Journal of Kerbala University , Vol. 8 No.1 Scientific . 2010

N_3O_3 Hexanuclear Complexes type are Synthesized and Characterised from the reaction of Diphenylmonoxime with ($Mn^{(II)}$,$Co^{(II)}$,$Ni^{(II)}$,$Cu^{(II)}$,$Zn^{(II)}$, and $Hg^{(II)}$) ions.

معقدات نوع N_3O_3 سداسية المنح حضرت وشخصت من تفاعل الليكاند Diphenylmonoxime مع ايونات (Mn (II), Co (II), Ni (II), Cu (II), Zn (II) and Hg (II))

Ahmad Thabet Numan
Department of chemistry, College of Education, Ibn Al-Haitham, University of Baghdad,
P.O. 4150, Adhamiyah , Baghdad ,Iraq .

Abstract:

The new Hexadentate complexes type $[M(H_3L_3)]K$ were prepared from the condensation reaction of Diphenylmonoxime and KOH with (Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Hg(II)) in methanol with 3:1 ligand : metal ratio to give a series of new complexes of the general formula $[M(H_3L_3)]K$ (where: M(II) = Mn ,Co ,N ,Cu ,Zn and Hg).All compounds have been Characterized by spectroscopic methods [I.R, U.v-Vis, atomic absorption and microanalysis (C.H.N) along with conductivity measurements. The stability constant K and Gibbs free energy ΔG were calculated for $[Co (H_3L_3)] K$, $[Ni (H_3L_3)] K$ and $[Cu (H_3L_3)] K$ and complexes using spectrophotometer method. The obtained values indicate that these complexes stable in their solution. From the above data the proposed molecular structure for complexes (Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Hg(II)) is octahedral structure about the metal ions.

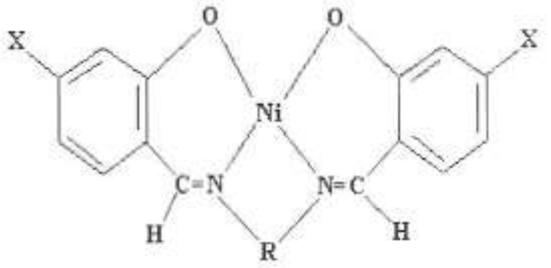
الخلاصة:

تضمن البحث تحضير وتشخيص معقدات جديدة سداسية المنح ذلك من مفاعلة الليكاند Diphenylmonoxime مع الايونات (Mn(II), Co(II), Ni(II), Cu(II),Zn(II) and Hg(II)) تحت التصعيد الارجاعي في الميثانول وسطاً للتفاعل وبنسبة (3:1) وبوجود هيدروكسيد البوتاسيوم تكونت سلسلة جديدة من المعقدات ذوات الصيغة العامة $[M (H_3L_3)] K$

M (II) = Mn, Co, Ni, Cu, Zn and Hg
وبنسبة مولية (3:1) تم تشخيص المعقدات المحضرة بواسطة التحليل الدقيق للعناصر (C.H.N) والمطيافية الذرية وقياسات التوصيلية المولارية ومحتوى الكلور وقياس درجة الانصهار واطياف الاشعة والاشعة فوق البنفسجية. وقد تبين ان البنية المقترحة هي ثمانية السطوح وان دراسة تركيب واستقرارية المعقدات طيفياً بطريقة النسبة المولية اكدت ان النسبه المولية L:M = (3:1) .

Introduction:

Vic-Dioximes have great importance since they are used as chelating agents because of their stable complexes with transition metals. Transition metals complexes with Vic-Dioximes have attracted attention of many researchers because of their similarity to vitamin B_{12} [1, 2].In (Fig-A) the spectra of several chelates with four equivalent ligand atoms of unknown symmetry were better assigned in tetragonal than in tetrahedral symmetry in each example considered.



