The interest for the chemistry of 1,3,4-mercapto-thiadiazole comes from their utility in the numerous scientific and technical domains. Following our previous studies, four metal complexes with a thiadiazole ligand were synthesized and characterized, corresponding to Cu(II), Co(II) and Mn(II), respectively. The composition of these complexes was deduced from their thermal behaviour and elemental analysis, and it was proven that the final decomposition products are CuO, CoO and MnO respectively.

Keywords: alkylated 1,3,4-thiadiazole; metal complex; thermal analysis; FTIR spectroscopy.

The interest for the chemistry of 1,3,4-mercapto-thiadiazoles is represented mainly by the fact that these derivatives have numerous applications in fields such as analytical chemistry and biosensors [1,2], as well as corrosion inhibitors [3,4], stabilizers [5], electrotechnical materials [6,7] and pharmaceuticals [8].

The coordination behaviour of the S-alkylated derivatives of 2,5-dimercapto-1,3,4-thiadiazoles resides on their structural planar and rigid geometry, and on the presence of an increased number of electronegativity heteroatoms which favourize the mono-, bi- and tridimensional supramolecular assembly. These structures can be compared with the ones observed for trithiocyanuric acid compound with zeolite properties, where supramolecular structures consisting in nanocavities and channels can be generated [9,10].

Thermal analysis is one of the most widely used techniques for the analysis of material samples, from pharmaceuticals to metallic glass [11] and metal complexes containing functionalized 1,3,4-thiadiazoles [12-15].

Following these considerations regarding the importance of the chemistry of thiadiazoles, we continued the study of derivatives containing (3H-2-thioxo-1,3,4-thiadiazol-5-yl)thioacetic moiety. The presence of this functionalized derivatives have numerous applications in fields such as analytical chemistry and biosensors [1,2], as well as corrosion inhibitors [3,4], stabilizers [5], electrotechnical materials [6,7] and pharmaceuticals [8].

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It is well known that several transition cations are involved in numerous biochemical processes, and their bioactivity can be modulated by coordinate-compound formation equilibria. Thus, coordination compounds containing nitrogen and sulphur donors from heterocyclic ligands were studied as structural, spectroscopic or functional models of biological systems [17]. In our previous papers, we have described the spectroscopic properties of sodium and potassium salts of (3H-2-thioxo-1,3,4-thiadiazol-5-yl)thioacetic acid, and as well for the metal coordination compounds containing Co(II), Ni(II), Cu(II) and Zn(II) transitional cations [18] and Mg(II), Ca(II), Sr(II) and Ba(II), respectively [19]. We have also presented the crystalline structure of sodium (3H-2-thioxo-1,3,4-thiadiazol-5-yl)thioacetate [20], followed by the thermal characterization and solid state structure of a new Ni(II) coordination compound with (3H-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetate ligand [21].

Experimental part

Materials and methods

The reagents (CuSO₄·5H₂O, Co(NO₃)₂·6H₂O and MnCl₂·4H₂O) were commercial products with analytical purity and were used as received, without further purification. The alkylated thiadiazole (L) was obtained in our laboratory by a method mentioned in literature [22]. The monodeprotonated form of the ligand (LNa) was used for the synthesis of metal complexes of Cu(II), Co(II) and Mn(II) and was prepared in mildly alkaline aqueous medium, by treating (3H-2-thioxo-1,3,4-thiadiazol-5-yl)thioacetic acid with sodium hydrogen carbonate in equimolar ratio. The complete protocol applied for the synthesis of metal complexes, and the spectroscopic description (FTIR and Raman) was elsewhere described [18].
The metal complexes were analyzed by TG, DTG and DTA using a TGA/SDTA 851-LF 1100 METTLER apparatus. The thermal behaviour of the samples was studied in the temperature range of 25-1000°C, using a heating rate of 10°C min⁻¹. Samples with masses of about 20 mg were weighed in platinum crucibles of 150 μL. The experiments were completed in a synthetic air atmosphere at a flow rate of 50 mL min⁻¹.

The composition of the metal complex (C, H, N and S) was obtained by means of elemental analysis using a VarioEL Elementar Analysensysteme GmbH. The metal content from metal complexes was determined after deagregation of complexes by complexometric titration, by a standard analytical procedure.

Results and discussions

Metal complexes were prepared from the sodium salt of (3H-2-thioxo-1,3,4-thiadiazol-5-yl)thioacetic acid and were precipitated from aqueous solution by the interaction of the above mentioned thiadiazole and an aqueous solution of M²⁺ (M=Cu, Co, Mn), according to the following equation:

\[
\text{ML}_2(\text{OH}_2)_n \rightarrow 2\text{Na}^+ + 2\text{Na}^+ + \text{L}_2\text{M}^{2+} + n \text{H}_2\text{O}
\]

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\[
2(\text{LNa})_aq + M^{2+} \text{aq} \xrightarrow{\text{intense stirring / r.t.}} 1-2\text{h} \quad \text{ML}_2(\text{OH}_2)_n + 2\text{Na}^+_aq
\]

Fig. 2. Synthesis of metal complexes

The results of the elemental analysis for the analyzed complexes are presented in table 1.

