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Ligational Behavior of Tridentate Schiff Base towards Transition Metal Ions

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ABSTRACT

The ligational behavior of Schiff base ligand obtained by the condensation of cyanoacetylhydrazine and dehydroacetic acid towards some first transition series bivalent ions has been studied. The ligand on complexation yielded metal complexes of type ML_2 where, L=anion of Schiff base ligand, cyano-acetic acid [1-(4-hydroxy-6- methyl-2-oxo-2H-pyran-3-yl)-ethylidene]-hydrazide; M=Co(II), Ni(II), Cu(II) or Zn(II)]. These complexes have been characterized on the basis of elemental analysis, molar conductivity, magnetic susceptibility, spectroscopic techniques (IR, UV-Visible, and NMR). The spectral studies suggested octahedral or distorted octahedral geometry around transition metal ion where Schiff base acted as tridentate ligand ONO coordinated through azomethine nitrogen and oxygen atoms of hydroxyl and carbonyl group to divalent metal ion.

Keywords: Cyanoacetylhydrazine, Metal complexes, Octahedral geometry, Complexation

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INTRODUCTION

Schiff base ligands containing azomethine group are privileged ligand as they can easily be prepared by simple one pot condensation of a carbonyl compounds and primary amines. Schiff bases of aliphaticaldehyde groups are less stable and easily pollymerizable as compared to one with aromatic aldehydes because of conjugation system. They are of particular interest because of existing in lactam (keto) or lactim (enol) tautomeric forms giving variation to donating properties to form Schiff base complexes. The structural, spectral and chemical behavior of these complexes depends upon the nature of the ligands and the reaction conditions [1-3]. Since many of these complexes provide biological models for understanding the structure of biomolecules and biological processes for which they are of special interest to bioinorganic chemists [4]. Schiff bases and their transition metal complexes exhibit a broad range of biological activity such as antibacterial, antifungal [5] anti HIV, peroxidase, anticancer and antitumor because of their specific structures [6-9]. In the present work, dehydroacetic acid has been used as one component for the preparation of Schiff base which have been reported to act as fungicides [10] and bactericides [11]. It is however, noteworthy that the biological activity is enhanced upon complexation to metal atom [12]. It has been reported that many drugs possess modified pharmacological and toxicological potentials when given in the form of their metal complexes. Many microorganisms have already become resistant to most of the commonly used organic drugs. The main aim of this work is to introduce metal ions specially Co(II), Ni(II), Cu(II) and Zn(II) as they form low molecular weight complexes to biological active ligand in order to study the effect of complexation on their biocidal activity and to explore the possibility of their use as potential biocide.

EXPERIMENTAL SECTION

Material and methods

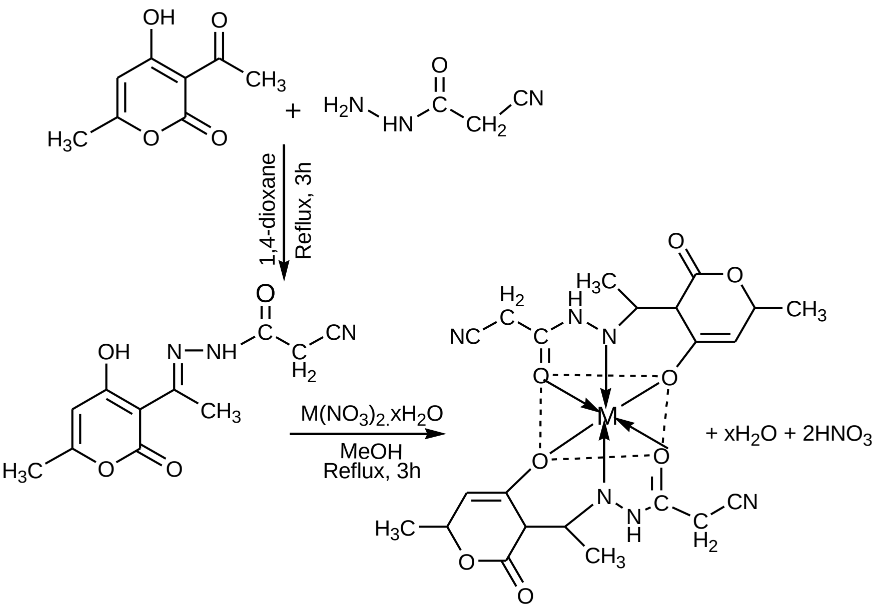
All the chemicals used were of analytical grade. All metal salts were used as nitrates salts obtained from Aldrich and used as such without any further purification. IR spectra were recorded on Shimadzu IR affinity-I 8000 FTIR spectrometer using KBr disc. ^{1}H-NMR and ^{13}C-NMR were recorded on Bruker Avance II 300 MHz NMR spectrometer and all chemical shifts are reported in parts per million relative to TMS as internal standard in $CDCl_3$. UV spectra were recorded on UV-VIS-NIR Varian Cary-5000 spectrometer in DMF. Elemental analysis was carried out on Perkin Elmer 2400. Metal contents were determined using standard gravimetric methods, cobalt as cobalt pyridine thiocyanate, nickel as nickel dimethylglyoximate, copper as cuperous thiocyanate and zinc as zinc ammonium phosphate.

