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Further investigation into the phenomenal paramagnetic shift influence of Cu(II) ion on ferrocene-thiosemicarbazone-based bimetallic complexes

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ABSTRACT

A Cu(II) bimetallic ferrocene-thiosemicarbazone-based ligand complex* containing a phenyl fragment has been synthesized and analyzed. Paramagnetic Shift studies of ^{1}H NMR and ^{13}C NMR have been conducted on the complex. A comparison has been made with a similar that containing a methyl fragment. It has been found that whereas the Cu(II) paramagnetic influence may shift or even block the ^{1}H NMR signals of the ligand in the complex, it completely inhibits the appearance of ^{13}C NMR signals in the complexes studied. * Structure of ligand LH is given in Fig. 1.

Keywords: Paramagnetic shift, Cu(II) ion, Ferrocene-thiosemicarbazone bimetallic complexes.

INTRODUCTION

Currently paramagnetic shift influence of lanthanide ions especially Eu(III),Yb(III) and Pr(III)[1-2] is being applied in the elucidation of geometries of complex molecules encountered especially in organic chemistry and biochemistry disciplines. Furthermore, complexes with paramagnetic properties are of great research interest due to enormous potential for applicability in the design of molecular magnets that may revolutionalize the computer industry by producing high speed computers[3-4].

Recently, we discovered the existence of paramagnetic influence in some thio-based Cu(II) complexes[5]. Not long ago, we aslo encountered metal complexes containing imidazolidine free radical ligands with very high paramagnetic shift influence[6].This paper carries out further paramagnetic shift studies on another Cu(II) bimetallic complex containing a ferrocene-thiosemicarbazone-based ligand (LH) system to determine the extent of the Cu(II) paramagnetic shift influence. We hereby report the findings.

EXPERIMENTAL

Synthesis of the Acetylferrocene-thiose micarb-azone Ligand(LH) with a Phenyl Frag-ment (see Fig. 1)

Acetylferrocene(2.0g) was dissolved in methanol(140mls). 4-phenyl-3-thiosemic-arbazide (1.46g, 99%) was also dissolved in methanol (100ml). The two solutions were then mixed in a beaker and transferred to a refluxing flask. Acetic acid(2.5ml of) was added drop wise and the mixture was refluxed for 3 hours.

After refluxing, the solution was transfer to a refrigerator at temperature of 5°C for 24 hours and a brown precipitate was formed. This was filtrated

off, washed with ethanol and ether. It was air-dried with the suction pump for 30 minutes. It was recrystallized from methanol giving a yield of 1.5g with a melting point of 179°C. The product is soluble in ethanol, methanol, chloroform, acetone, and ether.

Synthesis of the Copper(II) Complex, $[Cu(LH_2]Cl_2$

Copper chloride, $CuCl_2.4H_2O$(1.0g) was dissolved in water(50ml). The ligand LH (0.44g) was also dissolved in acetone(150ml). The two solutions were mixed and a green precipitation was formed immediately. The product was filtrated off, washed with water, ethanol and ether. It was then dried with the aid of a water suction pump for 40 minutes. It was then recrystallized from acetone giving a yield of 1.03g. The green complex is soluble in chloroform, acetone, dimethylsulphoxide and dimethylformamide.

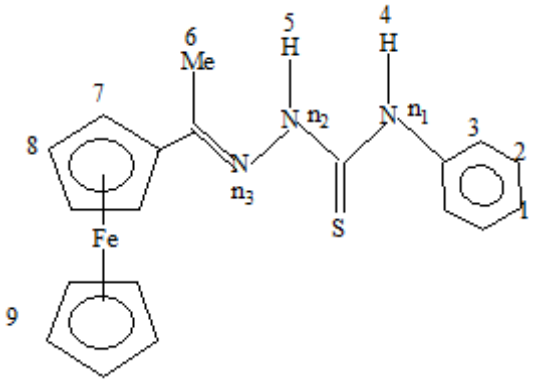

Fig. 1 : The Structure of Ligand HL and H numbering

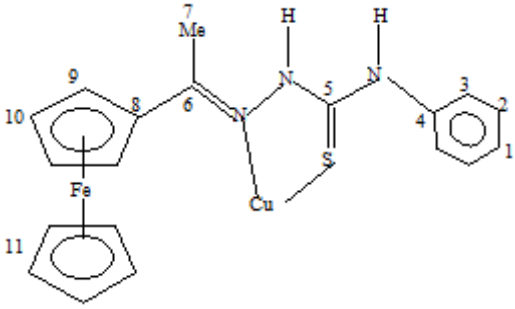

Fig. 2 : The Structure of half Copper $[Cu(HL)_2]Cl_2$ complex and C numbering

Table 1: Analytical Data of LH ligand and its complex $[Cu(LH)_2]Cl_2$

Compound	Found (Calculated)% C	H	N
LH	60.46 (60.49)	5.19 (5.04)	11.03 (11.14)
$[Cu(LH)_2]Cl_2$	51.61 (51.34)	4.30 (6.03)	9.32 (9.46)

