Monatsh Chem
DOI 10.1007/s00706-016-1727-5

ORIGINAL PAPER

A novel schiff base ligand and its Ni(II) complex: synthesis and characterization

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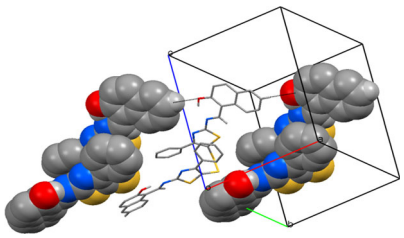
Received: 6 June 2015 / Accepted: 7 March 2016

Abstract In this paper, synthesis of a novel Schiff base ligand based on bis(2-amino-4-pheny1-5-thiazolyl)disulfide and its corresponding Ni(II) complex was reported. This ligand was prepared through the formation of an imine bond between 2-hydroxy-1-naphthaldehyde and bis(2-amino-4-phenyl-5-thiazol)disulfide in absolute methanol as solvent. The characterizations were performed by FT-IR, ^{1}H NMR, ^{13}C NMR, elemental analysis, and single crystal X-ray analysis. In the molecular structure, the ligand possessed *anti*-conformation around –S–S– bond and monomeric moieties were linked into the chains through the C–H···O and $\pi\cdots\pi$ interactions. The reaction of the synthesized ligand with $NiCl_2$ in methanol afforded the corresponding Ni(II) complex. The resulting product was further investigated by thermal gravimetric and differential thermal analysis, which confirmed the formation of desired polymeric complex. The electrochemical behavior and formation of Ni(II) complex in dimethyl sulfoxide (DMSO) solution were investigated by means of cyclic voltammetry and UV–Vis titration, respectively.

Graphical abstract



Keywords Schiff base · Thiazoline · Disulfide bond · Transition metal complex · UV/Vis spectroscopy · Cyclic voltammetry

Introduction

Schiff bases (known as azomethines), possessing a carbon–nitrogen double bond (C=N) functional group, are considered as important organic compounds. These systems play a critical role in coordination chemistry due to their ability to encapsulate metal ions using donor atoms in their backbones [1, 2]. So far, many biologically important Schiff bases possessing antibacterial, antifungal, anti-HIV, herbicidal, antitubercular, and anticancer activities have been reported in the literature [3–8]. These materials can easily coordinate with a wide range of transition metal ions, yielding stable and intensely colored metal complexes which exhibit interesting physical, chemical, biological, and catalytic properties [9–14]. Most commonly used Schiff bases have NO or N_2O_2-donor atoms. However, the oxygen atoms can be replaced by other atoms such as sulfur, nitrogen, or selenium atoms. To improve the

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Published online: 30 March 2016

medicinal properties of Schiff bases, the incorporation of thiazoline groups as chelating moieties in ligands is considered as effective models for executing important biological reactions [15].

Thiazole is a five-membered heterocycle having two hetero atoms (S, N) and one –C=N– bond. In recent years, thiazole and its derivatives have been the structural motif of many natural compounds including vitamin B1 (thiamine), penicillin, and carboxylase. Among them, 2-aminothiazole derivatives possess an antitumor activity through the inhibition of the kinases [16]. They have also been employed in the preparation of different drugs required for treatment of allergies, hypertension, inflammation, schizophrenia, bacterial and HIV infections [17]. From the chemistry point of view, the structure of 2-amino-4-phenylthiazole Schiff base derivatives has already been investigated in detail [18]. In addition, the molecular structures of two corresponding compounds, 2-amino-4-phenylthiazole hydrobromide monohydrate and 2-aminothiazole have been reported [19, 20]. Recently, some multi-substituted Schiff base-type ligands derived from 2-(2-aminothiazol-4-yl)-4-methylphenol and anisaldehyde have been developed [21]. Moreover, the complexes of Zn(II), Co(II), and Cu(II) with these ligands were synthesized and characterized. The prepared metal complexes were tested in vitro to their antibacterial activities against bacteria *E. coli*, *S. aureus*, *P. aeruginosa*, *K. pneumoniae*, and fungi *C. albicans* and *S. cerevisiae* [22]. In another study, 2-amino-4-phenyl-5-phenylazothiazole was prepared by coupling of phenyldiazonium chloride with 2-amino-4-phenylthiazole and was screened for antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* [23].

Although the biological and medicinal functions of thiazole have been widely noticed, to our knowledge, studies on substituted bi(thiazole) Schiff base systems and their related complexes have been limited. Quite recently, we found that a disulfide compound, bis(2-amino-4-phenyl-5-thiazolyl)disulfide, could be obtained and separated as a by-product during the previously reported reaction for the preparation of bis(2-amino-4-phenyl-5-thiazolyl)sulfide [24].

Here we report the synthesis and characterization of a novel Schiff base ligand prepared by the condensation reaction between this disulfide compound and 2-hydroxy-1-naphthaldehyde. The structure of the synthesized Schiff base is then investigated by single crystal X-ray analysis (Scheme 1). The Ni(II) complex of this ligand is also prepared and characterized by several analytical methods.

Results and discussion

The molecular structure together with the crystallographic numbering scheme of **2** is shown in Fig. 1, with thermal ellipsoids drawn at 50 % probability level. A summary of crystal data, experimental details, and refinement results is also given in Table 1. As shown, the molecule adopts *anti* configuration with respect to the disulfide (–S–S–) bond. The torsion angle of C14–S2–S2^{i}–C14^{i} is 63.32(19)° [symmetry code (i): $-x + 1, y, -z + 1/2$] and supports the *anti* configuration of this molecule and indicates that it is twisted around the disulfide bond.

