www.sphinxsai.com

ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.9 No.12, pp 813-822, 2016

Synthesis, Identification of Mn(ll), Nb(ll) and Pt(lV) Complexes with the Ligand Mixture (Ethylendiamine+ Glycine) and Study their Physical Properties and their Thermodynamic Stabilities

Jassem M. Abd Al Hassein

Chemistry Department, College of Science, University of Babylon, Hilla/Iraq

Abstract : The complexes of Mn(ll), Nb(ll) and Pt(lV) were synthesized by using the Ligand Mixture(Ethylendiamine + Glycine with the ratio 2 : 1)as a ligand. They were characterized by many techniques such as the element analysis, FTIR spectroscopy and UV.VIS. spectroscopy. Their physical properties such as electric conductivity and magnetic features were determined. Their stepwise and overall stability constants and their thermodynamic functions (ΔG^O, ΔS^O and ΔH^O) were determined. It was found that Mn(ll) and Nb(ll) complexes have paramagnetic features, whereas Pt(IV) has diamagnetic features. All the complexes have good conductivity. The formula of the complexes under this paper were detected by using the mole ratio method which lead to the formation of (1 : 3) metal : ligand formula for all the complexes under this paper. In all the complexes the coordination was through N atoms of the amino groups and O atom of the hydroxyl group. The suggested geometrical shapes of the complexes were the octahedral shape due to the d^2sp^3 hybridization. Their stepwise stability constants were determined, it was found that for all the complexes they were increased toward the addition of ligand that because of the chelate effect. Their overall stability constants were determined, it was found that for all the complexes were high that because of the chelate effect. Their thermodynamic functions (ΔG^O, ΔS^O and ΔH^O) were had negative value, that refer to good stability for the complexes and these results were satisfied with the spontaneous reaction and high stability complexes.

Keywords : ethylenediamine, glycine stepwise stability constant, overall stability constant, Nb(ll) complex.

1 - Introduction

The high molecular weight coordination complexes have a wide importance in field of clinical and analytical chemistry in recent days that because of their high stability and their wide use[1-3]. The organic reagent which have the chelating properties, have been used as a photometric reagents in analytical chemistry due to their visibly complexes with transition ions[4-5]. The coordination of these compounds with metal ions depends upon the nature of the metal, its valence, the number of the donor atoms, the type of the chelating rings and the pH of thereaction medium[6]. The ability to coordinate and the probability to produce stable complexes increased if the ligand contains rather thanone donor atom which localized on suitable place within the ligand molecule[7]. Complexes are compounds containing a central atom or ion which usually ametal with vacant orbitals (Lewis acid) surrounded by several electron donor items (Lewis bases) that are recognized as ligands[8]. The coordination of a polydentate ligand to an ion leads to the formation of a chelating complex so as do a saturated diamines such as 1,2-ethandiamine (en) which forms more flexible five chelate ring[9]. Of the 20 amino acids present in proteins, only arelatively small number are potential metal ligands, glycine is one of these[10]. The metal ion in aqueous solution is hydrated for example the ion ($[M(H_2O)_6]^{z+}$), by the addition of neutral ligand to its solution that lead to the formation of a series of complexes:$[M(H_2O)_5L]^{z+}$,$[M(H_2O)_4L_2]^{z+}$…………$[ML_6]^{z+}$[11]. The chelate effect enhanced the stability of the chelating complex system as compared to a similar non – chelating complex, so to understand the chelate effect properly we must study the thermodynamic stability of the complexes[11]. Pt(lV) salts are the primary materials for the Pt(ll) salts which are yet used as the primary materials for the preparation the cis – platinum chemotherapy drugs[13]. The oxidation state and the ionic size of the central atom are an important factor which effects on the complex stability, the high oxidation state leads to high stability and the high ionic size lead to low stability[14].

2 - Practical Part

Materials:

All the materials which were used in this paper were so sensitive to moisture that they had been kept in dry containers.

The water used was double distilled water.

Metal ion solutions (0.01 M) were prepared from theirs chloride salts.

All the reagents were of high purity, they had been get from BDH and FULKA companies.

Ammonium nitrate (2M) was used as a background electrolytic solution.

