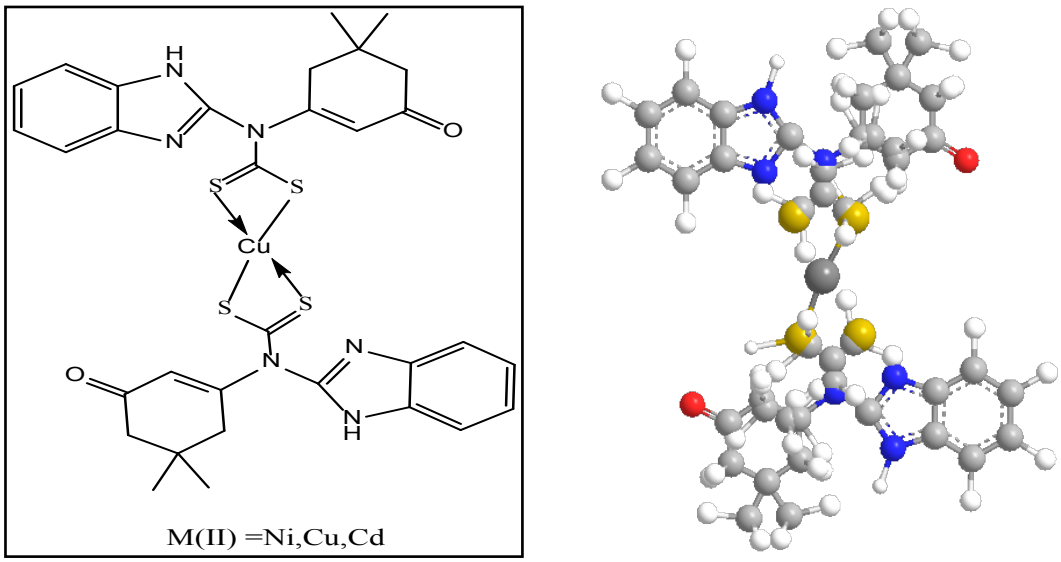
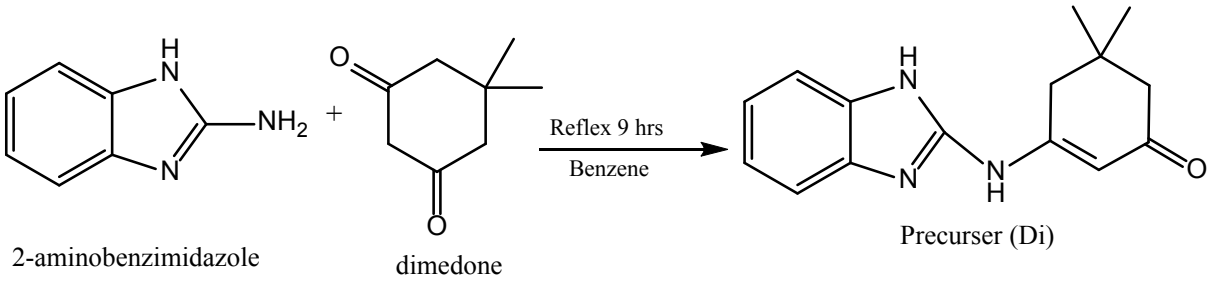
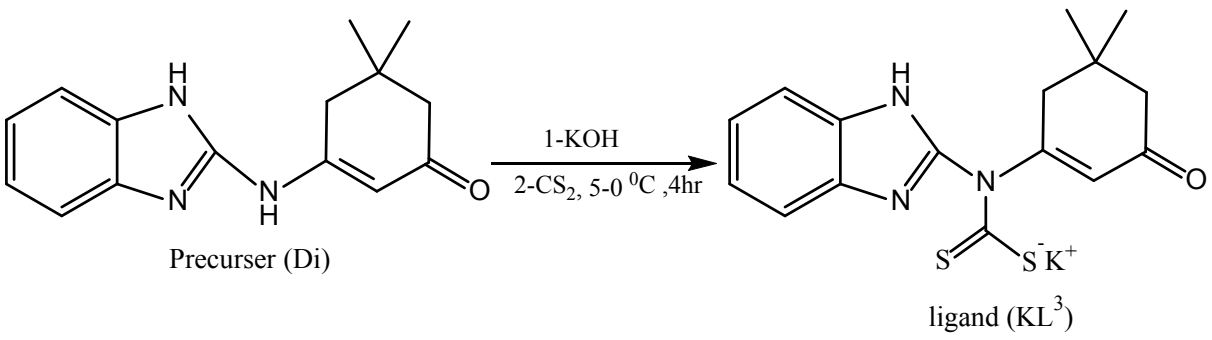


Fig. (13): Suggested structure of tetrahedral geometry [$M(L_2)$]



Scheme (1): Synthesis of precursor(Di)



Scheme (2): Synthesis of Ligand(KL^3)

