Diala , Jour , Volume , 42 , 2010

Synthesis and characterization of Fe(II),Co(1I),Ni(Il),Cu(II) and Zn(ll) mixed lizards complexes with Salicylaldoxime and Schiff Base

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Abstract:

A new mixed lizards complexes have been prepared by using salicylaldoxime and 2,3-dimethyl-l-phenyl-4salicylaidene-3-pyrazoline-5-one with Fe(II),Co(11),Ni(l1),Cu(I1) and Zn(Il) 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 IHL2CI) with M= geometrical in the general formula: KIML Fe(Il) ,Co(11) , Ni(11) , Cu(ll) and Zn(11) .

Introduction :

Generally, the chelating lizards are polyfunctional molecules which can encage heavy metals in an organic sphere.
Many types of Schiff base ligands are know and the properties of their metal chelators have been investigated(1-3) acyc lic lizards 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 the these compounds as agents has given rise to an intensification in to 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

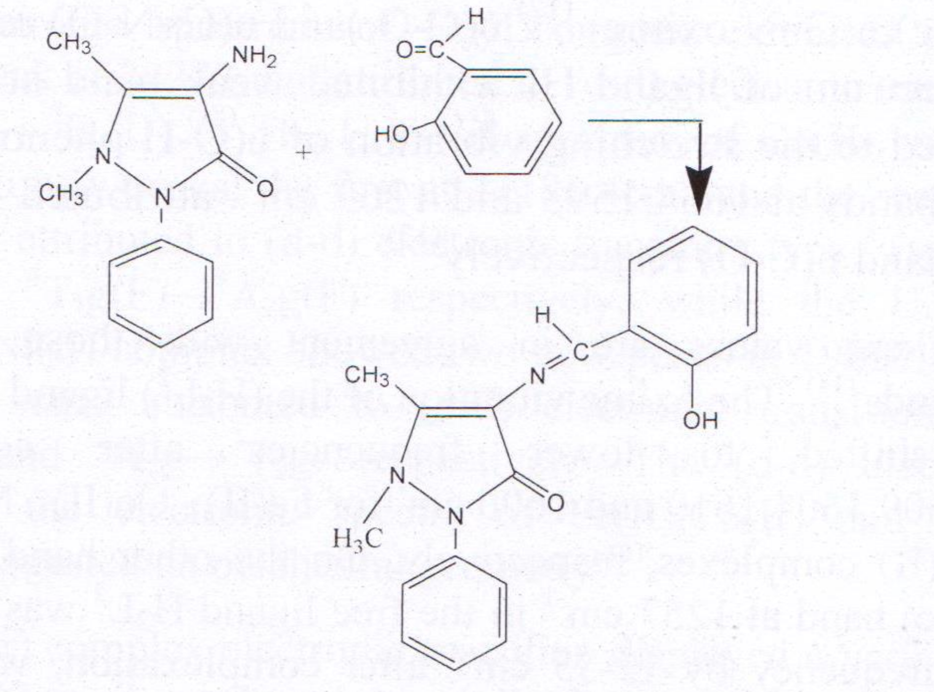
importance on the illuminate of the biological structures have increased(5.6) Copper complexes are known to have a broad . upper comp spectrum of biological action(7) .many copper complexes used as anti-inflammatory, anti-arthritic, anti-ulcer, anti-convul the reported an anti-tumor sent and anti-tumour agents(8) ,and copper salicylaldoxime (CUSAL-) complex which induces to poisomerase 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(l1) , Co(l1) , Ni(lI),Cu(I1) and Zn(I1) complexes with these two lizards (salicylaldoxime and 2.3-dimethyl-l-phenyl-4-salicylaidene-3pyrazoline-5-on)
.

