



Synthesis and Characterization of Cobalt(II), Nickel(II) and Copper(II) Complexes with Nitrogen-Oxygen Donor Ligand

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ABSTRACT

The complexes of ML_2 were synthesized where $M = Co(II), Ni(II)$ and $Cu(II)$ and $L = 2$ -Butyl thioquinazoline 4 (3H)- semicarbazone (BTQS). The ligand have been synthesized by condensation of thioquinazoline-4(3H)-one with semicarbazide hydrochloride characterized by molar mass, elemental analysis, Infrared spectra, electronic spectra, magnetic susceptibility and molar conductance measurements. The ligand BTQS acts as neutral bidentate chelating agent and coordinated to metal ions through azomethine nitrogen and carbonyl oxygen of semicarbazone moiety. The remaining Coordination centres are satisfied by anions such as Cl^- , Br^- , I^- and NO_3^- .

Key words : Schiff base / BTQS / $Co(II)$, $Ni(II)$ and $Cu(II)$ / Complexes

INTRODUCTION

Transition metal complexes of Schiff base have been intensely investigated by Coordination chemists due to their interesting structural properties and their wide ranging applications¹⁻⁵. The coordination ability of Schiff bases with transition element, particularly with first row, afford the study of the metals in such system. Keeping the above facts in mind and in continuation of our recent work⁶⁻²¹ we now, present the results of our investigations on

the synthesis, spectral and the theoretical studies of $Co(II)$, $Ni(II)$ and $Cu(II)$ complexes with ligand, 2-butyl thioquinazoline 4(3H) semicarbazone (BTQS).

EXPERIMENTAL

All the reagents herein used were of analytical grade. The metal contents of the complexes were estimated using standard procedures²². The IR spectra (Table-2) were recorded on Perkin-Elmer-577 spectrophotometer using KBr disc.

Magnetic susceptibility were measured on Gouy balance using $\text{Hg}[\text{CO}(\text{NCS})_4]$ as a calibrant. Electronic spectra were recorded on Systronics conductivitymeter model 303 using DMF as a solvent.

Preparation of the Ligand :

Ethanolic solution of 2-butyl thioquinazoline 4(3H) one (0.01m) was treated with semicarbazide hydrochloride (0.01 m) dissolved in minimum amount of sodium acetate in ethanol. The resulting mixture was heated for 2 and half hour with occasional stirring. The product crystallized from ethanol and dried. m.p. $263 \pm 1^\circ\text{C}$. Yield 65%.

Preparation of the complexes

The complexes of Cu(II), Co(II) and Ni(II) have been prepared by reacting solution of metal halides with solutions of the ligand BTQS in molar ratio 1:2. The solid coloured complexes which was separated on cooling were filtered, washed with ethanol, dried in oven. Yield in all cases 60-65%.

RESULTS AND DISCUSSION

I.R. Spectra

IR spectra of the ligand and complexes were recorded on Perkin Elmer Spectrophotometer Model 577 using KBr disc.

The IR spectra of the ligand exhibit strong and broad band at 1560 cm^{-1} assignable²³⁻²⁵ to $\nu_{\text{C=N}}$. The band is shifted to lower wave number after complex formation, proposes involvement of

azomethine N in the bonding with metal ions. The appearance of a band in far IR region at $425\text{-}395\text{ cm}^{-1}$. In the complexes assignable²⁴⁻²⁶ to $\nu_{\text{M-N}}$. The IR spectra of the ligand exhibits strong and broad band at 1760 cm^{-1} assignable²⁵⁻²⁸ to $\nu_{\text{C=O}}$. This band undergoes to shift after complex formation, proposes coordination of metal ion through carbonyl oxygen. It is further supported by the appearance of a new far IR band at $525\text{-}505\text{ cm}^{-1}$ in the complexes which is assignable²⁴⁻²⁶ to $\nu_{\text{M-O}}$. The linkage with halogen is indicated by the appearance of another band in the far IR region $320\text{-}280\text{ cm}^{-1}$ assigned²⁴⁻²⁶ to $\nu_{\text{M-X}}$ (X= Cl⁻, Br⁻ or I⁻). The coordination with halogen is supported by the low molar conductivity of the complexes in the range $11.2\text{-}13.7\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$.

