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Synthesis and Antifungal Investigation of Co(II), Ni(II) Complexes with Nitrogen, Oxygen and Sulphur Donor Ligands

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Mixed ligand complexes of the type [$M(LH_2)B_2$] where M = Co(II) and Ni(II), L = 1-hydroxy-10-mercapto-1,2:5,6:9,10-tribenzo-3,7-diaza-1,3,5,7,9-decapentene (LH_2), B = water, ammonia, phenyl isocyanide, quinoline, pyridine and α, β and γ-picolines. The ligand as well as metal complexes were characterized by physico-chemical technique. On the basis of above observations the geometry of the complexes were proposed to be octahedral. The LH_2 behaves as binegative tetradentate ligand. The remaining coordination sites are satisfied by neutral molecules. The ligand as well as metal complexes were screened for their antifungal activity.

Key Words: Co(II), Ni(II), Complexes, Spectroscopy, Antifungal activity.

INTRODUCTION

The formation of mixed ligand complexes of metal and two competing ligands has attracted attention concerning their structure and stability. The mixed ligand complexes are reported by many workers[1-5]. In continuation of our previous work[6] on transition metal complexes with nitrogen, oxygen and sulphur containing mixed ligand complexes, we report herein the synthesis and characterization of Co(II) and Ni(II) complexes of 1-hydroxy-10-mercapto-1,2:5,6:9,10-tribenzo-3,7-diaza-1,3,5,7-decapentene.

EXPERIMENTAL

All the reagents used were either BDH or E. Merck quality. The metal contents were determined using standard methods[7]. Molar conductance values were made on systronics conductivity meter model 303 using DMF as a solvent. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer. The electronic spectral values were recorded with Hitachi-320 spectrophotometer. Magnetic susceptibility values of the complexes were determined by Guoy method using mercury tetraisothiocyanatocobaltate as a calibrant.

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Preparation of the ligand: The ligand 1-hydroxy-10-mercapto-1,2:5,6:9,10-tribenzo-3,7-diaza-1,3,5,7,9-decapentene was synthesized in two steps. 12.1 g of 2-amino benzaldehyde was dissolved in ethanol was treated with 10.9 g of 2-amino phenol dissolved in ethanol. The resulting solution was refluxed for 2 h on water bath. The resulting solution after cooling, furnish faint yellow colour 1-hydroxy-6-amino-1,2:5,6-dibenzo-3-aza-1,3,5-hexene. 21.2 g ethanolic solution of 1-hydroxy-6-amino-1,2:5,6-dibenzo-3-aza-1,3,5-hexene was treated with 13.8 g *ortho* mercapto benzaldehyde dissolved in ethanol. The resulting mixtures were heated under reflux on water bath for 1 h. After cooling, the refluxed solution yellow colour solid was obtained which was separated by filteration, washed and finally dried and crystallized with tetrahydrofuran to furnish 1-hydroxy-10-mercapto-1,2:5,6:9,10-tribenzo-3,7-diaza-1,3,5,7,9-decapentene as yellow silky prismatic needles m.p. 276 ± 1 ºC, yield 60-65 %.

Preparation of the complexes: The ethanolic solution of metal acetates/chlorides (0.01 m) was allowed to react with ethanolic solution of ligand LH_2 (0.01 m) in molar ratio 1:1. The resulting mixtures was refluxed on water bath 2-3 h. The solution was then cooled and treated with neutral bases, water/ammonia/quinoline/phenyl isocyanide/pyridine/α-, β- or γ-picolines separately. The resulting mixture were again heated on waterbath for 1-2 h. The procedure carried out in each case were similar with slight variation of timing of reflux. On cooling solid coloured complexes separated out which was filtered, washed with ethanol, dried and recrystallized with tetrahydrofuran. Yield in all cases 60-65 %.

RESULTS AND DISCUSSION

The analytical data, colour magnetic susceptibility, molar conductance data and electronic spectral data have been recorded in Table-1.

The ligand (LH_2, Fig. 1) act as tetradentate molecule through deprotonated oxygen (OH), sulphur (SH) and two aldimine N atoms with metal ion.