The commercial name of the ligands are ethylenediamine, abbreviation as en and glycine, abbreviation as Gly.

Preparation the complexes:

Specific weight of the metal salt (metal chloride) dissolved in DW and specific amount of the liganddissolved in ethanol then the two solutions mixed together and heated to 70 °C for 30 minutes, aprecipitate of the complexes were formed, separated, washed and dried.

Determination λ_{max} of the complexes:

Maximum wave length (λ_{max}) for each complex solution (10^{-3} M) was obtained by using UV. VIS. Spectroscopy scanning (UV – 1650 PC shimadzu spectroscopy with quartz cells). The figures (1 – 4) shows the electronic spectra for the ligand and the complexes.

FTIR Spectra:

FTIR spectrum for the complexes were recorded by using FTIR – 84005 shimadzu spectroscopy with KBr discs in the range 400 – 4000 cm^{-1}. Figures (5 – 8) shows these spectra. Table (1) shows the important absorption bands of groups of the ligand and the complexes.

Table (1):Important FTIR absorption bands for the ligand (en + gl) and the complexes

Assigment	**Ligand(en + gl)**	**Pt + L**	**Mn + L**	**Nb + L**
N-H	3433	3400	3450	3420
O-H	3327	…………	…………	…………
C=O	1647	1640	1635	1650
C-N	1635	1498	1550	1450
C-O	1354		1386	1375
C – H (STR.)	3015 2914	3050 ……….	2950 ……….	2914 ………
C – H (BEN.)	1118	1186	1205	1120
M - N	…………	below 500	below 500	below 500

Determination the formula of complexes:

The formula of each complex was determined by using the continuous variation method. The formula (1 : 3) metal : ligand ratio, for all complexes under this research, was found.

Element Analysis:

Element analysis were measured for the solid complexes by using EURO element analyzer and shimadzu – AA – 160 atomic absorption – flame emission spectrophotometer. Table (2) shows the results of the element analysis.

Table (2): The results of the element analysis for the prepared complexes

M. F	[Pt(en)2(gly)]Cl3	[Mn(en)2(gly)]Cl	[Nb(en)2(gly)]Cl
O	4.04 (4.01)	7.88 (7.01)	6.09 (5.87)
C	6.01 (6.00)	12.83 (11.98)	10.67 (10.34)
H	2.00 (1.89)	4.27 (4.01)	3.55 (3.20)
N	7.01 (6.89)	14.9 (14.10)	12.45 (11.98)
Cl	36.09 (35.91)	38.50 (37.42)	32.01 (31.57)
M	48.87 (47.90)	29.41 (28.89)	41.30 (40.80)

Molar conductivity study:

Molar conductivity for the aqueous solutions of the complexes (10^{-3} M) at 25 ^{o} C were measured by using INOIL AB 740 potentiometer. Table (3) shows the results of this study.

Table (3): Physical properties of the prepared complexes

The complex	[Pt(en)2(gly)]Cl3	[Mn(en)2(gly)]Cl	[Nb(en)2(gly)]Cl
M.W.	399	187	225
Am(ms/cm	4.55	3.21	3.01
µeff (BM)	0.1	1.4	3.1

Magnetic properties study:

Magnetic susceptibility of the complexes were established due to Gouy Balance Method by using MSB – MKI magnetic susceptibility measurement balance. The effective magnetic momentum (μ_{eff}) at 25 ^{o} C was calculated and the results are shown in table (3).

3 - Theoretical calculations:

Thermodynamic stability studies[15-17]:

To calculate the concentration of the metal ion, the experiment had been done by using ion selective electrode technique in 2 M NH_4NO_3 aqueous solution and the concentration of the metal salt and the ligand was 0.01 M. The stability constant (K), for the formation of the complex below, obtains as follow:

$$[M(H_2O)_6]^{Z+}\ L \rightleftharpoons [M(H_2O)_4L]^{Z+} + 2H_2O$$

$$K = \frac{[M(H_2O)_4L]}{[M(H_2O)_6][L]}$$

At equilibrium:

$[M(H_2O)_4L] + [M(H_2O)_6] = 0.01$

$[M(H_2O)_6] = [L]$

So:

$$K = \frac{0.01 - [M(H_2O)_6]}{[M(H_2O)_6]^2}$$

$[M(H_2O)_6]$can be obtain from the electric cell (ion selective electrode) and K can be obtain from the above equation.

