

**Synthesis and characterization of (L- proline) amino acid
with (Mn⁺² , Fe⁺² , Co⁺² , Zn⁺² and Cd⁺²)**

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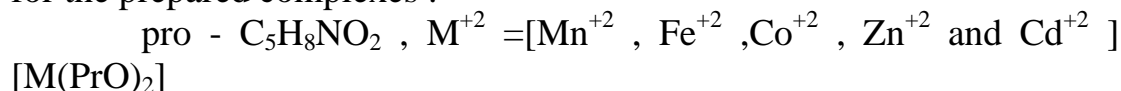
Abstract:

This paper includes the synthesis and characterization of the complexes of the amino acid (L-proline) = C₅H₉NO₂) symbolized (proH)-with some metal . The ligand and metal ions were brought into reaction in ethanolic medium using (1:2) metal : ligand molar ratios as required.

Products were found to be solid crystalline complexes, which have been characterized through the following techniques : Melting points, Solubility, Molar conductivity.

Determination the percentage of the metal in the complexes by (AAS). chloride ion content were also evolution by (mhor method) . Spectroscopic Methods (FT-IR and UV-Vis), and. The proposed structure of the complexes using program , chem office 3D(2004) .

from the results obtained the following general formula have been given for the prepared complexes .



Where The results showed that the deprotonated ligand (Proline acid) to (Prolinateate ion) (Pro⁻) by using (NaOH) coordinated to metal ions as bidentate ligand through the nitrogen atom of the imine group(N-h) and the oxygen atom of the carboxylate group (-COO⁻).

Introduction :

In recent years, the chemistry of N-heterocyclic carbines and their transition-metal complexes have attracted much attention because these carbines are readily generated from the corresponding imidazolium salts(1) and act as efficient lizards in a great variety of catalytic processes including alkene metathesis(2), hydrogenation(3), C-C (4) and C-N (5) bond construction. On the other hand, although a few examples of choral NHC-metal complexes have proven exhibiting good or excellent enantio sensitivities (6-(10), Traditionally, the very inert platinum(II) is modeled by palladium(II)in studies, still there are relatively few publications

describing solution equilibrium of palladium (III-amino acid systems. Besides some new platinum(II) and palladium(II) complexes, 11, 12 some organotin(13) lanthanide, (14) gold, (15) and copper (16-18) complexes were also found to be biologically active.

In this paper we present the synthesis and study of some transition metal complexes with amino acid (L-proline).

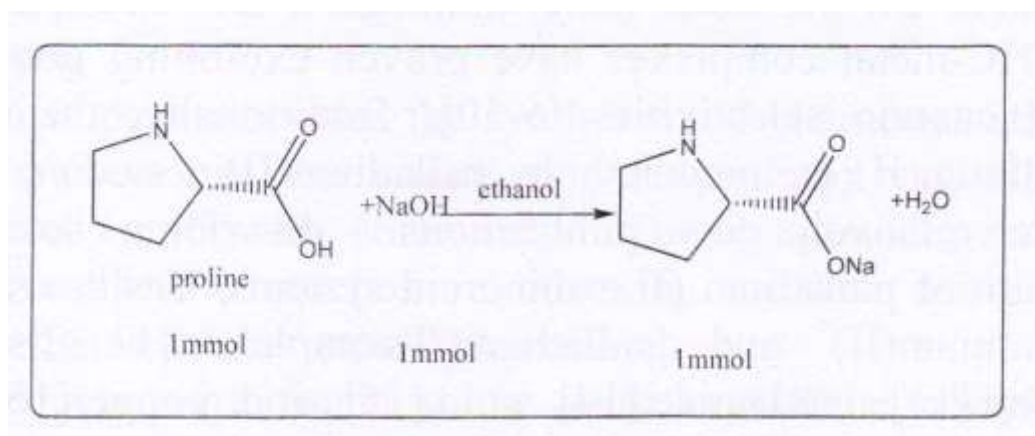
Experimental :

1-Reagents and instruments : L-proline was purchased from (Merck), metals chloride and solvents from (B.D.H). The reagents were applied without further purification.

