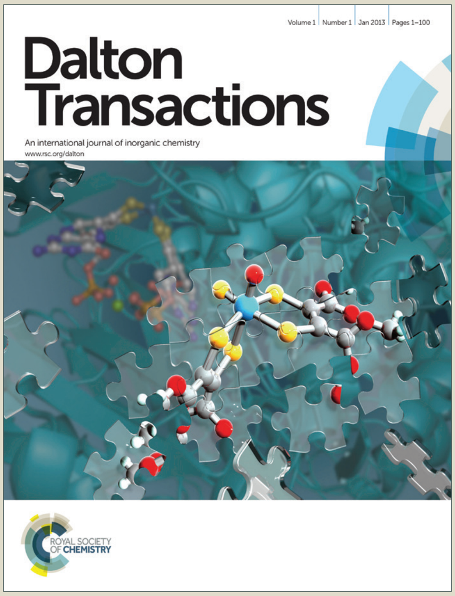
# Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

# Novel tandem synthesis of bis(μ-NN′-tetrazolate) bridged dinuclear nickel(II) Schiff base complex via [3 + 2] cyclo-addition at ambient condition

**Mithun Das[a], Klaus Harms[b], Shouvik Chattopadhyay[a,*]**

[a] *Department of Chemistry, Inorganic Section, Jadavpur University, Kolkata – 700 032, India. e-mail:* shouvik.chem@gmail.com Tel. +913324572941

