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STUDY OF THE THERMAL DECOMPOSITION OF BROMAZEPAN-THIOCYANATE COMPLEXES OF Fe(II), Co(II), Ni(II) AND Cu(II)

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ABSTRACT

The thermal behaviour of bromazepan thiocyanate complexes of Fe(II), Co(II), Ni(II) and Cu(II) has been studied by TG and DSC techniques. The complexes decompose in three steps: pyridine elimination, SCN oxidation and total decomposition to metal oxides. Different behaviour for Fe(II) with respect to other metal ion complexes was observed.

INTRODUCTION

The complexes of bromazepan with M(II) (Co, Ni, Cu and Zn) and X^{n-} (ClO_4^-, Cl^- and SO_4^{2-}) were characterized [1,2] and their thermal behaviour studied [3] in previous work and correlation between the dehydration temperatures and the coordinating ability of X^{n-} was observed. The anhydrous products decompose above 300°C by a well-defined step at 270–370°C with a narrow exothermic peak corresponding to the loss of two mol of pyridine per mol of compound.

We have synthesized and characterized the thiocyanate complexes of M(II)-bromazepan [4], and have proposed tentatively an idealized octahedral structure where the coordination sites are two N(imine), two N(pyridine), N(NCS) and S(NCS) donor atoms.

There is no information in the literature on the thermal behaviour of these compounds, although that of $M(II)(Py)_4(NCS)_2$ complexes has been reported [5,6].

EXPERIMENTAL

Samples

The complexes studied, whose synthesis and characterization have been previous reported [4], were: $FeB_2(NCS)_2$, $CoB_2(NCS)_2$, $NiB_2(NCS)_2$ and $CuB_2(NCS)_2$.

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Apparatus

TG curves were obtained under a static air atmosphere in a Mettler TA 3000 thermobalance at a heating rate of 10°C min^{-1}. The DSC curves were recorded in a Mettler differential scanning calorimeter (model DSC-20), over a 35–500°C temperature range, using a heating rate of 5°C min^{-1}. Samples weighed between 1.50 and 4.70 mg. X-ray powder diffraction patterns were obtained with a Kristalloflex 810 Siemens diffractometer.

RESULTS AND DISCUSSION

Thermogravimetric analysis curves for the isolated complexes are given in Fig. 1 and differential scanning calorimetry curves are given in Fig. 2.

All the complexes are anhydrous and stable below 200°C. Above this temperature thermal decomposition occurs in three overlapping steps: (i) elimination of molecules of pyridine at 200–400°C; (ii) the elimination of SCN at 400–500°C; and (iii) pyrolytic decomposition and metal oxide

