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THERMAL BEHAVIOUR OF COMPLEXES OF ANTIPYRINE DERIVATIVES

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Abstract

Parent and mixed ligand complexes of cobalt and copper with antipyrine derivatives of 1,2-ethanediamine or piperazine and with 2-aminobenzothiazole (TAB) were synthesized and their thermal behaviour was investigated. The complexes contain N,N'-bis(4-antipyrylmethyl)-piperazine (BAMP) or N,N'-tetra(4-antipyrytmethyl)-1,2-diaminoethane (TAMEN) or/and TAB as ligand, and Cl^-, ClO_4^- or SCN^-. The complexes decompose with the evolution of heat. The decomposition route depends on the presence of ClO_4^-. If the ClO_4^- is not coordinated, it oxidizes the TAB and BAMP or TAMEN and the decomposition is explosive.

Keywords: Co(II) and Cu(II) ions, mixed ligand complexes, pyrazolonic Mannich bases, thermal behaviour, 2 aminobenzothiazole

Introduction

Antipyrine and its derivatives exhibit antipyretic and analgesic activity [1, 2]. Their complexes with some metal ions, including Pt(II) and Co(II) ions, have been shown to act as antitumor substances [3]. In a search for new ligands and new complexes which will probably have antitumor activity, some first row metal complexes of the Mannich bases of antipyrine (N,N'-bis(4-antipyrylmethyl)-piperazine (BAMP) and N,N'-tetra(4-antipyrylmethyl)-1,2-diaminoethane (TAMEN) have been prepared and characterized [4–7]. Besides the parent complexes of BAMP and TAMEN, mixed ligand complexes of Cu(II) and Co(II), in which 2-aminobenzothiazole (TAB) acts as second ligand, were prepared and investigated [8].

The choice of TAB as ligand is based on the biological importance of the thiazole group, which contains N and S as possible donor sites. The amino group at position 2 also provides a donor atom, due to the similar basicities of the N atoms in TAB.

Many methods are available with which structural information may be obtained on these complexes, but the number of methods that give information on their stabilities is low. Thermoanalytical studies were therefore performed in order to obtain information on the stabilities of the investigated complexes.

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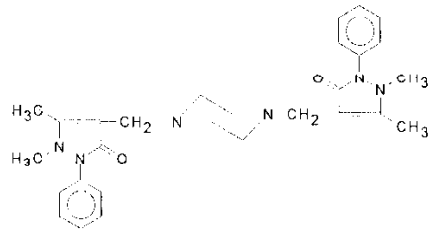
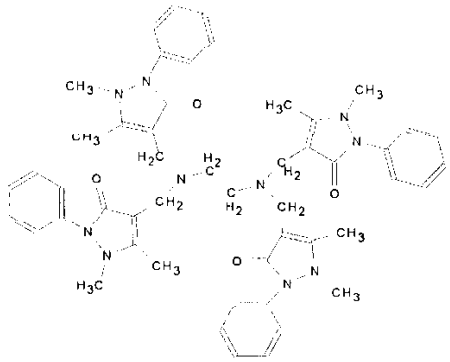
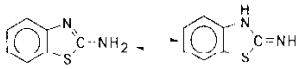


N,N'-bis(antipyrylmethyl) piperazine (BAMP)



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



Different tautomeric forms of 2-aminobenzothiazole (TAB)

Experimental

Preparation and characterization of complexes

The general procedure for the preparation of the complexes was as follows: the ligand and the metal halide in stoichiometric ratio were dissolved in methanol and $NaClO_4$ or NH_4SCN was added to precipitate the solid complex. The solid compounds were washed, and dried by the usual methods, and their compositions were determined by the usual analytical methods. The procedures for the preparation of the complexes are given in reference [8]. The following complexes were prepared:

$Co(BAMP)(SCN)_2$ (**1**)
$Co_2(BAMP)(ClO_4)_4$ (**2**)
$Co(TAB)_2Cl_2$ (**3**)
$Cu(TAB)_2Cl_2$ (**4**)
$Co_2(TAB)_2(BAMP)(SCN)_4$ (**5**)
$Co_2(TAB)_2(BAMP)(ClO_4)_4(H_2O)_2$ (**6**)
$Cu_2(TAB)_4(BAMP)(ClO_4)_4$ (**7**)
$Co_2(TAB)_2(TAMEN)(ClO_4)_4$ (**8**)
$Cu_2(TAB)_4(TAMEN)(ClO_4)_4$ (**9**)

Thermoanalytical studies

The thermal analyses were performed with a computer-controlled MOM derivatograph, using 5–100 mg samples. Measurements were made between room temperature and 1000°C. A heating rate of 10°C min^{-1}, ceramic crucibles and a nitrogen atmosphere were used. The reference substance was α-Al_2O_3.

