Thermochimica Acta, 200 (1992) 169–185
Elsevier Science Publishers B.V., Amsterdam

A thermoanalytical approach to the interpretation of the proposed isomerism of some nickel(II) benzimidazole complexes

R. Curini, G. D'Ascenzo, S. Materazzi and A. Marino

Department of Chemistry, University "La Sapienza" Rome, Rome (Italy)

(Received 10 February 1992)

Abstract

The proposed isomerism of some NiL_4Cl_2 complexes where L is benzimidazole, is investigated by thermoanalytical techniques coupled with an FT-IR system and supported by spectroscopic techniques.

The proposed compounds, unsolvated NiL_4Cl_2 (two isomers), acetone-solvated NiL_4Cl_2S and $NiL_4Cl_2S_2$ (three isomers), where S is aceton, appear to be the same compounds at different solvation levels, where water takes part in the solvation process for one of the six compounds. Reflectance and IR spectra were obtained at room temperature. Analysis of the data obtained supports the hypothesis that two possible main structures are present: (i) a distorted, octahedral, dimeric cationic structure where one chloride acts as a bridge between two nickel ions, the planar field being occupied by four benzimidazole neutral molecules; (ii) a distorted, octahedral, monomeric neutral structure where two chlorides are in both axial sites.

The dimeric cationic structure changes to the monomeric neutral structure by a temperature-induced anation reaction, as demonstrated by an exothermic process at 145°C.

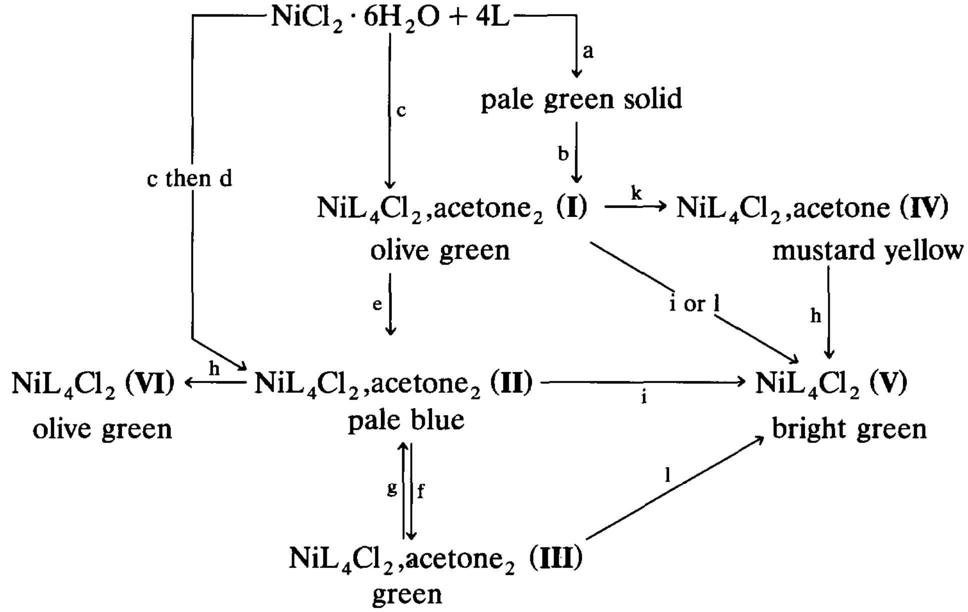
The interaction of acetone with the complexes described is also discussed and a new thermal procedure is suggested for obtaining some of the compounds investigated.

INTRODUCTION

Previous papers of this series concerning the thermal properties of coordination compounds obtained by reaction of imidazole and its related structures with divalent metal ions [1–3], have shown that different parameters such as basicity of the ligands, π-acceptor ability, steric factors, hydrogen bonding, and anion choice influence either the structure or the thermal characteristics of these compounds. Nickel(II) complexes of these

---

Correspondence to: G. D'Ascenzo, Dipartimento di Chimica, Universita di Roma "La Sapienza", Piazza A. Moro 5, 00185 Roma, Italy.



Scheme 1. Key: a, reflux for 15 min in acetone; b, same as stage a, but reflux for 24 h; c, reflux for 3 h in acetone + 1% H_2O; d, stand corked under mother-liquor for 2 days; e, as stage d, but for 12 days; f, dissolve solid in dry acetone, add L, stand sealed for several days; g, stand solid in acetone + 1% H_2O; h, heat at 75°C; i, heat at 130°C; l, heat at 110°C; k, leave solid loosely corked at room temperature.

sterically hindered heterocyclic nitrogen ligands are highly interesting. By suitable substitution of the ligand, and by proper choice of the anions and of the solvent forming the reaction surroundings, different kinds of stereochemical environments can be built around nickel(II). In addition, the tendency of bivalent nickel to form tetragonally distorted octahedral complexes and to give rise to isomeric species is well known.

Goodgame et al. [4] report the preparation and the study of a series of nickel(II) complexes with benzimidazole as the neutral ligand, which show complex isomerism and unusual magnetic behaviour. These same authors also affirm that the exact preparation conditions for many of these compounds are very critical, this being particularly true for the desolvation processes. The complexes obtained in the above study [4] with nickel chloride and their interrelationships are shown in Scheme 1, where each compound is identified by Roman numerals (because of the large number of isomers).

After careful examination of the compound preparation, as well as of the referred data and of the incongruities of some of their magnetic properties, it seemed interesting to apply thermoanalysis in association with spectroscopic techniques to an analytical study of these compounds.

EXPERIMENTAL

Instrumentation

A Perkin-Elmer thermobalance (model TGA7) coupled with a Perkin-Elmer FT-IR (model 1720) and differential scanning calorimeters (models DSC-2B and DSC7) both equipped with a data station were used. The heating rate ranged between isothermal behaviour and 10°C min^{-1}. The atmosphere was air at a flow rate of 50–100 ml min^{-1}. The IR spectra were recorded using a Perkin-Elmer FT-IR model 1720. The reflectance spectra were recorded using a Beckman DK-2A.

Synthesis of the compounds

Benzimidazole was obtained from Aldrich Chemical Co.; the other chemicals used were of reagent grade.

The compounds were initially prepared following the scheme proposed by Goodgame et al. [4].

RESULTS

On the basis of the described properties of these compounds, the thermoanalytical study was carried out following their thermal behaviour with time.

The TG curve of compound **I** (Fig. 1a) shows that 1.5 molecules of acetone are present and are released in two well-defined steps, the first corresponding to half a molecule and the second to one molecule of acetone.

FT-IR spectra of the decomposition products confirm that in both steps acetone is lost. Subsequently, the unsolvated compound decomposes through a series of superimposed processes with the loss of two molecules of benzimidazole, followed by a third molecule of ligand and then by oxidative decomposition to give NiO.

