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1

Syntheses, crystallographic characterization, catecholase activity and magnetic properties of three novel aqua bridged dinuclear nickel (II) complexes

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Abstract

Three novel μ_2 -aqua bridged dinuclear Ni(II) complexes, $[Ni_2(HL^1)_4(H_2O)]$ (1), $[Ni_2(HL^2)_4(H_2O)]$ (2) and $[Ni_2(HL^3)_4(H_2O)]$ (3) have been synthesized using Schiff base ligands derived from 5-amino-1- pentanol and salicylaldehyde (H_2L^1) , 5-bromo salicylaldehyde (H_2L^2) and 3-methoxy salicylaldehyde (H_2L^3) respectively. They are characterized by a variety of physical techniques including elemental analysis, infrared and UV-Vis spectroscopy, NMR, cyclic voltammetry, variable temperature magnetic measurements and single crystal X-ray diffraction. X-ray crystallographic analysis reveals that all the three complexes possess distorted octahedral environment with a bridging aqua ligand. Complexes 1 and 3 exhibit 3D supramolecular architecture whereas 2 demonstrates a 2D netlike arrangement along ab plane. Catecholase activity of the dinuclear Ni(II) systems are investigated using 3, 5-di-tertbutylcatechol as the substrate. The complexes are efficient catalysts with turnover numbers 1.87 x 10⁴, 1.79 x 10⁴ and 1.38 x 10⁴ h⁻¹ for 1, 2 and 3 respectively. The probable structures of the intermediates formed during the process are proposed on the basis of kinetic and spectral analyses. The magnetic data disclose that weak ferromagnetic couplings are transmitted between the metal centers and the magnetic properties are correlated with the structural features around the Ni(II) centers.

Keywords: Dinuclear Ni(II) complex; Aqua bridged; Crystal structure; Catechol oxidation; Ferromagnetic

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2

1. Introduction

Dinuclear Ni(II) complexes bridged by water, hydroxide ion or oxo group emerge as an interesting class of compounds because of their relevance to the active site of the hydrolytic enzyme urease [1-5]. In the literature, octahedrally coordinated polynuclear Ni(II) complexes are an interesting class of compound because of a variety of molecular structures and magnetic interactions [6]. Again, magnetic study of various di-, tri- and polynuclear Ni(II) complexes with different bridging groups like carboxylates and the μ -1,1-azido bridges derives its interest from their potential to use as molecular magnetic materials [7,8]. The bridging abilities of the phenolate oxygen atom have been exploited extensively for the purpose of designing dinuclear species featuring generally antiferromagnetic behaviour, though a couple of complexes showing ferromagnetic coupling have also been described in the literature [4e, 9-11]. A large number of structural parameters affect the super-exchange mechanism in these systems, such as the Ni–O–Ni bridging angle, Ni–O bond distance and dihedral angle between the Ni–O–Ni plane and the remaining coordination plane [6c,12]. Among the several reports of double phenoxide bridged Ni(II) dimers [8d,8e,6c,13], the presence of an aqua bridge in dinuclear Ni(II) complexes is relatively scanty [4e,12b-d,14].

It is well documented that bimetallic skeletons exist at active sites of many enzymes and play an essential role in biological systems [15]. There are a couple of recent reports describing phenoxide bridged dinickel(II) complexes that serve to mimic dinuclear biological active sites. For instance, phenoxo bridged dinickel(II) complexes are developed with labile coordination site(s) for the hydrolysis of phosphate esters [16]. Recently, Das et al and Biswas et al have reported catalytic activity of a dinuclear nickel(II) complex towards the oxidation of 3,5-ditert-butylcatechol under aerobic condition [17].

Therefore, the chemistry of bridged dinuclear nickel complexes is extensively investigated due to their potential applications in bioinorganic chemistry, magneto chemistry, materials chemistry and catalysis. In order to explore these possibilities, we have carried out a thorough investigation of a series of dinickel(II) complexes, $[Ni_2(HL^1)_4(H_2O)](1)$, $[Ni_2(HL^2)_4(H_2O)](2)$ and $[Ni_2(HL^3)_4(H_2O)](3)$ using Schiff base ligands derived from 5-amino-1- pentanol and salicylaldehyde(H_2L^1), 5-bromo salicylaldehyde(H_2L^2) and 3-methoxy salicylaldehyde(H_2L^3) respectively.

2. Experimental section

2.1. Materials

5-amino-1-pentanol, salicylaldehyde, 5-bromo salicylaldehyde and 3-methoxy salicylaldehyde were procured from Sigma-Aldrich. Solvents were used as received commercially.

2.2. Methods

Elemental (C, H and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were recorded in the region 400–4000 cm⁻¹ on a Bruker-Optics Alpha– T spectrophotometer with samples as KBr disks. ¹H NMR spectra were recorded in the CDCl₃ solvent on a Bruker AV 300 MHz Supercon NMR system dual probe. Cyclic voltammetric (CV) measurements were done using a BASi Epsilon-EC electrochemical analyzer. The concentration of the supporting electrolyte, tetrabutylammonium perchlorate(TBAP) was 0.1 M, while that of the complex was 1 mmol. Cyclic voltammetry measurements were carried out in DMF solution at 295 K with a glassy carbon disk working electrode and the scan rate was 100 mVs⁻¹. Electronic spectra were recorded on a MICROMASS Q-TOF mass spectrometer. Magnetic measurements in the temperature range 1.8-300 K were performed using a Quantum Design SQUID-based MPMSXL-5-type magnetometer. The SQUID magnetometer was calibrated with the palladium rod sample (Materials Research Corporation, measured purity 99.9985%). The superconducting magnet was generally operated at a field strength ranging from 0 to 5 T. Measurements were

3

made at a magnetic field of 0.5 T. Corrections are based on subtracting the sample – holder signal and contribution χ_D estimated from the Pascal constants [18]. Magnetization measurements were conducted at 2 K in the magnetic field from 0 to 5 T. EPR measurement was done by Magnettech GmbH MiniScope MS400 spectrometer equipped with a temperature controller TC H03 (microwave frequency was measured with a frequency counter FC400) at77 K.

2.3. Syntheses of the ligands

The ligands H_2L^1 , H_2L^2 , H_2L^3 (Scheme 1) were prepared by refluxing 5-Amino-1- pentanol(1.032 g, 10 mmol) with salicylaldehyde (1.08 mL, 10mmol), 5-Bromo-2-hydoxybenzaldehyde (2.01 g, 10 mmol) and 2-hydroxy-5- methoxy benzaldehyde (1.521 g, 10 mmol) respectively in methanol (40 mL) for 30 minutes. The volatile components were removed in vacuo to give the bidentate Schiff base ligands H_2L^1 , H_2L^2 and H_2L^3 which were subsequently used for complex formation.

 H_2L^1 : Yield 87%. Anal. Found (Calc.) (%) for $C_{12}H_{17}N_1O_2$ (MW = 207.125 g/mol): C, 69.35(69.53); H, 8.39 (8.27); N, 6.54 (6.76).¹H NMR (300 MHz, CDCl₃): δ 8.17 (s, 1H, CH=N), 7.20 – 7.15 (m, 1H, Ar–H), 7.12–7.09 (m, 1H, Ar–H), 6.87 (d, J = 8.4 Hz, Ar–H), 6.76 – 6.71 (m, 1H, Ar–H), 3.52 – 3.42 (m, 4H, CH₂N, CH₂OH), 1.63 – 1.53 (m, 2H, CH₂CH₂OH), 1.50–1.43(m,2H, CH₂CH₂N), 1.37–1.30 (m,2H,CH₂CH₂CH₂OH).

