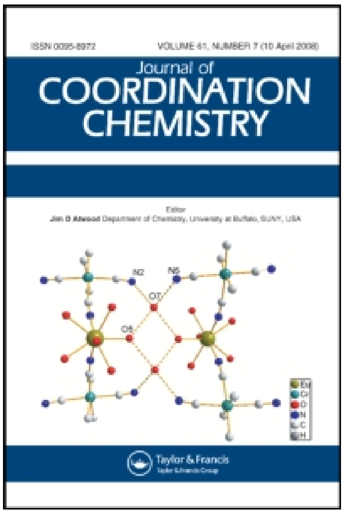

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Synthesis, spectral, thermal, solid state d.c. electrical conductivity and biological studies of Co(II), Ni(II) and Cu(II) complexes with 3-substituted-4-amino (indole-3-aldehydo)-5-mercapto-1,2,4-triazole Schiff bases

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A series of cobalt(II), nickel(II) and copper(II) complexes have been synthesized with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and indole-3-aldehyde in ethanol. These complexes have been characterized by elemental analyses, magnetic, spectroscopic (IR, UV-Vis, H-NMR, ESR, FAB-mass), thermal, electrochemical (CV) and solid state d.c. electrical conductivity studies. The elemental analyses confirm 1 : 2 stoichiometry of the type $ML_2 \cdot 2H_2O$ (M = Co/Ni) and ML_2 (M=Cu). The complexes are colored solids and non-electrolytes in DMF and DMSO. Magnetic and spectral data suggest octahedral geometry for Co(II) and Ni(II) complexes and square-planar geometry for Cu(II) complexes. The presence of coordinated water in Co(II) and Ni(II) complexes was confirmed by thermal and IR data of the complexes. The complexes are insoluble in water and common organic solvents and decompose at higher temperature. All these ligands and their complexes have also been screened for antibacterial (*Bacillus cereus*, *Staphylococcus aureus*, *Escherichia coli and Pseudomonas aeruginosa*) and antifungal activities (*Aspergillus niger* and *Aspergillus fumigates*) by the cup plate method.

Keywords: Synthesis; Biological activity; 1,2,4-triazole; Schiff bases; Metal complexes

1. Introduction

Metal complexes of 1,2,4-triazole derivatives have been extensively investigated and reported from our laboratory [1–5]. There is growing interest in metal complexes of Schiff bases derived from substituted triazoles and indoles which are well known as bactericides [6], pesticides [7], insecticides [8], and potential fungicides [9]. A number of attempts have been made to obtain Co(II), Ni(II), Cu(II) and Zn(II) complexes with Schiff bases derived from cinnamaldehyde and 4-amino 3-ethyl-5-mercapto-s-triazole and 4-amino-5-mercapto-3-n-propyl-s-triazole [10]; cobalt(II), nickel(II) and copper(II) complexes with Schiff bases derived from furfuraldehyde and

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3-substituted-4-amino-5-mercapto-s-triazole have been isolated and characterized by elemental analyses, magnetic, spectral (IR, UV-Vis, ^{1}H-NMR, EPR) and thermal studies [11].

No work has been carried out on the synthesis of metal complexes with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole with indole-3-aldehyde. These ligands have two donor sites of SN sequence with varied coordinating abilities. Such ligands with biological activity of the indole moiety have aroused our interest in elucidating structures of Co(II), Ni(II) and Cu(II) complexes.

In the present article, we report the synthesis, spectral, magnetic, thermal, electrochemical, solid state d.c. electrical conductivity studies and biological properties of Co(II), Ni(II) and Cu(II) complexes with the ligands shown in figure 1.

2. Experimental

All chemicals used were of reagent grade; indole-3-aldehyde was purchased from Acros Organic Chemicals. The metal contents were estimated gravimetrically by the standard method [12]. Carbon, hydrogen, nitrogen and sulfur were estimated using a C, H, N & S analyzer. The results of elemental analyses and molar conductance values are listed in table 1.