In the DSC curve (Fig. 2a) two peaks appear for the acetone release, with maxima at 94°C and 136°C respectively.

After leaving the compound in a closed vessel in order to avoid acetone loss, the TG curve changes with time, reaching a steady state after 28 days (Figs. 1b and 2b). At this point, the acetone amount does not change in the two steps, while the decomposition processes, involving three molecules of benzimidazole and an oxidative decomposition, change drastically.

Compound **II** starts to decompose (Fig. 3a) at room temperature through two overlapping processes. The FT-IR spectra of the decomposition gases account for an initial loss of water followed by loss of acetone. Quantitative analysis shows that one molecule of water and then two molecules of

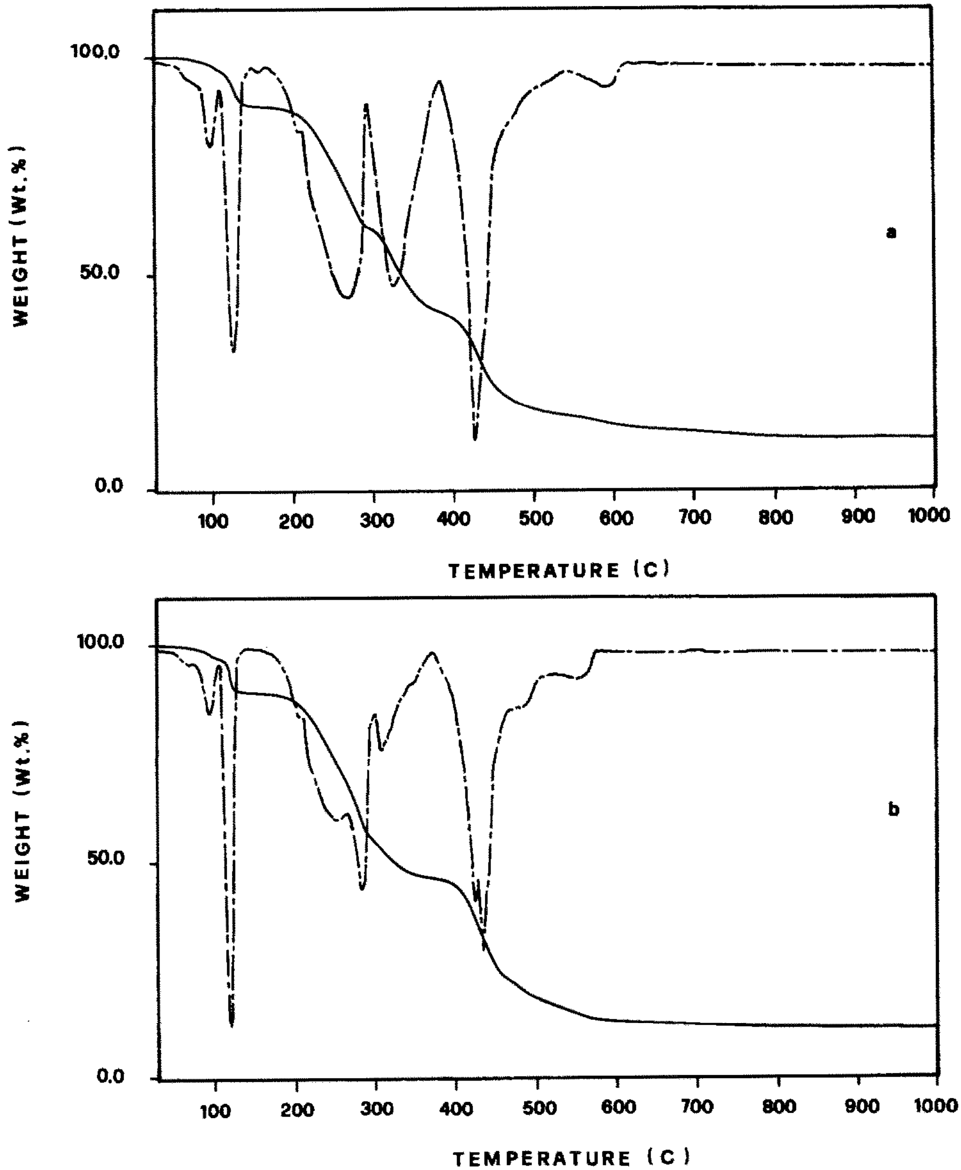


Fig. 1. a, TG and DTG curves of compound **I**: air atmosphere; heating rate, 10°C min^{-1}. b, TG and DTG curves of compound **I** after 28 days: air atmosphere; heating rate, 10°C min^{-1}.

acetone are released in this temperature range. After a plateau, the decomposition starts through the release of three molecules of benzimidazole in a series of very overlapping and unresolved processes, followed by an oxidative decomposition.

The DSC curve (Fig. 4a) reveals a first wide peak due to the superimposition of two processes: the first corresponds to one water molecule and the