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

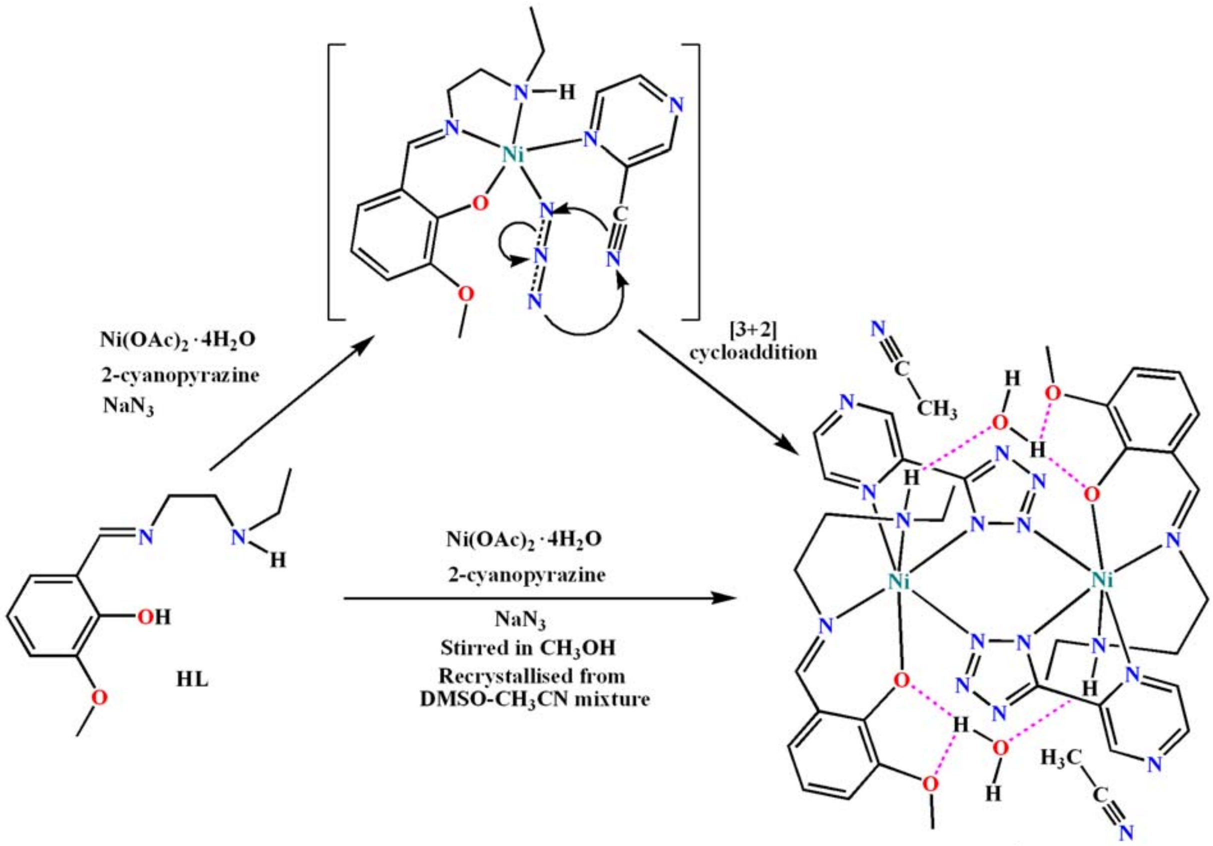
## Abstract

A novel bis(μ-NN′-tetrazolate) bridged centrosymmetric dinuclear nickel(II) Schiff base complex $[Ni_2(L)_2(PTZ)_2]\cdot 2H_2O\cdot 2CH_3CN$ (*HL* is a tridentate Schiff base, 2-((2-(ethylamino)ethylimino)methyl)-6-methoxyphenol and *HPTZ* is 5-pyrazinyltetrazole) has been synthesized via [3+2] cyclo-addition reaction of 2-cyanopyrazine and sodium azide in presence of nickel(II) acetate tetrahydrate and *HL*. The structure of the complex is confirmed by single crystal X-ray diffraction analysis. Combination of H-bonding and C–H···π interactions creates $3^6$-**hxl** topological supramolecular network. The acetonitrile molecule is encapsulated as a hydrophobic guest within the 2D supramolecular network.

**Key words:** Nickel(II); dinuclear; cyclo-addition; 5-pyrazinyltetrazolate; Schiff base

The rational design and synthesis of homo- and hetero-metallic coordination polymers using organic and inorganic linkers to develop new materials are of continuing interest as they found uses as single-molecule transistors[1], single-molecule magnets,[2] catalysts,[3] sensors, storage and separation devices.[4] Among several synthetic schemes, the in-situ generation of tetrazole-based ligands to produce coordination polymers by a hydrothermal process is well-known.[5] The chemistry of tetrazoles and their complexes has received a vast attention now-a-days.[6] The tetrazole functional group has found a wide range of applications in coordination chemistry as ligands,[7] in medicinal chemistry as a metabolically stable surrogate for a carboxylic acid group[8] and in material science, as high density energy materials.[9] The coordination ability of the tetrazolate through the four nitrogen atoms allows it to serve as either a multi-dentate or a bridging building block in supra-molecular assemblies and this is of particular interest to supramolecular chemists.[10] However, among the several synthetic methods reported so far, most of them have some drawbacks like drastic reaction conditions, water sensitivity and presence of highly toxic, explosive and volatile hydrazoic acids.[11] It was shown some time ago that performing the reaction on a metal site facilitated the 1,3-dipolar addition.[12] More recently, the preparation of a variety of 5-substituted-1H-tetrazoles using various transition metals as catalysts has been reported.[13] On the other hand, the metal tetrazolate complexes containing Schiff bases as blocking ligands are very few in literature. Best to our knowledge, only two such examples with two different metal atoms (nickel and platinum) are known.[14] In the present paper, we would like to report the tandem synthesis of a dinuclear nickel(II) Schiff base complex bridged by a substituted tetrazolate formed by the reaction of 2-cyanopyrazine, sodium azide, nickel(II) acetate and a Schiff base ligand *HL* under stirring condition in methanol. X-ray diffraction study has confirmed the structure of the complex.

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



**1**

**Scheme 1:** Graphical representation of synthetic route and possible reaction pathway for the tandem synthesis of complex **1**.

A methanol solution (20 ml) of N-ethyl-1,2-diaminoethane (1 mmol, 0.1 ml) and 3-methoxysalicylaldehyde (1 mmol, 152 mg) was refluxed for ca. 1 h. A methanol solution (5 ml) of 2-cyanopyrazine (1 mmol, 105 mg) was then added to it, followed by the addition of methanol solution (5 ml) of nickel(II) acetate tetrahydrate (1 mmol, 249 mg) with constant stirring. A solution of sodium azide (2 mmol, 130 mg) in methanol-water solution was added to it and the stirring was continued for additional 2 h. An initial precipitation was filtered off. Crystalline complex started to separate on standing the resulting solution at room temperature and it was collected by filtration after ca. 2 days. Red single crystals, suitable for X-ray diffraction, were obtained from acetonitrile–DMSO mixture. (See notes and references for details).‡

The ligand, *HL*, was prepared by the 1:1 condensation of 3-methoxysalicylaldehyde with the N-ethyl-1,2-diaminoethane in methanol following the literature method.[15] Nickel(II) acetate tetrahydrate was then reacted with this tridentate ligand, followed by 2-cyanopyrazine and sodium azide to form bis(tetrazolate) bridged dinuclear nickel(II) complex **1** (Scheme 1).

