



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

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ABSTRACT

Complexes of general molecular formula $[M(AQTC)_2X_2]$, where M = cobalt(II), nickel(II) and copper(II), AQTC = 2 phenyl quinoxaline thiosemicarbazone, X = Cl⁻, Br⁻, I⁻ and NO₃⁻ have been synthesized. Complexes were characterised by analytical analyses, IR spectra, electronic spectra, molar mass, conductivity measurements. The compound AQTC acts as a neutral, bidentate ligand and bonded to the metal ion through azomethine N and sulphur atom of thiosemicarbazone moiety. The remaining coordinating positions are satisfied by anions such as Cl⁻, Br⁻, I⁻ and NO₃⁻. Electronic spectral and magnetic susceptibility values reveals octahedral geometry for the complexes. 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 : AQTC/ cobalt(II)/nickel(II)/ copper(II)/ Schiff base/ antimicrobial/ antifungal activity.

INTRODUCTION

Schiff base ligands and their transition metal complexes have been extensively studied over past few decades¹⁻³. Schiff base and their metal complexes are very popular due to their diverse chelating ability⁴. They play important role in both synthetic and structural research, because of their preparative accessibility and structural diversity⁵. In

addition to variable magnetic property and catalytic activity, the Schiff base complexes can also serve as efficient model for the metal containing sites in metallo-proteins and enzymes^{6,7}. In continuation⁸⁻¹³ of earlier work on Schiff base complexes and their biocidal activities, preparation and characterization of cobalt(II), nickel(II) and copper(II) complexes with 2-phenyl quinoxaline thiosemicarbazone are reported in this paper.

EXPERIMENTAL

Material and method

All the chemicals used were of AnalaR grade. The complexes were analysed using standard procedures¹⁴. 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 $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant. The molar conductance values were done on Systronics conductivity meter using DMF as a solvent.

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

Preparation of the ligand

2-phenyl quinoxaline was prepared by modifying the earlier reported method¹⁵. Ethanolic solution of 2-phenyl quinoxaline (0.01 M) was treated with thiosemicarbazide hydrochloride (0.01 M) dissolved in ethanolic solution of sodium acetate in tetrahydro furan. The resulting mixture were heated on water bath for 3-4 h with occasional stirring. The precipitate was washed with water, treated with dilute sodium carbonate solution and filtered. The solid was washed thoroughly with water and recrystallized with tetrahydrofuran to furnish 2-phenyl quinoxaline thiosemicarbazone as colourless compound. m.p. $129 \pm 1^\circ\text{C}$, yield 60-65%.

Preparation of the complexes

The complexes of cobalt(II), nickel(II) and copper(II) have been prepared by reacting an ethanolic solution of the ligands AQTC and ethanolic solution of corresponding metal salts in molar ratio 2:1. The resulting mixtures were heated on waterbath for 2-3 h when the compounds separated out which were filtered, washed with ethanol followed by diethyl ether and dried in an electric oven. Yield in all cases 60-70%.

RESULTS AND DISCUSSION

Infrared spectra

The IR spectrum of the ligands AQTC

shows a broad band of medium intensity at 3460 cm^{-1} which can be assigned^{16,17} to $\nu_{\text{N-H}}$ vibrations. In the spectra of the complexes this band remains unaffected, indicating non involvement of either primary amino or secondary amino group in coordination with metal ion. The IR spectrum of the ligand shows a broad band of medium intensity at 1460 cm^{-1} assigned^{16,18} $\nu_{\text{C=N}}$. In the spectra of the complexes this band shows red shift with slightly reduced intensity. The shift of the band and change in intensity suggest coordination of the azomethine N. The linkage of metal ion with azomethine N is further supported by the appearance of a far ir band, in the region $475\text{-}455\text{ cm}^{-1}$ in the complexes assigned¹⁹ to $\nu_{\text{M-N}}$. The other ir band of structural significance in the spectra of the ligand appears $\sim 800\text{ cm}^{-1}$ assigned^{16,20} to $\nu_{\text{C=S}}$. In the spectra of the complexes this band shows red shift indicating coordination through thione S atom of thiosemicarbazone moiety. The linkage through S atom was further supported by appearance of a new band in the far IR region at $425\text{-}395\text{ cm}^{-1}$ assigned^{16,21} to $\nu_{\text{M-S}}$. The evidence of metal halogen linkage are indicated by the appearance of bands in the far IR regions at $320\text{-}265\text{ cm}^{-1}$ assigned to $\nu_{\text{M-X}}$ ($\text{X} = \text{Cl}, \text{Br}$ or I) The evidence of metal halogen is confirmed by the low value of molar conductance of the complexes in the range $2.8\text{-}4.9\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ (Table 1) which indicate non electrolytic nature²² of the complexes. The evidence of monocoordinate linkage of nitrate ion with metal ions are supported^{23,24} by the appearance of a significant IR band at 1320 cm^{-1} and 1200 cm^{-1} with a separation of 120 cm^{-1} .