Experimental :

Material and instrumentation Metal salts (FeC12,CoCl2.6H2O ,NiCl2 .6H2O ,CuCl2.2H2O
and ZnC12) were obtained from Riedel - Dehaenage in high purity , salicylaldehydes, P-Amino-2,3-dimethyl-l-phenyl-3pyrazolin-5-one ethanol , methanol and salicylaldoxime dimethyl foramaide, dimethyl sulphoxied from B.D.H. Melting point were recorded on Gallen Kamp melting point apparatus and were uncorrected.FT.IR spectra were recorded as Csl discs using FT-1R.3800 Shimadzu in the range of (4000-200cm-1) .Electronic spectra were obtained using UV-160 shimadzu spectrophotometer at room temperaturet(1o-3 M) in .

Conductivity was measured by capacitor analyzer and in DMF solution (1x10-3 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-l-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) .



Scheme (1) Formation reaction of the ligand (HL^1)

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.mo1e) was added followed by the solution of ligand 30-0 50g) (2.06-3.44m molel.dissolved in ethanolic (H2L2) (0030-0.50g)(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 lizards are given in table 1 .which lists the stretching frequency (v) 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 v(O-H oximel),(ll) v(O-Hphenolicl), v(C=N oxime)12, v(C-O) and v(C=N-O) respectively.

The spectrum of ligand HL1 exhibited weak band at 3298 cm-1 attributed to the stretching vibration of v(O-H phenolicl),but thestrong bands at 1654,1593 and 1263 cm-1 attributed to v(C=O) , V(C=N)and V(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(1l) , Co(1I) , Ni(1l),Cu(11)

and Zn(1l) complexes, respectively. On the other hand, the v(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 metat 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(1I),Ni(l1),Cu(lI) and Zn(II) complexes, respectively. On the other hand, the v(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 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(ll) , Co(11) , Ni(ll),Cu and Zn(1I) 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

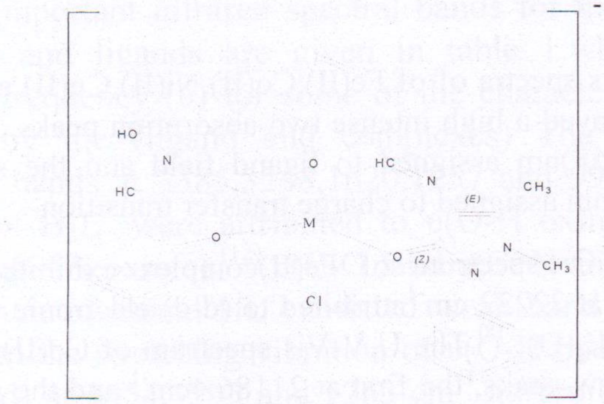
free ligand h HL 1showed a strong peak at 256 nm attributed to u-----u (10)* and anther at 340,362nm due to n--u* . The salicylaldoxime spectrum show absorption bands at 301nm refer to electronic tramsition n--.+u*. (3) The U.V-Vis spectra of of Fe(Il),Co(Il),Ni(1l),Cu(I1) and Zn(I1) complexes displayed 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(ll)complex exhibited a new absorption peak at 22222 cm-1attr ibited to(d-d)electronic transition type 5T2g (D)___5Eg(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 4T1g(F)____4T1g(p) and 4T1 g(F)____4A2g(F) respectively, while the U.V-Vis
spectrum of Ni(Il) complex showed two new peaks at 19607.8

cm-1and 18518.5 cm-1 attributed to (d-d) electronic transition type
3A2g ___3T1g and 3A2g____3T2g . respectively. The (d-d) electronic transition in the electronic spectra of Fe(1I),Co(1l) and Ni(I1) complexes suggested an octahedral geometry(19) . The Cu(I1) complex electronic transition displayed a very broad peak at14322cm-1 attributed to (d-d) electronic transition type 2Eg____2T2g,in fact this result an a good agreement with the previous work of Cu(1l) complex of distorted octahedral geometry because of Ja hn-Teller effect (19) The UV-Vis spectrum of Zn(lI) complex showed no absorption peak in range (378-1000)nm ,that is indicates no(d-d) electronic transition happened (d10-system)in the visible region, that is a good result for Zn(1I) octahedral complexes .

