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Synthesis and characterization of (Cu^{II}, Zn^{II}, Ni^{II}) complexes with Mixed Ligands Aspartic Acid and N-phenylene diamine

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Abstract:-

The reaction mixed ligand aspartic acid and N-phenylene diamine with metal ions (Ni^{II}, Cu^{II} and Zn^{II}) in aqueous ethanol with 1:2:1 molar ratio yielded a series neutral complexes of the general formula [M $(a.a)_2N$].

The prepared complexes were characterized by using flame atomic absorption, FT.IR and U.V-Vis spectroscopy as wellas magnetic susceptibility and conductivity measurements. From the above data suggested octahedral structure for all complexe

Introduction :-

Amino acids is a molecule contining both amino carboxylic functional groups. These molecules are particularly important in biochemistry [(1)].Metal amino acid complexes have long been interested as models for metal-ligand systems and interaction which may occur in nature[(2)]. Biological importance of several amino acids their complexes with transition metals is well documented[(3-5)] .Amino acids are critical to life, and have a variety proteins also in many other drugs and biological molecules, such as forming parts of conenzymes, and the production of drugs and chiral catalysts These Compounds are Studied in many Fields of Chemistry especially ,bio inorganic chemistry .[(6-8)] Mixed Ligand complexes are finding increasing application as plant and animal growth stimulants .[(7)] In this paper, the synthesis and study of some transition metal complexes with mixed ligand , aspartic acid and N-phenylene diamine .

Experimental

a- Materials :- All chemicals used were of grade and were used without further purification $NiCl_2.6H_2O$,$CuCl_2.2H_2O$ $ZnCl_2$(Fluka) . Aspartic acid ,
N-phenylene diamine (Merck).

b- Instrumentation:- UV-Vis spectra were recorded on a (Shimadzu UV-160A) Ultra violet-visble Spectrophotometer . IR spectra were taken on a (Shimadzu, FT.IR-8400S Fourier Transform Infrared) Spectrophotometer(4000-400) cm^{-1} with samples prepared as KBr discs .Atomic absorption measurement were obtained using (Shimadzu A.A 160) Atomic Absorption / Flame Emission Spectrophotometer. Conductivites were measured for 10^{-3} M of complexes in ethanol at 25ºc using (Philips Pw.Digital Conductimeter) . In addition melting points were obtained using (Stuart Melting point Apparatus).

Preparation of Metal Complexes (general method)

All complexes were prepared by dissolving 0.45g, 0.32g and 0.25g (l mmole) of $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ respectively in ethanol solution .The solution was added gradually with stirring to ethonolic KOH solution of aspartic acid (0.5g, 2 mmole) ,then added to N-phenylene diamine (0.20g,lmmole). The mixture was stirred until the colored precipitate was appeared .The solution mixture was filtered off and washed several times within ethanol.

Results and Discussion:-

The isolated complexes were crystalline solids soluble in ethanol,methanol and DMSO. The conductivity measurements in ethanol 10^{-3} M at 298 k indicated the non-electrolyte type[9] .(Table-1) includes the physical properties of all prepared complexes.

The FT.IR spectrum of N-phenylene diamine (Fig-1) exhibited two bands at 3375cm^{-1} and 3302cm^{-1} which were assigned to the stretching mode of $\upsilon(NH_2)$[10], suffered a great change in the intensity and position on complexation with metal ion. The spectrum of a spartic acid (Fig-2) showed two bands at 3140cm^{-1} and 3012cm^{-1} which were assigned to the $\upsilon(NH_2)$ vibration[11].

These bands shifted to higher frequency on complexation with metal ions.

The band at 1685cm^{-1} in the spectrum of aspartic acid refer to υ(C=O) asymmetric, suffered to lower frequency in the all spectra of the prepared complexes (Fig-3) . Strong band at 1611cm^{-1} in the spectrum of aspartic acid due to υ(C=O) symmetric. This band shifted to higher frequency on complexation with metal ions[12]. Metal-nitrogen and metal-oxygen bands further confirmed by the presence of the bands around (644-513)cm^{-1} and (478-439)cm^{-1} respectively[13,14]. (Table-2) gives the characteristic absorption for the ligands and its complexes.

