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Synthesis, Characterization and Antimicrobial Screening of Cobalt(II), Nickel(II) and Copper(II) Complexes with Schiff Base Derived from 2-Aroyl Quinoxaline Semicarbazone

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Complexes of general formula $[M(AQSC)_2X_2]$, where M = cobalt(II), nickel(II) and copper(II), AQSC = 2-aroyl quinoxaline semicarbazone, $X = Cl^-$, Br^-, I^-, NO_3^- and ClO_4^- have been prepared. Complexes were characterized by analytical analyses and physico-chemical methods. The ligand, 2-aroyl quinoxaline semicarbazone behaves as a neutral, bidentate chelateing agent and bonded to the metal ion through azomethine nitrogen and oxygen atom of semicarbazone moiety. The remaining coordinating sites are occupied by anions such as Cl^-, Br^-, I^-, NO_3^- and ClO_4^-. Electronic spectra and magnetic susceptibility measurements reveal octahedral geometry. The complexes were found to be non-electrolytic in nature on the basis of low value of molar conductance. The ligand as well as metal complexes have been screened for their antibacterial and antifungal activity.

Key Words: 2-Aroyl quinoxaline semicarbazone, Co(II), Ni(II), Cu(II), Schiff base, Antimicrobial, Antifungal activity.

INTRODUCTION

Quinoxaline derivative are reported as biologically active compounds[1-5]. Schiff bases and their metal complexes have been found to posses significant biological activities. Schiff base complexes continue to attract many researchers because of its wide application in the field of agriculture as pesticides and in medicine with their highly effective antibacterial and anticoagulant activities[6-9]. They acts as herbicides, insecticides, nematocides, rodenticides and plant growth regulators. Keeping the above facts in mind and in continuation of our earlier[10-20] work on Schiff base metal chelates, the preparation and characterization of Co(II), Ni(II) and Cu(II) complexes of with ligands 2-aroyl quinoxaline semicarbazone are reported.

EXPERIMENTAL

All the chemicals used were of analaR grade. The complexes were analyzed using standard procedures[21]. IR spectra were recorded on Perkin-Elmer-577 spectrophotometer using KBr disc. The electronic spectra of the complexes were recorded on a Cary 2390 spectrophotometer. Magnetic susceptibilities were measured using Gouy balance using mercury tetraisothiocyanatocobaltate as a calibrant. The molar conductance data was made on Systronics conductivity meter using DMF as the solvent.

Analytical, colour, magnetic moment, conductivity, electronic, spectral data and decomposition temperature are recorded in Table-1 and salient features of IR spectral data are recorded in Table-2.

TABLE-1
ANALYTICAL COLOUR, MAGNETIC SUSCEPTIBILITY, ELECTRONIC SPECTRAL AND CONDUCTIVITY MEASUREMENT VALUES FOR LIGAND AND ITS METAL COMPLEXES

Compounds (Colour)	m.w.	Elemental analysis (%): Found (calcd.)				μ_{eff} (BM)	λ_{max} electronic (cm^{-1})	Ω_m (ohm^{-1} cm^2 mol^{-1})	DT (ºC)
		M	C	H	N				
AQSC	292.000	–	65.87	23.82	4.72	–	–	–	–
(Colourless)			(65.75)	(23.97)	(4.79)				
$[Co(AQSC)_2Cl_2]$	713.930	8.29	53.91	19.73	3.98	5.04	10700, 14700,	4.1	288
(Brown)		(8.23)	(53.78)	(19.60)	(3.97)		21600		
$[Co(AQSC)_2Br_2]$	807.748	7.12	47.41	17.24	3.39	5.07	10400, 14910,	3.9	274
(Brown)		(7.29)	(47.53)	(17.33)	(3.46)		21660		
$[Co(AQSC)_2I_2]$	896.740	6.70	42.71	15.74	5.06	4.89	10200, 14800,	3.7	267
(Brown)		(6.57)	42.81)	(15.61)	(5.12)		21900		
$[Co(AQSC)_2(NO_3)_2]$	766.930	7.59	50.21	18.38	3.60	4.91	10340, 15000,	4.3	243
(Brown)		(6.68)	(50.06)	(18.25)	(3.65)		21800		
$[Co(AQSC)_2(ClO_4)_2]$	841.930	7.08	45.57	16.74	3.37	4.96	10600, 15100,	4.2	263
(Brown)		(6.99)	(45.60)	(16.62)	(3.32)		21200		
$[Ni(AQSC)_2Cl_2]$	713.710	8.29	53.68	19.72	3.87	3.23	12600, 17920,	2.7	291
(Greenish yellow)		(8.22)	(53.80)	(19.61)	(3.92)		24610		
$[Ni(AQSC)_2Br_2]$	802.528	7.39	47.63	17.33	3.92	3.18	12900, 18300,	2.6	278
(Greenish yellow)		(7.31)	(47.84)	(17.94)	(3.48)		23100		
$[Ni(AQSC)_2I_2]$	896.520	6.71	42.74	15.76	3.07	3.17	12990, 18040,	2.4	261
(Greenish yellow)		(6.54)	(42.83)	(15.61)	(3.12)		23300		
$[Ni(AQSC)_2(NO_3)_2]$	766.710	7.58	50.24	18.18	3.59	3.10	13000, 18200,	2.9	281
(Greenish yellow)		(7.65)	(50.04)	(18.25)	(3.65)		24500		
$[Ni(AQSC)_2(ClO_4)_2]$	841.710	7.06	45.49	16.76	3.38	3.22	12800, 18290,	2.5	279
(Greenish yellow)		(6.97)	(45.62)	(16.63)	(3.32)		24580		
$[Cu(AQSC)_2Cl_2]$	718.540	8.92	53.31	19.60	3.82	1.87	13160, 16310	3.8	301
(Green)		(8.84)	(53.44)	(19.48)	(3.89)				
$[Cu(AQSC)_2Br_2]$	807.358	7.93	47.68	17.21	3.39	1.94	13200, 16260	4.5	288
(Green)		(7.87)	(47.56)	(17.34)	(3.46)				
$[Cu(AQSC)_2(NO_3)_2]$	771.540	8.16	49.89	18.23	3.67	1.88	13000, 16500	4.6	289
(Green)		(8.23)	(49.77)	(18.14)	(3.62)				
$[Cu(AQSC)_2(ClO_4)_2]$	816.540	7.58	45.28	16.62	3.36	1.90	13060, 16400	4.4	280
(Green)		(7.50)	(45.36)	(16.53)	(3.30)				

