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Synthesis and Structural Characterization of a Linkage Isomer to a Mononuclear Nickel(II) Complex: Experimental and Computational Depiction of Phosphoesterase Efficiency

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Synthesis and Structural Characterization of a Linkage Isomer to a Mononuclear Nickel(II) Complex: Experimental and Computational Depiction of Phosphoesterase Efficiency

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characterization of a Synthesis and structural linkage isomer. bis(2,2'dipyridylamine)dithiocyanato(k-S)nickel(II), [Ni(dpa)₂(k-SCN)₂] (1) of a previously reported Ni(II) complex, $[Ni(dpa)_2(k-NCS)_2]$ (dpa = 2,2'-dipyridylamine; SCN = thiocyanate) has been reported herein. X-ray structural analysis of 1 reveals that Ni(II) complex crystallizes in monoclinic system with $P2_1/c$ space group and exists in *trans* configuration. The coordination geometry for 1 adopts a tetragonal structure. Supramolecular aspects of the Ni(II) complex indicate that N atom of SCN behaves as a donor and H atom of dpa ligand acts as a receptor in growing 1D crystalline structure along b axis in solid state. The aromatic rings in 1 prefer to exist in face-centred stacking with interplanar distance of 3.426 Å and supports strongly to form self-assembled 3D crystalline architecture. Hirshfeld surface analysis further recommends this crystalline assembly in solid state. 1 exhibits promising phosphatase activity towards disodium(4-nitrophenyl)phosphate (PNPP) in aqueous-methanolic medium. The hydrolytic phosphatase efficiency for 1 is determined in terms of turnover number (k_{cat}) as 3.38×10⁴ h⁻¹. Moreover, density functional theoretical computations closely replicate the structural parameters and spectroscopic behaviour of 1.

Keywords: Bio-mimicking Chemistry, DFT Study, Linkage Isomer, Nickel(II), Phosphatase Activity, X-ray Structure

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1. Introduction

In this modern era, investigation and exploration of new molecular properties for transition metal based coordination compounds raised the peak of demand in the advancement of functional materials [1-3]. Ligational motif with varying degree of coordination for different ligands may lead to an improvement in morphologies of the coordination compounds and physico-chemical properties as well as structural properties of the compounds may alter in significant manner [4-6]. Nickel(II) compounds with N,N-donor ligand exhibit diverse applications in modern science like fundamental catalysis, magnetism, bio-materials and so on [7-10].

Among the transition metal ions, nickel(II) is very attractive towards scientific community for its diverse functionality to serve as bio-enzymes like hydrogenase, generator of H_2 gas, etc. Among the available bio-relevant metalloenzymes, alkaline phosphatase enzyme contributes significantly in different biological functions ranging DNA fragmentation to RNA replication to bone metabolism as well as bio-remediation of organophosphate pesticides [11]. Active site of Phosphatase enzyme is surrounded by N or O coordination environment using histidine and aspartate groups [12]. Recently, it is also observed that nickel(II) complexes play key role in phosphatase activity [13] and approved as a well-accepted alternative in pursuing catalyzing hydrolytic reactions. Literature survey indicates that existence of Ni(II) coordination compounds with N,N linkages are well documented [11-14]. L. Dobrzańska et al. [15] have reported same mononuclear Ni(II) complex with dpa ligand having (k-N) mode of coordination by NCS ligands. L. Dobrzańska et al. have synthesized this isostructural Ni(II) complex with k-N mode of coordination by SCN ligand while we are able to produce its linkage isomer through k-S ligational mode in coordination of thiocyanate using a different synthetic approach. The spectroscopic properties of the previously reported Ni(II) compound have been reported earlier [16]. Nevertheless, there are quite a few crystallographic reports on [Ni(chelatingN,N-ligand)₂(NCS)₂] complexes with *trans*- [17] or *cis*-octahedral geometry [18]. In this present study, we have prepared a nickel(II) complex, bis(2,2'-dipyridylamine) dithiocyanato(k-S) nickel(II) with tetragonal coordination geometry. Exploration on supramolecular aspects of the Ni(II) complex indicate that N atom of SCN behaves as a donor and H atom of dpa acts as a receptor in growing 1D and 3D crystalline structure along b axis in solid state. The preference of face-centred stacking between aromatic rings in 1 with interplanar distance of 3.426 Å pursues strongly to assemble 3D structure in crystalline state. Moreover, this compound is quite efficient to cleave phosphoester bond hydrolytically with good catalytic efficacy, k_{cat} (h⁻¹)= 2.24×10³.

