Thermochimica Acta, 161 (1990) 297–307
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL BEHAVIOUR OF BIOLOGICALLY INTERESTING COORDINATION COMPOUNDS OF BENZIMIDAZOLE WITH DIVALENT METAL IONS

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(Received 24 October 1989)

ABSTRACT

The imidazole nucleus and its related structures, especially benzimidazole, are known to play a crucial role in the structure and functioning of a number of biologically important molecules, generally by virtue of their ability to coordinate to metal ions. Different parameters such as basicity of the ligands, π-acceptor ability, steric factors, hydrogen bonding, etc., influence either the structures or the thermal characteristics of the coordination compounds obtained by reaction of imidazole and benzimidazole with transition metal ions. The thermal properties of coordination compounds obtained by reaction of benzimidazole with $Co(NO_3)_2$, $Ni(NO_3)_2$ and $Cu(NO_3)_2$ are studied here by means of thermoanalytical techniques, supported by IR and reflectance spectroscopy, and compared with the previously published results for the coordination compounds obtained by reaction of the same ions with imidazole and *N*-methylimidazole. The compounds obtained were $Me(LH)_n(NO_3)_2$ and $Me(L)_2$ ($Me \equiv Co^{II}, Ni^{II}, Cu^{II}$; $n = 2$ or 4).

INTRODUCTION

The imidazole nucleus and its related structures are known to play a crucial role in the structure and functioning of a number of biologically important molecules, generally by virtue of their being coordinated to metal ions. Imidazole and benzimidazole are amphoteric, being moderately strong organic bases able to accept protons at N-3, as well as very weak acids capable of losing a proton from N-1. In near neutral solution, the neutral species that usually act as ligands via the unshared pair of electrons on N-3 predominate. Bonding via the N-1 is quite unlikely as there is no 'unshared pair' at the pyrrole nitrogen because the electrons are delocalised throughout the π-system. Thus the neutral molecules of imidazole and its derivatives have only one energetically favourable coordination site, the N-3 nitrogen.

The N-3 nitrogen displays weak negative σ- and π-electronic charges and is, therefore, a modest electron acceptor [1]. The activity of imidazole and its derivatives as ligands is especially correlated with their basicity and π-electron-acceptor capability. The fusion of a benzene ring at positions 4 and 5 in benzimidazole does not dramatically perturb the electronic structure of the heterocyclic molecule: the basicity is lowered, with pK_a being 5.6 as compared with 7.1 for imidazole [2,3]. In addition, in the solid state, there are other parameters that play an essential role in determining the structural types of coordination compounds that can be obtained, as well as their thermal characteristics, including steric factors, the requirement for imidazole to retain the aromaticity of the ring [4], hydrogen bonding and the possibility of polymeric reactions.

The aim of this research was to study the thermal characteristics of coordination compounds obtained by reaction of Co^{II}, Ni^{II} and Cu^{II} with benzimidazole and to discuss them in comparison with the published results for the coordination compounds of the same cations with imidazole and *N*-methylimidazole [5].

The compounds studied were $Me(LH)_x(NO_3)_2$ and MeL_2: $Me \equiv Co^{II}$, Ni^{II} and Cu^{II}; $LH \equiv$ benzimidazole, $L \equiv$ unprotonated benzimidazole; $x = 4$ and 2 (in the case of Co^{II} only). Nitrate was selected as the counter ion because of its very low coordination ability and because it shows characteristic absorption bands in its IR spectrum.

EXPERIMENTAL

Instrumentation

A Perkin-Elmer thermobalance (model TGS-2) and differential scanning calorimeter (model DSC-2 B), both equipped with a data station, were used. The heating rate ranged between 2.5 and 10 °C min^{-1}. The atmosphere was air or very pure nitrogen (99.99%) at flow rates of 50–100 ml min^{-1}. The IR spectra were recorded using a Nicolett 510 instrument. The reflectance spectra were recorded using a Beckman DK-2 spectroreflectometer.

