COMPLEXES OF Cu(II) AND Mn(II) WITH ACYLATED AMINOACIDS DERIVED FROM GLYCINE AND α-ALANINE

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abstract: a series of complexes of Cu(II) and Mn(II) with 4-(4'-halobenzenesulfonyl)-benzoyl glycine and 4-(4'-halobenzenesulfonyl)-benzoyl α-alanine with formula $[M(L\text{-}H)_2(H_2O)_2]$ have been synthesized and characterized as mononuclear species on the basis of elemental chemical analysis, electronic and infrared spectra and molar conductibility measurements. The IR spectra indicated the presence of aminoacid derivative as coordinated through nitrogen atom and the oxygen from the carboxylic group. The experimental data suggest that the ligands act as bidentate and adopt an octahedral stereochemistry.

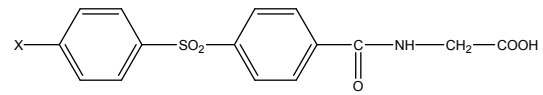
keywords: aminoacids, copper(II), manganese(II), complexes

Introduction

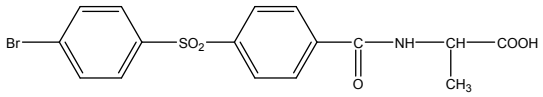
Interactions between transitional metal ions and aminoacids are very interesting in the biological applications.

Complexes of some metal ions with aminoacids can be used as models to study the pharmaco-dynamic effects of drugs or for increasing the biocompatibility and minimize toxic effects of some metal ions [1,2]. The Cu(II) complexes with gluconic acid is the main drug used in the treatment of infectious, inflammatory and virological conditions, while a number of complexes based on Mn(II) are used in treating allergies, heart diseases and anaemia [3-8].

In this paper we proposed to prepare a series of Cu(II) and Mn(II)complexes with acylated aminoacids derived from glycine and α-alanine:



X = Br (**L**[1]), Cl (**L**[2])



(**L**[3])

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Experimental

Materials and Methods

All reagents were of analytical grade and were used without further purification. The chemical analyses were performed by using the well-known micro methods. The diffuse reflectance spectra were recorded in the range 350 – 800 nm on VSU2-Carl Zeiss Jena spectrophotometer, using MgO as standard. The IR spectra were recorded in the 400 – 4000 cm^{-1} range with a BIO-RAD FTS 135 spectrophotometer using KBr pellets.

Molar conductivities were measured in freshly prepared solutions 10^{-3} M in DMF at room temperature with a digital conductivity meter Consort C 533.

Synthesis of Ligands

Ligands were prepared using the reaction between 4-bromo and 4-chlorobenzene sulphonyl benzoic acids with tionyl chloride in DMF [9,10].

The acid chloride obtained in this reaction was treated further with aminoacids following the Steiger procedure [11].

Synthesis of Complexes

A solution of sodium hydroxide 30% was added over the aqueous solution of anhydrous $MnSO_4$ (2 mmole in 20 ml H_2O) or cooper acetate monohydrated (2mmole in 20 ml H_2O) until a precipitate was formed. The precipitate was filtered off and was treated further with hot aqueous aminoacid solution (4 mmole in 40 ml H_2O). The M(II): aminoacid ratio was 1:2. The resulting mixture was refluxed for one hour and then the solution was cooled down. Pink pale crystals in the case of Mn(II) complexes and blue-violet crystals in the case of Cu(II) complexes separated out the solution. These crystals were filtered, washed with water and dried over P_4O_{10}. The pH value must be adjusted to 6-7 using 0.1N solution of NaOH.

