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Deactivation of Catecholase-like Activity of a Dinuclear Ni(II) Complex by Incorporation of an Additional Ni(II)

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Graphical abstract



Two new Ni(II) complexes $[Ni_2L_2(PhCOO)(H_2O)_2]ClO_4$ (1) and $[Ni_3L_2(PhCOO)_4]$ (2) has been synthesized by reacting Ni(II), HL¹ and benzoate in a different ratio. complex 1, of reduced Schiff base ligand (which is redox innocent) shows significant catecholase-like activity, but complex 2 is inactive towards catechol oxidation. From the magnetic point of view, Ni(II) centres are antiferromagnetically coupled in 1 but ferromagnetically coupled in 2.

Research Highlights

- Synthesis of nickel complexes with reduced Schiff base ligand.
- Mimicking catecholase like activity with 3,5-di-tert-butylcatechol (3,5-DTBC).
- Magneto-structural correlation for mixed bridged Ni(II) complexes.
- DFT calculations support the experimental findings.

Abstract

A new dinuclear Ni(II) complex $[Ni_2L_2(PhCOO)(H_2O)_2]ClO_4$ (1) has been synthesized by reacting Ni(ClO_4)_2.6H_2O with a reduced Schiff base ligand [(3-dimethylamino-propylamino)-methyl]-phenol (HL¹) in presence of benzoic acid in 1:1:1 ratios. Structural analysis reveals that complex 1 is a di- μ_2 -phenoxo-bridged dinuclear Ni(II) complex and has an additional *syn-syn* benzoate bridge. Enzyme kinetic studies reflect that it (1) is effective in mimicking catecholase like activity with 3,5-di-tert-butylcatechol (3,5-DTBC) as the substrate. Kinetic measurements suggest that the rate of catechol oxidation follows first order kinetics with respect to the catalyst. The possible intermediates during the course of reaction are identified from ESI-MS spectra. The

characteristic EPR spectra of the complex in the presence of 3,5-DTBC supports the formation of nickel(II)-semiquinonate as an intermediate species during the catalytic oxidation. When the synthesis is carried out with Ni(II): HL ratio of 3:2, a different compound [Ni₃L₂(PhCOO)₄] (**2**) is produced incorporating an additional Ni(II)-benzoate. **2** possesses a linear trinuclear structure with the tridentate reduced Schiff base ligand coordinated to the terminal nickel atoms which are linked to the central Ni(II) by phenoxo and carboxylate bridges. Unlike **1**, it does not show any catalytic activity towards catechol oxidation. Variable temperature magnetic susceptibility measurements have also been performed for **1** and **2**. Complex **1** indicates the presence of intradimer antiferromagnetic interactions (J = -5.65 cm⁻¹). In contrast to complex **1**, ferromagnetic coupling (J = 3.55 cm⁻¹) is observed in complex **2**.

Keywords: Nickel(II)/ Reduced Schiff base/ Crystal structure/ Catecholase activity/ Magnetic measurements

Introduction

Nature uses transition metals in different biological processes and it drives the quest of the scientist to understand the fundamental principles of its functionality, which eventually helps to develop different structural and more importantly functional model systems [1–8]. Transition metal induced several biological processes are well known over the years. Apart from these, many new molecules have been also developed over the years showing interesting properties like antibacterial, antifungal, antimicrobial activity where the transition metal ion performs crucial role in terms of structural organization and overall functionality [9-12]. Especially the presence of two transition metal ions in close proximity at the active site of several metallo-proteins and metallo-enzymes has simulated interest in the synthesis and study of multinuclear transition metal complexes. There is also continuing interest in mechanistic studies on the catalytic oxidation of catechols by transition metal complexes because this reaction plays key role in the metabolism of aromatic compounds [13-34]. Oxidation of a range of o-diphenols (catechols) in presence of the enzyme catecholase to corresponding quinone is known as catecholase activity. Although crystal structure determination of the met-form of catecholase revealed that the active site of the enzyme consists of a hydroxo bridged dicopper(II) centre, many other metal ions e.g. Mn(II/III), Fe(III), Co(II/III), Zn(II) have also been reported in literature that mimic catecholase

activity [26-34] Study of the Ni(II) complexes in this field is comparatively rare. Only few mono- and dinuclear Ni(II) complexes have been studied for the possible catechol oxidase like properties [13,19-25,66-71]. All the previous findings, mainly with copper-based model complexes reveal that the metal ion oxidation state, ligand environment, nuclearity of the complexes, etc. play important role(s) in catalyzing catechol and its derivative to their corresponding quinones. However, for catecholase-like activity of Ni(II) complexes, no such clear structural correlations have been drawn because the number of complexes studied for this purpose are comparatively rare.

We have synthesised a new dinuclear Ni(II) complex, $[[Ni_2L_2(PhCOO)(H_2O)_2]ClO_4]$ with N,N,O donor reduced Schiff base ligand (3-dimethylamino-propylamino)-methyl]-phenol (HL¹)). Examination of catecholase-like activity for the complex reveals that complex **1** acts as catalysts for the areal oxidation of 3,5-di-tert-butylcatechol to the corresponding o-quinone. A monomeric nickel(II)-semiquinonate intermediate which is identified through EPR and ESI-MS measurements is thought to be responsible for this oxygenation reaction. ESI-MS positive spectra also signify the presence of a bis(μ -oxo)dinickel(II) intermediate during the aerobic oxidation of catechol.

We were further curious to observe the structural, magnetic and catalytic effect of excess Ni(II) to the dinuclear entity. Hence, we added excess Ni(II) to complex **1** in different ratios in solution and finally succeeded to isolate a trinuclear entity $[Ni_3L_2(PhCOO)_4]$ (**2**) with Ni(II): HL: benzoate 3:2:4. Interestingly, unlike **1**, complex **2** does not show any catalytic activity towards catechol oxidation. Magnetic susceptibility measurements indicate antiferromagnetic exchange interaction mediated between the Ni(II) centers in **1** and ferromagnetic coupling in **2**. Further insight in magneto-structural correlations, we have also performed theoretical calculations to find the dependence of *J* on various bridging pathways. Hence, these two compounds demonstrate nicely the importance of the ratio of different constituents (i,e metal, ligand and carboxylate) in determining the nuclearity of the complexes and their effect on catalytic activity.