2. Experimental

2.1. Preparation of the complex

(a) Chemicals, solvents and starting materials

Pure 2,2'-dipyridylamine (Alfa-Aesar, UK), nickel(II) chloride hexahydrate (E-Merck, India), ammonium thiocyanate (E-Merck, India), disodium salt of 4-nitrophenylphosphate (Sigma-Aldrich, USA) and all other materials were purchased from commercial sources. All other chemicals and solvents were of analytical grade and were used as received without further purification.

(b) General procedure for the synthesis of Ni(II) compound (1)

A methanolic solution of 2,2'-dipyridylamine (0.3421 g, 1.998 mM in 20 mL) was added dropwise to an aqueous solution of hydrated nickel(II) chloride (0.2384 g, 1.002 mM in 10 mL) followed by addition of solid ammonium thiocyanate (0.1524 g, 2.002 mM). The reaction mixture was kept on magnetic stirrer for 1h. The blue coloured solution was filtered and kept in a capped glass tube for slowest evaporation. The beautiful blue-violet coloured single crystals were grown in the reaction mixture and were separated out from the solution after ~50 days.

Yield: ~0.1830 g (~76.76% based on metal salt). Anal. Calc. for $C_{22}H_{18}N_8S_2Ni$ (1): C, 51.08; H, 3.51; N, 21.66. Found: C, 51.12; H, 3.47; N, 21.72. IR (KBr, cm⁻¹): 3216-3311 (v_{N-H}), 2159 (v_{SCN}), 1631($v_{C=N}$).

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. Fourier Transform Infrared (FT IR) spectra (KBr discs, 4000-400 cm⁻¹) were recorded using a FTIR-8400S SHIMADZU spectrophotometer in the range 4000-400 cm⁻¹. Ground state absorption spectral measurements were operated with a JASCO model V-730 UV-Vis spectrophotometer. The ¹H NMR spectra were recorded on a Bruker DPX-500 MHz spectrometer. Electrospray ionization (ESI) mass spectrum was

recorded using a Q-tof-micro quadruple mass spectrometer. Molar conductivity measurement was done using a Horiba LAQUA Benchtop DS 70 conductivity meter.

2.3. X-ray diffraction study

Single crystal X-ray diffraction data of the nickel(II) complex were collected using a Rigaku XtaLABmini (Fixed 2Theta and Distance) diffractometer equipped with Mercury375R (2×2 bin mode) CCD detector. The data were collected with graphite monochromated Mo-K α radiation (λ =0.71073 Å) at 100 K using ω scans. The data were reduced using CrysAlisPro 1.171.38.46 [19] and the space group determination was done using Olex2. The structure was resolved by dual space method using SHELXT-2015 [20a] and refined by full-matrix least-squares procedures using the SHELXL-2015 [20b] software package through OLEX2 suite [20c].

2.4. Hirshfeld surface calculations of 1

Hirshfeld surfaces and fingerprint plots were generated using Crystal Explorer 17.5 [21] using data of single crystal X-ray diffraction study. The function d_{norm} was a ratio of the distances of any surface point to the nearest interior (d_i) and exterior (d_e) atom and the van der Waals radii of the atoms [22,23]. The negative value of d_{norm} indicated that the sum of d_i and d_e was shorter than the sum of the relevant van der Waals radii, which was considered to be a closest contact and was visualized in red colour. The white colour denoted intermolecular distances close to van der Waals contacts with d_{norm} equal to zero whereas contacts longer than the sum of van der Waals radii with positive d_{norm} values were coloured with blue. A plot of d_i versus d_e was a fingerprint plot that identified the presence of different types of intermolecular interactions.

