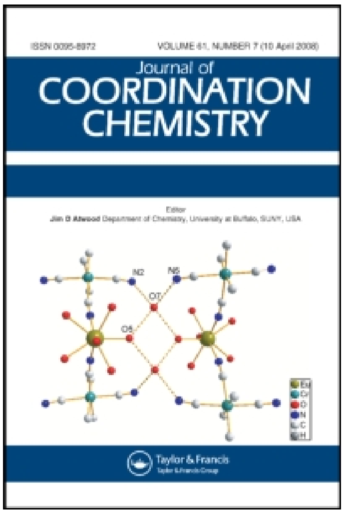

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Construction of mononuclear transition metal(II) complexes with bi- and tridentate, neutral hydrazone ligands with a quinoxaline hub

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Construction of mononuclear transition metal(II) complexes with bi- and tridentate, neutral hydrazone ligands with a quinoxaline hub

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A series of Co(II), Ni(II), Cu(II), and Zn(II) complexes of bi- and tridentate hydrazones were prepared. Ligands L^1 and L^2 were synthesized by the condensation of 2-mercapto-3-hydrazinoquinoxaline with 2-hydroxy-3-formylquinoline and 3-acetylcoumarin, respectively. The compounds were characterized by various spectro-analytical techniques and magnetic moment studies. The complexes are found to be monomeric and non-electrolytes. In these complexes, $[CuL^1Cl_2]$ has square pyramidal geometry and others have octahedral. The copper complexes are electrochemically active in the applied potential range.

Keywords: Quinoxaline; Quinoline; Coumarin; SNO donor system

1. Introduction

Hydrazones have versatility in coordinating metals and exhibit pharmacological and biological activities [1, 2]. The biological activities range from antibacterial to chemotherapy [3, 4]. The coordination chemistry of heterocyclic hydrazones constitutes one of the most important classes of sulfur, oxygen, and nitrogen donor ligands [5]. The formation of many metal complexes from these ligands shows their importance in coordination and bioinorganic chemistry. These hydrazones have also outstanding potential for inhibiting the growth of various pathogenic microorganisms, providing insight into new drug systems. Ligational behavior of multidentate ligands, especially chelates with different donors, is very interesting in coordination chemistry. The most popular donor set involves ONS or NNS displaying versatile coordination with monomers having one or two ligands attached to the metal, or dimers, in which the metal centers can be bridged through either the sulfur or oxygen of ligand skeleton or co-ligand (i.e., Cl, N_3, NCS, and CH_3COO) [6]. Structural features (stereochemical arrangement) of heterocyclic or acyclic cores which contain these donors play an

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important role in the coordination behavior [7]. Numerous examples of metal complexes derived from S, N, and O donors are of immense interest because of their versatile structural and functional properties and their applications in biochemistry, catalysis, medicine, and material research [8–10]. With all these findings, we prefer quinoxaline derivatives as the core moiety for the synthesis of metal complexes.

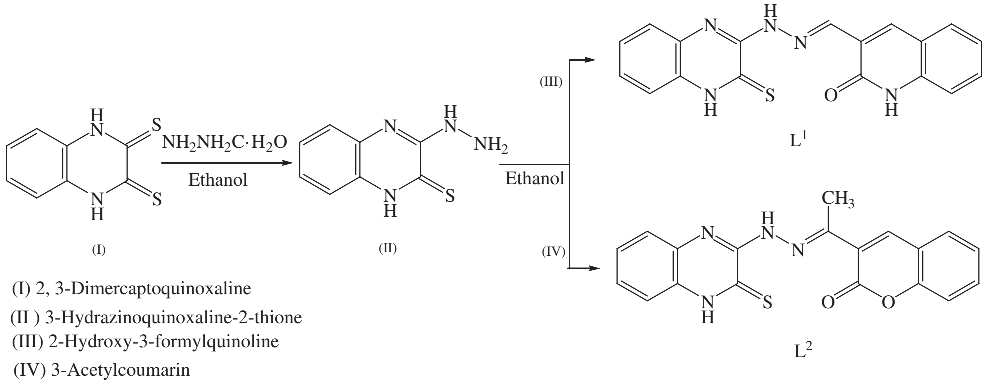
Quinoxaline derivatives are a very important class of nitrogen-heterocycles, widely used as pharmaceutical [11, 12] and electrical/photochemical materials [13–15]. Also, they can serve as a backbone for the construction of multidentate ligands [16, 17]. Quinoline, being the backbone for most of the natural products, is used for designing many compounds that have diverse pharmacological applications [18, 19]. Coumarin derivatives are well-known precursors for the design of ligands and complexes with multiple applications [20]. We have selected 3-hydrazinoquinoxaline-2-thione as a core for the synthesis of SNO donors. 3-Formylquinolinone and 3-acetylcoumarin scaffolds are condensed with the hydrazinoquinoxaline *via* Schiff base condensation and the resulting ligands are treated with transition metal(II) ions to form complexes. The ligational behavior of the ligands, the structural features and electrochemical behavior of the compounds are investigated.