(Fig-A)

Oxim compounds and their complexes with transition metals play a great importance in medicine, chemistry industry and biochemistry and chemistry [3]. This in turn has stimulated research into the coordination chemistry of ligands having other functions in addition to the oxime function [4].One of the analytical application of oxime compounds is their use as an organic precipitants for transition metals [5] . Oxime amine compounds play an important role in Radiopharmaceuticals and related nuclear medicine [6-8].In (2009) Ersin Guler synthesized unsymmetrical vic-dioximes: anilino-1-acetyl-1-cyclohexeneglyoxime ($C_{14}H_{17}N_3O_2$), benzylamino-1-acetyl-1-cyclohexeneglyoxime($C_{15}H_{19}N_3O_2$), p-toluidino-1-acetyl-1-cyclo hexane glyoxime ($C_{15}H_{19}N_3O_2$) and Their transition metal complexes with Ni(II) and Cu(II) have been synthesized. ^{1}H n.m.r, conductivity measurements, magnetic properties, I.R spectra, elemental analyses and thermal characterizations data of ligands and complexes are given [9].

Experimental:

Reagents were purchased from Fluka and Rediel – Dehenge Chemical Co. I.R spectra were recorded as (KBr) disc 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 solution in (DMF) at 25^0C using a Shimadzu 160 spectrophotometer with $1cm^{-1}$ matched quartz cell .Elemental microanalyses were performed on a (C.N.H) analyzer, model 1106(Carlo-Erba).While metal contents of the complexes were determined by atomic absorption (A.A) technique using a Shimadzu A.A 680G atomic absorption spectrophotometer. Electrical conductivity measurements of the complexes were recorded at 25^0C for 10^{-3}M solutions in (DMF) as a solvent using a PW 9526 digital conductivity meter.

Synthesis of the complexes.

Synthesis of [Mn (H_3L_3)] K.

A 0.25g, (1.26 mmole) of $(MnCl_2.4H_2O)$ was dissolved in (10ml) methanol. A solution of 0.861g (3.78 mmole) of $[H_2L]$ in (10ml) methanol was added to the above mixture. The reaction was allowed to reflux for (2 hrs), during which time the color of the mixture became a brown solution. The solution was allowed for a slow evaporation and a brown precipitate was formed, m.p (160° C), Yield (30%), (1.12g).

Synthesis of [Co (H_3L_3)] K, [Ni (H_3L_3)] K, [Cu (H_3L_3)] K, [Zn (H_3L_3)] K and [Hg (H_3L_3)] K Complexes.

The method used to prepare these complexes was similar to that mentioned in the case preparation [Mn (H_3L_3)] K complex. Table (1) shows the stated weight of starting materials, % yield and some physical properties of the prepared complexes.

Study of formation and stability of complexes:

The ratio L: M was determined by mole ratio method for that a series of solutions of constant molar concentration (10^{-3} mol L^{-1}) of metal ions with a progressive increasing in color concentration of ligand. The optical absorption was measured for each solution at (λ_{max}) of formed complex. Then the ratio of M: L was evaluated by Mole-Ratio Method Fig. (4a).

A series of solutions are prepared which contain equal concentrations of a metal ion but different concentrations of the ligand. The absorbance of each solution is then measured and a plot of the absorbance against the ratio of the number of moles of metal ion to the number of moles of ligand, the stoichiometric formula of the complex can be found by extrapolating the straight-line portions of the graph, which is to say that the point at which these lines intersect corresponds directly to the ratio of metal to ligand in the complex [10].

Also the stability constant K and Gibbs free energy ΔG were calculated.

Results and discussion

The (I.R) spectrum for $[H_2L]$ Fig (2a), display band at (1491) cm^{-1} due to the υ(C=N) stretching frequency for the oxime group [11].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 vibration. While (U.V-Vis) spectrum of the ligand Fig (3a) showed two high intense absorption peaks at (278 nm), ($35971 cm^{-1}$) (ε_{max} = 1570 molar $^{-1}.cm^{-1}$),(300 nm),(33333 cm^{-1}), (ε_{max} = 1514 molar^{-1}cm^{-1}) which assigned to of ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions respectively [12].

The reaction of ligand $[H_2L]$ with the metals [Mn(II),Co(II),Ni(II),Cu(II),Zn(II),and Hg(II)] was carried out in methanol under reflux. These complexes are stable in solution and electrolyte (1:1) systems in DMF (Table-3). The analytical and physical data (Table-1) and spectral data (Table-2) are compatible with the suggested structures.

