During the past two decades, the chemistry of the metal complexes of Schiff bases containing nitrogen and other donor atoms has attracted a great deal of attention due to their stability, biological activity [1] and potential applications in many fields such as oxidation catalysis [2], electrochemistry [3] etc.

Amino acids, a significant class of organic-based compounds, contain potential donor sites such as COOH and/or NH₂ which have good ability to coordinate with the metal ions [4]. Chohan et al. [5] synthesized Co(II), Ni(II), Cu(II), and Zn(II) complexes with amino acid derived Schiff bases and characterized them by various methods like IR, NMR, UV etc. Antibacterial and antifungal screening data showed that these metal complexes are more active than the uncomplexed Schiff base ligands. Moreover, they found that the zinc complexes show higher activity than other metal complexes. The researchers synthesized Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cu(OH)₂ complexes with Schiff base derived from 2-furancarboxaldehyde and 2-amino benzoic acid and characterized them by varying methods like IR, NMR, UV etc. Antibacterial and antifungal screening data showed that these metal complexes are more active than the uncomplexed Schiff base ligands. Moreover, they found that the zinc complexes show higher activity than other metal complexes.

The authors synthesized Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and UO₂(II) complexes with Schiff base derived from 2-furancarboxaldehyde and 2-amino benzoic acid and characterized them by various methods and also studied their antibacterial activity [6]. Antibacterial test results also indicate an increase in activity by coordination with the metal ions and a more pronounced biological activity of the Zn(II) complex compared to the Fe(III), Co(II), Ni(II) and Cu(II) complexes.

In this paper is presented the synthesis and the characterization of Zn(II) binuclear complexes with three Schiff bases derived from 2,2'- (propane-1,3-diyldioxy) dibenzaldehyde, 2-aminobenzoic acid and zinc chloride in absolute ethanol, while the compounds of the [Zn₂L₂(OAc)₂(H₂O)₄] type, where L = (C₉H₇O₄N₂)²⁻ or (C₇H₆O₈N₂)²⁻, were obtained by condensation of 2,2'- (propane-1,3-diyldioxy) dibenzaldehyde, L-tryptophane or tyrosine (in alkaline medium) and zinc acetate in methanol. These binuclear complexes were characterized using the data obtained from elemental analyses, molar conductivity, IR, electronic, emission spectra and thermal analysis.

Keywords: dialdehyde, Zn(II) binuclear complexes, IR spectra

Analytical and physical measurements

The elemental analysis (C, H, N) was carried out with a Costech 2002 analyzer. The zinc content was determined by flame atomic absorption spectrometry using a Spectra AA-220 Varian spectrophotometer. The infrared spectra (in KBr pellets) were recorded on a Bruker Alpha FTIR spectrophotometer in the 4000-400 cm⁻¹ range. The UV-Vis-NIR electronic spectra (200-2200 nm) were recorded with a UV-Vis-NIR spectrophotometer in diffuse reflectance, JASCO V 670. The fluorescence measurements were made with a JASCO FP 6500 spectrofluorimeter at room temperature. The molar conductivity measurements were conducted using an inoLab conductometer. The thermal analysis measurements (TG, DTG and DTA) of the zinc (II) complexes were carried using a horizontal “Diamond” Differential/Thermogravimetric Analyzer from Perkin Elmer Instruments in dynamic nitrogen atmosphere (150 mL min⁻¹) in the 20-1000°C temperature range, with the heating rate of 10°C min⁻¹. The melting points were measured in glass capillary tubes on a Gallenkamp/Sanyo apparatus.