Experimental section

Caution! Perchlorate salts of metal complexes are potentiallyexplosive; and caution should be exercised when dealing with such derivatives.

Materials and General Methods.

Reagents and solvents were purchased from various commercial sources and used without further purification unless otherwise stated.

Synthesis of the Schiff-base ligand [(3-dimethylamino-propylamino)-methyl]-phenol (HL¹) A methanolic solution of salicyldehyde (0.52 ml, 5 mM) and N,N-dimethyl-1,3-propanediamine (0.63 ml, 5 mM) has been refluxed for 1 h at 60°C. The methanolic solution was subsequently cooled to 0°C and solid sodium borohydride (210 mg, 6 mM) was added slowly with constant stirring. After completion of the addition, the resulting reaction mixture was acidified with concentrated HCl (5 mL) and then evaporated to dryness. The reduced Schiff-base ligand HL¹ was extracted from the solid residue with methanol; the methanolic solution obtained (ca. 20 mL) was used for preparation of the coordination compounds.

Synthesis of the complex [Ni₂L₂(PhCOO)(H₂O)₂]ClO₄ (1)

A methanolic solution of Ni(ClO₄)₂·6H₂O(1.828 g, 5 mM) was added to a methanolic solution (10 mL) of the reduced Schiff base (HL¹) (5 mmol) with constant stirring. After ca.10 min a methanolic solution of benzoic acid, PhCOOH (0.610 g, 5 mM) was added with slow stirring followed by addition of triethylamine (0.70 mL, 5 mM). After evaporation of the solvents to dryness, the resulting green solid was filtered and washed with diethyl ether and dissolved in CH₃CN. Slow evaporation of the resulting green solution gave X-ray quality deep-green single crystals of compound **1**.Yield: 1.37 g.(70%). *Anal* Calc. for C₃₁H₄₇ClN₄Ni₂O₁₀: C, 47.22; H, 6.01; N, 7.10. Found: C, 47.25; H, 6.00; N, 7.02. IR (KBr pellet): IR (KBr pellet): v(O-H)broad, 3465cm⁻¹, v(N-H), 3275 cm⁻¹, v(C-N), 1569 cm⁻¹, v_{asym} (C=O), 1610 cm⁻¹, v_{sym} (C=O), 1480 cm⁻¹.

Synthesis of the complex [Ni₃L₂(PhCOO)₄] (2)

Ni(ClO₄)₂·6H₂O(1.828 g, 5 mM), dissolved in 10 mL of methanol, was added to a methanolic solution (10 mL) of complex **1** (3.94 g, 5 mM) with constant stirring. After ca.25 min a methanolic solution of benzoic acid, PhCOOH (1.22 g, 10 mM) was added with slow stirring followed by addition of triethylamine (1.40 mL, 10mM). Removal of solvent results a dark green solid. The green solid was then washed with diethyl ether and dissolved in CH₃CN. Layering the acetonitrile solution with Et₂O result X-ray quality deep-green single crystals of compound **2**.

Yield: 1.43 g.(80%). *Anal* Calc. for C₅₂ H₅₈ N₄ Ni₃ O₁₀: C, 58.09; H, 5.44; N, 5.21. Found: C, 58.10; H, 5.40; N, 5.18. IR (KBr pellet): v(N-H), 3224 cm⁻¹, v(C-N), 1564 cm⁻¹ v(C=O), 1459 cm⁻¹. $v_{asym}(C=O)$, 1600 cm⁻¹, $v_{sym}(C=O)$, 1484 cm⁻¹

Alternative method for the synthesis of compound 2

This deep green compound was also prepared in the same method as described for Complex **1**. Only difference is the proportion of the added reagent - Ni(ClO₄)₂·6H₂O, Schiff base (HL¹) and benzoic acid, PhCOOH (0.488 g, 4 mM) ratio is maintained at 3:2:4 instead of 1:1:1 as in case of complex **1**.

Physical Measurements.

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra in KBr pellets (4500-500 cm-1) were recorded using a Perkin-Elmer RXI FT- IR spectrophotometer. Electronic spectra (1500-250 nm) were recorded in a Hitachi U-3501 spectrophotometer. The X-band (9.13 GHz) EPR experiment were carried out using a JEOL JES-FA 200 instrument at liquid nitrogen temperature (77 K) in methanol. Temperature-dependent molar susceptibility for powdered sample of **1-2** were measured with a superconducting quantum interference device vibrating sample magnetometer (SQUID-VSM, Quantum Design) with an applied field 500 Oe throughout the temperature range 2–300 K. Isothermal magnetizations measurements were performed at 2K up to 5 Tesla.

For the investigation of catecholase activity of the complexes, complex **1** was treated with 100 equiv. of 3,5-di-tert-butylcatechol (3,5-DTBC) in methanol under aerobic condition at room temperature. The reaction was monitored spectrophotometrically with the increase in the absorbance at 400 nm (Quinone band maxima) as a function of time (time scan).For determination of hydrogen peroxide during the catalytic reaction, iodometric method was followed as reported earlier [30].

Computational Methodology

The theoretical calculation based on broken symmetry DFT has been used to estimate the coupling constant (J) of these complexes and consequently, the J values have been derived from the Equation 1 as proposed by Ruiz et al [35]. The SCF calculations were accomplished with consideration of experimental X-ray structures. The hybrid B3LYP functional [36-38] and

widely employed TZVP [39] basis set has been considered in all calculations as implemented in the ORCA package [40]. The zeroth-order regular approximation (ZORA) has been included to describe scalar relativistic effects[41]. RI approximation with auxiliary TZV/J coulomb fitting basis set and tight SCF convergence criteria (Grid4) have also been incorporated [42].

$$2J = \frac{E_{bs} - E_{hs}}{2S_1 S_2 + S_1}$$
 Where S1 \ge S₂(1)

Crystal Data Collection and Refinement.

