

New mixed ligand Complexes of Mn(II), Fe(II), Co(II), Ni(II), Zn(II), and Cd(II) with amino acids (L-proline and L-threonine)
معقدات ليكاندات مختلطة جديدة ل Mn(II) ، Fe(II) ، Co (II) ، Ni(II) ، Zn(II) و Cd(II)

مع حوامض أمينية من نوع (L-proline and L-threonine)

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Abstract

A series of few mixed ligand complexes of, manganese(II), iron(II), cobalt(II), nickel(II), zinc (II) and cadmium(II), have been synthesized with The mixed ligand complexes have been characterized by, spectroscopic spectral measurements (FT-IR, U.V- Vis), molar conductance, magnetic measurements, and chloride content (Mohr Method) , metal contents of the complexes were determined by Atomic Absorption . The results suggest that the Mn(II), Fe(II), Co(II), Ni(II), Zn(II), and Cd(II) have distorted tetrahedral geometry . The following general formulae were proposed for the prepared complexes: $[M(\text{pro})(\text{Thr})]$, where $\text{pro}^- = \text{C}_5\text{H}_8\text{NO}_2^-$ Thr = $\text{C}_4\text{H}_9\text{NO}_2^-$, $M^{+2} = \text{Mn(II), Fe(II), Co(II), Ni(II), Zn(II), and Cd(II)}$. Molar conductance of a 10^{-3} M solution in (DMF) indicates that all the complexes are non-electrolytes.

الخلاصة:

تم تحضير سلسلة من المعقدات للأيونات الثنائية للمغنيز والحديد والكوبلت والنيكل والزنك والكاديوم من خلال إضافة نوعين من الحوامض الأمينية هما البرولين و الثريونين، حضرت المعقدات بطريق الإضافة الكاملة الى النوعين من الحوامض الأمينية الى الأيون الفلزي لتنتج معقدات ذات الصيغة العامة $[M(\text{pro})(\text{Thr})]$:

where $\text{pro}^- = \text{C}_5\text{H}_8\text{NO}_2^-$ Thr = $\text{C}_4\text{H}_9\text{NO}_2^-$, $M^{+2} = \text{Mn(II), Fe(II), Co(II), Ni(II), Zn(II), and Cd(II)}$

تم تشخيص المعقدات المحضرة بتقنية مطيافية الأشعة تحت الحمراء و فوق البنفسجية – المرئية والتوصيلية المولارية والحساسية المغناطيسية إضافة الى قياس محتوى الكلور بطريقة مور وتقنية الامتصاص الذري لتعيين نسبة الفلز في المعقدات اوضحت الدراسات اعلاه ان الشكل الفراغي المقترح هو رباعي السطوح المشوة وقد عززت قياسات التوصيلية المولارية ذلك حيث بينت ان جميع المعقدات المحضرة هي غير الكتروليتية.

Introduction :

Mixed ligand complexes are well known to play a significant role in biological systems [1]. Synthesis, structural studies and some other properties of mixed ligand transition metal complexes formed with histidine and adenine or guanine [2] and other amino acids have been reported [3-5]. The study of the coordinated systems metal ion - amino acids has become increasingly important in recent times, and from different points of view. [6]. Ganesh and Co-worker[7] were prepared and characterized of mixed ligand diox-ouranium(VI) and thorium(IV) complexes of 8-hydroxyquinoline as a primary ligand and amino acids such as L-proline(ProH) and 4-hydroxy-L-proline (Hyp) as secondary ligands. Cobalt complex with histidine ligand showed the significant antibacterial and antifungal activity in comparison with commercial antibiotics [8].

A few molybdenum(VI) peroxo L--amino acid complexes, $\text{MoO}(\text{O}_2)_2(-\text{aa})(\text{H}_2\text{O})$, [where -aa = glycine, alanine, proline, valine, leucine, serine, asparagines, and glutamine acid] have been synthesized and characterized [9].

Literature survey shows that no studies on the synthesis and characterization of mixed ligand complexes of L-proline and L-threonine have been reported. Hence the present paper reports the preparation, coordination and structure of new mixed ligand M(II) complexes formed with amino acids (L-prolin and L-threonine).

