



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



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ABSTRACT

Two new bis(μ -tetrazolato-NN') bridged dinuclear nickel(II) Schiff base complexes $[\text{Ni}_2\text{L}_2^1(\text{PTZ})_2] \cdot 2(\text{CH}_3)_2\text{SO} \cdot 2.69\text{H}_2\text{O}$ (**1**) and $2[\text{Ni}_2\text{L}_2^2(\text{PTZ})_2] \cdot 3\text{H}_2\text{O}$ (**2**) (HL^1 and HL^2 are Schiff bases, $\text{HL}^1 = 2-((2-(\text{dimethylamino})\text{ethylimino})\text{methyl})\text{phenol}$, $\text{HL}^2 = 2-((2-(\text{methylamino})\text{ethylimino})\text{methyl})-6\text{-methoxyphenol}$ 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. The change in the denticity of the Schiff base blocking ligand is shown to have no effect in controlling the molecular structures of the complexes. The supramolecular self assemblies are also explored.

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1. 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 and N_2O donor salicylaldimine Schiff bases as blocking ligands to prepare such complexes [10–15]. The ability of the phenoxo oxygen atom to bridge the metal centers and also to participate in hydrogen bonding interaction to form various supramolecular architectures has also inspired the researchers to use such Schiff bases in preparing new complexes [16,17]. Tetrazoles have also been used by several groups as bridging ligands [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-ligand was 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 intention was to examine the variation in molecular architectures, if any, on changing the denticity of Schiff bases.

We would also like to investigate the variation in supramolecular architectures of complexes. Supramolecular systems based on coordination complexes have already received immense attention for their potential uses in various fields [33,34]. Synthesis and characterization of a large number of supramolecular systems have also been reported in last decades [35,36]. The components of a supramolecule are held together by a variety of non-covalent forces, e.g. hydrogen bonding, $\pi \cdots \pi$, C–H $\cdots \pi$ interactions, etc. [37–40]. Herein, we report the tandem syntheses, structural features, spectroscopic characterization and supra-molecular architectures of two new bis(μ -tetrazolato-NN') bridged nickel(II) complexes with two Schiff base blocking ligands.

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2. Experimental

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 $[\text{Ni}_2\text{L}_2^1(\text{PTZ})_2]\cdot 2(\text{CH}_3)_2\text{SO}\cdot 2.69\text{H}_2\text{O}$ (**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). Methanol solution (5 mL) of nickel(II) acetate tetrahydrate (1 mmol, 250 mg) was added followed by the addition of methanol solution (5 mL) of 2-cyanopyrazine (1 mmol, 110 mg) in stirring condition. A methanol–DMSO (2:1 mixture) solution (15 mL) of sodium azide (1 mmol, 70 mg) was 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 $\text{C}_{36}\text{H}_{53.38}\text{N}_{16}\text{Ni}_2\text{O}_{6.69}\text{S}_2$ (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} ($\text{L mol}^{-1} \text{cm}^{-1}$)] (DMSO): 379 (9037), 555 (51), 725 (101), 912 (151).

2.2.2. Complex $2[\text{Ni}_2\text{L}_2^2(\text{PTZ})_2]\cdot 3\text{H}_2\text{O}$ (**2**)

It was prepared in a similar method as that of Complex **1**, except that here N-methyl-1,2-diaminoethane (1 mmol, 0.09 mL) and 3-methoxysalicylaldehyde (1 mmol, 153 mg) were used instead of N,N-dimethyl-1,2-diaminoethane and salicylaldehyde respectively. 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 $\text{C}_{64}\text{H}_{78}\text{N}_{32}\text{Ni}_4\text{O}_{11}$ (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} ($\text{L mol}^{-1} \text{cm}^{-1}$)] (DMSO): 386 (20567), 549 (62), 774 (162), 859 (207).

2.3. Physical measurements

Elemental analyses were 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:

$$\langle \tau \rangle = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i}$$

2.4. Crystal data collection and refinement

Single crystals having suitable dimensions were used for the X-ray crystallographic analysis. ‘Bruker D8 QUEST’ diffractometer

equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 100 K has been used for data collection of **1**. On the other hand, ‘Bruker SMART APEX II’ diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 123 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 potential 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 base blocking ligands.

Both 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 (Scheme 1). 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. The potential tetradentate Schiff base, HL^2 , behaves like a tridentate one. Thus

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

Complex	1	2
Formula	$\text{C}_{36}\text{H}_{53.38}\text{N}_{16}\text{Ni}_2\text{O}_{6.69}\text{S}_2$	$\text{C}_{64}\text{H}_{78}\text{N}_{32}\text{Ni}_4\text{O}_{11}$
Formula weight	998.86	1706.42
Crystal size (mm)	$0.13 \times 0.10 \times 0.09$	$0.21 \times 0.25 \times 0.28$
T (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 [$I > 2\sigma(I)$]	2781	12322
R_{int}	0.0874	0.025
R_1, wR_2 (all data)	0.0844, 0.1134	0.0518, 0.1322
R_1, wR_2 [$I > 2\sigma(I)$]	0.0449, 0.0985	0.0461, 0.1277
Largest difference in peak and hole (e \AA^{-3})	0.688, −0.601	2.16, −1.37

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