

Synthesis, Spectral Investigation and Biological Studies of New Transition Metal Complexes with Flouren Drived Schiff-base ligand

Hasan A. Hasan , Khaola M. Sultan , Riyadh M. Ahmed , Enaam I. Yousif

Department of Chemistry, College of Education Ibn Al-Haitham , University of Baghdad, Baghdad , Iraq

Email: hassan_salehy2001@yahoo.com

Abstract:

The new Schiff-base ligand [H₂L] 1-(9H-flouren-9-ylidene)-4-phenylthiosemicarbazide and its metal complexes with Mn(II),Co(II),Zn(II)andCd(II) are reported. The ligand derived from the condensation reaction of (4a,9a-Dihydro-flouren-9-one) with (4-phenylthiosemicarbazide) in mole ratio of 1:1. Upon complex formation, the ligand behaves as a dianionic bidentate species forming monomeric complexes of general formula [M(L)₂] and [M(L)₂(H₂O)₂] , (M=Mn(II), Co(II), Zn(II) and Cd(II)). The modes of bonding and overall geometry of the complexes were determined through (FTIR, UV-Vis, ¹H.NMR) along with elemental analysis, metal content, and conductance. These studies revealed octahedral geometry for the Mn(II) complex and tetrahedral for the Co(II), Zn(II) and Cd(II) complexes. Biological activity of the ligand and its metal complexes against gram positive bacterial strain *Bacillus* (G+) and gram negative bacteria *Pseudomonase* (G-) revealed that the metal complexes become less resistive to the microbial activities as compared to the free ligand.

Keywords: Schiff-base ligand (1-(9H-flouren-9-ylidene)-4-phenylthiosemicarbazid); transition metals; Spectral and biological studies.

Introduction:

The development of Schiff-base species based on transition metal compounds and polydentate ligands has been the subject of extensive research due to their potential applications in materials science [1, 2], environmental chemistry and medicine. In principle thiosemicarbazide reacts with wide variety of aldehydes and ketones to form thiosemicarbazones, which may be used as a ligand. Compounds formed in this way are structurally interesting since both sulfur and nitrogen atoms may be involved in coordination, and many transition metal complexes of thiosemicarbazones have been reported [3]. Thiosemicarbazone moiety without substitute attached to the thion sulfur coordinates as either neutral or anionic (N,S) bidentate ligand depending on the method of complex preparation [4]. When an additional coordinating functionality is presented in the proximity of the donating centers, the ligands bind in a tridentate manner NNS, ONS. This occurs with either the neutral molecule or the mono basic anion upon loss of a hydrogen from N(2) [5]. Schiff-base metal complexes also have applications in biomedical [6, 7], biomimetic and catalytic systems [8, 9] and in supporting liquid crystalline phases [10]. Furthermore, metal complexes of chromium, manganese, nickel, copper, zinc and ruthenium with a wide variety of Schiff-bases have been used as catalysts for carbonylation, hydrogenation, hydroformylation and epoxidation reactions [11, 12]. In this paper, the synthesis and spectral charecterisation of some transition metal complexes with (1-(9H-flouren-9-ylidene)-4-phenylthiosemicarbazid) [H₂L] are reported.

Experimental

Materials: All reagents were commercially available and used without further purification. Solvents were distilled from appropriate drying agents immediately prior to use.

Physical measurements: Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. IR spectra were recorded as (KBr) disc using a Shimadzu 8400 FTIR spectrophotometer in the range 4000-400 cm⁻¹. Electronic spectra of the prepared compounds were measured in the region 250-1100 nm for 10⁻³M solutions in DMSO at 25°C using a Shimadzu 160 spectrophotometer with 1.000±0.001 cm⁻¹ matched quartz cell. ¹H, NMR, spectrum was acquired in DMSO-d₆ solution using a Bruker AMX300 MHz spectrometer with tetramethylsilane (TMS) as an internal standard for ¹H NMR at AL-al-Bayt University, Jordan. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Chloride was determined using potentiometer titration method on a (686-Titro processor- 665Dosimat-Metrohm Swiss). Conductivity measurements were made with DMSO solutions using a PW 9526 digital conductivity meter.

