Synthesis and characterization of mixed ligand complexes of some metals with 1-nitroso-2-naphthol and L-leucin

F.H, Ghanim

Chemistry Department .Ibn -Al-Haithem College of Education,
University of Baghdad-IRAQ

Receiving Date: 2010/12/23 - **Accept Date:** 2011/5/8

Abstract

The mixed ligand complexes of Mn(II),Fe(II),Co(II),Cd(II), and Pb(II) with 1- nitroso-2-naphthol ($C_{10}H_7NO_2$), symbolized (NNPhH)] and amino acid [L-leucin **(**$C_6H_{13}NO_2$**)**, symbolized (LeuH), were synthesized and characterized by: Melting points, Solubility, Molar conductivity, and determination the percentage of the metal in the complexes by flame(AAS), magnetic susceptipibility , Spectroscopic Method [FT-IR and UV-Vis], And Program [Chem office- CS.Chem.- 3D pro 2004] was used.

The results showed that the deprotonated two ligands acts as a bidentate ligand , (leu-) was coordinated to the metal ions through the oxygen of the carboxylic group and the nitrogen of the amine and the 1-nitroso-2-naphthol ligand was coordinated to the metal ions through the oxygen and nitrogen atoms . Octahedral geometry for M(II) are proposed.

تحضير وتشخيص معقدات مختلطة الليكاند من (1- نتروزو 2- نفثول وحامض الليوسين) مع بعض أيونات العناصر الانتقالية

فائزة حسن غانم

جامعة بغداد / كلية التربية - ابن الهيثم / قسم الكيمياء

Synthesis and characterization of mixed ligand complexes of some metals with 1-nitroso-2-naphthol and L-leucin

F.H, Ghanim

تضمن هذا البحث تحضير وتشخيص معقدات ذات ليكاندات مختلطة للأيونات الفلزية وPb(II) من الليكاند (1- نتروز 2- نفثول) ($C_{10}H_7NO_2$) بالرمز (NNPhH) Mn(II),Fe(II),Co(II),Cd(II) مع حامض الليوسين ($C_6H_{13}NO_2$) بالرمز (LeuH) .

المعقدات المحضرة بلورات صلبة درست من النواحي الأتية:

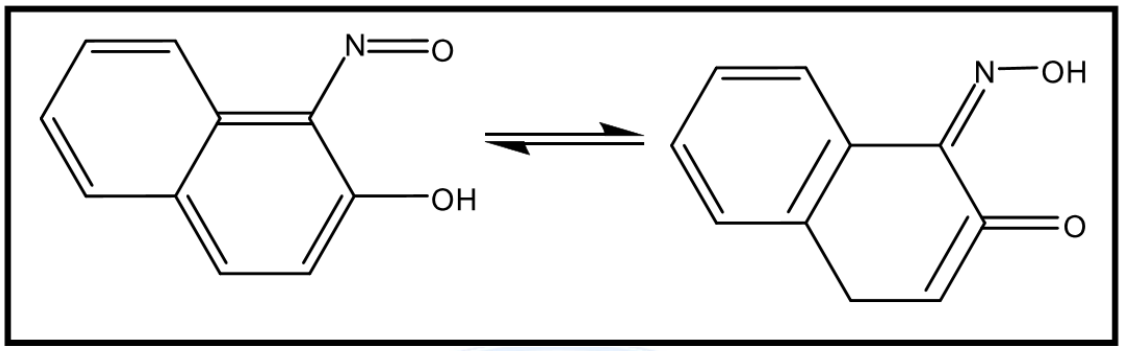
درجات الانصهار، التوصيلية الكهربائية المولارية، الذوبانية، الخواص المغناطيسية، تقدير النسبة المئوية للأيون الفلزي في المعقدات بوساطة مطيافية الامتصاص الذري، الدراسات الطيفية: وتضمنت أطياف (الأشعة تحت الحمراء، الأشعة فوق البنفسجية – المرئية، مع استعمال البرنامج (Chem. Office- Cs. chem- 3D pro 2004) في رسم أشكال المعقدات.

INTRODUCTION

1-nitroso-2-naphthol (IUPACName:1-nitrosonaphthalen-2-ol)

($C_{10}H_7NO_2$)

is crystalline solid, sparingly soluble in water and readily soluble in alcohol ,ether and common organic solvent. The melting point is equal to 103-106° C, Orthosubstituted nitrosonaphthols can undergo tautomerisation to give oxo-oximes. (Figure- 1) In the case of 1-nitroso-2-naphthol, the equilibrium is greatly displaced toward keto-form and the compound has, in the solid state and in solution, a predominately quinone which is a hybrid of resonance forms of the type [1-5]. Disodium 1-nitroso-2-naphthol-3,6-disulfonate (nitroso-R salt) was introduced in 1921 by Van Klooster for the detection of cobalt(II) and then subsequently used by various investigators for the determination of small quantities of metals in various samples. It is also a sensitive and specific reagent for Fluor metric determinations of tyrosine residues in proteins and peptides [6] Along with other phenols and naphthols, it belongs to biologically important com pounds, especially because of its cytotoxic action.