Suitable single crystals of each of the two complexes were mounted on a Bruker SMART diffractometer equipped with a graphite monochromator and Mo–K α ($\lambda = 0.71073$ Å) radiation. The crystals were positioned 60 mm from the CCD. 360 frames were measured with a counting time of 5 s. The structures were solved by the Patterson method by using SHELXS 97. Subsequent difference Fourier synthesis and least-squares refinement revealed the positions of the remaining non-hydrogen atoms. However, for complex 1, the four oxygen atoms of the perchlorate anion was refined in a disordered manner in six positions. The non-hydrogen atoms were refined with independent anisotropic displacement parameters. All calculations were carried out by using SHELXS 97, [43] SHELXL 97, [44] PLATON 99, [45] ORTEP-32, [46] and WinGX Ver-1.64 [47]. Data collection and structure refinement parameters as well as the crystallographic data for the two complexes are given in Table 1. CCDC 852926 (for 1), and 852928 (for 2) contain the supplementary crystallographic data for this paper. These data can be obtained free charge Cambridge Crystallographic Data of from Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

Syntheses of the complexes

Complex **1** was obtained as a consequence of reaction of reduced tridentate Schiff base ligand, HL^1 with nickel (II) perchlorate in methanol, followed by addition of benzoic acid in 1:1:1 molar ratio. Increase the Ni/L ratio leads to the formation of dinuclear complex **1** alongwith a trinuclear complex. Finally, when the Ni/L ratio reached 3:2, the pure free trinuclear compound (2) was obtained. Hence compound **2** has been prepared by addition of methanolic solution of ligand (HL¹) to the methanolic solution of Ni(II) perchlorate and PhCOOH with HL¹:Ni:PhCOOH

2:3:4 ratio, In an alternative method, complex **2** has also been prepared by addition of Ni(II) perchlorate to the methanolic solution of complex **1** followed by addition of benzoic acid (Scheme 1). The deprotonation of the benzoic acid in both cases was achieved with the required equimolar amounts of triethylamine. For both of the complexes, x-ray quality single crystals have been obtained by slow evaporation of the acetonitrile solution.

IR and UV-Vis Spectra of Complexes.

A moderately strong, sharp peak due to a N–H stretching vibration, at 3275 and 3224 cm⁻¹ for complexes **1** and **2**, respectively is obtained. In the IR spectra of complex **1**, the broad band near 3465 cm⁻¹ may be attributed to the presence of the O-H stretching of the water molecule. In **1**, the strong band at 1610 cm⁻¹ and 1480 cm⁻¹ are likely to be due to the antisymmetric and symmetric stretching mode of the carboxylate group and similarly in **2**, the strong bands at 1600 cm⁻¹ and 1484 cm⁻¹ can be attributed to the antisymmetric and symmetric stretching modes of the carboxylate group respectively. In complex **1**, the characteristic strong peak of the stretching vibration of uncoordinated perchlorate is observed at 1113 cm⁻¹.

The solid-state reflectance spectra of the complexes show a broad band centered at 1115, 1008 nm for complexes **1** and **2**, respectively. These broad bands are well-separated from the second transition observed at ca. 630, and 642nm for **1** and **2**, respectively. All these bands are the typical ones for octahedral Ni(II) complexes.

Structure of [Ni₂L₂(PhCOO)(H₂O)₂]ClO₄ (1).

Single-crystal X-ray diffraction studies on the crystals revealed a dimeric structure of **1** with the molecular formula $[Ni_2L_2(O_2CPh)(H_2O]^+$. A view of the molecule is shown in Figure 1. A non coordinated ClO₄⁻ anion counterbalances the charge on the cation. In this dinuclear entity, both the nickel(II) centres are in an octahedral environment being coordinated by two bridging μ_2 -phenoxo oxygen atoms O(10) of the Schiff-base ligand, O(2) of a bridging bidentate benzoate ligand (1 κ O:2 κ O²), by the two amino nitrogen atoms N(18) and N(22) of the Schiff base ligand and an oxygen atom O(1) from a water molecule (trans to the benzoate O(2) atom, Figure 1). Schiff base ligand (L¹) coordinates the metal centre in meridional fashion. The Ni-O (10), Ni-N(18), and Ni-N(22) bond distances (Table 2) are similar to those found in other related complexes [48-53]. The two Ni atoms are separated by 3.11(1) Å and the Ni-O(11)-Ni angle is

97.56(12)°. A bifurcated H-bond is formed between one of the hydrogen atoms of the two coordinated water molecule (H5W) and oxygen atom (O8) of noncoordinated perchlorate molecule. Other two oxygen atoms of perchlorate (O5 and O6) are engaged in weak hydrogen bonding with H29 of benzoate and H20b of amine forming a 2D porous sheet (Figure S1).

Structure of [Ni₃L₂(O₂CPh)₄] (2). Single crystal X-ray diffraction (XRD) study demonstrates trinuclear structure of complex 2 (Figure 2). Three nickel(II) ions form a linear array. The coordination geometry around the three nickeI(II) centre is approximately octahedral. Two terminal nickel(II) ions are coordinated by the two amine nitrogen atoms (N(18) and N(22)) and a phenoxo oxygen atom O(10) of tridentate reduced Schiff base ligand. The remaining site is coordinated by O(2) of a bridging bidentate benzoate ligand and two oxygen atoms O(3) and O(4) of a second chelating bidentate benzoate ligand. The bond lengths and bond angles, as summerised in Table 3 are similar to the previously reported complexes [54-59]. The tridentate reduced Schiff base ligand coordinates the metal centre in meridional fashion. The central metal ion Ni(2) is also octahedrally coordinated by two bridging phenoxo oxygen atoms, O(10) and $O(10^{\circ})$, two oxygen atoms, O(1) and $O(1^{\circ})$ from two bridging benzoate groups and two more oxygen atoms O(3) and O(3') from the second bridging bidentate benzoate ligand $(1\kappa O:2\kappa O')$. Two benzoate ligands show different coordination modes (1 κ O:2 κ O') and (1 κ O:2 κ ²O,O') to the nickel centre. The long distance between Ni(1) and Ni(2) (3.093(4)Å), indicates the absence of any bond between the two nickel centers and are similar to those found in other previously reported complexes [54-59]. The Ni(1)-O(3)-Ni(2) and Ni(1)-O(10)-Ni(2) bridge angles are 91.90(1) and 99.60(9), respectively. The amino N(18)-H forms a weak hydrogen bond with O(4) of benzoate.