2.1. *Physical measurements*

The IR spectra of the ligands and their Co(II), Ni(II) and Cu(II) complexes were recorded on a HITACHI-270 IR spectrophotometer in the 4000–250 cm^{-1} region in KBr disks. The electronic spectra of the complexes were recorded in DMF on a VARIAN CARY 50-BIO UV-spectrophotometer in the region 200–1100 nm. The ^{1}H-NMR spectra of ligands (**I–IV**) and one representative Ni(II) complex **6** were recorded in $CDCl_3$ on a BRUKER 300 MHz spectrometer at room temperature using TMS as an internal reference. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using Argon/Xenon (6 KV, 10Am) as the FAB gas. The accelerating voltage was 10 KV and the spectra were recorded at room temperature; *m*-nitrobenzyl alcohol was used as the matrix. The mass spectrometer was operated in the +ve ion mode. Electrochemical measurements of Cu(II) complexes were recorded on a CHI1110A-electrochemical (HCH Instruments)

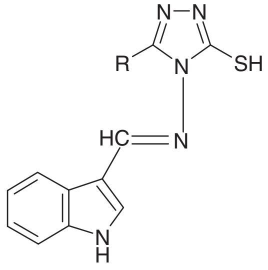

Figure 1. Schiff bases (R = H, CH_3, C_2H_5 and C_3H_7).

Table 1. Elemental analyses of Schiff bases (**I–IV**) and their Co(II), Ni(II) and Cu(II) complexes, molar conductance and magnetic data of Co(II), Ni(II) and Cu(II) complexes.

Complex No.	Empirical formula	C%		H%		N%		S%		M%		Molar conductance $\mathrm{Ohm^{-1}\,cm^{-2}\,mole^{-1}}$ 10^{-3} M	μ_{eff} BM
		Obsd.	Calcd	Obsd.	Calcd	Obsd.	Calcd	Obsd.	Calcd	Obsd.	Calcd		
I	$(C_{11}H_9N_5S)$	54.31	54.32	3.65	3.7	28.75	28.8	13.13	13.16	–	–	–	–
II	$(C_{12}H_{11}N_5S)$	56	56.03	4.22	4.28	27.16	27.23	12.42	12.45	–	–	–	–
III	$(C_{13}H_{13}N_5S)$	57.48	57.56	4.75	4.79	25.8	25.83	11.75	11.8	–	–	–	–
IV	$(C_{14}H_{15}N_5S)$	58.91	58.94	5.18	5.26	24.49	24.56	11.15	11.22	–	–	–	–
1	$Co(C_{11}H_8N_5S)2 \cdot 2H_2O$	45.58	45.6	2.72	2.76	24.15	24.18	11	11.05	10.15	10.17	25.12	4.72
2	$Co(C_{12}H_{10}N_5S)2 \cdot 2H_2O$	47.42	47.45	3.24	3.29	23.05	23.06	10.51	10.54	9.68	9.7	23.24	4.84
3	$Co(C_{13}H_{12}N_5S)2 \cdot 2H_2O$	49.04	49.14	3.75	3.78	22.01	22.05	10.05	10.08	9.25	9.27	24.32	4.95
4	$Co(C_{14}H_{14}N_5S)2 \cdot 2H_2O$	50.54	50.68	4.18	4.22	21.08	21.11	9.58	9.62	8.86	8.88	25.01	4.86
5	$Ni(C_{11}H_8N_5S)2 \cdot 2H_2O$	45.56	45.62	2.65	2.76	24.15	24.19	11.01	11.06	10.1	10.12	28.46	3.24
6	$Ni(C_{12}H_{10}N_5S)2 \cdot 2H_2O$	47.32	47.47	3.23	3.29	23.04	23.07	10.51	10.55	9.63	9.66	26.13	3.26
7	$Ni(C_{13}H_{12}N_5S)2 \cdot 2H_2O$	49.1	49.16	3.71	3.78	22.02	22.06	10.05	10.08	9.2	9.23	25.32	3.22
8	$Ni(C_{14}H_{14}N_5S)2 \cdot 2H_2O$	50.66	50.7	4.18	4.22	21.08	21.12	9.61	9.65	8.82	8.84	24.45	3.28
9	$Cu(C_{11}H_8N_5S)2$	48.14	48.21	2.86	2.92	25.55	25.57	11.64	11.68	11.56	11.59	27.56	1.72
10	$Cu(C_{12}H_{10}N_5S)2$	50.02	50.04	3.41	3.47	24.31	24.32	11.08	11.12	11.01	11.03	25.18	1.82
11	$Cu(C_{13}H_{12}N_5S)2$	51.62	51.69	3.92	3.97	23.17	23.19	10.57	10.6	10.49	10.52	26.24	1.78
12	$Cu(C_{14}H_{14}N_5S)2$	53.16	53.2	4.4	4.431	22.11	22.16	10.08	10.13	10.01	10.05	24.12	1.9

analyzer (made in U.S.A). Thermogravimetric analyses were measured from room temperature to 1000°C at a heating rate of $10^\circ C\,min^{-1}$. The data were obtained by using a PERKIN-ELMER DIAMOND TG/DTG instrument. Solid state d.c. electrical conductivities of solid complexes were measured using a digital micro voltmeter model DMV-001. Molar conductivity measurements were recorded on a ELICO-CM-82 T conductivity bridge with a cell having cell constant 0.51. The magnetic moment was carried out on a Faraday balance.

