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Synthesis and Characterization of some Cr^{+3}, Fe^{+3}, Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} Complexes with N-Phthalyl amino acid ligands

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Abstract

Two new sodium N-phthalyl amino acid ligands (L^1) and (L^2) were prepared by the reaction of phthalic anhydride with glycine or alanine amino acids the sodium salt of the above ligand were prepared by the reaction with sodium hydroxide. The mono and dinuclear complexes of Cr^{+3}, Fe^{+3}, Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} were prepared by the reaction of the above ligands with the metal chloride in (1:1)or (1:2) metal to ligands ratio. The ligands and their complexes have been characterized by their analytical, spectral data, conductivity and magnetic measurements. Electronic spectra and magnetic measurements indicates that the mononuclear complexes contain tetrahedral environment, while the dinuclear complexes have octahedral geometry.

Keywords: Synthesis, characterization, complexes, n-phthalyl amino acid, ligands.

Introduction

Interactions between transition metal and amino acids are very interesting in the biological applications. Complexes of some metals ions with amino acids can be used as models to study the pharmacodynamic effects of drugs or for increasing the biocompatibility and minimize toxic effects of some metal in Schroev and Abram U.[1], Grecu I., Sandulescu R. and Neamtu M.[2] and Grecu I., Neamtu M. and Enescn L.[3].

There are many reports in the literature on mixed ligand complex of amino acids. Srivastava and Gupta et.al[4-6] reported the synthesis and characterization of mixed ligand transition metal complexes formed with glycine, alanine, uracil, 2-thiouracil, thymine, adenine, histamine, valine and Lucien. A series of complexes of Cu(II) and Mn(II) with 4-(4'-halobenzene sulfonyl) benzoyl glycine and 4-(4'-halobenzenesolfonyl) – benzoyl – alanine with formula $[M(L\text{-}H)_2(H_2O)_2]$ have been synthesized and characterized as mononuclear species on the basis of elemental chemical analysis, electronic and infrared spectra and molar conductivity measurements. The IR spectra indicated the presence of amino acid derivatives as coordinated through nitrogen atom and the oxygen from carboxylic group. The experimental data suggest that the ligands act as bidentate and adopt an octahedral stereochemistry[7]. The coordination properties of the novel conjugate to wards copper ions were investigated. The performed studies exhibited the unusual binding properties of the ligand molecule having two potential strong coordination sites, namely dipeptide chain and pyridyl nitrogens. On the bases of potentiometric and spectroscopic studies the binding at the low pH values to the aromatic entity is suggested, while the rise of pH yielded the dimeric head to tail complex formation[8].

The use of a ligand directed strategy in the assembly of discrete cluster, 2D layer and 3D networks, using N-substituted glycine derivatives with o-iodobenzoyl (a bulky substituted) or pyrimidyl, create a new possibility in the design of coordination networks . The synthesis and crystalline structure of the ligand N(pyrimidyl) glycine (1), its sliver derivatives [Ag (pyr-gly)] 0.5 H_2O (2) and the sliver derivatives of o-iodohippuric acid [Ag(I-hip)] 1.25 H_2O (3) are described by Oliver M.B. et al[9].

In this paper we proposed to prepare a series of Cr^{+3}, Fe^{+3}, Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} complexes with sodium phthalated amino acids derived from glycine and alanine.

Material and Methods

Experimental: All chemical were of reagent grade quality and were purchased from commercial sources (BDH and Fluka). They were used without further purification.

Physical characterization: Elemental analysis of isolated complexes (C,H,N) were accomplished by the microanalytical laboratory at Dicle University Science and Technology Center (Du BTAM) Turky. Metal content analyses were made on Shimadzu AA670 atomic absorption spectrophotometer. Infrared spectra were recorded using the Fourier-Transform Spectrophotometer Tesor 27Co Bruker in the range 4000-200 cm^{-1} with CsI pellets. The electronic spectra were recorded on a Shimadzu UV160 for the 10^{-3} M solution of complex in dimethyl- formamide (DMF) at 25°C. Conductivity measurements were carried out with 10^{-3} M solution of complexes in DMF at ambient temperature using a Jenway 4070 conductivity meter. The magnetic measurements were carried out on the solids by Faraday's method using Bruker BM6 instrument.

Synthesis of ligands: Ligands were prepared using the reaction between Phthalic anhydride with the recommended amino acid. (glycine or alanine)[10].

