crucial role of the redox active Mn^{III} centre here as it is involved in the electron transfer process from the substrate to the molecular oxygen. The probable mechanism of the catalysis reaction is shown in Scheme 3.



Scheme 3 Proposed mechanism for the catalytic cycle of the oxidation of 3,5-di-*tert* butylcatechol.

It is to be noted here that, in literature, there are several examples of manganese complexes showing catecholase-like activity where the metal ion is in (+2) or (+3) or in (+4) oxidation state (Table S3). The k_{cat} values for the complexes are reported to be in the ranges 48.8 h⁻¹ to 1038.0 h⁻¹ for Mn^{II,9b,33c,34a,34b} 19.5 h⁻¹ to 7200.0 h⁻¹ for Mn^{III 34(d-g)} and 136.0 h⁻¹ to 8690.0 h⁻¹ for Mn^{IV 33e,34h} complexes. On the other hand, there are three mixed valence Mn^{II/III} hexanuclear,^{9b,34k} one tetranuclear,^{34j} three dinulcear^{34j,34i} and three trinuclear^{33g,34g} systems, view Article Online catecholase like activity of which have been studied. The k_{cat} values of these complexes have been found to be 7.5 h⁻¹ to 9011.0 h⁻¹. Till date, catecholase activity of only one mixed valence (Mn^{II/III}) polymer has been reported with k_{cat} value of 2547 h⁻¹. Therefore, complex **1** is only the second mixed valence polymeric complex whose catecholase-like bio-mimetic activity is reported here.

Phenoxazinone synthase-like activity and kinetic studies

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The phenoxazinone synthase mimicking activity of complex 1 was studied by observing the oxidation of o-aminophenol spectrophotometrically in dioxygen-saturated methanol at 25 °C.



Scheme 4 Catalytic oxidation of o-aminophenol (OAPH) to phenoxazinone in methanol.

To serve this purpose, (4×10^{-5}) M solution of the complex was treated with 100 equivalents of the substrate under dioxygen saturated methanol at 25 °C. The time dependent representative spectral changes for a period of ~ 1 h after the addition of *o*-aminophenol are shown in Fig. 5. The spectral scans revealed the continuous increase of peak intensity at *ca.* ~420 nm, characteristic of phenoxazinone chromophore, signifying catalytic oxidation of *o*-aminophenol in aerobic condition. It may be noted here that a blank experiment without catalyst did not show significant growth of the band at ~420 nm in an identical reaction condition (Fig. S11). This spectral behaviour concludes that the complex exhibits phenoxazinone synthase-like activity in aerobic condition.



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Fig. 5 UV-Vis spectral scan for the oxidation of *o*-aminophenol (4.0×10^{-3}) M catalyzed by the complex 1 (4×10^{-5}) M for up to ~1 h of reaction in dioxygen-saturated methanol at 25 °C.

Kinetic studies were performed to understand the extent of the catalytic efficiency. For a particular complex–substrate mixture, time scan at the maximum band of 2-aminophenoxazine-3-one was done for a period of 60 min. The initial rate of the reaction *versus* concentration of the substrate data shows rate saturation kinetics as can be seen from Fig. 6 for complex **1**. This observation indicates that 2-aminophenoxazine-3-one formation proceeds through a relatively stable complex–substrate adduct, followed by the redox decomposition of the adduct at the rate determining step. This type of saturation rate dependency can be easily explained by the Michaelis–Menten model, originally developed for the enzymatic kinetics, which on linearization gives double reciprocal Lineweaver–Burk plot to investigate values of various parameters like V_{max} , K_M , and k_{cat} .



Fig. 6 Plot of initial rates *versus* substrate concentration for the oxidation reaction of *o*-amino phenol catalyzed by complex **1**. Inset shows the Lineweaver–Burk plot.

Analysis of the experimental data yielded Michaelis binding constant ($K_{\rm M} = 1.67 \times 10^{-2}$ (Std. error = 3.85 x 10⁻⁴) M) and maximum initial rate ($V_{\rm max} = 2.46 \times 10^{-4}$ (Std. error 2.31 x 10⁻⁴)

M min⁻¹), and the turnover number ($k_{cat} = 738.0 \text{ h}^{-1}$) value is obtained by dividing the V_{max} by the concentration of the complex used. Thus this complex can be suitably used as a functional model for phenoxazinone synthase like activity.