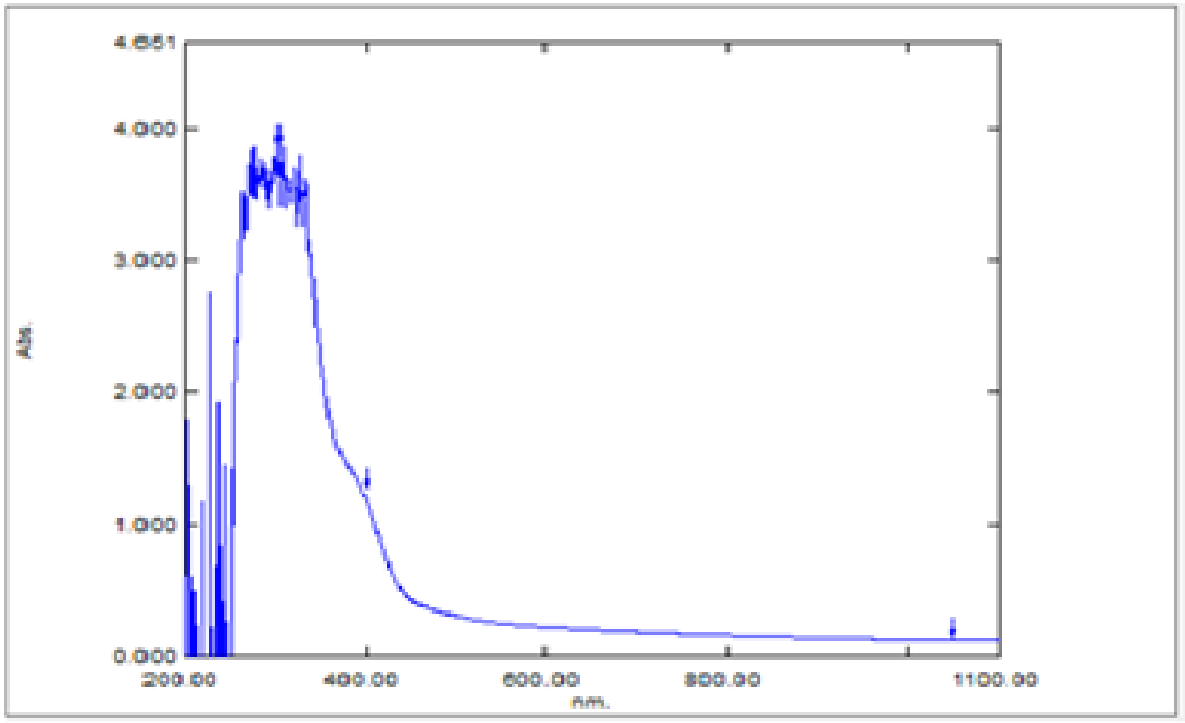


Fig.(11): Electronic spectrum of $[Cu(L^3)_2]$ complex

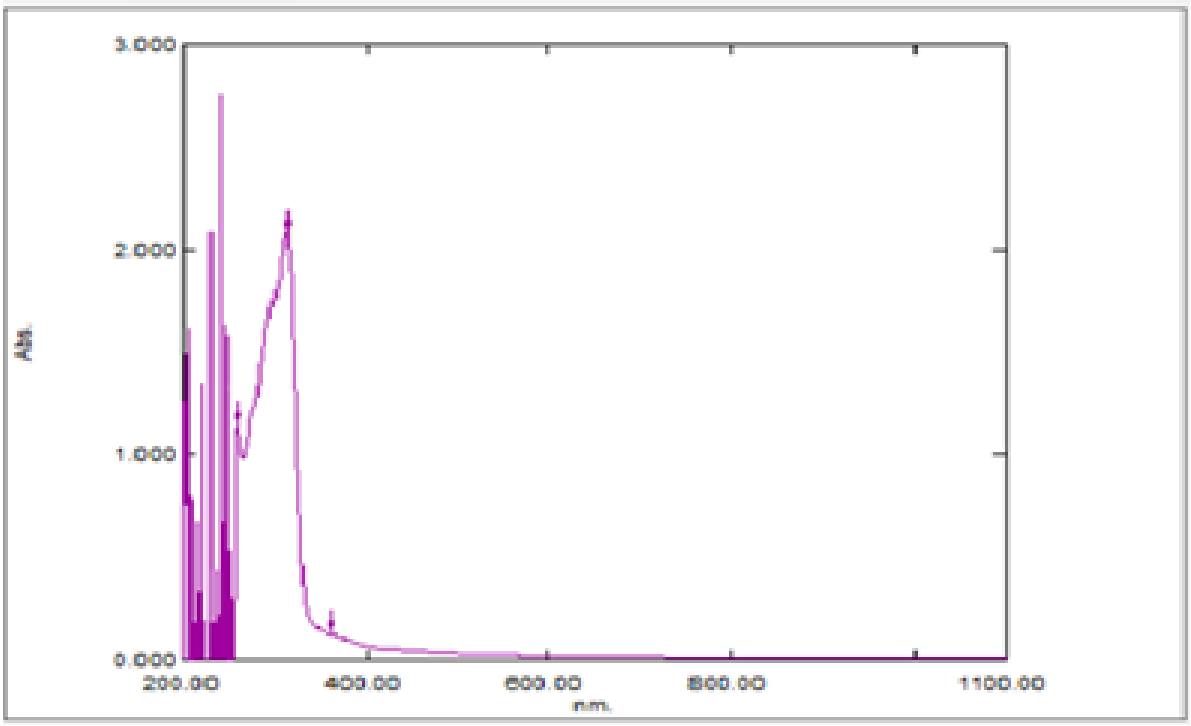


