



Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Ni(II)-tetrahedral complexes: Characterization, antimicrobial properties, theoretical studies and a new family of charge-transfer transitions

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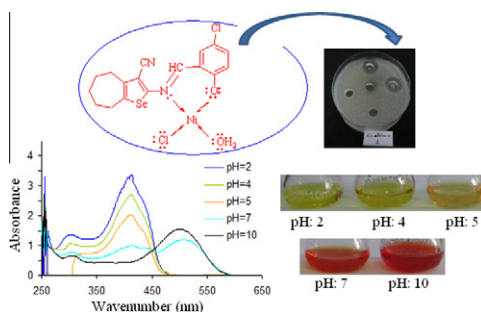
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HIGHLIGHTS

- ▶ Novel Ni(II)-tetrahedral complex with selenium ligand has been synthesized by means of template method and characterized.
- ▶ [Ni(SeSchCl)(H₂O)Cl] complex shows different properties of synthesized Ni(II) complexes.
- ▶ This complex changes color from yellow to orange in the range pH 5–7.
- ▶ [Ni(SeSchCl)(H₂O)Cl] complex is more potent bactericides than all of the substances synthesized.

GRAPHICAL ABSTRACT

Five new Schiff bases involving Selenium [(SeSchX)(X: -H, F, Cl, Br, CH₃)] and Ni(II) complexes ([Ni(SeSchX)(H₂O)₂]Cl/[Ni(SeSchCl)(H₂O)Cl]) are synthesized and characterized. [Ni(SeSchCl)(H₂O)Cl] complex exhibits metal-centered color-changing in between pH 5–7 and is a more potent bactericide than other complexes.



ARTICLE INFO

Article history:

Received 25 September 2012

Received in revised form 14 December 2012

Accepted 17 December 2012

Available online 4 January 2013

Keywords:

Charge-transfer transitions
Cyclic seven-membered ring
DFT
Amine containing selenium
Antimicrobial properties

ABSTRACT

A new amine containing selenium and their five imine, (SeSchX)(X: -H, F, Cl, Br, CH₃), and Ni(II) complexes, [Ni(SeSchX)(H₂O)₂]Cl/[Ni(SeSchCl)(H₂O)Cl], were synthesized. The compounds were characterized by means of elemental analyses, ¹³C and ¹H NMR (for imine), FT-IR, UV-Visible spectroscopy, TGA/DTA and elemental analyses. [Ni(SeSchCl)(H₂O)Cl] complex from Ni(II) complexes changes color from yellow to orange in the range pH 5–7. [Ni(SeSchCl)(H₂O)Cl] complex has ligand-to-metal charge-transfer (LMCT) transitions in the basic medium. Excitation characteristics and energetic of [Ni(SeSchCl)(H₂O)Cl] complex, examined via TD-DFT calculations, reveals transitions of LMCT and $\pi \rightarrow \pi^*$ character that matches the experimental values. [Ni(SeSchCl)(H₂O)Cl] complex showed the highest antibacterial activity when compared to other complexes reported in this work.

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Introduction

The coordination chemistry of transition metal complexes with azomethine ligands has been widely studied, partly due to the use of such compounds as antibacterial drugs in the field of medicine [1]. In particular, titanium (IV), platinum (II) and silver (I) complexes have been used in the treatment of numerous diseases [2–

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4]. Researchers have become increasingly interested in the coordination chemistry of nickel complexes as models for the active sites in nickel containing enzymes [5]. Nickel (II)-azomethine complexes have attracted attention in recent years due to their well-defined spectroscopic, photochemical and electrochemical properties [6–8]. Complexes of Nickel (II) can be prepared in various conformational structures, each having an extensive number of examples. This is probably the reason whereby Ni(II) is one of the most spectroscopically studied metal ions.

Molecules involving selenium are still efficient and encouraged in medicinal chemistry due to the structural features are retained and softer atom which can be served as hydrogen-bond acceptor or electron donor [9]. Selenium compounds were found playing important roles in protecting the heart, preventing cancer and cardiovascular diseases [10]. Because selenium functions as an antioxidant works in conjunction with vitamin E [11]. Selenium containing compounds have gained attention as potential antioxidants for preventing some metal ions mediated oxidative damage. Therefore, systematic investigation of molecules containing selenium is very important for bioinorganic area [12]. So, it would be interesting to investigate the structural and antimicrobial properties of complexes including selenium and Nickel (II) ion.