 H_2L^2 : Yield 83%. Anal. Found (Calc.) (%) for $C_{12}H_{16}N_1O_2Br$ (MW = 285.036 g/mol): C, 50.40 (50.37); H, 5.61 (5.64); N, 4.95 (4.89). ¹H NMR (300 MHz, CDCl₃): δ 8.37 (s, 1H, CH=N), 8.23 (d, 1H, J = 2.7 Hz, Ar–H), 8.20 – 8.16 (dd, 1H, $J_1 = 3$ Hz, $J_2 = 9.3$ Hz, Ar–H), 6.94 (d, 1H, J = 9 Hz, Ar–H), 3.71 – 3.66 (m, 4H, CH₂N, CH₂OH), 1.84 – 1.75 (m, 2H, CH₂CH₂OH), 1.68 – 1.59 (m, 2H, CH₂CH₂N), 1.55 – 1.45 (m, 2H, CH₂CH₂CH₂OH).

 H_2L^3 : Yield 84%. Anal. Found (Calc.) (%) for $C_{12}H_{19}N_1O_3$ (MW = 237.136 g/mol): C, 65.73 (65.8); H, 8.29 (8.07); N, 6.01 (5.90).¹H NMR (300MHz, CDCl₃): δ 8.22 (s, 1H, CH=N), 6.90 – 6.87 (m, 2H, Ar–H), 6.73 (d, 1H, *J* = 2.4 Hz, Ar–H), 3.73 (s, 3H, CH₃O), 3.61 – 3.52 (m, 4H, CH₂N, CH₂O), 1.72–1.60(m, 2H, CH₂CH₂OH), 1.57–1.53 (m, 2H, CH₂CH₂N), 1.46 – 1.38 (m, 2H, CH₂CH₂CH₂OH).

2.4. Syntheses of the complexes

2.4.1. Synthesis of $[Ni_2(HL^1)_4(H_2O)]$ (1)

5 mL methanolic solution of NiCl₂.6H₂O (0.832 g, 3.5 mmol) was added to 20 mL methanolic solution of H₂L¹ (1.45 g, 7 mmol) under stirring condition. The green color was intensified when methanolic solution of triethylamine (0.707 g, 7 mmol) was added slowly to the mixture. Then the resulting mixture was stirred for 3 h. The resulting dark green solution was evaporated to dryness and recrystallised from minimum amount of DMF. Good X-ray diffraction quality single crystals were obtained after 2 days.Yield 70%. Anal. Found (Calc.) (%) for C₄₈H₆₆N₄Ni₂O₉ (1) (MW = 964.45 g/mol): C, 59.836 (60.025); H, 7.031 (6.926); N, 5.688 (5.833). IR (KBr-cm⁻¹): v(O-H),3325;v(C=N),1630;v(C-O,1°alcohol),1031; v(C-O,phenoxide),1195.

2.4.2. Synthesis of $[Ni_2(HL^2)_4(H_2O)]$ (2)

In a manner similar to that for **1**, NiCl₂.6H₂O (0.832 g, 3.5 mmol), H_2L^2 (2.0 g, 7 mmol) and triethylamine (0.707 g, 7 mmol) gave complex **2**. Yield 69%. Anal. Found (Calc.) (%) for $C_{48}H_{62}Br_4N_4Ni_2O_9$ (**2**) (MW = 1276.03 g/mol): C, 45.293 (45.180); H, 4.735 (4.897); N, 4.467 (4.390). IR(KBr- cm⁻¹): v(O-H), 3496; 2930; v(C-O,1°alcohol),1038; v(C=N),1630; v(C-O,phenoxide), 1214.

2.4.3. Synthesis of $[Ni_2(HL^3)_4(H_2O)]$ (3)

In a similar way, NiCl₂.6H₂O (0.832 g, 3.5 mmol), H₂L³ (1.66 g, 7 mmol) and triethylamine (0.707 g, 7 mmol) gave complex **3**.Yield 64%. Anal. Found (Calc.) (%) for $C_{52}H_{74}N_4Ni_2O_{13}$ (**3**) (MW = 1112.52 g/mol): C, 57.836 (57.800); H, 6.811 (6.092); N, 5.225 (5.185). IR(KBr-cm⁻¹): v(O-H), 3402; v(sp²C-H), 2859; v(aromatic C-H), 2927; v(C=N), 1632; v(C-O, 1 alcohol), 1027; v(C-O, phenoxide), 1216.

4

2.5. Crystal data collection and refinement

The crystallographic data of the compounds are summarized in Table 1. Diffraction data were collected on a Nonius APEX-II diffractometer with CCD-area detector at 150 K using graphite-monochromated Mo K α radiation (k = 0.71073 Å). Crystal structure was determined by direct methods and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-squares refinements on F² using SHELXL-97 [19a]. Absorption correction was done by Multiscan Absorption Correction method. The contribution of the electron density associated with disordered solvent molecules were removed by the SQUEEZE subroutine in PLATON [19b]. Prior to SQUEEZE, all non-hydrogen atoms were made anisotropic and all hydrogen atoms were inserted at their calculated positions, riding on the atoms to which they are attached. The hydrogen atoms were refined isotropically, while the non hydrogen atoms were refined anisotropically.

3. Results

3.1. Synthesis of ligand and metal complexes

The Schiff base ligands H_2L^1 , H_2L^2 , H_2L^3 were synthesized by adopting a modified procedure described by Darensbourg et.al. [20a], taking respective aldehyde and 5-amino-1-pentanol under refluxing condition in MeOH and characterized by FTIR and¹H NMR spectroscopy. (Figs. S1a, S1b and S1c in the supporting information). The preparation of the nickel compounds of the present series followed almost the same method (Scheme 2). Treatment of these ligands with NiCl₂.6H₂O afforded dark green block shaped crystals **1**, **2** and **3** after recrystallization from DMF suitable for X-ray diffraction study. The complexes retain their integrity both in solid and solution phase.

3.2. Spectroscopic characterization

3.2.1. FTIR spectroscopy

The infrared spectra of the three compounds are very similar (Figs. S2a, S2b and S2c in the supporting information). Focus is mainly on the stretching vibrations of the azomethine C=N and C-O(phenoxide) of the ligands because of the possibility to infer their coordination modes. A diagnostic sharp absorption at ca. 1630-1632 cm⁻¹ is due to the C=N stretching of the Schiff base ligand. The medium intensity bands at ca. 1195-1216 cm⁻¹ are assigned to the C-O (phenoxide) stretching. The O-H stretching vibrations are observed at 3325 cm⁻¹, 3496 cm⁻¹ and 3402 cm⁻¹ respectively.