The I.R spectra of complexes are presented in (Table-2). The I.R spectra of the complexes(1), (2), (3), (4), (5) and (6) show the bands at 3286, 3367, 3255, 3379,3254 and 3369 cm^{-1} respectively which assigned to υ (HO…H) stretching vibration of the hydrogen bonding .This band was shifted to higher frequency in comparison with that of the free ligand at 3233 cm^{-1} [13-14] . The strong band in free ligand (H_2L) at 1491cm^{-1} for the oxime groups (C=N) was shifted to higher frequency by 1597, 1598, 1599, 1595,1600 and 1599 cm^{-1} for the complexes (1), (2), (3) ,(4), (5) and (6) respectively [15-17]. Showing a reducing in the bond order. This can be attributed to delocalization of metal electronic density in the π system of the ligand (HOMO-LUMO) [18].

Where HOMO = highest occupied molecular orbital.
LUMO = lowest unoccupied molecular orbital

The strong υ (N-O) stretching bands at (1014) and (986) cm^{-1} for the free ligand are shifted markedly to higher frequency by ca. (20) cm^{-1}, this is presumably due to coordinated (N-O) with group metal ions [19]. These results are a good agreement with those reported by Bigatto and co-workers [20] The bands at (543-451) cm^{-1} and (500-400) cm^{-1} were assigned to υ(M-N) and υ(M-O) stretching, indicating that the oxime nitrogen's and Oxygen of hydroxyl group were involved coordination with metal ion [21,22] .

The molar conductance data of the complexes in (DMF) (10^{-3}M) found in the range (35-51) Λ_m (Ω^{1}.cm^{2}.$Mole^{-1}$) (Table 3) which indicates that the complexes are electrolyte (1:1) ratio [23].

(U.V-Vis) spectra of complexes display absorption bands at the range (287-301) nm, which assigned to the ligand field and charge transfer transition (24). In the Mn (II) complex (Fig-3b) the band at (357) nm is attributed to d-d electronic transition of type ($^{4}Eg\ (G) \leftarrow {}^{6}A_{1}g$). The bands present in Co (II) complex at (608) and (671) nm were assigned to ($^{4}T_{1}g \leftarrow {}^{4}T_{2}g$), ($^{4}A_{2}g \leftarrow {}^{4}T_{2}g$) respectively [24] (Fig-3c). In the Ni (II) complex the band at (374) nm may be assigned to ($^{4}T_{1}g\ (p) \leftarrow {}^{4}T_{1}g$). While in the Cu (II) complex the band at (430) nm is attributed to d-d electronic transition of type ($^{3}T_{1}g\ (p) \leftarrow {}^{3}A_{2}g$). The absence of d-d transition in the complexes (Zn) and (Hg) are due to the configuration (d^{10}) structure for the metal ions .The positions of the bands in (U.v-Vis.) spectra suggest a octahedral structure to Mn(II), Co(II) , Ni(II) ,Cu(II), Zn(II) and Hg(II).

The atomic absorption analysis and the chloride content results of the complexes are in a good agreement with suggested formula $[M\ (H_3L_3)]\ K$ [25].

The stability constant K and Gibbs free energy were calculated using the method shown above in the experimental part (10) .the equilibrium of the complex metal ion and the ligand for 1:3 mole ratios and K for this ratio is expressed by:

$$M_x^{+2} + 3H_2L \rightarrow [M\ (H_3L_3)]^{-} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$K = \frac{[M\ (H_3L_3)]^{-}}{[M^{+2}]\ [H_2L]^{3}} \quad \ldots\ldots\ldots\ldots\ldots (2)$$

To calculate K, equation 2 was transformed into

$$K = \frac{1 - \alpha}{\alpha^{2}\ C} \quad \ldots\ldots\ldots\ldots\ldots (3)$$

Where C and a the concentration and degree of decomposition of the complex respectively The value α were determined from the equation

