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Synthesis, Characterization and Thermal studies of Schiff base complexes of Co(II),Ni(II),Cu(II),Zn(II),Cr(III), Fe(III),Mn(III),VO(IV) and Zr(IV)

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Abstract: Solid Complexes of Co(II), Ni(II),Cu(II),Zn(II), Cr(III), Fe(III), Mn (III),VO(IV) and Zr(IV) with Schiff base [LH_2] derived from 2,4–dihydroxy benzophenone and isonicotinoyl hydrazide have been synthesized and characterized on the basis 0f elemental analysis, infrared, ^{1}H NMR, molar conductance, magnetic susceptibilities, electronic spectra and thermogravimetric analysis.The Schiff base acts as monobasic bidentate ligand commonly coordinates through the oxygen atom of the deprotonated phenolic group and the nitrogen atom of azomethine group. which is confirmed by IR spectral data. Thermal analysis indicates the lattice and coordinated water molecules in the complexes which is also IR spectral data. The analysis of magnetic susceptibility, thermal analysis and electronic spectral data indicate square planar geometry for the Cu(II) & Ni(II) complexes, square pyramidal geometry for the Mn(III) and VO(IV) complexes, while octahedral geometry for the other complexes.

Keywords: Schiff base, Magnetic susceptibility, Thermogravimetric analysis.

Introduction

Schiff bases are an important class of ligand in coordination chemistry. Schiff bases or their metal complexes have many applications in different fields[1]. Schiff bases derived from hydrazones and aroyl hydrazines have been widely used as ligand for the synthesis of transition metal complexes[2]. Hydrazones, heteroaroyl hydrazones ligands and their metal complexes are biologically active. Heteroaroyl hydrazones forms stable metal complexes with transition metal ions and inner transition metal ions due to complexing ability of ligand through keto-enol tautomerism and availability of other donar sites in the ligand .Pyridine 4-carbonyl hydrazide i.e. isonicotinoyl hydrazide is one of the drug in chemotherapy of tuberculosis[5].Due to its biological potency, pharmacological properties and synthetic flexibility of Schiff base derived from isonicotinicacid hydrazide. The aim of present investigation is to synthesize various transition metal complexes of Schiff base derived from 2,4 –dihydroxy benzophenone and isonicotinoyl hydrazide.

Experimental

All the chemicals were of A.R. grade and used as received isonicotinoyl hydrazide(IH) was obtained from E. Merk (India), 2,4 –dihydroxy benzophenone(DHB) was obtained from S.D.Fine chemicals. Manganese(III) acetate dihydrate was prepared by Christensen's method [6] and the solvents were purified by standard methods.[7]

Synthesis of 2,4 –dihydroxy benzophenone isonicotinoyl hydrazone[DHBIH]:

A solution of isonicotinoyl hydrazide (0.02M) in 25ml of ethanol was added to an etanolic solution(25ml) of 2,4–dihydroxy benzophenone (0.02M) and the reaction mixture was refluxed on a water bath for 4h.,Then cooled to room temperature.

The resulting pale yellow coloured solid was washed with ethanol, crystallized from DMF and dried under reduced pressure at ambient temprature The purity of ligand was checked by elemental analysis, mp. and TLC. It was also characterized by IR and ^{1}H NMR spectral studies. Yield:70% MP. 268-270 ^{0}C.

Preparation of complexes

All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand DHBIH (0.02M) in 25ml of ethanol a suspension of respective metal salts [chlorides of Zn(II),Fe(III),Cr(III), acetates of Co(II),Ni(II), Cu(II),Mn(III) and $VOSO_4 .5H_2O$] was added drop wise with constant stirring. The reaction mixture was refluxed on a water bath for 4-6 h. The precipitated complexes were filtered.washed with ethanol. followed by ether and dried over fused calcium chloride. Yield : 45-50%

