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THERMAL PROPERTIES OF SOME COMPLEXES OF NICKEL(II) WITH PYRIDINE-2-ALDOXYME

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ABSTRACT

The thermal properties of some complexes of the Ni(II) with the pyridine-2-aldoxyme (PaOH), where the ligand appears either as ion (PaO^-) or as a neutral molecule, were determined using TG, DTA, HTRS and DRS techniques.

The thermal stability, as determined by procedural decomposition temperatures, was

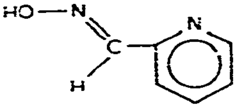
$$[Ni(PaOH)(PaO)(CH_3COO)H_2O] > [Ni(PaOH)_2Cl_2] > [Ni(PaOH)_2(CH_3COO)_2] > [Ni(PaOH)_3]I_2 \cdot 2H_2O$$

The thermal stability is discussed in terms of the intermolecular bonds of the solid lattice and of the electronegativity of the ligands.

The thermal decomposition mechanism of the $[Ni(PaOH)_2Cl_2]$ is also examined.

INTRODUCTION

The pyridine-2-aldoxime (PaOH)



reacts with the nickel(II) to give some complexes[1,2] where the ligand appears either as ion (the ionization occurs at the level of the proton bound to the oxime group and can be represented as

$$PaOH \rightleftharpoons H^+ + PaO^-)$$

or as neutral molecule.

The studied compounds are: $[Ni(PaOH)_2Cl_2]$; $[Ni(PaOH)_2(CH_3COO)_2]$; $[Ni(PaOH)_3I_2] \cdot 2H_2O$; and $[Ni(PaOH)(PaO)(CH_3COO)H_2O]$.

EXPERIMENTAL

Instrumentation

The TG, and DTA curves were obtained using a DuPont Model 990 DTA cell and a Model 951 thermobalance.

The high temperature reflectance spectra HTRS and the DRS (dynamic reflectance spectroscopy)[3,4] were recorded using a Beckman DB–GT spectroreflectometer equipped with the heated sample holder previously described[5].

The heating rate used was 10°C min^{-1} on samples whose sizes ranged in mass from 1 to 10 mg. The furnace atmosphere consisted of either dry pure nitrogen or air, at flow-rates of 50–100 ml min^{-1}.

All temperatures were corrected for thermocouple non-linearity and are, of course, procedural decomposition temperatures (pdt's).

Preparation of compounds

The pyridine-2-aldoxime used was purchased from Aldrich Chemical Co. Inc., Milwaukee, Wisc. The other chemicals employed were all of reagent grade quality.

The complexes have been prepared and purified according to Krause[1].

Thermogravimetry was used in order to determine the water content and the residual metal oxide; the metal content was also established by complexometric titration.

RESULTS

[Ni(PaOH)$_2$Cl$_2$]

The TG in air and in nitrogen and the DTA in air for the [Ni(PaOH)$_2$Cl$_2$] are shown in Fig. 1. The TG curve shows that the compound is anhydrous. The decomposition takes place in several steps, the first one corresponding to a loss of one

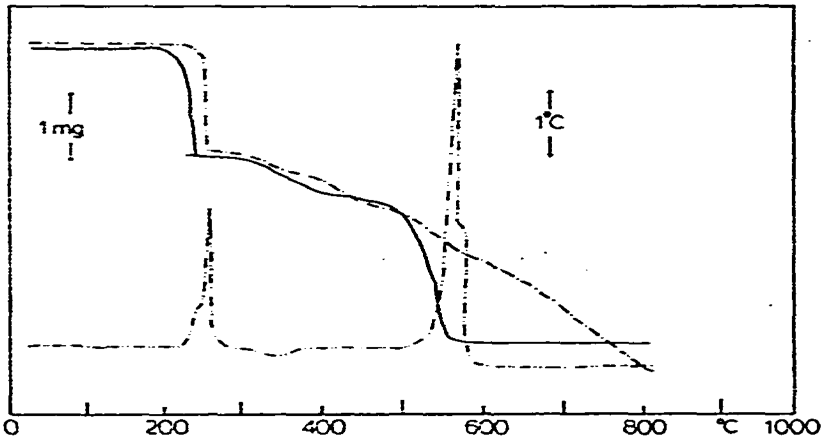


Fig. 1. TG and DTA curves of [Ni(PaOH)$_2$Cl$_2$]. ———, TG and —..—..—, DTA curves in air atmosphere; —.—.—., TG curve in nitrogen atmosphere. Heating rate 10°C min^{-1}.

pyridine group and one chloride (30.5% found; 30.65% calc.). The second step corresponds to the evolution of a $CH_2=N-OH$ group (11.9% found; 12.04% calc.), while the third step gives the oxide NiO (20.2% found; 19.99% calc.).

