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THERMAL BEHAVIOUR OF BIOLOGICALLY INTERESTING COORDINATION COMPOUNDS OBTAINED BY REACTION OF SOME DIVALENT METAL IONS WITH IMIDAZOLE AND *N*-METHYL IMIDAZOLE

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ABSTRACT

The imidazole ring appears in a number of biological ligands and many different parameters, such as basicity of the ligands, π-electron acceptor ability, steric factors, hydrogen bonding, etc., play an essential role either on the structural types of coordination or on the thermal characteristics of the coordination compounds obtained by reaction of imidazole and its derivatives with transition metal ions.

The influence of some of these parameters on the thermal properties of coordination compounds obtained by reaction of imidazole (Im) and *N*-methyl imidazole (NmIm) with $Co(NO_3)_2$, $Ni(NO_3)_2$ and $Cu(NO_3)_2$ is studied here by means of thermogravimetric and differential scanning calorimetric methods supported by infrared spectroscopy. The compounds obtained were $Me(L)_n(NO_3)_2$ (Me=Co(II), Ni(II), Cu(II); $n = 4, 6$).

The imidazole complexes are always more stable than the corresponding *N*-methyl imidazole complexes and the ΔH value corresponding to metal–ligand bond breaking is higher for the imidazole compounds.

The decomposition mechanisms are also discussed.

INTRODUCTION

The imidazole ring functions as a ligand towards transition metal ions in a variety of biologically important molecules. Binding between metal(II) ions and the imidazole ring is represented in nature by several metalloproteins, by vitamin B_{12} and its derivatives, by iron–heme systems, etc.

Imidazole can be considered to be constructed from a trigonal nitrogen with two electrons in the unhybridized *p* orbital (N-1 nitrogen), a trigonal nitrogen with a lone pair in a hybrid orbital and a single electron in the *p* orbital (N-3 nitrogen), and three trigonal carbons each with one electron in a *p* orbital (an aromatic sextet is then available). Imidazole is indeed generally

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TABLE 1

Net charges at the imidazole nitrogen atoms [1]

	σ	π
N-1	-0.84	$+0.40$
N-3	-0.16	-0.10

regarded as being aromatic. The N-3 nitrogen shows weak, negative σ and π electronic charges, and so is a modest electron acceptor [1]. The N-1 nitrogen donates quite a high fraction of electronic charge to the π system, but withdraws a higher fraction of electronic charge from the σ orbitals so that the net result is a gain of -0.44 electronic charge, Table 1 [1].

Concerning the behaviour of imidazole as a ligand, there is only one pair of unshared electrons, the pair on N-3. The electrons of N-1 are part of the aromatic sextet, and the chance of a proton or metal ion binding at N-1 is considered to be very unfavourable. Thus, the neutral molecule of the imidazole shows only one energetically favourable coordination site, the N-3 nitrogen. The activity of the imidazole as a ligand is especially correlated with two properties: basicity and π-electron acceptor capability, and it is convenient to compare the imidazole with ammonia and pyridine. The basicity scale is pyridine < imidazole < ammonia while the π-electron acceptor capability is the reverse of this, and is nil for ammonia.

Looking at the stability constants of these ligands with Co(II), Ni(II) and Cu(II) [2–4], the scales obtained are always pyridine < ammonia < imidazole. That means that imidazole possesses the best combination of the two properties. Besides, in the solid state other parameters take part, such as steric factors, requirement for the imidazole to retain the aromaticity of the ring [5], hydrogen bonding, possibility for polymeric reactions to play an essential role either on the structural types of coordination compounds that can be obtained, or on their thermal characteristics.

The aim of this reserach is to study the influence of these parameters on the thermal characteristics of coordination compounds, obtained by reaction of Co(II), Ni(II) and Cu(II) with imidazole and its derivatives chosen in order to obtain a homogeneous and sequential mutation of the ligand structure, and then of the parameters of interest.

Firstly, we studied the coordination compounds of Co(II), Ni(II) and Cu(II) obtained by reaction with imidazole and *N*-methyl imidazole. *N*-Methyl imidazole exhibits an almost identical pK_a value to that of imidazole and the stability constant values of the complexes of the two ligands studied are the same [6,7], while *N*-methyl imidazole does not show hydrogen bonding [8] and the 1-methyl group should introduce sufficient steric bulk to influence the characteristics of the coordination compounds.

The compounds studied are $Me(L)_x(NO_3)_2$ (Me=Co(II), Ni(II), Cu(II);

L = imidazole (Im), *N*-methyl imidazole (NmIm), $x = 4, 6$). Nitrate has been selected as the counter-ion because of its very low coordination ability with respect to halogen ions and because it shows characteristic absorption bands in its infrared spectrum.

Thermochemical investigations on imidazole compounds are restricted to $Me(Im)_6X_2$ (Me=Co(II), Ni(II); X=Cl, Br, I) $Co(Im)_6(NO_3)_2$ [9], $Ni(Im)_nX_2$ ($n = 1, 2, 4, 6$; X=Cl, Br, I, NCS) [10], $Cu(LH)_nX_2$ (LH = Im, NmIm; $n = 2, 4$; X = Cl, Br) [11] and Pd(II) compounds [12].

