

Synthesis and characterization of Fe(II),Co(II),Ni(II),Cu(II) and Zn(II) mixed ligands complexes with Salicylaldehyde and Schiff Base

**Asst.Dr.Shaimaa Hameid Shakir
Chemistry Department
College of Science for Women
University of Baghdad**

Abstract:

A new mixed ligands complexes have been prepared by using salicylaldehyde and 2,3-dimethyl-1-phenyl-4-salicylidene-3-pyrazoline-5-one with Fe(II),Co(II),Ni(II),Cu(II) and Zn(II) ions the prepared complexes were isolated and characterized by (FT-IR)and (UV-Vis) spectroscopy, Flame atomic absorption technique and determination of yield chloride for all complexes. in addition to magnetic susceptibility and conductivity measurement. The complexes are octahedral $M(L)_2Cl_2$ with M= geometrical in the general formula: $M(L)_2Cl_2$ Fe(II) ,Co(II) , Ni(II) , Cu(II) and Zn(II) .

Introduction :

Generally, the chelating ligands are polyfunctional molecules which can encage heavy metals in an organic sphere. Many types of Schiff base ligands are known and the properties of their metal chelators have been investigated(1-3) acyclic ligands containing nitrogen oxygen and sulphur donor atoms in their structures can act as effective chelating agents for the importance of the transition and non transition metal ions .

coordination in biological structures, the increasing proportion of the application and utilization of these compounds as agents has given rise to an intensification in the investigations of the complexes, especially "vic-dioxime compounds" in technique ,owing to resemble of the vic-dioxime compounds to

vitamin B12 and chlorophyll as a color material of the plants ,the

importance on the illuminate of the biological structures have increased(5.6) Copper complexes are known to have a broad . upper comp spectrum of biological action(7) .many copper complexes used as anti-inflammatory, anti-arthritis, anti-ulcer, anti-convul the reported an anti-tumor sent and anti-tumour agents(8) ,and copper salicylaldehyde (CUSAL-) complex which induces to poimerase 11 to form single-strand nicks in DNA and poisons its activity, which could be one of the possible mechanisms for This paper reports the anti-cancer activity of the complex(9) synthesis and characterization of some new Fe(II) , Co(II) , Ni(II),Cu(II) and Zn(II) complexes with these two lizards (salicylaldehyde and 2,3-dimethyl-1-phenyl-4-salicylaldehyde-3pyrazoline-5-on)

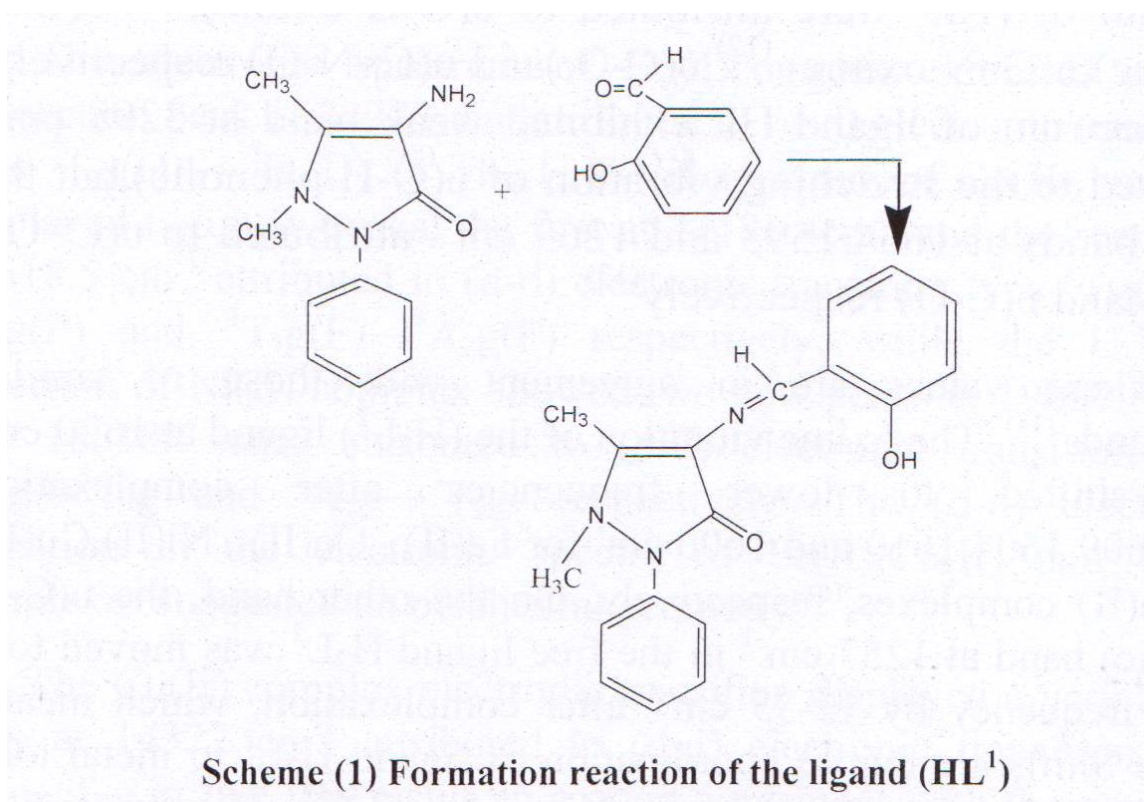
Experimental :

