

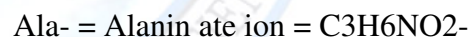
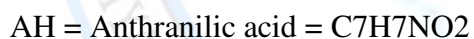
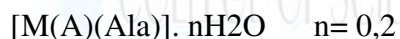
Synthesis and characterization of the mixed ligand complexes (L-alanine and anthranilic acid) with some transition Ions

BY

T.H.AL-Noor, A.T.AL-Jeboori, F.H, Ghanim
Chemistry Department .Ibn -Al-Haithem College of Education,
University of Baghdad-IRAQ

Abstract

This paper presents the synthesis and study of some new mixed-ligands complexes containing anthranilic acid and amino acid L-alanine (Ala) with some metals. The resulting products were found to be solid crystalline complexes which have been characterized by using (FT-IR,UV-Vis) spectra , melting point, molar conductivity , chloride ion content were also determined by (mohr method) and determination the percentage of the metal in the complexes by (AAS).The proposed structure of the complexes was suggested using program , Chem Office 3D(2004) .The general formula have been given for the prepared complexes :



Introduction

The characterization and quantitative investigation of the binding properties of amino acids towards transition metal ions plays an important role in our understanding of metal~protein interactions (1). There are many reports on the metal-anthranilate complexes along with the structure of many of these compounds. Some transition metal anthranilates have capability for aren't hydrogenation. (2, 3). During the recent years, there has been significant interest in the coordination chemistry , the structural properties and the reactivity of metal complexes of amino

acids.(4-8).Metal amino acid complexes have long been of interest as models for metal–ligand systems and interaction which may occur in nature(9-13).In this paper we reported the synthesis, spectroscopic and structural of complexes of M+2 ions using amino acid alanine as a primary ligand and anthranilic acid - as a secondary ligand.

Experimental

A: chemicals and instruments

chemicals were purchased from Fluka & Redial-Deheng Co.I.R spectra were recorded as KBr discs using Perkin-Elmer1330 Infrared Spectrophotometer and fourier transform infrared spectrophotometer ,Shimadzu 24FT-I.R8300. 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-160A Ultra Violet Visible-Spectrophotometer with 1.000 ± 0.001 cm matched quartz cell, while metal contents of the complexes were determined by v (A.A)technique using Japan A.A-670 Shimadzu. Electrical conductivity measurements of the complexes were recorded at 25°C for 10⁻³ M solutions of the samples in DMF using PW9527 Digital conductivity meter (Philips). Melting points were recorded using Stuart melting point apparatus. The proposed molecular structure of the complexes was determined by using Chem Office 2004, 3DX program.

B: General synthesis:

Sodium anthranilate (Na+Anth-) and sodium alaninate (Na+Ala-) were prepared by anaturalization of anthranilic acid(AH) [0.137gm(1mmol)] solution and alanine (AlaH) [0.09gm(1mmol)]solution with [0.04 gm(1mmol)]of sodium hydroxide solution .The complexes were prepared by the addition of (Na+Anth-) and (Na+Ala-) to warm stirred aqueous solution of the respective metal (II) chloride in the stoichiometric ratio metal:ligand (M:A:Ala) in (10 min) after cooling of the solution pink well-shaped crystals of the cobalt and manganese compounds formed . The compounds are insoluble in water, but soluble in DMF, the crystals were filtered , washed with acetone and dried at room temperature .

Results and Discussion

The complexes are air-stable, non-hygroscopic, colored solids, insoluble in water, partly soluble in ethanol and methanol, and soluble in DMSO and DMF. The observed molar conductance (Table 1) values measured in DMF in 10⁻³M solution fall in the range (1.44-8.20 Sem .cm².Mol⁻¹). These observed values of the molar conductance are well within the expected range for non- electrolytic nature (14-15) The (A.A.S) measurements and chloride content results for the complexes in a good agreement with calculated values, (Table-1) include the physical properties and chloride ion content. The magnetic measurements (Table-2) showed the cobalt ion in its pale brown complex to be paramagnetic with d⁷ configuration in distorted tetrahedral environment (15, 16). (Table-3 and 4) are computable with the suggested structure (Figs.1 and 2). This suggestion is supported by the number of maxima observed in uv – vis. spectrum of the complex, which show 3 maxima and be assigned to the transition 4A₂→4T₂,