2.5. Phosphatase activity by the nickel(II) complex

Disodium salt of (4-nitrophenyl)phosphate (PNPP) was used as a convenient substrate to explore the nature of cleavage of PNPP in aqueous-methanolic solution following a previously reported procedure [24]. An initial screening of the hydrolytic tendency of Ni(II) complex was performed until 2% formation of 4-nitrophenolate (2 hours) was reached, and then its kinetic data were collected. The cleavage rate of PNPP in the presence of the nickel complex was determined through initial rate method. The incremental optical band in absorption spectrum

was fixed at 414 nm owing to release of p-nitrophenolate ion in aqueous-methanolic solution at 25 °C. The electronic spectra were recorded by adding a solution of 1×10^{-4} M Ni(II) complex with 1×10^{-3} M PNPP during the course of wavelength scan for 2 hours. Blank experiment with PNPP in absence of Ni(II) complex under identical reaction conditions didn't exhibit any phosphatase activity.

Kinetic experiments of the phosphoester cleavage of PNPP in presence of Ni(II) complex were performed by monitoring the growth of the p-nitrophenolate band at 414 nm as a function of time under the condition of excess substrate (PNPP). Kinetic experiment was performed with **1** (at a constant concentration of 1×10^{-4} M) and PNPP (varying the concentration from 1×10^{-3} M to 1×10^{-2} M) in aqueous-methanolic solution adopting UV-Vis spectrophotometer. The incremental effect of absorbance in the electronic spectrum was recorded for a period of 2 hours at 8 min intervals. All measurements were performed in triplicate.

2.6. Computational methodology

Avoiding symmetrical restrictions all quantum mechanical computations were performed using Gaussian 09W programme suite [25]. For all atoms including the metal ion, B3LYP theoretical model and widely used 6-311G basis set [26] were compiled with Density Functional Theory (DFT) for ground state calculations. Initially, the preliminary structures were optimized in vacuum and then in acetonitrile (ϵ =35.688) employing well-established Integral Equation Formalism Polarizable Continuum Model (IEFPCM) [27]. Thereafter, the stability of all the complexes in vacuum and acetonitrile were confirmed separately through stability and IR frequency calculations. The images of molecular structure and frontier molecular orbitals (FMOs) were extracted from checkpoint files using GaussView 5.0.8 [25]. For more details of computational methodology readers could follow somewhere else [28].

3. Results and discussion

3.1. Synthesis and formulation

The $[Ni(dpa)_2(k-SCN)_2]$ complex has been prepared (**Scheme 1**) in the form of single crystals by addition of hydrated nickel(II) chloride with the chelator (dpa) in aqueous methanolic medium in a sealed glass tube. The structural formulation has been determined through different analytical techniques. The geometry of the Ni(II) complex (1) is confirmed

by single crystal X-ray diffraction study. We have employed several attempts to produce similar linkage isomers employing sodium cyanate but failed to produce corresponding compound using our reaction methodology. Our synthetic approach is highly useful for the production of thiocyanate based linkage isomers.



Scheme 1. Preparative procedure of Ni(II) complex (1).

3.2. Depiction of X-ray structure and supramolecular aspects of long range crystalline architectures

X-ray diffraction analysis of the nickel(II) complex reveals that nickel(II) compound crystallizes in a monoclinic system with $P2_1/c$ space group. The ellipsoidal plot of the mononuclear nickel(II) complex is displayed in Figure 1. The nickel(II) ion exists in tetragonal coordination geometry where the square plane consists of two units of dpa ligands. Two thiocyanate ions coordinate at axial position to the Ni(II) centre in this centrosymmetric structure and satisfies the cationic charges of Ni(II) ion. Bond distances and bond angles measurement in the primary zone of coordination indicates that Ni(II) ion adopts a tetragonal coordination geometry in crystalline phase. Two independent bond angles, \angle N1-Ni1-N3 and \angle N3-Ni1-N1* in square plane are found to contain 86.20°(7) and 93.80°(7) respectively whereas only one symmetry adopted bond angle, \angle S1-Ni1-S1* is found as 180°. Two independent Ni–N bond lengths are also observed of about 2.0240(17) and 2.0085(2) Å although one Ni1-S1 bond length is found as 2.8880(6) Å. The single crystal X-ray diffraction refinement parameters for **1** are shown in Table 1. Important bond lengths and angles for **1** are also summarized in Table 2.