In nitrogen atmosphere the decomposition still occurs in three steps, but the last one does not reach constant weight.

The DTA curve in air revealed a first sharp exothermic peak followed before by a little endothermic peak and then by a large exothermic one.

The analysis of the evolved gas in nitrogen atmosphere corresponding to the first TG step revealed the presence in the gas stream effluent from the balance of chlorine and pyridine.

$[Ni(PaOH)_2(CH_3COO)_2]$

The TG curves in air and in nitrogen atmosphere (Fig. 2) account for an anhydrous compound. The decomposition is a three-stage process whether in air or in nitrogen, but in air the last step gives the oxide NiO (17.8% found; 17.75% calc.) while in nitrogen it does not reach a constant weight.

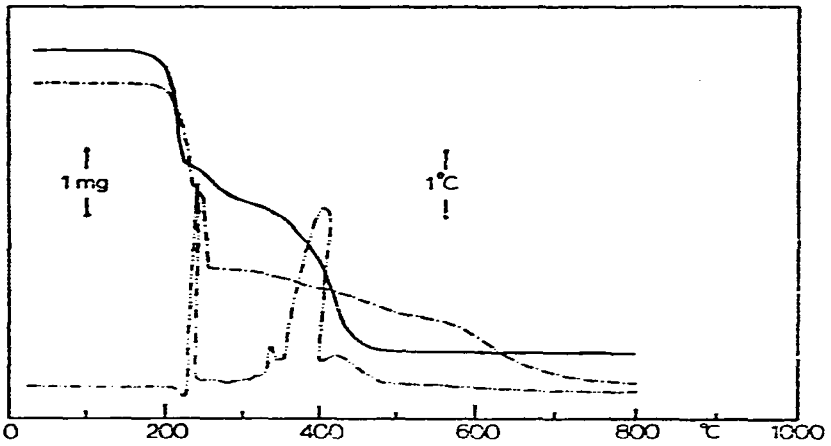


Fig. 2. TG and DTA curves of $[Ni(PaOH)_2(CH_3COO)_2]$. ———, TG and –..–..–, DTA curves in air atmosphere; –.–.–., TG curve in nitrogen atmosphere. Heating rate 10 °C min^{-1}.

The DTA curve in air atmosphere for the decomposition of the compound indicates a first sharp exothermic peak followed by a little endothermic one and then a triplet exothermic peak corresponding to the third step of the TG curve.

$[Ni(PaOH)_3]I_2 \cdot 2H_2O$

The TG curves in air and in nitrogen atmosphere and the DTA curve in air atmosphere of this compound are given in Fig. 3.

The first mass loss observed in the TG curve corresponds to the dehydration reaction (5.0% found; 5.04% calc.) and happens in only one step, while the DTA curve shows for the same process two superimposed endothermic peaks.

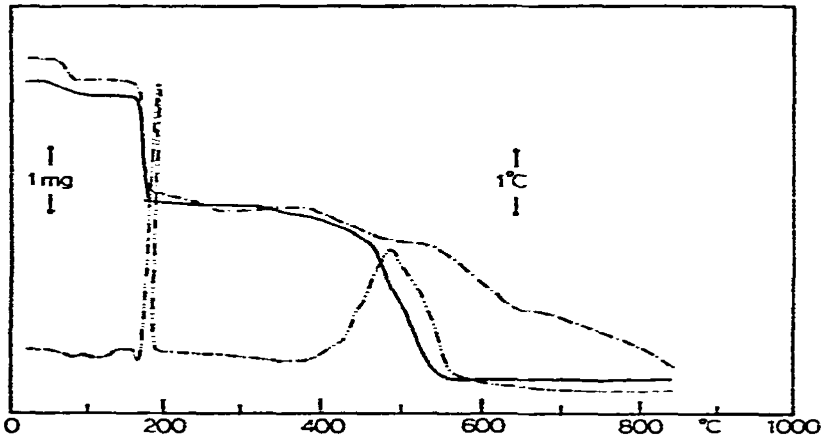


Fig. 3. TG and DTA curves of $[Ni(PaOH)_3]I_2 \cdot 2H_2O$. ———, TG and –..–..–, DTA curves in air atmosphere; –.–.–., TG curve in nitrogen atmosphere. Heating rate 10 °C min^{-1}.

The decomposition takes place in two steps in air giving the oxide NiO (10.5% found; 10.45% calc.) while in nitrogen the second process becomes a multistep process and does not reach a constant weight.

The DTA curve indicates for the decomposition reaction a little endothermic peak that suddenly changes to a sharp exothermic one, characteristic of this series of compounds. There is another broad exothermic peak corresponding to the second TG step for the decomposition of the anhydrous compound in air atmosphere.

