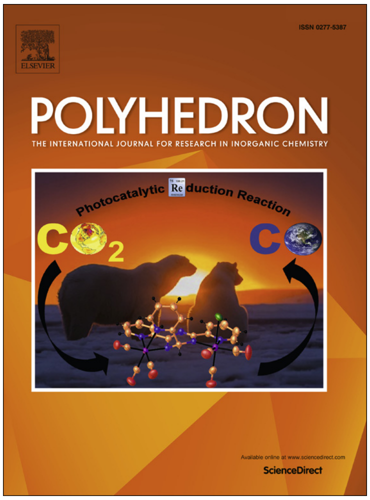


Bis(μ-tetrazolato-NN′) bridged dinuclear nickel(II) Schiff base complexes: Tandem synthesis, structure and self assembly

Mithun Das, Klaus Harms, Biswa Nath Ghosh, Kari Rissanen, Shouvik Chattopadhyay

PII: S0277-5387(14)00719-0
DOI: http://dx.doi.org/10.1016/j.poly.2014.11.012
Reference: POLY 11060

To appear in: *Polyhedron*

Received Date: 30 August 2014
Accepted Date: 12 November 2014

Please cite this article as: M. Das, K. Harms, B.N. Ghosh, K. Rissanen, S. Chattopadhyay, Bis(μ-tetrazolato-NN′) bridged dinuclear nickel(II) Schiff base complexes: Tandem synthesis, structure and self assembly, *Polyhedron* (2014), doi: http://dx.doi.org/10.1016/j.poly.2014.11.012

Bis(μ-tetrazolato-NN′) bridged dinuclear nickel(II) Schiff base complexes: Tandem synthesis, structure and self assembly

Mithun Das[a], Klaus Harms[b], Biswa Nath Ghosh[c], Kari Rissanen[c], Shouvik Chattopadhyay[a,*]

[a] *Department of Chemistry, Inorganic Section, Jadavpur University, Kolkata – 700 032, India.*

E-mail: shouvik.chem@gmail.com   Tel:+91-33-24572941

[b] *Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, D-35032 Marburg, Germany.*

[c] *Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, 40014 Jyväskylä, Finland.*

Abstract

Two new bis(μ-tetrazolato-NN′) bridged centrosymmetric dinuclear nickel(II) Schiff base complexes $[Ni_2L^1_2(PTZ)_2]\cdot 2(CH_3)_2SO\cdot 2.69H_2O$ (**1**) and $2[Ni_2L^2_2(PTZ)_2]\cdot 3H_2O$ (**2**) (HL^1 and HL^2 are Schiff bases, HL^1 = *2-((2-(dimethylamino)ethylimino)methyl)phenol*, HL^2 = *2-((2-(methylamino)ethylimino)methyl)-6-methoxyphenol* and *HPTZ* is *5-pyrazinyltetrazole*) have been synthesized via [3+2] cyclo-addition of 2-cyanopyrazine and sodium azide in presence of nickel(II) acetate tetrahydrate and the respective Schiff bases. The structures of the complexes are confirmed by single crystal X-ray diffraction analysis. Both complexes show fluorescence with fluorescence life times in the range 1 - 6 ns. The change in the denticity of the Schiff base blocking ligand was shown to have no effect in controlling the molecular structures of the complexes. The supramolecular self assemblies were also explored.

Key words: Nickel(II); Schiff base; 1,3-dipolar cycloaddition; 5-pyrazinyltetrazolate; Dinuclear.

Introduction

Di and polynuclear complexes of nickel(II) are widely used as materials for non-linear optics [1,2], as catalysts for diverse reactions [3] and as suitable models for the active sites of many enzymes [4-6] and also as magnetic materials [7-9]. Several researchers have used carboxylates and pseudohalides as bridging ligands [10-12]. N_2O donor tridentate Schiff bases, prepared simply by refluxing N-substituted diamines with salicylaldehyde or its derivatives, as blocking ligands in preparing such di and polynuclear complexes [13-15]. The ability of the phenoxo oxygen atom to bridge the metal centres and also to participate in hydrogen bonding interaction to form various supramolecular architectures has also inspired the researchers to use the above-mentioned Schiff bases in preparing new complexes [16,17]. Tetrazoles have also been used by several groups in forming bridges the nickel(II) centers [18-20]. The application of tetrazole functional groups in medicinal chemistry as a metabolically stable surrogate for a carboxylic acid group [21-23] and in material science as high density energy materials [24-26] and also in coordination chemistry as ligands with versatile coordination ability through its four nitrogen atoms [27,28] are well established. However, the use of Schiff bases as blocking ligands in preparing tetrazolato bridged di and polynuclear transition metal complexes is very rare. In our previous papers, we have reported three such complexes of nickel(II) [29,30]. Synthesis of few more nickel(II) complexes was also reported by a different group [31,32]. Two different methods were used in preparing the complexes. In the first case, the nickel(II) Schiff base complex with azide co-ligands were isolated in solid state followed by the reaction of this azide complex with 2-cyanopyridine to prepare the tetrazolato bridged dinuclear nickel(II) complexes with Schiff base blocking ligand. In the second case, the azide complex was not isolated, instead tandem synthesis of the tetrazolato bridged nickel(II) Schiff base complexes was reported. In the present work, we have used two different Schiff bases as blocking ligands and substituted tetrazolate to prepare two bis(μ-tetrazolato-NN′) bridged dinuclear nickel(II) complexes by tandem synthesis using 2-cyanopyrazine, sodium azide, nickel(II) acetate and respective Schiff base ligand under stirring condition in methanol. Our intension was to examine the variation in molecular architectures, if any, on changing the denticity of the Schiff bases.

We would also like to investigate the variation of the supramolecular architectures of the complexes. Supramolecular systems based on coordination complexes have received much attention now-a-days because of their potential use in photonic devices, catalysis, host-guest chemistry etc. [33,34]. A significant number of supramolecular metal complexes have been synthesized in the last several years [35,36]. The components of a supramolecule are held together by a variety of non-covalent forces, e.g. hydrogen bonding, π···π, C-H···π, etc. [37-40]. Herein, we report the tandem synthesis, structural features, spectroscopic characterization and supra-molecular architectures of two new bis(μ-tetrazolato-NN′) bridged nickel(II) complexes with N_2O donor Schiff base blocking ligands.

2. Experimental Section

2.1. Materials

All starting materials were commercially available, reagent grade, and used as purchased from Sigma-Aldrich without further purification.

2.2. Preparations

2.2.1. Complex $[Ni_2L^1{}_2(PTZ)_2]\cdot 2(CH_3)_2SO\cdot 2.69H_2O$ (**1**)

A methanol solution (20 ml) of N,N-dimethyl-1,2-diaminoethane (1 mmol, 0.1 ml) and salicylaldehyde (1 mmol, 0.1 ml) was refluxed for ca. 1 h to produce the ligand *2-((2-(dimethylamino)ethylimino)methyl)phenol* (HL^1). Then methanol solution (5 ml) of nickel(II) acetate tetrahydrate (1 mmol, 250 mg) followed by methanol solution (5 ml) of 2-cyanopyrazine (1 mmol, 110 mg) was added in stirring condition. A methanol-DMSO (2:1 mixture) solution (15 ml) of sodium azide (1 mmol, 70 mg) was then added and stirred further for ca. 1 h. X-ray quality single crystals were obtained after several weeks on slow evaporation of the mother liquor in a refrigerator. Yield: 360 mg (72%, based on nickel). Anal. Calc. for $C_{36}H_{53.38}N_{16}Ni_2O_{6.69}S_2$ (998.86): C, 43.29; H, 5.39; N, 24.40%. Found: C, 43.6; H, 5.7; N, 24.7%. FT-IR (KBr, cm^{-1}): 3442 (OH), 1641 (C=N), 1452, 1415 (tetrazolate). UV–Vis, λ_{max} (nm) [ε_{max}(L mol^{-1} cm^{-1})] (DMSO): 379 (9037), 555 (51), 725 (101), 912 (151).