Material and instrumentation Metal salts (FeCl_2 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2) were obtained from Riedel - Dehaenage in high purity , salicylaldehydes, P-Amino-2,3-dimethyl-1-phenyl-3pyrazolin-5-one ethanol , methanol and salicylaldehyde dimethyl foramide, dimethyl sulphoxide from B.D.H. Melting point were recorded on Gallen Kamp melting point apparatus and were uncorrected. FT-IR spectra were recorded as CsI discs using FT-1R.3800 Shimadzu in the range of $(4000-200\text{cm}^{-1})$.Electronic spectra were obtained using UV-160 shimadzu spectrophotometer at room temperature(10^{-3} M) in .

Conductivity was measured by capacitor analyzer and in DMF solution (1×10^{-3} DM) at room temperature. Magnetic susceptibility by Balance magnetic measurements were obtained at 25 C susceptibility model MSB-MKI. The metal

percent in the complexes were determined by using the Hitachi Atomic Absorption the Chloride contents of complexes were determined by potentiometric titration method using (686-Titro processor-665. Dosimeter Metrohn Swiss).

Preparation of the Schiff base (HL1): The Schiff base ligand was prepared by the condensation of the P-amino-2,3-dimethyl-1-phenyl-3-pyrozoline-5-on (0.5g , 2.47mmo1) with the (0.26ml,2.47mmol) salicylaldehyde in methanol (15ml) the resulting mixture was then reflexed for (1h) the yellow precipitate formed was filtered and - recrystallied from absolute ethanol to give yellow needles (10) .



General method for preparation of the Complexes : To the aqueous solution of the meta salts (0.5 g) an ethanolic KOH solution of ligand (HL1) (0-64-1.06g)(2.08 .

3.44m.mole) was added followed by the solution of ligand 30-0.50g) (2.06-3.44m mole). dissolved in ethanolic (H₂L₂) (0.030-0.50g)(2.06-3.44m mole).

KOH. the reaction mixture was stirred continuously. The required product was shortly precipitated at room temperature.

The precipitates were filtered off .washed with (1:1) (ethanol: water) crystallized from ethanol and dried at (60 °C). Table shows the physical properties of the prepared Complexes .

Results and Discussion :

The important infrared spectral bands for the synthesized complexes and ligands are given in table 1 .which lists the stretching frequency (ν) for some of the characteristics groups exhibited by the (ligand and complexes) The ligand H₂L₂ absorption bands at 3385,3248,1620,1257 and 991 cm⁻¹ in the spectrum of H₂L₂ were attributed to ν (O-H oxime), (II) ν (O-H phenolic), ν (C=N oxime), ν (C-O) and ν (C=N-O) respectively.