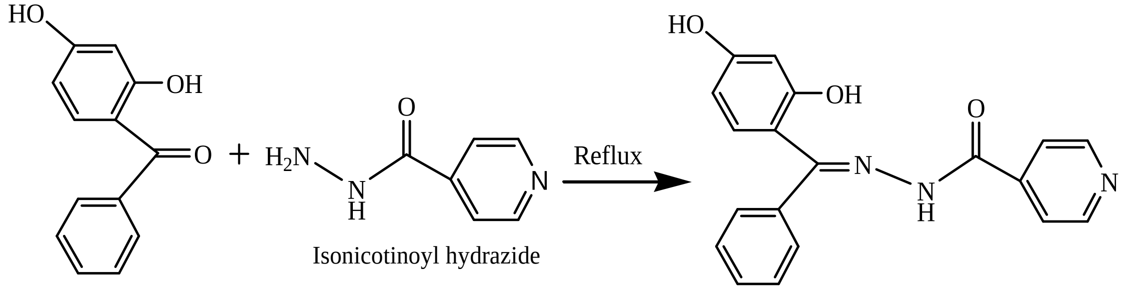
Preparation of Zr(IV) complex

A ethanolic solution of sodium acetate (0.04m,15ml) was added to a ethanolic solution of Zirconyl oxycholirde (0.02m,15ml) with constant stirring and the separated NaCl was filtered off. The solution of DHBIH (0.02M) was added and refluxed for 4h. The resulting solid was filtered and washed with hot water followed by ethanol and finally dried over fused calcium chloride.(Yield: 60%)

The complexes are soluble in DMSO and DMF but insoluble in water and common organic solvents. The metal chloride content of complexes were analyzed by standard methods[8]. The ^{1}H NMR spectra of ligand was recorded and obtained from RSIC Chandigarh. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000cm^{-1}, Carbon, Hydrogen and Nitrogen analysis were carried out at RSIC, Punjab university, Chandigarh. The molar conductance of the complexes at 10^{-3} M dilution in DMF were determined using equiptronic digital conductivity meter EQ-660 with a cell constant 1.00 cm^{-1} at room temperature. The magnetic moment measurement were made on a Gouy balance at room temperature using $[HgCo(SCN)_4]$ as the calibrant. The thermogravimetric analysis were performed on laboratory set up apparatus in air atmosphere at 10^0 C min^{-1} heating rate. The molecular weights of the complexes were determined by Rast method.

Table1. Analytical data of the Ligands.

Sr. No.	Ligand	Molecular Formula	Formula Weight	Color and nature	Elemental Analysis		
					C% found (Cal.)	H% Found (Cal.)	N% Found Cal.
1.	DHBIH	$C_{19}H_{15}N_3O_3$	333	Yellow Crystalline	(68.37) 68.46	(4.39) 4.50	(12.50) 12.61



Scheme 1-Synthesis of the ligand (LH_2)

Table 2. Analytical data and molar conductance of the compounds

Compounds	Colour	Mol.wt.	Analysis % Found (calc.) M	C	H	N	μ_{eff} B.M.	Λ_M ($\Omega^{-1}cm^2mol^{-1}$)
$[Co(LH)_22H_2O]$ $H_2$0	Brown	776.9	7.66 (7.58)	58.46 (58.69)	4.21 (4.37)	10.62 (10.81)	4.8	3.5
$[Ni(L)H_2O]2H_2$0	Green	443.7	13.35 (13.28)	51.12 (51.38)	3.67 (3.83)	9.21 (9.46)	Dia	7.19
$[Cu(LH)_2]$ $3H_2$0	Green	781.5	8.22 (8.13)	58.09 (58.34)	4.22 (4.35)	10.54 (10.74)	1.81	5.84
$[Zn(LH)_22H_2O]$ $2H_2$0	Yellow	801.3	8.26 (8.15)	55.87 (56.90)	4.31 (4.49)	10.23 (10.48)	Dia	---
$[Cr(LH)_2(H_2O)Cl]H_2$0	Rust	787.5	6.93 (6.60)	56.50 (57.90)	3.97 (4.06)	5.14 (5.33)	3.8	23.8
$[Mn(L)(H_2O)(OAC)H_2$0	Brown	480.9	11.55 (11.42)	51.96 (52.40)	4.10 (4.15)	8.57 (8.73)	4.9	8.1
$[Fe(LH)_2(H_2O)Cl]H_2$0	Brown	791.34	7.28 (7.05)	57.23 (57.62)	3.92 (4.04)	10.43 (10.61)	6.0	12.4
$[VO(L)_2]$	Brown	729	7.10 (6.99)	62.58 (62.55)	3.59 (3.56)	11.56 (11.52)	1.79	16.0
$[Zr(LH)_2(OH)_2]3H_2$0	Brown	843.22	10.96 (10.81)	53.84 (54.07)	4.17 (4.26)	9.58 (9.96)	Dia	12.2

Result and Disscution

The ligand DHBIH and its complexes have been characterized on the basis of ^{1}H NMR, IR spectral data, elemental analysis, diffused reflectance spectra, molar conductance, magnetic succeptibility measurements and thermogravimetric analysis data .