ΔG^O can be obtain from the relation:

$\Delta G^O = - RT\ln K$

ΔH^O can be obtaining by using thermometric titration calorimetry method, in which the ligand adds slowly to the metal and the temperature record as the addition prpcceds.

ΔS^O can be obtaining from the relation:

$\Delta G^O = \Delta H^O - T\Delta S^O$

The stepwise stability constants(K_n) for the formation of the complex $[M L_3]^{z+}$ are:

$$[M(H_2O)_6]^{Z+}\ L \rightleftharpoons [M(H_2O)_4L]^{Z+} + 2H_2O$$

$$K_1 = \frac{[M(H_2O)_4L]}{[M(H_2O)_6][L]}$$

$$[M(H_2O)_4L]^{Z+} + L \rightleftharpoons [M(H_2O)_2L_2]^{Z+} + 2H_2O$$

$$K_2 = \frac{[M(H_2O)_2L_2]}{[M(H_2O)_4L][L]}$$

$$[M(H_2O)_2L_2]^{Z+} + L \rightleftharpoons [ML_3]^{Z+} + 2H_2O$$

$$K_3 = \frac{[M L_3]}{[M(H_2O)_2L_2][L]}$$

The overall stability constant (β) is:

$\beta = K_1\, K_2\, K_3$

$\log \beta = \log K_1 + \log K_2 + \log K_3$

$$[M(H_2O)_6]^{Z+} + L_3 \rightleftharpoons [ML_3]^{Z+} + 6H_2O$$

$$\beta = \frac{[M\,L_3]}{[M(H_2O)_6][L]^3}$$

4 - Results and Discussion:

The results of the stepwise stability constants (K_n) and overall stability constant (β) for the complexes are shown in table (4), and the results of the thermodynamic functions (ΔG^O, ΔS^O and ΔH^O) are shown in table (5). Figures (8, 9 and 10) show the relation between the number of ligand moles and log K for the complexes. All the measurements established at 303 ^{o}K.

Table (4): The results of the stepwise and overall stability constants

The ione	no. of moles of ligand	conc. of ione sol. (M)	stepwisestab. conct. (K)	log K	log β	overall stab. const. (β)
Pt (IV)	1	0.0034	K1 = 570.9	2.76	log β1 = 2.76	2×10^9
Pt (IV)	2	0.0025	K2 = 1209.6	3.12	log β2 = 5.88	
Pt (IV)	3	0.0017	K3 = 2862.1	3.45	log β3 = 9.30	
Mn (II)	1	0.0036	K1 = 493.8	2.69	log β1 = 2.67	8×10^8
Mn (II)	2	0.0030	K2 = 777.7	2.89	log β2 = 5.58	
Mn (II)	3	0.0025	K3 = 1200.0	3.08	log β3 = 8.90	
Nb (III)	1	0.0062	K1 = 100.0	2.00	log β1 = 2.00	
Nb (III)	2	0.0050	K2 = 200.0	2.30	log β2 = 4.30	
Nb (III)	3	0.0041	K3 = 347.0	2.54	log β3 = 6.60	4×10^6

Table (5): The results of the thermodynamic functions

complex	ΔH_O(KJ/mol)	ΔG_O(KJ/mol)	ΔS_O(KJ/mol)
$[Pt(en)_2(gly)]^{3+}$	- 67.90	- 53.88	- 0.046
$[Mn(en)_2(gly)]^{+}$	- 70.90	- 51.55	- 0.063
$[Nb(en)_2(gly)]^{+}$	- 41.30	- 38.80	- 0.013

The FTIR spectra of the ligand and the complexes show the most important absorption bands within the range (4000 – 400) cm^{-1}. The important stretching bands in the ligand spectrum belongs to O-H, N-H, C=O, C-O,C-N, C-H and C-C bands. The shifting observed in the absorption bands, after the coordination with the metal ions under this research, supports that the coordination had been occurred between the metal ion and the ligands via the NH_2 and OH groups.

