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Synthesis and Antimicrobial Screening of Bivalent Metal Ion Complexes with Schiff Base Derived from 3,4-Diethyl Isoquinolone†

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The Co(II), Ni(II) and Cu(II) complexes have been synthesized with 3,4-diethyl isoquinolone thiosemicarbazone [DIQT]. All the complexes were identified and confirmed by elemental analyses, IR spectra, electronic spectra, molar conductivity, molar mass and magnetic susceptibility data. The molar conductance measurements revealed that the prepared complexes are non-electrolytic in nature. The magnetic susceptibility and electronic spectral data indicates the geometry of the complexes is octahedral in nature. Their spectral data proposed the coordination sites of the free ligand with the central metal ion through azomethine N and thione S. The remaining coordination positions are satisfied through negative ions such as Cl^-, Br^-, I^-, NO_3^- and ClO_4^-. The ligand and its metal complexes were tested for their antimicrobial activity against *Aspergillus niger* and *Aspergillus flavous*.

Key Words: Schiff base, 3,4-Diethyl isoquinolone thiosemicarbazone, Co(II), Ni(II) and Cu(II) complexes, Spectral study, Antimicrobial screening.

INTRODUCTION

The coordination compounds of thisemicarbazone constitute an interesting study both from the point of view of the adopted structure as for most important practical applications in various fields, from technical to medical literature survey reveal these complex combinations have several biological properties such as, antitumour[1], antifungal[2] and antibacterial[3]. Schiff bases and their metal complexes have been studied because of their interesting and important properties such as their ability to reversibly bind oxygen and their use in oxygenation and oxidation reaction of organic compounds, redox systems in biological processes[6], Aldol reactions[7], in textile industries[8], in radiopharmaceuticals[9], oxidation of DNA[10] and also in host of other important spheres. Keeping the above facts in mind and in continuation of our earlier work[11-18] in this field we herein report the synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes with, 3,4-diethyl isoquinolone thiosemicarbazone.

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EXPERIMENTAL

All the chemicals used of AR grade. The solvents were used without any purification. The metal contents were determind using standard method[19]. The analytical data of the complexes and their molar conductance values are given in Table-1. Conductivity measurements were made using Systronics conductivity meter model 303 in DMF. Electronic spectra of the complexes were recorded in DMF on Cary-2390 spectrophotometer. The IR spectra of ligands and its complexes were taken on Perkin-Elmer model 577 using KBr disc. Magnetic susceptibility were measured by Gouy method using $Hg[Co(NCS)_4]$ as a calibrant.

Preparation of the ligand: The ligand 3,4-diethyl isoquinolone thiosemicarbazone [DIQT] was prepared by condensation of ethanolic solution of 3,4-diethyl isoquinolone with thiosemicarbazide hydrochloride dissolved in 10 % ethanolic solution of sodium acetate. The resulting reaction mixture was refluxed on water bath for 3-4 h with occasional stirring. After cooling the refluxed solution, colourless solid was obtained which was separated by filtration, washed and finally dried and crystallized with tetrahydrofuran to furnish 3,4-diethyl isoquinolone thiosemicrbazone as colourless prismatic needles m.p. 223 ± 1 ºC. Yield 60-70 %.

Preparation of the complexes: The complexes of Co(II), Ni(II) and Cu(II) were prepared by the reaction between ethanolic solution of respective metal chloride/ metal nitrate (0.01 M) with ethanolic solution of ligand 3,4-diethyl isoquinolone thiosemicarbazone (0.02 M). The resulting reaction mixture was heating on water bath for 2-3 h with occasional stirring. The procedure carried out in each case were similar with slight variation of timing of reflux. On cooling solid coloured complexes separated out which was filtered, washed with ethanol, dried and recrystallized with tetrahydrofuran. Yield in cases 60-65 %.

RESULTS AND DISCUSSION

A careful interpretation of infrared spectral bands (Table-2) of the ligand DIQT and the complexes $[M(DIQT)_2X_2]$ reveals that there are certain bands of the ligand which are appreciable affected after the complex formation indicating the donor atoms of coordination position of the ligand to form the linkage with metal ions. The ligand exhibit a sharp and strong band at 3400 cm^{-1} assignable[20,21] to ν(N-H) vibration. In spectra of all the complexes this band without change in position and intensity, clearly indicating non involvement of nitrogen atom of either amino of imino group in the coordination with metal ion. A broad and sharp band obtained at 1520 cm^{-1} in the ligand assignable[20,22,23] to ν(C=N) vibration. This band has been reduced by 20-30 cm^{-1} in complexes suggesting coordination of azomethine N with metal ion. The next IR band of the ligand shows a broad and strong band at 780 cm^{-1} assignable[20,23,24] to ν(C=S) vibration. After complexation this band shows red shift with slightly reduced intensity. The shift of the band and change in intensity indicate coordination of thione sulphur with metal ion.