2. Experimental

All chemicals used were of reagent grade and the solvents were distilled prior to use. The metal estimation was done by standard methods [21]. Carbon, hydrogen, nitrogen, and sulfur analyses were carried out on a Thermo quest elemental analyzer. Molar conductance measurements were made on an ELICO-CM-82 conductivity bridge with a cell having cell constant 0.51 cm^{-1}. Magnetic measurements were made on a Faraday balance at room temperature by using $Hg[Co(SCN)_4]$ as calibrant. Electronic spectra of the compounds in dimethyl sulfoxide (DMSO) were recorded using a VARIAN CARY 50 Bio UV-Vis spectrophotometer. Infrared (IR) spectra of ligands and their complexes were recorded as KBr pellets from 4000 to 400 cm^{-1} on a Nicolet 170 SX FT-IR spectrometer. ^{1}H-NMR spectra of ligands and zinc(II) complexes were recorded in DMSO-d_6 on a Bruker 300 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. Electron paramagnetic resonance (EPR) spectra of copper(II) complexes were recorded at room temperature on a Varian E-4 X-band spectrometer using tetracyanoethylene (TCNE) as g-marker. Electrochemical measurements were carried out on a CHI 1110A electrochemical analyzer (USA) at room temperature. Glassy carbon, Pt wire, and non-aqueous Ag^+/AgCl were used in the analysis as working electrode, counter electrode, and reference electrode, respectively, and tetramethylammonium chloride was used as the supporting electrolyte. Precursors, 2,3-dimercaptoquinoxaline [22], 2-hydroxy-3-formylquinoline [23], 3-acetylcoumarin [24], were prepared by the method reported earlier.

2.1. *Preparation of 2-mercapto-3-hydrazinoquinoxaline*

Hydrazine hydrate (0.025 mol, 50 mL) was added dropwise to hot ethanolic solution of 2,3-dimercaptoquinoxaline (0.005 mol, 50 mL) and then the reaction mixture was



(I) 2, 3-Dimercaptoquinoxaline
(II) 3-Hydrazinoquinoxaline-2-thione
(III) 2-Hydroxy-3-formylquinoline
(IV) 3-Acetylcoumarin

Scheme 1. Schematic representation for the preparation of ligands.

refluxed for 3–4 h in a water bath. The resulting light orange solid was filtered hot, washed with hot alcohol, and dried.

2.2. *Preparation of the ligand*

An ethanolic solution of 2-hydroxy-3-formylquinoline (0.005 mol, 0.86 g) was added to a hot ethanolic solution of 3-hydrazinoquinoxaline-2-thione (0.005 mol, 0.96 g) and refluxed for 3–4 h in a water bath; the resulting orange solid product was filtered hot, then washed with hot alcohol and dried (scheme 1). The same procedure was followed for the preparation of L^2 by using 3-acetylcoumarin (0.005 mol, 0.94 g; scheme 1).

2.3. *Synthesis of the complexes*

Appropriate amount of L^1 (0.002 mol, 0.69 g) was taken in 30–40 mL of hot ethanol. To this mixture, hot ethanolic solution of metal(II) chloride {$CoCl_2 \cdot 6H_2O$ (0.002 mol, 0.475 g), $NiCl_2 \cdot 6H_2O$ (0.002 mol, 0.475 g), $CuCl_2 \cdot 2H_2O$ (0.002 mol, 0.341 g), and $ZnCl_2$ (0.002 mol, 0.272 g)} was added dropwise with stirring at 60–65°C. After completely adding the metal salt solution, the reaction mixture was stirred for another 30–40 min at the same temperature and refluxed for 3–4 h in a water bath. The isolated complexes were filtered while hot, washed with hot aqueous ethanol and dried. The same procedure was followed for the preparation of complexes of L^2 (0.002 mol, 0.756 g). Data for C, H, and N analysis are given in table 1.

3. Results and discussion

3.1. *IR spectral studies*

IR absorptions of both L^1 and L^2 and their metal complexes along with assignments are summarized in table 2. L^1 and L^2 show sharp bands at 1608 and 1596 cm^{-1},

Table 1. Analytical, conductivity, and magnetic data for the ligands and complexes.

