SYNTHESIS AND SPECTRAL 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 2,3-dihydroxybenzaldehyde and 2,4-dihydroxybenzaldehyde 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 (C=N) and as mononegative tridentate ones towards Cr (III), Mn (II) and Fe(III) bonding additionally through Nitrogen of ring C=N group. The geometry and the bonding characterstics of the complexes have been deduced from the relevant data.*

1. 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 mycology[1-7].

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 intrest 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 2,3-Dihydroxybenzaldehyde-1-(3-chloro-2-quinoxalinyl)hydrazone [DHBCQH] and 2,4-dihydroxybenzaldehyde-1-(3-chloro-2-quinoxalinyl)hydrazone [DHCQOH] .

2, 3-Dihydroxybenzaldehye-1-(3-chloro-2-quinoxalinyl)hydrazone [DHBCQH]
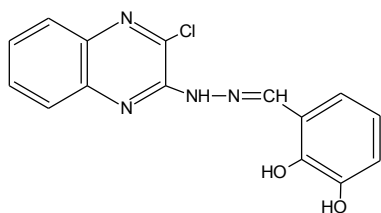
2, 4-dihydroxybenzaldehyde-1-(3-chloro-2-quinoxalinyl)hydrazone [DHCQOH]
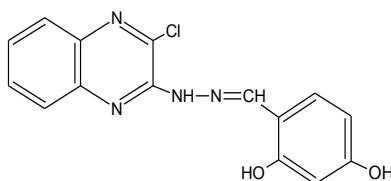
2. EXPERIMENTAL:

All the chemicals used were of A.R or B.D.H grade. The ligands DHBCQH and DHCQOH were prepared by stirred an equimolar mixture of 3-Chloro-2-hydrazinoquinoxaline[8]   with 2,3-dihydroxybenzaldehyde and 2,4-dihydroxybenzaldehyde in DMF at room temperature for about 2 hours. When the solid separation completed, it was filtered, washed with water and recrystalled from CHCl$_3$-hexane. The colour, yield %, m.p(^{0}C) and elemental analysis(%) of DHBCQH and DHCQOH are respectively, bulk orange 66; 223-225 ^{0}C;[Found(%) C,56.74; H,3.45; N,17.48; C$_{15}$H$_{11}$N$_4$OCl requires C,57.24; H,3.52; N,17.80] and bulk orange, 69; 230-232^{0}C;[Found(%) C,58.09; H,3.83; N,16.85; C$_{16}$H$_{13}$N$_4$O$_2$Cl requires C,57.24; H,3.52; N,17.80];

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 effect 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 $Hg[Co(NCS)_4]$ as the standard. Diamagentic corrections were applied using Pascals's constants[9]. The infrared spectra of the ligands and the metal complexes were recorded in KBR pellets in the range 4000–400cm^{-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}H-NMR spectra of the ligands were recorded in DMSO-d_6 solution employing Bruker avance 300 MHz and Variangemini 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.

3. 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 DHBCQH and DHCQOH in dimethylformaamide at 10^{-3}M concentration are given in Table.

Molar conductance (Ohm^{-1}. cm^2. mole^{-1}.) data for the present metal complexes:

S.No.	Metal complex	Molar conductance
1	VO(DHBCQH-H)$_2$	12
2	[Cr(DHBCQH-H)2]Cl	71
3	[Mn(DHBCQH-H)$_2$]	12
4	[Fe(DHBCQH-H)$_2$]Cl	73
5	[VO(DHCQOH-H)$_2$]	10
6	[Cr(DHCQOH-H)$_2$]Cl	68
7	[Mn(DHCQOH-H)$_2$]	10
8	[Fe(DHCQOH-H)$_2$]Cl	75

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 thermogravimetric analysis of VO(IV) and Fe(III) complexes of DHBCQH has been studied. The thermograms of these complexes of thermal data are presented in table.

Per cent pyrolysis of the metal complexes of DHBCQH

Complex	Wt. of the complex taken (mg)	Per cent pyrolysis	
		Experimental	Theoretical (Metal oxide as the final product)
[VO(DHBCQH-H)$_2$]	6.7	83	85
[Fe(DHCQOH-H)$_2$]Cl	10.5	74	77

The thermograms of the complexes indicates that they are thermally stable to different temperatures. They lose weight on heating almost in a continuous manner attaining constancy in weight at different temperatures, for VO(IV)

complex above 520^0C and   Fe(III) complex above 690^0C. The per cent weight loss as computed from the thermograms of the complexes suggests that the final product of decomposition in all the cases, corresponds, within the permissible experimental error, to the respective metal oxide. It may be noted that the thermogravimetric analysis of the complexes gives further support to the composition of the complexes proposed on the basis of their elemental analysis data.