Synthesis of Schiff base (cyano-acetic acid [1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-ethylidene]hydrazide, HL)

Cyanoacetylhydrazine (1.98 g, 20 mmol) in 1,4-dioxane (30 ml) was added to solution of dehydroacetic acid (3.36 g, 20 mmol) in same solvent (30 ml). The reaction mixture was refluxed for 3 h and after cooling to room temperature it was poured into beaker containing ice-cold water. The solid product formed was filtered and dried to give white solid, that was recrystallized from ethanol to give desired Schiff base hydrazide (HL) which was dried under vacuum (yielding 70%).

Synthesis of metal complexes

The methanolic solution of ligand (2.49 g, 10 mmol) was added to the solution of metal nitrate hydrate $Co(NO_3)_2.6H_2O$ (1.45 g, 5 mmol) in same solvent with constant stirring. The resulting solution was refluxed for 3 h. On cooling to room temperature, the solid product separated out was filtered off and washed with hot methanol or petroleum ether to remove excess of metal nitrates and ligand and finally dried in vacuum (Scheme 1).



M = Co (II), Ni(II), Cu(II) and Zn(II)
x = 1,6

Scheme 1: Synthesis of ligand and its metal complexes

RESULTS AND DISCUSSION

Schiff base ligand (HL) was obtained by the condensation of cyanoacetylhydrazine and dehydroacetic acid. The purity of this ligand was monitored by TLC. The metal complexes of type ML_2, where, L=anion of cyano-acetic acid[1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-ethylidene]-hydrazide and M= Co(II), Ni(II), Cu(II) or Zn(II)]. The analytical data of these complexes are given in Table 1. All these complexes are crystalline solids, stable at room temperature, hygroscopic in nature and insoluble in most of the common organic solvents except Dimethyl Sulfoxide (DMSO) or Dimethylformamide (DMF). The low molar conductance values (3.5-8.1 Ω^{-1} cm^2 mol^{-1} in dry DMSO of metal complexes indicates non-electrolytic nature.

Table 1: Physical and analytical data of compounds

Compounds	Molecular formula (Molecular weight)	m/z found	color	Yield (%)	Elemental analysis, found (cal)				(ΩM) Molar conductance × 10^{-3}
					C	H	N	o	
HL	$C_{11}H_{11}N_3O_4$	249.01	white	80	53.13	4.28	16.63	---	---
	-249.22				-53.01	-4.45	-16.86		
$Co(L)_2$	$C_{22}H_{20}N_6O_8Co$	555.5	green	72	47.36	3.98	15.52	10.43	6.4
	-555.36				-47.58	-3.63	-15.13	-10.61	
$Ni(L)_2$	$C_{22}H_{20}N_6O_8Ni$	555.8	brown red	71	47.41	3.32	15.38	10.84	8.1
	-555.12				-47.6	-3.63	-15.14	-10.57	
$Cu(L)_2$	$C_{22}H_{20}N_6O_8Cu$	560.2	dark green	75	47.43	3.87	15.34	11.54	4.7
	-559.98				-47.19	-3.6	-15.01	-11.35	
$Zn(L)_2$	$C_{22}H_{20}N_6O_8Zn$	561.4	colorless		47.42	3.87	15.07	11.93	3.5
	-561.82				-47.03	-3.59	-14.96	-11.64	