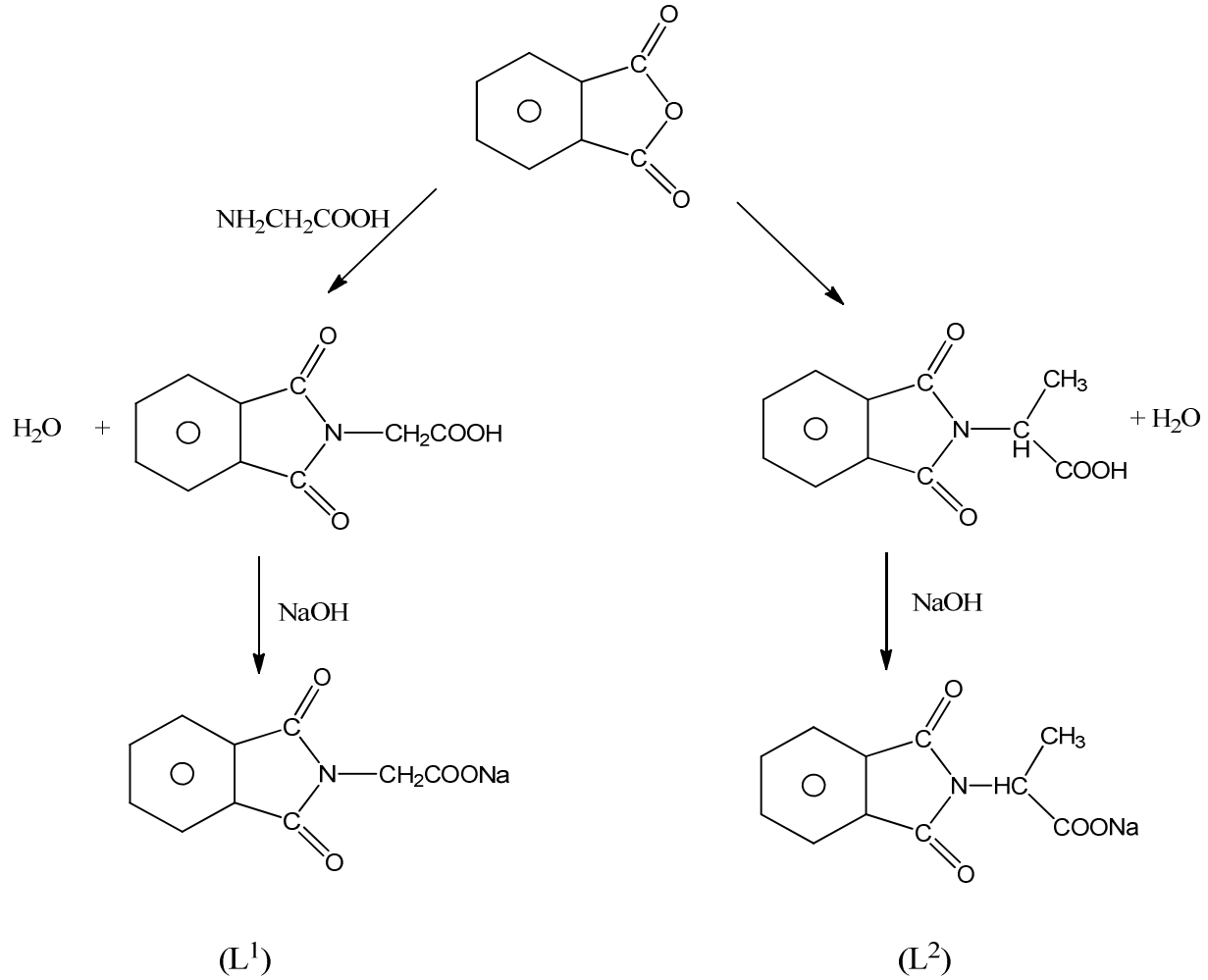
Properties of sodium salt of (L^1) and (L^2): The reaction of equimolar amount of phthalyl glycine (0.21g, 0.001 mol) or phthalyl alanine(0.22g, 0.001 mol) in 20 ml ethanol with NaOH (0.04g, 0.001 mol) in 20 ml ethanol. The mixture was boiled under reflux for 2 h. The product was obtained through evaporation of the solvent, then the precipitate was wash several times with ethanol and diethylether, then dried under vacuum for several hours.

preparation the complexes [M(L)Cl] M=Co^{+2},Ni^{+2},Cu^{+2},Zn^{+2} : A solution $CoCl_2$.$6H_2O$ (0.24g, 0.001 mol) in ethanol 10 ml was added drop wise to a solution of sodium phthalyl glycine (0.23g,0.001 mol) or sodium phthalyl alanine (0.24g, 0.001) in 10 ml methanol. The mixture was refluxed for 2 h, then the solution was allowed to cool to room temperature. The solid thus formed was filtered off, washed with ethanol followed by diethylether and dried under vacuum for 4h.The other complexes were prepared similarly.

