تحضير وتشخيص بعض المعقدات الفلزية الجديدة لليكاند

(5-*C*-dimethyl malonyl-pentulose-γ-lactone-2,3-enedibenzoate)

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الخلاصة

تم تحضير بعض المعقدات الفلزية الجديدة من الليكاند

(5-*C*-dimethyl malonyl-pentulose-γ-lactone-2,3-enedibenzoate) (L)

مع ايونات (الكالسيوم، الكوبلت، النيكل، النحاس، الخارصين، الكادميوم والزئبق) الثنائية التكافؤ وشخصت بالطرائق الطيفية المتوافرة ومنها طيف الرنين النووي المغناطيسي (^{1}H and ^{13}CNMR) وطيف الاشعة تحت الحمراء وطيف الاشعة فوق البنفسجية والمرئية فضلا" عن تعيين نسبة الفلز في المعقدات بوساطة طيف الامتصاص الذري وقياس التوصيلية المولارية لمحاليل المعقدات في مذيب ثنائي مثيل سلفوكسايد (DMSO) وقياس العزم المغناطيسي المؤثر في المعقدات الصلبة. ومن نتائج هذه الدراسات التشخيصية امكن اعطاء الصيغة العامة لهذه المعقدات وكماياتي [M(L)Cl$_2$]، إذ M = الايون الفلزي (Ca^{+2}، Co^{+2}، Ni^{+2}، Cu^{+2}، Zn^{+2}، Cd^{+2} و Hg^{+2}) ،

L = (5-*C*-dimethyl malonyl-pentulose-γ-lactone-2,3-enedibenzoate).

الكلمات المفتاحية: ثنائي مثيل المالونيل، لاكتون، بنزويت، معقدات.

Synthesis and Characterization of Some New Metal Complexes of (5-*C*-Dimethyl Malonyl-Pentulose-γ-Lactone-2,3-Enedibenzoate)

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Abstract

The synthesis of complexes for (Ca^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2} and Hg^{+2}) with new ligand (5-*C*-dimethyl malonyl-pentulose-γ-lactone-2,3-enedibenzoate) (L) have been successfully prepared and characterized by (^1H and ^{13}CNMR, FTIR, (U.V-Vis) spectroscopy, Atomic absorption spectrophotometer (A.A.s), Molar conductivity measurements and Magnetic moment measurements, and the following general formula has been given for the prepared complexes $[M(L)Cl_2]$ where M = (Ca^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2}),

L = (5-*C*-dimethyl malonyl-pentulose-γ-lactone-2,3-enedibenzoate).

Key words: dimethyl malonyl, lactone, benzoate, complexes.

Introduction

Numbers of transition metals with malonic esters have been isolated and characterized and tested for their antifungal, antibacterial and anti-inflammatory activities[1-4]. Nasman[5] reported the synthesis a novel series of 15-membered diaza-dithiamacrocyclic complexes $[ML_1Cl_2]$ and $[ML_2Cl_2]$ (M^{+2} = Fe, Co, Ni, Cu and Zn) by the template condensation reaction of *o*-thiosalicylic acid with aliphatic or aromatic diamines and diethyl malonate in the presence of transition metals. Also Pothiraja and co-workers[6] reported the synthesis new Hf and Zr malonate from reaction of metal amides with different malonate ligands as dimethyl malonate, diethyl malonate, di-tert-butyl malonate and bis(trimethylsilyl) malonate. We have investigated in this paper, the preparation and properties of some new metal ion complexes with (5-*C*-dimethyl malonyl-pentulose-γ-lactone-2,3-enedibenzoate) (L).

Experimental

Materials and Measurements

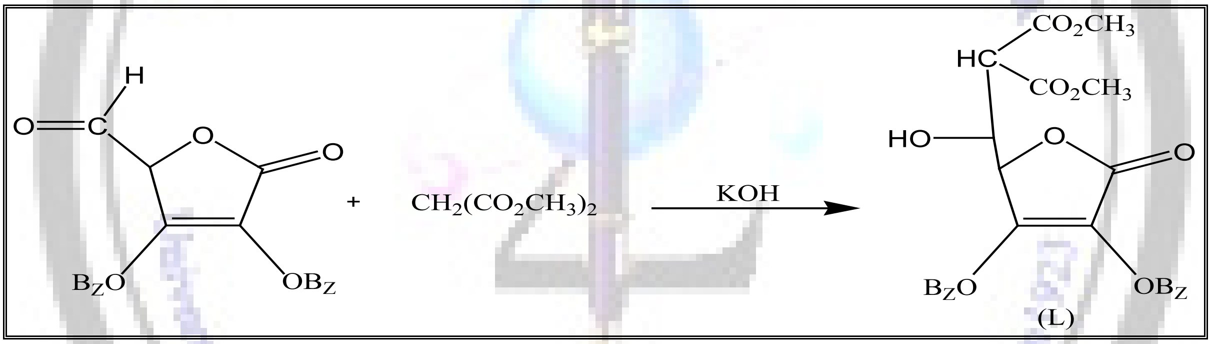
Metal salts ($CaCl_2.6H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2.H_2O$ and $HgCl_2$) were obtained from Fluka, Merck in high purity, Dimethyl malonate, KOH (BDH).