2.2.2. Complex $2[Ni_2L^2{}_2(PTZ)_2]\cdot 3H_2O$ (**2**)

A methanol solution (20 ml) of N-methyl-1,2-diaminoethane (1 mmol, 0.09 ml) and 3-methoxysalicylaldehyde (1 mmol, 153 mg) was refluxed for ca. 1 h to produce the ligand *2-((2-(methylamino)ethylimino)methyl)-6-methoxyphenol* (HL^2). After then same procedure had been performed as **1**. Single crystals Suitable for X-ray diffraction were obtained after several weeks on slow evaporation of the mother liquor in a refrigerator. Yield: 310 mg (73%, based on nickel).

Anal. Calc. for $C_{64}H_{78}N_{32}Ni_4O_{11}$ (1706.42): C, 45.05; H, 4.61; N, 26.27%. Found: C, 45.2; H, 4.5; N, 26.4%. FT-IR (KBr, cm^{-1}): 3436 (OH), 3260 (NH), 1646 (C=N), 1445, 1413 (tetrazolate). UV–Vis, λ_{max} (nm) [ε_{max}(L mol^{-1} cm^{-1})] (DMSO): 386 (20567), 549 (62), 774 (162), 859 (207).

2.3. Physical measurements

Elemental analysis was performed using a PerkinElmer 240C elemental analyzer. IR spectra in KBr (4500–500 cm^{-1}) were recorded using a PerkinElmer Spectrum Two FT-IR spectrophotometer. Electronic spectra in DMSO (1000–300 nm) were recorded in a PerkinElmer LAMBDA 35 UV/Vis spectrophotometer. Fluorescence spectra were obtained on SHIMADZU RF-5301PC spectrofluorophotometer at room temperature. Lifetime measurements were recorded using Hamamatsu MCP photomultiplier (R3809) and were analyzed by using IBHDAS6 software. Intensity decay profiles were fitted to the sum-of exponentials series

$$I(t) = \sum_i A_i exp(-t/\tau_i)$$

where A_i is a factor representing the fractional contribution to the time-resolved decay of the component with a lifetime of τ_i. The intensity-averaged life times (τ_{av}) are determined using the following equation:

$$< \tau > = \sum_i A_i \tau_i^2 / \sum_i A_i \tau_i$$

2.4. Crystal data collection and refinement

A single crystal having suitable dimensions of both complexes were used for the X-ray crystallographic analysis. A ‘Bruker D8 QUEST’ diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 100 K has been used for data collection of

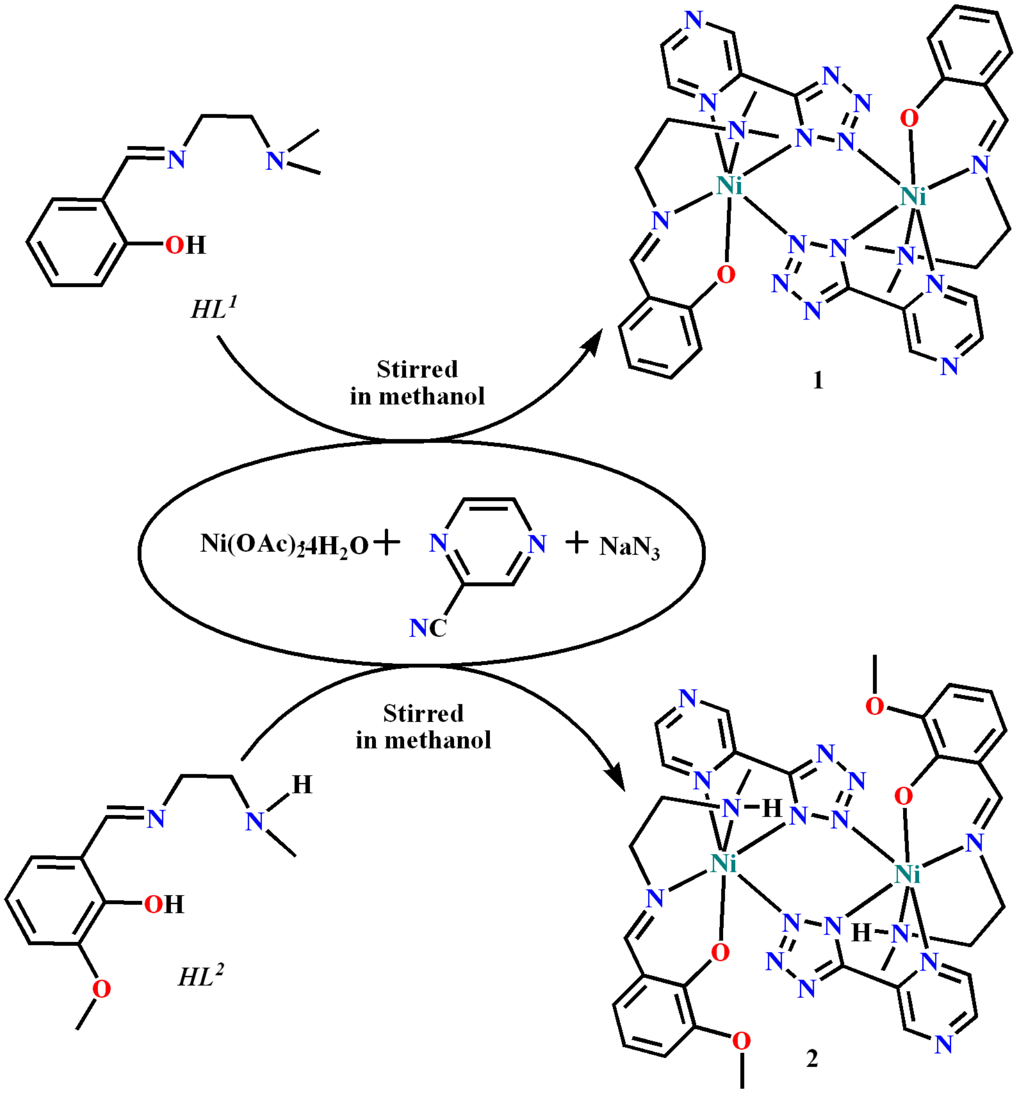
1. A ‘Bruker SMART APEX II’ diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) at 293 K has been used for **2**. In both cases, the molecular structures were solved by direct methods and refinement by full-matrix least squares on F^2 using the SHELX-97 package [41]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Hydrogen atoms of water molecules were located by difference Fourier maps and were kept fixed. Multi-scan empirical absorption corrections were applied to the data of **2** using the program SADABS [42]. Significant crystallographic data are summarized in Table 1.

3. Results and Discussions

3.1. Synthesis

In current investigation, we use one tridentate Schiff base (HL^1) and a tetradentate one (HL^2) as blocking ligands to prepare tetrazolato bridged nickel(II) complexes. HL^1 is prepared by the condensation of salicylaldehyde with N,N-dimethyl-1,2-diaminoethane whereas, HL^2 is prepared by refluxing 3-methoxysalicylaldehyde with N-methyl-1,2-diaminoethane in methanol following the literature methods [29,31]. The ligands are not isolated and used for the preparation of nickel(II) complexes. On the other hand, the tetrazolates are prepared in situ by 1,3-dipolar cycloaddition of cyanide and azide [32]. Our intension is to judge the change in the molecular architecture of the tetrazolato bridged complexes with the variation in the denticity of the Schiff bases blocking ligand.

Both the complexes are prepared in situ by the reaction of nickel(II) acetate tetrahydrate, 2-cyanopyrazine and sodium azide with the corresponding Schiff base (HL^1 for **1** and HL^2 for **2**) under stirring condition using methanol-DMSO mixture (2:1) as solvent. In both cases, bis(μ-tetrazolato-NN′) bridged dinuclear nickel(II) Schiff base complexes are resulted. The molecular structures of both the complexes are very similar. Thus the denticity of the Schiff base blocking ligands do not have any effect in the molecular structures of tetrazolato bridged nickel(II) complexes.



Scheme 1: Synthetic route for preparation of complexes **1** and **2**.