2- Instruments : ft.i.r 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 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-67 Shimadzu. Electrical conductivity measurements of the solutions of the complexes were recorded at 25°C or samples in DMF using pw9527 Digital conductivity meter (Philips). Melting points were recorded by using Stuart melting point apparatus.

The proposed molecular structure of the complexes were regenerated by using chem. office prog, 3dx (2004).

3-General Method for the Syntheses: a- Sodium proline: dissolve (0.115 gm) (1mmol) of ligand solution with (0.04 gm (1mmol) of sodium hydroxide in ethanol was deprotonated according to the following reaction



b- Synthesis of complexes: An aqueous solution of the metal salt was added to the solution of the ligand in ethanol using stoichiometric amounts ((1:2) (metal : ligand molar ratio as required, the mixture was stirred for half an hour at room temperature, crystalline precipitates observed. The resulting precipitates were filtered off recrystallized from ethanol and dried at room temperature.

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 they are not soluble in water. All complexes dissolved in DMF solvent. The atomic absorption measurements (Table-1) for all complexes gave approximated values for theoretical values.

The molar conductance values of the complexes in DMF at to be (2.1 0. - 4.55) $\mu\text{s}\cdot\text{cm}^{-1}$ for 10^{-3} M concentration are found , i dilating their non- complexes of composition $[\text{M}^{11} (\text{Pro})_2]$ indicating their non electrolytic nature (19) Spectral Studies: Tables (2 and 3) describes the important absorptions and assignments for the free ligand and its complexes.

The FT- Infra red spectrum of free ligand (Fig -1) Table (2) corresponds to exhibited a strong band around (3056) cm^{-1} that the stretching vibration of $\nu (\text{N-H}) + \nu (\text{O-H})$, while another which strong absorption band at (1624-1600) cm^{-1} is appease could explained as $\nu (\text{OCO})_{\text{asym}}$ where the $\nu (\text{OCO})_{\text{sym}}$ was noticed at (1450 -1377) cm^{-1} . (20,21).

In the infrared spectra for complexes, Table (2) (fig- 2) absorption band for $\nu (\text{OCO})_{\text{sym}}$ was noticed at the range shiked to higher position while the band (1488-1327) cm^{-1} caused by $\nu (\text{OCO})_{\text{asym}}$ appeared between (1624-1 508) cm^{-1} , which indicates the coordination of the carboxylic group to the central metal ion. (20,21) The strong band of $\nu(\text{c-n})$ stretching in the FT- Infra red for the imine spectrum of free ligand (proline) at (1473) cm^{-1} or group was shifted to lower frequency and appeared in the FTIn feared spectra of all complexes at range (1419-1458) cm^{-1} suggesting the possibility of the coordination of the ligand (pro-) through the nitrogen atom at the imine group (21). Absorption bands in the (549-624) cm^{-1} region are considered to be due to metal-nitrogen vibrations (21,22) whilst those occurring thought to arise from metal-oxygen around (474- 432) cm^{-1} are thought vibration . (20)

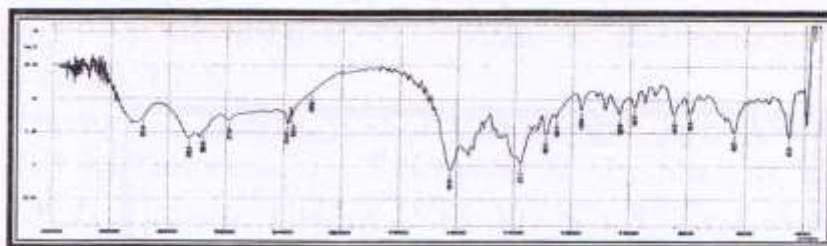


Fig .(1)FT- IR spectrum of (C₅H₉NO₂)

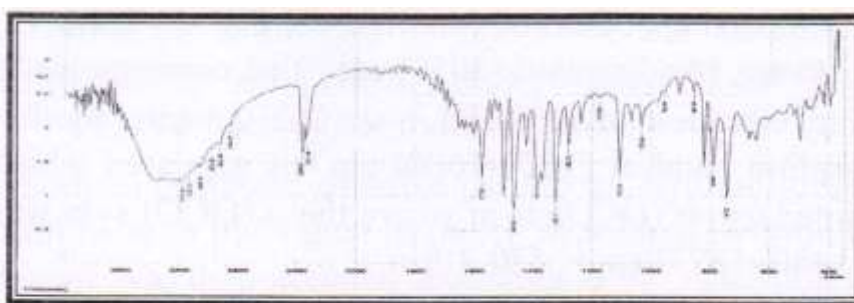


Fig .(2)FT- IR spectrum of Mn (C₅H₈NO₂)₂

The electronic spectrum of the free ligand and its complex are listed in Table (3) together with the proposed assignments.

