

New creatinine complexes of nickel(II)

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Abstract

Following recent work on creatinine complexes of copper(II), creatinine complexes of nickel(II) with various anions have been prepared for the first time and characterised by elemental analysis, solid state infrared spectroscopy and thermal analysis methods. Analysis of the gases evolved during thermal analysis with a coupled FTIR spectrometer provided support for the proposed decomposition sequence. In the case of the complex chloride, $[\text{Ni}(\text{creat})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ the loss of coordinated water has been shown to be reversible. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The complexation ability of creatinine (2-amino-1-methyl-imidazolin-4-one) (creat) is well recognised and studies on the metal ion interactions with creatinine may be helpful in deciphering creatine metabolic pathways [1–6]. However, so far, apart from recent work on copper(II) complexes [11], no thermoanalytical characterisations have been done, and often the complexes have been synthesised in very different reaction media, with different charged molecules or anions [2–4,7–9], as also reported by Mitewa in his review on the co-ordination properties of the bioligand creatinine [10].

In a previous work, the thermal characterisation of copper(II) complexes with creatinine was reported [11]. To compare the different behaviour and the thermal stability of the creatinine co-ordination compounds when changing the central metal ion, the syntheses and thermal characterisation of nickel(II) complexes with creatinine were carried out and the results are reported. New complexes, never described before, have been precipitated and characterised.

The coupling of the thermogravimetric analyser with the FTIR spectrometer provided information supporting the proposed decomposition mechanism of the complexes.

A new chloride complex $[\text{Ni}(\text{creat})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ showed reversible structural changes, the loss of coordinated water being reversible.

A solid state IR characterisation of the complexes is also reported.

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2. Experimental

2.1. Materials

Creatinine and the nickel(II) salts were purchased from Aldrich Chemical and used without further purification. All the solvent used were RPE grade.

2.2. Syntheses of the complexes

2.2.1. $[Ni(creat)_6](NO_3)_2$

250 ml of an organic solution of creatinine (6 mmol in acetone) and 250 ml of an organic solution of $Ni(NO_3)_2 \cdot 5H_2O$ (1 mmol in acetone) were mixed and heated at 80°C with constant stirring. The resulting precipitated complex was washed with acetone and dried in vacuo.

2.2.2. $[Ni(creat)_4](NO_3)_2$

250 ml of an organic solution of creatinine (2 mmol in acetone) and 250 ml of an organic solution of $Ni(NO_3)_2 \cdot 5H_2O$ (1 mmol in acetone) were mixed and heated at 80°C with constant stirring. The resulting precipitated complex was washed with acetone and dried in vacuo.

2.2.3. $[Ni(creat)_4](ClO_4)_2$

250 ml of an organic solution of creatinine (4 mmol in acetone) and 250 ml of an organic solution of $Ni(ClO_4)_2 \cdot 2H_2O$ (1 mmol in acetone) were mixed and heated at 60–70°C with constant stirring. The resulting precipitated complex was washed with acetone and dried in vacuo.

2.2.4. $[Ni(creat)_2(H_2O)_2]SO_4$

250 ml of an organic solution of creatinine (4 mmol in acetone) and 250 ml of an organic solution of $NiSO_4 \cdot 5H_2O$ (1 mmol in methanol) were mixed and heated at 95°C with constant stirring. The resulting precipitated complex was washed with acetone and dried in vacuo.

2.2.5. $[Ni(creat)_6]Cl_2$

250 ml of an organic solution of creatinine (8 mmol in acetone) and 250 ml of an organic solution of $NiCl_2 \cdot 2H_2O$ (1 mmol in acetone) were mixed and heated at 80°C with constant stirring. The resulting precipitated complex was washed with acetone and dried in vacuo.

2.2.6. $[Ni(creat)_2(H_2O)_2]Cl_2$

250 ml of an organic solution of creatinine (2 mmol in acetone) and 250 ml of an organic solution of $NiCl_2 \cdot 2H_2O$ (1 mmol in acetone) were mixed and heated at 80°C with constant stirring. The resulting precipitated complex was washed with acetone and dried in vacuo.