3.2. Structure descriptions

3.2.1. Complex $[Ni_2L^1{}_2(PTZ)_2]\cdot 2(CH_3)_2SO\cdot 2.69H_2O$ **(1)**

Complex **1** crystallizes in orthorhombic space group *Pbca* and features a centrosymmetric bis(μ-tetrazolato-NN′) bridged dinuclear nickel(II) moiety with two dimethyl sulphoxide and four lattice water molecules. Two of the lattice water molecules present in the unit cell, has been refined with occupancy of 0.344(8) per molecules. A perspective view of the complex with selective atom numbering scheme is shown in Figure 1. Selected bond lengths and bond angels are given in Table S1. Within the dinuclear unit, each nickel(II) center is six-coordinated and assumes distorted octahedral geometry. Ni(1) is coordinated by an oxygen atom, O(1), and two nitrogen atoms, N(1) and N(4), of a deprotonated Schiff base ligand in meridional fashion and two nitrogen atoms, N(14) and N(21), of deprotonated 5-pyrazinyltetrazolate. A nitrogen atom, N(22)*, from a symmetry related (1−x,1−y,1−z) deprotonated 5-pyrazinyltetrazolate of the centrosymmetric dimer coordinates Ni(1) to complete its distorted octahedral geometry. It should be noted that the (μ-NN′) bridging geometry of the deprotonated 5-pyrazinyltetrazolate is considerably asymmetric, which can be seen from the inequality in the bridging angles (Ni(1)–N(21)–N(22) = 141.9(2)° and Ni(1)*–N(22)–N(21) = 125.1(2)°) as was also observed in similar complex [29]. The saturated five membered ring [Ni(1)–N(1)–C(2)–C(3)–N(4)] has an envelope conformation on C(2) with puckering parameters Q(2) = 0.425(4) Å and $\phi(2)$ = 78.4(4)° [43].

There are four hydrogen atoms, H(3C), H(3D), H(4A) and H(4B), available for hydrogen bonding interactions from two water molecules present in asymmetric unit. Hydrogen atoms, H(3C) and H(4B), of two water molecules show two different hydrogen bonding interactions with oxygen atom, O(2), of dimethyl sulphoxide molecule. Another hydrogen atom, H(3D), available from one of those two water molecule is hydrogen bonded with phenoxo oxygen atom, O(1), of deprotonated Schiff base ligand creating a discrete chain as shown in Figure 2. The detail geometric features of hydrogen bonding interactions are given in Table 2.

The complex also shows significant C–H···π interactions. One N-methyl hydrogen, H(12A), attached with C(12) of deprotonated Schiff base ligand and another methyl hydrogen, H(26C), attached with C(26) of solvent molecule DMSO show two C–H···π interactions with tetrazole ring Cg(3) and pyrazine ring Cg(6) respectively, of a neighboring deprotonated 5-pyrazinyltetrazolate. A methylene hydrogen, H(13A) attached with C(13) of deprotonated Schiff base ligand is involved in C–H···π interactions with the phenyl ring Cg(7) of neighboring deprotonated Schiff base ligand. Considering the centrosymmetric dimer each of these interactions is duplicated and produce two dimensional layer structure in the crystal packing of **1** (Figure S1). Geometric features of the C–H···π interactions are given in Table 3.

3.2.2. Complex 2[$Ni_2L^2_2(PTZ)_2$]·$3H_2O$ (**2**)

Complex **2** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit consists of two bis(μ-tetrazolato-NN′) bridged dinuclear nickel(II) moieties with three noncoordinated water molecules. A perspective view of one dinuclear unit with selective atom numbering scheme is shown in Figure 3. Selected bond lengths and bond angels are given in Tables S2 and S3 respectively. Within that dinuclear unit, nickel(II) is coordinated meredonially by one phenoxy oxygen atom and two nitrogen atoms [O(1), N(1) and N(2) for Ni(1) and O(3), N(9) and N(10) for Ni(2)] of one depronated Schiff base ligand, along with two nitrogen atoms [N(3) and N(7) for Ni(1); N(11) and N(15) for Ni(2)] of deprotonated 5-pyrazinyltetrazolate. The sixth coordination site of each nickel(II) is occupied by a nitrogen atom [N(12) for Ni(1) and N(4) for

Ni(2)] of another deprotonated 5-pyrazinyltetrazolate bonded to second nickel atom, constructing a bis(μ-tetrazolato-NN′) bridged nickel(II) complex. It should be noted that the (μ-NN′) bridging geometry of the deprotonated 5-pyrazinyltetrazolate is considerably asymmetric, which can be seen from the inequality in the bridging angles (Ni(1)–N(3)–N(4) = 140.1(2)°, Ni(2)–N(4)–N(3) = 122.7(2)° and Ni(2)–N(11)–N(12) = 139.2(2)°, Ni(1)–N(12)–N(11) = 124.01(19)°) as was also observed in similar complex [30]. The saturated five membered ring, Ni(1)–N(1)–C(8)–C(9)–N(2), has twisted geometry over C(8)–C(9) with puckering parameters Q(2) = 0.421(3) Å and $\phi(2)$ = 97.9(3)°, whereas Ni(2)–N(9)–C(24)–C(25)–N(10) ring has an envelope conformation on C(25) with puckering parameters Q(2) = 0.432(3) Å and $\phi(2)$ = 284.3(3)° [43].

There are three hydrogen atoms, H(2), H(10) and H(26), available from two dinuclear complexes and six hydrogen atoms, H(9D), H(9E), H(10D), H(10E), H(11D) and H(11E), available from three water molecules creates a supramolecular tetramer of dinuclear units through hydrogen bonding interactions (Figure 4). The hydrogen atoms, H(2) and H(10), of one dinuclear unit, show hydrogen boding interactions with water and phenoxy oxygen atoms, O(9) and O(1), respectively. Then two hydrogen atoms, H(9C) and H(9D), attached to water oxygen atom, O(9), show two hydrogen bonding interactions with two other oxygen atoms, O(3) (phenoxy) and O(4) (methoxy) respectively. The combination of these hydrogen bonding interactions resulted a supramolecular species as shown in Figure 5A. The hydrogen atom, H(26), of second dinuclear unit shows hydrogen bonding with water oxygen atom, O(10) and hydrogen atom, H(10E), attached to O(10) then creates hydrogen bonding with phenoxy oxygen, O(5) of the same dinuclear unit. Two hydrogen atoms, H(11D) and H(11E), attached to water oxygen atom, O(11), show two hydrogen bonding interactions with water oxygen atoms, O(10) and tetrazole nitrogen atom, N(22)†, of a symmetry related († = 3-x,-y,3-z) dinuclear unit respectively creating a centrosymmetric tetranuclear species as shown in Figure 5B. Another hydrogen atom, H(10D) attached to water oxygen atom O(10), available from centrosymmetric tetranuclear species shows hydrogen bonding with pyrazine nitrogen atoms, N(8)$^{\#}$, of symmetry related ($^{\#}$ = 3-x,-y,2-z) dinuclear unit. Considering the centrosymmetric tetranuclear unit this interaction is duplicated and produces a supramolecular tetramer of dinuclear units (Figure 4). The details of hydrogen bonding interactions are given in Table 2.

There are two significant π···π stacking interactions present in the complex. First π···π stacking has been observed between two pyrazine ring Cg(11) and Cg(24) attached with Ni(2) and Ni(4) respectively of two dinuclear nickel(II) moiety present within the asymmetric unit. Again one pyrazine ring Cg(10) attached with Ni(1) shows the second π···π stacking with another pyrazine ring Cg(23) attached with Ni(3) of a symmetry related dinuclear moiety. These two π···π stacking creates a one dimensional chain structure of **2** (Figure S2). Complex shows five significant C–H···π interactions. Hydrogen atoms, H(43B) and H(59A), attached with methoxy carbon atoms, C(43) and C(59), of two depronated Schiff base ligands in one dinuclear moiety are involved in C–H···π interactions with the phenyl rings Cg(26) and Cg(25) respectively. Another two hydrogen atoms, H(16) and H(32), attached with carbon atoms, C(16) and C(32) of two $(PTZ)^{-}$ present in another dinuclear moiety are involved in C–H···π interactions with the phenyl rings Cg(25) and Cg(26) respectively. Combination of these four C–H···π interactions produce a two dimensional layer structure as shown in Figure S3. The fifth C–H···π interactions has been observed between two layers involving a hydrogen, H(27B), attached with methoxy carbon atom, C(27), and phenyl ring Cg(13) creating a double layer structure (Figure S4). Geometric features of the C–H···π and π···π stacking are given in Tables 3 and 4 respectively.

