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# Transition metal complexes with hydrazides and hydrazones.
# Part 5. Thermal decomposition of some copper(II) complexes with acetone 1-naphthoylhydrazone

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## Abstract

A study was made of the synthesis and thermal decomposition of copper(II) complexes of general formula $Cu(HL)X_2$ (X = Cl, Br), $Cu(HL)_2X_2$ (X = Cl, $NO_3$) and $CuL_2$, where HL and L are the neutral and monoanionic form of the organic ligand acetone 1-naphthoylhydrazone. On the basis of spectral and magnetic measurements, it was established that copper(II) coordination in all complexes is square-planar except for that of nitrate, which is octahedrally coordinated. A detailed analysis of the thermal decomposition of the complexes showed that they undergo endothermic decomposition followed by oxidation of the resulting fragments by atmospheric oxygen. The decomposition of the complexes is completed at 760°C and CuO is formed as the final product.

## INTRODUCTION

In our previous papers [1, 2] we have reported the synthesis and some physico-chemical characteristics of the octahedral bis(ligand) complexes of nickel(II) with the bidentate acetone 1-naphthoylhydrazone. The present paper describes the preparation, thermal decomposition, IR and reflectance spectra, magnetic and conductometric measurements of the mono(ligand) $Cu(HL)X_2$ (X = Cl, Br), bis(ligand) $Cu(HL)_2X_2$ (X = Cl, $NO_3$); and $CuL_2$ complexes, where HL and L are the neutral and monoanion forms of acetone 1-naphthoylhydrazone shown in Scheme 1.

## EXPERIMENTAL

### Chemicals

All chemicals used were analytical reagents of different makes.

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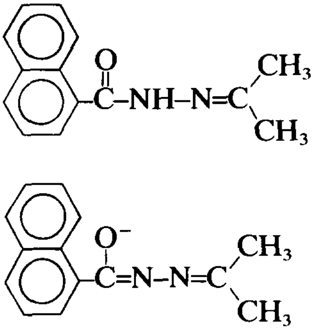


(HL)

(L)

Scheme 1. Neutral (HL) and monoanionic (L) forms of acetone 1-naphthoylhydrazone.

### *Preparation of the ligand*

The ligand acetone 1-naphthoylhydrazone was prepared as described earlier [1].

### *Preparation of the complexes*

*Cu(HL)Cl₂*

A warm solution of 0.02 g (1.2 mmol) of $CuCl_2 \cdot 2H_2O$ in 5 $cm^3$ of acetone was added to a hot suspension of 0.23 g (1.0 mol) of the ligand in 10 $cm^3$ of acetone, and the mixture was heated to complete dissolution of the ligand. The obtained brown solution was kept at room temperature for about 30 h. During filtration and washing with acetone, the brown–yellowish crystals became green; this change was accompanied by a decrease in their mass, probably due to removal of "crystalline" acetone. The product achieved stable mass after being kept at room temperature for 20 h. As could be concluded on the basis of the results of elemental analysis, the isolated $Cu(HL)Cl_2$ complex was insufficiently pure. A properly pure product was obtained after keeping the crystals in the solution until they were completely transformed into the green modification. This was achieved after concentrating the solution by mild heating. From the reduced volume of the solution the crystals were separated by filtration and washed with acetone and ether. Yield: 0.28 g (76.4%).

*Cu(HL)Br₂*

A mixture consisting of 0.23 g (1 mmol) of the ligand, 7 $cm^3$ of ethanol and 3 $cm^3$ of acetone was gently heated and to the incompletely dissolved ligand was added 0.22 g (1 mmol) of $CuBr_2$ in 3 $cm^3$ of acetone. The mixture was heated to complete dissolution of the ligand and the obtained solution was left at room temperature. After 40 h, the crystals formed were separated by filtration and washed with ethanol. Yield: 0.21 g (45.9%). The same complex was also obtained by the reaction of $CuBr_2$ and the ligand in the mole ratio 1:2.

*$Cu(HL)_2Cl_2$*

To a warm suspension of 0.45 g (2 mmol) of the ligand in 20 cm$^3$ of acetone was added 0.17 g (1 mmol) of $CuCL_2 \cdot 2H_2O$ in 10 cm$^3$ of acetone, and the mixture was heated to complete dissolution of the ligand. After keeping the solution at room temperature for 20 h, the green crystals were separated by filtration and washed with acetone. Yield: 0.28 g (47.7%).

*$Cu(HL)_2(NO_3)_2$*

A warm suspension of 0.23 g (1 mmol) of the ligand in 10 cm$^3$ of acetone was added to a solution of 0.12 g (0.5 mmol) of $Cu(NO_3)_2 \cdot 3H_2O$ in 5 cm$^3$ of acetone. The mixture was heated to dissolve the ligand, with the concurrent formation of green crystals. After 10 h the crystals were filtered off and washed with acetone. Yield: 0.25 g (76.4%).

