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THERMOANALYTICAL STUDIES ON SOME TRANSITION METAL NITROSODICYANOMETHANIDE TETRAPYRIDINE COMPLEXES: $M[ONC(CN)_2]_2(Py)_4$ ($M = Fe^{2+}, Ni^{2+}, Co^{2+}$; $Py = C_5H_5N$)

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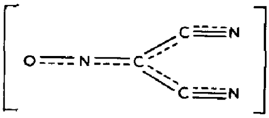
ABSTRACT

Simultaneous thermoanalysis of Fe(II), Ni(II) and Co(II) nitrosodicyanomethanide tetrapyridine complexes was performed in static air and dynamic nitrogen atmospheres using a derivatograph. The three complexes behave differently in the two atmospheres. The iron (II) complex is the least stable; its thermogram reveals that it has a different structure in comparison with those of the Co(II) an Ni(II) complexes. Complete depyridinization of the three complexes is possible in nitrogen if careful temperature control is carried out. In air a small part of the NOC group is always lost with the last escaping pyridine molecule, which means that separation of $M[ONC(CN)_2]_2$ is impracticable. The degradation of these complexes in nitrogen leads to the evolution of pyridine vapours, NO, CO and $(CN)_2$, in addition to the free metals and their oxides. Correlation between the thermal stabilities, the structures of the complexes and magnetic data (available from the literature) is performed. The three complexes decompose without melting. It is possible to identify the three complexes through their differential thermogravimetry (DTG) curves. Entities such as $Fe[ONC(CN)_2]$, $Ni[ONC(CN)_2]$ and $Co[ONC(CN)_2]$ cannot be detected experimentally, although thermogravimetry (TG) calculations predict their formation.

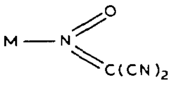
INTRODUCTION

Divalent transition metals form coordination complexes with nitrosodicyanomethanide anion [$(CNC(CN)_2^-$) as well as with other ligands. The structure of the anion is assumed to be unsymmetrical



Complexes of the type $M(ONC(CN)_2)_2 \cdot (Py)_4$ are obtained by reaction of aqueous solutions of $ONC(CN)_2^-$ with M^{2+} and Py (pyridine) [1]. The structures of the complexes resemble those of nitro and nitrato complexes.

According to Köhler and Seifert [2] the anionic ligand is bound to the metal through a nitrogen atom



Studies of the molecular spectrophotometry [2,3], magnetic susceptibility, magnetic dipole moment [1,2] and polarographic behaviours [4] of these complexes have been described. According to ref. 1 two of the pyridine molecules dissociate in aqueous solution. The isotopic effects using ^{15}N have been reported [3].

Several workers have studied the thermal behaviour of cyano complexes of pyridine with various metals. Liptay and coworkers [5,6] and Jona and Stramko [7] have investigated the thermal degradation of tetrapyridine nickel(II) dithiocyanate and have shown that the pyridine molecules are lost in two steps. Lee and Hambright [8] have reported that the temperatures of dissociation parallel the formation constant of addition pyridine ligands to metalloporphyrin in solution and the theoretical effective ion charge.

The thermoanalysis of the three title complexes has not been studied previously. Thermal analysis was performed using simultaneous thermogravimetry (TG), differential thermogravimetry (DTG), differential thermal analysis) (DTA) and thermogas titrimetry (TGT) techniques.

EXPERIMENTAL

The three complexes were prepared as described previously [1,2]. The ferrous complex is dark red, the nickel complex is brown and the cobalt complex is red–brown. They are crystalline substances.

Measurements were performed in a MOM derivatograph for simultaneous TG, DTG and DTA using the following instrument sensitivities: TG, 100 mg; DTG, 0.1 mg, DTA, 0.1 mg. The reference and sample were heated in MOM cyclindrical platinum crucibles. Heating was performed at a rate of 5 °C min^{-1} in static air or in a stream of nitrogen (60 ml min^{-1}). α-Al_2O_3 which had been heated at 1300 °C for 2–3 h was used as reference material. Powdered samples of 100 mg were used for each experiment. Temperature calibration was carried out using the crystalline phase change of pure quartz at 573 °C. Elemental analysis of some decomposition products was performed by the Analytische Laboratorien von Alfred Bernhardt, FRG. A Philips X-ray powder diffractometer was used to identify intermediate and final residues. A thermo-gas titrimeter was used to identify gaseous products.