3.3. IR and electronic spectra and photo-physical study

The infrared spectra of both complexes are quite similar to each other. The distinct band due to azomethine (C=N) group at 1641 and 1646 cm^{-1} are noticed in IR spectra of **1** and **2** respectively [44]. Broad band around at 3442 cm^{-1} and 3436 cm^{-1} has been noticed indicating the presence of water molecule in complex **1** and **2** respectively [45]. The sharp band due to the amino NH group appears at 3260 cm^{-1} in the spectrum of complex **2** [46].

The electronic spectra of the complexes are similar to each other in DMSO at room temperature and display absorption bands within the range of 549–555 nm and 859–912 nm with a shoulder band in the region 725–774 nm. These bands are assigned to the spin allowed transitions $^3A_2g \rightarrow {}^3T_1g(F)$, $^3A_2g \rightarrow {}^3T_2g(P)$ and spin forbidden transition $^3A_2g \rightarrow {}^1Eg$ (shoulder band) respectively [29]. The higher energy d–d transitions, corresponding to $^3A_2g \rightarrow {}^3T_1g(P)$ are obscured by strong ligand to metal charge transfer transitions at 379 nm (for **1**) and 386 nm (for **2**), which are characteristic of transition metal complexes with Schiff base ligands [30].

The emission spectral behavior of complexes **1** and **2** has also been studied at room temperature in DMSO solution. The complexes **1** and **2** on excitation at 300 nm shows emissions at 419 nm and 422 nm with exited state mean lifetimes 5.467 ns and 1.642 ns respectively at room temperature. It can be attributed to intra-ligand fluorescent $^1(\pi \rightarrow \pi^*)$ emissions of the coordinated ligand [47]. The photoluminescence lifetime spectra and time-resolved photoluminescence decays have been depicted in Figure 6 and 7 for complexes **1** and **2** respectively.

3.4. Electrochemical studies

The redox properties of complexes **1** and **2** were explored by cyclic voltammetry (see Experimental for details). Both the complexes show one oxidative quasi reversible Ni(III)/Ni(II) couple at $E_{1/2} = 0.79$ V (for **1**) and 0.77 V (for **2**) (vs. Ag/AgCl) which corresponds to the first electron abstraction from the corresponding complex. The reductive quasi reversible Ni(II)/Ni(I) couple at $E_{1/2} = -0.62$ V (for **1**) and -0.63 V (for **2**) can be assigned to the electron addition to Ni(II) compound to form Ni(I) species. It has been observed that no well defined oxidative or reductive responses could be observed on running further in the positive or negative potential. The single-electron nature of the voltammograms has been confirmed by the comparison of current heights for the compounds and that of a simple $[Fe(bipy)_3]^{2+}$ compound under identical conditions [48]. The criteria of reversibility were checked by observing constancy of peak–peak separation ($\Delta E_p = E_{pa} - E_{pc}$) and the ratio of peak heights (i_{pa}/i_{pc}~1) with variation of scan rates [49]. The results of cyclic voltammetry also closely resemble that of the similar reported compounds, which serve as further evidences for similar structural and electronic properties [30]. All the redox signals remain virtually invariant under different scan rates (0.01–1.0 Vs^{-1}) in the temperature range 300–280 K. Solvent dependent shift and change in electrochemical reversibility of red-ox couples are not noteworthy.

4. Summary

The whole work can be concluded in two statements. Firstly, the synthesis of two new bis(μ-tetrazolato-NN′) bridged dinuclear nickel(II) Schiff base complexes under non-hydrothermal and non-microwave reaction conditions using a simple in situ 1,3-dipolar cyclo-addition and their characterization by physico-chemical and structural studies afford a convenient synthetic route for these types of complexes at room temperature and opens up new possibilities for the syntheses of tetrazolato bridged transition metal complexes with Schiff bases as blocking ligands. This is particularly important because, although pseudohalide bridged di and polynuclear transition metal complexes are frequently found in literature, tetrazolato bridged complexes with Schiff base co-ligands are limited. Secondly, the change in the denticity of the Schiff base blocking ligand was shown to have no effect in controlling the molecular structure of such complexes.

Acknowledgment

SC acknowledges DST, India under FAST Track Scheme (Order No. SR/FT/CS-118/2010, dated 15/02/2012). K.R. gratefully acknowledges the financial support from the Academy of Finland (project No’s. 122350. 140718, 256259, 265328 and 263256).

Appendix A. Supplementary data

CCDC 1021604 and 1021611 contains the supplementary crystallographic data for complexes **1** and **2** respectively. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail:deposit@ccdc.cam.ac.uk.

References

[1] L.-J. Zhang, J.-H. Yu, J.-Q. Xu, J. Lu, H.-Y. Bie, X. Zhang, Inorg. Chem. Commun. 8 (2005) 638–642.

[2] E.A. Mikhalyova, S.V. Kolotilov, O. Cador, F. Pointillart, S. Golhen, L. Ouahab. V.V. Pavlishchuk, Inorg. Chim. Acta 363 (2010) 3453–3460.

[3] F.E. Jacobsen, R.M. Breece, W.K. Myers, D.L. Tierney, S.M. Cohen, Inorg. Chem. 45 (2006) 7306–7315.

[4] T. Tekeste, H. Vahrenkamp, Inorg. Chem. 45 (2006) 10799–10806.

[5] E.T. Papish, M.T. Taylor, F.E. Jernigan III, M. J. Rodig, R.R. Shawhan, G.P.A. Yap, F.A. Jove, Inorg. Chem. 45 (2006) 2242–2250.

[6] M. Ji, B. Benkmil, H. Vahrenkamp, Inorg. Chem. 44 (2005) 3518–3523.

[7] J. Ferrando-Soria, J. Pasán, C. Ruiz-Pérez, Y. Journaux, M. Julve, F. Lloret, J. Cano, E. Pardo, Inorg. Chem. 50 (2011) 8694–8696.

[8] C.L. Pereira, E.F. Pedroso, A.C. Doriguetto, J.A. Ellena, K. Boubekeur, Y. Filali, Y. Journaux, M.A. Novak, H.O. Stump, Dalton Trans. 40 (2011) 746–754.

[9] S.V. Kolotilov, O. Cador, P. Pointillart, S. Golhen, Y.L. Gal, K.S. Gavrilenko, L. Ouahab, J. Mater. Chem. 20 (2010) 9505–9514.

[10] Z. Serna, N. De la Pinta, M.K. Urtiaga, L. Lezama, G. Madariaga, J.M. Clemente-Juan, E. Coronado, R. Cortés, Inorg. Chem. 49 (2010) 11541–11549.

[11] I. Muga, J.M. Gutiérrez-Zorrilla, P. Vitoria, A. Luque, M. Insausti, P. Román, F. Lloret, Eur. J. Inorg. Chem. (2000) 2541-2547.

[12] Z. Setifi, F. Setifi, M. Ghazzali, M. El-Ghozzi, D. Avignant, O. Pérez, J. Reedijk, Polyhedron 75 (2014) 68–72.

[13] N. Mondal, , S. Mitra, V. Gramilich, S.O. Ghodsi, K.M.A. Malik, Polyhedron 20 (2001) 135–14.

[14] M. Das, B.N. Ghosh, A. Valkonen, K. Rissanen, S. Chattopadhyay, Polyhedron 60 (2013) 68–77.

[15] S.M.E. Khalil, H.S. Seleem, B.A. El-shetary, M. Shebl, J. Coord. Chem. 55 (2002) 883–899.

[16] M. Das, S. Chattopadhyay, Transition Met Chem 38 (2013) 191–197.

[17] M. Das, S. Chatterjee, S. Chattopadhyay, Inorg. Chem. Commun. 14 (2011) 1337–1340.

