

Structure and Chromotropic Properties of 2-Picolylamine-Ni(II) Complex

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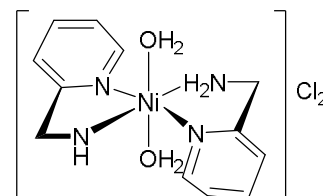
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A symmetric complex $[\text{NiL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$, where L = 2-picolylamine was synthesized and characterized by spectroscopic and structural methods. Single crystal X-ray studies reveal that the Ni(II) center located in a pseudo-octahedral N_4O_2 environment with bidentate ligands L placed in basal and two water molecules in the apical position. The complex is solvatochromic, ionochromic and thermochromic. The observed positive solvatochromism in polar solvents is due to the substitution of water molecules by the solvent. It was found that the complex is ionochromic towards cyanide and bromide anions in the presence of other halides and pseudo-halide anions and it can be served as a “naked-eye” indicator for the qualitative detection of these anions. The observed reversible thermochromism in solid-state is due to dehydration and hydration process of the compound.

Keywords: Chromotropism, 2-Picolylamine, Ni(II) complex

INTRODUCTION

Over the past decade or so, we have focused on the chromotropism of transition metal complexes, mainly copper(II) complexes [1-10]. This is due to wide variety of their potential applications as thermosensitive materials [11], imaging [12], photo-switching materials [13], sensor materials [14] molecular switches [15,16], pollutant sensors [17] and Lewis-acid-base color indicators [18]. Chromotropism is defined as the reversible change in color of a compound owing to the physical and chemical properties of its ambient surrounding medium, such as temperature (thermochromism), solvent (solvatochromism), pressure (piezochromism), light (photochromism), ion (ionochromism), pH (halochromism) and electro-redox reaction (electrochromism) [19]. It has been observed that many researchers have focused on chromotropism of the organic molecules. However, studies of metal complexes have received less attention and their potential application has not fully discovered. Among the metal complexes, transition metal complexes have received much less



Scheme 1. Complex under study

attention, and their enormous potential as chromotropic material remains mainly unexploited. Nickel(II) complexes have been proved to be particularly suitable candidates as chromotropic compounds because of their variable structures and rich photophysical properties that are sensitive to environmental variations [19]. On the other hand, appropriate ligand design is an important factor in the synthesis of a successful chromotropic complex. 2-picolylamine is a bidentate chelating ligand that makes a stable five-membered ring system with nickel(II) that is required for a thermodynamically stable chromotropic compound. Herein, we report the synthesis and chromotropic properties of nickel(II) with 2-picolylamine ligand shown in Scheme 1.

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EXPERIMENTAL

Reagents and Apparatus

2-Picolylamine (Aldrich) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Fluka) were used as received. A Bruker FT-IR spectrometer was used to record infrared spectra measurements, using KBr disk, in the range of $400\text{--}4000\text{ cm}^{-1}$. Conductance measurements were made at $25\text{ }^\circ\text{C}$ with a Jenway 400 conductance meter on concentrations of 1.00×10^{-3} . The UV-Vis spectra of the solutions were recorded with a Braic 2100 spectrophotometer with quartz cells of 1 cm optical path. Elemental analyses (C, H and N) were performed using a LECO 600 elemental analyzer. Absolute metal percentages were determined by a Varian-spectra A-30/40 atomic absorption-flame spectrometer. The solvents employed, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethanol (EtOH), methanol (MeOH) and deionized water were used without further purification in solvatochromism study. The buffer solution of $\text{pH} = 7.0$ for ionochromism study was prepared by mixing potassium dihydrogen phosphate (0.5 g) and dipotassium hydrogen phosphate (1.1 g) in deionized water (90 mL).

