

## Nickel(II) benzimidazole bromide complexes: discussion of the proposed isomerism by thermoanalytical investigation

S. Materazzi, G. D'Ascenzo \*, R. Curini and L. Fava

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

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### Abstract

The suggested isomerism of some  $\text{NiL}_4\text{Br}_2$  complexes (where L is benzimidazole) was investigated by thermoanalytical techniques coupled with an FT-IR system and supported by spectroscopic techniques. Starting from compound  $\text{NiL}_4\text{Br}_2 \cdot (\text{acetone})_2$  two main routes of thermal decomposition were found, the first one corresponding to a family of tetragonally distorted octahedral compounds and the second corresponding to square planar complexes. Reflectance and IR spectra were obtained at room temperature.

Analysis of the data supports the theory that in the family of tetragonally distorted octahedral compounds two main structures are possible: (i) a dimeric cationic structure where the axial position is occupied by three bromide ions, one acting as a bridge between two nickel(II) ions while the fourth bromide is the counter ion; and (ii) a monomeric neutral structure where two bromides are in both axial sites. The dimeric structure changes to the monomeric one by a temperature-induced anation reaction.

Two chloroform solvate compounds were also prepared. Desolvation mechanisms are discussed, new procedures are suggested for obtaining the already known compounds, and some new compounds of the series have also been prepared.

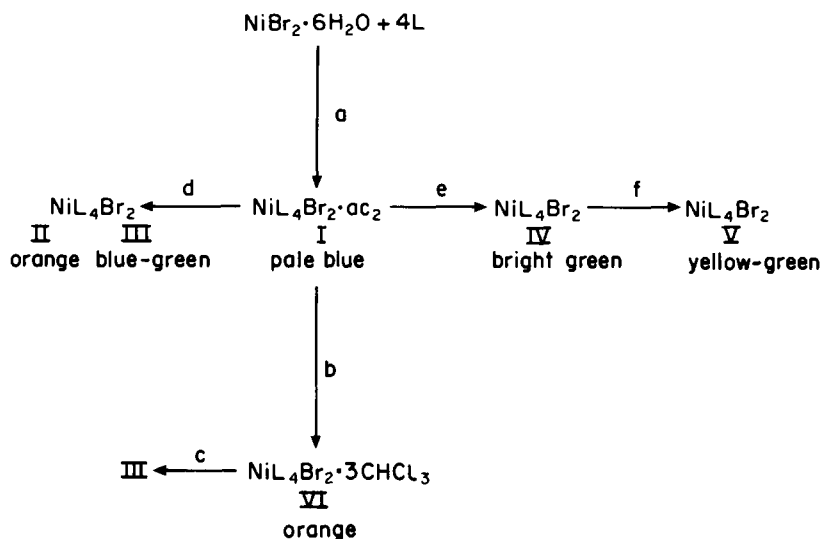
### INTRODUCTION

The tendency of bivalent nickel to give rise to isomeric species is well known, and of particular interest are the isomers of Ni(II) coordination compounds obtained by reaction with sterically hindered heterocyclic nitrogen ligands. By suitable choice of the surrounding chemical environment, different stereochemical reaction routes can be realized.

Goodgame et al. [1] report the preparation and some properties of a series of isomers of nickel(II) complexes with benzimidazole (L) as ligand of the type  $\text{NiL}_4\text{Br}_2$ . Acetone and chloroform solvates have also been isolated. Preparation conditions are critical, as the authors say, and "this was particularly true for the process of desolvation of  $\text{NiL}_4\text{Br}_2 \cdot (\text{acetone})_2$ ,

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\* Corresponding author.



Scheme 1. Key: a, reflux 4 h in acetone; b, under  $\text{CHCl}_3$  in sealed tube for several months; c, heat at  $110^\circ\text{C}$ ; d, heat at  $140^\circ\text{C}$  in an uncapped weighing bottle (VIII) or in a drawn-out ignition tube (IX); e, heat at  $140^\circ\text{C}$ , then at  $160^\circ\text{C}$ ; f, cool to room temperature.

and the procedure to obtain a given desolvation product is difficult to define precisely". Scheme 1 shows the complexes obtained in the above study [1] and their interrelationships. Each compound is identified by a roman numeral.

Previous papers of this series [2–5] have shown that different parameters, such as  $\sigma$  and  $\pi$  electronic charge, steric factors, hydrogen bonding, choice of anion and the solvent forming the reaction environment, influence the compounds' stereochemistry.

Thermoanalytical methods, also associated with spectroscopic techniques, appear to be a suitable tool for an analytical study of these compounds, especially to elucidate such problems as desolvation processes and correlation between the proposed isomerism and some incongruities in the obtained data.

## EXPERIMENTAL

### Instrumentation

A Perkin-Elmer thermobalance (model TGA7) coupled with a Perkin-Elmer FT-IR spectrometer (model 1760X) and differential scanning calorimeters (models DSC-2B and DSC7) each equipped with a data

station were used. The heating rate ranged from isothermal operation to  $10^{\circ}\text{C min}^{-1}$ . The atmosphere was air, nitrogen or argon at a flow rate of  $50\text{--}100\text{ ml min}^{-1}$ . The IR spectra were recorded using a Perkin-Elmer FT-IR spectrometer, model 1760X. 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 Scheme 1, proposed by Goodgame et al. [1], and subsequently were prepared following Scheme 2. The roman numerals in the results and discussion sections refer to Scheme 2.

## RESULTS

The TG, DTG and DSC curves of compound I (Figs. 1 and 2) show that two molecules of acetone are present and are released in four steps, the first corresponding to half a molecule, the second to one molecule, and the sum of the third and the fourth steps, which overall as the TG curve shows, correspond to another half molecule of acetone.

