$Co^{(II)}$ and $Cd^{(II)}$ Mixed-Ligands Complexes Prepared From N'-(4-methylsulfanyl-benzoyl)-hydrazine Carbodithioic Acid Methyl Ester; Synthesis and Physico-Chemical Characterisation

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Received in:13/November/2016,Accepted in:12/December/2016

Abstract

This work is based on the synthesis of Cobalt(II) and Cadmium(II) mixed-ligands compounds obtained from the reaction of N'-(4-methylsulfanyl-benzoyl)-hydrazine carbodithioic acid methyl ester as a ligand and using ethylendiamine (en), 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) as a co-ligand. The synthesis of ligand (HL) was based on multi-steps synthetic procedure. The reaction of 4-methylsulfanyl-benzoyl chloride with hydrazine gave 4-methylsulfanyl-benzoic acid hydrazide. This compound was reacted with carbon disulfide and potassium hydroxide in methanol to yield N'-(4-methylsulfanyl-benzoyl)-hydrazine potassium thiocarbamate, which upon reaction with methyl iodide resulted in the formation of the ligand. A range of physico-chemical techniques was used to characterise the new ligand and its mixed-ligand metal complexes. These include; IR, UV-Vis, ^{1}H, ^{13}C NMR, elemental micro analyses, magnetic susceptibility, atomic absorption, chloride content, and melting point. The physico-chemical analyses indicated the formation of complexes of the general formula $[M(L)_2X]$, (X = ethylene diamine (en), 2,2` bipyridine (bipy) and 1,10 phenanthroline (phen)), in which the coordination sphere about metal centre is octahedral.

Keywords: N'-(4-Methylsulfanyl-benzoyl)-hydrazine carbodithioic acid methyl ester, Dithiocarbamate derivative; Mixed-ligands complexes.

Introduction

Transition metal complexes that derived from dithiocarbamate (DTC) species, in particular that with heterocyclic backbone, have shown medicinal and industrial applications [1-3]. The presence of sulfur atoms in these type of compounds enhanced their anti-tumour properties [4] and allowed them to be used as fungicides and pesticides agents [5]. Further, dithiocarbamate (DTC) compounds have displayed cytotoxic properties and applied in the treatment of metal poising [6- 8]. The preparation of substituted dithiocarbamate ligands containing heteroatoms can facilitate these ligands to behave as a bidentate [9], tridentate [10, 11] or multidentate [12] chelating agent, upon complexation. Mixed ligands complexes are an interesting type of species that having at least two different kinds of ligands linked with the same metal ion in a complex. The formation of complexes with more than one ligand allowed researcher varying complex properties and obtaining complexes with interesting physical and chemical properties, compared with that containing one ligand [13-15]. In this work, the formation and structural characterisation of cobalt(II) and cadmium(II) mixed-ligands compounds that obtained from dithiocarbamate heterocyclic ligand and ethylene diamine (en), 2,2 bipyridine (bipy) and 1,10 phenanthroline (phen) co-ligand are reported. The physical and analytical analyses indicated the synthesis of complexes with octahedral coordination sphere around atom centre.

Experimental

Reagents

Reagents were acquired from Aldrich, Fluka and Acros and applied as received.

Instruments

(C. H. N) analyses were conducted on a EuroEA 3000 analyzer. IR samples were measured as solids, KBr discs, from 4000-400 cm^{-1} on a Shimadzu 8400 S FTIR spectrophotometer. UV-Vis samples were recorded from 200-1100 nm for 10^{-3}-10^{-5} M in DMSO medium at 23 °C with a Shimadzu 160 spectrophotometer. A Brucker AMX300 MHz spectrometer was used to obtain ^{1}H- ^{13}C-NMR data in DMSO–d_6 solutions. Positive Electrospray mass spectroscopy technique (ESMS) was used to achieve the mass spectrum. SMP40 apparatus was used to measure melting points of compounds. Metal content was determined using atomic absorption technique on a Shimadzu instrument model 680 G. A titration method using a 686 Titrp processor with 665 Dosimat -Metrohm Swiss instrument was conducted to determine chloride content in complexes. Molar conductance in DMSO solutions was run on a PW 9526 conductance bridge. Magnetic susceptibility measeurments at 30 °C were performed on a Sherwood Scientific Devise.

Synthesis

Preparation of HL:

The synthesis of HL was performed following a standard procedure stated in [16] in three steps and as follows:

Synthesis of the ligand: A solution of 4-methylsulfanyl-benzoyl chloride (1.0 g, 5.35 mmol) in 10 mL of MeOH was added dropwise to hydrazine (99%, 0.17 g, 5.30 mmol) with stirring for 1 h. The product was filter and washed with diethyl ether, which yielded (0.79 g, 81%). The product 4-methylsulfanyl benzoic acid hydrazide (0.7 g, 3.84 mmol) was dissolved in methanolic solution (10 mL) of KOH (0.211 g, 3.83 mmol). The mixture was allowed to cool and then CS_2 (0.292 g, 3.83 mmol) was added dropwise with stirring. The obtained solid of N'-(4-methylsulfanyl-benzoyl)-hydrazine potassium thiocarbamate (0.83 g, 73%) was collected by filtration and then reacted with methyl iodide (0.396 g, 2.79 mmole) in methanol medium (20 mL). The mixture was allowed to reflux for 2 h, and the required ligand N'-(4-methylsulfanyl-benzoyl)-hydrazinecarbodithioic acid methyl ester that isolated by filtration was rinsed with diethyl ether and allowed to dry under vaccu. Yield: (0.53 g, 70%), m.p=187 °C. Infra-red $\nu_{(cm-1)}$, (Figure 1): 3329; 3111 cm^{-1} ν(N-H) of amide and hydrazide, respectively, 1667 ν(C=O), 1637 δ(N-H), 1618 ν(C=C), 1527 ν(C=S-NH), 1113 ν(N-N), 972 ν(C=S). ^1H NMR data (ppm), δ_H (300 MHz, DMSO-d_6), (Figure 4): 1.99 (CS_2-CH_3), 2.038 (S-CH_3), 2.97 (NH-C=S), 6.70 and 7.50 (protons of ring), 8.33 (C=O-NH); ^{13}C NMR data (ppm), δ_C (100.63 MHz, DMSO-d_6), (Figure 5): 17.51 (S_2CH_3), 19.2 (SCH_3), 119.16, 123.20, 124.60, 135.72 (carbon of ring), 173.42 (C=O), 187.18 (C=S). ESMS of HL gave m/z, (Figure 8), 272 (57 %) $(M)^+$ indicates the ion peak of the ligand. Peaks observed at m/z 181 (31 %), 124 (100%), 78 (60%), assigned to the $[M-(CS_2-CH_3)]^+$, $[M-(CS_2-CH_3)+(NH-NH-C=O)]^+$ and $[M-(CS_2-CH_3)+(NH-NH-C=O)+(S-CH_3)]^+$, respectively.

Formation of complexes with mixed-ligands

A solution of metal chloride (1 mmole) in MeOH (10 mL) was added to a mixture of HL (2 mmole) in MeOH and $CHCl_3$ (25 mL, 50 V/V). The mixture was allowed to stirring for 2 h at room temperature followed by addition of co-ligands (ethylene diamine, 2,2-bipyridine and 1,10-phenanthroline) (1 mmole) in methanol (5 mL) that yielded a clear yellow solution. This solution was filtered and kept for slow evaporation, which gave coloured solids that washed with ether (2x5 mL). Physical and chemical data for products are stated in (Table 1).

Results and discussion

Chemistry:

The new multidentate ligand (HL) was obtained in a good yield *via* a three-step procedure using a mixture of MeOH and $CHCl_3$ medium. The reaction of 4-methylsulfanyl benzoic acid hydrazide with CS_2 and KOH yielded N'-(4-methylsulfanyl-benzoyl)-hydrazinepotassium thiocarbamate. This compound was reacted with methyl iodide (0.40 g, 2.79 mmol) at reflux to give the ligand N'-(4-methylsulfanyl-benzoyl)-hydrazinecarbodithioic acid methyl ester (Scheme 1). The ligand was characterised by C.H.N.S analyses (Table 1), Infra-Red analysis (Table 2), Electronic data (Table 3), and NMR spectra. The formation of monomeric mixed ligands complexes with cobalt(II) and cadmium(II) were obtained from the mixing of (1 mmol) of metal chloride salts, (2 mmol) of HL and (1 mmol) of co-ligands (ethylene diamine, 2,2-bpyridine and 1,10-phenanthroline) in MeOH medium. Neutral species of the general composition $[M(L)_2X]$, (M = $Co^{(II)}$, and Cd $^{(II)}$), X= en, bipy, phen, were isolated, see Scheme 2.

The solid complexes are stable in air that showed solubility in DMF and DMSO. The coordination spheres of the complexes were based on their physical and chemical data, see Table 1. Table 2 includes the IR data of the HL and its complexes.

NMR and IR Spectra

The NMR data were used to deduce the chemical structure of the ligand. Proton NMR spectrum of HL in DMSO-d_6 solvent, Figure 4: revealed peaks at 1.99 and 2.83 ppm assigned to (CS_2-CH_3) and (S-CH_3), respectively which appeared as expected at lower chemical shift. Signal at 2.97 ppm assigned to (N*H*-C=S) that observed up-field due to its neighbouring to (C=S) group that lead to increase the density on (N-H) group and causes the shielding. The signal of ring protons was observed at 6.70 and 7.50 ppm, while the chemical shift at 8.33 ppm attributed to (C=O-N*H*). The appearance of this peak down-field can be attributed to intra- or intermolecular-hydrogen bonding to the oxygen atom and/or to the NMR solvent, respectively. Such interaction causes a decrease in the electrons density on the (N-*H*) moiety. The ^{1}H NMR of $[Cd(L)_2(en)]$, (Figure 6), indicated the disappearance of proton signal that attributed to (N*H*-C=S) segment. This is due to loss of hydrazinic proton and confirming the involvement of nitrogen in coordination with Cd(II) ion. The spectrum showed signal at 2.25 ppm attributed to CH_2 group. Peak at 2.95 ppm assigned to (NH_2) of the ethylenediamine co-ligand. The down-field appearance of this peak, compared with that in ethylendiamine, may attribute to the involvement of the nitrogen atoms in the coordination to the Cd(II) ion. ^{13}C NMR spectrum (ppm), (Figure 7): δ_C, 18.44 (SCH_3), 19.74 (S_2CH_3), 44.16 (CH2), 116.01, 123.78, 127.57, 139.16 (carbon of ring), 167.82 (C=O), 192.67 (C=S).