Figur-1:Tautomerisation in 1-nitroso-2-naphthol

During the recent years , there has been significant interest in the coordination chemistry , the structural properties and the reactivity of metal complexes of amino acids . [7-10]

L-leucin is one of the twenty major amino acids and is considered an essential amino acid. Inorganic elements like transition metals are vital to the proper functioning of the body's processes. Metal ions have the ability to form strong bonds and be stable in more than one oxidation state.[11]

Experimental

a- Reagents and instruments: L-leucin was purchased from (Merck) ,1 -Nitroso-2-naphthol a Fluka Chemie AG, metals chloride and solvents from (B.D.H). The reagents were used without further purification .

b- Instruments: FT-I.R spectra were recorded as KBr discs using Fourier transform Infrared Spectrophotometer Shimadzu 24 FT-I.R 8400s. Electronic spectra of the prepared complexes were measured in the region (200- 1100) nm for 10^{-3}M solutions in ethanol at 25°C using shimadzu-U.V-160. A Ultra Violet Visible-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 Japan A.A-67G Shimadzu. Electrical conductivity measurements of the complexes were recorded at 25°C for 10^{-3} M solutions of the samples in Ethanol using pw 9527 Digital conductivity meter (Philips). Melting points were recorded by using Stuart melting point apparatus.

The proposed molecular structure of the complexes were determinated by using chem. office prog, 3DX (2004).

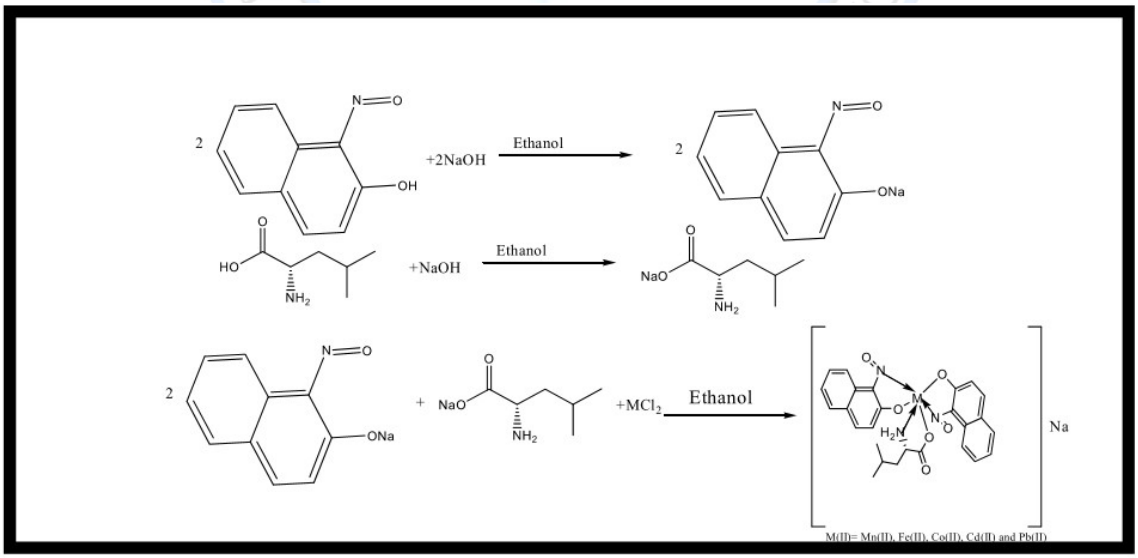
c- **General synthesis :**

a) Sodium leucinate(Na^+Leu -) : L-leucin [0.131 gm, 1 mmol] was dissolved in 10 ml ethnol and added to 10 ml of ethnolic solution containing [0.04 gm (1mmol)] of the sodium hydroxide , the solution was deprotonated according to the following reaction (scheme -1)

b) sodium 1-Nitroso-2-naphthol ate (Na^+NNPh -):

1-nitroso-2-naphthol ((NNPhH)**]**) [0.346 gm(2mmol)] was dissolved in 10 ml ethanol and added to (10) ml of ethanolic solution containing [0.08 gm (2mmol)] of the sodium hydroxide , the solution was deprotonated according to the following reaction (scheme -1)

c) Synthesis of complexes: The complexes were prepared by the addition of ethnolic solutions of the (Na^+NNPh $^-$) and (Na^+Leu $^-$) to warm stirred ethnolic solution of therespective metal (II) chloride in the stoichiometric ratio matel:ligand (M:2 NNPh: Leu) in (20 min). The mixture was stirred for half an hour at room temperature , crystalline precipitates was observed . The resulting precipitates were filtered off , recrystallized from ethanol and dried at 50°C○ . according to the following reaction (scheme -1).



Scheme (1): Synthesis of the Na [M ($C_{26}H_{24}N_3O_6$)] complexes

Results and Discussion

All the complexes are colored, non-hygroscopic and thermally stable solids (Table1), indicating a strong metal-ligand bond. The complexes are insoluble in water but soluble in common organic solvents such as ethanol, ethyl alcohol, acetone, chloroform ,DMF and DMSO.

The observed molar conductance (Table1) values measured in ethanol in 10^{-3}M solution lie in the (37-42) Ω^{-1} cm^2 mol^{-1} range, indicating their electrolytic nature with(1:1).[12-13]

The atomic absorption measurements (Table-1) for all complexes gave approximated values for theoretical values.