Synthesis

Preparation of the H₂L : Preparation of the (1-(9H-flouren-9-ylidene)-4-phenylthiosemicarbazid).A solution of 4a,9a-Dihydro-flouren-9-one (0.928 g, 5.16 mmole) in methanol(5ml) was added to 4-phenylthiosemicarbazide (1g , 5.16 mmole) dissolving in methanol (5ml),and then(2-4) drops of glacial acetic acid was added slowly to the reaction mixture. The mixture was refluxed for 4 hrs, and allowed to dry at room temperature for (24) hrs. Orange solid metal was obtained. Yield (1.26 g , %66), m.p =215⁰C .IR data (cm⁻¹): 3300,3160 ν (N-H), 896,1387 (w)ν(C=S), 1639 ν (C=N). The ¹H NMR spectrum of the ligand in DMSO-d₆ showed peaks at; δH(300 MHz, DMSO-d₆): 7.15-8.20 (Ar-H); 11.35, 10.51 (N-H-2) and (N-H-4), 9.15 (H-C-N-N), 4.80 (S-H).

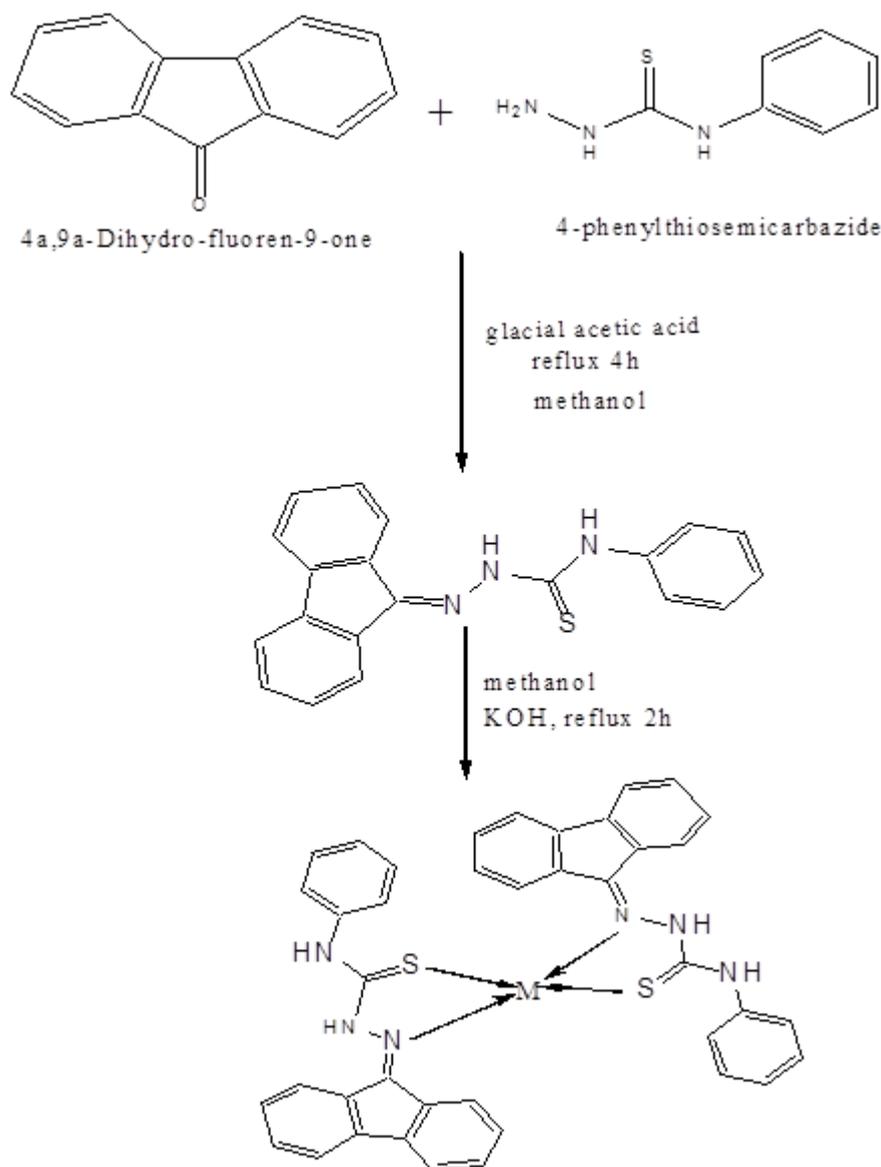
General synthesis of the complexes: A methanolic solution (10 mL) of the metal salt (metal (II) salts are hydrated chloride; $MCl_2 \cdot XH_2O$; where: $M = Mn^{II}$: $X = 4$, Co^{II} : $X = 6$, Cd^{II} : $X = 2$ respectively, Zinc chloride was none hydrated) was stirred into methanolic solution of the Schiff-base ligand (2 mmol) in methanol (15 mL) with (2 mmol) KOH in methanol (15 mL). The reaction mixture was then refluxed for 2 hrs on a water bath until a coloured precipitate formed which was collected by filtration, washed with cold ethanol (5 mL) and dried at room temperature. Elemental analysis data, colours, and yields for the complexes are given in (Table 1).

