

Binuclear metal complexes of polydentate Schiff-base: synthesis, characterisation and antibacterial studies

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Abstract:

The new Co(II), Cu(II), Zn(II) and Cd(II) complexes with a multidentate Schiff-base ligand [Benzen1,4-dicarboxaldehyde bis-Semicarbazone] [H₂L] are reported. The ligand H₂L was derived from the condensation reaction of Benzen1,4-dicarboxaldehyde and Semicarbazidehydrochloride. The complexes were prepared from the reaction of the corresponding metal chloride with the ligand. The ligand and its metal complexes were characterised by spectroscopic methods (FTIR, UV-Vis, ¹H NMR, A.A), chloride content, conductance and melting point measurements. These studies revealed complexes of the general formulae [M₂(L)₂] with tetrahedral geometries for Co^{II}, Zn^{II} and Cd^{II} complexes while square planar geometries have been suggested for Cu^{II} complex. 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; Benzen1,4-dicarboxaldehyde bis-Semicarbazone; Binuclear complexes; structural and antibacterial studies.

Introduction:

Schiff bases derived from condensation of semicarbazide with carbonyl compounds have been reported as complexing agents for various transition metal ions. 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..One interesting application in the field of coordination chemistry has been to investigate the use of Schiff-base ligands to develop

phenoxo-bridged binuclear complexes with homometallic and/or heterometallic centres. This includes design molecules containing paramagnetic metal centres are able to self-assemble through metal-ligand interactions rendering supramolecular assemblies with interesting structural and magnetic properties.[3-7]. Schiff-base metal complexes also have applications in biomedical [8,9], biomimetic and catalytic systems [10,11]. Recently, we reported the Metal-assisted assembly of dinuclear metal (II) dithiocarbamate Schiff-base macrocyclic complexes: Synthesis and biological studies potassium 2,2'-(1*E*,1'*E*)-(1,2-diphenylethane-1,2-diylidene)bis(azan-1-yl-1-ylidene) bis (2,1-phenylene)dithiocarbamate [12]. In this paper, the synthesis and spectral characterisation of some transition metal complexes with [Benzen-1,4-dicarboxaldehyde bis-Semicarbazone] H₂L are reported .

Experimental

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 250-900 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- 665 Dosimat-Metrohm Swiss). Conductivity measurements were made with DMSO solutions using a PW 9526 digital conductivity meter.

Synthesis

Preparation of the H₂L:

A solution of Benzen 1,4-dicarboxaldehyde (0.5g , 3.7mmol) in methanol (5 mL) was added to a mixture of Semicarbazid (0.831g , 7.4mmol) in methanol (5 mL), and 2-4 drops of glacial acetic acid. The reaction mixture was refluxed for 4 h. The Schiff base was obtained as a yellow solid which was collected by filtration, washed with diethyl ether (10 mL), and then recrystallised from ethanol and dried at room temperature. Yield (0.25 g, 71%), m.p = 180 °C. The ¹H NMR spectrum of the ligand in DMSO-d₆ showed peaks at; δH(300 MHz, DMSO-d₆): 7.71-7.96 (Ar-H); 10.3 (N-H-2); 6.53 (N-H-4),

General synthesis of the complexes:

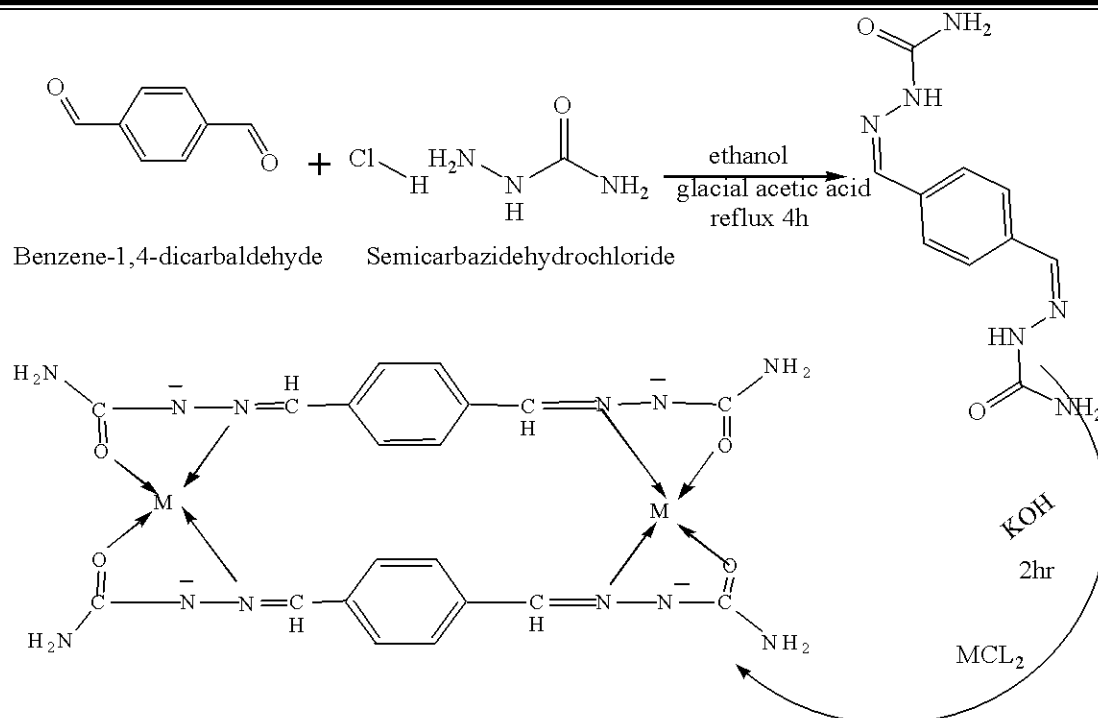
A methanolic solution (10 mL) of the metal salt (metal (II) salts are hydrated chloride; $MCl_2 \cdot XH_2O$; where: $M = Co^{II}$: $X= 6$, Cu^{II} : $X= 2$ and Zinc chloride was non hydrated, was stirred into methanolic solution of the Schiff-base ligand (2 mmol) in methanol (15 mL) with (2 mmol) in methanol (15 mL) KOH. The reaction mixture was then refluxed for 2 h on a water bath until a coloured precipitate formed which was collected by filtration, washed with cold ethanol (5 mL), ether (10 mL) and dried at room temperature. Elemental analysis data, colours, and yields for the complexes are given in (Table 1).

Determination of Antibacterial 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 centres 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 condensation reaction of Benzen1,4-dicarboxaldehyde and Semicarbazidehydrochloride. in mole ratios of 1:2 gave the ligand in good yield (Scheme 1). The Schiff-base ligand was characterised by elemental analysis (Table 1), IR (Table 2), UV–Vis (Table 3) spectroscopy and 1H NMR spectrum. The complexes are air-stable solids, soluble in EtOH, DMSO and DMF. The complexes are sparingly soluble in MeOH and not soluble in other common organic solvents. The coordination geometries of the complexes were deduced from their spectra. The analytical data (Table 1) agree well with the suggested formulae. Conductivity measurements of the complexes in DMSO solutions lie in the (11-17) $cm^2\Omega^{-1}mol^{-1}$ range, indicating their non-electrolytes behavior (Table 1) [14].



Scheme (1): Synthesis diagram of the Schiff-base Ligand H_2L and its complexes

IR and NMR Spectra:

The important infrared bands for the ligand and its metal complexes together with their assignments are listed in Table 2. The IR spectra of the ligand shows characteristic bands at (3275,3151), 3469,1683 ,1615 and 1350 cm^{-1} due to the $\nu(NH_{asy})$, $\nu(N-H_{sy})$, $\nu(NH-2)$ $\nu(C=O)$, $\nu(C=N)$ imine and $\nu(C-N)$ functional groups respectively. Figure (1) represents the IR of the ligand. The IR spectra of the complexes exhibited ligand bands with the appropriate shifts due to complex formation [15], (Table 2). The $\nu(C=N)$ imine at 1615 cm^{-1} in the free Schiff-base ligand is shifted to lower frequency and observed in the range 1593-1585 cm^{-1} for the complexes. The bands are assigned to a $\nu(C=N)$ stretch of reduced bond order. This can be attributed to delocalization of metal electron density (t_{2g}) to the π -system of the ligand [16, 17], indicating coordination of nitrogen of the $C=N$ moieties to the metal atoms [18]. Also the $\nu(C=O)$ carbonyl band at 1685 cm^{-1} in the free Schiff-base ligand is shifted to lower frequency and observed in the range 1675-1667 cm^{-1} for the complexes. Upon complex formation, at lower frequency the complexes exhibited bands around 574–536 and 470-435 cm^{-1} which are due to $\nu(M-N)$ and $\nu(M-O)$ stretching respectively suggesting that the oxygen atom in addition to the nitrogen are involved in coordination with the metal ion [11,17].These bands indicated that the imine nitrogens of the ligand is involved in coordination with metal ion. The