Preparation of complexes $[M(L)_2]Cl_2$ M=Fe^{+3} and Cr^{+3}: A solution of $CrCl_3$. H_2O (0.27g , 0.001 mol) in ethanol 10 ml was added for a solution of sodium phthalyl glycine (0.46 g, 0.002 mol) of sodium phthalyl alanine (0.48g , 0.002 m0l) in 10 ml ethanol, the mixture was refluxed for 3h , the solution was cooled to room temperature .The isolated solid was filtered off, washed several times with ethanol in order to remove the formed NaCl salt, then diethylether and dried under vacuum for several hours.

Results and Discussion

Sodium phthalyl glycine (L^1) and sodium phthalyl alanine (L^2) were prepared the by reaction of phthalic anhydride with glycine or alanine (amino acid) heated in a sand bath (scheme 1) and then treated with a sodium hydroxide.



Scheme-1
Preparation of the ligands

The complexes were prepared through direct substitution of chloride by the relevant phthalyl ligands as oxygen donors for the metal ions.

All complexes are thermally stable and insoluble in organic solvent, however fair solubility was attributed in DMSO (dimethyl solfoxide) and DMF (dimethylformamide). The 10^{-3} M solution for, Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} complexes display molar conductance equal to 20-50 $ohm^{-1}.cm^2.mol^{-1}$ (table 1) indicating neutral nature of the complexes, while the, Cr^{+2} and Fe^{+2} complexes have molar conductance of 130-172 $ohm^{-1}.cm^2.mol^{-1}$ indicating a 1:2 electrolytic nature[11], this is consistent with stoichiometry for the complexes on the basis of analytical data.

The most important diagnostic feature of IR spectra of the complexes were listed in table 2. The most significant information on the geometry of these complexes were came from the analysis carboxylate and carbonyl absorption region. Stretching frequencies of these functional groups are closely related to the way in which they are coordinated to the metal ions[12]. The ligands band due to carboxylate group may be coordinated to the metal ions either in monodentate or in bidentate manner. The FTIR consistent with the formation of well defined compound with the above composition. The carboxylate group is able to coordinate to metal ions in different mode[13].

When the carboxylate group coordinate to metal ion in mono-deutate manner, the difference between the wave number of a symmetric and symmetric stretching band ($\Delta\upsilon = \upsilon_{asym}COO-\upsilon_{sym}COO$) is larger than observed for ionic compounds, when the ligand chelate is bidentate $\Delta\upsilon$ considerably smaller than that for acetate group in ionic compounds.

Two bands are observed at 1626-1587 and 1414-1427 cm^{-1} and the difference in $\Delta\upsilon COO$ 141-194 cm^{-1} table 2 are indicative of bidentate nature of the carboxylate groups[14]. However, the bands observed at 1697-1722 cm^{-1} for the complexes may be assigned to the free carbonyl groups, and the other carbonyl groups are shared in coordination Further support for this argument came from IR of the complexes which showed new bands at 530-577 cm^{-1} and also a band at 290-330cm^{-1} which may attributable to υ (M-O) and υ(M-Cl) respectively[15]. The IR spectra of Ni(II) and Fe(II) complexes are shown in figure 2.

The electronic spectra of the ligands and their complexes are summarized in table 2. The results obtained are in good agreement with other spectra and the literature[16].

The bands observed at 34246 and 33113 cm^{-1} are due to the n-π or π-π* transitions with in the ligands.

The magnetic moment values of chromium complexes (1,7) are 3.75-3.89 B.M suggest the presence of three unpaired electro, which reveal the spin free nature of the complexes corresponding an octahedral geometry[17].

The electronic spectra of Cr(III) complexes show two bands at 17241,17301 and 23584 and 23696 cm^{-1} which may be assigned to $^3A_2g(F)$, $^4T_2g(F)(\upsilon_1)$ and $^4A_2g(F)$ $^4T_1g(F)(\upsilon_2)$ in octahedral geometry.

