Synthesis and Characterization of some transition metal Complexes of Schiff base derived from isonicotinic hydrazide and O-Vanillin.

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Abstract

A new series of transition metal complexes of Cu(II) , Co(II) , Ni(II) , Cd(II) , Zn(II) and VO(IV) were synthesized from the Schiff base (L) derived from isonicotinic acid hydrazide and o-vanilline . Structural features were obtained from their metal analysis ,magnetic susceptibility , molar conductance , IR and UV-Vis spectral studies . the data showed that these complexes have the composition of ML3 type for Cu(II) , Co(II) , Ni(II) while ML2 type for Zn(II), Cd(II) and VO(IV) .According to the the UV-Vis , magnetic susceptibility data of the complexes an octahedral geometry was suggested for Cu(II) , Co(II) & Ni(II) metal ions and a tetrahedral geometry for Cd(II) & Zn(II) metal ions, while a square-pyramidal geometry was suggested for VO(IV) ion .

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Introduction

Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions in the periodic table. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species.[1-3]

Interest in the study of hydrazones has been grown because of their antimicrobial, antituberculosis, and antitumour activity[4-8]. The coordination compounds of aroylhydrazones have been reported to act as enzyme inhibitors[9] and are useful due to their pharmacological applications[5-6].

Hydrazones derived from condensation of isonicotinic acid hydrazide with pyridine aldehydes have been found to show better antitubercular activity than INH (isonicotinic acid hydrazide)[10]. The remarkable biological activity of acid hydrazides R−CO−NH−NH_2, their corresponding aroylhydrazones R−CO−NH−N=CH−R′, and the dependence of their mode of chelation with transition metal ions present in the living system have been of significant importance in the past [11-14]. In view of the versatile importance of hydrazones, we herein describe the synthesis and identification of some transition metal complexes of N-isonicotinamido-2-hydroxy-3-methoxy benzalaldimine.

Experimental

$MCl_2 . nH_2O$ ($M = Co^{2+}$, Cu^{2+} , Zn^{2+} , Cd^{2+} and Ni^{2+}) were obtained from Fluka chemicals and were used as such except oxovanadium (IV) chloride was prepared by treating vanadium pentoxide with concentrated hydrochloric acid in the presence of few drops of ethanol .[15]

The ligand N-isonicotinamido-2-hydroxy-3-methoxy benzalaldimine was synthesised in the laboratory of Education college of Kalar by dissolving Isonicotinic acid hydrazide (1.1 m.mol) in 20 mℓ of 95% ethanol. To this solution, the aldehyde (Vanilline)(1.1 m.mol) was added in 95% ethanol (20 mℓ). The reaction mixture was refluxed on a water bath for 24 hours , then allowed to cool at room temperature. The crystalline solid were separated out and purified by recrystallization from the same solvent . The main characteristics and analytical data are recorded in(table 1).

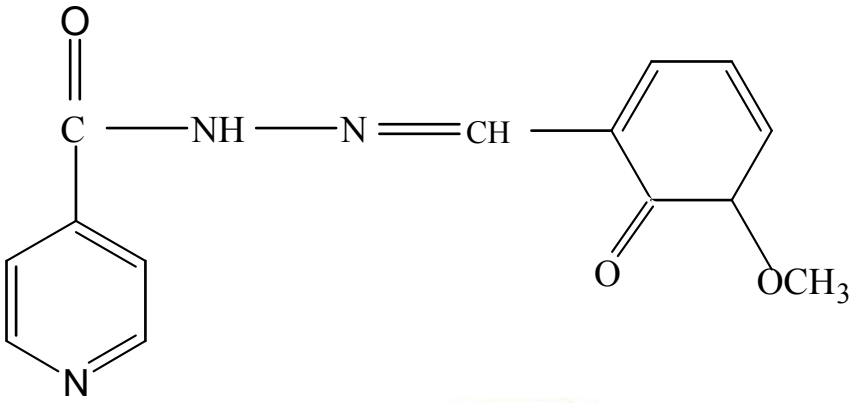


Fig-1.Structure of N-isonicotinamido-2-hydroxy-3-methoxy benzalaldimine.

Synthesis of the complexes :

A general method was used for the preparation of all the complexes. A hot ethanolic solution of the corresponding metal salts $MCl_2 . nH_2O$ (M = Co^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Ni^{2+}) was mixed with a hot ethanolic solution of the ligand (in 1 : 2 or 1 : 3 molar ratio). The reaction mixture was refluxed on water bath for about 2-3 hours. On cooling at room temperature, the coloured complexes precipitated out in each case. They were filtered, washed with ethanol , recrystallized , and dried under vacuum.

Results and Discussion

The analytical data for the ligand and complexes together with some physical properties are summarized in Table 1.