main peaks of ^1H NMR of H_2L and Zn-complex in DMSO are collected in the experimental section “preparation of H_2L and presented in Figure (3). The resonance peaks associated with the aromatic groups are observed in the range 7.71-7.96 ppm. A resonance around 10.3 ppm equivalent to two protons assigned to the secondary amine group (N-H-2). While the chemical shift at 6.53 ppm may assigned to the primary amine group (N-H-4), the shift to high field may be caused by intra molecular hydrogen bonding (N-H...O), while in the Zn-complex spectra in Figure (4) the resonance peaks associated with the aromatic groups are observed in the range 7.79-8.10 ppm. No resonance around 10.3 ppm was observed because of the deprotonation caused by addition of KOH. While the chemical shift at 6.52 ppm may assigned to the primary amine group (N-H-4), the shift to high field may be caused by intra molecular hydrogen bonding (N-H...O).

Electronic spectra and measurements:

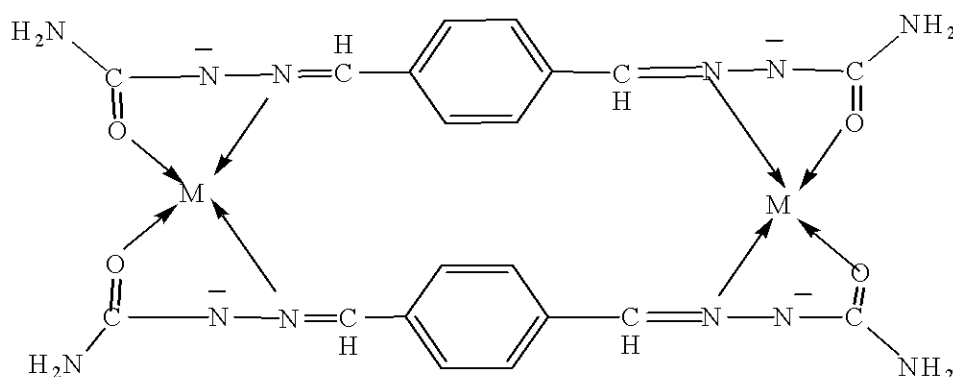
The electronic spectra of the ligand and its complexes are summarised in (Table 3). The UV-Vis spectrum of H_2L exhibits a high intense absorption peaks at 278 and 333nm, assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively. The electronic spectra of the complexes Co(II) and Cu(II) exhibit a high intensity peak around 267-303 nm related to the intra-ligand field transition. Bands exhibit around 407-334 nm assigned to the charge transfer (CT) transitions. The spectrum of the Co(II) complex exhibited two bands which can be attributed to $^4\text{T}_{1g}^{(F)} \rightarrow ^4\text{T}_{1g}^{(P)}$ and $^4\text{T}_{1g}^{(F)} \rightarrow ^4\text{A}_{2g}^{(F)}$ characteristic of tetrahedral Co(II) complex [20-23]. The electronic spectrum of the Cu(II) complex shows three bands which can be attributed to $^2\text{B}_{1g} \rightarrow ^2\text{B}_{2g}$ transition, corresponding to square planar geometry [20,24]. The spectrum of the Zn(II) and Cd(II) complexes exhibited bands assigned to ligand $\pi \rightarrow \pi^*$ and L \rightarrow M charge transfer [20,26]. The metal normally prefers tetrahedral coordination.