The magnetic moments of octahedral high spin iron(III) complexes are normally very close to the spin only value of 5.92B.M [18].

The electronic spectra of the prepared iron (III) complexes (table 2), the complexes exhibited absorption bands in the region (10224 and 10309) cm^{-1} referred for ^5T_2g ^5Eg transition the absorption position for iron (III) complexes are consistent with be six coordinate octahedral iron (III) complexes.

The magnetic moment values of Co(II) complexes (3 and 9) are (4.00-4.53)B.M These values correspond to get tetrahedral configuration, the Co(II) complexes gave more intense bands in the d-d electronic spectra at14880 and 15974 cm^{-1} which may be assigned to $^4A_2(F)$ $^4T_2(p)$ transition indicating tetrahedral geometry[19].

The magnetic moment values of Ni(II) complexes are 3.36 and 3.01 B.M at 25°C, suggest the presence of two unpaired electrons, which reveals the spin free nature of the complexes corresponding a tetrahedral stereochemistry. The nickel complexes show a bands at15060 and 14925 cm^{-1} due to $^3T_1$ (F) $^3T_1(p)(\upsilon_3)$ transition indicated for tetrahedral geometry[20] and as showing in figure 2.

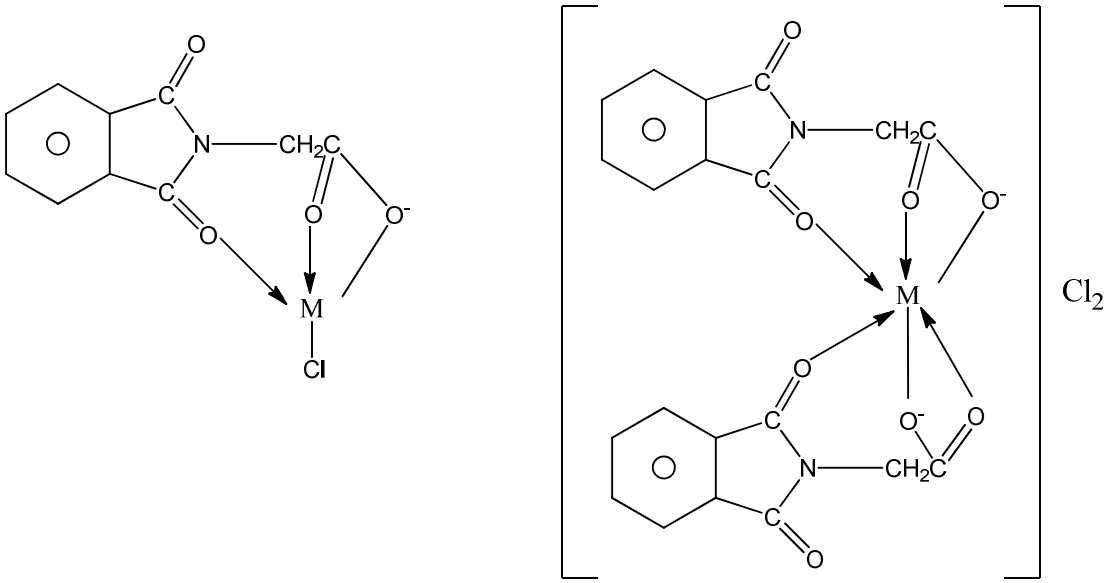
The magnetic moments for copper (II) complexes vary in the range 1.81-1.89 B.M. This indicates that the complexes are monomeric in nature and in agreement with distorted tetrahedral geometry. The copper (II) complexes show a bands at14204 and 14044 cm^{-1} which correspond to the transition of the ^2T_2g ^2E_2g consistent with distorted tetrahedral geometry[21].

The Zn(II) complexes are diamagnetic and do not show any d-d transition bands indicating a tetrahedral geometry.

Conclusion

The results of this study indicated that the ligand is coordinated to the metal ions as monobasic tridentate from carboxylate and carbonyl groups in mononuclear and binuclear complexes.

The magnetic moment and electronic spectral a studies suggest a tetrahedral and octahedral environment for the metal complexes at show in figure 1.



