Synthesis and Characterization of Tetradentate Complexes Type N_2O_2 From the Reaction of 2-Hydroxy -1, 2-Diphynel-Ethanone Oxime [H_2L] With Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Hg^{II} Ions

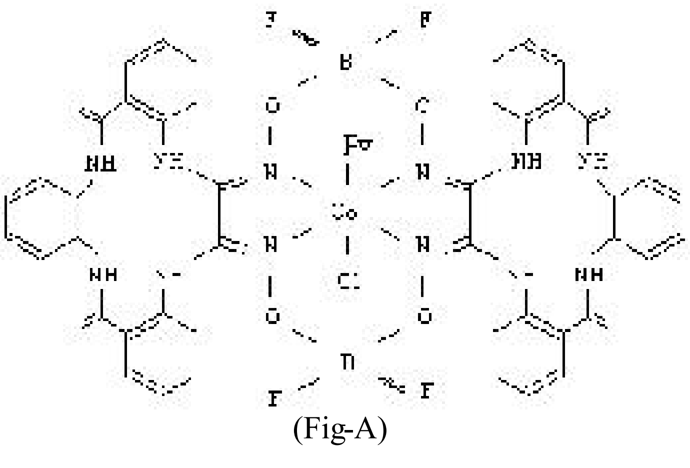
A.Th. Numan*, E. I. Alsalehe and J. H. Aldulaimi
Department of Chemistry, College of Education, Ibn Al-Haitham,
University of Baghdad

Abstract

Tetradentate complexes type [M $(HL)_2$] were prepared from the reaction of 2-hydroxy -1, 2-diphynel-ethanone oxime [H_2L] and KOH with (Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Hg^{II}), in methanol with (2:1) metal: ligand ratio. The general formula for Cu^{II} and Mn^{II} complexes are [M $(HL)_2$ $Cl.H_2O$] K, for Co^{II} [Co $(HL)_2$. H_2O] and [M $(HL)_2$] for the rest of complexes. All compounds were characterised by spectroscopic methods, I.R, U.V-Vis, H.P.L.C, atomic absorption and conductivity measurements chloride content. From the data of these measurements, the proposed molecular structures for Fe^{II} and Hg^{II} complexes are tetrahedrals, while Mn^{II} and Cu^{II} complexes are octahedrals, Ni^{II} complex adopting square planar structure and the complex of Co^{II} ion showed a bipyramidal structure

Introduction

Amino oxime metal complexes have been known since a long time (1)' The different coordination modes of oxime and oximato species indicated a versatile electronic distribution within the ligand. This, in turn suggested that the chemistry of metal-bonded oximes should be rich. The inspection of data accumulated in the literature confirmed these assumptions (2).Transition metal complexes of vic- dioximes are of particular interest as biological model compounds. Numerous chemical studies have been made on the cobalt (III) –bis (dimethyl glyoxime) system which has been called a model system for B12 moiety (3,4). Although these efforts metl with a considerable success. There are some species which do not appear to behave according to the existing theories (i.c., the dioxime of glyoxal). It was felt that stability constant studies would be of value in showing the inherent differences in the chelating ability of closely related metal ions (5). The synthesis of some cobalt (III) dioxime complexes with ligands containing macrocyclic frame on the backbone was reported (6,7). The template synthesis of these compounds involve linking of two tetraazamacrocycle containing components through dioxime coordinate to Co(II) then an aerial oxidation of this ion to Co(III)is done in the presence of (axial coordinating) pyridine and chloride ligands, (Fig. A).



(Fig-A)

This paper reports the synthesis and characterisation of new complexes derived from the reaction of [2-hydroxy -1, 2-diphynel-ethanone oxime] with (Mn^{II}, Fe^{II}, Co^{II}, Ni^{II} , Cu^{II} and Hg^{II}) metal ions.

Experimental

Reagents were purchased from Fluka and Redial – Dehenge Chemical Co. I.R spectra were recorded as (KBr) discs using a Shimadzu 8300 FTIR spectrophotometer in the range (4000-400) cm^{-1}. Electronic spectra of the prepared compounds were measured in the region (200-1100) nm for 10^{-3} M solutions in (DMF) at 25°C using a Shimadzu 160 spectrophotometer with 1.000±0.001 cm matched quartz cell ,while metal contents of the complexes were determined by atomic absorption (A.A) technique using a Shimadzu AA 680G atomic absorption spectrophotometer. Electrical conductivity measurements of the complexes were recorded at 25°C for 10^{-3} M solutions of the samples in (DMF) using a PW 9526 digital conductivity meter. The H.P.L.C. chromatograms of the complexes were obtained using H.P.L.C. type shimadzu LC-6H (Koyoto–Japan) in an isocratic system (MeCN: H_2O), (70–30). as a solvent.