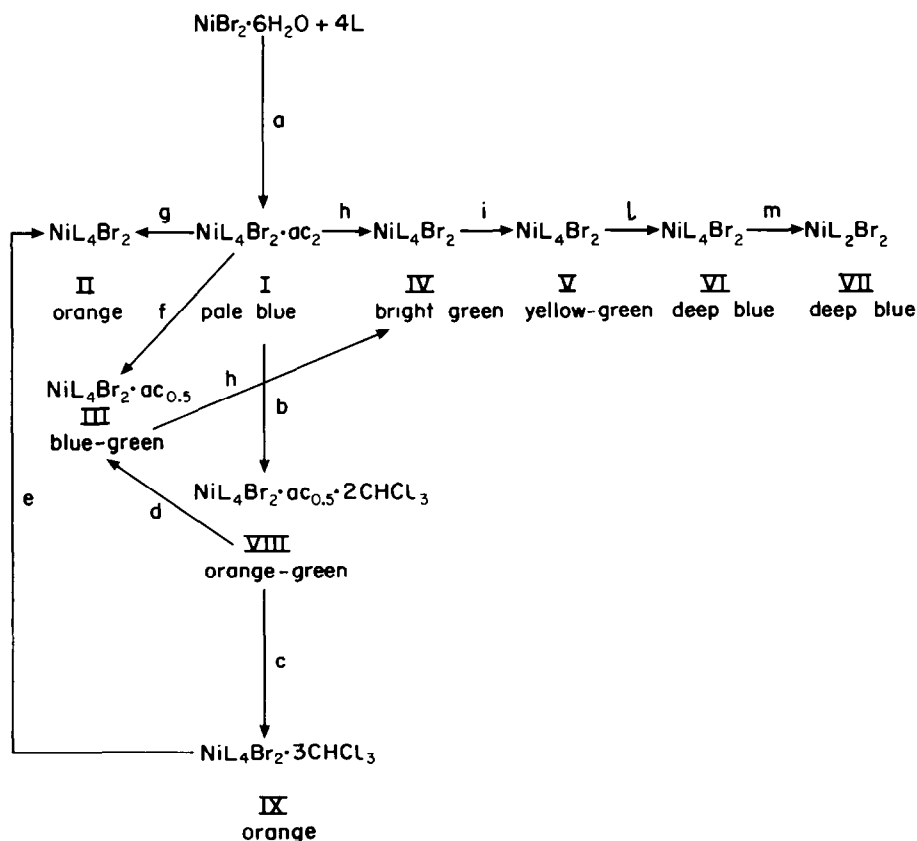
FT-IR spectra of the four stepwise decomposition products confirm that the released vapour comprises only acetone. The unsolvated compound decomposes through a series of incompletely resolved processes losing two molecules of benzimidazole followed by a third molecule of ligand, and then undergoing oxidative decomposition, in an air atmosphere, to give NiO.

Four peaks appear in the DSC curve (Fig. 2) corresponding to the release of acetone, the third one being endo and the fourth exothermic, very overlapped, immediately followed by two other very overlapped endothermic peaks, with maxima at  $157$  and  $170^{\circ}\text{C}$ ; a further peak at  $184^{\circ}\text{C}$  corresponds to the melting process. Figure 3 shows the FT-IR spectra as a function of the temperature corresponding to acetone release.

Thermoanalytical study was also carried out, monitoring the thermal behaviour with time after leaving the compound in a closed vessel. The thermal release of acetone changes with time; at 30 days (Fig. 4(a)) a new peak appears at  $69^{\circ}\text{C}$  and the areas of the first and second peaks at  $84$  and  $101^{\circ}\text{C}$  decrease.

After ageing the compound the acetone content undergoes further reduction, also changing (Fig. 4(b)) the shape of the curve. At 90 days the solvent present corresponds to one molecule of acetone.

The unsolvated compound II decomposes (Fig. 5) via a series of highly



Scheme 2. Key: a, reflux 4 h in acetone; b, reflux in  $\text{CHCl}_3$  in presence of trace of acetone for 1 h; c, reflux in  $\text{CHCl}_3$  for several weeks; d, heat on the TG apparatus until chloroform removal; e, heat on TG until chloroform removal; f, heat on TG until the loss of 1.5 acetone molecules; g, heat on TG in a large, flat crucible in isothermal mode at  $135^\circ\text{C}$  to constant weight; h, heat on the DSC instrument at  $175^\circ\text{C}$  until the end of the corresponding endothermic process; i, cool, with shaking, to room temperature; l, heat just after the melting point and then cool; m, heat on TG to removal of the first two benzimidazole molecules.

overlapped steps and the decomposition starts releasing benzimidazole, as shown by analysis of the collected thermal decomposition deposit represented by a sublimed white powder corresponding to undecomposed benzimidazole. The residual NiO percentage corresponds to a formula of  $\text{NiL}_4\text{Br}_2$ . On the DSC curve before decomposition, still represented by a series of very overlapped processes, only one endothermic peak corresponding to melting appears.

Compound III loses (Fig. 6) 0.5 molecule of acetone, as confirmed by the FT-IR spectra of the evolved gas, in the temperature range  $130\text{--}152^\circ\text{C}$ . Two molecules of benzimidazole are lost in the first thermal decomposition step of the unsolvated compound, and a third is lost before the oxidative

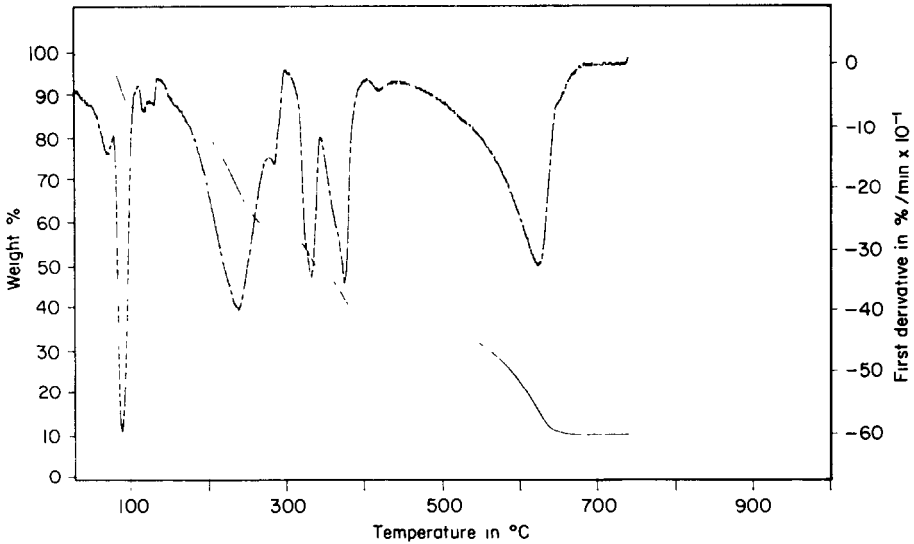


Fig. 1. TG and DTG curves of compound I: air atmosphere; heating rate,  $10^{\circ}\text{C min}^{-1}$ .

reaction, which in air yields nickel oxide. The DSC curve (Fig. 7) shows a first endothermic peak in correspondence with the TG step for acetone loss overlapped by an exothermic one and immediately followed by two other highly overlapping endothermic peaks. Finally, an endothermic peak, corresponding to melting, appears at  $184^{\circ}\text{C}$ .