ESI-Mass spectrometric study

To get better understanding of the probable complex-substrate intermediate in the oxidative dimerization reaction of o-amino phenol (OAPH), ESI-MS spectra of the 1/1 mixture (v/v) of complex 1 and substrate in methanol within 5 minutes of mixing was recorded (Fig. S16-S18). The spectrum shows two peaks at $\{m/z = 183.57 \text{ (calc. } 183.57)\}$ (Fig. S16) and $[m/z] = \frac{\sqrt{2}770}{1030778} \frac{1}{10000000}$ (calc. 279.01)} (Fig. S17) due to formation of $[Mn^{II}(bpy)_2]^{+2}$ and $[Mn^{III}(L)(CH_3OH)]^{+1}$ species respectively. These peaks have previously appeared in the mass spectrum of the complex. The appearance of three new peaks at m/z = 319.03 (calc. 319.05), 403.07 (calc. 403.07) and m/z =330.04 (calc. 330.07) (Fig. S18) assignable to species $[Mn^{II}(bpy)(OAP^{-})]^{+1}$, $[Mn^{III}(bpy)(L)]^{+1}$ and [Mn^{II}(L)(CH₃OH)₄]H⁺¹ respectively, is very important as they clearly establish the substratecatalyst binding via replacement of one bpy moiety in the Mn^{II} centre and subsequent reduction in the Mn^{III} centre during catalytic dimerization of OAPH. The peak at m/z = 357.06 (calc. 357.01) (Fig. S18) appears due to loss of one of the proton from the metal coordinated amino group of OAP i.e. $[Mn^{II}(bpy)(OAP^{2-})]K^{+1}$. In addition, the peak due to the protonated 2aminophenoxazine-3-one appears at m/z 212.01 (Fig. S17) indicating catalytic conversion of the reactant to product. During this process, we have checked that no H₂O₂ is formed as by-product, so, water is produced rather as a side product.

Mechanistic insight

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On the basis of thorough ESI-Mass Spectrometric Study, a probable mechanism is proposed here. The complex in solution at first dissociates into its two constituent fragments i.e. $[Mn^{III}(L)(CH_3OH)]^{+1}$ (A) and $[Mn^{II}(bpy)_2]^{+2}$ (B) respectively. Then, after addition of OAPH, it gets coordinated to the Mn^{II} centre after the loss of the phenolic hydrogen of the same and during this process, one of the previously coordinated bpy ligands is replaced from the Mn^{II} centre and gets coordinated to Mn^{III} centre explaining the formation of [Mn^{III}(bpy)(L)]⁺¹ (C) and $[Mn^{II}(bpy)(OAP^{-})]^{+1}$ (D). In the next step, one of the proton from the coordinated amino (-NH₂) group in (D) is lost to form (E) which is converted into an aminophenolate radical (G) which is associated with subsequent reduction of the metal centre in (C) to form $[Mn^{II}(L)(CH_3OH)_4]H^{+1}(F)$. In the last step, Areal oxygen oxidizes the coordinated organic radical into the product to make it release from the Mn^{II} centre and Mn^{II} in (F) to Mn^{III}. Thus the species (A) and (B) are regenerated after the end of process and is used for the next catalytic cycle. During the entire process, $3/2 O_2$ is reduced to form $3H_2O$.

We have checked whether one of our synthetic precursor $Mn(bpy)_2^{2+}$ is also active in the present catalysis reaction. In order to do so, we have monitored spectrophotometrically the increase of characteristic band at 420 nm in the identical condition like that of the complex (Fig. S12). Interestingly, no such significant increase of the phenoxazinone band at 420 nm after 30 minutes is observed. This clearly validates the role of Mn^{III} as a redox-active metal centre in

order to transfer electron from substrate to molecular oxygen where as Mn^{II} behaves as a lewis acidic centre to bind the substrate molecule. The probable scheme of the catalysis is shown in Scheme 5.



Scheme 5 Proposed mechanism for the catalytic cycle of the oxidation of o-aminophenol.

In the literature a few mononuclear or dinuclear Mn complexes with tetradentate or tridentate ligands in which the metal ion is in +2 or +3 or +4 oxidation state are known to exhibit phenoxazinone synthase-like activity. Interestingly, the k_{cat} value obtained for complex 1 is much higher than all these reported compounds (Table S4). To the best of our knowledge, complex 1 is the first example of mixed valence manganese coordination polymer showing phenoxazinone synthase-like activity and a detailed mechanistic insight is provided here.

Magnetic Property

The temperature dependent magnetic susceptibility for the complex **1** was investigated in the temperature range 2–300 K in the applied field of 0.05T. The direct current (dc) magnetic property of the complex in the form of $\chi_M T$ versus T for the complex (χ_M being the magnetic susceptibility of two Mn^{II}Mn^{III} units and T being the absolute temperature) is shown in Fig. 7. Since the complex shows two different Mn^{II...}Mn^{III} separation (5.571 Å and 5.584Å, vide infra), four consecutive manganese centres are taken as molecular unit for our magnetic calculations.



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Fig. 7 Variation of $\chi_M T$ with temperature for four consecutive manganese centres taken as molecular unit. The points are the experimental data and the solid line created from the best fitted curve.