4A₂ → 4T₁(F) and 4A₂ → 4T₁(p), Table (3) . The Racah parameter B⁻, B and the value of 10 Dq = 14836 cm⁻¹ where calculated by reference to Tanabe – Sugano diagram for d⁷ configuration (17) .

$$B^- = \frac{V_3 + V_2 - 3V_1}{15} 292.7 =$$

$$= \beta \frac{B^-}{B} = \frac{292.7}{971} 0.30 =$$

The spectrum of the free ligand (Ala⁻) in DMF solvent show a high intensity band in wave length 277 nm (36101cm⁻¹) ε max (343 l.mol⁻¹.cm⁻¹) assigned to (π→ π) and in wave length 304 nm (32894cm⁻¹) ε max (391 l mol⁻¹.cm⁻¹) assigned to (n → π*) (16) and free ligand (A) show a high intensity band in wave length in 337 nm (29673cm⁻¹) (2337.mol⁻¹.cm⁻¹) assigned to (π→ π*) and in wave length 360 nm (27777cm⁻¹) ε max (1108 l.mol⁻¹.cm⁻¹) assigned to (n → π*). (17)

The assignments of some of the most characteristic FT-IR band of the complexes are shown in (Table -3) together with those of sodium alalinate and sodium anthranilate recorded for comparative purposes and facilitate the spectral analysis. Absorption bands in the (634-518) cm⁻¹ region are considered to be due to metal-nitrogen vibrations (18,19) whilst those occurring around (410-514)cm⁻¹ are thought to arise from metal-oxygen vibration . (20,21) and finally the sharp bands at (3276-3330) cm⁻¹ are attributed to the N-H stretching vibration . (22).

Nomenclature of prepared complexes

Table (5) shows empirical formula and nomenclature (IUPAC) with abbreviated.

Proposed molecular structure

Studying complexes on the basis of the above analysis shows, the existence of tetra coordinated $[M(\text{Ala})(\text{A})]$, $M(\text{II}) = \text{Fe}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Zn}(\text{II})$ and $\text{Cd}(\text{II})$. Hexa coordinated $[M(\text{Ala})(\text{A})] \cdot 2\text{H}_2\text{O}$, $M(\text{II}) = \text{Cu}(\text{II}), \text{Mn}(\text{II})$. A proposed models of the species were built with Chem 3D shows in Figs (1 and 2).

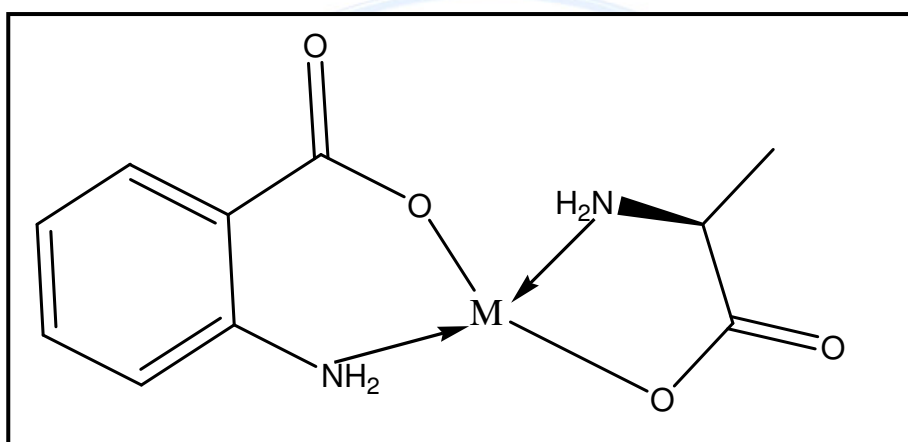
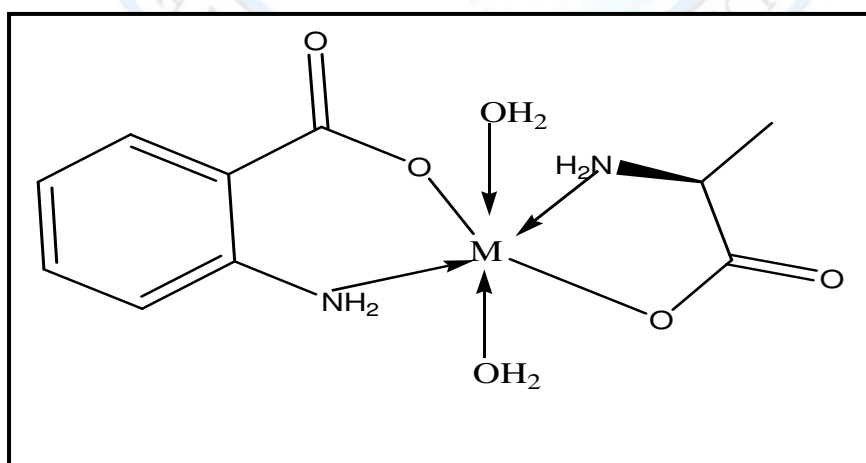