Compound IV is unsolvated and the first part of the TG and DTG curves

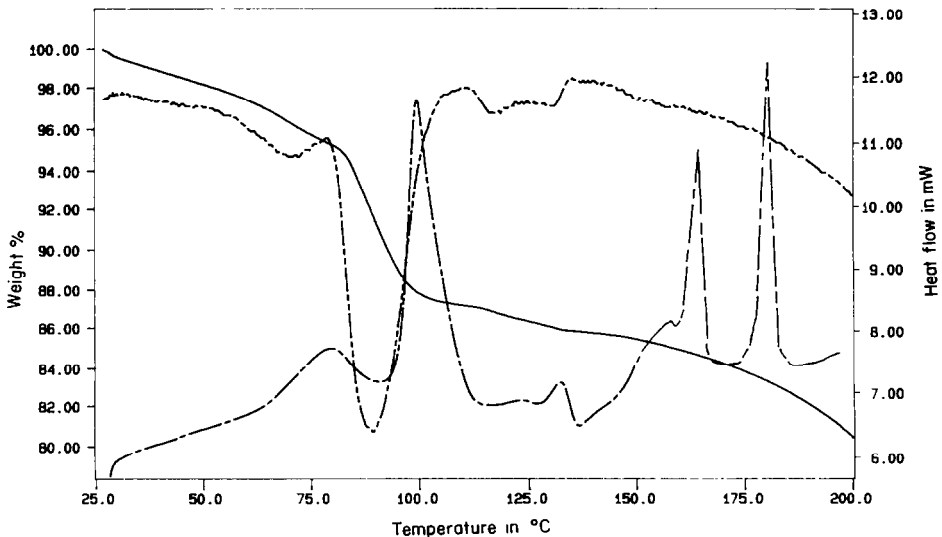


Fig. 2. TG, DTG and DSC curves of compound I: nitrogen atmosphere; heating rate,  $10^{\circ}\text{C min}^{-1}$ .

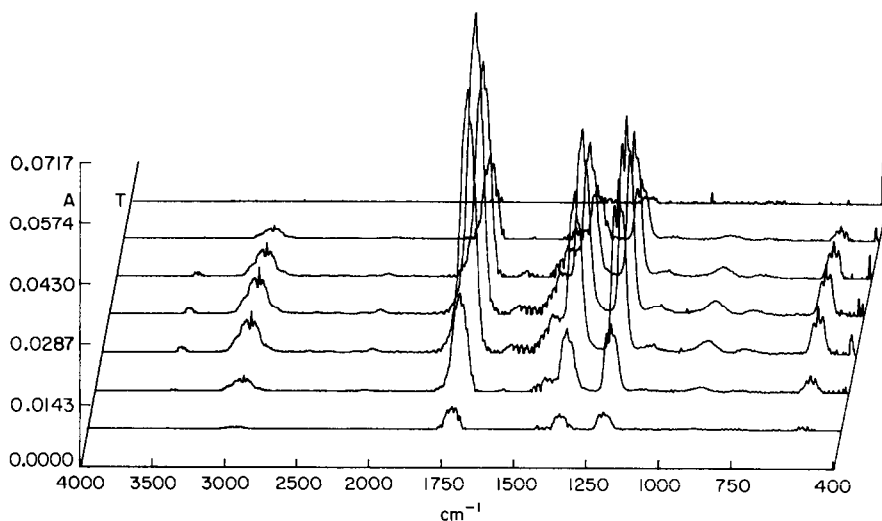


Fig. 3. FT-IR spectra of the evolved gas of compound I as a function of the temperature in nitrogen atmosphere.

(Fig. 8) still accounts for a loss of two and then one benzimidazole molecules in thermal decomposition behaviour similar to that of the compounds described before. The oxidative decomposition of the residue follows a different thermal route to give NiO. The DSC curve in the range 25–200°C (Fig. 9) shows only one endothermic peak, with its maximum at 184°C, corresponding to melting.

Compound V is unsolvated and the thermal decomposition (Fig. 10) still corresponds initially to the loss of two benzimidazole molecules; the TG and DTG curves then show a series of superimposed processes that lead, in an air atmosphere, to NiO. In the DSC curve (Fig. 11) only two endothermic processes appear: the first has a maximum at 148°C, located in a thermal region where no processes appear in the TG, DTG and TG–FTIR curves, and the second at 184°C corresponding to melting.

The deep-blue compound VI obtained by cooling immediately after melting is a vitreous form of  $\text{NiL}_4\text{Br}_2$  and obviously shows the thermal behaviour of the series of compound I, III and IV after melting.

Compound VII, deep-blue, which is obtained by thermal decomposition of compound I, III, IV or V after the liberation of two benzimidazole molecules, has the formula  $\text{NiL}_2\text{Br}_2$ .

Compound VIII loses two molecules of chloroform in the range 60–108°C (Fig. 12) and then in two steps loses 0.5 molecule of acetone between 108 and 159°C. FT-IR analysis of the evolved vapour has confirmed the nature of the solvents. The decomposition of the desolvated