On the basis of above IR spectral bands assignments, it is proposed that the compound AQTC behaves as neutral bidentate ligand and coordination proposed through azomethine N and thione sulphur of thiosemicarbazone moiety. The remaining coordinating positions are occupied by anions such as $\text{Cl}^-, \text{Br}^-, \text{I}^-$ and NO_3^- .

Electronic spectra and magnetic susceptibility of the complexes

Electronic spectra of the complexes of Cobalt(II), Nickel(II) and Copper(II) with ligand AQTC were recorded in the region $10,000\text{-}25000\text{ cm}^{-1}$. The complexes of cobalt(II) display three bands in the regions, $10660\text{-}10200$, $15400\text{-}14800$, $21860\text{-}21400$

Table 1: Analytical, colour, molar mass, magnetic susceptibility, electronic spectra and conductivity measurement data for ligand aqtc and its metal complexes

Compounds/ Colors	Molar Mass	% Analysis found (Calculated)				μ_{eff} B.M.	λ_{max} electronic cm^{-1}	Ω_m $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$	Decomposition Temp. $^{\circ}\text{C}$
		M	C	N	H				
AQTC	308.00		62.42	22.81	4.61				
Colorless			(62.33)	(22.72)	(4.54)				
$[\text{Co}(\text{AQTC})_2\text{Cl}_2]$	745.93	7.81	51.58	18.83	3.69	5.04	10200, 14800,	3.1	272
Brown		(7.90)	(51.47)	(18.76)	(3.75)		21500		
$[\text{Co}(\text{AQTC})_2\text{Br}_2]$	839.74	6.93	45.85	16.59	3.26	5.07	10410, 14940,	3.03	278
Brown		(7.01)	(45.72)	(16.67)	(3.33)		21680		
$[\text{Co}(\text{AQTC})_2\text{I}_2]$	928.74	6.29	41.26	14.93	2.96	4.89	10240, 14980,	3.02	269
Brown		(6.34)	(41.34)	(15.07)	(3.01)		21800		
$[\text{Co}(\text{AQTC})_2(\text{NO}_3)_2]$	798.93	7.28	48.20	17.61	3.46	4.99	10360, 15020,	3.00	273
Brown		(7.37)	(48.06)	(17.52)	(3.50)		21860		
$[\text{Ni}(\text{AQTC})_2\text{Cl}_2]$	745.71	7.82	51.57	18.81	3.79	3.19	12600, 17300,	4.8	263
Greenish yellow		(7.87)	(51.49)	(18.77)	(3.75)		23400		
$[\text{Ni}(\text{AQTC})_2\text{Br}_2]$	834.52	7.09	45.86	16.68	3.27	3.16	12800, 17870,	4.7	288
Greenish yellow		(7.03)	(46.01)	(16.77)	(3.33)		23200		
$[\text{Ni}(\text{AQTC})_2\text{I}_2]$	928.52	6.39	41.22	15.11	2.97	3.12	12800, 18140,	4.3	286
Greenish yellow		(6.32)	(41.35)	(15.07)	(3.01)		23600		
$[\text{Ni}(\text{AQTC})_2(\text{NO}_3)_2]$	798.51	7.26	47.91	17.62	3.55	3.24	12840, 18240,	4.6	301
Greenish yellow		(7.35)	(48.08)	(17.53)	(3.50)		23250		
$[\text{Cu}(\text{AQTC})_2\text{Cl}_2]$	750.54	8.52	51.28	18.72	3.67	1.87	13600, 16800	2.7	281
Green		(8.46)	(51.16)	(18.65)	(3.73)				
$[\text{Cu}(\text{AQTC})_2\text{Br}_2]$	839.35	7.50	45.59	16.78	2.28	1.86	13500, 16600	2.8	290
Green		(7.57)	(45.74)	(16.67)	(2.35)				
$[\text{Cu}(\text{AQTC})_2(\text{NO}_3)_2]$	803.54	7.82	47.69	17.53	3.43	1.93	13400, 16300	2.9	292
Green		(7.90)	(47.78)	(17.42)	(3.48)				