The measured magnetic moment (ueff)(table-3) for the prepared complexes Fe(11),Co(11),Ni(1l) and Cu(l1) exhibit magnetic moment 5.02,4.45,3.8 1 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 beehives al diamagnetic.

The observed molar conductance of the complexes in 10-3M solutions in DMSO at room temperature are in the range (40-50c 1cm2mol-1 table 3) This is consistent with the (1:1) electrolytic nature of th ese complexes(22) .

The metal to ligands ratio of all the complexes are (1:1:1) a 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	υ(O-H) oxime	υ(O-H) phenol	υ(C=O)	υ(C=N) azometh	υ(C=N) oxime	υ(C-O)	υ(N-O)	υ(M-N) υ(M-O) υ(M-Cl)
HL^1		3298	1654	1593		1260		-
H_2L^2	3385	3248			1620	1257	991	-
$K[FeL^1HL^2Cl]$	3372	-	1641	1570	1602	1285	1002	542 460 397
$K[CoL^1HL^2Cl]$	3380	-	1639	1580	1609	1271	1009	551 472 401
$K[NiL^1HL^2Cl]$	3332	-	1643	1554	1604	1292	1018	537 480 375
$K[CuL^1HL^2Cl]$	3387	-	1630	1563	1610	1269	1022	555 497 401
$K[ZnL^1HL^2Cl]$	3354	-	1626	1566	1600	1270	1019	535 482 392