$\alpha = (A_m - A_s) / A_m$

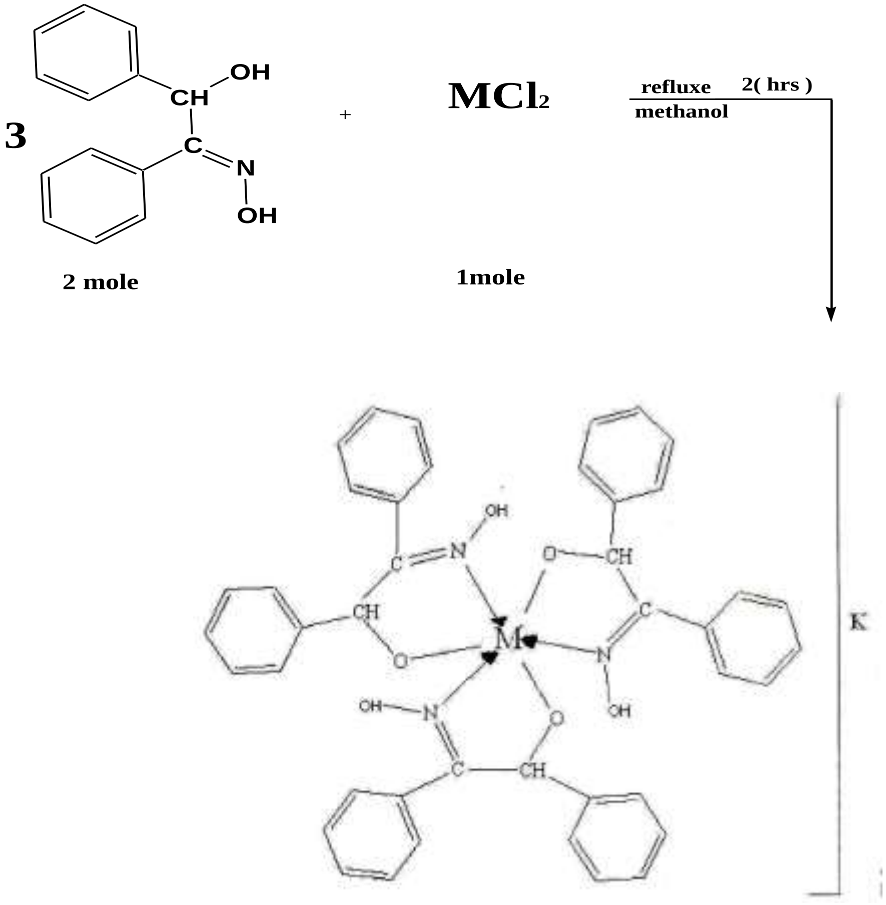
As and Am, are the absorption of the M: L =1:1, M: L=1:2, M: L=1:3, M: L=1:4 and M: L=1:5 respectively. The calculation of ΔG at 300°K was carried out according to following expression

$\Delta G = - 2.303RT \log k$

Where R=8.31 J. $mole^{-1}.K^{-1}$ and T=300°K.

The obtained data is listed in table (4) which shows that the complexes are stable ($\Delta G < 0$)

and there stability increase in the order Ni (II) > Co (II) >Cu (II) because The ionic radius is decrease regularly from Ni to Cu and the crystal field stabilization energy (CFSE) for Ni(II) more than Co(II) and Cu(II) [26].



Scheme (1): Preparation of the metal complexes

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

Compound	M.p ^0C (dec)	M.W	Metal chloride	Color	Weight of metal chloride		Weight of product (g)	Yield %	Found% , (Calc.) %			
					g	m mole			C	H	N	Metal
[H_2L]	-	227.2	-	White	-	-	-	-	(74.92) 73.52	(5.72) 5.43	(6.16) 5..90	-
[Mn (H_3L_3)] K	160	772.8	$MnCl_2.4H_2O$	brown	0.25	1.26	1.12	30	(65.21) 65.02	(4.65) 3.44	(5.43) 5..39	(7.10) 6.98
[Co (H_3L_3)] K	210	776.8	$CoCl_2.6H_2O$	brown Yellow	0.25	1.05	0.87	36	(64.88) 64.77	(4.63) 4.50	(5.40) 5..37	(7.19) 6.03
[Ni (H_3L_3)] K	270	777.6	$NiCl_26H_2O$	Mustard	0.25	1.46	1	41	(64.42) 64.18	(4.62) 4.51	(5.40) 5..26	(7.54) 7.44
[Cu (H_3L_3)] K	170	781.4	$CuCl_2.2H_2O$	Deep green	0.25	1.46	1.22	29	(64.49) 64.37	(4.60) 4.30	(5.37) 5..20	(8.21) 8.02
[Zn (H_3L_3)] K	134	783.3	$ZnCl_2$. H_2O	White	0.25	1.61	1.36	36	(64.43) 64.31	(4.59) 4.40	(5.36) 5..11	(8.35) 8.16
[Hg(H_3L_3)] K	285	918.5	Hg Cl_2	pale Yellow	0.25	0.92	0.78	31	(54.87) 54.60	(3.92) 3.86	(4.57) 4.18	(21.8) 21.70