The spectrum of the free ligand (proh) In DMF solvent (Fig- 3) shows intensity band at wave length 332nm (30120 cm^{-1}) cmax ($150 \text{ L, mol}^{-1} \cdot \text{cm}^{-1}$) assigned to ($n \rightarrow \pi^*$). (23)

The (UV-Vis) spectra of the complexes $[\text{M}(\text{C}_5\text{H}_8\text{NO}_2)_2]$
 $\text{M} = \text{Fe}^{+2}, \text{Co}^{+2}, \text{Zn}^{+2}, \text{Mn}^{+2}$

(Fig-4) displayed absorptions band at (319.7-366.8)nm assigned for ligand field . (23,24) The complete $[\text{Cd}(\text{C}_5\text{H}_8\text{NO}_2)_2]$, displayed absorptions at, λ assigned to the charge transfer (418.4nm) (23900 cm^{-1}) was assigned (C.T).

From the above data ,we suggested that the geometry of the all complexes are tetrahedral (23,24)

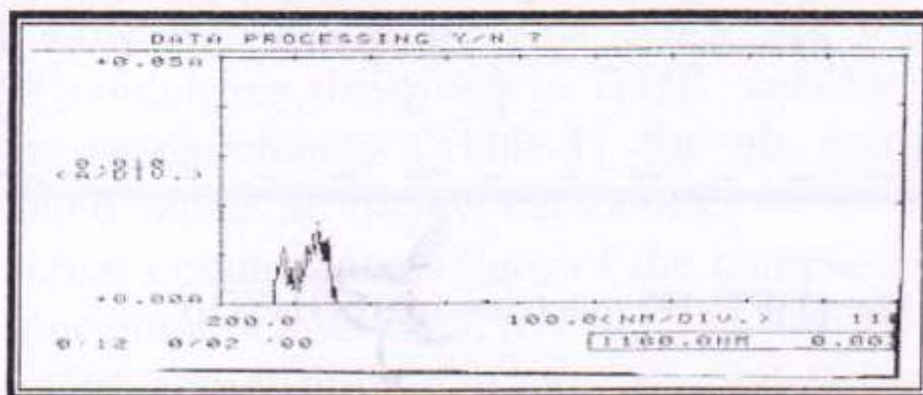


Fig. (3) Electronic spectrum of $(C_5H_9NO_2)$

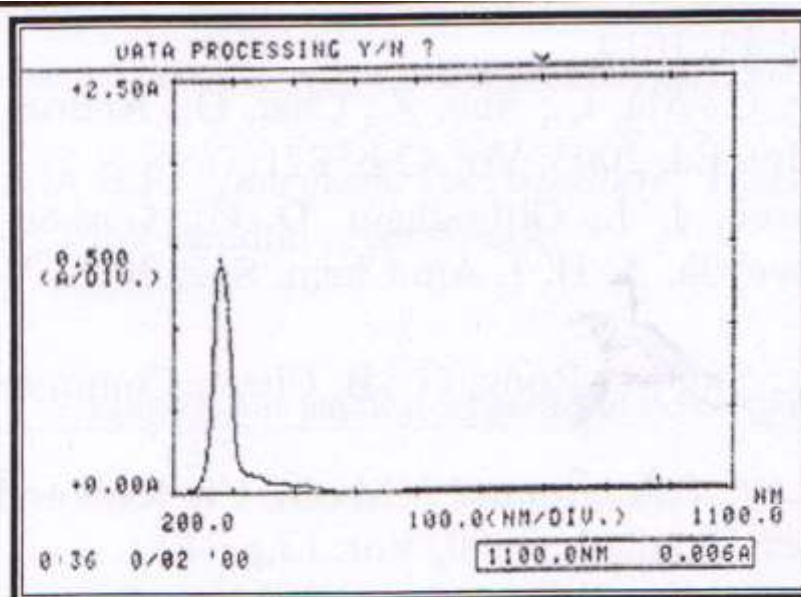


Fig. (4) Electronic spectrum of $Mn(C_5H_8NO_2)_2$

Nomenclature of prepared complexes : Table (4) shows empirical formula and nomenclature (IUPAC)