Catecholase-like Activity Studies:

Catecholase like activity of the synthesized metal complexes was studied by using 3,5-di-tert butylcatechol (3,5-DTBC) as the substrate due to its low redox potential for the quinone–catechol couple, (Scheme 2), and its bulky substituents, which make further oxidation reactions such as ring opening slower. The reactions were monitored by the UV-Vis spectroscopic technique as the oxidised product 3,5- DTBQ shows a maximum absorption at about 400nm. To

determine the catecholase activity of complexes 1 and 2, 100 equiv of 3,5-di-tertbutylcatechol (3,5-DTBC) in methanol were added to 10^{-4} M solutions of 1 or 2 in methanol under aerobic condition at room temperature. The progress of the reaction was investigated by UV-vis spectra of the mixture at 5 min interval times. Complex 1 show gradual increase of an absorption band around 400 nm in UV-vis spectroscopy but complex 2 does not show any such changes. This indicates that only complex 1 catalyzes the oxidation of 3,5-DTBC to 3,5-DTBQ. Hence, the detailed kinetic studies were only performed on complex 1. Figure 3 presents the variation of the spectral behavior of complex 1 in the presence of 3,5-DTBC. From the figure, it is clear that the spectra of 1 in methanol solution shows drastic changes immediately after addition of 3,5-DTBC. To understand the kinetic aspects, the rate was determined, by traditional initial rate methods by following the growth of the quinone band at 400 nm as a function of time. The rate constant for a particular complex substrate mixture was determined from the $\log[A_{\alpha}/(A_{\alpha} - A_{t})]$ vs time plot (Figure 4). The substrate concentration dependence of the oxidation rates and various kinetic parameters were determined by using 10^{-4} M solutions of **1** with different concentrations of 3.5-DTBC under aerobic conditions. In all cases, a first-order kinetic dependence was observed at low concentrations of 3,5-DTBC, whereas higher concentrations resulted in saturation kinetics. The Michaelis-Menten model was applied to analyse the observed rate versus substrate concentration data of enzymatic kinetics. The Michaelis-Menten constant (KM) and maximum initial rate (Vmax) were determined by linearization using Lineweaver– Burk plots and values of kinetic parameters Vmax, K_M, and K_{cat} was also calculated. Both the observed rate vs [substrate] and Lineweaver–Burk plot for complex 1 are shown in Figure 4. The kinetic parameters for both cases are listed in Table 4. The k_{cat} values can be calculated by dividing the V_{max} values by the concentration of the corresponding complexes (Table 4). To determine the substrate concentration dependence of the rate and to determine various kinetic parameters, 10^{-4} M solutions of the different complexes were treated with 10, 30, 50, 70, and 100 equivalents of substrate.

The catalytic action of many dinuclear copper complexes has been developed over the past few decades.¹⁻¹² It has been proposed that reaction goes always via dinuclear active species. On the contrary, for the Ni(II) systems, previous reports have shown that the dinuclear Ni(II) complexes retain it's Ni₂ structural core in solution and behaves as an active species in catechol oxidation

whereas the mononuclear complexes respond to catechol oxidation in it's mononuclear active species form. In both the cases, reaction goes *via* radical intermediate species. Moreover, most of the previously reported Ni(II) complexes, showing catecholase-like activity are of Schiff base ligands and it is presumed that the Schiff base undergoes one electron reduction during the catalytic cycle. But in this study we have shown here that the Ni(II) complexes of redox innocent reduced Schiff base can also show significant catecholase-like activity. We have also proposed a mechanism for the catalytic cycle of the oxidation of 3,5-di-tert butylcatechol . In the present system, we have shown for the first time that the initial dinuclear core breaks into mononuclear one and this mononuclear species becomes catalytically active. This phenomena has not been clearly shown in the previously reported Ni(II) complexes. Hence to rationalize the probable mechanism (Scheme 3) of catecholase activity of **1**, we have investigated the probable complex-substrate intermediate through ESI-MS, EPR spectroscopy and qualitative as well as quantitative detection of the I_3^- band (~353 nm.) by UV-Vis spectroscopy for indication of formation of H_2O_2 during the catalytic oxidation procedure.

The binding of 3,5-DTBC to the complexes has been investigated by mass spectrometry (ESI; positive mode); hence, ESI-MS spectra have been recorded in methanol. ESI-MS for a 1 : 100 mixture of the proportionate complex 1 and 3,5 DTBC, recorded after 5 min of mixing. The base peak at m/z = 651.05 (100%) observed in the mass spectra of 1 can be assigned to the cationic species $[Ni_2(L)_2(PhCOO)]^+$ (Figure S2, Supporting Information). It thus appears that dinickel(II) species are maintained in solution. After addition of 3,5- DTBC to methanol solution of 1, it exhibits two additional major peaks at m/z = 243 and 463 respectively (Figure S3). These two peaks correspond respectively to the quinone-sodium aggregates [(3,5-DTBQ)Na]⁺ and $[(3,5-DTBQ)_2Na]^+[16]$. The peak at m/z = 973.49 [B+H]⁺ and 995.47 [B+Na]⁺ (Figure S4) could be due to the formation of complex-substrate aggregate ("B" in Scheme 3). It proves that the dinuclear unit is capable of binding two units of 3,5- DTBC, which allows its metal-mediated oxidation to 3,5- DTBQ. Another peak at m/z 486.23 (Figure S5) could be due to the mononuclear radical intermediate "D" (Scheme 3). Hence it may be expected that the dinuclear entity first binds with two units of 3,5- DTBC, followed by its cleavage to a mononuclear entity. The formation of radical intermediate has also been proved by solution EPR spectra, which is dominated by an isotropic signal around giso=1.99 with a peak-to-peak line width of ca. 40 G (Figure 5). The g value of the signal is closed to 2.0023 (value for a free electron), a value that is

characteristic for organic radicals, such as a phenoxyl-type radical [23]. Based on the above observations, we have proposed a probable mechanism for the catalytic cycle of the oxidation of 3,5-di-tert butylcatechol and it is predicted that the dioxygen of the atmosphere is reduced to H_2O_2 during the oxidation process.