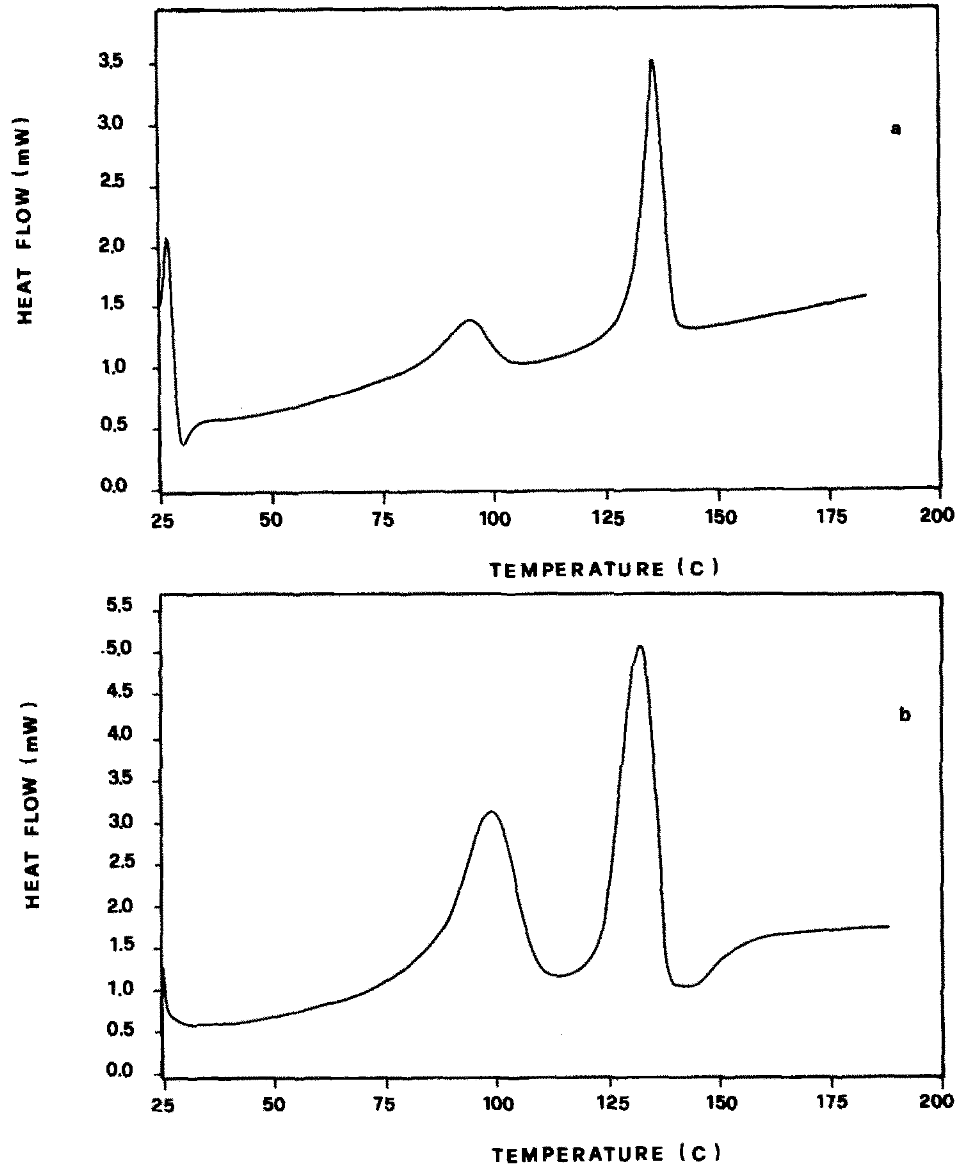


Fig. 2. a, DSC curve of compound I: air atmosphere; heating rate 10°C min^{-1}. b, DSC curve of compound I after 28 days: air atmosphere; heating rate, 10°C min^{-1}.

second to one acetone molecule, which is followed by another peak corresponding to one acetone molecule. Finally, an exothermic process (peak at 148°C) appears, corresponding to a TG plateau.

With time, the TG and DSC curves change dramatically. At 28 days, the process corresponding to solvent release is quite different (Figs. 3b and 4b). The first peak corresponds to the evolution of one water molecule and 1.75

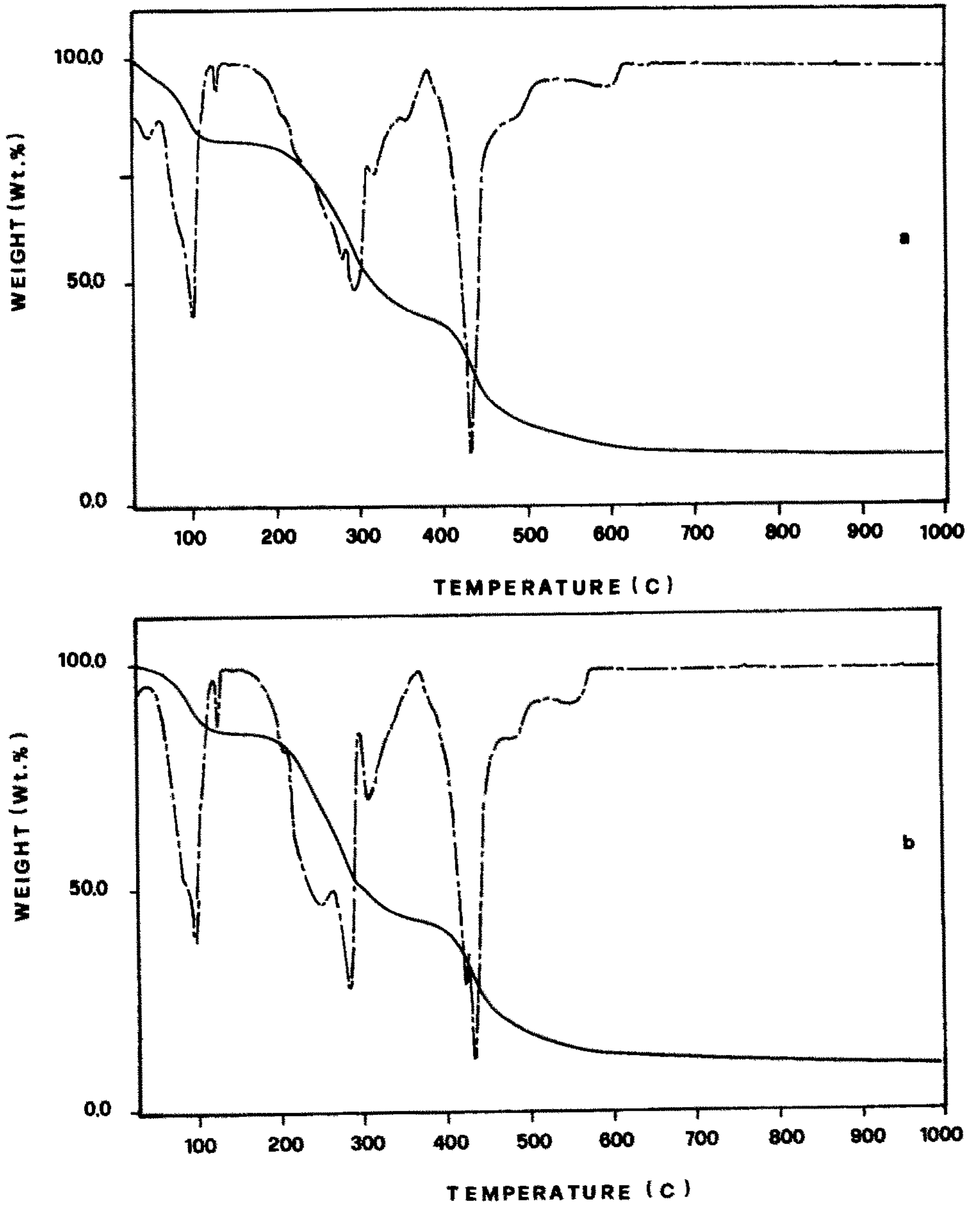


Fig. 3. a, TG and DTG curves of compound II: air atmosphere; heating rate 10°C min^{-1}. b, TG and DTG curves of compound II after 28 days: air atmosphere; heating rate, 10°C min^{-1}.

molecules of acetone, while the second peak corresponds to 0.25 molecules of acetone. The exothermic process in the DSC curve does not change either in position or in the heat evolved ($\Delta H = -51.8$ J g^{-1}).