Fig.(12): Electronic spectrum of $[Cd(L^3)_2]$ complex

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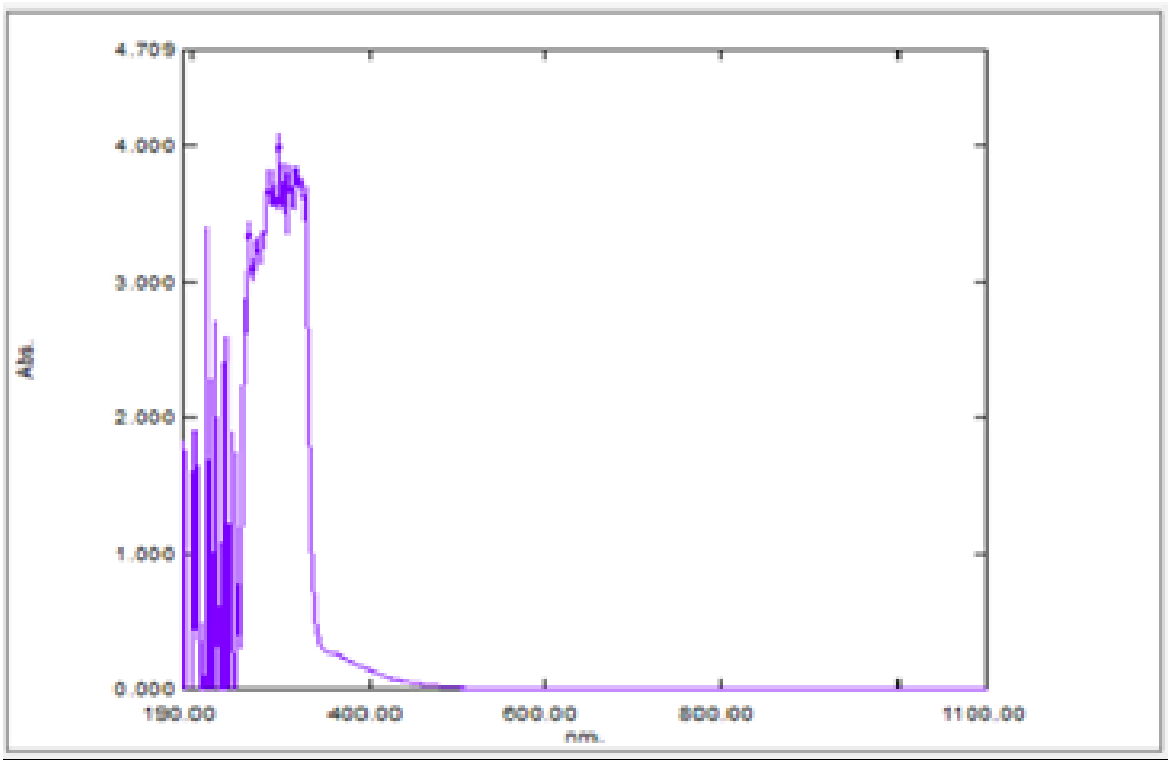