When the sample is cooled from room temperature (300 K), the $\chi_M T$ values slowly decreased down to ~80 K. Below ~80 K, $\chi_M T$ shows an abrupt decrease and reaches a value of *ca*. 2.9 cm³ K mol⁻¹ at 2 K. The nature of the curve indicates weak intra-chain antiferromagnetic interactions between the Mn^{III} and Mn^{II} centres. At room temperature $\chi_M T$ shows a value of 14.43 cm³ K mol⁻¹ which is close to the calculated value of 14.76 cm³ K mol⁻¹ for magnetically isolated two Mn^{III} and two Mn^{II} centres (for g = 2.00). Moreover, the isothermal magnetizations curve at 2 K show no saturation as magnetic field increased, confirming the presence of weak antiferromagnetic coupling (Fig. 8). Also, the magnetization value at 5T is much lower compared with the value for ideal non-interacting {Mn^{II}Mn^{III}}₂ tetramer.

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Fig. 8 Field dependence of molar magnetizations considering four consecutive manganese centres for the compounds at 2 K.

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The experimental magnetic data were fitted using the method that was introduced by Fisher³⁶ for a chain magnets and later modified for alternate magnetic centres by Drillon et al.³⁷ The Hamiltonian of said system can be represented as,

$$H = -J \sum_{i=1}^{2n} S_i S_{i+1}$$
(1)

Here, S_i can be considered as current spin vector of the *i*th centre. The expression for bulk susceptibility derived by Drillon can be presented as,

$$\chi_{\rm M} T = \frac{N\beta^2}{3k} \left[g^2 \frac{1+{\rm u}}{1-{\rm u}} + \delta^2 \frac{1-{\rm u}}{1+{\rm u}} \right]$$
(2)

With,

$$g = (g_{A}^{e} + g_{B}^{e})/2$$
$$\delta = (g_{A}^{e} - g_{B}^{e})/2$$
$$u = \operatorname{coth}(J^{e}/kT) - (kT/J^{e})$$

To correlate the parameter for classical spin S_A and S_B , the effective *g*-factors (g_A and g_B)and effective interaction parameter (J^e) are scaled through the following relations.

$$g_{\rm A}^e = g_{\rm A} [S_{\rm A} (S_{\rm A} + 1)]^{1/2}$$

$$g_{\rm B}^e = g_{\rm B} [S_{\rm B} (S_{\rm B} + 1)]^{1/2}$$

$$J^{e} = J[S_{A}(S_{A} + 1)S_{B}(S_{B} + 1)]^{1/2}$$

For the present case, the equation is satisfactory for Mn^{III}-Mn^{II} 1D chain with adequate number of local spins *viz*. $S_A = 5/2$ and $S_B = 2.^{38}$ From the crystallographic data, two consecutive Mn^{III}...Mn^{II} distances are slightly different (5.711Å, 5.584Å, Fig. 9), however, the other structural parameters that control superexchange coupling are very similar (vide infra). So, the magnetic coupling constant (J) can be considered same for the consecutive magnetic centres. The least square fit of the data using equation (2) yields the best fitted parameter J = -0.98 (2) cm⁻¹ with R² = 0.998 with the aim to avoid over-parametrization, the *g* factors was fixed to 2.00 $(g_{Mn(II)} = 2.00, g_{Mn(II)} = 2.00)$.



Fig. 9 Graphical description showing different Mn^{...}Mn separation distances for repeating units and *syn-anti* carboxylate bridging connecting two consecutive Mn^{II} and Mn^{III} centres.

In the present complex, the consecutive Mn^{III} and Mn^{II} ions are connected through threeatom (µ1,3) carboxylate bridge in syn-anti fashion. However, syn-anti carboxylate bridged complexes are rare compared to syn-syn bridged.³⁸ In our present case, Mn^{II} centres are connected to two carboxylate O atoms in syn fashion (Mn-O_{syn} = 2.113Å, 2.116Å and \angle Mn–O_{syn}–C = 141.31°, 136.40°) whereas, the Mn^{III} centers are connected to two carboxylate oxygen with anti fashion (Mn–O_{anti} = 2.054Å, 2.100Å and \angle Mn–O_{anti}–C = 116.51°, 116.58° respectively, Fig. 9). The anti Mn-O distances are found to be smaller than the syn Mn-O distance due to the greater positive charge on that Mn centre. Since, the efficient overlap between the 3d magnetic orbital of the Mn centre and the 2p orbital of the carboxy of oxygen at on 14E would lead to weak antiferromagnetic interaction through the $\mu_{1,3}$ -carboxylate bridge, the extent and nature of magnetic interactions are expected to be dependent on the carboxylate coordination modes. A syn-syn mode generally shows small metal-metal distances due to good overlap of magnetic orbitals and also provides stronger antiferromagnetic coupling. Whereas, syn-anti carboxylate bridges provide comparatively smaller J values because of the expanded metallic core and a mismatch in the orientation of magnetic orbitals.^{39,40} However, these factors are not conclusive controlling factors to regulate the superexchange of magnetic orbitals. The superexchange could also be affected by several other factors too. For instance, the small variations of Mn-O distance and the Mn-O-C angles can affect the overlap through the carboxylate group.⁴¹

Table 3 shows some structural parameters for mixed valent($\mu_{1,3}$) carboxylate bridged Mn^{III}Mn^{II} complexes. The coordination mode of carboxylate in all of these reported mixed valence complex is *syn-syn*. The magnitude of coupling constants for these complexes ranges from (-1.5) to (-1.7) cm⁻¹. In our present case, the bridging mode of carboxylate is *syn-anti* and the coupling is antiferromagnetic with J = -0.98 (2) cm⁻¹. The lower magnitude of *J* compared to the *syn-syn* bridged system is attributable to the less efficient overlap of magnetic orbitals as discussed above. Moreover, apart from carboxylate bridge, the reported complexes also contain additional oxo bridge connecting Mn^{II} and Mn^{III} centres and thus, additional super exchange modes may also play a vital role on their coupling constant values.