3.2.2. UV-Visible spectroscopy

The absorption bands in the electronic spectra, taken in methanol solution, exhibit very similar spectral patterns for all the three complexes. They depict a distinct band at 617 nm, 631 nm and 620 nm for **1**, **2** and **3** respectively which may be assigned to the spin allowed d-d transition ${}^{3}T_{1g} \leftarrow {}^{3}A_{2g}$. Another broad band centered at 1067 nm for **1**, **2** and **3** is assignable to the spin allowed d-d transition ${}^{3}T_{2g} \leftarrow {}^{3}A_{2g}$ (Fig. S6a in supporting information). The electronic spectra of **1**, **2** and **3** resemble the spectra of the six coordinate Ni(II) complexes depicted in literature [20(b)]. The solid state reflectance spectra of the complexes show a broad band centred at 1054 nm, 1039 nm and 1056 nm for complexes **1**, **2** and **3** respectively assignable to the spin allowed d-d transition ${}^{3}T_{2g} \leftarrow {}^{3}A_{2g}$. The bands for ${}^{3}T_{1g} \leftarrow {}^{3}A_{2g}$ transition appear at 619 nm, 606 nm and 621 nm respectively for complexes **1**, **2** and **3**. The solid state spectrum further shows a very small, sharp feature at 1193, 1191 and 1200 nm region due to spin forbidden ${}^{1}E \leftarrow {}^{3}A_{2}$ transition. The intense bands appeared at 347 nm, 365 nm and 410 nm for **1**, **2** and **3** respectively are due to L \rightarrow M charge transfer transition. (Fig. S6b in the supporting information). All these spectral features for **1-3** are in agreement with their crystal structures described below.

3.3. Description of the solid state structures of complexes 1, 2 and 3

The crystal structures of complexes **1-3** are determined by the X-ray diffraction study. The atom numbering scheme for these complexes is provided in Scheme 3 and the selected bond lengths and bond angles are gathered in Table 2.

The crystal structure of 1 consists of a discrete dinuclear unit [Ni₂(HL¹)₄(H₂O)] containing two independent nickel atoms, Ni1 and Ni2, surrounded by four Schiff base ligands that involve their imine nitrogen and phenoxide oxygen atoms for bonding to the metal centers (Fig. 1a). Out of these four Schiff bases, the phenoxide oxygen atoms of two Schiff bases are involved in bridging the two nickel centers. In addition to that the two nickel centers are further capped by an aqua ligand resulting in a triple oxygen bridged Ni₂O₃ species. Each nickel(II) center bonds with two imine nitrogen atoms, three phenoxide oxygen atoms from the Schiff bases and an aqua ligand forming a distorted octahedral environment. The two nickel atoms are separated by 2.988 Å [21]. The two phenoxide bridging angles, Ni(1)-O(3)-Ni(2) and Ni(1)-O(2)-Ni(2) are 92.86(10)° and 92.57(10)° respectively, and the water bridge angle Ni(1)–O(1)–Ni(2) is 80.11(11)°. It is worth noting that the double phenoxide bridge connecting both Ni(II) ions is asymmetric because each Ni(II) ion is closer to its own phenoxide oxygen atom (Ni1 – O3= 2.005(2) Å) than to the phenoxide oxygen atom of another Schiff base (Ni1 – O2 = 2.131(3) Å) as observed in other similar phenoxide bridged species [14c]. The bridging water molecule is slightly asymmetrically bonded between the two metal atoms [Ni(1)–O(1) 2.334(3)Å; Ni(2)–O(1) 2.310(3)Å]. These distances are rather longer compared to those found in other aqua-bridged dinuclear Ni(II) complexes, where it lies in the range of 2.09–2.25 Å [14b,22a,22b]. Argument in support of the unusually longer bond lengths can be provided in terms of bond angle of Ni(2)-O(1)-Ni(1) as $80.11(11)^{\circ}$ which is smaller than other reported complexes [14b]. Therefore, angle strain may play an important role in lengthening the Ni – O (water) bonds. Again O(1) participates in hydrogen bonding with a pendant –OH group of a Schiff base ligand which can also rationalize the lengthening of the Ni - O (water) bonds. The Ni - Nimine bond distances range from 2.030(3) to 2.065(4)Å; the Ni – Ophonexo distances are in the range of 1.987(3) - 2.131 Å similar to those found in related systems [8e, 13c, 13e, 20c].

The four pendant -OH groups present in **1** play significant role in stabilizing the crystal lattice by participating in extensive hydrogen bonding (Table 3). Each of the four pendant –OH groups offers a bifurcated hydrogen bonding provision to its neighbour [22c]. Here two different kinds of hydrogen bondings are operative. Two of the pendant – OH groups are engaged in H-bonding interaction with pendant –OH groups of adjacent moieties via O(7)-H(7A)…O(9) =2.732(9)Å and O(9)-H(9)…O(7) =2.908(10) Å. As a result of this interaction, one pendant arm coming from four neighbouring dinickel moieties each congregates at the center to form a rectangular core in the packing diagram (Fig. 1b). Other two pendant arms are actively involved in strong H-bonding with the phenoxide oxygen atoms and the bridging water molecule (O(8)-H(8)…O(4) = 2.627(4)Å, O(1)-H(49)…O(6) = 2.778(5)Å, O(6)-H(6)…O(5) = 2.659(4) and O(1)-H(51)…O(8) = 2.749(5)Å). Combined effect of these H-bonding interactions result in the final architecture as a 3D supramolecular network for **1** as depicted in Fig. 1c.

As depicted in Fig. 2, the dimeric structure contains a crystallographic two-fold axis through the bridging water molecule O(1) and can be expressed as $[Ni(HL^2)_2(1/2H_2O)]_2$ consisting of a Ni₂O₃ core like complex **1**. The bridging water molecule symmetrically binds the two nickel atoms with Ni – O_{water} bond length of 2.300(4)Å and the Ni atoms are separated by 2.971 Å with phenoxide bridging angle, Ni(1) – O(3) – Ni(1_a) = 92.50(9)° and the water bridge angle Ni(1) – O(1)– Ni(1_a) is 80.46(15)°. The average Ni – O_{phenoxo} bond length is 2.045 Å while the Ni – N_{imine} bond distance is 2.050(3) Å.

For complex 2, the H-bonding pattern is quite different from 1 (Table 3). Unlike 1, here only two pendant –OH groups participate in H- bonding. Here each dinuclear unit connects two neighbouring units via two pendant –OH groups $(O(4)-H(15)\cdots O(2) = 2.684(4)\text{Å})$. Again this unit is connected to other two adjacent moieties utilizing the bridging aqua ligand and phenoxide oxygen $(O(1)-H(31)\cdots O(4) = 2.745(4)\text{Å})$ (Fig. S3a). This type of interconnection propagates to afford a two dimensional net like architecture along ab plane (Fig.S3b).

The coordination features of **3** closely resemble those of **1** and **2**. Similar to complex **1**, the dinuclear structure of complex **3** can be formulated as $[Ni_2(HL^3)_4(H_2O)]$ with nickel(II) ions located in distorted octahedral environment as shown in Fig. 3. The two Ni atoms are separated by 2.984 Å with two phenoxide bridging angles, Ni(1)–O(10) – Ni(2) of 93.26(12)° and Ni(1) – O(4) – Ni(2) of 92.81(12)° and the water bridge angle Ni(1) – O(13) – Ni(2) of 79.69(11)°. The Ni–N_{imine}, Ni–O_{phenoxo} distances are in the ranges 2.049Å - 2.030Å and 1.975Å - 2.128Å respectively and the average Ni – O_{water} length is 2.328 Å.