EXPERIMENTAL

Instrumentation

A Perkin-Elmer Thermobalance (model TGS-2) and differential scanning calorimeter (model DSC-2b), both equipped with a data station, were used. Heating rate ranged between 2.5 and 10°C min^{-1}. Atmosphere: air or very pure nitrogen (99.99%) at flow rates of 50–100 ml min^{-1}. The IR spectra were recorded using a Beckman IR 12 instrument.

Synthesis of the compounds

Imidazole and *N*-methyl imidazole were obtained from Aldrich Chemical Co., other chemicals employed were of reagent grade.

Imidazole (Im), *N*-methyl imidazole (NmIm), Co(II), Ni(II) and Cu(II) nitrate salts were dissolved in absolute ethanol. To obtain coordination compounds of general formula $Me(Im)_6(NO_3)_2$ and $Me(NmIm)_6(NO_3)_2$, a warm solution of the metal salt was added to a warm solution of the ligand to obtain a final metal–ligand ratio of 1 : 12. To prepare coordination compounds of general formula $Me(Im)_4(NO_3)_2$ and $Me(NmIm)_4(NO_3)_2$, a warm solution of the ligand was added to a warm solution of the metal salt to obtain a final metal–ligand ratio of 1 : 4 or 1 : 2.

The mixtures obtained were cooled and left at room temperature until a precipitate was obtained. If a precipitate was not formed, ethyl ether was added. The precipitates obtained were washed with a mixture of absolute ethanol and ethyl ether (1 : 1), then with ether, and dried under vacuum. By this method, the following compounds were obtained: $Co(Im)_6(NO_3)_2$; $Ni(Im)_6(NO_3)_2$; $Cu(Im)_6(NO_3)_2$; $Cu(Im)_4(NO_3)_2$; $Co(NmIm)_6(NO_3)_2$; $Ni(NmIm)_6(NO_3)_2$; and $Cu(NmIm)_4(NO_3)_2$.

All attempts to prepare $Co(Im)_4(NO_3)_2$ and $Ni(Im)_4(NO_3)_2$ in solution, according to Davis and Smith [13], Taylor and Underhill [14] and Eilbeck et al. [15], and $Cu(NmIm)_6(NO_3)_2$, resulted in the formation, respectively, of $Co(Im)_6(NO_3)_2$, $Ni(Im)_6(NO_3)_2$ and $Cu(NmIm)_4(NO_3)_2$.

Coordination compounds at lower ligand number were only obtained by fusing together the metal salt and imidazole in the correct molar proportion [14].

The purity of the compounds was checked by elemental analysis and by thermogravimetric techniques, and the analytical results for all the compounds were good.

RESULTS

From the experimental data it can be derived that the hexakis complexes of imidazole, of general formula $Me(Im)_6(NO_3)_2$, decompose in air in the following way

$$Me(Im)_6(NO_3)_{2(s)} \rightarrow Me(Im)(NO_3)_{2(s)} + 5\ Im_{(g)} \qquad (I)$$

The resulting $Me(Im)(NO_3)_2$ then decomposes by a sharp exothermic process involving decomposition of the nitrate group, loss and oxidation of imidazole and formation of the metal oxide, Figs. 1–3.

In nitrogen atmosphere, reaction (I) does not change and the second reaction does not happen abruptly and commonly does not reach a constant weight in the operational temperature field, Figs. 1–3.

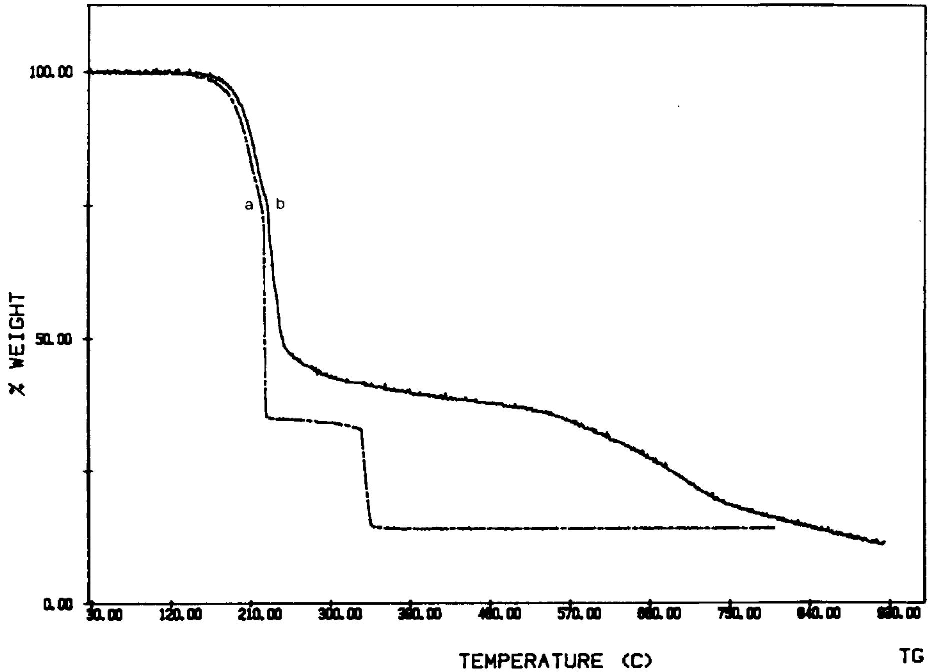

Fig. 1. TG curves of $Co(Im)_6(NO_3)_2$: (a) air atmosphere; (b) nitrogen atmosphere; heating rate, 10°C min^{-1}.