(^1H and ^{13}CNMR) spectra were recorded using Ultra Shield 300 MHz, Bruker, Switzerland, at University of Al al-Bayt, Jordan. IR spectra (in KBr discs) were recorded on Shimadzu FT infrared spectrophotometer. The (U.V-Vis) were recorded using (Shimadzu U.V- Vis 160A), (U.V-Vis) spectrophotometer in dimethyl sulphoxide solution (10^{-3} M). Metal contents of the complexes were determined by Atomic absorption technique by using Shimadzu (AA680G), Atomic absorption spectrophotometer. The magnetic moments (μ_{eff} B.M) were calculated on Faraday method by using (Balance Magnetic Susceptibility Model MSBMKT). Melting points were determined by using (Stuart-melting point apparatus). Conductivity measurements were carried out using Philips PW.Digital. The Thin Layer Chromatography was performed on aluminum plates coated with layer of silica gel, supplied by Merck.

Synthesis of ligand, (5-*C*-dimethyl malonyl-pentulose-γ-lactone-2,3-enedibenzoate) (L)

The mixture of potassium hydroxide (1.9g, 34mmol) and dimethyl malonate (3.9ml, 34mmol) was stirred for 30 minutes, a solution of (pentulosono-γ-lactone-2,3-enedibenzoate)[7] (10g, 28.4mmol) in absolute ethanol (60ml) was added.

After stirring for 24 hours at room temperature, monitored by TLC showed that the reaction was complete eluted by (benzene: methanol, 4:6) and the resulting mixture was filtered then the solvent was evaporated, the combined residue was washed with chloroform and then petroleum ether (60-80˚C) to give (72.7%) as a white crystals (scheme 1), m.p (dec.240˚C), R_f (0.65).



Scheme (1): Synthesis route for ligand (L)

Synthesis of complexes

Ethanolic solution of the metal salts (Ca^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2} and Hg^{+2}), ethanolic solution of (L) in (1:1) (Ligand:Metal) molar ratios was mixed. After stirring 6 hours, precipitates formed at room temperature, the solids were filtered, washed with (1:1) mixture of water:ethanol. Recrystallized from ethanol and dried at (50 ˚C).

Results and Discussion

The isolated complexes were crystalline solids, soluble in some of common solvents like dimethyl formamide (DMF), dimethyl sulphoxide (DMSO). The conductivity measurements in DMSO indicated the non-electrolyte behavior; Table (1) includes the physical properties. The analytical data confirmed the (1:1) (Metal:Ligand) composition of the complexes. The magnetic measurements (μ_{eff} B.M) for the complexes are also listed in Table (1).

Spectral studies

^{1}H and ^{13}CNMR spectra of the ligand (L). The ^{1}H and ^{13}CNMR spectra were recorded in DMSO and $CDCl_3$.

A) ^{1}HNMR spectrum for the ligand (L)

The ^{1}HNMR spectrum of (L), Fig. (1) showed the following signals: singlet (s) at δ(2.50) ppm for (DMSO), doublet (d) at δ(2.72) ppm for (1H, CH malonate), singlet (s) at δ(3.16) ppm for (1H, OH), singlet (s) at δ(3.56-3.58) ppm for (6H, $2CH_3$ malonate) and multiplet (m) at δ(7.14-8.86) ppm for aromatic protons.

B) ^{13}CNMR spectrum for the ligand (L)

The ^{13}CNMR spectrum of (L), Fig. (2) showed the following signals: signal at δ(168.82) ppm for carbon (C=O) of the ester, lactone ring, signal at δ(135.26) ppm for C-3, signal at δ(131.55) ppm for C-2, signals at δ(129.58,128.40) ppm for aromatic carbons, signal at δ(51.63) ppm for C-4, signal at δ(44.67) ppm for C-5 and signals at δ(40.78-39.11) ppm for C-6, and carbon ($2CH_3$ malonate)[8].