Nitrate complexes show characteristic medium intensity bands at 1360 and 1180 cm^{-1} with a separation 140 cm^{-1} due to monodentate linkage of nitrate groups. Combination band at 1660 cm^{-1} and 1640 cm^{-1} with a separation of 20 cm^{-1} conforming the monodentate behavior of the nitrate²⁹ group.

Electronic Spectra and Magnetic Susceptibility of the Complexes

The Co(II) complexes exhibit two spectral bands in the region at $13400\text{-}12860\text{ cm}^{-1}$ and $2100\text{-}20300\text{ cm}^{-1}$ assigned to the transitions, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ proposing octahedral^{30,31} geometry. The proposed geometry of Co(II) complexes are further supported by the high magnetic susceptibility value in the range $4.92\text{-}5.12\text{ B.M.}$ The Ni(II) complexes display three spectral

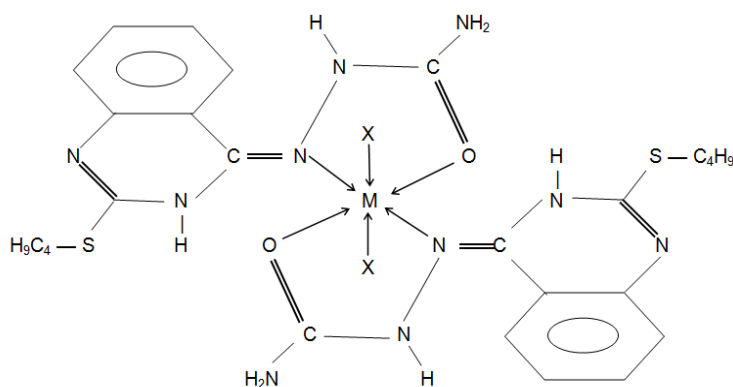


Fig.1 $[\text{M}(\text{BTQS})_2]$

M = Co(II) and Ni(II); X = Cl⁻, Br⁻, I⁻ or NO₃⁻.

M = Cu(II); X = Cl⁻, Br⁻ or NO₃⁻.

Table 1 : Physical Analysis of Ligands and Its Complexes

Compounds (Colour)	Molar Mass	% Analysis found (calculated)				H	μ_{eff} B. M.	Ω_m ohm ⁻¹ cm ² mol ⁻¹	λ_{max} electronic cm ⁻¹
		M	C	N	N				
BTQS (Colourless)	291		53.41 (53.60)	23.90 (24.05)	5.79 (5.84)				
[Co(BTQS) ₂ Cl ₂] Yellowish red	711.93	8.18 (8.27)	43.68 (43.82)	19.53 (19.66)	4.71 (4.77)	4.99	12930, 20300	11.9	
[Co(BTQS) ₂ Br ₂] Yellowish red	800.74	7.28 (7.35)	38.81 (38.96)	17.36 (17.48)	4.20 (4.24)	5.04	12860, 20700	11.2	
[Co(BTQS) ₂] Yellowish red	894.70	6.49 (6.58)	34.75 (34.87)	15.53 (15.64)	3.76 (3.80)	5.12	13400, 20600	11.6	
[Co(BTQS) ₂ (NO ₃) ₂] Yellowish red	764.93	7.62 (7.70)	40.62 (40.78)	18.11 (18.30)	4.39 (4.44)	4.92	13100, 21000	12.2	
[Ni(BTQS) ₂ Cl ₂] Orange	711.71	8.16 (8.24)	43.64 (43.83)	19.55 (19.67)	4.72 (4.77)	3.11	10300, 15800, 23800	13.1	
[Ni(BTQS) ₂ Br ₂] Orange	800.52	7.26 (7.33)	38.80 (38.97)	17.35 (17.48)	4.19 (4.24)	3.04	10060, 15300, 24000	12.8	
[Ni(BTQS) ₂] Orange	894.50	6.48 (6.56)	34.74 (34.87)	15.50 (15.65)	3.75 (3.80)	3.15	10200, 16000, 24700	11.4	
[Ni(BTQS) ₂ (NO ₃) ₂] Red	764.71	7.61 (7.67)	40.60 (40.79)	18.14 (18.30)	4.38 (4.44)	3.13	10600, 16100, 24500	12.3	
[Cu(BTQS) ₂ Cl ₂] Blue	716.54	8.78 (8.86)	43.38 (43.54)	19.40 (19.53)	4.70 (4.74)	1.88	12700, 15700	13.6	
[Cu(BTQS) ₂ Br ₂] Blue	805.35	7.79 (7.88)	38.60 (38.74)	17.23 (17.38)	4.18 (4.22)	1.86	12400, 16300	13.3	
[Cu(BTQS) ₂ (NO ₃) ₂] Blue	769.54	8.18 (8.25)	40.40 (40.54)	18.04 (18.19)	4.36 (4.41)	1.94	11700, 15900	13.6	