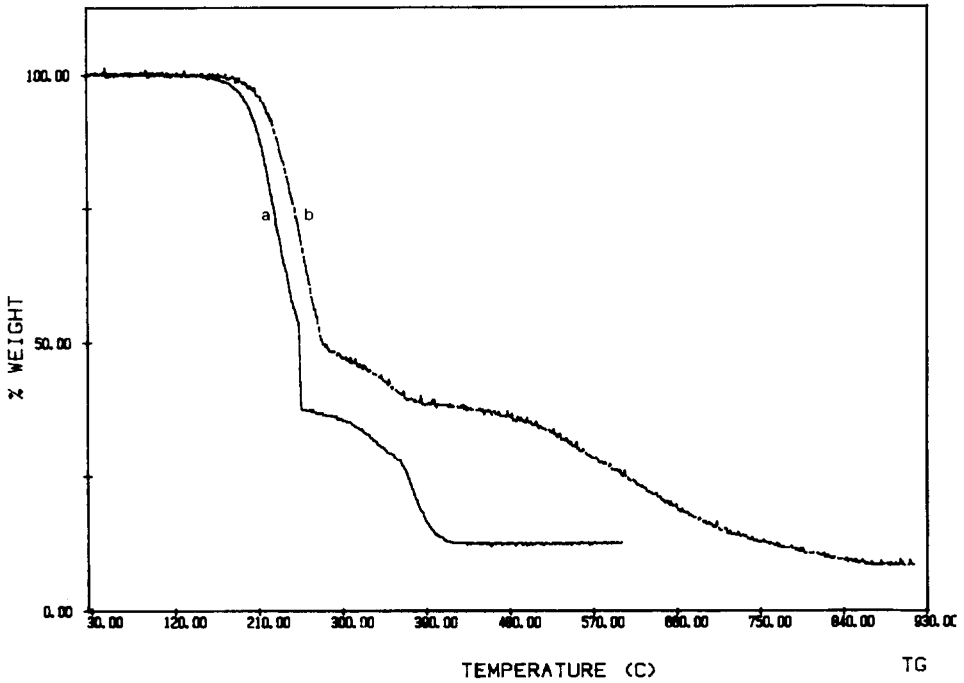

Fig. 2. TG curves of $Ni(Im)_6(NO_3)_2$: (a) air atmosphere; (b) nitrogen atmosphere; heating rate, 10°C min^{-1}.

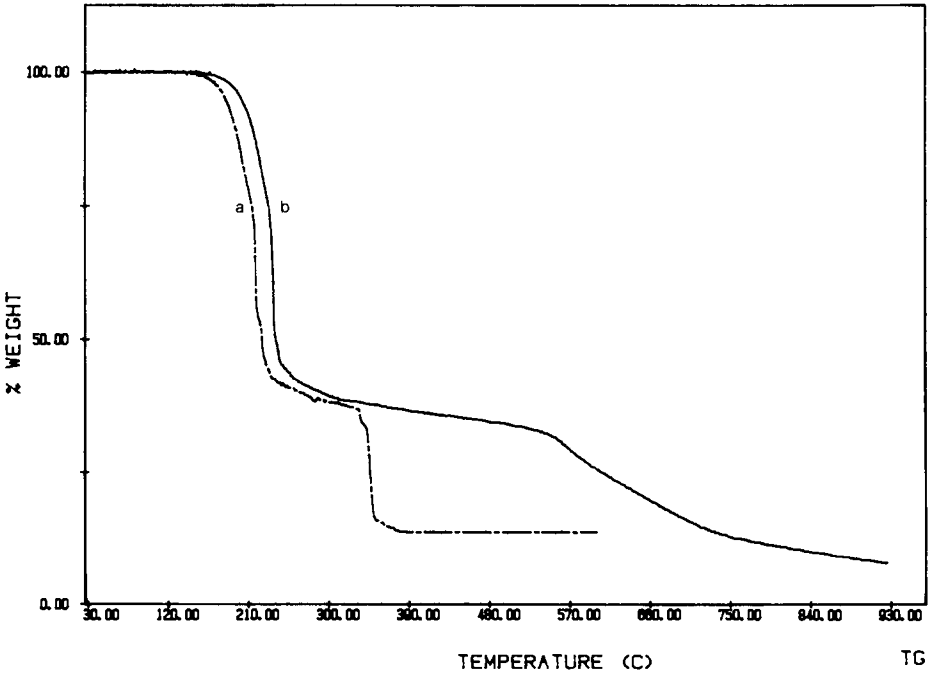

Fig. 3. TG curves of $Cu(Im)_6(NO_3)_2$: (a) air atmosphere; (b) nitrogen atmosphere; heating rate, 10°C min^{-1}.

