

Synthesis and Characterization of New Complexes Fe(II), Co(II) and Ni(II) Ions with Azo Ligand Derived from 4-Aminoantipyrene

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Abstract

The ligand (4-(7-hydroxy-4-methylcoumarin-8-ylazo)-1-phenyl-2,3-dimethyl pyrazol-5-one 4-yl) derived from 4-aminoantipyrene and 7-hydroxy-4-methyl coumarin. The synthesized ligand was characterized by ¹³C, ¹H NMR, FT-IR and UV-Vis spectra. Complexes of Fe(II), Co(II) and Ni(II) with the ligand were prepared in aqueous methanol with a (1:2) M:L ratio. The prepared complexes have been characterized by using flame atomic absorption, FT-IR, UV-Vis spectra as well as magnetic susceptibility and conductivity measurements. On the basis of physicochemical data octahedral geometries were attributed for the complexes.

Keywords: 4-aminoantipyrene, azo dye, coumarin.

1. Introduction

The studies of azo dyes with interesting physical and spectrophotometric properties have been active area of research. They are very important class of chemical compounds containing a heterocyclic moiety which have been attracted the attention of many researchers in the recent years [1]. 4-aminoantipyrene and its complexes are a good analytical reagent in the medicine field [2].

With an end goal to enhance bio-available, medicinal in addition to toxic properties of the compound derived from the azo-compound named 4-aminoantipyrene, numerous creators centered their exploration on the amalgamation, identification and natural assessment of metallic complexes for this group of natural materials [3-4]. The spectroscopically and magnetically investigations of Fe⁺³ complex of hydroxyl (aryl) azo-dyes, got from antipyrene, prompted. Rawther & Nair to propose from the FT-IR information that the OH group join in coordination by Nitrogen double bond Nitrogen and carbonyl group of ring of pyrazolone [5,6].

Azo gatherings show frail contributor properties however in conjunction with other solid gives like OH, NH₂ or C=O they form exceptionally stable chelates.

The stability of the chelates, as mentioned earlier, depends on the number of atoms

involved in ring formation. So chelates with five or six membered rings are the most stable ones. For the same reason, complexes of tridentate azo compounds are more stable than the ones of bidentate azo compounds. Moreover, the strongly basic ligands form the most stable complexes and the strongly acidic ones the least stable complexes [7].

Metallic azo compounds might be subdivided to first category and second category, named the azogroups were involve by bonding but the others in which they were not. Former could be derived to azocompounds that had donor groups (OH, NH₂, COOH, SH) in a congenial position to produce 6 or 5 metallic membered compound [9].

Metal complexes of azo-compounds might be separated into two classes, to be specific ones that the azogathering is included in holding & the others that they were most surly not. Previous are gotten from azocompounds that had benefactor capacities, for example, OH, NH₂, COOH, SH, and so forth., in a congenial position in order to frame 6 or 5 metallic membered compound [9].

2. Experimental Section

2.1 General

The reagents and solvents were of analytical grade and used without further purification. 4-aminoantipyrene, 7-hydroxy-4-

methylcoumarin, ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) were obtained from Fluka Company, ethanol, methanol and sodium nitrite (NaNO_2) were obtained from B.D.H. Company. Infrared spectra were recorded as KBr plates utilizing a Shimadzo FT-IR 8400S spectrophotometer, at the Chemistry Department, Al-Mustansyriyah University. UV/ visible on a UV-Visible spectrophotometer produced by Shimadzu in range 200nm-800nm utilizing 0.001M concentration of metallic compounds and ligand in methanolic solvent, that had utilized as blank. The ^{13}C , ^1H NMR spectra (dissolvable DMSO- d_6) had been noted on Bruker DMX-500 spectrophotometer-300 MHz spectrometer with TMS as interior standard which were made at Chemistry Department, Al-Bayt University, Jordan. The dissolving purposes of the readied compounds were gotten utilizing Gallenkamp M.F.B-600.

F Melting Point Apparatus. The metal percent in the compounds were resolved utilizing the nuclear retention Shimadzu 680cc-fire/Japan. Magnetic susceptibility estimations were gotten at room temperature by equalization magnetic susceptibility of Bruke Magnet B.M.6, England. Conductivity was estimated in Conductometer/WTW/England.