The infrared chart of the free ligand, Figure 1, exhibited typical bands related to ν(N-H), ν(C=O), δ(N-H), ν(C=C) and ν(C=S-NH), ν(C=S) functional groups. The distinct frequency around 3329, 3111 cm^{-1} assigned to ν(N-H). The band at 1667 can be attributed to ν(C=O) [17]. Bands noticed at 1637 and 1618 cm^{-1} allocated to ν(C=N) and ν(C=C), respectively [18]. Peaks at 1527 and 972 cm^{-1} related to ν(C=S-NH) and ν(C=S), respectively [19]. The infrared spectra of the complexes confirmed HL bands with the suitable changes and the M-N and M-O vibrations, confirming complexation (Table 2). Upon complex formation, new bands appeared at 3305, 3113 and 3328, 3188 cm^{-1} attributed to ν(NH_2), confirming the involvement of ethylenediamine group in the coordination to metal ion in complexes 1 and 2, respectively. The ν(C=O) and δ(N-H) is shifted, to lower frequency, and detected around 1642-1653 and 1606-1624 cm^{-1} for the complexes indicating the coordination of the N-H of hydrazide and oxygen of carbonyl amide group to the metal ions, compared with that in the free ligand [20-22]. The negative shift of 14-25 cm^{-1} in ν(C=O) value and the presence of new two bands at 422-590 cm^{-1} related to ν(M-N) suggests bonding of metal ions with ethylene diamine, bpy and 1,10-phenanthroline and one of hydrazinic nitrogen, after loss of a proton. The involvement of hydrazinic nitrogen in bonding is supported by positive shifts (10-48) cm^{-1} in ν(N-N) in all complexes [20, 23]. Further, complexes displayed new bands around 551-615 cm^{-1} that allocated to ν(M-O) and confirming the involvement of oxygen atom in complexation [18, 19], Figure 2 and 3.

Electronic spectra, magnetic measuerments and molar conductance:

The UV-Vis spectrum of HL displays a peak at 245 nm related to $\pi \rightarrow \pi^*$. Peaks at 305 and 423 nm assigned to $n \rightarrow \pi^*$ transitions. The UV-Vis spectra of the complexes showed peaks assigned to ligand field $\pi \rightarrow \pi^*$ and to the charge transfer transitions (Table 3). The $[Co^{II}(L)_2en]$ spectrum, Figure 8, showed band in the d-d region attributed to $^4T_2g^{(F)} \rightarrow {}^4A_2g^{(F)}$ transition [24, 25]. The electronic information and the μ_{eff} value confirmed an octahedral arrangment about the Co(II) atom [26]. The spectra of $[Co^{II}(L)_2bipy]$, Figure 9, and $[Co^{II}(L)_2phen]$ also show one additional peak at 650 and 633 nm, respectively`attributed to spin forbidden transition and confirming octahedral geometry [24, 25, 26]. The $\mu_{eff}$ value of Co(II) complexes confirmed a high spin`octahedral`structure. The UV-Vis data of Cd(II) species showed bands related to ligand`field and intra-ligand interaction [26]. As expected, these compounds are diamagnetic, d^{10} system The conductivity measurements indicate a non-electrolyte complexes, Table (1) [27].

Conclusion

A range of mixed-ligands Co(II) and Cd(II) complexes are reported. The complexes were obtained from the interaction of the multidentate ligand (HL) with Co(II) and Cd(II) metal ions and co-ligand ethylenediamine, 2,2-bipyridine or 1,10-phenanthroline. The entity and chemical structure of the complexes were deduced using a range of analytical and physical techniques. These methods indicated the formation of distorted octahedral geometries about metal centres.

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Table(1): Colours, yields, elemental analyses, and conductivity values.

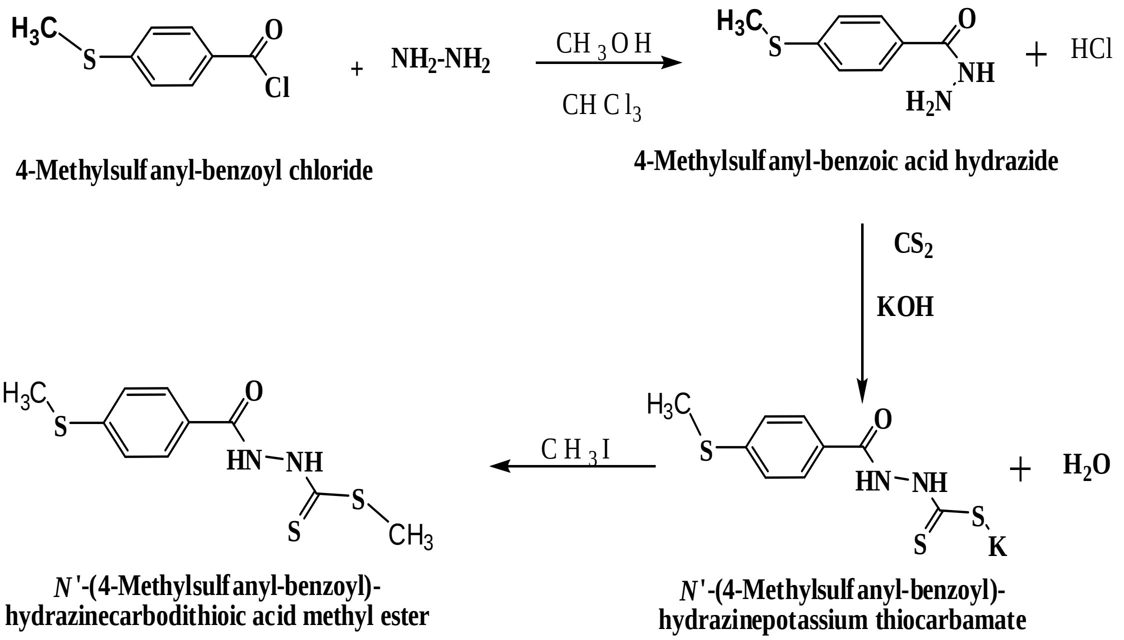
Comp.	Colo.	Yield	m.p	Found (Calcd.) (%)					Λ_M ($cm^2\Omega^{-1}mol^{-1}$)
				M	C	H	N	Cl	
HL	yellow	70	187		43.48 (44.09)	4.52 (4.44)	9.77 (10.28)	-	-
$[Co^{II}(L)_2en]$	yellow	68	276	8.12 (8.90)	39.37 (39.92)	4.67 (4.57)	12.87 (12.70)	- -	7
$[Cd^{II}(L)_2en]$	yellow	64	292	15.78 (15.71)	35.72 (36.94)	4.08 (4.23)	11.27 (11.75)	- -	6
$[Co^{II}(L)_2bpy]$	orange	69	289	7.56 (7.78)	46.73 (47.54)	3.67 (3.99)	10.19 (11.09)	- -	8
$[Cd^{II}(L)_2bpy]$	orange	72	284	13.17 (13.85)	43.96 (44.41)	3.42 (3.73)	10.07 (10.36)	- -	4
$[Co^{II}(L)_2phen]$	pale yellow	66	271	7.24 (7.54)	48.75 (49.15)	3.41 (3.87)	10.42 (10.75)	- -	8
$[Cd^{II}(L)_2phen]$	yellow	63	283	12.83 (13.46)	45.74 (46.01)	3.47 (3.62)	9.68 (10.06)	- -	6