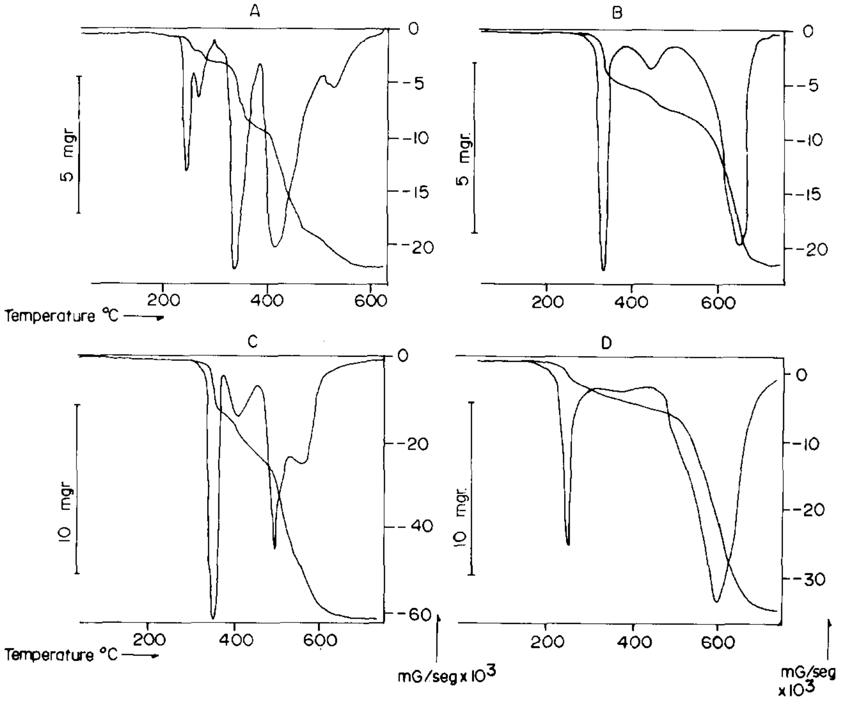

Fig. 1. TG and DTG curves of $FeB_2(NCS)_2$ (A); $CoB_2(NCS)_2$ (B); $NiB_2(NCS)_2$ (C); $CuB_2(NCS)_2$ (D).

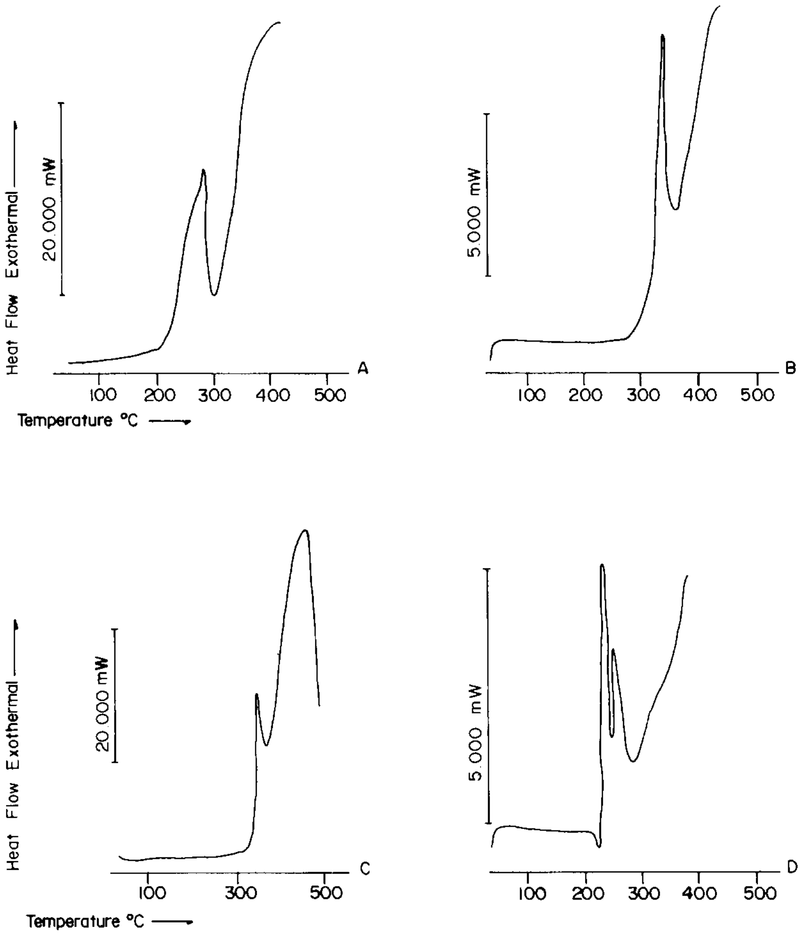

Fig. 2. DSC curves of $FeB_2(NCS)_2$ (A); $CoB_2(NCS)_2$ (B); $NiB_2(NCS)_2$ (C); $CuB_2(NCS)_2$ (D).

formation. The DSC curves show two exothermic peaks for the first and second processes.