The ligand electronic spectrum shows that there are four principle bands,350 nm,430 nm445 nm and 525 nm which belong to the charge transfer band[18]. Clear displacement of the principal band of the ligand (445 nm) had occurred after the formation of the complexes, that refer to that the electronic environment of the coordinated atom had been changed. This result agree with the published papers which used like this ligand[19,20].

The results of the molar conductivity measurements indicate that the complexes have good conductivities due to the positive charge on the coordination core and the negative on the neighbor ion.

The magnetic properties indicate that the Pt complex has diamagnetic properties, whereas Mn and Nb complexes have paramagnetic properties[21].

The suggested geometrical shape of the complexes are octahedral shape (d^2sp^3 hybridization). Figure (9) shows the shape of these complexes.

The thermodynamic study shows that the value of Pt (lV) complex stabilities was get close to the value of Mn (ll) complex stabilities that due to the high positive charge of Pt (lV) ion and the smallness of the ionic size of Mn (ll) ion.

The results of the thermodynamic stability study agree with the Irving – Williams Principle, which deals with the relation between the ionic size of the central atom and its complex stability[22].

The values of stability constants (K) increased as the reaction forward, that because of the chelate effect of the bidentate ligand (en + gly).

The negative charge of ΔG^{O} refers to that the complexes were thermodynamically stable according to the below gradation:

$[\,Pt(en)_2(gly)\,]^{3+} > [\,Mn(en)_2(gly)]^{+} > [\,Nb(en)_2(gly)]^{+}$

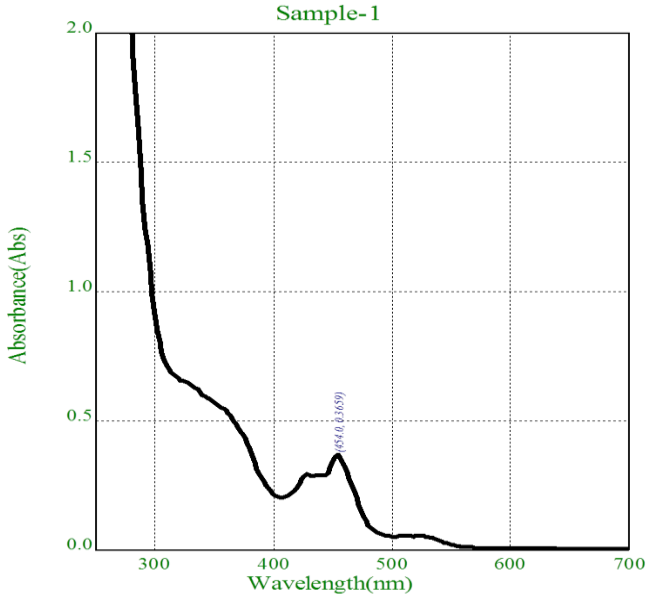

Figure (1): The electronic spectra for the (en+ gly) ligand

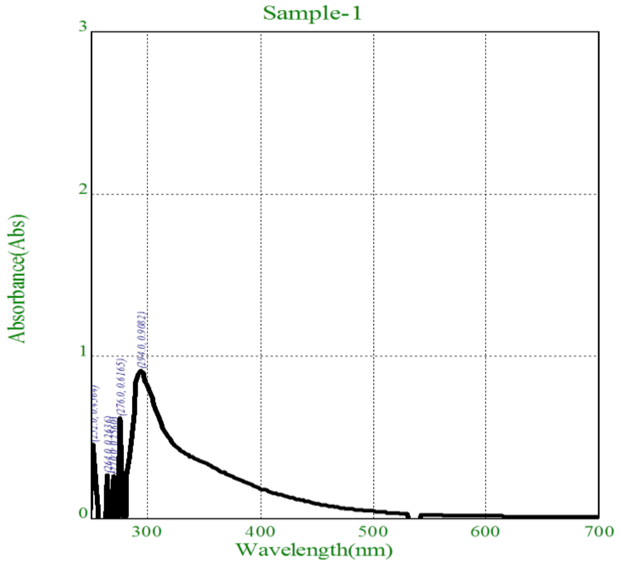

Figure (2): The electronic spectra for the complex (Mn^{2+}+L)