	Compounds	Elemental analysis (%) found/Calcd						Molar conductance, λ_M (mho cm^{-2} mol^{-1})	Magnetic moment, μ_{eff} (B.M.)
		C	H	N	S	M	Cl		
L^1	$(C_{18}H_{13}N_5OS)$	62.14/62.24	3.25/3.74	19.93/20.17	9.08/9.22	–	–	–	–
1	$[Co(C_{18}H_{13}N_5OS)Cl_2 \cdot H_2O]$	43.18/43.72	2.84/3.03	14.02/14.17	6.14/6.47	11.72/11.94	13.98/14.17	8.3	5.22
2	$[Ni(C_{18}H_{13}N_5OS)Cl_2 \cdot H_2O]$	43.32/43.76	2.93/3.03	14.04/14.18	6.13/6.48	11.06/11.8	13.97/14.18	8.9	2.95
3	$[Cu(C_{18}H_{13}N_5OS)Cl_2]$	44.51/44.95	2.26/2.70	14.17/14.56	6.26/6.65	13.02/13.25	14.23/14.56	9.4	1.73
4	$[Zn(C_{18}H_{13}N_5OS)Cl_2 \cdot H_2O]$	43.03/43.20	2.88/3.00	14.76/14.00	5.97/6.40	12.92/13.08	13.85/14.00	6.9	Diamagnetic
L^2	$(C_{19}H_{14}N_4O_2S)$	62.45/62.98	3.25/3.86	15.18/15.46	8.41/8.83	–	–	–	–
5	$[Co(C_{19}H_{14}N_4O_2S)_2Cl_2] \cdot H_2O$	52.02/52.35	3.10/3.44	12.31/12.85	7.19/7.34	6.29/6.77	7.89/8.03	12.5	5.18
6	$[Ni(C_{19}H_{14}N_4O_2S)_2Cl_2] \cdot H_2O$	52.14/52.37	3.09/3.44	12.24/12.86	7.15/7.35	6.59/6.73	7.84/8.04	13.6	3.2
7	$[Cu(C_{19}H_{14}N_4O_2S)_2Cl_2] \cdot H_2O$	51.90/52.08	3.11/3.42	12.17/12.79	7.15/7.31	7.03/7.25	7.63/7.99	15.4	1.98
8	$[Zn(C_{19}H_{14}N_4O_2S)_2Cl_2] \cdot H_2O$	51.61/51.97	3.24/3.41	12.05/12.76	6.89/7.29	7.11/7.45	7.45/7.97	11.2	Diamagnetic

Table 2. IR spectral data of the ligands and their complexes.

Compound	ν(C=N) (Azomethine) (cm^{-1})	ν(C=O) (Quinoline) (cm^{-1})	ν(C=S) (cm^{-1})	ν(C=O) (Coumarin) (cm^{-1})	$\nu(H_2O)$ (cm^{-1})
L^1	1608	1660	1255	–	3431
1	1556	1636	1228	–	3406
2	1597	1638	1222	–	3385
3	1545	1639	1220	–	3419
4	1598	1638	1223	–	3401
L^2	1596	–	1246	1725	–
5	1609	–	1236	1728	3432
6	1609	–	1218	1729	3434
7	1609	–	1230	1724	3430
8	1608	–	1211	1728	3402

respectively, assigned to ν(C=N). This band shifts to low frequency for **1**–**4** and to high frequency for **5**–**8** due to the coordination of azomethine nitrogen to metal [25]. Bands at 1660 and 1725 cm^{-1} are attributed to ν(C=O) of quinoline [26] and coumarin [20], respectively. The absence of a band at 2500 cm^{-1} attributable to ν(S–H) in both ligands rules out thione–thiol tautomerism and suggests the stable thione form of the ligand. The coordination of the quinoline carbonyl is evidenced by negative shift for ν(C=O) in complexes. The ν(C=O) of coumarin remains unaltered upon complexation suggesting non-involvement in coordination. The ν(C=S) in **1**–**8** shifts lower and decreases in intensity due to the thione sulfur coordination [27], further supported by the presence of ν(N–H) in spectra of the complexes and ^{1}H-NMR. Bands at 3300–3400 cm^{-1} indicate the presence of coordinated/crystal water.