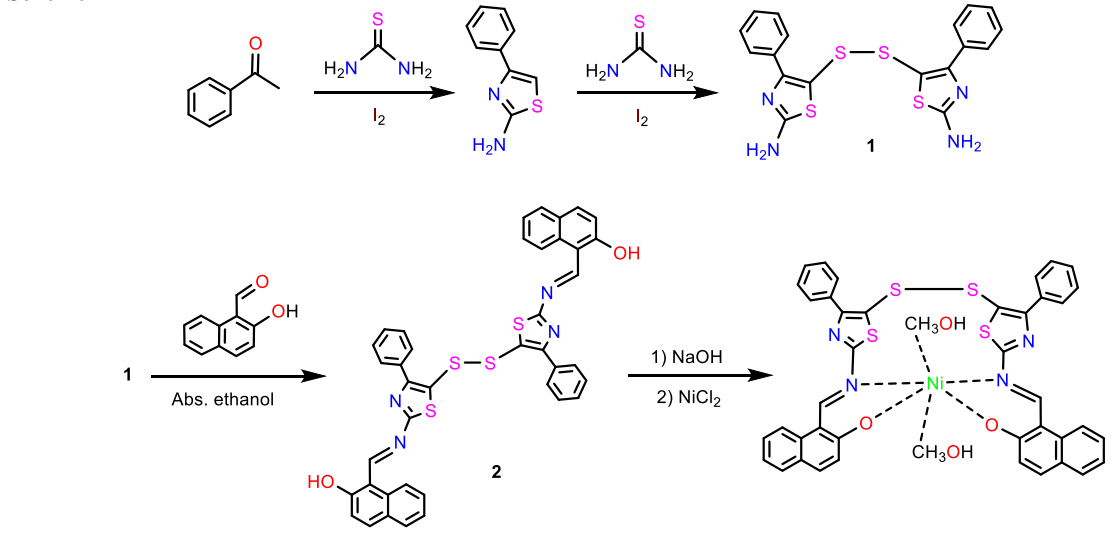
In comparison with the average S–S bond length reported for almost similar structures (2.02 ± 0.03 Å) [25–28], the S–S bonds in this present Schiff base were somewhat elongated as 2.0969(18) Å (Table 2). The dihedral angle between the planes of phenyl and naphthyl groups with thiazole ring is 32.95(16)° and 22.07(14)°, respectively. The C12–S1–C14 angle is smaller with that of 2-amino-4-phenylthiazole hydrobromide monohydrate (89.4° vs. 90.17°) [19]. The exocyclic (C11–N1 and C12–N1) and heterocyclic (C12–N2 and C13–N2) bond distances are 1.297(5), 1.370(5), 1.314(5), and 1.383(5) Å, respectively, in which an excellent agreement is observed between Fehlmann's data and those of **2** [29, 30].

It was expected that the C–N bond distances would be dissimilar as a consequence of different bond order between these atoms. The C13–C15 bond distance in **2** is 1.473(5) Å. Compared with the value of 1.506 Å found in 2-amino-4-phenylthiazole hydrobromide monohydrate, there is a greater double bond character of the C13–C15 bond in **2**. The inter-ring distance of C13–C14 is 1.389(5) Å. The internal bond angles show the characteristic reduction from 120° which is usual in five-membered heterocyclic molecules. The angle of 89.4(2)° at the sulfur atom (C12–S1–C14) is common for substituted thiazole molecules.

As shown in Table 3, the structure of **2** contains an intermolecular hydrogen bond between the hydrogen atom of the phenolic group and the nitrogen atom of imine fragment. In addition, non-classic C20–H20···S2 hydrogen bond with D···A distance of 3.330(4) Å is present. An interesting feature of this compound is the formation of a chain structure through the connection of individual molecules to each other by C3–H3···O1^{ii} [(ii): $x - 1/2, y + 1/2, z$] hydrogen bond in [11] direction (Fig. 2).

Furthermore, the symmetric π–π stacking interaction with centroid–centroid distance of 3.777(3) Å exists between parallel aromatic naphthyl rings of *Cg*1···*Cg*2 (Fig. 3); *Cg*1 and *Cg*2 are centroids for C5–C10 and C1–C5,C10 rings, respectively.

Scheme 1



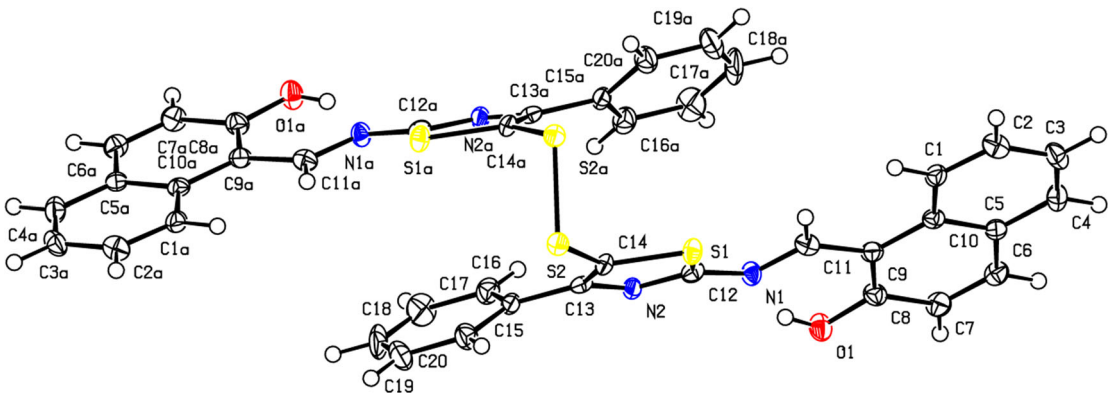


Fig. 1 The molecular structure together with the crystallographic numbering of **2**, with thermal ellipsoids drawn at 50 % probability level