Determination of Bacteriological Activity: Bioactivities were investigated using agar-well diffusion method [13]. The wells were dug in the media with the help of a sterile metallic borer with centers at least 24 mm. Recommended concentration (100 μ L) of the test sample 1 mg/mL in DMSO was introduced in the respective wells. The plates were incubated immediately at 37°C for 20 hours. Activity was determined by measuring the diameter of zones showing complete inhibition (mm). In order to clarify the role of DMSO in the biological screening, separate studies were carried out with the solutions alone of DMSO and they showed no activity against any bacterial strains. Ligand found to be potentially active against these bacterial strains compared with its complexes.

Results & Discussion: The ligand [H_2L] was prepared in one step according to the general method of preparation of Schiff base ligand [14] shown in Scheme (1). The infrared spectrum of the ligand [H_2L], Fig. (1) was recorded within the 4000-400 cm^{-1} range and compared with those of the new complexes (Table 1). The IR spectra of the ligand shows characteristic bands at 3300, 3160, 1639 and 896, 1387 (w) cm^{-1} due to the $\nu(N-H-2)$, $(N-H-4)$, $\nu(C=N)$ imine and $\nu(C=S)$ functional groups respectively [15,16]

The thiole (S-H) group resulted from the reasonanse (N-C-S) shows a band at (1485-1460). The IR spectra of the complexes exhibited ligand bands with the appropriate shifts due to complex formation (Table 2). The $\nu(C=N)$ imine at 1639 cm^{-1} in the free Schiff-base ligand is shifted to lower frequency and observed in the range 1600-1625 cm^{-1} for the complexes. The bands are assigned to a $\nu(C=N)$ stretch of reduced bond order. This can be attributed to delocalisation of metal electron density (t_{2g}) to the π -system of the ligand [17, 18], indicating coordination of nitrogen of the C=N moieties to the metal atoms [19]. Upon complex formation, The $\nu(N-H-4)$ band at 3160 cm^{-1} in the free ligand is shifted to higher wave number for the complexes [19]. At lower frequency the complexes exhibited bands around 692-648, 545-595 and 418-493 cm^{-1} which could be assigned to $\nu(M-O)$, $\nu(M-N)$ and $\nu(M-S)$ vibration mode [17] (Table 3). These bands indicated that the imine nitrogen and the thione sulphur of the ligand is involved in coordination with metal ion. Finally the H_2O molecule in Mn complex shows a broad band at 3442 cm^{-1} .