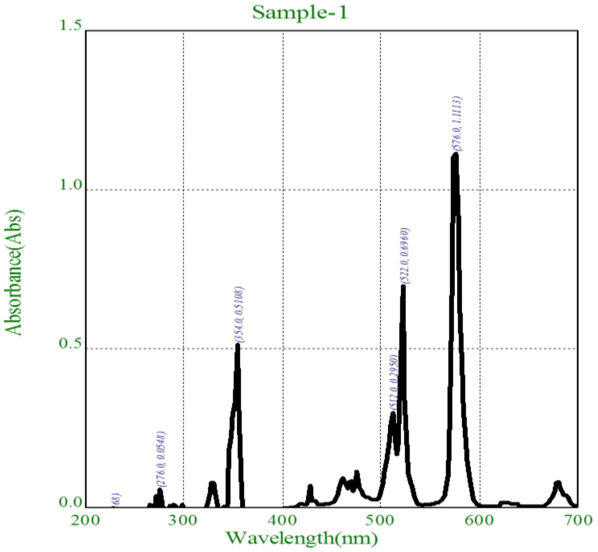

Figure (3): The electronic spectra for the complex (Nb^{2+}+L)

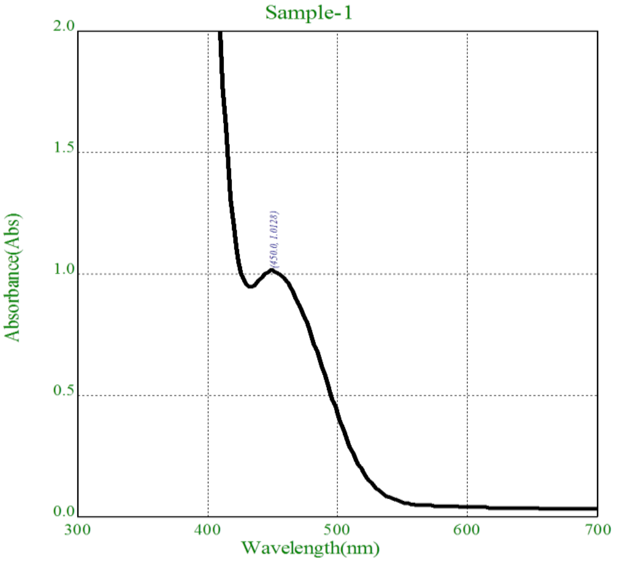

Figure (4): The electronic spectra for the complex (Pt^{4+}+L)

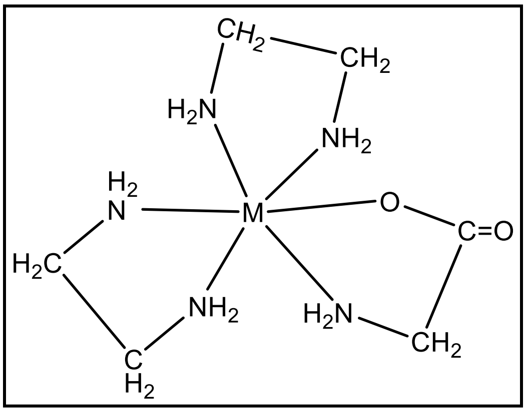

Figure (9): The geometrical shape of thecomplexs (M = Mn^{2+}, Nb^{2+}, Pt^{4+})