Infrared spectra

The infrared spectra of ligand (L) and its complexes are given in Table (2). The strong absorption band at (1720) cm^{-1} in the free ligand due to υ(C=O) ester,[9,10] in the complexes spectra this band have been found in the range between (1712-1604) cm^{-1} shifted to lower frequencies by (8-16) cm^{-1},[11,12] which indicates the coordination of the oxygen atom at the υ(C=O) group[11]. New bands appeared in the spectra of metal complexes at (524-432) cm^{-1} and (439-405) cm^{-1} which attributed to the (M-O) and (M-Cl) respectively. The FTIR spectra for the ligand and its copper complex were shown in the Figures (3) and (4).

Electronic spectra

The absorptions and assignments related to the ligand and their complexes are listed in Table (3). The ligand, Fig. (5) exhibited an absorption band in (U.V) region at (297) nm (33670) cm^{-1} could be attributed to ($n \longrightarrow \pi^*$) and ($\pi \longrightarrow \pi^*$) transitions[13,14].

The spectra of the complexes

- [$CoLCl_2$] complex

The spectrum of the deep-blue complex of Co(II), Fig. (6) show the following bands at (33444) cm^{-1}, (23803) cm^{-1}, (16743) cm^{-1} and (11494) cm^{-1} which have been assigned to (C.T), $^{4}A_2 \xrightarrow{V_3} {}^{4}T_1(p)$, $^{4}A_2 \xrightarrow{V_2} {}^{4}T_1(F)$ and $^{4}A_2 \xrightarrow{V_1} {}^{4}T_2$ respectively.

The Racah interelectronic repulsion parameter ($\acute{B}$) found to be (404) cm^{-1}, the ratio $\beta = \acute{B} / B_\circ$ comes out to be (0.416) ($B_\circ$ is equal 971cm^{-1})[15]. These parameters are accepted for cobalt(II) tetrahedral complexes[16,17].

- [$NiLCl_2$] complex

The spectrum of the green complex exhibited the following absorptions at (33898) cm^{-1}, (28571) cm^{-1}, (16891) cm^{-1} and (12787) cm^{-1}, these bands[17] are characteristic of tetrahedral nickel(II) complex and were assigned to the transitions (C.T), ${}^3T_1(F) \xrightarrow{V_3} {}^3T_1(P)$, ${}^3T_1(F) \xrightarrow{V_2} {}^3A_2$ and ${}^3T_1(F) \xrightarrow{V_1} {}^3T_2$ respectively.

The Racah interelectronic repulsion parameter ($\acute{B}$) found to be (473.4) cm^{-1}, the ratio $\beta = \acute{B} / B_\circ$ comes out to be (0.454) ($B_\circ$ is equal 1030 cm^{-1})[15].

- [CuLCl$_2$] complex

The spectrum of the green complex of Cu(II) gave two bands at (32894) cm^{-1} caused by (C.T) transition and weak band appeared at (12820) cm^{-1} may be ${}^2B_{1g} \longrightarrow {}^2B_{2g}$ transition in square planar geometry[19-21].

- [CaLCl$_2$], [ZnLCl$_2$], [CdLCl$_2$] and [HgLCl$_2$] complexes

The white complexes [CaLCl$_2$], [ZnLCl$_2$], [CdLCl$_2$] and [HgLCl$_2$] showed absorption bands at (34364) cm^{-1}, (34722) cm^{-1}, (34602) cm^{-1} and (33898) cm^{-1} respectively attributed to charge transfer because the electronic configuration of (Ca^{+2}, Zn^{+2}, Cd^{+2} and Hg^{+2}) which confirms absence of any (d-d) transition[22,23].

According to spectral data as well as those obtained from elemental analysis, the chemical structure of the complexes suggested as:

1- Tetrahedral for [M(L)Cl$_2$], where M = (Ca^{+2}, Co^{+2}, Ni^{+2}, Zn^{+2}, Cd^{+2} and Hg^{+2}), Fig. (7).

2- Square planar for [Cu(L)Cl$_2$], Fig. (8).

References

1. Baba, S.; Ogura, T.;Kawaguchi, S. (1980) Bull. Chem. Soc., 53: 665

2. Kawato, T.; Uechi, T.; Kayama, H.; Kanatomi, H. and Kawanami, Y. (1984) “Preparation, structure, and properties of central-carbon-bonded diethyl malonato complexes of palladium(II) with bis-(μ-chloro) and μ-oxalato bridges” Inorg. Chem., 23: 764-769.