The spectrum of ligand HL1 exhibited weak band at 3298 cm⁻¹ attributed to the stretching vibration of ν (O-H phenolic),but the strong bands at 1654,1593 and 1263 cm⁻¹ attributed to ν (C=O) , ν (C=N)and ν (C-O) respectively¹³ These values are in agreement with those of similar compounds⁽¹⁴⁾. The oxide vibration of the (H₂L₂) ligand at 1620 cm⁻¹ was shifted to lower frequencies after complexation 1602,1609,1604,1610 and 1600 cm⁻¹

for Fe(II) , Co(II) , Ni(II),Cu(II)

and Zn(II) complexes, respectively. On the other hand, the ν (C-O phenolic) band at 1257 cm⁻¹ in the free ligand H₂L₂ was moved to a higher frequency by 12-35 cm⁻¹ 12-25 cm⁻¹ after complication, which means that the Shifts are due to coordination of ligand H₂L₂ to metal ions by the oxide metal ions by the oxime nitrogen and phenolic oxygen (15). The

practically unchanged O-H at 3385 cm⁻¹ of .

the oxide group confirm that the o-h oxide itself does not coordinate to metal atoms by oxygen atom (16) and the azomethine and carbonyl vibration of the HL1 at 1593 and 1654 cm⁻¹ was shifted to lower frequencies frequencies after complication ,(1570 and 1641), (1580 and 1639), (1554 and 1643) ,(1563, and 1630), and (1566 and 1626)cm⁻¹ for Fe(II),Co(II),Ni(II),Cu(II) and Zn(II) complexes, respectively. On the other hand, the $\nu(\text{C-Ophenolic})$ i the free ligand HL was moved to a band at 1260 cm⁻¹ in fter complication, which means that higher frequency by 9-32 cm⁻¹ a to metal ions by the the Shifts are due to coordination of ligand HL azomethine nitrogen and phenolic oxygen and carbonyl oxygen (17).

The electronic spectra of the ligand HL and H2L2and the Fe(II) , Co(II) , Ni(II),Cu and Zn(II) complexes were recorded in DMF at room temperature. the UV spectral data of the lizards and its complexes are given in table 2 .The spectrum of

free ligand h HL 1showed a strong peak at 256 nm attributed to $\pi \rightarrow \pi^*$ (10)* and anther at 340,362nm due to $n \rightarrow \pi^*$. The salicylaldoxime spectrum show absorption bands at 301nm refer to electronic transition $n \rightarrow \pi^*$. (3) The U.V-Vis spectra of of Fe(II),Co(II),Ni(II),Cu(II) and Zn(II) complexes displayed a high intense two absorption peaks , The first at range (227-358)nm assigned to ligand field and the second ot range (352-377)nm assigned to charge transfer transition.

The electronic spectrum of Fet(II)complex exhibited a new absorption peak at 22222 cm⁻¹attr ibited to(d-d)electronic transition type $5T_{2g}(D) \rightarrow 5E_g(D)$ (18)

The U.v-vis spectrum of Co(II) complex and the second at displayed two new peaks, the first at 21 186-4cm⁻¹ and the second at 185cm⁻¹ attributed to (d-d) electronic transition type $4T_{1g}(F) \rightarrow 4T_{1g}(p)$ and $4T_{1g}(F) \rightarrow 4A_{2g}(F)$ respectively, while the U.V-Vis

spectrum of Ni(II) complex showed two new peaks at 19607.8

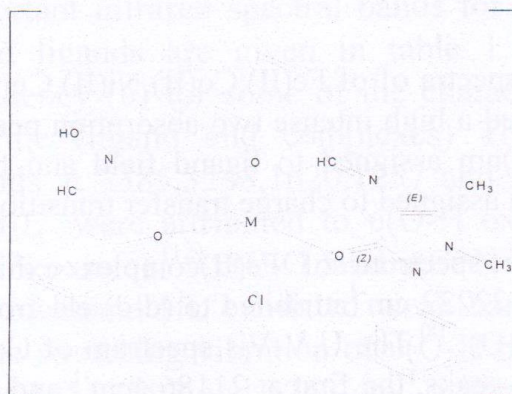
cm⁻¹ and 18518.5 cm⁻¹ attributed to (d-d) electronic transition type

$3A_{2g} \rightarrow 3T_{1g}$ and $3A_{2g} \rightarrow 3T_{2g}$. respectively. The (d-d) electronic transition in the electronic spectra of Fe(II), Co(II) and Ni(II) complexes suggested an octahedral geometry (19) . The Cu(II) complex electronic transition displayed a very broad peak at 14322 cm⁻¹ attributed to (d-d) electronic transition type $2E_g \rightarrow 2T_{2g}$, in fact this result is in a good agreement with the previous work of Cu(II) complex of distorted octahedral geometry because of Jahn-Teller effect (19) The UV-Vis spectrum of Zn(II) complex showed no absorption peak in range (378-1000) nm, that indicates no (d-d) electronic transition happened (d¹⁰-system) in the visible region, that is a good result for Zn(II) octahedral complexes .