Interestingly, we have collected Ni(II) complex in *trans*-form as blue-violet coloured crystals from the solution and more surprisingly S-end of the thiocyanate ions are used to coordinate Ni(II) ion. Probably, effect of creating strong hydrogen bonds by N atom of SCN ligand with the H atoms of dpa facilitates the coordination by S-end of SCN to Ni(II) ion along axial side.

Investigation on the nature of growth of supramolecular architectures in crystalline phase for this Ni(II) complex, it is revealed that H-atoms attached to dpa and N-atom of the thiocyanate act significant role in constructing a 1D H-bonded network along *b* axis. N2-H2...N4 and C4-H4...N4 are the main responsible force in the construction of 3D crystalline architecture in solid state (Fig. 2, Table S1). Furthermore, face-centred stacking between aromatic rings has provided additional stability in forming self assembled 3D crystalline architecture in solid state. The Ni(II) complex has been found to have face-centred stacking between the aromatic rings. The pyridine rings of one dpa ligand are stacked with another pyridine ring of other dpa unit with centroid-centroid distance of 3.426 Å and interplanar distance of 3.476Å.

Comparison of structural aspects between the Ni(II) compound prepared by L. Dobrzańska *et al.* [15] and its linkage isomer, $[Ni(dpa)_2(k-SCN)_2]$ (1), it has been observed that both the linkage isomers has been found to exist in trans configuration. The isomers are crystallized in monoclinic system with identical space group, $P2_1/c$. Both the compounds have and displayed close relationship between bond distances and bond angles around Ni(II) ion. However, some important structural parameters like cell volume, cell dimension, resolution factor, H bonding interactive distances, and face-centred stacking between aromatics for our synthesized Ni(II) complex differ largely from its linkage isomer reported by L. Dobrzańska.

3.3. Hirshfeld analysis of nickel(II) complex

Hirshfield surface area of Ni(II) complex has been determined to reveal the nature of H bonding and face-centred stacking between aromatics in forming supramolecular structure for this Ni(II) complex. The nickel(II) complex has been found to have 528.41Å^3 surface volume and 428.47Å^2 surface area (Fig. S1). Red area shows close contact present in the molecules with other adjacent molecules in crystalline phase. This molecular interaction has presented the N-H...N strong hydrogen bonding with nitrogen atom of SCN molecule as displayed in Fig 3. Percentage share of each element in close interaction (Table S2) and fingerprint plots (Figure 3) display the same type of interaction by the surface area. Fingerprint plot of H_{in} - All_{out} and All_{in} and N_{out} has showed of intense interaction between N-H of molecule and N of SCN which have exhibited by the sharp point peaks in the 2D fingerprint plot.

3.4. Theoretical modelling of the structure and frontier molecular orbitals

Computational modeling has been performed to correlate the structural information between X-ray structure and optimized Ni(II) structure. The optimized molecular structure of **1** in vacuum (Fig. 4) exhibits close similarity with the X-ray structure. Subsequently, the bond lengths and bond angles have been observed in well agreement with the experimental values (Table 2). The optimized structure in vacuum has also defined the same degree of coordination motifs for dipyridyl amine and thiocyanate ions and has attested the formation of Ni(II) structure in *trans* conformation. We have also superimposed the XRD structure with computationally optimized structure using PyMOL 1.3 software and presented in Fig. S2. The experimental and theoretical geometry parameters for this Ni(II) linkage isomer are already summarized in Table 2. Both the structures well superimposed on each-other. There is little discrepancy in orientation of SCN groups of computationally optimized structures. Probably this is due to ignorance of hydrogen bonding in computational calculations as observed in experimental XRD structure between two asymmetric units. The green and brown structure presents the experimental XRD and computationally optimized structure respectively.

Calculation of energies of the frontier orbitals of the nickel(II) linkage isomer in MeCN exhibit that the energy gap between HOMO \rightarrow LUMO and HOMO-1/2 \rightarrow LUMO+1/2 (Fig. 5) portray a clear picture about the electronic activity of **1** in solution. It is well established that low energy gap between HOMO and LUMO provides higher chemical activity. It is found that electronic cloud of HOMO, HOMO-1 and HOMO-2 orbitals locate majorly on Ni(II) ion; however electronic cloud of LUMO, LUMO+1 and LUMO+2 orbitals dominate extensively over ligand moieties. Such large and prominent shift of electronic cloud indicates the possibility of LMCT behaviour. Also, HOMO-LUMO, (HOMO-1)-(LUMO+1) and (HOMO-2)-(LUMO+2) transition energies 2.36 eV (525 nm), 2.62 eV(473 nm) and 2.85 eV (435 nm) respectively have been well justified the experimental absorption spectrum of **1** in acetonitrile medium.