Synthesis of the compounds

Benzimidazole was obtained from Aldrich Chemical Co.; the other chemicals employed were of reagent grade. Benzimidazole and Co^{II}, Ni^{II} and Cu^{II} nitrate salts were dissolved in absolute ethanol. For coordination compounds of general formula $Me(LH)_4(NO_3)_2$, 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. All attempts to prepare coordination compounds of general formula $Me(LH)_6(NO_3)_2$ failed as did attempts to synthesise compounds with a final metal–ligand ratio of 1 : 100. To prepare coordination compounds of general formula $Me(LH)_2(NO_3)_2$, 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 : 2. Only $Co(LH)_2(NO_3)_2$ was obtained. It was also impossible to obtain similar compounds for nickel(II) and copper(II) using metal–ligand ratios of 10 : 1. The mixtures were cooled and left at room temperature until a precipitate was obtained. If a precipitate was not formed ethyl ether was added. The precipitates were washed with a mixture of absolute ethanol and ether (1 : 1 v/v), then with ether, and were then dried under vacuum. The following compounds were obtained by this method: $Co(LH)_4(NO_3)_2$, $Ni(LH)_4(NO_3)_2$, $Cu(LH)_4(NO_3)_2$ and $Co(LH)_2(NO_3)_2$.

Coordination compounds of general formula $Me(L)_2$ were obtained as suggested by Goodgame and Cotton [6]. Using this method, the following compounds were obtained: $Co(L)_2$, deep purple, $Ni(L)_2$, blue-grey, and $Cu(L)_2$, brick red. The purity of the compound was checked by elemental analysis and by thermogravimetric techniques, and the analytical results for all the compounds were good.

RESULTS

The TG curves in air show that the tetrakis complexes of benzimidazole, of general formula $Me(LH)_4(NO_3)_2$, start to decompose by losing ligand molecules, Figs. 1–3.

$Co(LH)_4(NO_3)_2$ loses three molecules of benzimidazole in the first step; then the residual compound decomposes abruptly by an exothermic process involving decomposition of the nitrate group, loss and oxidation of benzimidazole and formation of the metal oxide. The DTG and DSC curves, Fig. 4, indicate that the first three molecules are not, in fact, isoenergetically bonded and that they are eliminated by two quite different overlapping processes.

$Ni(LH)_4(NO_3)_2$ behaves in a similar manner, but the beginning of the second process, which yields the oxide by a mechanism similar to that of the cobalt compound, overlaps with the first process, thus masking the completion of the loss of the first three ligand molecules. The DTG and DSC curves, Fig. 4, also confirm that in the case of the nickel compound the first three molecules of ligand are not isoenergetically bonded.

The TG curve of $Cu(LH)_4(NO_3)_2$ shows that this compound loses the first three molecules of benzimidazole in two well-resolved steps, the first corresponding to two ligand molecules. The final part of the second step, corresponding to loss of one ligand molecule, overlaps with the final decomposition reaction, which appears to be almost explosive. The DTG and DSC curves, Fig. 4, confirm that $Cu(LH)_4(NO_3)_2$ loses the first three ligand molecules in two clearly different steps. In nitrogen atmosphere, the