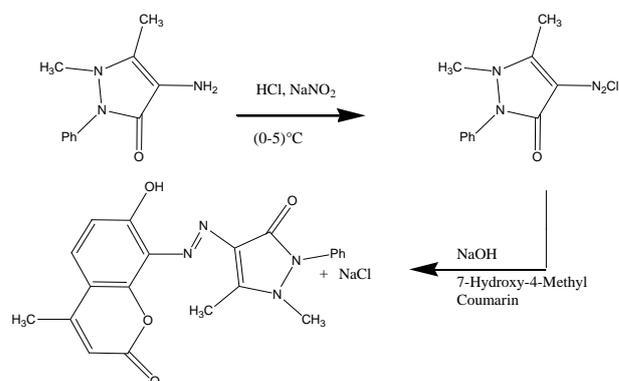
2.2 Synthesis of 4-aminoantipyrine diazonium salt.

4-aminoantipyrine (2.0324 gm., 0.01mole) was diazotised by dissolving in dilute hydrochloric acid 20.25 ml in 4 ml water. The resulting solution is stirred for 10 min. A solution of sodium nitrite (0.76 gm., 0.011 mole) in water (2.5 ml) was added slowly dropwise to previous solution (keeping the temperature at $0-5^\circ\text{C}$). The solution where clear.

2.3 Synthesis of ligand (HL).

The solution of unstable compound (diazonium-salt) had been spontaneous add wisely to alkaline well cooled mixture. Solution of 7-hydroxy-4-methylcoumarin (1.7620g, 0.01 mole) in ethanol and 10% NaOH (15 ml). After the completed addition,

the mixture was stirred for further 20 min. The mixture had been allowed to stand for one h. Yellowish/orange product of the ligand had been formed. Filtered then washed with water. Boiling ethanol has been used as recrystallization solvent then reducing the water by utilizing ofr anhydrous CaCl_2 for one night in a desiccator (yield 85%, M.p. $176-178^\circ\text{C}$) (Scheme (1)).



Scheme (1): Synthesis of HL ligand.

2.4 Synthesis of metal ion complexes

To methanolic solution (10 ml) of HL (0.392 g, 1 mmol), a metal salt solution (0.5 mmol) (0.995 g, 0.119 g and 0.119 g of, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ respectively) in methanol has been add drop/wise with stirring. The mixture had been refluxed for 2-3 hrs. The ratio of metal to ligand was 1:2 for all studied metals. Complexes had been washed with water/methanol and filtered. All complexes had been recrystallized from absolute ethanol and kept in a desiccators over anhydrous CaCl_2 .

Results and Discussion

HL ligand was synthesized by diazotised of 4-aminoantipyrine with 7-hydroxy-4-methyl coumarin. The reaction of HL ligand with metals salts in a 1:2 metal to ligand mole ratio resulted in the formation of solid complexes with the general composition $[\text{ML}_2]_n\text{Cl}$ ($\text{L} = \text{C}_{21}\text{H}_{18}\text{N}_4\text{O}_4$, $\text{M} = \text{Fe}^{\text{II}}$, Co^{II} and Ni^{II} ; $n = 1$ when $\text{M} = \text{Fe}^{\text{II}}$ or Co^{II} while $n = \text{zero}$ when $\text{M} = \text{Ni}^{\text{II}}$). The ligand and their complexes were characterized through elemental analysis, electrical conductance, infrared, electronic spectra, and magnetic susceptibilities at room temperature. The

analytical data for the ligand and complexes together with some physical properties are summarized in Table (1). The lower conductivity value of the Ni^{II} complex support

the non-electrolytic nature, while Fe^{II} and Co^{II} complexes show the electrolytic nature. All the data and remarks are found in Table (1).

Table (1)
Physical parameters with CHN analysis for the metallic compounds with ligand.

Comp.	Formula	Yield (%)	Colour	Mp. (°C)	M% Calc. (found)	Cond.* μS. cm ²
Ligand HL	C ₂₁ H ₂₀ N ₄ O ₄	85	Yellowish orange	176-178	--	--
[FeL ₂]	C ₄₂ H ₃₈ N ₈ O ₈ FeCl	81	Black	155-157	7.17 (7.32)	50 Cond.
[CoL ₂]	C ₄₂ H ₃₈ N ₈ O ₈ CoCl	46	Brownish Green	120-122	7.57 (7.81)	40 Cond.
[NiL ₂]	C ₄₂ H ₃₈ N ₈ O ₈ Ni	58	Pale yellow	140-142	7.54 (7.73)	10 Noncond.