The main peaks of 1H NMR of [H_2L] are collected in the experimental section "preparation of H_2L and presented in Figure (5). The resonance peaks associated with the aromatic groups are observed in the range 7.15-8.20 ppm. A resonance around 11.3 ppm equivalent to one proton assigned to the secondary amine group (N-H-2). While the chemical shift at 10.5 ppm may assigned to the (N-H-4) amine group. The spectrum involves two chemical shifts at 9.15 ppm and 4.80 assigned to S-H and H-C-N-N groups resulted from the two kinds of resonance (N-C-S) and (N-N-C) achieved in the ligand structure. Finally in the Zn-complex spectrum, Figure (6) no resonance around 11.3 and 4.8 ppm was observed because of the deprotonation of N-2-H caused by addition of KOH.



Scheme (1): Synthesis diagram of the Schiff-base Ligand H₂L and its complexes.

Electronic spectra measurement: The UV-Vis spectrum of [H₂L] exhibits a high intense absorption peaks at 267 and 375 nm, assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively. The electronic spectra of the complexes Mn (II) and Co (II) exhibit a high intensity peak around 266-285 nm related to the intra-ligand field transitions. Bands exhibit around 379-426 nm assigned to the charge transfer (CT) transitions. Spectrum of the Mn (II) complex exhibited band which can be attributed to ${}^6A_{1g}^{(S)} \rightarrow {}^4T_{1g}^{(G)}$ characteristic of octahedral Mn (II) complex [20-23]. The electronic spectrum of the Co (II) complex shows band which can be attributed to ${}^4T_{1g}^{(F)} \rightarrow {}^4A_{2g}^{(F)}$ transition, corresponding to tetrahedral geometry [20, 24], while the spectrum of the Zn(II) and Cd(II) complexes exhibited bands assigned to ligand $\pi \rightarrow \pi^*$ and L \rightarrow M charge transfer [20,25]. the metals normally prefers tetrahedral coordination.

Conductivity measurements of the complexes lie in the (8.3-14.6) $\text{cm}^2\Omega^{-1}\text{mol}^{-1}$ range, indicating their non-electrolytes behavior (Table 3) [26]. The atomic absorption analysis and the chloride content results of the complexes are in a good agreement with suggested formula $[M(L)_2]$ and $[M(L)_2(H_2O)_2]$.

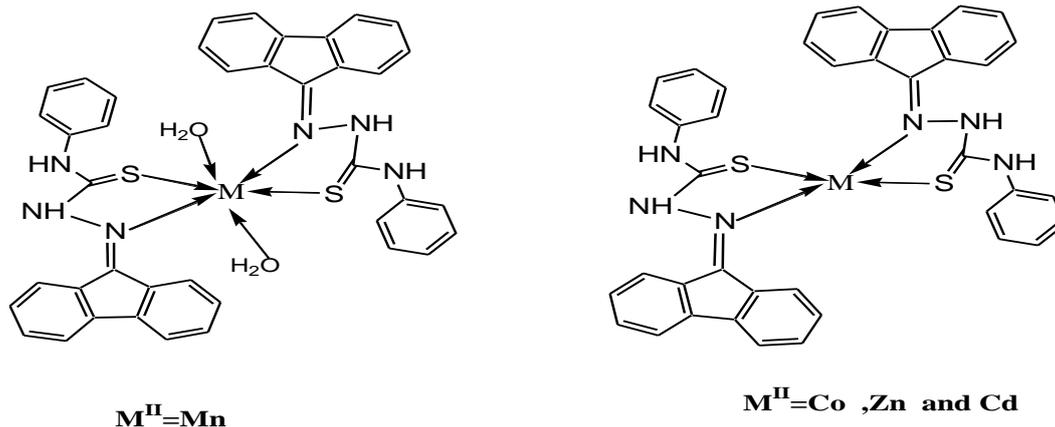
Antimicrobial activity: The free Schiff-base ligand and its metal complexes were screened against *Bacillus* (G+) and *Pseudomonase* (G-) to assess their potential as an antimicrobial agent by disc diffusion method. The measured zone of inhibition against the growth of various microorganisms is listed in Table 4. It is found that the ligand has higher antimicrobial activity than its metal complexes. This can be explained as follows: The biological activity of the Schiff-base ligand is related to the imine moiety, which plays a key role in the inhibition of the tested bacteria. The lower antimicrobial activity of the metal