Complex **1** crystallizes in the monoclinic space group $P2_1/c$. The complex features a centrosymmetric bis(μ-NN′-tetrazolate) bridged dinuclear nickel(II) moiety $[Ni_2L_2(PTZ)_2]$ with two non-coordinated water and two acetonitrile molecules. Perspective view of **1** is shown in Figure 1. 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(8), and two nitrogen atoms, N(3) and N(6), of a depronated tridentate Schiff base $(L)^-$ in meridional fashion and two nitrogen atoms, N(14) and N(21), of 5-pyrazinyltetrazolate. A nitrogen atom, N(22)$^*$, from a symmetry related (2-x,-y,2-z) $(PTZ)^-$ ligand 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 $(PTZ)^-$ ligand is considerably asymmetric, which can be seen from the inequality in the bridging angles (Ni(1)–N(21)–N(22) = 139.8(1) and Ni(1)$^*$–N(22)–N(21) = 124.6(1)) involving the bridging nitrogen atoms, as was also observed in similar complex.[14] The saturated five membered ring [Ni(1)–N(3)–C(4)–C(5)–N(6)] has an envelope conformation on C(4) with puckering parameters Q(2) = 0.448(2) Å and $\phi(2) = 252.3(2)°$.[16]

The complex shows significant supramolecular interactions (H-bonding and C–H···π interactions[17]). The H-bonding interactions between centrosymmetric dimer and lattice water molecules produce two-dimensional H-bonded network (Figure S1 in ESI). Furthermore, C–H···π interactions (Figure S2 in ESI) made this H bonded network to a $3^6$-**hxl** topological supramolecular network as shown in Figure S3 (ESI).[18] The details of supramolecular structure analysis are provided in ESI.

In the IR spectrum (Figure S4, ESI), distinct band due to the azomethine (C=N) group at 1641 $cm^{-1}$ has been noticed.[19] A broad band around 3473 $cm^{-1}$ is assigned to the OH stretching vibration of the water molecule, which is involved in hydrogen bonding.[20] The sharp band due to the amino NH group appears at 3217 $cm^{-1}$.[21] The peaks at 1444 and 1404 $cm^{-1}$ are due to the tetrazolate moiety which are consistent with those of other tetrazolate-based metal complexes in previous reports.[22] The electronic spectrum (Figure S5, ESI) shows an absorption band at 539 nm and a broad band at 883 nm with a shoulder peak at 778 nm in DMSO. These bands are respectively assigned to the following transitions of an octahedral nickel(II) complex: $^3A_2g \rightarrow {}^3T_1g(F)$, $^3A_2g \rightarrow {}^3T_2g(P)$ and $^3A_2g \rightarrow {}^1Eg$ (shoulder band).[23] The higher energy d–d band $^3A_2g \rightarrow {}^3T_1g(P)$ is obscured by strong ligand to metal charge transfer transitions at 385 nm, which is also characteristics of transition metal complexes with Schiff base ligand.[24] The emission spectral behavior has been studied at room temperature using DMSO solution. The complex on excitation at 385 nm shows emissions at 413 nm and 436 nm with exited state mean lifetimes 1.322 ns and 0.914 ns respectively at room temperature. It can be attributed to intra-ligand fluorescent $^1(\pi \rightarrow \pi^*)$ emissions of the coordinated ligand. The details of the Photoluminescence lifetime data and spectrum have been depicted in Table S2 (ESI) and Figure 2 respectively. The room temperature magnetic susceptibility measurements show that the magnetic moment of the complex is 3.1 BM per nickel atom, indicating the presence of two unpaired electrons as expected for octahedral nickel(II) complex.

The present complex exhibits a reduction peak at $E_{pc}$ = -0.98 V with a direct oxidation peak at $E_{pa}$ = -0.66 V corresponding to the formation of a quasi reversible Ni(II)/Ni(I) couple with $E_{1/2}$ = -0.82 V. The peak separation of this couple ($\Delta E_p$) is 320 mV. A representative cyclic voltammogram is shown in Figure S6 (ESI). The single-electron nature of the voltammogram has been confirmed by the comparison of current heights for the complex and that of a simple $[Fe(bipy)_3]^{2+}$ complex under identical condition.[25] The criteria of reversibility has been 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.[26] 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 redox couples are not noteworthy.

In the present work, we have reported the synthesis and characterization of a bis(μ-NN′-tetrazolate) bridged dinuclear nickel(II) Schiff base complex via [3+2] cycloaddition reaction between metal coordinated azide and 2-cyanopyrazine. The syntheses of tetrazoles by microwave iradiations or under solvo-thermal conditions are frequently reported by several groups. But the tetrazolate bridged transition metal complexes with Schiff bases as co-ligands are extremely rare in literature. We have prepared a bis(tetrazolate) bridged dinuclear nickel(II) complex with Schiff base as the blocking ligand under non-hydrothermal and non-microwave reaction condition. During the course of the reaction, a metal Schiff base complex with azide as co-ligand is formed and this is then made to undergo [3+2] cycloaddition reaction to form tetrazole, which is then deprotonated. Participation of tetrazolate in a (μ-NN′) fashion forms a dinuclear nickel(II) complex. The facile synthesis of the complex would, therefore, afford a convenient synthetic route for this type of complexes and opens up new possibilities for the synthesis of tetrazolate bridged transition metal complexes with Schiff base co-ligands.

Work is in progress to improve the yield of the reaction and to develop more systems based on this strategy to generalize the concept.