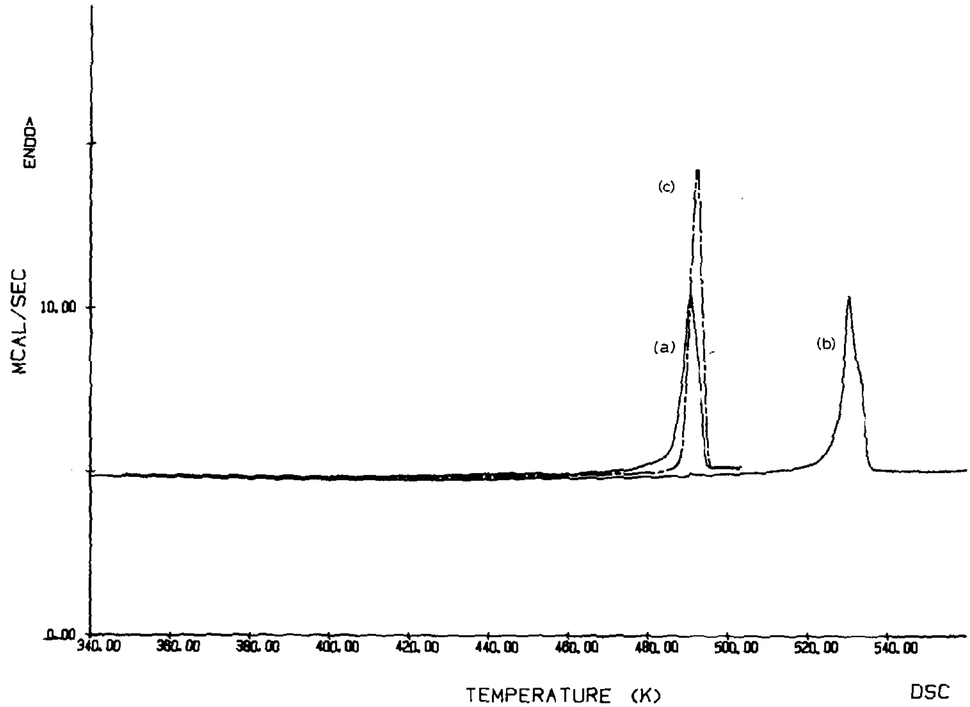

Fig. 4. DSC curves of: (a) $Co(Im)_6(NO_3)_2$; (b) $Ni(Im)_6(NO_3)_2$; (c) $Cu(Im)_6(NO_3)_2$ obtained by stainless-steel O-ring capsules. Nitrogen atmosphere; heating rate, 10 K min^{-1}.

Generally, the first process is not perfectly defined in weight in an air atmosphere, because it starts as an endothermic process but suddenly becomes exothermic and the temperature increase, due to the oxidative reaction, causes overlapping of the two decomposition steps. Decreasing the sample mass decreases the overlapping and sometimes it is possible to separate the two reactions.

The DSC curves have been obtained working with special stainless-steel O-ring sample containers with a pressure limit of 24 atm and filling and

TABLE 2

Values of ΔH_{exp} and ΔH_{exp} divided by m, the number of ligand molecules released, for the complexes studied

	Peak temp. (K)	ΔH_{exp} (kcal mol^{-1})	$\Delta H_{exp}/m$ (kcal mol^{-1})
$Co(Im)_6(NO_3)_2$	490	24.0 ± 0.4	4.8
$Ni(Im)_6(NO_3)_2$	530	24.5 ± 0.3	4.9
$Cu(Im)_6(NO_3)_2$	493	28.0 ± 0.3	5.6
$Co(NmIm)_6(NO_3)_2$	486	18.1 ± 0.3	4.5
$Ni(NmIm)_6(NO_3)_2$	515	18.5 ± 0.3	4.6

sealing the capsule in a dry box purged with very pure nitrogen to avoid any oxidation phenomena, Fig. 4.

By this method, it has been possible to avoid the passage of imidazole in the gaseous phase so that the ΔH value measured (Table 2) for reaction (I) can be correlated with the breaking of the metal–ligand bonds.

The vaporisation process connected with the empty disposable space inside the capsule does not give appreciable signals at temperatures corresponding to reaction (I) for the complexes examined as shown by DSC curves obtained on samples of pure imidazole and carried out under the same conditions. The DSC processes corresponding to eqn. (I) are endothermic, under the conditions described, which implies no decomposition of the nitrate ions with a consequent oxidation phenomenon induced by the products of thermal decomposition of the anion.

The copper tetrakis complex, $Cu(Im)_4(NO_3)_2$, decomposes in air and in nitrogen through a single sharp step whose weight loss is intermediate between three and four imidazole molecules (Fig. 5) and is influenced by the sample mass. The DSC curves (Fig. 6) show that the decomposition starts with a sharp endothermic peak that suddenly becomes exothermic for the concurrent decomposition of the nitrate and localized at a temperature higher than that corresponding to reaction (I) of the copper hexakis complex.