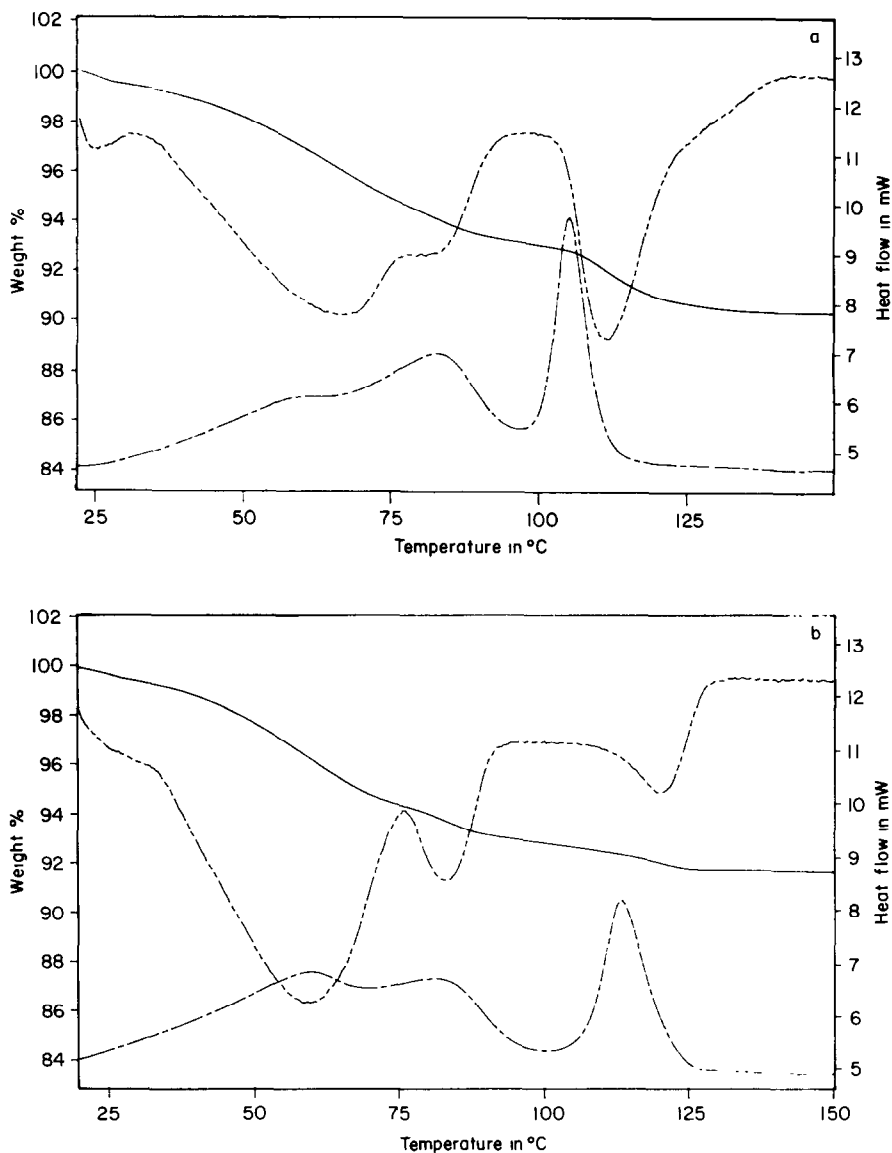


Fig. 4. (a) TG, DTG and DSC curves of compound I after 30 days; nitrogen atmosphere; heating rate,  $10^{\circ}\text{C min}^{-1}$ . (b) TG, DTG and DSC curves of compound I after 90 days; nitrogen atmosphere; heating rate,  $10^{\circ}\text{C min}^{-1}$ .

compound happens exactly in the same way as that of compound III. The first endothermic peak in the DSC curve (Fig. 13), in a nitrogen atmosphere, corresponds to the release of two chloroform molecules and is followed by two peaks, the first endo and the second exothermic, corresponding to the release of acetone.

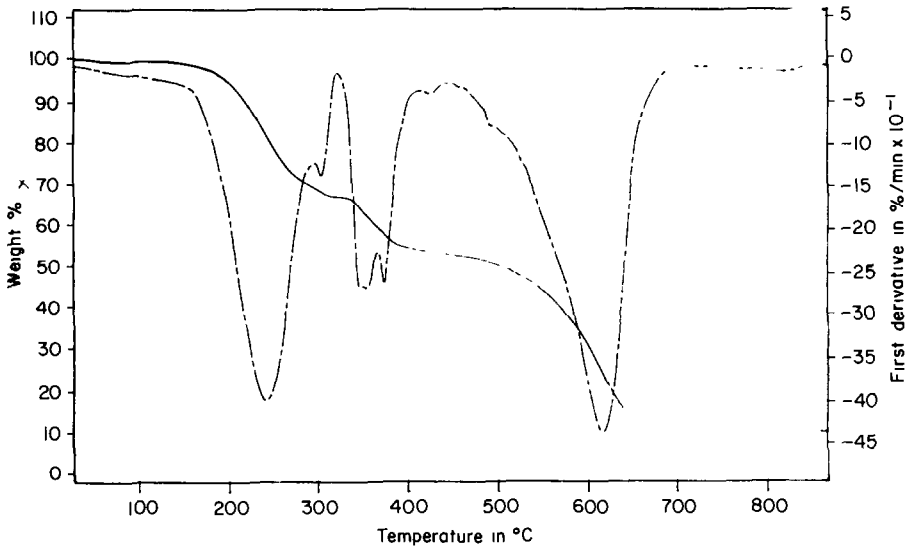


Fig. 5. TG and DSC curves of compound II: air atmosphere; heating rate  $10^{\circ}\text{C min}^{-1}$ .

With time, the interaction of the solvents with the complex changes: the amount of chloroform decreases (Fig. 14) after 15 days and the release of this solvent is split into two processes: a first slight one starting at ambient temperature followed by a second much more pronounced process in the same temperature range as for the freshly prepared compound; there then

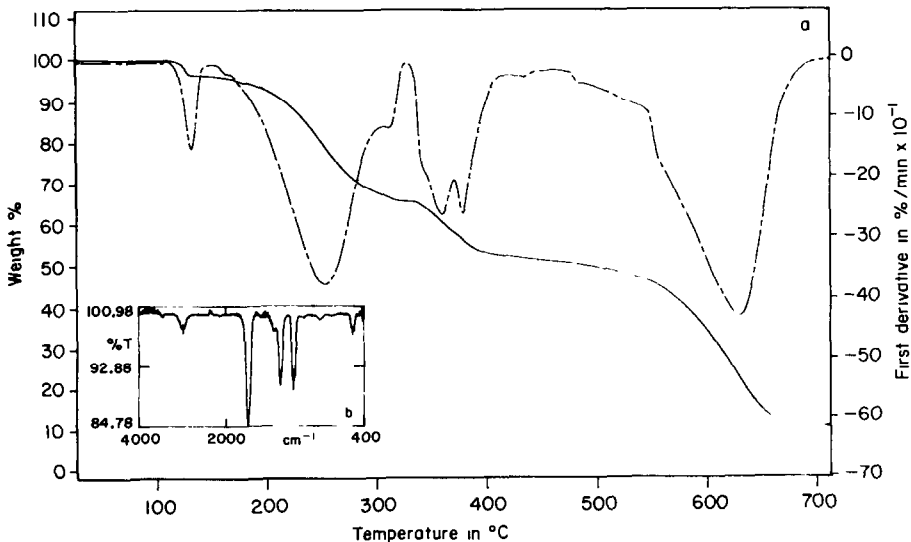


Fig. 6. (a) TG, DTG curves of compound III: air atmosphere; heating rate  $10^{\circ}\text{C min}^{-1}$ ; (b) FT-IR spectrum of the evolved solvent; nitrogen atmosphere.