* The conductivity measured in DMSO solvent of (1x10⁻³ mole/L) complexes at room temperature.

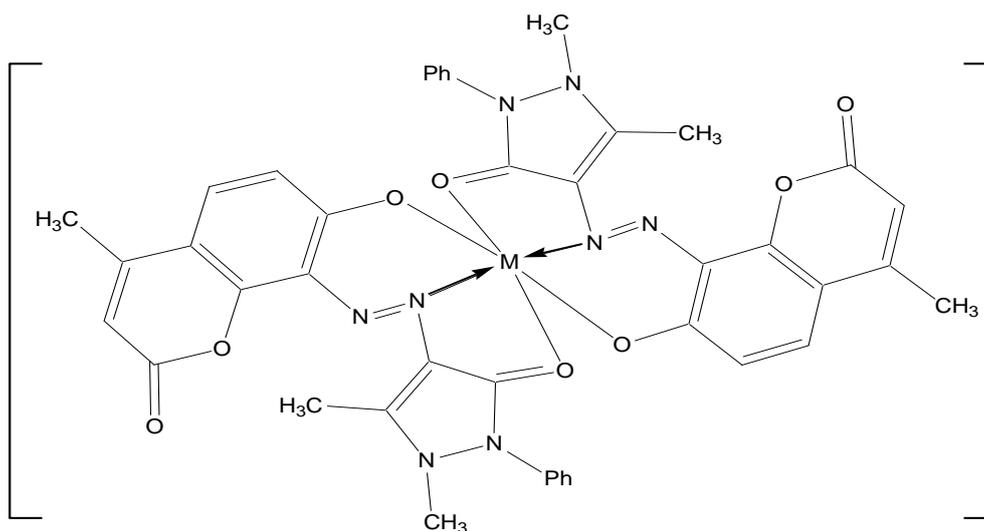


Fig.(3): The proposed structure of the complexes. When $M = Fe^{II}$ or Co^{II} , $n = 1$, when $M = Ni^{II}$, $n = 0$.

3.1 Electronic Spectra and magnetic moments of Free Ligand and their complexes

The spectrum of the free ligand HL show as a strong bands at 202 and 217nm, which is attributed to $\pi \rightarrow \pi^*$ transition. Another two bands were also observed at 325 and 373 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively [10,11]. These values do not change more between free ligand and their complexes except the last value (373 nm) which shifted to higher wave, in all complexes this mean corporation the pair of electrons of azo group in binding with metal.

The electronic spectrum of Fe^{II} complex showed three peaks at 205,219,323nm due to ligand field. Other two peaks at 422, 551 nm which were assigned to charge transfer and (d-d) electronic transition type $^5T_{2g} \rightarrow ^5E_g$ [12]. The spectrum of Co^{II} complex appeared peaks at 207,221 and 323 nm were attributed to ligand field. The peaks at 429, 450, and 620nm were ascribed to charge transfer and electronic transition $^4T_{1g} \rightarrow ^4T_{2g} (P)$ and $^4T_{1g} \rightarrow ^4A_{2g}(F)$, these results agree well with the observed values of magnetic moments, $\mu = 3.98$ B.M, [13]. which clearly indicate for six coordinated octahedral.

The electronic spectrum of the Ni (II) complex display three peaks at 208, 222 and 323 nm due to ligand field other peak at 357nm which was assigned to charge transfer with electronic transition ${}^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$ the two peaks at 437, 670 nm due to electronic transition type ${}^3A_{2g(F)} \rightarrow {}^3T_{2g(F)}$ and ${}^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$ respectively [14].

The magnetic moment μ_{eff} for complexes in the solid state shows that all complexes are

paramagnetic at room temperature. The complexes of Fe^{II} (d^6), Co^{II} (d^7) and Ni^{II} (d^8) were found to be 4.93 B.M, 3.98 B.M and 3.01 B.M respectively, which within the expected spin-only values. The higher value of μ_{eff} of the $\text{Ni}^{+2}(d^8)$ complexes 3.01 B. M may be due to the orbital contribution [15, 16], as show in Table (2).