2.2. *Synthesis of Schiff bases I–IV*

A series of 3-substituted-4-amino-5-mercapto-1,2,4-triazoles were synthesized by reported methods [13, 14]. A mixture of 3-substituted-4-amino-5-mercapto-1,2,4-triazole and indole-3-aldehyde in 1 : 1 molar proportions in an alcoholic medium containing a few drops of concentrated HCl were refluxed for 3–4 h. The products separated on evaporation of the alcohol and were recrystallized from EtOH. Yield 60–70%, m.p. 250–270°C.

2.3. *Synthesis of Co(II), Ni(II) and Cu(II) complexes 1–12*

An alcoholic solution of Schiff bases (**I–IV**) (2 mmol) was refluxed with 1 mmol of $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ in ethanol on a water bath for 1 h. Then 2g of sodium acetate was added to the reaction mixture and refluxing was continued for 3 h. The separated complex was filtered, washed thoroughly with water, ethanol and ether and finally dried in vacuum over fused calcium chloride.

3. Results and discussion

All the cobalt(II), nickel(II) and copper(II) complexes are colored non-hygroscopic solids stable in air. They are sparingly soluble in common organic solvents, but soluble in DMF and DMSO. The elemental analyses show that the cobalt(II), nickel(II) and copper(II) complexes have 1 : 2 stoichiometry of the type $CoL_2 \cdot 2H_2O$, $NiL_2 \cdot 2H_2O$ and CuL_2. The molar conductance values are too low to account for any dissociation of non-electrolytes in DMF.

3.1. *IR spectra*

The important IR frequencies of the Schiff bases and their Co(II), Ni(II) and Cu(II) complexes are mentioned below.

(1) The free ligands exhibit a medium intensity band in the region $3110–3097\,cm^{-1}$ due to ν(NH) indicating the thion form, while a weak broad band observed around $2400\,cm^{-1}$ due to ν(SH) vibrations suggest that the Schiff bases exhibit thiol-thione tautomerism [15, 16].

(2) Another characteristic band of medium to high intensity in the region $1630–1620\,cm^{-1}$ is ascribed to ν(C=N), indicating the presence of indole-3-aldehyde.

(3) These ligands contain NCSH and NHCS groups with the expectation of delocalized thiamide vibrations. The medium to high intensity bands around

1310 cm^{-1} have been assigned to the thiamide-II vibration [15, 16]. Bands due to thiamide-III vibrations are located in the region around 1020 cm^{-1}. The thiamide-IV band, mainly from ν(C=S), is located around 750 cm^{-1} for these Schiff bases.

In the complexes we observed the following changes.

(1) The characteristic band due to ν(C=N) appears around 1600 cm^{-1} for these Co(II), Ni(II) and Cu(II) complexes. The low frequency shift suggests that C=N is coordinated to the metal ion through nitrogen. Bands due to ν(C=N) of the heterocyclic ring for the complexes appears almost in the same region as observed in the ligands.

(2) The disappearance of ν(NH) and ν(SH) vibrations in the complexes is due to deprotonation of the thiol and complexation through sulfur. A weak band appears around 750 cm^{-1} due to ν(C=S). The weakening further indicates coordination through sulfur.

(3) The Co(II), Ni(II) and Cu(II) complexes exhibit a broad band around 3400 cm^{-1}, attributed to the symmetric and antisymmetric–OH stretching modes. There is also a medium to high intensity band around 850 cm^{-1} assigned to coordinated water.

(4) In the light of previous assignments [5, 17, 18] the medium intensity bands found in the region 580–535 cm^{-1} are assigned to the ν(M–N) vibrations coupled with ligand vibrations, and medium intensity bands in the region 380–335 cm^{-1} are due to the ν(M–S) vibration [19, 20].

3.2. *Electronic spectra*

The electronic spectra of Co(II) complexes exhibit absorption bands in the region 8000–10000 cm^{-1} and 18000–20000 cm^{-1} corresponding to ν_1 and ν_3 transitions, respectively ($^4T_{1g}$ (F) → $^4T_{2g}$ (F) (ν_1); $^4T_1$g (F) → $^4T_1$g (P) (ν_3)). These bands are characteristic of high spin octahedral Co(II) complexes. The ν_2 transition is not observed in these Co(II) complexes because of its proximity to the strong ν_3. In complexes **1**–**4** we observe two bands in the region 9540–9682 and 19000–19276 cm^{-1} for ν_1 and ν_3.