TABLE-1
ANALYTICAL, COLOUR, MOL. MASS, MAGNETIC SUSCEPTIBILITY, MOLAR CONDUCTIVITY, ELECTRONIC SPECTRA AND DECOMPOSITION TEMPERATURE OF THE LIGAND DIQT AND ITS METAL COMPLEXES

Compound (colour)	Mol. mass	Elemental analysis (%): Found (calcd.)				μ_{eff} (BM)	Ω_m (ohm^{-1} cm^2 mol^{-1})	λ_{max} electronic (cm^{-1})	DT (°C)
		M	C	H	N				
DIQT (Colourless)	273.00	–	61.41 (61.53)	20.40 (20.51)	6.14 (6.22)	–	–	–	–
[Co(DIQT)$_2$Cl$_2$] (Red)	675.93	8.62 (8.71)	49.58 (49.70)	16.45 (16.56)	4.97 (5.03)	5.12	12.7	9360, 17410, 21718	236
[Co(DIQT)$_2$Br$_2$] (Rose red)	764.748	7.61 (7.70)	43.87 (43.93)	14.53 (14.64)	4.38 (4.44)	5.16	13.3	9390, 17320, 21732	249
[Co(DIQT)$_2$I$_2$] (Light pink)	858.73	6.79 (6.86)	38.94 (39.12)	12.95 (13.04)	3.87 (3.95)	4.89	13.4	9370, 17460, 21732	241
[Co(DIQT)$_2$(NO$_3$)$_2$] (Pink)	728.93	7.93 (8.08)	45.89 (46.09)	15.24 (15.30)	4.58 (4.66)	4.99	13.7	9400, 17430, 21760	239
[Ni(DIQT)$_2$Cl$_2$] (Green)	675.71	8.57 (8.68)	49.58 (49.72)	16.48 (16.57)	4.94 (5.03)	3.14	17.4	13560, 18300, 25300	211
[Ni(DIQT)$_2$Br$_2$] (Pale green)	764.52	7.58 (7.67)	43.83 (43.91)	14.53 (14.64)	4.36 (4.44)	3.12	17.9	15600, 18310, 25320	214
[Ni(DIQT)$_2$I$_2$] (Light green)	858.51	6.77 (6.83)	39.04 (39.13)	12.93 (13.04)	3.89 (3.96)	3.10	18.4	13260, 17980, 24700	222
[Ni(DIQT)$_2$(NO$_3$)$_2$] (Yellow)	728.71	87.97 (8.05)	45.92 (46.10)	15.27 (15.36)	4.59 (4.66)	3.17	19.7	13330, 18260, 24770	226
[Cu(DIQT)$_2$Cl$_2$] (Blue)	680.54	9.26 (9.33)	49.24 (49.37)	16.33 (16.45)	4.92 (4.99)	1.89	10.4	12100, 22900	230
[Cu(DIQT)$_2$Br$_2$] (Blue)	769.34	8.17 (8.25)	43.55 (43.67)	14.39 (14.55)	4.36 (4.41)	1.87	9.3	12300, 22960	240
[Cu(DIQT)$_2$(NO$_3$)$_2$] (Deep blue)	733.54	8.60 (8.66)	45.62 (45.80)	15.14 (15.26)	4.57 (4.63)	1.94	8.6	12400, 23610	248

DT = Decomposition temperature.

The conclusive evidence of bonding of ligand to metal through oxygen atom of nitrate, nitrogen atom of azomethine group and sulphur atom of thiosemicarbazone moiety is indicated by the appearance of far IR region bands due to ν(M-O)[25,26] at 530-505 cm^{-1}, ν(M-N)[25,26] at 475-455 cm^{-1} and ν(M-S)[25,26] at 425-395 cm^{-1}, respectively. The evidence of metal halogen linkage is supported by the low molar conductance value of the complexes in the range 8.6-19.7 ohm^{-1} cm^2 mol^{-1} and appearance of a band in the far IR region at 325-265 cm^{-1} assigned[25-27] to ν(M-X) (X = Cl$^-$, Br$^-$, I$^-$). The next IR bands at 1630 and 1500 cm^{-1} with a separation of 120 cm^{-1} suggest mono coordinated behaviour of nitrate group[28].