[18] A.J. Mota, A. Rodríguez-Diéguez, M.A. Palacios, J.M. Herrera, D. Luneau, E. Colacio, Inorg. Chem. 49 (2010) 8986–8996.

[19] K. Darling, W. Ouellette, A. Prosvirin, S. Walter, K.R. Dunbar, J. Zubieta, Polyhedron 58 (2013) 18–29.

[20] S.V. Voitekhovich, R. Syre, J. Lach, V.E. Matulis, P.N. Gaponik, O. A. Ivashkevich, B. Kersting, Eur. J. Inorg. Chem. (2010) 5387–5393.

[21] A.H. McKie, S. Friedland, F. Hof, Org. Lett. 10 (2008) 4653–4655.

[22] R.J. Herr, Bioorg. Med. Chem. 10 (2002) 3379–3393.

[23] H. Singh, A.S. Chawla, V.K. Kapoor, D. Paul, R.K. Malhotra, Prog. Med. Chem. 17 (1980) 151–183.

[24] T.M. Klapötke, J. Stierstorfer, J. Am. Chem. Soc. 131 (2009) 1122–1134.

[25] T. Fendt, N. Fischer, T.M. Klapötke, J. Stierstorfer, Inorg. Chem. 50 (2011) 1447–1458.

[26] A. Hammer, T.M. Klapötke, H. Nöth, M. Warchhold, G. Holl, M. Kaiser, U. Ticmanis, Inorg. Chem. 40 (2001) 3570–3575.

[27] L. Liang, G. Peng, L. Ma, L. Sun, H. Deng, H. Li, W. Li, Cryst. Growth Des. 12 (2012) 1151–1158.

[28] A.J. Calahorro, A. Salinas-Castillo, J.M. Seco, J. Zuñiga, E. Colacio, A. Rodríguez-Diéguez, CrystEngComm 15 (2013) 7636–7639.

[29] M. Das, K. Harms, S. Chattopadhyay, Dalton Trans. 43 (2014) 5643–5647.

[30] M. Das, S. Chatterjee, K. Harms, T.K. Mondal, S. Chattopadhyay, Dalton Trans. 43 (2014) 2936–2947.

[31] B.G. Mukhopadhyay, S. Mukhopadhyay, M.F.C. Guedes da Silva, M.A.J. Charmier, A.J.L. Pombeiro, Dalton Trans. (2009) 4778–4785.

[32] M. Saha, R. Nasani, M. Das, A. Mahata, B. Pathak, S.M. Mobin, L.M. Carrella, E. Rentschler, S. Mukhopadhyay, Dalton Trans. 43 (2014) 8083–8093.

[33] R.J. Forster, T.E. Keyes, Coord. Chem. Rev. 253 (2009) 1833–1853.

[34] C.M. McGuirk, C.L. Stern, C.A. Mirkin, J. Am. Chem. Soc. 136 (2014) 4689–4696.

[35] J.P. Byrne, J.A. Kitchen, T. Gunnlaugsson, Chem. Soc. Rev. 43 (2014) 5302-5325.

[36] S. Hazra, S. Biswas, A.M. Kirillov, A. Ghosh, Polyhedron 79 (2014) 66–71.

[37] W. Yang, T. Tian, H.-Y. Wu, Q.-J. Pan, S. Dang, Z.-M. Sun, Inorg. Chem. 52 (2013) 2736–2743.

[38] R. Medishetty , R. Tandiana, J.J. Vittal, Cryst. Growth Des. 14 (2014) 3186–3190.

[39] M. Das, S. Chattopadhyay, Polyhedron 50 (2013) 443–451.

[40] M. Das, S. Chatterjee, S. Chattopadhyay, Polyhedron 68 (2014) 205–211.

[41] G.M. Sheldrick, Acta Cryst. A 64 (2008) 112.

[42] G.M. Sheldrick, SADABS, Bruker Analytical X-ray system Inc, Madison, Wisconsin, 2008.

[43] D. Cremer, J.A. Pople, J. Am. Chem. Soc. 97 (1975) 1354-1358.

[44] M. Das, S. Chattopadhyay, J. Mol. Struct. 1051 (2013) 250–258.

[45] M. Das, S. Chattopadhyay, Inorg. Chim. Acta 378 (2011) 303–306.

[46] P.K. Bhaumik, K. Harms, S. Chattopadhyay, Polyhedron 68 (2014) 346–356.

[47] M. Das, B.N. Ghosh, K. Rissanen, S. Chattopadhyay, Polyhedron 77 (2014) 103–114.

[48] K. Mitra, S. Biswas, C.R. Lucas, B. Adhikary, Inorg. Chim. Acta 2006 (1997) 359-

[49] D.H. Evans, K.M. O'Connell, R.A. Petersen, M.J. Kelly, J. Chem. Educ. 60 (1983) 290–293.

Table 1: Crystal data and refinement details in complexes **1** and **2**

Complex	**1**	**2**
Formula	$C_{36}H_{53.38}N_{16}Ni_2O_{6.69}S_2$	$C_{64}H_{78}N_{32}Ni_4O_{11}$
Formula Weight	998.86	1706.42
Crystal Size [mm]	0.13 x 0.10 x 0.09	0.21 x 0.25 x 0.28
Temperature (K)	100(2)	123
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca*	$P\bar{1}$
a(Å)	15.120(2)	11.6034(2)
b(Å)	13.454(2)	19.7734(4)
c(Å)	21.715(2)	20.2261(4)
α (°)	90	118.240(2)
β (°)	90	99.2964(17)
γ (°)	90	95.7235(17)
Z	4	2
d_{calc} (g cm^{-3})	1.502	1.434
μ(mm^{-1})	1.013	1.707
F(000)	2092	1772
Total Reflections	20047	25366
Unique Reflections	4108	14171
Observed data [I > 2 σ (I)]	2781	12322
R(int)	0.0874	0.025
R1, wR2 (all data)	0.0844, 0.1134	0.0518, 0.1322
R1, wR2 [I > 2 σ (I)]	0.0449, 0.0985	0.0461, 0.1277
Largest diff. in peak and hole (eÅ^{-3})	0.688, -0.601	2.16, -1.37

Table 2: Hydrogen bond distances (Å) and angles (º) for complexes **1** and **2**.

Complexes	D–H···A	D–H	D···A	H···A	∠D–H···A
1	O(3)–H(3C)···O(2)	0.82(5)	2.869(5)	2.09(4)	159(5)
	O(3)–H(3D)···O(1)	0.84(5)	2.738(4)	1.92(5)	164(5)
	O(4)–H(4B)···O(2)	0.87(5)	2.89(1)	2.18(2)	139(5)
2	N(2)–H(2)···O(9)	0.9300	3.105(3)	2.1800	171
	O(9)–H(9C)···O(3)	0.90(5)	2.891(3)	2.02(5)	164(5)
	O(9)–H(9D)···O(4)	0.67(6)	3.025(3)	2.54(5)	132(6)
	N(10)–H(10)···O(1)	0.9300	3.221(3)	2.3100	165
	N(10)–H(10)···O(2)	0.9300	3.126(3)	2.5100	124
	O(10)–H(10D)···N(8)$^{\#}$	0.74(5)	3.036(4)	2.37(6)	151(6)
	O(10)–H(10E)···O(5)	0.91(6)	2.776(4)	1.88(6)	167(4)
	O(11)–H(11D)···N(22)†	0.84(5)	2.917(3)	2.08(5)	175(4)
	O(11)–H(11E)···O(10)	1.02(6)	2.820(4)	1.85(6)	158(5)
	N(26)–H(26)···O(10)	0.9300	3.088(3)	2.2200	155

Symmetry transformations, $^{\#}$ = 3-x,-y,2-z; † = 3-x,-y,3-z for complex **2**.

Table 3: Geometric features (distances in Å and angles in °) of the C–H···π interactions in **1** and **2**.