2.3. Instrumental

The IR spectra were recorded from KBr pellets with a Perkin Elmer FTIR spectrometer, model 1760X (30 scans at a resolution of 4 cm^{-1}).

The thermoanalytical curves were obtained using a Perkin Elmer TGA7 thermobalance (range 20–1000°C) and a Perkin Elmer DSC7; the atmosphere was either pure nitrogen or air, at a flow rate of 100 $ml\ min^{-1}$; the heating rate was varied between 5 and 40°C min^{-1} , with the best resolution achieved at a scanning rate of 10°C min^{-1} .

To obtain the IR spectra of the gases evolved during the thermogravimetric analysis, the thermobalance is coupled with a Perkin Elmer FTIR spectrometer, model 1760X; the TGA7 is linked to the heated gas cell of the FTIR instrument by means of a heated transfer line, and the temperatures of the cell and of the transfer line are independently selected.

3. Results

3.1. Elemental analysis

Results from the elemental analysis are listed in Table 1.

3.2. Thermal analysis

The thermal profiles of the complexes are reported in Figs. 1–6.

The $[Ni(creat)_6](NO_3)_2$ complex shows a thermal behaviour similar to the $[Cu(creat)_6](NO_3)_2$ complex, with the loss of four creatinine molecules in the temperature range 180–500°C and the following final decomposition involving the nitrate ions (Fig. 1a and b). The loss of the creatinine molecules is proved by the IR spectra of the gases evolved in this temperature range, which are the same as for the decomposition of

Table 1
Elemental analysis of the precipitated complexes^a

Complex	Ni	C	H	N
[Ni(creat) ₆](NO ₃) ₂	7.00 (6.81)	33.40 (33.43)	4.80 (4.87)	32.60 (32.50)
[Ni(creat) ₄](NO ₃) ₂	9.10 (9.24)	30.40 (30.22)	4.20 (4.40)	30.85 (30.85)
[Ni(creat) ₄](ClO ₄) ₂	8.25 (8.26)	27.00 (27.03)	4.00 (3.94)	23.80 (23.66)
[Ni(creat) ₂ (H ₂ O) ₂] ₂ SO ₄	14.00 (14.07)	23.00 (23.02)	4.50 (4.31)	20.00 (20.14)
[Ni(creat) ₆]Cl ₂	7.30 (7.26)	35.85 (35.62)	5.25 (5.20)	31.10 (31.17)
[Ni(creat) ₂ (H ₂ O) ₂]Cl ₂	15.00 (14.98)	24.50 (24.50)	4.65 (4.59)	21.50 (21.43)

^a Values found (and calculated).

creatinine. A stacked plot of the spectra collected at different temperatures is shown in Fig. 1c.

The [Ni(creat)₄](NO₃)₂ complex behaves differently, being less stable than the 1:6 nitrate compound, and showing a larger first decomposition process (Fig. 2). Both the complexes are characterised by the loss of the hydrogen-bonded creatinine molecules in the first step, with the following break down of the fundamental structure to obtain the metal oxide.

The [Ni(creat)₄](ClO₄)₂ complex loses two creatinine molecules in two well defined steps, clearly shown by the derivative curve in Fig. 3: the thermal stability is similar to the [Cu(creat)₂(H₂O)₂](ClO₄)₂ compound, but the final decomposition process to give the oxide is sharper for the nickel(II) compound.

The first TG step of the [Ni(creat)₂(H₂O)₂]₂SO₄ complex is the loss of the water molecules (Fig. 4a and b) that is again confirmed by the IR spectra of the evolved gases collected in this temperature range (Fig. 4c). It is followed by the release of one ligand molecule and then by the final decomposition, involving the sulphate ion, to give NiO. This complex shows a thermal stability similar to the corresponding copper compound but with different decomposition steps. This could be due to the fact that the water molecules

are inside the fundamental structure of the nickel(II) compound, but outside of the copper(II) complex.