3.5. Phosphatase activity of [Ni(dpa)₂(k-SCN)₂] and its mechanistic implications

The cleavage efficiency of the Ni(II) complex has been examined in aqueous-methanolic medium by spectrophotometry. Disodium (4-nitrophenyl)phosphate hexahydrate (PNPP) is considered as a standard substrate. Evolution of 4-nitrophenolate in aqueous-methanolic medium is monitored by scanning wavelength from 200 to 900 nm at 25 °C. Furthermore, the

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structural stability of the Ni(II) linkage isomer has been examined through time dependent measurements of molar conductance and electronic spectra in solution phase with 30 mins interval. Initially, the optical spectrum for this Ni(II) liknage isomer in methanolic solution exhibits sharp electronic transitions at 249 and 308 nm which are assignable to the π - π * / n- π * electronic transitions of ligand origin (Fig. S3) [2d]. After 30 mins, the positions of existing electronic bands are shifted promptly to lower energy region (260 & 328 nm; Red shift) along with development of a broad optical band at 623 nm. The positional variation of the optical bands strongly recommend about the changes in ligand coordination to Ni(II) centre or most probably the displacement of thiocyanate ion from Ni(II) centre in methanol medium [29]. Further measurement with another 30 min interval i.e., after 1 h, the position of the electronic bands remains very close to position of the bands appeared in measurements after 30 mins. The electrical molar conductivity measurements of 1 in 10^4 M dry methanolic solution show a non-electrolytic behaviour with molar conductance value of 07 Scm²mol⁻¹. After 30 mins, the solution of the Ni(II) isomer exhibits molar conductance value 93 Scm²mol⁻¹ which is a definite signature for the 1:1 electrolytic behavior in solution phase. With progress of time (with 30 mins interval till 2h), molar conductivity value is found as 99 Scm²mol⁻¹ which consolidates the dissociation of one thiocyanate ion and represents a 1:1 type electrolyte during a period of 2h (Fig. S4). The changes in electronic bands and molar conductance value with the progress of time are indicative of structural instability of this nickel complex in solution phase.

Characteristics changes in the spectral bands upon addition of Ni(II) complex to PNPP have been observed and is shown in Fig. 6. The spectra have been recorded for 2 hours at 8 min intervals. Upon addition of Ni(II) complex to the solution of PNPP, a new optical band at 414 nm with incremental absorbance (Fig. 6) has been detected during the spectrophotmetric titration. A close inspection on absorbance vs time plot at 414 nm has revealed that the changes of absorbance difference remain almost parallel to time and maintain a first order kinetics. The incremental absorption band at 414 nm is assignable to the evolution of 4-nitrophenolate in solution. Phosphatase activity has also been measured employing 10^{-4} M aq. methanolic solution of hydrated nickel(II) chloride and dipyridylamine ligand (dpa) independently under similar experimental conditions. However, independent addition of 10^{-4} M solution of NiCl₂.6H₂O and dpa to 10^{-3} M PNPP didn't produce any significant effect in optical region which strongly recommends about non-functional activity of NiCl₂.6H₂O and dpa in solution (Fig. S5).

The details of kinetics for phosphatase activity have been carried out following the initial slope method. The calculated first order rate constant, $V(min^{-1})$ is found as 1.61×10^{-4} (Error = 2.81×10^{-6}) (Fig. S6). The kinetic parameters (V_{max} , K_M , k_{cat}) for Ni(II) complex catalyzed reactions have been calculated using Michaelis-Menten approach of enzymatic kinetics (Table 3). Important kinetic parameters for phosphoesterase activity by the nickel(II) complex have been determined through plotting of log[$A_{\alpha}/(A_{\alpha} - A_t)$] values against time. Moreover, a comparison has also been made to examine the catalytic efficacy of this linkage isomer with other reported nickel(II) complexes in Table 3 and it is found that this Ni(II) complexes [24,30,31].