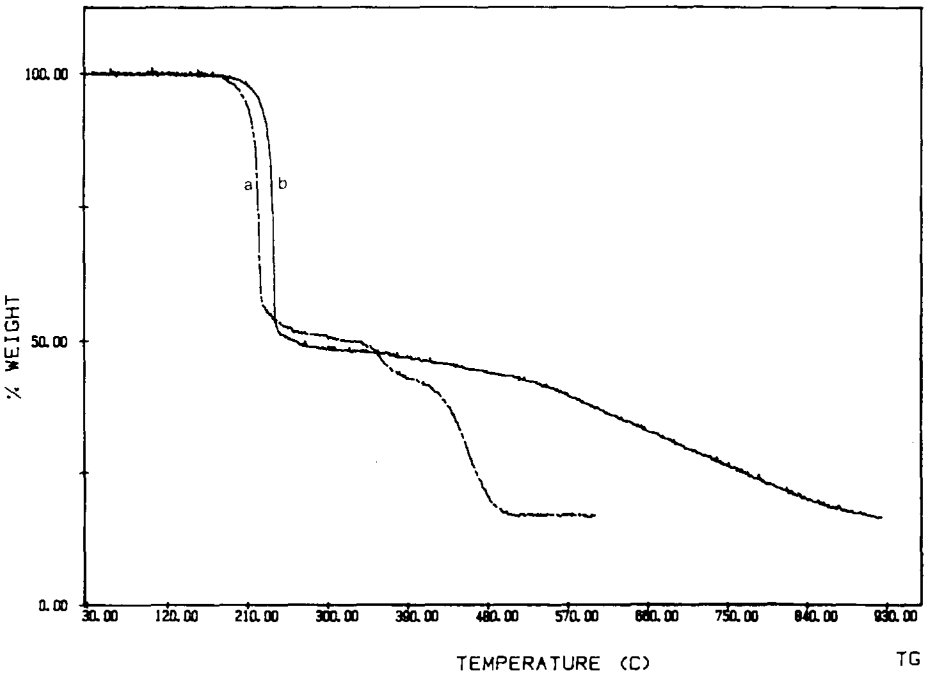

Fig. 5. TG curves of $Cu(Im)_4(NO_3)_2$: (a) air atmosphere; (b) nitrogen atmosphere; heating rate, 10°C min^{-1}.

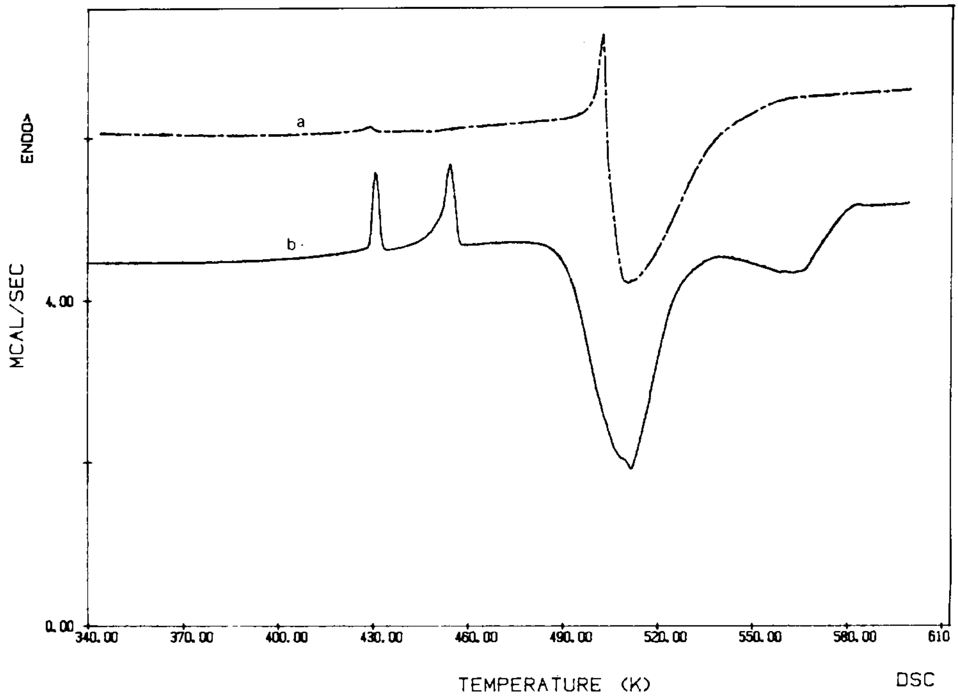

Fig. 6. DSC curves of: (a) $Cu(Im)_4(NO_3)_2$; (b) $Cu(NmIm)_4(NO_3)_2$ obtained by stainless-steel O-ring capsules. Nitrogen atmosphere; heating rate, 10 K min^{-1}.