Conclusion

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In the present paper, we have structurally characterized for the first time a moanionic bis-chelate of Mn^{III} of the tridentate Schiff base which is derived from alanine and salicyladehyde by growing the single crystals with the help of $[Mn(bpy)_2(H_2O)(ClO_4)]^+$. The resulted species $[{Mn^{III}(L)_2} {Mn^{II}(2,2'-bpy)_2}(ClO_4)(H_2O)_{0.5}]_n$, $(H_2L = N-salicylidene-L-alanine and bpy = 2,2'$ bipyridine) is an unprecedented mixed-valence one-dimensional alternating chain of Mn^{III} andMn^{II} bridged by*syn-anti*carboxylate. The complex shows moderately high catalytic activity for $oxidation of catechol to quinine with <math>k_{cat}$ value (126.9 h⁻¹). It is also found to be catalytically active for oxidation of *o*-amino phenol to 2-aminophenoxazine-3-one and is the first mixed valence Mn^{II/III} compound whose phenoxazinone synthase-like activity is studied with k_{cat} value (738.0 h⁻¹). Magnetic measurement shows that the Mn^{II} and Mn^{III} ions are antiferromagnetically coupled through the *syn-anti* carboxylate bridge and the $\chi_M T$ values have been reproduced very satisfactorily in the whole temperature range with the alternating chain model. The nature and magnitude of the coupling constant are in agreement with the reported *syn-anti* carboxylate bridged Mn^{II} and Mn^{III} complexes.

Supporting Information (see footnote on the first page of this article)

Powder XRD, TGA, IR, UV-Vis, ESI-mass spectra of the complex **1** and mass spectra of $[Mn^{II}(bpy)_2(ClO_4)(H_2O)](ClO_4)$, UV-Vis spectrum of 3,5-DTBC (blank) and OAPH (blank) and of $[Mn^{II}(bpy)_2(ClO_4)(H_2O)](ClO_4)$ with 3,5-DTBC and OAPH, mass spectra of complexies for the literature and their k_{cat} values for which catecholase-like and phenoxazinone synthase-like activities have been analyzed.

CCDC-1818765 (for 1) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References

Published on 19 April 2018. Downloaded by Fudan University on 19/04/2018 17:16:52

1 (a) G. Christou, Acc. Chem. Res., 1989, 22, 328–335; (b) G. Davies, Coord. Chem. Rev., 1969, 4, 199–224.

2 (*a*) R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141–143; (*b*) S. Piligkos, G. Rajaraman, M. Soler, N. Kirchner, J. Slageren, R. Bircher, S. Parsons, H. Güdel, J. Kortus, W. Wernsdorfer, G. Christou and E. K. Brechin, *J. Am. Chem. Soc.*, 2005, **127**, 5572–5580; (*c*) G. Rajaraman, M. Murugesu, E. C. Sañudo, M. Soler, W. Wernsdorfer, M. Helliwell, C. Muryn, J. Raftery, S. J. Teat, G. Christou and E. K. Brechin, *J. Am. Chem. Soc.*, 2004, **126**, 15445–15457; (*d*) J. T. Brockman, J. C. Huffman and G. Christou, *Angew. Chem., Int. Ed.*, 2002, **41**, 2506–2508; (*e*) M. Soler, E. Rumberger, K. Folting, D. N. Hendrickson and G. Christou, *Polyhedron*, 2001, **20**, 1365–1369; (*f*) S. Naiya, S. Biswas, M. G. B. Drew, C. J. Gómez-García and A. Ghosh, *Inorg. Chem.*, 2012, **51**, 5332–5341; (g) P. Kar, P. M. Guha, M. G. B. Drew, Y. Ida, T. Ishida and A. Ghosh, *Dalton Trans.*, 2011, **40**, 3295–3304.

3 M. Liu, D. Q. Zhang and D. B. Zhu, *Dalton Trans.*, 2010, 39, 1781–1785.

4 (a) J. Milios, A. Prescimone, A. Mishra, S. Parsons, W. Wernsdorfer, G. Christou, S. P. Perlepesd and E. K. Brechin, *Chem. Commun.*, 2007, 153–155.

5 M. R. Razali, N. F. Chilton, A. Urbatsch, B. Moubaraki, S. K. Langley, K. S. Murray, G. B. Deacon and S. R. Batten, *Polyhedron*, 2013, **52**, 797–803.

