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Metal Complexes of Biologically Potential Quinazoline Schiff Base

KUMAR RAJEEV KISHORE† and B.K. RAI*
Department of Chemistry, L.N.T. College, Muzaffarpur-842 002, India
E-mail: binodkr_rai@yahoo.co.in

Metal complexes of Co(II), Ni(II) and Cu(II) with Schiff base, 3- amino-2-phenyl-4(3*H*)quinazoline semicarbazone (APQS) have been synthesized and characterized by elemental analyses, molar mass, molar conductance, magnetic susceptibility, IR, UV-visible studies. These studies proposed tridentate behaviour of the ligand and coordination takes place through azomethine nitrogen, carbonyl oxygen and secondary amino group of quinazoline side chain. Electronic spectra and magnetic susceptibilities value proposes octahedral geometry for the complex. The molar conductance value indicates complexes were electrolytic in nature of the 1:2 type. The ligand APQS and its metal complexes were also screened for their antibacterial and antifungal activities.

Key Words: Schiff base, Co(II), Ni(II) and Cu(II), Semicarbazone, Antimicrobial, Antifungal screening.

INTRODUCTION

Presently the Schiff base possesses strong ability to form coordination compounds[1,2] and they have been extensively studied because of their broad spectrum of biological activities[3,4]. Synthetic flexibility of Schiff bases may permit the synthesis of multidentate ligands of diverse structure. Schiff bases possess anticancer, antibacterial properties and they have important effect to stimulate enzymes[5-7]. In continuation of our earlier work[8-14] on Schiff base complexes and in view of the importance of Schiff base complexes, some new complexes of Co(II), Ni(II) and Cu(II) with 3-amino-2-phenyl-4(3*H*)quinazoline semicarbazone are reported in this paper.

EXPERIMENTAL

All the chemicals and solvents used were of analytical reagent grade. Electronic spectra of the complexes were recorded in DMF on a carry 2390 spectrophotometer. The IR spectra of the ligand and their complexes were scanned on Perkin-Elmer 577 using KBr disc. The analysis of C, H and N were estimated by microanalytical techniques. Metal contents were estimated by precipitating metal extract in dilute HCl with diammonium hydrogen phosphate. Magnetic susceptibility of the complexes were measured by Gouy method using $Hg[Co(NCS)_4]$ as a calibrant. The molar conductance measurements were done on Systronics conductivity meter model 303 using DMF as a solvent.

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†Department of Chemistry, B.R.A. Bihar University, Muzaffarpur-842 001, India.

Preparation of the ligand: Ethanolic solution of 3-amino-2-phenyl-4(3*H*)-quinazoline-4-one 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 occasional stirring. After cooling, the precipitate was collected, washed with ether, treated with dilute sodium carbonate solution and filtered. The solid was washed thoroughly with water and crystallized with ethanol to furnish 3-amino-2-phenyl-4(3*H*)quinazoline semicarbazone as a colourless compound. m.p.186 ± 1 ºC, yield 60-65 %.

Preparation of the complexes: The complexes of Co(II), Ni(II) and Cu(II) have been synthesized by reacting an ethanolic of the ligand APQS (0.001 M) with ethanolic solution of corresponding salts [metal halide/metal nitrate] (0.001 M). The resulting mixture were heated on water bath for 2 h. The procedure carried out in each case was of similar nature with a slight variation of timing of reflux. The coloured 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 oven (yield 60-65 %).

TABLE-1
ANALYTICAL, COLOUR, MOL. MASS, MAGNETIC SUSCEPTIBILITY, CONDUCTIVITY MEASUREMENT AND DECOMPOSITION TEMPERATURE OF LIGAND APQS AND ITS METAL COMPLEXS