complexes compared with that in the ligand may be due to the strong interaction between the imine moieties and the metal ions. Such interaction will reduce the activity of the imine moiety in the inhibition.

Conclusion:

In this paper, the synthesis and coordination chemistry of some monomeric metal complexes derived from the Schiff base H_2L are investigated. The complexes were prepared by mixing at reflux 2

mmole of the Schiff-base ligand with 1 mmole of the appropriate metal chloride. Complexes of the general formula $[M(L)_2]$ and $[M(L)_2(H_2O)_2]$, (where $M = Mn(II), Co(II), Zn(II)$ and $Cd(II)$) was obtained. Physico-chemical analysis indicated the formation of four coordinate and six coordinate metal complexes. Biological activities revealed that the ligand has higher antimicrobial activity than its metal complexes.



Scheme(2): Proposed structures of complexes

Table (1) : some physical properties of the ligand and complexes and their reactants quantities .

| Compound | M.p ⁰ C | Color | Yield % | Metal content Prac (Theo.) | chloride content Prac (Theo.) |
|--------------------------|--------------------|-------------|---------|-------------------------------|----------------------------------|
| $[H_2L]$ | 215 | orange | 66 | - | - |
| $[Mn^{II}(L)_2(H_2O)_2]$ | 280 | brown | 67 | 6.22 (7.34) | nill |
| $[Co^{II}(L)_2]$ | 245 | Drak brown | 56 | 7.33 (8.23) | nill |
| $[Zn^{II}(L)_2]$ | 275 | yellow | 46 | 8.67 (9.05) | nill |
| $[Cd^{II}(L)_2]$ | 240 | pale orange | 60 | 13.38 (14.61) | nill |