## Acknowledgement

This work was supported by the DST, India under FAST Track Scheme (Order No. SR/FT/CS-118/2010, dated 15/02/2012). We are thankful to Dr. Saurabh Das, Department of Chemistry, Jadavpur University, India for providing facilities for UV-Vis spectral studies and Mr. Kallol Bera for fluorescence life-time measurements.

## Notes and References

‡ Yield: 330 mg (68%, based on nickel(II) salt). Anal. Calc. for $C_{19}H_{25}N_9O_3Ni$ (972.38): C, 46.9; H, 5.2; N, 25.9%. Found: C, 46.8; H, 5.4; N, 25.7%. FT-IR (KBr, $cm^{-1}$): 3473 (broad, s, OH), 3217 (m, NH), 1641 (s, C=N), 1444 (s, *PTZ*), 1403 (m, *PTZ*). UV–Vis, $\lambda_{max}$ (nm) [$\varepsilon_{max}$($dm^3$ $mol^{-1}$ $cm^{-1}$)] (DMSO): 843(76), 778(61), 539(54), 385(8694). Magnetic moment: 3.1 B.M. Elemental analysis (carbon, hydrogen and nitrogen) was performed using a PerkinElmer 240C elemental analyzer. IR spectrum in KBr (4000–450 $cm^{-1}$) was recorded using a PerkinElmer Spectrum Two FT-IR spectrometer. Electronic spectrum in DMSO (1100–300 nm) was recorded in a JASCO V-630 spectrophotometer. The magnetic susceptibility measurements were done with an EG & PAR vibrating sample magnetometer, model 155 at room temperature and diamagnetic corrections were made using Pascal's constants for all the constituent atoms. Fluorescence spectrum was obtained on Hitachi F-7000 Fluorescence Spectrophotometer at room temperature. Electrochemical measurement was performed in DMSO solution under a dry nitrogen atmosphere in conventional three-electrode configurations using a Pt diskworking electrode, Pt

auxiliary electrode and Ag/AgCl reference electrode, with tetrabutylammonium hexafluorophosphate as supporting electrolyte in the potential range from -2 to 2 V and were uncorrected for junction contribution. The value for the Fc–$Fc^+$ couple under our conditions was 0.39 V. Fluorescence total emission intensity decay measurement was carried out on a fluorescence lifetime spectrometer with components from Edinburgh Analytical Instruments (EIA, UK) and EG&G ORTEC (USA) and operated in the time-correlated-single-photon-counting mode. Excitation was provided by a pulsed high-pressure 1.5 atm N -lamp operating at 25 kHz repetition rate, the pulse profile having a FWHM of 1.3 ns. Slits of bandwidth 16 nm were used in both excitation and emission channels. 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 $\tau_i$. Best fit parameters were estimated using software supplied by Edinburgh Instruments (UK), implementing a non-linear least-squares iterative fitting procedure. Mean lifetime was calculated using the relation

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

A single crystal having suitable dimensions was used for the X-ray crystallographic analysis using a ‘Bruker SMART APEX II’ diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda$= 0.71073 Å) at 100 K. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm.[27] Data were corrected for absorption effects using the multi-scan method (SADABS).[28] The structure was solved and refined using the Bruker SHELXTL Software Package[29] using the space group $P2_1/c$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 300 variables converged at R1 = 3.67% for the observed data and wR2 = 7.29% for all data. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. H atoms of water molecules were located by difference Fourier maps and were kept fixed. CCDC reference number 956491.

Crystal data: formula = $C_{38}H_{50}N_{18}Ni_2O_6$, formula weight = 972, crystal size [mm] = 0.17 x 0.18 x 0.23, temperature (K) = 100, crystal system = Monoclinic, space group = $P2_1/c$, a = 13.3833(8) Å, b = 9.8759(6) Å, c = 17.7659(11) Å, β = 110.1600(10)°, Z = 2, $d_{calc}$ ($gcm^{-3}$) = 1.465, μ ($mm^{-1}$) = 0.921, F(000) = 1016, total reflections = 25325, unique reflections = 5029, observed data [$I > 2\sigma(I)$] = 4049, R(int) = 0.03, R1, wR2 (all data) = 0.0557, 0.0729, R1, wR2 [$I > 2\sigma(I)$] = 0.0367, 0.0675.

1 (a) J. Otsuki, T. Akasaka and K. Araki, *Coord. Chem. Rev.*, 2008, **252**, 32–56; (b) D.-H. Chae, J. F. Berry, S. Jung, F. A. Cotton, C. A. Murillo and Z. Yao, *Nano lett.*, 2006, **6**, 165-168; (c) T. Albrecht, A. Guckian, A. M. Kuznetsov, J. G. Vos and J. Ulstrup, *J. Am. Chem. Soc.*, 2006, **128**, 17132-17138.