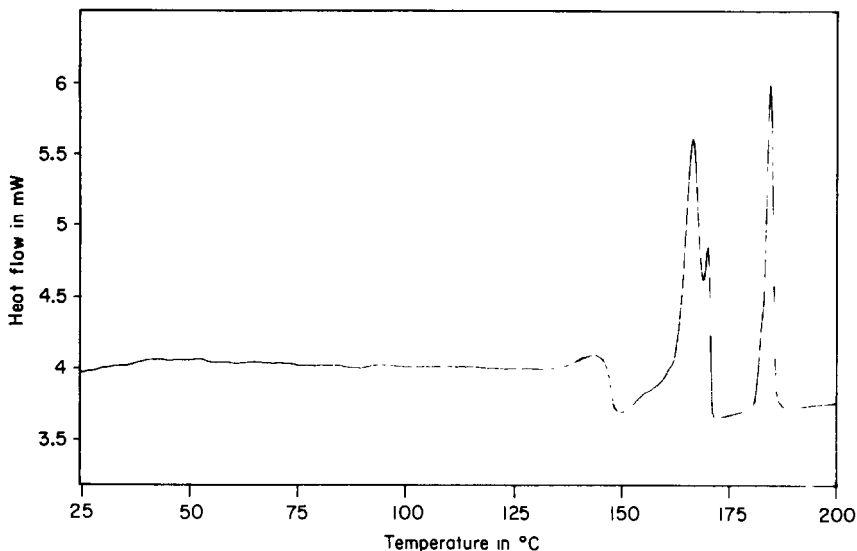


Fig. 7. DSC curve of compound III: nitrogen atmosphere; heating rate  $10^{\circ}\text{C min}^{-1}$ .

appears an endothermic peak overlapped by an exothermic one in a nitrogen or argon atmosphere. Finally, at  $184^{\circ}\text{C}$  the melting peak appears.

Compound IX loses three molecules of chloroform in the range  $60\text{--}110^{\circ}\text{C}$  (Fig. 15), as confirmed by TG–FT-IR analysis. The remaining unsolvated compound follows exactly the same trend of that of compound II. In the DSC curve only one endothermic peak appears corresponding to chloroform release, followed only by a melting process as for compound II.

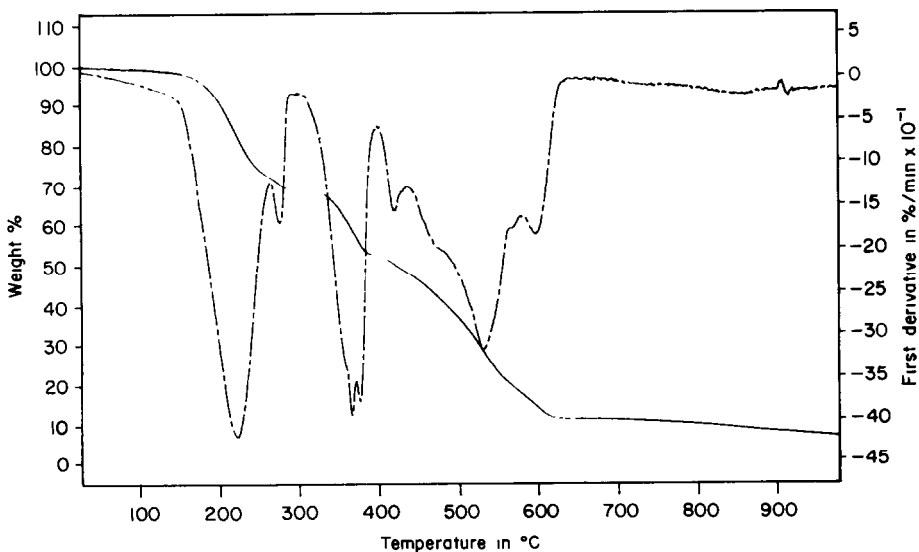


Fig. 8. TG and DTG curves of compound IV: air atmosphere; heating rate  $10^{\circ}\text{C min}^{-1}$ .

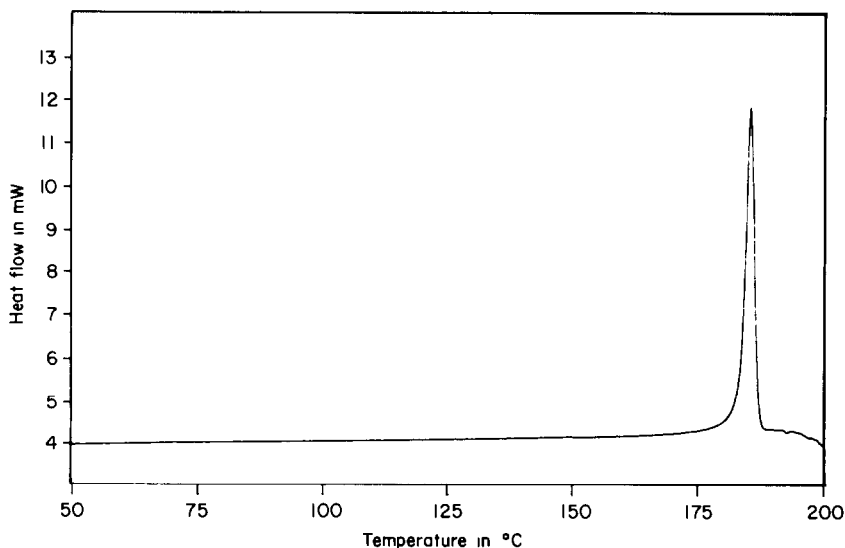


Fig. 9. DSC curve of compound IV: nitrogen atmosphere; heating rate  $10^{\circ}\text{C min}^{-1}$ .

After ageing the compound, the release of chloroform is split in two processes, but nothing changes in the remaining part of the curves.

## DISCUSSION

The experimental data obtained do not completely agree with Scheme 1 as proposed by Goodgame, but some compounds show thermoanalytical behaviour corresponding to the different solvation states as proposed in Scheme 2, where some new means of preparation are also suggested. The proposed scheme is in agreement with the obtained elemental analysis data.

