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THERMAL ANALYSIS OF OXATHIOAMIDATE COMPLEXES

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Abstract

Oxathioamidates ($CSNR_1R_2COOK$ $R_1=R_2=H$ (A), $R_1=H$ and $R_2=CH_3$ (B), $R_1=R_2=CH_3$ (C)) can act as O, S donors and form pentaatomic ring systems with divalent metals (M(II) = Mn, Fe, Co, Ni, Cu, Zn). Vibrational spectra and thermal analysis provide information on the amount and nature of associated water molecules. The dehydration of $MA_2(H_2O)_2$ (M=Mn, Fe, Co, Ni) can be very well explained by the C.F.S.E. (crystal field stabilization energy) for weak field octahedral complexes. The complexes with ligand A and B decompose to form polymers by deprotonation on the thioamide group. The proposed structures are confirmed by the vibrational spectra. For ligand C no stable intermediates are formed during heating, degradation proceeds until metal sulphide remains.

Keywords: complexes, oxathioamidate

Introduction

For several years our laboratory is interested in the physico-chemical study of amides and thioamides [1–4]. As a part of our research on metal(II) complexes with thioamides we synthesized some new original ligands ($CSNR_1R_2COOK$ $R_1=R_2=H$ (A), $R_1=H$ and $R_2=CH_3$ (B), $R_1=R_2=CH_3$ (C)) in which the thioamide group is linked to a carboxylate function. The carboxylate function (COO^-) [5–7] and the thioamide functions ($CSNH_2$, $CSNHCH_3$, $CSN(CH_3)_2$) [8, 9] have separately been investigated by several groups, but until now no combination of the two functional groups in one molecule has been made. Recently we published a well defined structure together with a complete vibrational analysis of ligand A and C [10, 11]. This article describes the thermal decomposition and the formation of stable intermediates for these thiooxamates and their complexes, mainly based on results from infrared spectroscopy and Raman spectroscopy.

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Experimental

All the products under investigation have been synthesized in the laboratory. The ligands have been prepared according to the literature data [10, 11]. The M:L = 1:2 complexes are formed in aqueous media by adding a metal chloride solution in a 1:2 ratio to a neutral solution of the ligand and they can be described by the following general formula: $[ML_2(H_2O)_x]yH_2O$ (M(II)=Mn, Fe, Co, Ni, Cu and Zn; L=A, B, C; x=0, 1, 2; y=0 or 2). In alkaline medium (0,1 N KOH) ligand A and B form polymers with general formula $MA{\cdot}H_2O$ (M(II)=Co, Ni, Zn) and $MB{\cdot}H_2O$ (M(II)=Mn, Co, Ni, Cu and Zn) which can be prepared by adding one equivalent of the ligand to one equivalent of a metal chloride. For ligand C under these circumstances no stable products can be isolated as the ligand can not be deprotonated.

The infrared spectra of the solid state were recorded with a Bruker IFS 113v Fourier transform spectrometer equipped with a Globar source. For the 4000–500 cm^{-1} region a liquid N_2 cooled MCT detector was used and the product was pressed in KBr. For the 500–50 cm^{-1} region a DTGS detector was used while the sample was prepared as a polyethylene pellet. The Raman spectra were recorded on a Bruker IFS 66v using a FRA 106 FT-Raman Accessory, a CW Nd:YAG laser source and a liquid N_2 cooled Ge detector. A Seiko 200TG/DTA model and a DuPont R90 thermal analyser, equipped with a 951 TGA Cahn Balance, were used for the thermal measurements, which were carried out under dry nitrogen atmosphere.

Results and discussion

A. Complexes with oxathioamidate (ligand A)

In neutral medium oxathioamidate forms 1:2 *cis* or 1:2 *trans* complexes dependent on the hardness of the metal [12]. In this medium the metal will always coordinate to the S- and O-atoms of the ligand to form a bidentate complex. Structural and spectroscopic data (IR-, Raman-, UV/VIS-spectra and magnetic