Synthesis of [Mn (HL)$_2$ .Cl.H_2O] K

A 0.25g, (1.26mmole) of $MnCl_2.4H_2O$ was dissolved in 10ml methanol. A solution of 0.56g, (2.46mmole) of [H_2L] in 10ml ethanol was added to the above mixture. Then of KOH dissolved in methanol and added to the above mixture. The reaction was refluxed for 2 hrs and during thes time, the colour of the mixture became brown. The solution was allowed for slow evaporation and a brown precipitate was formed. Yield 0.62g (43 %), m.p 255°C.

Synthesis of [Fe (HL)$_2$]

The method used to prepare [Fe (H_2L_2)] was analogous to the procedure given for the complex [Mn (HL) $_2$.Cl.H_2O] K, but with $FeCl_2.4H_2O$ 0.25g, (1.25mmole) instead of $MnCl_2.4H_2O$. The quantities of the other regents were adjusted accordingly and an identical work-up procedure gave red purple precipitate 0.76g (60%), m.p 175°C.

Synthesis of [Co (HL)$_2$.H_2O]

In 50 ml round bottomed flask 0.25g, (1.05mmole) of $CoCl_2.6H_2O$ was dissolved in 10ml methanol. A solution of 0.572g, (2.09mmole) of [H_2L] in 10ml ethanol was added to the above mixture, and the reaction was allowed to reflux for 2 hrs. The pale brown precipitated solid which formed upon standing over 24 hrs, was collected, washed with 2ml ether, and dried to give 0.88g (80%) of the title compound, m.p 190 °C.

Synthesis of [Ni (HL)$_2$]

A similar procedure to that described for the complex [Co(HL)$_2$.H_2O] was used to prepare [Ni(HL)$_2$)] but with $NiCl_2.6H_2O$ 0.25g, (1.05mmole) in place of $CoCl_2.6H_2O$ with 0.478g, (2.10mmole) [H_2L] to give an orange precipitate ,which was washed with 2 ml ethyl ether to yield 0.60g (56%) m.p 165°C.

Synthesis of [Cu (HL)$_2$. Cl.H_2O] K

A 0.25g of $CuCl_2$.2H2O, (1.46mmole) was dissolved in 10 ml ethanol. A solution of 0.666g, (2.90mmole) of [H_2L] in 10ml methanol was added and allowed to reflux for 2 hrs. A deep green precipitate was formed, washed with 2 ml ether in order to give 0.68g (31%) m.p 240°C.

Synthesis of [Hg (HL) $_2$]

The method used to prepare [Cu (H_2L_2) Cl.H_2O] was analogous to the procedure given for the complex [Hg (H_2L_2)] but with $HgCl_2$. (0.25g, 0.92mmole) instead of $CuCl_2.2H_2O$.The quantities of the other regents were adjusted according to an identical work-up procedure in order to give a mustard precipitate (0.57g) (48%), m.p 135°C.

Results and Discussion

The I.R spectrum for (H_2L) ligand (Fig.2A), displayed aband at 1491 cm^{1-} due to the υ C=N stretching frequency for the oxime group (8). The band at 3233 cm^{-1} is attributed to the υ O—H stretching of the oxime group. The strong bands at 1014 and 986 cm^{-1} are attributed to υ N—O stretching.

While U.V-Vis aspectrum (Fig.3A) exhibits a high intense absorption peak at 278 nm, 35971 cm^{-1}, ε_{max} =1570 M^{-1} .cm^{-1} and 300nm, 33333cm^{-1} , ε_{max} =1514M^{-1} .cm^{-1} which were assigned to overlap $\pi \rightarrow \pi^*$and n $\rightarrow \pi^*$ transitions(9).

The reaction of [H_2L] ligand with the metals (Mn^{II}, Fe^{II}, Co^{II}, $Ni^{II,}$ Cu^{II} and Hg^{II}) was carried out in methanol under reflux.

All complexes are stable in the solid state and in the solution. The analytical and physical data (Table-1) and spectral data (Table-2 and 3) are compatible with the suggested structures (Fig.1).

The I.R spectral data of the complexes are presented in (Table -2). These spectra, in general show bands at the range 1552-1599 cm^{-1} assigned to the υ C=N stretching for the oxime groups. The shifting to a higher frequency is made in comparison with that of the free ligand, this shifting can be attributed to the delocalisation of metal ion electronic density into the ligand (π- system) (10, 11).

The strong υ N—O stretching bands at 1014 and 996 cm^{-1} for the free ligand are shifted markedly to higher frequencies by ca. 100 cm^{-1}. This is presumably due to coordinated N—O group with the metal ions (12). These results are in agood agreement with those reported by Bigatto and co-workers (13).