The preparation conditions proposed by Goodgame et al. [1], which are highly critical, particularly for the process of desolvation of  $\text{NiL}_4\text{Br}_2 \cdot (\text{acetone})_2$ , can be discussed by means of an analysis of the TG, DTG and DSC curves of the compounds.

As can be seen from Scheme 2, all compounds are prepared starting from compound I, and the different proposed ways of preparation, except that corresponding to stages b and c (Scheme 2), can be discussed in terms of the thermal behaviour of this compound.

On heating compound I at  $115^{\circ}\text{C}$  in a nitrogen atmosphere, compound III is obtained by the release of 1.5 molecules of acetone; this desolvation must be carried out very carefully.

Compounds I and III have electronic spectra (Table 1) typical of nickel(II) ions in a tetragonally distorted octahedral environment.

Compound IV is obtained by heating compound I or II at  $175^{\circ}\text{C}$ , a temperature immediately following the very overlapped endothermic peaks and located before the melting process at  $184^{\circ}\text{C}$ . Looking at the DSC

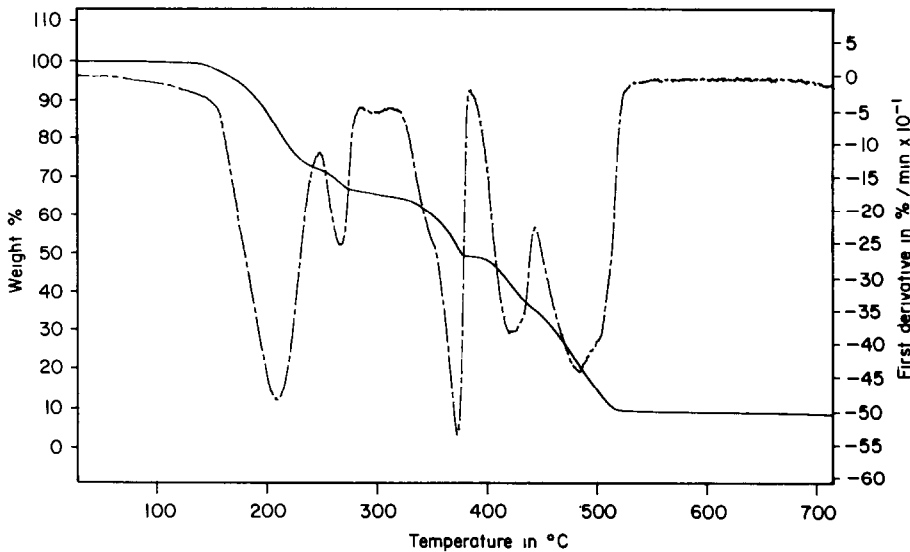


Fig. 10. TG and DTG curves of compound V: air atmosphere; heating rate  $10^{\circ}\text{C min}^{-1}$ .

curves, it is possible to see that compounds I and III show an exothermic process (peak at  $148^{\circ}\text{C}$ ), in a nitrogen or argon atmosphere, overlapping the endothermic peak corresponding to the last acetone release. As for  $\text{NiL}_4\text{Cl}_2 \cdot (\text{acetone})_2$  [5–7],  $\text{NiL}_4\text{Br}_2 \cdot (\text{acetone})_2$  also probably has a dimeric cationic structure as shown in Scheme 3, and the exothermic process corresponds to an anation reaction to give the monomeric neutral species  $\text{NiL}_4\text{Br}_2$ , compound IV.

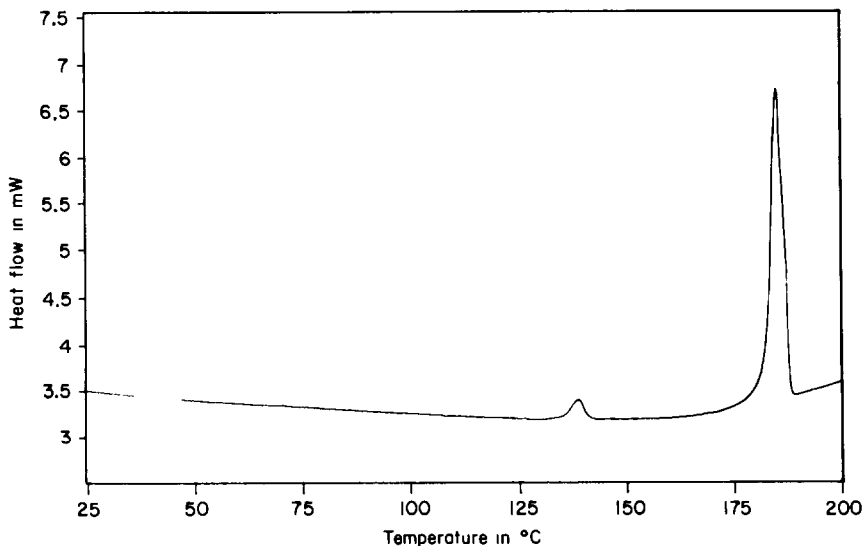


Fig. 11. DSC curve of compound V: nitrogen atmosphere; heating rate  $10^{\circ}\text{C min}^{-1}$ .

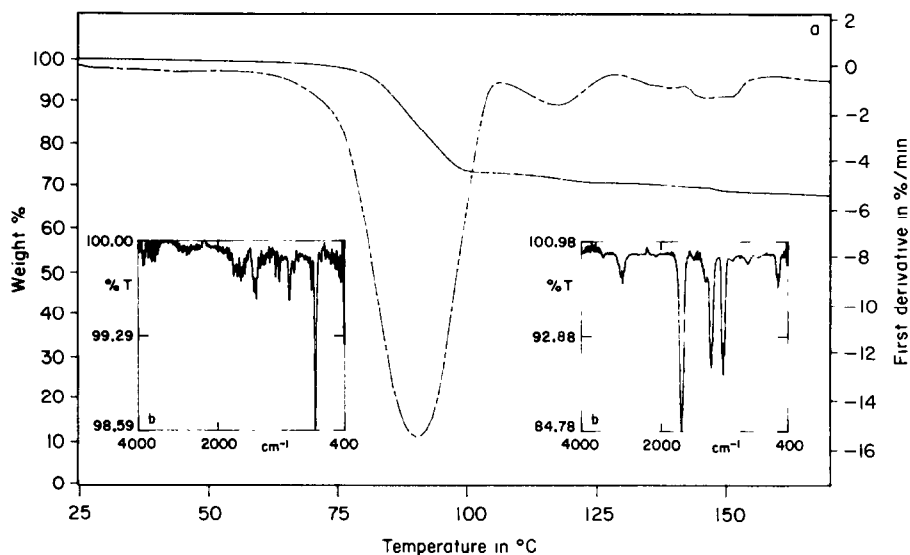


Fig. 12. (a) TG, DTG curves of compound VII: air atmosphere; heating rate  $10^{\circ}\text{C min}^{-1}$ ; (b) FT-IR spectra of the evolved solvents; nitrogen atmosphere.