3.2. *^{1}H-NMR study*

^{1}H-NMR spectra of the ligands and Zn(II) complexes were recorded in DMSO-d_6 from 0 to 16 ppm. The peak observed at 8.62 ppm in L^1 is assigned to azomethine proton, which shifts downfield upon complexation, confirming coordination of the azomethine nitrogen [28]. Quinoxaline ring –NH resonates at 11.62 and 10.64 ppm, respectively, for L^1 and L^2, and quinoline ring –NH for L^1 resonates at 12.02 ppm. A multiplet at 6.93–7.91 ppm is assigned to aromatic protons of the ligands. Relative to the free ligands, zinc complexes show small shifts in proton resonance frequencies, attributable to variation in electron density and steric constraints brought about in the compounds upon complexation [29]. ^{1}H-NMR data of ligands and complexes are given in "Supplementary material" (table 3).

3.3. *Molar conductivity*

Molar conductance values of the complexes measured at room temperature in DMSO at 10^{-3} mol dm^{-3} concentration fall in the range of 6.9–15.4 $\Omega^{-1} cm^2 mol^{-1}$ (table 1), which is in agreement with non-electrolytes [30].

3.4. *Electronic spectra*

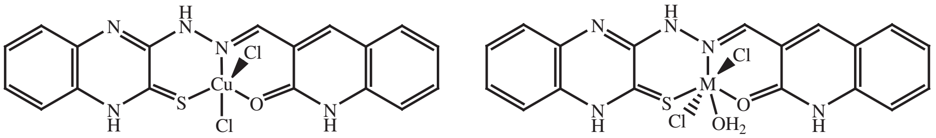
Electronic spectra of the ligands and their complexes were measured in dimethylformamide (DMF). The free ligands exhibit strong absorptions at 275–292 nm ($\varepsilon \sim 15{,}000\,\mathrm{L\,cm^{-1}\,mol^{-1}}$) due to intraligand π–π^* transitions; these bands are almost unchanged in spectra of complexes. Absorptions at 350–370 nm ($\varepsilon \sim 12{,}000\,\mathrm{L\,cm^{-1}\,mol^{-1}}$) are attributed to the n–π^* transition associated with azomethine, and a red shift of these absorptions upon complexation indicates the coordination of azomethine nitrogen [31, 32]. In the electronic spectra of cobalt (**1** and **5**), bands at 465–434 nm ($\varepsilon \sim 20{,}000\,\mathrm{L\,cm^{-1}\,mol^{-1}}$) are assigned for ligand-to-metal charge transfer (LMCT) transitions. A broad distinct peak observed at 550 nm ($\varepsilon \sim 200\,\mathrm{L\,cm^{-1}\,mol^{-1}}$) assignable to ${}^4T_{1g} \rightarrow {}^4A_{2g}$ suggests octahedral structure for the complexes [33]. Both the nickel complexes (**2** and **6**) have LMCT transitions at 423 nm ($\varepsilon \sim 20{,}000\,\mathrm{L\,cm^{-1}\,mol^{-1}}$) and d–d transitions around 600 nm ($\varepsilon \sim 150\,\mathrm{L\,cm^{-1}\,mol^{-1}}$) [34] assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}$ indicating octahedral geometry. Electronic spectra of copper complexes exhibit a broad intense peak at 445 nm ($\varepsilon \sim 25{,}000\,\mathrm{L\,cm^{-1}\,mol^{-1}}$) assignable to S → Cu(II) LMCT and **3** exhibits a broad peak at 565 nm ($\varepsilon \sim 100\,\mathrm{L\,cm^{-1}\,mol^{-1}}$) with low energy shoulder, assigned for square pyramidal geometry [35]. In **7**, a band at 565 nm is attributed to d–d transition. Cu(II) can adopt square-planar, square-pyramidal, trigonal-bipyramidal, octahedral, and tetrahedral geometries, which are generally distorted from idealized structures. The d–d spectra shown by these coordination geometries are distinctive only in the case of the tetrahedral environment where the absorptions occur at much lower energies and generally show well-separated absorptions. For all other distorted geometries, spectra show closely spaced absorption manifolds. Hence it is difficult to predict the accurate structure for the complexes only on the basis of electronic spectra. Zinc(II) complexes (**4** and **8**) show strong absorptions at 370–390 nm for charge transfer.