Elemental analysis results and conductibility measurements values are:

$[Cu(L^1\text{-}H)_2(H_2O)_2]$: Found (%): C:39.85; H:2.50; Cu:7.01; Require(%): C: 40.10;H:2.60; Cu:7.09; $\Lambda_M=5.3\Omega^{-1}cm^2mol^{-1}$

$[Cu(L^2\text{-}H)_2(H_2O)_2]$: Found (%): C:43.50; H:2.50; Cu:7.70; Require(%): C:44.02;H:2.60; Cu:7.81; $\Lambda_M=4.10\Omega^{-1}cm^2mol^{-1}$

$[Cu(L^3\text{-}H)_2(H_2O)_2]$: Found (%): C:40.75; H:2.85; Cu:6.50; Require(%): C:41.10;H:3.05; Cu:6.88; $\Lambda_M=2.90\Omega^{-1}cm^2mol^{-1}$

$[Mn(L^1\text{-}H)_2(H_2O)_2]$: Found (%): C:40.30; H:2.80; Mn:5.79; Require(%): C:40.68; H:2.93; Mn:6.19; $\Lambda_M=6.10\Omega^{-1}cm^2mol^{-1}$

$[Mn(L^2\text{-}H)_2(H_2O)_2]$: Found (%): C:45.10; H:3.14; Mn:6.50; Require(%): C:45.22;H:3.26; Mn:6.88; $\Lambda_M=5.40\Omega^{-1}cm^2mol^{-1}$

$[Mn(L^3\text{-}H)_2(H_2O)_2]$: Found (%): C:41.85; H:3.10; Mn:5.82; Require(%): C:42.05; H:3.28; Mn:6.00; $\Lambda_M=4.50\Omega^{-1}cm^2mol^{-1}$

Results and Discussions

The results of the elemental chemical analysis of complexes obtained indicate a molar ratio of M(II):LH=1:2.

The values of molar conductivity for Mn(II) and Cu(II) complexes suggest that they are in non-electrolytes form in solution. To establish the structural formula of these complexes IR and UV-VIS spectra were recorded. The positions and assignments of the absorption bands in the UV-VIS spectra are presented in Table 1.

Table 1. Electronic Spectra Data

Compound	λ(nm)	Transitions
$C_{15}H_{12}BrNO_5S(L^1)$	230	$n\rightarrow\pi^*$
	262	$\pi\rightarrow\pi^*$
$[Cu(L^1\text{-}H)_2(H_2O)_2]$	235	$n\rightarrow\pi^*$
	270	$\pi\rightarrow\pi^*$
	415	TS
	620	$d\text{-}d(^2Eg\rightarrow{}^2Tg)$
$[Mn(L^1\text{-}H)_2(H_2O)_2]$	220	$n\rightarrow\pi^*$
	250	$\pi\rightarrow\pi^*$
	340-350	$^6A_{1g}\rightarrow{}^4T_{1g}(P)$

The UV-VIS spectra of Cu(II) complexes with the three ligands show two absorption bands assigned to intraligands transitions and a large band around 620 nm (≈16000 cm^{-1}). The presence of the later band support an octahedral stereochemistry for these complexes.

The UV-VIS spectra of Mn(II) complexes show two bands corresponding to the ligand and a weaker band around 340-350 nm that can be attributed to the d – d spin forbidden transition $^6A_{1g}\rightarrow{}^4T_{1g}(P)$. It is possible that this absorption band appears because of linear combinations of forbidden transitions: $^6A_{1g}\rightarrow{}^4T_{1g}(P)$ and $^6A_{1g}\rightarrow{}^4A_{2g}(F)$ [12].

The study of IR spectra can give valuable information regarding the ligands and the nature of the donor atoms. The bands assignments were done in agreement with the literature data [13-15] and are given in table 2.

Table 2. IR Spectral Data (cm^{-1})

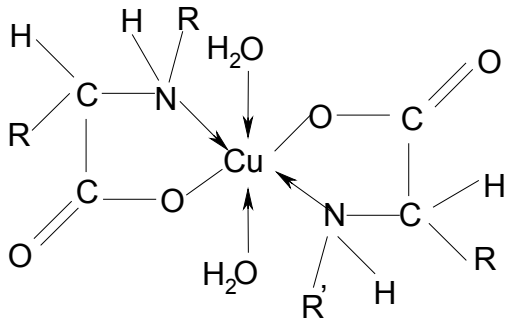
Compound	$\nu s_{(COO-)}$	$\nu as_{(COO-)}$	δ_{NH}	$\nu_{OH(H2O)}$	ν_{M-N}	ν_{M-O}
$[Cu(L^1\text{-}H)_2(H_2O)_2]$	1400	1600	1520	3220	450	495
$[Cu(L^2\text{-}H)_2(H_2O)_2]$	1402	1605	1510	3250	440	490
$[Cu(L^3\text{-}H)_2(H_2O)_2]$	1405	1600	1515	3400	445	495
$[Mn(L^1\text{-}H)_2(H_2O)_2]$	1400	1610	1520	3240	430	490
$[Mn(L^2\text{-}H)_2(H_2O)_2]$	1403	1605	1525	3300	435	490
$[Mn(L^3\text{-}H)_2(H_2O)_2]$	1405	1600	1530	3280	430	495

