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THERMAL BEHAVIOUR OF COMPLEXES OF ANTIPYRINE DERIVATIVES Part III.

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The thermal behaviour of the mixed-ligand complexes of cobalt(II) and copper(I) ions with antipyrine derivatives of 1,2-ethanediamine or piperazine (BAMP and TAMEN), with water and with 2-mercapto-benzothiazole (Hmbt) was investigated. The complexes contain 2-mercaptobenzothiazole (Hmbt, in the case of cobalt(II) ion) or dimercaptobenzothiazine (mbt–mbt, in the case of copper(I) ion) molecules as ligands and perchlorate (ClO_4^-) or thiocyanate (SCN^-) ion as counterion. By heating, water and ligands release the solid phase at lower temperature. At higher temperatures process of different organic reactions of ligands (e.g. polymerization, polycondensation) could be suggested to interpret the relative high final mass values.

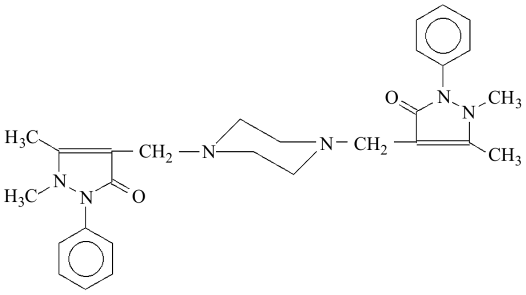
Keywords: *complexes of Co(II) ion, complexes of Cu(I) ion, 2-mercaptobenzothiazole, mixed-ligand complexes, pyrazolonic Mannich bases, thermal behaviour*

Introduction

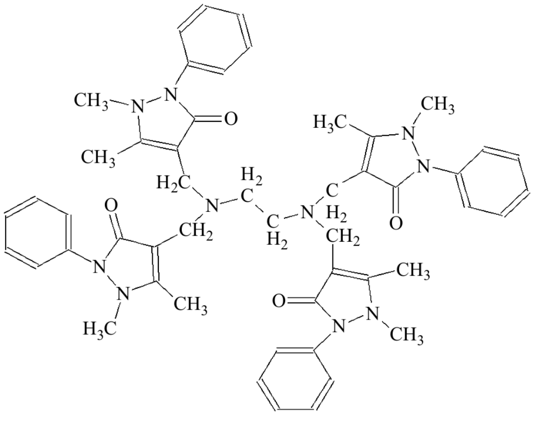
The interest in Mannich bases containing antipyrine as active group is mainly due to their pharmaceutical activity [1]. There have been many reports on metal complexes of antipyrine or its derivatives that exhibit antitumour and antipyretic properties [2–8]. This explains the recent syntheses and structural and studies of some 3d metal complexes with binucleating Mannich bases as ligands, e.g. N,N'bis-(antipyrylmethyl)-piperazine (BAMP) and N,N'-tetra(antipyrylmethyl)-1,2-diaminoethane (TAMEN) [9–16].

Within such studies of the structures and biological activities of metal complexes, not only the parent complexes, but also mixed-ligand complexes are of interest. In the parent complexes of BAMP and TAMEN, a tetrahedral coordination sphere is formed around the metal ions, while the ligands act as bis-bidentate and bis-tridentate ligands, respectively, and the anion or water molecules occupy the remaining coordination sites. In the mixed-ligand complexes, a second ligand molecule may coordinate to the metal ion, thereby changing the properties and even the biological activity of the metal complexes.

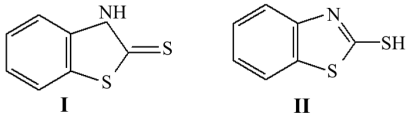
Besides BAMP and TAMEN, thioazobenzene and imidazole have been used as second ligand, and their mixed-ligand complexes with copper and cobalt ions have been prepared and investigated in our laboratory [1, 2]. Following this study, we have now chosen 2-mercaptobenzothiazole (Hmbt) as second ligand, and its mixed-ligand complexes of copper(I) and cobalt(II) ions with BAMP and TAMEN as ligands have been synthesized and investigated (Schemes 1–3).