Results and discussion

Composition and general description of complexes

A tetrahedral coordination sphere was revealed around the metal ion by IR spectroscopy and magnetic susceptibility measurements in all the investigated complexes except complex **1**, in which the cobalt(II) ion has an octahedral coordination sphere. The ligand BAMP act as a bis-bidendate ligand via two pyrazolone oxygen atoms and two piperazine nitrogen atoms. TAMEN is coordinated as a bis-bidendate ligand (copper complexes (**9**)) or a bis-tridentate ligand (cobalt complexes (**8**)) via the pyrazolone oxygen atoms or the pyrazolone oxygen atoms and the ethylenediamine nitrogen atoms. TAB act as a monodentate ligand in all cases.

Thermoanalytical studies

Decomposition of the investigated complexes was accompanied by an exothermic effect, except for the release of water molecules from complex **6**. This means that the decomposition is accompanied by a chemical reaction. In some cases, this chemical reaction did not allow determination of the different steps of the decomposition route. The following trends were found in the decompositions of the complexes.

Parent complexes of cobalt(II) perchlorate and thiocyanate with BAMP (complexes **1** and **2**)

The thermoanalytical curves of complex **1** are shown in Fig. 1. Similar curves were observed in the course of decomposition of complex **2**. The following reactions could be suggested:

$$2Co(BAMP)(SCN)_2 \rightarrow Co_2(BAMP)_2(SCN)_4 + BAM \quad (250–350^{\circ}C)$$
$$Co_2(BAMP)_2(SCN)_4 \rightarrow Co_2(BAMP^-)_2(SCN)_2 + 2HSCN \quad (350–450^{\circ}C)$$
$$Co_2(BAMP)_2(ClO_4)_4 \rightarrow Co_2(BAMP^-)_2(ClO_4)_2 + 2HClO_4 \quad (350–450^{\circ}C)$$

The decomposition of the intermediates $(Co_2(BAMP^-)_2(SCN)_2$ and $Co_2(BAMP^-)_2(ClO_4)_2)$ is doubtful. There is no synchrony between the DTA and the DTG curves. The reason for this phenomenon is the simultaneous presence of both endothermic and exothermic effects. The release of molecules from the solid phase without a chemical reaction must be accompanied by an endothermic effect. Simultaneously with the endothermic process, an exothermic effect will occur because of the chemical reaction or combustion of the ligands.

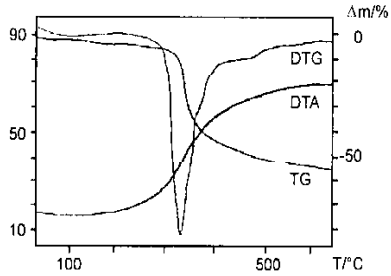


Fig. 1 Thermoanalytical curves of complex **1** ($Co(BAMP)SCN_2$)

The octahedral coordination sphere in complex **1** changes to tetrahedral during the decomposition. The stability of the tetrahedral coordination sphere around the cobalt(II) ion is similar for the thiocyanate and the perchlorate complexes. BAMP is able to form an anion and coordinate to the cobalt(II) ion. The final decomposition product is probably is $CoCl_2$ (**2**) or $Co(SCN)_2$ (**1**), containing polymeric compounds or carbon.

Parent complexes of TAB (complexes **3** and **4**)

The parent complexes of cobalt(II) and copper(II) with TAB (complexes **3** and **4**) decompose in different ways. The copper(II) complex decomposes in one step between 200 and 1000°C to give $CuCl_2$ as final product. On heating, one TAB molecule replace one Cl^- in the cobalt(II) complexes **3** (Fig. 2). The suggested decomposition scheme is as follows:

$$Co(TAB)_2Cl_2 \rightarrow Co(TAB)(TAB^-)Cl + HCl \quad (280–300°C)$$
$$Co(TAB)(TAB^-)Cl \rightarrow Co(TAB^-)Cl \quad (450–550°C)$$

The decomposition of $Co(TAB^-)Cl$ between 550 and 1000°C is doubtful. A mixture of CoS and $CoCl_2$ could be suggested as final product. Similarly to the decomp positions of complexes **1** and **2**, there is no synchrony between the DTA and DTG curves, owing to the presence of both endothermic and exothermic effects.

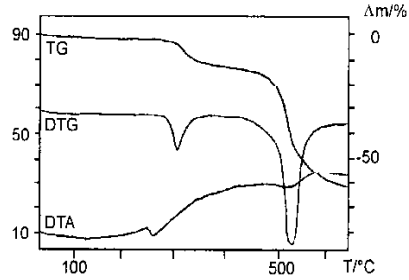


Fig. 2 Thermoanalytical curves of complex **3** ($Co(TAB)_2Cl_2$)

TAB is able to form an anion and replace Cl^- in the coordination sphere of the cobalt(II) ion, but it is not able to form an anion in the copper(II) complex. TAB can form an anion at a lower temperature than BAMP can.