Synthesis

Bis(aquo)bis(2-picolylamine)nickel(II) dichloride, $[\text{NiL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$, was prepared by addition of an ethanolic solution (15 mL) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.94 g, 4 mmol) into 2-picolylamine (0.86 g, 8 mmol) in ethanol (10 mL). The resultant purple color solution was stirred for 2 h. The pink precipitate was separated by filtration. The obtained crude solid was recrystallized by slow diffusion of diethyl ether into an ethanolic solution of the compound. Yielded 0.367 g (47%) as pink crystal. Selected IR data (v/cm^{-1} using KBr disk): 3254 (br, OH str.), 3150, 3082 (s, NH_2 str.), 2939 (m, C-H str.), 1607 (s, C=N str.) 1436 (m, N-H bend). Anal. Calcd. for $\text{C}_{12}\text{H}_{20}\text{N}_4\text{O}_2\text{NiCl}_2$ (MW = 381.91 g M^{-1}): C, 37.74; H, 5.28; N, 14.67, Ni, 15.37; Found: C, 37.69; H, 5.37; N, 14.49; Ni, 15.14%. M. P. $> 300\text{ }^\circ\text{C}$.

X-ray Structural Analysis

The X-ray measurement of $[\text{NiL}_2(\text{OH}_2)_2]\text{Cl}_2$ was made on a Bruker Apex-II CCD single crystal diffractometer at room temperature by using graphite-monochromated Mo-K α radiation. Data was collected and reduced by SMART

and SAINT softwares [20] in the Bruker packages. The structure was solved by direct method [21,22] and subsequent Fourier difference techniques and refined using the full-matrix weighted least-squares procedure on F^2 [23] with anisotropic thermal parameters for all non-hydrogen atoms. The position and isotropic displacement parameter of the OH_2 apical hydrogens have been refined with only a suitable O-H bond distance restrain. A summary of crystal data and structure determination is reported in Table 1.

RESULTS AND DISCUSSION

The stoichiometry of the complex resulting from the reaction of nickel(II) dichloride with 2-picolylamine in ethanol showed the presence of water molecules, while the molar conductance values in different solvent solutions (Table 2) suggested that the chloride anions are free of coordination [24].

Electronic spectral data of the complex in methanolic solution is shown in Fig. 1. Under an ideal condition, in a tetragonal distortion octahedral system (D_{4h}), four spin-allowed transitions are expected to be observed arisen from ground term $^3A_{2g}$, among which three bands are observed in the near-IR region. In the electronic spectra of the complex, a band at near-IR region shows the further splitting of the d-d band indicating trans-configuration of octahedral nickel(II) complex [25]. The electronic spectral data of the complex shows absorption maxima at 881 nm ($\epsilon = 10\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) and 570 nm ($\epsilon = 8\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) assigned to $^3A_{2g} \rightarrow ^3T_{2g}$ and $^3A_{2g} \rightarrow ^3T_{1g}$, respectively (assuming the *N* and *O* site symmetry). This indicates pseudo-octahedral geometry around nickel(II) [25]. The bands located at UV region are associated with the pyridine to Ni(II) charge transfer transition (LMCT), which appears at 261 nm ($\epsilon = 17530\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ solution) [25].

In the IR spectrum, the bands arising from the stretching vibrations of the primary amino group [26] are shifted significantly to lower frequencies compared with the free ligand and are observed at 3150 and 3082 cm^{-1} . Alternatively, the band appeared in the spectrum of the ligand at 1591 cm^{-1} that is assigned to the stretching vibration of the aromatic C=N bond shifted to a higher frequency while in the spectrum of the complex occurred at 1607 cm^{-1} , signifying that the electronic density of the

Table 1. Crystal Data and Structure Refinement of $[\text{NiL}_2(\text{OH}_2)_2]\text{Cl}_2$