RESULTS AND DISCUSSION

$Fe(ONC(CN)_2)_2(Py)_4$ (complex I)

This complex starts to decompose at 50 ° C. In air the DTG curve (Fig. 1) shows three small clearly defined endothermic peaks at $T_{max} = 100$, 140 and 190 ° C due to the stepwise elimination of three molecules of pyridine; these correspond to weight losses of 0.68, 0.82 and 1.48 mol of pyridine respectively (Fig. 2). The shape of the TG curve is typical for this complex and can be used for its identification (Fig. 1). The part of the DTA curve which corresponds to the loss of 1.48 mol of pyridine is more exothermic than that corresponding to the loss of 0.68 and 0.82 mol. The exothermicity is due to the disruption of the C≡N bond of Py which is lost at high temperatures. The loss of the fourth Py molecule is complete at 315 ° C. The 250–315 ° C step is less steep than the previous steps, indicating that the dissociation of this Py molecule is slower because it is more strongly bonded than its predecessors. The large broad exothermic peak at 315–475 ° C is due to the

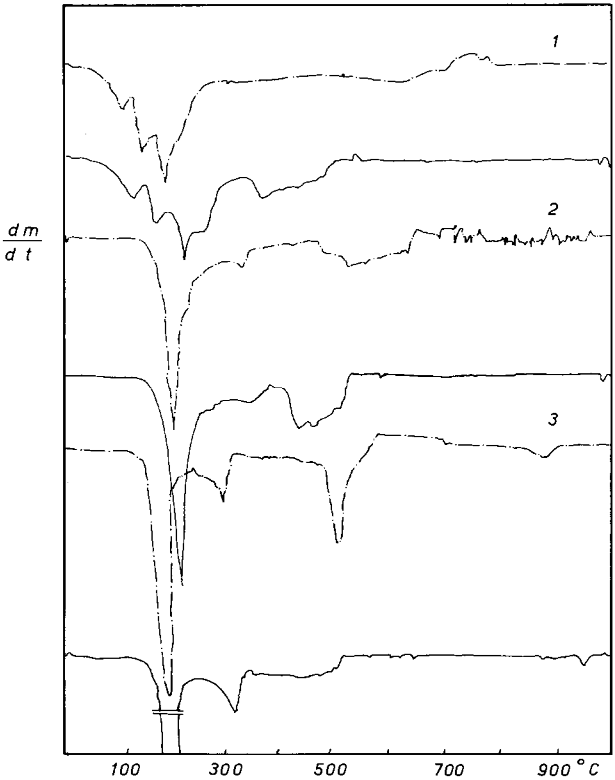


Fig. 1. DTG curves of (1) complex **I**, (2) complex **II**, (3) complex **III**; (———) in air; (·–·–·) in nitrogen.

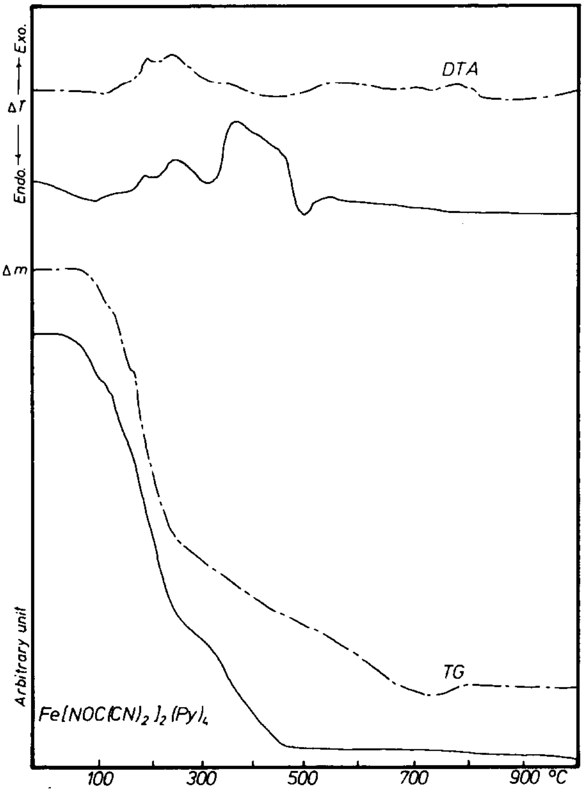


Fig. 2. TG and DTA curves of Fe[ONC(CN)$_2$]$_2$(Py)$_4$ complex I; (———) in air; (·–·–·) in nitrogen.