HL^1=2,3-dimethyl-1-phenyl-4-salicylaidene-3-pyrazoline-5-on

H_2L^2= salicylaldoxime

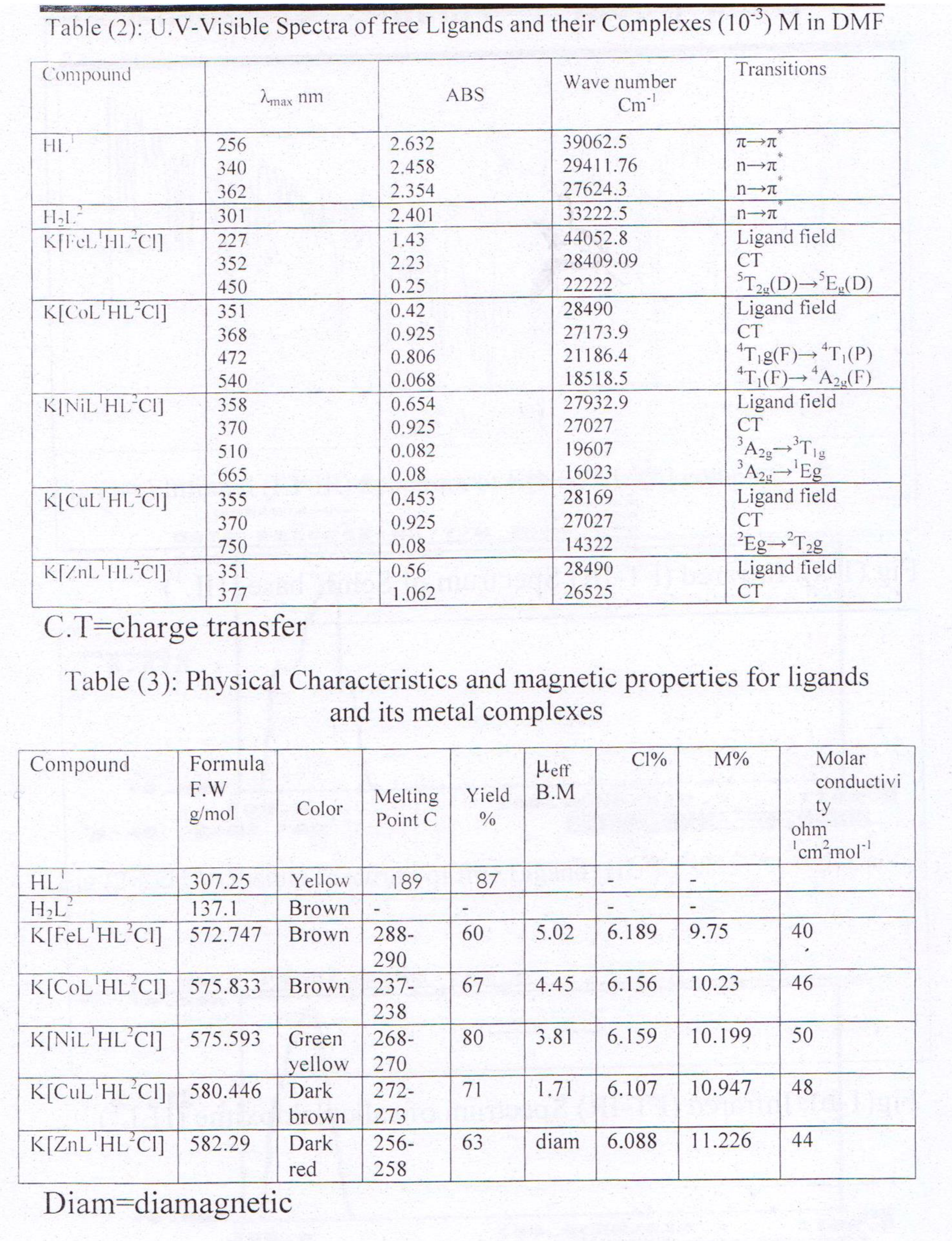


Table (2): U.V-Visible Spectra of free Ligands and their Complexes (10^{-3}) M in DMF

Compound	λ_{max} nm	ABS	Wave number Cm^{-1}	Transitions
HL^1	256 340 362	2.632 2.458 2.354	39062.5 29411.76 27624.3	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $n \rightarrow \pi^*$
H_2L^2	301	2.401	33222.5	$n \rightarrow \pi^*$
$K[FeL^1HL^2Cl]$	227 352 450	1.43 2.23 0.25	44052.8 28409.09 22222	Ligand field CT $^5T_{2g}(D) \rightarrow {}^5E_g(D)$
$K[CoL^1HL^2Cl]$	351 368 472 540	0.42 0.925 0.806 0.068	28490 27173.9 21186.4 18518.5	Ligand field CT $^4T_1g(F) \rightarrow {}^4T_1(P)$ $^4T_1(F) \rightarrow {}^4A_{2g}(F)$
$K[NiL^1HL^2Cl]$	358 370 510 665	0.654 0.925 0.082 0.08	27932.9 27027 19607 16023	Ligand field CT $^3A_{2g} \rightarrow {}^3T_{1g}$ $^3A_{2g} \rightarrow {}^1Eg$
$K[CuL^1HL^2Cl]$	355 370 750	0.453 0.925 0.08	28169 27027 14322	Ligand field CT $^2Eg \rightarrow {}^2T_2g$
$K[ZnL^1HL^2Cl]$	351 377	0.56 1.062	28490 26525	Ligand field 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 $ohm^{-1}cm^2mol^{-1}$
HL^1	307.25	Yellow	189	87		-	-	
H_2L^2	137.1	Brown	-	-		-	-	
$K[FeL^1HL^2Cl]$	572.747	Brown	288-290	60	5.02	6.189	9.75	40
$K[CoL^1HL^2Cl]$	575.833	Brown	237-238	67	4.45	6.156	10.23	46
$K[NiL^1HL^2Cl]$	575.593	Green yellow	268-270	80	3.81	6.159	10.199	50
$K[CuL^1HL^2Cl]$	580.446	Dark brown	272-273	71	1.71	6.107	10.947	48
$K[ZnL^1HL^2Cl]$	582.29	Dark red	256-258	63	diam	6.088	11.226	44