The υ O—H stretching band of the oxime group in the free ligand at 3233 cm^{-1} is still present at the (3025-3459) cm^{-1} rang for these complexes.

The bands at 635-523 $cm^{-1}$and 494-635 cm^{-1} were assigned to υ M—N and υ M—O stretching, indicating that the oxime nitrogen and oxygen of hydroxyl group were involved in coordination with metal ion (14-16). The bands at the range 630-660 cm^{-1}, 732-760 cm^{-1} and 829-919 cm^{-1} in the I.R. spectra of complexes Mn, Co and Cu respectively are attributed to υ O—H stretching frequency for coordinated H_2O molecules with metal ion(17). Fig (2B), (2D and (2F) represent the I.R spectra for the complexes Mn, Co and Cu respectively. The electronic spectral data of the complexes are summarised in (Table-3). The U.V-Vis spectra of the complexes displayed absorptions at 275-344 nm assigned to the ligand field and charge transfer (18). In the [Mn (HL) $_2$ .Cl.H_2O] K and [Cu $(HL)_2$.Cl.H_2O] K complexes the peaks at 500nm and 432nm are attributed to d -d electronic transitions type $^4Eg(G) \leftarrow {}^6A_1g$ and $^2B_1g \leftarrow {}^2B_2g$ respectively , suggesting an octahedral structure about Mn and Cu ions. The peak at 855nm in the spectrum of [Fe (H_2L)] (Fig.3C) is assigned to ($^5T_2 \leftarrow {}^5E$ (d -d) electronic transitions, suggesting tetrahedral structure about Fe ion. In the U.V-Vis spectrum of [Ni (HL) $_2$] (Fig.3E), the peak at 747 nm is attributed to (d-d) electronic transition type $^3T_1$ (p) $\leftarrow$ $^3T_1$suggesting asquare planar structure about Ni ion. The U.V-Vis spectrum of [Hg $(HL)_2$] suggests asquare planar structure about Hg ion too. While the peak at 400 nm in the spectrum of the [Co (HL) $_2$) H_2O] is attributed to (d-d) electronic transition type ^4E (F) ← $^4A_2$ suggesting a trygonal bipyramidal structure about Co ion [18]. The molar conductance of the complexes in DMF lies in the 22.9─5.22 ohm^{-1}.cm^2.mole^{-1}range (Table-3) indicates the complexes that are to be neutral (Mn and Cu complexes are electrolyte with 1:1 ratio) (19). The H.P.L.C chromatograms for these complexes [Mn (HL) $_2$) Cl.H_2O] K, [Fe (HL) $_2$] and [Co (HL) $_2H_2O$] Figs. (4-a, b, c) respectively, exhibit one signal at aretention time (t_R= 2.8 min), (t_R= 3.4 min) and (t_R= 4.6 min) indicate the purity of the complexes and appear as a single species in a solution.

References

1. Murmann,R.K. (1957) J. Am. Chem. Soc., 79: 521,
2. Kukushkin ,V. Yu. et al(1996) Coordination Chemistry Reviews 156 :333-362,
3. Finke,R. G .; Schiraldi, D. A. and Mayer,B . (1984).J. coord. Chem. Rev., 54: 1
4. Schrauzer, G. N. (1968) Accounts chem. Res., 1:97
5. Gok, Y. and Kantchin,H. (1997).Polyhedron, 16:2413
6. Gok, Y. and Kantckin,H. (1997) Acta. Chem. Scand., 51:664
7. Kemp,W. (1987)."Organic Spectroscopy" 2nd. Edition, 144,
8. Hadzi, D. and Premru, L. (1967) Spectrochim. Acta, 23A, 35,
9. Abdul-Rahman, A. A. (2002). Ph D. Thesis, Collage of Education Ibn- Al-Heaitham University of Baghdad
10. Hadzi,D. (1956) J. Chem. Soc., 15: 2725,
11. Bigatto,A. ;Costa,G.; Galasso V. and Dealti,G. (1939), (1970) Spectrochim. Acta, 26,
12. Nakamoto ,K. (1996) “Infrared Spectra of Inorganic and Coordination Compounds”4th. Ed. J. Wiely and Sons, New York,
13. Ferraro,J. (1971) “Low Frequency Vibrations of Inorganic and Coordination Compounds ” Ed. Plenum, New York,
14. Najappan, P. ; Ramalingam, K.; Pirro, S. J.; Narr, R. K.; Nowotinik ,D. P.; Nunn, A. D. (1992).Abstracts of papers, Ninth International Symposium on Radiopharmaceutical Chem. Paris 6-10 April
15. EL-Tabl, A. S. (2002)Transition Metal Chemistry, 27:166,
16. Geary,W. J. (1971) Coord. Rev., 7: 81,
17. Green Wood, N.N. and Earnshow,A. (1998)Chemistry of the Elements, Ed. J. Wiley and Sons Inc. New York, 18.A. B. P. Lever, “Inorganic Electronic Spectroscopy”, Ed. New York, (1968).
19. Geary, W. J. (1971) “The use of conductivity measurements in organic solvents for the characterization of coordination compounds”. Coord. Chem. Rev; 7:(81-115)