slow dissociation of Fe(ONC(CN)$_2$)$_2$ in air. Data from elemental analysis and the TG curve indicate that a weight equivalent to $\frac{1}{2}$ONC is lost with the fourth molecule. X-ray diffraction (XRD) patterns of the final residue confirm the presence of Fe_3O_4 and a trace of carbon. The small exotherm on the DTA curve (500–549 °C) indicates the oxidation of FeO to Fe_3O_4 and reveals the strong link between Fe^{2+} and $ONC(CN)_2^-$. Figure 2 shows that Fe(ONC(CN)$_2$)$_2$(Py)$_4$ does not melt and its degradation occurs directly from the solid state. The stability of the complex is attributed to its relatively high dipole moment (5.3 μ_B).

In nitrogen the loss of the first three pyridine molecules is similar except that the three endothermic peaks shown on the DTG curve (Fig. 1) are sharper (faster rate of change of weight) and the corresponding weight loss is steeper (Fig. 2). The starting temperature of the slow dissociation of the fourth Py molecule overlaps with that of the third step and ends at 340 °C. The DTA curve (340–560 °C) indicates that the degradation of Fe(ONC(CN)$_2$)$_2$ is an endothermic process resulting in the formation (TGT curve, not shown for brevity) of CO, NO and (CN)$_2$. The broad exothermic peak observed between 720 and 810 ° C is due to the slow oxidation (due to the presence of traces of O_2) of Fe^{2+} to FeO and finally to Fe_3O_4. Carbon could not be detected. It is worth noting that the thermal degradation of the complex occurs over a wider range of temperatures in nitrogen compared with that in air; this shows that complex **I** is more stable in an inert atmosphere than it is in air and that aging will affect its chemical nature if left or stored in air.

Figures 1 and 2 infer that complex **I** is unstable beyond 45 ° C and thus should be stored below this temperature; this instability is due to the dissociation of pyridine.

It was not possible to calculate adequately the molar degradation enthalpy of $Fe(ONC(CN)_2)_2$ because of technical difficulties.

$Ni(ONC(CN)_2)_2$ (complex II)

Figure 3 shows that this complex is stable up to 122 ° C; thereafter it decomposes rapidly in one step losing 42 mg (equivalent to three Py

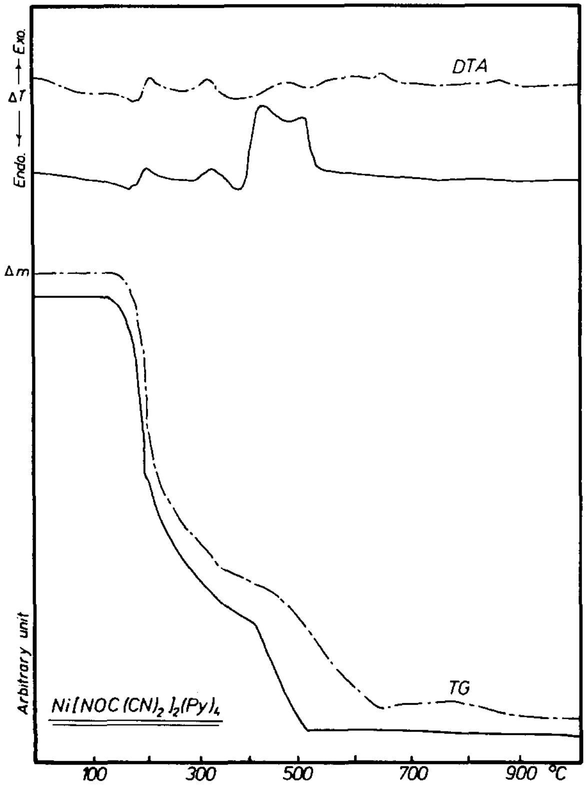


Fig. 3. TG and DTA curves of $Ni[ONC(CN)_2]_2(Py)_4$ complex **II**; (———) in air; (·–·–) in nitrogen.