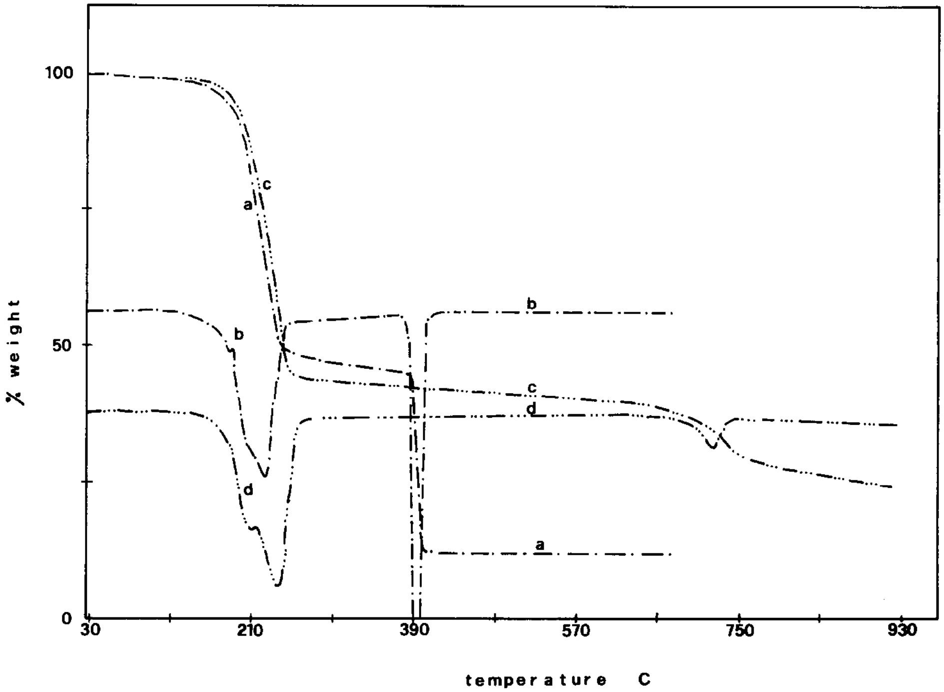

Fig. 1. TG and DTG curves of $Co(LH)_4(NO_3)_2$: a and b, air atmosphere; c and d, nitrogen atmosphere; heating rate 10 °C min^{-1}.

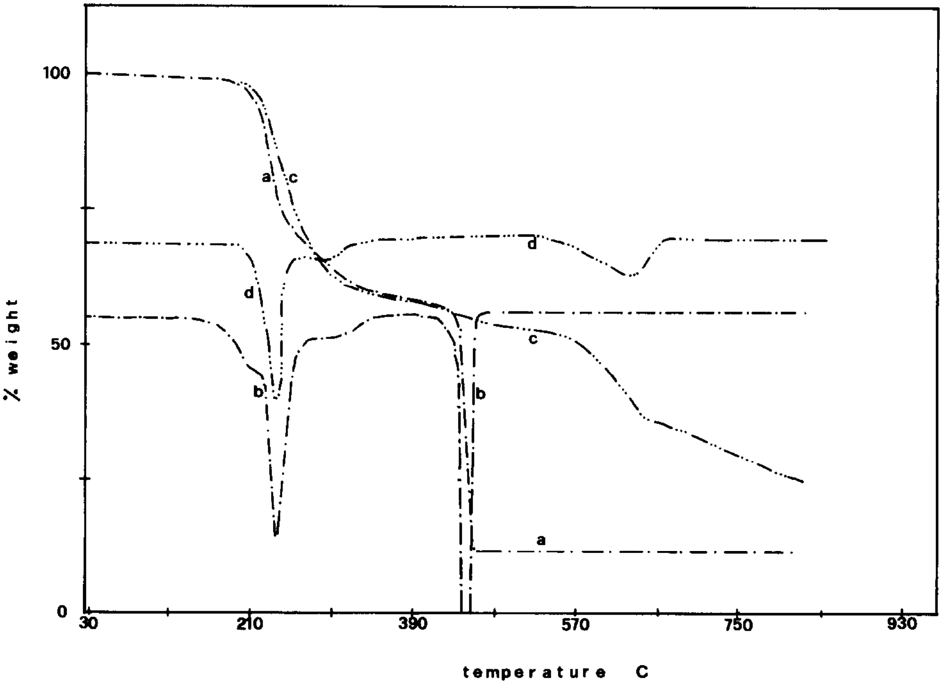

Fig. 2. TG and DTG curves of $Ni(LH)_4(NO_3)_2$: a and b, air atmosphere; c and d, nitrogen atmosphere; heating rate 10 °C min^{-1}.