6 M. Murugesu, J. Raftery, W. Wernsdorfer, G. Christou and E. K. Brechin, *Inorg. Chem.*, 2004, **43**, 4203–4209.

7 S. K. Langley, K. J. Berry, B. Moubarakia and K. S. Murray, Dalton Trans., 2009, 973–982.

8 Z. Sun, P. K. Gantzel and D. N. Hendrickson, Inorg. Chem., 1996, 35, 6640-6641.

9 (a) P. Karsten, A. Neves, A. J. Bortoluzzi, J. Strahle and C. M. Mossmer, *Inorg. Chem. Commun.*, 2002, 5, 434–438; (b) P. Kar, Y. Ida, T. Kanetomo, M. G. B. Drew, T. Ishida and A. Ghosh, *Dalton Trans.*, 2015, 44, 9795–9804; (c) P. Kar, R. Haldar, C. J. Gómez-García and A. Ghosh, *Inorg. Chem.*, 2012, 51, 4265–4273; (d) A. Dimitrakopoulou, C. D. Samara, A. A. Pantazaki, M. Alexiou, E. Nordlander and D. P. Kessissoglou, *J. Inorg. Biochem.*, 2008, A102, number 618–628; (e) P. Kar, M. G. B. Drew, A. Ghosh, *Inorg. Chim. Acta*, 2013, 405, 349–355; (f) P. Seth, M. G.B. Drew, A. Ghosh, *J. Mol. Catal. A: Chem.*, 2012, 365, 154–161.

10 (*a*) H. Caot and S. L. Suib, *J. Am. Chem. Soc.*, 1994, **116**, 5334-5342; (*b*) J. Limburg, J. S. Vrettos, H. Chen, J. C. D. Paula, R. H. Crabtree and G. W. Brudvig, *J. Am. Chem. Soc.*, 2001, **123**, 423-430.

11 T. C. Stamatatos, K. A. Abboud, W. Wernsdorfer and G. Christou, *Angew. Chem. Int. Ed.*, 2008, **47**, 6694–6698.

12 (a) A. Das, G. M. Rosair, M. S. E. Fallah, J. Ribas and S. Mitra, *Inorg. Chem.*, 2006, **45**, 3301–3306; (b) D. Deguenon, G. Bernardinelli, J. P. Tuchagues and P. Castan, *Inorg. Chem.*, 1990, **29**, 3031–3037; (c) G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483–3538.

13 (*a*) T. C. Stamatatos, K. A. Abboud and G. Christou, *J. Mol. Struct.*, 2008, **890**, 263–271; (*b*) H. Oshio, N. Hoshino, T. Ito, M. Nakano, F. Renz and P. Gutlich, *Angew. Chem., Int. Ed.*, 2003, **42**, 223–225.

14 (a) A. R. Schake, J. B. Vincent, Q. Li, P. D. W. Boyd, K. Folting, J. C. Huffman, D. N. Hendrickson and G. Christou, *Inorg. Chem.*, 1989, 28, 1915–1923; (b) E. E. Moushi, A. J. Tasiopoulos and M. J. Manos, *Bioinorg. Chem. Appl.*, 2010, 367128–367135; (c) D. M. Low, E. K. Brechin, M. Helliwell, T. Mallah, E. Rivière and E. J. L. McInnes, *Chem. Commun.*, 2003, 2330–2331; (d) J. Kim and H. Cho, *Inorg. Chem. Commun.*, 2004, 7, 122–124.

15 (a) P. Gerbier, D. Ruiz-Molina, J. Gomez, K. Wurst and J. Veciana, *Polyhedron*, 2003, **22**, 1951–1955; (b) L. A. Kushch, G. V. Shilov, R. B. Morgunov and E. B. Yagubskii, *Mendeleev Commun.*, 2009, **19**, 170–171.

16 (*a*) J. Vanco, Z. Travnicek, J. Marek and R. Herchel, *Inorg. Chim. Acta*, 2010, **363**, 3887– -3896; (*b*) A. Li, Y. H. Liu, L. Z. Yuan, Z. Y. Ma and C. L. Zhao, *J. Inorg. Biochem.*, 2015, **146**, 52–60; (*c*) H. Liu, L. Li, Q. Guo, J. Dong, J. Li, C. Z. Xie, W. G. Bao and J. Y. Xu, *Transition Met. Chem.*, 2013, **38**, 441–448; (*d*) F. Sevgi, U. Bagkesici, A. N. Kursunlu and E. Guler, *J. Mol. Struct.*, 2018, **1154**, 256–260.

17 Y. Rodríguez-Martín, J. González-Platas and C. Ruiz-Pérez, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1999, **55**, 186–188.