*DT = Decomposition temperature.

Preparation of the ligand: 2-Aroyl quinoxaline was prepared by modifying the earlier reported method[22]. Ethanolic solution of 2-aroyl quinoxaline was treated with semicarbazide hydrochloride dissolved in 10 mL ethanolic solution of sodium acetate. The resulting mixtures were heated on water bath for 3-4 h with frequent stirring. The precipitate was collected, washed with ether, treated with dilute sodium carbonate solution. The solid was washed thoroughly with water and recrystallized with ethanol to furnish 2-aroyl quinoxaline semicarbazone as colourless compound. m.p. 186 ± 1 ºC, yield 70-75 %.

TABLE-2
INFRARED SPECTRAL BANDS OF LIGAND AQSC AND ITS METAL COMPLEXES

Compounds	ν(C=N)	ν(C=O)	ν(M-O)	ν(M-N)
AQSC	1620 b	1780 s,b	–	–
$[Co(AQSC)_2Cl_2]$	1590 m,b	1755 m,b	510 m	405 m
$[Co(AQSC)_2Br_2]$	1625 m,b	1750 m,b	500 m	410 m
$[Co(AQSC)_2I_2]$	1595 m,b	1750 m,b	515 m	400 m
$[Co(AQTC)_2(NO_3)_2]$	1625 m,b	1755 m,b	510 m	405 m
$[Co(AQSC)_2(ClO_4)_2]$	1590 m,b	1755 m,b	520 m	410 m
$[Ni(AQSC)_2Cl_2]$	1630 m,b	1750 m,b	515 m	410 m
$[Ni(AQSC)_2Br_2]$	1595 m,b	1755 m,b	500 m	415 m
$[Ni(AQSC)_2I_2]$	1630 m,b	1755 m,b	500 m	410 m
$[Ni(AQTC)_2(NO_3)_2]$	1595 m,b	1755 m,b	495 m	415 m
$[Ni(AQSC)_2(ClO_4)_2]$	1625 m,b	1750 m,b	490 m	405 m
$[Cu(AQSC)_2Cl_2]$	1595 m,b	1750 m,b	500 m	400 m
$[Cu(AQSC)_2Br_2]$	1630 m,b	1755 m,b	505 m	400 m
$[Co(AQTC)_2(NO_3)_2]$	1590 m,b	1755 m,b	505 m	410 m
$[Co(AQSC)_2(ClO_4)_2]$	1635 m,b	1755 m,b	500 m	415 m

Preparation of the complexes: The complexes of cobalt(II), nickel(II) and copper(II) have been formed by reacting an ethanolic solution of the ligands 2-aroyl quinoxaline semicarbazone. The procedure carried out in each case was of similar nature with a slight variation of timing of reflux. The complexes obtained in each case were cooled, filtered and washed with ethanol several times to remove any excess of the ligand. Finally complexes were washed with anhydrous diethyl ether and dried in an air oven. Yield 70-75 %.

RESULTS AND DISCUSSION

Infrared spectra: IR spectrum of the ligands 2-aroyl quinoxaline semicarbazone shows a broad band at 3100 cm^{-1} assigned[23,24] to ν(N-H) vibrations. In the spectra of the complex this band remains unaffected, indicating non-involvement of either terminal amino or secondary amino group in coordination. IR spectrum shows a broad band of medium intensity at 1620 cm^{-1} assigned[25] to ν(C=N). In the spectra of the complexes this band shows red shift with silghtly reduced intensity. The shift of the band and change in intensity suggest coordination of the azomethine nitrogen with metal ions. The linkage with azomethine nitrogen is further supported by the appearance of a far ir band, in the region 420-400 cm^{-1} in the complexes may be assigned[26] ν(M-N). The next IR spectra of the ligand AQSC shows a sharp and strong band at 1780 cm^{-1} which can be assigned[27] to ν(C=O). In the spectra of the complexes this band also shows red shift appearing in the region at 1750 cm^{-1} suggesting coordination through carbonyl oxygen of semicarbazone moiety. The linkage with oxygen atom is further supported by the appearance of a band in the far IR region at 520-495 cm^{-1} which may be assigned[28,29] as ν(M-O). The evidence of metal halogen is confirmed by the low value of molar conductance of the complexes in

the range 2.4-4.6 ohm^{-1} cm^2 mol^{-1} (Table-2) which indicate non-electrolytic nature of the complexes.