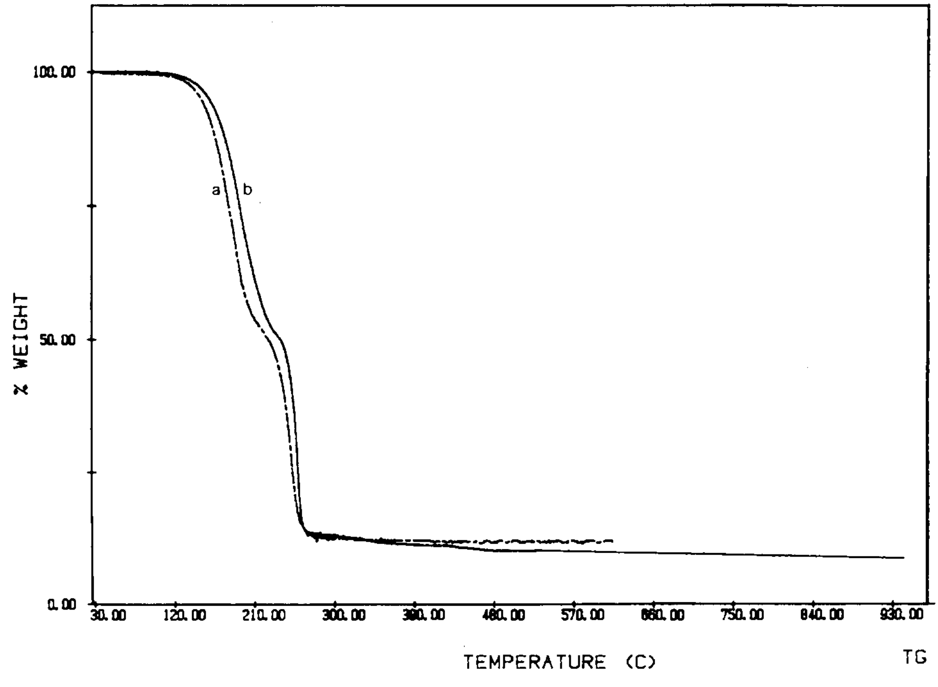

Fig. 7. TG curves of $Co(NmIm)_6(NO_3)_2$: (a) air atmosphere; (b) nitrogen atmosphere; heating rate, 10°C min^{-1}.

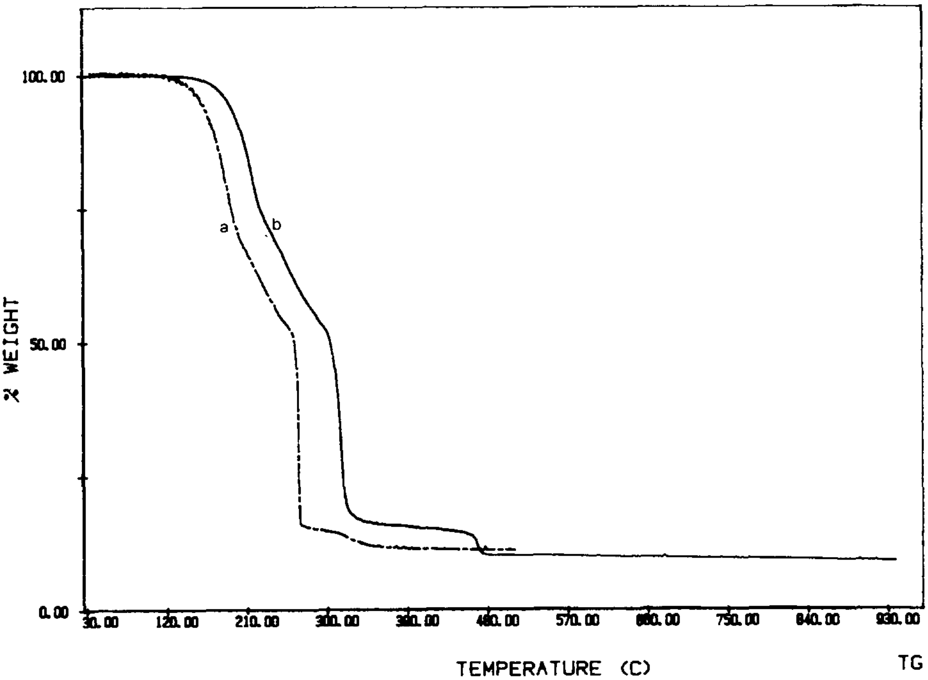

Fig. 8. TG curves of $Ni(NmIm)_6(NO_3)_2$: (a) air atmosphere; (b) nitrogen atmosphere; heating rate, 10°C min^{-1}.

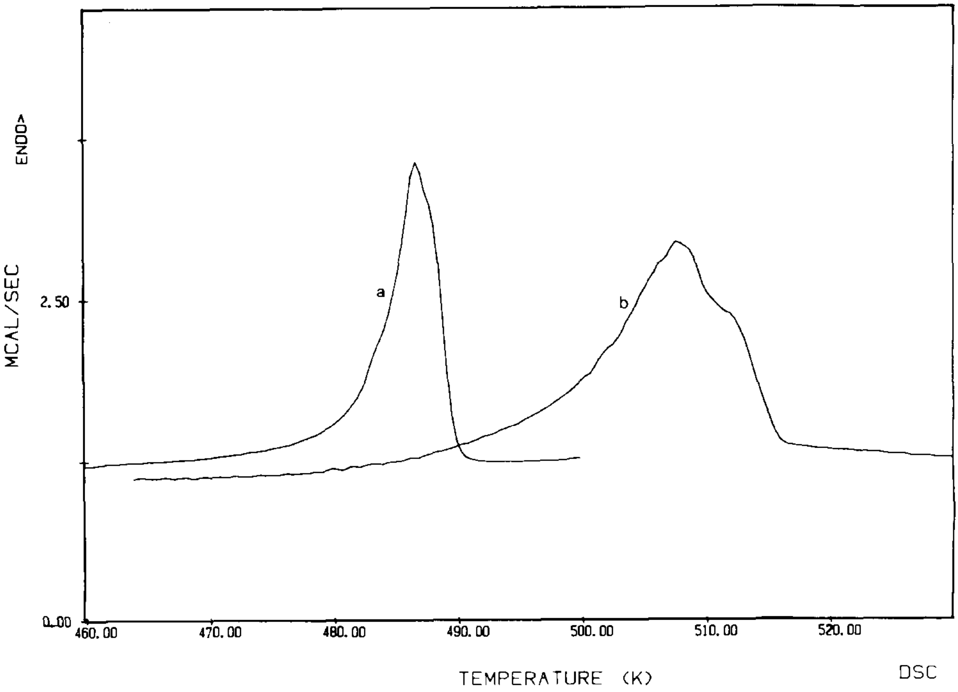

Fig. 9. DSC curves of: (a) $Co(NmIm)_6(NO_3)_2$; (b) $Ni(NmIm)_6(NO_3)_2$ obtained by stainless-steel O-ring capsules. Nitrogen atmosphere; heating rate, 10 K min^{-1}.