18 C. M. Rajesh and M. Ray, Dalton Trans., 2014, 43, 12952-12960.

19 G. A. Bain and J. F. Berry, J. Chem. Educ., 2008, 85, 532-536.

Published on 19 April 2018. Downloaded by Fudan University on 19/04/2018 17:16:52

20 G. M. Sheldrick, SHELXS-97, Program for solution of crystal structures, University of Gottingen, Germany, 1997.

21 SAINT, version 6.02, SADABS, version 2.03, Bruker AXS Inc., Madison, WI, 2002.

22 T. Gruene, H. W. Hahn, A. V. Luebben, F. Meilleur and G. M. Sheldrick, J. Appl. Crystallogr., 2014, 47, 462–466.

23 J. Lübben, C. Volkmann, S. Grabowsky, A. Edwards, W. Morgenroth, F. P. Fabbiani, G. M. Sheldrick and B. Dittrich, *Acta Crystallogr., Sect. A: Found. Adv.*, 2014, **70**, 309–316.

24 PLATON, Molecular Geometry Program: A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7-13.

25 L. J. Farrugia, J. Appl. Crystallogr., 1997, 30, 565-565.

26 L. J. Farrugia, J. Appl. Crystallogr., 1999, 32, 837-838.

View Article Online DOI: 10.1039/C8NJ00414E

27 (*a*) A. Neves, L. M. Rossi, A. J. Bortoluzzi, B. Szpoganicz, C. Wiezbicki, E.Schwingel, W. Haase and S. Ostrovsky, *Inorg. Chem.*, 2002, **41**, 1788–1794; (*b*) E. Monzani, L. Quinti, A. Perotti, L. Casella, M. Gullotti, L. Randaccio, S. Geremia, G. Nardin, P. Faleschini and G. Tabbi, *Inorg. Chem.*, 1998, **37**, 553–562.

28 (*a*) W. Liu and H. H. Thorp, *Inorg. Chem.*, 1993, **32**, 4102–4105; (*b*) A. A. Alaimo, A. Worrell, S. D. Gupta, K. A. Abboud, C. Lampropoulos, G. Christou and T. C. Stamatatos, *Chem. - Eur. J.*, 2018, **24**, 2588–2592.

29 (*a*) İ. Şakiyan, N. Gündüz and T. Gündüz, *Synth. React. Inorg. Met.-Org. Chem.*, 2001, **31**, 1175–1187; (*b*) Í. Sakıyan, E. Logoglu, S. Arslan, N. Sari and N. Sakıyan, *BioMetals*, 2004, **17**, 115–120; (*c*) Í. Sakıyan, *Transition Met. Chem.*, 2007, **32**, 131–135.

30 (*a*) P.A.N. Reddy, M. Nethaji and A. R. Chakravarty, *Eur. J. Inorg. Chem.*, 2004, **2004**, 1440–1446; (*b*) P. A. N. Reddy, M. Nethaji and A. R. Chakravarty, *Inorg. Chim. Acta*, 2002, **337**,450–458; (*c*) Z. Z. Li, L. Du, J. Zhou, M. R. Zhu, F. H. Qian, J. Liu, P. Chen and Q. H. Zhao, *Dalton Trans.*, 2012, **41**, 14397–14403.

31 (a) M. R. Mendoza-Quijano, G. Ferrer-Sueta, M. Floresálamo, N. Aliaga-Alcalde, V. Gomez-Vidales, V. M. Ugalde- Saldívara and L. Gasque, *Dalton Trans.*, 2012, 41, 4985–4997;
(b) J. Ackermann, F. Meyer, E. Kaifer and H. Pritzkow, *Chem. - Eur. J.*, 2002, 8, 247–258.

32 (*a*) J. Balla, T. Kiss and R. F.Jameson, *Inorg. Chem.*, 1992, **31**, 58–62; (*b*) K. Selmeczi, M. Règlier, M. Giorgi and G. Speier, *Coord. Chem. Rev.*, 2003, **245**, 191–201.

33 (a) S. K. Dey and A. Mukherjee, *Coord. Chem. Rev.*, 2016,**310**, 80–115; (b) A. Hazari, L. K. Das, R. M. Kadam, A. Bauzá, A. Frontera and A. Ghosh, *Dalton Trans.*, 2015, **44**, 3862–3876;
(c) J. Adhikary, A. Chakraborty, S. Dasgupta, S. K. Chattopadhyay, R. Kruszynski, A. Trzesowska-Kruszynska, S. Stepanovic, M. Gruden-Pavlovic, M. Swartf and D. Das, *Dalton Trans.*, 2016, **45**, 12409–12422; (d) L. K. Das, A.Biswas, J. S.Kinyon, N. S. Dalal, H. Zhou and A. Ghosh, *Inorg. Chem.*, 2013, **52**, 11744–11757; (e) A. Guha, T. Chattopadhay, N. D. Paul, M. Mukherjee, S. Goswami, T. K. Mondal, E. Zangrando and D. Das, *Inorg. Chem.*, 2012, **51**, 8750–8759; (f) N. Sarkar, K. Harms, A. Frontera and S. Chattopadhay, *New J. Chem.*, 2017, **41**, 8053–8065; (g) M. Pait, M. Shatruk and D. Ray, *Dalton Trans.*, 2015, **44**, 11741–11754.