FT-IR study

In the FT-IR spectrum of **1**, absorptions at 3281, 3191, and 1628 cm^{-1} suggested the presence of NH_2, CH, and C=C functionalities, respectively. The intense band at 1570 cm^{-1} is assigned to $\bar{\nu}$(C=N). Also, the bands near 3423 and 1318 cm^{-1} are assigned to $\bar{\nu}$(O–H) and $\bar{\nu}$(C–O) stretching of the phenolic group. The downfield shift of the $\bar{\nu}$(C=N) vibration (1538 cm^{-1}) suggests that the nitrogen atom of imine group participates in coordination to the Ni(II) atom. Also, the band at 1318 cm^{-1}, which is ascribed to the stretching vibration of the phenolic oxygen, undergoes a shift toward higher frequency (1362 cm^{-1}) in the Ni(II) complex spectra. The complex formation is further proved by the appearance of new bands around the absorption range 420–700 cm^{-1} due to (M–N) and (M–O) vibrations [31].

NMR study

In the ^{1}H NMR spectra of **1**, the signal at 7.05 ppm is assigned to the amino groups. The protons of the pendant phenyl ring are also observed at 7.28–7.66 ppm. Since only seven signals are observed in the ^{13}C NMR spectrum of **1**, a symmetry element is present in this molecule. In the ^{1}H NMR spectrum of **2**, the broad signal at 13.53 ppm is assigned to the proton of the OH group. The single proton of –CH=N has chemical shift at 8.79 ppm. In the ^{13}C NMR spectrum, the carbon atoms of –CH=N and C–O groups show resonances at 162.3 and 158.8 ppm, respectively. As

Table 1 Crystallographic and structure refinement data for compound **2**

Formula	$C_{40}H_{26}N_4O_2S_4$
Formula weight/g mol^{-1}	722.93
Crystal system	Monoclinic
Space group	C2/*c*
a/Å	16.136 (3)
b/Å	10.567 (2)
c/Å	20.949 (4)
β/°	111.32 (3)
Volume/Å^3	3327.5 (13)
D/g cm^{-3}	1.311
F(000)	1496
Temperature/K	120 (2)
Crystal size/mm	0.23 × 0.15 × 0.11
θ range for data collection/°	2.36–29.16
Index ranges	$-21 \le h \le 22$, $-14 \le k \le 12$, $-28 \le l \le 28$
Z	4
Wavelength/Å	0.71073
Absorption coefficient/mm^{-1}	0.33
Data collected	4482
Unique data (R_{int})	2535, 0.1298
Parameters/restraints	230/0
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0827$, $wR_2 = 0.1187$
R indices (all data)	$R_1 = 0.1609$, $wR_2 = 0.1392$
Goodness of fit on F^2 (*S*)	1.018
Largest diff. peak and hole/e Å^{-3}	0.43 and −0.36

the nickel(II) complex exhibits extremely broad ^{1}H NMR signals, hence no analysis can be performed in this regard.

VSM study

As mentioned before, elementary ^{1}H NMR study reveals that this complex should be paramagnetic. For further investigation, magnetization measurements on Ni(II) complex are performed using vibrating sample magnetometer (VSM) at room temperature. Figure 4 shows the hysteresis loop obtained from the magnetization *M* versus field *H* data for Ni(II) complex. The shape of the hysteresis loop is characteristic of superparamagnetic (weak ferromagnetic) behavior. From Fig. 4, the coercive field (Hc) and the remanent magnetization (Mr) are estimated to be only 60 Oe and 0.003 emu/g.

Thermal study

The Ni(II) complex is thermally investigated by TGA and DTA analysis and its thermal degradation is shown in Fig. 5. The decomposition process of the Ni(II) complex occurs in two steps. At the beginning, the weight loss of 8 % at 200 °C corresponds to removal of the hydrated and coordinated solvent molecules from the complex which can be supported with an exothermic peak in the thermogram. The Ni(II) complex is stable up to 200 °C and its decomposition starts after this temperature and ends at 500 °C. The loss percentage of Schiff base ligand is found as 82 % (calculated = 81 %). The process of removal of this fragment can be explained with the sharp exothermic peaks between 200 and 450 °C. By further heating above 500 °C, it decomposes to stable metal oxides as final products.