The measured magnetic moment (μ_{eff}) (table-3) for the prepared complexes Fe(II), Co(II), Ni(II) and Cu(II) exhibit magnetic moment 5.02, 4.45, 3.81 and 1.71 B.M respectively, which can be a normal values for high spin complexes compared with that have been found in the literature (20,21) Zn(II) complex behaves as diamagnetic.

The observed molar conductance of the complexes in 10⁻³ M solutions in DMSO at room temperature are in the range (40-50 cm² mol⁻¹ table 3) This is consistent with the (1:1) electrolytic nature of these complexes (22) .

The metal to ligands ratio of all the complexes are (1:1:1) according to elemental analyses results



Suggested Structure of the Octahedral complexes (M=,Fe(II) ,Co(II) ,Ni(II) Cu(II) and Zn(II)

Table (1) the characteristic of FT-IR bands of the ligands and the complexes

Compound	$\nu(\text{O-H})$ oxime	$\nu(\text{O-H})$ phenol	$\nu(\text{C=O})$	$\nu(\text{C=N})$ azometh	$\nu(\text{C=N})$ oxime	$\nu(\text{C-O})$	$\nu(\text{N-O})$	$\nu(\text{M-N})$ $\nu(\text{M-O})$ $\nu(\text{M-Cl})$
HL ¹		3298	1654	1593		1260		-
H ₂ L ²	3385	3248			1620	1257	991	-
K[FeL ¹ HL ² Cl]	3372	-	1641	1570	1602	1285	1002	542 460 397
K[CoL ¹ HL ² Cl]	3380	-	1639	1580	1609	1271	1009	551 472 401
K[NiL ¹ HL ² Cl]	3332	-	1643	1554	1604	1292	1018	537 480 375
K[CuL ¹ HL ² Cl]	3387	-	1630	1563	1610	1269	1022	555 497 401
K[ZnL ¹ HL ² Cl]	3354	-	1626	1566	1600	1270	1019	535 482 392

HL¹=2,3-dimethyl-1-phenyl-4-salicylidene-3-pyrazoline-5-on

H₂L²= salicylaldoxime

Table (2): U.V-Visible Spectra of free Ligands and their Complexes (10^{-3}) M in DMF

Compound	$\lambda_{\max}$ nm	ABS	Wave number Cm^{-1}	Transitions
HL^1	256	2.632	39062.5	$\pi \rightarrow \pi^*$
	340	2.458	29411.76	$n \rightarrow \pi^*$
	362	2.354	27624.3	$n \rightarrow \pi^*$
H_2L^2	301	2.401	33222.5	$n \rightarrow \pi^*$
$\text{K}[\text{FeL}^1\text{HL}^2\text{Cl}]$	227	1.43	44052.8	Ligand field
	352	2.23	28409.09	CT
	450	0.25	22222	$^5\text{T}_{2g}(\text{D}) \rightarrow ^5\text{E}_g(\text{D})$
$\text{K}[\text{CoL}^1\text{HL}^2\text{Cl}]$	351	0.42	28490	Ligand field
	368	0.925	27173.9	CT
	472	0.806	21186.4	$^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_1(\text{P})$
	540	0.068	18518.5	$^4\text{T}_1(\text{F}) \rightarrow ^4\text{A}_{2g}(\text{F})$
$\text{K}[\text{NiL}^1\text{HL}^2\text{Cl}]$	358	0.654	27932.9	Ligand field
	370	0.925	27027	CT
	510	0.082	19607	$^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}$
	665	0.08	16023	$^3\text{A}_{2g} \rightarrow ^1\text{E}_g$
$\text{K}[\text{CuL}^1\text{HL}^2\text{Cl}]$	355	0.453	28169	Ligand field
	370	0.925	27027	CT
	750	0.08	14322	$^2\text{E}_g \rightarrow ^2\text{T}_{2g}$
$\text{K}[\text{ZnL}^1\text{HL}^2\text{Cl}]$	351	0.56	28490	Ligand field
	377	1.062	26525	CT