Synthesis of Zn(II) binuclear complex with Schiff base derived from the reaction of 2,2'- (propane-1,3-diyldioxy) dibenzaldehyde with 2-aminobenzoic acid, [Zn₂(C₇H₆O₈N₂)(OH)₂(H₂O)₄] (1)

A solution of 2-aminobenzoic acid (anthranilic acid) (0.27 g, 2 mmol) in absolute ethanol (5 mL) was added to a solution of dialdehyde [2,2'- (propane-1,3-diyldioxy) dibenzaldehyde] (0.28 g, 1 mmol) in absolute ethanol (5 mL). The resulting mixture was refluxed for 2 h, after which the solution acquired a yellow color indicating the formation of the Schiff-base and then an ethanolic solution 1M of NaOH (2 mL) was added. The reflux and stirring processes were continued for 10-15 min. In the next step the zinc chloride (2 mmol) in absolute ethanol (10 mL) were added to the Schiff base ligand solution under continuous stirring. The reaction mixture was further stirred under reflux for another 4 h and left standing overnight. The obtained white product was separated by filtration, washed with distilled water, cooled ethanol (0°C), ethyl...
Synthesis of Zn(II) binuclear complex with Schiff base derived from the reaction of 2,2’-(propane-1,3-diyldioxy)dibenzaldehyde with tyrosine, \([\text{Zn}_2(\text{C}_{35}\text{H}_{32}\text{O}_8\text{N}_2)(\text{OAc})_2(\text{H}_2\text{O})_4]\) \((2)\)

A solution of 2,2’-(propane-1,3-diyldioxy)dibenzaldehyde (0.2 g, 0.7 mmol) in 5 mL methanol was added, dropwise, to a mixture of tyrosine (0.253 g, 1.4 mmol) and KOH (0.078 g, 1.4 mmol) in 25 mL methanol. The resulting mixture was refluxed for 3 h, after which the solution acquired an orange color indicating the formation of the Schiff base. Zinc acetate (0.31 g, 1.4 mmol) was dissolved in 10 mL methanol and added to the Schiff base ligand solution under stirring. The reaction mixture was stirred under reflux for another 4 h and left standing overnight. The obtained colored product was separated by filtration, washed with distilled water, ethanol, ethyl ether and dried under vacuum. The complex was obtained in a 40 % yield.

Results and discussions

Because the Schiff bases obtained from this dialdehyde hydrolyze easily, the complexes were obtained without isolation of the Schiff base.

The complex \([\text{Zn}_2(\text{C}_{35}\text{H}_{32}\text{O}_8\text{N}_2)(\text{OAc})_2(\text{H}_2\text{O})_4]\) \((1)\) was obtained by a reaction, consisting of refluxing the ethanolic solutions of 2,2’-(propane-1,3-diyldioxy)dibenzaldehyde, 2-aminobenzoic acid and zinc chloride in a 1:2:2 molar ratio, with medium yield. The complexes \([\text{Zn}_2(\text{C}_{35}\text{H}_{32}\text{O}_8\text{N}_2)(\text{OAc})_2(\text{H}_2\text{O})_4]\) \((2)\) and \([\text{Zn}_2(\text{C}_{35}\text{H}_{32}\text{O}_8\text{N}_2)(\text{OAc})_2(\text{H}_2\text{O})_4]\) \((3)\) were synthesized by condensation of the methanolic solutions of the dialdehyde, L-tryptophane / tyrosine (in alkaline medium) and zinc acetate in a 1:2:2 molar ratio, with medium yields.

These compounds were insoluble in common organic solvents and in water, but soluble in some extent (less soluble) in DMF and DMSO. For this reason it was not possible to record NMR spectra of these complexes.

All of the resulting solid complexes were characterized by elemental and physico-chemical analysis. The results are presented in table 1.

Molar conductivity measurements

The molar conductivity values of the Zn(II) binuclear complexes in DMF, solutions 10⁻¹ M, lie in the range of non-electrolytes [8] as shown in table 1. The three values suggest that no anions are present outside the coordination spheres.

IR spectra

The IR bands that can provide structural evidence for the coordination of the Schiff base ligands to the zinc ion are given in table 2. The assignments of the characteristic IR frequencies from the IR spectra of the Zn(II) complexes are as follows.