In conclusion, our investigation this suggest that the ligands L-leucin and 1-nitroso-2- naphthol coordinate with M (II) forming Octahedral geometry (Figur-2) .

Figure (3), Table (2), displays the (FT-IR) spectrum for the (L-leucin) exhibited a band around υ (3417) cm^{-1} that corresponds to the stretching vibration of υ (N-H) +υ (O-H), while another strong absorption band at υ (3070) cm^{-1} is due to the υ (NH_2) sym while the bands at (1585) cm^{-1} and (1415)cm^{-1} were assigned to the υ (- COO)asy and υ (-COO)sym respectively. υΔ (-COO)asy-sym =170 cm^{-1}. [14]

Figure (4) ,Table (2), displays the (FT-IR) spectrum for the(1-nitroso-2-naphthol) which exhibits very strong band at (1616)cm^{-1} due to υ(C=O) stretching vibration. [14-15] The band at (3425)cm^{-1} is due to the υ(O–H) stretching vibration [14] . The band at (1523)cm^{-1} is due to the υ(C=N) while the bands at (1450) and (2790)cm^{-1} were assigned to the υ(C=C) aromatic and υ(C–H) aromatic stretching respectively. The band at (3066)cm^{-1} were assigned to υ(HO---H) hydrogen bonding [15,16] and the band at (1153) cm^{-1} is due to the υ(N-O) stretching vibration. The complexes show band at (590-520) and (470-489) cm^{-1} rang, due to the ν(M-N) and ν (M-O) vibrations respectively. [14-16]

Electronic spectra

The electronic spectral data of the free ligands 1-nitroso-2-naphthol and L-leucin and their complexes are summarized in table-3. The u.v-vis spectra of the free ligand (1-nitroso-2-naphthol) in ethanol solvent appeared a high, intense absorption bands at (**304**nm) (**32894** cm^{-1}) ($\in$max=**937** $molar^{-1}.cm^{-1}$) and at (**383**nm) (26109cm^{-1}) ($\in$max =**2238** $molar^{-1}.cm^{-1}$).

These bands are attributed to ($\pi\rightarrow\pi^*$)and ($n\rightarrow\pi^*$) transitions respectively. The electronic spectra of leucin show an absorption band at 305 nm (32786cm^{-1}) in ethanol . The (UV-Vis) spectra of the complexes displayed absorptions at (301-334) nm assigned for ligand field. the (UV-Vis) spectrum of $[Co(C_{26}H_{24}N_3O_6)]$-complex band observed at (412) nm are attributed to (d-d) transitions of type $T_{1g}(F)\rightarrow {}^4T_{2g}(P)$. [17-18]

The complex of $[Cd(C_{26}H_{24}N_3O_6)]$- complex exhibits two bands at (304 and 385) nm assigned to charge –transfer transitions [17]. Figures(7-10) From the above data ,we suggested that the geometry of the all complexes are octahydral.

Table 1-The physical properties of the complexes

Compound / Ligand	M.wt	Color	M.p°c (de) °c	Λm $\mu Scm^{-1}.Mol^{-1}$	Metal%		CI%
					theory	exp	
$C_6H_{13}NO_2$ (leu)	131.18	white	289	1.24	-	-	-
1-nitroso-2-naphthol ($C_{10}H_7NO_2$)	173.17	dark-Brown	106	1.77	-	-	-
$[Mn(C_{26}H_{24}N_3O_6)]Na$	529.45	dark-Brown	240 de	37	10.83	11.2	Nill
$[Fe(C_{26}H_{24}N_3O_6)]Na$	530.36	green	228 de	39	10.53	11	Nill
$[Co(C_{26}H_{24}N_3O_6)]$ Na	533.51 3	red	265 de	38	11.05	13	Nill
[Cd ($C_{26}H_{24}N_3O_6$)] Na	586.92	green	206 de	42	19.15	21	Nill
$[PMC_{26}H_{24}N_3O_6)]$ Na	681.71	green	236 de	40	30.40	29	Nill

Λm = Molar Conductivity de = decomposition

Table (2) FT-IR spectral data of the Ligands and their complexes

Compound	υ(N-H) + υ (O-H)	υ $(C-H)_{cy}$ $(C-H)_{ali}$	υ (C=O)	υ (C=N)	υ (N-O)	υ $(-COO)_{asy}$	υ $(-COO)_{sym}$	M-N	M-O
$C_6H_{13}NO_2$ (leu)	3417m	1580s	-	-	-	1585vs	1415vs	-	-
1-nitroso-2-naphthol ($C_{10}H_7NO_2$)	3425s-br-3066w	2790vw	1616vs	1523vs	1153m	-	-	-	-
$[Mn(C_{26}H_{24}N_3O_6)]Na$	3471s 3062m	2931s 2870w	1616s	1589vs	1134vs	1508vs	1411s	532s	489s
$[Fe(C_{26}H_{24}N_3O_6)]Na$	3402vs	2924m	1610vs	1550m	1139vs	1506vs	1355vs	590m	480vs
$[Co(C_{26}H_{24}N_3O_6)]$ Na	3444vs 3062w	2954w	1647m	1597s	1268m	1516vs	1357m	559m	489s
$[Cd\ (C_{26}H_{24}N_3O_6)]$ Na	3444s 3259w	2954w	1616m	1593m	1246s	1543vs	1346s	578m	470s
$[Pb(C_{26}H_{24}N_3O_6)]$ Na	3448vs 3043w	2954w	1624s	1558s	1288s	1477m	1361 m	520m	470s