(Calc): Calculated (dec.): decomposed

Table (2) I.R spectral data of the ligand and its complexes

Compound	υ(O-H) oxime	υ (C-N) oxime	υ(C-H) alph υ(C-H) aroma	υ (N-O)	M-N M-O	Additional peaks
$[H_2L]$	3233(w)	1491(w)	2920(br) 3030(w)	987(s) 1014 (s)	- -	υ (C=C) ring 1590 υ (CH_2)1387
$[Mn (H_3L_3)]$ K	3286(w)	1597(s)	2930(w) 3075(w)	988(s) 1069 (s)	523(w) 500(w)	υ (C=C) ring 1492
$[Co (H_3L_3)]$ K	3367(br)	1598(sh)	2945(w) 3055(br)	1002(s) 1035 (s)	543(s) 404(w)	υ (C=C) ring 1492
$[Ni (H_3L_3)]$ K	3255(w)	1599(sh)	2930(br) 3035(br)	987(w) 1016 (s))	451(sh) 400(w)	υ (C=C) ring 1492
$[Cu (H_3L_3)]$ K	3379(w)	1595(br)	2890(br) 3085(br)	1013(w) 1042 (br)	512(br) 500(w)	υ (C=C) ring 1491
$[Zn (H_3L_3)]$ K	3254(br)	1600(s)	2930(W) 3040(br)	987(s) 1037 (w)	487 (br) 469(sh)	υ (C=C) ring 1491
$[Hg(H_3L_3)]$ K	3369(w)	1599(s)	2910(Wr) 306a0(w)	1014(br) 1027 (br)	524(w) 499(sh)	υ (C=C) ring 1551

Recorded as KBr

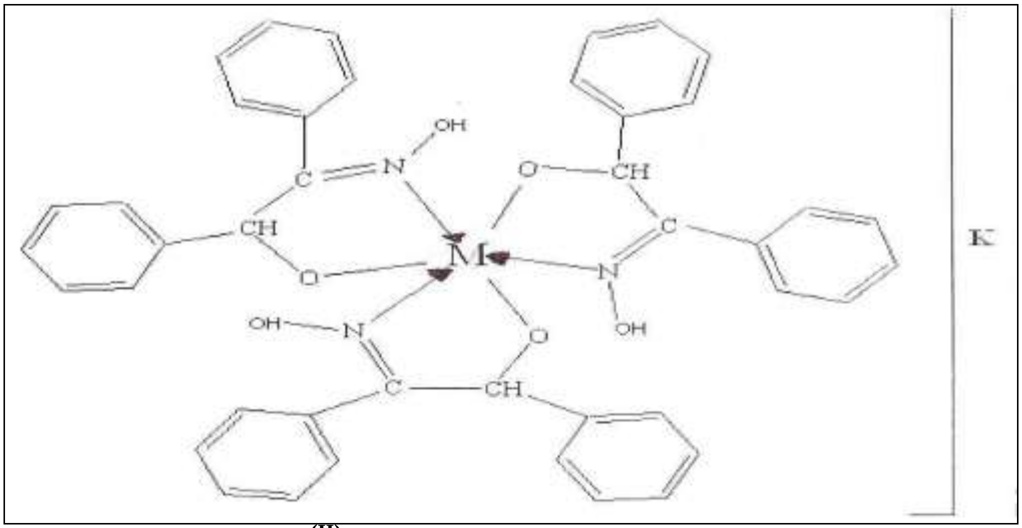
s:strong m:medium w:weak br:broad w.br: weak broad

Table (3): Electronic spectral data, and conductance measurement for the ligand $[H_2L]$ and its complexes