The broad and medium band observed in the region 3321-3450 cm⁻¹ in the IR spectra of all the complexes is assigned to the stretching vibrations of O-H group from the coordinated water molecules [9]. In the same time, the IR spectrum of the complex 1 shows a sharp band at 3300 cm⁻¹ which can be assigned to the coordinated OH group (fig. 3 – chemical structure) [9]. The medium band at 3412 cm⁻¹ in the IR spectra of the complex 2 can be attributed to the N-H stretching vibration of tryptophan moiety. In the spectra of the complex 3 a band at 3331 cm⁻¹ was also observed which may be assigned to the O-H stretching vibration of tyrosine moiety.

It was noted that the band corresponding to ν\text{asym(NH)} stretching vibrations appeared at 3494 cm⁻¹ in the IR spectrum of 2-aminobenzoic acid but was absent in the IR spectrum of the complex 1. The band corresponding to ν\text{sym(NH)} stretching vibrations appeared at 3060 cm⁻¹ and 3018 cm⁻¹ in the IR spectra of tryptophane and tyrosine, respectively, is not present in the IR spectra of the complexes 2 and 3. Furthermore, no strong absorption band was observed in the spectra of all the complexes at 1680 cm⁻¹, indicating the absence of the >C=O group of dialdehyde and confirming thus the condensation of the carbonyl group of dialdehyde with the amino group of 2-aminobenzoic acid, tryptophan and tyrosine, respectively [10]. The complex 1 shows a strong band at 1610 cm⁻¹ which can be assigned to C=N stretching vibration [11]. This band appears in the IR spectrum of the isolated free Schiff base ligand derived from dialdehyde and 2-aminobenzoic acid at 1616 cm⁻¹ [12]. The shift of this band in the IR spectra of the complex 1 suggests the coordination of the azomethine nitrogen to the zinc ion. The IR spectrum of the complex 2 shows a strong band at 1625 cm⁻¹ which may be attributed to C=N stretching vibration [11]. In this case any attempt to isolate the free Schiff base ligand derived from dialdehyde and L-tryptophan was unsuccessful [12]. The IR spectrum of the isolated free Schiff base ligand derived from dialdehyde and tyrosine shows a band at 1613 cm⁻¹ which may be assigned to C=N stretching vibration [12]. This band shifts at 1600 cm⁻¹ in the IR spectrum of the complex 3 which suggests Table 1

<table>
<thead>
<tr>
<th>Complex</th>
<th>Color</th>
<th>M.p. (°C)</th>
<th>Molecular Weight (g mol⁻¹)</th>
<th>C % exp. (calc.)</th>
<th>H % exp. (calc.)</th>
<th>N % exp. (calc.)</th>
<th>Zn % exp. (calc.)</th>
<th>(\Lambda_m) (Ω⁻¹ cm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>white</td>
<td>&gt;350</td>
<td>756.74</td>
<td>49.65 (49.15)</td>
<td>4.19 (4.49)</td>
<td>3.55 (3.70)</td>
<td>17.50 (17.27)</td>
<td>6.5</td>
</tr>
<tr>
<td>2</td>
<td>orange</td>
<td>&gt;250</td>
<td>974.74</td>
<td>53.14 (52.92)</td>
<td>5.16 (4.92)</td>
<td>5.84 (5.74)</td>
<td>12.91 (13.41)</td>
<td>9.7</td>
</tr>
<tr>
<td>3</td>
<td>cream</td>
<td>&gt;250</td>
<td>928.74</td>
<td>50.72 (50.39)</td>
<td>5.23 (4.95)</td>
<td>3.15 (3.01)</td>
<td>13.80 (14.07)</td>
<td>13.3</td>
</tr>
</tbody>
</table>
the involvement of the azomethine nitrogen atom in coordination to the zinc ions.

It is mentioned that the band appearing at 1600 cm\(^{-1}\) in the spectrum of the complex 3 can be considered as an overlapped band due to two stretching vibrations of C=N and asymmetric coordinated COO\(^{-}\).