Iodometric method has been followed to detect the formation of hydrogen peroxide during the catalytic reaction [20]. The formation of H_2O_2 has been estimated both qualitatively and quantitatively; estimation of H_2O_2 clearly shows that, the % of generation of H_2O_2 at first gradually increases with time and after 1 h of oxidation, it become saturated with generation of 64.67% of H_2O_2 , generated with respect to the formation of 3,5-DTBQ (Table 5). A plot of % of generation of H_2O_2 vs time has been shown in Figure 6. Comparison of the catecholase activity of mono and dinuclear Ni(II) complexes in MeOH and MeCN solvent has been depicted in Table S4 [22,23,66-71].

The activity of the dinuclear complex 1 may be attributed to the fact that presence of two weekly coordinated solvent water molecules can be removed to facilitate catalyst binding whereas complex 2 being a neutral rigid molecule has no option to interact with catechol and hence does not show any catalytic activity.

Magnetic properties

The thermal variation of the product of the molar magnetic susceptibility with temperature ($\chi_M T$) for compound **1** is displayed in Figure 7a. It is seen that the compound shows room temperature $\chi_M T$ values of ca. 2.25 cm³ K mol⁻¹ and it is in agreement with a magnetically noninteracted Ni(II) dimer having spin only value of 2.0 cm³ K mol⁻¹ for g = 2 at 300K. On cooling, $\chi_M T$ value slowly goes down; however, a more pronounced rapid decrease is seen at very low temperature and finally the value reaches to 0.025 cm³ K mol⁻¹ at 1.8 K. The nature of the curve indicates for antiferromagnetic exchange interaction between the Ni(II) centers. Isothermal magnetizations curve at 2K indicates that the molar magnetization is almost linear up to 5T and attained a maximum value of 1.53 μ_B as shown in Figure S6a. This linear nature of the magnetization curve and the smaller saturation value (expected value of ca. 2 μ_B) also imply the presence of dominant antiferromagnetic exchange interactions. To estimate the strength of magnetic interaction, we have fitted with relevant van Vleck's susceptibility equation of the magnetic susceptibility based on the isotopic Heisenberg Hamiltonian (H =–2JS₁S₂) as shown in Equation 2 [23]. The best

fitted result provides the following parameters: $g = 2.16 \pm 0.10$, $J = -5.65 \pm 0.04$ cm⁻¹ and R = 4.6×10^{-5} . Here, R represents the agreement factor and it can be defined as $R = \sum [(\chi_M T)_{exp} - (\chi_M T)_{calc}]^2 / \sum [(\chi_M T)_{exp}]^2$.

$$\chi_{M}T = \frac{Ng^{2}\beta^{2}}{k} \times \frac{2e^{2x} + 10e^{6x}}{1 + 3e^{2x} + 5e^{6x}} \quad x = J/kT$$
(2)

The thermal variation of $\chi_M T$ for linear trimeric Ni(II) complex **2** is shown in Figure 7b. The room temperature $\chi_M T$ value, ca. 3.91 cm³ K mol⁻¹ is close to the expected spin only value for magnetically non-interacted Ni(II) trimer (3.0 cm³ K mol⁻¹). Upon cooling from room temperature, $\chi_M T$ slowly increases down to ca. 150K, after that the value rises rapidly to attain a maximum value of ca.5.71 cm³ K mol⁻¹ at ca. 8K.

Thereafter, at very low temperature an abrupt decrease of $\gamma_{M}T$ value is observed and a value of ca. 4.33 cm³ K mol⁻¹ is reached at 2 K. This behavior suggests for the presence of a dominant ferromagnetic coupling. The sharp decrease at very low temperature should be attributed to the presence of a zero field splitting and/or intertrimer antiferromagnetic interactions [59]. Isothermal molar magnetization at 2K shows that the saturated molar magnetization value at 5T is $5.5\mu_{\rm B}$ as shown in Figure S6b. The intertrimer interaction and ZFS factor might cause the slight lowering from the ideal value. To calculate the J value, we have considered the relevant van Vleck's susceptibility equation corresponding to isotropic spin Hamiltonian H=- $2J(S_1S_2+S_2S_3)$ for linear Ni^{II} trimeric system. We have considered molecular field approximation to take account of the intermolecular interaction and zero field splitting factor (ZFS). It is worth to note that the molecular field approximation provides combined result for the contribution of intermolecular interaction and ZFS; therefore it is not possible to extract separate contributions for both of them. Taking consideration of isotropic spin Hamiltonian with molecular field approximation, we have fitted the magnetic susceptibility data with Equation 3 and the best fitted data provide the following parameters: $g = 2.25 \pm 0.04$, $J = 3.55 \pm 0.01$ cm⁻¹, $zJ' = -0.025 \pm 0.001$ cm^{-1} and $R = 5 \times 10^{-5}$ [59].

$$\chi_{\rm m}^{\rm trimer} = \frac{2{\rm Ng}^2\beta^2}{3{\rm k}} \times \left[\frac{3+42{\rm e}^{4{\rm x}}+15{\rm e}^{2{\rm x}}+18{\rm e}^{-2{\rm x}}+3{\rm e}^{-6{\rm x}}}{3+7{\rm e}^{4{\rm x}}+5{\rm e}^{2{\rm x}}+8{\rm e}^{-2{\rm x}}+{\rm e}^{-4{\rm x}}+3{\rm e}^{-6{\rm x}}}\right] \quad {\rm where} \ {\rm x}={\rm J/kT}$$

$$\chi_{\rm m}^{\rm total} = \frac{\chi_{\rm m}^{\rm trimer}}{\left[1 - \left(\frac{2zJ'\chi_{\rm m}^{\rm trimer}}{Ng^2\beta^2}\right)\right]} \dots \dots \dots (3)$$

Magneto-structural correlations

Since last two decades, several magneto-structural correlations have been drawn for different polynuclar transition metal systems. The correlation for hydroxo or phenoxo bridged Cu(II) dimer is most common one and well-established. Irrespective of metal ion, all these correlations show that the exchange interaction (*J*) has a strong dependence on metal bridging angle(s). For example, the di-phenoxido bridged Ni(II) dimers show almost linear dependence of J with Ni-O-Ni bridging angle [60-61]. If the angle is less than a critical value of ~97°, the effective overlap of magnetic orbitals is less and ferromagnetic interaction occurs due to orthogonality of magnetic orbital; however, for larger angles the overlap of magnetic orbitals is enhanced and as a result, antiferromagnetic coupling is observed. Based on theoretical calculation, Alvarez and his coworkers reported that the out-of-plane shift of the phenoxido rings and the hinge distortion of the M₂O₂ core framework can also change the *J* value [62]. A large out-of plane shift of the phenoxido rings results in lowering of antiferromagnetic contribution.