The decomposition process of the unsolvated compound, after a series of changes taking place with time, reaches a steady state at 28 days, exactly

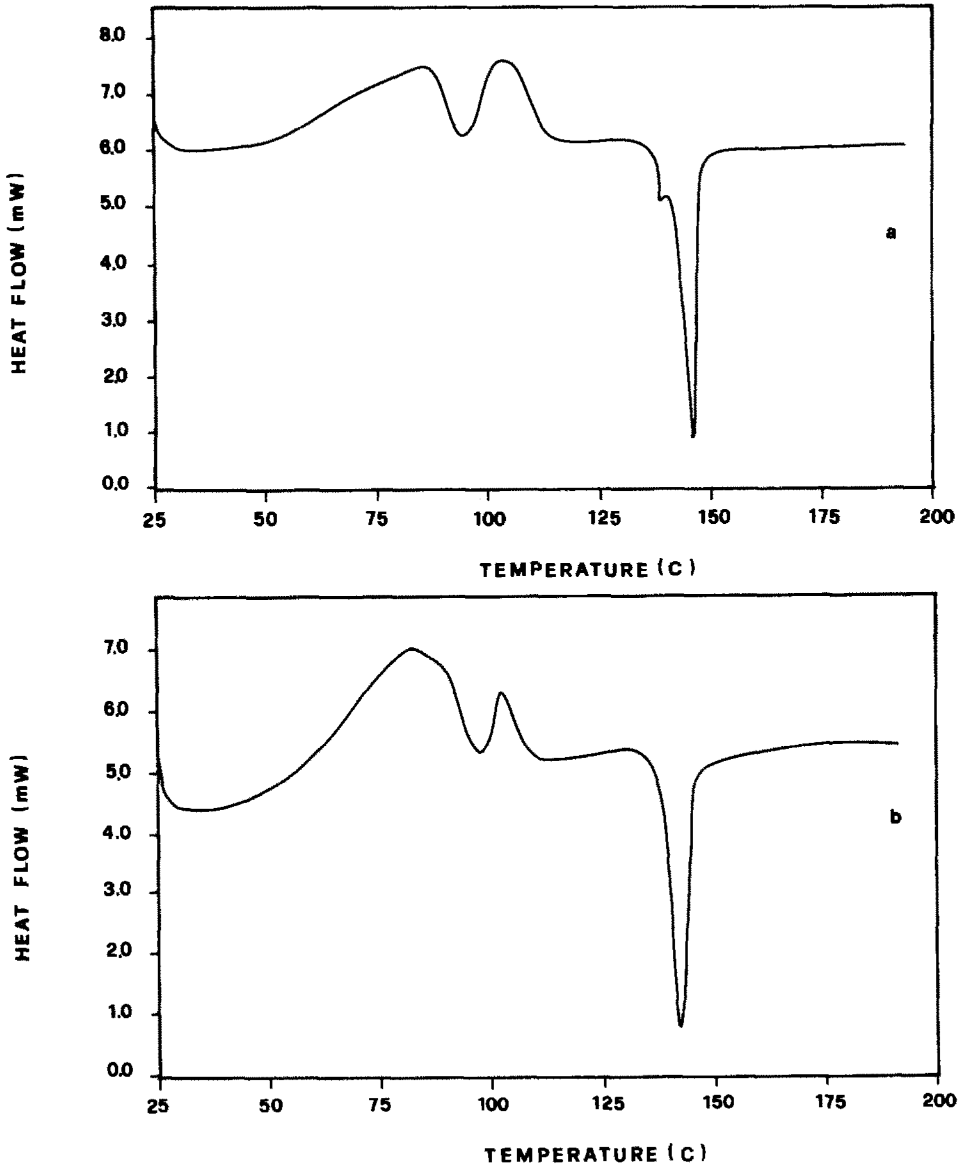


Fig. 4. a, DSC curve of compound **II**: air atmosphere; heating rate, 10°C min^{-1}. b, DSC curve of compound **II** after 28 days: air atmosphere; heating rate, 10°C min^{-1}.

overlapping at this time the decomposition behaviour of unsolvated compound **I** at 28 days.

Compound **III** loses two molecules of acetone (Fig. 5a) in the first process, at about 95°C, and the TG curve shows that such loss is the result of the superimposition of two processes, the first being much more pronounced than the second.