*$CuL_2$*

The solution obtained by dissolving 0.10 g (0.5 mmol) of $Cu(CH_3COO)_2 \cdot 2H_2O$ in 10 cm$^3$ of methanol was, after filtration, heated gently and added to a warm solution of 0.23 g (1 mmol) of the ligand in 3 cm$^3$ of methanol and 3 cm$^3$ of acetone. Green needle-like crystals soon formed, and were separated by filtration after 5 h and washed with methanol. Yield: 0.17 g (52.0%).

## *Elemental analysis*

The elemental analysis and all physico-chemical measurements were performed using air-dried substances. Analysis (C, H, N) was carried out by standard micromethods. Analytical data are given in Table 1.

TABLE 1

Analytical and some physico-chemical data of the complexes

| Complexes | Colour | $\mu_{eff}$ (BM) | $\lambda_M$ (S cm$^2$ mol$^{-1}$) | Found (calcd.) | | |
|---|---|---|---|---|---|---|
| | | | | C(%) | H(%) | N(%) |
| $Cu(HL)Cl_2$<br>($CuC_{14}H_{14}N_2OCl_2$) | green | 1.41 | 26 | 46.21<br>(46.61) | 4.10<br>(3.91) | 7.64<br>(7.77) |
| $Cu(HL)Br_2$<br>($CuC_{14}H_{14}N_2OBr_2$) | black | 1.39 | 76 | 36.38<br>(37.39) | 3.28<br>(3.14) | 7.39<br>(6.26) |
| $Cu(HL)_2Cl_2$<br>($CuC_{28}H_{28}N_4O_2Cl_2$) | light green | 1.91 | 110 | 57.19<br>(57.29) | 4.76<br>(4.81) | 9.36<br>(9.54) |
| $Cu(HL)_2(NO_3)_2$<br>($CuC_{28}H_{28}N_6O_8$) | light green | 1.70 | 135 | 52.58<br>(52.54) | 4.75<br>(4.41) | 13.13<br>(13.13) |
| $CuL_2$<br>($CuC_{28}H_{26}N_2O_4$) | green | 1.81 | 3 | 66.15<br>(65.42) | 5.34<br>(5.10) | 10.88<br>(10.90) |

## *Infrared spectra*

Infrared absorption spectra (KBr discs) of the ligand and its complexes were obtained on a Perkin-Elmer 457 spectrophotometer.

## *Diffusion-reflection spectra*

The reflection spectra were measured in the 10 000–45 000 cm$^{-1}$ range at room temperature using an SPM-2 monochromator (VEB Zeiss, Jena)

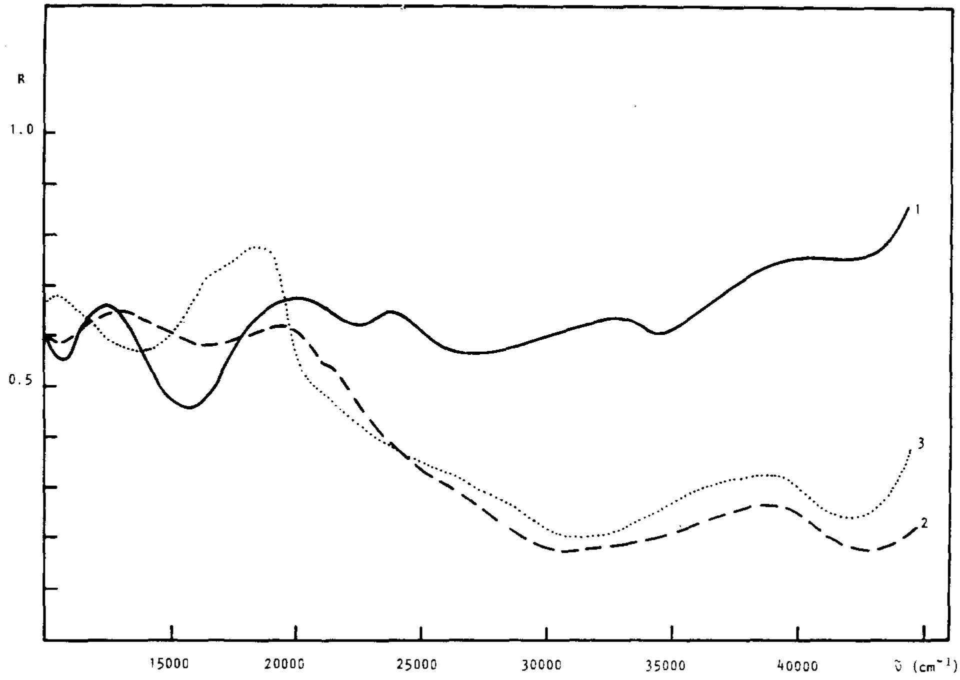


Fig. 1. Reflection spectra of $CuL_2$ (1), $Cu(HL)_2Cl_2$ (2) and $Cu(HL)_2(NO_3)_2$ (3) complexes.