For a better insight in magnetic exchange pathway, we adopted spin-flip DFT calculations using broken symmetry approach to calculate J values as well as spin density maps. The DFT calculation provides the values of J = -6.74 cm⁻¹ for **1** and +3.63 cm⁻¹ for **2**, which agree well with the experimentally obtained values of J = -5.65 cm⁻¹ and +3.55 cm⁻¹ respectively. The molecular structure of complex **1** shows that the Ni(II) atoms are connected with each other via two phenoxido bridges and one μ_2 -1,3 carboxylate bridge. It can be assumed that the overall exchange coupling (*J*) is the vector sum of three individual contributions from three bridges and it is mediated through two distinct exchange pathways viz. (i) two phenoxido bridges and (ii) μ_2 -1,3 carboxylate bridge. It has been established that the magnetic exchange through multiple bridges can add or counterbalance their effects through different interaction between the HOMOs of each of the bridging ligands with the combinations of the magnetic orbitals of metal centers and the phenomena are called as orbital complementarity and countercomplementarity, respectively [63]. In case of complex **1**, the effect of orbital complementarity or countercomplementarity is expected. The individual magnetic exchange for phenoxido group is expected to be antiferromagnetic as the Ni(II)...O_{phenoxido}...Ni(II) angle

 (97.56°) exceeds the critical value of 97° . It is well known that the syn-syn bridging coordination mode of carboxylate groups usually causes AF coupling. However, the contribution through carboxylate can also be ferromagnetic due to countercomplementarity effect. To check the existence of ferro- or antiferromagnetic contribution through syn-syn carboxylate bridge, we performed DFT calculations on model structure. Initially, we have taken the structure of complex 1 and then a model structure was built by replacing the syn-syn carboxylate group with two nonbridging water molecules and kept the rest of the structure unaltered. It is worth to note that the oxygen atoms of carboxylate group for complex 1 and the oxygen atoms in non-bridging water molecules in model structure are placed in same crystallographic coordinate. The result shows that the model complex exhibits stronger antiferromagnetic $(J = -12.4 \text{ cm}^{-1})$ interaction compared with complex 1 (J = -6.74 cm⁻¹). The increased antiferromagnetic coupling for the model compound indicates ferromagnetic contribution of syn-syn carboxylate bridge in the complex. Therefore, a countercomplementarity effect is working between ferromagnetic interaction of synsyn carboxylate group and the antiferromagnetic contribution of di-phenoxido bridging group and the antiferromagnetic contribution dominates over the ferromagnetic one leading to a weak negative J.

The spin density mapping can also help us to identify the nature of exchange interaction through *syn-syn* carboxylate bridge. If the carbon atom of *syn-syn* coordinating carboxylate possesses a negative spin density in high spin state, then ferromagnetic interaction mediates through spin polarization mechanism, otherwise antiferromagnetic interaction dominates as a result of spin delocalization. According to MO theory, larger the negative spin density at carboxylate carbon atom, stronger is the ferromagnetic interaction [64]. The Mulliken's spin density at high spin state of carboxylate carbon atom of **1** is calculated to be -0.00505 au and hence it should provide weak ferromagnetic coupling. Conversely, the dominance of antiferromagnetic contributions as result of effective spin delocalization through di-phenoxido bridging group is also noticed from spin density plot and Mulliken's atomic spin densities as depicted in Figure S7 and Table S1, respectively. In this context, the spin delocalization is seen from density at phenoxido oxygen and it follows a σ -type exchange pathway involving the $d_{x^2-y^2}$ and d_{z^2} orbitals of the Ni(II) ions and the *p*-orbitals of the phenoxido group. It is also to be noted that the small value of plane shift of the phenoxido ring ($\tau = 12.2^\circ$) and hinge distortion of Ni₂O₂ plane ($\beta=30.7^\circ$) (Figure S9) in this complex might have weakened the AF coupling *via*

phenoxido bridges but their effects are not high enough to make the overall coupling ferromagnetic [65].

The molecular structure of complex 2 shows that Ni(II) ions are connected with each other through one phenoxido, one μ_2 -1,3 carboxylate (1 κ O:2 κ O) and one μ_2 -1,1 carboxylate ((1 κ O:2 κ^2 O) bridges. Indeed here, both Ni-O_{phenoxido}-Ni angle (99.59°) and Ni-O_{μ 2-1,1 carboxylate}-Ni bond angle (91.93°) play a major role on J value through σ -type exchange mechanism. Additionally, μ_2 -1,3 carboxylate bridging should also contribute weak ferro- or antiferromagnetic coupling depending on other structural parameters as mentioned previously. The Figure S8a shows that spin density located at phenoxido-oxygen atom is equally spread on both sides of Ni ion which signifies spin delocalization and as well as antiferromagnetic exchange interaction as is expected from the bridging angle of 99.59°. On the other hand, it can be noticed that spin density carried by μ_2 -1,1 carboxylate-oxygen atom is localized and directed towards the terminal nickel sites and therefore it mediates ferromagnetic exchange as a results of spin localization or accidental orthogonality of magnetic orbital through a σ -type exchange. The orthogonality of magnetic orbital can be visualized from singly occupied molecular orbital diagram as shown in Figure S8b. The $d_{x^2-y^2}$ lobe is seen in the central Ni(II) centers, where as dz^2 lobe is located at terminal Ni(II) atoms. The atomic spin density (Table S2) of high spin state pointed out that the phenoxido oxygen has a larger positive spin density compared to μ_2 -1,1 carboxylate-oxygen indicating a larger spin delocalization as well as antiferromagnetic contribution via phenoxido bridge. In case of μ_2 -1,3 carboxylate bridge, as we have discussed earlier that the spin density of central carbon atom decides the nature exchange. The negative spin density at high spin state of carboxylate carbon atom (-0.00297 au) suggests for weak ferromagnetic coupling through this bridge.

