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THERMAL BEHAVIOUR OF COMPLEXES OF ANTIPYRINE DERIVATIVES II[*]

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Abstract

Parent and mixed ligand complexes of cobalt(II) and copper(II) ions with N,N'-bis-(4-antipyrylmethyl)piperazine or N,N'-tetra(4-antipyryl-methyl)-1,2-diaminoethane or/and imidazole as ligand and ClO_4^- or SCN^- as counterion were synthesised and their thermal behaviour was investigated.

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

Introduction

Numerous artificial organic compounds are known which alone or in the presence of different metal ions display therapeutic activity. To elucidate the mechanisms of therapeutic action of these compounds and their metal complexes, their characterisation is required. A knowledge of the physical and chemical properties of a compound and its metal complexes may help to clarify their biological (therapeutic) activity and allow the prediction of new compounds or complexes with similar or more higher therapeutic activity.

For study of the correlation between the therapeutic activity and the physical and chemical properties, antipyrine derivatives were chosen as model compounds, because they exhibit antipyretic and analgesic activity [2, 3]. Their complexes with certain metal ions, e.g. Pt(II) and Co(II) ions, exert antitumor activity [4].

Metal complexes of the antipyrine derivatives, N,N'-bis(antipyrylmethyl)-piperazine (BAMP) and the N,N'-tetrakis(antipyrylmethyl)-1,2-diaminoethane (TAMEN) were studied earlier [5–10], and their mixed ligand complexes with imidazole (IA) were also prepared and investigated. As previously [5–10], in the present work the thermal studies were chosen to

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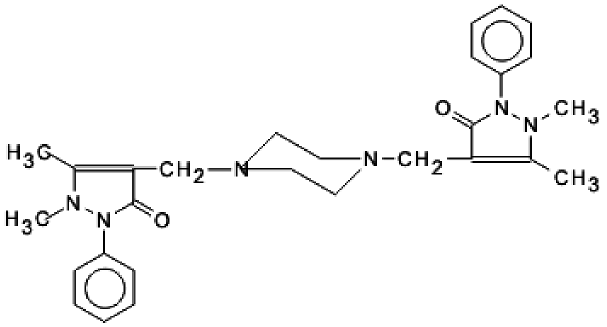
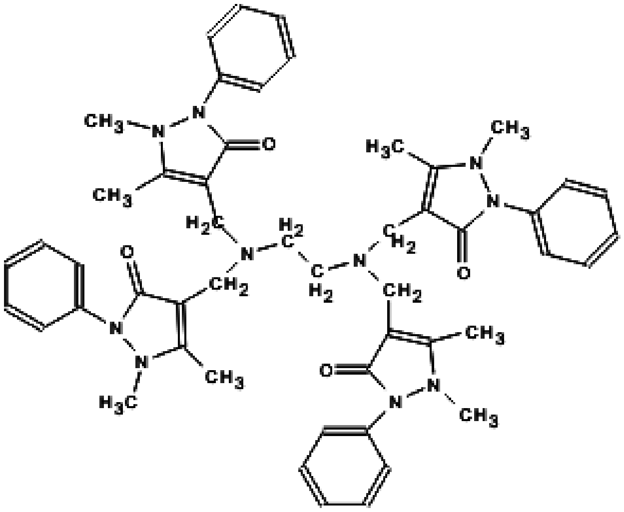
obtain information on the stabilities of the investigated complexes. This method is often used to characterise different organic compounds and their metal complexes of potential therapeutic use [11–15].



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



N, N’-tetrakis(antipyrylmethyl)-1,2-diaminoethane (TAMEN)

Experimental

Preparation and characterisation of complexes

The general procedure for the preparation of the complexes was as follows: The ligands and the metal(II) chloride in stoichiometric ratio were dissolved in methanol or ethanol, and $NaClO_4$ or NH_4SCN was added to precipitate the solid complex. The solid product was washed, then dried by the usual methods and its composition was

The structure of imidazole (IA)

determined by the usual analytical methods. The procedures for the preparation of the complexes and for the determination of their compositions are described in detail in [10]. Complexes with the following composition were prepared:

$$Cu_2(BAMP)(IA)_4(ClO_4)_4{\cdot}2H_2O \qquad (1)$$

$$Cu_2(TAMEN)(IA)_4(ClO_4)_4 \qquad (2)$$

$$Co_2(BAMP)(IA)_4(SCN)_4 \qquad (3)$$

$$Co_2(BAMP)(IA)_4(ClO_4)_4{\cdot}2H_2O \qquad (4)$$

The following BAMP parent complexes, with known properties [1, 8], were also prepared:

$$Co(BAMP)(SCN)_2 \qquad (5)$$

$$Co_2(BAMP)(ClO_4)_4 \qquad (6)$$

Thermoanalytical studies

Thermal analyses were performed with a computer-controlled MOM derivatograph. Measurements were made between room temperature and 1000ºC at a heating rate of 10ºC min^{-1}. Ceramic crucibles and a nitrogen atmosphere were used, with α-Al_2O_3 as reference substance.