Table 3- Electronic Spectral data, magnetic moment, of the studied complexes and two Ligands

Compounds	λ (nm)	υ′(cm^{-1})	ε(max) L.mol. cm^{-1}	μ_{eff} (BM)	Assignment
$C_6H_{13}NO_2$ (leu)	305	32786	310	-	$\pi\rightarrow\pi^*$
l-nitroso-2-naphthoI ($C_{10}H_7NO_2$)	304 383	32894 26109	937 2238	-	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$
[Mn($C_{26}H_{24}N_3O_6$)]Na	301 417 827	33222 32980 12091	1134 1760 365	5.92	Ligand field $A^6 1g\rightarrow {}^4T_2g$ (G) $A^6{}_{1g}\rightarrow T_{1g}$ (G)
[Fe($C_{26}H_{24}N_3O_6$)]Na	304 378 798	32894 26455 12531	470 798 176	4.90	Ligand field C.T $^5T_{2g}\rightarrow {}^5E_{2g}$
[Co($C_{26}H_{24}N_3O_6$)] Na	314 412	31847 24271	2242 2328	3.87	Ligand field $T_{1g}(F)\rightarrow {}^4T_{2g}(P)$
[Cd ($C_{26}H_{24}N_3O_6$)] Na	304 385	3289 25974	1290 1865	Diamag	C.T C.T
[PM$C_{26}H_{24}N_3O_6$)] Na	339 377	29498 26525	2475 2446	---	Ligand field C.T

C.T= Charge transfer

Proposed molecular structure :

Studying complexes on bases of the above analysis , the existence of hexa coordinated $[M(C_{10}H_6NO_2)_2\ (C_6H_{12}NO_2)]^-$,were M(II)= Mn(II), Fe(II), Co(II), Cd(II) and Pb(II). proposed models of the species were built with chem3D shows in **Figure** -2.

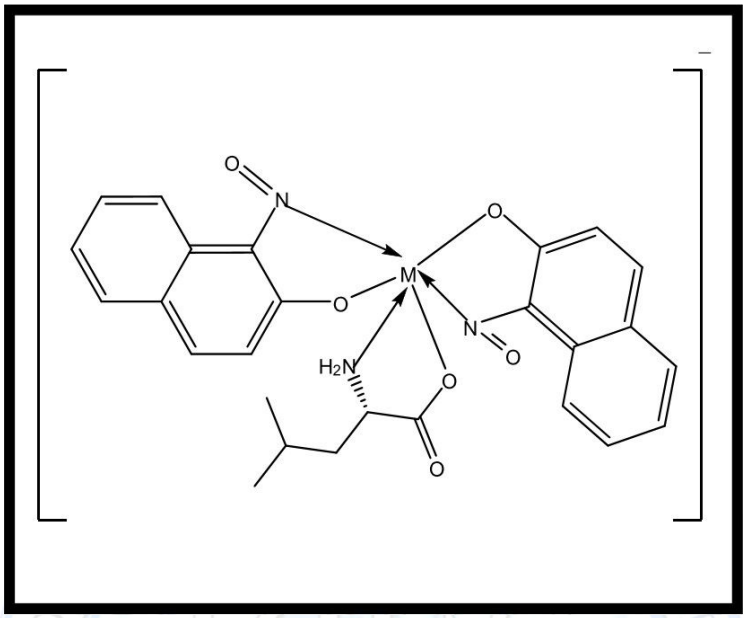


Figure (2):The suggested structure for the complexes $Na[M(C_{10}H_6NO_2)_2 (C_6H_{12}NO_2)]$
M(II)= Mn(II), Fe(II), Co(II), Cd(II) and Pb(II).

Nomenclature of prepared complexes:

Table (4) shows empirical formula and nomenclature (IUPAC) with abbreviated.

Table (4) Nomenclature of prepared complexes

Complexes	Nomenclature	Abbreviation
Na $[Mn(C_{26}H_{24}N_3O_6)]$	Sodium(L-leucinato)bis(1-nitroso-2-aphtholato)manganese(II).	$[Mn(NNPh)_2(leu)$ Na
Na $[Fe(C_{26}H_{24}N_3O_6)]$	Sodium (L-leucinato) bis (1-nitroso-2-naphtholato) ferrate(II)	$Na[Fe (NNPh)_2(leu)]$
Na $[Co(C_{26}H_{24}N_3O_6)]$	Sodium (L-leucinato) bis (1-nitroso-2-naphtholato)cobalt (II)	$Na[Co(NNPh)_2(leu)]$
Na $[Cd (C_{26}H_{24}N_3O_6)]$	Sodium (L-leucinato) bis (1-nitroso-2-naphtholato)cadmium(II)	$Na[Cd(NNPh)_2(leu)]$
Na $[Pb(C_{26}H_{24}N_3O_6)]$	Sodium (L-leucinato) bis (1-nitroso-2-naphtholato)lead(II)	$Na[Pb(NNPh)_2$ (leu)]

