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Synthesis, characterization and DFT study of nickel(II) complexes of a N_2O donor Schiff base with different pseudo-halides: Formation of supra-molecular architectures by C–H···π interactions

Subrata Jana [a,*], Prasanta Kumar Bhaumik [a], Klaus Harms [b], Shouvik Chattopadhyay [a,*]

[a] *Department of Chemistry, Inorganic Section, Jadavpur University, Kolkata 700 032, India*
[b] *FachbereichChemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, 35032 Marburg, Germany*

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ABSTRACT

Four new mono-nuclear square planar nickel(II) complexes *[Ni(L)(N_3)]* (**1**), *[Ni(L)(NCO)]* (**2**), *[Ni(L)(NCS)]* (**3**) and *[Ni(L)(NCSe)]* (**4**), where *HL* = 2-(1-(2-(diethylamino)ethylimino)ethyl)naphthalen-1-ol, have been synthesized and characterized by elemental analysis, IR, UV–Vis, fluorescence spectroscopy and single crystal X-ray diffraction studies. The ligand is so designed that there is no possibility of hydrogen bonding interactions in all the four complexes. However, the C–H···π interactions lead to the formation of one-dimensional chain in complex **2** and two-dimensional sheets in the other three complexes. The geometries of all complexes are optimized in the singlet ground states by DFT calculation. Electronic spectra of the complexes are explained using TD DFT calculation.

1. Introduction

Nickel(II) is present in the active sites of many metalloproteins, such as urease and nickel hydrogenases [1]. The potential role played by nickel(II), present in these metalloproteins, has stimulated the design of new ligand frames and their nickel(II) complexes as models for providing a better understanding of biological systems [2]. Nickel(II) complexes with several chelating ligands are also used to prepare several materials with potential applications in catalysis, magnetism, non-linear optics, etc [3–5]. Schiff bases are very well-known chelating ligands to the synthetic inorganic chemists and are already used by several groups to prepare various mono-, di- or poly-nuclear nickel(II) complexes. Definitely, the N_2O_2 donor H_2salen type Schiff bases, prepared from the condensation of various diamines with salicylaldehyde or its derivatives, are receiving the most attention among all the Schiff bases, as they can form poly-nuclear complexes exploiting the bridging ability of phenoxo oxygen atoms. N_2O donor tridentate Schiff bases could also be prepared easily and used to synthesize several nickel(II) complexes [6].

In the present work, we have used a tridentate Schiff base to prepare nickel(II) complexes with four different pseudo-halides as co-ligands. In each case, we get mono-nuclear complexes, in spite of the presence of the pseudo-halides with potential bridging ability. The steric crowding in the tridentate Schiff base probably restricts polymerization. In recent years, there have been immense interests in studying supra-molecular structures [7]. The inspiration for this is not only to know the role of fundamental interactions in both chemical and biological molecular recognition, but also to discover their potential for technological applications in a number of areas of material science [8–10]. The most commonly used approach for engineering the crystal structures of such systems is to employ hydrogen bonds within them [11–13]. The molecular as well as crystalline architectures of the complexes can also be managed by π···π, C–H···π and anion···π interactions [14–15]. The tridentate Schiff base, in the present work, is so designed that it cannot participate in H-bonding interaction. Thus the supra-molecular architecture is totally guided by other interactions. Herein, we report the synthesis, spectroscopic characterization and X-ray crystal structures of four new nickel(II) complexes as well as their interesting crystalline architectures formed by supra-molecular interactions.

2. Experimental

2.1. Materials

All chemicals were of reagent grade and used without further purification.

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* Corresponding author. Tel.: +91 33 24572941.
E-mail addresses: subrata.chem87@gmail.com (S. Jana), shouvik.chem@gmail.com (S. Chattopadhyay).

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2.2. Preparation

2.2.1. Preparation of the ligand {HL = 2-(1-(2-(diethylamino)ethylimino)ethyl)naphthalen-1-ol}

The tridentate Schiff base, *HL*, was synthesized by refluxing N, N-diethyl-1,2-diaminoethane (1 mmol, 0.14 ml) with 1-hydroxy-2-acetonaphthone (1 mmol, 186 mg) in methanol for ca. 1 h. The ligand was not isolated and used directly for the synthesis of the complexes.

2.2.2. Preparation of [Ni(L)(N$_3$)] (**1**)

A methanol solution (20 ml) of nickel(II) perchlorate hexahydrate (1 mmol, 365 mg) was added to the methanol solution of the ligand (1 mmol) and stirred for 1 h. A methanol solution of sodium azide (1 mmol, 65 mg) was then added to it and stirred further for ca. 1 h. Deep green precipitate separated out and was collected by filtration. Diffraction quality single crystals were obtained after a few days by slow evaporation of a dark green acetonitrile solution of the complex in open atmosphere.

Yield: 0.25 g (65%). *Anal.* Calc. for $C_{18}H_{23}N_5NiO$ (384.10): C, 56.29; H, 6.04; N, 18.23. Found: C, 56.1; H, 6.4; N, 18.4%. IR (KBr, cm^{-1}): 1570 ($\nu_{C=N}$), 2040 (ν_{N3}), UV–Vis, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (acetonitrile), 317 (14430), 418 (4880). Magnetic moment: diamagnetic.