2. Experimental part

2.1. Materials and instruments

A- All chemicals were purchased from Merck and BDH.. ($\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , CdCl_2 , H_2O , and NaOH) from Merck . Methanol, ethanol, DMF, chloroform , acetone , L-proline and L-threonine from BDH. and were used without further purifications

B- Instruments: FT-IR 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 N,N-dimethyl formamide(DMF) 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 (DMF) using pw 9527 Digital conductivity meter (Philips). Melting points were recorded by using Stuart melting point apparatus.

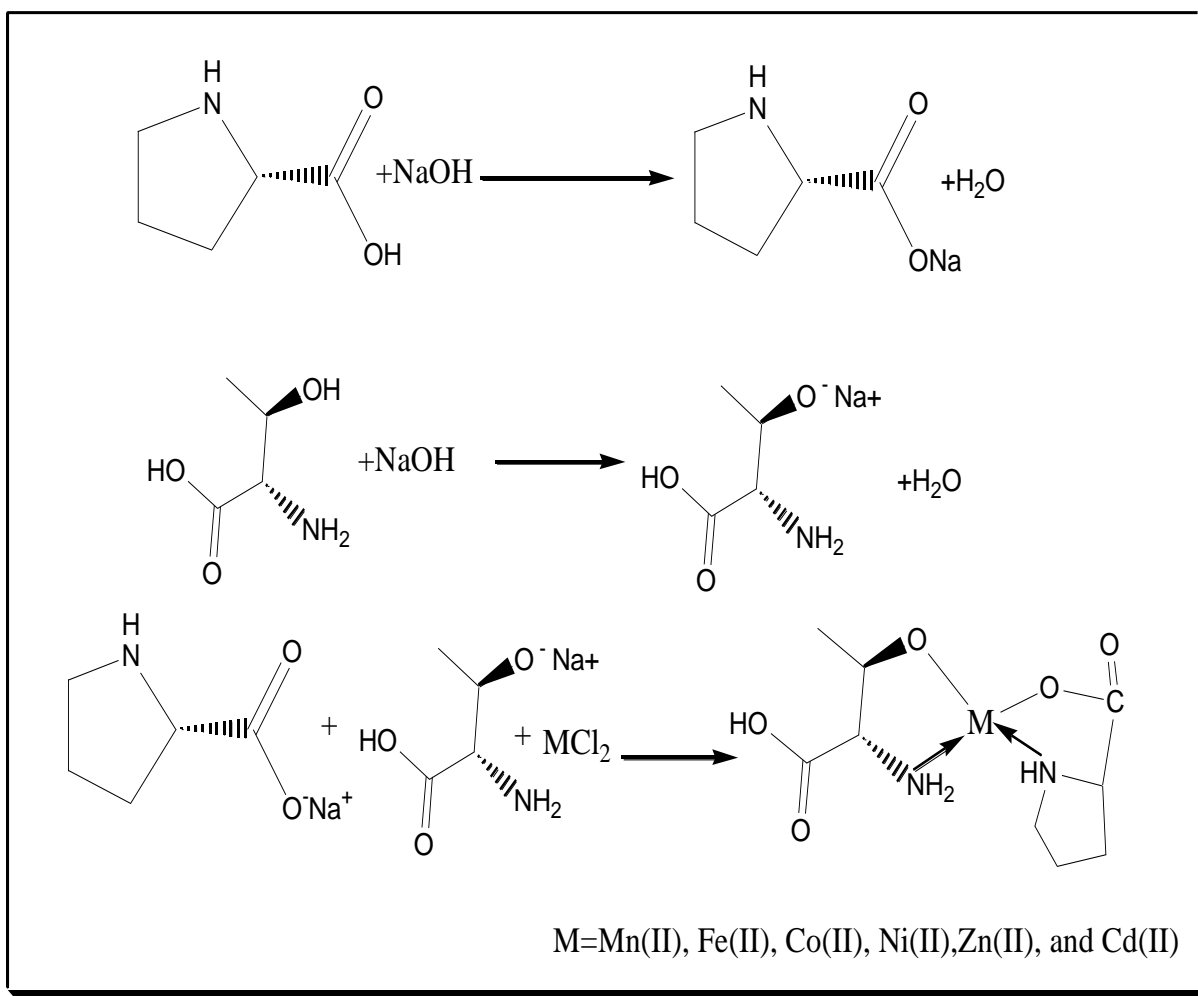
The proposed molecular structure of the complexes were determinated by using chem. office prog, 3DX (2006).