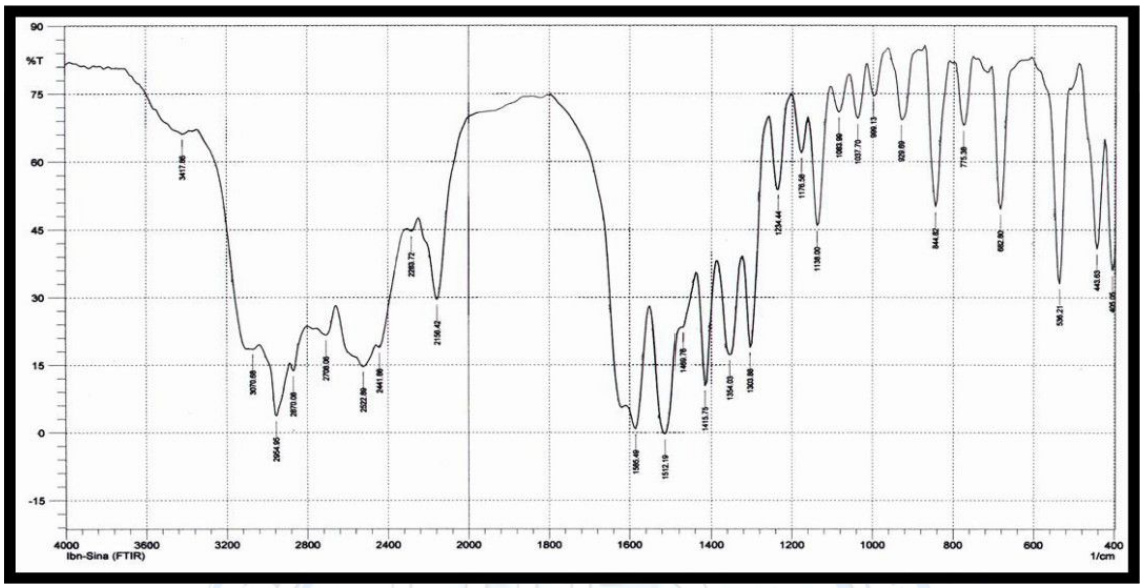


Figure .(3) FT- IR Spectrum of leucine $C_6H_{13}NO_2$

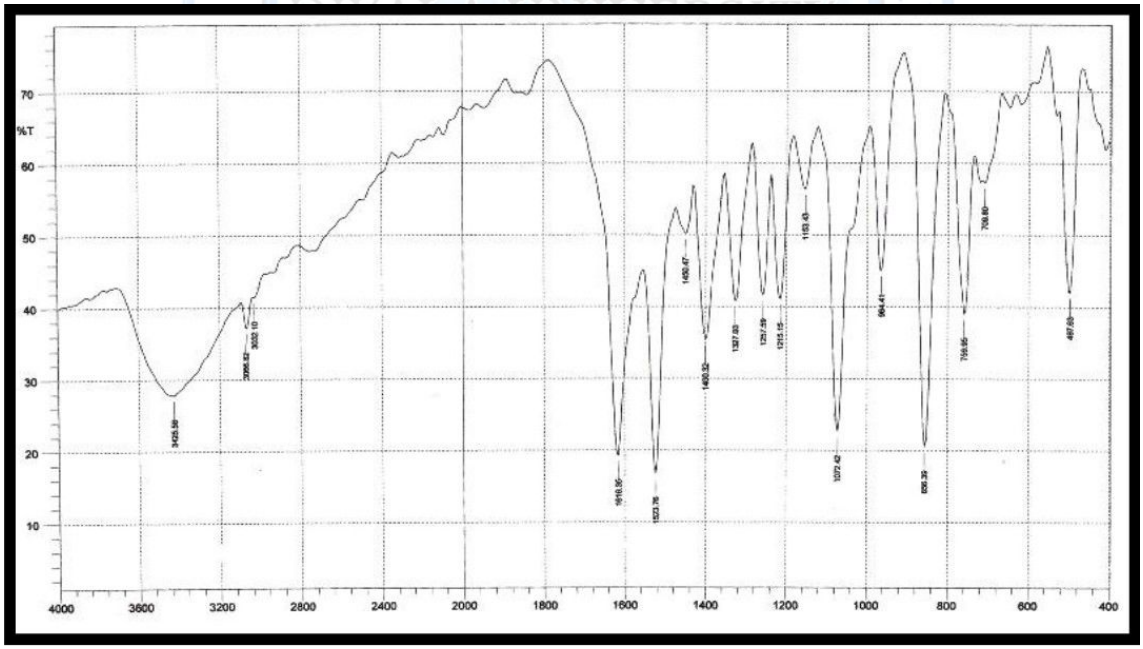


Figure .(4)FT- IR Spectrum of 1-nitroso-2-naphthol ($C_{10}H_7NO_2$)

Synthesis and characterization of mixed ligand complexes of some metals with 1-nitroso-2-naphthol and L-leucin