Diam=diamagnetic

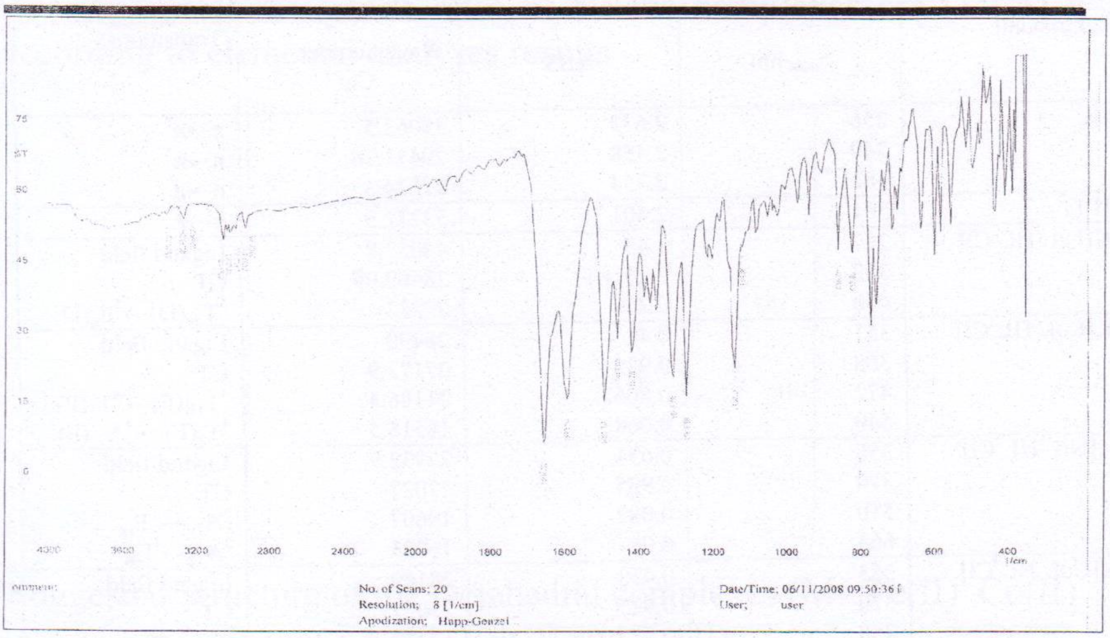
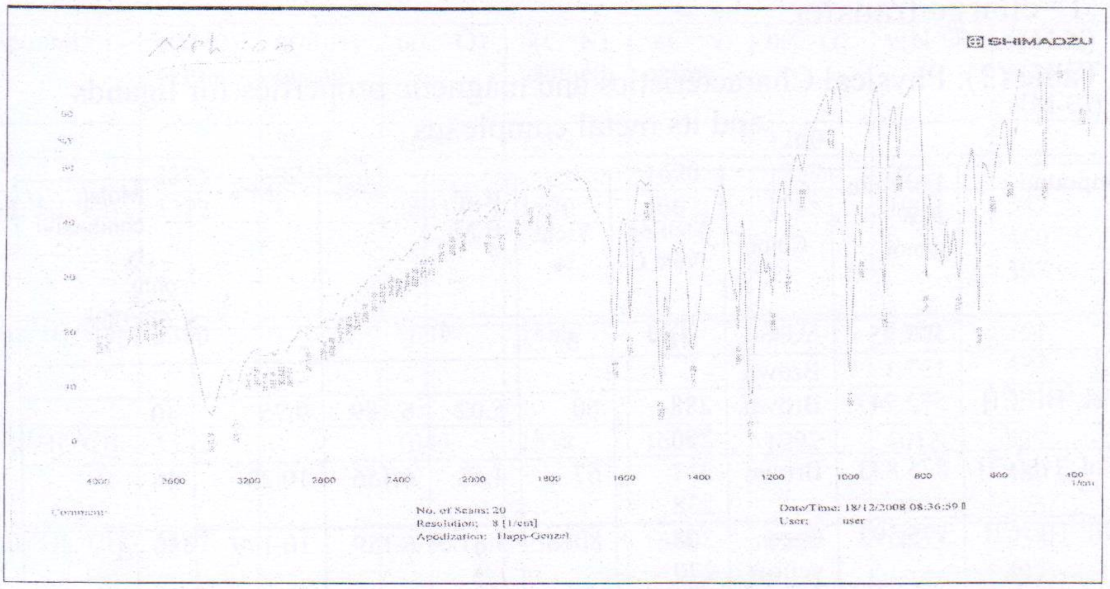