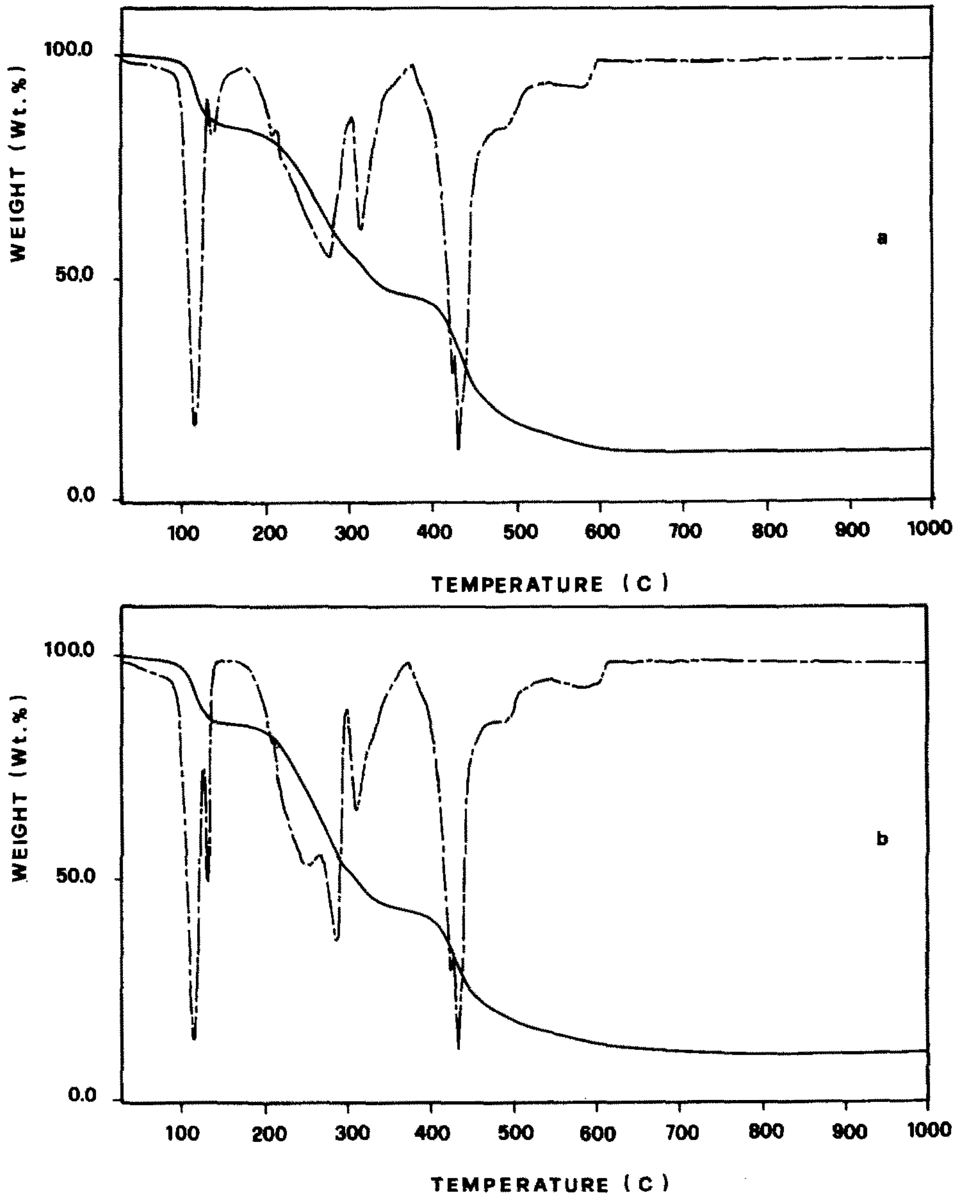


Fig. 5. a, TG and DTG curves of compound III: air atmosphere; heating rate, 10°C min^{-1}. b, TG and DTG curves of compound III after 28 days: air atmosphere; heating rate, 10°C min^{-1}.

The FT-IR of the evolved gas accounts for the presence of acetone only. Thermal degradation of the unsolvated compound still occurs through the release of three molecules of benzimidazole in a series of overlapping processes, and is then followed by an oxidative degradation process to give NiO.

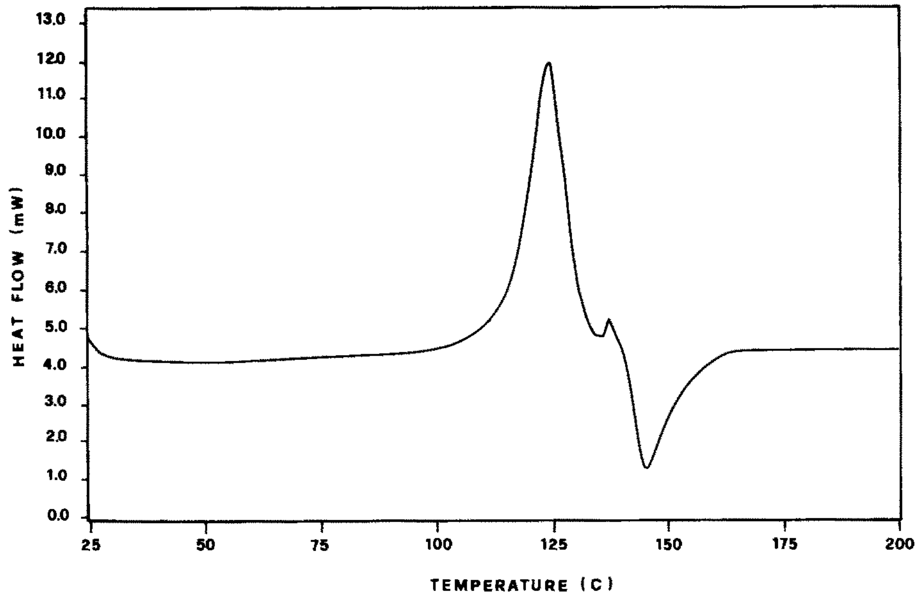


Fig. 6. DSC curve of compound III: air atmosphere; heating rate, 10°C min^{-1}.

The DSC curve (Fig. 6) shows a first endothermic process (peak at 125°C) followed by a second one of lower intensity, immediately masked by an exothermic process (peak at 145°C, $\Delta H = 45.93$ J g^{-1}).

With time, TG and DTG curves (Fig. 5b) change and at 28 days the desolvation process is clearly divided into two steps, the first corresponding to 1.75 and the second to 0.25 molecules of acetone. The decomposition of the unsolvated compound also changes at 28 days, assuming exactly the same behaviour as that of compounds **I** and **II** when they are 28 days old.

In the DSC curve of compound **III** at 28 days there still appears to be a pronounced endothermic process (peak at 125°C), followed by a more evident second endothermic peak, which is, however, still masked by an exothermic process (peak at 145°C), this being characterized by a lower value of ΔH ($\Delta H = 35.99$ J g^{-1}).

The desolvation process of compound **IV** (Fig. 7) implies the loss of one acetone molecule and is represented by one step only. The corresponding DTG peak appears very sharp and perfectly symmetrical. The decomposition behaviour of the freshly prepared compound **IV** is exactly the same as that of compounds **I**, **II** and **III** when they are 28 days old, remaining unchanged with time. The DSC curve (Fig. 8) confirms this desolvation process through the existence of only one symmetrical endothermic reaction (peak at 133°C).

Exothermic peaks are not present in the temperature range corresponding to the TG plateau before the decomposition of the unsolvated compound.

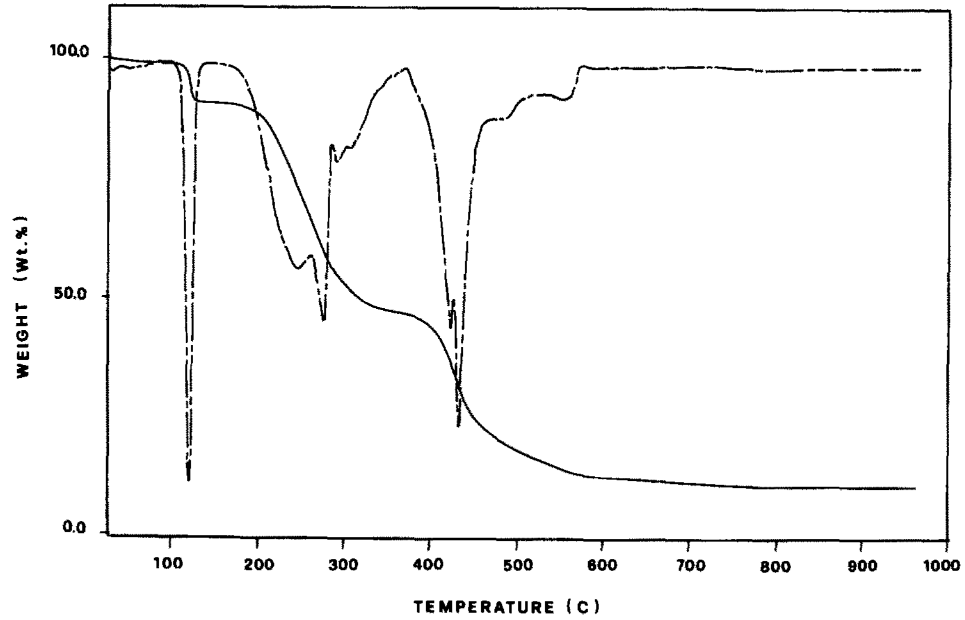


Fig. 7. TG and DTG curves of compound IV: air atmosphere; heating rate, 10°C min^{-1}.