Table 2: ^{1}H NMR Of the Ligand LH (δppm)

Peak Position	Hydrogen number	Possible Fragment
1.300	6	Me
2.214	6	Me
4.186	9	C_p
4.416	7	C_p*
4.650	8	C_p*
7.250	1	Ph
7.400	2	Ph
7.700	3	Ph
8.700	4	N(1)H
9.300	5	N(2)H

Table 3: ^{1}H NMR OF $[Cu(LH)_2]Cl_2$ Complex (δppm)

Peak Position	Hydrogen number	Possible Fragment
1.30	6	Me
1.60	6	Me
2.00	6	Me
2.90	8	C_p*
4.20	9	C_p
4.90	7	C_p*
5.90	1,2,3	Ph
6.60	1,2,3	Ph
7.10	1,2,3	Ph
8.10	4	N(1)H
11.20	5	N(2)H

Table 4: ^{13}C NMR of the Ligand LH(δppm)

Peak Position	Carbon number	Possible Fragment
15.0	7	Me
25.0	7	Me
67.0-71.0	8-11	$C_p + C_p^*$
77.0	Solvent	$CDCl_3$
124.0-129.0	1,2,3	Ph
138.5	5	C=S
150.0	6	C=N

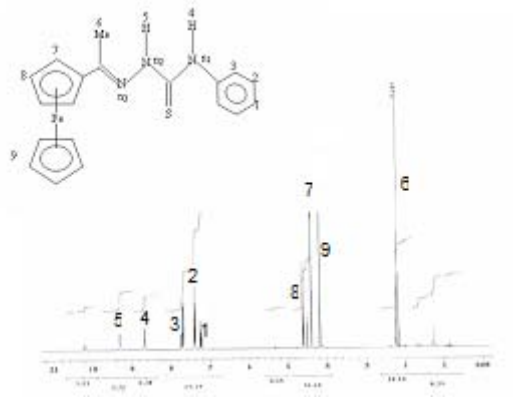

Fig. 3: Proton NMR of LH

Table 5: Paramagnetic Shifts of $[Cu(LH)_2]Cl_2$ relative to Ligand LH

Ligand Fragment	Shift Average (Δppm)
Ph	-0.92
N(1)H	-0.60
N(2)H	+1.90
Me	-0.61
C_p*-7	+0.48
C_p* -8	-1.75
C_p – 9	+ 0.01

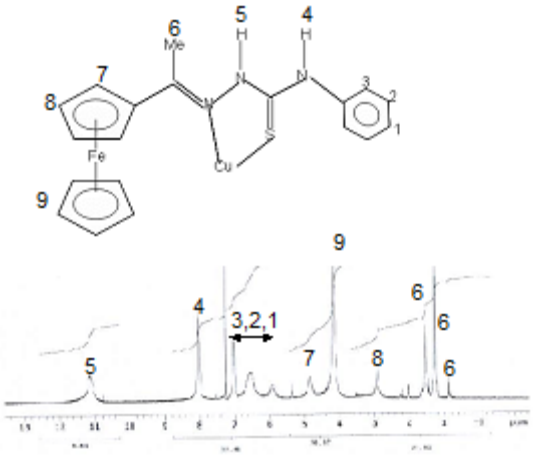

Fig. 4: Proton NMR of $[Cu(LH)_2]Cl_2$

Table 6: Paramagnetic Shifts of $[CuACl]_2$ relative to Ligand HA^+

Ligand Fragment	Shift Average (Δppm)
Me-1	-0.19
N(1)H	+1.65
Me-2	-0.19
C_p*-5	+0.079
C_p*-6	+0.201
C_p	+0.033

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* Substituted cyclopentadienyl ring .