Empirical formula	$\text{C}_{12}\text{H}_{20}\text{N}_4\text{O}_2\text{NiCl}_2$
Formula weight	381.93
Color	Needle, pink
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
Crystal size (mm)	$0.40 \times 0.20 \times 0.12$
Unit cell dimensions	
a (Å)	8.4187(17)
b (Å)	7.5198(15)
c (Å)	12.764(3)
β (°)	94.79
V (Å ³)	805.2(3)
Z	2
Calculated density (mg m ⁻³)	1.575
F (0 0 0)	396
θ range for data collection (°)	3.15-27.00
	$-10 \leq h \leq 10$
Index ranges	$-9 \leq k \leq 9$
	$-16 \leq l \leq 14$
Reflections collected/unique	5403/1745 [R(int.) = 0.0490]
Completeness to $\theta = 27.00$	99.5%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-square on F ^{2a}
Data/restraints/parameters	1745/0/113
R indices ^a [2806 with I > 2 σ (I)] ^b	R1 = 0.0289, wR2 = 0.0723
Goodness-of-fit on F ^{2c}	1.019
R indices (all data)	R1 = 0.0323, wR2 = 0.0735
Largest diff. peak and hole (e Å ⁻³)	0.498 and -0.341
CCDC	2006284

^aR = $\sum(|F_o| - |F_c|)/\sum|F_o|$. ^bwR = $\{[(\sum[F_o^2 - F_c^2]^2)/\sum w(F_o^2)^2]\}^{1/2}$. ^cS = $\sum[w(F_o^2 - F_c^2)^2]/(N_{\text{obs}} - N_{\text{param}})$.

Table 2. Molar Conductivities Data (Λ_m) of the Complex ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) at 25 °C in Different Solvents

Complexes	EtOH	MeOH	DMF	H ₂ O
1	73	2122	121	241
1:2 Electrolyte ^a	70-90	160-220	130-170	235-337

^aTaken from Ref. [24].

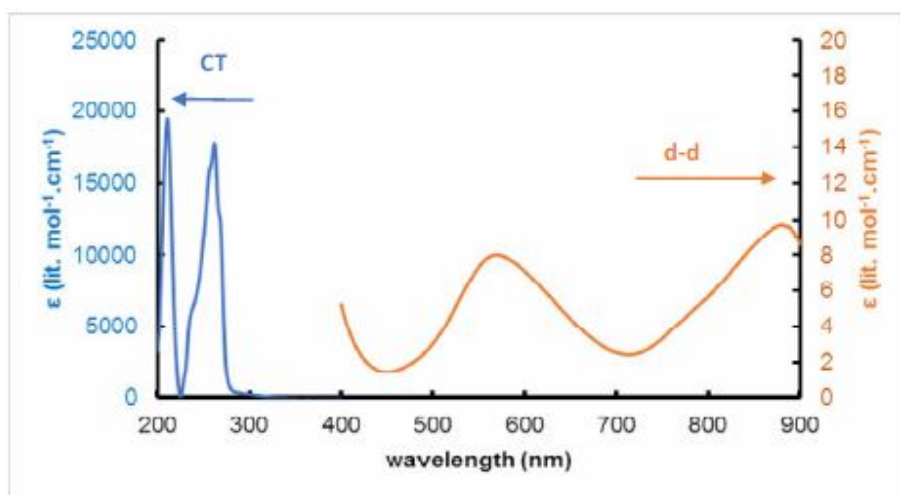


Fig. 1. The UV-Vis spectrum of the complex in methanol.

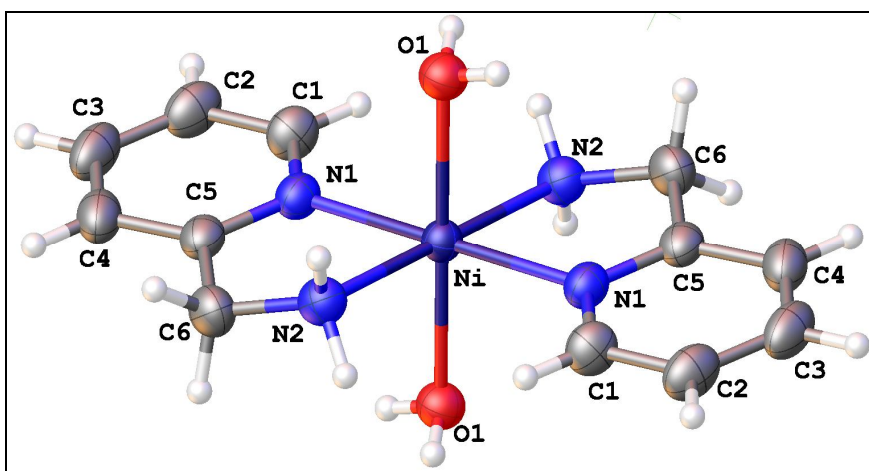


Fig. 2. ORTEP view of cationic part of $[\text{NiL}_2(\text{OH}_2)_2]\text{Cl}_2$.

