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THERMAL DECOMPOSITION OF DINITROGEN COMPLEXES OF Cr(III)

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ABSTRACT

The thermal behaviour of two dinitrogen complexes of chromium with EDTA and CDTA have been studied using DTA and TG. IR spectroscopy is used for the characterization of intermediate products. The loss of dinitrogen occurs at 240°C in both cases.

INTRODUCTION

Thermogravimetry (TG) and differential thermal analysis (DTA) are the two analytical techniques most widely used in the study of the thermal behaviour of coordination compounds. However, the results obtained by applying only these techniques are insufficient to determine exactly the elimination sequence of the different groups of compounds. It is necessary to make use of an auxiliary technique to resolve this problem. Infrared spectroscopy is a very good auxiliary technique. The changes in the shape and intensity of the bands of the original compound and the appearance of new bands permit the nature of intermediate products in the decomposition process to be elucidated.

Previously, our investigation group used these techniques successfully for the study of complexones [1–3], complexes of metals of the platinum group with complexones [4,5], and dinitrogen complexes of Fe(II) with chelating agents [6].

This paper describes the thermal behaviour of complexes of Cr(III) with dinitrogen and aminopolycarboxylic ligands.

EXPERIMENTAL

The syntheses of the compounds $Na[Cr(EDTA)N_2] \cdot 2H_2O$ and $Na[Cr(CDTA)N_2] \cdot 2H_2O$ (EDTA = ethylenediaminetetracetate; CDTA = 1,2-diamine-cyclohexanetetraacetate) have been reported in a previous paper

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[7]. DTA and TG curves were obtained using a Mettler TA-HE-20 system with Pt/Pt–10% Rh thermocouples; α-Al_2O_3 was used as reference material in the DTA measurements. The heating rate was 10°C min^{-1} in all cases. The experiments were carried out in an atmosphere of static air. Infrared spectra of solid intermediate products were recorded in KBr pellets using Pye-Unicam SP 3-300 spectrophotometer.

RESULTS AND DISCUSSION

The TG and DTA curves corresponding to the EDTA and CDTA complexes are shown in the Figs. 1 and 2, respectively. The IR spectra of some intermediate products of the thermal decomposition are shown in Figs. 3 (EDTA complex) and 4 (CDTA complex).

The observed weight loss for both complexes and the range of temperatures are indicated in Table 1.

Between 50 and 200°C, a weight loss is observed (Figs. 1 and 2) corresponding approximately to the elimination of two molecules of crystallization water. Some proportion of this loss could be the adsorbed water due to the hygroscopic character; however, previous to the thermal study, the samples are left over P_2O_5 until constant weight.

The loss of crystallization water is not confirmed on heating the intermediate products between 100 and 200°C. Infrared spectra still show the

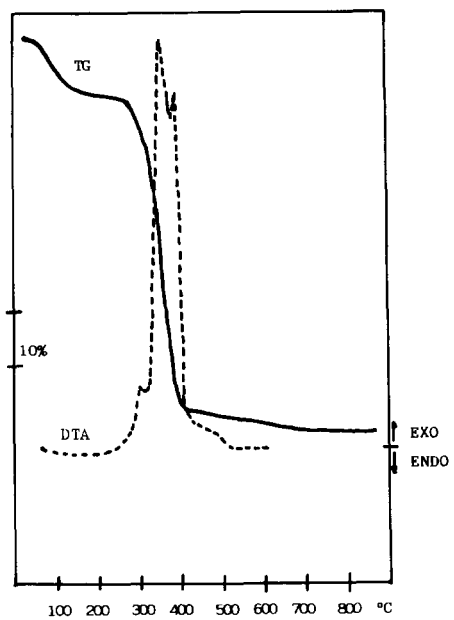

Fig. 1. DTA and TG curves for $Na[Cr(EDTA)N_2]\cdot 2H_2O$.

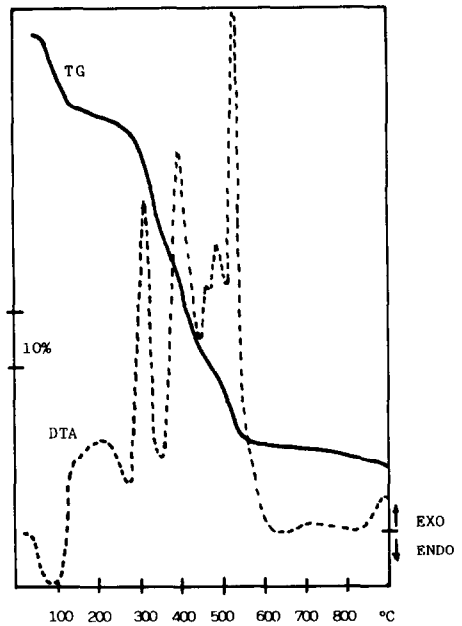

Fig. 2. DTA and TG curves for $Na[Cr(CDTA)N_2]\cdot 2H_2O$.

band at 3400 cm^{-1} (ν_{O-H}) (Figs. 3 and 4). Possibly, the elimination of water is not complete or the samples absorb water during cooling at room temperature. Other significant variations are not observed in the infrared spectra, which seems to indicate that the elimination of other groups does not occur.