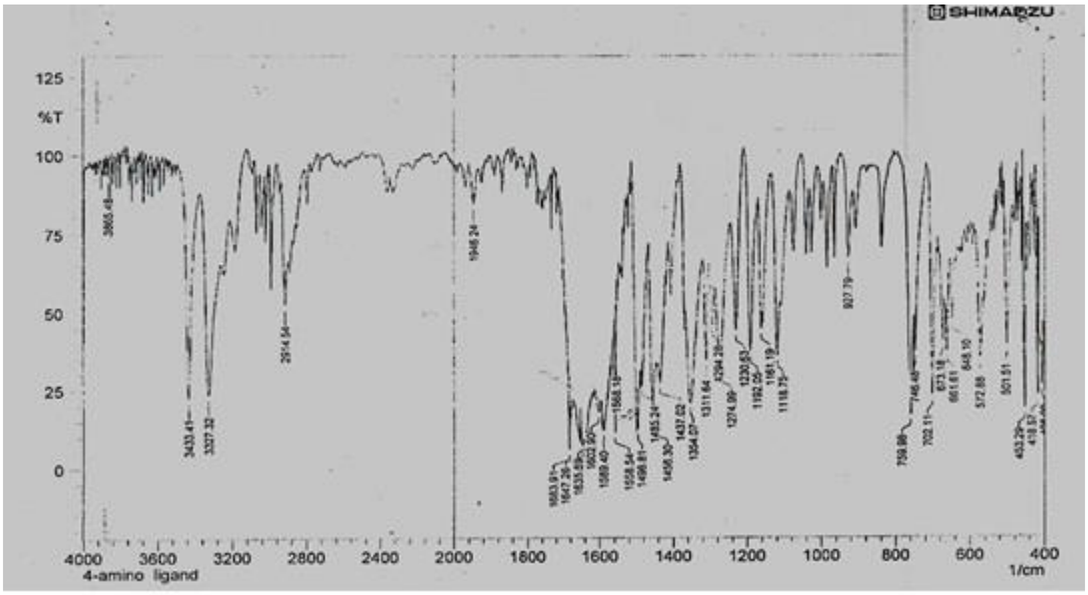

Figure (10): FTIR spectra for the (en + gly) ligand

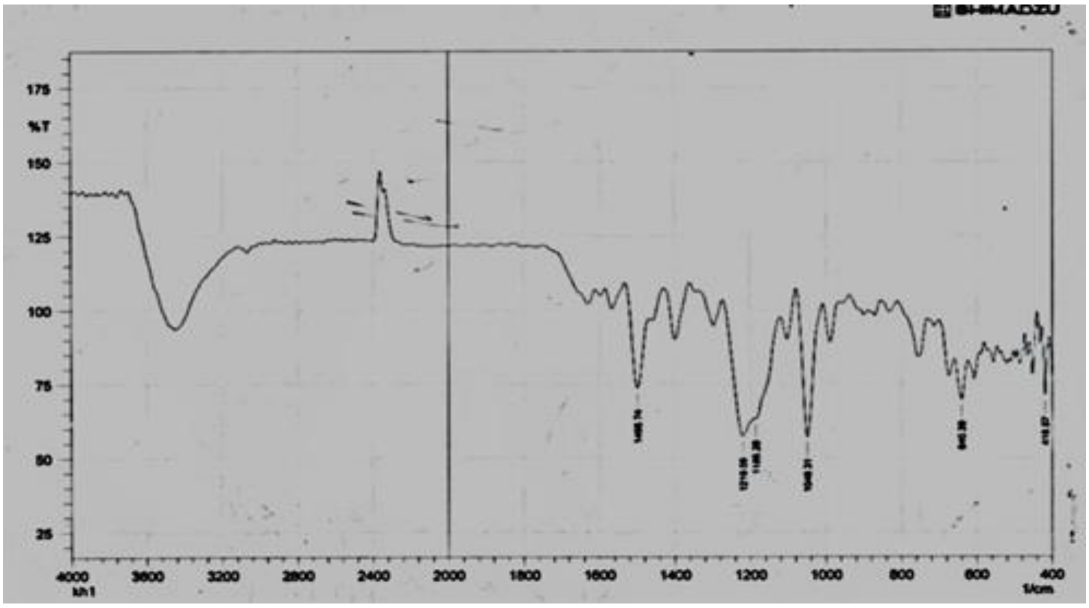

Figure (11): FTIR spectra for the (en + gly) ligand + Pt(IV)