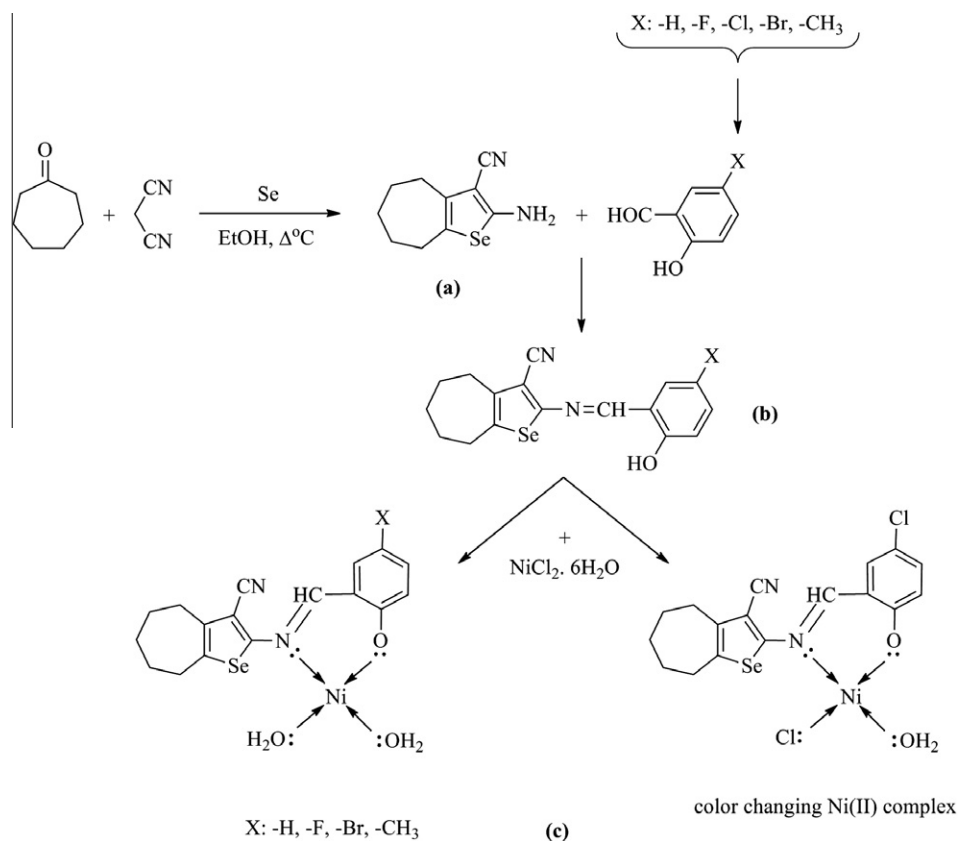
Here we report the synthesis, characterization, antimicrobial properties of new azomethine (Schiff bases) and their Ni (II) complexes (Scheme 1). Motivated by the presence of heterocyclic seven-membered rings in numerous biologically active natural products and pharmaceuticals (such as tuberostemonine), a new amine 2-Amino-5,6,7,8-tetrahydro-4H-cyclohepta[b]selenophene-3-carbonitrile (**1**) was synthesized using the Gewald methods [13,14]. Then, its five Schiff bases (**2**) prepared from the reaction of 2-aminocycloheptaselenophene-3-carbonitrile and salicylaldehyde derivatives and their Ni (II) complexes (**3**) were synthesized by means of condensation and template method, respectively.

[Ni(Se-SchCl)(H₂O)Cl] complex showed different property than other Ni (II) complexes. This complex was observed color change depends on pH. Ligands or complexes that change color have attracted a great deal of interest because of their useful photochemical properties and potential applications in many fields, such as chemosensors [15], photocatalysts and light-emitting diodes (LEDs) [16]. In this study, [Ni(Se-SchCl)(H₂O)Cl] complex showed change color in different pH unlike from other synthesized Ni(II)-tetrahedral complexes. So, we decided to study electronic spectra of [Ni(Se-SchCl)(H₂O)Cl] complex. Furthermore calculated spin densities the triplet ground states for all Ni (II) complexes bear two unpaired electrons residing in Ni d-based orbital.

Experimental section

Materials and physical measurements

All chemicals used in the study were reagent grade and were purified when it was necessary. The aldehydes (salicylaldehyde, 5-fluorosalicylaldehyde, 3-chloro-5-fluorosalicylaldehyde, 3-bromo-5-fluorosalicylaldehyde and 5-fluoro-3-methylsalicylaldehyde), cycloheptanone, selenium and morpholine were purchased from Sigma–Aldrich. Elemental analyses were performed with a LECO-CHNS-9320 instrument. Metal contents were determined by using a Philips PU 9285 atomic absorption instrument. ¹H and ¹³C NMR spectra were recorded with a Bruker DPX-300 MHz and 100 MHz using TMS as an internal standard and CDCl₃ as solvent. Electronic spectra were recorded on a UV-1800 ENG240V spectrophotometer in ethanol. IR spectra were recorded on a Mattson-5000 FTIR instrument in KBr pellets. Melting points were determined with a Barnstead-Electrothermal-9200 melting point apparatus. The molar conductivities were measured with an inoLab Cond 730 conductivity meter (10⁻³ mol L⁻¹ in DMF solution). The



Scheme 1. The Synthetic route of Ni(II) complexes.

TGA curves were obtained on General V4.1C Du Pont 2000 between 30 and 900 °C at a heating rate of 10 °C min⁻¹ in nitrogen atmosphere. Magnetic measurements were performed with a Sherwood Scientific magnetic susceptibility balance (Model No: MK 1) at 21 °C with Hg[Co(NCS)₄] as a calibra.

Synthesis

Synthesis of 2-amino-5,6,7,8-tetrahydro-4H-cyclohepta[b]selenophene-3-carbonitrile, (1), [Se-NH₂]

2-Aminoselenophene-3-carbonitrile (1) was prepared according to the procedure described by Gewald [14,17]. To the stirred solution of 5.61 g (0.05 mol) cycloheptanone, 3.30 g (0.05 mol) malononitrile, and 3.95 g (0.05 mol) of selenium in 50 ml anhydrous ethanol, 4.36 g (0.05 mol) of morpholine was added drop wise at room temperature. Then the reaction was refluxed for 48 h. After the reaction mixture was poured into the ice-water. The resulting solid was collected and recrystallized from ethanol (m.p.: 125–127 °C, 71% yield).

Synthesis of imine compounds: general procedure, (2), ([Se-SchH], [Se-SchF], [Se-SchCl], [Se-SchBr], [Se-SchCH₃])

A mixture of aldehyde (0.443 g, 0.308 g, 0.344 g, 0.442 g, 0.268 g, 0.022 mol, respectively, salicylaldehyde, 5-fluorosalicylaldehyde, 3-chloro-5-fluorosalicylaldehyde, 3-bromo-5-fluorosalicylaldehyde and 5-fluoro-3-methylsalicylaldehyde) and 2-Aminoselenophene-3-carbonitrile compound (0.536 g of [Se-NH₂], 0.022 mol) in 20 ml of ethanol was refluxed for 2 h and then cooled at room temperature. The precipitated solid was collected, washed with cold ethanol, and recrystallized from ethanol. All imine compounds were prepared by using the same procedure.

