

SYNTHESIS AND CHARACTERIZATION OF OXOVANADIUM (IV), Cr (III), Mn (II) AND Fe(III) COMPLEXES OF SOME QUINOXALINE SCHIFF BASES

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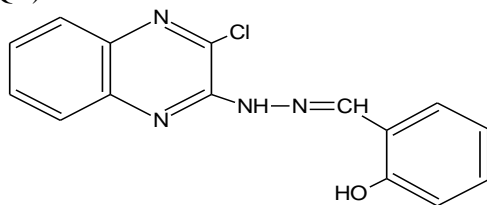
ABSTRACT

The complexes VO(IV), Cr (III), Mn (II) AND Fe(III) of Quinoxaline based Schiff Bases derived from the condensation reaction of 3-Chloro-2-hydrazinoquinoxaline with 2-Hydroxybenzaldehyde and 2-Hydroxy-3-methoxybenzaldehyde have been prepared and characterized. These two ligands function as uni-negative bidentate co-ordinating ligand with VO(IV) ions through phenolic oxygen and free azomethine nitrogen ($\text{N}=\text{C}$) and as mononegative tridentate ones towards Cr (III), Mn (II) AND Fe(III) bonding additionally through Nitrogen of ring $\text{C}=\text{N}$ group. The geometry and the bonding characteristics of the complexes have been deduced from the relevant data.

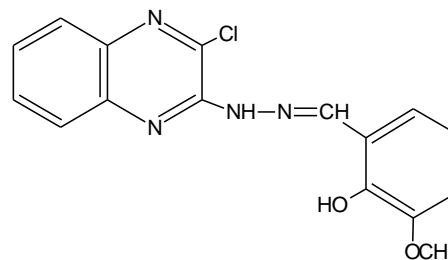
Key words: Metal complexes, Quinoxaline based Schiff bases, Synthesis, Spectral studies

INTRODUCTION

Quinoxalines are a class of fused six-membered nitrogen heterocyclics containing two nitrogens in mutually para disposition. These compounds have a wide range of applications in pharmacology, bacteriology and mycology¹⁻⁷. Quinoxaline and its derivatives have received attention as complexing agents owing to the presence of two potentially metal binding nitrogen centers at 1,4 positions. Further, significant chelating abilities could be developed in these systems by introducing suitable substituents in the heterocyclic ring or benzene ring. Metal complexes of various Quinoxaline derivatives have been synthesized and characterized over the years. Quinoxalines attract an immense interest because of their diverse pharmacological applications. Owing to the importance associated with this class of compounds. We present herein the synthesis and characterization of VO(IV), Cr(III), Mn(II) and Fe(III) complexes of Quinoxaline-based Schiff bases namely 2-Hydroxybenzaldehyde-1-(3-chloro-2-quinoxaliny)hydrazone (HBCQOH) and 2-Hydroxy-3-methoxybenzaldehyde-1-(3-chloro-2-quinoxaliny)hydrazone (HMBCQH).



HBCQOH



HMBCQH

MATERIALS AND METHODS

All the chemicals used were of A.R or B.D.H grade. The ligands HBCQOH and HMBCQH were prepared by stirred an equimolar mixture of 3-Chloro-2-hydrazinoquinoxaline with 2-Hydroxy benzaldehyde and 2-hydroxy-3-methoxy benzaldehyde in DMF at room temperature for about 2 hours. When the solid separation completed, it was filtered, washed with water and recrystallized from CHCl_3 -hexane. The colour, yield %, m.p($^{\circ}\text{C}$) and elemental analysis(%) of HBCQOH and HMBCQH are respectively, yellow 68; 175-176 $^{\circ}\text{C}$; [Found(%) C,59.72; H,3.54; N,18.39; $\text{C}_{15}\text{H}_{11}\text{N}_4\text{OCl}$ requires C,60.31; H,3.71; N,18.75] and bulk yellow, 72; 214-216 $^{\circ}\text{C}$; [Found(%) C, 58.09; H,3.83; N,16.85; $\text{C}_{16}\text{H}_{13}\text{N}_4\text{O}_2\text{Cl}$ requires C,58.46; H,3.99; N,17.04];

The Cr(III) and Fe(III), complexes with the two ligands were prepared using respective metal chlorides, Mn(II) complexes using respective metal acetates and VO(IV) complexes using sulphate.

In the preparation of all the metal complexes, the metal and the ligand were combined in 1:2 mole ratio (the metal being in slight excess of what the ratio required) using required quantities of methanol or aqueous methanol for the metal salts and methanol for the ligands so as to affect their solubility. The contents were refluxed on a water bath for 2-3 hours and the solid that separated was filtered, washed with water, hot methanol and ether and dried in air.