IR spectra

The infrared spectra of complexes were compared with that of Schiff base ligand to ascertain the coordination sites on the basis of shifts in the frequency of various groups and absence of certain absorptions may be due to changes in electronic environment of the ligand after formation of metal ligand bond. A strong band observed at 1670 cm^{-1} due to υ(C=O) group in spectra of ligand were shifted to 1635-1650 cm^{-1} respectively in complexes thereby indicated that hydrazone ligand has coordinated to metal center through carbonyl oxygen. The IR spectra of complexes have absorption bands at 1550-1560 cm^{-1} assigned to υ(C=N) stretching frequencies whereas for free ligand these bands were observed at 1585 cm^{-1}. The shift to lower frequencies (as compared to free ligand) suggested donation of lone pair of electrons on azomethine nitrogen to metal center [13]. Donation of lone pair of electron on nitrogen atom has been strengthened by shift of υ(N-N) band from 1014 cm^{-1} in free ligand to 1025-1050 cm^{-1} in complexes. In the spectrum of ligand stretching vibration of υ(C=O, lactone) at 1726 cm^{-1} remains unaltered on complexation and indicated non-involvement of this group in coordination. On complexation, the absence of absorption band at 3420 cm^{-1} due to OH group attached to pyran moiety in ligand indicated deprotonation and coordination through oxygen. Furthermore, the appearance of new bands of low frequency observed at 420-440 cm^{-1} and 480-510 cm^{-1} assigned to υ (M-O) and υ (M-N) vibrations respectively in complexes [14].

NMR spectra

The NMR (^1H, ^{13}C) spectra of free ligand and its zinc(II) complex were recorded in $CDCl_3$ containing small amount of DMSO-d_6 with TMS as the internal reference (Table 2). On comparing ^1H-NMR of free ligand and its zinc(II) complex $Zn(L)_2$, absence of peak at δ=11.26 due to OH proton suggested the deprotonation of OH group and peak at δ=15.68 observed due to NH proton was almost same as that of ligand showed coordination through keto form. The signals due to CH_2, CH (attached to C_5), methyl group attached to CH=N (C_8) and CH_3 group (attached to C_6) appeared at δ=3.56, δ=5.90, δ=2.21 and δ=2.58 showed small shift. It was observed that DMSO has no coordinating effect in metal complexes.

In ^{13}C-NMR of complexes, the signals due to carbon (C_4) to which OH group is attached was shifted from δ=189.87 to δ=184.62. On complexation, while carbon of azomethine group (C_7) shifted from δ=162.57 to δ=160.05 indicated involvement of azomethine nitrogen in bonding and carbonyl carbon (C_{10}) shifted from δ=182.75 to δ=179.37. The signals due to other carbon atoms remains almost unaltered on complexation.

Table 2: ^1H and ^{13}C-NMR of ligand and its zinc(II) complex

Ligand	^1H-NMR ($CDCl_3$) δ in ppm	^{13}C-NMR ($CDCl_3$) δ in ppm
HL	15.68 (s, 1H, NH), 11.26 (s, IH, OH), 5.90 (s, 1H, C_5-H), 2.21 (s, 3H, C_8-H), 2.58 (s, 3H, C_9-H), 3.56 (s, 2H, C_{11}-H)	163.97 (C_2), 97.43 (C_3), 189.87 (C_4), 106.72 (C_5), 156.51 (C_6), 162.57 (C_7), 12.70 (C_8), 18.80 (C_9), 182.75 (C_{10}), 35.49 (C_{11}), 138.14 (C_{12})
$Zn(L)_2$	15.70 (s, 1H, NH), 5.83 (s, 1H, C_5-H), 2.36 (s, 3H, C_8-H), 2.50 (s, 3H, C_9-H), 3.42 (s, 2H, C_{11}-H)	156.51 (C_2), 106.72 (C_3), 184.62 (C_4), 107.43 (C_5), 156.32 (C_6), 160.05 (C_7), 12.70 (C_8), 18.80 (C_9), 179.37 (C_{10}), 35.49 (C_{11}), 138.14 (C_{12})