Scheme 1 N,N'-bis(antipyrylmethyl)-piperazine (BAMP)



Scheme 2 N,N'-tetra(antipyrylmethyl)-1,2-diaminoethane (TAMEN)



Scheme 3 Tautomeric forms of 2-mercaptobenzothiazole (Hmbt)

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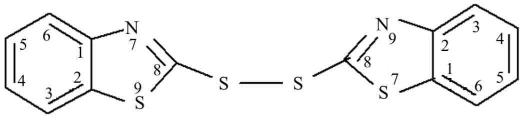
The importance of the thioamide group in biological systems is well known. Its activity is interpreted in terms of the interactions between the thioamide group and certain trace metal ions [17]. The Hmbt exists in two tautomeric forms and it may take part in redox reactions too, which leads additional interest to its coordination modes [18–24].

Experimental

Preparation and composition of complexes

The procedures for the preparation of the complexes and their characterization are detailed in [16]. In the course of the preparation of the copper complexes, copper(I) was formed. The redox reactions between copper(II) ion and thiols are well known [18], with the reduction of copper(II) ion followed by the formation of a bis(benzothiazol-2-yl-disulfide (mbt–mbt) (Scheme 4).



Scheme 4 The dimercaptobenzothiazine (bis(benzothiazol-2-yl-disulfide, mbt–mbt)

The following complexes were prepared and investigated:

$Cu_2(TAMEN)(mbt–mbt)(ClO_4)_2{\cdot}2H_2O$ (**1**)
$Cu_2(BAMP)(mbt–mbt)_2(ClO_4)_2{\cdot}2H_2O$ (**2**)
$Cu_2(BAMP)(mbt–mbt)(SCN)_2{\cdot}2H_2O$ (**3**)
$Co_2(BAMP)(Hmbt)_2(ClO_4)_4{\cdot}2H_2O$ (**4**)
$Co_2(BAMP)(Hmbt)_2(SCN)_4{\cdot}2H_2O$ (**5**)

Thermoanalytical studies

The thermal analyses were performed with a computer-controlled MOM derivatograph. The mass of the investigated samples was 70–100 mg. The measurements were made between room temperature and 1000°C, at a heating rate of 10°C min^{-1}, in ceramic crucibles under static atmosphere of nitrogen, with α-Al_2O_3 as reference substance.

Results and discussion

Composition and general description of the complexes

Mixed-ligand complexes of copper(I) perchlorate with TAMEN, BAMP and mbt–mbt (complexes **1** and **2**)

The TAMEN complex (**1**) and the BAMP complex (**2**) contain one and two mbt–mbt ligands, respectively. As TAMEN and BAMP are bis-tridentate (six donor atoms) and bis-bidentate (four donor atoms) ligands, respectively, and copper(I) ion forms tetrahedral coordination sphere, it is presumed that remained (two and four) coordination sites around the two copper(I) ions are occupied by mbt–mbt ligands. The perchlorate anion is presumed not to be coordinated; this is supported by the IR spectroscopic data [16].

Mixed-ligand complexes of copper(I) with BAMP and mbt–mbt with perchlorate, and thiocyanate anions (complexes **2** and **3**)

In the presence of the perchlorate anion (complex **2**), two mbt–mbt ligand coordinate to the copper(I), whereas in the presence of the thiocyanate anion (complex **3**) only one mbt–mbt ligand can coordinate to copper(I) ion. With regard to the tetrahedral coordination sphere around both copper(I) ions, and to the fact that BAMP has four coordinating donor atoms and to the ability of mbt–mbt to participate in bis-mono- or bidentate binding, the thiocyanate ions are presumed to be coordinated in complex **3**. The band maxima at 2109 cm^{-1} in the IR spectra of **3** support this hypothesis [16]. This maxima significantly differ from the same value (2053 cm^{-1}) of the free thiocyanate ion, which refer to the coordination of the thiocyanate ion to the copper(I) ion.

Mixed-ligand complexes of cobalt(II) perchlorate and thiocyanate with BAMP and Hmbt (complexes **4** and **5**)

In the presence of cobalt(II) ion, there is no possibility for a redox reaction between the metal ion and the ligand at the temperature of the preparation. The Hmbt therefore acts as ligand. Independently from the anion, one cobalt(II) ion can coordinate two molecules of Hmbt. According to the electronic spectra and magnetic susceptibility data [16], in these complexes the cobalt(II) ion has a tetrahedral coordination sphere. Consequently, both the perchlorate and the thiocyanate anion have to be uncoordinated. This is supported by the IR spectra of these complexes [16]. The bands maxima (1111, 932 and 623 cm^{-1}) of perchlorate ion in the spectra of complex **4** are characteristic – as in the case of the complexes **1** and **2** – for the uncoordinated perchlorate ion. In contrast to the complex **3**, the complex **5** has a strong band with maxima at 2063 cm^{-1}, which is close to the band maxima 2053 cm^{-1}, characteristic for free thiocyanate ion [25].