Electronic Spectra

The U.V-Visble spectra data for the free ligands and all metal complexes are listed in (Table-4) . The UV-Vis spectrum of N-phenylene diamine (Fig-4) shows two peaks at 301 and 394 nm which were assigned to the (π-π^*) and (n-π^*) respectively[15].The spectrum of aspartic acid (Fig-5) observed two peaks at 246 and 304 nm due to (π-π^*) and (n-π^*) respectively[16] .

Electronic Spectra of Complexes

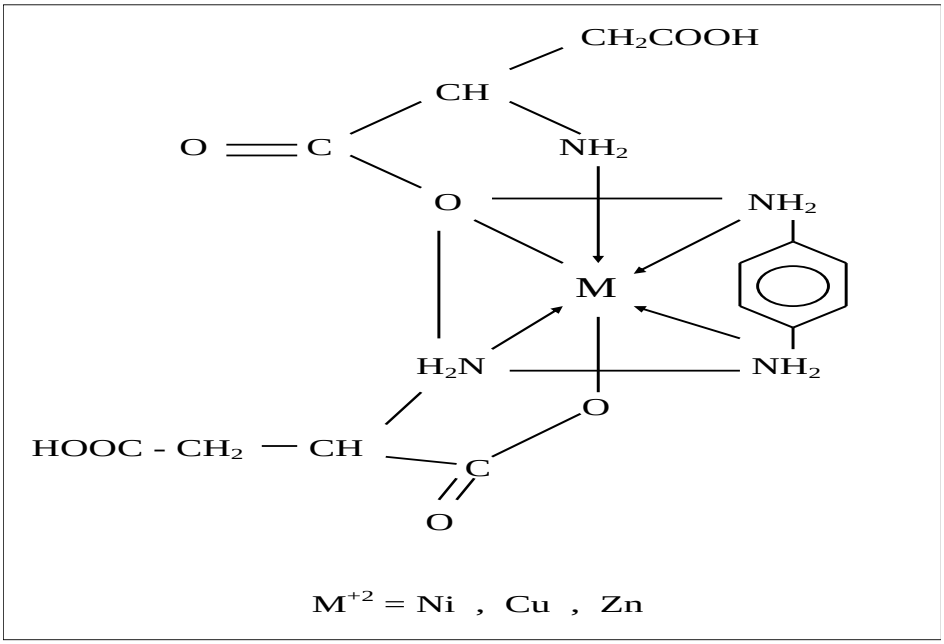
1- $[Ni(a.a)_2N)$:- The spectrum (Fig-1) showed an absorption peak at 304nm related to charge transfer (C.T) . Other peak at 496nm was found to be caused by (d-d) electronic transition[17] type $^4A_{g(F)} \rightarrow {}^4T_{g(P)}$.

2- $[Cu(a.a)_2N)$:- The spectrum gave absorption peak at 316nm refer to charge transfer, and only one absorption peak at 496nm was attributed to (d-d) electronic transition type[17] $^2E_g \rightarrow {}^2T_{2g}$.

3- $[Zn(a.a)_2N)$:- The spectrum appeared peak at 327nm could be due to charge transfer[17] .

According to the results obtained and spectral analyses, the chemical

structures of the complexes may be suggested as octahedral geometry



Scheme-1-The Suggested Structure For The Complexes

Table(1):- Physical Properties of the Ligand and its Metal Complexes

No.	Compounds	Color	M.P.C°	M% Calc (found)	Conductivity	μ_{eff}(BM)
1-	Aspartic acid	White	270	-	-	-
2-	N-phenylene diamine	Black	145	-	-	-
3-	$[Zn(a\text{-}a)_2N]$	Grew	150 dec	49.49	11.36	
4-	$[Cu(a\text{-}a)_2N]$	Brown	310	49.33	18.4	1.62
5-	$[Ni(a\text{-}a)_2N]$	Black	160	48.83	10.2	2.3