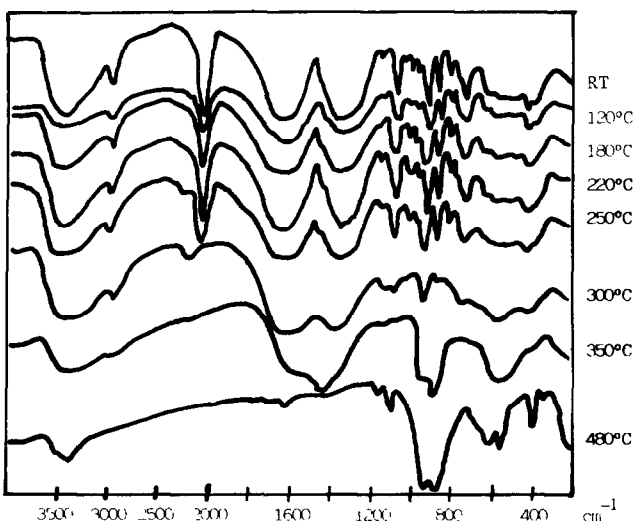

Fig. 3. IR spectra of some intermediate products in the decomposition of $Na[Cr(EDTA)N_2]\cdot 2H_2O$.

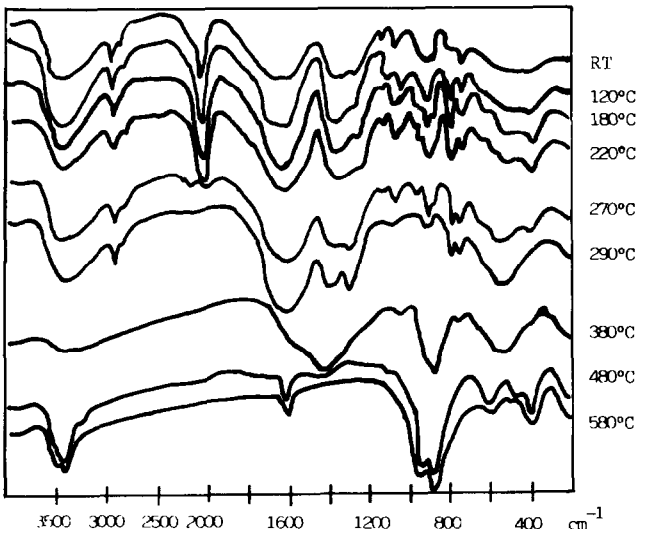

Fig. 4. IR spectra of some intermediate products in the decomposition of $Na[Cr(CDTA)N_2]\cdot 2H_2O$.

In the thermal decomposition of dinitrogen complexes, the elimination of N_2 is normally observed at temperatures ranging from 20 to 200°C [8,9]. The stretching of N≡N appears in the spectra of samples (RT) at 2070 cm^{-1}. Infrared spectra of intermediate products heated at temperatures higher than 200°C show a progressive loss of intensity of this band until its disappearance. However, a new band appears, centered at ca. 2200 cm^{-1}. Similar effects are observed in the thermal decomposition of analogous complexes of Fe(II) [6].

In the thermal study of sodium salts of EDTA [2] a similar band was observed at 2200 cm^{-1} which was assigned to a resonant doubles bond between C and N. Therefore, an overlapping of dinitrogen elimination with the first stage of the pyrolysis of the compound can be postulated. It causes differences between the theoretical values of weight loss for the elimination of one dinitrogen molecule (6.55 and 5.82% for the complexes of EDTA and CDTA, respectively) and the experimental values found between 200 and 300°C in TG (Table 1).

TABLE 1

Weight loss (%) and temperatures for both complexes

T (°C)	$Na[Cr(EDTA)N_2]\cdot 2H_2O$	$Na[Cr(CDTA)N_2]\cdot 2H_2O$
50–200	9.0	10.0
150–250	7.0	7.5
250–475	53.5	55.5
475–900	3.0	6.0

The DTA curves (Figs. 1 and 2) show several exothermic effects at temperatures higher than 300°C. In Table 1 the initial and final temperatures of the pyrolysis process and the weight loss observed between both temperatures in TG are given. The appearance of several peaks in the DTA curves suggests that this pyrolysis process occurs in different overlapping steps.

The infrared spectra of these intermediate products (Figs. 3 and 4) are completely different to those corresponding to the samples at RT. The disappearance of the $\nu^{s}_{COO^-}$ (1400 cm^{-1}) and $\nu^{as}_{COO^-}$ (1600 cm^{-1}) bands shows that this step of the decomposition process consists of the loss of carboxylate groups associated with cracking and the release of CO_2, CO, NH_3 and traces of hydrocarbons as shown in the thermal decomposition of sodium salts of EDTA and CDTA [2,3].

The thermal behaviour of Cr(III) complexes is different to that of the analogous complexes of Fe(II) [6]. At temperatures ca. 380°C, the characteristic bands of carbonate groups appear in the IR spectra (1400, 900 cm^{-1}). However, for intermediate products heated at 480°C, two bands (between 800 and 900 cm^{-1}) are observed. The colour of these products is orange but changes to yellow during cooling. This fact can be explained supposing that the final product of pyrolysis is sodium dichromate (orange) and that this changes into sodium chromate (yellow) during cooling. The infrared spectra of the yellow samples show characteristic bands of chromate groups (846, 890 cm^{-1}).

The theoretical weight losses corresponding to the formation of $Na_2Cr_2O_7$ from anhydrous samples are 60.92 and 65.31% for the EDTA and CDTA complexes, respectively. The average experimental weight losses corresponding to the dinitrogen elimination and pyrolysis (Table 1) are 60.5 and 63.0%, respectively.

At the final pyrolysis temperatures (900°C), an additional weight loss is still observed in the TG curves (Figs. 1 and 2) of both compounds with values of 3.0 and 6.0% for the EDTA and CDTA complexes, respectively. The decomposition of sodium chromate with Cr_2O_3 and Na_2O formation can explain these final weight losses.

The formation of these products from the original complexes must be accomplished with theoretical weight losses of 75 (EDTA complex) and 77.8% (CDTA complex). In fact, these values of the total weight loss for the formation of these products are in agreement with the experimental values (Table 1) for both complexes.

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