Unlike complex 1 and 2, here three pendant –OH groups are involved in H –bonding to propagate the network. The phenoxide oxygen and the bridging aqua ligand undergo extensive H – bonding interaction with two of the pendant –OH groups of another moiety $(O(6) - H(60) \cdots O(7) = 2.644(5) \text{ Å}, O(9) - H(90) \cdots O(1) = 2.651(5), O(13) - H(10) \cdots O(9) = 2.738(5) \text{ Å} and O(13) - H(20) \cdots O(6) = 2.727(6) \text{ Å}) (Fig.S4a). The third pendant arm is utilized in H – bonding with –OCH₃ group <math>(O(3) - H(30) \cdots O(8) = 2.850(6) \text{ Å})$ generating as a whole a 3D supramolecular layer architecture (Fig.S4b).

6

3.4. Catecholase activity

A couple of recent reports on catecholase activity promoted by dinickel (II) complexes led to this investigation of interaction between 3,5-di-tertbutylcatechol (3,5-DTBCH₂) and the dinuclear nickel center in 1, 2 and 3. A detailed kinetic investigation of catechol oxidation reaction was therefore undertaken. In most of the cases, the study of catecholase activity is performed with 3, 5 DTBCH₂ as a model substrate as its low redox potential makes it easy to oxidize and the bulky tertbutyl substituents prevent further oxidation reactions such as ring-opening [23]. The oxidized product 3, 5- di-tertbutylquinone shows maximum absorption at 402 nm in pure methanol. For studying the catecholase activity of the synthesized complexes, 10⁻⁴ M methanolic solutions of the three complexes were treated with 10⁻² M 3, 5-di-tert butyl catechol, under aerobic conditions. All the three dinuclear nickel(II) complexes display significant catalytic activity towards oxidation of 3, 5-di-tertbutylcatechol (3, 5 DTBCH₂) to 3,5-di*tert*butylquinone (3,5-DTBQ) in methanolic medium. Complex **1** has a broad peak at 407 nm which upon addition of 3.5 DTBCH₂ gradually disappear with progress in time. Ultimately it gets vanished and subsequently a peak is generated at 402 nm characteristic of 3,5-DTBO. The spectral outputs are depicted in Fig. 4a.(See supporting information Figs. S5a-f for 2 and 3). The kinetics of the 3, 5-DTBCH₂ oxidation was determined by the initial rates method by monitoring the increase of the product 3,5-DTBQ at constant temperature of 20 °C. The rate constant for a particular complex-substrate couple was eluicidated from absorbance vs time plot by employing initial rate method. The substrate concentration dependence of the oxidation rate was examined under aerobic conditions, using 1×10^{-4} M solutions of 1, 2, and 3 and increasing amounts of 3,5-DTBCH₂ from 0.005 (M) to 0.02 (M). In all cases, first order dependence was observed at low substrate concentrations, whereas saturation kinetics was found at higher substrate concentrations. The substrate concentration dependence suggests that the initial step of the catalytic cycle is the binding of the substrate to the catalyst. Michaelis-Menten kinetics was applied to analyze the data obtained, and the Michaelis–Menten constant (K_M) and maximum initial rate (V_{max}) were determined by linearization using Lineweaver-Burk plots. The turnover number (kcat) values can be calculated by dividing the Vmax values by the concentration of the corresponding complexes. Different kinetic parameters for catecholase activity are listed in Table 4. It is seen from the Table 4 that the catecholase activity of the complexes are almost similar. The observed k_{cat} values in the range of 1.38 – 1.87 x 10⁴ h⁻¹ indicate that the three complexes are very efficient catalysts for catechol oxidation as compared with similar systems reported earlier [17,24] (Table 5). Biswas et al. have critically assessed the catalytic activity of the complexes on basis of the mode of binding the two active Ni(II) centers by the ligand. It is argued that a binucleating ligand that can hold the two metal centers, offer more feasibility towards electron shuttling between the metal centres [8d]. In a similar line of argument, it can be stated that since in the present work, the nickel centers are held by a binucleating ligand as well as a bridging water molecule, the systems possess the potentiality to act as efficient catalysts. As it is evident that in the oxidation of 3,5-DTBC to 3,5-DTBQ aerial oxygen can be reduced to H_2O_2 or H_2O_3 in order to clarify this fact we performed a reported procedure for the detection of H_2O_2 in the catalytic process which clearly demonstrated the generation of H_2O_2 in the mixture of 3,5-DTBC and catalyst(Complex 1/2/3).

As stated earlier, it can be presumed that the initial step of the catalytic cycle is the binding of the substrate to the catalyst. It is important to mention here that for dicopper complexes behaving as catalysts, Krebs and co-workers had proposed a monodentate asymmetric coordination of the substrate and Solomons and co-workers coined the idea of simultaneous coordination of the substrate to both metal centers in the bidentate bridging mode [15]. In order to get an insight regarding the probable structure of the substrate-catalyst species, ESI-MS (positive) studies for the complexes are carried out in methanol maintaining [Complex]:[3,5-DTBCH₂] as 1:100 (see supporting information Figs. S7a-b for representative example of 1). The adduct having a peak at m/z 1001.03 amu (m/z calcd 1001.33) is clearly attributable to the species $\{[Ni_2(HL^1)_3(L^1)(\mu_2-H_2O)]^- + 2Na^+\}^+$ confirming that the dinuclear form is maintained in the solution. After addition of 3,5-DTBCH₂, new peaks are generated in the mass spectral output. The ESI-MS (positive) is recorded immediately after addition of 3, 5 DTBCH₂ and again after 20 minutes interval. The spectral pattern now displays two important sets of peaks at m/z 1201.37 and 1186.30 amu consistently in both the cases. Keeping the propositions of Krebs et al and Solomon et al in mind, it can be deduced that the substrate binds to the catalyst forming two step intermediates IA and IB which can be attributed to the substrate-catalyst intermediates as $\{[Ni_2(HL^1)_4(\mu_1-H_2O)(3,5-DTBCH)] + H^+ + Na^+\}^+$ (m/z calcd 1202.48, exptl 1201.37) and $\{[Ni_2(HL^1)_4(3,5-DTBC^2)] + 2H^+ + Na^+\}^+$ (m/z calcd 1187.49, exptl 1186.30) respectively, as depicted in Scheme 4.

3.5. Results of electrochemical studies and EPR

The cyclic voltammograms of complexes 1-3 in DMF are similar in appearance. They display irreversible reductive responses at $E_{pc} = -1.79$ V, -2.03 V and -2.36 V respectively (Fig. S8, supporting information), which is attributed to the Ni^{II}/Ni¹ couple. The oxidation peak corresponding to the conversion of Ni^{II} to Ni^{III} is observed at around +0.7 V for all the three complexes. Prior works also demonstrated the similar potential ranges for Ni^{II}/Ni¹ and Ni^{II}/Ni^{III} couples [8d,21c,25,26,27].