C.T=charge transfer

Table (3): Physical Characteristics and magnetic properties for ligands and its metal complexes

Compound	Formula F.W g/mol	Color	Melting Point C	Yield %	μ_{eff} B.M	Cl%	M%	Molar conductivity $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$
HL^1	307.25	Yellow	189	87		-	-	
H_2L^2	137.1	Brown	-	-		-	-	
$\text{K}[\text{FeL}^1\text{HL}^2\text{Cl}]$	572.747	Brown	288-290	60	5.02	6.189	9.75	40
$\text{K}[\text{CoL}^1\text{HL}^2\text{Cl}]$	575.833	Brown	237-238	67	4.45	6.156	10.23	46
$\text{K}[\text{NiL}^1\text{HL}^2\text{Cl}]$	575.593	Green yellow	268-270	80	3.81	6.159	10.199	50
$\text{K}[\text{CuL}^1\text{HL}^2\text{Cl}]$	580.446	Dark brown	272-273	71	1.71	6.107	10.947	48
$\text{K}[\text{ZnL}^1\text{HL}^2\text{Cl}]$	582.29	Dark red	256-258	63	diam	6.088	11.226	44

Diam=diamagnetic

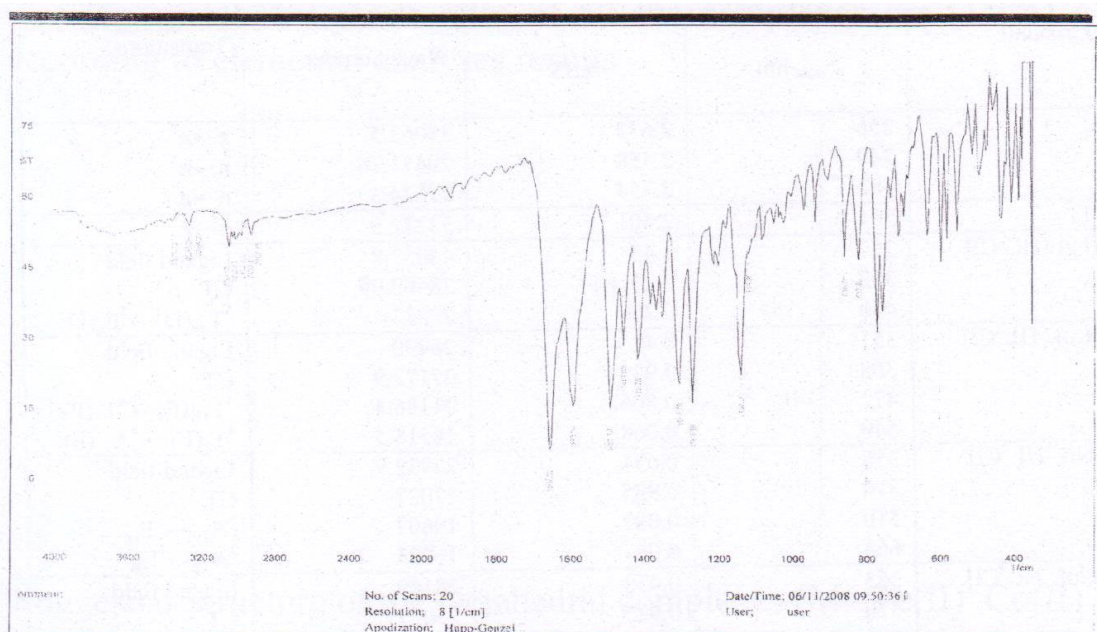
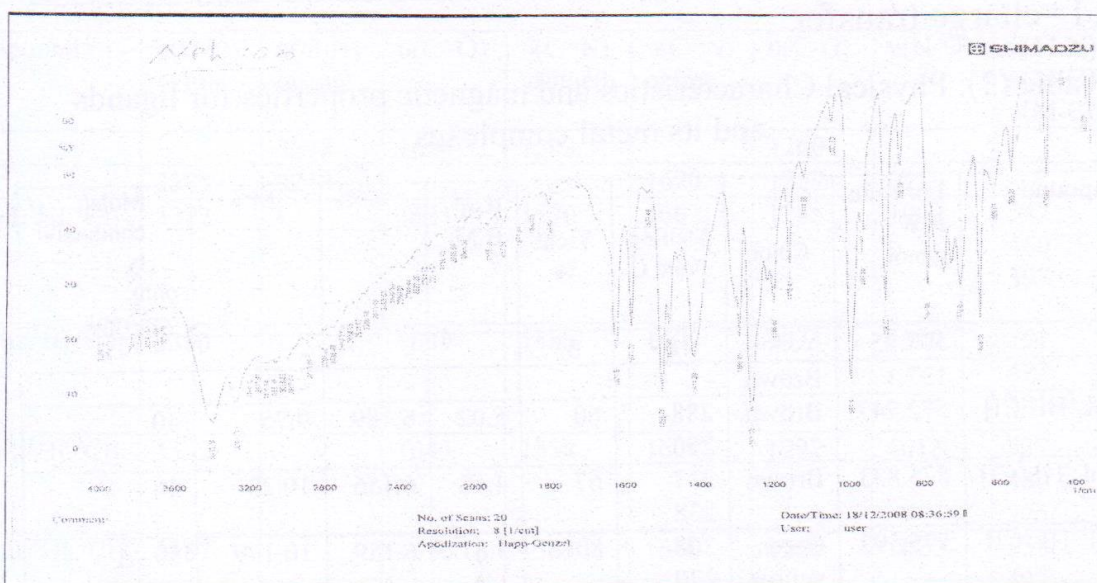