Fig.(9): Electronic spectrum of ligand KL^3

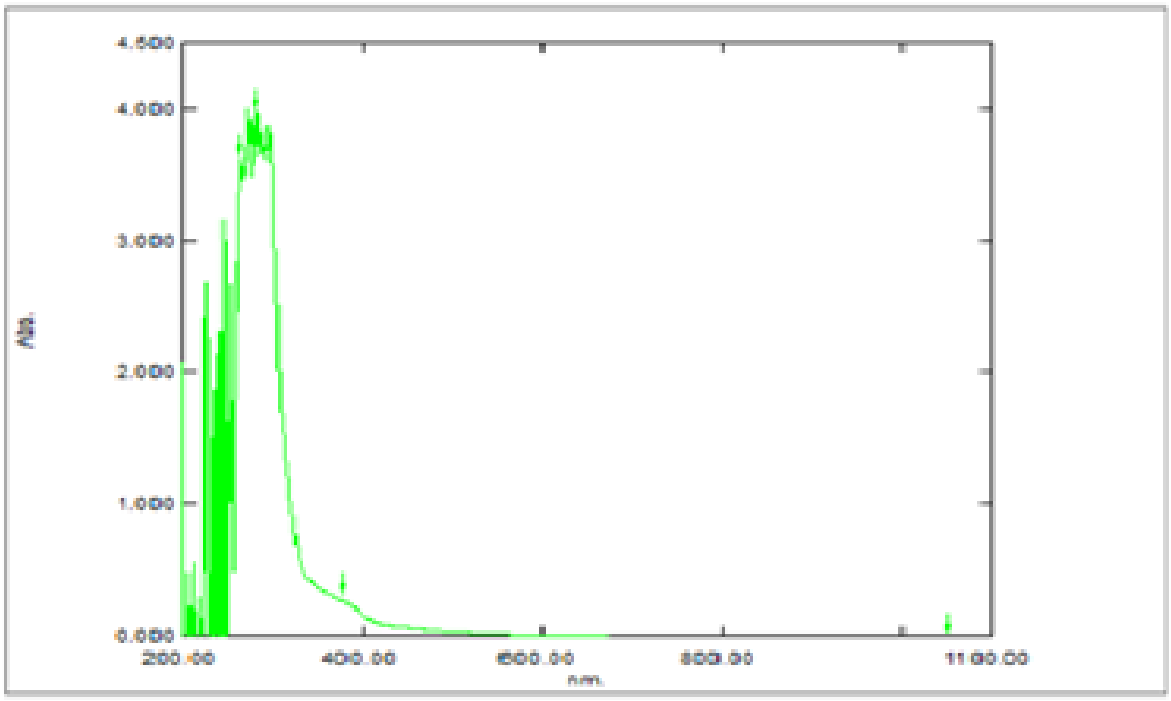

Fig.(10): Electronic spectrum of $[Ni(L^3)_2]$ complex

Fig.(7): FTIR Spectrum of $[Cu(L^3)_2]$ complex

Fig. (8): FTIR Spectrum of $[Cd(L^3)_2]$ complex

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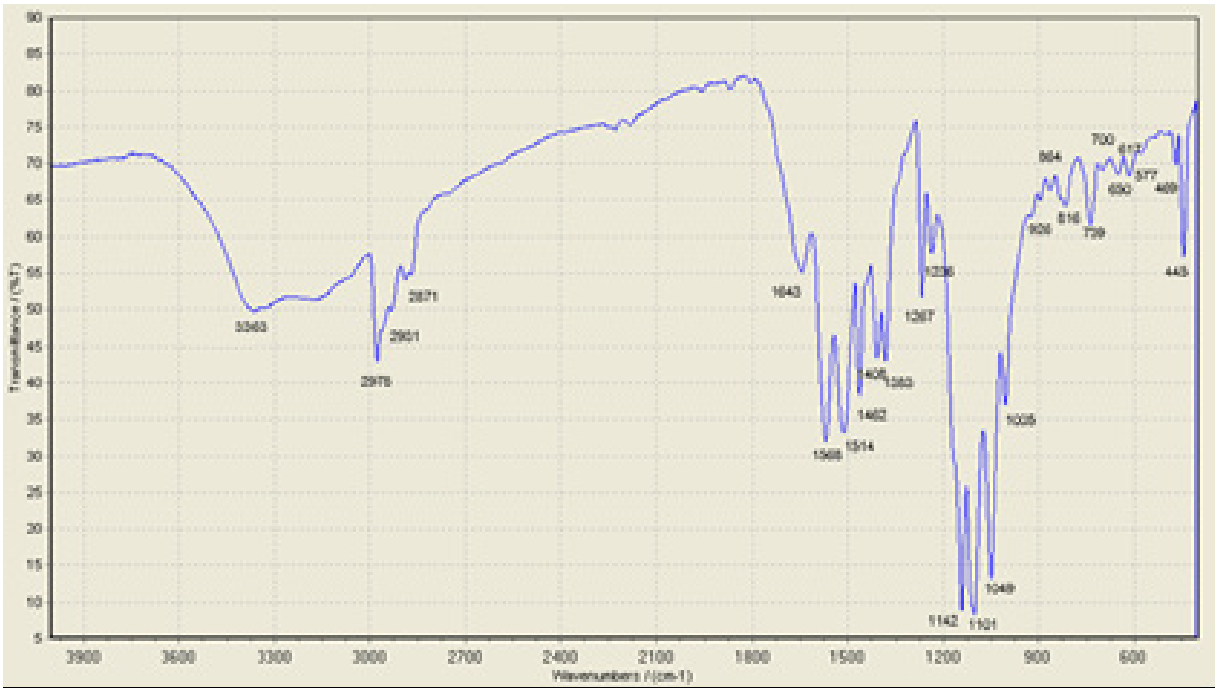