Fig (1) : The proposed structure of the complexes $[M(\text{A})(\text{Ala})]$.

$\text{Fe}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Zn}(\text{II}), \text{Cd}(\text{II})$. $M(\text{II}) =$



**Fig (2) :The proposed structure of the complexes $[M(\text{A})(\text{Ala})] \cdot 2\text{H}_2\text{O}$
 $M(\text{II}) = \text{Cu}(\text{II}), \text{Mn}(\text{II})$**

References

1. R.H. Prager and G.R. Skurray , Aust. J. chem , 21 , p. 1037 (1968) .
2. A.F. Borowski and D.J. Cole-Hamilton , Polyhedron , 12 , p. 1757 (1993) .
3. T.Huey Lu , P. hattopadhyay , F.L , Liao and J.Mau Lo , J.Analytical sciences , 17 , pp. 905-906 (2001) .
4. P.Gurcan , N.Sari , N.J. Inorg . Chem., 38, p. 2807-2817 (1999) .
5. Y.yang , S.Zhang , J.Spectro chim Acta .,59, pp.1205-1209, (2003) .
6. V.Kataline , Helga . Suli-Varha Danielle sane , Giovanni , Micera and S.Imer . J.Inorg chem., Acta , 339 , p.373-382 (2002) .
7. A, m. Ahmed , syntheses and characterization of some Lanthanides (III) complexes with Amino acids Leucine and phenylalanine . M. Sc. thesis , ,college of education(Ibn Al-Haitham, university of Baghdad (2004) .
8. M.A. Al-Khuzae , syntheses and characterization of some Lanthanides (III) complexes with Antranilic acide and phenylalanine.M.Sc. thesis ,college of education(Ibn Al-Haitham, university of Baghdad (2003) .
- 9.S.L.Gao,Y.D.Hou,M.Ji,S.P.ChenandQ and Z.Shi, J.Thermo Chim. Acta,35, p.47 (2000).
10. L.Zhu and N.N.Kostic; J. Inorg. Chem. Acta, 21 , p. 217 (1994) .
11. T.N.Parac; N.M.kostic; J. Inorg. Chem. , 37 , p. 2141 (1998) .
12. G.Karet and N.M.Kostic; J. Inorg . Chem. , 37 , p. 1021 (1998) .
13. M.R.Ermarcora; D.W.Ledman; R.O.Fox. Nat. struct. Biol. , 3 , p. 59 (1996) .
14. S.Cakir , E.Bicer , H. Icbudak , P.Naumov, H.Korkmaz and O.Cakir . J.Che, 75, p. 371-377 (2001) .