Complex	C–H····Cg(Ring)	H····Cg	C–H····Cg	C····Cg
1	C(12)–H(12A)···Cg(3)	2.81	3.638(4)	143
	C(13)–H(13A)···Cg(7)	2.69	3.643(5)	166
	C(26)–H(26C)···Cg(6)	2.97	3.830(5)	147
2	C(16)–H(16)···Cg(26)[$]	2.95	3.770(3)	145
	C(27)–H(27B)···Cg(13)[#]	2.69	3.524(4)	144
	C(32)–H(32)···Cg(25)	2.68	3.447(3)	139
	C(43)–H(43B)···Cg(26)[¥]	2.88	3.566(4)	128
	C(59)–H(59A)···Cg(25)[§]	2.68	3.588(3)	155

Cg(3) = Centre of gravity of the ring [N(21)–N(22)–N(23)–N(24)–C(20)], Cg(6) = Centre of gravity of the ring [N(14)–C(15)–C(16)–N(17)–C(18)–C(19)], Cg(7) = Centre of gravity of the ring [C(6)–C(7)–C(8)–C(9)–C(10)–C(11)] for **1** and Cg(13) = Centre of gravity of the ring [C(17)–C(18)–C(19)–C(20)–C(21)–C(22)], Cg(25) = Centre of gravity of the ring [C(33)–C(34)–C(35)–C(36)–C(37)–C(38)], Cg(26) = Centre of gravity of the ring [C(49)–C(50)–C(51)–C(52)–C(53)–C(54)] for **2**. Symmetry transformations [*] = 1-x,1-y,1-z; [◊] = -1/2+x,1/2-y,1-z; [‡] = 3/2-x,1/2+y,z; [$] = -1+x,y,-1+z; [#] = 3-x,-y,2-z; [¥] = -1+x,y,z; [§] = 1+x,y,z.

Table 4: Geometric features (distances in Å and angles in °) of the π···π stacking in **2**.

Cg(I)-Cg(J)	Cg-Cg	α	β	γ	Cg(I)-Perp	Cg(J)-Perp
Cg(10)-Cg(23)$^{\$}$	3.872(2)	24.0(2)	7.90	30.60	3.333(1)	3.835(1)
Cg(11)-Cg(24)	3.647(2)	13.4(2)	18.00	30.43	3.144(2)	3.468(1)

Cg(10) = Centre of gravity of the ring [N(7)–C(13)–C(14)–N(8)–C(15)–C(16)], Cg(11) = Centre of gravity of the ring [N(15)–C(29)–C(30)–N(16)–C(31)–C(32)], Cg(23) = Centre of gravity of the ring [N(23)–C(61)–C(62)–N(24)–C(63)–C(64)], Cg(24) = Centre of gravity of the ring [[N(31)–C(45)–C(46)–N(32)–C(47)–C(48)]. Symmetry transformations $^{\$}$ = -1+x,y,-1+z.

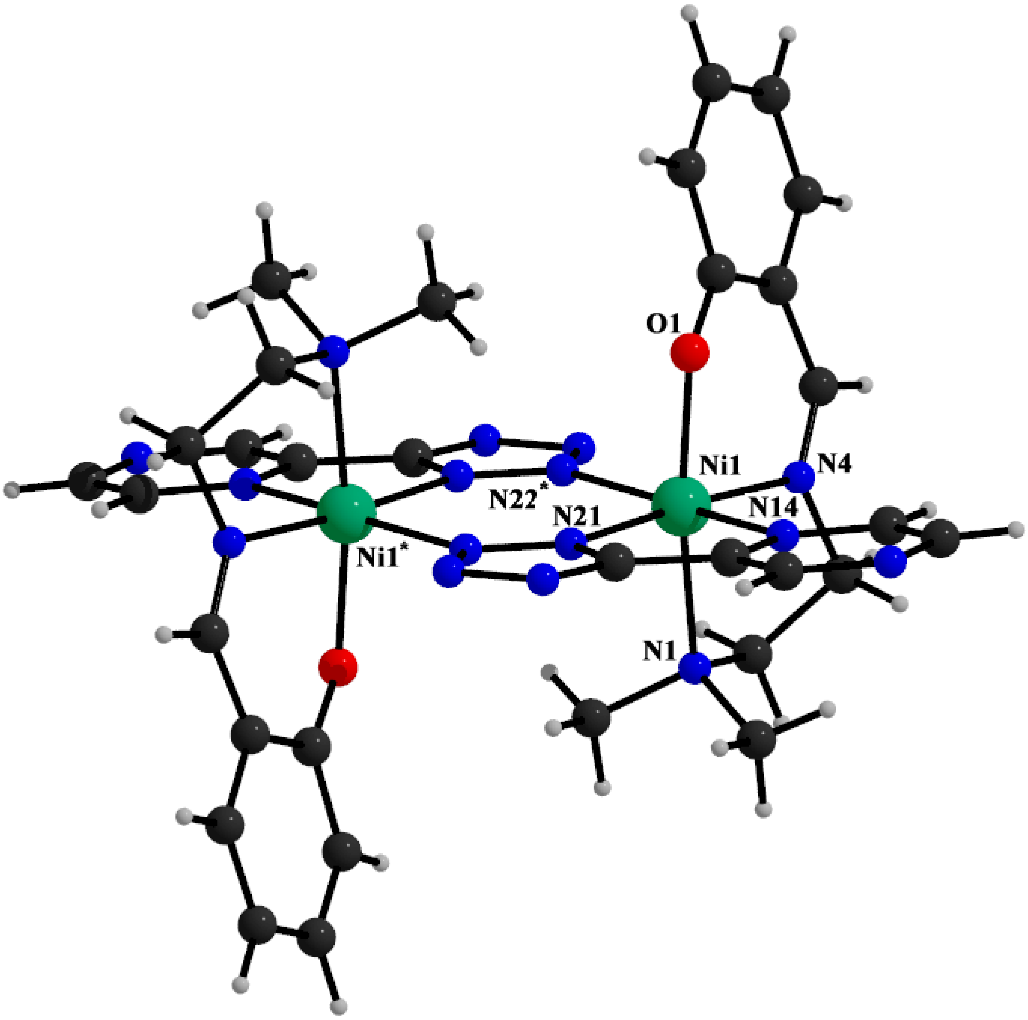


Figure 1: A perspective view of dimeric nickel(II) structure with selective atom numbering scheme of complex **1**.

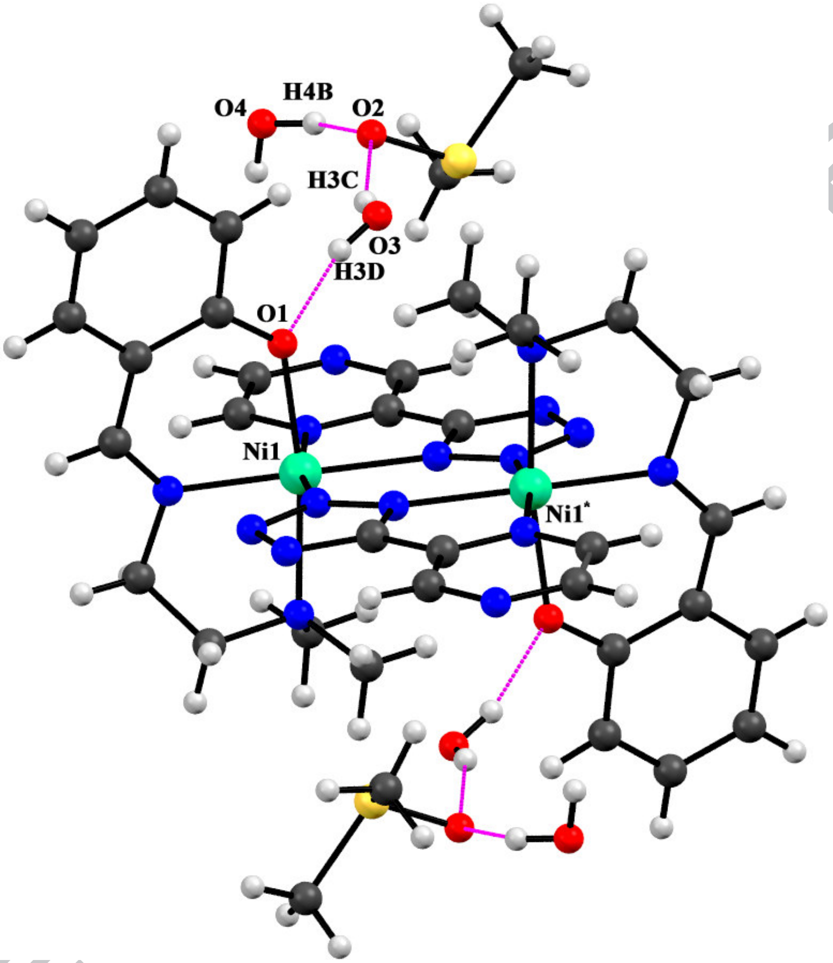


Figure 2: A perspective view of hydrogen bonded interactions in complex **1**.