Table 2: Infrared spectral bands of ligand AQTC and their metal complexes

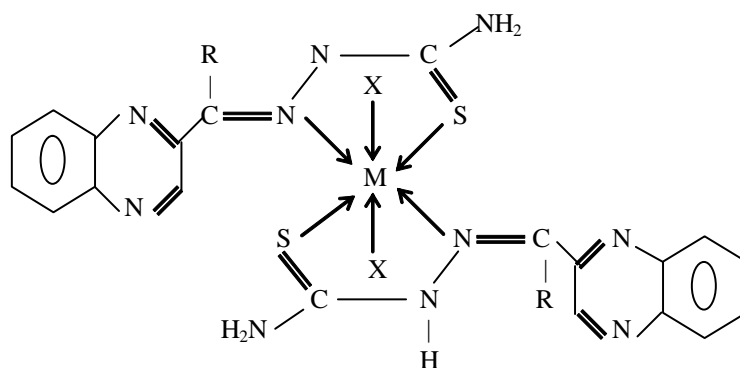
Compounds	$\nu_{C=N}$	$\nu_{C=}$	$\nu_{C=S}$	ν_{M-N}	ν_{M-S}	ν_{M-X}
AQTC	3460 m,b	1460 m,b	800 s,b			
[Co(AQTC) ₂ Cl ₂]	3460 m,b	1440 m,b	775 s,b	455 m	395 m	310 m
[Co(AQTC) ₂ Br ₂]	3460 m,b	1405 m,b	770 m,b	460 m	410 m	290 m
[Co(AQTC) ₂ I ₂]	3460 m,b	1435 m,b	770 m,b	460 m	400 m	275 m
[Co(AQTC) ₂ (NO ₃) ₂]	3460 m,b	1440 m,b	775 m,b	465 m	405 m	
[Ni(AQTC) ₂ Cl ₂]	3460 m,b	1440 m,b	770 m,b	470 m	410 m	320 m
[Ni(AQTC) ₂ Br ₂]	3460 m,b	1435 m,b	770 m,b	465 m	415 m	295 m
[Ni(AQTC) ₂ I ₂]	3460 m,b	1435 m,b	775 m,b	465 m	410 m	265 m
[Ni(AQTC) ₂ (NO ₃) ₂]	3460 m,b	1440 m,b	775 m,b	460 m	415 m	
[Cu(AQTC) ₂ Cl ₂]	3460 m,b	1440 m,b	775 m,b	465 m	400 m	315 m
[Cu(AQTC) ₂ Br ₂]	3460 m,b	1440 m,b	770 m,b	465 m	400 m	310 m
[Cu(AQTC) ₂ (NO ₃) ₂]	3460 m,b	1435 m,b	775 m,b	460 m	410 m	

cm⁻¹ which is 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 octahedral²⁵ geometry for the cobalt(II) complexes. The proposed octahedral geometry of the Cobalt(II) complexes are further supported^{24,25} by high magnetic moment value in the range 4.89 - 5.07 BM. The electronic spectra of all the Nickel(II) complexes displays three bands in regions, 13000-12600, 18280-17300, 23560-23200 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^{25,30} geometry for all the Nickel(II) complexes. The proposed octahedral geometry for

all the Nickel(II) complexes are further supported^{27,28,31} by magnetic moment value in the range 3.10-3.23 BM. The complexes of Copper(II) exhibits two spectral bands in the regions 13600-13200 cm⁻¹ and 16800-16260 cm⁻¹ assigned to ${}^2T_{2g} \leftarrow {}^2E_g$ and charge transfer bands respectively which support distorted octahedral^{25,32} geometry. The proposed geometry of copper(II) complexes are further supported^{27,28,33} by the magnetic moment value in the range 1.87 - 1.94 BM.

Antimicrobial activity

Antimicrobial and antifungal activity of ligand AQTC and their cobalt(II), nickel(II) and



[M(AQTC)₂X₂]; M = Co(II), Ni(II); X = Cl⁻, Br⁻, I⁻ and NO₃⁻.

M = Cu(II); X = Cl⁻, Br⁻ and NO₃⁻; R = Phenyl

Fig. 1.

copper(II) complexes have been tested by disc diffusion technique³⁴ at concentration level of 2.0 and 0.2% (w/v medium were used). The ligand AQTC and its metal complexes were screened for their antimicrobial activity against Gram negative bacteria, *Escherichia coli*. The antifungal activity were screened against, *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°C. Results were compared with known antibiotics tetracycline at the same concentration. It is observed that majority of compounds show moderate activity against different strains of bacteria and fungi. On comparison with reference to ligand complexes of cobalt(II), nickel(II) and copper(II) are more effective than ligand AQTC. Better activities of some of the metal complexes as compared to the ligand can be explained by chelation theory³⁵. The theory explains that decrease

in polarizability of the metal could enhance the lipophilicity of the complexes which leads to the breakdown to permeability of the cells resulting in interference with normal cell process³⁶.

CONCLUSION

Thus on the basis of above studies it may be concluded that the complexes possess the octahedral geometry around the central metal ion as shown in Fig.1.

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