UV–Vis studies

The electronic absorption spectral bands of the Schiff base and its Ni(II) complex are recorded over the range 200–600 nm in DMSO as solvent. The electronic spectrum of the Schiff base ligand shows two absorption bands at 343 and 428 nm. The short-wave band may be attributed to electron transitions in the aromatic rings (intraligand (IL) *n*–*π**), and the longer wavelength band at 428 nm is assigned to *π*–*π** transition in the azomethine chromospheres in the Schiff base ligand [32, 33]. On complexation, the absorption band at 428 nm undergoes a bathochromic shift compared to the free ligand as a result

Table 2 Selected bond distances and angles for **2**

S2–S2^i	2.0969 (18)	C11–N1	1.297 (5)
C8–O1	1.336 (5)	C12–N1	1.370 (5)
C12–S1	1.748 (4)	C13–N2	1.383 (5)
C14–S1	1.731 (4)	C12–N2	1.314 (5)
C14–S2	1.733 (4)	C13–C14	1.383 (5)
		C13–C15	1.471 (5)
C11–N1–C12	120.0 (3)	S1–C14–S2	119.9 (2)
C13–C14–S2	129.8 (3)	S2^i–C14–S2	100.83 (12)
C12–S1–C14	89.4 (2)	C14– S2–S2^i–C14^i	63.32 (19)

Symmetry code (i): $-x+1, y, -z+1/2$

Table 3 Selected hydrogen bonding geometries for **2**

D–H···A	d(D–H)/Å	d(H···A)/Å	d(D···A)/Å	<(D–H····A)/°
O1–H1A···N1	0.86	1.76	2.538 (4)	150
C3–H3···O1^{ii}	0.95	2.53	3.386 (5)	149
C20–H20···S2	0.95	2.79	3.330 (4)	117

Symmetry code (ii): $x - 1/2, y + 1/2, z$

of coordination via the nitrogen atoms of the azomethine groups. The Ni(II) complex displays absorption bands at 330 nm and 474 nm, respectively.

Solution studies

In this study, we also represent further support for the polymeric character of Ni(II) complex. It is important to note that the method used in this research has some advantages over the Jobs analysis. In fact, a limited number of samples (10 samples for instance) with different volume ratios should be prepared in Jobs analysis. However, in the UV–Vis titration desired amount of metal (5×10^{-3} mol dm^{-3}) is added to the ligand solution

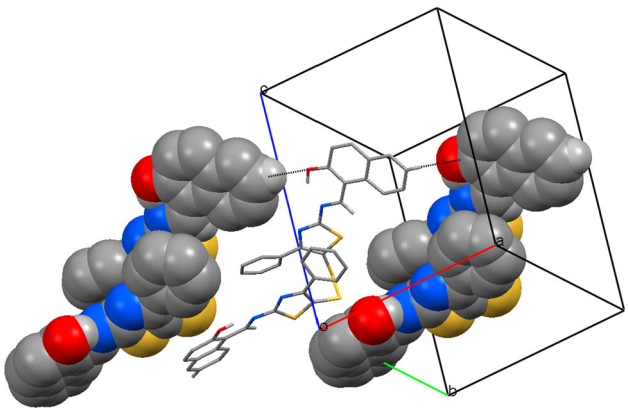


Fig. 2 The individual molecules of **2** are connected to each other by C3–H3···O1^{ii} (symmetry code (ii): $x - 1/2, y + 1/2, z$) hydrogen bond in [11] direction, forming a chain structure. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity

(5.0×10^{-5} mol dm^{-3}) in one cell and then this addition continues up to 40 times. The absorbance spectrum of the mixture is recorded after each addition. Therefore, the numbers of obtained points are higher in this method and the accuracy would definitely be better. Performing all additions in one UV–Vis quartz cell compared to using ten cells in Jobs analysis is another advantage of the method utilized in this present study.

In a typical procedure, 2.0 cm^3 of ligand solution in methanol is placed in the spectrophotometer cell and the absorbance of the solution is measured. Then an appropriate amount of the concentrated solution of $NiCl_2$ in methanol is added in a stepwise manner using a 10-mm^3 Hamilton syringe. The absorbance spectrum of the solution is recorded after each addition. The Ni(II) solution was continually added until the desired metal to ligand mole ratio was achieved. The electronic absorption spectra of the Schiff base ligand **2** in the presence of increasing concentration of $NiCl_2$ in MeOH at room temperature are shown in Fig. 6. The resulting absorbance against [HL]/[Ni^{2+}] mole ratio plot is shown in the inset of Fig. 6. As mentioned, the injection point at ligand-to-metal molar ratio of about ten indicates the formation of polymeric compound [34]. It seems that these compounds have different behavior in the solid state and in solution.

Electrochemical studies

Electrochemical experiments are performed with a μAUTOLAB TYPE III electrochemical workstation (ECO CHEMIE, the Netherlands). A standard three-electrode cell is used for the electrochemical experiments and a 2-mm-

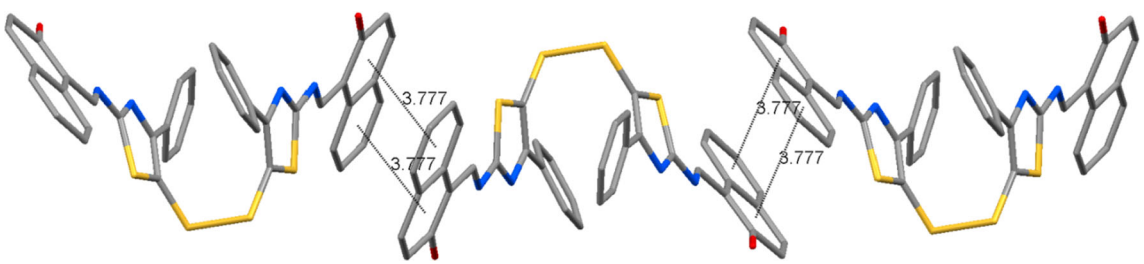


Fig. 3 π–π stacking interaction with face-to-face distance of 3.776(3) Å between parallel aromatic naphthyl rings