34 (a) J. Kaizer, G. Baráth, R. Csonka, G. Speier, L. Korecz, A. Rockenbauer and L. Párkányi, J Inorg Biochem., 2008, 102, 773–780; (b) S. C. Kumar, A. K. Ghosh, J. D. Chen and R. Ghosh, Inorg. Chim. Acta, 2017, 464, 49–54; (c) N. C. Jana, P. Brandão and A. Panja, J Inorg Biochem., 2016, 159, 96–106; (d) N. Sarkar, K. Harms and S. Chattopadhay, Polyhedron, 2018, 141, 198–207; (e) K. S. Banu, T. Chattopadhyay, A. Banerjee, M. Mukherjee, S. Bhattacharya, G. K. Patra, E. Zangrando and D. Das, Dalton Trans., 2009, 8755–8764; (f) M. U. Triller, D. Pursche, W. Y. Hsieh, V. L. Pecoraro, A. Rompel and B. Krebs, Inorg. Chem., 2013, 42, 6274–6283; (g) K. Chattopadhyay, G. A. Craig, M. J. H. Ojea, M. Pait, A. Kundu, J. Lee, M. Murrie, A. Frontera, and D. Ray, *Inorg. Chem.*, 2017, **56**, 2639–2652; (*h*) D. Mondal and M. C. Majee, *Inorg. Chim. Acta*, 2017, **455**, 70–77; (*i*) A. Panja, N. C. Jana, S. Adak and K. Pramanik, *Inorg. Chim. Acta*, 2017, **459**, 113–123; (*j*) A. Jana, N. Aliaga-Alcalde, E. Ruiz and S. Mohanta *Inorg. Chem.*, 2013, **52**, 7732–7746; (*k*) P. Seth and A. Ghosh, *RSC Adv.*, 2013, **3**, 3717–3725.

35 (*a*) A. Panja, *Polyhedron*, 2014, **79**, 258–268; (*b*) N. Sarkar, M. Das and S. Chattopadyay, *Inorg. Chim. Acta*, 2017, **457**, 19–28; (*c*) S. Banerjee, P. Brandão, A. Bauzá, A. Frontera, M. Barcelo-Oliver, A. Panja and A. Saha, *New J. Chem.*, 2017, **41**, 11607–11618; (*d*) N. Sarkar, K. Harms, A. Frontera and S. Chattopadhay, *ChemistrySelect*, 2017, **2**, 2975–2984.

36 M. E. Fisher, Am. J. Phys., 1964, 32, 343-346.

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37 M. Drillon, E. Coronado, D. Beltran and R. Georges, Chem. Phys., 1983, 79, 449-453.

38 O. Kahn, Molecular Magnetism, VCH, Weinheim, Germany, 1993.

39 *a*) D. K. Towle, K. Hoffmann, W. E. Hatfield, P. Singh and P. Chaudhuri, *Inorg. Chem.*, 1988, **27**, 394–399; (*b*) E. Colacio, J. M. Dominguez-Vera, J. P. Costes, R. Kivekãs, J. P. Laurent, J. Ruiz and M.Sundberg, *Inorg. Chem.*, 1992, **31**, 774–778.

40 (*a*) R. L. Carlin, K. Kopinga, O. Kahn and M. Verdaguer, *Inorg. Chem.*, 1986, **25**, 1786–1786; (*b*) F. Lloret, M. Julve, R. Ruiz, Y. Journeaux, K. Nakatani, O. Kahn and J. Sletten, *Inorg. Chem.*, 1993, **32**, 27–31.

41 P. Kar, R. Biswas, Y. Ida, T. Ishida and A. Ghosh, Cryst. Growth Des., 2011, 11, 5305–5315.

42 C. J. Milios, C. P. Raptopoulou, A. Terzis, R. Vicente, A. Escuer and S. P. Perlepes, *Inorg. Chem. Commun.*, 2003, **6**, 1056–1060.

43 C. J. Milios, C. P. Raptopoulou, A. Terzis, R. Vicente, A. Escuer and S. P. Perlepes, *Dalton Trans.*, 2005, 501–511.

Complex	1
Formula	C ₄₀ H ₃₅ Mn ₂ N ₆ O _{10.5} Cl
Formal weight	913.05
Crystal system	Monoclinic
Space group	P21
a/Å	12.519 (2)
<i>b</i> /Å	14.724(2)
c/Å	13.436(2)
$\alpha^{\prime \circ}$	90
$eta\!/^{\circ}$	117.480(4)
γ/°	90
V/Å ³	2197.2(6)
Z	2
$D_c/g \text{ cm}^{-3}$	1.377
μ/mm^{-1}	0.696
F (000)	932
R(int)	0.05
Total reflections	23090
Unique reflections	8067
Data with $I > 2\sigma(I)$	6149
R_1^a on $I > 2\sigma(I)$	0.047
wR_2 (all data) ^b	0.1284
GOF^c on F^2	1.02
Temperature (K)	257(2)