3-General Method for the Synthesis:

a- Sodium prolinatate: dissolve [(0.115 gm)1m.mol]of L-prolin with [0.04 gm (1mmol)] of sodium hydroxide (10ml) distilled water was deprotonated according (scheme -1).

b- Sodium threoninate: dissolve [(0.119 gm)1m.mol]of L- threonin with [0.04 gm (1mmol)] of sodium hydroxide in(10ml) distilled water was deprotonated according to the following reaction (scheme -1).

c) Synthesis of complexes: The complexes were prepared by the addition of aqueous solutions of the ($\text{Na}^+ \text{thr}^-$) and ($\text{Na}^+ \text{Pro}^-$) to warm stirred aqueous solution of the respective metal (II) chloride in the stoichiometric ratio matel: ligands(1:1:1) ($\text{Na}^+ \text{thr}^-$: M: $\text{Na}^+ \text{Pro}^-$). The mixture was stirred for 30 minutes at room temperature , and then formed the products were filtered off, washed and recrystallized with mixture of (1:1) water: ethanol and dried at 50°C . according to the following reaction , scheme -1



Scheme (1): Synthesis of the $[M(C_9H_{16}N_2O_5)]$ complexes

Results and Discussion :

The Physical properties listed in(Table -1). Some the complexes are colored, non-hygroscopic, and appears as powders with high melting points .

Solubility – The complexes are insoluble in water, ethanol, Methanol, chloroform , acetone, but soluble in N,N-dimethyl formamide (DMF) solvents.

The molar conductance :

The molar conductance values of the complexes in DMF at 10^{-3} M concentration are found to be (3.85. - 10.51) $\mu\text{S}\cdot\text{cm}^{-1}$, for complexes of composition $[M(\text{Pro})(\text{thr})]$ indicating their virtually non- electrolytes nature [10].

The atomic absorption measurements :

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

Table 1-The physical properties of the complexes

Compound	M.wt	Color	M.p °c (de) °c	Λ _m μS.cm ² .Mol ⁻¹	Metal%		Cl%
					theore tical	Exp.	
Ligand							
C ₅ H ₉ NO ₂ (proH)	115.13	White	222	5.45	-	-	-
(C ₄ H ₉ NO ₂) (Thr H)	119.12	White	238	2.74	-	-	-
[Mn(C ₉ H ₁₆ N ₂ O ₅)]	287.18	brown	230 dec.	4.50	19.13	18.2	Nil
[Fe(C ₉ H ₁₆ N ₂ O ₅)]	288.08	red brown	265 dec.	4.25	19.39	18	Nil
[Co(C ₉ H ₁₆ N ₂ O ₅)]	291.24	pale brown	240 dec.	9.78	11.05	13	Nil
[Ni(C ₉ H ₁₆ N ₂ O ₅)]	290.96	green	232 dec.	10.51	19.15	21	Nil
[Zn (C ₉ H ₁₆ N ₂ O ₅)]	297.63	White	166de	3.85	21.98	21	Nil
[Cd(C ₉ H ₁₆ N ₂ O ₅)]	344.65	White	268de	3.90	32.62	31.8	Nil

Λ_m = Molar Conductivity

dec. = decomposition

Fourier-transform infrared spectra :

The most important infrared spectral bands that provide conclusive structural evidence for the coordination of the ligands to the central metal ions . The characteristic vibrations and assignments of ligands (L- proline) and (L-threonine) and their complexes as KBr spectrum discs are described (Table -2) , Figures(1 - 4) .