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 complexes derived from the Schiff-base Benzen1,4-dicarboxaldehyde bis-Semicarbazone are investigated. The complexes were prepared by mixing at reflux 2 mmole of the Schiff-base ligand with 2 mmole of the appropriate metal chloride. Complexes of the general formulae $[M_2 (L)_2]$ (where $M = Co^{II}, Cu^{II}, Zn^{II}, Cd^{II}$) was obtained. Physico-chemical analysis indicated the formation of four coordinate dicationic metal complexes. Biological activities revealed that the ligand has higher antimicrobial activity than its metal complexes.



Scheme(2): Proposed structures of complexes

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Table 1: Colours, yields, elemental analyses, and molar conductance values.

Compound $\Lambda_M(\text{cm}^2\Omega^{-1}\text{mol}^{-1})$	Colour	Yield (%)	m.p °C		Found(Calc.)	
			M	Cl		
H ₂ L	Yellow	84	188	-	-	-
[Co ₂ (L) ₂]	pink	90	210	19.03 (19.18)	nill	15.87
[Cu ₂ (L) ₂]	Pall green	75	200	19.29 (20.38)	nill	18.12
[Zn ₂ (L) ₂]	white yellow	69	250	20.09 (20.84)	nill	11.34
[Cd ₂ (L) ₂]	White	86	260	29.32 (31.16)	nill	7.03

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Table 2: FTIR frequencies (cm^{-1}) of the compounds .

Compound	$\nu(\text{NH}_2)$	$\nu(\text{NH})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C-N})$	$\nu(\text{N-N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
H ₂ L	3275	,3151	3469	1683	1615	1350	933	-
[Co ₂ (L) ₂] 435	3228	,3154	-	1667	1591	1322	913	536
[Cu ₂ (L) ₂] 439	3223	,3155	-	1670	1587	1348	922	534
[Zn ₂ (L) ₂] 470	3219,	3153	-	1675	1593	1335	918	536
[Cd ₂ (L) ₂] 455	3219	,3153	-	1675	1585	1340	915	574

Table 3: U.V-Vis spectral data in DMSO solutions.

Compound	Band position (λ_{nm})	Extinction coefficient $\epsilon_{\text{max}}(\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})$	Assignments
H ₂ L	278	1532	$\pi \rightarrow \pi^*$
	333	3082	$n \rightarrow \pi^*$
[Co ₂ (L) ₂]	267	865	$n \rightarrow \pi^*$
	407	221	CT
	609	38	${}^4\text{T}_{1\text{g}}^{(\text{F})} \rightarrow {}^4\text{T}_{1\text{g}}^{(\text{P})}$
[Cu ₂ (L) ₂]	671	62	${}^4\text{T}_{1\text{g}}^{(\text{F})} \rightarrow {}^4\text{A}_{2\text{g}}^{(\text{F})}$
	303	993	$\pi \rightarrow \pi^*$
	334	573	CT
	495	123	${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{E}_{\text{g}}$
	635	106	${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{B}_{2\text{g}}$
Zn ₂ (L) ₂]	648	136	$\text{B}_{1\text{g}} \rightarrow {}^2\text{B}_{2\text{g}}$
	276	490	$\pi \rightarrow \pi^*$
	340	889	CT
[Cd ₂ (L) ₂]	265	786	$\pi \rightarrow \pi^*$
	360	642	CT

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

Compounds	<i>Bacillus</i> (G+)	<i>Pseudomonase</i> (G-)
H ₂ L	+++	+++
[Co ₂ (L) ₂]	++	+
[Cu ₂ (L) ₂]	+	++
[Zn ₂ (L) ₂]	+	++
[Cd ₂ (L) ₂]	++	++

(-) = No inhibition = inactive, (+) = (2-4) mm = active, (++) = (5-7) mm = more active, (+++) = (8- 13) mm = highly active