Table (1): Analytical and physical data of the ligand and its complexes

Compound	Molecular weight M.W	Colour	m.p°C	Yield %	Found, (Calc.)%	
					Cl	Metal
$[H_2L]$	227.27	white			-------	-
$[Mn(HL)_2Cl.H_2O)]K$	599.94	Brown		43	(5.93) 4.86	(9.15) 9.00
$[Fe(HL)_2]$	508.34	Red purple	175	60	------	(10.97) 10.50
$[Co(HL)_2\ H_2O]$	529.54	Pale Brown	190	80	-------	(11.12) 10.90
$Ni(HL)_2]$	511.34	Orange	165	56	-------	(11.47) 11.21
$[Cu(HL)_2Cl.H_2O]K$	608.54	deep green	240	31	(5.84) 3.44	(10.43) 10.11
$[Hg(HL)_2]$	653.14	mustard	135	48	-------	(30.71) 30.53

(Calc.): calculated

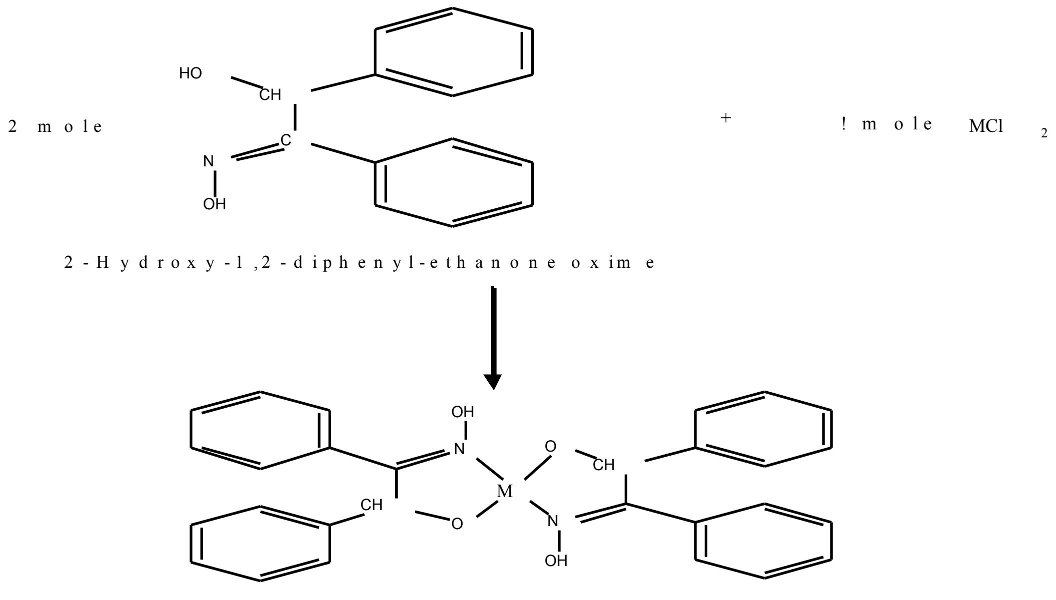
Table (2): I.R spectral data of the ligand and it's complexes

Compound	υ(O-H) oxime υ(O-H) H_2O	υ(C-H) aliph υ(C-H) aroma	υ(C=N) oxime	υ(N-O)	υ(M-N) υ(M-O)	Additional peaks
$[H_2L]$	3233(b) _	2920(w) 3023(w)	1491(sh)	996(sh) 1014(sh)	–	1387 υ(CH_2) 1590 υ(C=C)ring
$[Mn(HL)_2Cl.H_2O)]K$	3350(w) 3249(w)	2925(w) 3057(w)	1552(s)	987(s) 1013(s)	523(w) 501(sh)	1491(C=C) ring
$[Fe(HL)_2]$	3342(br)	2910(w) 3075(br)	1597(sh)	988(s) 1015(s)	591(s) 479(br)	1491υ(C=C) ring
$[Co(HL)_2H_2O]$	3459(w) 3250(w)	2915(br) 3060(br)	1598(sh)	1001(w) 1066(s)	657(sh) 537(w)	1492υ(C=C ring
$[Ni(HL)_2]$	3416(w)	2905(br) 3052(br)	1599(br)	1019(w) 1068(br)	695(sh) 635(w)	1492(C=C)ring
$[Cu(HL)_2Cl.H_2O]K$	3379(br) 3233(w)	2881(w) 3057(br)	1595(s)	1004(s) 1045(w)	597(br) 511(br)	1577(C=C)ring
$[Hg(HL)_2]$	3025(w)	2950(w) 3025(w)	1567(s)	1013(br) 1110(br)	623(w) 494(sh)	1500υ(C=C)ring