Template method for Ni (II) complexes, (3)

Ni (II) complexes were prepared by following a general method: A solution of 1 (0.119 g, 5 × 10⁻⁴ mol) and aldehyde (0.061 g, 0.070 g, 0.078 g, 0.100 g, 0.068 g, 5 × 10⁻⁴ mol; respectively, salicylaldehyde, 5-fluorosalicylaldehyde, 3-chloro-5-fluorosalicylaldehyde, 3-bromo-5-fluorosalicylaldehyde and 5-fluoro-3-methylsalicylaldehyde) are dissolved in 1,1',2,2'-tetrachloro-ethane (25 mL). The solution refluxed for 2 h. The solution was stirred magnetically and heated NiCl₂·6H₂O (0.12 g, 5 × 10⁻⁴ mol) dissolved in methanol (5 mL) was added dropwise to the solution of the amine-aldehyde mixture. The reaction mixture was, after refluxing for 2 h, concentrated through evaporation until half of the volume [18]. After keeping it another 2 days, the solid complexes formed were collected by filtration and then dried in a desiccator over CaCl₂.

Detection of antimicrobial activity

The bacterial subcultures chosen were *Listeria monocytogenes* 4b ATCC19115, *Staphylococcus aureus* ATCC25923, *Escherichia coli* ATCC1280, *Salmonella typhi* H NCTC-901.8394, *Brucella abortus* (A.99, UK-1995) RSKK03026, *Staphylococcus epidermis* sp., *Micrococcus luteus* ATCC9341, *Shigella dysenteria* type 10 NCTC 9351, *Pseudomonas putida* sp., *Bacillus cereus* RSKK-863. An antifungal susceptibility test was used by *Candida albicans* Y-1200-NIH, Tokyo. The ligands and the complexes were tested for their antimicrobial activity by the well-diffusion method. Each ligand and complex were kept dry at room temperature and dissolved (0.25 µg/mL) in DMF. DMF was used as solvent and also for control. It was found to have no antimicrobial activity against any of the tested organisms. 1% (v/v) of 24 h broth culture containing 10⁶ CFU/mL was placed in sterile Petri dishes. Mueller- Hinton Agar (MHA) (15 mL) kept at 45 °C was then poured into the Petri dishes and allowed to solidify. Then 6 mm diameter wells were punched carefully by using a sterile cork borer and were entirely filled with

the test solutions. The plates were incubated for 24 h at 37 °C. On completion of the incubation period, the mean value obtained from the two holes was used to calculate the zone of growth inhibition of each sample. Bacterial subcultures and fungus were tested for resistance to five antibiotics (produced by Oxoid Ltd., Basingstoke, UK): ampicillin (preventing the growth of gram-negative bacteria), nystatin (binding to sterols in the fungal cellular membrane, altering the permeability and allowing leakage of the cellular contents), kanamycin (used in molecular biology as agent to isolate bacteria), sulphamethoxazol (bacteriostatic antibacterial agent that interferes with folic acid synthesis in susceptible bacteria), amoxycillin (β-lactam antibiotic used to treat bacterial infections caused by susceptible microorganisms).

Studies of spectroscopy under different pH for [Ni(Se-SchCl)(H₂O)Cl]

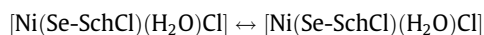
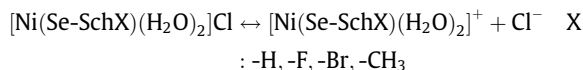
[Ni(Se-SchCl)(H₂O)Cl] complex was dissolved in DMF (10 mL, 1 × 10⁻³ M) at room temperature. Buffer solution pH 10, 7, 5, 4 and 0.01 M standard HCl solution were purchased from Sigma-Aldrich. Buffers dissolved in water (1 mL) were added dropwise to the solution of 1 × 10⁻³ M [Ni(Se-SchCl)(H₂O)Cl] complex. It was then stirred and color was obtained as follows (Fig. 1).

Computational method

UB3LYP/LANLNDZ level of theory is employed throughout all calculations. Geometries of all species are fully optimized and confirmed for having no imaginary frequencies, thus verifying the authenticity of global minima. TD-DFT calculations utilize the polarizable continuum model (PCM). A dielectric medium of ε = 36.6 is used, instead of the experimental DMF (ε = 38.3). Complexes VII-X are experimentally observed whereas IX' is modeled to provide insight on suggested MLCl(OH₂) structure instead of ML(OH₂)₂. All calculations were performed using Gaussian 03 program suite [19].

Results and discussion

Analytical data and some of the physical properties of the Schiff bases and their complexes are summarized in Table 1. The complexes are only soluble in DMF and DMSO, but insoluble in organic solvents like C₂H₅OH, CCl₄ and benzene. The molar conductance values of the four Ni (II) complexes are found to be 12.97–14.79 µS/cm in 10⁻³ M DMF solutions were indicated the 1:1 electrolytic nature of the compounds [18]. [Ni(Se-SchCl)(H₂O)Cl] complex were nonelectrolytic.



IR, UV-Visible and NMR spectra of ligands

Table 2 summarizes the main IR and UV-Visible bands of the azomethine (Schiff bases) and their Ni(II) complexes. 2-Aminoselenophene-3-carbonitrile ([Se-NH₂]) spectra show three medium broad band in the region 3228–3433 cm⁻¹ and another band at 2197 cm⁻¹, assigned to the νNH₂ and νCN groups, respectively [20]. The IR showed the disappearance of the NH₂ bands together with the presence of CH=N band. IR bands of azomethines in the 1553–1567 cm⁻¹, 3387–3467 cm⁻¹, 2197–2225/1601–1651 cm⁻¹ regions are characteristic of ν(CH=N), ν(OH), and ν(CN)/ν(Se-C), respectively [18,20]. The bands in the 2857–2917 cm⁻¹ and 3058–2979 cm⁻¹ regions may, respectively, ascribe to νCH_{aliphatic}