15. C.Preti and G.Tosi , J.Inorg.Nucl. chem, 36, p. 3725 (1974) .
16. A.B.P, Lever, “Inorganic electronic spectroscopy” New York (1968).
19. A.Klienstien and I.Gabe An.St .Univ, Lasi XIV, p. 139 (1968) .
20. J.D.During and D.W.Wertz .A “Inorganic electronic spectroscopy” New York (1968)
17. G.W, Watt , and D.S, Klett. Inorg. Chem., 5, p. 1278 (1966) .
18. K.Nakamoto; Infrared spectra of Inorganic and coordination compounds “4ED th ; J.Wiely and Sons, New york, (1996).
21. D.A.Buckingham and D.Jones; J. Inorg, Chem., 4, p. 1387 (1965) .
22. A.Klierstien and G.A.Webb; J. Inorg. Nucl, Chem, 33 , p. 405 (1971) .

Table (1) the physical properties of the prepared complexes

| Compounds | M.wt | Colour | M.P °c (de) °c | M.C Sem cm ² .M ol ⁻¹ | Metal% | | Cl% |
|---------------------------------|---------|-------------|-------------------|--|--------|-------|-----|
| | | | | | theory | exp | |
| Alanin(Ala) | 89.09 | white | 314 | 1.0 | - | - | - |
| Anthranilic(A) | 137.14 | Pale-yellow | 146 | 6.2 | - | - | - |
| [Mn(Ala)(A)] .2H ₂ O | 315.18 | Pale brown | 240 de | 1.44 | 17.43 | 17.79 | Nil |
| [Fe(Ala)(A)] | 280.06 | Red-brown | 244 de | 1.64 | 19.94 | 21.05 | Nil |
| [Co(Ala)(A)] | 283.15 | Pale-pink | 265 de | 7.83 | 20.18 | 19.52 | Nil |
| [Ni(Ala)(A)] | 282.191 | Pale-green | 272 de | 8.20 | 20.75 | 21.74 | Nil |
| [Cu(Ala)(A)].2H ₂ O | 323.07 | Pale-blue | 228 de | 2.30 | 19.63 | 18.31 | Nil |
| [Zn(Ala)(A)] | 289.60 | Pale-yellow | 290 de | 7.18 | 22.57 | 21.05 | Nil |
| [Cd(Ala)(A)] | 336.61 | white | 260 de | 6.12 | 33.39 | 33.37 | Nil |

Table (2) The magnetic measurements data of the prepared complexes

| Compounds | λ (nm) | ν (cm ⁻¹) | ϵ_{\max} L.mol ⁻¹ . cm ⁻¹ | Assignment | coordination |
|---|-------------------|---------------------------|---|--|--------------|
| Ala= (C ₃ H ₇ NO ₂) | 277 304 | 36101 32894 | 343 391 | $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ | - |
| A=(C ₇ H ₇ NO ₂) | 337 360 | 29673 27777 | 2337 1108 | $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ | - |
| [Mn(Ala)(A)] 2H ₂ O | 330 686 816 | 30303 14577 12254 | 1867 17 11 | C.T $A_{1g}^6 \rightarrow {}^4T_{2g}(G)$ $A_{1g}^6 \rightarrow {}^4T_{1g}(G)$ | Oh |
| [Fe(Ala)(A)] | 343 351 | 29154 28490 | 1191 763 | C.T ${}^5E \rightarrow {}^5T_2$ | Td |
| [Co(Ala)(A)] | 674 520 344 | 14836 19230 29069 | 210 144 331 | ${}^4A_2 \xrightarrow{\nu_1} {}^4T_2$ ${}^4A_2 \xrightarrow{\nu_2} {}^4T_1(f)$ ${}^4A_2 \xrightarrow{\nu_3} {}^4T_1(p)$ | Td |
| [Ni(Ala)(A)] | 388 344 315 | 25773 29069 31746 | 1335 2108 1137 | ${}^3T_1(f) \xrightarrow{\nu_1} {}^3T_2(f)$ ${}^3T_1(f) \xrightarrow{\nu_2} {}^3A_2$ ${}^3T_1(f) \xrightarrow{\nu_3} {}^3T_1(p)$ | Td |
| [Cu(Ala)(A)].2H ₂ O | 300 316 432 | 33333 31645 23148 | 1450 1563 386 | C.T C.T ${}^2E_g \rightarrow {}^2T_{2g}$ | Oh |
| [Zn(Ala)(A)] | 361 337 | 27700 29673 | 1132 2308 | C.T C.T | Td |
| [Cd(Ala)(A)] | 323 | 30959 | 1815 | C.T | Td |