The IR spectrum of the complex 1 shows a band at 1560 cm\(^{-1}\) which may be attributed to \(v_{\text{sym}}(\text{COO}^-)\) stretching vibration. The IR spectra of the complexes 2 and 3 show a band at 1600 cm\(^{-1}\) which can be assigned to \(v_{\text{asy}}(\text{COO}^-)\) stretching vibration. This last two bands also appear in the IR spectra of amino acids at 1592 cm\(^{-1}\) and 1589 cm\(^{-1}\) for tryptophane and tyrosine respectively. These results prove the ligands coordination to the zinc ion through the oxygen atom of amino acid deprotonated carboxylate [13]

A band at 1408 cm\(^{-1}\) in the IR spectrum of the complex 1 may be assigned to \(v_{\text{asy}}(\text{COO}^-)\) stretching vibration [13]. A medium band at 1383 cm\(^{-1}\) and 1390 cm\(^{-1}\) in the IR spectra of the complex 2 and 3 respectively, can be also attributed to \(v_{\text{sym}}(\text{COO}^-)\) stretching vibrations. This last two bands also appear in the IR spectra of tryptophane and tyrosine around 1415 cm\(^{-1}\). These results confirm the ligands coordination to the zinc ion through the oxygen atom of amino acid deprotonated carboxylate. It is mentioned that for the complexes 2 and 3, the bands due to \(v_{\text{sym}}(\text{COO}^-)\) and \(v_{\text{asy}}(\text{COO}^-)\) stretching vibrations from coordinated acetate groups overlap with the bands due to \(v_{\text{sym}}(\text{COO}^-)\) and \(v_{\text{asy}}(\text{COO}^-)\) stretching vibrations of the carboxylate groups from the Schiff base ligands. The \(\Delta v(\text{sym}(\text{COO}^-) - v_{\text{asy}}(\text{COO}^-))\) values for the complexes 2 and 3 were higher than 144 cm\(^{-1}\), which suggests that the acetate group is acting as monodentate [9, 14].

Furthermore, a medium absorption band at 1357 cm\(^{-1}\) and 1355 cm\(^{-1}\) in the spectra of the complexes 2 and 3 respectively, may be assigned to \(\delta_{\text{sym}}(\text{CH}^-)\) deformation vibrations, confirming the acetate group coordination to the central metal ion [15]. The ring skeletal vibrations (C=C) were observed in the region 1454-1458 cm\(^{-1}\) of the spectra of all the complexes.

In the spectra of the complexes, a medium band at 1240-1245 cm\(^{-1}\) was due to \(v_{\text{sym}}(\text{Ar-O-C})\) stretching vibrations and a weak band at 1051-1077 cm\(^{-1}\) was due to \(v_{\text{sym}}(\text{Ar-O-C})\) stretching vibrations [15]. This last band is found in the spectrum of dialdehyde at 1104 cm\(^{-1}\). These results provide evidence for the coordination through the Ar-O-R etheric oxygen atom. The bands present at 515-583 cm\(^{-1}\) in all the complexes may be assigned to \(v_{\text{Zn-O}}\) stretching vibrations [16]. The spectra of the complexes also show bands in the region 416-430 cm\(^{-1}\) corresponding to \(v_{\text{Zn-N}}\) stretching vibrations, which give insight into the coordination of the azomethine nitrogen to the zinc ion [16, 17].

Therefore, the IR spectra confirm the in situ obtaining of the Schiff base ligands and their coordination to the central metal ions through the deprotonated carboxylate oxygen, the azomethine nitrogen and the Ar-O-R etheric oxygen atoms.

Electronic spectra and magnetic moments

The electronic spectra of the complexes were recorded in the solid state at room temperature.

The electronic spectra of all the zinc complexes exhibit an intense band at 30765-29412 cm\(^{-1}\) (325-340 nm). This band is most probably due to \(\pi \rightarrow \pi^*\) transitions of the azomethine chromophore from the Schiff base ligands. These transitions are also observed in the spectra of the isolated free Schiff base ligands [12], but at lower frequencies, confirming the coordination of these ligands to the zinc ions.