Complex(3-6,9-12) Complexes (1 and 2)

Figure-1
Suggested structures for the complexes

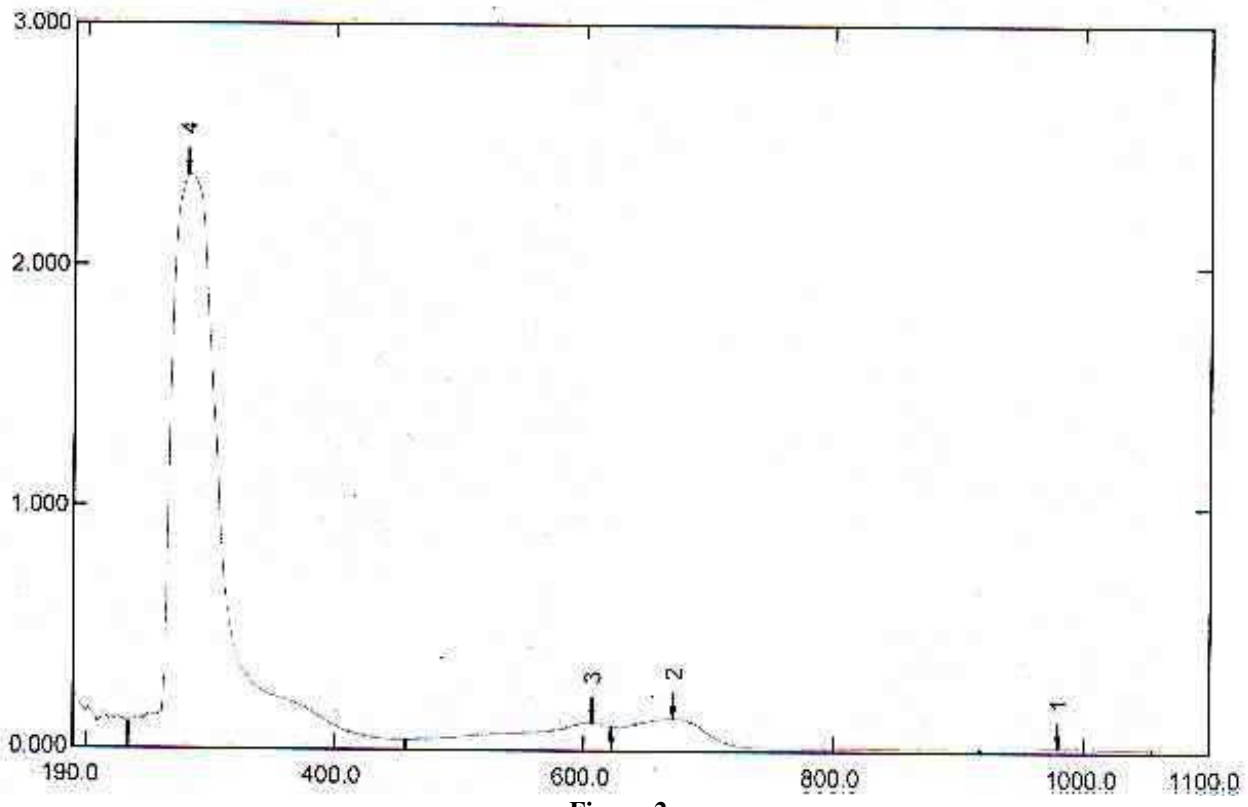
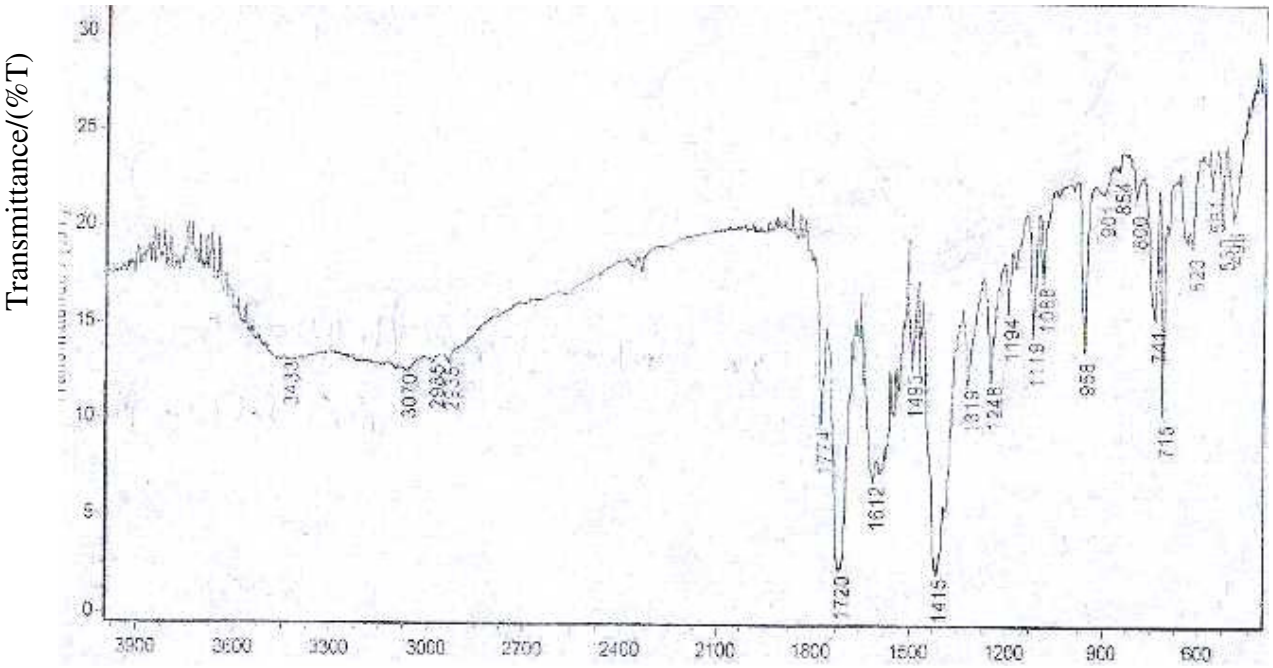
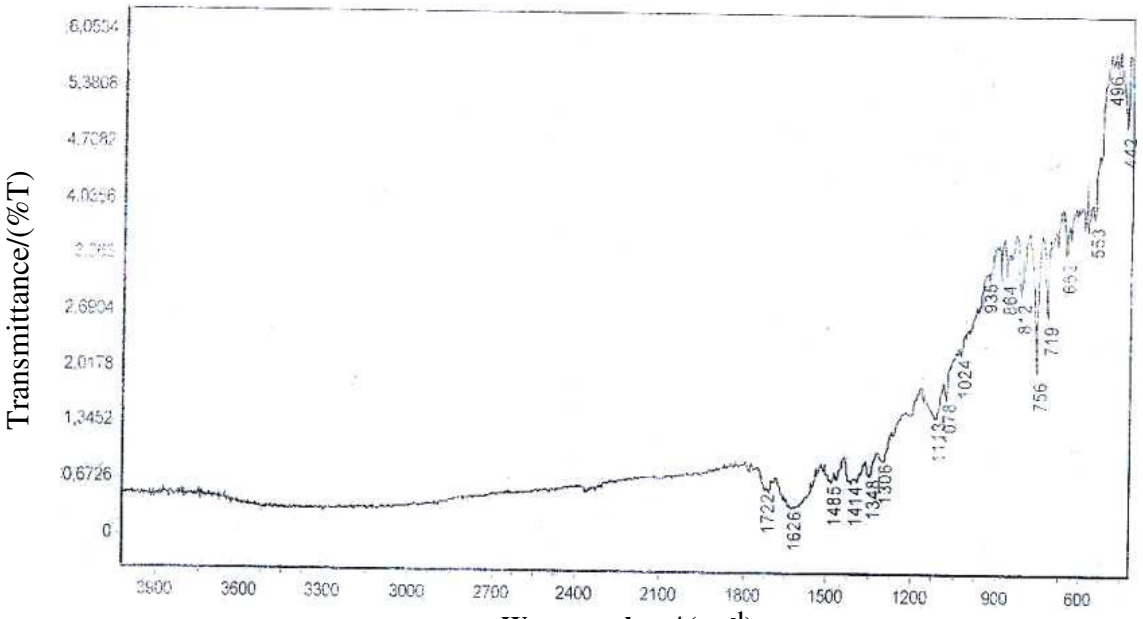