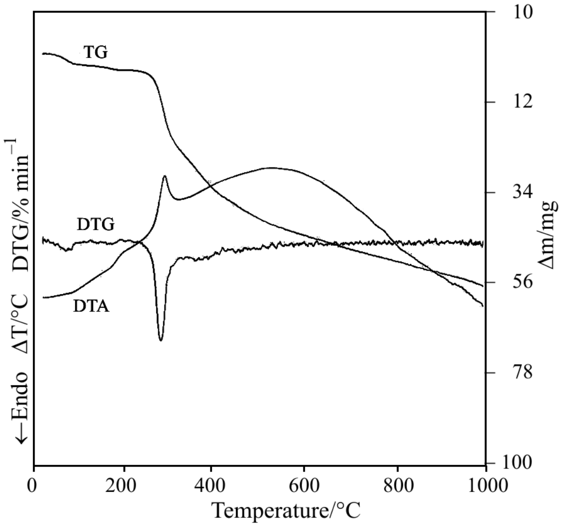


Fig. 1 Thermoanalytical curves of complex **1** (*m*=71.32 mg)

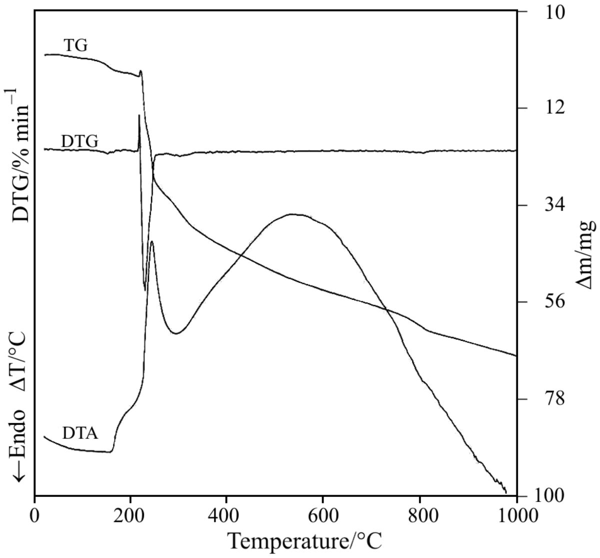


Fig. 2 Thermoanalytical curves of complex **2** (*m*=78.60 mg)

Thermoanalytical studies

Copper complexes

Mixed-ligand complexes of copper(I) perchlorate with TAMEN or BAMP and mbt–mbt (complexes 1 and 2)

Typical thermoanalytical curves of complexes **1** and **2** are shown in Figs 1 and 2. The decomposition behaviour of these complexes is similar. Both complexes decompose in three steps. In the first step, water molecules are released from the solid material below 200°C (in an endothermic process). In the second step (250–320 and 220–250°C, respectively), there is a fast decomposition (a sharp peak in the DTG curve and an extra peak in the DTA curve). This step is explosion-like for complex **2** (BAMP complex).

In the third step (320–1000 and 250–1000°C, respectively), a continuous loss in mass is observed. Both decomposition steps are accompanied by an exothermic effect. The mass losses formally indicate that $CuClO_4$ and CuCl could be the final products of decomposition of complexes **1** and **2**, respectively. However, these compounds do not exist in these high temperatures. Therefore it is more possible, that by heating, after the cleavage of the chemical bonds, there are processes of different reactions of the ligands (or their fragments). These reactions could be result a polymeric or condensed type of organic residues with unknown composition, which leave the solid material continuously by heating. The suggested decomposition schemes at lower temperature are the followings:

1
$\downarrow$<200°C
$\mathrm{Cu_2(TAMEN)(mbt{-}mbt)(ClO_4)_2}$
$\downarrow$250–320°C
$\mathrm{Cu_2(TAMEN)(ClO_4)_2}$

2
$\downarrow$<200°C
$\mathrm{Cu_2(BAMP)(mbt{-}mbt)_2(ClO_4)_2}$
$\downarrow$220–250°C
$\mathrm{Cu_2(BAMP)(mbt{-}mbt)(ClO_4)_2}$

Comparing the thermal behaviour of the TAMEN (**1**) and BAMP (**2**) complexes, it could be state, that the BAMP bound less strongly to the copper(I) ion and/or more easily oxidizable by perchlorate ion as the TAMEN ligand.