<table>
<thead>
<tr>
<th>Complex formulae</th>
<th>Elemental analysis (%) found/calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>C₆H₁₈N₆S₅O₂Co</td>
<td>17.65/17.61</td>
</tr>
<tr>
<td>C₆H₁₈N₆S₅O₂Cu</td>
<td>19.86/20.10</td>
</tr>
<tr>
<td>C₆H₁₈N₆S₅O₂Mn</td>
<td>17.71/19.01</td>
</tr>
</tbody>
</table>

Table 1

**ELEMENTAL ANALYSIS DATA**

**Thermal analysis**

Thermal techniques are an important tool for determining the structure, composition and degradation conditions of metal complexes [22-27]. The establishment of a mechanism of the thermal degradation of the biological active compounds with transitional metal ions which play a vital role in different biological processes is an important step for development of new metallotherapeutics [28-33]. To obtain this information, the thermal behaviors of metal complexes were accomplished by simultaneous TG/DTG/DTA analyses in dynamic air atmosphere and using a heating rate of 10°C min⁻¹. The thermoanalytical curves of these complexes are presented in figure 3 and the data corresponding to these curves are summarized in table 2.

The first step of thermal degradation of Co(II) and Mn(II) complexes consists in an endothermic peak corresponding to the water elimination up to 160 °C (DTA peak Co complex=139 °C; DTA peak Mn complex=115 °C). The thermal decomposition of anhydrous complexes begins at 200 °C with a mass loss corresponding to 35% for Co complex and 48.15% for Mn complex, respectively. These processes are accompanied by several endothermic effects, according to the DTA curves. The next step is not a single one, but an overlapping of multiple processes, according to the profile of the DTA curve. The degradation of thiadiazole heterocyclic moiety proceeds with a mass loss of = 23% in the case of Mn complex and 11.14% in the case of Co complex. These processes are accompanied by small exothermic peaks observed in the 300-900°C temperature range and are probably due to simultaneous endo and exothermic reactions which consist in some breaking and rearrangement of bonds and some oxidative degradation. All these decompositions lead to CoO and MnO as final products with a found and calculated overall mass loss:
13.8/13.7 for Co complex and 11.80/11.71 (found/calculated) for Mn complex respectively.

The formation of CoO is also sustained by the fact that the equilibrium presented in figure 4, which indicate that cobalt(II) oxide, CoO, converts to Co3O4 if heated to ~700 °C in air. At temperatures higher then 900 °C, CoO is stable [34].

The final decomposition product obtained for the decomposition of Mn(II) complex was identified both by the analysis of the TG curve of the complex, and the results were correlated as well with the thermodynamic transformations that occur in oxidative media between manganese oxides. Literature indicate that manganese dioxide (MnO2) decomposes at temperature higher than 520 °C to manganese(III) oxide (Mn2O3), according to reactions presented in figure 4. At higher temperatures, the mixed-valence compound Mn3O4 is stable, and at higher temperatures (~1000 °C), MnO is formed.

In the case of Cu complex, the TG/DTG and DTA curves indicate that the thermal degradation follows 4 steps (fig. 1b). This coordination compound is stable as anhydrous substance, with no crystallization and/or lattice water present in the structure, and as a consequence, the thermal degradation begins at 160 °C. The pattern of this thermal decomposition is different from that of previous presented complexes (fig. 1). The final step contains multiple exo- and endothermic processes presented on the DTA curves and as a result of these reactions, the final decomposition product identified was copper (II) oxide with the mass loss (found/calculated) 16.8/16.64%.

The water content of the two metal complexes with Mn and Co was determined by thermal analysis, and was calculated by the mass loss in the 40-165 °C range: the mass loss corresponds to a number of moles of water of approx. 2.06 for complex with Mn and 4.08 for the complex with Co. The molar mass of the complexes was also determined from the thermogravimetric curve, being presented in table 3. The molar mass was calculated by the means of the final decomposition product (after the thermal treatment of the complexes at 1000 °C), which was confirmed to be the metal oxide.

The results obtained by thermal analysis are in good agreement with the ones obtained by elemental analysis. As elemental analysis suggest, Cu(II) metal complex does not contain crystallization or lattice water. Mn(II) and Co (II) loose, in the first step, the contained water by the formation of the anhydrous complexes which start decomposing around 200 °C. The process associated with the degradation of the thiadiazolic ligand is a continuous one and took place up to 900 °C.

Conclusions

The thermoanalytical curves of the metal complexes obtained during heating at ϑ=10 °C·min−1 in air atmosphere exhibit a multistadial decomposition route. For Co(II) and Mn(II) complexes, the first step in the temperature range 40-140 °C represents the dehydration step. The decomposition of the anhydrous complex commences at temperatures higher than 200 °C, the final decomposition product was confirmed to be the divalent metallic oxide, for each coordination compound. It can be noticed that the decomposition process is different for each complex: the Cu(II) complex decomposes in four major steps, Co(II) in three and Mn(II) in two, respectively.

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References


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