The Ni(II) complexes **5**–**8** show three bands in the region 26160–26296, 15675–15842 and 9578–9820 cm^{-1}, assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$(P) ($\nu_3$), $^3A_{2g} \rightarrow {}^3T_{1g}$(F) ($\nu_2$) and $^3A_{2g}$(F) → $^3T_{2g}$(F) (ν_1) transitions, respectively, indicating octahedral geometry [21]. The ligand field parameters D_q, β, B', ν_2/ν_1 and LFSE have been calculated using the procedure given by Drago [22] (table 2).

Table 2. Ligand field parameters of Ni(II) complex with 3-substituted-4-amino (indole-3-aldehydo)-5-mercapto-1,2,4-triazole Schiff bases (**I**–**IV**).

	Transitions (cm^{-1})			ν_2 Calcd			%			μ_{eff}		
Complex No.	ν_1	ν_2	ν_3	cm^{-1}	D_q cm^{-1}	$B1$ cm^{-1}	Distortion	ν_2/ν_1	LFSE	Calcd. BM	β	β°%
5	9752	15842	26296	15813.08	975.2	856.87	0.183	1.624	33.435	3.196	0.811	18.857
6	9820	15782	26172	15859.94	982	838.13	0.491	1.607	33.669	3.193	0.794	20.632
7	9578	15675	26160	15594.8	957.8	868.05	0.514	1.637	32.839	3.202	0.822	17.798
8	9646	15764	26240	15685.77	964.6	865.85	0.499	1.634	33.072	3.2	0.82	18.006

In Cu(II) complexes a band observed at 18000 cm^{-1} was assigned to the transition $^2Eg \rightarrow {}^2T_{2g}$, which is characteristic of square-planar geometry. (Octahedral complexes have a diffused band in the 13000–18000 cm^{-1} region followed by a band in the 21000–23000 cm^{-1} region [23, 24].) The fluctuation of the band over a narrow range suggests that the complexes have the same coordination number and stereochemistry. The nature and shape of the band maxima compare very well with the well characterized square-planar copper(II) complexes. In addition to this band, the complexes show a high intensity ligand to metal charge transfer band in the region 25654–23552 cm^{-1}.

3.3. *^{1}H-NMR spectra*

The ^{1}H-NMR spectra of **I–IV** exhibited signals at 13.58, 9.65 and 7.2–7.5 ppm due to –NH, –CH=N and aromatic protons, respectively. In addition to these signals, a sharp signal at 3.5 ppm is attributed to SH protons. These observations suggest that the ligands exist in thiol-thione tautomerism.

The ^{1}H-NMR spectrum has been studied for only one representative complex, **6**. The resonance due to NH proton (13.58 ppm) disappears in the spectrum of **6** suggesting that the ligands react with metal in the thiol form via deprotonation. The resonance due to azomethine proton in the complex appears at 10.02 ppm indicating a downfield shift with respect to **II** (9.65 ppm). This suggests coordination of the azomethine through nitrogen to the metal ion. Further support for coordination of azomethine nitrogen to the metal has been inferred from the downfield shift of the indole moiety (7.35–7.68 ppm) with respect to **II** (7.25–7.5 ppm). The signal due to water in the complex appears at 5.52 ppm. All these observations support the IR interpretation.

3.4. *Magnetic data*

The magnetic moments obtained at room temperature are listed in table 1. The Co(II) complexes show magnetic moments in the range 4.7–4.95 BM, well within the expected range 4.7–5.2 BM [2, 25] for octahedral complexes.

The Ni(II) complexes show magnetic moments in the range 3.24–3.28 BM; octahedral Ni(II) complexes exhibit magnetic moments in the range 2.5–3.5 BM [25, 26].

For the Cu(II) complexes the magnetic moments fall in the range 1.72–1.90 BM, consistent with the expected spin only values of 1.75–2.20 BM [25], indicating the absence of spin-spin interactions.