above-mentioned bond was increased after coordination. A broad vibration band at 3254 cm^{-1} suggested that the water is coordinated to the nickel(II) ion [27]. Further evidence of the ligation of 2-picolylamine as a bidentate ligand and the coordination of water was obtained from the X-ray diffraction analysis that is discussed below.

Crystallography

In the unit cell of the compound, there are two nickel atoms. The molecular structure of the compound consists of $[\text{NiL}_2(\text{H}_2\text{O})_2]^{2+}$ cation and two chloride anions, in which two bidentate ligands coordinated to the nickel via nitrogen atoms of the amine and pyridine as well as the oxygen atoms of water molecules. A view of the complex with the atom-labeling scheme is shown in Fig. 2. The selected bond distances and angles are listed in Table 3. The nickel atom is surrounded by four nitrogen and two oxygen atoms symmetrically positioned in a distorted octahedral environment. The six-coordinate structure of the complex assembled by four nitrogen atoms of the ligand in the basal plane and two oxygen atoms of water molecules in the axial positions. The bond distance of the two oxygen atoms ($2.1599(12)\text{ \AA}$) is much longer than the usual distance in Ni-O(water) compounds [28]. Hence, the forces holding the water molecules are weak and can be cleaved in coordinating solvents, which led to the observed solvatochromism. Additionally, the long Cu-O bonds indicate appreciable tetragonal distortion. In fact, in the immediate vicinity of nickel is found only the four nitrogen atoms that lie in a plane encompassing the nickel center that is nearly coplanar; the deviations from the least-squares plane are N(1) 0.000, N(2) 0.330, N(#1) 0.000, N(#2) -0.330 and Cu(1) 0.00 \AA . The aromatic moiety of the ligand is completely planar and in the same plane also lies the carbon atom (C6) that links the pyridine ring with the amino group. The five-membered chelate ring is puckered with a torsion angle of N(1)-C(5)-C(6)-N(2) which is $15.33(5)^\circ$. The bite angle of the five-membered chelate ring, N(1)-Cu(1)-N(2) is $80.77(6)^\circ$. The primary amine nitrogen (N2) and the nitrogen atom of the pyridine (N1), respectively, located *trans* to each other. Charge neutralization is affected by the chloride anions that distanced $4.607(5)\text{ \AA}$ from the nickel atom and symmetrically disposed so that the metal atom becomes an inversion center. The chloride counter

ions are positioned in such a way to interact strongly with hydrogen atoms of the water molecules which was further linked to neighboring chloride ion extending to a 1-D supramolecular architecture along the b-axis (dotted lines in Fig. 3). The most interesting structural feature, at the supramolecular level, consists of the stacking interactions involving the pyridyl moieties of neighboring entities. The weak intramolecular π - π stacking overlap leads to infinite chains (Fig. 4). The hydrogen bonding and π - π stacking interaction are probably responsible for the low solubility of the compound in low and non-polar solvents but the strongly polar ones.

Chromotropism Study

The complex is chromotropic in solution and displays well-defined color change. The color changes are due to change in absorption maxima of the d-d transition (${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$) of nickel(II) with d^8 electron configuration in pseudo octahedral structure.