Table (3) Electronic Spectra of the ligands and there complexes

| Complex | S | L | Term Symbol | μ_s | μ_s+L | Exp _{eff} |
|---------------------------------|-----|---|----------------|---------|-----------|--------------------|
| [Mn(Ala)(A)] .2H ₂ O | 5/2 | 0 | ⁶ S | 5.92 | 5.92 | 5.75 |
| [Fe(Ala)(A)] | 2 | 2 | ⁵ D | 4.90 | 5.94 | 3.40 |
| [Co(Ala)(A)] | 3/2 | 3 | ⁴ F | 3.87 | 5.20 | 4.5 |
| [Ni(Ala)(A)] | 1 | 3 | ³ F | 2.83 | 4.47 | 2.72 |
| [Cu(Ala)(A)].2H ₂ O | 1/2 | 2 | ² D | 1.73 | 3.00 | 2.80 |
| [Zn(Ala)(A)] | 0 | 0 | 0 | 0 | 0 | D.M |
| [Cd(Ala)(A)] | 0 | 0 | 0 | 0 | 0 | D.M |

Table (4) FT-IR spectral data of the Ligands and their complexes

| Compounds | ν (N-H) _{asy} | ν (N-H) _{sym} | C=C aromatic | ν (-COO) _{asy} | ν (-COO) _{sy} m | $\Delta\nu$ (-COO) as-sy | M-N | M-O |
|--|----------------------------|----------------------------|--------------|-----------------------------|---------------------------------|-----------------------------|----------|-----------|
| Alanine(Ala) =C ₃ H ₇ NO ₂ | 3379 m | 3087m | - | 1618 vs | 1411 s | 207 | - | - |
| Anthranilic(A) =C ₇ H ₇ NO ₂ | 3370s | 3320 vs | 1532 s | 1590 s | 1400 s | 190 | - | - |
| [Mn(Ala)(A)] .2H ₂ O | 3305v s | 3143 s | 1589 s | 1614 s | 1407 vs | 207 | 634 | 514 |
| [Fe(Ala)(A)] | 3328 w | 3164 m | 1595 m | 1565 s | 1407 s | 158 | 530 | 480 |
| [Co(Ala)(A)] | 3309 s | 3137 s | 1591 b | 1546 b | 1409 s | 137 | 516 m | 420 m |
| [Ni(Ala)(A)] | 3305 s | 3128 s | 1595 b | 1548 b | 1406 vs | 142 | 518 m | 424 m |
| [Cu(Ala)(A)]. 2H ₂ O | 3276 vb | 3126 s | 1614 vb | 1548 v.b | 1409 vs | 139 | 518 m | 424 m |
| [Zn(Ala)(A)] | 3300 wb | 3126 m | 1591 s | 1541 vs | 1407 vs | 134 | 524 s | 410 vw |
| [Cd(Ala)(A)] | 3330 vb | 3060 w | 1589 vs | 1569 vs | 1452 m.s | 117 | 518 m | 425 w |

Table (5) Nomenclature of prepared complexes

S= sharp , vs = very sharp , ms= middle sharp , w= weak , b= broad , v.b = very broad

(Ala-H) = C₃H₇NO₂ , (A-H) = C₇H₆NO₂

| Complexes | Nomenclature |
|---------------------------------|---|
| [Mn(Ala)(A)] .2H ₂ O | (L-alaninato)(anthranilato)manganese(II).2hydrate |
| [Fe(Ala)(A)] | (L-alaninato)(anthranilato)iron(II) |
| [Co(Ala)(A)] | (L-alaninato)(anthranilato)cobalt(II) |
| [Ni(Ala)(A)] | (L-alaninato)(anthranilato)nickel(II) |
| [Cu(Ala)(A)].2H ₂ O | (L-alaninato)(anthranilato)copper(II).2hydrate |
| [Zn(Ala)(A)] | (L-alaninato)(anthranilato)zinc(II) |
| [Cd(Ala)(A)] | (L-alaninato)(anthranilato)cadmium(II) |