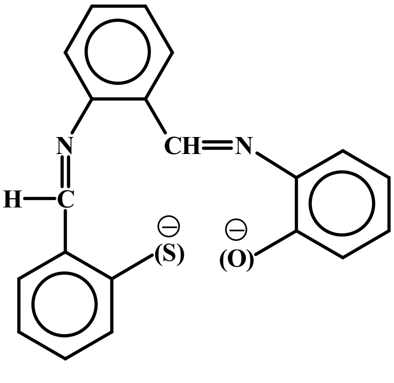

Fig. 1. Structure of ligand, 1-hydroxy-10-mercapto-1,2:5,6:9,10- tribenzo-3,7-diaza-1,3,5,7,9-decapentene (LH_2)

TABLE-1
ANALYTICAL, COLOUR, MAGNETIC SUSCEPTIBILITY, ELECTRONIC SPECTRA, MOLAR CONDUCTANCE DATA OF LIGAND LH_2 AND ITS METAL COMPLEXES

Compounds (colour)	Elemental analysis (%): Found (Calcd.)				μ_{eff} (BM)	λ_{max} (electronic cm^{-1})	Ω_m (ohm^{-1} cm^2 mol^{-1})
	M	C	H	N			
LH_2 (Yellow)		72.15 (72.28)	4.85 (4.81)	8.47 (8.43)			
$[Co(LH_2)(H_2O)_2]$ (Pinkish brown)	13.80 (13.86)	56.36 (56.48)	6.65 (6.58)	4.28 (4.13)	4.90	9100, 7100, 20900	8.3
$[Co(LH_2)(NH_3)_2]$ (Light brown)	13.86 (13.92)	56.64 (56.75)	13.30 (13.24)	4.78 (4.72)	4.85	9250, 16600, 20600	9.4
$[Co(LH_2)(C_9H_7N)_2]$ (Yellowish brown)	9.02 (9.10)	70.37 (70.49)	8.72 (8.65)	4.36 (4.32)	4.80	9150, 16700, 20700	9.1
$[Co(LH_2)(C_6H_5NC)_2]$ (Orange brown)	9.78 (9.90)	68.49 (68.58)	9.48 (9.41)	4.09 (4.03)	4.81	9300, 16900, 20800	9.4
$[Co(LH_2)(C_5H_5N)_2]$ (Light chocolate)	10.68 (10.76)	65.71 (65.82)	10.29 (10.23)	4.44 (4.38)	4.88	9400, 10500, 20500	9.2
$[Co(LH_2)(C_5H_4NH_3)_2$ (α-pic$)_2]$ (Yellowish brown)	10.16 (10.24)	66.68 (66.79)	9.80 (9.74)	4.88 (4.87)	4.96	9450, 16400, 21100	11.3
$[Co(LH_2)(\beta\text{-pic})_2]$ (Dirty brown)	10.20 (10.24)	66.75 (66.79)	9.82 (9.74)	4.90 (4.87)	4.94	9435, 16200, 20600	11.7
$[Co(LH_2)(\gamma\text{-pic})_2]$ (Brownish chocolate)	10.12 (10.24)	66.66 (66.79)	9.76 (9.74)	4.94 (4.81)	4.92	9200, 16300, 20500	12.6
$[Ni(LH_2)(H_2O)_2]$ (Faint green)	13.70 (13.82)	56.40 (56.51)	6.66 (6.50)	4.25 (4.23)	3.20	9950, 14600, 23200	12.8
$[Ni(LH_2)(NH_3)_2]$ (Light green)	13.76 (13.88)	56.65 (56.77)	13.30 (13.24)	4.75 (4.73)	2.96	9890, 14650, 23600	13.8
$[Ni(LH_2)(C_9H_7N)_2]$ (Yellowish green)	9.01 (9.07)	70.41 (70.51)	8.71 (8.65)	4.36 (4.32)	3.10	9840, 14610, 23900	10.1
$[Ni(LH_2)(C_6H_5NC)_2]$ (Brownish green)	9.76 (9.87)	68.58 68.60)	9.45 (9.41)	4.07 (4.03)	3.15	9940, 14560, 23100	10.3
$[Ni(LH_2)(C_5H_5N)_2]$ (Pinkish green)	10.71 (10.73)	65.70 (65.84)	10.30 (10.24)	4.42 (4.38)	3.10	9860, 14590, 23400	18.2
$[Ni(LH_2)(\alpha\text{-pic})_2]$ (Sky green)	10.12 (10.21)	66.71 (66.81)	9.81 (9.74)	4.95 (4.87)	3.00	9890, 14580, 23300	18.6
$[Ni(LH_2)(\beta\text{-pic})_2]$ (Blush green)	10.14 (10.21)	66.68 (66.81)	9.80 (9.74)	4.90 (4.87)	2.96	9910, 14530, 23500	20.1
$[Ni(LH_2)(\gamma\text{-pic})_2]$ (Light green)	10.10 (10.21)	66.70 (66.81)	9.78 (9.74)	4.91 (4.87)	3.08	9930, 14540, 23800	19.3

A careful interpretation of infrared spectral bands of the ligand LH_2 and the complexes $[M(LH_2)B_2]$ reveals that there are certain bands of the ligand which are appreciable affected after the complex formation indicating the donar atoms of coordination sites of the ligand to form the linkage with metal ions. Some new bands, which are totally absent in the ligand appears in the complexes also indicate the formation of bond between the metal and donor atoms of the ligand.