Fig. (5): FTIR Spectrum of ligand KL^3

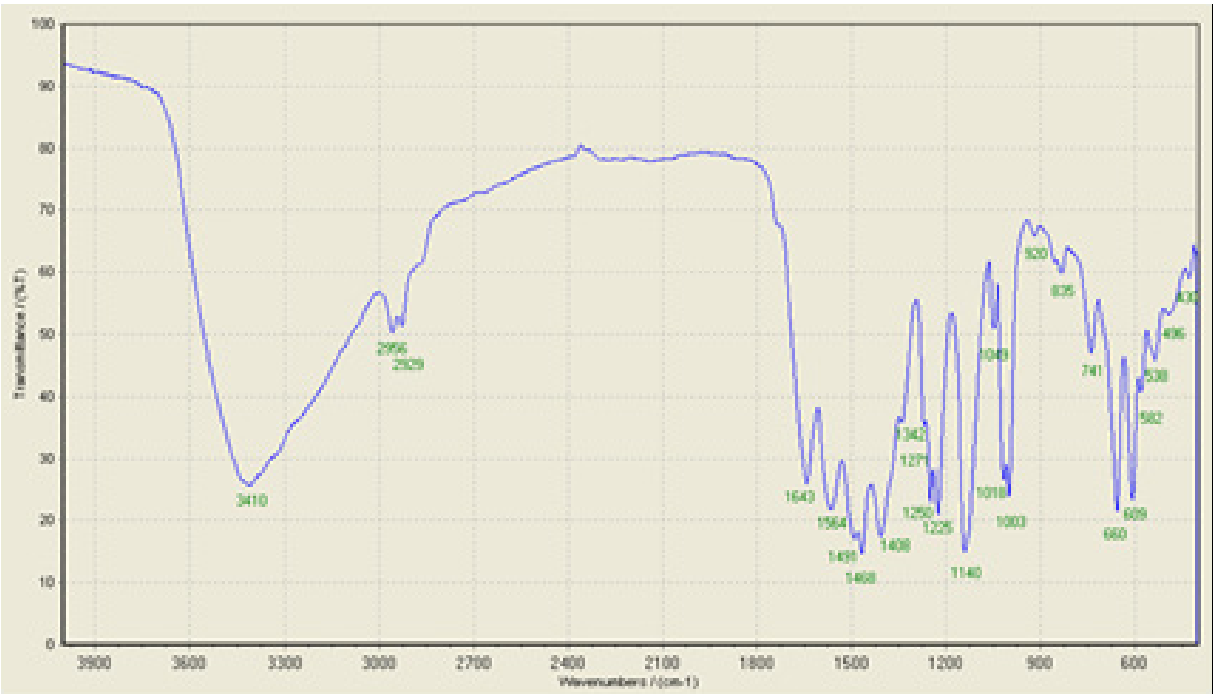

Fig. (6): FTIR Spectrum of $[Ni(L^3)_2]$ complex

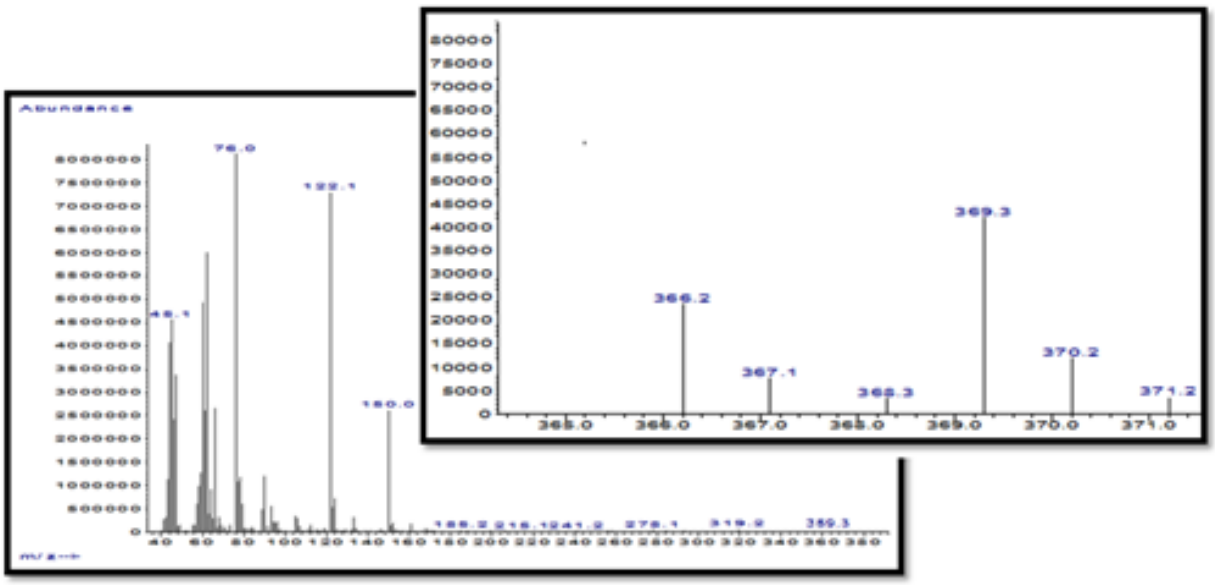

Fig. (3): Mass spectrum of ligand KL^3

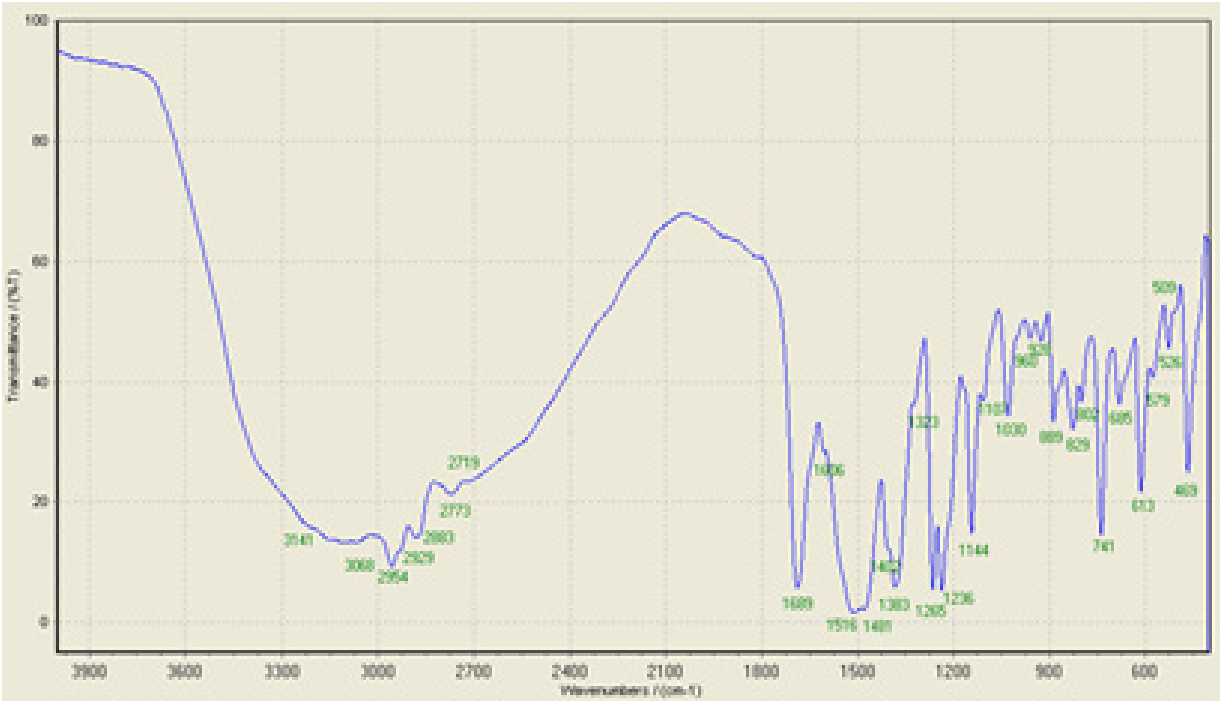

Fig.(4): FTIR spectrum of of precursor (Di).