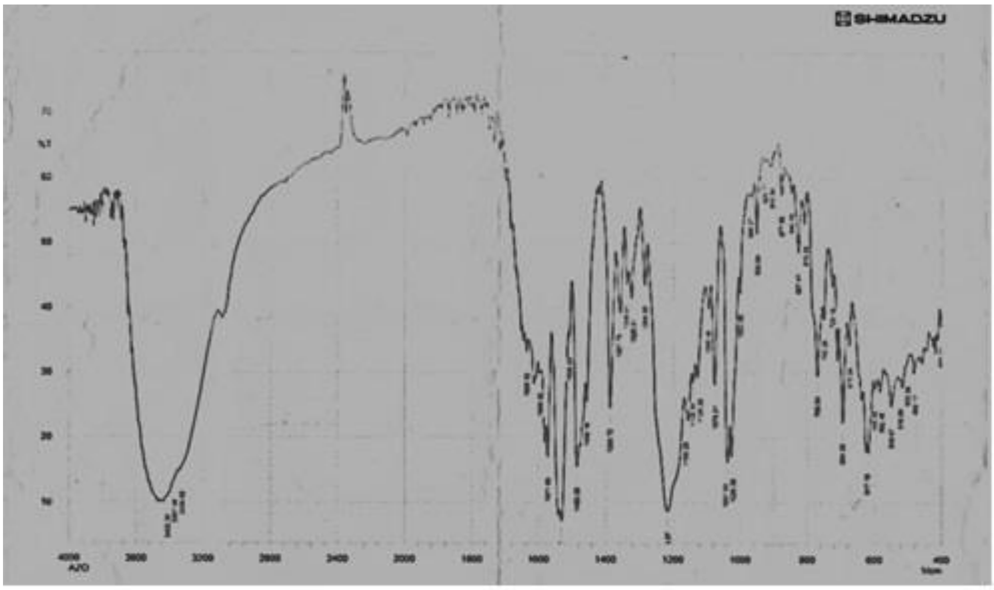

Figure (12): FTIR spectra for the (en + gly) ligand + Mn (II)

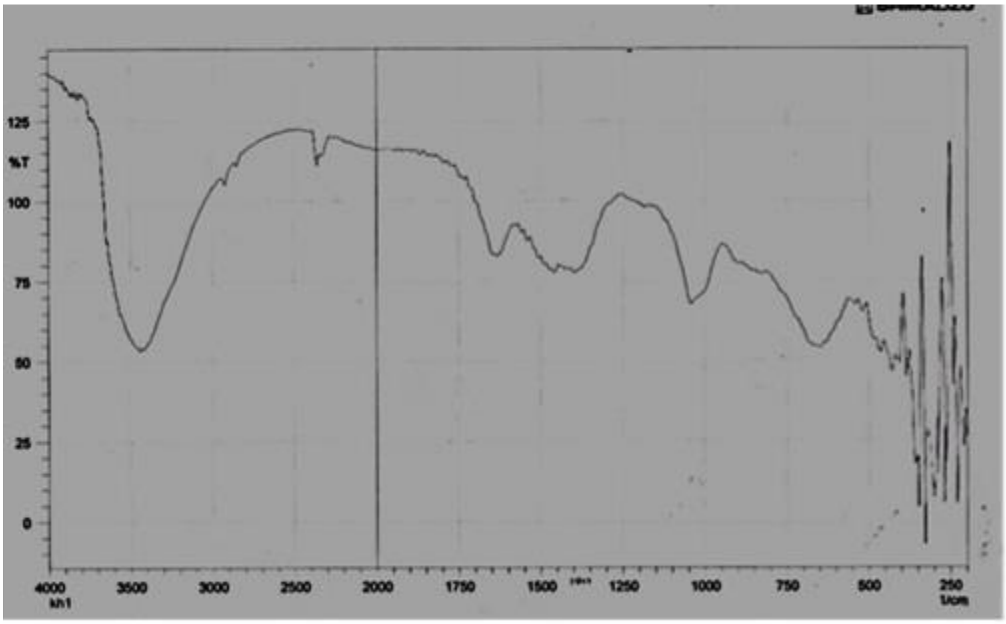

Figure (13): FTIR spectra for the (en + gly) ligand + Nb (II)

References:

1. Sieron L, Bukowska- Strzyzewska M. (1999);Catena-Poly[[[diaqua(pyridine-2-carboxamide-N 1,O)copper(II)]--(sulfato-O:O)] monohydrate]. Acta Crystallographica Section C: Crystal Structure Communications. 55(4): 491-494.
2. Malathy Sony SM, Kuppayee M, Ponnuswamy MN, et al. (2004);Crystal structure of a copper(II) complex: 4-chloro-3-methyl-6(3-N,N-dimethylamino-1-iminomethyl)phenolatocopper(II) acetate. Analytical Sciences: X-ray Structure Analysis Online. 20(3): x85-x86.
3. Malathy Sony SM, Saraboji K, Ponnuswamy MN, Manonmani J, Kandasamy M, Fun HK. (2004);Structure and conformation of a nickel complex: {2-hydroxo-3-piperidine-1-yl-methyl-N,N(bis-

5-bromobenzylpropylenediimine) nickel(II) perchlorate}. Crystal Research and Technology. 39(2): 185-192.