The elemental analyses were carried out by Carlo Erba 1108 elemental analyzer at RSIC, CDRI, Lucknow. Conductance measurements on the complexes were made in DMF at 10^{-3}M concentration on a Digisun digital conductivity meter, DI 909 model with a cell calibrated with 0.1M KCl solution was employed to measure conductance of the metal complexes in DMF at 10^{-3}M concentration. The magnetic susceptibilities of the complexes were recorded on a Faraday balance (CAHN-7550-03) at room temperature using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the standard. Diamagnetic corrections were applied using Pascals's constants. The infrared spectra of the ligands and the metal complexes were recorded in KBR pellets in the range $4000\text{--}400\text{cm}^{-1}$ on Perkin Elmer-BX spectrophotometer at central Instrumentation center, Kakatiya University. The electronic spectra of the metal complexes in DMF were recorded on ELICO SL-159 UV-Vis spectrophotometer. The $^1\text{H-NMR}$ spectra of the ligands were recorded in DMSO-d_6 solution employing Bruker avance 300 MHz and Variagemin 200 MHz. The Chemical shifts are given in ppm downfield from

tetramethylsilane. The JEOL FE1X ESR spectrometer operating in the frequency range 8.8 - 9.6GHz was employed in recording ESR spectra of the VO(IV) complexes of all the ligands in DMF at liquid nitrogen temperature.

RESULTS AND DISCUSSION

All the metal complexes are coloured, stable at RT and are non hygroscopic. They are insoluble in water and soluble in DMF and DMSO. All the metal complexes which are non –electrolytic in DMF give satisfactory C, H, N and M analyses corresponding to 1:2 metal-organic ligand stoichiometry. The magnetic studies reveal that VO (IV), Cr (III), Mn (II) and Fe(III) complexes of the two ligands are paramagnetic to the extent of one ,three, five and five unpaired electrons respectively.

The molar conductance values observed for the present VO (IV), Cr (III), Mn (II), and Fe (III) complexes of HBCQOH and HMBCQH in dimethylformamide at 10^{-3} M concentration are given in Table.1.

Table.1.Molar conductance ($\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$) data for the present metal complexes

Metal complex	Molar conductance
[VO(HBCQOH-H) ₂]	16
[Cr(HBCQOH-H) ₂]Cl	72
[Mn(HBCQOH-H) ₂]	12
[Fe(HBCQOH-H) ₂]Cl	75
[VO(HMBCQH-H) ₂]	12
[Cr(HMBCQH-H) ₂]Cl	68
[Mn(HMBCQH-H) ₂]	13
[Fe(HMBCQH-H) ₂]Cl	72

An examination of the data in table indicates at the Cr(III) and Fe(III) complexes of the ligands are 1:1 electrolytes and VO(IV) and Mn(II) complexes are non electrolytes.

The ligands HBCQOH and HMBCQH show in their spectra a medium intensity band in the region $3200\text{--}3330 \text{ cm}^{-1}$ that has been assigned to $\nu\text{O-H}$. This band disappears in the spectra of their complexes indicating that deprotonation of the group has taken place. A small or medium intensity band around 1230 cm^{-1} in the ligands assignable to $\nu\text{C-O}$ is seen to have undergone a positive shift by $30\text{--}50\text{ cm}^{-1}$ in the complexes suggesting coordination through phenolic oxygen. The positive shift observed may be attributed to the drift of electron density from oxygen to the metal ion resulting in greater ionic character of the C-O bond and a consequent increase in its vibration frequency. The ligands record a somewhat broad, medium intensity band around 3430 cm^{-1} attributable to free $\nu\text{N-H}$. This band remains either unshifted or higher shifted in the complexes indicating nonparticipation of nitrogen of this group in coordination. Further, the ligands reveal bands around 1620 cm^{-1} due to free $\nu\text{C=N}$ and around 1580 cm^{-1} due to ring $\nu\text{C=N}$. While the band due to free $\nu\text{C=N}$ has got lower shifted by $10\text{--}20\text{ cm}^{-1}$ in all the complexes, the band due to ring $\nu\text{C=N}$ is lower shifted by $20\text{--}30\text{ cm}^{-1}$ in the Cr(III), Mn(II) and Fe(III) complexes and remains unshifted in VO(IV) complexes. This suggests that the ligands act as mononegative, bidentate ones bonding through phenolic oxygen and nitrogen of free C=N group in VO(IV) complexes and as mononegative, tridentate ones coordinating additionally through nitrogen of ring C=N in Cr(III), Mn(II) and Fe(III) complexes.