To monitor the solution behaviour during catecholase action, methanol solution of the mixture of complex 1 and 3, 5-DTBC is investigated and the cyclic voltammetric output, taken after 20 minutes, exhibits two reductive responses at -1.37V and -0.78V as illustrated by the representative voltammogram in Fig.5. It is easily presumable that since catechol to quinone oxidation is a two electron process, therefore, complexes containing two nickel centers that turn between Ni(II) and Ni(I) during the cycle are desirable. Therefore, the appearance of two reduction peaks can be interpreted by considering participation of both the nickel centers as follows Ni^{II}Ni^{II} $-Ni^{II}Ni^{II}$

 \rightarrow Ni¹Ni¹ [26]. Our mass spectral output is also along the same line with the proposition of involvement of both nickel centers. However, no oxidation peak corresponding to the 3,5-DTBC to 3,5-DTBQ conversion is observed in methanol - a feature usually encountered in acetonitrile solvent. A very recent publication by Das et al[27] have also reported similar cyclic voltammetric profile.

In the attempt to further characterize the products, X-band EPR spectroscopy is a useful tool as recently demonstrated by Das et al. [27]. The species generated after mixing complex 1 and 3,5-DTBC (1:100) in methanol, exhibits a sharp EPR signal at g =2.004, signifying the formation of semiquinone type S = 1/2 organic radical (Fig.6). As Fig.6 depicts, the presence of anisotropy in the signal strongly suggests that the radical interacts with the metal centres. But whether a concerted mechanism involving both the metal centres and the radical is operative or not is still a subject of intensive research.

Comparison to other dinickel (II) catalysts

By far the most efficient catalysts showing catecholase activity are reported by Das and co-workers which presents k_{cat} value upto 3.24 x 10⁴ h⁻¹[28]. In other publications they have come up with a couple of other efficient dinickel(II) catalysts that have been run under similar conditions to our studies and show comparable results to our catalysts [17,24,28]. In a recent characterization of nickel based catalysts, they have tested eight dinickel(II) complexes and found the k_{cat} values in the order of ~10² h⁻¹. Ghosh *et al.* used three dinuclear nickel (II) complexes and 3,5-DTBCH₂ to monitor the conversion in acetonitrile and the highest k_{cat} value was 81.7 h⁻¹ [27]. Thus, a comparison of k_{cat} values shows that our complexes 1, 2 and 3 are among the best performing dinickel(II) based catalysts showing catecholase activity (Table 5).

Furthermore, the authors obtained good assignments of the fragments by assuming the existence of dinuclear species providing indirect evidence for metal mediated oxidation of 3,5-DTBCH₂. They have also observed an isotropic signal at $g = \sim 2.00$ in X-band EPR spectrum corresponding to an organic radical reinforcing the proposition of radical pathway. By combining the analyses of ESI- MS, cyclic voltammetry and X-band EPR, our findings are also consistent with literature reports.

3.6. Magnetic studies

The study of the magnetic susceptibility data for the examined complexes has been performed within the temperature range of 1.80 - 300 K. The experimental data, plotted as thermal variations of the χ_M and $\chi_M T$, are shown in Figs. 7a-c (1-3). The three samples show very similar properties. The χ_M curve starts at 0.00814 cm³mol⁻¹ (1), 0.008 cm³mol⁻¹ (2), 0.0076cm³mol⁻¹ (3) at room temperature (300K) and increases in uniform way to 1.147 cm³mol⁻¹(1), 0.972 cm³mol⁻¹(2), 1.245 cm³mol⁻¹ (3) at 1.8 K. Plots of $\chi_M T$ vs T for all compounds show typical ferromagnetic behaviour : an increase in the effective magnetic moment with decreasing temperature. At 300K they show $\chi_M T$ values of 2.38, 2.40 and 2.43 cm³mol⁻¹K for 1, 2 and 3, respectively. This quantity increases up to maximum values of 3.09 cm³mol⁻¹K at 10 K for 1, 2.77 cm³mol⁻¹K at 9 K for 2 and 3.02 cm³mol⁻¹K at 9 K for 3. Below this temperature, $\chi_M T$ decreases gradually indicating the contribution of zero – field splitting of ground state (S = 2) and/or antiferromagnetic intermolecular interactions between the dinuclear entities.

At the first step to interpreted quantitatively magnetic data, we applied standard dimeric equation for Ni(II) with only two parameters χ (g, J) [29]. The fit was acceptable only at high temperature range (much above the maximum on $\chi_M T$ vs T curve). For 1 - 3 Ni(II) dimers where the maximum is resolved, the situation requires the addition of higher order effect. In such case the variable – temperature susceptibility data were analysed using the isotropic

8

Ginsberg model from the Hamiltonian [30], which includes a crystal field splitting term (D) characteristic for axially distorted octahedral symmetry and a molecular field term (zJ'). The equation will be referred to as χ (g, J, D, zJ').

$$H = -2J\hat{S}_{1}\hat{S}_{2} - D(\hat{S}_{1z}^{2} + \hat{S}_{2z}^{2}) - 2zJ'\hat{S}_{i}\langle\hat{S}_{i}\rangle - g_{i}BH\hat{S}_{i}$$

The molar magnetic susceptibility for a dinuclear Ni²⁺ complex is given in supplementary part.

The fitting are much better using more parameters in the equations described above. However at low temperature the very small discrepancies were visible. Probably it can be due to the presence of two different bridge between Ni(II) ions, which will be described later.

Least-square fits to the experimental data were obtained for $J = 2.46 \text{ cm}^{-1}$, $D = -2.11 \text{ cm}^{-1}$, $zJ' = -0.25 \text{ cm}^{-1}$, g = 2.091 and $R = 2.37 \times 10^{-4}$ for (1), $J = 1.86 \text{ cm}^{-1}$, $D = -3.56 \text{ cm}^{-1}$, $zJ' = -0.37 \text{ cm}^{-1}$, g = 2.12 and $R = 3.04 \times 10^{-4}$ for (2), $J = 1.73 \text{ cm}^{-1}$, $D = -3.84 \text{ cm}^{-1}$, $zJ' = -0.39 \text{ cm}^{-1}$, g = 2.10 and $R = 1.25 \times 10^{-4}$ for (3). Our calculations shown that the parameters D and zJ' are strongly correlated with each other but are only weakly correlated with g and J. The value of the D-parameter for the {NiN₂O₄} chromophore spans the interval for the other Ni(II) centers [31]. However, the identification of its sign is rather problematic. The best technique for such a target is the high-frequency/high-field electron spin resonance.

The magnetic properties of the examined compounds can be interpreted in terms of the two different bridging groups (-O, H_2O) and the geometrical consequences of the twisted bridging arrangement. The double phenoxide Ni – O – Ni bridge angles are lower than 100° (around 93° for all three complexes) and presented as an almost ideal structure for weak ferromagnetism and dominate the overall exchange process.