F.H, Ghanim

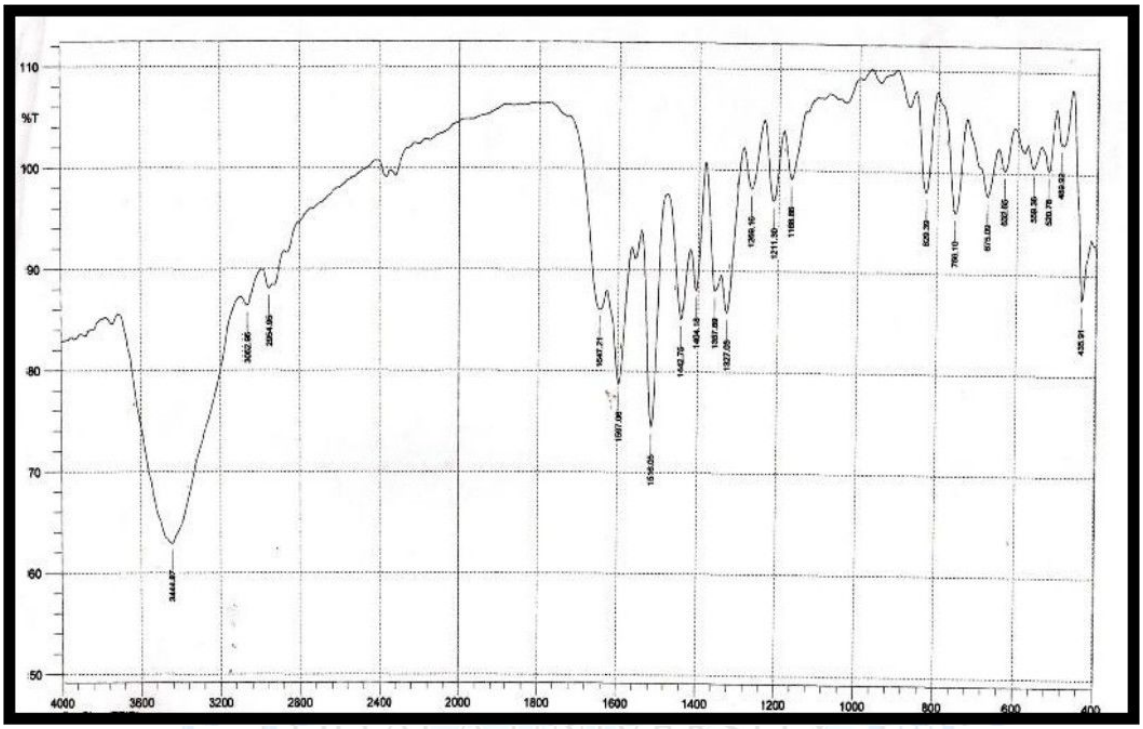


Figure .(5)FT- IR spectrum of $Na[Co(C_{26}H_{24}N_3O_6)]$

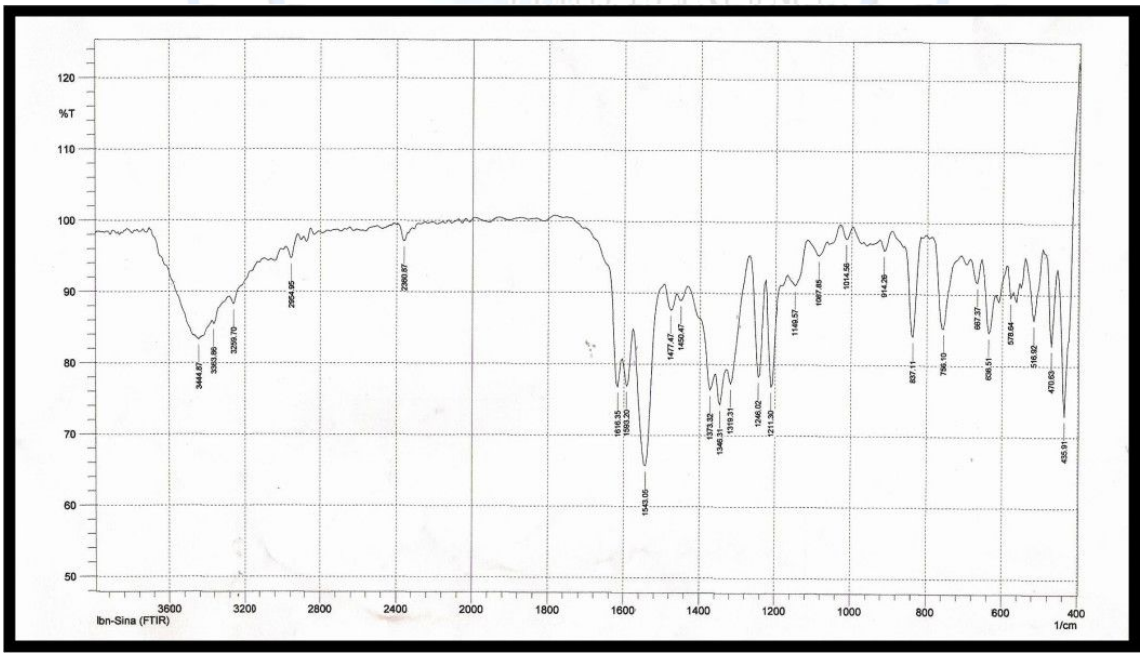


Figure .(6)FT- IR Spectrum of $Na[Cd(C_{26}H_{24}N_3O_6)]$

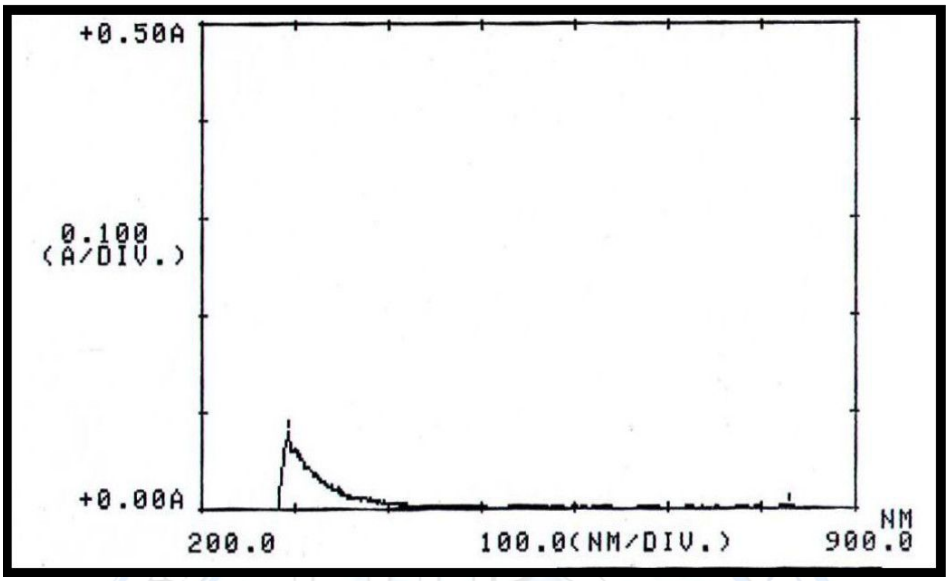