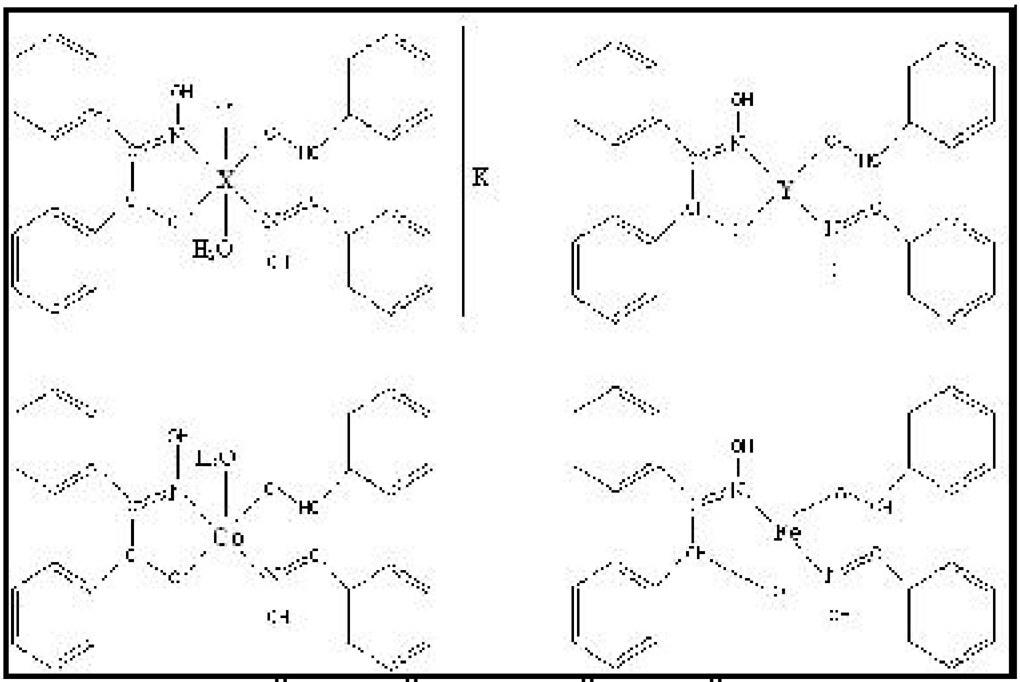
s: strong m: medium w: weak br: broad w.br: weak broad

Table (3): Electronic spectral data, HPLC and conductance measurements of $[H_2L]$ and its complexes

Compound	λ nm	ϵ_{max} $M^{-1}.cm^{-1}$	assignments	M.C* ($ohm^{1}.cm^{2}.mole^{-1}$)	(HPLC) Min.	solvent	Ratio
$[H_2L]$	278	1570	($\pi \rightarrow \pi^*$)	-------	-------		
	300	1514	($n \rightarrow \pi^*$)				
$[Mn(HL)_2Cl.H_2O)]K$	275	551		53	2.8	DMF	1:1
	340	112					
	500	17	($^4Eg(G) \leftarrow {}^6A_1g$)				
$[Fe(HL)_2]$	300	2352		15.43	3.4	DMF	neutral
	342	2127					
	384	1188					
	855	4	($^5T_2 \leftarrow {}^5E$)				
$[Co(HL)_2\ H_2O]$	314	2436		22.9	4.6	DMF	neutral
	400	1700					
	879	5	($^4E(F) \leftarrow {}^4A_2$)				
$[Ni(HL)_2]$	300	1796		12.45	-----	DMF	neutral
	344	1809					
	469	1014					
	747	2	($^3T_1(p) \leftarrow {}^3T_1$)				
$[Cu(HL)_2Cl.H_2O]K$	297	1477		54	-----	DMF	1:1
	432	461	($^2B_1g \leftarrow {}^2B_2g$)				
$[Hg(HL)_2]$	292 450	1154 125	C.T	5.22	-------	DMF	neutral