Results and discussion

Compositions of the complexes

BAMP may act as a bis bidendate ligand, via two pyrazolonic O atoms and two piperazine N atoms. TAMEN can coordinate to metal ions as a bis bidendate or a bis tridentate ligand, via the four pyrazolonic O atoms and two ethylenediamine N atoms (the pyrazolonic O and the piperazine or ethylenediamine N atoms always form a chelate ring).

ClO_4^- can act as a mono-, bi-, tri- or tetradentate ligand, but its mono- and bidentate binding modes are common and it is only a weak complexing agent. SCN^- can act as a monodentate (via the N or S atom) or bidentate ligand towards metal ions, but the monodentate mode is the common one. The water molecule can also act as a monodentate or bidentate ligand and may complete the coordination sphere around a metal ion. IA can act as a monodentate or bidentate ligand via one or two N atoms.

As concerns the compositions of the complexes and the general sequence of coordination ability of the ligands, the BAMP or TAMEN, IA and SCN$^-$ are candidates as participants in the first coordination sphere of the metal ions. SCN$^-$, ClO_4^- and H_2O are suggested to be present in the second coordination sphere, or in the first coordination sphere, if there are not enough coordinating donor atoms in the complexes.

Information on coordination sphere and the coordination modes of the different ligands, water and anions can be obtained from the electronic spectra, the IR spectra and the magnetic susceptibility data relating to the complexes [10].

The electronic spectra [10] suggested a distorted tetrahedral coordination sphere for both the copper and the cobalt complexes 1–4. The IR spectra reveal changes in the characteristic bands of BAMP, TAMEN and IA, indicating that these ligands are located in the first coordination sphere around the metal(II) ion. The differences between the complexes of the two large ligands (BAMP and TAMEN) are the presence of H_2O in complexes 1 and 2, and the IR spectra of the ClO_4^-.

It is presumed that the H_2O, ClO_4^- and SCN$^-$ are located in the second coordination sphere of the metal(II) ion, bound by hydrogen-bonds or electrostatic interaction. Probably the larger size and the presence of the 5th and the 6th donor atoms in the TAMEN ligand (complex 2) or the presence of SCN$^-$ in the BAMP complex (complex 3) prevent the binding of H_2O. Both the ν_4 and ν_2 bands of the ClO_4^- are split to a small extent to two (complexes 1 and 4) or to three (complex 2) bands, caused by the presumed hydrogen-bonds via two and one O atoms of the ClO_4^-, respectively. The characteristic band of SCN$^-$ (ν(C=S)) is split (2080 and 2063 cm^{-1}), as a sign of the different surroundings of the SCN$^-$ in the molecule.

In complexes 5 and 6, octahedral and distorted tetrahedral coordination spheres were suggested [6] around the cobalt(II) ion; the four donor atoms of the BAMP, the SCN$^-$ and the ClO_4^- are coordinated.

Thermoanalytical studies

Copper(II) complexes

Mixed ligand complexes of copper(II) perchlorate with BAMP or TAMEN and IA (complexes 1 and 2):

Complexes 1 and 2 decompose in a similar way. The thermoanalytical curves for complex 1 and 2 are shown in Figs 1 and 2, and the suggested decomposition scheme is presented in Fig. 3.

The curves reveal the release of H_2O from the solid compound in the interval 50–150ºC. This step is not observed in the course of the decomposition of complex 2. A sharp change may be observed in the TG and DTG curves, at 275 and 310ºC for complexes 1 and 2, respectively, which may be attributed to an explosion-like decomposition.

At higher temperatures the samples decompose in two steps, and the masses suggest CuCl (376 and 468°C) and Cu_2O (600°C) as intermediate and end-product.