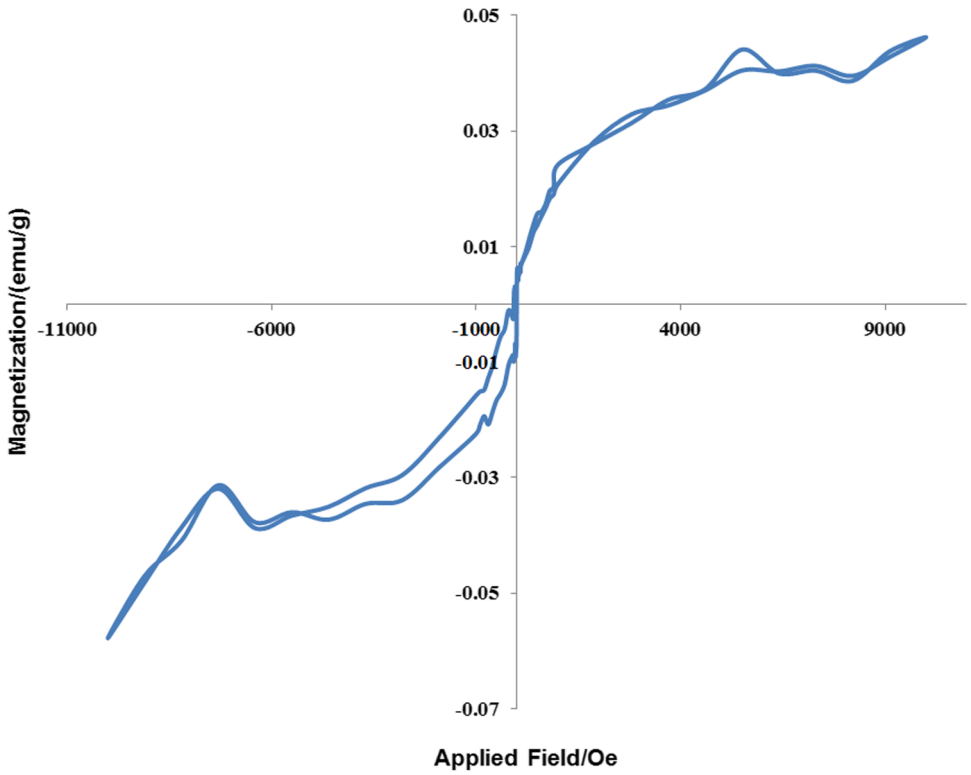


Fig. 4 Magnetization versus applied magnetic field at room temperature and hysteresis loop of Ni(II) complex

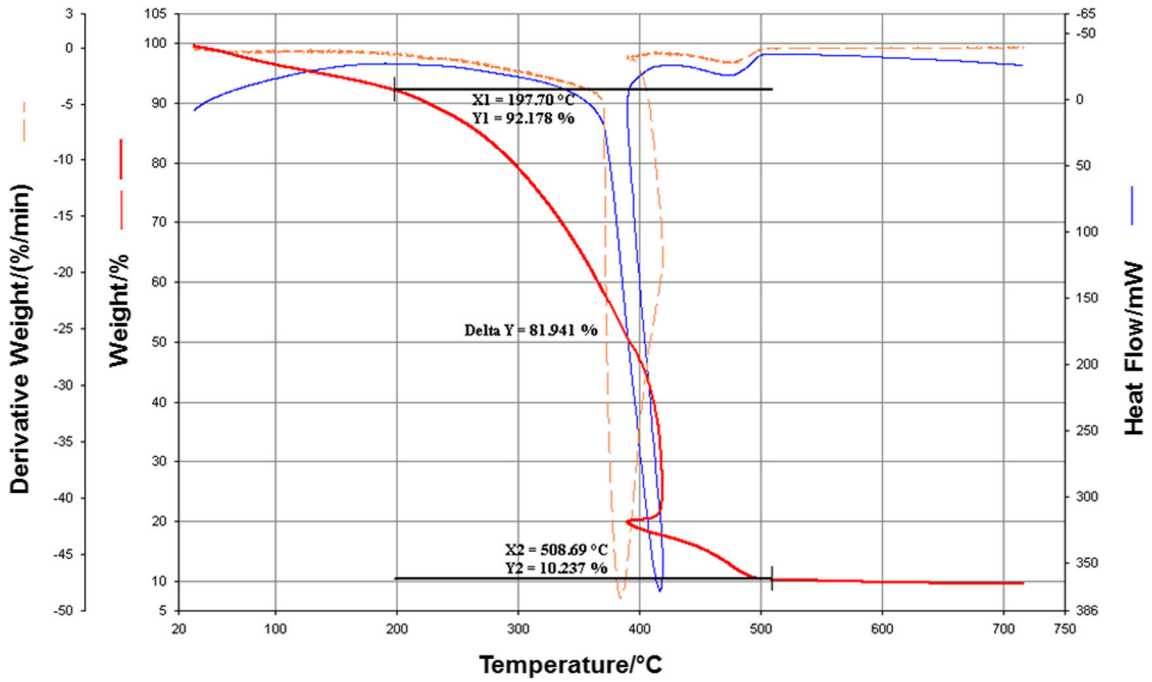


Fig. 5 The TGA and DTA analysis and decomposition process of the Ni(II)

diameter GC is utilized as the working electrode. A silver/silver chloride (Ag/AgCl) electrode and a platinum electrode are also used as the reference and the counter electrodes, respectively.