In Fig. 5, the thermogravimetric curve of the [Ni(creat)₆]Cl₂ complex shows that four creatinine molecules are released in three different steps, and the final decomposition to NiO follows.

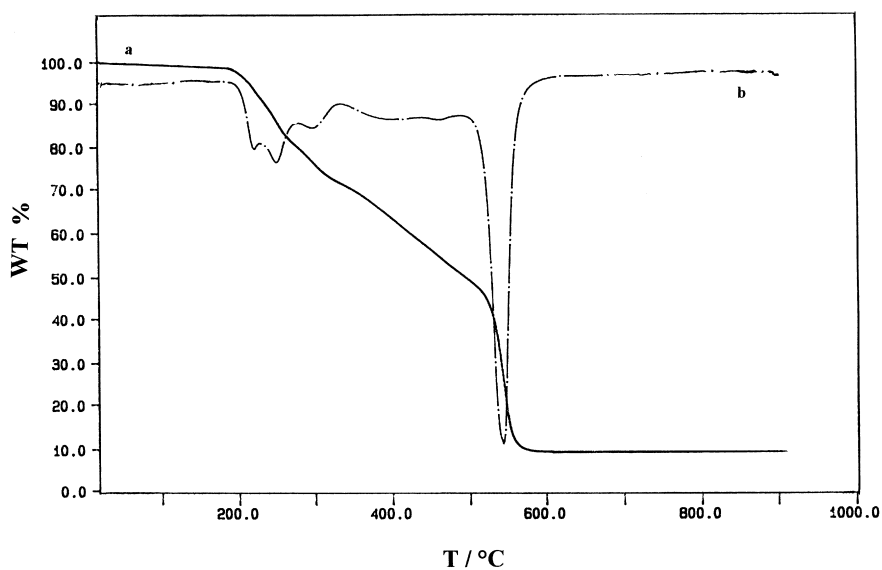
The [Ni(creat)₂(H₂O)₂]₂Cl₂ complex is more stable than the 1:6 chloride compound previously described in Fig. 6a; a TG plateau can be observed up to 300°C. The decomposition occurs with the loss of the water molecules and one creatinine molecule, followed by the final process to give the nickel oxide. With time, this compound undergoes a structure modification, with the water molecules shifted out from the original conformation. This modification has been monitored by TG and DSC as a function of the time, and the resulting curves are collected in Fig. 6 (b and c profiles) and Fig. 7 (DSC profiles), with the steady state reached after 30 days from the synthesis.

3.3. IR spectroscopy

In Table 2, the IR characteristic frequencies of the complexes (KBr pellets) are collected and compared with those of creatinine.

Table 2
Selected IR frequencies (cm⁻¹) of the complexes

Complex	Assignment				
	ν_{as} NH ₂	ν_s NH ₂	δ NH ₂	ν CO	ν CN
[Ni(creat) ₆](NO ₃) ₂	3380	3180	1665	1710	1597
[Ni(creat) ₄](NO ₃) ₂	3380	3160	1660	1715	1605
[Ni(creat) ₄](ClO ₄) ₂	3370	3195	1682	1720	1610
[Ni(creat) ₂ (H ₂ O) ₂] ₂ SO ₄	3110	3020	1620	1708	1600
[Ni(creat) ₆]Cl ₂	3320	3150	1660	1690	1685
[Ni(creat) ₂ (H ₂ O) ₂]Cl ₂	3320	3160	1670	1692	1684
Standard creatinine	3250	3040	1690	1665	1500