3. Singh, B. and Singh, V. L. (1999) “Mono and trinuclear lanthanide complexes of 13-membered tetraaza macrocycle: Synthesis and characterization”, Journal of Chemical Sciences, 111: 639-650.

4. He, H.S.; Zhao, Z.X.; Wong, W.K.; Li, K.F.; Meng, J.X. and Cheah, K.W. (2003) “Synthesis, characterization and near-infrared photoluminescent studies of diethyl malonate appended mono-porphyrinate lanthanide complexes”, Dalton Trans. 980-986.

5. Nasman, O. S. M. (2008) “N_2S_2-Donor macrocycles with some transition metal ions: Synthesis and characterization”, Phosphorus, Sulfur and Related Elements, 183: 1541-1551.

6. Pothiraja, R.; Milanov, A.; Parala, H.; Winter, M.; Fischer, R. A. and Devi, A. (2009) “Monomeric malonate precursors for the MOCVD of HfO_2 and ZrO_2 thin films”, Dalton Trans., 4: 654-663.

7. Al-Ogiady, R. M. R. (2010) Ph. D. Thesis, “Synthesis of New Malonate and Barbiturate Derivatives of D-Erythroascorbic Acid and their Metal Complexes”, College of Education / Ibn-Al-Haitham, University of Baghdad.

8. Carey, F. A. (2006) “Organic Chemistry”, 6th Ed., the McGraw-Hill Companies, Inc., New York.

9. Lappert, M. F. (1962) “Coordination compounds having carboxylic esters as ligands. Part II. Relative acceptor strengths of some Group III and IV halides”, J. Chem. Soc., 542.

10. Dalton, F. et al. (1960) “The infrared spectra of deuterium compounds. Part I. The C–H stretching bands of OMe and NMe groups”, J. Chem. Soc., 2927-2929.

11. Nakamoto, K. (1996) “Infrared Spectra of Inorganic and Coordination Compound”, 4th Ed., John Wiley and Sons, New York.

12. Veit, R.; Girerd, J. J.;Kahn, O.; Robert, F.; Jeannin, Y. and ElMurr, N. (1984) “Amino acid amides of dithiooxalic acid: Spectroscopic, electrochemical, and magnetic properties of copper(II) binuclear complexes and crystal structure of [N,N′-(1,2-dithioxoethane-1,2-diyl)bis(methylmethioninato)]bis(bromocopper(II))”, Inorg. Chem., 23: 4448-4454.

13. Silverstein, R. M.; Bassler, G. C. and Morrill, T. C. (1981) “Spectrometric Identification of Organic Compound”, 4th Ed., John Wiley and Sons, Inc., New York.

14. Dyer, R. J. (1965) “Application of Absorption Spectroscopy of Organic Compounds” Prentice-Hall, Inc., Englwood Cliffs, N. J., London.

15. Sutton, D. (1968) “Electronic Spectra of Transition Metal Complexes”, McGraw-Hill, New York.

16. Blum, P. R.; Wei, R. M. C. and Cummings, S. C. (1974) “Square-planar transition metal complexes with tetradentate thioiminato Schiff base ligands”, Inorg. Chem., 13 (2): 450-456.

17. Ferraro, J. R.; Murray, B. B. and Wieckowicz, N. J. (1972) “Cobalt(II) halide complexes of 2,2′-dithiodipyridine and 4,4′-dithiodipyridine”, Inorg. Nucl. Chem., 34: 231-235.

18. Menabaue, L.; Pellcani, G. C. and Saladini, M. (1979) “Cobalt(II), nickel(II) and zinc(II) complexes of peptide-group containing amino acids. Bis(N-Acetyl-DL-valinate)metal(II) complexes and their amine adducts”, Inorganic Chimica Acta, 32: 149-155.

19. Burger, K. (1973) “Coordination Chemistry, Experimental Methods”, Butter Worth, London.

20. Massy, A. C.; and Johnson, B. F. G. (1975) “The Chemistry of Copper, Silver and Gold”, Pergamon Press, Oxford, Vol. (20 and 41), London.