Table(2): The Infrared Spectra for the Mixed Ligand and its Complexes

No.	Compounds	υ(NH) Aspertic Acid+υ(NH) N-phenylene diamine	υ(coo)asym	υ(coo) sym	υ(M-N)	υ(M-O)
1.	Aspartic acid	3140(b) 3012(b)	1685(m)	1612(m)	……..	……
2.	N-phenlyendiamine	3375(vs) 3302(b)	……	……..	…….	……
3.	$[Zn(a.a)_2N]$	3140(vw) 3016(vw)	1558(w)	1612(w)	644(vs)	478(vs)
4.	$[Cu(a.a)_2N]$	3290(w) 3233(w)	1411(s)	1708(s)	559(s)	439(s)
5.	$[Ni(a.a)_2N]$	3236(b) 3163(b)	1411(m)	1516(m)	513(s)	447(s)

Where:-vs= very strong , vw = very weak, s= strong, b= broad

Table (3): The Electronic Spectra for the Mixed Ligand and itsComplexes

No.	Compounds	λnm	ABS	Wave number (cm-1)	$E_{max}(L.Mol^{-1}.cm^{-1})$
1-	Aspartic acid	246 304	0.210 0.668	40650 32894.73	210 688
2-	N-phenylene diamine	394 301	0.265 0.368	25380.71 33222.59	265 368
3-	$[Zn(a-a)_2N]$	327	1.132	30581.03	1132
4-	$[Ni(a-a)_2N]$	304 496 252	1.334 1.423 0.139	32894073 24752.47 2016.29	1334 926 1423
5-	$[Cu(a-a)_2N]$	496 316	0.242 2.263	20120.72 31645.56	242 2263