IR spectra of the evolved gas

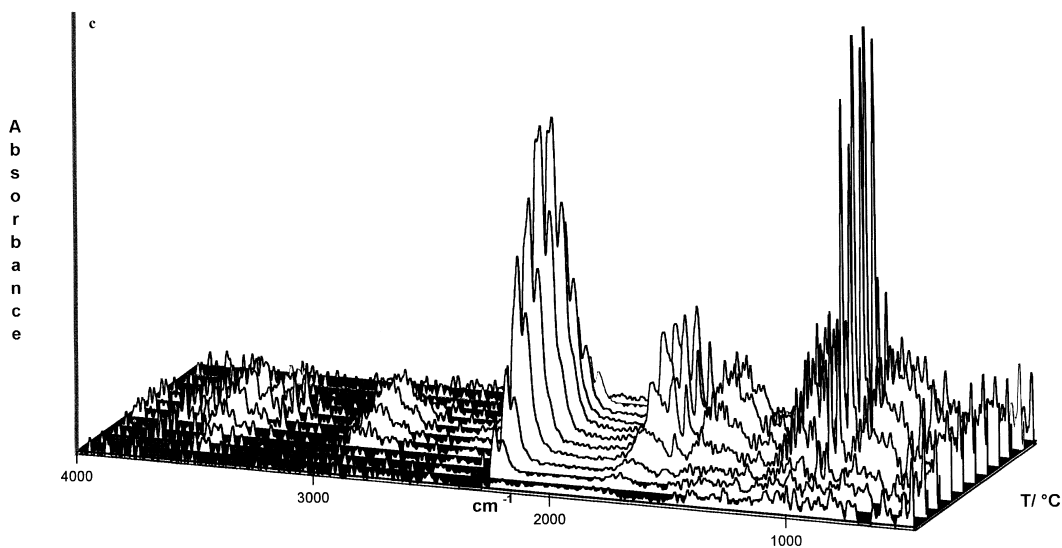


Fig. 1. $[\text{Ni}(\text{creat})_6](\text{NO}_3)_2$: (a) TG curve; (b) DTG curve; scanning rate: $10^\circ\text{C min}^{-1}$; air flow at 100 ml min^{-1} ; (c) stacked plot of the IR spectra of the evolved gases for the first process in air, temperature range $180\text{--}300^\circ\text{C}$; resolution: 8 cm^{-1} .

4. Discussion

It has been shown that no complexation of nickel(II) with creatinine proceeds in water [8]; several different complexes have been established in organic media [7–9] but under very different conditions. Moreover,

the thermoanalytical data regarding creatinine complexes are often incomplete or not available. The purpose of this work was the syntheses and thermal characterisation of new nickel(II)-creatinine complexes, obtained by reaction in organic medium, to compare the thermal stability when changing the

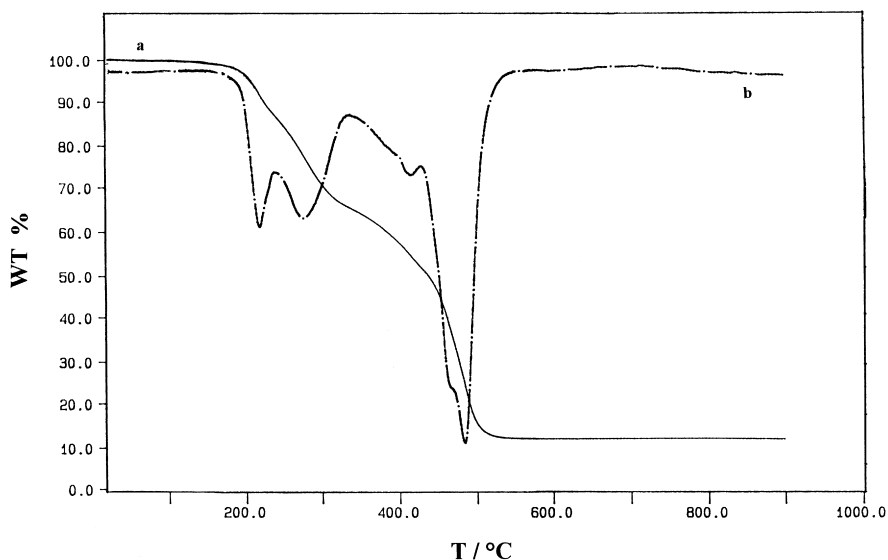


Fig. 2. $[\text{Ni}(\text{creat})_4](\text{NO}_3)_2$: (a) TG curve; (b) DTG curve; scanning rate: $10^\circ\text{C min}^{-1}$; air flow at 100 ml min^{-1} .

metal ion or the anion and to determine the decomposition mechanisms by means of the thermogravimetry coupled to the IR spectroscopy as evolved gas analysis.