Figure. (7)The (UV-Vis) Spectra of L-leucin

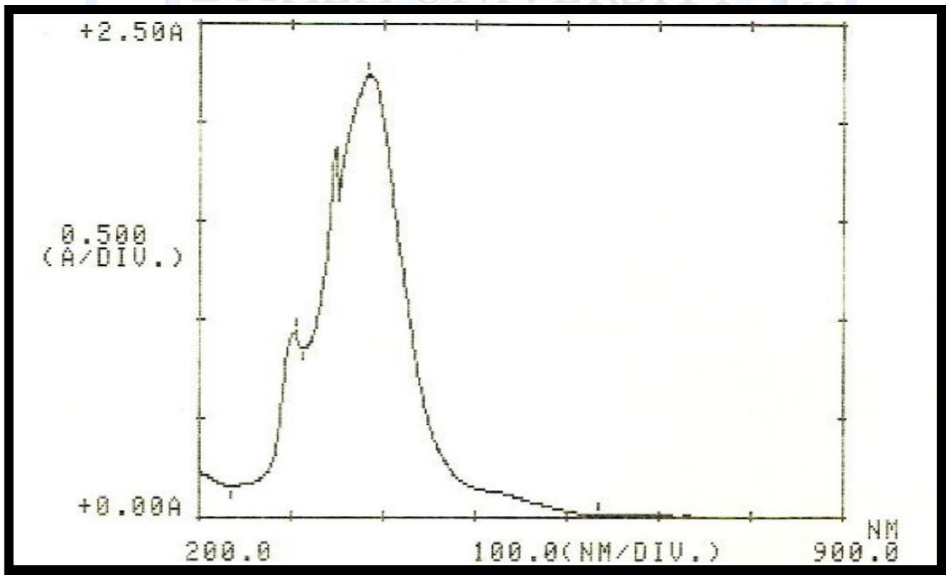


Figure.(8)The (UV-Vis) Spectra of 1-nitroso-2-naphthol

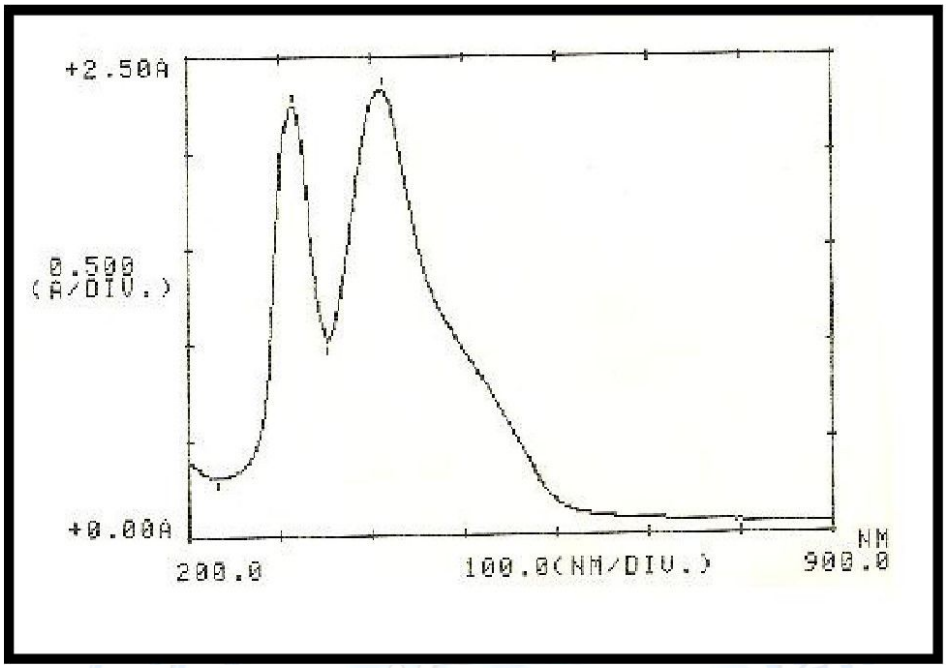


Figure.(9) The (UV-Vis) Spectra of Na[Co($C_{26}H_{24}N_3O_6$)]