To explicate the involvement of active species in studying phosphoester cleavage activity in aqueous-methanol medium, ESI mass spectral analysis of PNPP in presence of Ni(II) complex has been recorded in positive mode. In situ ESI-MS spectral measurements of the reaction mixture remain helpful in predicting the mechanistic pathway of the phosphoesterase activity in aqueous-methanol. The reaction mixture between Ni(II) complex and PNPP of 1:10 ratio in aqueous-methanol has exhibited the rising of new characteristics peaks with isotropic distribution pattern. In the solution of mixture between Ni(II) complex and PNPP, characteristics peaks in ESI-Ms have been observed at m/z 161.90, 478.07 and 637.25 which are assignable to $[Na-nitrophenolate]^+$ (Theoretical m/z 161.09), $[Ni(dpa)_2(k-SCN)(H_2O)]H^+$ (Theoretical m/z 478.2) and [Ni(dpa)₂(PNPP)(H₂O)] (Theoretical m/z 637.19) adducts in solution (Fig. S7). Initially, it is believed that the Ni(II) complex undergoes hydrolysis to form an aquatic Ni(II) complex which in presence of PNPP has made an adduct between substrate and catalyst. In the later stage, the coordinated aqua molecules have made a nucleophilic attack that probably formed a P-O-Ni cycle and subsequently rearranged to release nitrophenolate and phosphoric acid through cleavage of phosphor-ester linkage (Scheme 2). Most of the proposed adducts and chemical species have been identified through ESI-Ms in aqueous methanolic medium. The experimental findings have been further attested by the energy and stability of the optimized reaction intermediates in solution phase.



Scheme 2. Proposed catalytic cycles for the phosphatise activity of Ni(II) linkage isomer

With our own curiosity, we have optimized few adducts those have been probably operative in the course of catalytic cycle and calculated the stabilization energy values for those intermediates. The proposed reactive intermediates and adducts including their stabilization energies are given in **Scheme 3**. The stabilization energy (ΔE) of the possible intermediates has been calculated by considering the difference between potential energy of the Ni(II) complex (E_{complex}) and summation of the potential energies of the individual ions (Ni²⁺, SCN⁻)/molecules (water).

$$\Delta E = E_{\text{Complex}} - E_{\text{Components}}$$

Where, ΔE = Stabilization energy or binding energy of the metal-ligand complex; $E_{Complex}$ = Potential energy of metal-ligand complex; $E_{Component}$ = Summation of potential energies of the individual ions (Ni^{II}, SCN⁻ etc.)/molecules (water).



Scheme 3. Optimized structures of the proposed reactive intermediates during catalytic phosphoester cleavage of PNPP with Ni(II) complex with corresponding stabilization energy values.

Theoretical calculations reveal that the 2nd intermediate has highest binding energy (-900.04 kJ Mol⁻¹) (1st row, **Scheme 3**) among the three intermediates and strongly recommends in favour of better stability of the 2nd intermediate. Consequently, it is also justified that conversion from dithiocyanato-Ni(II) to thiocyanato-aqua-Ni(II) complex during solubilisation of the nickel(II) complex in aq. methanolic medium is in accordance with computational calculations and depicted in **Scheme 2**. On the other hand, upon addition of PNPP to aq. methanolic solution of Ni(II) complex, theoretical calculations have preferred the lowest interaction energy (1403.06 kJ Mol⁻¹) of the hydrogen bonded PNPP complex (2nd row, **Scheme 3**) and clearly justified the possibility of formation of hydrogen bonded intermediate during the course of phosphatase activity as proposed in **Scheme 2**.

On the basis of ESI mass spectrum for the reaction mixture and theoretical calculations, it may be considered that the primary stage of Ni(II) complex in aq. methanolic solution provides simple substitution at Ni(II) centre which has attested the most possible existence of second structure in solution phase of as most stable structure (1st row images, **Scheme 3**). While enhanced stabilization energy of the second intermediate in second row structures (1st row images, **Scheme 3**) has clearly suggested it as the most probable substrate-catalyst intermediate for the course of phosphoestarase cleavage activity by this Ni(II) complex. The

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m/z values of the possible intermediates and adducts have been obtained through ESI-MS that has well resembled with theoretical values calculated for those adducts (**Scheme 3**).