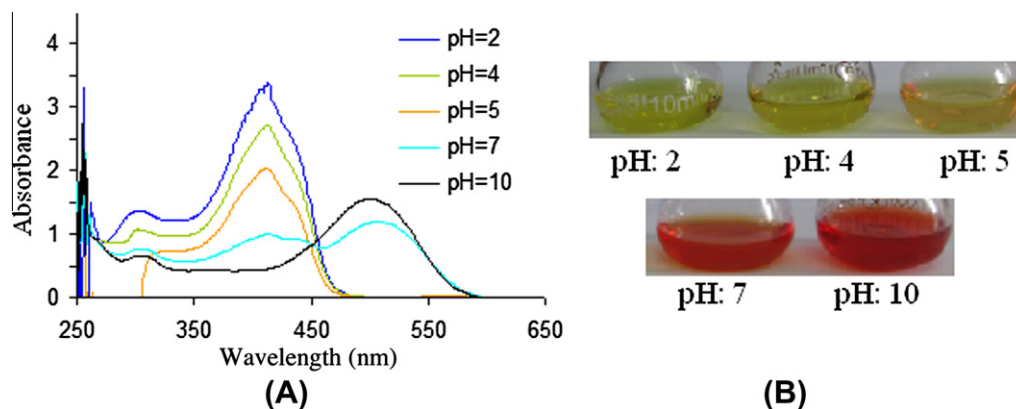


Fig. 1. UV-Visible spectra and color change imaging of $[\text{Ni}(\text{Se-SchCl})(\text{H}_2\text{O})\text{Cl}]$ in between pH = 2–10.

Table 1

Analytical data and some of the physical properties of synthesized molecules.

Compound	Chemical formula, M_w	Color μ_{eff} , BM	Elemental analysis Found (calculated) %			
			C	H	N	Ni
$[\text{Se-NH}_2]$	$\text{C}_{10}\text{H}_{12}\text{N}_2\text{Se}$ (238.96)	Brown 117–118	50.77 (50.21)	4.36 (5.02)	12.32 (11.71)	
$[\text{Se-SchH}]$	$\text{C}_{17}\text{H}_{16}\text{N}_2\text{SeO}$ (342.96)	Cream 172–174	59.44 (59.48)	4.12 (4.66)	8.14 (8.16)	
$[\text{Se-SchF}]$	$\text{C}_{17}\text{H}_{15}\text{N}_2\text{SeOF}$ (360.95)	Yellow 221–223	56.56 (56.51)	3.76 (4.15)	7.82 (7.76)	
$[\text{Se-SchCl}]$	$\text{C}_{17}\text{H}_{15}\text{N}_2\text{SeOCl}$ (377.46)	Yellow 232–234	53.93 (54.04)	3.53 (3.97)	7.39 (7.42)	
$[\text{Se-SchBr}]$	$\text{C}_{17}\text{H}_{15}\text{N}_2\text{SeOBr}$ (421.86)	Yellow 243–245	47.96 (47.86)	3.16 (3.55)	6.61 (6.64)	
$[\text{Se-SchMe}]$	$\text{C}_{17}\text{H}_{15}\text{N}_2\text{SeOCH}_3$ (356.96)	Brown 201–203	59.01 (58.15)	4.49 (4.20)	7.69 (7.84)	
$[\text{Ni}(\text{SeSchH})(\text{H}_2\text{O})_2]\text{Cl}$	$\text{C}_{17}\text{H}_{19}\text{N}_2\text{SeO}_2\text{ClNi}$ (456.10), 288	Green 2.72	43.45 (44.72)	3.99 (4.16)	6.36 (6.13)	13.70 (12.71)
$[\text{Ni}(\text{SeSchF})(\text{H}_2\text{O})_2]\text{Cl}$	$\text{C}_{17}\text{H}_{17}\text{N}_2\text{SeO}_2\text{FCINi}$ (473.20), 256	Clear green 2.97	42.89 (43.11)	3.88 (3.59)	6.06 (5.91)	12.40 (12.26)
$[\text{Ni}(\text{SeSchCl})(\text{H}_2\text{O})_2]\text{Cl}$	$\text{C}_{17}\text{H}_{15}\text{N}_2\text{SeOCl}_2\text{Ni}$ (470.96), 280	Green 3.74	43.40 (43.32)	3.20 (3.18)	6.00 (5.94)	12.30 (12.32)
$[\text{Ni}(\text{SeSchBr})(\text{H}_2\text{O})_2]\text{Cl}$	$\text{C}_{17}\text{H}_{17}\text{N}_2\text{SeO}_2\text{BrClNi}$ (533.36), 273	Green 2.69	37.45 (38.24)	3.64 (3.18)	5.20 (5.25)	10.74 (10.87)
$[\text{Ni}(\text{SeSchMe})(\text{H}_2\text{O})_2]\text{Cl}\cdot\text{H}_2\text{O}$	$\text{C}_{18}\text{H}_{18}\text{N}_2\text{SeOCINi}$ (485.5), 235	Green 2.31	41.33 (42.01)	4.33 (3.70)	5.58 (5.76)	12.30 (11.95)