Table (2): I.R frequencies (cm^{-1}) of the ligand and complexes

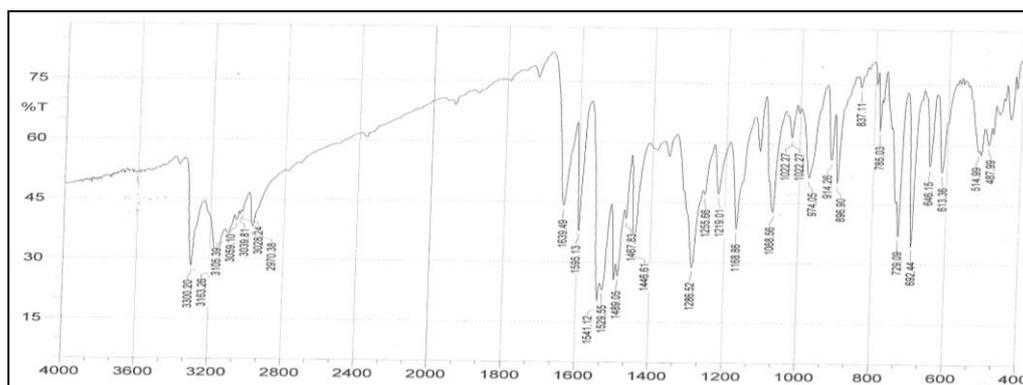
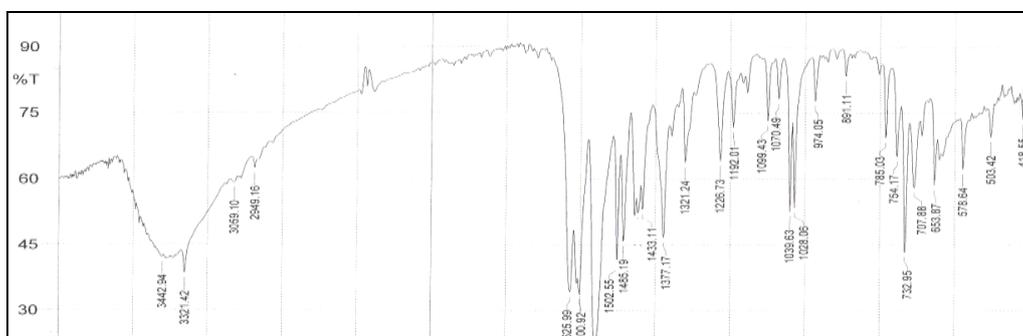
| Compound | $\nu(N-H)$ | $\nu(C=N)_{imin}$ | $\nu(-N-C-S)$ | $\nu(C=S)$ | $\nu(N-N)$ | $\nu(M-O)$ | $\nu(M-N)$ | $\nu(M-S)$ |
|--------------------------|------------|-------------------|---------------|--------------|------------|------------|------------|------------|
| $[H_2L]$ | 3300,3160 | 1639 | 1446 | 896,1387 (w) | 1022 | - | - | - |
| $[Mn^{II}(L)_2(H_2O)_2]$ | 3442 | 1625 | 1485 | 891,1377 (w) | 1028 | 653 | 578 | 418 |
| $[Co^{II}(L)_2]$ | 3381 | 1600 | 1463 | 815,1357 (w) | 1018 | 692 | 592 | 493 |
| $[Zn^{II}(L)_2]$ | 3388 | 1602 | 1460 | 821,1311(w) | 1020 | 648 | 595 | 491 |
| $[Cd^{II}(L)_2]$ | 3373 | 1608 | 1468 | 813,1313(w) | 1019 | 690 | 545 | 455 |

Table (3) : Electronic spectral data and conductance measurement for the ligand and complexes

| Compound | λ nm | ϵ_{\max} Molar Cm^{-1} | Assignment | Δm ($\Omega^1 \cdot \text{cm}^2 \cdot \text{Mole}^{-1}$) | Propose structure |
|--|--------------|--|---|---|-------------------|
| [H ₂ L] | 267 | 3743 | $\pi \rightarrow \pi^*$ | - | - |
| | 375 | 3800 | $n \rightarrow \pi^*$ | | |
| [Mn ^{II} (L) ₂ (H ₂ O) ₂] | 285 | 2328 | Ligand field | 14.6 | octahedral |
| | 379 | 1146 | charge transfer | | |
| | 568 | 110 | ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ | | |
| [Co ^{II} (L) ₂] | 266 | 3522 | Ligand field | 8.3 | Tetrahedral |
| | 426 | 1138 | charge transfer | | |
| | 690 | 26 | ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ | | |
| [Zn ^{II} (L) ₂] | 268 | 3340 | Ligand field | 6.15 | Tetrahedral |
| | 420 | 3245 | charge transfe | | |
| [Cd ^{II} (L) ₂] | 270 | 3345 | Ligand field | 1.03 | Tetrahedral |
| | 410 | 3378 | charge transfe | | |

Table (4) : Antibacterial activities of the synthesised Schiff-base and metal complexes.

| Compounds | <i>Bacillus</i> (G+) | <i>Pseudomonase</i> (G-) |
|---|----------------------|--------------------------|
| [[H ₂ L] | 2.8 | 3 |
| [[Mn ^{II} (L) ₂ (H ₂ O) ₂] | 2 | 2 |
| [Co ^{II} (L) ₂] | 2 | 1 |
| [Zn ^{II} (L) ₂] | 2.2 | 1.5 |
| [Cd ^{II} (L) ₂] | 0.5 | 1.8 |