Table 1 Crystal data and structure refinement of complex 1

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 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| \sum |F_{o}|, \ {}^{b}wR_{2} \ (F_{o}^{2}) = \left[\sum [w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w \ F_{o}^{4}\right]^{\frac{1}{2}} \text{ and } {}^{c}GOF = \left[\sum [w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{params})\right]^{\frac{1}{2}}$

1							
Bond distances (Å)	ond distances (Å)						
Mn(1)-O(1)	1.954(5)	Mn(1)-O(2)	1.974(6)				
Mn(1)-O(3)	2.054(4)	Mn(1)-O(4)	2.100(5)DC				
Mn(1)-N(1)	1.983(7)	Mn(1)-N(2)	1.986(6)				
Mn(2)-O(5)	2.116(4)	Mn(2)-N(3)	2.290(5)				
Mn(2)-N(4)	2.267(6)	Mn(2)-N(5)	2.258(6)				
Mn(2)-N(6)	2.245(7)	Mn(2)-O(6) ^a	2.113(5)				
Bond angles(°)							
O(1)-Mn(1)-O(2)	92.2(2)	O(1)-Mn(1)-O(3)	169.4(3)				
O(1)-Mn(1)-O(4)	90.1(2)	O(1)-Mn(1)-N(1)	89.4(2)				
O(1)-Mn(1)-N(2)	99.6(2)	O(2)-Mn(1)-O(3)	90.65(19)				
O(2)-Mn(1)-O(4)	166.8(3)	O(2)-Mn(1)-N(1)	99.8(3)				
O(2)-Mn(1)-N(2)	88.6(2)	O(3)-Mn(1)-O(4)	89.43(18)				
O(3)-Mn(1)-N(1)	80.1(2)	O(3)-Mn(1)-N(2)	90.7(2)				
O(4)-Mn(1)-N(1)	93.2(2)	O(4)-Mn(1)-N(2)	78.2(2)				
N(1)-Mn(1)-N(2)	167.5(2)	O(5)-Mn(2)-N(3)	162.3(2)				
O(5)-Mn(2)-N(4)	89.88(19)	O(5)-Mn(2)-N(5)	89.18(19)				
O(5)-Mn(2)-N(6)	104.4(2)	$O(5)-Mn(2)-O(6)^{a}$	91.35(19)				
N(3)-Mn(2)-N(4)	72.6(2)	$N(3)-Mn(2)-O(6)^{a}$	90.7(2)				
N(3)-Mn(2)-N(6)	92.5(2)	$O(6)^{a}-Mn(2)-N(3)$	89.7(2)				
N(4)-Mn(2)-N(5)	97.4(2)	N(4)- Mn(2)-N(6)	162.2(2)				
$O(6)^{a}-Mn(2)-N(4)$	85.8(2)	N(5)-Mn(2)-N(6)	72.6(2)				
$O(6)^{a}-Mn(2)-N(5)$	176.8(2)	$O(6)^{a}-Mn(2)-N(6)$	104.2(2)				
Symmetry Element ^a =	$= 1 - x \frac{1}{2} + y \frac{1}{2}$	-7					

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Table 2 Selected bond distances (Å) and angles (°) for complex 1

Compund	Mn ^{III} -	Mn ^{II} -	Mn	∠Mn ^{III} -	∠Mn ^{II} -	J	refe	rence
1	O _{syn} Å	O _{syn} Å	 Mn Å	O _{syn} -C	O _{syn} view Ar I: 10.1039/C81	tic cm - NJD04141		INSCI
$[Mn^{II}_{2} Mn^{III}_{2}(O_{2}CPh)_{2}Br_{2}\{(py)_{2}CNO\}_{2}\{(py)_{2}CO_{2}\}_{2}]$	2.068	2.120	3.430	134.16	132.40	- 1.7	42	Mah
$[Mn_{2}^{II}Mn_{2}^{III}(O_{2}CMe)_{2}Br_{2}\{(py)_{2}CNO\}_{2}\{(py)_{2}CO_{2}\}_{2}]$	2.089	2.140	3.419	132.52	133.20	- 1.5	42	6d
$[Mn^{II}_{2}Mn^{III}_{2}(O_{2}CMe)_{2}Br_{2}\{(py)_{2}CNO\}_{2}\{(py)_{2}CO_{2}\}_{2}].2MeCN$	2.089	2.140	3.419	132.52	133.20	- 1.7	43	ept
$[Mn_4(O_2CMe)_2\{(py)_2CO_2\}_2\{(py)_2CNO\}_2Br_2]\cdot 2MeCN$	2.079	2.152	3.432	133.05	133.83	- 1.5	43	ACC
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Table 3 Structural parameters of some mixed valence carboxylate bridged Mn^{II}Mn^{III} polynuclear complexes and their corresponding magnetic interaction parameters $(J \text{ cm}^{-1})$.

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A one-dimensional mixed-valence Mn^{II}/Mn^{III} chain has been synthesized using N-salicylidene-L-alanine and 2,2'-bipyridine. The complex shows moderate catecholase and phenoxazinone synthase-like activity.

