Preparation Of Polyamid Macrocycle Dinuclear Complexes Containing Mn(II), Fe(II), Co(II), Ni(II) ,Cu(II) and Zn(II)Ion's

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Abstract : In this work we prepared some transition metal complexes with tetraamid [N8] macrocyclic ligand L-dicyclohexan 2,13,16,27 tetraoxo-3,6,9,12,17,20,23,26 decaazacyclohexa decane. The dinucleating with two metal ion's one of them Zn(II) nuclei in macrocyclic cavity. The structure was studied based on metal analysis FT-IR , electronic spectral magnetic measurements indicate that the compounds have octahedral and distortedoctahedral environment in the region of the metal ions.

Keywords: Macrocyclic ligand,Polyamid ligand,Dinuclear complexes,Transaition elements.

Introduction :

The combination of transition element macrocyclic compound is a constantly twist region in diagnostic in inorganic and bioinorganic chemistry[1-3], According to its application to study the functions of redox [4], of a lot of metallo-enzymes.

The redox active copper (II) compounds with saleen and relevant Schiff bases were exploited as structuralchemical nucleases [4] and DNA destructive agents [5].

The polydentate ligands having the donor atoms they contain at least three donor atoms and the ring should have at least nine atoms[6],poly macrocyclic complexes Settlement with tetra and hexaamide function a cyclic tetra peptide moieties inthe flip-flop connect element ions without deprotonation method of the amide set and make stability in the little oxidation states of the element ions[7]

The many method has been widely described audex ploited for the preparation of number of different types of metal-laminated macrocyclic complexes. However the importance of non-template procedure for isolating metal ion-free poly aremacro cycles have also been assert by some authors[8]. According to the above applications, it is preferable to preparation and investigation transition element compounds using such a ligand[9-11].

In this work, the synthesis and characterization of dinuclear complexes with [N8] polyamide L derived from tri ethylene tetra amine has been reported, as shown in Fig (1).

Experimental :

The ligand was synthesized according to the following method[12]. The hot ethanol(20ml) was used to dissolve the hexahydrophthalic anhydride (7.8g, 0.05mol) and combine slowly by a hot ethanolic solution (20ml) of tri ethylen tetra amine (7g , 0.05mol) with stirring. At ~ 85˚C, (2 ml conc) HCl is added to the mixture and then refluxed to 7h. Upon cooling the mixture, a white precipitate was formed. After that, it was filtered, washed using cold ethanol absolute and dried under vacuum Fig (1).

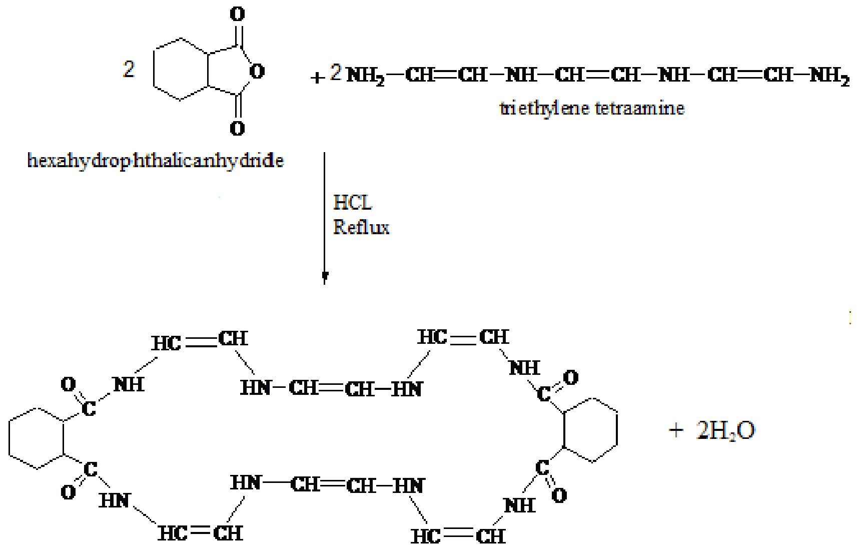

Fig (1): Preparation and structure of the ligand

A: preparation of the metal compounds :

The hot ethanolic solution of both the ligand and Zinc Chloride salt of concentration (0.001 mol /20ml) were mixed together with stirring. After that a hot ethanolic solution of Manganese(II), Iron(II),Cobalt(II), Nickel(II) , Copper(II) and Zinc(II) Chloride salt's (0.001 mol /20 ml) were mixed every metal alone in 1:1 molar ratio. Cooling the mixture after refluxed it for 2h at 80˚C, gives a colored

precipitate of the compounds. All the complexes of 1:1 molar ratio metals filtered and washed by cold ethanol and then desiccated under vacuum. All the physical properties shown in Table (1).