The figure 1 shows the electronic spectrum of the complex 2 as an example.

All the complexes are diamagnetic (\(\mu_{\text{eff}} = 0\) B.M.), as expected for a d\(^{10}\) configuration [18].

Emission spectra

The photoluminescent behaviour of the complexes were investigated in the solid state at ambient temperature. The figure 2 shows the emission spectra of the complexes.

The zinc complex 1 exhibits a strong luminescence at 391 nm upon excitation at 300 nm (fig. 2 - a). The complex 2 exhibits emission maxima at 471 nm and additional shoulder peak at 520 nm upon excitation at 390 nm (fig. 2 - b) and the zinc complex 3 shows emission band at 507 nm upon excitation at 400 nm (fig. 2 - c). The luminescence of these compounds should be assigned to the \(\pi \rightarrow \pi^*\) intraligand transitions [19, 20].

Thermal analysis

Thermal analysis of the metal complexes is used to obtain information about their physical properties and thermal stability, as well as for the nature of the intermediates and final decomposition products [21-29].

Table 3 shows the thermogravimetric analysis results of the zinc complexes.
The decomposition curve of the complex 1 shows four steps within the temperature range 100-680°C. The first step of the decomposition within the temperature range 100-250°C corresponds to the loss of four coordination water molecules with a mass loss of 9.54% (calc. 9.51%). The subsequent steps (250-680°C) correspond to the removal of the organic part of the ligand and of two coordination hydroxyl groups leaving 22.36% ZnO as a residue (calc. 21.50%). The second decomposition is a medium heat absorption process.

The decomposition curve of the complex 2 shows three steps in the 100-550°C temperature range. The first step (100-250°C), which is accompanied by a small endothermic effect, corresponds to the loss of four coordination water molecules. The second decomposition step (250-420°C) involves the loss of 2CO₂, 2CO, C₂H₆ and 2HCN molecules, with a mass loss of 23.20% (calc. 23.39%). The last step of the decomposition within the 420-550°C temperature range corresponds to the removal of the bulk organic part of the complex (the C₁₅H₁₄O₂ group and 2C₁₀H₉N groups), leaving 16.00% ZnO as residue (calc. 16.69%). The overall mass loss was 84.00% (calc. 83.29%).

The decomposition curve of the complex 3 also shows three decomposition steps in the 100-525°C temperature range. The first step (100-200°C) corresponds to the loss of four coordination water molecules. This decomposition step is accompanied by a weak endothermic effect. The second decomposition step (200-400°C) involves the loss of C₂H₆O group and 2C₂H₄O groups, leaving 18.43% ZnO as residue (calc. 17.52%).

Based on all these experimental data obtained through the used analysis methods, the proposed structures for the zinc complexes are as follows:

![Fig. 2. The emission spectra of the complexes: 1 – a, 2 – b and 3 – c](image)

![Fig. 3. The proposed structures for the zinc complexes](image)
Conclusions

In this study, three Zn(II) binuclear complexes with the Schiff bases derived from 2,2'-(propane-1,3-diyldioxy) dibenzaldehyde and some amino acids (2-aminobenzoic acid, L-tryptophane and tyrosine) were obtained and characterized by various physico-chemical methods. The IR spectra confirm the \textit{in situ} obtaining of the Schiff base type ligands and their coordination to the zinc ions through the deprotonated carboxylate oxygen atom, the azomethine nitrogen atom and the Ar-O-R etheric oxygen atom. The low molar conductivity values of the complexes indicate them to be non-electrolytes. Thermogravimetric analysis results are in good agreement with the proposed composition of the complexes. The emission spectra suggest that these compounds have the luminescent properties.

Acknowledgments: The authors are grateful to Professor Stelian Florea (Faculty of Chemistry, University of Craiova) for the useful discussions and for the help he provided in writing this paper.

References