The measurements are carried out in a dimethyl sulfoxide and 0.1 mol dm^{-3} tetrabutylammonium perchlorate as a supporting electrolyte at room temperature. Figure 7 represents the cyclic voltammetry curve of the synthesized

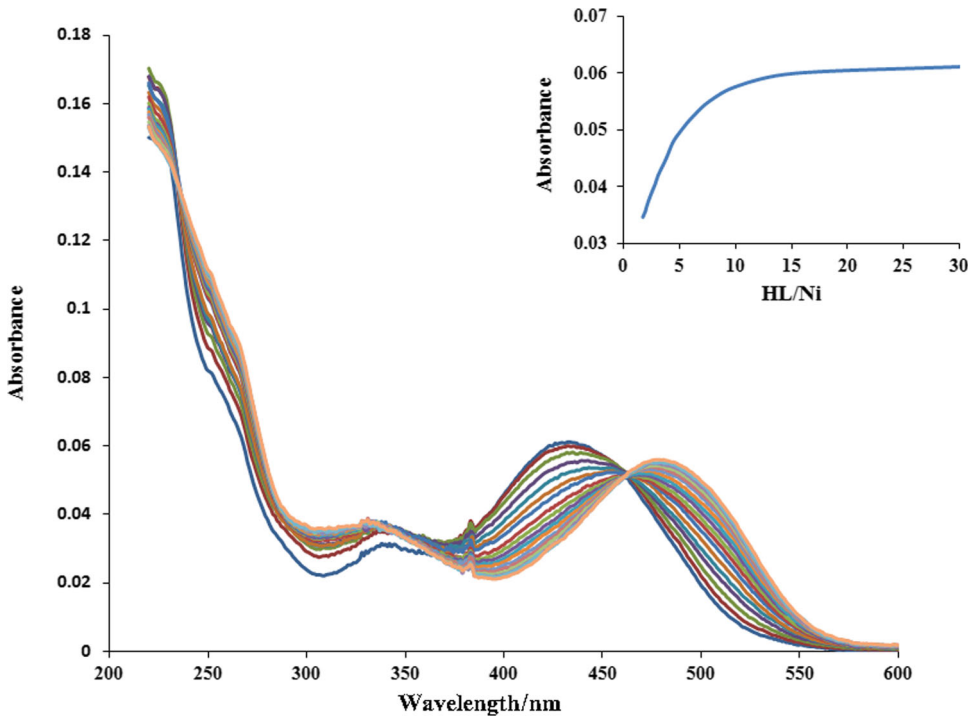


Fig. 6 **a** Electronic absorption spectra of the ligand **2** in MeOH in the presence of increasing concentration of $NiCl_2$ at room temperature. **b** Corresponding mole ratio plot of HL/Ni^{II}

Schiff base (curve T1). As shown, a pair of redox peak attributes to the phenolic moiety in which the anodic peak appears at 0.06 V and cathodic peak appears at −0.35 V vs. Ag/AgCl. Moreover, one total irreversible cathodic peak appears at −0.82 V which can be arisen from the reduction of sulfur moiety. The cyclic voltammetry curve of the Ni(II) complex is also recorded and shown in Fig. 7 (curve T2). It seems that this complex has the same feature of the free ligand and is not an electro-active solid.

Conclusion

In summary, a novel Schiff base ligand based on bis(2-amino-4-phenyl-5-thiazolyl)disulfide was synthesized and fully characterized including X-ray crystallography. Non-covalent forces such as C–H···O hydrogen bonding and π···π interactions in **2** connect the monomeric moieties into chains and help to stabilize the constructed framework. The Ni(II) complex of this ligand was prepared and the obtained product was further investigated by TG and DT analysis. Finally, in this study, UV–Vis data support a square planar Ni(II) ion, while paramagnetism (from NMR and VSM study) suggests octahedral geometry for a d^8 configuration. Therefore, it seems that the actual structure of the Ni(II) complex is ambiguous. We suppose that the structure might have a highly distorted octahedral geometry with two elongated bonds of coordinated solvent molecules, hence approaching a square planar environment.

Experimental

All chemicals were purchased from Merck and used without further purification. The required starting material, 4-phenylthiazol-2-amine, was prepared from acetophenone, iodine, and thiourea following the procedure developed by Dodson and King [24].

FT-IR spectra were recorded in the frequency range of 4000–400 cm^{-1} using Perkin-Elmer RXI spectrometer using KBr disks at room temperature. Elemental analysis was carried out using a Perkin-Elmer 2400(II) CHNS/O analyzer. ^1H NMR and ^{13}C NMR spectra were recorded with Bruker Avance 300 spectrometer using DMSO-d_6 as solvent. UV–Vis spectra were recorded with a Perkin-Elmer Lambda 25 spectrophotometer, using two matched 10-mm quartz cells. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out with a STA-1500 Instrument at a heating rate of 10 °C/min in air.

