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THERMOANALYTICAL BEHAVIOUR OF NITROSODICYANMETHANIDE TETRAPYRIDINIUM COMPLEXES OF Mn^{II}, Cu^{II} AND Zn^{II}

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ABSTRACT

The thermoanalytical behaviour of the nitrosodicyanmethanide tetrapyridinium complexes of Mn^{II}, Cu^{II} and Zn^{II} was studied under static air and dynamic nitrogen atmospheres. At high temperatures both Mn^{II} and Cu^{II} complexes exhibited a gradual degradation leading to the elimination of one of the $[ONC(CN)_2]_2$ groups. The Zn^{II} complex showed a different decomposition mechanism in which only a fraction of this group was lost. The final stages of the decomposition of the complexes are atmosphere dependent. Ageing the Mn and Cu complexes influences their decomposition.

INTRODUCTION

Several authors have reported on the structure and properties of pyridine halogenide complexes of divalent metal ions [1–4]. Tetrapyridinium complexes have monomeric transoctahedral structures [3,4] and have been used in clathrate chromatography to separate various compounds [5]. In tetrapyridinium nickel(II) dithiocyanate, pyridine molecules are lost in two steps [6]. The decomposition temperatures have been shown [7] to parallel the formation constants of addition of pyridine ligands to the metalloporphyrin in solution and the theoretical effective metal ion charge [8].

This study reports the thermal behaviour of tetrapyridino-bis(nitrosodicyanmethanide) complexes of the divalent ions of manganese, copper and zinc using simultaneous thermogravimetry (TG), derivative thermo-

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gravimetry (DTG), and differential thermal analysis (DTA), aided by chemical analysis and X-ray diffraction of intermediate and final products.

EXPERIMENTAL

Apparatus

The TG, DTG and DTA measurements were carried out on a MOM derivatograph. Elemental analyses of some decomposition products were performed by Analytische Laboratorien (Alfred Bernhardt, West Germany). A Philips X-ray powder diffractometer was used to identify intermediate and final products. For the derivatographic runs, the sample size was 100 mg and the heating rate was 5 °C min^{-1}.

The three complexes were prepared as described in a previous paper [1,2].

RESULTS AND DISCUSSION

Thermal decomposition of $Zn[ONC(CN)_2]_2(Py)_4$ (I)

There are two main reactions in the thermal decomposition of complex **I**, both having a significant dependence on the atmosphere (Fig. 1). Above 70 °C the complex started to lose the pyridine ligands, showing a varying thermal curve. The process started endothermically with melting of the complex at 124 °C (peak temperature). After melting, the decomposition rate increased significantly and was accompanied by the release of heat (exothermic peak) between 145 and 220 °C.

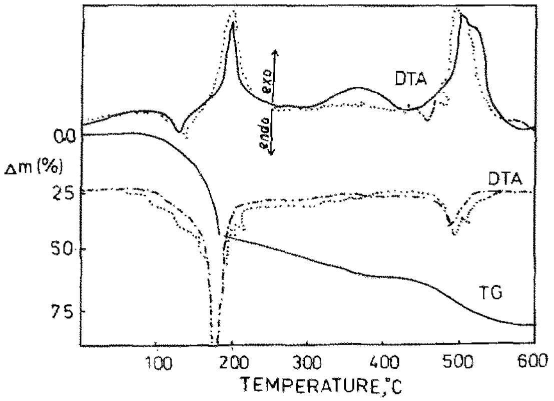

Fig. 1. TG, DTG and DTA curves for the zinc(II) complex.

Under nitrogen a stable monopyridino complex could be identified on the TG curve at 250 ° C. However, melting may help the rearrangement of the molecules of the intermediate dipyridino complex into chains bridged by the nitrosodicyanomethanides, thus facilitating the formation of the monopyridino complex. Such a chain formation was reported in the case of dipyridinocadmium chloride bridged by two chloride ions [4].

Under air, the decomposition proceeded until the four pyridine molecules were lost. However, the experimental conditions were very important in determining the shape of the thermograms of tetrapyridinonickel(II) thiocyanate [8]. Masuda et al. [9] have demonstrated a stepwise decomposition for tetra(4-methylpyridino)cadmium chloride under a nitrogen atmosphere. The process of weight loss slowed down in the last stages as a result of the formation of a solid surface layer of the product material which restricted the release of pyridine vapour from the interior. Thus, the pyridine molecules which are lost in the final stages are no more strongly bonded to the central metal ion than the others [10]. Above 460 ° C, $Zn[ONC(CN)_2]_2$ decomposed to zinc oxide in an endothermic process with some multistep character resulting from the complex nature of the nitrosodicyanmethanide anion. The exothermicity was greater under air than under nitrogen because of the expected oxidation. The formation of ZnO was confirmed by quantitative evaluation of the TG curve and X-ray diffraction of the product at 550 ° C.