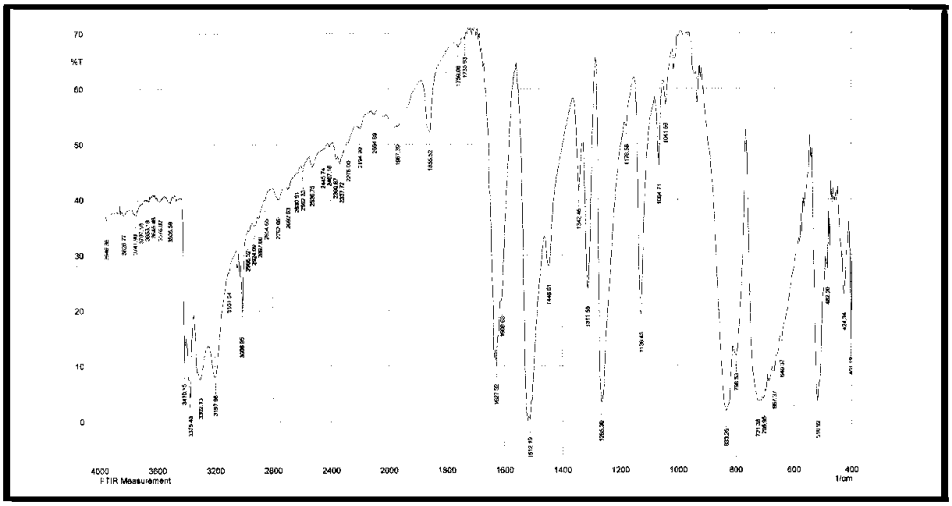


Fig (1) :- FTIR Spectrum Of The N- Phenylene di amine

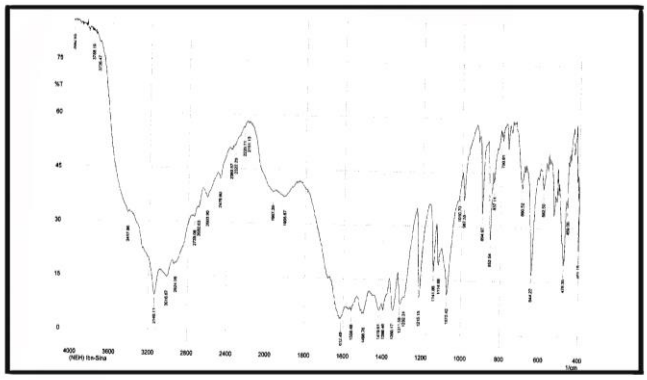
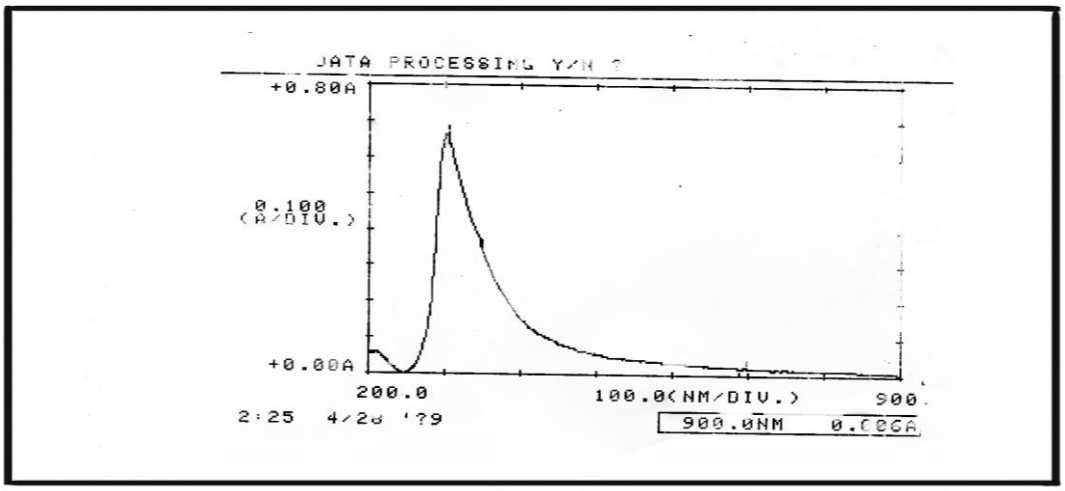


Fig (2) :- FTIR Spectrum Of The Aspartic acid



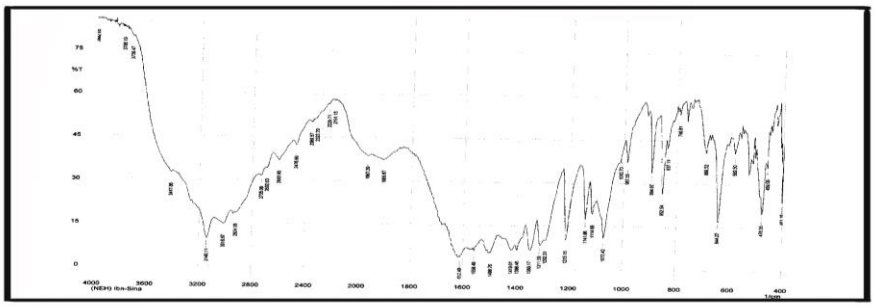


Fig (3) :- FTIR Spectrum Of The [Zn(a.a)$_2$]

