Synthesis and Spectral Characterization of Metal Complexes of Quinaxaline Schiff Base

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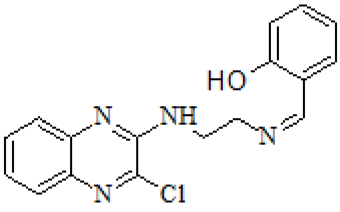
Abstract: ***The VO(IV), Pd(II), Zn(II), Cd(II), Hg(II), Ru(III), Au(III) and UO_2(VI) complexes of Schiff bases derived from N-(3-choloroquinoxaline-2-yl)ethane-1,2-diamine and 2-hydroxy benzaldehyde has been synthesized and characterized by physico-chemical data. The ligand behaves towards the metal ions as mononegative, bidentate ones co-ordinating through phenolic oxygen and azomethine nitrogen. The geometry and the bonding characteristics associated with the complex have been deduced from the relevant spectral data.***

Keywords: Choloroquinoxaline Schiff base complexes, Synthesis, Characterization

1. Introduction

Quinoxaline derivatives are biologically active and find application in medicinal use[1]. These compounds have potent donor groups and despite this, the studies directed towards exploring the ligational behaviour of these compounds are limited. For this reason, we report, herein, the synthesis and chracterization of VO(IV), Pd(II), Zn(II), Cd(II), Hg(II), Ru(III), Au(III) and UO_2(VI) complexes of Schiff base namely 2-(2-hydroxy benzylamino)-3-chloro ethylene diamine quinoxaline(HBCEQ).



Ar = C_7H_5O

2. Experimental

N-(3-choloroquinoxaline-2-yl)ethane-1,2-diamine was synthesized according to reported procedure and all other chemicals used were of A.R. or B.D.H. grade. The ligands HBCEQ was synthesized by refluxing equimolar methanolic solutions *N*-(3-choloroquinoxaline-2-yl)ethane-1,2-diamine and the respective salacialdehyde in presence of a few drops of piperidine for 6 hrs. The solids that separated during reflux was filtered, washed with methanol and re-crystallised from hot dry methanol. The colour, yield%, mp (°C) and elemental analysis (%) of HBCEQ, are dirty white, 38, 230°C (Found C 66.70, H 4.86, N 18.03; $C_{17}H_{15}ClN_4$ requires C 65.70, H 4.86, N 17.92).

The Zn(II), Cd(II) and UO_2(VI) complexes were prepared taking respective metal acetates, Pd (II), Ru(III) and Au(III) complexes using metal chlorides and VO(IV) complexes using vanadyl sulphate. In the preparation of VO(IV), Pd(II), Zn(II), Cd(II), Hg(II), Au(III) and UO_2(VI) complexes, the metal and the ligand were combined in 1:2 mole ratio while in the case of Ru(III) complexes they were mixed in 1:3 ratio using aqueous methanol for the metal salts and methanol-DMF (20:1) mixture for ligand. The contents were refluxed on a water bath for about 3h, the solid that separated was filtered, washed with water, hot methanol and ether and dried in air.

The elemental analyses of the ligand and the complexe were carried out by CDRI, Lucknow. Conductance measurements were made in DMF at 10^{-3} M concentration on a Digisun digital conductivity meter DI 909 model. Gouy balance calibrated with $Hg[Co(SCN)_4]$ was used to measure the magnetic susceptibility of the metal complexes at room temperature. The IR spectra of the ligands and the metal complexes in KBr were recorded in the range 4000-400 cm^{-1} using Brucker FT/IR 5300 spectrophotometer. The electronic spectra of the metal complexes in DMF were recorded on Systronics UV-VIS spectrophotometer. The Varian E4 X-band spectrophotometer operating in the frequency range 8.8-9.6 GHz available with RSIC, IIT, Chennai was employed in recording the ESR spectra of VO(IV) complexes in DMF solution at LNT.

3. Results and Discussion

All the metal complexes (Table 1) are stable at room temperature and are non-hygroscopic. The metal complexes decompose upon heating without melting. The ligands and its metal complexes are insoluble in water, slightly or very slightly soluble in methanol and acetone and fairly soluble in dimethyl formamide. With the exception of Au(III) complexes which are 1:1 electrolytes with molar conductance in the range (78-85), all others are non-electrolytes showing only residual conductance (10-14). The magnetic moment data indicate that VO (IV) and Ru(III) complexes are paramagnetic to the extent of one unpaired electron while all others are diamagnetic. The ligand show broad intensity band in the region 3365-3400cm-1 assigned to ν-NH remains unshifted in the complex indicates –NH group is not participate in the bonding, The ligand show, in its spectra, a medium intensity band in the region 3190-3200cm^{-1} that has been assigned to νO-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 1230cm^{-1} in the ligand assignable to νC-O is seen to has undergone a positive shift by 30-50cm^{-1} in the complexes suggesting coordination through phenolic oxygen[2]. 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 νC-O bond and a consequent increase in its vibration frequency[3]. Further, the ligand reveal band around 1660cm^{-1} due to free νC=N and around 1580cm^{-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 remains unshifted in the complexes. These observations suggest that the ligands act as mononegative, bidentate ones bonding through phenolic oxygen and nitrogen of free νC=N group [4-6].