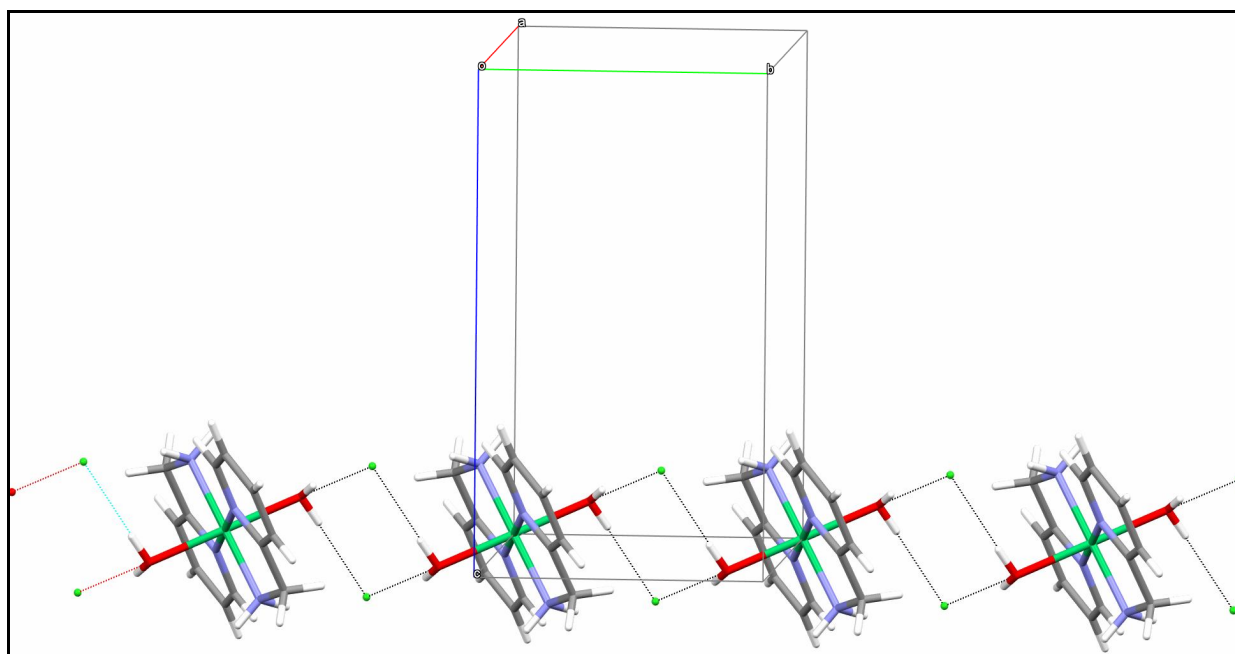
Solvatochromism

The complex is soluble in polar solvents and solvatochromic and shows a diverse color in different solvents. Its solvatochromism was investigated in methanol, ethanol, water, dimethylformamide, and dimethyl sulfoxide. The visible spectra in the above-mentioned solvents are shown in Fig. 5 and the shifts in wavelength maxima are collected in Table 4. The origin of the color change is due to the change in the d-d band of Ni(II) center. The shift in d-d band by variation of the solvent point to change in the ligand field strength around the nickel ion due to substitution of coordinated water molecules by solvent molecules as evidenced by good correlation with experimental values and donor number (DN) of solvent molecules as shown in Fig. 6. Donor number is a scale for solvent Lewis basicity [29]. In fact, solvents with donor power higher than water ($\text{DN}_{\text{H}_2\text{O}} = 18$) can be exchanged with coordinated water due to the presence of a copious number of solvent molecules in the solution. As it is clear the absorption band in near IR region do not show marked changes in different solvent ($\Delta\lambda = 9\text{ nm}$) in comparison to the d-d band in the visible region ($\Delta\lambda = 42\text{ nm}$). Since the ligand field strength is mainly changed along the z-axis by substitution of coordinated water with solvent molecules

Table 3. Selected Bond Lengths (Å) and Angles (°) for Complex $[\text{NiL}_2(\text{OH}_2)_2]\text{Cl}_2$

Bond lengths (Å)	
Ni(1)-N(1)	2.0873(14)
Ni(1)-O(1)	2.1599(12)
Ni(1)-N(2)	2.0767(14)
Bond angles (°)	
N(1)-Ni(1)-O(1)	89.02(5)
N(1)-Ni(1)-N(2)	80.77(6)
O(1)-Ni(1)-N(2)	89.40(6)
N(1)-Ni(1)-N(1)#1	180.0(3)
N(1)-Ni(1)-O(1)#1	90.98(5)
N(2)-Ni(1)-N(2)#1	180.0(3)
N(2)-Ni(1)-O(1)#1	90.60(6)
N(2)-Ni(1)-N(1)#1	99.23(6)
N(4)-Ni(1)-O(1)#1	180.00(3)

Symmetry transformations used to generate equivalent atoms: #1-x+2,-y,-z+2.