All the complexes are stable and can be stored for long periods at room temperature. They are generally soluble in common organic solvents , do not have sharp melting points but decompose above 250ºc .[16]

The molar conductance values of all the complexes were recorded in DMF at room temperature , the higher conductance value of Co(II), Cu(II)& Ni(II) complexes supports their electrolytic nature , while the others show non-electrolytic nature.[17]

Metal analysis of the complexes indicates the stoichiometry to be 1:2 (metal: ligand) (Schiff base).

Table 1. Physical properties of Schiff base and its corresponding metal complexes

Compound	Molecular formula	Colour	Yield %	Melting point °C
L	$C_{14}H_{12}N_3O_3$	Yellow	85	122-124
$[CoL_3]Cl_2$	$CoC_{42}H_{36}N_9O_9Cl_2$	Red	72	189-191
$[CuL_3]Cl_2$	$CuC_{42}H_{36}N_9O_9Cl_2$	Dark-brown	79	222-224
$[NiL_3]Cl_2$	$NiC_{42}H_{36}N_9O_9Cl_2$	Yellowish-green	83	207-209
$[ZnL_2]Cl_2$	$ZnC_{28}H_{24}N_6O_6Cl_2$	White	67	178-180
$[CdL_2]Cl_2$	$CdC_{28}H_{24}N_6O_6Cl_2$	Yellow	75	256-258
$[VOL_2]Cl_2$	$VC_{28}H_{24}N_6O_7Cl_2$	Green	80	195-197

Magnetic susceptibility

The measured magnetic moments($\mu_{eff.}$) for the prepared complexes are listed in (table-2) .Magnetic moments of the solid cobalt(II) complex was found to lie in the range of 4.1- 4.6 BM. , indicative of three unpaired electrons per Co(II) ion in an octahedral environment [18].

The Cu(II)complex showed μ_{eff} value in the range 1.3-1.5 BM ,indicative of one unpaired electron per Cu(II) ion suggesting that this complex has a structure within the range consistent to spin-free distorted octahedral geometry [19].Similarly Ni (II) complex showed μ_{eff} in the range of 3.2-3.4 BM , corresponding to two unpaired electrons per Ni(II) ion for their ideal six-coordinated configuration[18].

Most Vanadyl (II)complex were magnetically simple having virtually "spin-only" moments of (1.73)BM , corresponding to one unpaired electron, the value of this complex was found to be 1.6 BM , showing quardivalent state of vanadium ion which contain VO(II) ion[20] .while the Zn(II) and Cd(II) complexes were found to be diamagnetic.

Table-2 Molar conductance , magnetic susceptibility and metal analysis data of the ligand and its metal complexes

Compounds	ΩM (Ohm cm^2 mol^{-1})	μeff (BM)	Metal analysis(%) Found (calcd)
L	—	—	—
$[CoL_3]Cl_2$	78	4.2	15.33(15.94)
$[CuL_3]Cl_2$	71	1.4	14.52(14.86)
$[NiL_3]Cl_2$	69	3.3	15.55(16.00)
$[ZnL_2]Cl_2$	42	—	10.09(10.34)
$[CdL_2]Cl_2$	55	—	6.11(6.43)
$[VOL_2]Cl_2$	38	1.6	10.12(10.27)

Infrared spectra

The IR spectra provide valuable information regarding the nature of functional groups attached to the metal atom . Study and comparison of the infrared spectra of the ligand and its metal complexes imply that the ligand is dentate with the phenolic-oxygen and azomethine-nitrogen as the 2-coordination sites. The presence of various ring vibrations and C-H absorption makes the spectra fairly complicated for complete assignments of individual bands. The partial infrared data are presented in table 3. Generally, all amides showed two absorption bands first: the carbonyl absorption band near 1640cm^{-1} known as amide-I-band and second,strong band in the 1600-1500cm^{-1} region (amide-II band). The amide-I band in INH-derivatives appeared in the 1685-1665 cm^{-1} region. The appearance of this peak in all the spectra of the complexes indicate that the carbonyl–oxygen group is free from complexation .The amide-II band appeared at the normal position in the N-H deformation frequency mode, the absorption in the 1565-1560 cm^{-1} region was assigned to amide-II absorption. The band due to NH-stretching in free ligands occured in the 3350-3230 cm^{-1} region and remained unaffected after complexation [21]. This precluded the possibility of coordination through the imine-nitrogen atom. Another important band, which occured at 1635 cm^{-1}, is attributed to (C=N) (azomethine) mode[21-22]. In the spectra of all the complexes, this band is shifted to lower frequency and appeared in the 1590-1630 cm^{-1} region, indicating the involvement of the N-atom of the azomethine group in coordination[19].