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Table (1) The physical properties of the compounds

| Compound | M.wt | Colour | M.p ^o c (de) | *M.C μS.cm ⁻¹ | Metal% | | Cl% |
|--|--------|--------------|-------------------------|-----------------------------|--------|-------|-----|
| | | | | | theory | exp | |
| Proline (ligand) | 115.13 | White | 222 | 5.45 | - | - | - |
| Mn(C ₅ H ₈ NO ₂) ₂ | 283.19 | Dark Brown | 278 de | 4.555 | 19.40 | 20.02 | Nil |
| Fe(C ₅ H ₈ NO ₂) ₂ | 284.10 | Red-Brown | 250 de | 3.36 | 19.66 | 21.03 | Nil |
| Co (C ₅ H ₈ NO ₂) ₂ | 287.25 | brown | 232 de | 4.55 | 20.52 | 19.50 | Nil |
| Zn (C ₅ H ₈ NO ₂) ₂ | 293.64 | White | 244 de | 3.5 5 | 22.27 | 24.07 | Nil |
| Cd (C ₅ H ₈ NO ₂) ₂ | 340.66 | Pale -yellow | 280 de | 2.10 | 33 | 34.4 | Nil |

M.C = Molar Conductivity

prolinato ion = pro⁻ = C₅H₈NO₂⁻

de = decomposition

Table (2) FT-IR spectral data of the Ligand and its complexes

| Compound | ν(N-H) + ν(O-H) | (C-N) _{as} | (C-H) _{est} | (N-H) _{est} | ν(-COO) _{as} | ν(-COO) _{sym} | M-N | M-O |
|--|-----------------|---------------------|----------------------|----------------------|-----------------------|------------------------|-----|-------|
| Proline (ligand) | 3419-2393br | 1473(964)s | 2958s | 640s | 1624-1564 | 1450-1377s | - | - |
| Mn(C ₅ H ₈ NO ₂) ₂ | (3419-2393)br | 1419s941s | 2970m | 594vs | 1624-1600 sh | 1445vs-1342w | 549 | 474m |
| Fe(C ₅ H ₈ NO ₂) ₂ | 3418 s | 1430m | 2978m | 671m | 1561vs- | 1445vs- | 576 | 456 m |
| Co (C ₅ H ₈ NO ₂) ₂ | 3410s | 1458m | 2985m | 671m | 1620vs | 1458w-1361vs | 624 | 432m |
| Zn (C ₅ H ₈ NO ₂) ₂ | 3356vs | 1419w(937s) | 2978m | 651m | 1561vs-1508vs | 1488 vs-1327m | 624 | 470w |
| Cd (C ₅ H ₈ NO ₂) ₂ | 3387vs | 1419vs | 2360s | 651m | 1624-1600 sh | 1415-1396s | 624 | 432w |

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

Table (3): The Electronic Spectra data for the Free Ligand (L-Proline) and its Complexes in DMF($10^{-3}M$)

| Compounds | λ (nm) | $\bar{\nu}$ (cm^{-1}) | ϵ (max)L.mol.m $^{-1}$ | Assignment | Coordination |
|----------------------------|----------------|---------------------------|---------------------------------|-----------------------|--------------|
| L-Proline=($C_5H_8NO_2$) | 332 | 30120 | 150 | $n \rightarrow \pi^*$ | - |
| Mn($C_5H_8NO_2$) $_2$ | 319.7 | 31279 | 417 | Ligand field | Td |
| Fe($C_5H_8NO_2$) $_2$ | 366.8 | 27277 | 592 | Ligand field | Td |
| Co ($C_5H_8NO_2$) $_2$ | 391.4 | 25549 | 340 | Ligand field | Td |
| Zn ($C_5H_8NO_2$) $_2$ | 355.4 | 28137 | 115 | Ligand field | Td |
| Cd ($C_5H_8NO_2$) $_2$ | 418.4 | 23900 | 73 | C.T | Td |