Scheme (1): The synthesis route of the complexes



Where X=Mn ^{II} and Cu ^{II}; and Y=Ni ^{II} and Hg ^{II}

Fig. (1): The suggested structures for the complexes

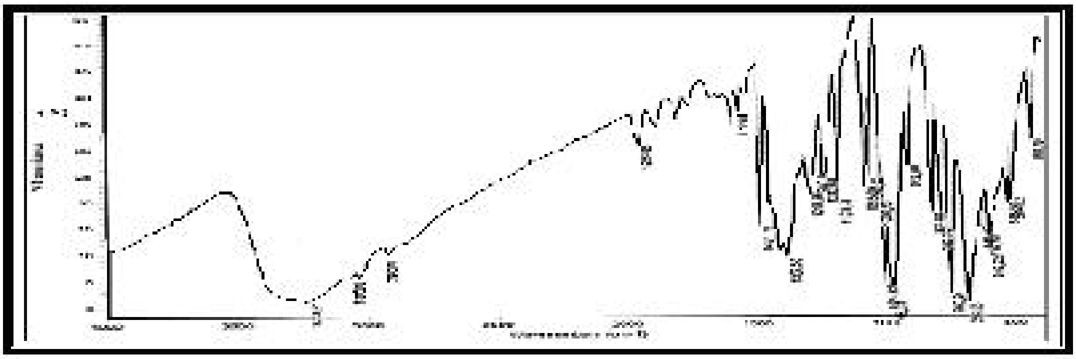


Fig. (2-A) :The (I.R) Spectra of ligand

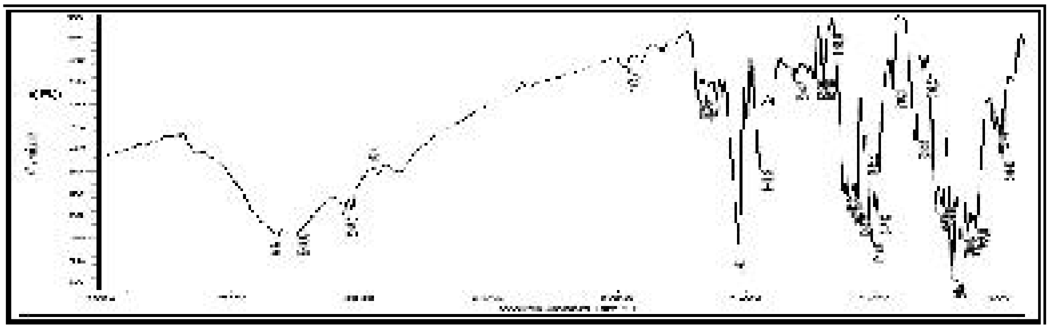


Fig. (2-B):The (I.R) Spectra of the Complex $[Mn (HL)_2.Cl.H_2O]K$

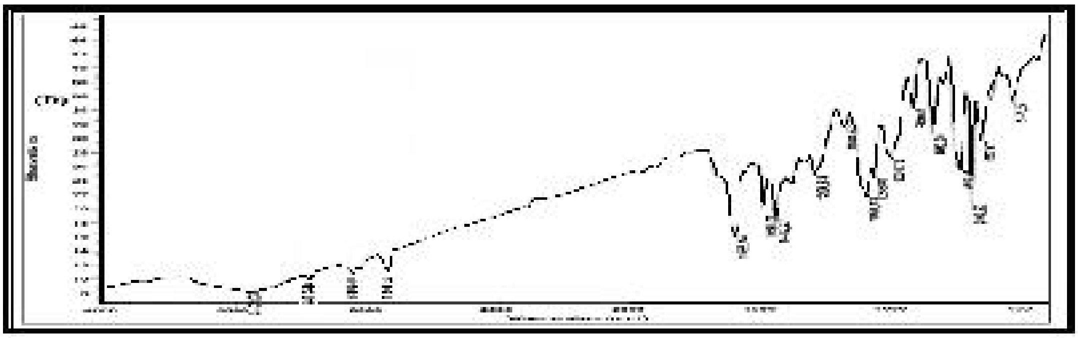


Fig. (2-D): The (I.R) Spectra of the Complex $[Co (HL)_2.H_2O]$