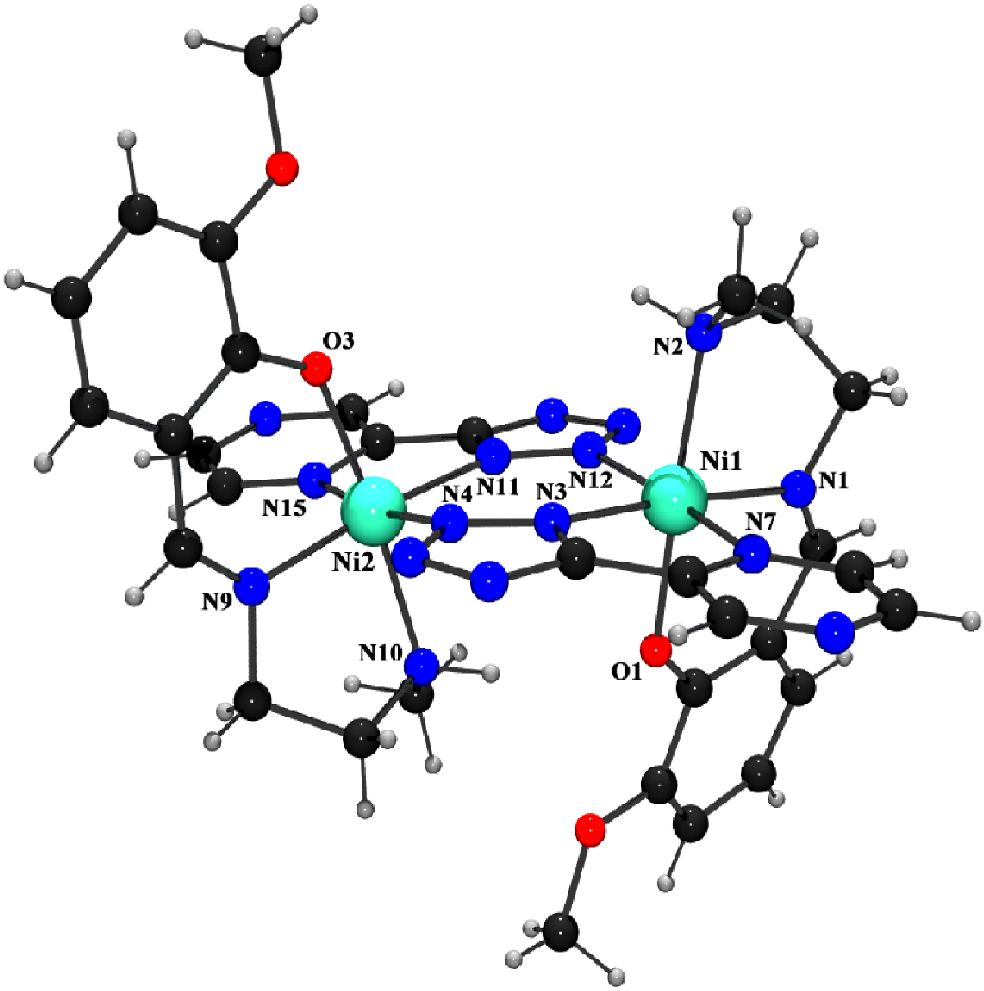


Figure 3: A perspective view of dimeric nickel(II) structure with selective atom numbering scheme of complex **2**.

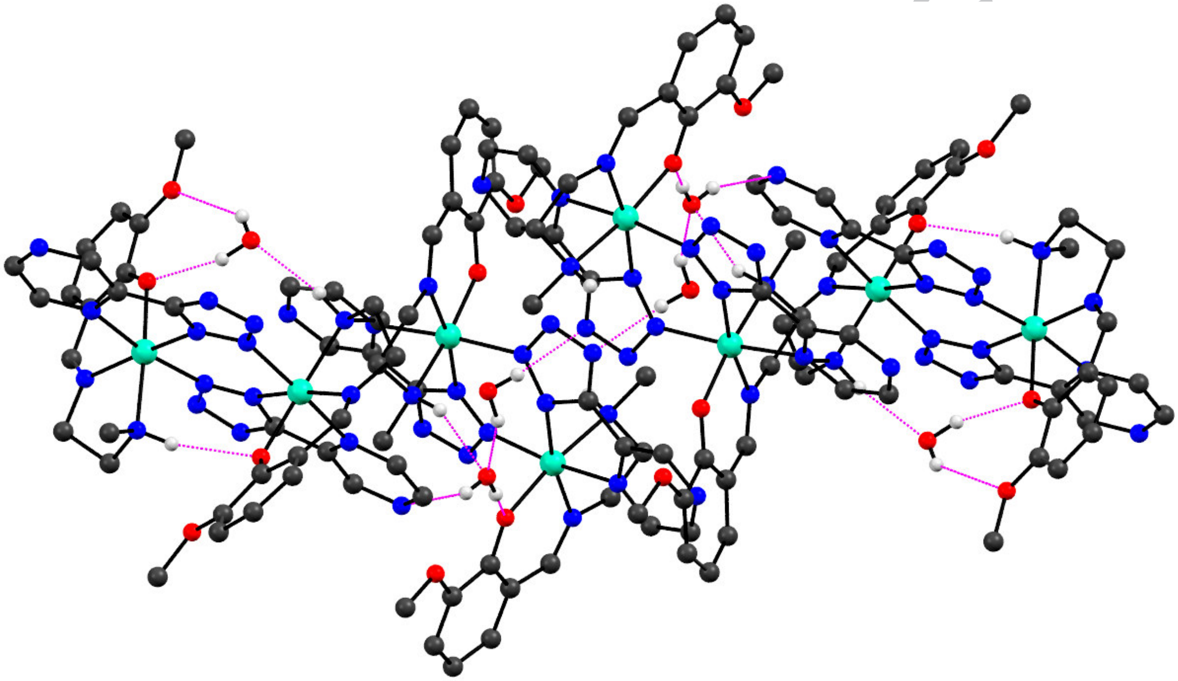


Figure 4: A perspective view of a hydrogen bonded supramolecular tetramer of dinuclear units in **2**. Only the relevant hydrogen atoms are shown for clarity.