Starting from the conditions described by Mitewa et al. [8], Gencheva et al. [9], and on the basis of the results obtained with the copper complexes [11], the methods of preparation were modified, resulting in

improvement of the yields and of the purity of the precipitated compounds.

For most of the complexes, the syntheses described in the literature gave low yields, even if the conditions were exactly reproduced: this fact is probably due to the high dependence of the results on the water/metal/ligand ratio; this dependence has also been shown to be critical for the copper(II) complexes. The nickel-

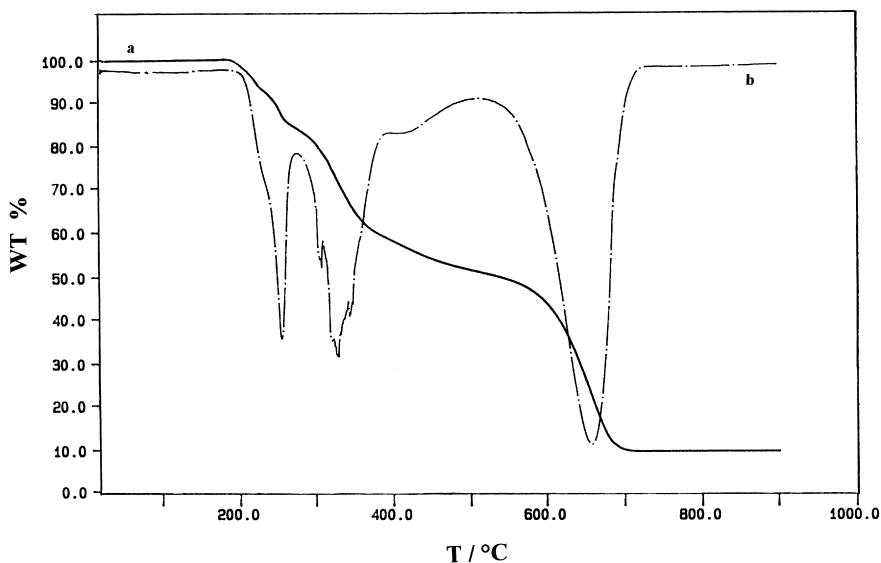
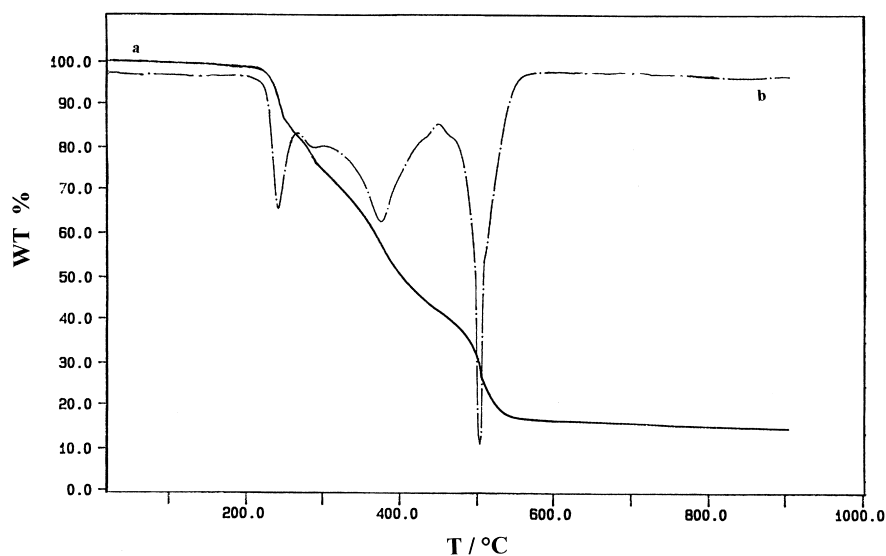