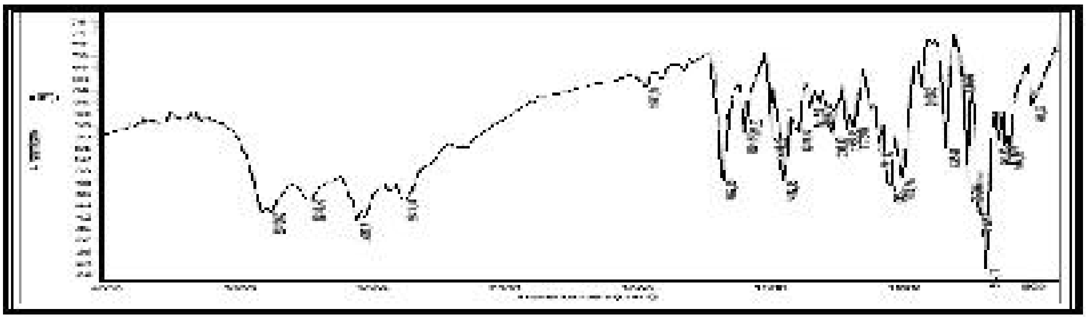


Fig. (2-F): The (I.R) Spectra of the Complex $[Cu (HL)_2.Cl.H_2O]$ K

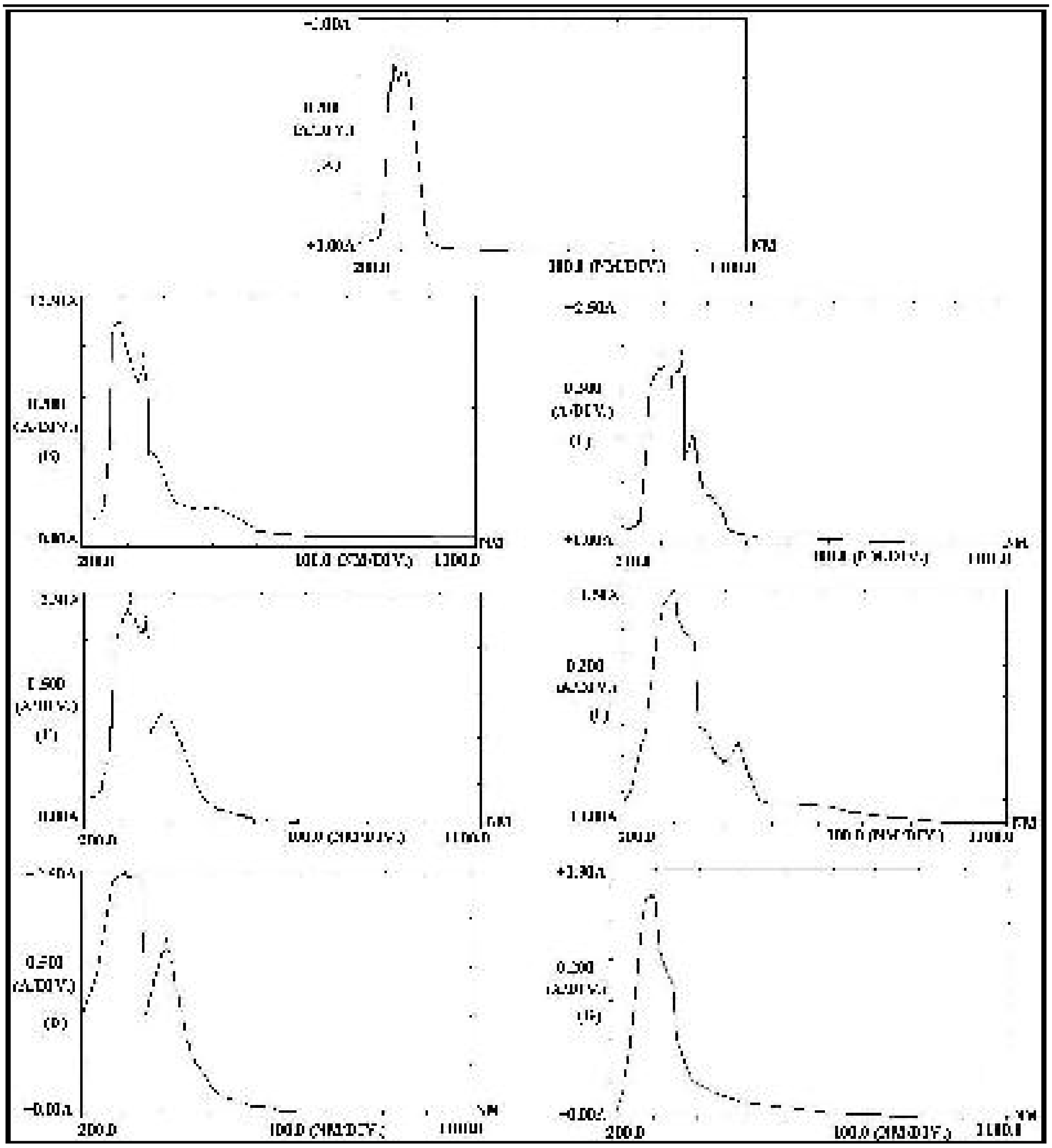


Fig . (3): The (UV-Vis) Spectra of:
(A) The ligand (H_2L)
(B) The complex [Mn (HL)$_2$. Cl.H_2O] K
(C) The complex [Fe (HL)$_2$)]
(D) The complex [Co (HL)$_2$. H_2O]
(E) The complex [Ni (HL)$_2$]
(F) The complex [Cu (HL)$_2$. Cl.H_2O] K
(G) The complex [Hg (HL)$_2$)]