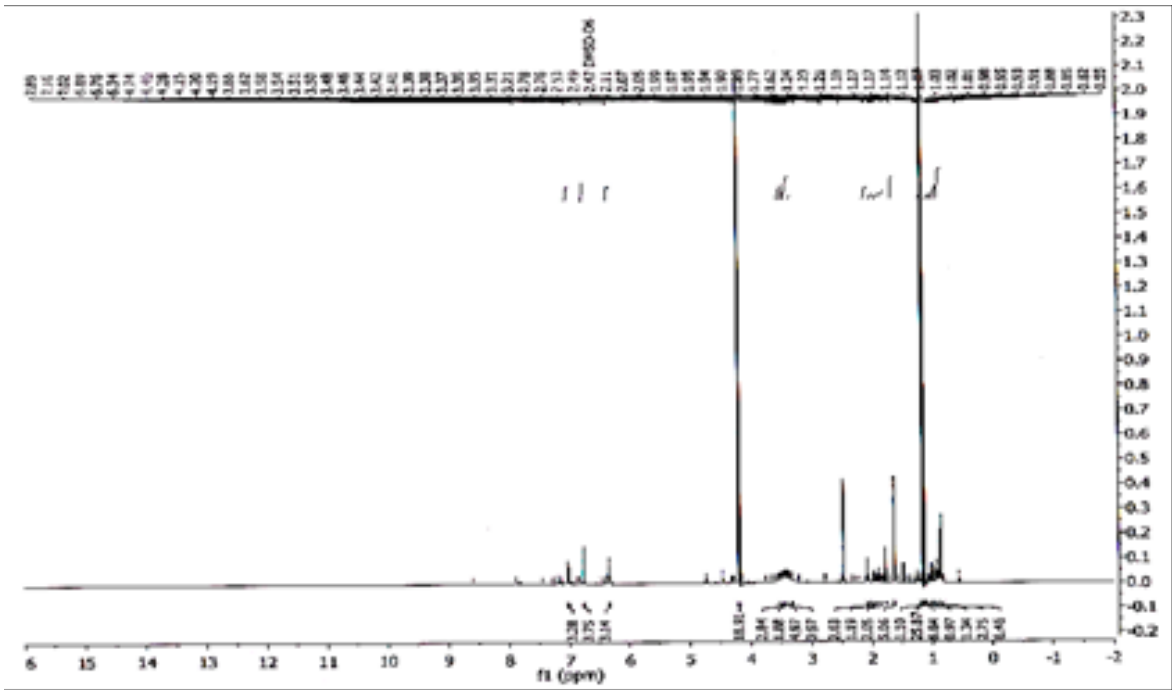

Fig.(1): ^{1} H NMR spectrum of ligand KL^{3} in DMSO

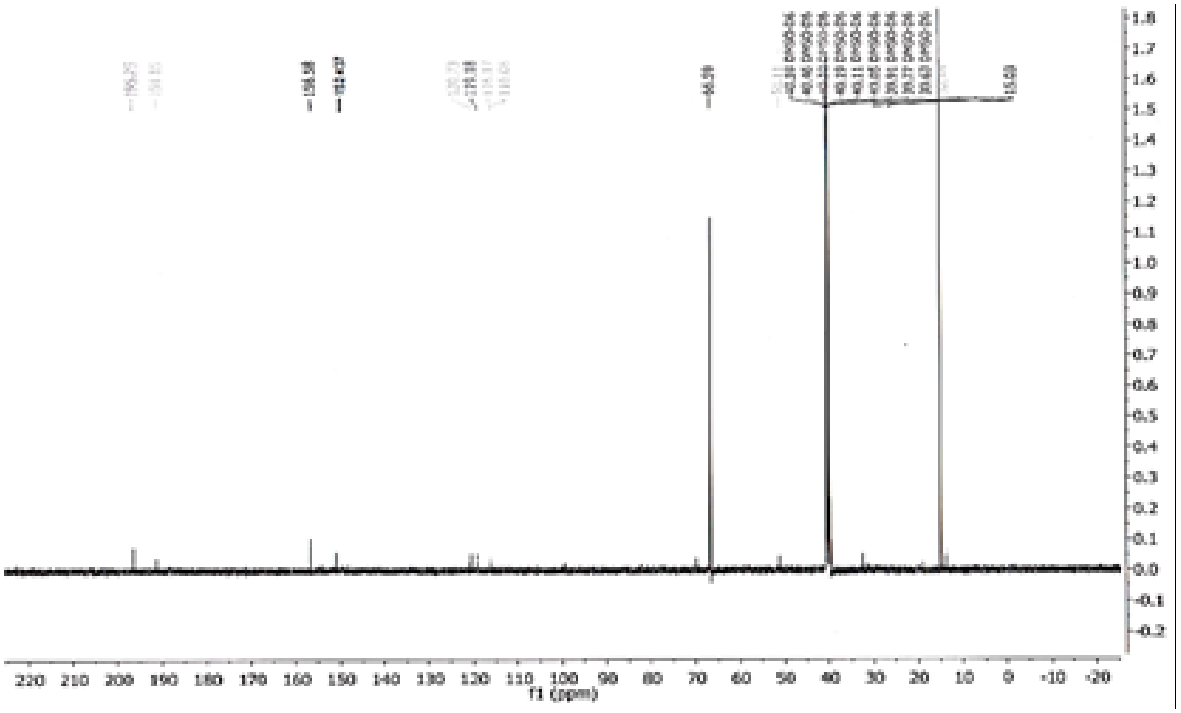

Fig. (2): ^{13} C NMR spectrum of ligand KL^{3} in DMSO

Table (3): UV-Vis spectral data of KL^3 complexes in DMSO solutions.

Com.	Wave length λ_{nm}	Wave number(cm^{-1})	ε_{max} ($moler^{-1}.cm^{-1}$)	Assignment	Suggested geometry
KL^3	264 299	37878 33444	3276 3917	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	–
$[Ni(L^3)_2]$	254 279 387 1049	39370 35842 25839 9532	3612 3984 295 185	Intra Ligand Intra Ligand C.T $^3T_1 \rightarrow {}^3T_{1(P)}$	Tetrahedral
$[Cu(L^3)_2]$	303 400 1049	33003 25000 9532	3864 1200 123	Intra Ligand C.T $^2E \rightarrow {}^2T_2$	Tetrahedral
$[Cd(L^3)_2]$	258 311 365	38759 32154 27397	1154 2089 150	Intra Ligand Intra Ligand C.T	Tetrahedral

Table(4): Magnetic moment of complexes.

Com.	μ_{eff}(B.M.)	Suggested Structure
$[Ni(L^3)_2]$	3.62	Tetrahedral
$[Cu(L^3)_2]$	2.06	Tetrahedral
$[Cd(L^3)_2]$	–	Tetrahedral

Table (2):
FTIR spectral data of complexes (cm^{-1})

Com.	ν. (N–H)	νalph. (C–H)	ν (C=O)	ν. (N–H)	νvin. (C=C)	ν (N–CS_2).	ν (C–N)	ν (C–S)sy. ν (C–S)asy.	ν (M–S)
KL_3	3363(m)	2998(m)–2875(m)	1658(w)	1643(w)	1568(w)	1462(w)	1142(s)	1049(m)–1005(w)	–
$[Ni(L^3)_2]$	3410(m)	2956(w)	1666(w)	1643(w)	1564(w)	1491(w)	1140(s)	1018(s)–1003(w)	364(w) 331(w)
$[Cu(L^3)_2]$	3435(w)	2976(w)	1738(w)	1662(w)	1562(w)	1496(w)	1194(w)	1034(s)–1007(m)	343(w) 322(w)
$[Cd(L^3)_2]$	3359(m)	2954(w)	1716(w)	1639(w)	1564(w)	1464(s)	1142(s)	1043(m)–1005(s)	318(w) 293(w)

Table (1):

Physical data and analysis of ligand and its complexes.