The anation reaction is induced by time also, as shown by the ageing of compound I. In fact, in the DSC curves of compound I that is 30 and 90 days old, the exothermic peak corresponding to the anation reaction has disappeared.

By cooling and shaking the bright-green compound IV, the yellow-green compound V is obtained. The DSC cooling curve of compound IV

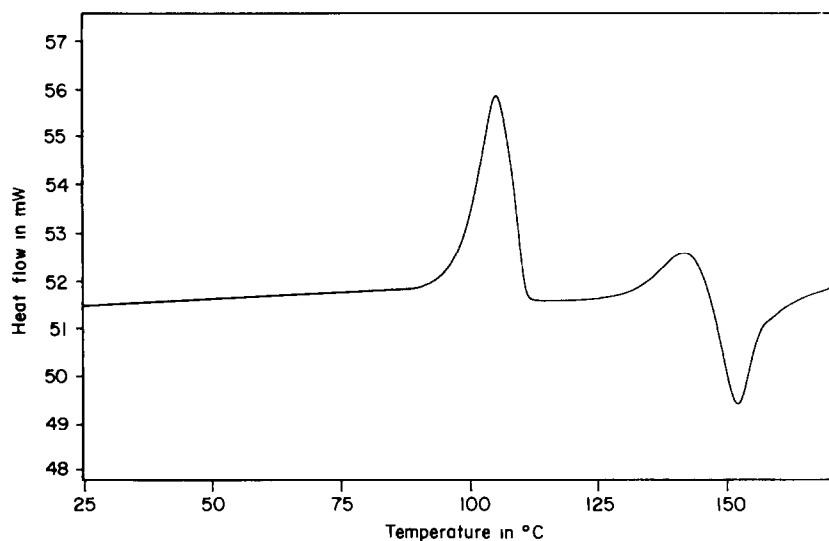


Fig. 13. DSC curve of compound VII: nitrogen atmosphere; heating rate  $10^{\circ}\text{C min}^{-1}$ .

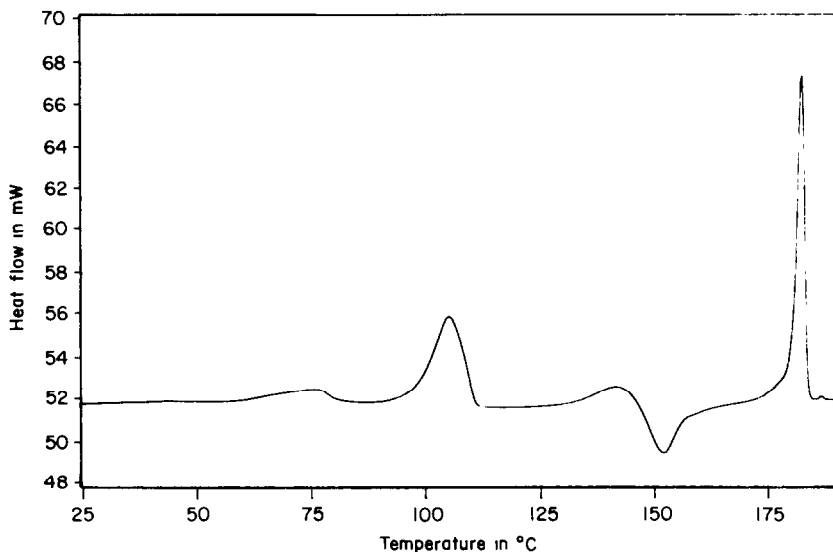


Fig. 14. DSC curve of compound VIII after 15 days; nitrogen atmosphere; heating rate  $10^{\circ}\text{C min}^{-1}$ .

(obviously obtained without shaking) does not show any discernible process. The DSC heating curve of compound IV shows only one endothermic peak at  $184^{\circ}\text{C}$  corresponding to melting, whereas in the DSC heating curve of compound V an endothermic peak at about  $160^{\circ}\text{C}$  appears,

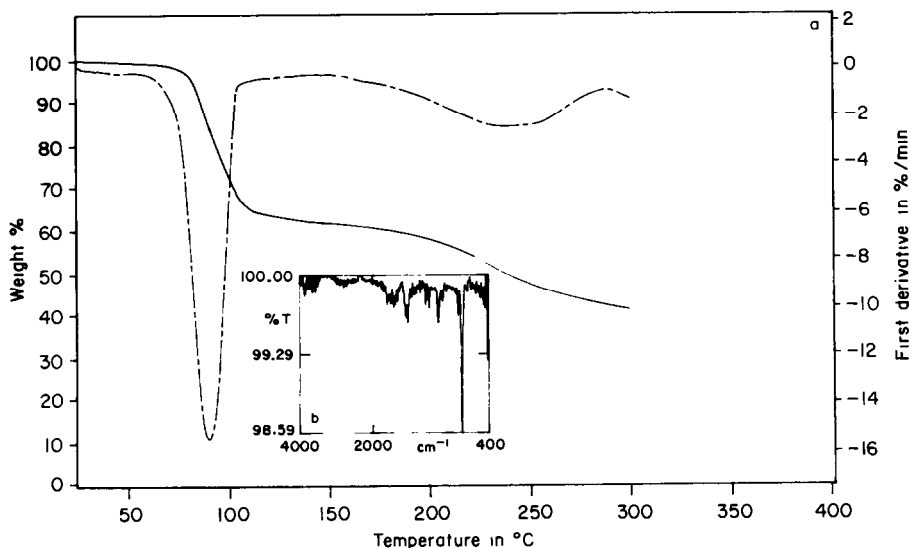


Fig. 15. (a) TG and DTG curves of compound IX: air atmosphere; heating rate  $10^{\circ}\text{C min}^{-1}$ ; (b) FT-IR spectrum of the evolved solvent; nitrogen atmosphere.