Fig (1-a): Infrared (FT-IR) Spectrum of Schiff base (HL¹)



Fig(1-b): Infrared (FT-IR) Spectrum of salicylaldoxime (H₂L²)

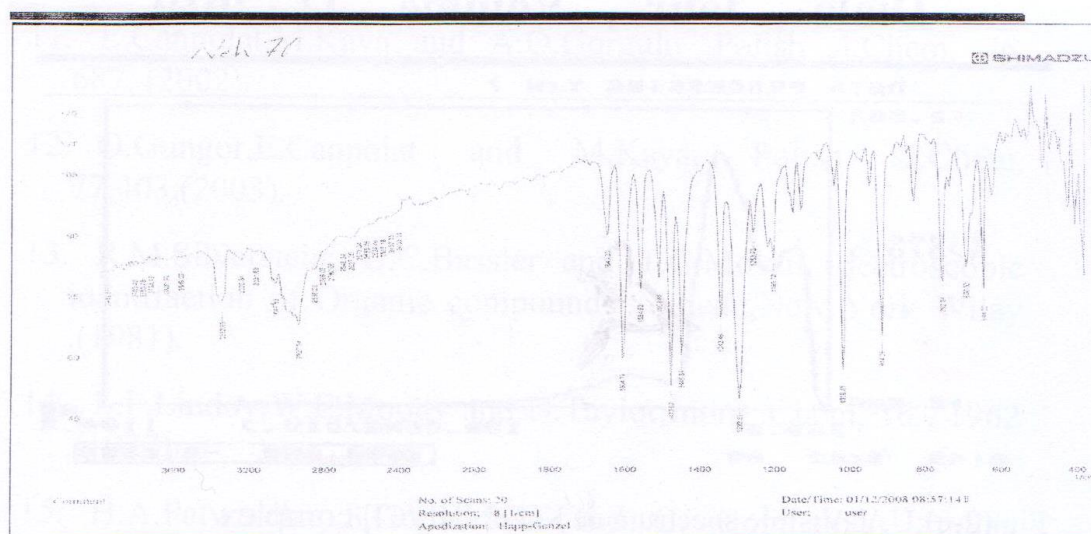


Fig (1-c):Infrared (FT-IR) Spectrum of $K[NiL^1HL^2Cl]$ complex

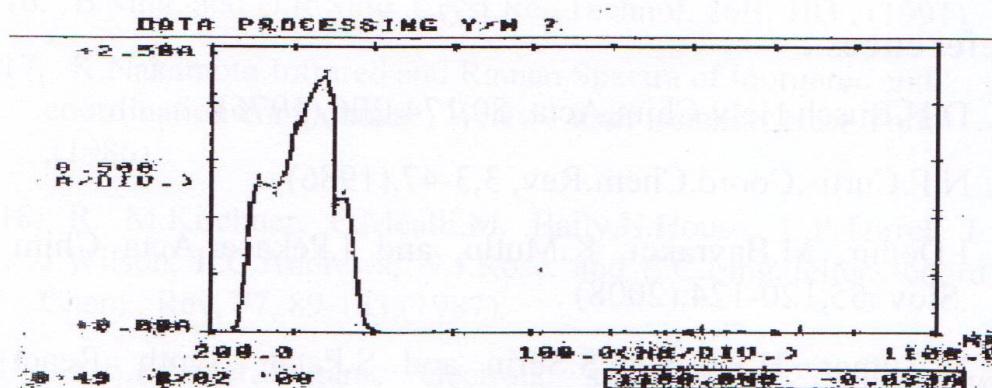


