COMPLEXATION TRENDS OF 5-CYANO-2,4-DIMETHYL-6-HYDROXYPYRIDINE TOWARDS DIVALENT TRANSITION METAL IONS

K. M. Khalifa[1], M.M. El-ajaily[2]*, G. A. El-Alttif[1], M. A. Aboubaker[1]
[1]Chemistry Department, Science Faculty,Sebha University, Sebha, Libya.
[2]Chemistry Department, Science Faculty, Garyounis University, Benghazi, Libya.
*E-mail: melagaily@yahoo.com

ABSTRACT

The Co(II), Ni(II) and Cu(II) ions of 5-cyano-2,4-dimethyl-6-hydroxypyridine were synthesized. All the synthesized complexes were characterized by elemental analysis, molar conductivity, infrared and electron paramagnetic resonance spectroscopies. The analytical data suggested the stoichiometric of 1:2 [M:L] ratios. From the infrared spectra, it is concluded that the ligand is coordinated to the metal ions through nitrogen atom of the cyano group and oxygen anion of the hydroxyl group. The electron paramagnetic resonance spectral data suggested a square planar structure for the synthesized complexes.

Key words: *5-cyano-2,4-dimethyl-6-hydroxypyridine, complexes, CHN elemental analysis, molar conductivity, Ir and EPR.*

INTRODUCTION

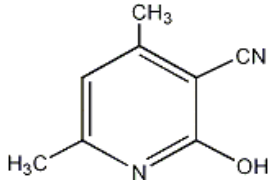
5-cyano-2,4-dimethyl-6-hydroxypyridine compound has donor sites through N,-OH and CN and it behaves as a bidentate ligand and form large number of metal complexes with many metal ions.[1] A copper(II) complex of the formula [Cu(Phen)(BPT)].0.5H_2O,(Phen represents phenanthroline and BPT is biphthalate) has been synthesized under ambient conditions and a square pyramid geometry was suggested for the Cu(II)complex.[2] The synthesis, characterization and some properties of thiourea derivatives and some of their transition metal complexes have been reported.[3-5] The coordination capacity of thiourea derivatives has been shown in several studies.[6-8]

The aim of this study is to synthesis and elucidate the geometrical structures of the 5-cyano-2,4-dimethyl-6-hydroxypyridine complexes with Co(II), Ni(II) and Cu(II) ions.

EXPERIMENTAL

Material

All chemicals used in this study were pure materials (BDH or Aldrich), including; $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, NH_4OH, C_2H_5OH, DMSO, 5-cyano-2,4-dimethyl-6-hydroxypyridine and double distilled water.



Synthesis of Cobalt (II) complex

The Co(II) complex was synthesized by adding 0.02 moles (2.96 g) of the 5-cyano-2,4-dimethyl-6-hydroxypyridine in 30 mL of ethanol to 0.1 mole (2.37 g) of $CoCl_2.6H_2O$ in the same amount of the solvent, then few drops of ammonia solution were added to adjust the pH at which the

complex even isolated and refluxed for two hours, filtered and washed with hot ethanol and kept in a desiccator over $CaCl_2$. The final product yielded 65%.

Synthesis of Nickel(II) complex

The Ni(II) complex was synthesized by adding 0.02 moles (2.96 g) of the 5-cyano-2,4-dimethyl-6-hydroxypyridine in 30 mL of ethanol to 0.01 mole (2.38 g) of $NiCl_2.6H_2O$ in 30 mL of ethanol. Few drops of ammonia solution were added to adjust the pH at which the complex even separated. The obtained mixture was refluxed for two hours, filtered and washed with hot ethanol and kept in a desiccator over $CaCl_2$. The final product yielded 65- 70%.

Synthesis of Copper(II) complex

The complex of Cu(II) ion was synthesized by adding 0.02 mole(2.96 g) of the 5-cyano-2,4-dimethyl-6-hydroxypyridine in 30 mL of ethanol to 0.1 mole (1.70 g) of $CuCl_2.2H_2O$ in the same amount of the solvent. Few drops of ammonia solution were added to adjust the pH at which the complex even isolated The resulted mixture was refluxed for two hours, filtered and washed with hot ethanol and kept in a desiccator over $CaCl_2$. The final product yielded 50-65%.