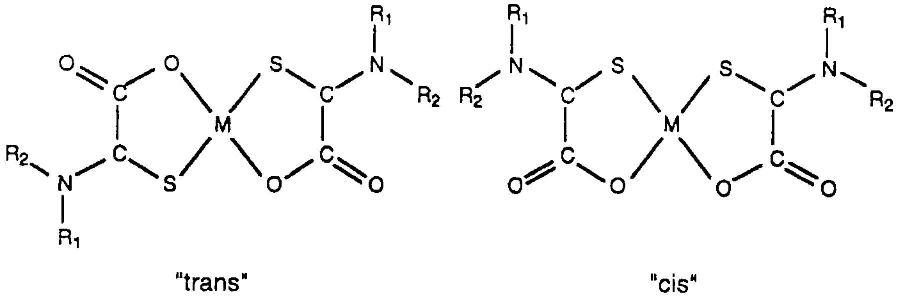

Fig. 1 The "*cis*" and "*trans*" configurations of oxathioamidate complexes

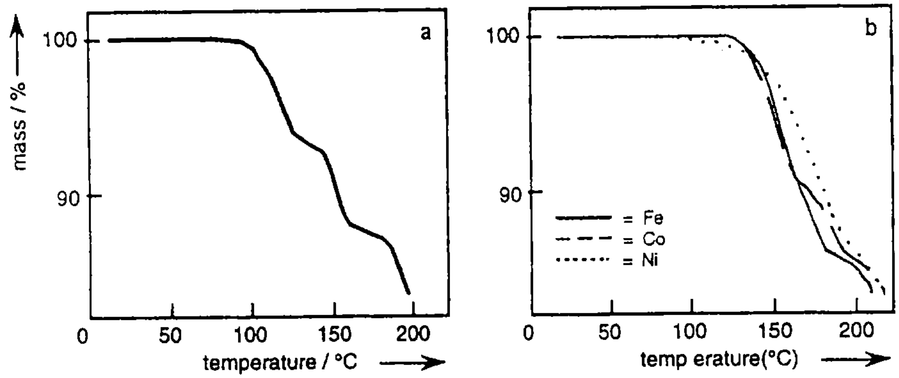

Fig. 2 TG curve of $MnA_2(H_2O)_2$ (a), TG curve of $MA_2(H_2O)_2$ (M=Fe, Co, Ni) (b)

measurements) indicate that the Mn(II) [13], Fe(II) [14], Co(II) and Ni(II) complexes all exhibit the same *trans*-planar structure with two water molecules in axial position. The Cu(II) complex is four-coordinated, *cis*-planar [15] and water-free. The axial coordination sites interact with O- and S-atoms of neighbouring units. The thermal analysis of this compound is discussed in part C of this paper. The Zn(II) complex is penta-coordinated in a *cis*-trigonal bipyramidal structure [14]. The *cis* and *trans* configurations are given in Fig. 1.

Thermal analysis confirms two-coordinated water molecules for the Mn(II), Fe(II), Co(II) and Ni(II) complexes, one water molecule for the Zn(II) complex and no water for the Cu(II) complex. As is shown in Figs 2a and b the two water molecules are released separately for the Mn(II) complex, while for the other complexes the loss of water occurs in one step. The high decomposition temperature, between 100 and 200°C, means that the water molecules are

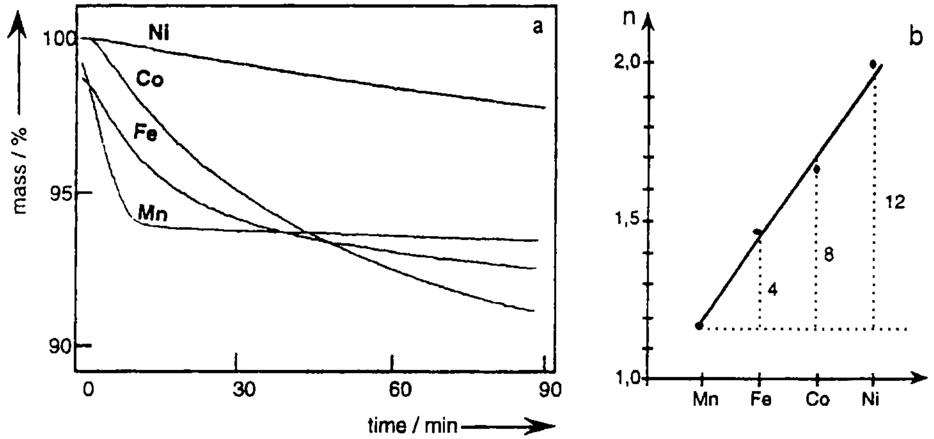

Fig. 3 Isotherm at 120°C for $MA_2(H_2O)_2$ (M=Mn, Fe, Co, Ni) (a), The number of remaining water molecules (n) after 10 min for the different metals (b)

coordinated, which is confirmed by the typical δ(OH) and π(OH) modes in the infrared spectrum of the Mn(II) complex at respectively 1664 and 650 cm^{-1}. After losing water all complexes decompose into a mixture of metal oxide and metal sulphide as the thermogram shows a curve with inflections but without a plateau. For some complexes the dehydration and decomposition overlap, so calculations of the activation energy gave no results, as there is more than one process involved.