There are some differences in the thermal behaviour of Co(II) and Ni(II) with respect to Cu(II) and Fe(II) complexes, as can be seen from the TG and DTG curves. In the former, the TG curves show a 19.5 and 18.2% weight loss which corresponds to the theoretical value required for elimination of two mol of pyridine per mol of compound (19.57%, 19.58%). In the second step, the Co(II) and Ni(II) complexes show elimination of NCS radicals as indicated by the weight loss (exp. 12.6%, 13.6%; calc. 14.7% in both compounds). Finally, pyrolytic decomposition takes place above 500°C.

However, in the Cu(II) complex the first process consists of elimination of one mol of pyridine per mol of compound, as shown by the experimental weight loss (9.0%) and the theoretical value (9.75%). The second step in the

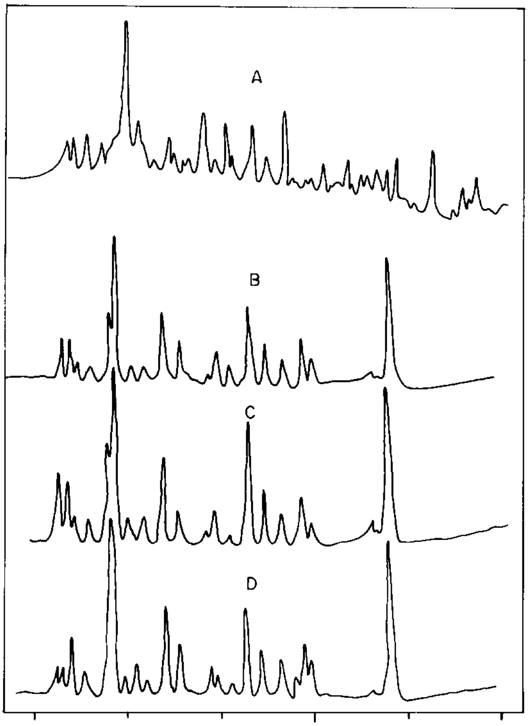

Fig. 3. X-ray spectra of $FeB_2(NCS)_2$ (A); $CoB_2(NCS)_2$ (B); $NiB_2(NCS)_2$ (C); $CuB_2(NCS)_2$ (D).

TG–DTG curves of the Cu(II) complex shows elimination of the second molecule of pyridine which takes place slowly in the 300–470°C temperature range with a corresponding weight loss of 9.0% (the total experimental weight loss is 18.0% in reasonable agreement with the theoretical value of 19.46%). The elimination of NCS and pyrolytic decomposition overlap for the Cu(II) complex.

The different behaviour of Cu(II) and the Co(II) and Ni(II) complexes cannot be attributed to their solid structures, since these are isomorphous complexes as shown by powder pattern X-ray diffractograms (Fig. 3). We propose that the Cu(II) complex loses the first pyridine molecule at lower temperatures and the second at higher temperatures than do the other complexes because the square pyramidal structure is more stable for the Cu(II) complex.

The thermal behaviour of the Fe(II) complex is more complicated than the other M(II)-bromazepan complexes. Here, there are also three steps: in the first, the pyridine molecule is lost at 220–295°C (one mol per mol of compound, exp. 10.0% and calc. 9.82%); in the second step one mol of pyridine and two mol of NCS are lost (exp. 24.4% and calc. 24.24%). Finally the third step corresponds to pyrolytic decomposition.

The following factors can be used to rationalize this behaviour: (i) oxidation of the Fe(II) ion; (ii) the solid structure of the Fe(II) complex which differs from the others, as indicated by X-ray diffraction pattern (Fig. 3). In previous work [4], we proposed the existence of two spin isomers in the Fe(II) complex. The experimental magnetic moment (2.4 BM), implies a mixture of both states ($^1A_1$ and $^5T_2$), i.e. low and high spin isomers in equal proportion. It has been shown that different spin isomers give rise to differences in X-ray powder patterns [7,8].

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