21. Jorgensen, C. K. (1964) “Absorption Spectra and Chemical Binding in Complexes”, Pergamon Press, Oxford, London.

22. Rabino Witch, E. and Mol, R. V. (1960) Phys., 14: 112, Jmorcus, R. (1960) Solar Energy, 4: 20.

23. Kashyap, B. C.; Taneja, A. D. and Banerji, S. K. (1975) “Complexes of some N-aryl,N′-2-(5-halo-pyridyl) thioureas with Cd(II) and Hg(II) chlorides”, J. Inorg. Nucl. Chem., 37 (6): 1542-1544.

Table (1): Physical properties of ligand and its complexes

Formula	Colour	M.p˚C or dec.	Metal % Found (Calc.)	Molar conductivity (S.cm^{2}mole^{-1}) in DMSO (10^{-3} M)	μ_{eff} (B.M)
$C_{24}H_{20}O_{11}$ [L]	White	240(dec.)	-	10.60	-
$[CaLCl_2]$	White	190(dec.)	6.50 (6.73)	18	0
$[CoLCl_2]$	Deep-blue	110(dec.)	10.46 (9.59)	20	4.43
$[NiLCl_2]$	Green	220(dec.)	10.07 (9.57)	23	3.22
$[CuLCl_2]$	Green	187(dec.)	9.56 (10.27)	24.5	1.74
$[ZnLCl_2]$	White	210(dec.)	11.72 (10.54)	16.95	0
$[CdLCl_2]$	White	210(dec.)	15.84 (16.84)	23.6	0
$[HgLCl_2]$	White	175(dec.)	27.62 (26.54)	15	0

Table (2): The characteristic infrared of the ligand (L) and its metal complexes

Compound	υ(C=O) Ester aliphat.	υ(C-H) Alipha.	M-O	M-Cl
$C_{24}H_{20}O_{11}$ [L]	1720(s)	2904(w)	-	-
$[CaLCl_2]$	1674(s)	2677(w)	524(w)	405(w)
$[CoLCl_2]$	1689(m)	2989(m)	432(w)	412(w)
$[NiLCl_2]$	1685(m)	2360(m)	459(w)	408(w)
$[CuLCl_2]$	1604(s)	2927(w)	474(w)	408(w)
$[ZnLCl_2]$	1612(s)	2985(m)	474(w)	405(w)
$[CdLCl_2]$	1708(s)	2935(w)	520(w)	439(w)
$[HgLCl_2]$	1712(s)	2985(m)	504(w)	435(w)

Where: s = strong, m = medium, w = weak

Table (3): Electronic spectra data of (L) complexes in DMSO solvent

Compound	λ_{max} nm	Wave number cm^{-1}	ε_{max} $Molar^{-1}cm^{-1}$	Assignment
[L]	297	33670	102	$n \longrightarrow \pi^*$
				$\pi \longrightarrow \pi^*$
$[CaLCl_2]$	291	34364	121	C.T
$[CoLCl_2]$	299	33444	444	C.T
	420.1	23803	150	${}^4A_2 \xrightarrow{V_3} {}^4T_1(p)$
	597.25	16743	97	${}^4A_2 \xrightarrow{V_2} {}^4T_1(F)$
	870	11494	18	${}^4A_2 \xrightarrow{V_1} {}^4T_2$
$[NiLCl_2]$	295	33898	193	C.T
	350	28571	85	${}^3T_1(F) \xrightarrow{V_3} {}^3T_1(P)$
	592	16891	38	${}^3T_1(F) \xrightarrow{V_2} {}^3A_2$
	782	12787	16	${}^3T_1(F) \xrightarrow{V_1} {}^3T_2$
$[CuLCl_2]$	304	32894	2163	C.T
	780	12820	41	${}^2B_{1g} \longrightarrow {}^2B_{2g}$
$[ZnLCl_2]$	288	34722	55	C.T
$[CdLCl_2]$	289	34602	77	C.T