Mixed ligand cobalt(II) complexes of TAB and BAMP with ClO_4^- and SCN^- (complexes **5** and **6**)

Complex **6** decomposes in three steps. First, the water molecules leave the solid phase. In the second step, two TAB molecules form anions and replace two ClO_4^-. This step has an explosive character; there is a sharp peak in the DTA curve. The decomposition in the third step (>300°C) is continuous; the final mass points to the decomposition of ClO_4^-.

$Co_2(TAB)_2(BAMP)(ClO_4)_4(H_2O)_2 \rightarrow Co_2(TAB)_2(BAMP)(ClO_4)_4$ (<20$_0$°C)
$Co_2(TAB)_2(BAMP)(ClO_4)_4 \rightarrow Co_2(TAB^-)_2(BAMP)(ClO_4)_2+HClO_4$ (200–300°C)

The DTG curve indicates that complex **5** decomposes in three steps between 200 and 1000°C (Fig. 3), but the steps are not separated. The final mass is less than that for $Co(SCN)_2$.

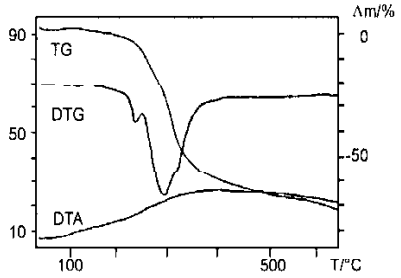


Fig. 3 Thermoanalytical curves of complex **5** ($Co(TAB)_2(BAMP)(SCN_4)$)

A similar decomposition scheme could be suggested for the SCN^- complex as for the ClO_4^- complex. The difference probably lies in the stability of the tetrahedral intermediate complexes ($Co_2(TAB^-)_2(BAMP)X_2$, X=ClO_4^- or SCN^-); the SCN^- complex is the less stable.

Mixed ligand complexes of cobalt(II) perchlorate with TAB and BAMP or TAMEN (complexes **6** and **8**)

There is a difference between the decomposition routes of complexes **6** (TAB and BAMP) and **8** (TAB and TAMEN). Complex **8** decomposes explosively in one step (270–280°C). In this case, the determination of the final mass is uncertain.

The ClO_4^- is not involved in the coordination sphere around the cobalt(II) ion in complex **8**, and the uncoordinated ClO_4^- is probably responsible for the explosive decomposition.

Mixed ligand complexes of copper(II) perchlorate with TAB and BAMP or TAMEN (complexes **7** and **9**)

Complex **7** (TAB and BAMP complex) decomposes explosively in one step. The final mass values indicates the presence of CuCl. In the decomposition of complex **9**, first the TAB molecules leave the solid phase:

$$Cu_2(TAB)_4(TAMEN)(ClO_4)_4 \rightarrow Cu_2(TAMEN)(ClO_4)_4 + 2TAB \quad (250–300^{\circ}C)$$

This step has an explosive character. TAMEN leaves the solid phase continuously between 300 and 1000°C and the final mass value indicates the presence of $CuCl_2$ (Fig. 4).

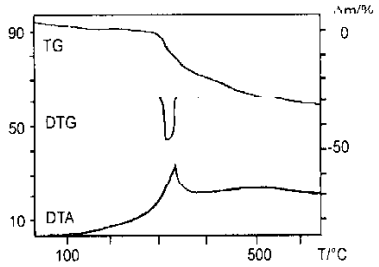


Fig. 4 Thermoanalytical curves of complex **9** ($Cu_2(TAB)_4(TAMEN)(ClO_4)_4$)

In complexes **7** and **9** (similarly as in complex **8**, the ClO_4^- is not involved in the coordination sphere, and the free ClO_4^- and the copper(II) ion can oxidize the TAB and TAMEN or BAMP explosively.

Discussion

BAMP and TAMEN form stable dimeric tetrahedral complexes with cobalt(II) and copper(II) ions. The coordination sphere containing BAMP or TAMEN or/and TAB and SCN^- or ClO_4^- is stable on heating to 200–300°C. The perchlorate complexes are less stable: their decompositions start at lower temperatures than those for the corresponding thiocyanate complexes. The high stability of the complexes is connected with the chelate-type coordination of BAMP and TAMEN.

The decomposition of each complex is accompanied by chemical reactions. The deprotonation of TAB and BAMP could be observed. The ClO_4^- is able to oxidize the ligands, especially in the presence of copper(II) ion. On heating of the thiocyanate complexes, degradation of the ligands and polymerization of the products can be suggested as occurring.

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