



Synthetic and Structural Studies of Some Bivalent Transition Metal Complexes with Oxygen and Nitrogen Containing Schiff Base

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ABSTRACT

The present communication deals with the result of the Schiff base ligand 3-amino 2 ethyl quinazoline 4(3H) Semicarbazone (AEQS) with bivalent transition metal ions, Cu(II), Co(II) and Ni(II). The ligand and its metal complexes are characterized on the basis of molar mass, elemental analyses, IR, electronic spectra, molar conductivity, magnetic moment measurement. The reaction of the ligand with Cu(II), Co(II) and Ni(II) resulted in the formation of the complexes have the general composition $[M(AEQS)_2]X_2$ where M= Cu(II), Co(II) and Ni(II). AEQS=3-amino 2 ethyl quinazoline 4(3H) semicarbazone and X = Cl⁻, Br⁻ or I⁻. The studies proposes a distorted octahedral geometry for Cu(II) complexes whereas octahedral geometry is assigned for Cu(II), Co(II) and Ni(II) complexes.

Key word: Semicarbazone/AEQS/ Cu(II), Co(II) and Ni(II)/complexes compound.

INTRODUCTION

Complexes of semicarbazone ligands exhibit remarkable attention, primarily due to bioinorganic relevance. Semicarbazone complexes exhibit wide medicinal applications such as antimalarial, antiviral, antibacterial, and antitumor¹⁻¹⁰. In order to consider above features of semicarbazone Schiff bases ligands and its complexes and in continuation of our recent works¹¹⁻¹⁵ in this field., we herein reported synthesis and characterization of Cu(II), Co(II) and Ni(II)

complexes with Schiff base, 3-amino 2- ethyl quinazoline 4(3H) semicarbazone.

EXPERIMENTAL

Analytical and physical data of the ligand and its metal complexes are given in Table-1. The ligand is soluble in common organic solvents, but the complexes are found to be soluble in DMF and DMSO. The molar conductance value in DMF (Table-1) adequately support the 1:2 electrolytic metal of the metal complexes. All the chemicals

used were of analytical grade. Metal contents were determined using standard procedures. IR Spectra of the ligand and complexes were recorded on Perkin Elmer model 577 spectrophotometer using KBr disc. Electronic spectra were recorded on Cary-2390 spectrophotometer using DMF as a solvent. Molar conductivity of the complexes were measured by using Systronic conductivity meter. Model 303 in DMF. Magnetic susceptibility was carried out by Gouy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$

Synthesis of the ligand, AEQS

A hot ethanolic solution of semicarbazide hydrochloride (0.02mol) and an ethanolic solution (20ml) of 3-amino 2-ethyl quinazoline-4(3H) one (0.02mol) were mixed slowly with constant stirring. This mixture was refluxed for 4h. On cooling, a colourless compound was precipitated out. It was filtered, washed with cold ethanol and dried in oven m.p. $160 \pm 1^\circ \text{C}$, yield 65%.

Preparation of the complexes

The complexes of Co(II), Ni(II) and Cu(II) have been synthesized by reacting ethanolic solution of the ligand (0.02mol) with respective metal halide (0.01mol). The reaction mixture was refluxed for 4–5 h. On cooling, a coloured compound was precipitated out in each case. The compound was filtered, washed with ethanol and dried in oven. Yield-65-70%.

RESULTS AND DISCUSSION

The important infrared frequencies of the ligand and its complexes along with their tentative assignments are given in Table-2. The IR spectra of the ligand exhibit strong and broad band at 3300 cm^{-1} assigned¹⁷ $\nu_{\text{N-H}}$ vibrations. In the spectra of the complexes this band suffered downward shift proposing coordination through N-atom of primary amino group. A medium intensity band at 1580 cm^{-1} in the ligand due to $\nu_{\text{C=N}}$ of azomethine¹⁸ is shifted to lower frequencies at 1555 cm^{-1} upon complexation because of coordination of azomethine nitrogen with metal ions. The next IR spectra of the ligand exhibit strong and broad band at 1700 cm^{-1} assigned¹⁹ to $\nu_{\text{C=O}}$. In the spectra of the complexes this band suffered downward shift clearly indicating coordination through carbonyl oxygen of semicarbazone. The linkage with N atom primary amino group as well as azomethine N and carbonyl/oxygen is further supported by two far IR spectral bands present at $535\text{-}505 \text{ cm}^{-1}$ and $425\text{-}395 \text{ cm}^{-1}$ assigned²⁰ to $\nu_{\text{M-O}}$ and $\nu_{\text{M-N}}$ respectively.