TABLE 1  
Reflectance spectra

Compound	Wavenumber/cm <sup>-1</sup>						
I	26300	20800w	16250	13700	11900		7800
II		21300		12500br, w			
III	25000	20000w	15600	13000sh	11100sh	8800w, sh	7250
IV	25100	20800sh	15200	12500w, sh	11400w, sh	9600	6300br
V	27700	25100sh	19700w	15300	12600	10500	8800w, sh
VI		24800	20000sh	15200	12500sh	11500sh	9900
VII			21700sh	17250	11700sh	10420	6800br
VIII	25100	20000w	15700	13000sh	11050sh	8800w, sh	7250
IX		21300		12700br, w			

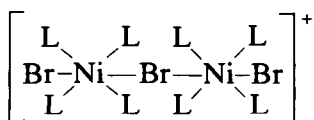
corresponding to a thermochromic transition to the bright-green compound IV.

By stopping heating immediately after melting, a deep-blue fluid is obtained that, on cooling gives a vitreous and hygroscopic deep-blue NiL<sub>4</sub>Br<sub>2</sub> complex which by simply crushing, gives a yellow–green complex with thermal and spectral characteristics corresponding to those of compound V. At 300°C on the TG curve, after a loss of two benzimidazole molecules, a deep-blue complex is obtained with the formula NiL<sub>2</sub>Br<sub>2</sub>.

The electronic spectrum of NiL<sub>2</sub>Br<sub>2</sub> (Table 1) permits the assignment to it of an essentially tetrahedral structure. The bands at 10 420 and 17 250 cm<sup>-1</sup> can be assigned as <sup>3</sup>T<sub>1</sub>(F) → <sup>3</sup>A<sub>2</sub> and <sup>3</sup>T<sub>1</sub>(F) → <sup>3</sup>T<sub>1</sub>(P) transitions respectively.

The IR spectrum of freshly prepared acetone solvated compound I shows the presence of a band at 1701 cm<sup>-1</sup> and another at 1728 cm<sup>-1</sup> ascribed to the C=O stretch of acetone, but in the IR spectrum of compound III only a 1701 cm<sup>-1</sup> band appears. With time the spectrum of compound I changes and the band at 1701 cm<sup>-1</sup> decreases in intensity until disappearing after 30 days; the band at 1730 cm<sup>-1</sup> changes too, with an intensity according with the thermal behaviour of acetone.

The presence of the band at 1701 cm<sup>-1</sup> may be due to an interaction between acetone and benzimidazole, probably at the level of hydrogen bonding involving –NH, bromide and the carbonyl group of acetone. The



Scheme 3.

higher hindrance and the lower residual charge of bromide with respect to chloride decreases the acetone–complex interaction.

Looking at the electronic spectra of the tetragonally distorted octahedral  $\text{NiL}_4\text{Cl}_2 \cdot (\text{acetone})_2$  [5],  $\text{NiL}_4\text{Br}_2 \cdot (\text{acetone})_2$  and  $\text{NiL}_4\text{Br}_2 \cdot (\text{acetone})_{0.5}$ , it is possible to see that the in plane ligand field is similar but slightly weaker for  $\text{NiL}_4\text{Br}_2 \cdot (\text{acetone})_{0.5}$ , whereas the axial field is stronger for  $\text{NiL}_4\text{Cl}_2 \cdot (\text{acetone})_2$ . The benzimidazole molecules will probably be forced, for steric reasons, to lie with their molecular planes at an angle to the  $\text{NiL}_4$  plane. There will therefore be some steric hindrance to the approach of larger anions resulting, because of the increased steric requirement and lower charge of bromide, in a longer nickel–bromide bond, so weakening the complex–acetone interaction.

Compound II can sometime be obtained by heating a massive quantity of compound I at 140°C in an uncapped weighing bottle, as suggested by Goodgame, but commonly a mixture has been obtained. By thermal methods, by heating compound I in a large, flat crucible in isothermal mode in a nitrogen atmosphere at 135°C to constant weight, compound II is obtained.

Looking at the two different thermal pathways of compound I, stages f and g correspond to desolvation processes, but although the electronic spectra of compound II, with a spectral band at 21 300  $\text{cm}^{-1}$  and another much weaker one at about 12 500  $\text{cm}^{-1}$  are consistent with a square planar environment, compound III, like compound I, has an electronic spectrum typical of a tetragonally distorted octahedral structure, so whereas step f is only a desolvation process, step g also involves a structural change.

Looking at the thermal behaviour and ageing of chloroform solvated compounds VIII and IX, compound VIII, when freshly prepared, loses two molecules of chloroform, and then the remaining half molecule of acetone is released via two overlapping steps.

The TG, DTG and DSC curves of compound VIII that is 15 days old show a very different way of thermal desolvation, where only one molecule of chloroform is still present and the remaining half molecule of acetone is released in only one step; the TG and DTG curves are exactly similar to those of compound III. The DSC curve after the chloroform release shows exactly the same behaviour as the curve of compound III, losing the half acetone molecule through an endothermic peak overlapped by an exothermic one corresponding to the anation reaction (Fig. 4(b)) as for compounds I and III.

Compound IV loses the three chloroform molecules in a single step to give compound II. So the chloroform solvation process happens by steps through a replacement of the acetone molecules, and when the last half molecule of acetone is extracted by chloroform the structure changes from a tetragonally distorted octahedral to a planar one, accounting for the influence of acetone on the structure.

The electronic spectrum of compound VIII (Table 1) is attributable to a tetragonally distorted octahedral environment similar to that of compounds I and III.

In the electronic spectrum of compound IX, only two bands appear, at  $21\,300\text{ cm}^{-1}$  and at  $12\,700\text{ cm}^{-1}$ ; the latter is much the weaker. The spectrochemical behaviour of compound IX indicates a square planar structure of the same type as for compound II.

Two different independent thermal pathways can be identified concerning compound I: (a) by loss of 1.5 molecules of acetone, dimeric compound I gives a dimeric compound III which, by loss of the remaining 0.5 molecule of acetone and through an exothermic anation reaction, gives the monomeric compound IV; (b) by complete loss of the two acetone solvation molecules, compound I gives the square planar compound II. This hypothesis is supported by the behaviour of chloroform solvated compounds, which, by the extraction of acetone by chloroform, are formed in two similar ways, giving in presence of the residual half molecule of acetone a tetragonally distorted octahedral compound VIII, and after complete extraction of acetone a square planar compound IX.

#### ACKNOWLEDGEMENT

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