Table (1) : Elemental analysis data and molar conductance of the compounds

No.	compound	color	M.p (C^{o})	Yield %	Molar conductance $\Omega^{-1}.cm^{2}.mol^{-1}$	Elemental analysis data Found (Calculated%)
	Ligand (L)	White	169-171	68	----	----
1.	$[Zn_2\ LCl_4]$	Pale yellow	182-184	67	8.5	13.59(13.71)
2.	$[Zn\ LMnCl_4]$	yellow	204-206	72	9.0	Mn% 5.71(5.82)
3.	$[Zn\ LFeCl_4]$	Brown	224-226	75	12	Fe% 5.88(5.92)
4.	$[Zn\ LCo\ Cl_4]$	Dark green	211-213	80	13	Co% 6.08 (6.22)
5.	$[Zn\ LNi\ Cl_4]$	Green	228-230	60	7	Ni% 5.99(6.20)
6.	$[Zn\ LCuCl_4]$	Brown	198-200	65	11	Cu% 6.58(6.68)

B. Physical measurements:

Metal analysis of the compounds were done using standard method. Using a Perkin-Elmer 580 B spectrophotometer, the I.R spectra (4000-400 cm^{-1}) was recorded as Potassium Bromide discs. Also Shimadzu UV/VS was used to obtain the electronic spectra at room temperature and the compounds taken in concentration of 10^{-3} M of the DMSO solvent. By a Faraday's method using BrukerBM6, magnetic measurements were performed at 25 ° C on the solid. Conductivity was measured by a conductivity meter mode PCMS –Jenway .

Results and discussion:

The infrared spectra of the ligand show no band related to free primary amine and (C–O–C) group (6) and four new bands emerge in the free ligand spectrum allocatable to amid I [ν(C=O)], amid II [ν(C–N) +δ (N–H)], amid (III)[δ (N–H)], and [ν (N–H)] of secondary amino set as shown in Table (2) [13-15].

The infrared spectra of the present compounds contain a band at 3388-3405cm^{-1}which moved to lower frequencies by ~25 cm^{-1}. Also the band of amid II propose the coordination from the nitrogen of NH group. More support comes from the emergence of average intensity band in rang 405-447 cm^{-1} credited to [ν(M–N)] as shown in Table (2) [14-16].

Table (2) : Selected infrared spectra bands and their assignment in cm^{-1}

No.	Compound	Amid I υ (C=O)	Amid II υ (C–N+δNH)	Amid III υ (NH)	υ (NH)	υ (M–N)
	Ligand (L)	1715	1638	1467	3448	----
1.	**[Zn_2 LCl_4]**	1719	1615	1478	3418	427
2.	**[Zn $LMnCl_4$]**	1720	1615	1433	3405	410
3.	**[Zn $LFeCl_4$]**	1700	1614	1456	3417	405
4.	**[Zn LCo Cl_4]**	1720	1623	1455	3405	447
5.	**[Zn LNi Cl_4]**	1708	1617	1457	3406	450
6.	**[Cu $LCuCl_4$]**	1714	1613	1455	3388	428

Zinc (II) and Manganese (II) compound:

In this compound the magnetic moment value at room temperature 5.92 B.M, if we propose that the Zinc (II) ion diamagnetic. This value may attributed to the Mn(II) ion and indicates an octahedral structure with five unpaired electron(8). The electrons spectra exhibit a bands at 27450,34814 cm^{-1} may attributed to charge transfer as shown in Table (3) [17,18].

Zinc (II) and Iron (II) compound:

The electron is spectra appears a band at 1142 cm^{-1} which may credited to the Fe(II) ion ($^5T_2g \longrightarrow {}^5Eg$) transition and can be devoted to octahedral structure. This compound has a magnetic moment at room temperature 4.72 B.M attributed to Fe(II) ion in accord with those having distorted octahedral too as shown in Table (3) [13,17].

Zinc (II) and Cobalt (II) compound:

The magnetic moment value for this complex 4.96 B.M and also when we propose the zinc(II) ion diamagnetic this value may attributed to Co(II) ion and related to three unpaired electrons[13,17]. The electronic spectra showed an absorption at 11580,15125,17990 and 35670 cm^{-1}, these bands probably devoted to the transitions:

$^4T_1g(F)^4 \longrightarrow T_2g(F)\ \nu_1$, $^4T_1g \longrightarrow {}^4A_2g\ \nu_2$and $^4T_1g(F) \longrightarrow T_2g(P)\ \nu_3$, respectively[18,19].

The forth band probably due to charge transfer. The location of electronic spectral band shows that the Co(II) ion in this compound have distorted octahedral geometry, as shown in Table (3).

Zinc(II) and Nickel(II) compound:

In this compound, the magnetic value of 3.18 B.M assigned to high spin shape and appears the present of the octahedral structure round nickel(II) ion[19,20]. The electronic spectrum indicates 3 bands at 10480, 16125 ,and 24264 cm^{-1}correspoinding to three spin-allowed transition ${}^3A_2g$ (F) $\longrightarrow$ ${}^3T_2g$ (F) ν_1, ${}^3A_2g$ $\longrightarrow$ ${}^3T_2g$ (F) ν_2, and ${}^3A_2g$ (F) $\longrightarrow$ ${}^3T_1g$ (p) ν_3, respectively as illustrated in Table (3). An inspection of the compound shows that the Ni(II) ion octahedral geometry as shown in fig(2) [19,20].