Fig (1-a): Infrared (FT-IR) Spectrum of Schiff base (HL^1)



Fig(1-b): Infrared (FT-IR) Spectrum of salicylaldoxime (H_2L^2)

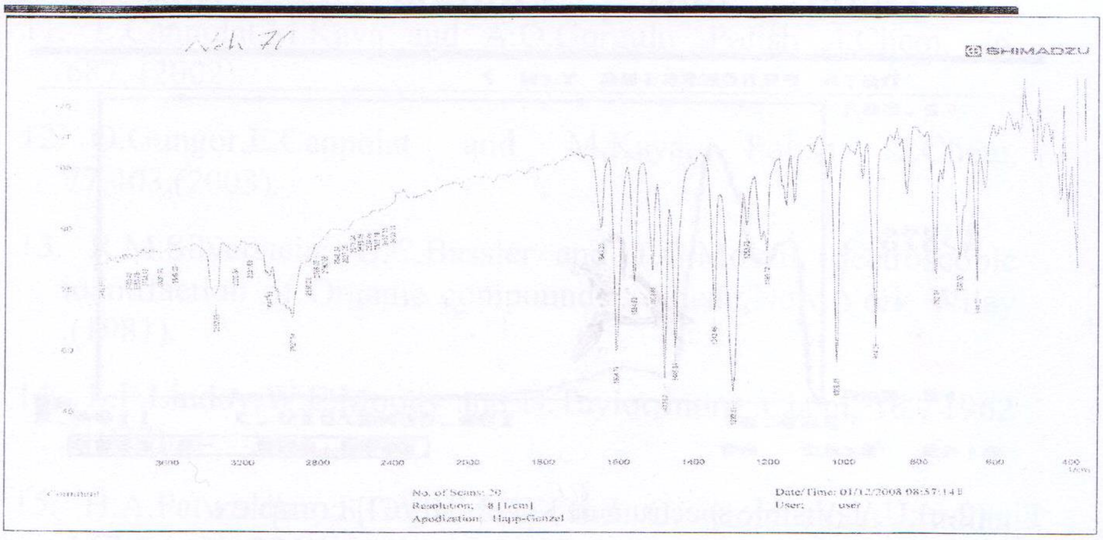


Fig (1-c):Infrared (FT-IR) Spectrum of K[NiL^{1}HL^{2}Cl] complex

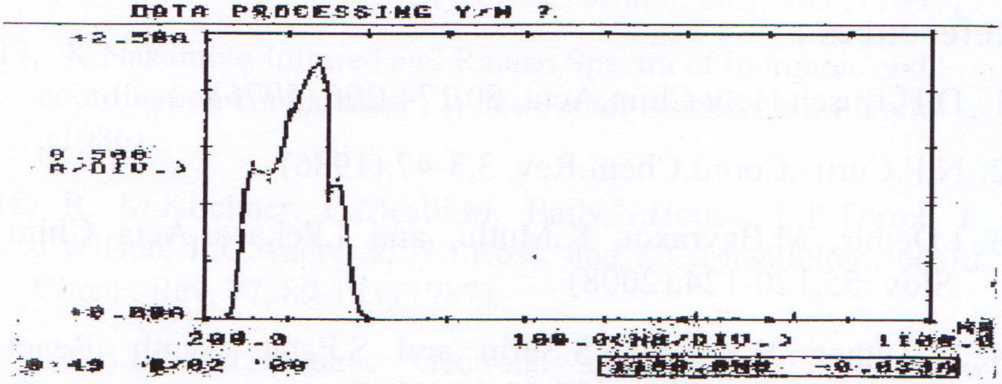


Fig (2-a):U.V-Visible spectrum of free Ligand (HL^1)