Fig (2-a):U.V-Visible spectrum of free Ligand (HL^1)

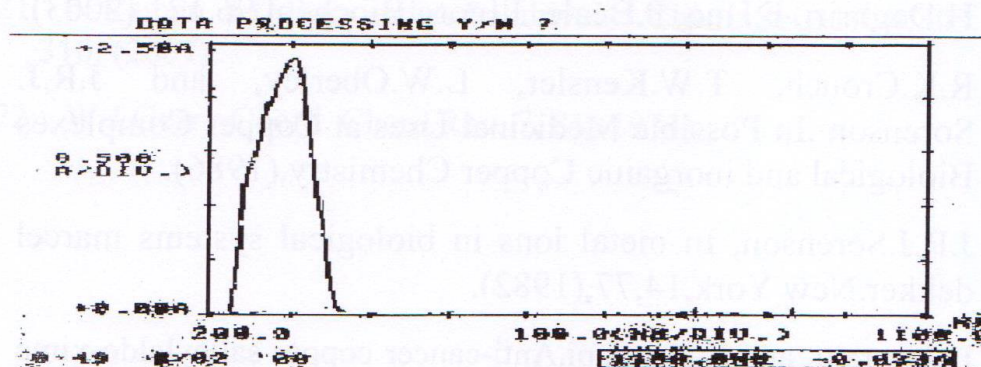


Fig (2-b):U.V-Visible spectrum of free salicylaldoxime (H_2L^2)

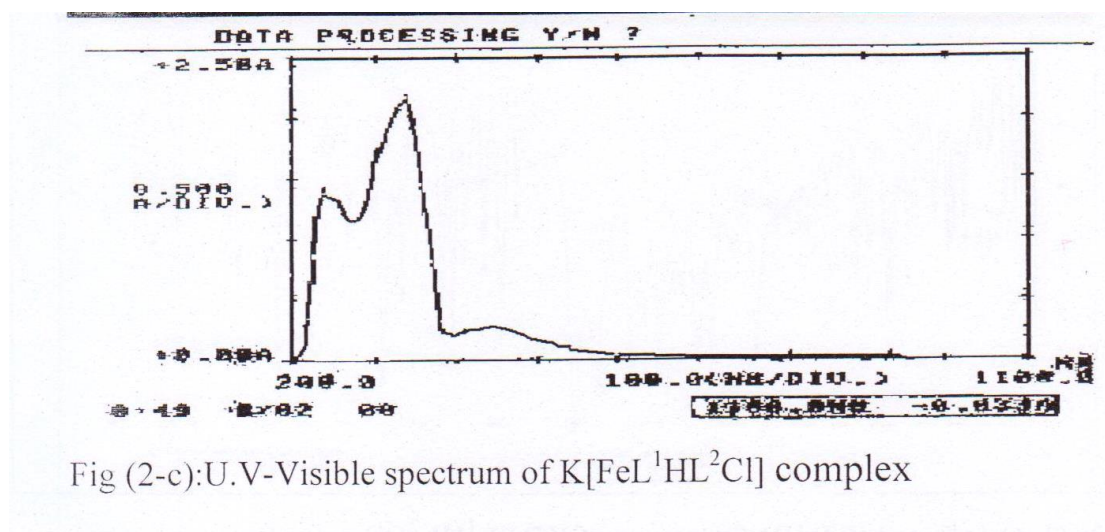


Fig (2-c):U.V-Visible spectrum of K[FeL¹HL²Cl] complex

References :