In air the TG curve reaches a plateau corresponding to CuO while in nitrogen it does not.

The thermal decomposition of the hexakis complexes of *N*-methyl imidazole, Me(NmIm)$_6$(NO$_3$)$_2$, can be described by the equation

$$\mathrm{Me(NmIm)_6(NO_3)_{2(s)} \rightarrow Me(NmIm)_2(NO_3)_{2(s)} + 4\ NmIm} \qquad \text{(II)}$$

Then Me(NmIm)$_2$(NO$_3$)$_2$ decomposes by a very sharp step corresponding to the loss and oxidation of the residual two molecules of *N*-methyl imidazole, to the decomposition of nitrate anions and to the formation of metal oxide, Figs. 7 and 8.

In nitrogen atmosphere, reaction (II) is the same while the second reaction still happens abruptly but does not give a plateau. The DSC curves, obtained as described for the imidazole compounds (Fig. 9) show, for the processes corresponding to eqn. (II), only endothermic peaks.

Figure 10 shows the TG curves of tetrakis Cu(NmIm)$_4$(NO$_3$)$_2$ in both air and nitrogen atmospheres. The decomposition starts losing *N*-methyl imidazole but a second reaction also involving the nitrate anions overcomes the first one giving an unresolved TG curve both in air and nitrogen atmospheres. In air the curve reaches a plateau corresponding to CuO while in nitrogen it does not. The DSC curve (Fig. 6) shows two endothermic peaks,

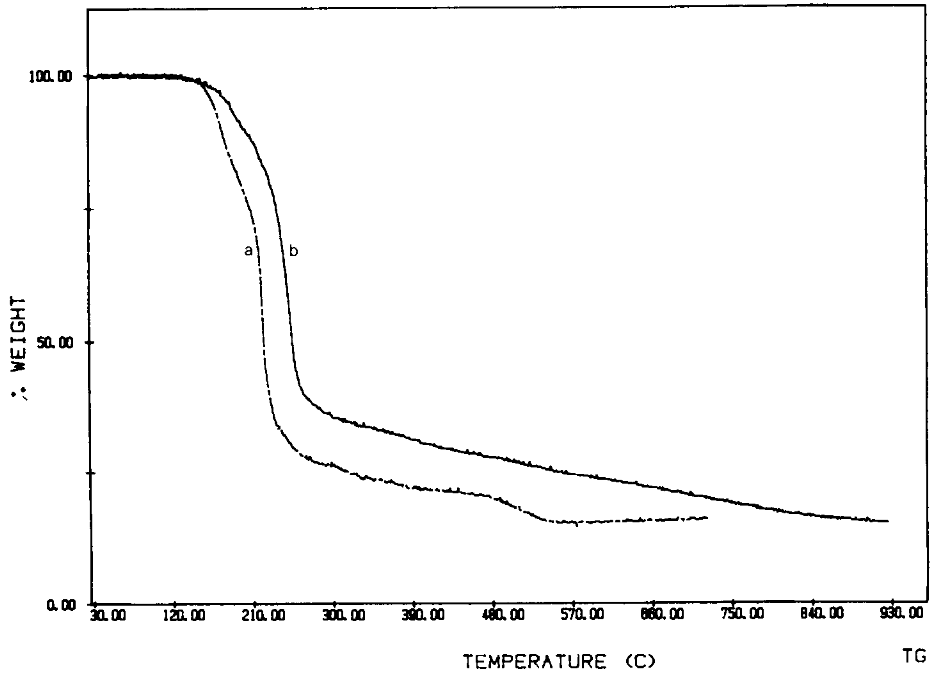

Fig. 10. TG curves of Cu(NmIm)$_4$(NO$_3$)$_2$: (a) air atmosphere; (b) nitrogen atmosphere; heating rate, 10°C min^{-1}.

the first one corresponding to melting of the compound and the second to loss of *N*-methyl imidazole, while a third peak, exothermic, corresponds to the final decomposition.

DISCUSSION

Imidazole, as demonstrated by the experimental data and as confirmed by the literature [15,16], shows a tendency to form hexakis complexes in contrast to the case of the pyridine, which preferably gives tetrakis compounds.

Two hypotheses have been proposed as an explanation for this difference [16]: π-acceptor ability is lower for imidazole than for pyridine; sequential addition of imidazoles determines a charge increase on the metal ion that inhibits entry of negatively charged ions so that all the coordination sites are occupied by neutral imidazole molecules. In the case of pyridine the higher π-acceptor ability produces a lower increase of electron density on the metal ion thus favouring tetrakis complex formation.