4. Conclusion

Herein, we have synthesized a linkage isomer of nickel(II) complex, bis(2,2'dipyridylamine)dithiocyanato(k-S)nickel(II), $[Ni(dpa)_2(k-SCN)_2](1)$ (dpa = 2.2'dipyridylamine) and structurally characterized employing different analytical techniques. Xray structural analysis reveals that nickel(II) ion in 1 adopts tetragonal coordination geometry and exists in a centrosymmetric structure. Nitrogen atoms of SCN ion and hydrogen atoms of dpa play an important role in constructing 1D and 3D supramolecular architecture along b axis in crystalline phase. Face-centred stacking between the pyridine rings of different dipyridyl amine ligands having interplanar distance of 3.426Å lead to a self assembled 3D crystalline architecture. The hydrolytic phosphatase activity for this mononuclear nickel complex has been determined in terms of high turnover number (k_{cat}) as 3.38×10^4 h⁻¹. Computational outcomes employing density functional theory has been used to correlate structural parameters and spectroscopic behaviour. More importantly, the coordination geometry for most of the linkage isomers has been determined through spectroscopic analysis although we have successfully prepared the blue-violet coloured single crystals for this nickel(II) linkage isomer. Furthermore, the mode of coordination for thiocyanate in complexation with metal ions is observed through nitrogen (k-NCS) and from this perception, this nickel(II) linkage isomer is a limited addition to the molecular library.

5. Supplementary data

Crystallographic data are available free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) upon request, quoting deposition number CCDC 1900185 for the Ni(II) compound.

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$\begin{array}{c} C_{22}H_{18}N_8S_2Ni\\ \\\hline 517.27\\ \hline 100 \ K\\ \hline 0.71073 \ \text{\AA}\\ \hline Monoclinic\\ \hline P2_1/c\\ \hline 7.5588(3)\text{\AA}, \ \ \alpha=90^\circ; \ b=17.4779(5)\text{\AA}, \ \ \beta=\\ .785(4)^\circ; \ c=8.3349(3)\text{\AA}, \ \ \gamma=90^\circ\\ \hline 1073.84(7) \ \ \text{\AA}^3 \end{array}$
517.27 100 K 0.71073 Å Monoclinic $P2_{1/c}$ $7.5588(3)\text{Å}, \ \alpha = 90^{\circ}; \ b = 17.4779(5)\text{Å}, \ \beta =$ $.785(4)^{\circ}; \ c = 8.3349(3)\text{Å}, \ \gamma = 90^{\circ}$ $1073.84(7) \text{ Å}^{3}$
100 K 0.71073 Å Monoclinic $P2_1/c$ 7.5588(3)Å, α= 90°; b = 17.4779(5)Å, β= .785(4)°; c = 8.3349(3)Å, γ = 90° 1073.84(7) Å ³
$\begin{array}{r} 0.71073 \text{ \AA} \\ \hline \\ Monoclinic \\ \hline P2_1/c \\ \hline \\ 7.5588(3)\text{\AA}, \alpha = 90^\circ; \ b = 17.4779(5)\text{\AA}, \beta = \\ .785(4)^\circ; \ c = 8.3349(3)\text{\AA}, \gamma = 90^\circ \\ \hline \\ 1073.84(7) \text{ \AA}^3 \end{array}$
Monoclinic $P2_1/c$ 7.5588(3)Å, $\alpha = 90^\circ$; $b = 17.4779(5)Å$, $\beta =$.785(4)°; $c = 8.3349(3)Å$, $\gamma = 90^\circ$ 1073.84(7) Å ³
$\frac{P2_{1}/c}{7.5588(3)\text{\AA}, \alpha = 90^{\circ}; \ b = 17.4779(5)\text{\AA}, \beta = .785(4)^{\circ}; \ c = 8.3349(3)\text{\AA}, \gamma = 90^{\circ} \\ 1073.84(7) \text{\AA}^{3}$
7.5588(3)Å, $\alpha = 90^{\circ}$; b = 17.4779(5)Å, ß= .785(4)°; c = 8.3349(3)Å, $\gamma = 90^{\circ}$ 1073.84(7)Å ³
1073.84(7) Å ³
2
1.60 g/cm^3
1.128 mm ⁻¹
7831
1887
0.031
1.08
$R1 = \frac{0.0339}{0.0339}, wR2 = 0.0919$
0.88 and <mark>-0.58</mark> e. Å ⁻³