The water Ni - O - Ni bridge angles are around 80°, therefore, it is reasonable to assume that any exchange via this bridge is not likely to be ferromagnetic, and in fact, it might be expected to propagate a weak antiferromagnetic contribution. The smaller water bridge angle than in most reported complexes, is a result of the long Ni – O bond length. Antiferromagnetic behavior was typical for hydroxide bridge binuclear copper(II) compounds [31] and phenoxide bridged binuclear nickel(II) complexes [10b, 33]. Such assumptions remain in good compliance with ab initio theoretical calculations on binuclear Ni – $(\mu$ -O) – Ni model compounds, which show strong correlation between the value of exchange coupling J and Ni-O-Ni angle: the coupling should be antiferromagnetic for angles below 85° and above 102°, but weakly ferromagnetic in between [32,34]. The geometry of the dimers determines the sign and magnitude of intradimer exchange. Consideration of the electronic states of weakly interacting metal centres have revealed, that the bridging ligand is most effective in supporting antiferromagnetic exchange interactions between the two metal ions if the bridge has available molecular orbitals that can interact with the bonding combination of the metals'd-orbitals [35,36]. The antiferromagnetic contribution reduces when the environment around metal atom changes from planar to tetrahedral geometry. Almost all reported dinuclear complexes derived from the macrocyclic ligand show antiferromagnetic coupling in a slightly distorted [Ni -(O)₂ -Ni] planar unit with an inversion center, where Ni – O – Ni angle is close to 99.5 - 105.7, with antiferromagnetic coupling, J, lying between -17.0 and -67.1 cm⁻¹ [10b, 31]. The substantial variation of the exchange parameter was the result of stereochemical changes (different axial ligands). The extent of antiferromagnetic interaction increases along this series as progressive increase in the intramolecular Ni \cdots Ni distance (3.10 – 3.206 Å) as well as bridge angle. Complexes 1, 2, 3 are different from most of the reported similar complexes for several reasons: the double phenoxide bridge connecting both Ni(II) ions is asymmetric (with one shorter Ni - O bond, and one similar as observed in other phenoxo bridged species), all contains an additional superexchange pathway involving the water bridge, which is perpendicular to the Ni_2O_2 pathway, as a result the Ni - O - Ni angles are comparatively lower (close to 93°) with shorter Ni ... Ni distance [2.988 Å for (1), 2.971 Å for (2), 2.984 Å for (3)] (see Table 6). In addition, the presence of an aqueous bridge causes an additional antiferromagnetic contribution to magnetic effects, thus weakening the dominant ferromagnetic interactions. This feature explain why the J value is positive and the lowest reported so far for these Ni(II) dinuclear complexes with two phenoxo bridging ligand.

The magnetization per formula unit adopts a value of 3.81M.B. for 1, 3.65 M.B. for 2 and 3.84 for 3 somewhat about 5T and T = 2.0 K [see the right inset in Figs. 7a-c]. These values are a little bit lower that those characteristic for completely polarized dimer of Ni²⁺ (S = 2), provides evidence for a parallel alignment of the spin of the nickel ions in the magnetic field. These small discrepancies is due to weak coupling between the magnetic centers and

9

evidences a sizable zero-field splitting for Ni(II) ions.

Below 9 K, $\chi_M T$ value decreases due to the combined effect of zero-field splitting, saturation and/or intermolecular antiferromagnetic couplings. In this procedure, a zJ' constant has been used to account for intermolecular interactions. Additionally, according to the crystal structure, in all three complexes oxygen atoms (from water) forms bifurcated hydrogen bonding pattern with a pendant -OH group of Schiff base ligand (O1-H49...O6 = 2.778(5) Å (1), O1-H31...O4 = 2.745(4) Å (2), O13-H10...O9= 2.738(5) Å (3)) and phenoxide oxygen atoms of another unit. These contacts may create a next magnetic exchange pathway between the Ni ions of neighbouring dimers in the crystal network. The small magnitude of this interaction is a result of the rather long Ni ...Ni separation (8.779 (8) Å for 1, 8.5987 (11) Å for 2 and 7.7009 (15) Å for 3). The obtained very small value of zJ' = -0.25 cm⁻¹ for 1, zJ' = - 0.37cm⁻¹ for 2 and zJ' = - 0.39 cm⁻¹ for 3 in comparison to large value of D_{Ni} parameter indicates a dominant zero-field splitting effect within the S=1 local ground states of each Ni(II) ions.

4. Conclusion

We have synthesized and characterized three dinuclear Ni(II) complexes, $[Ni_2(HL^1)_4(H_2O)](1)$, $[Ni_2(HL^2)_4(H_2O)](2)$ and $[Ni_2(HL^3)_4(H_2O)](3)$ using Schiff base ligands derived from 5-amino-1- pentanol and salicylaldehyde (H_2L^1) , 5-bromo salicylaldehyde (H_2L^2) and 3-methoxy salicylaldehyde (H_2L^3) respectively. All of them contain bridging aqua ligand - a feature observed only in a couple of dinuclear Ni(II) complexes in literature. All of them describe distorted octahedral structures and the dispositions of the pendant –OH groups are such so that they remain relaxed inside the crystal lattice providing a scope for H-bonding. Notably, the presence of coordinated bridging water molecules also leads to the formation of extensive H-bonding interactions resulting in 3D supramolecular network in 1 and 3, and a 2D netlike arrangement in 2. The coordinated water molecules having Ni(II) – O(water) bond lengths in the range of 2.3 Å, which is slightly longer than expected, enables these dinuclear Ni(II) complexes to act as efficient catalysts for the conversion of 3, 5-di-*tert*butylcatechol (3,5-DTBCH₂) to 3, 5- di-*tert*butylquinone (3,5-DTBQ) in methanolic medium. The cyclic voltammetry and X-band EPR studies are carried out in order to monitor the solution behaviour during catecholase action. The magnetic data suggest that weak ferromagnetic couplings exist between the Ni(II) centers. Simple magnetic considerations which are based on structural knowledge are employed to account for the weak magnetic interactions. From the structural and magnetic parameters, the Ni – O – Ni bond angle seems to be a considerable factor affecting the magnitude of magnetic couplings.

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Appendix A. Supplementary material

CCDC reference numbers of crystals **1–3** are, 917991,935266 and 917992 respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk</u>.

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12

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Figure Captions

Fig. 1a. Crystal structure of 1. Hydrogen atoms except aqua bridged are removed for clarity.

Fig. 1b. Rectagular core formed by four neighbouring dinickel moieties in 1.Blue broken line represents the H-bonding.

Fig. 1c. 3-dimensional supramolecular architecture formed in 1.

Fig. 2. Crystal structure of 2. Hydrogen atoms except aqua bridged are removed for clarity.

Fig. 3. Crystal structure of 3. Hydrogen atoms except aqua bridged are removed for clarity.

Fig. 4a. UV-Vis spectrum of 1 at 15 minutes time interval after addition of 3,5-DTBCH₂.

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Fig. 7b. Thermal dependence of $(\circ)\chi_M$ and $(\bullet)\chi_M$ T for 2. The inset show thermal dependence of inverse magnetic susceptibility (left) and field dependence of the magnetization (right). The solid lines are the calculated curves.

Fig. 7c. Thermal dependence of $(\circ)\chi_M$ and $(\bullet)\chi_M T$ for **3**. The inset show thermal dependence of inverse magnetic susceptibility (left) and field dependence of the magnetization (right). The solid lines are the calculated curves.



Scheme 2. Synthetic outline of the complexes

14



Symmetry transformations used to generate equivalent atoms: _a: 1-x, y, 1/2-z

Scheme 3. Bond length and bond angles of the metal centre of 1, 2 and 3 respectively.