**Fig. 3.** Packing diagram of the complex with H-bonding interactions viewed down *b*-axis (dotted lines).

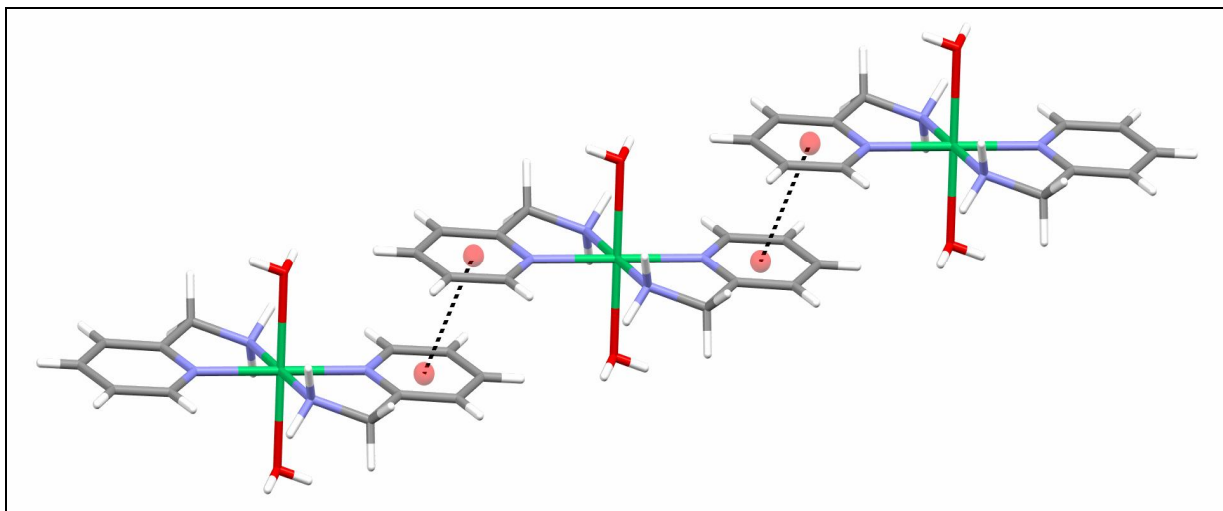


Fig. 4. Packing diagram of the compound showing the π - π stacking interactions.