The IR spectra of complexes show the characteristic bands of the aminoacids that are slightly shifted or weaker in case of the amino and deprotonated carboxyl groups.
The M-N and M-O stretching frequencies appear in the IR spectra between 430 - 450 cm^{-1} and 490-495 cm^{-1}. The stretching vibrations of the group OH corresponding to the coordinated water are located in the 3200-3400 cm^{-1} range. The uncoordinated COOH

group (ν_{CO2H}=1730 - 1775 cm^{-1}) could not be detected in the IR spectra, this fact indicating the coordination of the ligands to metal ions through the carboxilate anions.

All complexes show in the IR spectra a large absorption band in the 3200-2500 cm^{-1} range, a characteristic of transitional metal complexes with Aminoacids.

The correlation of all experimental data suggest that the geometry of Cu(II) and Mn(II) complexes prepared is octahedral.



Conclusions

Six new Cu(II) and Mn(II) complexes of 4-(4'-halobenzenesulfonyl)benzoyl glycine and 4-(4'- halobenzenesulfonyl)benzoyl α-alanine have been synthesized and characterized on the basis of their elemental analysis, electronic and infrared spectra, as well as by molar conductivity measurements. The correlation of the experimental data allowed the assignment of an octahedral stereochemistry to all the reported complexes.

REFERENCES:

1. Grecu,I., Sandulescu, R. and Neamtu M. (1986) *Rev. Chim.* **37(7)**, 589-595.
2. Asma,I.El-Said., Amna, S.A.Zidan., Mahmoud,S.El-Meligy., Aref, A.Aly and Omar, F.Mohamened (2001) *Synth.React.Inorg Met-Org Chem.* **31(4)**, 633-648.
3. Grecu,I., Neamtu, M. and Enescu, L. (1982) **Implicatii biologice si medicale ake chimiei anorganice**, Ed Dacia, Cluj-Napoca.
4. Anjaneyulu, Y. and Rao, R. P. (1986) *Synth. React. Inorg.Met-Org.Chem* **16**(21), 257-272.
5. Gupta, M. and Srivastrava, M. N. (1985) *Polyhedron* **4**(3), 475-479.
6. Gupta, M and Srivastrava, M. N. (1991) *Bull. Soc.Chim Fr.*, 859-863.
7. Saxena, V.K., Gupta, M. and Srivastrava, M. N. (1996) *Synth. React. Inorg. Met-Org.Chem* **26**(10), 1661-1676.
8. Ullah, M.R. and Bhattacharya, P.K. (1990) *Indian J. Chem. Sect A* **29A**(2), 150-153.
9. Schiketanz, I., Istrati, D., Draghici, C. and Balaban, A. T. (1999) *Rev. Roum. Chim.* **44**, 137.

10. Schiketanz, I., Draghici, C., Saramet, I. and Balaban, A. T. (2002) The Journal Arkivoc (Archive for Organic Chemistry) 64-72.

11. Steiger, R.E. (1994) *J. Org. Chem*. **9**, 396.

12. Lewis, J. and Wilkins, R.G. (1960) **Modern Coordination Chemistry Principles and Methods**, Interscience Publ.Inc., New York, 287.

13. Nakamoto, K. (1986) **Infrared and Raman Spectra of Inorganic and Coordination Compounds**, Wiley, New York, 201-206.

14. Balaban, A.T., Banciu, M. and Pogany I. (1983) **Aplicatii ale metodelor fizice inn chimia organica**, Ed. Stiintifica si Enciclopedica Bucuresti.

15. Schiketanz ,I; Draghici, C; Saramet, I and Balaban,A.T(2002) Rev. Roum. Chim. **47** (3-4) 235-238.