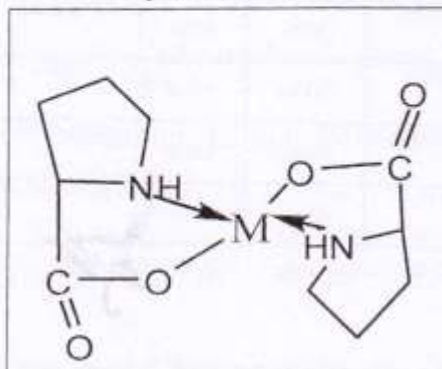
Table (4) Nomenclature of prepared complexes

| Complexes | Name | Abbreviation |
|--------------------------|-------------------------------|----------------|
| Mn($C_5H_8NO_2$) $_2$ | Di (prolinato) manganese (II) | Mn (Pro) $_2$ |
| Fe($C_5H_8NO_2$) $_2$ | Di (prolinato) iron(II) | Fe (Pro) $_2$ |
| Co ($C_5H_8NO_2$) $_2$ | Di (prolinato) cobalt (II) | Co (Pro) $_2$ |
| Zn ($C_5H_8NO_2$) $_2$ | Di (prolinato) zinc (II) | Zn (Pro) $_2$ |
| Cd ($C_5H_8NO_2$) $_2$ | Di (prolinato) cadmium (II) | Cd (Pro) $_2$ |

Proposed Molecular Structure

Studying complex on bases of the above analysis ,the existence of tetra coordinated $[M(C_5H_8NO_2)_2]$, $M^{+2}=[Mn^{+2}, Fe^{+2}, Co^{+2}, Zn^{+2}, Cd^{+2}]$.

A proposed models of the species were built with chem. 3D shows in Fig (3) .



Fig(3):The suggested structure for the complexes $[M (C_5H_8NO_2)_2]$ $M^{+2}=[Mn^{+2}, Fe^{+2}, Co^{+2}, Zn^{+2}, Cd^{+2}]$

تحضير وتتشخيص معقدات الحامض الاميني (البرولين)

الايونات ، cd^{+2} , mn^{+2} , fe^{+2} , co^{+2} , zn^{+2}

م.م. تغريد هاشم النور .م.م. فائزة حسن غانم ، م.م. عالية سلمان قنديل

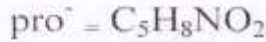
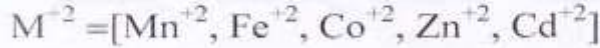
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الخلاصة

يتضمن البحث تحضير وتتشخيص خمسة من معقدات الليكاندا (proline) ومختصره (proh) وذلك من مفاعله مع الايونات الثنائية الشحنة الموجبة لبعض العناصر الفلزية وقد كانت التفاعلات في مذيب الايثانول بنسب مولية (1:2) المعقدات المحضرة بلورات صلبة بعضها ملون درست من النواحي الاتية:-

درجة الانصهار ، التوصيلية الكهربائية المولارية الذوبان تقدير النسبة المئوية للأيون الفلزي في المعقدات بواسطة مطيافية الامتصاص الذري محتوى الكلور بأستعمال طريقة مور الدراسات الطيفية وتضمنت اطيف (الاشعة تحت الحمراء ، الاشعة فوق البنفسجية - المرئية مع استعمال البرنامج chem. Office-cs-3dpro2004 في رسم اشكال المعقدات ومن الدراسات التشخيصية اقترحت الصيغة العامة الاتية لهذه المعقدات.

[M(pro)₂] اذ ان :



الليكاند (حامض البرولين) الفاقد البروتون الى (ايون البرولينيت

(pro⁻) = (prolinato) باستعمال (NaOH) يسلك سلوك ليكاند ثنائي السن

اذ يرتبط بالأيون الفلزي عن طريق ذرة النتروجين في مجموعة الأيمين

(-NH)(imine) وذرة الأوكسجين في مجموعة الكربوكسيل (-COO⁻).