5,5′-Disulfanediylbis(4-phenylthiazol-2-amine) (**1**, $C_{18}H_{14}N_4S_4$)

2-Amino-4-phenylthiazole (3.6 g) and 1.52 g of thiourea were dissolved in 50 cm^3 mixture of warm ethanol and distilled water. Iodine (7.6 g) was then added slowly to this solution with occasional stirring. After the addition was completed, the resultant red-brown mixture was refluxed for 3 h and then poured into cooled distilled water. The mixture was extracted with CH_2Cl_2 (3 × 50 cm^3). The

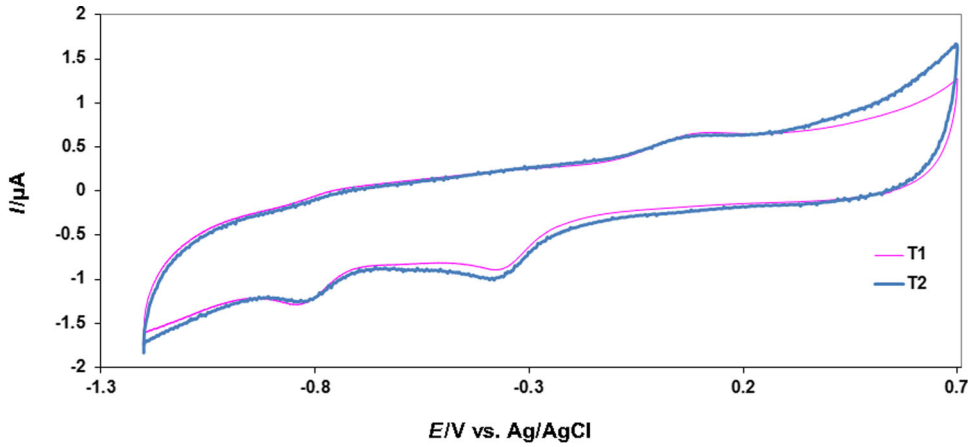


Fig. 7 The cyclic voltammetry curve of the synthesized Schiff base ligand (*T1 curve*) and its Ni(II) complex (*T2 curve*)

filtrate was concentrated and the crude product purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane, 2/3 v/v). The first and major fraction was then made alkaline with sodium hydroxide solution and was identified as bis(2-amino-4-phenyl-5-thiazolyl)sulfide. The second fraction containing the desired bis(2-amino-4-phenyl-5-thiazolyl)disulfide was then made alkaline with sodium hydroxide solution. A yellow precipitate was formed which further crystallized from water/acetic acid (3:1) to give **1** as a yellow solid. M.p.: 180–182 °C; FT-IR (KBr): $\bar{\nu}$ = 3281(m), 3191(m), 2425(br), 1682(s), 1628(s), 1515(s), 1471(s), 1438(w), 1355(m), 1277(s), 771(s), 690(s) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 7.05 (2H, NH_2), 7.28–7.66 (5H, aromatic) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 109.9, 128.4, 128.8, 129.8, 134.7, 159.4, 171.9 ppm.

1,1′-[(1E,1′E)-[[5,5′-Disulfanediylbis(4-phenylthiazole-5,2-diyl)]bis(azanylylidene)]bis(methanylylidene)]-bis(naphthalen-2-ol) (**2**, $C_{40}H_{26}N_4O_2S_4$)
To a stirred solution of 0.35 g 2-hydroxy-1-naphthaldehyde (2 mmol) in 25 cm^3 absolute methanol, 0.4 g bis(2-amino-4-phenyl-5-thiazolyl)disulfide (1 mmol) in methanol was added in presence of 2–3 drops of glacial acetic acid. After the addition, the prepared solution was refluxed overnight. Difficulties resulting from the poor chemical reactivity of the starting materials were overcome with azeotropical removal of water by a Dean-Stark trap. The obtained orange precipitation was filtered, washed with methanol and dried in vacuum. The orange plate-like crystals of the compound suitable for X-ray analysis were obtained by slow evaporation of the solvent (DMSO) within several weeks. M.p.: 240–242 °C; FT-IR (KBr): $\bar{\nu}$ = 3423(br), 1620(s), 1601(s), 1570(s), 1480(s), 1444(s), 1318(s), 1186(s), 8229 s), 775(s), 752(m), 695(s) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 8.79 (1H, N=CH), 7.21–8.13 (11H, aromatic), 13.53 (1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 109.7, 119.2, 122.0, 124.4, 127.7, 127.9, 128.5, 128.9, 129.2, 129.3, 132.3, 132.9, 137.9, 158.8, 162.3 ppm; UV–Vis (DMSO, $c = 2.10^{-5}$ mol dm^{-3}): λ_{max} = 428, 343 nm.

1,1′-[(1E,1′E)-[[5,5′-Disulfanediylbis(4-phenylthiazole-5,2-diyl)]bis(azanylylidene)]bis(methanylylidene)]-bis(naphthalen-2-olate)-dimethanol-nickel(II)
($C_{15}H_{15}N_3NiO_2$)
A solution of 0.1 g NaOH (2 mmol) in 5 cm^3 MeOH was added to a suspension of 0.7 g Schiff base (1 mmol) in absolute methanol to obtain a clear solution. To this solution, $NiCl_2$ salt was slowly added in absolute methanol. Subsequently, the reflux was continued overnight. The black precipitates were obtained from the reaction mixture. At the end, the precipitates were filtered and washed several times with methanol and then dried in vacuum. Regardless of testing several methods, our attempts to get suitable crystals for X-ray analysis were unsuccessful. FT-IR (KBr): $\bar{\nu}$ = 3338(br), 1618(s), 1576(s), 1538(s), 1477(m), 1362(s), 833(s), 771(s), 695(s), 456(w) cm^{-1}; UV–Vis (DMSO, $c = 2.10^{-3}$ mol dm^{-3}): λ_{max} = 474, 330 nm.