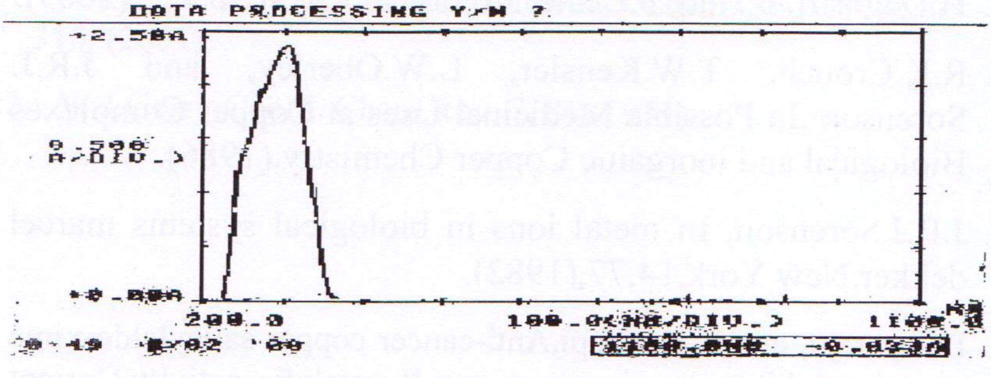


Fig (2-b):U.V-Visible spectrum of free salicylaldoxime (H$_2$L^2)

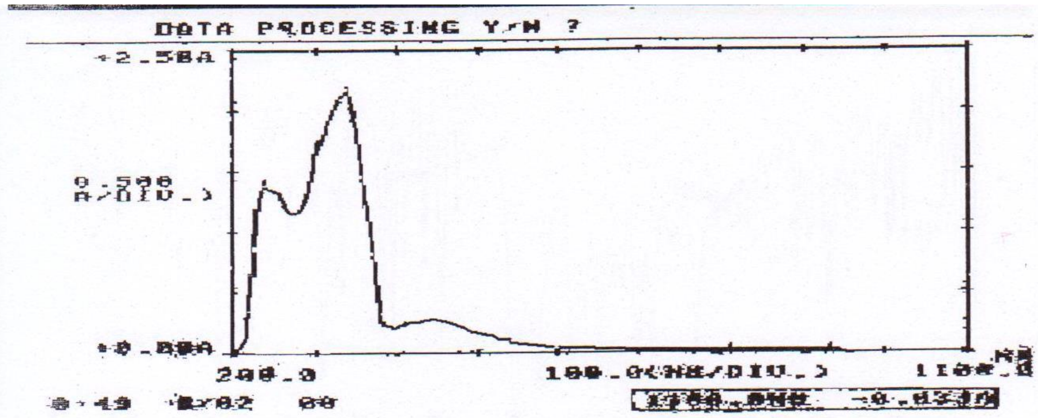


Fig (2-c):U.V-Visible spectrum of K[FeL^{1}HL^{2}Cl] complex

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Diala , Jour , Volume , 42 , 2010

تحضير وتشخيص معقدات مختلطة الليكاندات ل الحديد(II) والكوبلت (II) والنيكل (II) والنحاس (II) والخارصين(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 H2L2و3,2 ثنائي مثيل -1-فنيل -4- سلسلدائين -3- بايروزولين -5- اون (HL1مع ايونات الحديد والكوبلت والنيكل والنحاس والخارصين ثنائية التكافؤ . عزلت المعقدات المحضرة وتم تشخيصها بوساطة طيف الاشعة تحت الحمراء(FT.IRوطيف الاشعة فوق البنفسجية والمرئية (UV-Visتقنية الامتصاص الذري اللهبي للعناصر وتعيين النسبة المئوية للكلور فضلا عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية .اظهرت الدراسة ان المعقدات ثمانية السطوح وذات صيغة عامة K(ML1HL2C1حيث ان

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