Also a band at 3450 cm^{-1} attributed to OH stretching in the ligand[22] disappeared in its metal complexes , and instead a band appearing in the1378-1385 cm^{-1} region due to (C-O) stretching vibrations indicated the involvement of the phenolic-oxygen atom in the coordination

The strong bands observed at 1575-1520 cm^{-1} and 1080-1000 cm^{-1} are tentatively assigned [20,21] to asymmetric and symmetric (C=C) and (C=N) of pyridine ring and pyridine ring breathing and deformations respectively. These bands remain practically unchanged after complexation. These observations suggest the non-involvement of pyridinic-nitrogen in complex formation. The overall infrared spectral evidence suggests that the ligand acts as a bidendate ligand and coordinated through phenolic-oxygen and azomethinic-nitrogen atoms. The far infrared spectral bands in the ligands are practically unchanged in these complexes, however some new bands with medium to weak intensities appeared in the region of 425-465 cm^{-1} and 525-535cm^{-1} in the complexes under study, which are assigned to (M-O)/ (M-N) (metal-ligand) modes.[21,22]

Table 3. Infrared absorption frequencies (cm^{-1}) of ligand and its metal complexes .

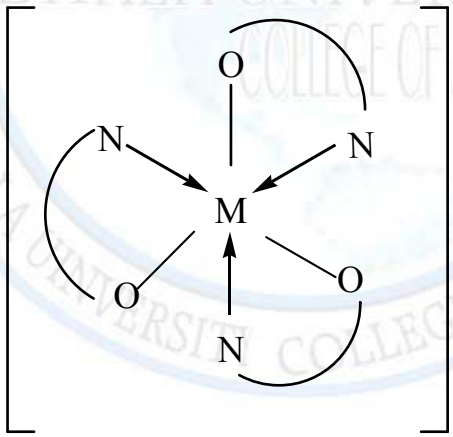
Compound	υ (C-O)	υ (C=N) azomethinic	υ (M-N)	υ (M-O)
L	1385	1635	–	–
$[CoL_3]Cl_2$	1380	1625	532	455
$[CuL_3]Cl_2$	1381	1620	563	506
$[NiL_3]Cl_2$	1380	1610	525	450
$[ZnL_2]Cl_2$	1377	1623	530	460
$[CdL_2]Cl_2$	1379	1625	535	504
$[VOL_2]Cl_2$	1380	1625	485	415