Mixed ligand complexes of cobalt(II) perchlorate and thiocyanate with BAMP and IA (complexes 3 and 4):

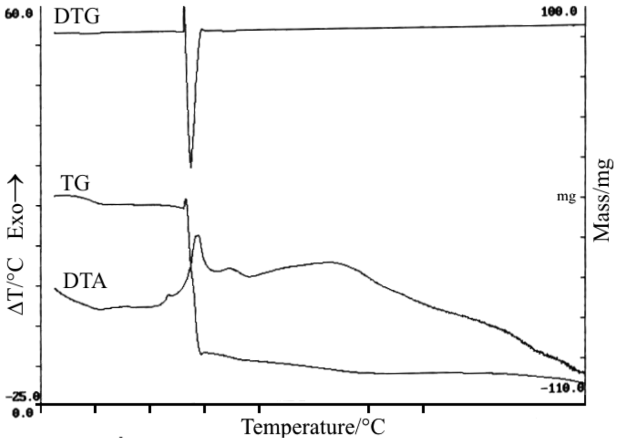


Fig. 1 Thermoanalytical curves of complex 1

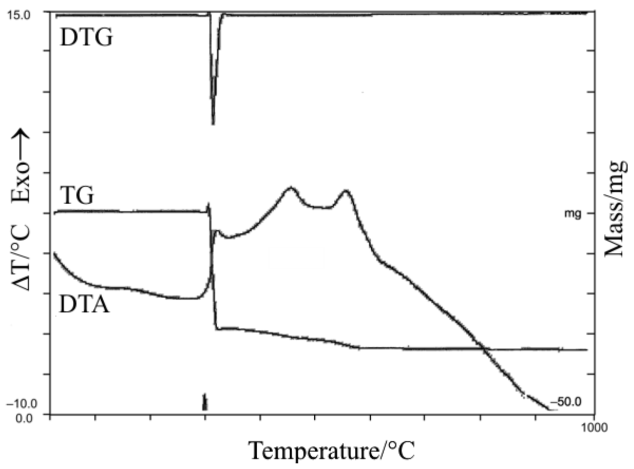


Fig. 2 Thermoanalytical curves of complex 2

$$Cu_2(BAMP)(IA)_4(ClO_4)_4{\cdot}2H_2O \xrightarrow{50\text{–}150^\circ C} Cu_2(BAMP)(IA)_4(ClO_4)_4 \xrightarrow{\sim 275^\circ C} CuCl \xrightarrow{275\text{–}600^\circ C} Cu_2O$$

$$Cu_2(TAMEN)(IA)_4(ClO_4)_4 \xrightarrow{310^\circ C} CuCl \xrightarrow{310\text{–}600^\circ C} Cu_2O$$

Fig. 3 Decomposition scheme of complexes 1 and 2

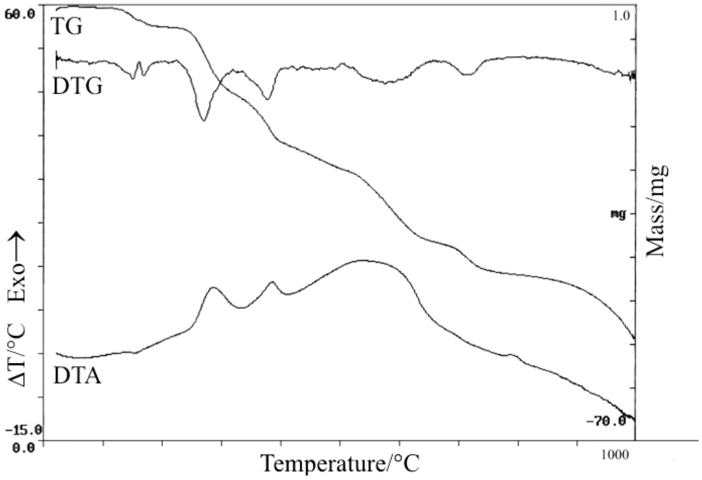


Fig. 4 Thermoanalytical curves of complex 3

There are many similarities and differences between the thermal behaviour of the ClO_4^- and SCN^- complexes; the thermoanalytical curves are shown in Figs 4 and 5.

Perchlorate complex

The ClO_4^- complex (complex 4) decomposes in five steps between 140 and 800°C. On the basis of the mass losses, the suggested decomposition scheme is shown in Fig. 6: H_2O, $HClO_4$, IA and BAMP molecules are released from the solid matrices in the first, second, third and fourth steps of the decomposition. $Co(ClO_4)_2$ and $Co(IA^-)_2$ are suggested as intermediates products. Finally, the $Co(IA^-)_2$ decomposes and CoO is formed.