2 (a) G. P. Guedes, S. Soriano, L. A. Mercante, N. L. Speziali, M. A. Novak, M. Andruh and M. G. F. Vaz, *Inorg. Chem.*, 2013, **52**, 8309−8311; (b) K. Wang, D. Qi, H. Wang, W. Cao, W. Li, T. Liu, C. Duan and J. Jiang, *Chem. Eur. J.*, 2013, **19**, 11162–11166; (c) J. Kan, H. Wang, W. Sun, W. Cao, J. Tao and J. Jiang, *Inorg. Chem.*, 2013, **52**, 8505−8510; (d) P. Zhang, Y.-N. Guo and J. Tang, *Coord. Chem. Rev.*, 2013, **257**, 1728–1763.

3 (a) R. K. Dean, K. Devaine-Pressing, L. N. Dawe and C. M. Kozak, *Dalton Trans.*, 2013, **42**, 9233–9244; (b) K. Press, V. Venditto, I. Goldberg and M. Kol, *Dalton Trans.*, 2013, **42**, 9096–

9103; (c) S.-C. Roşca, D.-A. Roşca, V. Dorcet, C. M. Kozak, F. M. Kerton, J.-F. Carpentier and Y. Sarazin, *Dalton Trans.*, 2013, **42**, 9361–9375.

4 (a) J. Reboul, S. Furukawa, N. Horike, M. Tsotsalas, K. Hirai, H. Uehara, M. Kondo, N. Louvain, O. Sakata and S. Kitagawa, *Nature Materials,* 2012, **11**, 717–723; (b) M. Meilikhov, S. Furukawa, K. Hirai, R. A. Fischer and S. Kitagawa, *Angew. Chem., Int. Ed.* 2013, **52**, 341–345; (c) C. Zhang, Y. Che, Z. Zhang, X. Yang and L. Zang, *Chem. Commun.*, 2011, **47**, 2336–2338; (d) M.-L. Ho, Y.-A. Chen, T.-C. Chen, P.-J. Chang, Y.-P. Yu, K.-Y. Cheng, C.-H. Shih, G.-H. Lee and H.-S. Sheu, *Dalton Trans.,* 2012, **41**, 2592-2600; (e) T. Fukushima, S. Horike, Y. Inubushi, K. Nakagawa, Y. Kubota, M. Takata and S. Kitagawa, *Angew. Chem., Int. Ed.* 2010, **49**, 4820–4824.

5 (a) X.-M. Zhang, Y. F. Zhao, H.-S. Wu, S. R. Batten and S. W. Ng, *Dalton Trans.,* 2006, 3170-3178; (b) X.-S. Wang, Y.-Z. Tang, X.-F. Huang, Z.-R. Qu, C.-M. Che, P. W. H. Chan and R.-G. Xiong, *Inorg. Chem.,* 2005, **44**, 5278-5285; (c) R.-G. Xiong, X. Xue, H. Zhao, X.-Z. You, B. F. Abrahams and Z. Xue, *Angew. Chem., Int. Ed.* 2002, **41**, 3800-3803; (d) S. Singh, D. K. Gupta, H. Noeth and A. Pandey, *J. Chem. Crystallogr.*, 2013, **43**, 82-90.

6 (a) P. Cui, Y.-G. Ma, H.-H. Li, B. Zhao, J.-R. Li, P. Cheng, P. B. Balbuena and H.-C. Zhou, *J. Am. Chem. Soc.*, 2012, **134**, 18892−18895; (b) C. Cook, F. Habib, T. Aharen, R. Clérac, A. Hu and M. Murugesu, *Inorg. Chem.*, 2013, **52**, 1825−1831; (c) N. Fischer, D. Izsák, T. M. Klapötke and J. Stierstorfer, *Chem. Eur. J.*, 2013, **19**, 8948–8957; (e) L. Liang, G. Peng, L. Ma, L. Sun, H. Deng, H. Li and W. Li, *Cryst. Growth Des.*, 2012, **12**, 1151−1158; (f) A. J. Calahorro, A. Salinas-Castillo, J. M. Seco, J. Zuñiga, E. Colacio and A. Rodríguez-Diéguez, *CrystEngComm,* 2013, **15**, 7636–7639.

7 (a) L. Sun, L. Ma, J.-B. Cai, L. Liang and H. Deng, *CrystEngComm*, 2012, **14**, 890-898; (b) S. Jeong, X. Song, S. Jeong, M. Oh, X. Liu, D. Kim, D. Moon and M. S. Lah, *Inorg. Chem.*, 2011, **50**, 12133−12140; (c) L. Ma, Y.-C. Qiu, G. Peng, J.-B. Cai and H. Deng, *Eur. J. Inorg. Chem.*, 2011, 3446–3453; (d) H.-F. Chen, W.-B. Yang, L. Lin, X.-G. Guo, X. Dui, X.-Y. Wu, C.-Z. Lu and C.-J. Zhang, *J. Solid State Chem.*, 2013, **201**, 215-221.