Table (2). IR data (cm^{-1}) of compounds.

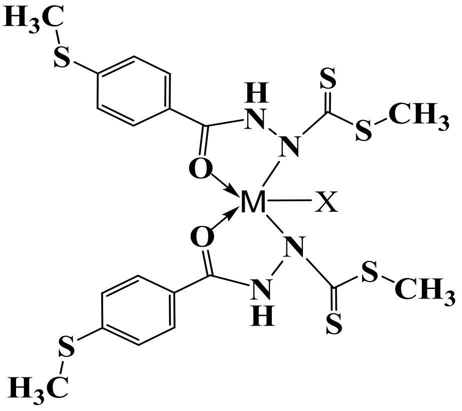
Compound	ν(N-H)	ν($N-H_2$)	ν(C=O)	δ(N-H)	ν(C=C)	ν(N- N)	ν(C= S)	ν(M-O)	ν(M-N)
HL	3329 3111	-	1667	1637	1618	1113	972	-	-
$[Co^{II}(L)_2en]$	3165	3305 3113	1653	1618	1618	1161	958	551	501, 422
$[Cd^{II}(L)_2en]$	3131	3328 3188	1649	1612	1612	1128	945	609	502, 455
$[Co^{II}(L)_2bipy]$	3119	-	1644	1566	1566	1149	918	615	476, 441
$[Cd^{II}(L)_2bipy]$	3141	-	1642	1618	1618	1123	916	565	549, 486
$[Co^{II}(L)_2phen]$	3149	-	1647	1573	1573	1143	950	557	480, 457
$[Cd^{II}(L)_2phen]$	3124	-	1645	1558	1558	1144	963	615	590, 515

Table(3). Magnetic values with electronic data in DMSO solutions.

Comp.	μ_{eff} (BM)	Band position (λnm)	Extinction coefficient ε_{max}(dm^3 mol^{-1}cm^{-1})	Assignments
Co^{II}(L)$_2$(en)]	2.44	240 421 626	861 680 630	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $^4T_2g^{(F)} \rightarrow {}^4A_2g^{(F)}$
[Cd^{II}(L)$_2$en]	3.03	260 325 422	2608 1354 100	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ CT
[Co^{II}(L)$_2$bipy]	0.79	245 370 650	631 800 340	L.F C.T $^4T_1g^{(F)} \rightarrow {}^4A_2g^{(F)}$
[Cd^{II}(L)$_2$bipy]	1.77	265 305	2163 1287	Intra-ligand C.T
[Co^{II}(L)$_2$phen]	1.55	235 395 633	727 510 500	L.F C.T $^4T_1g^{(F)} \rightarrow {}^4A_2g^{(F)}$
[Cd^{II}(L)$_2$phen]	0.38	245 422	413 120	L.F C.T