Compound V is the only unsolvated compound. Its decomposition behaviour is represented in Fig. 9, when the freshly prepared compound is obtained from compounds II and III, becoming with time identical to other

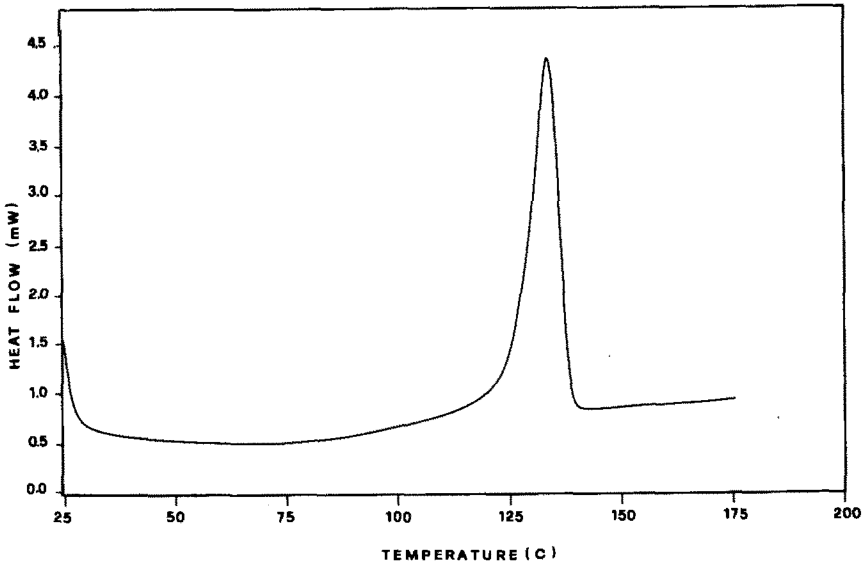


Fig. 8. DSC curve of compound IV: air atmosphere; heating rate, 10°C min^{-1}.

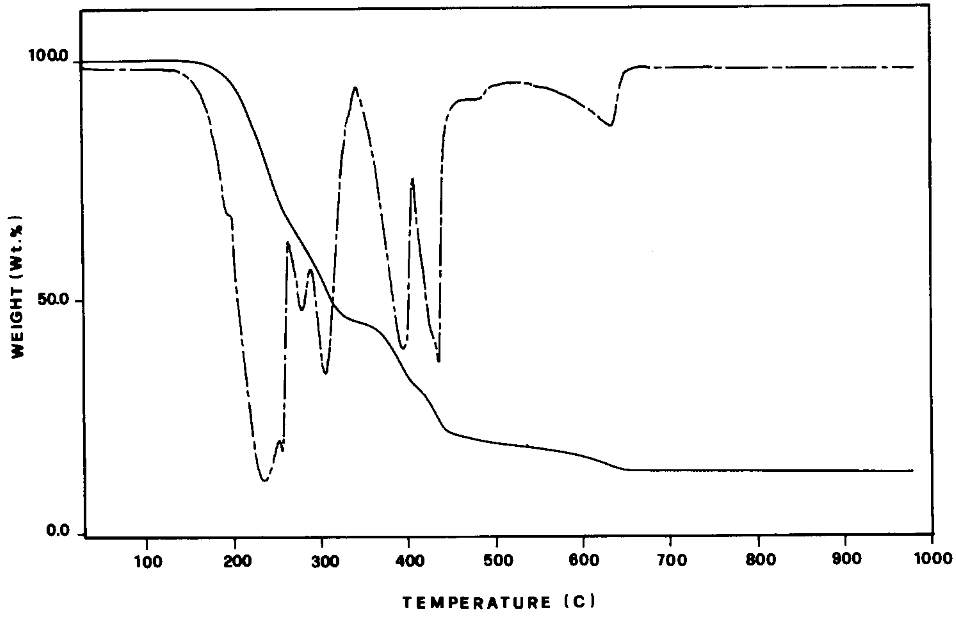


Fig. 9. TG and DTG curves of compound V: air atmosphere; heating rate, 10°C min^{-1}.

compounds when they are 28 days old. If compound **V**, on the other hand, is prepared from compound **IV**, as in Scheme 1 (stage h), its thermal behaviour immediately appears to be the same as that of the unsolvated compound **IV**.

In order to obtain compound **VI**, Goodgame et al. [4] suggest that compound **II** be heated at 75°C.

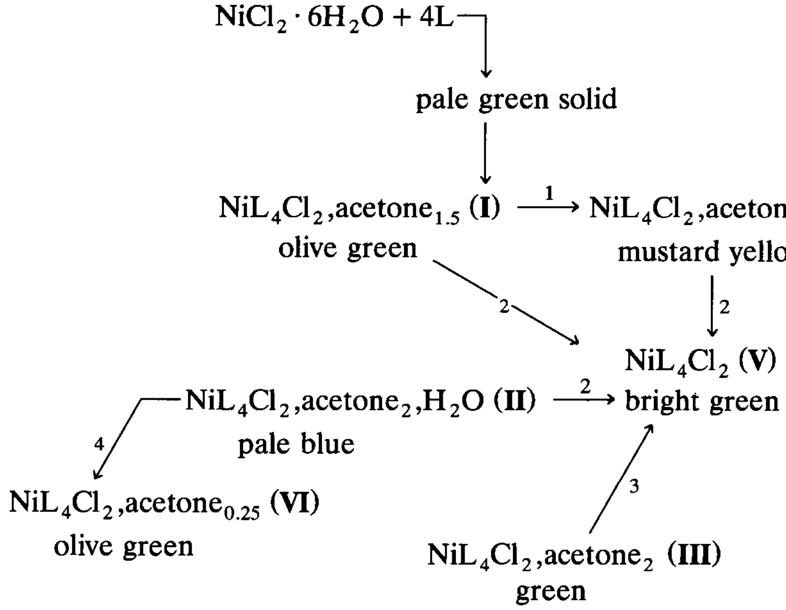
From the TG and DSC curves of compound **II**, it may be noted that isothermal heating at 75°C of compound **II** implies the elimination of one water molecule and of 1.75 acetone molecules, subsequently obtaining an $NiL_4Cl_2 \cdot 0.25$acetone like compound.