Compound (Colour)	Mol. mass	Elemental analysis (%): Found (Calcd.)				μ_{eff} (BM)	λ_{max} electronic (cm^{-1})	Ω_m (ohm^{-1} cm^2 mol^{-1})	DT (ºC)
		M	C	N	H				
APQS	204		61.07	28.47	4.71	–	–	–	–
(Colourless)			(61.22)	(28.57)	(4.76)				
$[Co(APQS)_2]Cl_2$	717.93	8.08	49.79	23.51	3.85	5.11	8100, 14800	126.4	220
(Red)		(8.20)	(50.14)	(23.40)	(3.90)		18900		
$[Co(APQS)_2]Br_2$	806.74	7.22	44.58	20.97	3.43	4.87	8630, 15000	131.2	236
(Reddish brown)		(7.30)	(44.62)	(20.80)	(3.47)		18400		
$[Co(APQS)_2]I_2$	900.74	6.47	39.88	18.57	3.06	4.91	8200, 14600	120.4	212
(Reddish brown)		(6.54)	(39.96)	(18.65)	(3.10)		18800		
$[Co(APQS)_2](NO_3)_2$	270.93	7.57	46.61	21.68	3.60	4.96	8700, 14200	128.3	201
(Red)		(7.64)	(46.69)	(21.79)	(3.63)		19200		
$[Ni(APQS)_2]Cl_2$	717.71	8.12	50.07	23.27	3.08	3.14	10900, 17300	117.4	242
(Green)		(8.18)	(50.15)	(23.40)	(3.90)		23100		
$[Ni(APQS)_2]Br_2$	806.52	7.21	44.53	20.72	3.42	3.15	10600, 17700	116.8	245
(Deep green)		(7.27)	(44.63)	(20.83)	(3.47)		23800		
$[Ni(APQS)_2]I_2$	900.52	6.59	39.88	18.57	3.16	3.13	10700, 17200	115.4	230
(Greenish brown)		(6.51)	(39.97)	(18.65)	(3.10)		23600		
$[Ni(APQS)_2](NO_3)_2$	770.71	7.50	46.58	21.68	3.68	3.16	10800, 17800	113.7	237
(Greenish brown)		(7.61)	(46.64)	(21.79)	(3.63)		23100		
$[Cu(APQS)_2]Cl_2$	722.54	8.67	49.77	23.20	3.80	1.92	12600, 24800	104.1	262
(Blue)		(8.79)	(49.82)	(23.25)	(3.87)				
$[Cu(APQS)_2]Br_2$	811.35	17.76	44.22	20.82	3.42	1.84	12200, 24900	109.8	253
(Blue)		(17.83)	(44.37)	(20.70)	(3.47)				
$[Cu(APQS)_2](NO_3)_2$	755.54	8.15	26.30	21.78	3.55	1.92	13000, 24300	111.3	248
(Blue)		(8.19)	(46.41)	(21.66)	(3.61)				

DT = Decomposition temperature.

RESULTS AND DISCUSSION

From the literature it is established that the semicarbazone ligand may be coordinated[15] as bidentate ligands, in most cases, *via* the azomethine nitrogen and carbonyl oxygen atom of semicarbazone moiety. The IR spectrum of the ligand APQS exhibits strong and broad band in the region 3200 cm^{-1} assigned[16,17] to ν(N-H). In the spectra of the complexes (Table-2) this band shows red shift with slightly reduced intensity. The shift of the band and change in intensity suggest coordination of secondary amino group with metal ion.

The IR spectrum of the ligand APQS exhibits strong and broad band at 1500 cm^{-1} assigned[17,18] to ν(C=N). In the spectra of complexes this band shows red shift with change in intensity. The shift of the band and change in intensity proposed coordination of the azomethine nitrogen with metal ion. The coordination of metal ion through secondary amino nitrogen and with azomethine N is further supported by the appearance of a far IR band in the region 425-395 cm^{-1} assigned[17,19] to ν(M-N).

TABLE-2
KEY IR SPECTRAL BANDS (cm^{-1}) OF LIGAND APQS AND ITS METAL COMPLEXES

Compounds	ν(N–H)	ν(C=N)	ν(C=O)	ν(M–O)	ν(M–N)
APQS	3200 s,b	1500 s,b	1720 s,b		
$[Co(APQS)_2]Cl_2$	3180 m,b	1470 m,b	1695 m,b	510 m	400 m
$[Co(APQS)_2]Br_2$	3175 m,b	1475 m,b	1700 m,b	515 m	410 m
$[Co(APQS)_2]I_2$	3180 m,b	1480 m,b	1700 m,b	525 m	395 m
$[Co(APQS)_2](NO_3)_2$	3180 m,b	1470 m,b	1700 m,b	490 m	400 m
$[Ni(APQS)_2]Cl_2$	3175 m,b	1475 m,b	1695 m,b	485 m	495 m
$[Ni(APQS)_2]Br_2$	3175 m,b	1475 m,b	1695 m,b	490 m	415 m
$[Ni(APQS)_2]I_2$	3170 m,b	1475 m,b	1690 m,b	490 m	410 m
$[Ni(APQS)_2](NO_3)_2$	3180 m,b	1475 m,b	1690 m,b	500 m	420 m
$[Cu(APQS)_2]Cl_2$	3175 m,b	1470 m,b	1690 m,b	510 m	425 m
$[Cu(APQS)_2]Br_2$	3180 m,b	1480 m,b	1690 m,b	510 m	395 m
$[Cu(APQS)_2](NO_3)_2$	3175 m,b	1480 m,b	1690 m,b	510 m	395 m