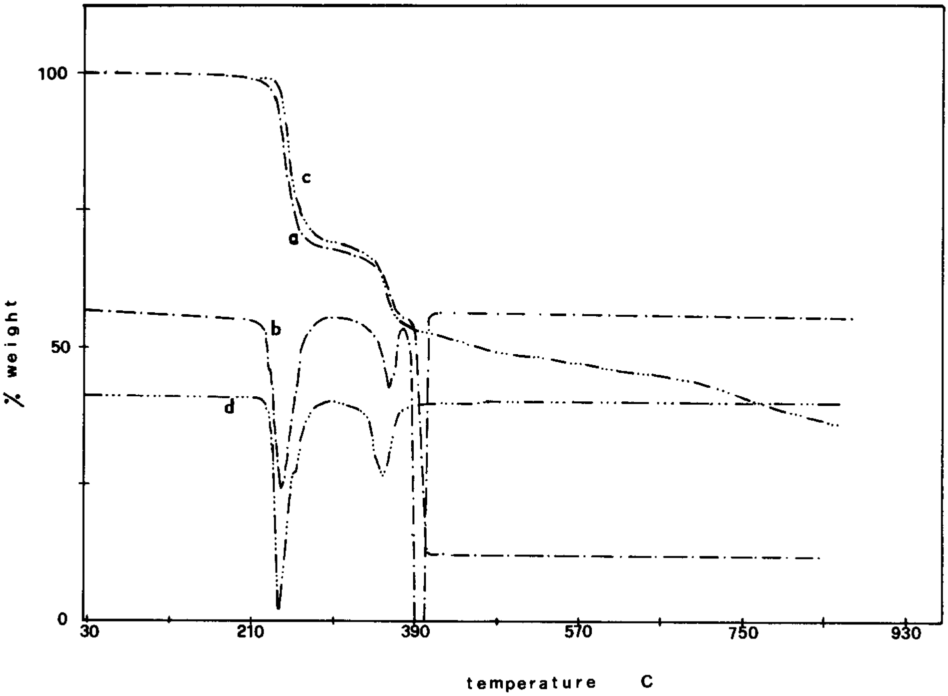

Fig. 3. TG and DTG curves of $Cu(LH)_4(NO_3)_2$: a and b, air atmosphere; c and d, nitrogen atmosphere; heating rate 10 °C min^{-1}.

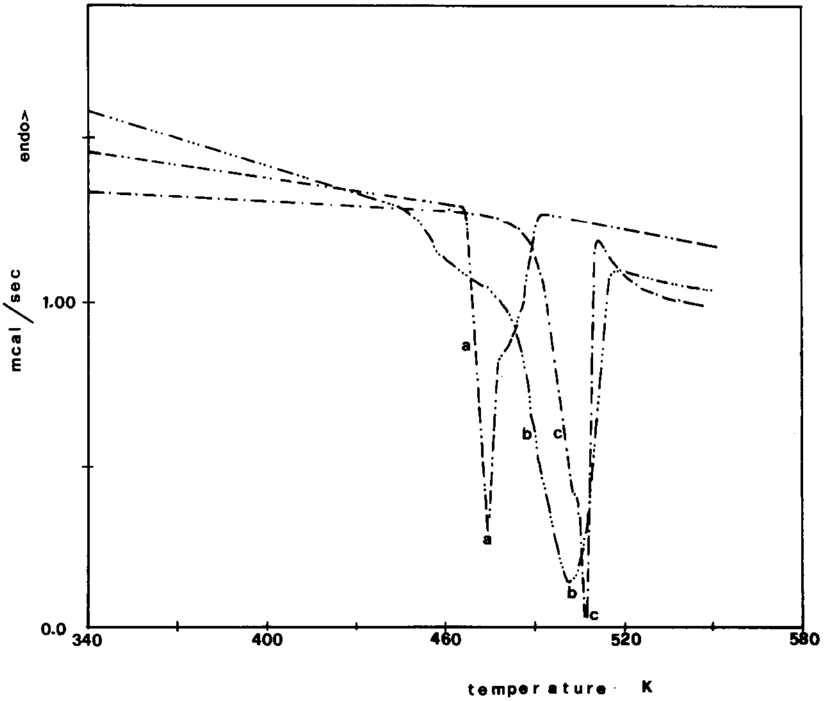

Fig. 4. DSC curves of: a, $Co(LH)_4(NO_3)_2$; b, $Ni(LH)_4(NO_3)_2$; c, $Cu(LH)_4(NO_3)_2$; nitrogen atmosphere; heating rate 10 °C min^{-1}.