Isothermal measurements at 120°C for Mn(II), Fe(II), Co(II) and Ni(II) are given in Fig. 3a. The loss of weight in this series of comparable complexes can very well be explained by the C.F.S.E. (crystal field stabilization energy) of weak octahedral complexes. This is shown in Fig. 3b where the number of remaining water molecules after 10 min (*n*) is scheduled against the number of *d*-electrons and is compared with the C.F.S.E. values. It is clear that the Ni(II) complex is the most stable product, in agreement with the C.F.S.E.- theory, which predicts the strongest metal-water bonding for a d^8-complex. After

Table 1 νM–O (w) frequencies of MA$_2$(H$_2$O)$_2$ (*M*=Mn, Fe, Co, Ni)

$\bar{\nu}$/cm^{-1}	Mn	Fe	Co	Ni
νM–O$_w$	255 ms	263 ms	270 m	283 mw

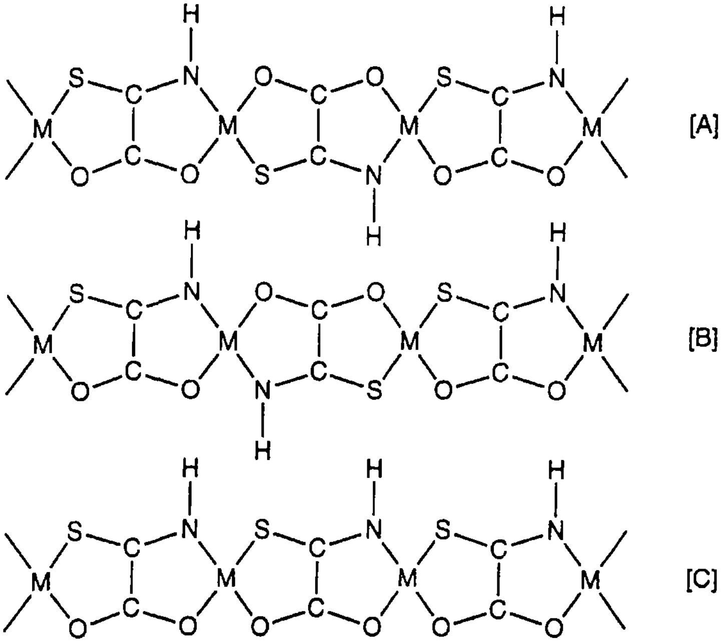

Fig. 4 Several structures for planar polymeric complexes

30 min the Mn(II) complex has lost 1 mole of water, while the dehydration of the other complexes has just started (Fe(II): 0,83 H_2O; Co(II): 0,45 H_2O; Ni(II): 0,12 H_2O). This indicates that the water molecule in the Mn(II) complex is less firmly bound to the metal ion. The νM–O(w) frequencies confirm this CFSE (Table 1).

Polymers are formed in alkaline medium by deprotonation of the thioamide function. The planar polymeric Co(II), Ni(II) and Zn(II) complexes can adopt several structures which are shown in Fig. 4. The fact that the far and mid in-