molecules). Between 205 and 325 ° C it loses a further 14 mg (equivalent to one Py molecule). In this step the weight loss is less steep because of the presence of electrostatic forces between the fourth Py molecule and $Ni(ONC(CN)_2)_2$. The comparatively low temperatures at which the first three Py molecules are lost indicate that they are linked to $Ni(ONC(CN)_2)_2$ by weak van der Waals' forces. The two small broad exothermic peaks at $T_{max} = 205$ and 325 ° C are due to the rupture of the C≡N bond of the volatilized Py molecules. In the range 395–518 ° C $Ni(ONC(CN)_2)_2$ is completely combusted, which is displayed by the large broad exotherm on the DTA curve; owing to the absence of a horizontal plateau the possibility of thermal isomerization of the $ONC(CN)_2^-$ anion is excluded. The XRD pattern of the final decomposition products infers the presence of NiO and traces of carbon. Thermo-gas titrimetric analysis indicates that the gaseous products are mainly CO_2 and NO_2. Traces of $(CN)_2$ are also detected.

In a nitrogen atmosphere the large broad exotherm (obtained in static air) disappears confirming that the degradation of $Ni(ONC(CN)_2)_2$ is an endothermic process. Figures 1 and 3 show that deflagration is observed which continues to the end of the heating programme. Here the decomposition products contain NO, CO, CO_2 and appreciable amounts of $(CN)_2$. In nitrogen, degradation of $Ni(ONC(CN)_2)_2$ begins at 484 ° C; in air it begins at 385 ° C. This is because the oxygen in the air enhances combustion. The XRD patterns of samples heated up to 640 ° C (discontinuity in the TG curve) indicate nickel metal; this is oxidized very slowly by traces of air to Ni_2O_3. The latter subsequently decomposes beyond 800 ° C to NiO and O_2.

$Co(ONC(CN)_2)_2(Py)_4$ (complex III)

The thermal analysis results obtained for complex **III** are given in Fig. 4. As can be seen from the TG curve, heating of the complex in air beyond 105 ° C leads to a sudden loss of 2.2 Py molecules per molecule of complex. Above 170 ° C, the less steep part of the TG curve indicates the slow dissociation of a further pyridine molecule. This is succeeded by a steeper exothermic change (275–290 ° C) which is due to the loss of the remaining 0.8 Py molecule and the abstraction of one ONC group per mole of complex. During the degradation of the first three Py molecules the DTA curve exhibits a very low endothermic enthalpy change reflecting the weak (van der Waals' forces) links between the Py molecules and the rest of the complex. Py is detected at this stage of heating. The exotherm of the dislocation and disruption or burning of the fourth Py molecule overlaps with that of the combustion of $Co(ONC(CN)_2)_2$. TG calculations and elemental analysis show that one ONC group is lost with the Py molecule. This means that the Co–CNO bond energies are different otherwise both NOC moieties would escape simultaneously and it may also reveal the asymmetric nature of complex **III**. Unfortunately, facilities for the measure-

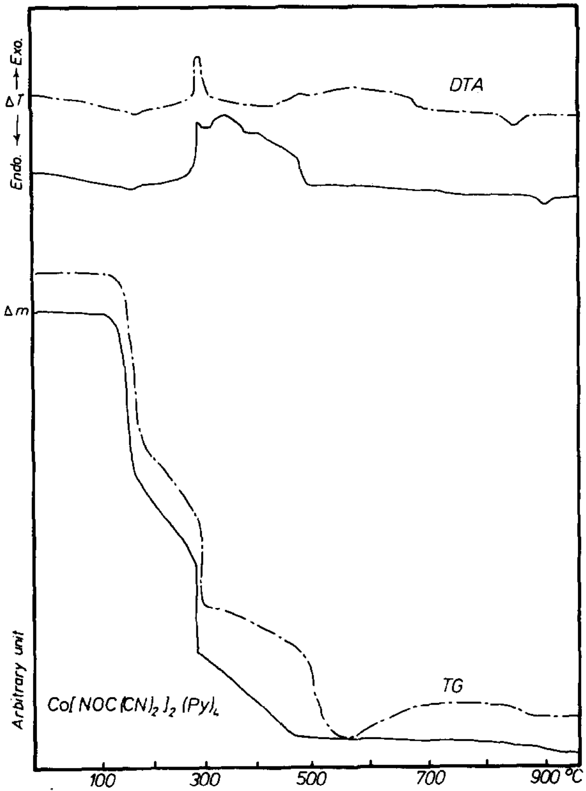


Fig. 4. TG and DTA curves Co[ONC(CN)$_2$]$_2$(Py)$_4$ complex III; (———) in air; (·—·—·) in nitrogen.