$[HgLCl_2]$	295	33898	432	C.T

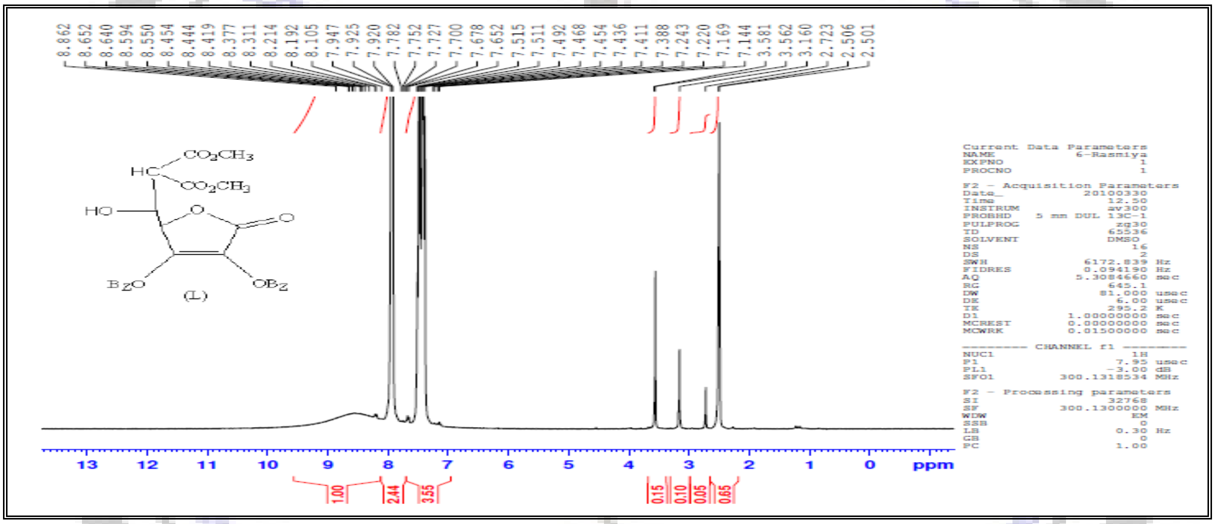


Fig. (1): ^{1}HNMR spectrum of ligand (L)

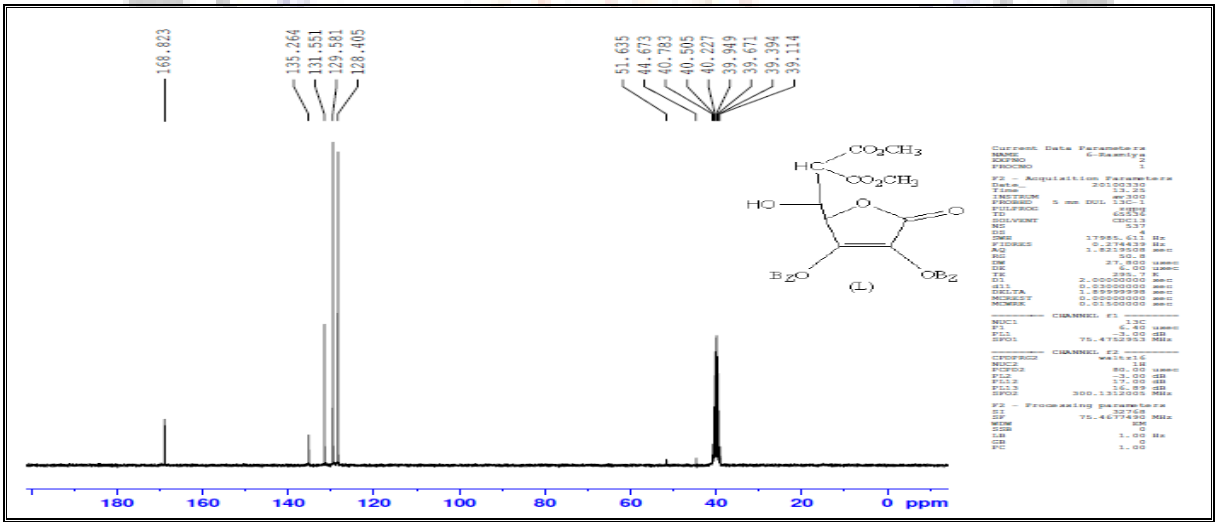


Fig. (2): ^{13}CNMR spectrum of ligand (L)