4. Sieroń L, Bukowska-Strzyzewska M. (1999);cis-bis(2-amino-1,3-benzothiazole-N 3)bis-(formato-O,Oâ€²)copper(II). Acta Crystallographica Section C: Crystal Structure Communications. 55(2): 167-169.
5. I TP, Nancollas GH. (1972);Thermodynamics of ion association. XXIV. The formation of mixed complexes of copper with glycine, alanine, serine, and valine. Inorganic Chemistry. 11(10): 2414-2425.
6. M. Geloch,(1990),Coord. Chem. Rev., 99, 117.
7. X.X. Liu and W.T. Wong, (2001)"Synthesis, characterisation and electrochemical behaviour of rhodium(III) complexes containing 1,2-naphthoquinone-2-oxime and formation of imine complexes through N-O bond cleavage", EUR J INORG, (2), :. 511-520
8. F. R. Hartly, C. Burgess and R. M. Alcock,(1980), Solution Equilibria, Ellis Horwood Limited.
9. Catherine E. Housecroft and Alan G. Sharpe,(2005), Inorganic Chemistry, Pearson Education Limited, Second Edition.
10. Robert R. Crichton,(2008), Biological InorganicChemistry An Introduction, Elsevier B. V.
11. Burgess J., (1979), Metal Ion in Solution, Chichester, Ellis Horwood Limited.12. F. Albert Cotton and Geoffrey Wilkinson,(1967), Advanced Inorganic Chemistry, Second Edition, John Wiley and Sons, Inc..
12. Sama Mehdi Hassan,(2016), MSC Thesis, Department of Chemistry, College of Science, University of Babylon.
13. N. N. Greenwood and A. Earnshaw,(1984), Chemistry of the Elements, Pergamon Press Ltd..
14. A. I. Vogel, Quantitative Inorganic Analysis, Text – Book, Third Edition,(1961),Longmar Group Limited, London, 415 – 420.
15. Christensen J. J. and Izatt R. M.,(1968), Physical Method in Advanced Inorganic Chemistry, Hill, H. A. O. and Day, pp. 554 – 576, London
16. Izatt RM, Johnson HD, Christensen JJ. (1972);Log Ki, Δh°i, and Δs°i values for the interaction of glycinate ion with H+, Mn2+, Fe2+, Co2+, Ni2+, Cu2+, Zn2+, and Cd2+ at 10, 25, and 40° Journal of the Chemical Society, Dalton Transactions. (11): 1152-1157.
17. R. Chang,(1972).Physical Chemistry, University Science Books
18. Schneider HJ, Xiao F. (1992);Binding and catalysis with a metal-induced ternary complex of an ethylenediamine-substituted cyclodextrin. Journal of the Chemical Society, Perkin Transactions 2. (3): 387-391.
19. Chen S.H. and Lai J.Y. (1996), ‘Polycarboante (N-N’-dialicylidene ethylenediamine) cobalt (II) complex membrane for gas separation’, J. Appl. Polym. Sci., Vol. 59, pp. 1129-1135.
20. Jassem M. A. Al-Hasien, Thamer A. A. Al- Alwani and Sadiq J. Baqir,(2009),Synthesis and Spectral Studies of Mn(II) and Cu(II) Complexes with 4,5 - dihydroxy - 3- (phpnylazo) -2,7- disulfonic acid disodium naphthalene salt , National Journal of Chemistry, 36, 745 – 753.
21. Jasim M. AL – Shamery and Hussein A. M. Salih(2006),Physical studioes of BTZ AzoNaphthioc acid and its complexes with heavy metal ion s, National Journalof Chemistry, 23, 305 – 313.

*****