3.5. *FAB mass spectrum of Ni(II) complex 6 of ligand II*

The FAB mass spectrum of **6** is depicted in figure S1, showing a molecular ion at *m*/*z* 606, equivalent to its molecular weight. The molecular ion by the loss of one indole molecule gave $[Ni(C_{15}H_{13}N_9S_2)\ 2H_2O]^+$ at *m*/*z* 477; loss of one water gave $[Ni(C_{15}H_{13}N_9S_2)\ H_2O]^+$ at *m*/*z* 459; loss of another water gave $[Ni(C_{15}H_{13}N_9S_2)]^+$ at *m*/*z* 441 and finally, loss of one triazole molecule gave $[Ni(C_{12}H_{10}N_5S)]^+$ at *m*/*z* 314. All these fragments lead to formation of $[Ni(L)]^+$ which undergoes demetallation to $[L + H]^+$ at *m*/*z* 257.

3.6. *ESR spectra of copper(II) complex 10*

The ESR spectrum of **10** is depicted in figure S2. The $g_{\|}$ and $g_{\perp}$ values are 2.041 and 2.028, respectively. The g_{av} calculated to be 2.032 and $g_{\|} < 2.3$ show covalent character of the metal-ligand bond; the unpaired electron is located in the $d_{x^2-y^2}$ orbital. The axial symmetry parameter $G = 1.464$, which is less than 4.0, indicates considerable exchange interaction in the solid complex [27].

3.7. *Thermal studies*

TG and DTG studies were carried out for some of the complexes. These complexes decompose gradually with formation of respective metal oxide above 550°C (figures S3A–S3C, supplementary data available online). The nature of proposed chemical change with temperature and the percent of metal oxide obtained are given in table 3. The thermal decompositions of **2** and **6** take place in three steps as indicated by DTG peaks around 100–115, 230–300 and 320–360°C corresponding to the mass loss of two coordinated water molecules, two indole moieties and two triazole moieties, respectively. Complex **10** decomposes in two steps as indicated by DTG peaks around 260–280 and 300–340°C corresponding to loss of two indole and two triazole moieties, respectively.

3.8. *Kinetic study*

The Freeman and Carroll procedure [28] was used to evaluate the kinetic parameters such as order of reaction and energy of activation from a single experimental curve (figure S4) from the plot of $(\Delta\log \mathrm{d}w/\mathrm{d}t)/\Delta\log W_r$ *versus* $(\Delta T^{-1})/\Delta \log W_r \times 10^3\,\mathrm{K}^{-1}$. In order to determine the thermal stability trend, the parameters T_{o} (temperature of onset of decomposition), T_{10} (temperature for 10% weight loss), $T_{\max}$ (temperature of maximum weight loss), activation energy and order of reaction were evaluated, and the determined order of reaction and energy of activation are listed in table S1.

Table 3. Thermogravimetric data of **2**, **6**, and **10** of 3-substituted-4-amino (indole-3-aldehydo)-5-mercapto-1,2,4-triazole Schiff base (**II**).

		% Weight loss		
Empirical formula	Decomposition temperature (°C)	Obsd.	Calcd	Inference
$Co(C_{12}H_{10}N_5S)2 \cdot 2H_2O$	100–125	5.90	5.93	Loss of coordinated water molecules
	230–275	42.48	42.51	Loss of indole moieties
	330–340	41.85	41.87	Loss of triazole moieties
$Ni(C_{12}H_{10}N_5S)2 \cdot 2H_2O$	100–220	5.92	5.95	Loss of coordinated water molecules
	270–300	42.50	42.53	Loss of indole moieties
	320–360	41.85	41.87	Loss of triazole moieties
$Cu(C_{12}H_{10}N_5S)_2$	260–280	44.79	44.83	Loss of indole moieties
	300–340	44.10	44.13	Loss of triazole moieties

The fractional values obtained for the order of reaction may be due to the determination in the air rather in vacuum. In **2**, the activation energy (E_a) was higher than in **6** and **10**, indicating that **2** is thermally more stable.

3.9. *Cyclic voltammetry*

The electrochemical behavior of **10** was examined by employing glassy carbon as working electrode, Ag/AgCl as reference electrode and platinum wire as auxiliary electrode. The working media consisted of DMF and n-Bu_4NClO_4 as supporting electrolyte. The cyclic voltammogram of **10** in 10^{-3} M solution was recorded at room temperature in the potential range −3.0V to +2.4V with a scan rate of $100\,mV\,s^{-1}$.

The complex shows a redox process corresponding to the Cu(II) → Cu(I) couple at $Ep_a = +1.19$ V and associated cathodic peak at $Ep_c = -0.65$ V. This couple is quasi-reversible as the peak separation between the anodic and cathodic potential is very high. The ratio between the anodic and cathodic currents suggests that the process is a one-electron, quasi-reversible process [29, 30].