The^{1}H NMR spectra of ligand DHBIH shows signals[9,10,11,12] at δ 12.51, (1H, s phenolic OH at C_2), δ 11.40 (1H, s, imino), δ 10.11 (1H, s, phenolic OH at C_4), δ 8.68-8.66 (4H, d, isonicotine), δ 7.76-7.38 (3H, m, phenyl) δ 6.38 to 3.34 (5H, m, phenyl). All these values and analytical data is consistent with proposed molecular formula of ligand . All the compounds are coloured solid and stable in air. All the compounds are insoluble in water but soluble in coordinating solvents like DMF and DMSO. The molar conductance values in DMF(10^{-3} M) solution at room temperature (Table1) shows all the complexes are non electrolytes.

IR spectra of ligand shows **V**(C=N) peaks at 1632 cm^{-1} and absence of C=O peak at around 1700 – 1750 cm^{-1} indicates the Schiff base formation. Other reported peaks are V(N-H) at 3250 cm^{-1} , V(OH) at 3435cm^{-1}, V(C=O) phenolic at 1498 cm^{-1}, pyridyl ring breathing peak at 1061 cm^{-1}, V(N=N) peak at 996 cm^{-1} and V(C=N) peak at 1632 cm^{-1}, A peak at 2875 cm^{-1}attributed to hydrogen bonded phenolic OH. The absence of peak at 2875 cm^{-1}due to V(OH/NH) in all the complexes indicates the coordination of phenolic oxygen ,which is further supported by increase in phenolic CO stretching frequencies in the spectra of complexes.[13] The V(C=N) peak of ligand is found to be shifted to lower frequencies by 18 – 25 cm^{-1} in the spectra of complexes indicating the coordination via the azomethine nitrogen[14],which is also confirmed by appearance of bands in the range of 440 – 420 cm^{-1} which have been assigned to V(M-N) band.The V(N-H) and V(C=O) bands remain unshifted in the complex of Co(II),Zn(II),Cr(III),Fe(III) and Zr(IV) indicating the non involvement of amide oxygen of ligand in the coordination.[15] It is therefore indicates that ligand behave as monobasic bidentate donor in these complexes. The spectra of Mn(III) and VO(IV) complexes do not shows bands due to V(N-H) and V(C=O) frequencies , indicating the destruction of carbonyl moiety as a result of enolisation and subsequent coordination of the enolic oxygen after proton replacement.[16] Thus the ligand behave as dibasic tridentate donar in these complexes. The V(C=O) peak shifted upward by 18cm^{-1} in the complex formation of Cu(II) and Ni(II) indicates the involvement of carbonyl oxygen in coordination.[17] It is thus inferred that the ligand is monobasic tridentate in nature.The coordination of acetate group in Mn(III) complex is indicated the appearance of two bands due to V(COO) and V(COO) at 1410 – 1400 $cm^{-1}$and at 1615 - 1605 cm^{-1} respectively. The magnitude of ΔV = 205 cm^{-1}

suggest the coordination of acetate group in monodentate fashion.[18] The presence of coordinated water molecules are indicated by the appearance of new bands at 837 – 835 and 747 – 742 cm^{-1}due to rocking and wagging modes of water molecule. In all the complexes except VO(IV) the lattice/ coordinated water molecules are indicated by the appearance of a broad band at 3500 – 3000 cm^{-1}.[19]The V(OH) at C_4 frequency of free ligand at 3435 cm^{-1}due remain unshifted in the spectra of complexes indicating the non involvement of the OH group in the coordination.The strong band at 978cm^{-1}in the VO(IV) complex and at 1113cm^{-1}in the Zr(IV) complex are assigned to V(C=O) and V(Zr—OH) respectively.[20-21]