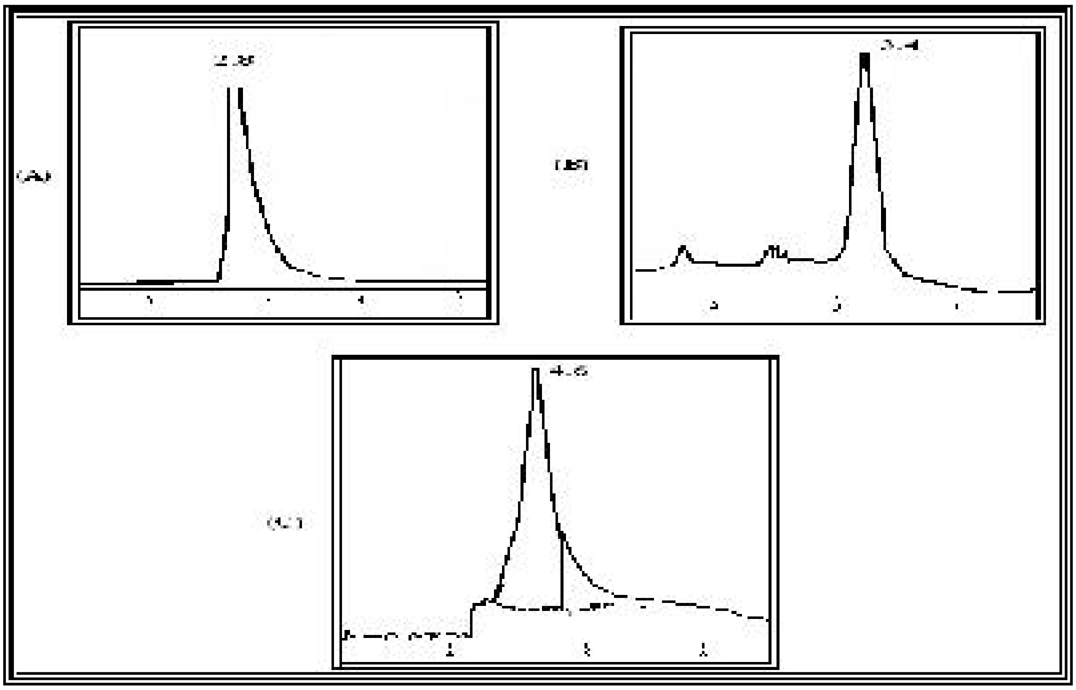


Fig. (4): The H.P.L.C. chromatogram for the complexes of:-
(t_R= min)
(a) [Ni $(HL)_2$] complex
(b) [Fe $(HL)_2$] complex
(c) [Co $(HL)_2$. H_2O] complex

تحضير وتشخيص معقدات رباعية المنح نوع N_2O_2 من تفاعل الليكند 2-hydroxy -1, 2-diphynel-ethanone oxime [H_2L] مع الايونات (Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Hg^{II})

احمد ثابت نعمان ،ايمان ابراهيم الصالحي ،جاسم هاشم الدليمي
قسم الكيمياء ،كلية التربية ابن الهيثم ،جامعة بغداد

الخلاصة

تضمن البحث تحضير وتشخيص المعقدات الجديدة رباعية المنح وذلك من مفاعلة الليكند 2-hydroxy -1, 2-diphynel-ethanone oxime [H_2L] مع الايونات (Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Hg^{II}) باستعمال الميثانول وهيدروكسيد البوتاسيوم وسطا للتفاعل وبنسبة فلز : ليكاند (1:2) تكونت سلسلة جديدة من المعقدات ذي الصيغة العامة:k [$M(HL)_2.Cl.\ H_2O$] و[$M^*(HL)_2.H_2O$] و[$M^{**}(HL)_2$] اذ:
(Where: $M=Mn^{II}$, Cu^{II}, $M^* = Co^{II}$, $M^{**}= Fe^{II}$, Ni^{II} and Hg^{II}.

تم تشخيص المركبات المحضرة بوساطة الطرائق الطيفية الاتية الاشعة تحت الحمراء ،الاشعة فوق البنفسجية والمرئية ، H.P.L.C ، ومطيافية التذرية كذلك قيست التوصيلية المولارية الكهربائيةومحتوى الكلور ومن النتائج المحصول عليها فان الشكل الفراغي المقترح لمعقد النيكل والزئبق هو مربع مستو بينما يتخذ معقد الحديد شكل رباعي السطوح والكوبلت خماسي السطوح وتتخذ معقدات كل من المنغنيز والنحاس شكل ثماني السطوح.