On comparing cyclic voltammograms, the variation in oxidation and reduction potential may be due to distortion in the geometry which arises due to different anions coordinated to the metal ion [31].

3.10. *Solid state d.c. electrical conductivity*

The d.c. electrical conductivity of the complexes were measured in pellet form (coated with silver paste) from 30°C to 225°C. The pellet was dried at 100°C around 24 h in air and then the sample was allowed to cool slowly to room temperature. Resistive behavior of these samples was studied as a function of temperature using the standard probe method.

Typical plot of electrical conductivity ($\log\sigma$) *versus* temperature (T^{-1}) for the above said complexes are shown in figure S5 and values are listed in tables S2–4. As the temperature increases there is a gradual decrease in d.c. resistivity. The values of electrical conductivity and activation energy (E_a) are listed in table 4. The increase in conductivity with temperature indicates that these complexes are semiconductors.

The increase in conductivity can be explained on the basis of clustering of ions, effectively lowering the concentration of stable bands, and conduction will be due to hopping. The calculated activation energy may be attributed to the interaction between the electrons of d-orbitals of a cation and the π-orbitals of the ligand. Thus, interaction will localize the π-electronic charge on the ligand [32].

Table 4. Electrical conductivity measurements of **2**, **6**, and **10** with Schiff base (**II**).

Complex No.	Empirical formula	Electrical conductivity σ (T) $\Omega\,cm^{-1} \times 10^{-8}$ (at 100°C)	Activation energy E_a (eV) (at 100°C)
2	$Co(C_{12}H_{10}N_5S)_2 \cdot 2H_2O$	0.130	10.656
6	$Ni(C_{12}H_{10}N_5S)_2 \cdot 2H_2O$	0.114	12.590
10	$Cu(C_{12}H_{10}N_5S)_2$	0.207	3.936

3.11. *Pharmacology*

3.11.1. *In vitro* antibacterial and antifungal assay. The biological activities of the newly synthesized Schiff bases (**I–IV**) and their metal complexes have been studied for antibacterial and antifungal activities by the cup plate method [33, 34]. The antibacterial activities were done by using gram positive organisms (*Staphylococcus aureus* and *Bacillus cereus*) and gram negative organisms (*Pseudomonas aeruginosa* and *Escherichia coli*). These bacterial strains were chosen as they are known pathogens and *Aspergillus niger* and *Aspergillus fumigates* were used for antifungal activities at 20 µg/ml concentrations in solvent DMF used as control. The bacteria were subcultured in agar medium. The Petri dishes were incubated for 24 h at 37°C. Standard antibacterial drug (Gentamycine) was also screened under similar conditions for comparison. The fungi were subcultured in potato dextrose agar medium with standard antifungal drug (Fluconazole) used for comparison. The Petri dishes were incubated for 48 h at 37°C.

The microbial results are systematized in table 5 (figures 2–5). Ligands **I–IV** were moderately active towards *B. cereus* and weakly active towards *P. aeruginosa*, *E. coli* and *S. aureus*. Complexes **2**, **5**, **6** and **10** show high activity; the remaining complexes show moderate activity against *B. cereus*. All complexes show weak activity or inactive towards *P. aeruginosa*, *E. coli* and *S. aureus*.

For antifungal activity **I–IV** show high activity against *A. niger*; **II** shows higher activity than the standard against *A. niger*. All ligands are weakly active towards *A. fumigates*. Complex **2** has high activity against *A. fumigates* but its corresponding ligand (**II**) has weak activity against *A. fumigates*. Remaining Co(II) complexes (**1**, **3–5**, and **12**) are moderately or weakly active towards *A. niger* and *A. fumigates*.

Table 5. Bacteriological results of Schiff bases and their Co(II), Ni(II) and Cu(II) complexes.