and $\nu_{\text{CH aromatic}}$ vibrations [17]. The ^1H NMR spectrum of 2-Aminosenophene-3-carbonitrile, recorded in CDCl_3 showed the following signals: $-\text{NH}_2$ proton at 4.80 ppm (t, 2H), $\text{aa}'_{(\text{cyclo})}$ proton at 2.56–2.67 ppm (m, 4H), $\text{bb}'_{(\text{cyclo})}$ proton at 1.60–1.68 ppm (m, 4H), $\text{c}_{(\text{cyclo})}$ proton at 1.77–1.87 ppm (d, 2H). The ^1H NMR spectrum of the ligands shows the following signals: $\text{aa}'_{(\text{cyclo})}$ proton at 2.76–2.91 ppm (s, 4H), $\text{bb}'_{(\text{cyclo})}$ at 1.60–1.75 ppm (s, 4H), $\text{c}_{(\text{cyclo})}$ proton at 1.86–1.93 ppm (d, 2H) phenyl as multiplet at 6.18–6.98 ppm (m, 4H or 3H), $-\text{CH}=\text{N}-$ at 8.23–8.30 ppm (s, 2H) and the peak at 11.85–11.90 ppm (s, 1H) is attributable to the phenolic $-\text{OH}$ group present in the aldehyde moiety. The ^{13}C NMR spectra data of the Schiff bases (Table 3) are in accordance with the proposed structures. The electronic spectra of the Schiff bases in DMSO show bands ca. 420 nm are attributed to the azomethine $n \rightarrow \pi^*_{(\text{CH}=\text{N})}$ transition. The bands at higher energies (253–398 nm) are associated with the benzene $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transition [20,21].

IR, UV-Visible spectra, thermal analyses (TGA/DTA) and magnetic susceptibilities of Nickel(II) complexes

The IR assignments for the important bands of the complexes are given in Table 2. The bands in the 2217–2225 cm^{-1} and 1574–1609 cm^{-1} region may be, respectively, ascribed to $\nu(\text{CN})$

and $\nu(-\text{CH}=\text{N})$ vibrations [22,23]. A shift at $\nu(\text{CN})$ bands is not seen in the complexes, lending further support to the suggestion that the atoms N in the $-\text{CN}$ do not coordinate with the metal ion [18] (Scheme 1(3)). The azomethine in the IR spectra of the complexes are in the 1574–1609 cm^{-1} range, somewhat lower than observed for the free ligands. These indicate that the azomethine nitrogen is coordinated to metal ion [18,21]. Assignment of the proposed coordination sites is further supported by the appearance of medium bands at 420–455 cm^{-1} which could be attributed to $\nu\text{M}-\text{N}$ respectively. In addition, the Nickel (II) complex shows a band at 483–490 cm^{-1} attributed to $\text{N}-\text{O}$ frequency.

The electronic absorption spectra of the Ni (II) complexes were recorded at 298 K. The absorption region, band assignment and the proposed geometry of the complexes are given in Table 2. The electronic spectra of the Ni (II) complexes shows two d–d bands at ca. 690 and 380 nm, respectively, the position of which is indicative of tetrahedral stereochemistry, assigned to $^3\text{T}_1(\text{F}) \rightarrow ^3\text{T}_2(\text{v}_2)$ and $^3\text{T}_1(\text{F}) \rightarrow ^3\text{A}_2(\text{v}_3)$ transitions. More intense bands in the d–d electronic spectra and high magnetic moment values support a tetrahedral configuration for the Ni (II) complexes [18].

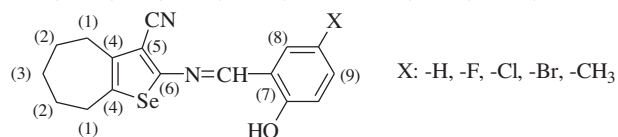
The TGA curves of the Ni (II) complexes are similar in the 50–400 $^\circ\text{C}$ range; the loss in weight is equivalent to degradation of the complexes. A weight loss (ca. 4.0%) between 55 and 155 $^\circ\text{C}$ for the $[\text{Ni}(\text{Se-SchMe})(\text{H}_2\text{O})_2]\text{Cl}\cdot\text{H}_2\text{O}$ complex is assigned to the loss

Table 2
Important IR vibration frequencies (cm^{-1}) and UV–Visible spectrum values (nm) of synthesized molecules.

Compound	$\nu(\text{O}-\text{H})$	$\nu(\text{C}-\text{CN})$	$\nu(\text{Se}-\text{C})$	$\nu(\text{C}-\text{H})_{\text{aliphatic}}$	$\nu(\text{C}-\text{H})_{\text{aromatic}}$	$\nu(\text{NH}_2)_{\text{asym. sym}}$	$\nu(\text{CH}=\text{N})$	$\nu(\text{M}-\text{O}), \nu(\text{M}-\text{N})$	$\lambda_{\text{max}} (\epsilon)$			
									$n \rightarrow \pi^*_{(\text{C}=\text{N})}$	$\pi \rightarrow \pi^*_{(\text{C}=\text{N})}$	$d \rightarrow d$	$d \rightarrow d$
[Se-NH ₂]	–	–	2922–2837	–	–	3433, 3336, 3228	–	–	261 (3580)	266 (3399)	298 (3875)	–
[Se-SchH]	2197	–	–	–	–	–	–	–	288–415 (3800–3900),	–	–	–
	1624	–	–	–	–	–	–	–	420–446 (3529–3413)	–	–	–
[Se-SchF]	3467	–	2917–2849	–	–	–	–	–	–	–	–	–
	2214	–	3064	–	–	1567	–	–	–	–	–	–
	1601	–	–	–	–	–	–	–	–	–	–	–
[Se-SchCl]	3455	–	2922–2854	–	–	–	–	–	263 (3055), 302 (3342),	–	–	–
	2219	–	3064	–	–	1562	–	–	400 (3926), 441 (3441)	–	–	–
	1632	–	–	–	–	–	–	–	–	–	–	–
[Se-SchBr]	3461	–	2917–2846	–	–	–	–	–	256 (2758), 306 (1256)	–	–	–
	2225	–	3063–2993	–	–	1553	–	–	417 (2728), 436 (3800)	–	–	–
	1638	–	–	–	–	–	–	–	–	–	–	–
[Se-SchMe]	3444	–	2922–2849	–	–	–	–	–	253 (2707), 304 (1262)	–	–	–
	2225	–	3058–2990	–	–	1556	–	–	417 (2328)	–	–	–
	1651	–	–	–	–	–	–	–	–	–	–	–
[Ni(SeSchH)(H ₂ O) ₂]Cl	3387	–	2917–2849	–	–	–	–	–	260 (2912), 308 (3854)	–	–	–
	2219	–	3058–2979	–	–	1567	–	–	398 (3214), 441 (3546)	–	–	–
	1620	–	–	–	–	–	–	–	–	–	–	–
[Ni(SeSchF)(H ₂ O) ₂]Cl	3426	–	2916–2846	–	–	–	–	–	401 (2216); 406 (2314)	–	–	–
	2217	–	Overlap	–	–	1581	–	–	549 (2,27)	–	–	–
	1602	–	–	–	–	434/490	–	–	–	–	–	–
[Ni(SeSchCl)(H ₂ O) ₂]Cl	3433	–	2923–2853	–	–	–	–	–	295(1307); 407 (1989)	–	–	–
	2218	–	Overlap	–	–	1574	–	–	606(987)	–	–	–
	1602	–	–	–	–	434/490	–	–	–	–	–	–
[Ni(SeSchBr)(H ₂ O) ₂]Cl	3433	–	2916–2846	–	–	1560	–	–	292 (2216); 408 (2314)	–	–	–
	2224	–	2993–3063	–	–	441/483	–	–	536 (227)	–	–	–
	1602	–	–	–	–	–	–	–	–	–	–	–
[Ni(SeSchMe)(H ₂ O) ₂]Cl·H ₂ O	3405	–	2923–2846	–	–	1609	–	–	290 (972); 407(2496)	–	–	–
	2225	–	Overlap	–	–	420/490	–	–	598 (4,86)	–	–	–
	1623	–	–	–	–	–	–	–	–	–	–	–
	3384	–	2916–2846	–	–	1581	–	–	295 (908); 408 (2107)	–	–	–
	2217	–	overlap	–	–	455/490	–	–	544 (12,94)	–	–	–
	1602	–	–	–	–	–	–	–	–	–	–	–