IR spectrum of the ligand also shows strong and broad band at 1720 cm^{-1} assigned[17,20] to ν(C=O). In the spectra of the complexes this band also shows red shift at 1700 cm^{-1} and appearance of a band at 520-495 cm^{-1} in the complexes assigned[17,20] to ν(M-O) confirms the coordination of carbonyl oxygen atom to the metal ion.

Thus on the basis of above IR data the, APQS behaves as neutral tridentate ligand and coordination proposed through secondary amino of quinazoline side chain, azomethine N as well as through carbonyl oxygen of semicarbazone moiety.

Electronic spectra and magnetic susceptibility value of the complexes: Electronic spectrum of the Co(II) complexes display three bands in the region 8700-8100, 15000-14200 and 19200-18400 cm^{-1} 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. The above transitions of Co(II) complexes indicate octahedral[21,22] complexes which are further supported[23,24] by μ_{eff} value in the range 4.89-5.11 BM. The Ni(II) complexes exhibit three spectral bands in the regions, 11300-10600, 17900-17200 and 23900-23100 cm^{-1} assigned to the transitions, $^3T_{2g}(F)\leftarrow{}^3A_{2g}(F)$, $^3T_{1g}(F)\leftarrow{}^3A_{2g}(F)$ and $^3T_{1g}(P)\leftarrow{}^3A_{2g}(F)$, respectively, which indicate octahedral[22,25] geometry for Ni(II) complexes. The octahedral geometry for Ni(II) complexes supported[23,24] by μ_{eff} value in the range 3.13-3.18 BM. The Cu(II) complexes display two ligand field bands in the regions 13000-12200 and 24900-23800 cm^{-1} which assigned to $^2T_{2g}\leftarrow{}^2E_g$ and charge transfer bands which indicate octahedral[22,26] geometry for the Cu(II) complexes. The magnetic susceptibility value[23,24] of Cu(II) complexes lies in the range 1.84-1.92 BM.

Molar conductance data: Molar conductance measurements were taken on Systronics conductivity meter model 303 using DMF as a solvent. The molar conductance data of the complexes were found to be in the range 104.1-131.2 ohm^{-1} cm^2 mol^{-1} indicating their electrolytic[27] nature of 1:2 type. On the basis of these studies the structure of present complexes are given in Fig. 1.

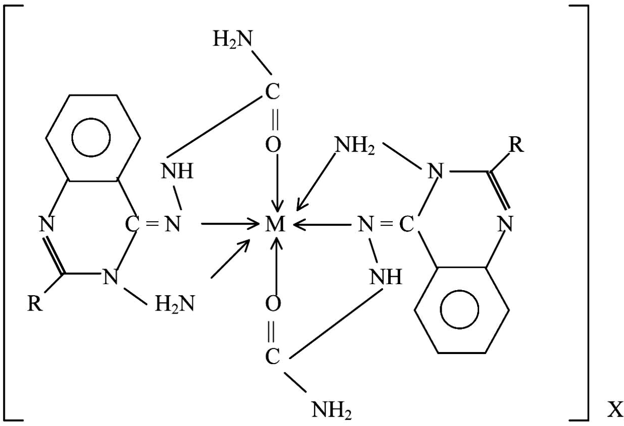

Fig. 1. [M(APQS)$_2$]X$_2$; M = Co(II) and Ni(II); X = Cl$^-$, Br$^-$, I$^-$ and NO$_3^-$; M = Cu(II); X = Cl$^-$, Br$^-$ and NO$_3^-$; R = Phenyl

Antimicrobial activity: The ligand APQS and its complexes of Co(II), Ni(II) and Cu(II) have been screened for antifungal activity against *Aspergillus niger* and *Penicillium expansum* by paper disc plate method[28] at the concentration levels of 2.0 and 0.2 %(w/v) medium. Filter paper disc after incubating for a period of 72 h at 25-30 °C. On comparison with reference to fungicide, the complexes were found to be more effective than free ligand due to chelation theory[29].

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