DT = Decomposition Temperature

Table 2 : IR spectral bands of ligand BTQS and its metal complexes

Compounds	$\nu_{C=O}$	$\nu_{C=N}$	ν_{M-O}	ν_{M-N}	ν_{M-X}
BTQS	1760 s,b	1560 s,b			
[Co(BTQS) ₂ Cl ₂]	1735 m,b	1530 m,b	515 m	410 m	275 m
[Co(BTQS) ₂ Br ₂]	1730 m,b	1530 m,b	510 m	410 m	280 m
[Co(BTQS) ₂ I ₂]	1730 m,b	1530 m,b	525 m	405 m	285 m
[Co(BTQS) ₂ (NO ₃) ₂]	1740 m,b	1540 m,b	515 m	305 m	
[Ni(BTQS) ₂ Cl ₂]	1735 m,b	1535 m,b	510 m	420 m	300 m
[Ni(BTQS) ₂ Br ₂]	1735 m,b	1535 m,b	505 m	400 m	510 m
[Ni(BTQS) ₂ I ₂]	1735 m,b	1540 m,b	520 m	410 m	320 m
[Ni(BTQS) ₂ (NO ₃) ₂]	1735 m,b	1540 m,b	525 m	425 m	
[Cu(BTQS) ₂ Cl ₂]	1740 m,b	1540 m,b	505 m	395 m	290 m
[Cu(BTQS) ₂ Br ₂]	1740 m,b	1535 m,b	505 m	400 m	295 m
[Ni(BTQS) ₂ (NO ₃) ₂]	1740 m,b	1535 m,b	510 m	410 m	

S = strong; m = medium; b = broad

bands in the regions, 10600-10000 cm⁻¹ 16100-15300 cm⁻¹ and 24700-23600cm⁻¹ assigned to the transitions, ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ respectively, suggested octahedral geometry^{30,34} for Ni(II) complexes. The proposed geometry of Ni(II) complexes is further supported by the magnetic susceptibility value in the range 3.04-3.15 B.M. The Cu(II) complexes exhibit two spectral bands in the regions, 11700-12400 cm⁻¹ and 16300-15700cm⁻¹ assigned to the transitions, ${}^2E_g \rightarrow {}^2T_{2g}$ and charge transfer band suggested octahedral^{30,35} geometry for the Cu(II) complexes. The magnetic susceptibility value of Co(II) complexes lies in the range 1.86-1.94 B.M.

Molar conductance measurement

Molar conductance value of the complexes of Co(II), Ni(II) and Cu(II) were found to be in the range 11.2-13.7 ohm⁻¹ cm²mol⁻¹ in the DMF which proposes their non-electrolytic nature. The molar conductance values also supported the structure

assigned on the basis of physico-chemical and spectroscopic measurements.

CONCLUSIONS

Thus on the basis of above mentioned studies, it is proposed that the ligand BTQS acts in a neutral bidentate manner and coordinates is proposed through azomethine nitrogen and carbonyl oxygen of semicarbozone moiety which is also supported by the literature. The remaining positions of metal ions are satisfied by negative ions such as Cl⁻, Br⁻, I⁻ and NO₃⁻. The geometry of Co(II), Ni(II) or Cu(II) complexes are proposed to be octahedral in nature as given in structure-I.

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