The suggested preparation process was carried out on a thermobalance, working in isothermal mode at 75°C, and compound **VI** was obtained after 6 h, with an experimental weight loss of 16.2% (theoretical, 16.24%).

The thermal behaviour of compound **VI** obviously follows the thermal behaviour of compound **II** after the first part of the desolvation process.

DISCUSSION

Our experimental data show that the compounds investigated are not a series of isomers, but one compound in different solvation states. A new series can therefore be represented (Scheme 2) where some new ways of preparation are also shown.



Scheme 2. Key: 1, TG in isothermal mode at 100°C; 2, TG in isothermal mode at 120°C or in dynamic mode at 2°C $\min^{-1}$ till a plateau; 3, TG in isothermal mode at 133°C; 4, TG in isothermal mode at 75°C.

The proposed scheme is in agreement with elemental analysis data (Table 1) obtained at present.

Elemental analysis data obtained by Goodgame et al. does not fit very well with the formula proposed in Scheme 1 for compounds **I**, **II** and **VI**. They fit much better with the formula proposed in Scheme 2, especially as far as the analysis of compound **II** is concerned. In this respect, the sum of the percentage contributions of the different atomic species is 96.99, while if the percentage contribution of oxygen is calculated as a difference (100 – the sum of all other species), a value is obtained that agrees quite well with the formula $NiL_4Cl_2 \cdot acetone \cdot H_2O$ proposed in Scheme 2.

Furthermore, the preparation of compound **II** is possible only if 1% water is present, and looking at stages f and g of Scheme 1, it may be noted that the preparation of compound **III** from compound **II** (stage f) is a dehydration induced by the presence of an excess of dry acetone, while stage g occurs only in the presence of 1% water. The preparation conditions proposed by Goodgame et al., very critical when desolvation processes are implied, can be easily explained by the thermoanalytical curves, where it is easy to see the desolvation processes, so that it is also possible to chose the best thermal conditions in order to obtain the different compounds.

The best procedure for obtaining identical intermediate compounds is direct preparation on TG, working either in isothermal mode as for

TABLE 1

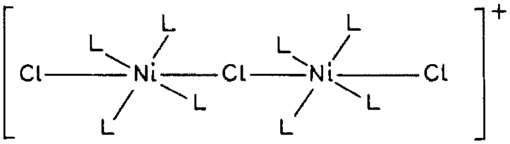
Elemental analysis

	Data of Goodgame et al. [4]			Present data			Theoretical data		
	I	**II**	**III**	**I**	**II**	**III**	NiL_4Cl_2 ·1.5acetone	NiL_4Cl_2 ·2acetone·1H_2O	NiL_4Cl_2 ·2acetone
C	55.5	54.7	56.75	56.4	55.5	56.7	56.63	55.45	56.85
H	5.0	5.05	4.85	4.9	5.3	5.1	4.82	5.20	5.05
Cl		9.6		10.3	9.6	9.8	10.29	9.63	9.87
N		15.4		16.1	15.3	15.5	16.26	15.22	15.60
Ni	8.2	8.0	8.15	8.7	8.0	8.3	8.51	7.97	8.17
O	4.3	4.24	4.5	3.6	6.3	4.6	3.48	6.52	4.45
	IV	**V**	**VI**	**IV**	**V**	**VI**	NiL_4Cl ·1acetone	NiL_4Cl_2	NiL_4Cl_2 ·0.25acetone
C		55.7	55.9	56.3	55.8	55.9	56.39	55.85	55.99
H		3.8	4.3	4.6	3.9	4.2	4.58	4.02	4.17
Cl	10.6			10.6	11.8	11.6	10.74	11.78	11.49
N				17.1	18.8	18.1	16.97	18.61	18.17
Ni	8.8	9.7	9.8	8.9	9.7	9.5	8.89	9.75	9.52
O	2.4			2.5		0.7	2.42		0.65

compound **VI**, or at low heating rate, then stopping the heating rate at the end of the thermal process of interest. Thus compound **IV** can be prepared by desolvation of compound **I**, either as suggested in Scheme 1 (stage k), or by desolvation on a thermobalance. Therefore when the compound is obtained by TG, it obviously shows the same thermal behaviour as freshly prepared compound **I** after loss of 0.5 acetone molecules. This behaviour changes with time, reaching a steady state at 28 days, whereas when prepared as suggested in Scheme 1, compound **IV** immediately appears to be in a steady state because of the long time necessary for its preparation.

The compounds studied show a characteristic change in TG and DTG thermal behaviour with time; all compounds which are 28 days old show thermal behaviour identical to the TG curve corresponding to the unsolvated compounds.

Looking at the DSC curves, it is possible to see that compounds **II**, **III** and **VI** show a characteristic exothermic process (peak at 145°C) immediately after complete solvent loss, in a temperature range corresponding to a TG plateau. This exothermic process accounts for a structural rearrangement towards a more stable structure. Therefore, as suggested by Drew et al. [5], compound **III** exhibits a dimeric cationic structure as shown in Scheme 3.



Scheme 3.

Its electronic spectrum (Table 2) shows band energies that can also be fitted with the energy-level scheme for square-pyramidal nickel(II) [6] although nickel ions in this compound are hexacoordinate.

Comparing benzimidazole complexes with those of pyridine, it seems that the increased steric requirement of benzimidazole results in a longer axial bond with a reduced axial field. The transition $^3B_1 \rightarrow {}^3B_2$ at 11400 cm^{-1}, representing the in-plane ligand field, has the same energy as that of compounds **I**, **II** and **IV**. This suggests that the major difference among the various forms lies in their axial field strength.

The electronic spectra of compounds **I**, **IV** and **V** still account for a distorted octahedral structure; looking at the axial field of these compounds, it may be noted that the axial field energy is higher than that for compounds **II** and **III**. Moreover, compounds **I**, **IV** and **V** respectively show one band at 21300 cm^{-1} (**I**), 21600 cm^{-1} (**IV**) and 21300 cm^{-1} (**V**), when prepared by TG from the freshly obtained compound **IV** (Table 2), corresponding to the main electronic band of a diamagnetic NiL_4Br_2 complex

TABLE 2

Reflectance spectra

Compound	Frequency (cm^{-1})						
I	25200	21300	15350	≈ 12850 sh	≈ 11000 sh		6000
II	25900	≈ 20800	16100	≈ 13600 sh	11400	8000	
III	25000	≈ 20800 w	15400	≈ 12800 sh	≈ 11400 sh	≈ 8800 wsh	6100
IV	≈ 25100	21600	16100	≈ 13000 sh	≈ 11500 sh	≈ 8800 wsh	7100
V (from compound IV)		21300		12500 w			
V (from compounds II and III)	24900	20800 sh	15200	≈ 12500 sh	≈ 11600 sh	9900	5700
VI	24200	20000 sh	14400		≈ 11650	≈ 8800 wsh	6900

[4]. On the contrary, compound **V** obtained in stages i or l of Scheme 1 shows electronic spectral behaviour consistent with the spectra of compounds **II** and **III**, where there is no band at 21 300 cm^{-1}.