To check the ferromagnetic contribution through *syn-syn* carboxylate bridge, we again performed a DFT calculations on model structure of complex **2**, which was built by replacing the *syn-syn* carboxylate groups with four non-bridging water molecules and kept the rest of the structure unaltered. The atomic dispositions of carboxylate oxygen atoms for complex **2** are kept constant with respect to non-bridging oxygen atoms for coordinated water molecule in model structure. The calculated J shows a significant lowering (65.8%) of ferromagnetic interaction $(J=1.24 \text{ cm}^{-1})$ in model complex with respect to complex **2** $(J=3.63 \text{ cm}^{-1})$. This lowering of J in

model structure provides the evidence of weak ferromagnetic contribution transmitted through *syn-syn* carboxylate bridge in the complex **2**.

The analysis of the magneto-structural data for isostructural triply bridged trinuclear Ni(II) complexes are listed in Table S3. It is noticed that most of the structurally alike complexes possess very close phenoxido bridging angle ($\theta_1 \sim 96-97^\circ$) and μ_2 -1,1 carboxylate bridging angle $(\theta_2 \sim 93-94^\circ)$. The overall J values are positive for all these complexes as the ferromagnetic contributions of the μ_2 -1,1 carboxylate and syn-syn carboxylate bridge dominate over the antiferromagnetic contribution of phenoxido bridge. Among these complexes, antiferromagnetic coupling is found only in FUSWUM, where a wider phenoxido bridging angle ($\theta_1 = 99.89^\circ$) and μ_2 -1,1 carboxylate (θ_2 =96.49°) causes for the dominance of antiferromagnetic interaction over the ferromagnetic contributions of and syn-syn carboxylate groups. The comparison of complex 2 and FUSWUM indicates that both of them have almost the same phenoxido bridging angle (~99°) but the Ni(II) centers of complex 2 are ferromagnetically coupled. The difference in magnetic behavior seems to lie in the θ_2 angle which is 91.93° for 2. In case of FUSWUM complex, both of the μ_2 -1,1 carboxylate (96.5°) and phenoxido bridge provide individual antiferromagnetic interaction which dominate over ferromagnetic contribution of syn-syn carboxylate group. In case of complex 2, both the μ_2 -1,1 carboxylate (91.9°) and syn-syn carboxylate groups transmit ferromagnetic interaction which dominate over the antiferromagnetic contribution of phenoxido bridge.

Conclusions

The reaction of the tridentate reduced Schiff-base ligand, HL^1 , with nickel(II) perchlorate and benzoic acid in 1:1:1 molar ratio afforded double phenoxido and an *syn-syn* carboxylate bridged dinuclear nickel(II) complex (1). Complex 1 catalyses oxidation of 3,5-ditertiarybutyl catechol to the corresponding quinone derivative in methanol. Each Ni(II) centre in the complex contains a coordinated solvent molecule which is removed easily to facilitate binding of catechol to the metal centres and subsequently breaks into mononuclear species. These catechol bound mononuclear species seems to take part in the catalytic cycle which passes through radical formation and H_2O_2 generation. Most of the previously reported Ni(II) complexes, showing catecholase-like activity are of Schiff base ligands and it is presumed that the Schiff base undergoes one electron reduction during the catalytic cycle. We have shown here that the Ni(II)

complexes of reduced Schiff base which is redox innocent can also show significant catecholaselike activity. In a previous system we had the similar observation. However, to get a clearer insight into the reaction pathway, study of complexes with similar ligand systems and redox innocent metals like Zn^{2+} are needed to be studied. Such work is in progress in our laboratory. Interestingly, the trinuclear compound (2) which contains an additional Ni(II) ion but similar bridging system (two oxido- and one *syn-syn* carboxylate) is inactive towards catechol oxidation activity. The reason seems to lie in the absence of solvent molecule in the coordination sphere that would have been replaced by catechol to be bonded to the metal centre.

From the magnetic point of view, Ni(II) centres are antiferromagnetically coupled in **1** but ferromagnetically coupled in **2**. DFT calculations reproduced well with experimentally observed *J* values. In complex **1**, both the phenoxido bridges are equivalent and mediate antiferromagnetic coupling but in **2** one of the phenoxido bridge mediates AF coupling while μ_2 -1,1 carboxylato bridge transmits ferromagnetic interaction as expected from the Ni–O–Ni angles. In both compounds, *syn-syn* carboxylate bridges are uniquely trying to implant ferromagnetic coupling through spin polarization mechanism, however its contribution is suppressed by other bridging groups as supported by DFT calculations.

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Note: Electronic supplementary information (ESI) available: Fig. S1- S9, Table S1-S4, CCDC 1475002 and 1475003 for **1** and **2**.

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Figure 1: ORTEP-3 view of the asymmetric unit of 1 with ellipsoids at 30% probability.



Figure 2: ORTEP-3 view of the asymmetric unit of 2 with ellipsoids at 30% probability.



Figure 3. Increase in absorbance around 401 nm, after addition of 100 equivalents of 3,5-DTBC to a 10^{-4} M methanol solution of **1**. The spectra were recorded every 5 min.



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



Figure 5: EPR spectrum of a methanol solution of $1(10^{-3} \text{ M})$ after addition of 3,5-DTBC, recorded at 77K.



Figure 6. Generation of % of H₂O₂ with time.



Figure 7. Variation of $\chi_M T$ as a function of temperature at 500 Oe applied field for **1** (left) and **2** (right).



Scheme 1: Synthesis of complexes 1 and 2.



Scheme 2. Catalytic Oxidation of 3,5-DTBC to 3,5-DTBQ in Air-Saturated Methanol solvent.