Compound	λ nm	ε_{max} Molar Cm^{-1}	assignments	Λm $(\Omega^{1}.cm^{2}.Mole^{-1})$
$[H_2L]$	278	1578	$\pi \rightarrow \pi^*$	
	300	1514	$n \rightarrow \pi^*$	
$[Mn (H_3L_3)] K$	299	2429	Ligand Field	35.1
	357	910	d-d transition	
$[Co (H_3L_3)] K$	218	1864	Ligand Field	45
	385	994	C.T	
	608	149	d-d	
	671	159	d-d	
$[Ni (H_3L_3)] K$	301	2501	Ligand Field	41.1
	374	1246	d-d transition	
$[Cu (H_3L_3)] K$	297	1610	Ligand Field	51.1
	320	1430	Ligand Field	
	370	1100	C.T	
	430	431	d-d transition	
$[Zn (H_3L_3)] K$	298	1109	C.T	48.3
$[Hg (H_3L_3)] K$	296	1332	Ligand Field	40.5
	330	970	C.T	

Table (4) stability constant and ΔG at 300°K of complexes

compounds	As	Am	α	°K	Log K	ΔG KJ/mole
$[Co(H_3L_3)]K$	0.62	0.651	0.047	431416.9	5.634	- 32.346
$[Ni(H_3L_3)]K$	1.25	1.29	0.031	1008324.66	6.003	- 34.465
$[Cu(H_3L_3)]K$	0.41	0.44	0.0681	200494.6	5.302	- 30,440