2.2.3. Preparation of [Ni(L)(NCO)] (**2**)

Complex **2** was prepared in similar method to that of complex **1** except that sodium cyanate (1 mmol, 65 mg) was added instead of sodium azide. Diffraction quality single crystals were obtained after a few days by slow evaporation of a dark green acetonitrile solution of the complex in open atmosphere.

Yield: 0.27 g (70.3%). *Anal.* Calc. for $C_{19}H_{23}N_3NiO_2$ (384.09): C, 59.41; H, 6.04; N, 10.94. Found: C, 59.1; H, 6.3; N, 11.1%. IR (KBr, cm^{-1}): 1576 ($\nu_{C=N}$), 2100 (ν_{OCN}), UV–Vis, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (acetonitrile), 319 (10760), 416 (5850). Magnetic moment: diamagnetic.

2.2.4. Synthesis of [Ni(L)(NCS)] (**3**)

Complex **3** was prepared in similar method to that of complex **1** except that sodium thiocyanate (1 mmol, 81 mg) was added instead of sodium azide. Diffraction quality single crystals were obtained after a few days by slow evaporation of a dark green acetonitrile solution of the complex in open atmosphere.

Yield: 0.28 g (70%). *Anal.* Calc. for $C_{19}H_{23}N_3NiOS$ (400.16): C, 57.03; H, 5.79; N, 10.50. Found: C, 56.9; H, 5.6; N, 10.7%. IR (KBr, cm^{-1}): 1575 ($\nu_{C=N}$), 2230 (ν_{SCN}), UV–Vis, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (acetonitrile), 313 (12450), 413 (6150). Magnetic moment: diamagnetic.

2.2.5. Synthesis of [Ni(L)(NCSe)] (**4**)

Complex **4** was prepared in similar method to that of complex **1** except that potassium selenocyanate (1 mmol, 144 mg) was added instead of sodium azide. Diffraction quality single crystals were obtained after a few days by slow evaporation of a dark green acetonitrile solution of the complex in open atmosphere.

Yield: 0.3 g (67%). *Anal.* Calc. for $C_{19}H_{23}N_3NiOSe$ (447.05): C, 51.05; H, 5.19; N, 9.40; Found: C, 51.2; H, 5.1; N, 9.6; IR (KBr, cm^{-1}): 1582 ($\nu_{C=N}$), 2103 (ν_{SeCN}), UV–Vis, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (acetonitrile), 311 (10460), 411 (5820). Magnetic moment: diamagnetic.

2.3. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin–Elmer 240C elemental analyzer. Infrared spectra in KBr (4000–400 cm^{-1}) were recorded using a Perkin–Elmer FT-IR spectrum two spectrophotometer. Electronic spectra in acetonitrile (1000–200 nm) were recorded on a Jasco V-630 UV–Vis spectrophotometer. Fluorescence spectra in acetonitrile were recorded on a Shimadzu RF-5301PC Spectrofluorophotometer at room temperature. The magnetic susceptibility measurements were done with an EG&PAR vibrating sample magnetometer, model 155 at room temperature.

2.4. X-ray crystallography

Single crystals of the complexes **1** and **3**, having suitable dimensions, were used for data collection using a 'Bruker SMART APEX II' diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 273 K. The molecular structure was solved by direct methods and refinement by full-matrix least squares on F^2 using the SHELX-97 package [16]. Non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Multi-scan empirical absorption corrections were applied to the data using the program SADABS [17].

Single crystals of **2** and **4** of suitable dimensions were mounted in inert oil and transferred to the cold gas stream of the cooling device. Data were collected at 100 K on a Bruker D8 QUEST area detector diffractometer using graphite monochromated Mo Ka radiation, and were corrected for absorption effects using multi-scanned reflections. Non hydrogen atoms were refined anisotropically. All other hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Programs used: SHELXS-97 [16], SHELXL-2013 [16], DIAMOND [18], ORTEP [19] and MERCURY [20]. A summary of the crystallographic data are given in Table 1. Selected bond lengths and angles are summarized in Table 2. CCDC reference numbers 973125, 963809, 973126 and 963810 contain the supplementary crystallographic data for complexes **1**, **2**, **3** and **4** respectively.

2.5. Theoretical calculations

Singlet ground state geometry optimizations of all the complexes were carried out using density functional theory (DFT) at the B3LYP level using the GAUSSIAN 03W suite of programs [21–24]. The single crystal X-ray geometry was used as an initial guess structure. The geometries of the complexes were fully optimized in gas phase without any symmetry constraints. All subsequent calculations were carried out based on the optimized structure. For C, H, N, O, S and Se atoms the 6-31G(d) basis sets were used, while for Ni the TZVP basis set was employed. Vertical electronic excitations based on B3LYP optimized geometries were computed for the complexes using the time-dependent density functional theory (TD-DFT) [25–27]. GAUSS SUM was used to calculate the fractional contributions of various groups to each molecular orbital [28].

3. Results and discussion

3.1. Synthesis

The ligand (*HL*) was prepared by 1:1 condensation of the N,N-diethyl-1,2-diaminoethane with 1-hydroxy-2-acetonaphthone in methanol following the literature method [29]. A methanol solution of nickel(II) perchlorate was then added to the methanol solution of the ligand, followed by the addition of methanol solution of sodium azide with constant stirring to prepare complex **1**. Deep green precipitate appeared within 1 h and was collected by filtration. Addition of a methanol solution of sodium cyanate instead of sodium azide produced complex **2**. Complex **3**, on the other hand, was prepared on adding sodium thiocyanate. The