Measurements

The synthesized complexes were subjected to C, H and N elemental analysis using 2400 elemental analyzer. The molar conductance measurements of the complexes were calculated by using conductivity meter model CM-1K. TOA company (Japan), at chemistry department, Garyounis University, Benghazi, Libya. The infrared spectra were carried out applying the KBr disc technique using IFS-25 DPUS/IR spectrometer (Bruker). The electron paramagnetic resonance spectra were recorded using EMXEPR spectrometer (Bruker).

RESULTS AND DISCUSSION

Microanalysis and Molar conductivity

All the synthesized complexes are microcrystalline powders by different colors, stable for a long time with high melting points. The analytical data indicate the formation of 1:2[M:L]ratio. The molar conductance measurements suggest the existence of a non- electrolyte nature,[9] Table 1.

Infrared spectra

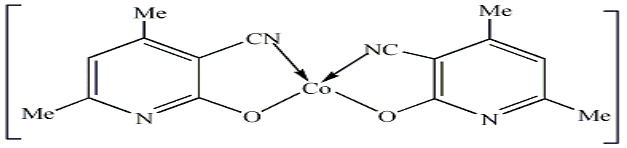
The infrared spectral data of the synthesized complexes are presented in table 1.The spectra of the complexes show a change in the position of CN group in the complexes in comparison with the free ligand (see the table). This change indicates the involvement of the group in complexation through nitrogen atom with the metal ions under investigation.[10] Meanwhile, the broad band in the range of 3444-3555 cm^{-1} assigned to the presence of water molecules in the complexes.[11] New bands in the range of 624-699 cm^{-1} and 716-842 cm^{-1} due to ν(M-N) and ν(M-O) vibrations. The appearance of these vibrations supports the participation of nitrogen and oxygen atoms in complexation.[12]

Electron paramagnetic resonance spectra

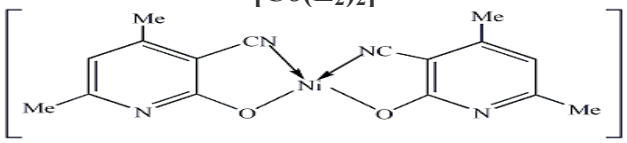
The electron paramagnetic resonance spectral data for the synthesized complexes show a g_{eff} values in the range of 1.40-1.86 . The small deviation of these values compared to the idea value (2.0023) is due to the existence of partial ionic character of the covalent bond between the metal ions and the ligand. The obtained geff values suggest a square planar configuration for the synthesized complexes. [13]

CONCLUSION

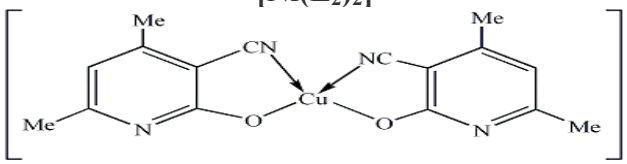
From the previous physiochemical analyses, one can draw the following geometrical structures:



$[Co(L_2)_2]$



$[Ni(L_2)_2]$



$[Cu(L_2)_2]$

Table-1: Elemental analysis and Infrared band assignments (Cm^{-1}) and Electron paramagnetic resonance spectral of 1:2[M:L] of Complexes

Ligands →	$C_8H_8N_2O$(L)	[Co($C_8H_8N_2O$)$_2$]	[Ni($C_8H_8N_2O$)$_2$]	[Cu($C_8H_8N_2O$)$_2$]
M.Wt.	148	354.93	390.7	359.54
%C Calc.	64.86	54.09	49.14	53.40
%C Found	60.80	54.06	51.14	51.00
%H Calc.	5.44	4.54	5.15	4.48
%H Found	4.51	4.38	5.23	3.75
%N Calc.	18.91	15.77	14.33	15.57
%N Found	17.10	15.60	16.66	15.29
%O Found	9. 88	9. 00	15.99	7..97
υ OH	3292	3555	3444	3440
υ C=N	1550	1643	1610	1600
C≡N	2206	2208	2208	2208
C-O υ	1113	1212	1213	1241
M-O υ	-	716	842	842
M-N	-	629	699	624
geff	-	1.40	1.85	1.75
Expected Geometry	-	Square Planner	Square Planner	Square Planner
Color	Light Yellow	Orange	Yello	Dark Green

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Education is the ability to listen to almost anything without losing your temper or your self-confidence.

-Robert Frost