The FT- Infra red spectrum of free ligand (L- proline) (Figure -1) exhibited a strong band around (3419-2393) cm⁻¹ that corresponds to the stretching vibration of ν (N-H) + ν (O-H), while another strong absorption band at (1624--1564) cm⁻¹ is appeared which could explained as ν (OCO)_{asym} where the ν (OCO) sym was noticed at (1450 -1377) cm⁻¹ . [13,14].

As regards chelation through amino acids, the IR spectra exhibit significant features in the νNH₂ and νCOO⁻ regions. It is worthwhile to mention here that free amino acids exist as zwitterions (NH₃AA.COO⁻) and the IR spectra of these cannot be compared entirely with those of metal complexes as amino acids in metal complexes do not exist as zwitterions. Some new bands of weak intensity observed in the regions around (505-645)cm⁻¹and (432-455) cm⁻¹ may be ascribed to M-N and M-O vibrations, respectively [14-15].It may be noted that, these vibrational bands are absent in the spectra of the ligands.

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

Compound	$\nu(\text{N-H}) + \nu(\text{O-H})$	$(\text{C-N})_{\text{cy}}$	$(\text{C-H})_{\text{cycl}}$	$(\text{N-H})_{\text{rock}}$	$\nu(-\text{COO})_{\text{asy}}$	$\nu(-\text{COO})_{\text{sym}}$	M-N	M-O
$\text{C}_5\text{H}_9\text{NO}_2$	3419-2393br	1473(964)s	2958s	640s	1624-1564	1450-1377s	----	----
$(\text{C}_4\text{H}_9\text{NO}_2)$	3167 -2515 br-vs	-----	----	702vs	1461-1454 vs	1419-1346vs	-----	-----
$[\text{Mn}(\text{C}_9\text{H}_{16}\text{N}_2\text{O}_5)]$	3356-2543 br	1493 (964)m	2971s	725	1442vs	1404vs	505m	455m
$[\text{Fe}(\text{C}_9\text{H}_{16}\text{N}_2\text{O}_5)]$	3359-2523 br	1493(966)s	2924w	735m	1373s	1397vs 1323 s	518m	459m
$[\text{Co}(\text{C}_9\text{H}_{16}\text{N}_2\text{O}_5)]$	3379- 2445 br	1458s(945)	2931s	734m	1604-	1396-1365s	518m	455m
$[\text{Ni}(\text{C}_9\text{H}_{16}\text{N}_2\text{O}_5)]$	3136 2854- br	1319br-s	2938s	725m	1469 vs	1377vs	657m	544m
$[\text{Zn}(\text{C}_9\text{H}_{16}\text{N}_2\text{O}_5)]$	3315s-3085m	1319m	2937w	754m	1467vs	1371vs	516m	432m
$[\text{Cd}(\text{C}_9\text{H}_{16}\text{N}_2\text{O}_5)]$	3410 sh	1315m(960)s	2979m	721m	1419vs	1396vs	645	432m

Sym: symmetric, asy: asymmetric, v.s: very strong, s: strong, m: medium, w: week, sh: shoulder



Figure .(1)FT- IR spectrum of L- proline ($\text{C}_5\text{H}_9\text{NO}_2$)