The ligands DHBCQH and DHCQOH   show, in their spectra, a medium intensity band at 3305 and 3315 cm^{-1} that has been assigned to νO-H (ortho and para). This band intensity decreases in the spectra of their complexes indicating that one of the phenolic group is involved, after deprotonation, in coordination to the metal. A small or medium intensity band around $1230cm^{-1}$ in the ligands assignable to νC-O is seen to have undergone a positive shift by $30-50cm^{-1}$ in the complexes suggesting coordination through phenolic oxygen[9]. 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[10]. The ligands record a somewhat broad, medium intensity band around $3440cm^{-1}$ attributable to free νN-H[11]. 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 $1640cm^{-1}$ due to free νC=N and around $1575cm^{-1}$ due to ring νC=N. While the band due to free νC=N has got lower shifted by $10-20cm^{-1}$ in all the complexes, the band due to ring νC=N is lower shifted by $20-30cm^{-1}$ 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[12-14] . An intense band that appears around $750cm^{-1}$ in all the ligands and their metal complexes has been assigned to νC-Cl[15] and fairly intense band that figures around $953cm^{-1}$ in the VO(IV) complexes has been attributed to νV=O[16].The coordination through phenolic oxygen and azomethine nitrogen(s) is further substantiated by the appearance, in all the complexes, of non-ligand bands in the far infrared region around 500 and $400cm^{-1}$ assignable repectively to νM-O and νM-N vibrations[17,18]. From the foregoing presentation, it may be concluded that the ligands DHBCQH and DHCQOH function as mononegative, bidentate ones towards VO(IV) coordinating through phenolic oxygen and free C=N nitrogen and as mononegative, tridentate ones towards Cr(III), Mn(II) and Fe(III).

The electronic spectral frequencies observed for the VO(IV), Cr(III), Mn(II) and Fe(III) complexes of DBCQH and DCQOH and the relevant ligand field parameters are presented in table. The spectral features of the complexes of a particular metal ion with the two ligands is same.

Electronic spectral data of the metal complexes of DHBCQH and DHCQOH.

S.No.	Metal complex	Frequency (cm^{-1})			ν_2/ν_1	10DQ cm^{-1}	B cm^{-1}	β
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	VO-DHBCQH	14700	17500	25000	---	---	---	---
2	Cr- DHBCQH	16480	23200	32000	---	---	---	---
3	Mn- DHBCQH	13160	18890	24150	---	---	---	---
4	Fe- DHBCQH	14230	20310	25350	---	---	---	---
5	VO-DHCQOH	14720	17800	24690	---	---	---	---
6	Cr-DHCQOH	16500	23000	31900	---	---	---	---
7	Mn-DHCQOH	13000	19000	24510	---	---	---	---
8	Fe- DHCQOH	14190	20200	25410	---	---	---	---

The present VO(IV) complexes show each three peaks in the frequency region 14700 - 25000 cm^{-1} (Table) which may be assigned to the transitions $^2B_2 \longrightarrow {}^2E_2, {}^2B_2 \longrightarrow {}^2B_1$ and $^2B_2 \longrightarrow {}^2A_1$ in the increasing order of frequency. These observations, coupled with the other data obtained for the complexes suggest square-pyramidal geometry for them[19-21].The present Cr(III) complexes show each three peaks in the frequency regions 16480 - $32000cm^{-1}$ assignable respectively to $^4A_{2g} \longrightarrow {}^4T_{2g}$, $^4A_{2g} \longrightarrow {}_{1g}(F)$ and $^4A_{2g} \longrightarrow {}_{1g}(P)$[22]. The Mn(II) and Fe(III) complexes of the ligands each show three weak bands respectively in the region 13000 – 24510 and 14190 – $25410cm^{-1}$ that could be assigned to the spin-forbidden transitions as given for the complexes of these metal ions in the previous section of the chapter. The complexes have been assigned octahedral geometry based on their electronic spectra, analytical and magnetic data[23-27].

The spectra of VO(IV) complexes are well resolved with eight parallel and eight perpendicular components due to hyperfine coupling with vanadium (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 dispositon[28]. For all the complexes $g_\parallel < g_\perp <$ g_e (g_e = free electron value) which indicates that the unpaired electron is in the d_{xy} orbital[29,30].

ESR parameters of VO(IV) and Cu(II) complexes

Complex	$g_\parallel$ *	$g_\perp$ *	g_{av} **	$A_\parallel$ x 10^4 (cm^{-1})	$A_\perp$ x 10^4 (cm^{-1})	A_{av} *** x 10^4 (cm^{-1})	α^2	β^2	γ^2	$-\lambda$ (cm^{-1})
VO-DHBCQH	1.94	1.99	1.97	107	57	73	---	---	---	---
VO-DHCQOH	1.94	2.00	1.98	125	50	80	---	---	---	---

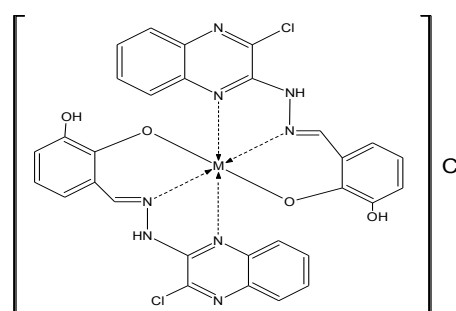* $g_\parallel$ and $g_\perp$ values have been calculated form the small and large intensity peaks respectively[31].
** g_{av} = 1/3 ($g_\parallel$ + 2$g_\perp$)　　　　　　　　　*** A_{av} = 1/3 ($A_\parallel$ + 2$A_\perp$)

The schematic drawing of metal complexes formed with the representative ligand HBCQOH is shown in figur
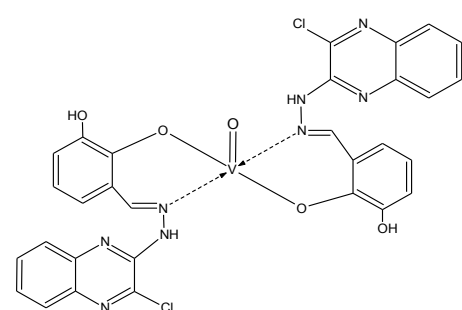
Structure of VO(IV) complexes of DHBCQH

M = Cr or Fe
Structure of Cr(III) and Fe(III)complexes of DHBCQH

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