Fig. 3. $[\text{Ni}(\text{creat})_4](\text{ClO}_4)_2$: (a) TG curve; (b) DTG curve; scanning rate: $10^\circ\text{C min}^{-1}$; air flow at 100 ml min^{-1} .



IR spectra of the evolved gas

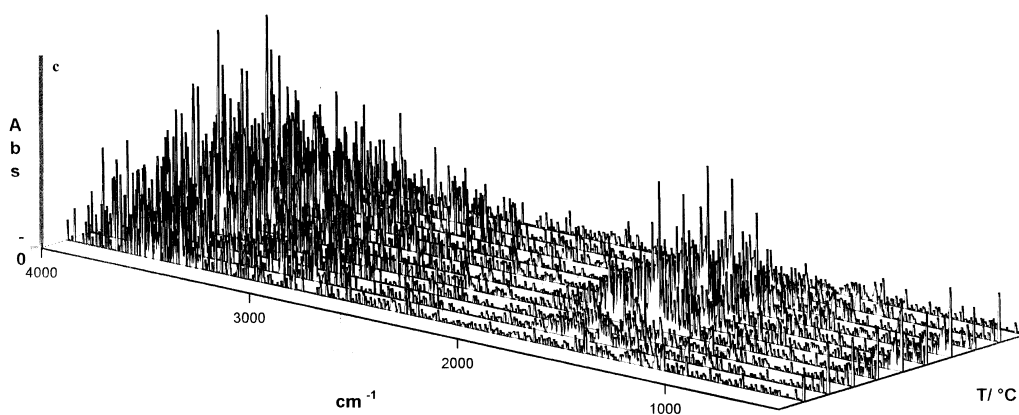


Fig. 4. $[\text{Ni}(\text{creat})_2(\text{H}_2\text{O})_2]\text{SO}_4$: (a) TG curve; (b) DTG curve; scanning rate: $10^\circ\text{C min}^{-1}$; air flow at 100 ml min^{-1} ; (c) stacked plot of the IR spectra of the evolved gases for the first process air, temperature range $210\text{--}250^\circ\text{C}$; resolution: 8 cm^{-1} .

nitrate complex shows the 1:4 metal/ligand co-ordination that has not been obtained for the copper(II) complexes, but all the attempts to precipitate the 1:2 metal/ligand nitrate complex failed.

The infrared characterisation of the solid state complexes (Table 2) indicates the presence of creatinine in the nitrate complexes in its amino form; evidently, the C=O group is not involved (vibration around 1700 cm^{-1} compared with the free ligand), and the $-\text{NH}_2$ vibration bands are rather broad, the participation in hydrogen bond being the logical

explanation. The data obtained for NO_3^- vibrations are typical for ionic compounds, thus, confirming the nitrate groups in the outer sphere of the complexes. In the case of the chloride complexes, the hydrogen bond participation is suggested again by the rather broad character of the $-\text{NH}_2$ bands, and the bands with C=N contribution exhibit intensity changes and important shifts, all these data suggesting binding between nickel and the endocyclic N atom of the ligand. These results are in good agreement with those reported in the literature [8,12].