.Com	Empirical formula	M.W g / mol	٪ Yield	m.p. °C	colour	٪ (. Microanalysis (calc				
						٪M	C	H	N	S
KL^3	$C_{16}H_{16}KN_3OS_3$	369.54	71.18		Yellow	-	51.90 (52.00)	4.32 (4.36)	11.51 (11.37)	17.38 (17.35)
$[Ni(L^3)_2]$	$C_{32}H_{32}N_6O_2S_4Ni$	721.77	73.98	*250	green	8.00 (8.13)	50.89 (51.07)	4.11 (4.43)	11.90 (11.63)	17.38 (17.73)
$[Cu(L^3)_2]$	$C_{32}H_{32}N_6O_2S_4Cu$	726.62	73.54	158-160	Green yellow	8.33 (8.74)	52.20 (52.84)	4.25 (4.40)	11.81 (11.56)	17.26 (17.61)
$[Cd(L^3)_2]$	$C_{32}H_{32}N_6O_2S_4Cd$	775.49	79.00	180-182	Light yellow	14.11 (14.49)	49.17 (49.51)	3.89 (4.12)	11.07 (10.83)	16.31 (16.50)

*** decomposition**

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to the intra ligand transition. The Ni(II) complex shows two absorption bands at (387, 1049) nm which was assigned to C.T and $^3T_1(F) \rightarrow {}^3T_1(P)$ transition in tetrahedral geometry [20]. The Cu(II) complex gives an absorption at (1049 nm)which corresponds to ($^2E \rightarrow {}^2T_2$) transition in tetrahedral geometry [21]. Finally the Cd(II) complex shows an absorption at 365nm which assigned to charge transfer [22,23]. **Fig.(10- 12)**, **Table(3)**.

Magnetic Susceptibility

The experimentally determined value of magnetic moment and the suggested structure [24] for all these complexes are listed in **Table (4)**.

Conclusion

This present work account the synthesis and identification of new DTCs ligand (KL3) and its complexes with Ni(II) , Cu(II) and Cd(II) metal ions. These compounds were described by accessible techniques. In synopsis, we have shown that all of these complexes have the tetrahedral suggested structure. The structural formulas of these complexes is suggested in **Fig (13)**.

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at m\z = 122.1 (85%), 76.0 (100%) corresponding to [$C_8H_{10}O$+], [CS_2+] , respectively.[16]

Preparation of metal complexes

Ethanol solution $NiCl_2$. $6H_2O$,$CuCl_2$. $2H_2O$ and $CdCl_2$. $2H_2O$ (0.3mmol) was added to solution of (0.1g,0.27 mmol) (KL^3) in (10ml) ethanol. The mixture was reflexed for 3 hrs with constant stirring, the precipitate was collected by filtration, washed with (1:1) mixture of water: ethanol, then with diethylether and dried at room temperature precipitate.

Results and Discussion

The analytical data in Table(1) indicates that KL^3 and all complexes were found to be stable in air and insoluble in water but soluble in dimethyl form amide (DMF) and dimethyl sulfoxid (DMSO). The notice molar conductance value of the complexes in DMSO were non electrolytic nature. The mole ratio method was used to determine the ratio of metal and ligand. The study shows the ligand coordinated to metal in 1:2 ratio. Physical data and analysis of ligand and its complexes are listed in **Table(1)**.

Infrared spectra

The FT-IR bands of the spectra of ligand and their complexes are listed in **Table (2)**, shown in **Fig. (5- 8)**. The DTCs complexes three main areas of FT-IR. First, the 1550- 1450 cm^{-1} zone. This was mostly associated with the stretching vibrations of C-N group of N-CSS- moiety [17]. The second area of vCS_2 was observed in the 1003-1051 cm^{-1} [18] it was shifting in simile to the corresponding band in the ligand signalize that the dithiocarbamate ligand coordinates with the metal through S atoms. FT-IR spectra offer a new band at 322- 366 cm^{-1} which is the proof for the coordination of metal sulfur v M-S [19].

Electronic spectra

The solution electronic spectra of the ligand and the complexes were booked in DMSO as solvent in the UV-Visible region. The electronic transition datum was given in the **Table (3)**. Bands at 264 nm 299nm related to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition of N-C-S set and electronic transition involving Ion pair of electrons find on the S atom, **Fig.(9)**. On complexation these bands have some change in wavelength. In the complexes, bands in range of (233- 400)nm are attributed

FTIR-600) Fourier Transform Infrared Spectrophotometer (4000- 400) cm^{-1} with samples as discs. Elemental analysis (C. H. N) was (EURO3000 Singl)), Conductivities were measured for 10^{-3} M of complexes in DMSO at 25oC using (Digitsl conductivity meter P, 9526), Magnetic moments were evaluate with a magnetic susceptibility (Xg) were carried out at 20oC by Faraday. Metal contents complexes were determined by atomic absorption (A.A) technique using a Atomic Absorption spectrophotometer- 680G.

Synthesis of 3- ((1H- benzo[d] imidazol -2- yl) amino) -5,5- dimethyl cyclohex -2- en -1- one (Di)[13]

Dimedone (7.14 mmol) was grinded together with 2-aminobenzimidazole (7.11mmol), then adding (25ml) of benzene and continuous stirring. To the solution a few drops of glacial acetic acid was added, then resulting was refluxed for (9) hrs, the reaction mixture was allowed to cool temperature, a pale yellow product was isolated by filtration and washed several times with benzene and dried to give a pale yellow precipitate, **Scheme (1)** . Yield 1.445(79.3%), M. P. (9092-oC). Anal.Cal for C15H17N3O (255.32): C,70.56, H, 6.71, N, 16.46%, Found: C,70.828, H, 6.558, N, 16.97%.