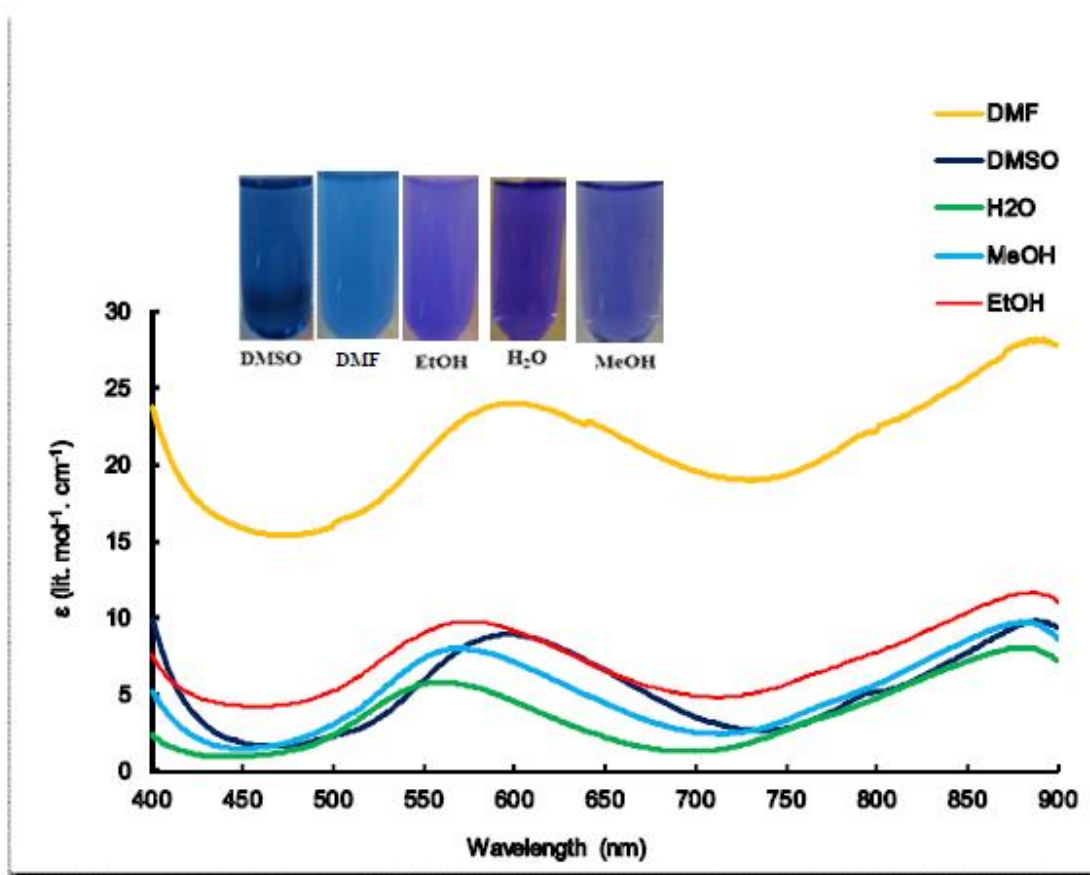


Fig. 5. Absorption spectra of the complexes in solvents used.

Table 4. The Solvent Donor Number Values and Electronic Spectra of the Compound in Selected Solvents λ_{\max} (nm) (ϵ (L cm⁻¹ mol⁻¹))

Solvent	DN ⁱ	Compound
DMSO	29.8	595 (6)
DMF	26.6	600 (24)
MeOH	19.0	570 (8)
EtOH	19.2	574 (10)
H ₂ O	18.0	558 (6)
$\Delta\lambda$ (nm)		42

ⁱThe values are taken from Ref. [29].

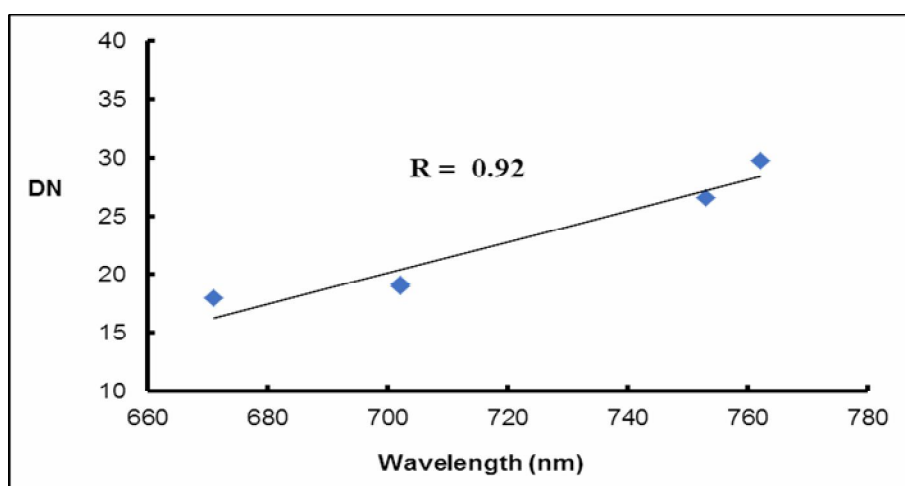


Fig. 6. Dependence of the λ_{\max} values of the complex on the solvent donor number values.

the ${}^3A_{2g} \rightarrow {}^3T_{1g}$ transition is predominantly affected.