Table 3
¹H NMR and ¹³C NMR spectral data in ppm (CDCl₃) of amine and azomethines.

Comp	¹ H NMR				¹³ C NMR	
	–NH ₂ /–OH	H _C =N	1, 1'	2, 2'	H _C =N	Ar–C ₁₋₁₀
[Se-NH ₂]	4.80/–	–	2.56–2.67	1.60–1.68	–	27.97,26.38,31.92,128.24,93.68
[Se-SchH]	–/11.90	8.3	2.77–2.91	1.7	161.16	31.98,26.86,30.00, 142.60,112.72,161.02, 118.47,132.58,132.58,134.36
[Se-SchF]	–/11.85	8.20	2.79–2.88	1.65–1.74	159.59	32.53,26.83,30.00, 143.53, 113.43, 154.13, 118.25, 118.15, 118.97, 121.40
[Se-SchCl]	–/11.85	8.20	2.77–2.91	1.65–1.74	159.39	32.53, 26.83,30.01,143.63, 113.52, 124.25 119.19,119.28, 131.26, 134.00
[Se-SchBr]	–/11.9	8.23	2.76–2.90	1.65–1.75	159.29	31.95, 26.83,30.01,143.63, 111.08, 119.92 115.49,119.68, 134.30, 136.76
[Se-SchMe]	–/11.9	8.24	2.76–2.91	1.7	161.10	31.98, 26.87,29.99,142.36, 112.47, 128.75 118.11,117.46, 132.41, 135.46



of hydrated water. For other the Ni (II) complexes, the first weight loss (8.5–9%) in the 50–200 °C range may be accounted for in terms of the loss of coordinated water [24]. The exothermic peaks lying at ca. 200–350 °C for all of the complexes were due to melting. This is followed by broad and stronger exothermic peaks, corresponding to decomposition of the complexes. The residues at the end of the decomposition for all of the complexes were found to be NiCl₂ + SeCO₃ + residues (Table 4).

Biological activity of Schiff bases and their complexes

The ligands and their Ni (II) complexes were screened for antimicrobial activity in DMF solvent as a control substance. The compounds were tested with the same concentrations in DMF solution (0.08 μg/mL). All the synthesized compounds and antibiotic exhib-

ited varying degree of inhibitory effects on the growth of different tested strains (Table 5). All the compounds were active against *Br. abortus* except [Ni(Se-SchBr)]. *Br. abortus* is a gram-negative bacterium that causes premature abortion of a cattle fetus. What makes this bacterium so dangerous is that it can be transferred from an animal to a human host. In humans, this disease causes both acute and chronic symptoms, but can be treated with antibiotics. This research indicates that Schiff bases of 2-Aminoselenophene-3-carbonitrile and their Ni (II) complexes are active against *Br. abortus* (Table 5). Synthesized Schiff bases were inactive against *S.typhi* H, whereas their complexes were active except [Ni(Se-SchBr)]. In general, the metal complexes are more potent bactericides than the ligand. This enhancement in activity may be explained on the basis of chelation theory [25]. Chelation reduces the polarity of the metal ion. Hence, a complex has lipophilic character, and in-

Table 4
TGA results of Ni (II) complexes.