Preparation of potassium [(1H - benzo [d]imidazol -2- yl) (5,5 - dimethyl -3- oxocyclohex -1- en -1- yl) carbamodithioate] (KL^3)

To a solution of (Di) (0.10 g, 0.30mmol) in 10 mL of ethanol, was added KOH (0.07 g, 1.25 mmol) dissolved in ethanol (2mL). The mixture was allowed to stir in an ice bath, and then a solution of carbon disulfide (0.07 g, 0.92mmol) was added dropwise with stirring. The mixture was allowed to stir at 0 °C for 2 h, during which the formation of the potassium dithiocarbamate salt was obtained as a yellow solid, Scheme (2), m.p= (110-112) ºC. Yield: (0.144)g, (71.18%),

^{1}H-NMR data (ppm) **Fig.(1)**: proton N-H group 1H (6.34)s, 4H (C_{12}, C_{13}) (7.89 - 6.76)s, 1H (C_5) (4.74)s, 4H (C_3,C_7) (4.20) m, 6H (C_1) (1.01)s. [14].

^{13}C-NMR data (ppm) **Fig.(2):** C_1 (15.03), C_2 (32,44) ,C_3,7 (56.54), C_5 (66.59) ,C_6 (156,58) ,C_8 (191,15), C_9 (152.4), C_{10} (120.73) ,C_{11} (116.17) ,C_{12} (119.18), C_4 (195.25). [15]

The mass spectrum **Fig.(3)** of the ligand KL^3 showed the peaks at m\z = 370.2 (3%) corresponding to parent ion. The other two peaks detected

Introduction

Dithiocarbamats (DTCs) are multipurpose ligands with a wide range of chemistry and plentiful applications in different areas such as medicine, materials science and in industrial applications in the vulcanization of rubber and in grasp [13-]. Furthermore DTCs derivatives are applied as precursors for nanoparticles while in the preparation of pesticides [4]. DTCs are often applied for the synthesis of transition metal complexes [5]. Their ability to connect transition metals, including lanthanide, actinide, and representative elements make them helpful ligands in both inorganic and bioinorganic chemistry. This is based on the turnout of the anionic CS_2^- moiety, that have a framework of binding modes; monodentate, bidentate or bridging, onto complexation [6-8]. Some dithiocarbamate complex recycled to strip NO in which the absorbed NO is reduced to nitrogen. In different direction, the most contaminating industries such as wastewater emptying by textile industries are known to contain large facts of toxic dyes, which can be extracted by DTCs modified starch materials[9,10]. DTCs have shown a set of requests in analytical chemistry. They have the volume to form a stable compound with transition metals and delegate elements. They have been employment in solvent extraction, spectrophotometric willpower of trace elements and eclectic chromatographic determination of metal ions[11,12]. In this study, we sitting the synthesis and characterization of Ni ,Cu and Cd complexes of ligand potassium [(1H-benzo [d]imidazol -2- yl) (5,5-dimethyl -3- oxocyclohex -1-en-1-yl) carbamo dithioate].

Experimental

Materials and Methods

All reagents and solvents were of analytical grade and used supplied from (Fluka , BDH or Merck) chemical firms.

Instrumentals

^{1}H and ^{13}C–NMR spectra were acquired in DMSO using Brucker, Model: Ultra 400 MHz, Switzerland for tetramethylsilane (TMS). Mass spectra were acquired by 5975CVL-MSD, UV-Vis spectra were recorded on (Shimadzu UV-1800) Ultra Violet –Visible spectrophotometer, FT-IR-spectra were taken on a (SIDCO,

doi.org/10.52866/esj.2020.05.16.10

Journal of Education and Scientific Studies Chemistry Science
JESCS Vol. 16, No. 5, August 2020, ISSN 2413 - 4759

Synthesis, Characterization of Ni(II) , Cu(II) and Cd(II) Complexes of new ligand potassium [(1H-benzo[d] imidazol-2-yl)(5,5-dimethyl-3-oxocyclohex-1-en-1-yl) carbamo dithioate]

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Abstract :

This study includes preparation and identification of new ligand potassium [(1H-benzo[d]imidazol-2-yl)(5,5-dimethyl-3-oxocyclohex-1-en-1-yl)carbamodithioate] and its metal (II) complexes were synthesized and characterized by spectral (UV-Vis, FT-IR) and $^{1}H,^{13}C$-NMR, Mass spectra, elemental micro analysis C.H.N.S., molar conductivity, magnetic susceptibility, atomic absorption ,melting points. Three new complexes have been prepared of some transition metals Ni(II) , Cu(II) and Cd(II).

Key words: Dithocarbamate(DTCs), dimedone, ligand complexes .

تحضير وتشخيص معقدات النيكل ,النحاس والكادميوم الثنائية لملح البوتاسيوم الليكاند الجديد [(1H- بنزو [د] إيميدازول -2-يل) (5،5-ثنائي ميثيل-3-أوكسي سيكلوهكس-1-ين-1-يل) كاربامودیثيوات]

احمد ثابت نعمان , ضحى فاروق حسين , عوف عبد الرحمن احمد
قسم الكيمياء, كلية التربية للعلوم الصرفة /ابن الهيثم ,جامعة بغداد, بغداد ,العراق

خلاصة :

تتضمن هذه الدراسة تحضير وتشخيص ملح البوتاسيوم لليكاند الجديد [(1H- بنزو [د] إيميدازول – 2 – يل) (5،5 –ثنائي ميثيل– 3 – أوكسي سيكلوهكس– 1 – ين – 1 – يل) كاربامودیثيوات] ، كما تم تحضير و تشخيص المعقدات الفلزية الثنائية بالطرق الطيفية المختلفة منها الاشعة المرئية – فوق البنفسجية والاشعة تحت الحمراء وطيف الرنين النووي المغناطيسي البروتوني والكاربوني وطيف الكتلة والتحليل الدقيق للعناصر والتوصيلية المولارية والحساسية المغناطيسية والامتصاص الذري ودرجات الانصهار. المعقدات الثلاثة الجديدة حضرت لبعض العناصر الانتقالية الثنائية (النيكل، النحاس والكادميوم).

الكلمات المفتاحية: ثنائي ثايوكارباميت ، دايميدون ، معقدات الليكاند .