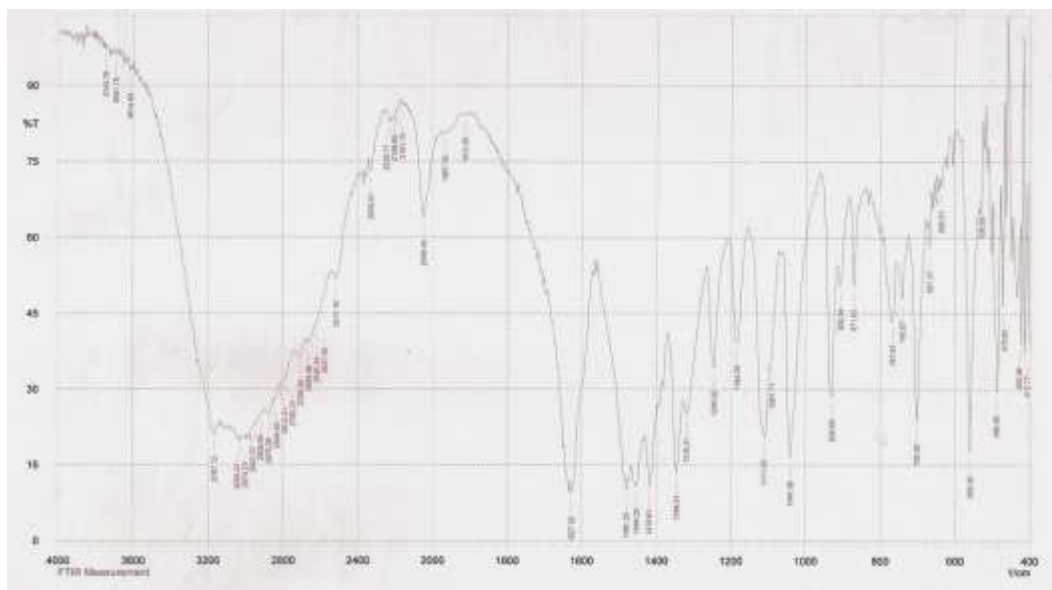


Figure .(2)FT- IR spectrum of **L-threonine (C₄H₉NO₂)**

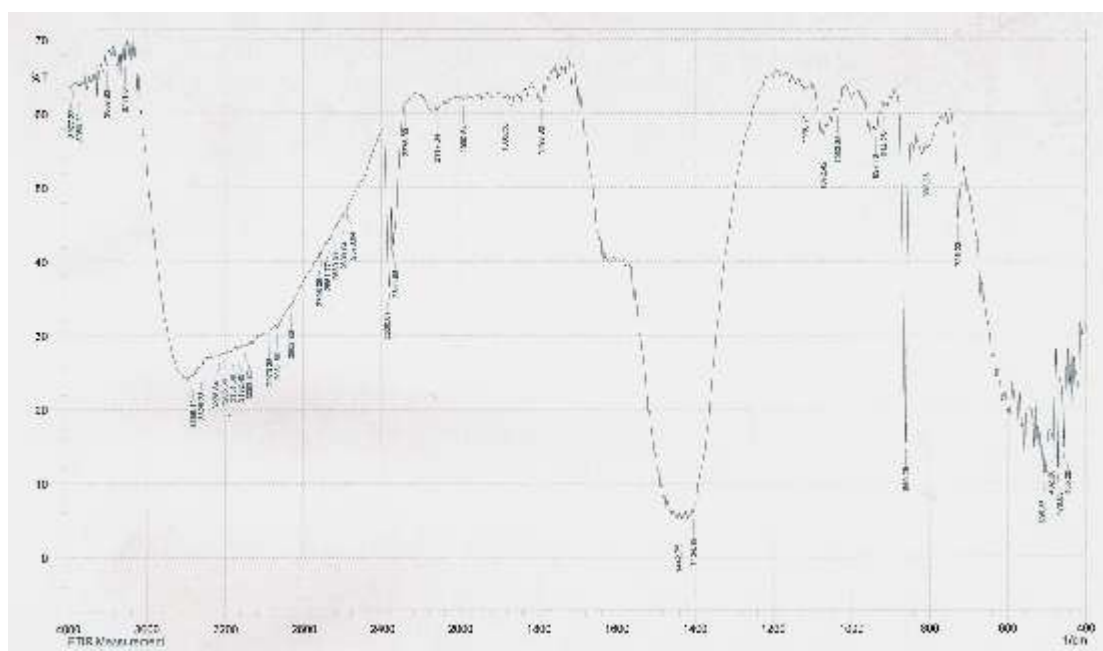


Figure .(3)FT- IR spectrum of **[Mn(C₉H₁₆N₂O₅)]**

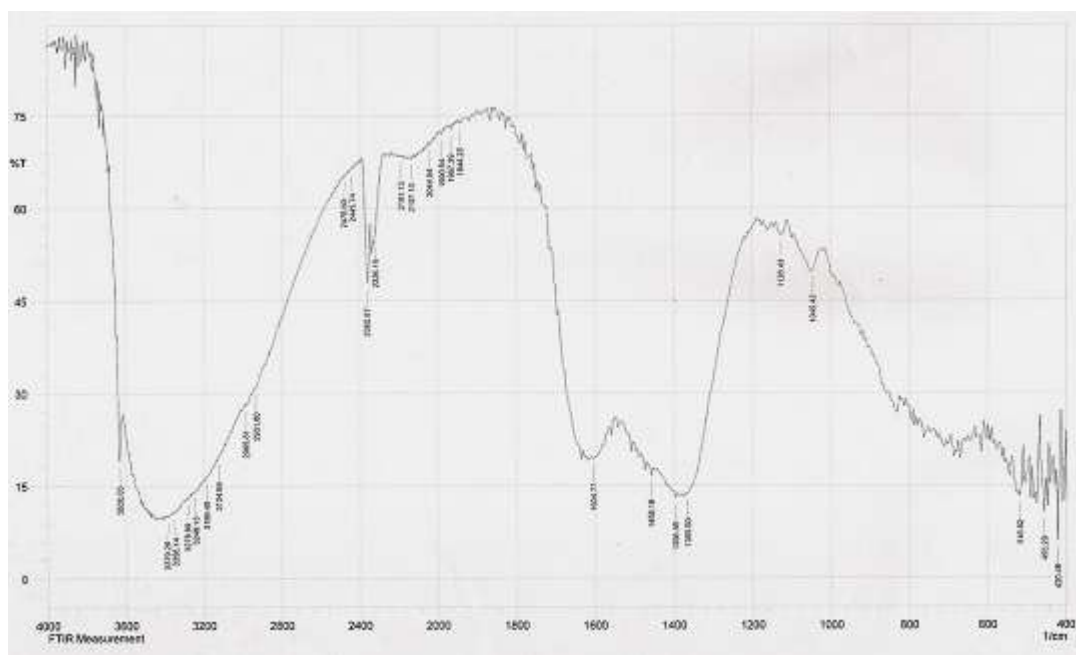


Figure .(4) FT- IR spectrum of [Co (C₉H₁₆N₂O₅)]

Electronic Spectra:

The UV- Vis spectra of the ligands and prepared complexes dissolved in DMF(10^{-3} M) have been measured the spectra appears the characteristic broad peaks for ligands at 276 and 274 nm due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ for (proH) and (ThrH) respectively. The complexes shows two types of transitions the first covered the ultra violet region respects the charge transfer and ligand field transition at (217),(268),(272),(280),(263,348,355),(274,345,370) nm for Mn, Fe, Co,Ni, Zn and Cd ions respectively, while the others peaks took places in the visible region respects the d-d transition at 344 nm assigned to $^4T_{1g} \rightarrow ^4A_{1g}$, for Mn(II), the peak at 420 nm can be assigned to $^5E_g \rightarrow ^5T_{2g}$ for Fe(II) ion, the peak at 389 nm assigned to $^4A_{2g} \rightarrow ^4T_{1g}$ for Co(II) ion, the peaks at 445 670 nm attributed to $^3T_{1(F)} \rightarrow ^3T_{2(F)}$ and $^3T_{1(F)} \rightarrow ^3T_{1(P)}$ for Ni(II) ion while the Zn(II) and Cd(II) doesn't have any d-d transition corresponding with d^{10} complexes since the electronic spectra supported the suggested tetrahedral geometry for the prepared complexes and the data obtained were included in (Table- 3).