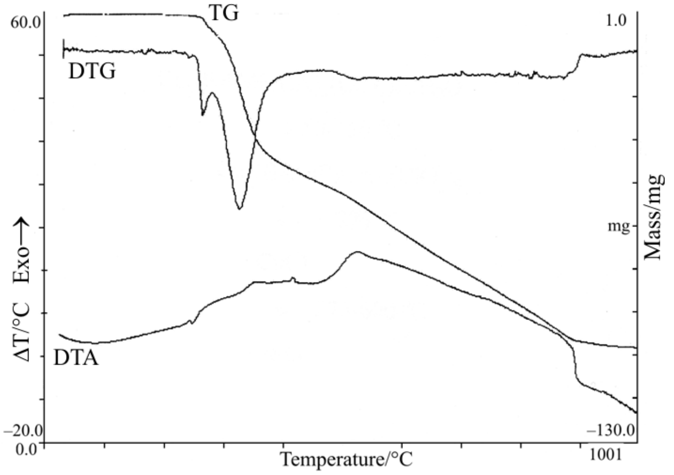


Fig. 5 Thermoanalytical curves of complex 4

$$\mathrm{Co_2(BAMP)(IA)_4(ClO_4)_4{\cdot}2H_2O}$$

$$\downarrow \quad 140\text{–}230^\circ\mathrm{C}$$

$$\mathrm{Co_2(BAMP)(IA)_4(ClO_4)_4}$$

$$\downarrow \quad 230\text{–}320^\circ\mathrm{C}$$

$$\mathrm{Co_2\ (BAMP)(IA)_2\,(IA^-)_2(ClO_4)_4{+}2\ HClO_2}$$

$$\downarrow \quad 320\text{–}420^\circ\mathrm{C}$$

$$\mathrm{Co_2(BAMP)(IA^-)_2(ClO_4)_2 + 2\ IA}$$

$$\downarrow \quad 420\text{–}660^\circ\mathrm{C}$$

$$\mathrm{Co(BAMP)_{1/2}(ClO_4)_2{+}\ Co(IA^-)_2 +\ (BAMP)_{1/2}}$$

$$\downarrow \quad 660\text{–}1000^\circ\mathrm{C}$$

$$\mathrm{Co(ClO_4)_2{+}CoO{+}(BAMP)_{1/2}}$$

$$\mathrm{Co_2(BAMP)(IA)_4(SCN)_4}$$

$$\downarrow \quad 250\text{–}270^\circ\mathrm{C}$$

$$\mathrm{Co_2(BAMP)(IA)_3(IA)(SCN)_3{+}HSCN}$$

$$\downarrow \quad 270\text{–}380^\circ\mathrm{C}$$

$$\mathrm{Co(BAMP)_{1/2}(SCN)_2{+}Co(AI)_2{+}IA{+}HSCN{+}1/2\ BAMP}$$

$$\downarrow \quad 380\text{–}1000^\circ\mathrm{C}$$

$$\mathrm{Co(SCN)_2{+}CoO}$$

Fig. 6 Decomposition scheme of complexes 3 and 4

Comparison of the decomposition schemes of complexes 4 and 6 [1] indicates that IA loses 2 protons (dissociation) at lower temperature than for the BAMP molecule [1] and it these results in the neutral form of BAMP in the course of the decomposition. If the complex does not contain IA (complex 6), the BAMP dissociates above 300ºC and the decomposition is accompanied by a continuous loss of mass to yield $\mathrm{Co(ClO_4)_2}$ as endproduct.

Thiocyanate complex

Complex 3 decomposes in three steps; the suggested decomposition scheme is shown in Fig. 6.

A comparison of the decomposition schemes of complexes 3 and 5 permits similar conclusions as for the $\mathrm{ClO_4^-}$ complexes. The IA dissociates at lower temperature than for BAMP, and a similar decomposition scheme can be suggested.

Conclusions

A comparison of complexes 1 and 2 demonstrates that the TAMEN complex has the higher thermal stability. It decomposes at higher temperature. The presence of the 5th and 6th donor atom in TAMEN may be responsible for the greater stability of complexes 2 and for the absence of H_2O molecules. The distorted tetrahedron around the copper(II) ion involves the amine N, pyrazolonic O and two imidazole N atoms. The free pyrazolonic O atoms in TAMEN may bind to ClO_4^- or to the imidazole molecules by hydrogen bonding and this interaction causes an increase in the stability of the complex.

It is not surprising that the complexes containing ClO_4^- undergo explosive-like decomposition. Comparison of the thermal behaviour of complexes 1 and 3 clearly indicate that the copper ion, even in the Cu(I) state, must be present for this phenomenon to be observed.

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