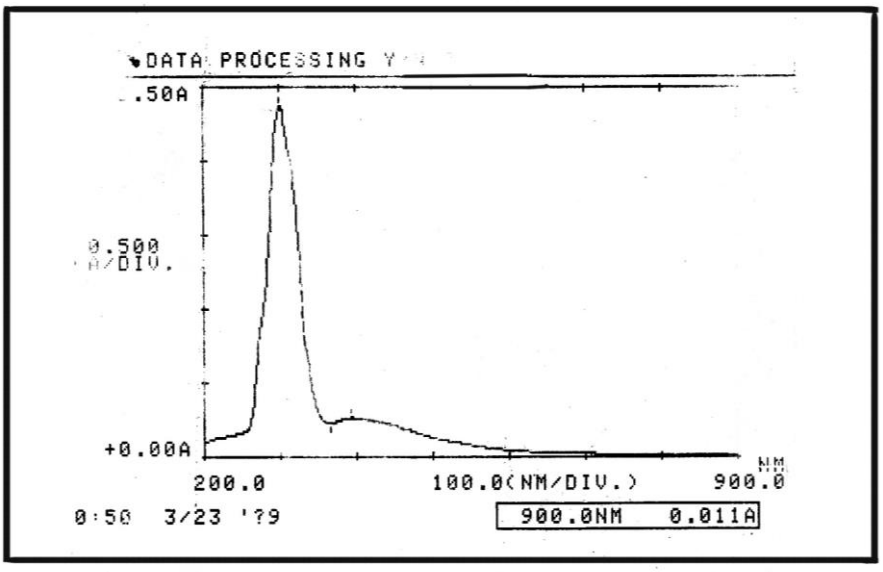


Fig (4) UV – Vis Spectrum of the N- phenylene diamine

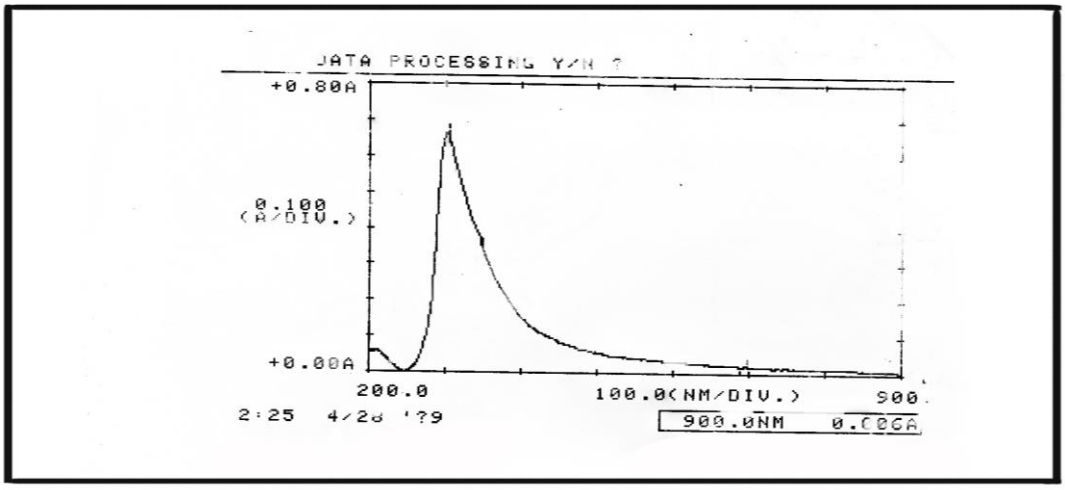


Fig (5) :- UV-Vis Spectrum Of The Aspartic acid

Fig (6) :- UV- Vis Spectrum of the [Ni (a-a)$_2$] complex

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تحضير وتشخيص معقدات النيكل (II) والنحاس (II) والزنك(II) مع ليكاندات مختلطة من حامض الاسبارتك و n – فيلين داي امين.

إنعام هاشم إبراهيم
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الخلاصة

يتضـــمن هذا البحث تحضـــير وتشـــخيص معقدات لبعض ايونات العناصـــر الانتقالية (Ni^{II},Cu^{II},Zn^{II}) وذلك من خلال مفاعلتها مع ليكاندات مختلطة من حامض الاسبارتك و N- فنيلين داي امين في وسط الايثانول وبنسبة 1:2:1 للحصول على سلسلة من المعقدات المتعادلة ذات الصيغة العامة $[M(a.a)_2N]$. شخصت المركبات المحضرة بوساطة طيف الاشعة تحت الحمراء والاشعة فوق البنفسجية-المرئية وقياس الامتصاص الذري فضلا عن قياسات التوصلية الكهربائية والحساسية المغناطيسية . ومن النتائج التي تم الحصول عليها تم اقتراح الشكل ثماني السطوح للمعقدات المحضرة.