ment of circular dichroism and optical rotatory dispersion were not available to confirm this.

Surprisingly the separation of the first three Py molecules is an endothermic process which is different from that observed for complexes **I** and **II** (Fig. 4).

In the temperature range 290–490 °C the straight, gradually descending portion of the TG curve represents a slow constant rate of combustion of the species Co(ONC(CN)$_2$)$^+$. The two discontinuities at 290 and 490 °C indicate that Co(ONC(CN)$_2$)$^+$ undergoes slow equilibrated degradation. The corresponding portion of the DTA curve exhibits a rather large broad distorted exotherm. Thermo-gastitrimetry of the decomposition products confirms the presence of NO_2, CO_2 and a trace of $(CN)_2$. The XRD patterns of the residues at about 500 °C show Co_3O_4, which on heating beyond 880 °C changes to CoO at $T_{max} = 910$ °C. Complex **III** (Fig. 4) shows similar degradation as far as the elimination of the four Py molecules is concerned, except that the degradation is shifted to higher temperatures and the decomposition of Co(ONC(CN)$_2$)$^+$ takes place slowly at first and then suddenly increases, a process which is accompanied by a sharp absorption of heat probably due to a secondary oxidation reaction of CO to CO_2. The gaseous products analysed in the range 300–495 °C contain CO, CO_2 and $(CN)_2$. The X-ray diffraction data of the remaining residue around 570 °C confirm the presence of metallic Co which, on further heating, slowly oxidizes (as shown by the gradual rise of the TG curve in the range 680–840 °C) to Co_3O_4, which in turn decomposes ($T_{max} = 910$ °C) to form CoO.

CONCLUSIONS

From thermoanalysis (simultaneous TG, DTG, DTA and TGT), elemental analysis and X-ray diffraction studies it is apparent that complex **I** is the least stable in both air and nitrogen. The decomposition mechanism indicates that the first three Py molecules are loosely linked to the complex by van der Waals' forces, whereas the fourth molecule is strongly bonded. The Py molecules of complexes **II** and **III** are lost in a similar manner although the degradation steps of complex **I** are more clearly resolved. The thermal stabilities of $M(ONC(CN)_2)_2$ for the three metals are different, revealing structural dissimilarities.

A correlation between the thermometric measurements obtained and the magnetic data available in the literature for the three complexes is proposed. References 1 and 2 report the molar magnetic susceptibilities χ_m used to calculate the number of unpaired electrons per mole of complex and the magnetic dipole moments μ_{eff} expressed in Bohr magnetons (μ_B) for some nitrosodicyanomethanide metal complexes: for $Co(ONC(CN)_2)_2(Py)_4$, $\mu_{eff} = 4.87\ \mu_B$; for $Ni(ONC(CN)_2)_2(Py)_4$, $\mu_{eff} = 3.23\ \mu_B$; for $Fe(ONC(CN)_2)_2(Py)_4$, $\mu_{eff} = 5.30\ \mu_B$. These data show that the nature of the electron distribution (paired or unpaired) in these complexes is different and hence their thermal behaviour will be different. Complete depyridinization of the three complexes to obtain intact $M(ONC(CN)_2)_2$ is extremely difficult thermally; a fraction of the ONC group is always lost with the fourth Py molecule. The DTG curves (Fig. 1) can be used to identify the complexes. The peculiar DTG curve of complex **I** shows the ferromagnetic nature of the complex (different from complexes **II** and **III**). To determine whether species such as $M(ONC(CN)_2)$ or $M(ONC(CN)_2)^+$ are formed a more elaborate hybrid technique, such as thermal analysis–mass spectrometry, is required.

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