Ligand size has also been proposed as a determining factor in the formation of hexakis complexes. However, it appears that steric hindrance is insufficient to account for most instances of six-coordination with imidazole and four with pyridine.

Considering imidazole and *N*-methyl imidazole, ligands whose basicity is almost the same and whose known stability constants are the same [6,7], it can be seen that the only difference is the steric hindrance due to the presence of the methyl group in position 1, which does not play a fundamental role, giving the two ligands the same complexes, apart from $Cu(Im)_6(NO_3)_2$. Considering now $Cu(Im)_6(NO_3)_2$, it is interesting to note that Goodgame et al. [16] suggested for this compound an unusual stoichiometry of the type $Cu(Im)_4(NO_3)_2 \cdot 2$ Im, where two imidazole molecules are uncoordinated. The bonding energy of two molecules should therefore be lower than the other four. The TG and DSC curves show a first process corresponding to the loss of five isoenergetic molecules of imidazole and the energy of metal–ligand bond strength fits well with those of the corresponding compounds of Co(II) and Ni(II) (Table 2), whose thermal behaviour is in agreement with that of the copper compound. In addition, the infrared spectra of $Co(Im)_6(NO_3)_2$ and $Cu(Im)_6(NO_3)_2$ are very similar to one another and to that of imidazole, according to Davis and Smith [13] and Eilbeck et al. [15]. All the compounds further show bands of medium intensity at 710 and 825 cm^{-1} and a very sharp band at 1375 cm^{-1}, typical of the ν_4, ν_2 and ν_3 frequencies, respectively, of non-coordinated nitrate ion [18], while $Cu(Im)_4(NO_3)_2$ shows a sharp, strong band at 1050 cm^{-1} and two other sharp bands at 1350 and 1405 cm^{-1} due to splitting of the ν_3 frequencies corresponding to a symmetry decrease of the coordinated nitrate anion.

Thus, the formulation $Cu(Im)_4(NO_3)_2 \cdot 2$ Im appears to be improbable. It has been suggested that, in these complexes, coordination of imidazole molecules takes place through the pyridine nitrogen, rather than through the pyrrolic nitrogen, and an octahedral geometry has been assigned to these complexes on the basis of their electronic spectra [13–17]. This hypothesis has been confirmed, in several cases [19,20], by structural studies.

Freeman and Szymanski [21] interpret this structural type as a requirement for the imidazole ring to retain its aromaticity. Moreover, it is considered that imidazole has strong intermolecular hydrogen bonding in the solid state [22] while no hydrogen bonding should occur in its complexes because the pyridine nitrogen is coordinated to the metal ion [15].

Looking now at the thermochemical data obtained it is possible to see that the thermal stability of imidazole complexes is always higher than that of the corresponding complexes of *N*-methyl imidazole. The ΔH value corresponding to the breaking of one metal–ligand bond was obtained by considering the reaction

$$Me(L)_n(NO_3)_2 \rightarrow Me(L)_{n-m}(NO_3)_2 + mL$$

Dividing the experimental ΔH value by the number m of ligand molecules released (Table 2) always gives a lower value for *N*-methyl imidazole compounds than for imidazole compounds, and the ΔH values obtained are in agreement with those of Van Dam et al. [10] for $Me(Im)_6X_2$ compounds ($X = Cl, Br, I$).

Therefore, considering that the only difference between the two ligands, as said before, is the presence of a methyl group in position 1, the thermal difference can only be ascribed to the presence of hydrogen bonding in the case of imidazole complexes involving the pyrrolic hydrogen, which is impossible in the case of *N*-methyl imidazole.

This hypothesis agrees with the structural studies of Santoro et al. [19] who found that the orientation of the imidazole ring with respect to a pair of adjacent nitrate groups, in a hexagonal unit cell containing three molecules of $Ni(Im)_6(NO_3)_2$, is consistent with hydrogen bonding. The order of metal–ligand bonding energy is (Table 2): Cu(II) > Ni(II) > Co(II) for the hexakis compounds of imidazole according to the order of stability constants in solution; and Ni(II) > Co(II) for the hexakis compounds of *N*-methyl imidazole. While the order of thermal stability is: Ni(II) > Cu(II) > Co(II) with an anomalous situation for Cu(II) with respect to the commonly found order [23] probably referrable to differences in hydrogen bonding at the lattice energy level.

Finally, it is interesting to note that the thermal decomposition mechanisms of the hexakis complexes of imidazole and *N*-methyl imidazole are exactly the same within the two series, but it is quite different between the two series losing the imidazole compounds' five ligand molecules in the first step, while *N*-methyl imidazole compounds lose only four ligand molecules in the first step.

Moreover, the second step happens abruptly, immediately after the first one, for *N*-methyl imidazole compounds, while it is smooth for imidazole compounds and also starts immediately after the first one. Tetrakis compounds, $Cu(Im)_4(NO_3)_2$ and $Cu(NmIm)_4(NO_3)_2$, show a distorted octahedral configuration with the nitrate anions coordinated as shown by infrared spectra.

The thermal stability of the imidazole complex is higher than that of the *N*-methyl imidazole one. The decomposition starts to lose ligand molecules, but immediately after the nitrate starts to decompose. This mechanism is probably due to the fact that the decomposition of the tetrakis compound begins at a temperature higher than that of the hexakis compound involving all the coordinated systems.

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