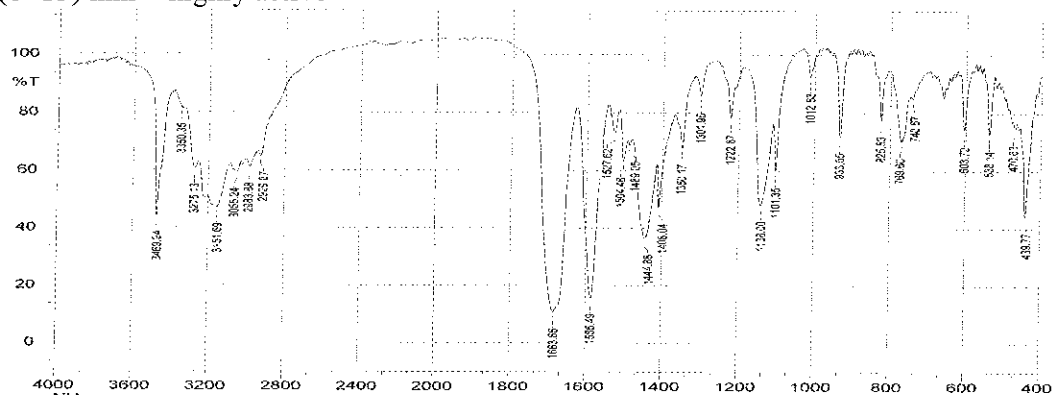


Figure 1: IR spectra for the ligand

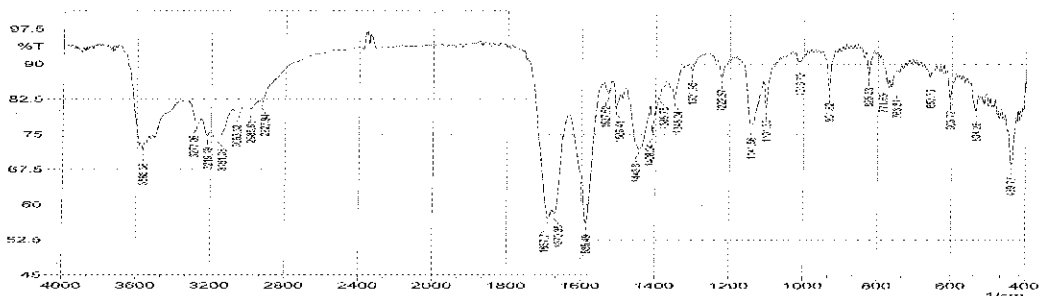


Figure 2: IR spectra for the Zn-complex

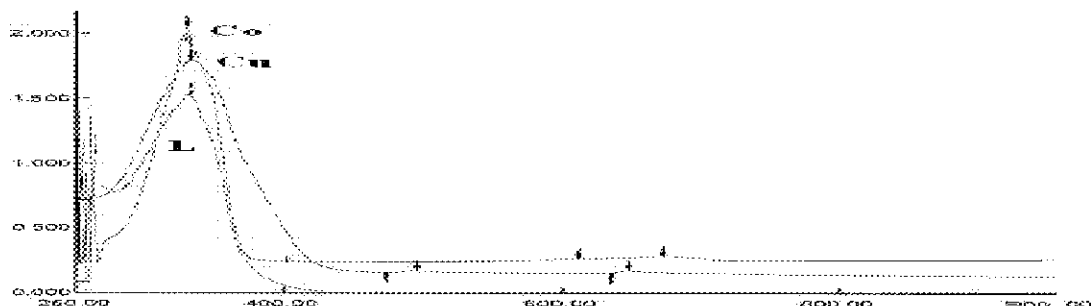


Figure 3: Electronic spectrum of the ligand and Co- and Cu- complexes

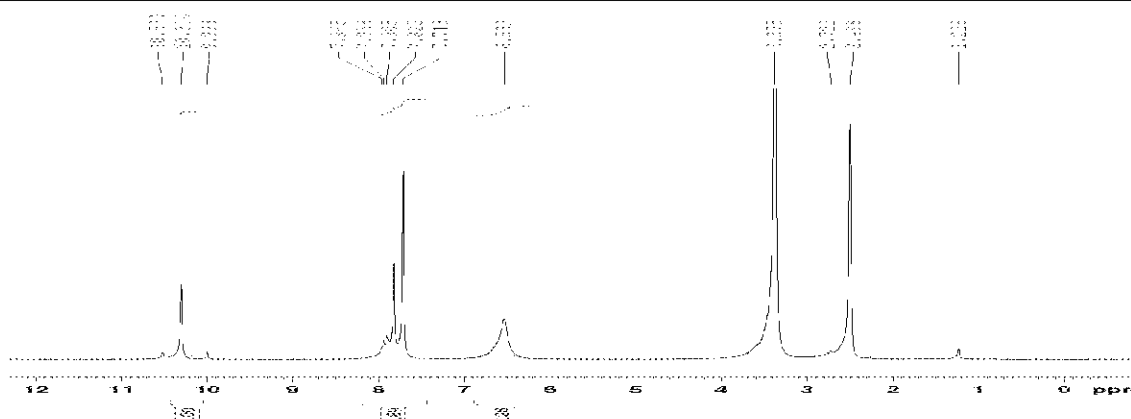


Figure 4: $^1\text{H-NMR}$ spectrum of the ligand H_2L in DMSO-d_6 solution.

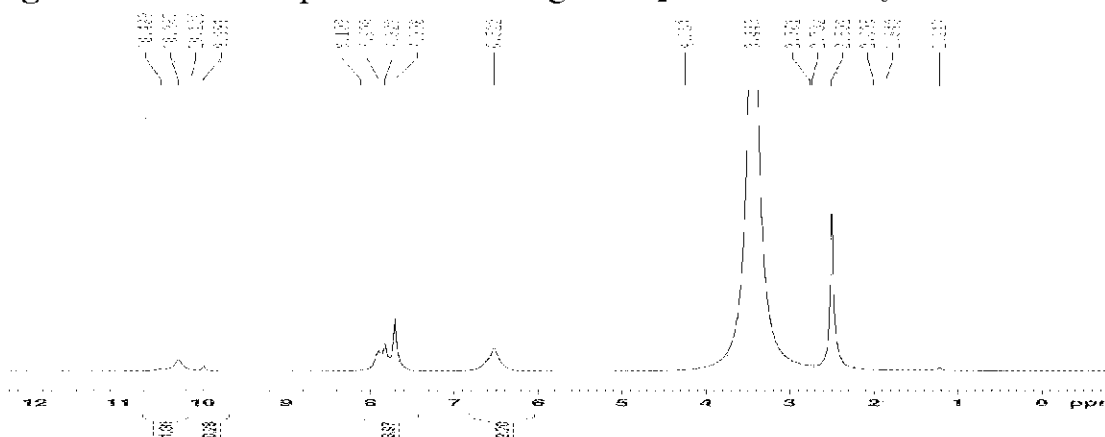


Figure 5: $^1\text{H-NMR}$ spectrum of the Zn-complex in DMSO-d_6 solution.

معقدات ثنائية النواة

لقاعدة شف متعددة الاسنان تحضير ، تشخيص و دراسة للمضاد الجراثيم

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الخلاصة

تضمن البحث تحضير الليكاند الجديد قاعدة شف [Benzen1,4-dicarboxaldehyde bis-Semicarbazone] (L) المشتق من Benzen1,4-dicarboxaldehyde و Semicarbazidehydrochlorid . ثم مفاعلة مع بعض املاح العناصر الفلزية باستخدام الميثانول وسطا للتفاعل وبنسبة (2:2) حيث تكونت معقدات جديدة ذات الصيغ العامة:
 $[M_2(L)_2]$
 حيث:

$M = \text{Co}^{(II)}, \text{Cu}^{(II)}, \text{Zn}^{(II)} \text{ and } \text{Cd}^{(II)}$

شخصت جميع المركبات بالطرق الطيفية التالية (الأشعة تحت الحمراء والأشعة فوق البنفسجية - المرئية ومطيافية الامتصاص الذري للعناصر، $^1\text{H-NMR}$ ، ومحتوى الكلور ودرجات الانصهار) ، مع قياس التوصيلية المولارية الكهربائية والفعالية البايولوجية. من النتائج أعلاه كان الشكل الفراغي المقترح لمعقدات الكوبالت ، الزنك و الكادميوم تتخذ شكل رباعي السطوح بينما النحاس هو مربع مستوي.