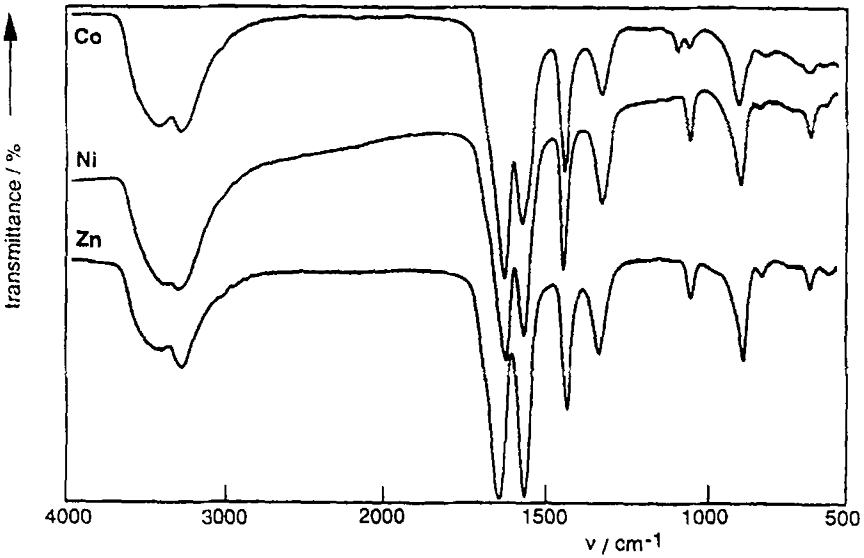

Fig. 5 Mid infrared spectra of $[M(CSNHCOO)]_n$ (M=Co, Ni, Zn)

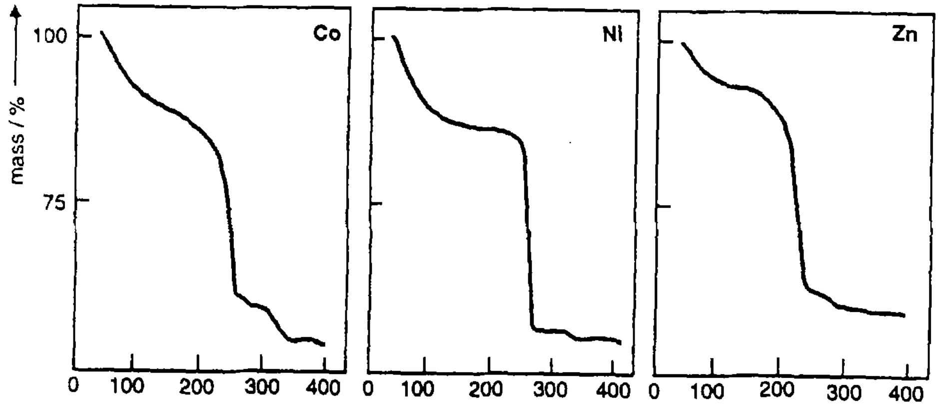

Fig. 6 The thermal breakdown of $[M(CSNHCOO)]_n$ (M=Co, Ni, Zn)

frared spectra are very simple (Fig. 5) indicates a high symmetry and led us conclude that structure A is the most probable one. The thermal breakdown of these polymers (Fig. 6) is very similar and starts with the loss of 1 mole of water over a wide temperature range, to form metal sulphide without formation of any stable intermediate. From these thermograms we expect that the three polymers have the same structure. This indeed is confirmed by the infrared spectra.

B. Complexes with N-methyl oxathioamidate (ligand B)

N-methyl oxathioamidate forms 1:2 complexes in neutral and 1:1 polymers in alkaline medium with the first row transition metals (Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)) in analogy with the ligand A. TG curves and vibra-