3.5. *Magnetic studies*

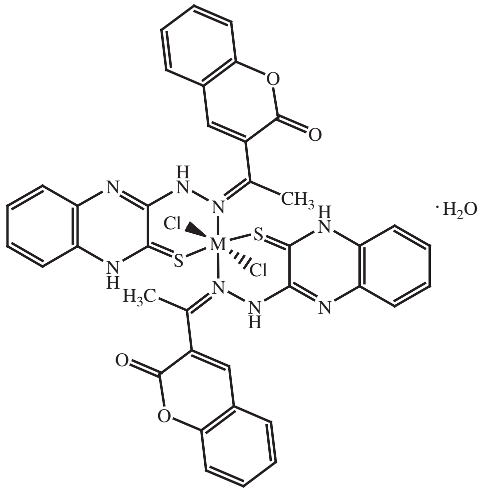
The magnetic moment values of the synthesized metal complexes are given in table 1. The magnetic moments of **1** and **5** are 5.22 and 5.18 B.M. at room temperature, indicating high-spin octahedral cobalt(II) complexes [36, 37]. For **2** and **6**, magnetic moment values are 2.95 and 3.2 B.M., respectively, indicating octahedral configuration [38], with two unpaired electrons. The effective magnetic moment values of copper **3** and **7** are 1.73 and 1.98 B.M. The higher magnetic moment values of these complexes can be rationalized in terms of the orbital contribution of donor atoms toward the spin-only value [36, 37].

3.6. *EPR spectral studies*

The solid state X-band EPR spectra of copper complexes **3** and **7** exhibit isotropic intense broad signals with g_{iso} values 2.06 and 2.08, respectively, without hyperfine splitting. No half field absorption was observed indicating the absence of metal–metal interaction. Similar type of spectra were reported for complexes bearing large organic ligand substituents having considerable covalent character for metal–ligand bonds [39].



Where M = Co, Ni and Zn



Where M = Co, Ni, Cu and Zn

Figure 1. Proposed structures of complexes.

3.7. *Fast atom bombardment mass study*

Fast atom bombardment (FAB) mass spectral studies provide supporting evidence for the proposed complexes (figure 1). The two copper complexes **3** and **7** show molecular ion peaks at *m*/*z* 486 and 882 that correspond to the formula weight [CuL^1Cl_2] and [$Cu(L^2)_2Cl_2$]·H_2O, respectively. Besides, the spectra show some prominent peaks corresponding to various molecular ion fragments. It is difficult to assign the fragmentation pattern and isotopic ratio of metal and chlorine due to the complex nature of the spectra. FAB mass spectra of both complexes are given in "Supplementary material" (figures 2 and 3).

3.8. *Cyclic voltammetry study*

Cyclic voltammetry is the most versatile electro-analytical technique used for the study of electrochemical properties of metallo-organic species. Important parameters of cyclic voltammograms are the magnitudes of the peak current (I_{pa}, I_{pc}) and peak potential (E_{pa}, E_{pc}). Electrochemical properties of L^1 and L^2 and **1–8** were studied in the potential range 1.2 to −1.6 V. Except for **3** and **7**, all the compounds are electrochemically inert in the potential range. Cyclic voltammograms of **3** and **7** show a well-defined redox process corresponding to the Cu(II)/Cu(I) couple. Complex **3** exhibits quasi-reversible process with cathodic peak at $E_{pc} = 0.51$ V corresponding to Cu(II) → Cu(I) and the respective anodic peak for Cu(I) → Cu(II) at $E_{pa} = 0.55\,V$. In **7**, E_{pa} and E_{pc} are 0.47 and 0.38 V, respectively. In both **3** and **7**, the value of ΔE_p, i.e., the separation between the anodic and cathodic peak potentials, is greater than 59 mV indicating quasi-reversible redox [40]. The dependency of peak potentials on scan rates and value (~1) for I_a/I_c (ratio of oxidative to reductive peak currents) indicates simple one-electron transfer [41]. Representative cyclic voltammogram of **3** is given in "Supplementary material" (figure 4).

4. Conclusion

In this study, the synthesis and structural investigations of sulfur-containing hydrazone ligands and their transition metal(II) complexes are presented. Structures of the ligands and complexes were confirmed by spectral and analytical techniques. The ligand-to-metal (L : M) stoichiometry is 1 : 1 and is 2 : 1 in case of L^1 and L^2, respectively. The ligands coordinate to metal in thione rather than thiol form and give evidence for non-involvement of lactonic oxygen (**5–8**). All the complexes have octahedral geometry except $[CuL^1Cl_2]$, which is square pyramidal. Only the copper complexes are electrochemically active in the applied potential range. Further studies are needed to understand the mechanism of electron transfer and to check their applicability as pharmaceuticals. These compounds can be used as structural and functional models for various metallobiosites. However, detailed studies are required to analyze the utility of these compounds as biomimetics.

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