Scheme (1). Synthetic route of ligand



M= Co^{II} and Cd^{II}

X= en, biby and phen

Scheme (2). General structure of complexes

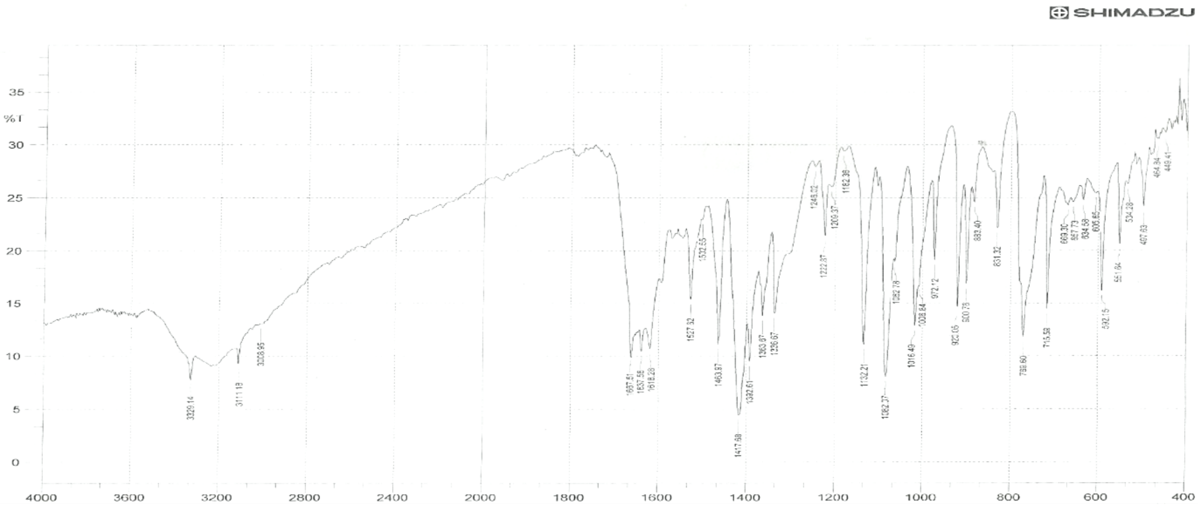


Figure (1): IR spectrum of L

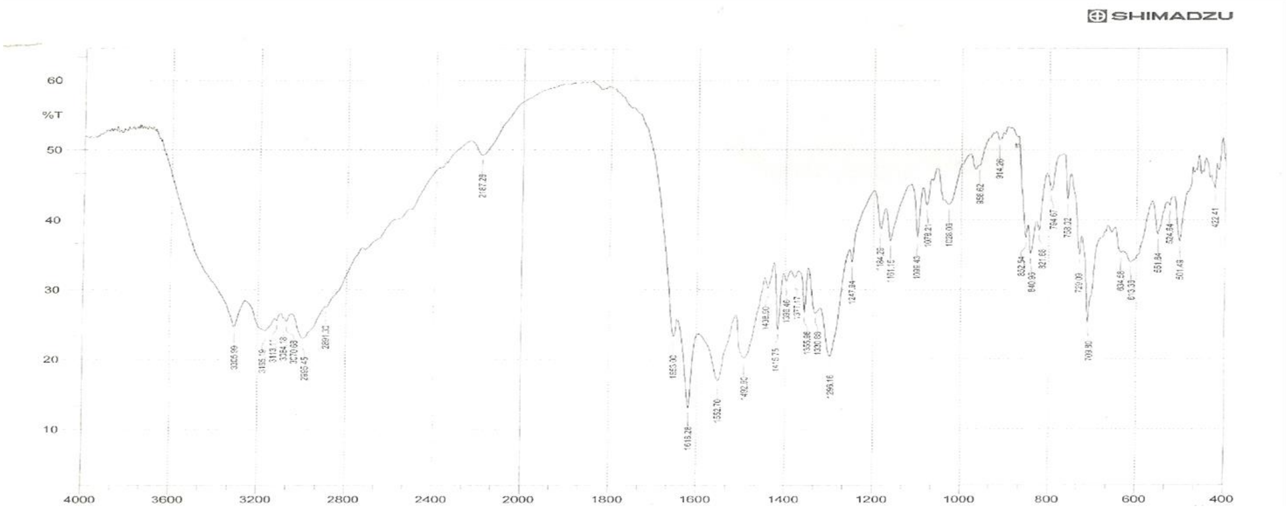