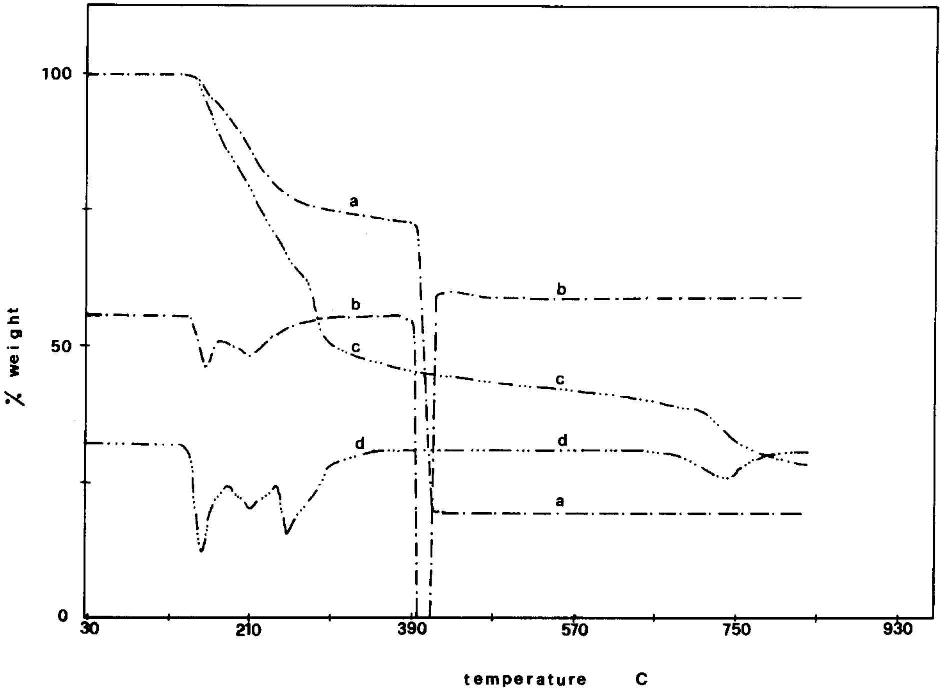

Fig. 5. TG and DTG curves of $Co(LH)_2(NO_3)_2$: a and b, air atmosphere; c and d, nitrogen atmosphere; heating rate 10 °C min^{-1}.

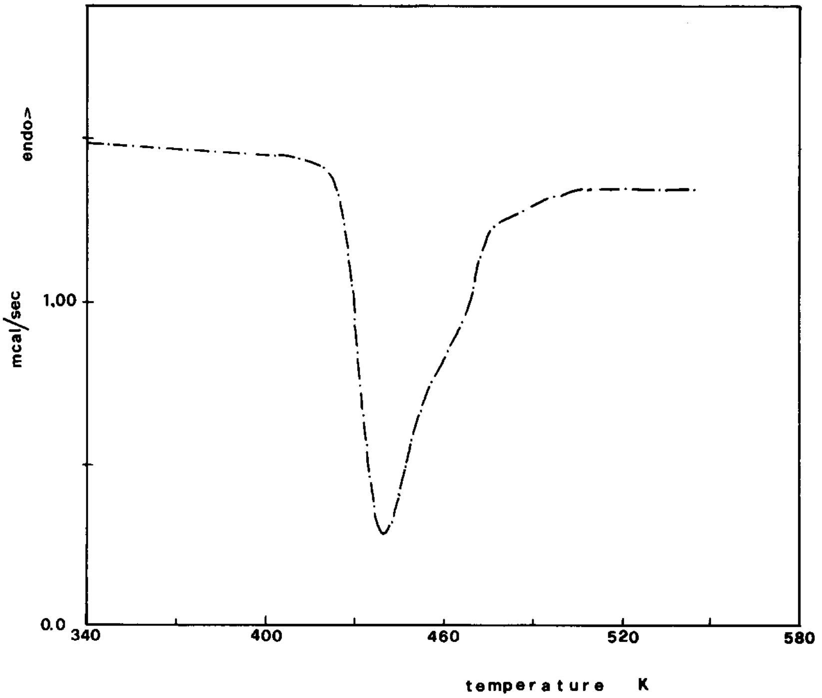

Fig. 6. DSC curve of $Co(LH)_2(NO_3)_2$: nitrogen atmosphere; heating rate 10 °C min^{-1}.