8 (a) A. H. McKie, S. Friedland and F. Hof, *Org. Lett.*, 2008, **10**, 4653-4655; (b) R. J. Herr, *Bioorg. Med. Chem.*, 2002, **10**, 3379–3393; (c) H. Singh, A. S. Chawla, V. K. Kapoor, D. Paul and R. K. Malhotra, *Prog. Med. Chem.*, 1980, **17**, 151-183.

9 (a) T. M. Klapötke and J. Stierstorfer, *J. Am Chem. Soc.*, 2009, **131**, 1122-1134; (b)T. Fendt, N. Fischer, T. M. Klapötke and J. Stierstorfer, *Inorg.Chem.*, 2011, **50**, 1447–1458; (c) A. Hammer, T. M. Klapötke, H. Nöth, M. Warchhold, G. Holl, M. Kaiser and U. Ticmanis, *Inorg. Chem.*, 2001, **40**, 3570-3575.

10 (a) S. Bhandari, C. G. Frost, C. E. Hague, M. F. Mahon and K. C. Molloy, *J. Chem. Soc., Dalton Trans.*, 2000, 663–669; (b) W. Wei, M. Wu, Q. Gao, Q. Zhang, Y. Huang, F. Jiang and M. Hong, *Inorg. Chem.*, 2009, **48**, 420-422; (c) Z. Li, M. Li, X.-P. Zhou, T. Wu, D. Li, and S. W. Ng, *Cryst. Growth Des.* 2007, **7**, 1992-1998; (d) C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885-3896.

11 (a) Z. P. Demko and K. B. Sharpless, *J. Org. Chem.*, 2001, **66**, 7945-7950; (b) F. Himo, Z. P. Demko, L. Noodleman and K. B. Sharpless, *J. Am. Chem. Soc.*, 2002, **124**, 12210-12216.

12 (a) Z. P. Demko and K. B. Sharpless, *Org. Lett.*, 2001, **3**, 4091-4094; (b) Z. P. Demko and K. B. Sharpless, *Org. Lett.*, 2002, **4**, 2525-2527; (c) Z. P. Demko and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2110-2113; (d) Z. P. Demko and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2113-2116.

13 (a) F. Himo, Z. P. Demko, L. Noodleman and K. B. Sharpless, *J. Am. Chem. Soc.,* 2003, **125**, 9983-9987; (b) G. Venkateshwarlu, A. Premalatha, K. C. Rajanna and P. K. Saiprakash, *Synth. Commun.,* 2009, **39**, 4479–4485; (c) S. Kamijo, T. Jin, Z. Huo, Y. S. Gyoung, J.-G. Shim and Y. Yamamoto, *Mol Divers,* 2003, **6**, 181–192; (d) P. Lin, W. Clegg, R. W. Harrington and R. A. Henderson, *Dalton Trans.,* 2005, 2388–2394; (e) J. Bonnamour and C. Bolm, *Chem. Eur. J.,* 2009, **15**, 4543–4545.

14 B. G.Mukhopadhyay, S. Mukhopadhyay, M. F. C. Guedes da Silva, M. A. J. Charmier and A. J. L. Pombeiro, *Dalton Trans.,* 2009, 4778–4785.

15 (a) S. Mukherjee and P. S. Mukherjee, *Dalton Trans.,* 2013, 4019-4030; (b) S.-J. Li, K. Li, X.-Y. Qiu and X.-J. Yao, *J. Chem. Crystallogr*., 2012, **42**, 879-883; (c) S. Hayami, S. Miyazaki, M. Yamamoto, K. Hiki, N. Motokawa, A. Shuto, K. Inoue, T. Shinmyozu and Y. Maeda, *Bull. Chem. Soc. Jpn*., 2006, **79**, 442-450.

16 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.,* 1975, **97**, 1354-1358.

17 (a) Y.-F. Jiang, C.-J. Xi, Y.-Z. Liu, J. Niclós-Gutiérrez and D. Choquesillo-Lazarte, *Eur. J. Inorg. Chem.*, 2005, 1585–1588; (b) P. M. Selvakumar, S. Nadella, K. J. Prathap, R. I. Kureshy, E. Suresh and P. S. Subramanian, *Inorg. Chim. Acta*, 2011, **375**, 106–113; (c) B. Čobeljić, Y, B. WarżAjtis, U. Rychlewska, D. Radanović, V. Spasojević, D. Sladić, R. Eshkourfu and K. Anđelković, *J. Coord. Chem*., 2012, **65**, 655–667.