Table (3) : Electronic Spectra of the studied complexes and ligands

Compounds	λ (nm)	ν' (cm^{-1})	Assignment	μ_{eff} (BM)
$\text{C}_5\text{H}_9\text{NO}_2$ (proH)	274	36496	$\pi \rightarrow \pi^*$ & $n \rightarrow \pi^*$	-
$(\text{C}_4\text{H}_9\text{NO}_2)$ (Thr H)	276	36232	$\pi \rightarrow \pi^*$ & $n \rightarrow \pi^*$	-
$[\text{Mn}(\text{C}_9\text{H}_{16}\text{N}_2\text{O}_5)]$	217 344	46083 29070	C.T ${}^4\text{T}_{1(\text{p})} \rightarrow {}^4\text{A}_1$	4.76
$[\text{Fe}(\text{C}_9\text{H}_{16}\text{N}_2\text{O}_5)]$	268 420	37313 23810	C.T ${}^5\text{E}_g \rightarrow {}^5\text{T}_2$	4.24
$[\text{Co}(\text{C}_9\text{H}_{16}\text{N}_2\text{O}_5)]$	272 389	36765 25707	C.T ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$	3.45
$[\text{Ni}(\text{C}_9\text{H}_{16}\text{N}_2\text{O}_5)]$	280 445 670	35714 22472 14925	charge transfer ${}^3\text{T}_{1(\text{F})} \rightarrow {}^1\text{T}_2$ ${}^3\text{T}_{1(\text{F})} \rightarrow {}^3\text{T}_{1(\text{p})}$	3.76
$[\text{Zn}(\text{C}_9\text{H}_{16}\text{N}_2\text{O}_5)]$	263 348 355	38023 28735 28169	Charge transfer & ligand field	0.00
$[\text{Cd}(\text{C}_9\text{H}_{16}\text{N}_2\text{O}_5)]$	274 345 370	36496 28986 27027	Charge transfer & ligand field	0.00

Magnetic Susceptibility:

Magnetic susceptibility was determined at room temperature using solid sample by Gouy method. The complexes of (Zn^{2+} , Cd^{2+}) ($d^{10} = e^4t^6$) (white complexes) were diamagnetic as expected from their electron configuration. The μ_{eff} value for the following high spin tetrahedral complexes was found to be as follows: for $\text{Co}^{2+}(d^7)$ complex was 3.45 B.M within the expected spin-only values [12]. The higher value of μ_{eff} for $\text{Ni}^{2+}(d^8)$ complex was 3.76 B.M which may be due to orbital contribution (e^4t^4) and . μ_{eff} for $\text{Mn}^{2+}(d^5)$ complex was 4.76 B.M within the expected spin-only values. [11,12].

Proposed Molecular Structure

Studying complex on bases of the above analysis ,the existence of tetra coordinated.

$[\text{M}(\text{C}_9\text{H}_{16}\text{N}_2\text{O}_5)]$, M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II), and Cd(II).

A proposed models of the species were built with chem.-3D shows in Figure-5

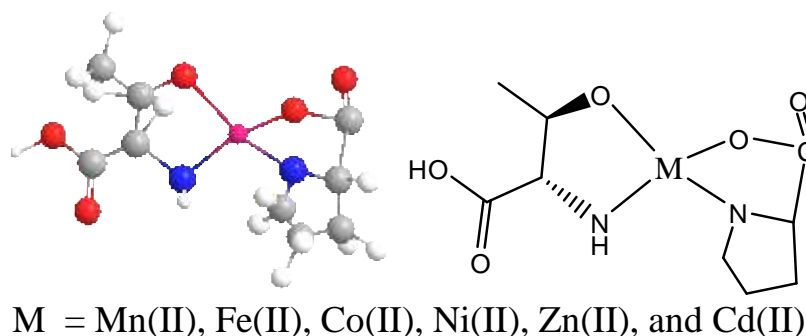


Fig (5):The suggested structure for the complexes [M (C₉H₁₆N₂O₅)]

Conclusion:

In this work a new mixed ligand complexes containing L- threonine and L- proline with the general formula [M(pro)(ther)] where Synthesis and Characterization of Mixed Ligand Complexes of L-threonine and L-proline with Mn(II), Fe(II), Co(II), Ni(II), Zn(II), and Cd(II) ions .

The molar conductivity of the complexes in DMF solution were non electrolyte and the configurations were performed to coordinate the threonine and proline through the nitrogen and oxygen atoms. Therefore, Conclusion Thus the evidences obtained from IR spectra, electronic spectra and magneto chemical measurements suggest an distorted tetrahedral configuration geometry around the central atom.

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