Figure (2): IR spectrum of $[Co(L)_2en]$ complex

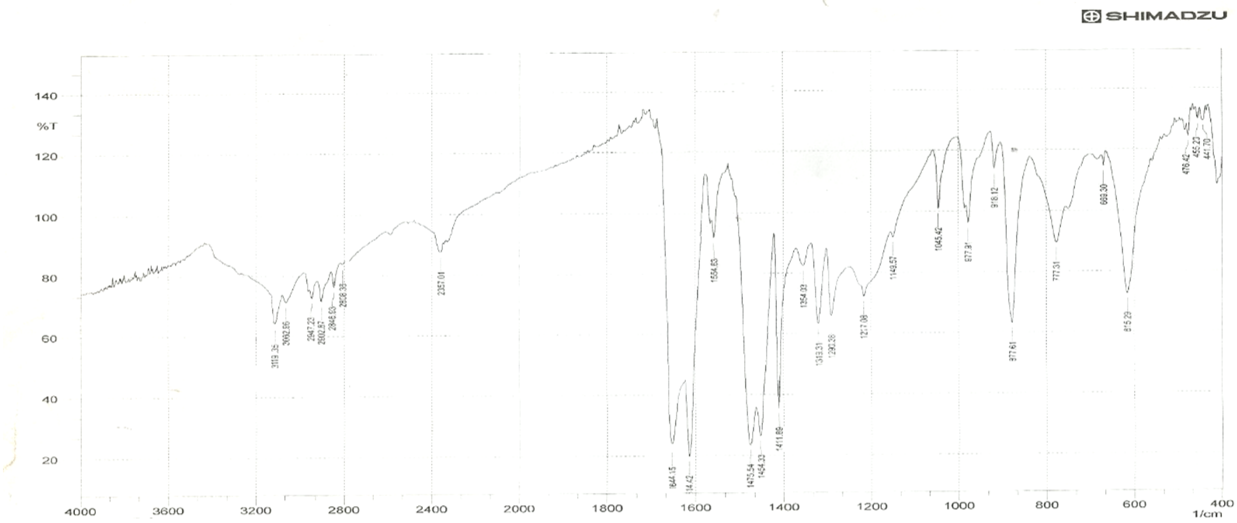


Figure (3): IR spectrum of $[Co(L)_2bipy]$ complex

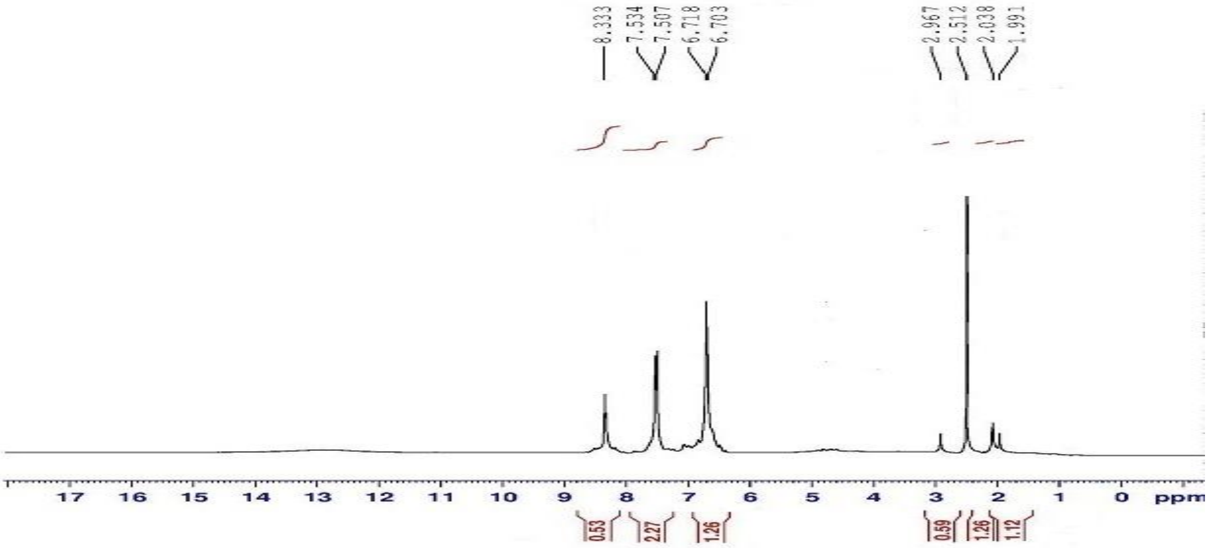


Figure (4): ^{1}H NMR spectrum of L

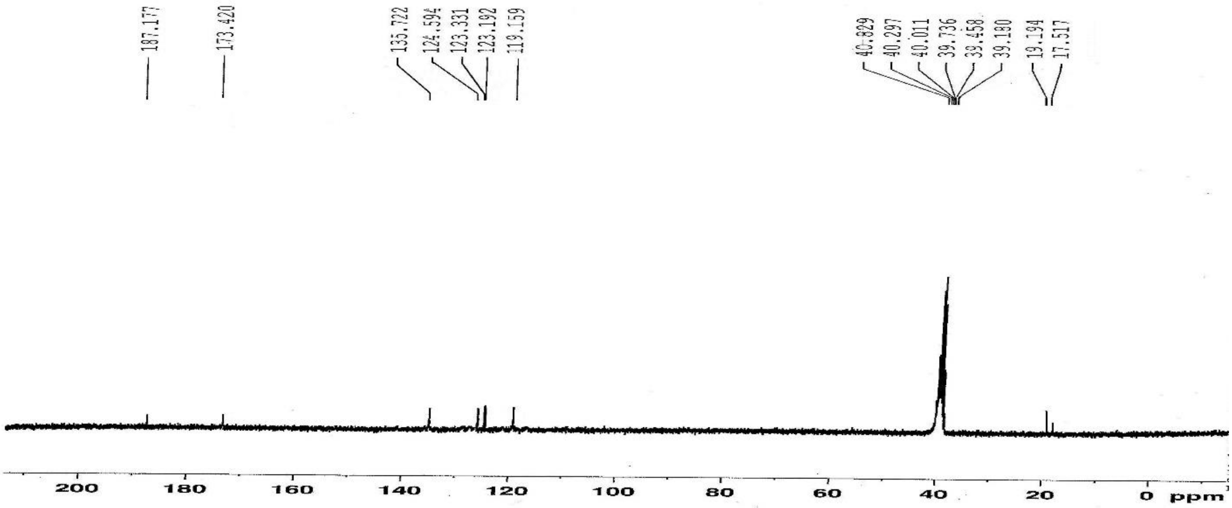


