



Synthesis and Study of Co(II), Ni(II) and Cu(II) Complexes with Schiff Base Ligands Derived from 3-Amino-2-phenyl-4(3H)-quinazoline One

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In the present work, complexes of hexacoordinated Co(II), Ni(II) and Cu(II) complexes of the type $[M(APQH)X_2]$ where $M = Co(II)$, Ni(II) and Cu(II), APQH = 3-amino-2-phenyl-4(3H)-quinazoline hydrazone, $X = Cl^-$, Br^- , I^- and NO_3^- . The prepared ligand APQH and its complexes have been characterized by elemental analyses, molar mass, molar conductance, infrared spectra, electronic spectra and magnetic susceptibility measurements. On the basis of above physico-chemical observations, the compound APQH acts as a neutral bidentate ligand and coordination proposes through azomethine nitrogen and primary amino group of quinazoline side chain. The remaining position of metal ions are occupied by negative ions such as Cl^- , Br^- , I^- and NO_3^- . The structure of the complexes are proposed to be octahedral in nature.

Key Words: 3-Amino-2-phenyl-4(3H)-quinazoline hydrazone, Schiff base, Complexes, Co(II), Ni(II) and Cu(II).

INTRODUCTION

Quinazoline derivatives have been used as a variety of biological activities¹⁻⁶ such as antihypertensive⁷, antibacterial⁸, antifungal⁹, CNS depressant¹⁰, antihistaminic¹¹, antiinflammatory¹², antipyretic¹³ and anticancer¹⁴. In continuation of earlier work¹⁵⁻²³ on quinazoline derivative and their preparation of Schiff base metal complexes, we have now reporting the synthesis and characterization of metal complexes of Co(II), Ni(II) and Cu(II) with 3-amino-2-phenyl-4(3H)-quinazoline hydrazone.

EXPERIMENTAL

All the chemicals used were of analytical grade and used without further purification. The melting points of the newly synthesized compounds were determined in open capillaries and were uncorrected.

Preparation of ligand APQH: The ligand 3-amino-2-phenyl-4(3H)-quinazoline hydrazone (APQH) was prepared in good yield by condensing 3-amino-2-phenyl-4(3H)-quinazoline one (0.001 M) with hydrazine hydrate in ethanol. The ligand APQH synthesized by refluxing the ethanolic solution of hydrazine hydrate with the solution of 3-amino-2-phenyl quinazoline-4-(3H)-one dissolved in a minimum volume of tetrahydrofuran in 1:1 ratio. After cooling the solution yellow coloured crystals were obtained which was filtered, washed with cold ethanol followed by ether and dried in oven.

Preparation of the complexes: Ethanolic solution of the ligand APQH was added to the solution of the respective metal halide/nitrates dissolved in tetrahydrofuran in the molar ratio 2:1 with constant stirring. Resulting mixture was refluxed on a water bath for 3 h, when coloured compounds separated out which was filtered and washed with ethanol followed by ether and dried in an electric oven.

The complexes were analyzed for metal contents by standard procedures²⁴. The carbon, hydrogen and nitrogen were determined by microanalytical techniques. The electronic spectra were recorded on a Cary-2390 spectrophotometer. The IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer using KBr disc. Magnetic moment was determined at room temperature by Gouy's method using $Hg[Co(NCS)_4]$ as a calibrant. The conductivity measurements were carried out on Systronics conductivity meter 303 using 10^{-3} M dimethyl formamide solution. Analytical data, colour, electronic spectral data, conductivity measurements and magnetic moments are recorded in Table-1 and important IR spectral band are recorded in Table-2.