Scheme 4. Plausible intermediate (IA, IB) formation during the coupling of dinuclear Ni(II) complex and 3,5-DTBCH₂(charge and counterions are omitted for clarity).

Table(s)

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Table 1.

Crystal data and structure refinement for 1 - 3.

Formula	C48 H66 N4 Ni2 On (1)	C48 H62 Br4 N4 Ni2 Oo (2)	C_{52} H ₇₄ N ₄ Ni ₂ O ₁₂ C H ₄ O (3)
M	060 43	1276	1112 52
	900.43	1270	1112.52
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	$P 2_1/c$	C 2/c	$P 2_1/c$
a/Å	21,5729(13)	17.6987(8)	12.2617(11)
h/ Å	11 70/3(7)	15 53/3(8)	31 6040(29)
	10 (412(12)	13.5545(0)	15 2000(14)
<i>C</i> / A	19.6413(13)	22.5002(12)	15.2099(14)
$\alpha(^{\circ})$	90.00	90.00	90.000
$\beta(^{\circ})$	92.863(2)	108.205(2)	107.020(1)
$\nu(^{\circ})$	90.00	90.00	90,000
$V/\dot{\Delta}^3$	4953 2(5)	5876 5(5)	5636 0(9)
7	49555.2(5)	5070.5(5)	5050.0(7)
Σ	4	4	4
$Dc/g \text{ cm}^{-1}$	1.292	1.429	1.187
μ/mm^{-1}	0.816	3.408	0.727
F(000)	2052	2568	2320
R(int)	0.0456	0.0649	0.0473
total Reflections	7745	9351	8849
unique reflections	6352	4602	6182
	0.0570 0.1409	4002	0.0507_0_1754
R1, WR2	0.0560, 0.1408	0.0565, 0.1439	0.0597, 0.1754
<i>T</i> /K	150(2)	150(2)	150(2)

Table(s)

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Table 2.

Selected bond distances (Å) and angles (deg)in the metal coordination spheres for 1-3.

	1	2		3	
Ni(1)-O(4)	1.988(2)	Ni(1)-O(2)	1.980(2)	Ni(1)-O(1)	1.975(3)
Ni(1)-O(3)	2.005(2)	$Ni(1)-O(3_a)$	2.003(2)	Ni(1)-O(4)	1.990(3)
Ni(1)-N(3)	2.030(3)	Ni(1)-N(24)	2.048(3)	Ni(1)-N(1)	2.033(4)
Ni(1)-N(2)	2.048(3)	Ni(1)-N(23_a)	2.050(3)	Ni(1)-N(2)	2.049(4)
Ni(1)-O(2)	2.131(3)	Ni(1)-O(3)	2.109(2)	Ni(1)-O(10)	2.101(3)
Ni(1)-O(1)	2.334(3)	Ni(1)-O(1)	2.300(4)	Ni(1)-O(13)	2.368(3)
Ni(2)-O(5)	1.987(3)			Ni(2)-O(13)	2.289(3)
Ni(2)-O(2)	2.002(2)			Ni(2)-(07)	1.988(3)
$N_1(2) - N(4)$	2.036(3)			$N_1(2) - O(10)$	2.002(3)
N1(2) - N(1) N2(2) - O(2)	2.065(4)			$N_{1}(2) - N_{1}(3)$	2.029(4)
NI(2) - O(3)	2.118(5)			-1NI(2) - 1N4	2.049(4)
NI(2) - O(1)	2.310(3)			NI(2)- 04	2.128(3)
O(1)-Ni(1)- O(2)	74.70(10)	O(1)-Ni(1)-O(2)	92.67(8)	O(1)-Ni(1)-O(4)	166.86(13)
O(1)-Ni(1)-O(3)	76.16(11)	O(1)-Ni(1)-O(3)	74.52(9)	O(1)-Ni(1)-N(1)	91.16(14)
O(1)-Ni(1)-O(4)	91.41(11)	O(1)-Ni(1)-N(24)	168.91(10)	O(4)-Ni(1)-N(1)	99.50(12)
O(1)-Ni(1)-N(2)	88.32(12)	O(1)-Ni(1)-O(3_a)	92.63(9)	O(1)-Ni(1)-N(2)	94.95(15)
O(1)-Ni(1)-N(3)	171.96(12)	O(1)-Ni(1)-O(23_a)	92.58(9)	O(4)-Ni(1)-N(2)	91.75(14)
O(2)-Ni(1)-O(3)	77.55(10)	O(2)-Ni(1)-O(3)	92.63(9)	N(1)-Ni(1)-N(2)	95.17(14)
O(2)-Ni(1)-O(4)	93.22(10)	O(2)-Ni(1)-N(24)	90.98(10)	O(1)-Ni(1)-O(10) 92.73(12)
O(2)-Ni(1)-N(2)	160.79(12)	O(2)-Ni(1)-O(3_a)	167.30(9)	O(4)-Ni(1)-O(10) 77.98(11)
O(2)-Ni(1)-N(3)	97.46(12)	O(2)-Ni(1)-N(23_a)	76.48(9)	O(10)-Ni(1)-N(1) 99.76(12)
O(3)-Ni(1)-O(4)	166.04(10)	O(3)-Ni(1)-N(24)	94.86(10)	O(10)-Ni(1)-N(2) 163.05(14)
O(3)-Ni(1)-N(2)	89.87(12)	O(3)-Ni(1)-O(3 a)	78.22(8)	O(1)-Ni(1)-O(13) 92.54(13)
O(3)-Ni(1)-N(3)	100.71(12)	O(3)-Ni(1)-N(23 a)	164.60(10)	O(4)-Ni(1)-O(13	76.09(11)
O(4)-Ni(1)-N(2)	96.18(13)	O(3 a)-Ni(1)-N(24)	98.51(10)	O(13)-Ni(1)-N(1) 172.97(12)
O(4)-Ni(1)-N(3)	90.77(12)	N(23_a)-Ni(1)-N(24	4) 97.42(10)	O(13)-Ni(1)-N(2	2) 90.45(13)
N(2)-Ni(1)-N(3)	99.13(13)	O(3 a)-Ni(1)-N(23)	a)90.74(10)	O(10)-Ni(1)-O(1	3)74.10(11)
O(1)-Ni(2)-O(2)	77.65(11)	Ni(1)-O(1)-Ni(1 a)	80.46(15)	O(7)-Ni(2)-O(10) 167.92(13)
() (=) - (=)				-(.,	,=(10)

Table 3.

Hydrogen bonding	distances (A°) for 1	-3.	
1		2	3
O(6)-H(6)…O(5)	2.659(4)	O(4)-H(15)···O(2) 2.684(4)	O(13)-H(10)O(9) 2.738(5)
O(7)-H(7A)···O(9)	2.732(9)	O(1)-H(31)···O(4) 2.745(4)	O(13)-H(20)···O(6) 2.727(6)
O(8)-H(8)…O(4)	2.627(4)		O(3)-H(30)····O(8) 2.850(6)
O(9)-H(9)…O(7)	2.908(10)		O(6)-H(60)····O(7) 2.644(5)
O(1)-H(49)…O(6)	2.778(5)		O(9)-H(90)···O(1) 2.651(5)

Table 4.