Figure-2
The electronic spectrum of [Ni(L^1)Cl] complex



Wave numbers/ (cm^{-1})
Figure-3
The IR spectrum of [Fe(L^1)Cl]



Wave numbers/ (cm^{-1})
Figure-4
The IR spectrum of [Ni(L^2)Cl]

Table-1
Physical properties and elemental analysis of the ligands and their complexes

Seq.	compound	Color	m.p (°c)	Yield %	Analysis ,found (calc.)%				(Λ) $cm^2.ohm^{-1}.mol^{-1}$	μ_{eff}
					C	H	N	M		
L^1	$C_{10}H_6O_4NNa$	Yellowish	193-196	82	52.79(52.86)	2.58(2.64)	6.18(6.16)	----	---	---
1	$[Cr(L^1)_2]Cl_2$	Olive	250d	75	45.00(45.19)	2.15(2.25)	5.20(5.27)	9.92(9.79)	170	3.75
2	$[Fe(L^1)_2]Cl_2$	Orange	160d	70	44.82(44.87)	2.29(2.24)	5.21(5.24)	10.03(10.44)	130	5.40
3	$[Co(L^1)Cl]$	Pink	260d	72	40.16(40.21)	1.99(2.01)	4.61(4.69)	19.69(19.74)	40	4.00
4	$[Ni(L^1)Cl]$	Green	220-222	80	40.15(40.21)	1.98(2.01)	4.59(4.69)	19.58(19.68)	46	3.01
5	$[Cu(L^1)Cl]$	Blue	230d	78	40.00(39.60)	1.83(1.98)	4.58(4.62)	20.88(20.95)	30	1.81
6	$[Zn(L^1)Cl]$	White	240d	74	39.41(39.35)	1.85(1.96)	4.50(4.59)	21.22(21.45)	45	Dia
L^2	$C_{11}H_9O_4NNa$	White	149-151	85	56.75(56.89)	4.00(3.88)	6.00(6.63)	---	---	---
7	$[Cr(L^2)_2]Cl_2$	Olive	230d	70	47.00(47.06)	3.19(3.21)	4.72(4.99)	9.25(9.21)	172	3.89
8	$[Fe(L^2)_2]Cl_2$	Orange	190-192	80	46.62(46.74)	3.11(3.18)	4.89(4.95)	9.95(9.89)	155	5.31
9	$[Co(L^2)Cl]$	Violet	116-118	75	42.30(42.11)	2.81(2.87)	4.45(4.47)	18.71(18.79)	20	4.53
10	$[Ni(L^2)Cl]$	Green	192[d]	72	42.10(42.15)	2.89(2.96)	4.41(4.47)	18.71(18.74)	40	3.36
11	$[Cu(L^2)Cl]$	Blue	150-152	79	41.60(41.51)	2.90(2.83)	4.35(4.40)	19.86(19.96)	50	1.89
12	$[Zn(L^2)Cl]$	White	181-183	81	41.11(41.26)	2.79(2.81)	4.31(4.37)	20.50(20.44)	40	Dia

d= decomposition temperature.

Table-2
Electronic and infrared spectral bands of the ligands and their complexes

Complex no.	Band maxima (λ_{max}) nm	IR spectral bands (cm^{-1})					
		υ_{as}(COO)	υ_s(COO)	$\Delta\upsilon(\upsilon_{as}-\upsilon_s)$	υ(CO)	υ(M-O)	υ(M-Cl)
L^1	34246	1593_s	1473_m	---	1649_s	---	---
1	17241,23584	1604_s	1415_m	189	1712_s	530_w	---
2	10224	1612_s	1415_m	197	1720_s	469_w	330_w
3	14880	1597_s	1425_m	172	1697_s	532_w	310_w
4	15060	1620_s	1422_m	198	1701_s	532_w	300_w
5	14204	1597_s	1421_m	176	1716_s	530_w	300_w
6	34013						$_w$
L^2	33112	1599_s	1480_m	---	1630_s	---	---
7	17301,23696	1562_s	1414_m	148	1720_s	530_w	290_w
8	10309	1600_s	1417_m	183	1722_s	577_w	300_w
9	15974	1593_s	1420_m	173	1700_s	535_w	310_w
10	14925	1626_s	1485_m	141	1722_s	553_w	300_w
11	14044	1631_s	1477_m	154	1697_s	532_w	310_w
12	35211	1626_s	1483_m	143	1722_s	553_w	290_w

S= strong, m=medium, w= weak.