[Ni(PaOH)(PaO)(CH₃COO)H₂O]

The TG curves in air and in nitrogen atmosphere (Fig. 4) start with a little step corresponding to a loss of one molecule of water (4.8% found; 4.75% calc.). Then

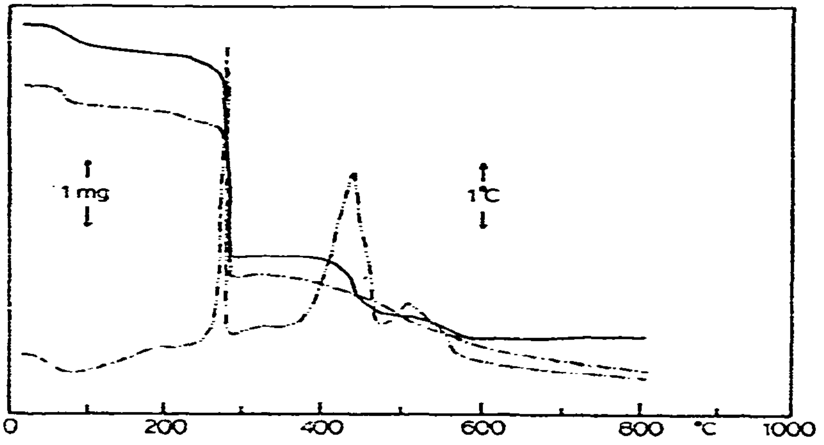


Fig. 4. TG and DTA curves of $[Ni(PaOH)(PaO)(CH_3COO)H_2O]$. ———, TG and –..–..–, DTA curves in air atmosphere; –.–.–., TG curve in nitrogen atmosphere. Heating rate 10 °C min^{-1}.

the decomposition takes place in air atmosphere through a three-step process, of which the first one is very large and fast, giving the oxide NiO (19.5% found; 19.71% calc.). The decomposition in nitrogen is quite different and gives only two steps, the second of which does not reach constant weight. The DTA in air atmosphere (Fig. 4) shows a first endothermic peak corresponding to the water loss, then there is a sharp exothermic one and finally a doublet broad exothermic peak.

The HTRS and the DRS evidences that during the water loss there is no change in the spectrum Figs. 5 and 6.

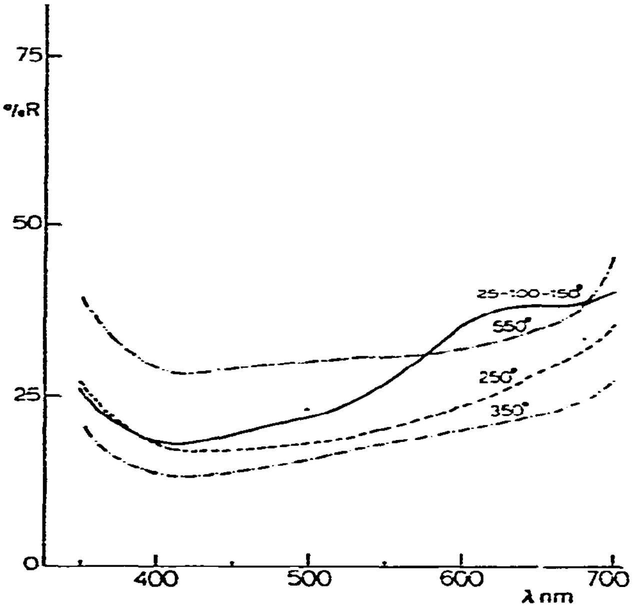


Fig. 5. High temperature reflectance curves of [Ni(PaOH) (PaO) $(CH_3COO)H_2O$].

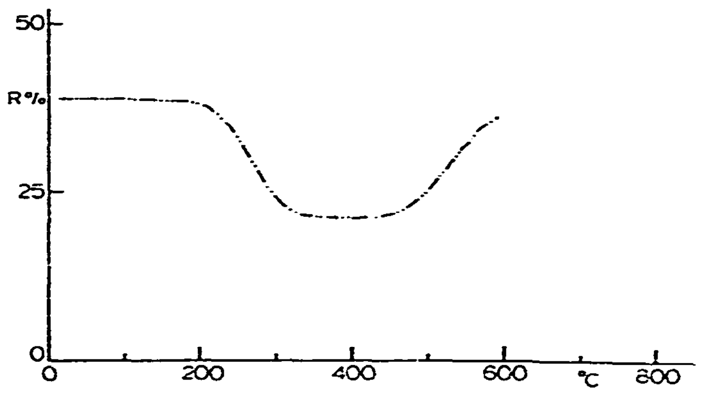


Fig. 6. Dynamic reflectance spectroscopy at 630 nm of [Ni(PaOH) (PaO) $(CH_3COO)H_2O$]. Heating rate 10°C min^{-1}.