The present VO(IV) complexes of HBCQOH, HMBCQH, HDICQH and HNCQOH each show three peaks in their electronic spectra around 14500 , 16600 and 25500 cm^{-1} which may be assigned respectively to the transitions, ${}^2\text{B}_2 \rightarrow {}^2\text{E}$, ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ and ${}^2\text{B}_2 \rightarrow {}^1\text{A}_1$. Based on these observations and the analytical and the other data obtained for the complexes, they have been assigned square pyramidal geometry. The Cr(III) complexes reveal each three peaks around 16500 , 23000 and 32000 cm^{-1} assignable respectively to ${}^4\text{A}_2\text{g} \rightarrow {}^4\text{T}_{2\text{g}}$, ${}^4\text{A}_2\text{g} \rightarrow {}^4\text{T}_{1\text{g}}(\text{F})$ and ${}^4\text{A}_2\text{g} \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})$. The Mn(II) complexes each show three very weak bands around 13000 , 19000 and 24500 cm^{-1} assignable respectively to ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}}(\text{G})$, ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}(\text{G})$ and ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{E}_{\text{g}}(\text{G})$. Fe (III) complexes show three weak bands around 12500 , 15600 and 20000 cm^{-1} . The ground state of Fe(III), in a weak octahedral field, is ${}^6\text{A}_{1\text{g}}$ with an electron in each d-orbital thus making the transitions spin –forbidden. The weak bands observed for the present complexes may be assigned in the increasing order of frequency to ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}}(\text{G})$, ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}(\text{G})$ and ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{E}_{\text{g}}(\text{G})$. Based on electronic spectral data the complexes of Cr(III), Mn(II), and Fe(III) are shows octahedral geometry.

Table.2.Electronic spectral data of the metal complexes of HBCQOH and HMBCQH

Metal complex	Frequency (cm^{-1})			ν_2/ν_1	10DQ cm^{-1}	B cm^{-1}	β
VO-HBCQOH	14480	16660	25500	---	---	---	---
Cr-HBCQOH	16500	23000	32000	---	---	---	---
Mn-HBCQOH	13120	19180	24610	---	---	---	---
Fe-HBCQOH	12500	15600	20000	---	---	---	---
VO-HMBCQH	14450	16680	25470	---	---	---	---
Cr-HMBCQH	16480	23750	31950	---	---	---	---
Mn-HMBCQH	13110	19190	25000	---	---	---	---
Fe-HMBCQH	12410	15550	20450	---	---	---	---

The spectra of all the four VO(IV) complexes are well resolved with eight parallel and eight perpendicular components due to hyperfine coupling with vanadium nucleus of $I = 7/2$. The g and A values obtained for the complexes are in agreement with those generally observed for a vanadyl complex with a square pyramidal geometry. For all the complexes, $g_{\parallel} < g_{\perp} < g_e$ (where g_e is free electron value) which indicates that the unpaired electron is in the d_{xy} orbital with 2B as the ground state.

Table.3.ESR parameters of VO (IV) complexes

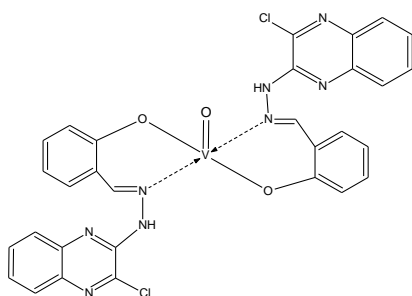
Complex	g_{\parallel}^*	g_{\perp}^*	g_{av}^{**}	$A_{\parallel} \times 10^4$ (cm^{-1})	$A_{\perp} \times 10^4$ (cm^{-1})	$A_{av}^{***} \times 10^4$ (cm^{-1})	α^2	β^2	γ^2	$-\lambda$ (cm^{-1})
VO-HBCQOH	1.95	1.99	1.98	147	34	72	---	---	---	---
VO-HMBCQH	1.94	2.00	1.98	140	45	80	---	---	---	---

* g_{\parallel} and g_{\perp} values have been calculated from the small and large intensity peaks respectively⁹⁸.

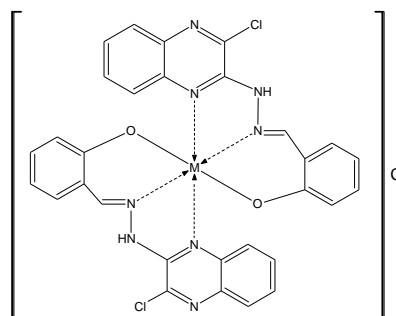
** $g_{av} = 1/3 (g_{\parallel} + 2g_{\perp})$

*** $A_{av} = 1/3 (A_{\parallel} + 2A_{\perp})$

The schematic drawing of metal complexes formed with the representative ligand HBCQOH is shown in figure.



Structure of VO(IV)-HBCQOH



Structure of Cr(III) and Fe(III) complexes of HBCQOH

CONCLUSION: Synthesis and characterization of oxovanadium (iv), cr (iii), mn (ii) and fe(iii) complexes of some quinoxaline schiff bases was done by following the above mentioned methods.

REFERENCES

- Singh, B., Singh, R.N. and Aggarwal, R.C., Synth. React. Inorg. Met. Org. Chem., 14, 1984, 815.
Demertzi, D. and Nicholls, D., Inorg. Chim. Acta, 73, 1983, 37.
Hursthouse, M.B., Amarasiri, S., Jayaweera, A. and Quick, A., J. Chem. Soc., Dalton Trans., 1979, 279.
Haran, R., Gairin, J. and Commenger, G., Inorg. Chim. Acta, 46, 1980, 63.
Murphy, T.B., Johnson, D.K., Rose, N.J., Aruffo, A. and Schomaker, V., Inorg. Chim. Acta, 66, 1982, 67.