References

1. Schroev and Abram U., Tetrameric rhenium complexes with a glycine-thiourea derivative, *Inorg.Chem.Commun*, **13(1),** 26-29 **(2010)**

2. Grecu I., Sandulescu R. and Neamtu M., Complexes of Cu(II) and Mn(II) with acylated amino acids, *Rev.Chim*., **37(7),** 589-595 **(1986)**

3. Grecu I., Neamtu M. and Enescn L., Implicatil biologice si medicate ake chimici anorganic, *Ed Dacia.Cluj-Napoca*., **(1982)**

4. Gupta M. and Srivastava M.N., Synthesis and characterization of mixed ligand complexes of copper (II), Nickal (II), Cobalt (II) and Zinc (II) with glycine and uracil or 2-thiouracil, *polyhedron*, **4(3),** 475-479 **(1985)**

5. Gupta M. and Srivastava M.N., Synthesis and characterization of complexes of copper (II), Nickal (II), Cobalt (II) and Zinc (II) with histidine and uracil, Thymine, *Bull .Soc. Chim. Fr.,* 859-863 **(1991)**

6. Gupta M. and Srivastava M.N., Synthesis and characterization of mixed ligand amino acid chelates of Cobalt (II), Nickal (II), copper (II) and Zinc (II) with alanine and uracil or 2-thiouracil, *Synth.React.Inorg.Met-Org.Chem*., **26(2),** 305-320 **(1996)**

7. Negoin M., Rosu T., Saramet I. and Matei C.A., Complexes of Cu(II) and Mn(II) with acylated aminoacids derived from glycine and α-alanine, *Chimie.Anul.*XIV, **I**, 129-133 **(2005)**

8. Szcze W., Panik, Mlynarz P., Stefanowicz P., Kalminska M.K., Amelis N.D., Mjkut A.O. , Staszewska A., Ratajska M. and Bojczuk M.G., Structural studies of Cu(II) bindinding to the novel peptidy derivative of quinoxaline glycine, *Polyhedron*, **30(1),** 9-15 **(2011)**

9. Oliver M.B., Tasada A., Fiol J.J., Raso Raso A.G., Terron A. and Molins E., Molecular arhitecture by means of interactions between Ag(I) and glycine derivatives, *Polyhedron*, **25(2),** 71-80 **(2006)**

10. Nogel's A., Text book of organic chemistry, *Iongman*, 828, **(1979)**

11. Geary W.J., The use of conductivity measurements in organic solvent for characterization of coordination compounds , *Coord.Chem.Rev*., **7,** 81-122 **(1971)**

12. Cinellu M.A. and Minghetti G., Gold (I) and Gold (III) complexes with anionic oxygen donor ligands, *Gold Bulletion*, **35(1)**, 11-20 **(2002)**

13. Nakamoto K., Infrared spectra of inorganic and coordination compounds, 3rd Ed., John Wiely, New York, 161 **(1978)**

14. Mrinalini L. and Singh A.K., Mixed ligand cobalt (III) complexes with 1-amidino-methyurea and aminoacids, *Res.J.Chem.Sci.,* **2(1),** 45-49 **(2012)**

15. Shukla M.H. , Solanki Y.K., Shah R., Shah P.J., Shah Shah A.L. and Raj D.S., Synthesis,characterization and antimicrobial studies of coordination polymers, *Res.J.Chem.Sci.*, **3(1),** 48-56 **(2013)**

16. Montazerozohori M., Musari S.A.R. and Jooharishiva , Synthesis, characterization and thermal behavior of some new mercury and cadmium halides coordination compounds of recently synthesized Schiff base, *Res.J.Recent,Sci.*, **1(11),** 9-15 **(2012)**

17. Kumar R. and Singh R., Chromium (III) complexes with different chromospheres mearocyclic ligands, Synthesis and spectroscopic studies, *Turk.J.Chem.*, **30**, 77-87 **(2004)**

18. Nicholls, The chemistry of iron, cobalt and nickel, Pergamon Press, Oxford 1st Ed. **(1973)**

19. Buttrus N.H. and Saeed F.T., Bis(N-methylbenzimidazolium -2-thiol) ethane, propane or butane diiodide and its Co(II),Ni(II), Cu(II) and Zn(II) ionic salts, *International J.Chem.*, **22(2),** 17-22 **(2012)**

20. Buttrus N.H. and Saeed F.T. ,Synthesis and structural studies on some transition metal complexes of bis (benzimidazole-2-thio) ether,propane and butane ligands, *Res.J.Chem.Sci*., **2(6),** 43-49 **(2012)**

21. Mohamed S.M.,Synthesis and characterization of Co^{+2},Ni^{+2},Cu^{+2} , Zn^{+2} and Hg^{+2} complexes with 1,1,2,2-tetrakis (sodium thiopropionate) ethylene, *Res.J.Chem.Sci.*, **3(7),** 9-14 **(2013)**