Figure (5): ^{13}C NMR spectrum of L

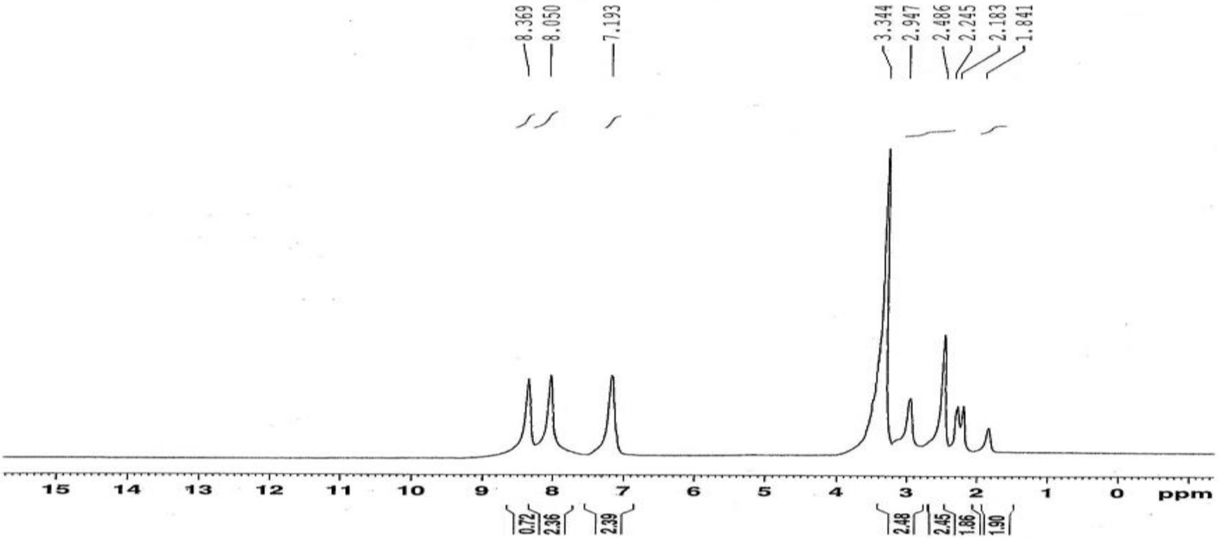


Figure (6): ^{1}H NMR spectrum of [Co(L)$_2$en] complex

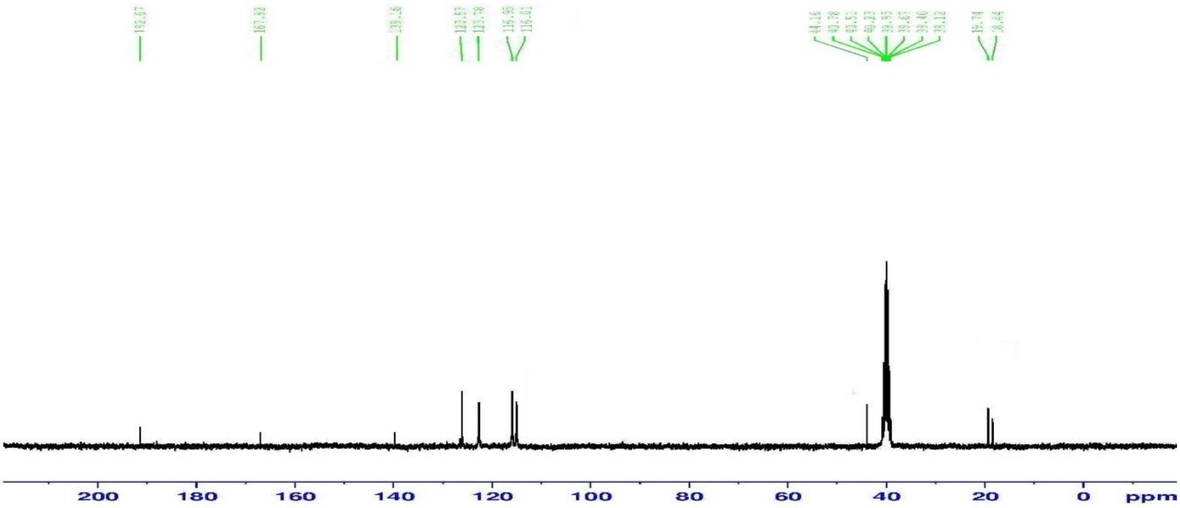
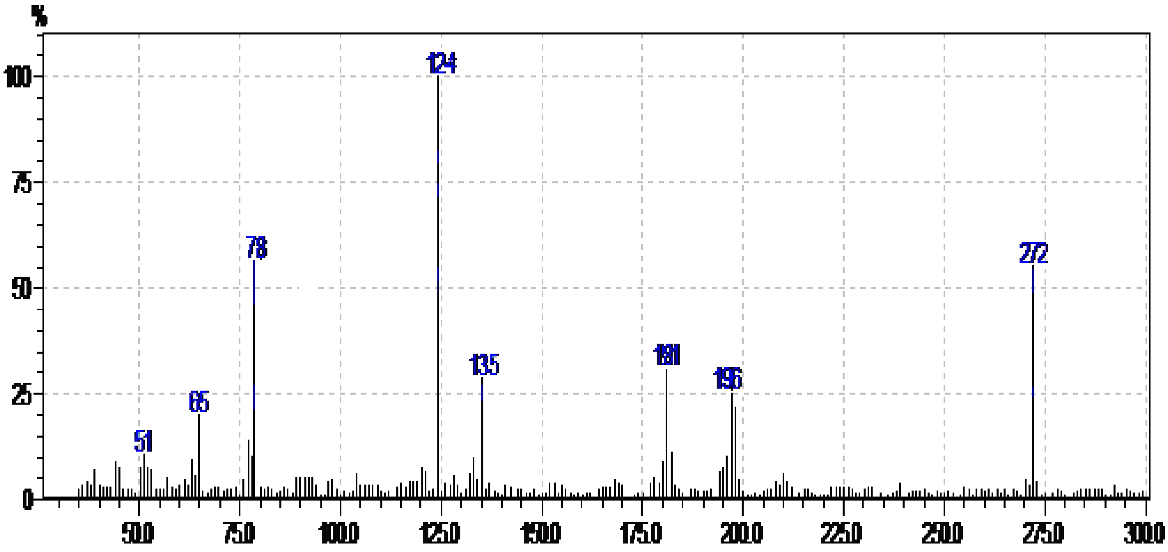
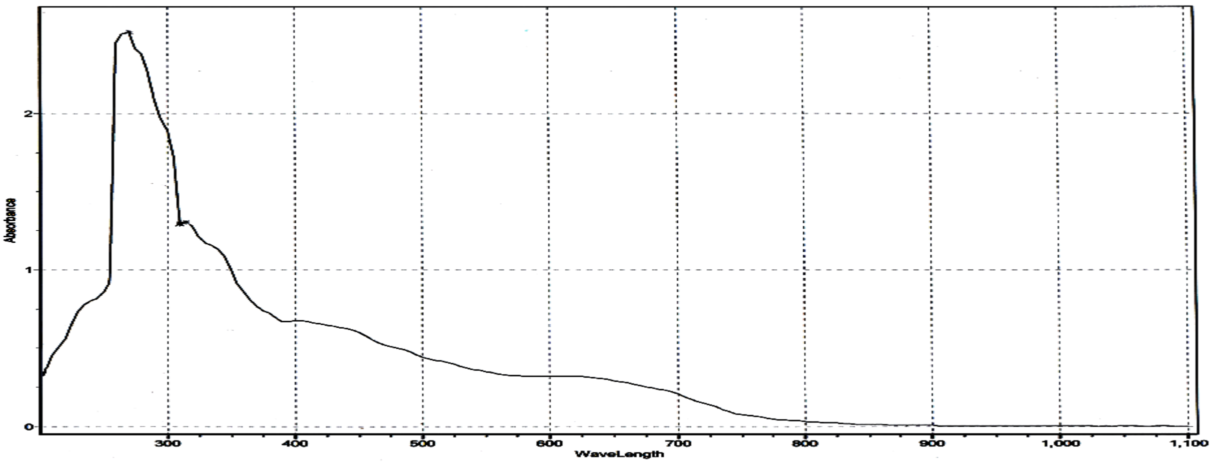