Table (2)

Uv/Visible data and magnetic moment of azo ligand and its metal complexes (nm).

Compound	$\pi - \pi^*$	$n - \pi^*$	$d-d$ transistons	μ_{eff} (B.M.)	
				Cal.	Fou.
Ligand (HL)	202, 217, 325	373	-	-	-
[FeL ₂]	205, 219	323, 422	551 (${}^5T_{2g} \rightarrow {}^5E_g$)	4.89	4.93
[CoL ₂]	207, 221	323, 429	450 (${}^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$) 620 (${}^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$)	3.87	4.7-5.2 High spin 2.0-2.7 Low spin
[NiL ₂]	208, 222	323, 437	357 (${}^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$) 670 (${}^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$)	2.83	3.01

3.2 FTIR spectra of ligand and its complexes

The data of the IR spectra of the ligand and its complexes were compared with the FTIR spectrum of the free ligand in order to determine the involvement of coordination sites in chelation and to detect the changes that might have taken place. The obtained data are summarized in Table (3) with some assignments of the important characteristic bands.

The FT/IR spectra for the ligand shown broad band at 3185 cm^{-1} , which was allocated to the extending vibration of ν (OH) group. This band was truant in the spectra of all synthesized complexes, which showed deprotonating and contribution of enol oxygen in chelation.

The band at 1701 cm^{-1} show up because of the stretching mode of ν (C=O), on appearance a moved with change in shape was seen from this band, while expanding in intensity was seen. Band normal for the azo extension vibration at 1550 cm^{-1} moved to lower frequency with change in shape of complexes, which means that the engagement of this

gathering in the coordination with metal ion. The appearances of new groups in the area of $466-560 \text{ cm}^{-1}$ are probably relegated to ν (M-N) and ν (M-O) (Metal-ligand) extending groups [18, 19].

Table (3)
FT-IR data of azo ligand and its metal complexes (cm^{-1}).

Compound	$\nu(\text{O-H})$	$\nu(\text{C-H})$ aro.	$\nu(\text{C-H})$ alph.	$\nu(\text{C=C})$ arom.	$\nu\text{C=O}$	$\nu(\text{N=N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
HL	3185	3103	2988	1502	1701	1550	-	-
[Fe(L ₂)]	-	3124	2989	1514	1674	1455	476	538
[Co(L ₂)]	-	3120	2985	1510	1676	1450	466	521
[Ni(L ₂)]	-	3159	2987	1516	1674	1452	479	560

3.3 HNMR spectrum of the ligand

The HNMR spectrum of the ligand in D₆-DMSO was demonstrated in Fig.(1). The spectrum might be shows four important signals, (Me-C=C) coumarin (d,3H,2.504-2.677), methyl (N-CH₃) for antipyrine (d,3H,3.144-3.365), H-for(C=C) in pyrone ring for coumarin (S,1H,6.118), aromatic C-OH proton at(6.696), aromatic ring for coumarin have 2H each proton give (d,1H) in (6.703-6.779) and (6.786-6.808), (5H)

benzene ring in antipyrine (7.393-7.594) [20-22].

Fig.(2) demonstrate the ¹³C/resonance of HL ligand, that records the absorptions at 161.6-160.7, 155-102, 40.2-1805 ppm that may correspond to C=O, C=C & CH₃ groups respectively. The obtained data from ¹³C/NMR as in Fig.(3) with results of ¹H NMR together supports the normal structure of azo/ligand.

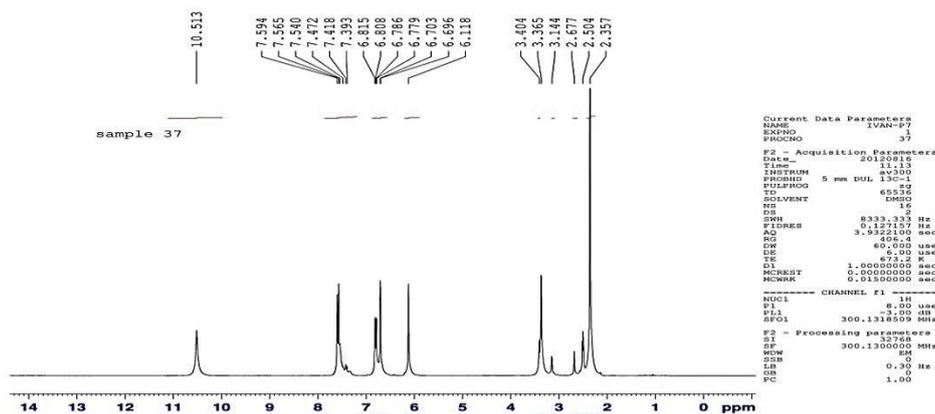


Fig.(1): ¹H NMR spectrum of HL ligand in DMSO-d₆.