		Activity against bacteria (mm)				Activity against fungi (mm)	
Complex No.	Empirical formula	*E. coli*	*P. aeruginosa*	*B. cereus*	*S. aureus*	*A. niger*	*A. fumigates*
I	$(C_{11}H_9N_5S)$	12	12	15	14	18	14
II	$(C_{12}H_{11}N_5S)$	13	12	16	12	20	16
III	$(C_{13}H_{13}N_5S)$	14	12	15	14	18	14
IV	$(C_{14}H_{15}N_5S)$	14	13	16	13	18	14
1	$Co(C_{11}H_8N_5S)_2 \cdot 2H_2O$	14	12	16	14	16	16
2	$Co(C_{12}H_{10}N_5S)_2 \cdot 2H_2O$	15	13	18	13	16	18
3	$Co(C_{13}H_{12}N_5S)_2 \cdot 2H_2O$	12	12	16	13	14	16
4	$Co(C_{14}H_{14}N_5S)_2 \cdot 2H_2O$	14	12	15	14	14	16
5	$Ni(C_{11}H_8N_5S)_2 \cdot 2H_2O$	12	12	17	14	12	14
6	$Ni(C_{12}H_{10}N_5S)_2 \cdot 2H_2O$	12	14	18	12	14	16
7	$Ni(C_{13}H_{12}N_5S)_2 \cdot 2H_2O$	13	13	16	12	14	13
8	$Ni(C_{14}H_{14}N_5S)_2 \cdot 2H_2O$	12	12	15	13	13	14
9	$Cu(C_{11}H_8N_5S)_2$	12	12	15	14	12	14
10	$Cu(C_{12}H_{10}N_5S)_2$	12	12	16	12	14	16
11	$Cu(C_{13}H_{12}N_5S)_2$	13	11	15	12	12	16
12	$Cu(C_{14}H_{14}N_5S)_2$	12	13	16	12	14	14
Gentamycine		20	20	20	20	–	–
Flucanazole		–	–	–	–	24	24
DMF		12	12	12	12	12	12

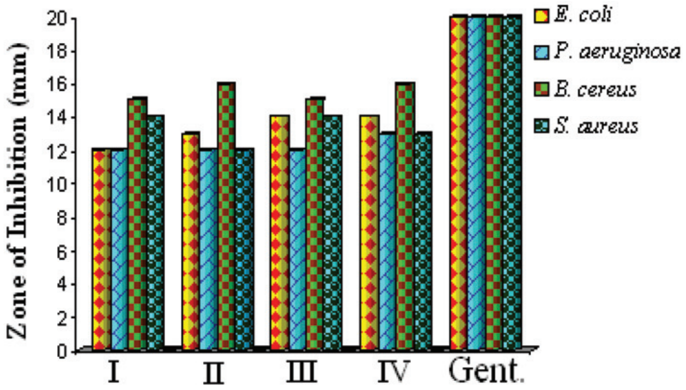

Figure 2. *In vitro* antibacterial spectrum of compounds (**I–IV** and gentamycine).

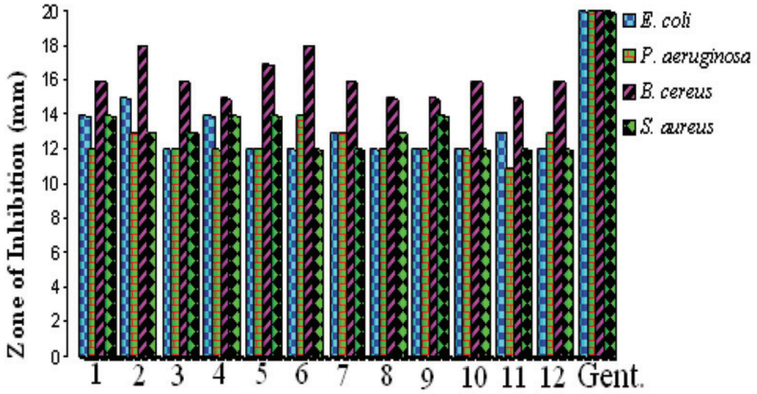

Figure 3. *In vitro* antibacterial spectrum of Co(II), Ni(II) and Cu(II) complexes and gentamycine.

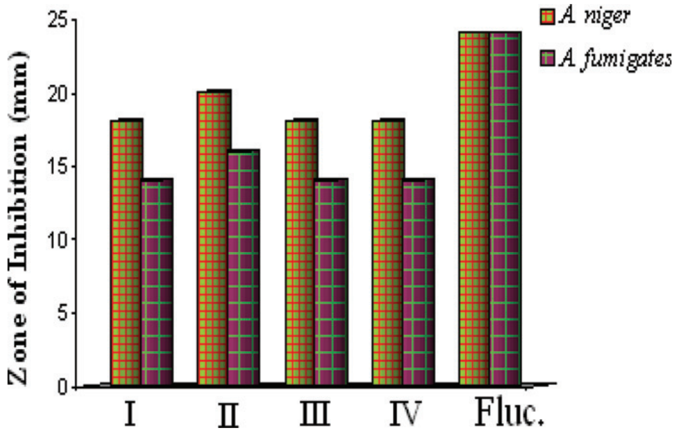

Figure 4. *In vitro* antifungal spectrum of compounds (**I–IV** and fluconazole).