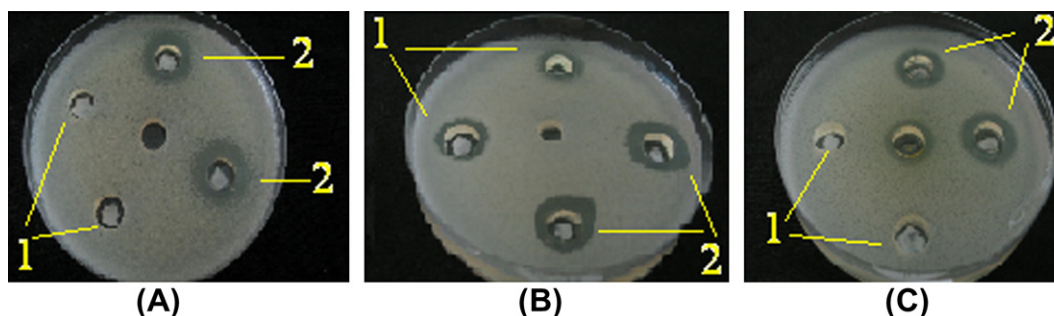
Compound	Thermally decomposed			Loss of mass at 900 °C (wt.%)	Residue formulae Found (calculated) %
	T_i	$T_{1/2}$	T_f		
[Ni(Se-SchH)(H ₂ O) ₂]Cl	50	70	80	44	1/2NiCl ₂ + C + 1/2NiO + SeCO ₃ 56 (57.7)
[Ni(Se-SchF)(H ₂ O) ₂]Cl	150	160	180	35	1/2NiCl ₂ + 1/2NiF ₂ + SeCO ₃ 68 (68.5)
[Ni(Se-SchCl)(H ₂ O)Cl]	65	85	90	39	NiCl ₂ + SeO + C 51 (50.1)
[Ni(Se-SchBr)(H ₂ O) ₂]Cl	155	175	190	31	1/2NiCl ₂ + 4C + 1/2NiBr ₂ + SeCO ₃ 69 (69.8)
[Ni(SeSchMe)(H ₂ O)Cl]·H ₂ O	155 55	160	200	38	1/2NiCl ₂ + 3C + 1/2NiCO ₃ + SeCO ₃ 62 (61.3)

T_i : temperature of initial degradation; $T_{1/2}$: temperature of half degradation.
 T_f : temperature of finally degradation.

Table 5
Antimicrobial activity of studied molecules (0.25 µg/ml) and standard reagents (diameter of zone inhibition (mm)).

		Schiff bases					Ni(II) complexes					DMF control	
		1	2	3	4	5	6	7	8	9	10		11
Gram (+)	<i>Sh.dys. typ 10</i>	–	12	–	10	–	15	11	18	12	15	–	
	<i>P. putida</i>	–	15	13	–	12	10	–	14	14	–	13	–
	<i>S. typhi</i> H	–	–	–	–	–	–	11	16	12	–	14	–
	<i>Br. Abortus</i>	–	15	12	13.5	14	13	15	–	14	–	15	–
	<i>L. monocytogenes</i> 4b	–	–	–	–	–	–	–	–	13	13	–	–
Gram (–)	<i>B. cereus</i>	–	–	–	–	–	–	–	12	–	–	15	–
	<i>S. aureus</i>	7	17	–	–	–	–	–	–	14	–	–	–
	<i>S. epidermis</i>	–	16	10.5	6.5	–	–	–	15	15	–	14	–
	<i>M. luteus</i>	–	12.5	–	7	11	8	–	16	16	–	15	–
	<i>E. coli</i>	–	12.5	–	10	14.5	–	–	15	14	–	15	–
Antifungal	<i>C. albicans</i>	–	–	–	–	–	–	19	21	–	20	–	
Positive control	<i>S. aureus</i>	<i>P. putida</i>	<i>E. coli</i>	<i>S. typhi</i> H	<i>Br. abortus</i>	<i>C. albicans</i>							
K30	25	14	25	20	–	–						SXT25, Sulphamethoxazol, 25 µg;	
SXT25	24	18	18	17	–	–						AMP10, Ampicillin 10 µg;	
AMP10	30	8	10	11	–	–						NYS100, Nystatin 100 µg;	
AMC30	30	15	14	19	–	–						SCF, Sulbactam (30 µg)	
NYS100	–	–	–	–	–	–						20	

(1) (Se-NH₂), (2) (Se-SchH), (3) (Se-SchF), (4) (Se-SchCl), (5) (Se-SchBr), (6) (SeSch-CH₃), (7) [Ni(Se-SchH)], (8) [Ni(Se-SchF)], (9) [Ni(Se-SchCl)], (10) [Ni(Se-SchBr)], (11) [Ni(Se-SchMe)].

**Fig. 2.** Imaging of the couple work of antimicrobial affect of (Se-SchCl) (1) and [Ni(Se-SchCl)(H₂O)Cl] complexes (2) against *P. putida* (A), *M. luteus* (B), *C. albicans* (C).

increases the interaction between the metal ion and the lipid is favored. This lead to the breakdown of the permeability barrier of the cell, resulting in interference with the normal cellular processes [26]. [Ni(Se-SchCl)] complexes were observed to be the most active against *Sh.dys. typ 10* (Fig. 2). It was interesting to note that methyl and chlorine groups in the metal chelates had an impact on the bactericidal activity. Furthermore, the antibacterial activity of these compounds was also compared with five commercial antibiotics, namely Sulfamethoxazol, Ampicillin, Nystatin and

Table 6
Transmittances of the [Ni(Se-SchCl)(H₂O)Cl] complexes in between pH = 2–10.

pH	Color	Wavenumber (nm), absorbans		
		$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	LMCT
2	Lemon-yellow	307 (1.35)	416 (3.35)	–
4	Lemon-yellow	306 (1.05)	417 (2.59)	–
5	Orange	309 (0.63)	416 (1.97)	–
7	Red	310 (0.65)	416 (0.99)	510 (1.19)
10	Dark-red	311 (1.02)	415 (1.02)	504 (0.62)