The ligand exhibit a band at 3260 cm^{-1} which assignable to ν(OH)[8] due to band disappears in almost all the complexes and a new band is obtained in the far IR region at 550 cm^{-1} due to ν(M-O) vibration[9] indicating deprotonation of phenolic OH and linkage with oxygen atom in the formation of the complex with the metal ions.

A broad and sharp band obtained at 2460 cm^{-1} in the ligand assignable to ν(S-H) vibration. This band disappears in almost all the complexes indicating deprotonation of (SH) group and a new band appears[10] in the far IR region at 380 cm^{-1} has been obtained in the complexes due to coordination of (SH) sulphur atom of ligand with metal ion. The bands due to ν(C-O) and ν(C-S) vibrations have been reduced by 25-30 cm^{-1} suggesting the deprotonation of OH and SH group present in the ligand.

The next IR band of the ligand shows a broad and strong band at 1650 cm^{-1} assignable[11] to ν(C=N) vibrations. This band has been reduced by 30-40 cm^{-1} in complexes proposes the linkage of both azomethine nitrogen atoms present in the ligand molecule in the complex formation.

Electronic spectra and magnetic moment data: The Co(II) complexes display three absorption bands in the regions, 9100, 17100 and 20900 cm^{-1} which assigned to $4T_{2g}(F) \rightarrow {}^4T_{1g}(F)$, ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and ${}^4T_{1g}(P) \rightarrow {}^4T_{1g}(F)$ transitions, respectively which indicate octahedral[12] geometry of the complexes. The proposed geometry of Co(II) complexes is further confirmed[13,14] by high magnetic moment value in the range. The electronic spectra of all the Ni(II) complexes shows three bands in the regions 10000, 14500 and 23500 cm^{-1} which may be assigned to ${}^3T_{1g}(P) \rightarrow {}^3A_{2g}(F)$, ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$, ${}^3T_{1g}(P) \rightarrow {}^3A_{2g}(F)$ transitions, respectively. The appearance of these bands suggest octahedral[12] geometry of the complexes. The octahedral geometry of Ni(II) complexes is further supported[13,14] by the magnetic moment values in the range 4.90-5.20 BM.

Conductivity measurement: Molar conductance values recorded on systronics conductivity meter model 303 using DMF as a solvent. All the complexes were found to be non-electrolytic[13] in nature giving conductivity value in the range 8.3-20.1 ohm^{-1} cm^{2} mol^{-1}. The molar conductance data of the complexes also supports the assigned structure on the basis of elemental analysis, spectral data, magnetic susceptibility value.

Antifungal activity: Fungicidal activity of the ligand and their metal complexes were carried out by disc method[14] on *Aspergillus flavus* and *Penicillin notatum*. The ligand and their corresponding metal complexes in DMF were screened antifungal activity. The ligand exhibited 20-25 and 30-35 % inhibition per 125 to 250 ppm concentration, respectively. It is observed that the metal complexes show enhanced antifungal activity than ligand. This is due to chelation which reduces the polarity of metal ion due to partial sharing of its positive charge with ligand. The chelation increases lipophilic character in the complexes and results in the enhancement of fungicidal activity. The inhibition of metal complexes has been increased by 30-65 and 40-70 % for 125 and 250 ppm concentration. The Ni complex exhibit greater fungicidal activity than Co complexes.

On the basis of elemental of analyses, IR, electronic spectral studies, magnetic susceptibility values and molar conductance data the ligand LH_2 acts in binegative tetradentate manner and linkage through deprotonated phenolic oxygen and two azomethine N atoms. The remaining two coordination sites are satisfied by neutral molecules like water, ammonia, quinoline phenylisocynide, pyridine or α-, β- and γ-picolins. The geometry of the complexes were proposed to be octahedral in nature as shown in Fig. 2.

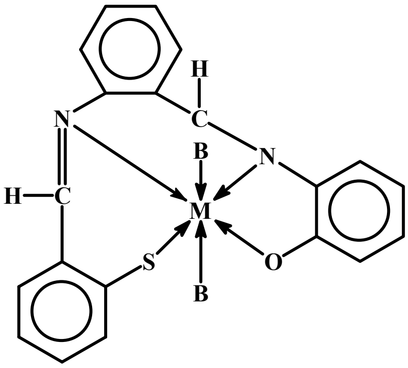

Fig. 2. $[M(LH_2)B_2]$; M = Co(II) and Ni(II)

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