Mass spectra

The LC-MS of ligand and its complexes were recorded and the mass spectrum of HL ($C_{11}H_{11}N_3O_4$) showed a well-defined molecular ion peak at m/z=249.22 while its corresponding Co(II) complex ($C_{22}H_{20}CON_6O_8$) has base peak at m/z=555.4. The molecular ion peaks in the spectra of other complexes were in well agreement with their molecular formula and given in Table 1.

Magnetic moment and electronic spectra of complexes

The observed magnetic moment for transition metal complexes is generally diagnostic of geometry around metal ion. The magnetic moments of complexes calculated from magnetic susceptibility are given in Table 3. The magnetic moment of Co(II) complex was found to be 4.03 BM. The electronic spectrum of this complex showed three d-d bands at 8723 cm^{-1}, 17150 cm^{-1}, 24925 cm^{-1} assignable to transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) respectively. The energy ratio ν_2/ν_1=1.96 is in range of octahedral configuration. The ligand field parameters B, β, Dq calculated by using band-fitting equation [15] for the Co(II) complex was found to be 630, 0.64, 842.7 respectively, these parameters along with the transition and magnetic moment value indicate d^7 high spin system and characteristics of octahedral geometry around metal in this complex [16]. The electronic spectrum of Ni(II) complex exhibited three bands at 9263 cm^{-1}, 14225 cm^{-1} and 24830 cm^{-1} due to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) respectively [17]. The energy ratio ν_2/ν_1=1.53 was in the range of octahedral configuration. The Racah interelectronic repulsion parameters B, β, Dq calculated for the Ni(II) complex is found to be 751, 0.72, 926.3 respectively. The effective magnetic moment of Ni(II) complex was found to be 2.99 BM due to two unpaired electrons indicating a triplet ground state have octahedral geometry with d8 high spin system around metal ion. The Racah interelectronic repulsion parameter B value is less than the free ion value because of the decreased interelectronic repulsion from electron delocalization suggested weak covalent bond. The copper complex has a magnetic moment of 1.98 BM which corresponds to single unpaired electron with significant orbital contribution. This increase from spin only value (1.73 BM) might be due to Jahn-Teller distortion [18]. A broad band at 15,898 cm^{-1} in electronic spectrum of Cu(II) complex was due to $^2E_g \rightarrow {}^2T_{2g}$ transition, broadness of band occur due to Jahn-Teller distortion, indicating the distortion from octahedral geometry, while another band at 24,324 cm^{-1} due to charge transfer which is closed to spin allowed values expected for d^9 configuration and indicative of octahedral geometry. In the electronic spectrum of Zn (II) complex only one band is observed due to LMCT transition indicating diamagnetic nature as expected for d^{10} configuration [19,20].

Table 3: Electronic absorption spectral data and magnetic moment (µ) of transition metal(ii) complexes of dehydroacetic acid hydrazone

Complexes	Absorption (cm^{-1})	Band assignment	B value	β value	Geometry	µ (BM)
$Co(L)_2$	24925 (ν_3)	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	630.69	0.64	Octahedral	4.01
	17150 (ν_2)	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$				
	8723 (ν_1)	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$				
$Ni(L)_2$	24830 (ν_3)	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	751.06	0.72	Octahedral	2.99
	14225 (ν_2)	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$				
	9263 (ν_1)	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$				
$Cu(L)_2$	24324	π N → Cu*	--	--	Distorted Octahedral	1.98
	15898	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$				
$Zn(L)_2$	22445	LMCT	--	--	Octahedral	--

CONCLUSION

Schiff base cyano-acetic acid [1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-ethylidene]-hydrazide acted as tridentate ligand ONO coordinating through hydroxyl oxygen, azomethine nitrogen and carbonyl oxygen to divalent metal ion forming complexes of type ML_2 with octahedral or distorted octahedral geometry.

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