Electronic absorbition spectra

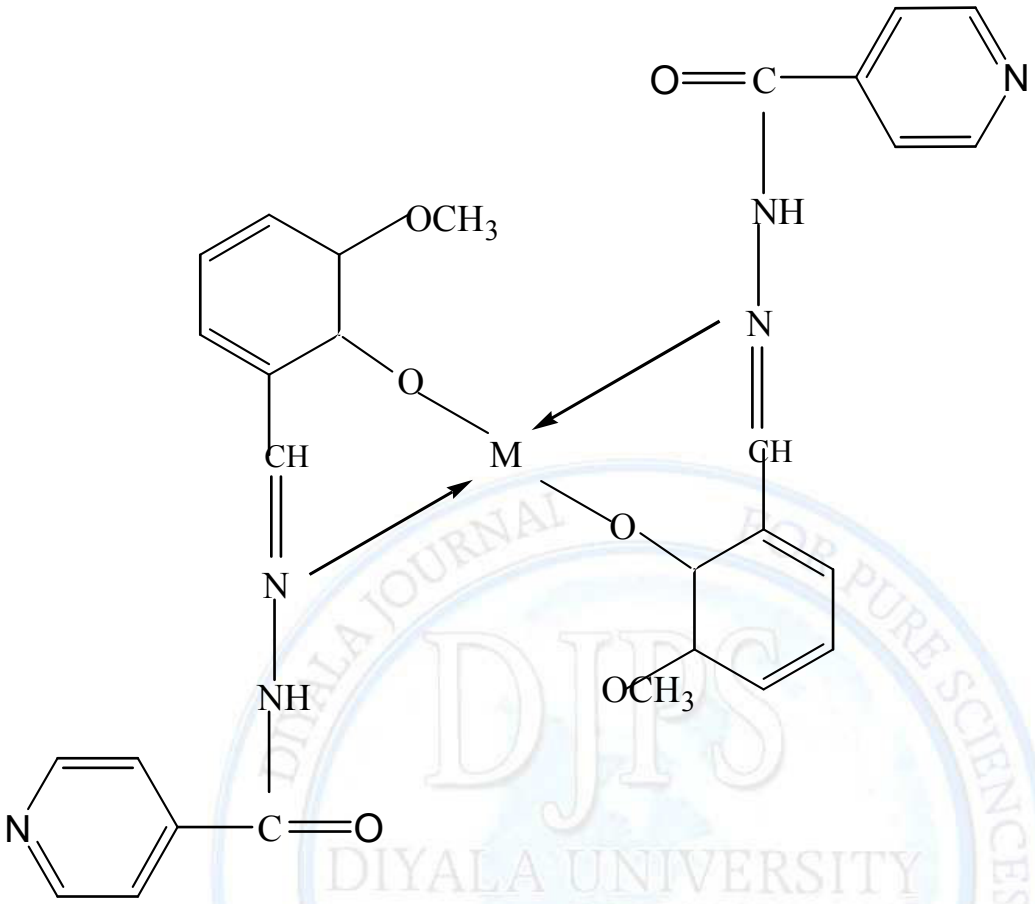
The electronic absorption spectra of the Schiff base, Co(II) , Cu(II) , Ni(II) and VO(IV) complexes were recorded in the range (200-1100) . The Electronic spectra of the Co(II) complexes showed three band at (30262 , 17776 , and 8807) cm^{-1} which may be assigned to $^4T_{1g} \rightarrow {}^4T_{2g(F)}$, $^4T_{1g} \rightarrow {}^4T_{1g(P)}$ and $^4T_{1g} \rightarrow {}^4A_{2g(F)}$ transitions, respectively, and suggested [22,23] octahedral geometry around the cobalt ions . the Ni(II) complex exhibited three band at (29956 , 15910 , and 9965) cm^{-1} assignable [23] respectively to the transition $^3A_{2g(F)} \rightarrow {}^3T_{2g(F)}$, $^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$ and $^3A_{2g(F)} \rightarrow {}^3T_{2g(P)}$ which are characteristic of Ni(II) in an octahedral geometry . The Cu(II) complex showed absorption band between 10Dq band for distorted octahedral geometry corresponding[23,24] to the transition $^2E_g \rightarrow {}^2T_{2g}$.The broadness of this band is also usually observed in simple octahedral copper (II) complexes, as a consequence of the Jahn-Teller effect, expected to be very important in the case of a d^9 electron configuration , In general oxovanadium(IV) complexes display 3 low intensity bands in the10,000-30,000 cm^{-1} range.The first and subsequent charge transfer transitions are predicted to occur at higher energies (beyond 30,000 cm−1) and often bandIII is not observed, but is thought to be buried beneath the low energy tail of the much more intense charge transfer band. Following the ordering of energy levels, the first band, which is centered at 13,000 cm^{-1}, is assigned to an unresolved band resulting from the ($^2B \rightarrow {}^2E$) transition. The second band (in region 15,000-16,000 cm^{-1}) is attributed to($^2B_2 \rightarrow {}^2B_1$) transitions. The band at about 23,000 cm^{-1} may either be assigned to the ($^2B_2 \rightarrow {}^2A_1$) transition or thought to be a low energy charge transfer band.In conclusion, due to steric interactions of the large size of the ligand the coordination number 5 was been assigned to this complex. And the geometry was square-pyramidal[20] .

Table 4. Electronic absorption spectral data of the complexes

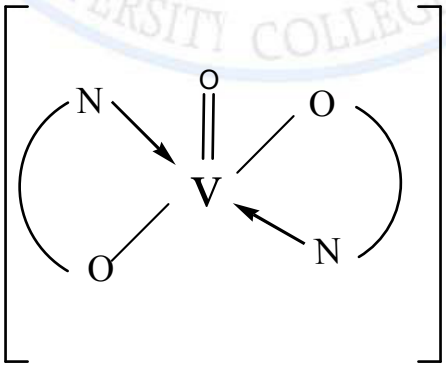
Complex	Absorption (cm^{-1})	Band assignment	Geometry
$[CoL_3]Cl_2$	30262 17776 8807	$^4T_{1g} \rightarrow {}^4T_{2g(F)}$ $^4T_{1g} \rightarrow {}^4T_{1g(P)}$ $^4T_{1g} \rightarrow {}^4A_{2g(F)}$	Octahedral
$[CuL_3]Cl_2$	30610 22360	$^2E_g \rightarrow {}^2T_{2g}$	Octahedral
$[NiL_3]Cl_2$	29956 15910 9965	$^3A_{2g(F)} \rightarrow {}^3T_{2g(F)}$ $^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$ $^3A_{2g(F)} \rightarrow {}^3T_{2g(P}$	Octahedral
$[VOL_2]Cl_2$	14300 15900 22900	$^2B \rightarrow {}^2E$ $^2B_2 \rightarrow {}^2B_1$ $^2B_2 \rightarrow {}^2A_1$	Square-pyramidal



1. Proposed structure for Cu(II) , Co(II) , Ni(II) Metals



2. Proposed structure for Cd(II) , Zn(II) Metals



3. proposed structure of VO(II) Metal

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