Molar Conductivity

The observed molar conductance of complexes of Co(II), Cu(II) and Ni(II) were taken 10^{-3} DMF solution are in the range $146.3\text{-}167.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. The molar conductance values are consistent with the electrolytic²¹ in nature of 1:2 type.

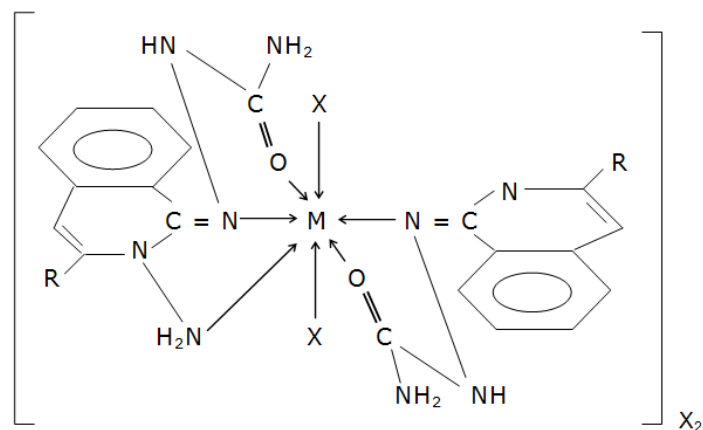


Fig. 1: $[\text{M}(\text{AEQS})_2] \text{X}_2$
 $\text{M} = \text{Co}(\text{II})$ and $\text{Ni}(\text{II})$; $\text{X} = \text{Cl}^-$, Br^- , NO_3^- , I^- ; $\text{M} = \text{Cu}(\text{II})$; $\text{X} = \text{Cl}^-$ and Br^-
 $\text{R} = \text{Ethyl}$

Table 1: Analytical, colour, mol. wt., magnetic susceptibility values, conductivity measurement and decomposition temperature of ligand AEQS and its metal complexes

Compounds (Colour)	Yield %	Molar mass	% Analysis found (calculated)				μ_{eff} B.M	Ω_m cm ² mol ⁻¹	DT °C.	λ_{max} cm ⁻¹
			M	C	N	H				
AEQS (Colourless)		246		53.48 (53.65)	34.02 (34.14)	5.62 (5.69)				
[Co(AEQS) ₂ Cl ₂] (Brown)		621.93	9.38	42.30 (9.47)	26.92 (42.44)	4.45 (27.01)	4.89 (4.50)	160.3	216	9300, 16100
[Co(AEQS) ₂ Br ₂] (Green)		710.738	8.20 (8.29)	36.98 (37.14)	23.52 (23.63)	3.88 (3.93)	4.81	165.2	202	9250, 16400
[Co(AEQS) ₂ I ₂] (Yellowish green)		804.748	7.23 (7.32)	32.68 (32.80)	20.78 (20.87)	3.43 (3.47)	5.1	164.1	213	9300, 16800
[Co(AEQS) ₂ (NO ₃) ₂] (Dark brown)		674.93	8.64 (8.73)	38.89 (39.11)	24.74 (24.89)	4.08 (4.14)	4.93	167.8	209	9400, 16700
[Ni(AEQS) ₂ Cl ₂] (Brown)		621.71	9.39 (9.44)	42.28 (42.46)	26.93 (27.02)	4.44 (4.50)	3.18	158.1	187	10100, 18300 , 26800
[Ni(AEQS) ₂ Br ₂] (Green)		710.51	8.18 (8.26)	36.94 (37.15)	23.50 (23.64)	3.87 (3.94)	3.20	155.1	193	10300, 18600 20400
[Ni(AEQS) ₂ I ₂] (Greenish yellow)		804.52	7.20 (7.29)	32.66 (32.81)	20.74 (20.88)	3.43 (3.48)	3.24	150.4	194	11100, 18100 26300
[Ni(AEQS) ₂ (NO ₃) ₂] (Violet)		674.71	8.62 (8.70)	38.86 (39.12)	24.76 (24.89)	4.09 (4.14)	3.26	148.6	197	10700, 18500 , 26200
[Cu(AEQS) ₂ Cl ₂] (Blue)		626.54	10.05 (10.14)	42.02 (42.13)	26.70 (26.81)	4.40 (4.46)	1.91	146.3	231	12300, 24300
[Cu(AEQS) ₂ Br ₂] (Blue)		715.48	8.79 (8.88)	36.78 (36.90)	23.35 (23.48)	3.87 (3.91)	1.87	149.6	226	12800, 24800
[Cu(AEQS) ₂ (NO ₃) ₂] (Blue)		679.54	9.28 (9.35)	38.70 (38.84)	24.61 (24.72)	4.07 (4.12)	1.88	147.1	223	12500, 25100