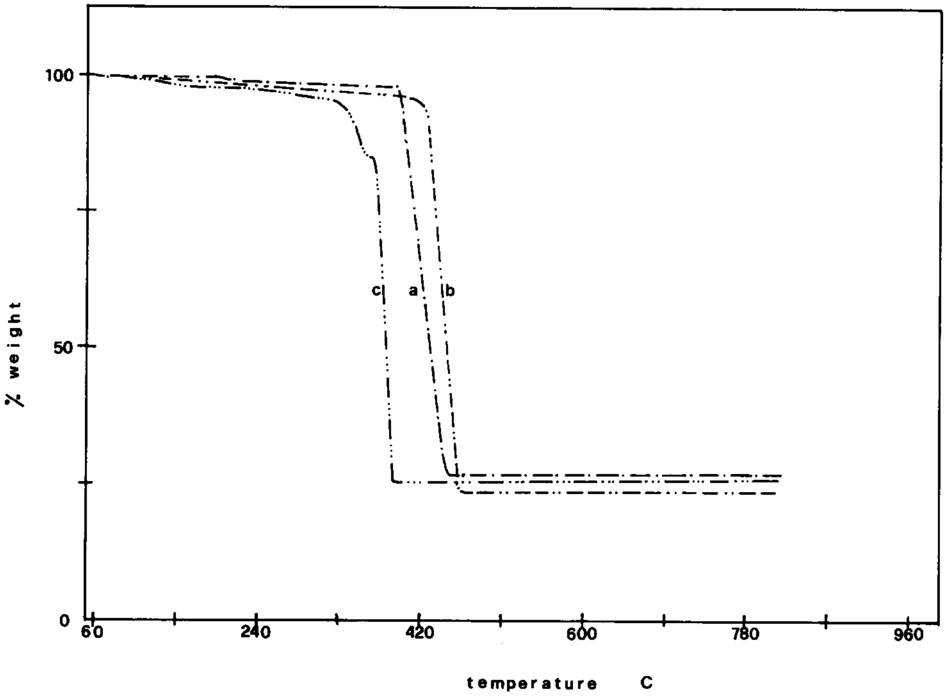

Fig. 7. TG curves of: a, $Co(L)_2$; b, $Ni(L)_2$; c, $Cu(L)_2$; air atmosphere; heating rate 10 °C min^{-1}.

initial part of the thermal reaction concerning the first three molecules of ligand does not change; however the following reactions do not occur abruptly, nor do they reach a constant weight within the operational temperature field, see Figs. 1–3.

$Co(LH)_2(NO_3)_2$ decomposes in air through two steps, see Fig. 5. The first step is smooth and corresponds to the loss of one molecule of benzimidazole; the second is sharp and almost explosive, corresponding to a process involving decomposition of the nitrate group, loss and oxidation of benzimidazole and formation of the metal oxide. In nitrogen atmosphere, the first process is unchanged, while the second becomes smooth and the thermal reaction does not reach a constant weight in the operational temperature field. The DSC curve, Fig. 6, shows that the first TG step is a single well-defined process.

The compounds of general formula $Me(L)_2$ are very stable and decompose at a temperature which is very high for a coordination compound, see Fig. 7. The decomposition in air of all three compounds is similar and happens almost explosively through a sharp exothermic process giving the oxides directly.

DISCUSSION

The maximum number of benzimidazole molecules found on a metal site is four, as demonstrated by the experimental data and confirmed in the literature [3,6–7]. This limit is presumably primarily imposed by steric factors. Johnston and Freiser [8] have postulated that the benzene part of the substituted benzimidazoles imposes steric effects in the chelation of metallic ions.

A comparison of the difference in the stability constants of the imidazoles [9] with those of benzimidazole [3] may provide evidence to suggest that the benzene portion of the molecule is sterically hindering the coordination. The basicity of benzimidazole is lower than that of imidazole and, as the electronic structure of the heterocyclic ring is not dramatically perturbed so that the δ- and π-electronic charges are almost similar, the lower values of the formation constants of the benzimidazole compounds with respect to those of the corresponding imidazole compounds can basically be ascribed to sterical hindrance factors. Benzimidazole [3] forms less stable coordination compounds relative to those of imidazole [9]. This is the result of two factors: the difference in the pK values being greater for the imidazole than for the benzimidazole compounds, and the steric hindrance of the bulky benzene ring attached to the imidazole.

Comparing the TG curves of $Cu(LH)_4(NO_3)_2$ with the corresponding tetrakis complexes of copper with imidazole and *N*-methylimidazole, Fig. 8, shows that the thermal stability of dinitratobis(benzimidazole)-Cu^{II} is higher than that of dinitratobis(imidazole)-Cu^{II} and much higher than that of dinitratobis(*N*-methylimidazole).

