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Spectral Characterization of Co(II), Ni (II) and Cu (II) complexes with 5-(4-Chlorophenyl)-3-(2-naphthyl)-1-phenyl-4,5-dihydro-1H-pyrazole

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ABSTRACT

The Co(II), Ni(II) and Cu(II) complexes of 5-(4-Chlorophenyl)-3-(2-naphthyl)-1-phenyl-4,5-dihydro-1H-pyrazole were synthesized and characterized by elemental analysis, molar conductivity, infrared and electron paramagnetic resonance spectroscopies. The analytical data suggested the stoichiometric of 1:1 and 1:2 [M:L] ratios. From the infrared spectra, it is concluded that the ligand is coordinated to the metal ions through nitrogen atoms of the ligand. The electron paramagnetic resonance spectral data suggested a square planar structure for Co(II and Ni (II) complexes and an octahedral geometry for Cu(II) complex.

Key words: 5-(4-Chlorophenyl)-3-(2-naphthyl)-1-phenyl-4,5-dihydro-1H-pyrazole, complexes, CHN elemental analysis, molar conductivity, Ir and EPR.

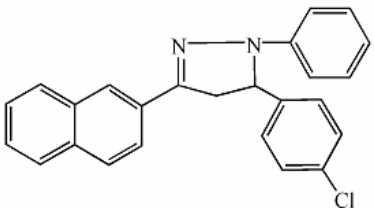
INTRODUCTION

5-(4-Chlorophenyl)-3-(2-naphthyl)-1-phenyl-4,5-dihydro-1H-pyrazole 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

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-(4-Chlorophenyl)-3-(2-naphthyl)-1-phenyl-4,5-dihydro-1H-pyrazole 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 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%.

Synthesis of Nickel(II) complex

The Ni(II) complex was synthesized by adding 0.02 moles (2.96 g) of the 5-(4-Chlorophenyl)-3-(2-naphthyl)-1-phenyl-4,5-dihydro-1H-pyrazole in 30 mL of ethanol to 0.01 mole (2.38 g) of $NiCl_2.6H_2O$ in 30 mL of ethanol. 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-(4-Chlorophenyl)-3-(2-naphthyl)-1-phenyl-4,5-dihydro-1H-pyrazole in 30 mL of ethanol to 0.1 mole (1.70 g) of $CuCl_2.2H_2O$ in the same amount of the solvent. 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

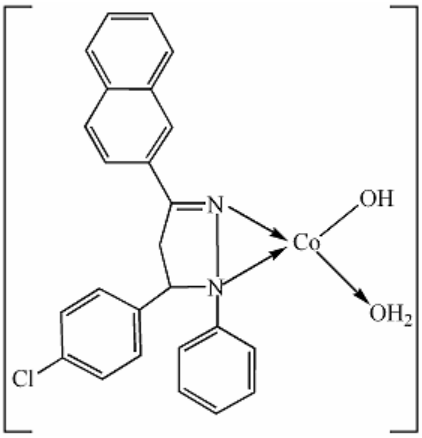
All the synthesized complexes are microcrystalline powders by different colors, stable for a long time with high melting points.

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

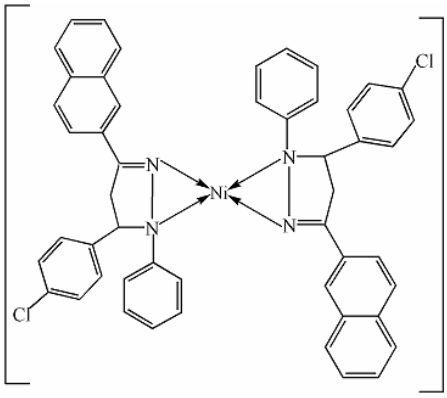
Ligand/ compounds	mol. wt	%C calc.	%C found	%H calc.	%H found	%N calc.	%N found	υOH CHNH	υC=N	υC-Cl	M-O υ	Geff values	Expected geometry	colour
$C_{25}H_{19}ClN_2$(L)	382	78.53	78.42	4.97	5.00	7.32	7.34	3042	1560	720	-	-	-	White
$[Co(C_{25}H_{19}ClN_2)(OH)(H_2O)]$	547.93	58.37	60.19	6.07	6.09	5.45	5.30	3505	-	720	592	1.20	Square plannar	Dark brown
$[Ni(C_{25}H_{19}ClN_2)_2]$	858.7	69.79	70.35	4.92	4.69	6.51	6.49	3356	1619	720	666	1.80	Square plannar	Light green
$[Cu(C_{25}H_{19}ClN_2)_2(H_2O)_2]$	861.54	68.40	63.10	4.45	4.89	6.47	5.98	3446	1630	720	617	2.00	Octahedral	Cyan

The analytical data indicate the formation of 1:1 and 1:2[M:L]ratios. The molar conductance measurements suggest the existence of a non-electrolyte nature[9] Table 1.

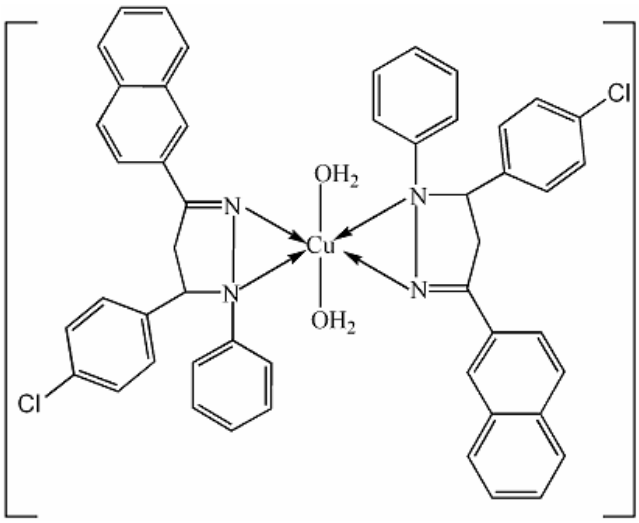
The infrared spectral data of the synthesized complexes are presented in table 1. The spectra of the complexes show a change in the position of ν(C=N) group in the complexes in comparison with the free ligand (see the table). This change indicates the involvement of the group in complexation through nitrogen atom with the metal ions under investigation[10,11]. Meanwhile, the broad band in the range of 3433-3545 cm^{-1} assigned to the presence of water molecules in the complexes[12]. The band at 1200-1350 cm^{-1} assigned to ν(C-N) vibration. The change of the position of this vibration during Complexation indicates the participation of this group in bonding with the metal ions[13]. New bands in the range of 587-720 cm^{-1} due



$[Co(C_{25}H_{19}ClN_2)(OH)(OH_2)]$



$[Ni(C_{25}H_{19}ClN_2)_2]$



$[Cu(C_{25}H_{19}ClN_2)_2(OH_2)_2]$

to ν(M-N) vibration. The appearance of this vibration supports the participation of nitrogen atoms in Complexation[14].

The electron paramagnetic resonance spectral data for the synthesized complexes show a g_{eff} values in the range of 1.20-2.00. 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 Co(II) and Ni(II) complexes and an octahedral geometry for Cu(II) complex[15].

CONCLUSION

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

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