Table 1 Crystallographic refinement parameters of [Ni(dpa)₂(k-SCN)₂] (1)

Table 2 Selected bond lengths (Å) and bond	angles (°) for [Ni(dpa) ₂ (k-SCN) ₂] (1) obtained
from the XRD structure and from DFT study	

Bond lengths (Å)					
	Experiment	DFT		Experiment	DFT
Ni1-S1	2.8880(6)	3.187	Ni1-N3	2.0085(18)	1.9239
Ni1-N1	2.0240(17)	1.9225			
Bond angles (°)				• 	
	Experiment	DFT		Experiment	DFT
S1-Ni1- <mark>N3</mark>	92.16(6)	92.70	N1-Ni1-N3	86.20(7)	86.45
S1-Ni1- <mark>N1</mark>	95.69(5)	91.79	N3-Ni1-N3*	180.00	177.40
S1-Ni1-S1*	180.00	174.53	N1-Ni1-N3*	93.80(7)	93.05
S1-Ni1- <mark>N3</mark> *	87.84(6)	89.75	N <mark>1</mark> -Ni1-N <mark>1*</mark>	180.00	176.84
S1-Ni1- <mark>N1</mark> *	84.31(5)	91.34			

*Symmetric atom occupies to trans position and applicable to centrosymmetric system

Table 3	Kinetic parameters	for hydrolytic	cleavage of PNPP	catalyzed by 1	l in aq. MeOH
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Complex	$V_{max}(M s^{-1})$	$K_m(M)$	$k_{\rm cat}$ (h ⁻¹)	Ref
1*	9.39×10 ⁻⁴	1.19×10 ⁻³	3.38×10^{4}	Present
$[Ni_2L_2(NCS)(OAc)(H_2O)_{0.5}(MeOH)_{0.5}]$	4.09×10 ⁻⁴	2.81×10 ⁻⁴	2.94×10^{4}	[24]
$[Ni(bpy)_2(OH_2)(NO_3)](NO_3)$	2.34×10 ⁻⁴	1.02×10 ⁻³	8.42×10^{3}	[2d]
$[Ni_4{}^{II}(\mu\text{-}OHCH_3)_2(L)_2(CH_3OH)_2]^{-2}CH_3OH$	1.65×10 ⁻⁵	5.78×10 ⁻³	5.92×10^{2}	[30]
$[Ni_2(L^1)(H_2O)_2(NCS)_3)]$			2.91×10^{2}	[31]

*Std. Error for V_{max} (MS⁻¹) = 2.46×10⁻⁵; Std. Error for K_m (M)= 1.10×10⁻⁴



Fig. 1. An ellipsoidal plot of nickel(II) complex with 30% ellipsoid probability



Fig. 2. Formation of 1D (Top) and 3D (Below) crystalline architectures through H^{...}N interactions (pink dotted) in **1**





Fig. 3. Fingerprint plot of Ni(II) complex.



Fig. 4. Optimized structure of 1 in vacuum using DFT/B3LYP/6-311G theoretical model.



Fig. 5. Frontier molecular orbitals of **1** along with the corresponding transition energy values calculated using TD-DFT/B3LYP/6-311G theoretical model and IEFPCM/acetonitrile solvent system.



Fig. 6. Enhancement of absorbance for gradual production of phenolate species at 414 nm upon addition of **1** to 100 equivalents of PNPP in aqueous medium. The spectra were recorded after every 8 min at 298 K.

Highlights

- Synthesis of bis(2,2'-• and X-ray structure a linkage isomer, dipyridylamine)dithiocyanato(k-S)nickel(II), [Ni(dpa)₂(k-SCN)₂] of a previously reported nickel(II) complex, [Ni(dpa)₂(k-NCS)₂]
- The nickel(II) complex efficiently cleave PNPP with TON, $3.38 \times 10^4 h^{-1}$. •
- The theoretical findings employing DFT have been well corroborated with the • experimental results.