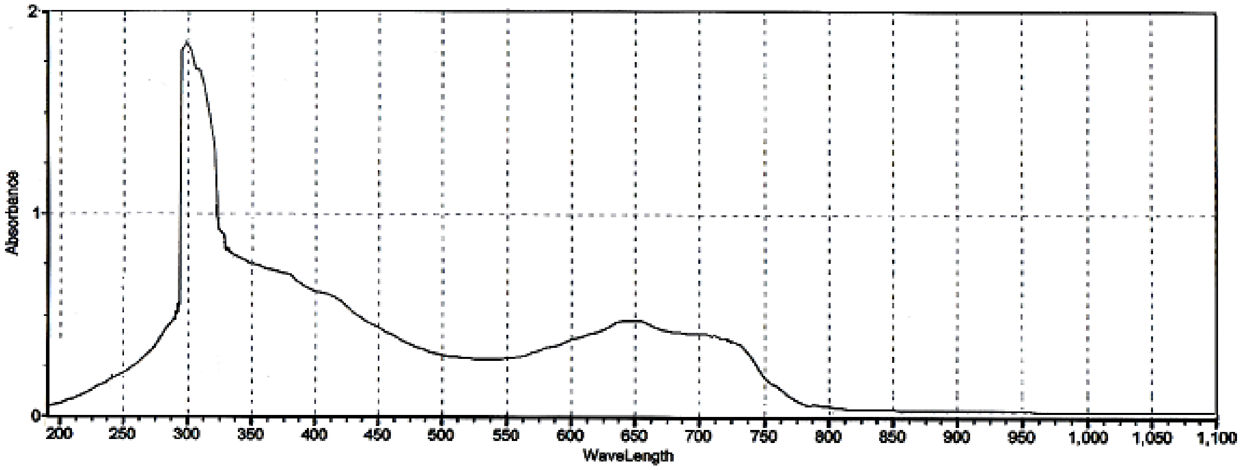
Figure (7): ^{13}C NMR spectrum of [Co(L)$_2$en] complex



Figure(8): Mass spectrum of L



Figure(9): UV-Vis spectrum of [Co(L)$_2$en] complex



Figure(10): UV-Vis spectrum of $[Co(L)_2bipy]$ complex

معقدات الـ Co(II) والـ Cd(II) مع ليكاندات مختلطة من N'-(4-Methylsulfanyl-benzoyl)-hydrazine Carbodithioic acid Methyl Ester ، تحضير وتشخيص فيزيو-كيميائي

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استلم البحث في:13/تشرين الثاني/2016،قبل في:12/كانون الأول/2016

الخلاصة

تضمن البحث تحضير معقدات الكوبلت والكادميوم مع ليكاندات مختلطة من تفاعل N'-(4-methylsulfanyl-benzoyl)-hydrazine carbodithioic acid methyl ester كليكاند واستخدام الـ ethylendiamine (en) 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) كمساعد ليكاند.

تم تحضير الليكاند بعدة خطوات ، حيث تم مفاعلة الـ 4-methylsulfanyl-benzoyl chloride مع الهيدرازين ليعطي 4-methylsulfanyl-benzoic acid hydrazide ، ومن ثم تم مفاعلة الناتج مع CS_2 وهيدروكسيد البوتاسيوم وباستعمال الميثانول ليعطي N'-(4-methylsulfanyl-benzoyl)-hydrazine potassium thiocarbamate والذي تم مفاعلته مع المثيل ايوديد ليعطي الليكاند.

تم استعمال مجموعة من التقنيات الفيزيو-كيميائية لتشخيص الليكاند الجديد والمعقدات لليكاند المختلط ومنها مطيافية IR, UV-Vis, ^{1}H, ^{13}C NMR وطيف الكتلة والتحليل الدقيق للعناصر، الحساسية المغناطيسية، الامتصاص الذري، محتوى الكلور ودرجة الانصهار. بينت التحاليل الفيزيو-كيميائية تكوين المعقدات بالصيغة $[M(L)_2X]$ حيث X= en, bipy and phen وان الكرة التتناسقية حول الفلز هو ثماني السطوح.

الكلمات المفتاحية: -(4- مثيل سولفانيل-بنزويل)-هيدرازين كاربوثنائي ثايويك اسد مثيل استر، مشتقات ثنائي ثايوكاربامات، معقدات ليكاندات مختلطة