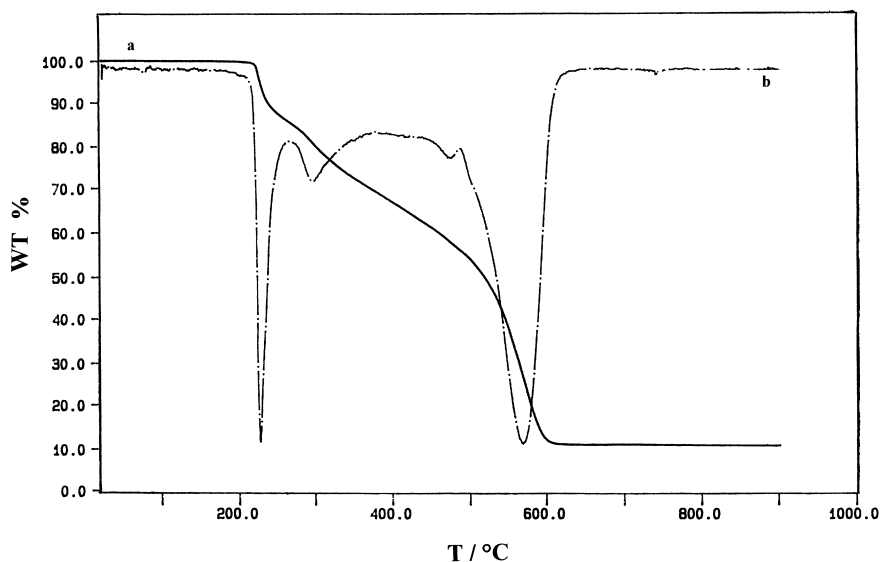


Fig. 5. $[\text{Ni}(\text{creat})_6]\text{Cl}_2$: (a) TG curve; (b) DTG curve; scanning rate: $10^\circ\text{C min}^{-1}$; air flow at 100 ml min^{-1} .

The thermal decomposition mechanism of the nickel compounds proves that all the complexes are built on a $[\text{Ni}(\text{creat})_2]\text{X}_2$ fundamental structure, the successive two or four creatinine molecules being linked by hydrogen bonds. In fact, if the synthesis is carried out with a lower temperature or for shorter time, the complex obtained is a $[\text{Ni}(\text{creat})_2]\text{X}_2$, more or less stable as a function of the reaction temperature. The same behaviour was observed for the copper complexes. However, the $[\text{Ni}(\text{creat})_2](\text{NO}_3)_2$ complex was never obtained; the 1:4 compound precipitated even at room temperature and without stirring or heating.

The thermally induced reactions are consequently different when the complex is broken in its fundamental structure or loses the hydrogen-bonded creatinine molecules. This difference is clearly shown by the evolved gas analysis. The IR spectra of the TG decomposition products show the bands related to the creatinine decomposition for the 1:2 complexes, instead of the bands of decomposed creatinine in the first step of the 1:6 and 1:4 compounds. This process can be enhanced if the TG atmosphere is changed from air or oxygen to pure nitrogen or argon.

The presence of two or four hydrogen-bonded creatinine molecules increases the thermal stability of the fundamental 1:2 structure with a shift to higher temperature of the final decomposition step.

The $[\text{Ni}(\text{creat})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ complex reversibly bonds the two water molecules in the structure. The compound obtained from the refluxing synthesis, with a TG plateau up to 300°C , undergoes with time a structure modification. The thermal profile consequently changes, showing a final steady state characterised by two well defined steps related to the loss of the water molecules (see Fig. 6). The aging steps can be observed in the DSC curves. The growing peak in Fig. 7 is related to the loss of water molecules, and is split into two peaks when the steady state is reached. The peak at 318°C , related to the break down of the fundamental structure, with time shows an increasing ΔH value because the removal of the water molecules increases the stability of the fundamental structure. The ΔH values are collected in Table 3. If the aged compound is refluxed in the presence of 2–3% water,

Table 3
 ΔH values (J g^{-1}) of the DSC peak at 318°C for the $[\text{Ni}(\text{creat})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ complex

Aging time	Water peak	Peak at 318°C
Fresh prepared	–	201.094
4 Days old	7.233	247.310
8 Days old	12.962	294.872
9 Days old	31.418	328.110
10 Days old	39.673	345.003
2 Months old	Split	402.247