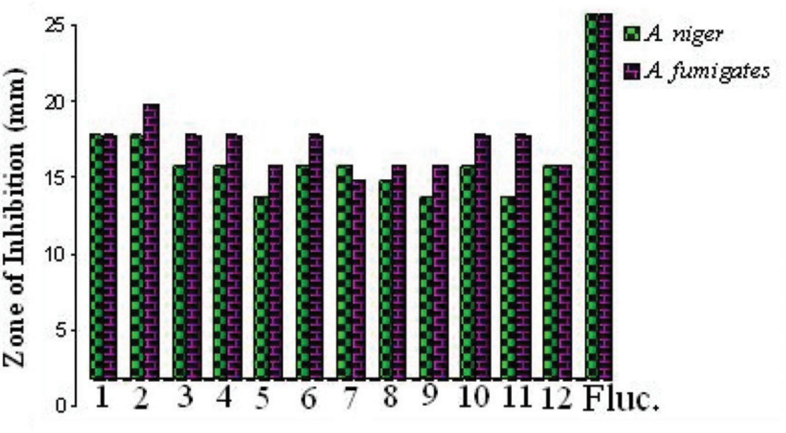

Figure 5. *In vitro* antifungal spectrum of Co(II), Ni(II) and Cu(II) complexes and fluconazole.

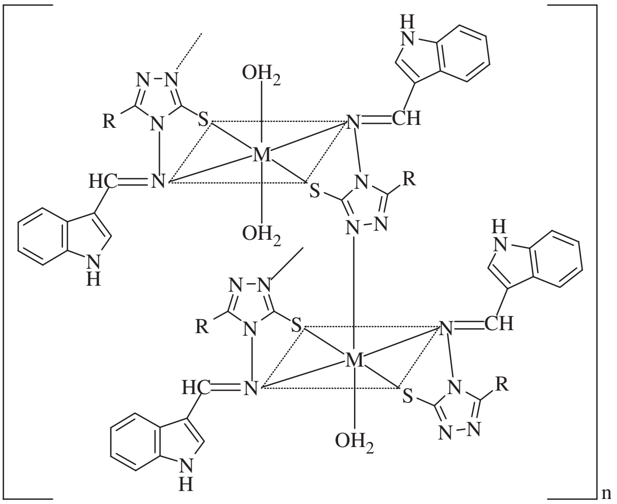

Figure 6. Octahedral structure of Co(II) and Ni(II) complexes (R=H, CH_3, C_2H_5 and C_3H_7; M = Co(II) and Ni(II)).

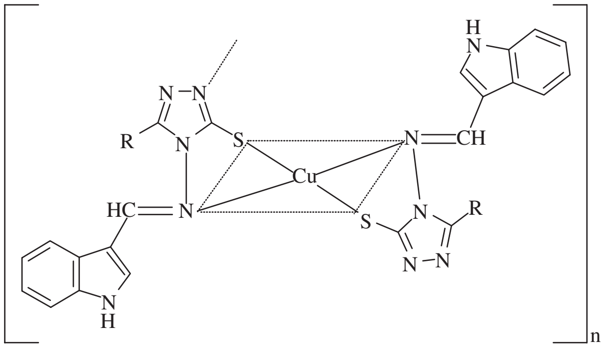

Figure 7. Square-planar structure of Cu(II) complexes (R=H, CH_3, C_2H_5 and C_3H_7).

4. Conclusion

The synthesized 3-substituted-4-amino (indole-3-aldehydo)-5-mercapto-1,2,4-triazole Schiff bases are bidentate ligands through coordination of azomethine nitrogen and sulfur to the metals, as confirmed by analytical, IR, PMR, ESR, electronic, magnetic, FAB mass and thermal studies. The semiconductor behavior has been inferred from solid state d.c. electrical conductivity studies.

Cobalt(II), nickel(II) and copper(II) complexes were most active towards *B. cereus* and moderately and weakly active against *S. aureus, P. aeruginosa* and *E. coli*. The activity of **2** and **II** were more than some commercial antibiotics. All compounds are insoluble in water and common organic solvents and decompose at higher temperatures, suggesting polymeric nature [35, 36].

All these observations indicate the structures shown in figures 6 and 7 for $CoL_2 \cdot H_2O$, $NiL_2 \cdot H_2O$ and CuL_2.

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