The higher thermal stability of the benzimidazole compounds with respect to those of imidazole is compatible with the fact that in homogeneous compounds the trend in thermal stability is the reverse of the trend in the stability constants in solution [10]. At the same time, the differences in the thermal stabilities among the three compounds can also be ascribed to the presence of hydrogen bonding in the imidazole and benzimidazole compounds, which involves the hydrogen at the N-1 pyrrolic site; according to the structural studies of Santoro et al. [11] on imidazole–nickel(II) compounds, this is impossible in the case of *N*-methylimidazole. The higher thermal stability of the benzimidazole derivative and the almost similar decomposition trends for benzimidazole and imidazole compounds, imply the presence of hydrogen bonding in the benzimidazole compounds also.

The reflectance spectra of dinitratobis(benzimidazole)-Cu^{II}, Fig. 9, are of the general type found for planar or tetragonally distorted octahedral copper(II).

The IR spectra show bands at 1402, 1318, 1032 and 822 cm^{-1}, characteristic of the nitrate. The bands at 1318 and 1402 cm^{-1} are due to the splitting of ν_3 frequencies corresponding to a decrease in the symmetry of the

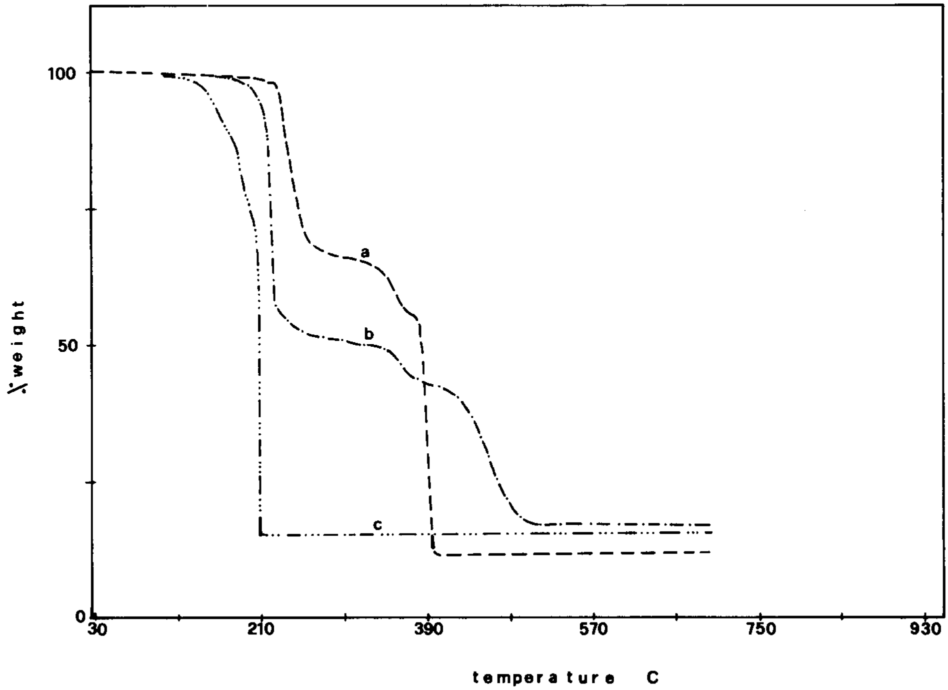

Fig. 8. TG curves of: a, Cu(benzimidazole)$_4$(NO$_3$)$_2$; b, Cu(imidazole)$_4$(NO$_3$)$_2$; c, Cu(*N*-methylimidazole)$_4$(NO$_3$)$_2$; air atmosphere; heating rate 10 °C min^{-1}.