Crystal structure determination and refinement

The X-ray diffraction measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Cell constants and orientation matrices for data collection were obtained by least-squares refinement of diffraction data from 2535 unique reflections for **2**. Data were collected to a maximum 2θ value of 29.16° for **2** in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [35] software package. A numerical absorption correction was applied using X-RED [36] and X-SHAPE [37] software. The data were corrected for Lorentz and Polarizing effects. The

structures were solved by direct methods [38] and subsequent difference Fourier maps and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [39]. The atomic factors were taken from the International Tables for X-ray Crystallography [40]. All refinements were performed using the X-STEP32 crystallographic software package [41].

CCDC number of 1059282 contains the supplementary crystallographic data for compound **2**. These 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. Holm RH, Everett GW, Chakravorty A (1966) Prog Inorg Chem 7:83
2. Mehta BH, More PS (2007) Asian J Chem 19:4719
3. Sakiyan I, Logoglu E, Arslan S, Sari N, Sakiyan N (2004) Biometals 17:115
4. Pandeya SN, Sriram D, Nath G, DeClecq E (1999) Eur J Pharm Sci 9:25
5. Chen H, Rhodes J (1996) J Mol Med 74:497
6. Molla BS, Rao BS, Shridhara K, Akberali PM (2000) Farmaco 55:338
7. Islam MR, Mirza AH, Huda QMN, Khan BR (1989) J Bang Chem Soc 2:87
8. Ali MM, Jesmin M, Sarkar MK, Salahuddin MS, Habib MR, Khanam JA (2008) Int J Biol Chem Sci 2:292
9. You ZL, Zhu HL, Liu WS (2004) Z Anorg Allg Chem 630:1617
10. You ZL, Zhu HL (2004) Z Anorg Allg Chem 630:2754
11. Abu-Raqabah A, Davies G, El-Sayed MA, El-Toukhy A, Shaikh SN, Zubieta J (1992) Inorg Chim Acta 193:43
12. Mukherjee P, Drew MGB, Figuerola A, Ghosh A (2008) Polyhedron 27:3343
13. Yilmaz I, Temel H, Alp H (2008) Polyhedron 27:125
14. Temel H, Alp H, Ilhan S, Ziyadanogullari B (2008) J Coord Chem 61:1146
15. Khandar AA, Hosseini-Yazdi SA, Zarei SA, Rabie UM (2005) Inorg Chim Acta 358:3211
16. Minghua L, Seung WK, Yoojin S (2010) Bull Korean Chem Soc 31:1463
17. Tsuji K, Ishikawa H (1994) Bioorg Med Chem Lett 4:1601
18. Sadigova SE, Magerramov AM, Allakhverdiev MA, Alieva RA, Chyragov FM, Vekilova TM (2003) Russ J Gen Chem 73:1932
19. Form GR, Raper ES, Downie TC (1974) Acta Crystallogr B 30:342
20. Caroni C, Capella L (1982) J Appl Crystallogr 15:106
21. Woodbridge RG, Dougherty G (1949) J Am Chem Soc 71:1744
22. Ghatole AM, Lanjewar KR, Gaidhane MK (2014) Int J Pharm Pharm Sci 6:142
23. Prajapati AK, Modi VP (2010) J Chil Chem Soc 55:240
24. Dodson RM, Carroll King L (1945) J Am Chem Soc 67:2242
25. Wang D, Behrens A, Farahbakhsh M, Gatjens J, Rehder D (2003) Chem Eur J 9:1805
26. Spek AL (2003) J Appl Crystallogr 36:7
27. Okamatsu T, Irie R, Katsuki T (2007) J Organomet Chem 692:645
28. Schroth W, Hintzsche E, Jordan H, Jende T, Spitzner R, Thondorf I (1997) Tetrahedron 53:7509
29. Fehlmann M (1970) Acta Crystallogr B 26:1736
30. Rofouei MK, Fereyduni E, Sohrabi N, Shamsipur M, Attar Gharamaleki J, Sundaraganesan N (2011) Spectrochim Acta A 78:88
31. Ferraro JR (1971) Low Frequency Vibrations of Inorganic and Coordination Compounds, 2nd edn. John Wiley, New York
32. Ramesh R, Maheswaran SJ (2003) J Inorg Biochem 96:457
33. Ahmed IS, Kassem MA (2010) Spectrochim Acta A 77:359
34. Nandini R, Vishalakshi B (2010) Spectrochim Acta A 75:14
35. Stoe & Cie (2005) X–AREA: Program for the Acquisition and Analysis of Data, Version 1.30. Stoe & Cie GmbH, Darmstadt, Germany
36. Stoe & Cie (2005) X-RED: Program for Data Reduction and Absorption Correction. Stoe & Cie GmbH, Darmstadt, Germany
37. Stoe & Cie (2004) X–SHAPE: Program for Numerical Absorption Correction, Version 2.05. Stoe & Cie GmbH, Darmstadt, Germany
38. Sheldrick GM (1997) SHELX97. University of Göttingen, Germany, Program for Crystal Structure Solution
39. Sheldrick GM (1997) SHELX97. University of Göttingen, Germany, Program for Crystal Structure Refinement
40. International Tables for X-ray Crystallography, vol C (1995) Kluwer Academic Publisher. The Netherlands, Dordrecht
41. Stoe & Cie (2000) X-STEP32: Crystallographic Package, Version 1.07b. Stoe & Cie GmbH, Darmstadt, Germany