RESULTS AND DISCUSSION

The IR spectra of the ligand APQH exhibits strong and broad band at the region 3220 cm^{-1} assigned²⁵⁻²⁸ to the $\nu(N-H)$. In the spectra of the complexes this band shift with slightly reduced intensity. The shift of the band and change in intensity

TABLE-1
 ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES OF THE LIGAND APQH

Compounds (Colour)	Molar mass	Yield (%)	Elemental analysis (%): Found (calcd.)				λ_{\max} electronic (cm ⁻¹)	μ_{eff} (BM)	DT (°C)	Ω_m (ohm ⁻¹ cm ² mol ⁻¹)
			M	C	N	H				
APQH (Colourless)	252.00	64	–	66.48 (66.66)	27.61 (27.77)	5.49 (5.55)	–	–	–	–
[Co(APQH) ₂ Cl ₂] (Brownish red)	633.93	70	9.20 (9.29)	52.83 (53.00)	21.98 (22.08)	4.37 (4.41)	8240, 15050, 19460	5.07	187	1.7
[Co(APQH) ₂ Br ₂] (Brown)	722.74	73	8.04 (8.15)	46.31 (46.48)	19.20 (19.37)	3.81 (3.87)	8310, 14800, 20100	5.10	192	1.3
[Co(APQH) ₂ I ₂] (Brown)	816.73	74	7.12 (7.21)	40.89 (41.13)	17.11 (17.14)	3.34 (3.42)	8360, 14950, 20170	4.94	181	2.4
[Co(APQH) ₂ (NO ₃) ₂] (Dark brown)	686.93	70	8.49 (8.57)	48.80 (48.91)	20.30 (20.38)	4.01 (4.07)	8140, 14700, 20300	4.96	201	0.96
[Ni(APQH) ₂ Cl ₂] (Green)	633.71	71	9.19 (9.26)	52.92 (53.02)	21.90 (22.04)	4.36 (4.41)	10060, 16960, 23430	3.11	184	0.94
[Ni(APQH) ₂ Br ₂] (Brownish green)	722.52	72	8.04 (8.12)	46.36 (46.50)	19.22 (19.37)	3.75 (3.87)	10200, 17300, 23530	3.08	196	0.96
[Ni(APQH) ₂ I ₂] (Deep green)	816.51	74	7.10 (7.19)	41.10 (41.15)	17.06 (17.14)	3.36 (3.42)	10140, 17240, 23640	3.12	198	4.8
[Ni(APQH) ₂ (NO ₃) ₂] (Greenish brown)	686.71	73	8.35 (8.54)	48.90 (48.97)	20.22 (20.38)	3.92 (4.07)	10160, 16980, 23700	3.14	204	4.6
[Cu(APQH) ₂ Cl ₂] (Blue)	638.54	74	9.88 (9.95)	52.54 (52.62)	21.83 (21.92)	4.31 (4.38)	12580, 25870	1.90	187	3.1
[Cu(APQH) ₂ Br ₂] (Blue)	727.35	75	8.72 (8.73)	46.04 (46.19)	19.11 (19.24)	3.78 (3.84)	12610, 25960	1.89	196	3.6
[Cu(APQH) ₂ (NO ₃) ₂] (Deep blue)	691.54	73	9.11 (9.18)	48.32 (48.58)	20.12 (20.21)	4.00 (4.04)	12740, 25600	1.87	190	3.9

DT = Decomposition temperature.

 TABLE-2
 IR SPECTRAL BAND (cm⁻¹) OF THE LIGAND APQH AND ITS COMPLEXES

Compounds	$\nu(\text{N-H})$	$\nu(\text{C=N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{M-X})$
APQH	3220 s,b	1480 s,b	–	–	–
[Co(APQH) ₂ Cl ₂]	3195 m,b	1450 m,b	–	480 m	315 m
[Co(APQH) ₂ Br ₂]	3195 m,b	1450 m,b	–	470 m	280 m
[Co(APQH) ₂ I ₂]	3195 m,b	1455 m,b	–	475 m	275 m
[Co(APQH) ₂ (NO ₃) ₂]	3195 m,b	1460 m,b	540 m	470 m	–
[Ni(APQH) ₂ Cl ₂]	3195 m,b	1460 m,b	–	440 m	325 m
[Ni(APQH) ₂ Br ₂]	3195 m,b	1455 m,b	–	445 m	295 m
[Ni(APQH) ₂ I ₂]	3195 m,b	1460 m,b	–	450 m	280 m
[Ni(APQH) ₂ (NO ₃) ₂]	3195 m,b	1455 m,b	530 m	455 m	–
[Cu(APQH) ₂ Cl ₂]	3195 m,b	1460 m,b	–	460 m	320 m
[Cu(APQH) ₂ Br ₂]	3195 m,b	1455 m,b	–	465 m	275 m
[Cu(APQH) ₂ (NO ₃) ₂]	3195 m,b	1450 m,b	515 m	470 m	–