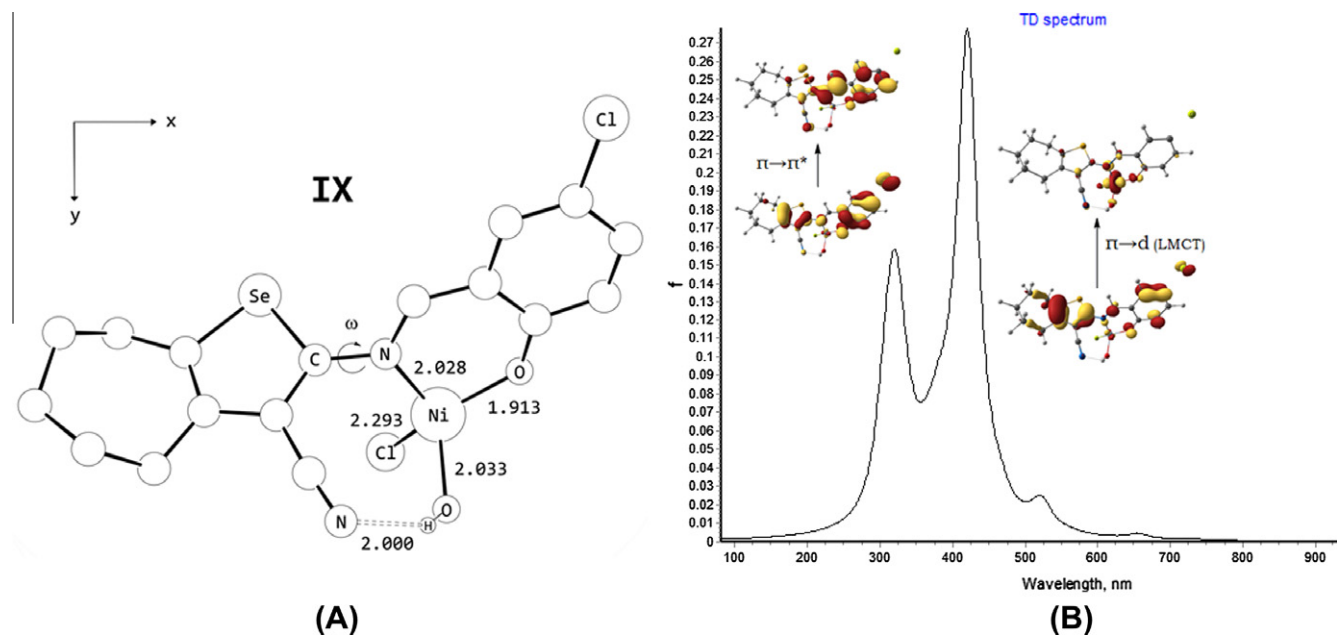


Fig. 3. (A) Selected bond lengths (Å) for IX. Hydrogens are omitted for clarity, except for the one involved in hydrogen bonding. (B) Simulated TD-DFT spectrum for IX. LMCT and $\pi \rightarrow \pi^*$ character dominates the transitions.

Table 7

Ligand environment and Mulliken atomic spin densities on Ni(II)-center of complexes studied in this work.

Species	Complex	X ₁	X ₂	ρ_{Ni}
VII	[Ni(SeSchH)(H ₂ O) ₂]Cl	H ₂ O	H	1.63
VIII	[Ni(SeSchF)(H ₂ O) ₂]Cl	H ₂ O	F	1.62
IX	[Ni(SeSchCl)(H ₂ O)Cl]	Cl	Cl	1.63
X	[Ni(SeSchBr)(H ₂ O) ₂]Cl	H ₂ O	Br	1.62
IX'	[Ni(SeSchCl)(H ₂ O) ₂]Cl	H ₂ O	Cl	1.62

Sulbactam. It was seen that the synthesized compounds were effective as the antibiotics mentioned.

The spectral studies for [Ni(Se-SchCl)(H₂O)Cl] complexes in between pH = 2–10

As shown in Table 6, the spectral studies were carried out at room temperature in the wavelength region of 340–700 nm. The absorption spectra of the [Ni(Se-SchCl)(H₂O)Cl] complexes under different pH are as shown that Fig. 2. [Ni(Se-SchCl)(H₂O)Cl] complexes can change its color from yellow to dark red along with the pH value decreasing. Between pH = 5 and pH = 7, [Ni(Se-SchCl)(H₂O)Cl] complexes gave rise to color change from yellow² to red in DMF which was clearly visible to the naked eye (Fig. 1B).

Theoretical assessment, calculated UV-spectrum and thermodynamic details of tetrahedral Ni(II) complexes

All complexes exhibit triplet ground state that lie 10–14 kcal/mol below the singlet. Singlet complexes assume the square planar geometry, whereas triplets are tetrahedral. IX has two conformers that lie 2.5 kcal/mol apart, which is attributable to the hydrogen

bonding interaction between nitrile and water for the more stable conformer (Fig. 3A). Two conformers differ in the y -axis orientation of the nitrile group and interconvert via change of the dihedral ω . Common features of the emission process are reproduced and assignments are in good agreement with the available data (Fig. 3B). Calculated spin densities given in Table 7 shows that the triplet ground states for all Ni(II) complexes bear two unpaired electrons residing in Ni d-based orbitals, consistent with the paramagnetic character observed experimentally.

The interesting observation of failure to obtain [Ni(SeSchCl)(H₂O)₂] (IX') well agrees with the computed thermodynamic stability difference between the Ni-chloro and Ni-aqua complexes



Conclusions

Coordination structures of Ni(II) complexes have been determined by spectral analyses. All of Ni(II) complexes have tetrahedral structure. The superior bactericide [Ni(Se-SchCl)(H₂O)Cl] (IX) exhibits pH-dependent color and has [ML(OH₂)Cl] coordination unlike the rest. Structural and electronic properties of all complexes were further studied computationally. Thermodynamic stability of IX relative to its hypothetical analog [ML(OH₂)₂]Cl (IX') well correlates with the experiment. TD-DFT spectra featured transitions mainly of LMCT and $\pi \rightarrow \pi^*$ character, and also closely matched the experimental values. We believe that, this novel bactericide, Ni(SeSchCl)(H₂O)Cl, can find practical applications in chemical, environmental and biological systems.

Acknowledgment

This work was supported by the Gazi University Research Fund (Project number: 05/2010-74).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2012.12.078>.

² For interpretation of color in Fig. 2, the reader is referred to the web version of this article.

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