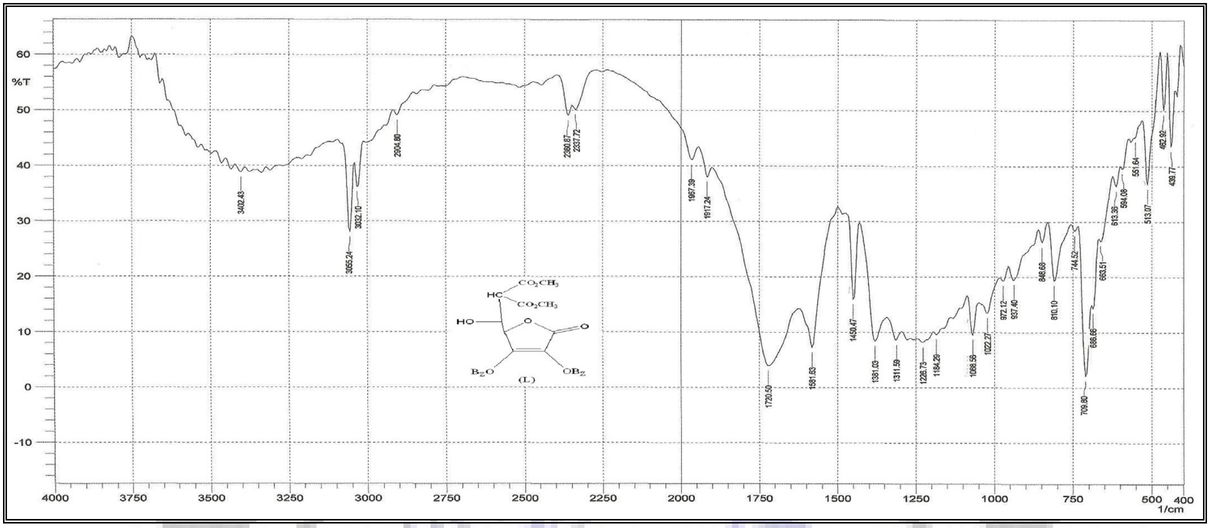


Fig. (3): Infrared spectrum of ligand (L)

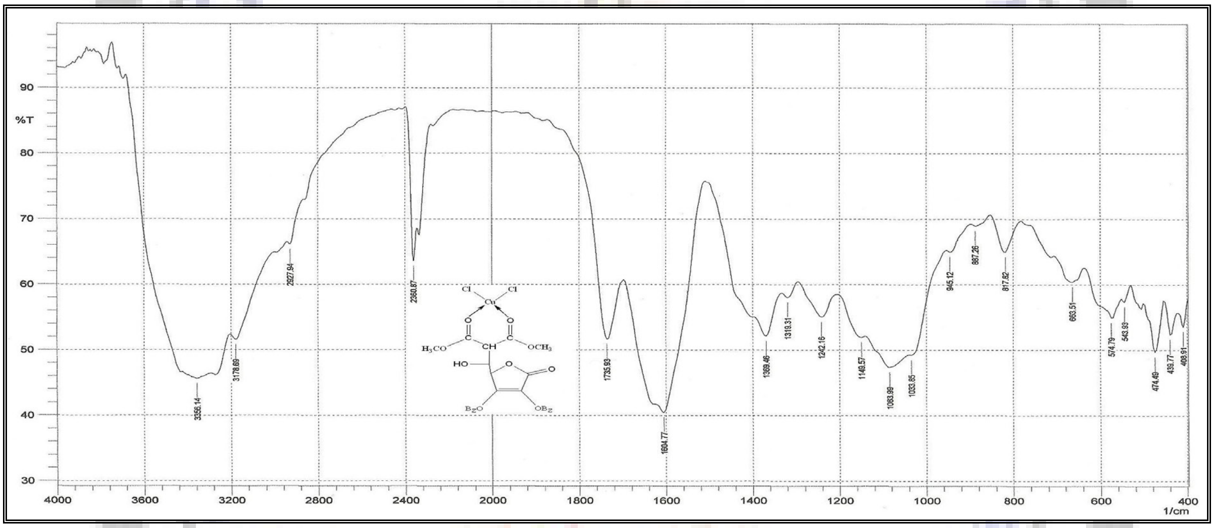


Fig. (4): Infrared spectrum of [CuLCl$_2$]