 $[(3,5-DTBQ)Na]^+ = 243.05$ $[(3,5-DTBQ)2Na]^+ = 463.17$

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

Complexes	1	2	
Formula	C ₃₁ H ₄₇ N ₄ Ni ₂ O ₁₀ Cl	C52H58N4Ni3O10	
М	788.56	1075.09	
Crystal System	Monoclinic	Triclinic	
Space Group	C2/c (No. 15)	P-1 (No. 2)	
a/Å	15.0693(9)	10.200(5)	
<i>b</i> /Å	16.7418(10)	11.073(5)	
c/Å	15.4511(9)	12.222(5)	
$\alpha / ^{\circ}$	90	63.825(5)	
<i>β</i> /°	110.155(2)	78.812(5)	
$\gamma^{\prime \circ}$	90	75.048(5)	
V/Å ³	3659.4(4)	1191.8(9)	
Z	4	1	
$D_c/g \text{ cm}^{-3}$	1.431	1.498	
μ/mm^{-1}	1.159	1.237	
F (000)	1656	562	
R(int)	0.032	0.066	
Total Reflections	22212	8380	
Unique reflections	3200	4163	
$I > 2\sigma(I)$	2900	2268	
R1, <i>w</i> R2	0.0561, 0.1621	0.0592, 0.1549	
Temp (K)	293	293	
GOF	1.049	0.968	

 Table 1. Crystal data and structure refinement of complexes 1 and 2.

	0	∂	
bond lengths (Å)		bond angles (°)	
Ni(1)–O(1)	2.156(3)	O(1)–Ni(1)–O(2)	178.78(14)
Ni(1)–O(2)	2.028(3)	O(1)-Ni(1)-O(10)	85.77(15)
Ni(1)–O(10)	2.070(3)	O(1)-Ni(1)-N(18)	89.85(15)
Ni(1)–N(18)	2.105(4)	O(1)-Ni(1)-N(22)	93.37(18)
Ni(1)–N(22)	2.168(5)	$O(1)-Ni(1)-O(10)^{a}$	90.73(15)
Ni(1)–O(10) ^{<i>a</i>}	2.065(3)	O(2)-Ni(1)-O(10)	93.78(13)
		O(2)-Ni(1)-N(18)	89.02(13)
		O(2)-Ni(1)-N(22)	87.15(16)
		$O(2)-Ni(1)-O(10)^{a}$	90.28(12)
		O(10)–Ni(1)–N(18)	91.20(15)
		O(10)-Ni(1)-N(22)	176.40(15)
		O(10)-Ni(1)-(O10) ^a	77.47(12)
		N(18)-Ni(1)-N(22)	92.30(17)
		O(10) ^e -Ni(1)-N(18)	168.57(16)
		$O(10)^{e}-Ni(1)-N(22)$	99.06(15)

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

Symmetry element: a = -x, y, 3/2-z

bond lengths (Å)		bond angles (°)	
Ni(1)–O(2)	1.999(4)	O(2)–Ni(1)–O(3)	98.81(16)
Ni(1)-O(3)	2.152(4)	O(2)-Ni(1)-O(10)	91.36(16)
Ni(1)–O(4)	2.202(4)	O(2)–Ni(1)–N(18)	92.50(17)
Ni(1)–O(10)	2.036(5)	O(2)-Ni(1)-N(22)	87.96(19)
Ni(1)–N(18)	2.086(5)	O(2)-Ni(1)-C(32)	129.5(2)
Ni(1)–N(22)	2.189(6)	O(3)–Ni(1)–O(4)	61.22(15)
Ni(2)–O(1)	2.066(4)	O(3)-Ni(1)-O(10)	79.49(17)
Ni(2)–O(3)	2.152(5)	O(3)–Ni(1)–N(18)	165.41(17)
Ni2-O(10)	2.014(4)	O(3)-Ni(1)-N(22)	93.63(19)
$Ni2-O(1)^a$	2.066(4)	O(3)–Ni(1)–C(32)	30.92(18)
$Ni2-O(3)^a$	2.152(5)	O(4)–Ni(1)–O(10)	88.51(15)
Ni2-O(10) ^a	2.014(4)	O(4)-Ni(1)-N(18)	107.80(17)
		O(4)-Ni(1)-N(22)	89.68(19)
		N(18)-Ni(1)-N(22)	96.0(2)
		O(10)-Ni(1)-N(18)	91.11(19)
		O(10)-Ni(1)-N(22)	172.91(19)
		O(1)-Ni(2)-O(3)	91.01(15)
		O(1)-Ni(2)-O(10)	88.01(15)
		$O(1)-Ni(2)-O(1)^{a}$	180.00
		$O(1)-Ni(2)-O(3)^{a}$	89.00(15)
		O(1)-Ni(2)-O(10) ^a	91.99(15)
		O(3)-Ni(2)-O(10)	79.95(17)
		$O(1)^{a}-Ni(2)-O(3)$	89.00(15)
		$O(3) - Ni(2) - O(3)^{a}$	180.00
		O(3)-Ni(2)-O(10) ^a	100.05(17)
		O(1) ^a -Ni(2)-O(10)	91.99(15)
		$O(3)^{a} - Ni(2) - O(10)$	100.05(17)
		$O(10) - Ni(2) - O(10)^{a}$	180.00
		$O(1)^{a}-Ni(2)-O(3)^{a}$	91.01(15)
		$O(1)^{a} - Ni(2) - O(10)^{a}$	88.01(15)
		$O(3)^{a} - Ni(2) - O(10)^{a}$	79.95(17)

Table 3. Selected bond lengths (Å) and bond angles (°) for complex 2

Symmetry element: a=1-x, 1-y, 1-z

Table 4. Kinetic parameters for the oxidation of 3,5-DTBC catalyzed by complex 1 in methanol.

complex	V _{max} (M min ⁻¹)	K _m (M)	K _{cat} (h ⁻¹)	$\begin{array}{c} K_{cat} / K_m \\ (s^{-1}M^{-1}) \end{array}$
1	1.397×10 ⁻⁴	3.31×10 ⁻³	167.64	14.06

Standard error for $V_{max}(M \text{ min}^{-1}) = 6.20 \times 10^{-6}$ and Standard error for $K_m = 4.99 \times 10^{-5}$.

Table 5. Generation of % of H₂O₂ with time.

Time(min)	% of H ₂ O ₂
1	48.64
2	50.56
3	53.00
5	55.40
7	60.10
10	70.01
20	70.05
40	74.45
60	74.67