Mixed-ligand complexes of copper(I) with BAMP and mbt–mbt with perchlorate, and thiocyanate anions (complexes 2 and 3)

The thermoanalytical curves of complexes **2** and **3** are shown in Figs 2 and 3, respectively. The TG, DTG and DTA curves of the complex **3** (thiocyanate anions) partly differ from that of complex **2** (perchlorate anion). Both complexes decompose in three main steps: In the first step (<200 and <235°C, respectively), the water molecules are released from the solid material, this process being accompanied by an endothermic effect. The second and the third steps are accompanied by exothermic effect. In the case of complex **2**, a sharp DTG peak, and an extra peak in the DTA curve can be observed, connected with the explosion-like decomposition. This extra peak is not present in the DTA curves of complex **3**, for which the mass loss is not explosion-like.

In the second step of decomposition of complex **3** three different processes can be distinguished on the basis of the DTG curves. This is connected with the complicated character of its decompositions and it could not

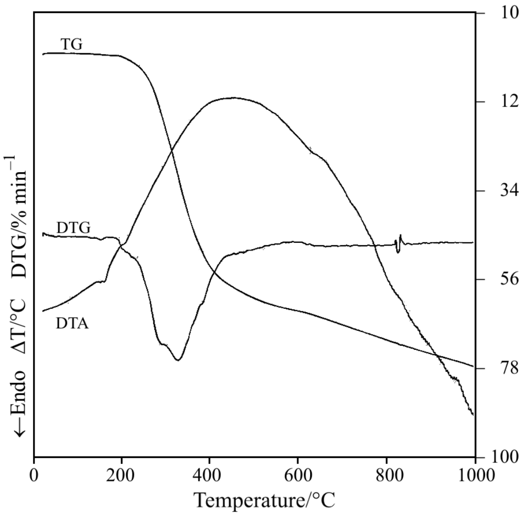


Fig. 3 Thermoanalytical curves of complex **3** (m=95.11 mg)

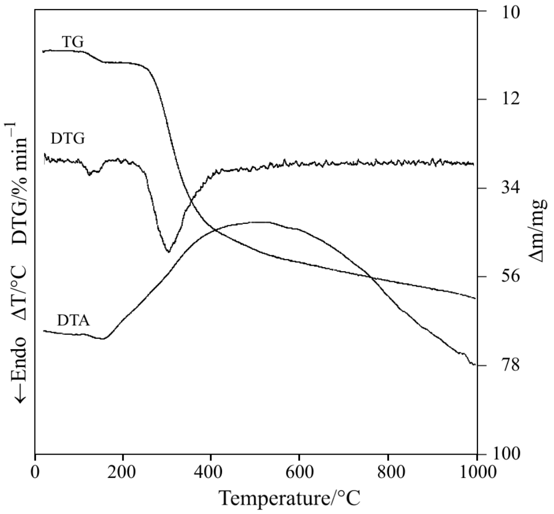


Fig. 4 Thermoanalytical curves of complex **4** (m=95.48 mg)

be suggest a defined decomposition scheme. In the third step a continuous loss of mass can be observed, but without an intensive peak in the DTG curve.

Formally CuCl (complex **2**) and CuSCN (complex **3**) could be proposed as final product, but as it was suggested before, the existence of these compounds at so high temperature is not presumable. As in the case of complexes **1** and **2**, the existence of different reactions of the ligands (or their fragments) could be suggested. In these cases also, these reactions could be resulted a polymeric or condensed type of organic residues with unknown composition, which leave the solid material continuously by heating.

Comparing the perchlorate and the thiocyanate anions, it could be stated that in the presence of the perchlorate anion the first reaction is explosive and it proceeds at lower temperature than in the case of the thiocyanate complex (complex **3**).

Cobalt complexes

Mixed-ligand complexes of cobalt(II) perchlorate and thiocyanate with BAMP and Hmbt (complexes **4** and **5**)

Both complexes decompose in three main steps (Figs 4 and 5). The first step is accompanied by endothermic, the second and third steps are followed by exothermic effect.