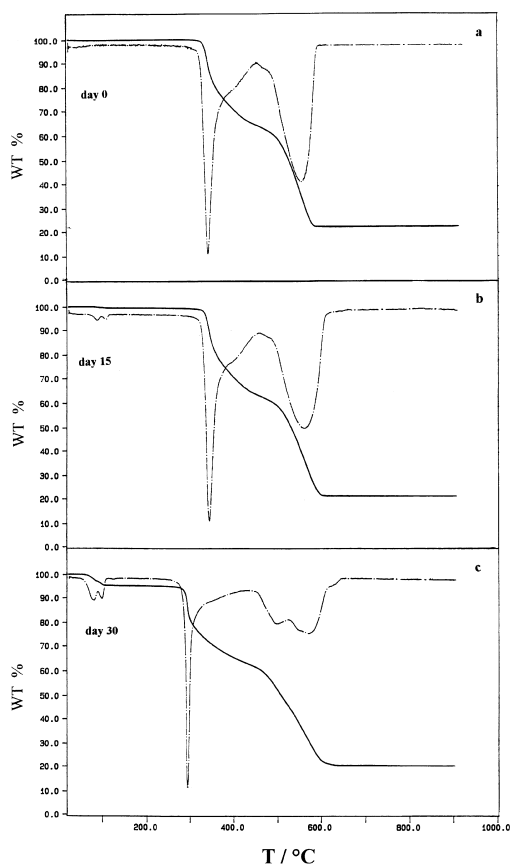


Fig. 6. $[\text{Ni}(\text{creat})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$: TG curves as a function of the aging time; scanning rate: $10^\circ\text{C min}^{-1}$; air flow at 100 ml min^{-1} .

the starting situation can be reversibly obtained and the complex undergoes a new aging modification to reach the steady state.

5. Conclusions

New nickel(II) complexes of creatinine have been synthesised in organic media. Thermal characterisation has been carried out by TG, DSC and coupled TG-FTIR techniques, and the results of a parallel qualitative analysis by solid state IR spectroscopy are reported.

By coupling the thermobalance with the FTIR spectrometer, the proposed decomposition stages of the complexes were confirmed by comparing the IR bands of the gases evolved from the TG furnace with the spectra of the standard ligand.

The thermoanalytical and spectroscopic behaviour of the nickel(II) complexes was compared with the related copper(II) complexes reported in a previous work.

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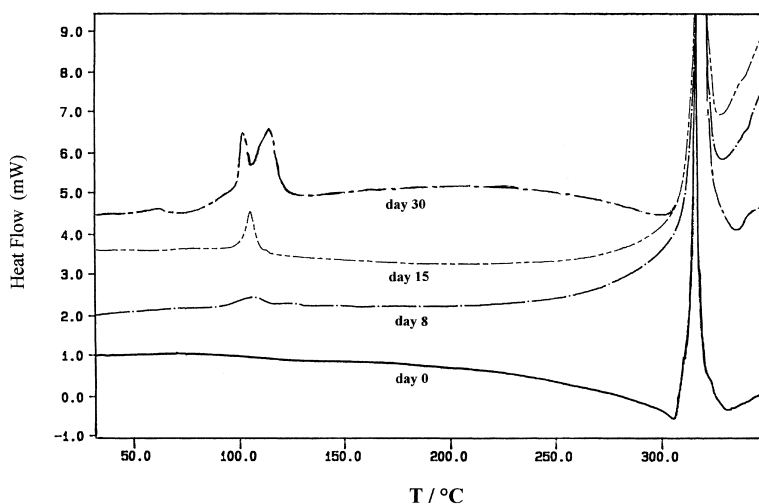


Fig. 7. $[\text{Ni}(\text{creat})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$: DSC curves as a function of the aging time; scanning rate: $10^\circ\text{C min}^{-1}$; air flow at 100 ml min^{-1} .

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