Different kinetic parameters for catecholase activity of 1-3.

compren	$V_{max} (M S^{-1})$	$K_{M}(M)$	$K_{cat}(h^{-1})$
1	$5.19 \pm 0.017 {\times} 10^{-4}$	$6.05 \pm 0.021 \times 10^{-3}$	1.87 x 10 ⁴
2	$4.97 \pm 0.035 \times 10^{-4}$	$8.14 \pm 0.011 {\times} 10^{\text{-3}}$	1.79 x 10 ⁴
3	$3.86 \pm 0.029 \times 10^{-4}$	$5.78 \pm 0.031 \times 10^{-3}$	1.38 x 10 ⁴
			55
6			

Table 5. Comparison of K_{cat} value for the oxidation of 3,5-DTBCH₂ to 3,5-DTBQ by different dinuclear Ni(II) Schiff base ligand complexes.

Complex	$K_{cat}(h^{-1})$		Reference	
	I n Methanol	In Acetonitrile		2
1	1.87 x 10 ⁴	n.d.	Present work	2
2	1.79 x 10 ⁴	n.d.	Present work	
3	1.38 x 10 ⁴	n.d.	Present work	.0
Σ Ni ₂ L ¹ ₂ (NCS) ₂	n.d.	64.1 ±4.1	8.(d)	2
Σ Ni ₂ L ² ₂ (NCS) ₂	n.d.	51.1 ± 6.2	8.(d)	
Σ Ni ₂ L ³ ₂ (NCS) ₂	n.d.	81.7 ±4.7	8.(d)	
$*[Ni_2(LH_2)(H_2O)_2(OH)(NO_3)](NO_3)_3$	1.4 x 10 ⁴	Inactive	24	
[§] [Ni ₂ L(NO ₃)(H ₂ O) ₃]NO ₃	1.5 x 10 ³	n.d.	17	
$\#[Ni_2(L^2)(N_3)_3(H_2O)_2]$	1.728×10 ²	n.d.	27	
$\#[Ni_2(L^4)(N_3)_3(H_2O)_2]$	2.641×10 ²	n.d.	27	
$f[Ni_2(L^1)(NCS)_3(H_2O)_2]$	3.60 x 10 ³	1.08 x 10 ⁴	28	
$\label{eq:constraint} \pounds \left[Ni_2(L^2)(CH_3COO)(NCS)_2(H_2O) \right]$	2.16 x 10 ⁴	3.24 x 10 ⁴	28	
$f[Ni_2(L^3)(NCS)_3]$	1.3 x 10 ³	2.95 x 10 ³	28	

 Σ L¹= 2-[1-(3-methylamino-propylamino)-ethyl]-phenolato

RCC

 $L^2=2$ -[1-(2-dimethylamino-ethylamino)-ethyl]-phenolato $L^3=2$ -[1-(3-dimethylamino-propylamino)-ethyl]-phenolato

* LH₂= 2,6-bis(N-ethylpiperazine-iminomethyl)-4-methyl-phenolato

^{\$}L=[1+2] condensation of 1,3-diaminopropane and 2,6-diformyl-4-tert-butylphenol)

L2= 4-tert-Butyl-2-[(2-dimethylamino)-methyl]-6-[(2-dimethylamino)-methyl]phenolato

L4= 4-tert-Butyl-2,6-bis-[(2-pyridin-2-yl-ethylimino)-methyl]-phenolato

 ${}^{\pounds}L^{l}{=}\ 2, 6{\text -}bis (N{\text -}ethylpyrrolidine iminomethyl){\text -}4{\text -}methylphenolato$

 $L^2 = 2,6$ -bis(N-ethylpiperidineiminomethyl)-4-methylphenolato

 $L^{3} = 2,6-bis\{N-ethyl-N-(3-hydroxypropyliminomethyl)\}-4-methylphenolato$

Table(s)

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Complex	J, cm ⁻¹	g	D, cm ⁻¹	zJ', cm ⁻¹	Ni…Ni, Å	Ni–O–Ni, deg	Ni–O–Ni, deg
$[Ni_2(HL^1)_4(H_2O)]$ (1)	2.46	2.091	-2.11	- 0.25	2.988 Å	92.57(10)	water 80.11(11)
$[Ni_2(HL^2)_4(H_2O)]$ (2)	1.86	2.12	-3.56	- 0.37	2.971 Å	92.80(10) 92.50(9)	80.46(15)
[Ni ₂ (HL ³) ₄ (H ₂ O)] (3)	1.73	2.10	-3.84	- 0.39	2.984 Å	93.26(12) 92.81(12)	79.69(11)
						6	
						9	
					2		
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Table 6. Comparison of magnetostructural data for 1 - 3.



Fig. 1a. Crystal structure of 1. Hydrogen atoms except aqua bridged are removed for clarity.



Fig. 1b. Rectangular core formed by four neighbouring dinickel moieties in 1. Blue broken line represents the H-bonding.

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Fig. 1c. 3-dimensional supramolecular architecture formed in 1.



Fig. 2. Crystal structure of 2. Hydrogen atoms except aqua bridged are removed for clarity.



Fig. 3. Crystal structure of 3. Hydrogen atoms except aqua bridged are removed for clarity.



Fig. 4a. UV-Vis spectrum of 1 at 15 minutes time interval after addition of 3,5-DTBCH₂.



Fig. 4b. Plot of the initial rates versus substrate concentration for the oxidation of 3,5-DTBCH₂ catalyzed by **1**. The inset shows Lineweaver–Burk plot.



Fig. 5. Cyclic voltammogram of methanolic solution of 3,5-DTBC and Complex **1** (as representative example).



Fig. 6. X-band EPR spectrum of mixture of 3,5-DTBC and Complex **1**(as representative) in methanol at 77K.

CCE



Fig. 7a. Thermal dependence of $(\bullet)\chi_M$ and $(\circ)\chi_M$ T for **1**. The inset show thermal dependence of inverse magnetic susceptibility (left) and field dependence of the magnetization (right). The solid lines are the calculated curves.



Fig. 7b.Thermal dependence of (•) χ_M and (•) χ_M T for 2. The inset show thermal dependence of inverse magnetic susceptibility (left) and field dependence of the magnetization (right). The solid lines are the calculated curves.

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Fig. 7c. Thermal dependence of $(\bullet)\chi_M$ and $(\circ)\chi_M$ T for **3**. The inset show thermal dependence of inverse magnetic susceptibility (left) and field dependence of the magnetization (right). The solid lines are the calculated curves.

22

GRAPHICAL ABSTRACT. Three novel μ^2 -aqua bridged dinuclear Ni(II) complexes, $[Ni_2(HL^1)_4(H_2O)]$ (1), $[Ni_2(HL^2)_4(H_2O)]$ (2) and $[Ni_2(HL^3)_4(H_2O)]$ (3) have been synthesized using Schiff base ligands derived from 5-amino-1- pentanol and salicylaldehyde (H₂L¹), 5-bromo salicylaldehyde (H_2L^2) and 3-methoxy salicylaldehyde (H_2L^3) respectively that are efficient models for catechol oxidation. Acception

Graphical Abstract - pictogram (for review)



23

Highlights

- Three dinuclear aqua bridged Ni(II) Schiff base complexes have been synthesized. •
- All the three complexes show high catecholase activity. ٠
- They exhibit weak ferromagnetism. •

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