**Figure 1: I.R. Spectrum of the ligand [H₂L]****Figure 2: IR spectra for the Mn-complex**

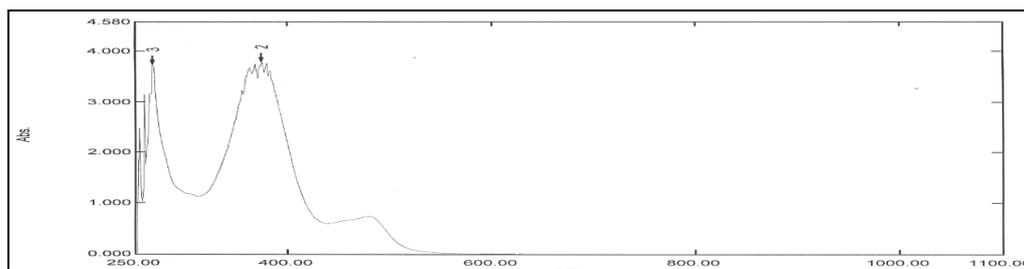


Figure 3: Electronic spectrum of the ligand [H₂L]

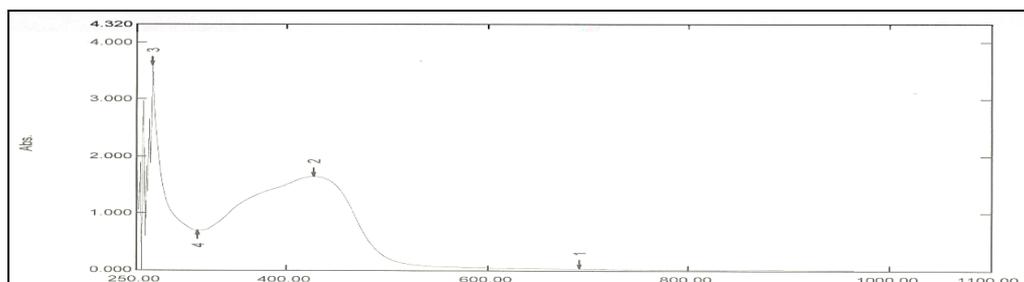


Figure 4: Electronic spectrum of the Co-complex

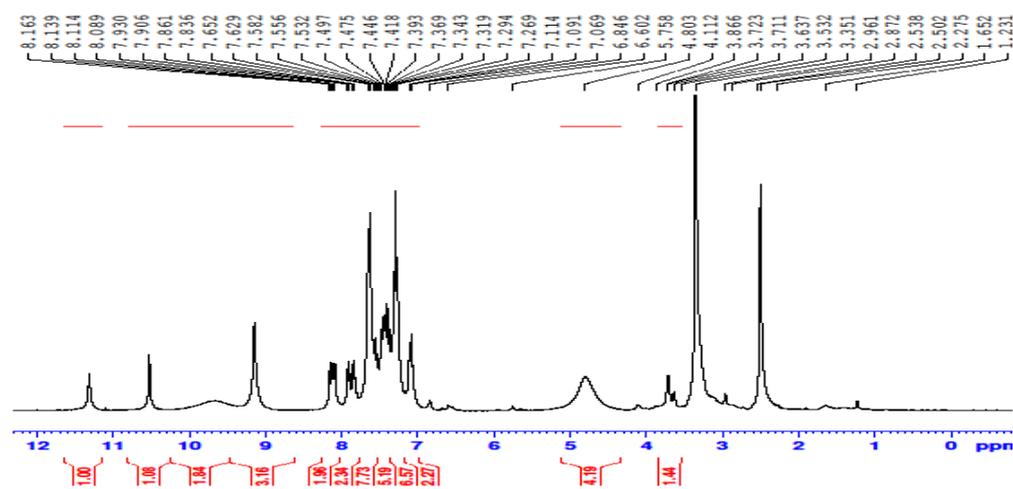


Figure 5: ¹H-NMR spectrum of the ligand H₂L in DMSO-d₆ solution.