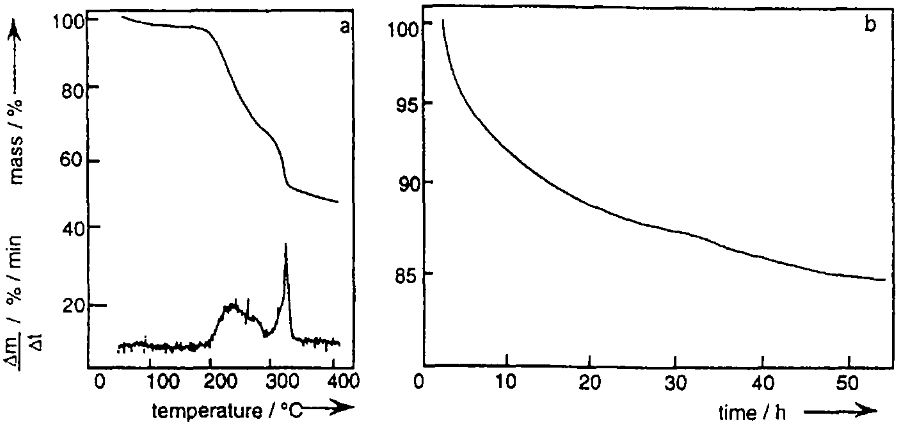

Fig. 7 TG curve (a) and isotherm at 175°C (b) of $[MnB_2(H_2O)_2]\cdot 2H_2O$

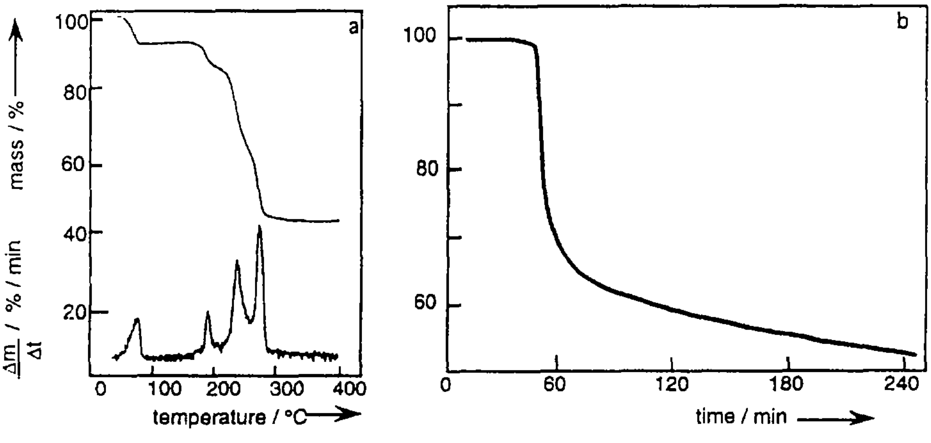

Fig. 8 TG curve (a) and isotherm at 230°C (b) of $[ZnB_2(H_2O)_2]\cdot 2H_2O$

tional spectra indicate two axial water molecules for all these complexes except for the Cu(II) complex (see part C for detailed study) and two water molecules for the Mn(II), Co(II), Ni(II) and Zn(II) complexes as hydrates. A typical TG curve is given for the Mn(II) complex in Fig. 7a. The loss of water occurs between 100 and 200°C and is endothermic. No stable intermediates are obtained. The best way to prepare the water-free compound is to heat the product isothermally. When the Mn(II) complex is heated for 50 h at a temperature of 175°C, a fairly constant mass level is reached at about 83.9%. The loss of weight of the two coordinated water molecules and one hydrate is shown in Fig. 7b.

The TG/DTG curve of $[ZnB_2(H_2O)_2]\cdot 2H_2O$ indicates an inflection point at 254°C without a distinct plateau (Fig. 8a). Yet, a stable intermediate can be isolated by heating this complex isothermally at 230°C (Fig. 8b)

$$x\mathrm{ZnB_2} \xrightarrow{230^\circ\mathrm{C}} (\mathrm{ZnB})_x + x\mathrm{B}\uparrow$$

The mid infrared spectrum of this intermediate $(ZnB)_x$ is the same as the spectrum obtained for the Zn(II) polymer prepared in alkaline medium. From these results we can conclude that these two products are identical and have the same structure with similar bonding of the ligand. The temperature for this formation is very critical as lower temperatures gives no polymer and direct decomposition of the polymer occurs above 230°C. The final residue, obtained after heating up to 600°C, contains in all cases a nitrile function ($C–C\equiv N$), as indicated by the infrared spectra.

C. Cu(II) complexes with ligand A, B and C

Due to tetragonal distorsion the Cu(II) complexes are all water-free. Their thermal stability can be related to the metal ligand bond strength. These compounds all decompose by an endothermic reaction, except CuC_2 where an exothermic reaction occurs to form copper sulphide. The temperature for maximum loss of mass $(\Delta m/\Delta t)_{max}$ for CuA_2, CuB_2 and CuC_2 are respectively 140.8°C, 194.7°C and 140.2°C. Clearly CuB_2 is the most stable product. This can be explained by the inductive donating effect of the methyl group which makes the metal-ligand bond more electron-rich and therefore stronger in com-

Table 2 Metal ligand IR frequencies of CuA_2, CuB_2, CuC_2

$\bar{\nu}/cm^{-1}$	CuA_2	CuB_2	CuC_2
$\nu M–S$	343 s 315 s	360 s	351 mw
$\nu M–O$	218 mw 183 mw	270 m	251 mw

parison with CuA_2. CuC_2 is less stable than CuB_2 due to sterical hindrance. This sequence of thermal stability is confirmed by the far infrared spectra (Table 2).

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