18 (a) M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *Acc. Chem. Res*., 2008, **41**, 1782-1789; (b) H. Chen, D. Xiao, J. He, Z. Li, G. Zhang, D. Sun, R. Yuan, E. Wang and Q.-L. Luo, *CrystEngComm*, 2011, **13**, 4988-5000; (c) X. Zhang, Y.-Y. Huang, J.-K. Cheng, Y.-G. Yao, J. Zhang and F. Wang, *CrystEngComm*, 2012, **14**, 4843–4849; (d) Y. Gong, Z. Hao, J. L. Sun, H.-F. Shi, P.-G. Jiang and J.-H. Lin, *Dalton Trans*., 2013, **42**, 13241–13250.

19 (a) P. Bhowmik, S. Chattopadhyay, M. G. B. Drew and A. Ghosh, *Inorg. Chim. Acta*, 2013, **395**, 24-32; (b) P. K. Bhaumik, K. Harms and S. Chattopadhyay, *Polyhedron*, 2013, **62**, 179-187.

20 M. Das and S. Chattopadhyay, *Polyhedron,* 2013, **50**, 443–451.

21 P. Bhowmik, S. Jana and S.Chattopadhyay, *Polyhedron*, 2012, **44**, 11–17.

22 (a) L. Ma, N. Yu, S. Chen and H. Deng, *CrystEngComm*, 2013, **15**, 1352–1364; (b) F. Wang, X.-Y. Wu, R. Yu and C.-Z. Lu, *Inorg.Chem. Commun.*, 2012, **25**, 21–25; (c) C. Jiang, Z. Yu, C. Jiao, S. Wang, J. Li, Z. Wang and Y. Cui, *Eur. J. Inorg. Chem.*, 2004, 4669-4674.