- 1 . D.H.Busch ,Helv.chim,Acta, 50,174-206,(1976) .
2. N.F.curtis,Coord.Chem.Rev, 3,3-47,(1986) .
3. I.Demir, M.Bayrakci, K.Mutlu, and I.pekacar,Acta Chim .Slov .55,120-124,42008) .
4. M.Tumer, H.Koksal, S.serin and s.patat, Synth React Inorg .Met.Org.chem, 27,59-68,41997).
5. A.chakravorty,cood.chem.Rev, 13,1-46,41974).
6. H.Daghriri, F.Huq, P.Beale, J.Inorg.Biochem 96,121,(2003).
7. R-K.crouch, T.W-Kensler, L.W.oberley, and J.R.J. Sorenson ,1n Possible Medicinal Uses at Copper Complexes Biological and inorganic Copper Chemistry,(1986)
8. J.R.J.sorenson, In metal ions in biological systems marvel

dekker, New York, 14, 77, (1982).

9. D. Jayaraju, and K. Kondapi, Anti-cancer copper salicylaldehyde complex inhibits topoisomerase II catalytic activity. *Current Science*, 81, 7, 787-792, (2001).

10. A. A. S. Alhamadani, *J. Umm Al-Qadisiyah Science*, 2, 2, 395-602 (2005).

11. E. Canpolat M. Kaya and A. O. Gorgulu, *Polish J. Chem*, 76, 687, (2002).

12. O. Güngör, E. Canpolat and M. Kay, *Polish J. Chem*, 77, 403, (2003).

13. R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectroscopic Identification of Organic Compounds*, 4th edn, New York Wiley (1981).

14. L. F. Lindoy, W. E. Moody and D. Taylor, *Inorg Chem*, 16, 1962 (1977).

15. H. A. Patwardhan, S. Gopinath and C. Gopinathan, *Indian J. Chem*, 16, 224, (1978).

16. B. Singh, and U. R. Singh, *Cryst. Res. Technol*, 26B, 103, (1991).

17. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York (1986).

18. R. M. Kirchner, C. Mealli, M. Bailly, N. House, L. P. Torrel, L. Wilson, L. C. Andrews, N. J. Rose, and E. C. Lingafelter, *Chem. Rev*, 77, 89-163, (1987).

1 9. A.B.p.lever, Inorganic electron spectroscopy 2nd edn NEW York., (1968).

20. M.M.Aboaly and M.M.H.Khalil, Spectrosc. Lett 34, 495 , (2002)
.

2 1. N.Raman, J.D.Raja and A.sakthivel, J.Chem Sci 119, 4, 303 - 310, (2007).

W.j.Geary, coord. Chem Rev, 7, 8 1, (1971).

تحضير وتشخيص معقدات مختلطة الليكاندات ل الحديد(II) والكوبلت (II) والنيكل (II) والنحاس (II) والخاصين(II) مع السلسدوكسيم وقاعدة شيف

م.د. شيماء حميد شاكر قسم الكيمياء – كلية العلوم للبنات-جامعة بغداد

الخلاصة:

حضرت معقدات فلزية جديدة ذات ليكاندات مختلطة من سلسدوكسيم H_2L_2 و H_2L_3 ثنائي مثيل - ١- فنيل - ٤- سلسلدائين - ٣- بايروزولين - ٥- اون (HL1) مع ايونات الحديد والكوبلت والنيكل والنحاس والخاصين ثنائية التكافؤ . عزلت المعقدات المحضرة وتم تشخيصها بواسطة طيف الاشعة تحت الحمراء (FT.IR) وطيف الاشعة فوق البنفسجية والمرئية (UV-Vis) تقنية الامتصاص الذري اللهب للعناصر وتعيين النسبة المئوية للكلور فضلا عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية. اظهرت الدراسة ان المعقدات ثمانية السطوح وذات صيغة عامة $K(ML_1HL_2C_1)$ حيث ان

$CU(II), ZN(II), Fe(II), CO(II), NI(II) = M$