TABLE-2
INFRARED SPECTRAL DATA (cm^{-1}) AND ITS COMPLEXES WITH Co(II), Ni(II) AND Cu(II)

Compounds	ν(N-H)	ν(C=N)	ν(C=S)	ν(M-O)	ν(M-N)	ν(M-S)	ν(M-X)
DIQT	3400 s,b	1520 s,b	780 s,b				
[Co(DIQT)$_2$Cl$_2$]	3400 s,b	1495 m,b	755 m,b		470 m	405 m	300 m
[Co(DIQT)$_2$Br$_2$]	3400 s,b	1495 m,b	760 m,b		470 m	410 m	325 m
[Co(DIQT)$_2$I$_2$]	3400 s,b	1490 m,b	755 m,b		475 m	415 m	315 m
[Co(DIQT)$_2$(NO$_3$)$_2$]	3400 s,b	1495 m,b	755 m,b	505 m	470 m	420 m	
[Ni(DIQT)$_2$Cl$_2$]	3400 s,b	1500 m,b	755 m,b		460 m	395	275 m
[Ni(DIQT)$_2$Br$_2$]	3400 s,b	1495 m,b	750 m,b		465 m	400	270 m
[Ni(DIQT)$_2$I$_2$]	3400 s,b	1490 m,b	750 m,b		465 m	400 m	
[Ni(DIQT)$_2$(NO$_3$)$_2$]	3400 s,b	1490 m,b	755 m,b	520 m	460 m	395 m	
[Cu(DIQT)$_2$Cl$_2$]	3400 s,b	1415 m,b	755 m,b		455 m	405 m	275 m
[Cu(DIQT)$_2$Br$_2$]	3400 s,b	1490 m,b	750 m,b		455 m	410 m	300 m
[Cu(DIQT)$_2$(NO$_3$)$_2$]	3400 s,b	1495 m,b	755 m,b	530 m	460 m	420 m	

Electronic spectra and magnetic susceptibility of the complexes: The Co(II) complexes display three band in the region 9400, 17400 and 21700 cm^{-1}, assigned to the transitions, $^4T_{2g}(F)\leftarrow{}^4T_{1g}(F)$, $^4A_{2g}(F)\leftarrow{}^4T_{1g}(F)$ and $^4T_{1g}(P)\leftarrow{}^4T_{1g}(F)$, respectively which indicate octahedral[29,30] geometry. The octahedral geometry of Co(II) complex supported[31-33] by high μ_{eff} value in the range 4.87-5.16 BM. The Ni(II) complexes exhibits three bands in the region 13600-13260, 18360-17980 and 25320-24890 cm^{-1} assigned to transition $^3T_{2g}(F)\leftarrow{}^3A_{2g}(F)$, ${}_3T_{1g}(F)\leftarrow{}^3A_{2g}(F)$ and $^3T_{1g}(P)\leftarrow{}^3A_{2g}(F)$, respectively which indicate octahedral[30-34] geometry for all the Ni(II) complexes, which is further supported[31,32,35] by the μ_{eff} value in the range 3.10-3.17 BM for all the Ni(II) complexes. The Cu(II) complexes display two ligand field bands in the region 12300-11700 and 23400-22960 cm^{-1} assigned to the transitions $^2T_{2g}\leftarrow{}^2E_g$ and charge transfer band, respectively. The electronic spectra of all the Cu(II) complexes suggesting octahedral[30,36] geometry around central metal ion. The magnetic moment value of Cu(II) complexes are lie in the range 1.87-1.94 BM[31,32,37].

Molar conductivity: Molar conductance data of the complexes were measured in the solvent DMF and the complexes were found to be non electrolytic[38] in nature. The molar conductance value of the complexes are in the range 8.6-19.7 ohm^{-1} cm^2 mol^{-1}.

Antifungal activity: Fungicidal activity of the ligand and their metal complexes were done by disc plate method[39] on *Pencillum expansum* and *Aspergillus flavus*. On comparison with reference to fungicide, the complexes were found to be more effective than free ligand due to chelation theory[40].

Conclusion

On the basis of above mentioned observations the complpexes were tentatively proposed monomeric octahedral geometry as shown in Fig. 1.

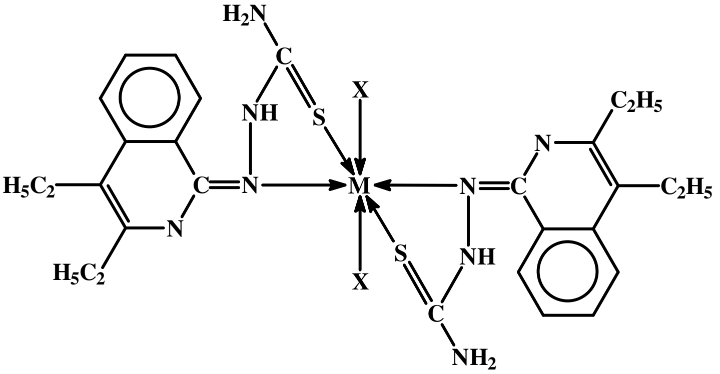

Fig. 1. [M(DIQT)$_2$X$_2$]; M = Co(II), Ni(II) and Cu(II); X = Cl^-, Br^-, I^-, or NO_3^-

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