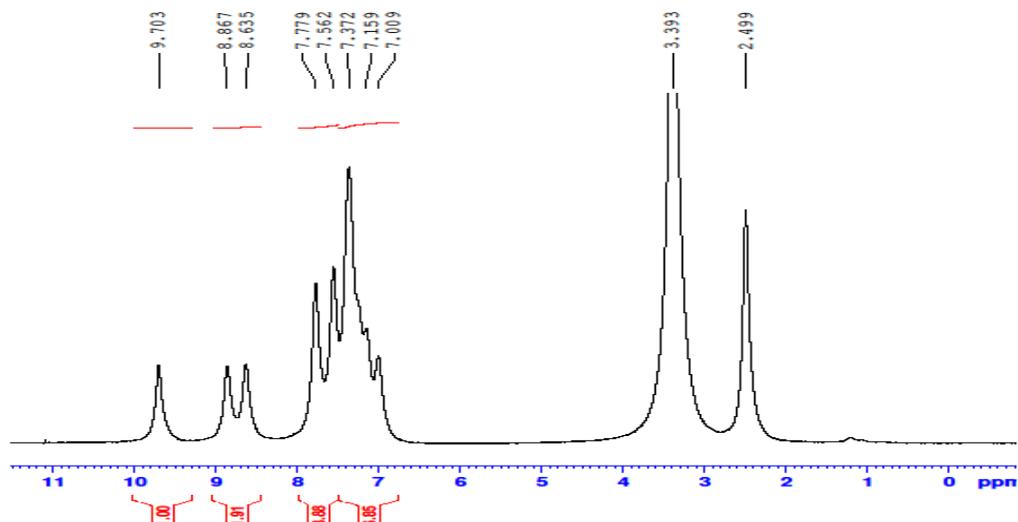


Figure 6: ¹H-NMR spectrum of the Zn-complex in DMSO-d₆ solution.

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تحضير , تحقيق طيفي و دراسة الفعالية البايولوجية لبعض معقدات الفلزات الانتقالية الجديدة مع ليكاند

(قاعدة شف) مشتق من الفلورين

حسن احمد حسن ، خولة محمد سلطان ، رياض محمود احمد ، انعام اسماعيل يوسف

قسم الكيمياء ، كلية التربية ابن الهيثم ، جامعة بغداد ، بغداد ، العراق

الملخص

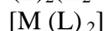
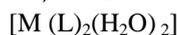
تضمن البحث تحضير الليكاند الجديد قاعدة شف

[1-(9H-flouren-9-ylidene)-4-phenylthiosemicarbazide] H₂L

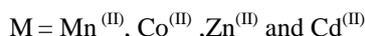
المشتق من

4a,9a-Dihydro-flouren-9-one و 4-phenylthiosemicarbazide

ثم مفاعلة مع بعض العناصر الفلزية باستخدام الميثانول وسطا للتفاعل وبنسبة (1 : 2) حيث تكونت معقدات جديدة ذات الصيغ العامة:



حيث:



شخصت جميع المركبات بالطرق الطيفية التالية (الأشعة تحت الحمراء والأشعة فوق البنفسجية – المرئية ومطيافية الامتصاص الذري للعناصر. وطيف الرنين النووي المغناطيسي) , مع قياس محتوى الكلور ودرجات الانصهار, التوصيلية المولارية الكهربائية والفعالية البايولوجية. من النتائج أعلاه كان الشكل الفراغي المقترح لمعقدات المنغنيز ثماني السطوح بينما الكوبالت, الزنك والكادميوم تتخذ شكل رباعي السطوح.