In the first step (<200°C), water molecules are released from the solid phase. In the second step there are four peaks in the DTG curve of complex **4** (perchlorate complex), but only one broad peak is observed in the DTG curve of complex **5** (thiocyanate complex) in the interval 200–420°C. In the third step, a continuous loss of mass and weak peaks in the DTG curves can be observed for both complexes. The suggested decomposition schemes at low temperatures (<510°C) are as follows:

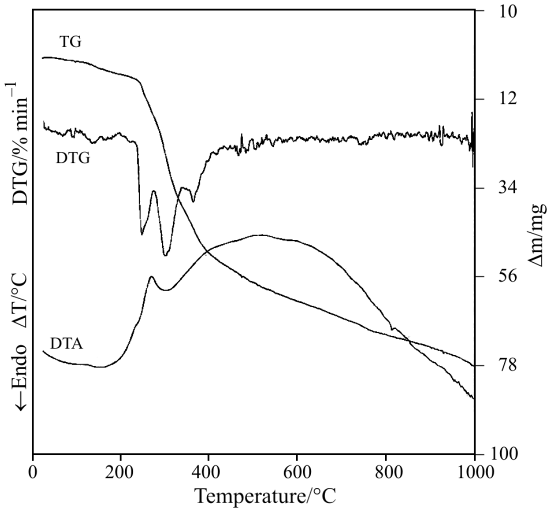


Fig. 5 Thermoanalytical curves of complex **5** (m=79.80 mg)

$$\mathbf{4}$$
$$\downarrow\!<\!200°\mathrm{C}$$
$$Co_2(BAMP)(Hmbt)_2(ClO_4)_4$$
$$\downarrow 210\text{–}510°\mathrm{C}$$
$$Co_2(BAMP^{2-})(ClO_4)_2$$

$$\mathbf{5}$$
$$\downarrow\!<\!200°\mathrm{C}$$
$$Co_2(BAMP)(Hmbt)_2(SCN)_4$$
$$\downarrow 200\text{–}420°\mathrm{C}$$
$$Co_2(BAMP^{2-})(SCN)_2$$

The values of the final masses of the decomposition are larger than the expected cobalt(II) oxide (or cobalt(III) oxide). This phenomenon could be interpreted in similar way as in the case of complexes **1**–**3**.

Conclusions

Compositions of complexes

The compositions of the prepared complexes correspond to the theoretical considerations. The first coordination spheres around the copper(I) and the cobalt(II) ions are occupied by the organic ligands (BAMP, TAMEN and Hmbt or mbt–mbt) and by the thiocyanate anions. The perchlorate anion and water molecules are located in the second coordination sphere.

In consequence of the redox property of the Hmbt molecule, it is not surprising that, instead of copper(II) complexes, only copper(I) complexes could be prepared in the presence of Hmbt.

Thermal behaviour of complexes

The investigated metal ions (Cu(I)) and (Co(II)) form a tetrahedral coordination sphere, and the donor atoms of the ligand and the thiocyanate anion occupy the first coordination sphere. In the second coordination sphere the water molecules and the perchlorate, tiocyanate anions are located. On increase of the temperature, first (<200–250°C) the water molecules are released from the solid material (endothermic process).

On further increase of the temperature, the organic ligands start to be released from the solid phase, to the accompaniment of an exothermic effect. The DTG curves show that this process takes place in one or three steps. Hmbt and mbt–mbt ligands release the solid material in this temperature range. In the case of cobalt complexes (complexes **4** and **5**) the deprotonation of the BAMP ligand also could be suggested. Probably the Hmbt and mbt–mbt are bound more weakly to the metal ion or their thermal stability is lower than the other ligands, and that (or both of them) is the reason why they leave the solid matrix at lower temperature. The exothermic heat effect refers to the importance of the thermal stability of ligands. The thermal decomposition of the ligands takes place through the cleavage of chemical bonds, which open a possibility for many organic reactions.

In the third steps a continuous loss of masses could be observed to 1000°C with final mass value larger than the expected one (metal-oxides are expected as final product). This phenomenon could be explained by the process of different organic reactions, which result final products with relatively high thermal stability in nitrogen atmosphere (e.g. carbon, condensed hydrocarbons).

Comparing the TAMEN and the BAMP, the later one seems to be taken part in these reactions more easily (compare the complexes **1** and **2**).

The role of the metal ions in this respect supported by the comparison of the thermal behaviour of the complexes **2** and **4** or **3** and **5**: both copper(I) and cobalt(II) can take part in these reactions.

The role of the anion is also interesting. The copper(I) complex with thiocyanate anion and with BAMP (complex **3**) shows a complicated decomposition scheme (in the second step of decomposition), while the cobalt(II)-thiocyanate complex decompose in this temperature range more simple way (with the same BAMP ligand).

In otherwise, the copper(I) complex with BAMP and perchlorate anion (complex **2** with BAMP) decompose in one explosive way). Finally it could be stated that the thermal behaviour of these antipyrine derivatives depend on the partner ligand and from the partner metal ions.

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