$M^{(II)}$ = Mn, Co, Ni, Cu, Zn and Hg

Figure (1) the suggested structure for the complexes

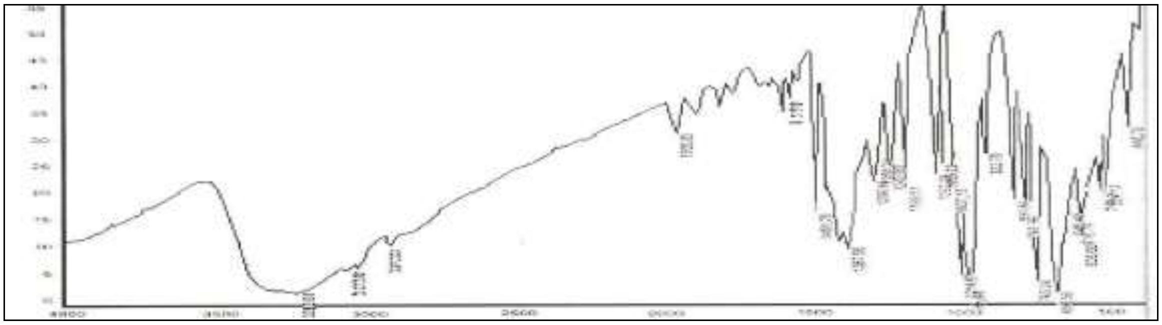


Fig (2a) .The I.R. Spectrum of the ligand $[H_2L]$

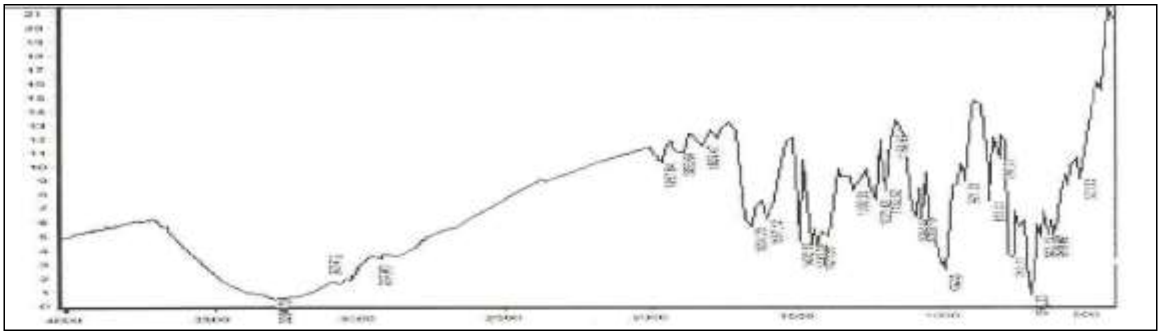


Fig (2b) .The I.R. Spectrum of the complex $[Mn (H_3L_3)]$ K

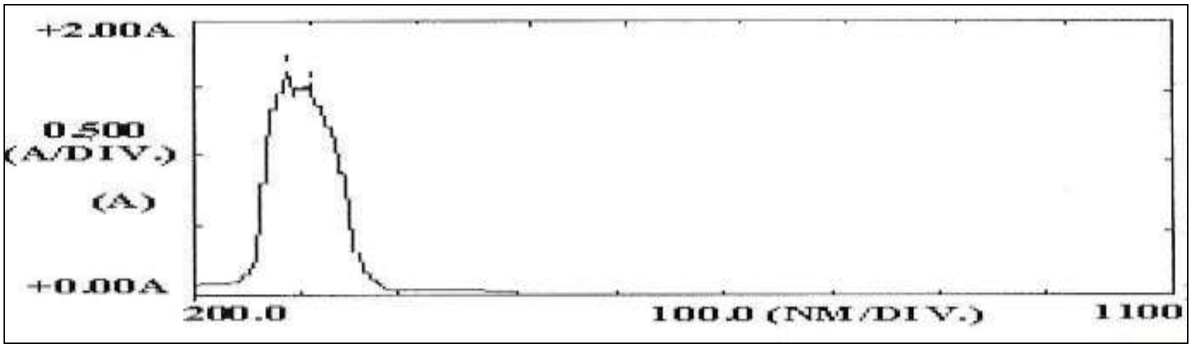


Fig (3a) .The U.V Spectrum of the ligand [H_2L] in DMF ($1x10^{-3}$ M)

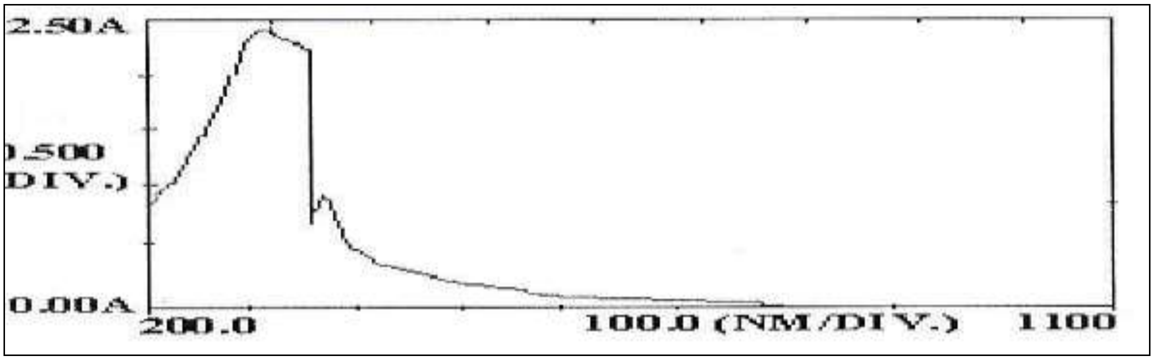


Fig (3b) .The U.V Spectrum of the complex [Mn (H_3L_3)] K in DMF ($1x10^{-3}$ M)

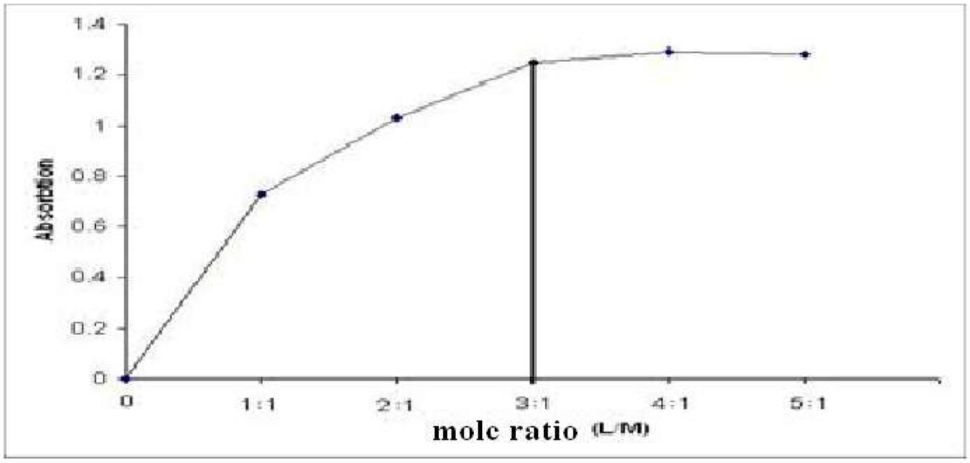


Fig (4a) The mole ratio curve to complex [Ni (H_3L_3)] K in solution (1×10^{-3} mole/L) at (λ= 374 nm)

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