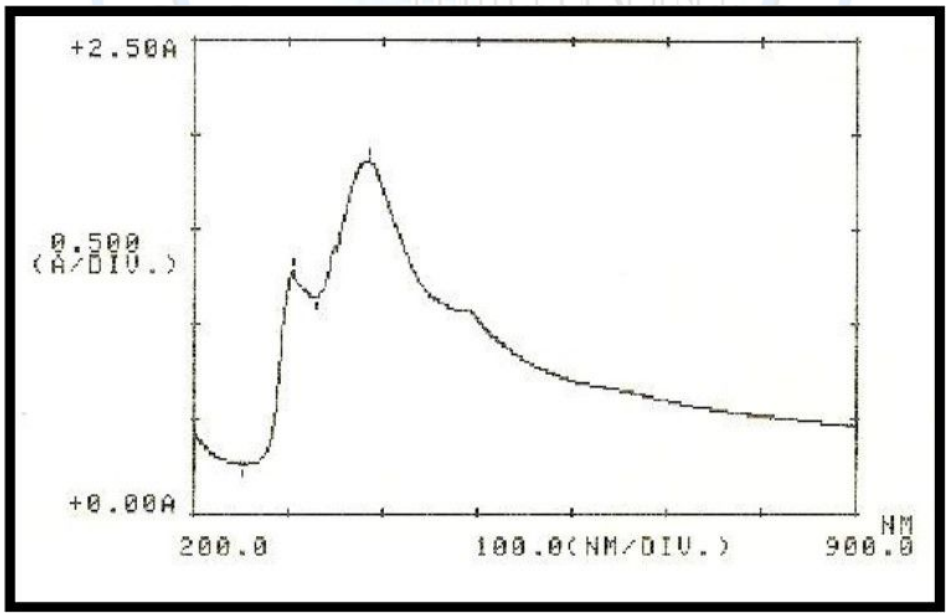


Figure.(10) The (UV-Vis) Spectra of Na[Cd ($C_{26}H_{24}N_3O_6$)]

REFERENCES

1. Bla`enka Foreti and Nicoletta Burger ,J Croatica Chemica Acta 75 (1) pp51-58 (2002)
2. M. Burawoy, M. Cais, J. T. Chamberlein, F. Liversedge, and A. R.Thompson, J Chem. Soc.pp 3727– .3733 (1955)
3. K. K. Chatterjee, Anal. Chim. Acta 20 pp423–427 (1959) .
4. M.A. Taher, Anal. Sci. 16, pp501-506 (2000) .
5. M.A. Taher, Quimica Anal. (Spain). 19(3),pp 143-149 (2000).
6. F. Sundler, L. J. Larsson, and R. Hakanson, Histochemistry 50, pp39–46 (1976).
7. T.Huey Lu , P. hattopadhyay , F.L , Liao and J.Mau Lo , J.Analytical sciences , Vol. 17 pp 905-906 (2001) .
8. S.sharma , V.K.Srivastave , A.Kumar , Eur J.Med . chem , Aug ; 37(8) pp 689-697, (2005).
9. P.Gurcan , N.Sari , N.J.Jnorg . chem., 38(12) pp 2807-2817 (1999) .
10. Y.yang , S.Zhang ., J.Spectro chim Acta. Mol Biomol spectrosc , 59(6) pp 1205-1209 (2003).
11. Tannistha Roy Barman and G n mukherjee, J. Chem. Sci., Vol. 118, No. 5, September, pp. 411– 418(2006).
12. W. J. Geary, Coord. Rev., 7, 81, (1971).
13. A .Ganesh. Thakur, V. Shrikant , Athlekarb, R.Sanjiv , Dharwadkr , Acta Poloniae Pharmaceutica ,Drug Research, 64 No. 1,. 9-15, (2007).
14. S. G. Mastrostamatis, M. S. Papadopoulos, I. C. Pirmettis, E. Paschali, A. D. Varvrigou, C. I. Sassinopoulou, C. P. Rapetopoulou, A. Teris and E. Chiotellis, J. Med. Chem., 37, 32112, (1994).
15. C. P. Prebhakaran and C. J. Patelc, J. Inorg. Nucl. Chem., 31, 3316, (1969).
16. K. Nakamoto," *Infrared Spectra of Inorganic and Coordination Compounds"* 4th Ed., J. Wiely nd Sons, New York, (1996).
17. M,Ketton, and A.B.P.Lever; Inorg. Chem; 10, No:1 (1971).
18. A.B.P. Lever.. *"Inorganic spectroscopy"* Elsverier publishing company London , New York. (1968).