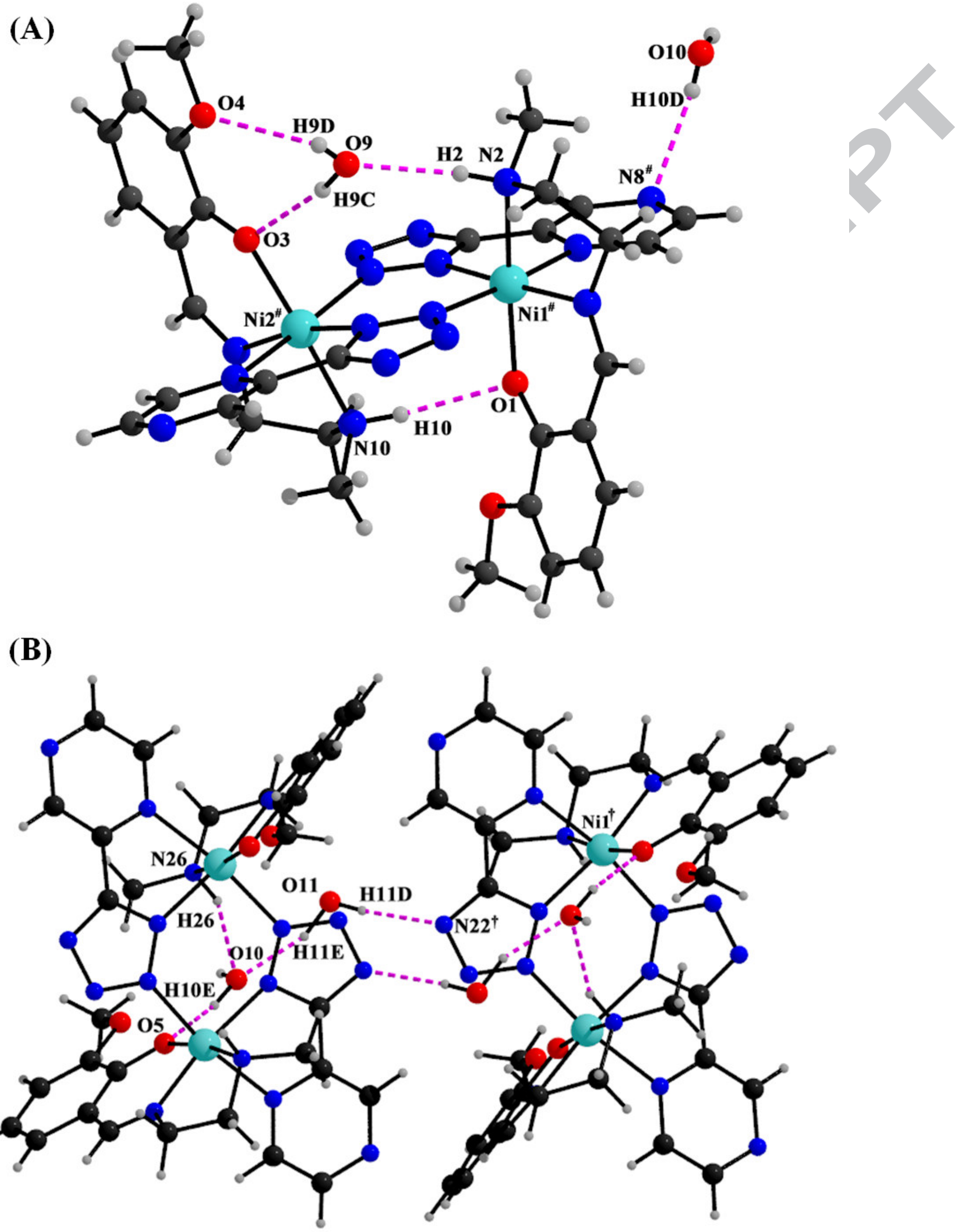


Figure 5: A perspective view of hydrogen bonded interactions in complex **2**.

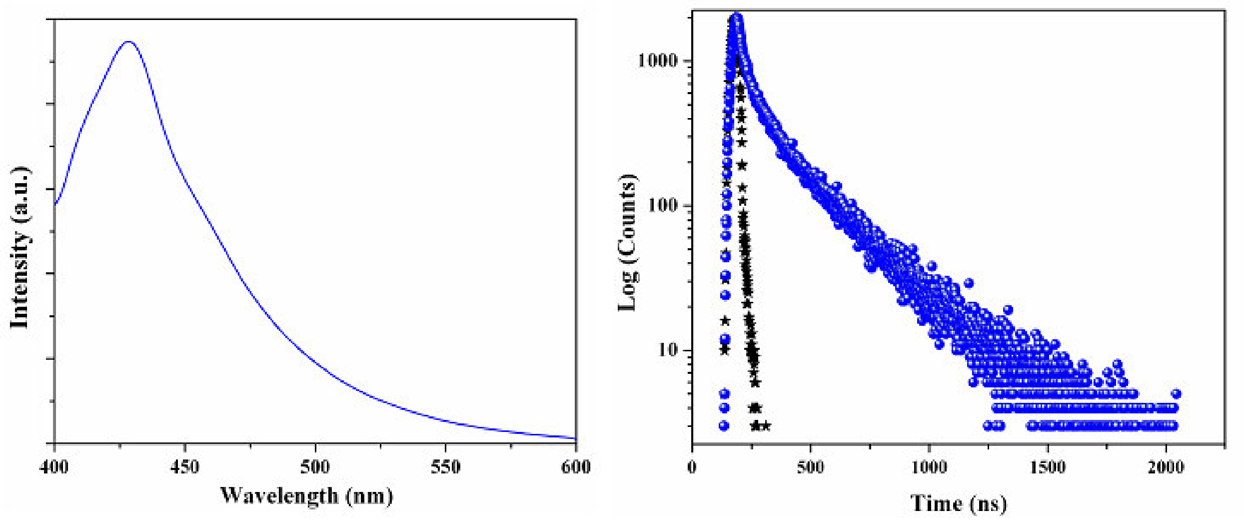


Figure 6: A perspective view of photoluminescence spectrum (left) and time-resolved photoluminescence decay profile (right) of **1** in DMSO at room temperature.

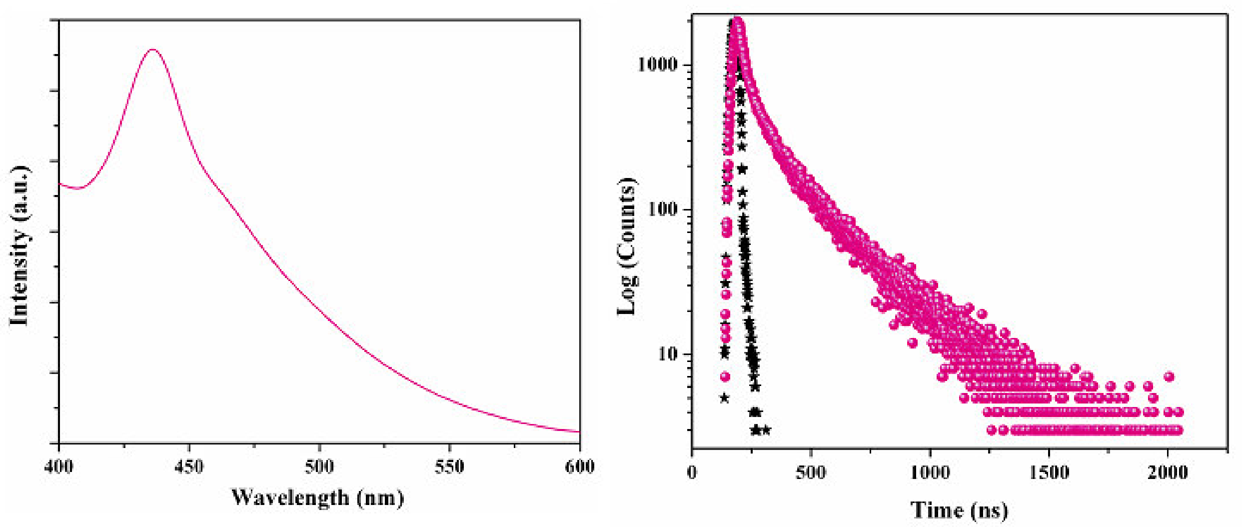


Figure 7: A perspective view of photoluminescence spectrum (left) and time-resolved photoluminescence decay profile (right) of **2** in DMSO at room temperature.

Bis(μ-tetrazolato-NN′) bridged dinuclear nickel(II) Schiff base complexes: Tandem synthesis, structure and self assembly

Mithun Das, Klaus Harms, Biswa Nath Ghosh, Kari Rissanen, Shouvik Chattopadhyay[*]

Facile synthesis of two new Bis(μ-tetrazolato-NN′) bridged dinuclear nickel(II) Schiff base complexes by 1,3-dipolar cyclo-addition of azide and cyanide at room temperature established that any change in denticity of the Schiff base blocking ligands does not have any significant effect in controlling the molecular structures of such complexes.

Bis(μ-tetrazolato-NN′) bridged dinuclear nickel(II) Schiff base complexes: Tandem synthesis, structure and self assembly

Mithun Das, Klaus Harms, Biswa Nath Ghosh, Kari Rissanen, Shouvik Chattopadhyay*