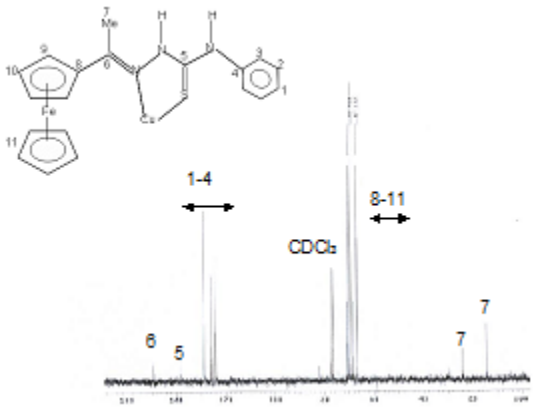

Fig. 5: Carbon-13 NMR of LH ligand

RESULTS

The ligand LH and the corresponding $[Cu(LH)_2]_2Cl_2$ complex were characterized by elemental analysis, ^1H NMR and ^{13}C NMR. The analytical data and the NMR spectra of the ligand and the complex are given in Tables 1-6 and Figs 4-5. The elemental analysis is consistent with the ligand formulation shown in Fig. 1 and the complex being formulated as $[Cu(LH)_2]Cl_2$. The ^1H NMR and ^{13}C NMR peaks have tentatively been assigned on the basis of the literature information[7-8].

DISCUSSION

The NMR signals have tentatively been assigned the positions shown in Figs 3-5 and tabulated in Tables 3-5 on the basis of the literature information[7-9]. The methyl protons usually exhibit signals within δ range of 0-2.6 ppm. The aromatic proton signals occur in the 6.0-9.0 region while the cyclopentadienyl ring protons in ferrocene systems are found in the 4.0-5.0 region. The signal positins of N-H protons vary widely[9]. However in the thiosemicarbazone ferrocene-based systems we have studied and from literature, the N-H signals tend to occur within 7.0-12 ppm range. The proton signal is very much sensitive to the electronegativity of the atom or functional group it is attached to. The higher the electronegativity of the atom/group attachment, the larger the δ value[7,9]. This effect also applies to ^{13}C NMR spectroscopy. The ^{13}C NMR assignments of signal positions shown in Fig.5 were based on literature[7-8]. The methyl C atom signal appears in the lower δ value region[2] of the carbon-13 spectrum (-20 to 30 ppm) and aromatic C atoms (110-135 ppm) range. The ^{13}C NMR signals around 65-75 ppm region in our complexes have been assigned to cyclopentadienyl C atom signals[8].

Paramgnetic shifts influence

The paramagnetic shift influence affects an NMR signal in several ways. First, a signal may be shifted downfield to a higher more positive δ value (to the left of its initial position)or it may be shifted up field to a less positive δ value (to the right of its original position) in the up field direction. The other paramagnetic influence characteristic is to broaden the signal or make it disappear completely. The paramagnetic influence comes about due to the presence of unpaired electron(s) in a system. Thus, transition metal and lanthanide ions which have unpaired electrons usually cause paramagnetic influence to a proton and/or carbon containing ligands when ^1H NMR or ^{13}C NMR spectra are recorded. The lanthanide ions Eu(III) with an f^6 electron configuration has six unpaired electrons and Yb(III) with f^{13} with one unpaired electron are utilized as shift reagents[2]. They form some interaction with the compound under investigation and bring about paramagnetic shifts downfield[2] due to the magnetic field arising from the existence of the unpaired electrons. On the other hand, the lanthanide ion Pr(III) with an f^2 electron configuration produce up field shifts[2]. In our previous paramagnetic shifts studies of ML_2 (M = Co, Ni, Cu, and Zn, L = mono deprotonated imidazolidine nitroxyl ligand)[6], we found that the proton NMR signals appeared in strikingly wide range of +30 ppm to -90 ppm.

In the present study of LH (see Fig.1) ligand and the $[Cu(LH)_2]Cl_2$ (see Fig.2) complex, the proton NMR signals appeared in the usual range of 0-11 ppm. However the signals shifted from their original positions some downfield and some upfield. The proton signals of both the methyl and phenyl fragments tend to be shifted to the up field positions (lower δ values). This is seen in both Tables 5- 6. In the case of cyclopentadienyl protons, the shift, with one exception, was downfield and was in the range of $\Delta\delta$ value s 0.01 to 0.50 ppm. Relative to the ligsnd. The nitrogen proton N(1)H shifted upfield in the LH ligand but down field in the case of HA. The factors that influence whether an NMR signal shifts or not or gets broadened or not are not clear.

The ^{13}C NMR spectra of the ligands LH and HA, as well as the corresponding Cu(II) complexes $[Cu(LH)_2]Cl_2$ and$[CuACl]_2$ were scrutinized for the possible existence of paramagnetic influence. Surprisingly, the paramagnetic shift influence was so great that no signal was observable in the case of the copper(II) complexes despite the corresponding ligands LH and AH exhibiting good ^{13}C NMR spectra.

Conclusion

The copper(II) ion with its one unpaired electron exerts significant paramagnetic shifts influence in both the proton and carbon-13 spectra

of the copper complexes studied. The extent of this phenomena in the ferrocenethiosemicarbazone complexes needs further investigations.

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