On the basis of above IR spectral assignments, it is proposed that ligand 2-aroyl quinoxaline semicarbazone behaves as neutral bidentate manner and coordination takes place through azomethine nitrogen and carbonyl oxygen of semicarbazone moiety. The remaining coordinating sites are occupied by anions such as Cl^-, Br^-, I^-, NO_3^- and ClO_4^-.

Electronic spectra and magnetic susceptibility of the complexes: The complexes of cobalt(II) display three bands in the regions, 10700-10200, 15300-14800, 21900-21200 cm^{-1} which may be assigned to $^4T_{2g}(F)\leftarrow{}^4T_{1g}(F)$, $^4A_{2g}(F)\leftarrow{}^4T_{1g}(F)$ and $^4T_{1g}(P)\leftarrow{}^4T_{1g}(F)$ transitions, respectively which proposes octahedral[30] geometry of the Co(II) complexes. The proposed octahedral geometry of the cobalt(II) complexes are further supported[31,32] by high magnetic moment value in the range 4.89-5.07 BM. The electronic spectra of all the nickel(II) complexes display three bands in regions, 13000-12600, 18300-17920, 24610-23020 cm^{-1} which may be assigned to $^3T_{2g}(F)\leftarrow{}^3A_{2g}(F)$, $^3T_{1g}(F)\leftarrow{}^3A_{2g}(F)$, $^3T_{1g}(P)\leftarrow{}^3A_{2g}(F)$ transitions, respectively, which proposed octahedral[30] geometry for all the nickel(II) complexes. The proposed octahedral geometry for all the nickel(II) complexes are further supported[31,32] by magnetic moment value for Ni(II) complexes in the range 3.10-3.23 BM. The complexes of copper(II) exhibit two spectral bands in the regions 13200-13000 and 16500-16260 cm^{-1}. These bands may be assigned to $^2T_{2g}\rightarrow{}^2E_g$ and charge transfer bands, respectively which support octahedral[30] geometry around central metal ion. The proposed geometry of copper(II) complexes is further supported[31,32] by magnetic moment value in the range 1.87-1.94 BM.

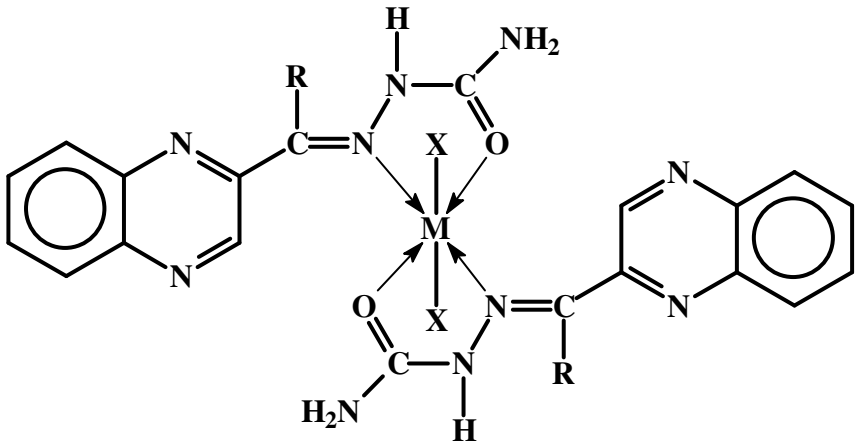

Fig. 1. $[M(AQSC)_2X_2]$; M = Co(II), Ni(II); X = Cl^-, Br^-, I^-, NO_3^- and ClO_4^-. M = Cu(II); X = Cl^-, Br^-, NO_3^- and ClO_4^-; R = Phenyl

Antimicrobial activity: Antimicrobial and antifungal activity of ligand 2-aroyl quinoxaline semicarbazone and their cobalt, nickel, copper complexeses have been tested by disc diffusion technique[33]. Following organism were used to find out antimicrobial activity, Gram negative bacteria *Escherichia coli* and fungi, *Aspergillus flavus* and *Aspergillus niger*. Filter paper discs of diameter 12 mm were used and the diameters of zones of inhibition formed around each disc after incubating for a period of 72 h at 25-30 ºC. Results were compared with known antibiotics tetracycline and dithane Z-78 sat same concentration. It is observed that on comparison with reference to antibiotic and fungicides, the complexes were found to be more effective than ligand 2-aroyl quinoxaline semicarbazone.

Conclusion

Thus on the basis of above studies it may be concluded that the complexes possess the octahedral geometry around the central metal ion.

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