proposing coordination of secondary amino group with metal ion which is also supported by appearance of a band at far IR regions at 480-440 cm⁻¹ assigned²⁹⁻³³ to $\nu(\text{M-N})$. The next IR spectrum of the ligand shows strong and broad band at 1480 cm⁻¹ assigned^{27-29,34} to $\nu(\text{C=N})$. In the spectra of the complexes this band shows red shift with slightly reduced intensity. The shift of the band and change in intensity suggests coordination of the azomethine Nitrogen with metal ion. The linkage with oxygen atom of nitrate group is indicated by the presence of a far IR band at 540-515 cm⁻¹ assigned²⁹⁻³³ to $\nu(\text{M-O})$. The coordination through metal halogen is indicated by the presence of a band in the far IR region 320-270 cm⁻¹ assigned²⁹⁻³³ to $\nu(\text{M-X})$. The evidence of metal halogen linkage is further supported by the low value of molar conductance in the range 0.94-4.8 ohm⁻¹ cm² mol⁻¹. The presence of band at 1580 and 1460 cm⁻¹ with a separation of 120 cm⁻¹ suggest mono coordinated nature of nitrate group³⁵.

Electronic spectra and magnetic susceptibility data of the complexes: Electronic spectrum of the complex [Co(APQH)₂X₂] exhibits three bands in the region 8360-8140, 15050-14700 and 20300-19460 cm⁻¹ assigned to ⁴T_{1g}(F) → ⁴T_{2g}(F), ⁴A_{2g}(F) and ⁴T_{1g}(P) transitions, respectively. The above transitions propose ϕ octahedral^{36,37} geometry for Co(II) complexes which is further supported³⁸⁻⁴⁰ by μ_{eff} value in the range 4.94-5.10 BM. The Ni(II) complexes exhibits three spectral bands in the regions, 10200-10160, 17240-16980 and 23700-23430 cm⁻¹ assigned to the transitions ³A_{2g}(F) → ⁴T_{2g}(F), ³T_{1g}(F) and ³T_{1g}(P), respectively, which proposes octahedral^{37,41} geometry for Ni(II) complexes. The octahedral geometry of Ni(II) complexes are further supported^{38,39,42} by μ_{eff} value 3.08-3.14 BM. The Cu(II) complexes exhibits two ligand bands in the region 12740-12610 and 25600-25960 cm⁻¹ assigned to ²E_g → ²T_{2g} and charge transfer band which proposes distorted octahedral^{37,43} geometry for Cu(II) complexes. The μ_{eff} value for Cu(II) complexes lie in the range 1.87-1.90 BM^{38,39,44}.

Molecular conductivity: Molar conductance measurements of the complex of Co(II), Ni(II) and Cu(II) 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 0.94-4.80 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating the non electrolytic behaviour of the complexes⁴⁵.

Conclusion

Hence on the basis of above discussion the complexes of the Co(II), Ni(II) and Cu(II) of the type $[\text{M}(\text{APQH})_2\text{X}_2]$ can be presumed to have octahedral geometry as shown in Fig. 1.

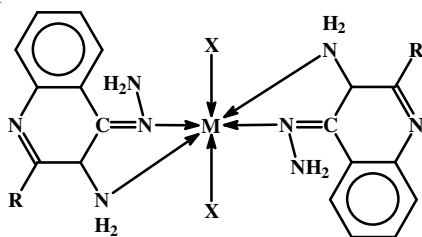


Fig. 1. $[\text{M}(\text{APQH})_2\text{X}_2]$ [R = Phenyl; M = Co(II) and Ni(II); X = Cl^- , Br^- , I^- and NO_3^- ; M = Cu(II), X = Cl^- , Br^- and NO_3^-]

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