Thermal decomposition of $Cu[ONC(CN)_2]_2(Py)_4$ *(II)*

The main features of the thermograms of complex **II** are similar to those of complex **I**, see Fig. 2A. The first decomposition stage of the freshly prepared sample started at 60 ° C and involved the loss of 1 mol of pyridine per mol of complex (calc. 13.92 wt.%; found 13.6 wt.%). The complex melted at 99 ° C. The characteristic temperatures of the second stage (loss of the three pyridine molecules) were identical to those for complex **I**. The third decomposition reaction was multistep under a nitrogen atmosphere with a weight loss of 24.6 wt.% which can be explained by the loss of one $[ONC(CN)_2]$ group (calc. 24.84%). Calculations based on elemental analysis of the product at 400 ° C confirmed the formation of $Cu[ONC(CN)_2]$ which means that the copper was reduced to the Cu^I state at this stage. The reaction was exothermic and yielded DTA peaks between 290 and 400 ° C with maxima at 325 and 365 ° C under the inert and oxidising atmospheres, although the resolution was better under air. Finally, the complex decomposed slowly to copper(II) oxide between 415 and 550 ° C.

A stock sample of complex **II**, stored for almost 3–4 years, decomposed directly into copper(II) oxide, the theoretically produced amount of oxide (14.0%) being far less than that found experimentally: 21.3% under nitrogen and 18.6% under air (Fig. 2B). This significant difference is attributed to the

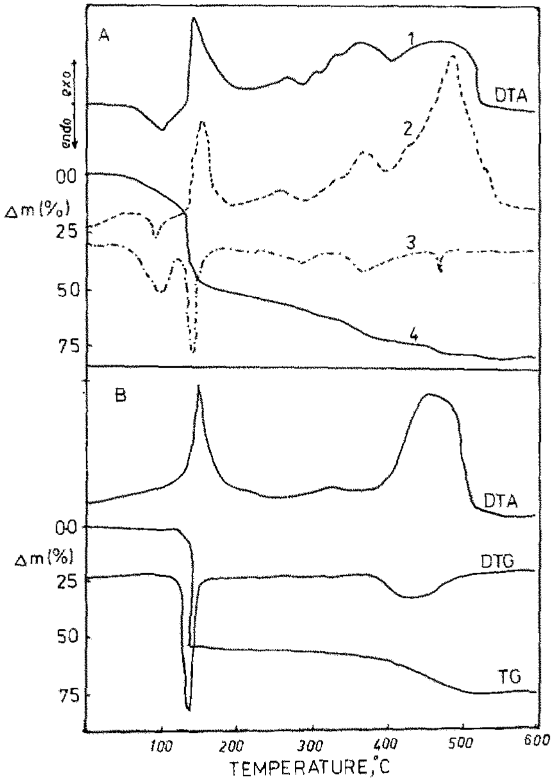

Fig. 2. TG, DTG and DTA curves for the copper(II) complex: A, fresh complex; B, stored complex. 1, DTA curve under a nitrogen atmosphere; 2, DTA curve under air; 3, DTG curve; 4, TG curve.

deterioration of the complex during storage. The elemental analysis of the product and the X-ray diffraction pattern indicated the presence of elemental carbon in addition to cupric oxide. Further heating, however, may reduce the amount of carbon by the formation of carbon oxides.

Thermal decomposition of $Mn[ONC(CN)_2]_2(Py)_4$ *(III)*

The decomposition of complex **III** occurred at well-separated stages. The first stage, between 73 and 128 °C, represented 8.1% weight loss; the second, between 128 and 167 °C, had a weight loss of 24.3%; and the third, between 167 and 218 °C, had a weight loss of 16.5%. However, because these stages are almost overlapping, isolation of the intermediate products was difficult. Attempts to correlate these results with the theoretical weight losses of complete pyridine molecules were not successful. It was thought that the loss of pyridine ligands from the complex follows the sequence: 4–3, 3–1 and 1–0. The calculations were corroborated in the case of the tripyridino complex, for which the three stages follow the sequence: 3–2.5, 2.5–1 and

1–0, i.e. 0.5, 1.5 and 1 mol of pyridine being lost in these consecutive stages. The elemental analysis of the decomposition product confirmed the presence of $Mn[ONC(CN)_2]_2$.

A stored sample of complex **III**, kept for almost 18 months, showed an initial weight loss in the range 112–245 ° C which was higher than that for the freshly prepared complex. Thus, the first decomposition step must have taken place during storage. A second sharp decomposition reaction was noticed at 245 ° C with a significant weight loss of 58.0%. The reaction was highly exothermic and exhibited a single exothermic peak with a maximum at 290 ° C. The product was analysed by X-ray diffraction and was identified as MnO, Mn_2O_3 and Mn_3O_4, in addition to another phase which matched $Mn_5C_2.28N$ in the ASTM index. However, the X-ray pattern also showed sharp lines at 7.865, 3.944 and 2.529 Å which could not be assigned.

The decomposition products underwent further weight-loss processes between 307 and 386 ° C. The C, H, N and Mn analysis showed a decrease in the carbon content of the products and a corresponding increase in the nitrogen content, which may possibly indicate the formation of manganese nitride. This is more favorable than formation of manganese carbide, particularly in the presence of Mn_2O_3 and Mn_3O_4 which can oxidise carbon to carbon monoxide. The exothermic nature of this process may support this explanation.

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