Thermochromism

The complex is thermochromic in solid-state. So that its purple color turns to light blue at a temperature about 85 °C. This phenomenon is reversible, so that by leaving it in a humid atmosphere or addition of few drops of water its original color re-appears. The lack of the appropriate instrument hinders to track record this phenomenon.

Ionochromism

Ionochromic materials, similar to other chromic materials, the color is varied in the presence of a ions. A flow of ions through an ionochromic material results in a reaction/color change from the material. Ionochromic substances are suitable for the detection of charged particles and are utilized as pM indicators in complexometric titrations [30]. The ionochromism of the complex was taken into consideration in presence of halides (F⁻, Br⁻ and I⁻) and some pseudo-halide anions (CN⁻, NO₂⁻, OCN⁻, SCN⁻ and

N_3^-) by the visible absorption spectroscopy in buffer solution (pH = 7.0). The solution of the complex was at a concentration of 7.0×10^{-2} M. The color and pH of the original aqueous solution of the complex is purple and 7.0, respectively. Upon addition of sodium cyanide (NaCN) and sodium bromide (NaBr), the absorption spectra show evidently ionochromic behavior, so that the original purple color of the solutions changed to red and bluish-green respectively, but with the addition of the other anions, the wavelength of the maximum absorbance was not changed appreciably as shown in Fig. 7. However, upon the addition of Br^- , the absorption band of the complex at UV region tailed into the visible region while the d-d band was almost no evidently changed. Although the identity of the compound was not identified, it seems that the coordinated water molecules are replaced by bromide anion. In the case of the addition of cyanide anion, the absorption wavelength at 560 nm shifted to higher energy (blue shift) due to its high coordination power. These results revealed that the complex is high-sensitive and selective toward CN^- and Br^- . Moreover, an anion competition was also performed by mixing anions salts, NaX ($X = F^-, Br^-, I^-, CN^-, NO_2^-, OCN^-, SCN^-$ and N_3^-) (one equivalent) in buffer solution (pH = 7.0) of the complex at room temperature. The color of the mixture became red indicating that none of the anions can compete effectively with CN^- ion. In another experiment, the same competition reaction was performed by excluding cyanide ion. It was found that the color of the original purple solution turned to bluish-green within a few seconds. These results indicate that the complex is high-sensitive and selective towards CN^- and Br^- anions.

CONCLUSIONS

We have successfully synthesized the $[NiL_2(H_2O)_2]Cl_2$. The Ni(II) ion is six-coordinate in distorted octahedral coordination by two bidentate 2-picolylamine ligands and two water molecules as a trans position. Spectral assignments in solution and solid-state supported to the structure of the complex. The crystal packing of complex is a composite of intramolecular hydrogen bonding and π - π stacking interactions. The compound is chromotropic with discrete color changes. The compound display sensitivity towards cyanide and bromide anions with the obvious color

changes in aqueous solution in the presence of other halides (F^- , Br^- and I^-) and pseudo-halide anions (CN^- , NO_2^- , OCN^- , SCN^- and N_3^-). So, these anions can be detected with the naked eyes. In other words, a signal can be simply read by the naked eye without help to any spectroscopic equipment. The solvatochromism properties of the compound in polar solvents are due to dissociation of weakly bonded water molecules on the top and below of the nickel center that allows the solvent molecules with different coordination power re-coordinate to the nickel(II) ion. This phenomenon changes the ligand field around the nickel(II) center that causes the shift in the absorption wavelength of the complex. In addition, the compound is thermochromic in solid-state and shows a reversible color change from blue to green perhaps due to dehydration and hydration process. However, the lack of the appropriate instrument hinders to track record this phenomenon.

Supplementary Data

CCDC 2006284 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* 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 336033; or e-mail: deposit@ccdc.cam.ac.uk.

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