DISCUSSION

The TG and DTA curves show a characteristic process for the thermal decomposition of the examined compounds corresponding to a first sharp exothermic peak whose maximum lies between 170 and 280°C. Assuming the pdt's of this process as the temperatures corresponding to the thermal stability of the compounds it is possible to obtain a scale:

$$[Ni(PaOH)(PaO)(CH_3COO)H_2O] > [Ni(PaOH)_2Cl_2] > \\ > [Ni(PaOH)_2(CH_3COO)_2] > \\ > [Ni(PaOH)_3]I_2 \cdot 2H_2O$$

This behaviour can be explained considering the intermolecular bonds of the solid lattice of the compounds and the electronegativity of the ligands around the central ion[6].

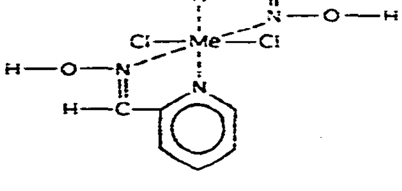
The highest thermal stability of $[Ni(PaOH)(PaO)(CH_3COO)H_2O]$ can be justified considering that the greater degree of conjugation, in the nickel complex, of pyridine-2-aldoxime favours the increase of the acid strength through resonance stabilization of the oxime conjugate base increasing the procedural decomposition temperatures[7].

In the same time the oximic oxygen of the PaO^- group is available as a binding agent on a second nickel ion[8,9] giving heteropolynuclear chelates whose reticulate lattice still increases the thermal stability of the compound. As a consequence the water must not be coordinated to the nickel.

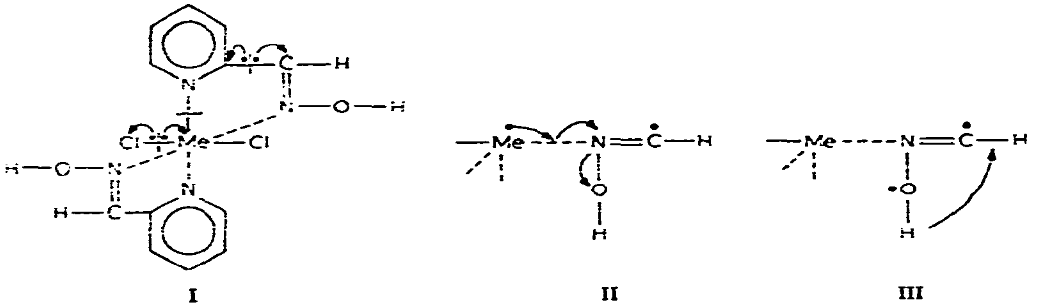
In accordance with this hypothesis the single first endothermic peak of the DTA curve shows that the water molecule is lost at a very low temperature and the HTRS and DRS curves show that there is no change in the shape of the spectrum during the water loss (Figs. 5 and 6) and then the compound should be represented as $[Ni(PaOH)(PaO)CH_3COO] \cdot H_2O$.

The thermal stability scale of the other three compounds agrees with the scale of the electronegativity of the ligands.

The thermal decomposition mechanism of the $[Ni(PaOH)_2Cl_2]$ has been studied. According to the literature[1,10] its structure is



The first break would be charged to the bond between the oxymic carbon and the pyridine ring, then there would be the break of the metal–chloride bond with an electronic rearrangement of the molecule



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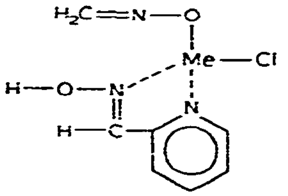
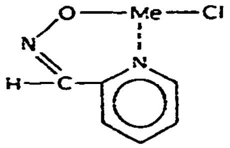
Now the negatively charged oxymic oxygen would bind to the positively charged metal ion giving



This structure agrees with the weight loss corresponding to one pyridine and one chloride (calc. 30.651%; found 30.4%) with the elemental analysis of the residue of the first TG step and with the analysis of the gas evolution of this step.

In the second step of the thermal decomposition it is possible to admit the releasing of a CH_2=N–OH group with a residual molecule of the type



obtaining in this way the enlargement of the chelate ring. This is in accord with the paper of Pattison and Wade[10] where they admit a six-membered ring only for complexes with a metal-ligand molar ratio 1:1.

In the last stage of the thermal reaction there is a complete decomposition of the residual molecule giving, in air, the oxide NiO.

ACKNOWLEDGEMENT

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