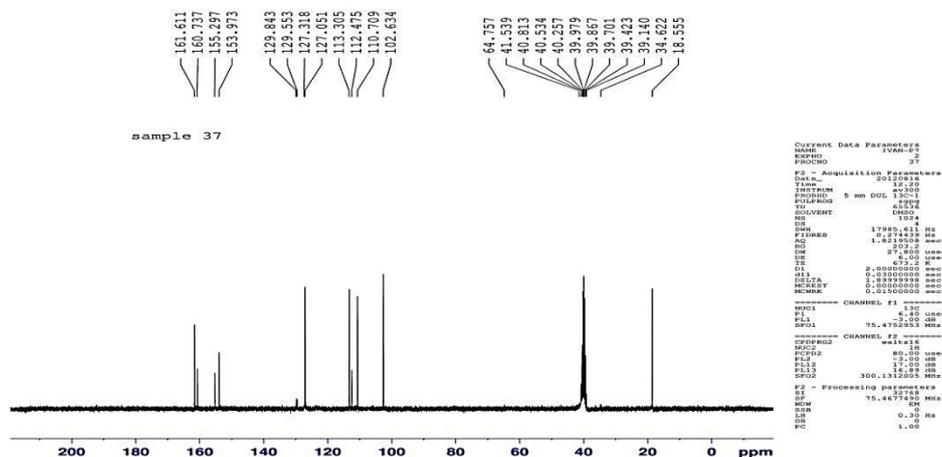


Fig.(2): ¹³C NMR spectrum of HL ligand in DMSO-d₆.

4. Conclusions

Our paper, coordination chemistry for series of Fe^{II}, Co^{II} and Ni^{II} metals with a new azo/ligand namely (4-(7-hydroxy-4-methylcoumarin-8-ylazo)-1-phenyl-2,3-dimethyl pyrazol-5-one 4-yl) were synthesized in good yield. The ligand with metal complexes had been identified on the basis of ¹H & ¹³C NMR, metal analyses, magnetic susceptibility, FT/IR with UV-Vis., spectroscopical outcomes. The structure of metallic compounds had been founded to be [ML₂]_nCl; were M= Fe^{II} or Co^{II}, n=1; M= Ni^{II}, n=0. The T/IR spectral data revealed that HL behaves as tri-dentate ligand via nitrogen atoms in –Nitrogen double bond Nitrogen-group with atoms name Oxygen from hydroxyl an carbonyl pyrazoline groups. As indicated by the outcomes acquired from natural investigations, molar/conductivity estimations in DMSO and magnetic/susceptibility information, the Oh-structures for all metallic compounds been proposed as appeared in Fig.(3).

5. References

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الخلاصة

حضر الليكند (4) - (7) هيدروكسي -4- ميثيل كيومارين
- 8 - ايل (ازو) -1- فنييل -3,2- ثنائي ميثيل بايروزول -5-
اون 4- ايل) من 7-هيدروسي -4-ميثل كومارين و 4-
امينو انتي بارين و شخص الليكند المحضر بواسطة اطياف
الرنين النووي المغناطيسي و الاشعة تحت الحمراء و فوق
البنفسجية -المرئية. حضرت معقدات الحديد و الكوبلت و
النيكل الثنائية الشحنة مع الليكند في وسط الميثانول وبنسبة
فلز: ليكند (2:1)، شخصت المعقدات المحضرة باستخدام
اطياف الاشعة تحت الحمراء و فوق البنفسجية - المرئية و
تقنية الامتصاص الذري، فضلا عن قياسات الحساسية
المغناطيسية و التوصيلية الكهربائية و من النتائج المحصول
عليها تم اقتراح الشكل الثماني السطوح للمعقدات المحضرة.