Magnetic and electronic spectral studies

The diffuse reflectance spectra of Co(II) complex shows three bands at 9174, 18867 and 21276cm^{-1}which was assigned to $^4T_1g(F)$ ---> $^4T_2g(F)$, $^4T_1g(F)$ ---> $^4A_2g(F)$ and),$^4T_1g(F)$--->$^4T_1g(P)$ transitions respectively.[22] The observed magnetic moment 4.80 B.M. favours the high spin nature and octahedral geometry of complex[23]. Ni(II) complex shows two bands at 16778 and 20578cm^{-1}these bands are assigned to ^1A_1g --->^1A_2g and ^1A_1g ---> ^1B_1g transitions respectively. The observed bands and diamagnetic nature of the complex suggest the square planar geometry of the complex.[24] The Cu(II) complex exhibits 1.81 B.M.magnetic moment value and two bands at 13623 and 19646 cm^{-1} in the diffuse reflectance spectra. these bands are assigned to ^2B_1g --->^2B_2g and ^2B_1g ---> ^2Eg transitions respectively.[25] suggesting the square planar geometry of the complex. The Zn(II) is found to be diamagnetic in nature and does not show any band in the electronic spectra, indicates no d-d transition as expected for $d^0$and d^{10} system, suggest octahedral geometry,also supported by IR,thermal and analytical data. The Cr(III) complex shows three bands at 18691,24390 and 28653cm^{-1}can be assigned to $^4A_2g(F)$ ---> $^4T_2g(F)$, $^4A_2g(F)$ ---> $^4T_1g(F)$ and $^4A_2g(F)$ --->$^4T_1g(P)$ transitions respectively.[26] The observed magnetic moment 3.68 B.M. which indicates the presence of three unpaired electrons in an octahedral field around Cr(III) ion.The Mn(III) complex exhibits a magnetic moment of 4.9 B.M. which is equal to spin only value of four unpaired electrons and shows band at 13793,16949,20202 and 25641cm^{-1} which are assigned to $^5B_1$ ---> $^5B_2$, $^5B_1$ ---> $^5A_1$, $^5B_1$ ---> ^5E and LMCT transitions respectively.[27]suggesting the square pyramidal geometry.The diffuse reflectance spectra of Fe(III) complex shows three bands at 13736,18050 and 23041cm^{-1}which was assigned to ^6A_1g ---> $^4T_1g(G)$, ^6A_1g ---> $^4T_2g(G)$ and ^6A_1g --->$^4A_1g(G)$,^4E_g transitions respectively.[28] and the observed magnetic moment 6.0 B.M. suggest the high spin octahedral geometry for this complex. The VO(IV) complex shows four absorption bands at 13717,16808,22172 and 29325cm^{-1} these bands are assigned to $^2B_2$ ---> ^2E, $^2B_2$ ---> $^2B_1$, $^2B_2$ ---> $^2A_1$ and LMCT transitions respectively.[29] The observed magnetic moment value 1.79 B.M.is found in close vicinity of spin only value of VO(IV) complexes[24]suggesting the square pyramidal geometry. The Zr(IV) is found to be diamagnetic as expected for d^0system. The diffuse reflectance spectra of this complex did not show any d-d transition but abroad band is observed in the region 23250 – 24260 cm^{-1} due to charge transfer transition suggest octahedral geometry for Zr(IV) complex

Thermogravimetric studies

Thermogravimetric study indicates all the complexes are stable up to 60-70^{0}C. All the complexes except Cu(II) and VO(IV) shows three stage decomposition pattern.The percentage weight loss data (Table 3) up to 140^{0}C indicates the loss of one water molecule from Co(II), Cr(III), Mn (III) and Fe(III) complexes each ,loss of two water molecule from Zn(II) and Ni(III) complexes and loss of three water molecules (lattice) from Cu(II) and Zr(IV) complexes each.Further loss in weight up to 220-240^{0}C was observed. The percentage weight loss data indicates loss of one coordinated water molecule from Ni(II),Cr(III), Mn (III) and Fe(III) complexes each, loss of two coordinated water molecule from Co(II) and Zn(II) complexes each. There is no weight loss at 220-240^{0}C in Cu(II) and Zr(IV) complexes indicates the absence of coordinated water molecule. The VO(IV) complex did not show any weight loss up to 260^{0}C indicates the absence of lattice or coordinated water molecule in this complex.[30]

Table: 3 The percentage weight loss data of complexes of DHBIH

Complexes	The percentage weight loss at		Half decomposition Temparature^{0}C
	110-140^{0}C observed (Calc.)	220-240^{0}C observed(Calc.)	
Co(II)	2.45 (2.31)	4.80 (4.63)	428
Ni(II)	4.50 (4.05)	4.25 (4.05)	468
Cu(II)	7.25 (6.90)	---	433
Zn(II)	4.75 (4.49)	4.60 (4.49)	425
Cr(III)	2.50 (2.28)	4.40 (4.28)	488
Mn(III)	4.12 (3.74)	3.90 (3.74)	440
Fe(III)	2.42 (2.27)	2.40 (2.27)	420
VO(IV)	---	---	445
Zr(IV)	7.10 (6.40)	---	412

Conclusions

All the complexes shows weight loss up to 320^{0}C indicates decomposition of ligand molecule. Further a horizontal curve was observed beyond 640^{0}C suggest the formation of final decomposition products i.e.stable metal oxides of respective metals. On the basis of half decomposition temperature the order of thermal stability is found to be Cr(III) > Ni(II) > VO(IV) > Mn(III) > Cu(II) > Co(II) > Zn(II) > Fe(III) > Zr(IV) . The analysis of magnetic moment, thermal analysis and electronic spectral data indicate square planar geometry for the Cu(II)& Ni(II) complexes, square pyramidal geometry for the Mn(III) and VO(IV) complexes, while octahedral geometry for the other complexes.

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