DT = Decomposition Temperature

Electronic spectra and magnetic susceptibility of the complexes

The Co(II) complexes exhibits three spectral bands in the regions 10700-11300cm⁻¹ 19330-19500 cm⁻¹ and 23100-23300 cm⁻¹ assigned to ⁴T_{2g}(F) ← ⁴T_{1g}(F) and ⁴A_{2g}(F) ← ⁴T_{1g}(F) and ⁴T_{1g}(P) → ⁴T_{1g}(F) transitions respectively. The above

mentioned spectral bands proposes octahedral²² geometry for Co(II) complexes. The octahedral geometry for Co(II) complexes is further supported^{23,24} by m_{eff} value in the range 4.89-5.13 B.M. The Ni(II) complexes exhibit three absorption bands in the regions, 9700-10200 cm⁻¹, 16100-16400cm⁻¹ and 24300-24700cm⁻¹ assigned to

Table 2: Important IR spectral bands (cm⁻¹) of ligand AEQS and its complexes

Compounds	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
AEQS	3300 s,b	1700 s,b	1580 s,b		
[Co(AEQS) ₂ Cl ₂]	3280 m,b	1670 m,b	1555 m,b	520 m	395 m
[Co(AEQS) ₂ Br ₂]	3280 m,b	1670 m,b	1555 m,b	520 m	395 m
[Co(AEQS) ₂ I ₂]	3280 m,b	1680 m,b	1555 m,b	520 m	405 m
[Co(AEQS) ₂ (NO ₃) ₂]	3280 m,b	1680 m,b	1555 m,b	535 m	415 m
[Ni(AEQS) ₂ Cl ₂]	3280 m,b	1680 m,b	1555 m,b	530 m	410 m
[Ni(AEQS) ₂ Br ₂]	3280 m,b	1680 m,b	1555 m,b	535 m	425 m
[Ni(AEQS) ₂ I ₂]	3280 m,b	1680 m,b	1555 m,b	520 m	425 m
[Ni(AEQS) ₂ (NO ₃) ₂]	3280 m,b	1680 m,b	1555 m,b	510 m	415 m
[Cu(AEQS) ₂ Cl ₂]	3280 m,b	1680 m,b	1555 m,b	510 m	415 m
[Cu(AEQS) ₂ Br ₂]	3280 m,b	1675 m,b	1555 m,b	505 m	420 m
[Cu(AEQS) ₂ (NO ₃) ₂]	3280 m,b	1670 m,b	1555 m,b	515 m	415 m

m = medium, s = strong, b = broad

³T_{2g}(F) ← ³A_{2g}(F), ³T_{1g}(F) ← ³A_{2g}(F) and ³T_{1g}(P) ← ³T_{2g}(P) transitions respectively. The above mentioned spectral bands of Ni(II) complexes propose octahedral²² geometry. The octahedral geometry of Ni(II) complexes is also supported^{23,24} by μ_{eff} value in the range 3.11-3.17 BM. The Cu(II) complexes display two ligands field bands in the regions, 12700-13100 cm⁻¹ and 18200-18430cm⁻¹ assigned ²T_{2g}(F) ← ²E_g and charge transfer band respectively, which proposes octahedral²² geometry for Cu(II) complexes. The magnetic susceptibility^{23,24} value of Cu(II) complex lies in the range 1.87-1.91 B.M.

CONCLUSION

The present studies show that the ligand AEQS behaves as neutral tridentate chelating ligand and coordination proposes through amine nitrogen, imine nitrogen and Carbonyl oxygen atom of semicarbozone moiety. Thus on the basis of above mentioned studies it is proposed that the complexes of Co(II) and Ni(II) have octahedral geometry where as distorted octahedral geometry is recorded for Cu(II) complexes [Fig-1].

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