23 D. Maity, S. Chattopadhyay, A. Ghosh, M. G. B. Drew and G. Mukhopadhyay, *Inorg. Chim. Acta*, 2011, **36**, 525-31.

24 P. Bhowmik, S. Chattopadhyay, M. G. B. Drew, C. Diaz and A. Ghosh, *Polyhedron*, 2010, **29**, 2637–2642.

25 K. Mitra, S. Biswas, C. R. Lucas and B. Adhikary, *Inorg. Chim. Acta*, 2006, **359**, 1997-2003.

26 D. H. Evans, K. M. O'Connell, R. A. Petersen and M. J. Kelly, *J. Chem. Educ.,* 1983, **60**, 290–293.

27 Bruker (2007) *SAINT,* Bruker AXS Inc., Madison, Wisconsin, USA.

28 G. M. Sheldrick, (1996). *SADABS.* University of Göttingen, Germany.

29 SHELXTL Software Reference Manual, Version 6.10, Dec. 5th, 2000, Bruker Analytical X-Ray System, Inc., Madison, WI.

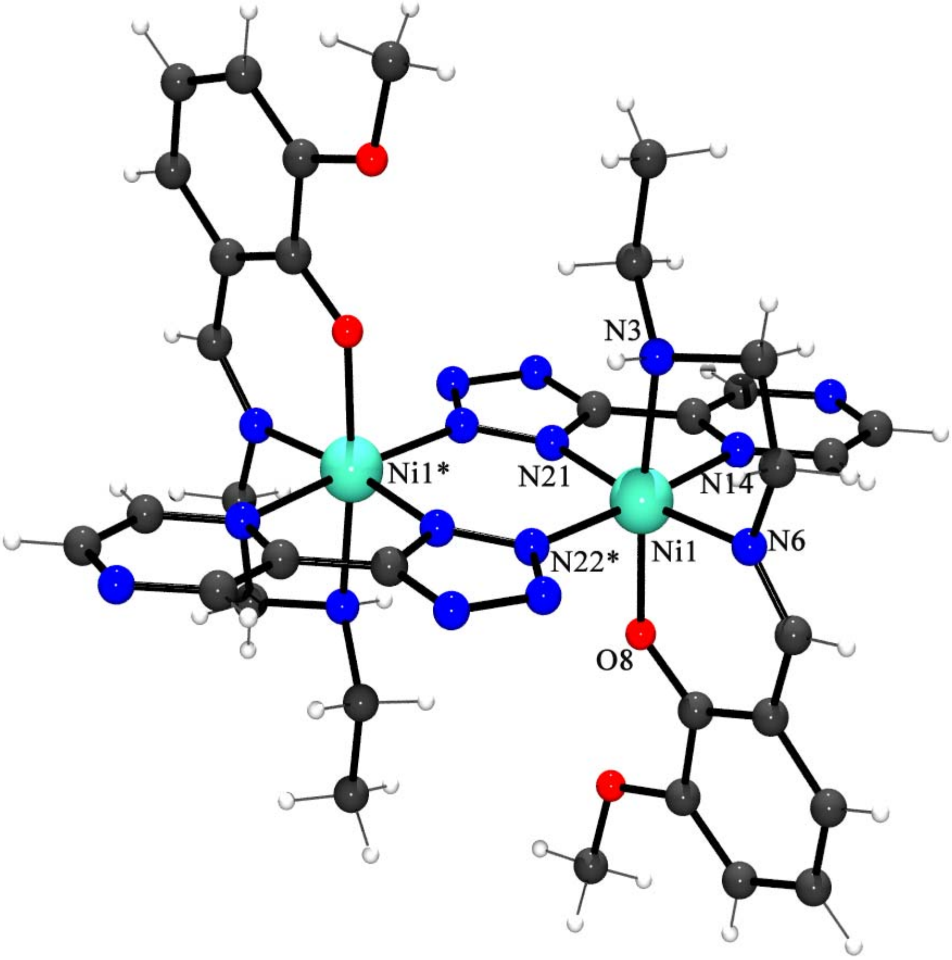


**Figure 1**: Perspective view of complex **1** with selective atom numbering scheme. The water and acetonitrile molecules have been omitted for clarity. Selected bond lengths: Ni(1)–N(3) = 2.1499(16), Ni(1) – N(6) = 1.9957(16), Ni(1) – N(14) = 2.1887(15), Ni(1) – N(21) = 2.0628(15), Ni(1) – N(22)$^{*}$ = 2.0666(15), Ni(1) – O(8) = 2.0152(13). Selected bond angles are given in Table S1 (ESI). Symmetry element $^{*}$ = 2-x,-y,2-z.

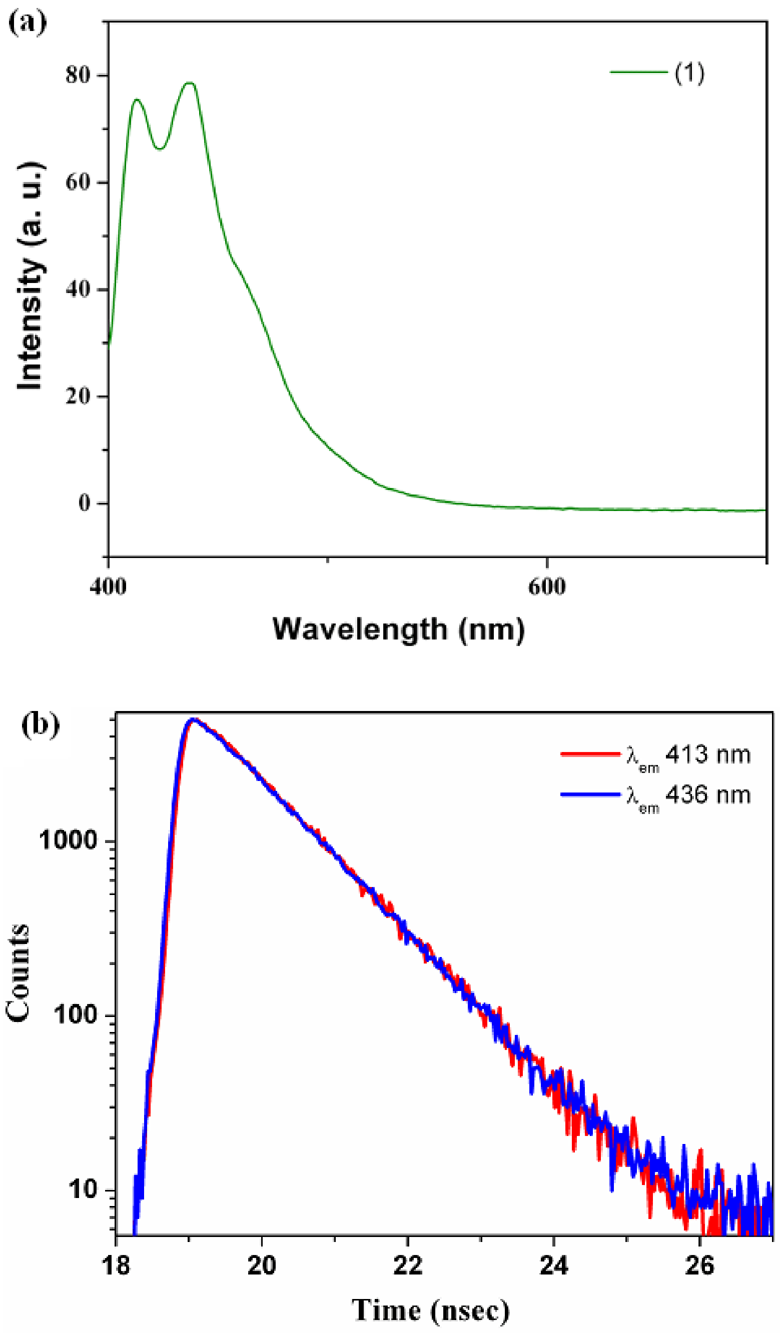


**Figure 2:** Perspective view of (a) photoluminescence spectrum and (b) time-resolved photoluminescence decays of complex **1** in DMSO at room temperature.