Zinc(II) and Copper(II) compound:

The magnetic moment of the compound 1.91 B.M and may point out that the Cu(II) ion has one unpaired electron and Zinc(II) ion diamagnetic illustrated as shown in Table (3), So the electronic spectra display band's at 10892, 16834 cm^{-1} devoted to ${}^2E_2g$ $\longrightarrow$ ${}^2T_2g$ transition in distorted octahedral for Cu(II) ion as shown in fig(2).

Table (3) : Electronic spectral data and magnetic moment of the compounds.

No.	Compound	μeff B.M (25°C)	λ max (cm^{-1})
1.	[Zn_2 LCl_4]	diamagnetic	28451,31435
2.	[Zn $LMnCl_4$]	5.92	27450, 34814
3.	[Zn $LFeCl_4$]	4.72	11420, 35718
4.	[Zn LCo Cl_4]	4.96	11580, 15125, 17990, 35670
5.	[Zn LNi Cl_4]	3.18	10480, 16125, 24264, 36782
6.	[Zn $LCuCl_4$]	1.91	10892, 16834, 28940

All these compounds have non-electrolytic nature which supports the proposed structure, see Table (1) and Fig (2) [18,21]. Based on the previous explanation we suggest the following configuration to the Metal(II) compound shown in Fig (2).

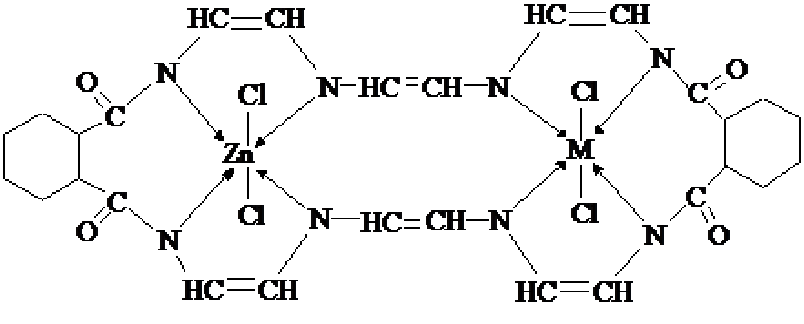

Fig.(2) Proposed structure of the compounds where M= Manganese(II), Iron(II),Cobalt(II), Nickel(II) , Copper(II) and Zinc(II)

References :

[1] BeswickCShaldersand R Swaddle T 1996 *Inorg.Chemi*35 991.
[2]Xiaoqi Yu and ZhangJi2018 *Macrocycli Polyamine Synthesis and Appliction* 1 ed. (Wiley-VCH , New Yourk) p 232.
[3]Al-Daher A and Al-Qassar I2018*Raf. J. Sci.*27(1) 52-64.
[4] CollmanJMarroccoMDenisevich PKoval Cand Anson F 1979*J.Electroanal Chem.* **101** 117.
[5]BurrowssC and MulterJ 1998 *Chem. Rev***98**1109.
[6]MohamadH andShreef K 2017 *Int. J. Curr. Res. Biosci. Plant Biol.* **4**(8)pp 15-21
[7] KantekinH and Dilber A2010*J. Org. Chem.***695**(8)pp1210 - 1214.
[8] Davis CDuck Worth PLindoy L and Mody W 1995*Aust. J.Chem***48** 1819.
[9] DawoodS and Thana Y2012*J. Edu. and Sci* ., **24**(1)pp22-28.

[10] Dawood S2011*J. Edu. and Sci* . **24**(4)pp 60 -67.
[11] DawoodSThana Y and IsraaA2010*Tikrit J. Pure Sci*. **15**(3)pp194-197.
[12]ChandraS Gupta L 2004 *SpectrochimicaActa*. A**60** 2767.
[13] Chandra S Gupta L 2002*Trans Met Chem*. 27329.
[14] Sulekh C and Lokesh K2005*SpectrochemicaActa*A**62** 1102-1106.
[15] Nacamoto K1997*Infrared and Raman Spectra of Inorganic and Coordination Compounds* 5th ed (John wily and Sons, Inc., New York) pp87-89.
[16] FalahM and Saad K2019 *Raf. J. Sci.***28**4pp 29-37.
[17] Ferguson J 1970 *Prog. Inorg. Chem*.**12**, 159.
[18] LeverA 1970 *crystal field spectra and electronic spectroscopy*(Wiley Inter science, New York) 101.
[19] Sulekh C andLokesh K2004*SpectrochemicaActa*. Part A. **60** pp 2767-2774 .
[20] SanKPaulsamy S and Hari N2007 *J. Inclphenommacrocycle Chem*. **959**pp 383-388.
[21]Chandra S and GauptaK 2001 *Synth React Met Org. Chem*. 31**4** pp661-672 .