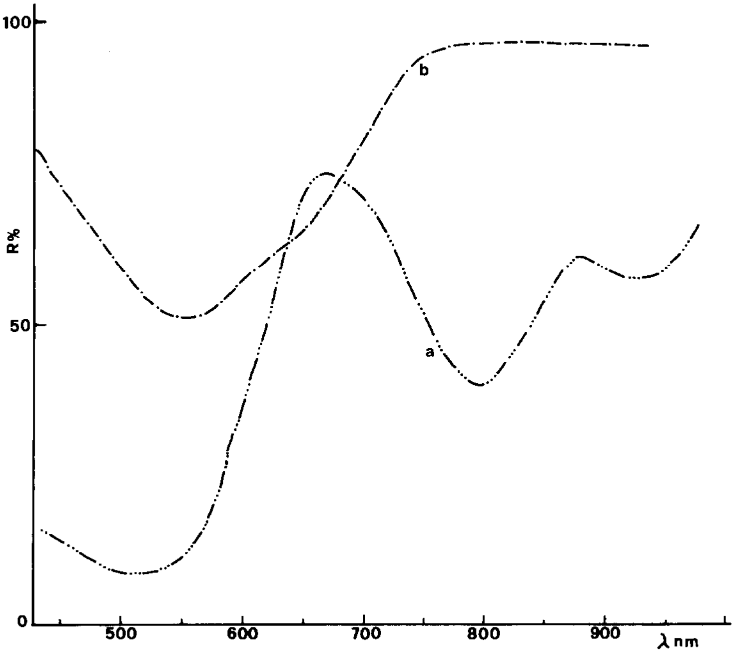

Fig. 9. Reflectance spectra of: a, Cu(LH)$_4$(NO$_3$)$_2$; b, Cu(L)$_2$.

coordinated nitrate ion. The comparative weakness of the 1032 cm^{-1} band, corresponding to a transition forbidden in uncoordinated nitrate but allowed in the bound nitrate, suggests that the nitrate is coordinated in this compound but that the bond is fairly weak. So it seems possible that the structure could be that of a tetragonally distorted octahedral copper(II) complex, with the four benzimidazole molecules in the x–y plane and the nitrate ion weakly coordinated on the z-axis.

The experimental data for the cobalt and nickel compounds suggest a tetrahedral structure, in accordance with Goodgame et al. [6,12].

The IR bands corresponding to nitrate ions are localised around 710 and 825 cm^{-1} (medium intensity), and 1370 cm^{-1} (very sharp), typical of ν_4, ν_2 and ν_3 frequencies, respectively, of an uncoordinated nitrate ion.

The order of thermal stability within the $Me(LH)_4(NO_3)_2$ series is $Cu^{II} > Ni^{II} > Co^{II}$, with Cu^{II} being in an anomalous position with respect to the commonly found order [10]. This is probably due to the differences in the structures, the copper(II) compound having a distorted octahedral structure with the two nitrate ions inside the coordination sphere, while the cobalt(II) and nickel(II) compounds appear to have a tetrahedral structure in which the nitrate ions are not coordinated.

$Co(LH)_2(NO_3)_2$ loses the two benzimidazole molecules in two steps: the first corresponds to one benzimidazole; the second fairly similar to the last decomposition step of $Co(LH)_4(NO_3)_2$ following the loss of three benzimidazoles.

The IR spectra show a sharp strong band at 1047 cm^{-1} and two other sharp bands at 1324 and 1405 cm^{-1} due, as before, to the splitting of the ν_3 frequencies corresponding to a symmetry decrease in the coordinated nitrate ion. The band at 1047 cm^{-1} is, comparatively, not very weak. Therefore, this implies a tetrahedral structure with the two nitrates coordinated to the Co^{II}.

The compounds of general formula $Me(L)_2$ show a thermal stability which is unusually high for coordination compounds and much higher than that of all the other compounds obtained by reaction with imidazole or its derivatives.

The reflectance spectrum of $Cu(L)_2$, Fig. 9, shows a behaviour corresponding to a distorted tetrahedral structure, according to Goodgame and Haines [7]. Similar behaviour is shown by the cobalt(II) and nickel(II) compounds.

This thermal and spectroscopic behaviour can be explained by the reasonable assumption that the structure of these compounds can be represented as an infinite polymer in which benzimidazole anions act as bidentate ligands at the N-1 and N-3 sites, forming bridges between metal ions, each metal being tetrahedrally surrounded by four nitrogens.

The order of thermal stability within the $Me(L)_2$ series is $Ni^{II} > Co^{II} > Cu^{II}$, in agreement with the commonly found trend for a homogeneous series of coordination compounds.

ACKNOWLEDGEMENT

The support of MPI (40 and 60%) is gratefully acknowledged.

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