An intense band that appears around 750cm^{-1} in the ligand and its metal complexes has been assigned to νC-Cl [7] and a fairly intense band that figures around 950cm^{-1} in all the VO(IV) complexe has been attributed to νV=O[8].

The coordination through phenolic oxygen and azomethine nitrogen is further substantiated by the appearance, in all the complexes, of non-ligand bands in the far infrared region around 590 and 450cm^{-1} assignable respectively to νM-O and νM-N vibrations [9-10].

The electronic spectral data for the VO(IV), Ru(III) and Pd(II) complexes are presented in Table 2.

The VO (IV) complexes each show three peaks in the region 11100 – 28570 cm^{-1} which may be assigned in the increasing order of frequency to the transitions $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightrightarrows {}^2B_1$ and $^2B_2 \rightrightarrows {}^2A_1$ of square pyramidal geometry [11].

The Pd(II) complexes each show three peaks in the region 12195-25000 cm^{-1} that are assignable, in the increasing order of frequency to the transitions, $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g}$, $^1B_{1g}$ and $^1A_{1g}$ ^1E_g of square planar geometry [12].

Based on these data, the complexes have been assigned square planar geometry.

The Ru(III) complexes reveal three peaks in the region 11490 – 25000 cm^{-1} which may be assigned in the increasing order of frequency to the transitions $^2T_{2g} \rightarrow {}^4T_{1g}$, $^2T_{2g} \rightarrow {}^4T_{2g}$ and $^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$ of octahedral geometry[13].

The Zn(II), Cd(II) and Hg(II) complexes of HBCEQ show, as expected, no d-d transitions in their electronic spectra and on the basis of analytical, conductance and infrared spectral data, they have been assigned tetrahedral geometry. The Au(III) and UO_2(VI) complexes show only charge transfer (above 35000cm^{-1}) but no d-d bands and based on this observation and the other data obtained for the complexes, Au(III) complexes have been assigned square planar geometry and the UO_2(VI) complexes, octahedral geometry.

The ESR spectral parameters calculated for the VO(IV) complexes using appropriate methods and equations [14].The spectra of the complexe is well resolved with eight parallel and eight perpendicular components due to hyperfine coupling with vanadium nucleus I = 7/2. The g values observed for the present complexes are in agreement with those generally observed for a vanadyl complex with a square pyramidal geometry[15]. For the complexe, $g_{\parallel} < g_{\perp} < g_e$ (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 [16].

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Table 1: Analytical & Physical Data of Metal Complexes

Metal complex	Per cent			Molar cond. Ω^{-1} cm^2 mol^{-1}	μ_{eff} B.M.
	C	H	N		
$[VO(C_{17}H_{15}ClN_4O)_2]$	56.78 (56.84)	3.78 (3.93)	15.57 (15.60)	10	1.78
$[Pd(C_{17}H_{15}ClN_4O)_2]$	53.84 (53.88)	3.70 (3.72)	14.75 (14.78)	12	--
$[Zn(C_{17}H_{15}ClN_4O)_2]$	56.88 (56.96)	3.92 (3.94)	15.59 (15.63)	14	--
$[Cd(C_{17}H_{15}ClN_4O)_2]$	53.40 (53.45)	3.62 (3.69)	14.65 (14.67)	11	--
$[Hg(C_{17}H_{15}ClN_4O)_2]$	47.90 (47.92)	3.29 (3.31)	13.05 (13.15)	10	--
$[Ru(C_{17}H_{15}ClN_4O)_3]$	56.72 (56.80)	3.91 (3.93)	15.53 (15.57)	10	1.79
$[Au(C_{17}H_{15}ClN_4O)_2]$ Cl	48.12 (48.13)	3.29 (3.33)	13.18 (13.21)	80	--
$[UO_2(C_{17}H_{15}ClN_4O)_2$	45.82 (45.91)	3.12 (3.17)	12.56 (12.60)	11	--

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Table 2: Electronic Spectral Data of Metal Complexes

Metal complex	Frequency (cm^{-1})		
VO-HBCMQ	11710	17240	28570
Pd-HBCMQ	12195	20000	25000
Ru-HBCMQ	11490	18870	25000

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