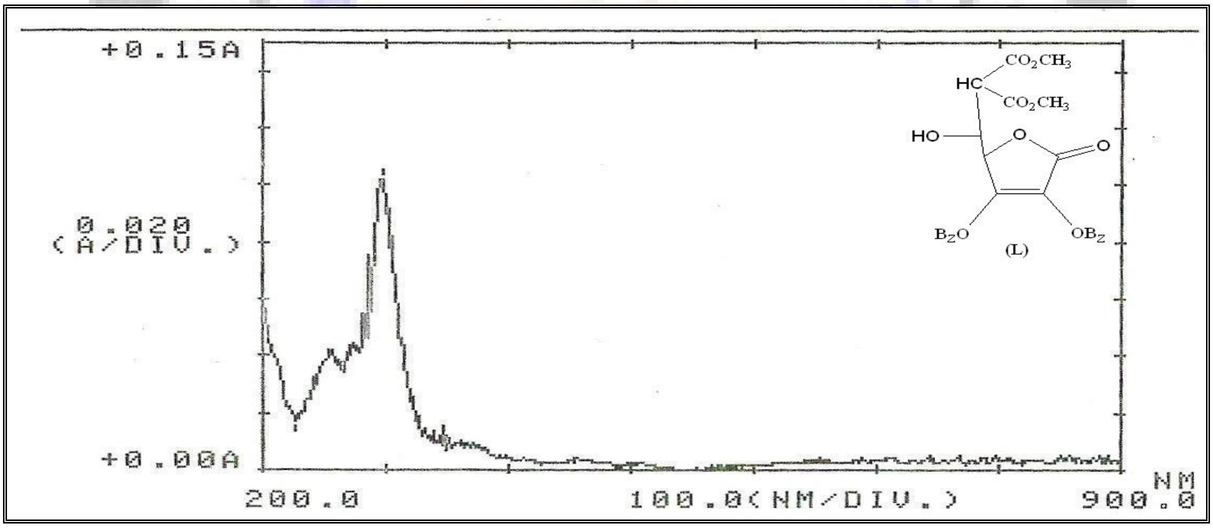


Fig. (5): Electronic spectrum of ligand (L)

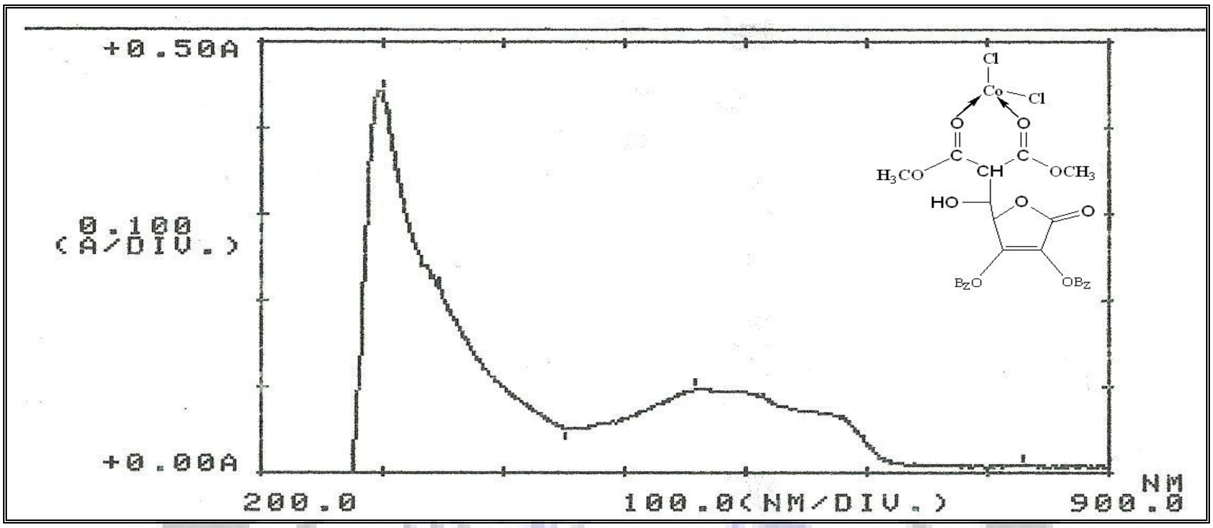


Fig. (6): Electronic spectrum of [$CoLCl_2$]

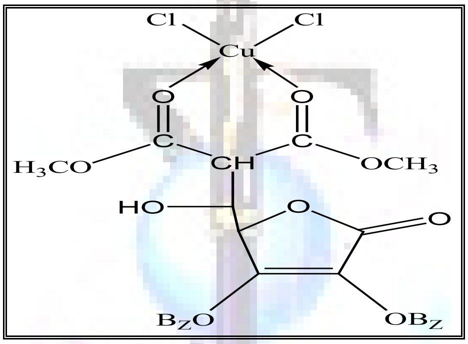


Fig. (7): Tetrahedral geometry of [$M(L)Cl_2$] complexes

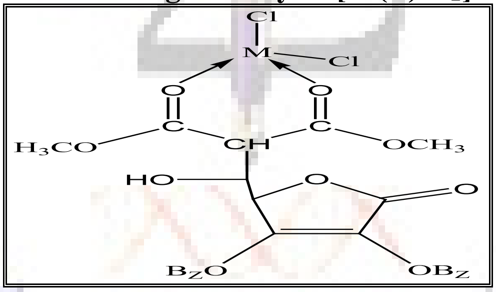


Fig. (8): Square planar geometry of Cu(II) complex