In the DSC curve of compounds **II** and **III** there appears to be an exothermic process, narrow and symmetrical (peak at 145°C), corresponding to a TG plateau, and suggesting a structural rearrangement. Presumably the quantity of solvent has an influence on the structure of different compounds. The structure is also correlated with the possible formation of hydrogen bonds between –NH, chloride and acetone molecules, so that two different structures become possible: (a) a dimeric cationic structure proposed by Drew et al.; (b) a monomeric structure where both the axial positions are occupied by chloride ions.

The DSC endothermic peak at 145°C could account for an anation reaction where the free chloride ion enters the coordination sphere to give the monomeric structure. This hypothesis is also supported by the thermal and IR spectral behaviour of these compounds. As shown by TG and DSC curves, especially for compound **II**, solvent interaction with the complex crystal structure changes with time. The acetone band of the freshly prepared compound, at 1628 cm^{-1}, suggests a strong interaction of acetone. This is probably due to hydrogen bonding between benzimidazole and acetone molecules involving the pyrrolic nitrogen atom of the imidazole ring and the carbonyl group of acetone.

As suggested by Nakanishi and Saloman [7], when intramolecular hydrogen bonds are formed, bands may be shifted lower than 50 cm^{-1} (Fig. 10a). After a very short time, the spectral behaviour starts to change and the acetone band moves towards higher frequencies, assuming at the end the spectral behaviour shown in Fig. 10b. This accounts for a decrease in the acetone interaction, probably through a break of hydrogen bonding owing

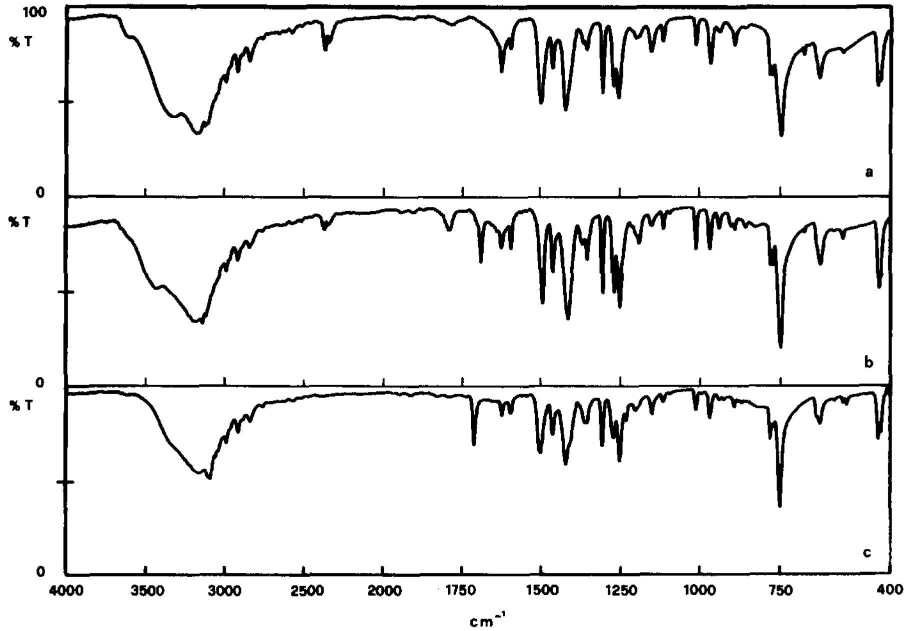


Fig. 10. a, FT-IR spectrum of freshly prepared compound **II**. b, FT-IR spectrum of compound **II** after a short time. c, FT-IR spectrum of compound **IV**.

to structural rearrangement, according to the DSC curves.

Both the freshly prepared compounds **I** and **IV** show one acetone spectral band at about 1700 cm^{-1}, while another weak band at 1732 cm^{-1} is present in the spectrum of compound **I**. With time, while the band at 1732 cm^{-1} changes very slightly and in its intensity only, the band at 1700 cm^{-1} moves to higher frequencies in both compounds, at the end being at 1709 cm^{-1} (Fig. 10c), thus suggesting a low acetone interaction.

This spectral and DSC behaviour is similar for the two compounds: in fact, the value of ΔH of the second endothermic process for compound **I** decreases from 105.08 J g^{-1} to 62.77 J g^{-1}, and compound **IV**, either obtained as suggested by Goodgame et al. or by TG, shows in the steady state for the corresponding process, a ΔH value of 62.27 J g^{-1}. Therefore, a dimeric cationic structure can be suggested for compounds **II**, **III** and **VI**, while a monomeric neutral structure can be suggested for compounds **I**, **IV** and **V**.

The different and inconsistent spectral behaviour of compound **V** can be explained by considering the preparation procedure. From compounds **I** and **IV** is obtained a compound **V** in a monomeric structure, while from compounds **II** or **III**, heating at 130°C, before exothermic transition, compound **V** is obtained in a dimeric structure that changes very slowly with time or changes suddenly through an exothermic process induced by temperature, to give the final monomeric structure.

This hypothesis can also justify the magnetic data obtained by Goodgame et al., which are inconsistent with the formula proposed in Scheme 1, with special reference to a series of compounds of monomeric structure.

ACKNOWLEDGEMENT

Financial support of CNR (National Research Council) and of MURST (Ministry for the University and for Scientific Research) is gratefully acknowledged.

REFERENCES

1 R. Curini, G. D'Ascenzo, G. De Angelis and A. Marino, Thermochim. Acta, 99 (1986) 259.
2 R. Curini, S. Materazzi, G. D'Ascenzo and G. De Angelis, Thermochim. Acta, 161 (1990) 297.
3 R. Curini, S. Materazzi and G. D'Ascenzo, Thermochim. Acta, 164 (1990) 237.
4 D.M.L. Goodgame, M. Goodgame and M.J. Weeks, J. Chem. Soc. A, (1967) 1125.
5 M.G.B. Drew, D.H. Templeton and A. Zalkin, Inorg. Chem., 7 (1968) 2618.
6 M. Ciampolini, Inorg. Chem., 5 (1966) 35.
7 K. Nakanishi and P.H. Solomon, Infrared Absorption Spectroscopy, 2nd edn., Holden Day, San Francisco, CA, 1977, p. 38.