TABLE 2

Electronic spectral data of Cu(II) complexes

| Compound | Transition ($10^3$ cm$^{-1}$) | | | IL1 ($10^3$ cm$^{-1}$) | IL2 ($10^3$ cm$^{-1}$) |
|---|---|---|---|---|---|
| | $b_{1g} \rightarrow a_{1g}$ | $b_{1g} \rightarrow b_{2g}$ | $b_{1g} \rightarrow e_g$ | | |
| $Cu(HL)Cl_2$ | 10.8 | 13.0 | 25.2 | 32.5 | 43.5 |
| $Cu(HL)Br_2$ | 10.6 | 14.4 | 21.0 | 31.5 | 42.2 |
| $Cu(HL)_2Cl_2$ | 10.6 | 16.8 | 21.2 | 31.0 | 43.0 |
| $CuL_2$ | 10.8 | 15.8 | 22.5 | 34.5 | 42.5 |
| | | $^2E_g \rightarrow {}^2T_{2g}$ | | | |
| $Cu(HL)_2(NO_3)_2$ | | 14.2 | | 31.6 | 42.2 |

with an R-45/0 type reflection cell. MgO was used as the "white" standard.

The reflection spectra are illustrated in Fig. 1. In order to identify the symmetry point group and the type of electronic transition in the complexes, reflection spectra were evaluated according to the Kubelka–Munk theory [3]. The electronic spectral data for the copper(II) complexes are given in Table 2.

### *Magnetic measurements*

Magnetic susceptibilities were measured by the Faraday method at room temperature, using $Hg[Co(NCS)_4]$ as the calibrant. The effective magnetic moments of the complexes are given in Table 1.

### *Thermogravimetric investigations*

Thermogravimetric investigations were carried out with a derivatograph. Each sample was heated from room temperature to 1000°C at the rate of $10°C\,min^{-1}$. The processes were carried out in an air atmosphere. $Al_2O_3$ was used as the reference material.

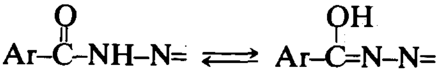
### *Molar conductivities*

Molar conductivities (Table 1) were measured for freshly prepared $1 \times 10^{-3}\,mol\,l^{-1}$ solutions (DMF) at room temperature using an MA 5961 conductivity meter (Iskra, Kranj).

## RESULTS AND DISCUSSION

### *Synthesis and general physico-chemical characteristics of complexes*

As can be seen from Table 1, acetone 1-naphthoylhydrazone forms with copper(II) both mono- and bis(ligand) complexes. General factors influencing the formation of these complexes are the nature of the anion present in the reaction mixture and the metal–ligand stoichiometry. Thus, the reaction of an acetone solution of $CuCl_2 \cdot 2H_2O$ or an ethanol–acetone solution of $CuBr_2$ with the ligand in the ratio 1:1 yields the mono(ligand) complexes of general formula $Cu(HL)X_2$ ($X = Cl$, Br). It should be pointed out that in the case of $CuBr_2$ the same complex is also formed when $Cu:HL = 1:2$. The bis(ligand) complexes $Cu(HL)_2X_2$ ($X = Cl$, $NO_3$) are formed by the reaction of acetone solutions of the copper(II) salt and the ligand in the ratio 1:2. Finally, the reaction of a methanol–acetone solution of the ligand and a methanolic solution of $Cu(CH_3COO)_2 \cdot H_2O$ yielded the bis(ligand) complex $CuL_2$, irrespective of the stoichiometry of



$$\mathrm{Ar{-}\overset{O}{\overset{\|}{C}}{-}NH{-}N{=}} \rightleftharpoons \mathrm{Ar{-}\overset{OH}{\overset{|}{C}}{=}N{-}N{=}}$$

Scheme 2. Reprotonation of the enolized aroylhydrazone fragment.

mixing the reactants. The anionic form of the ligand is formed by deprotonation of the enolized aroylhydrazone fragment as shown in Scheme 2. The reaction is facilitated by the presence of acetate as a proton acceptor.

The obtained complexes are crystalline substances stable in air, well soluble in DMF, less soluble in methanol, ethanol and acetone and insoluble in ether and water.

### *Structural considerations*

On the basis of the shifts of the $\nu$(C=O) and $\nu$(C=N) bands in the IR spectra of nickel(II) complexes with acetone 1-naphthoylhydrazone to lower energies with respect to their positions in the spectrum of the non-coordinated ligand, it has been supposed that the oxygen and nitrogen atoms of the respective groups are involved in coordination [4, 5]. The same effect has also been observed for the present copper(II) complexes. Besides, the isolation of the $CuL_2$ complex, containing the mono-deprotonated ligand, represents a chemical proof of the existence of the enolized oxygen of the C=O group. A preliminary X-ray analysis of the $Cu(HL)_2(NO_3)_2$ complex has confirmed the above supposition on the mode of the ligand coordination. It also showed that this complex has an octahedral configuration, which is realized via the two bidentate (N, O) ligand molecules and the two monodentate $NO_3$ groups. However, it should be noted that the IR spectrum (KBr) of the complex contains a strong band at 1385 $cm^{-1}$ which is characteristic of non-coordinated nitrate [6]. It is straightforward to conclude that the appearance of this band can be ascribed to the exchange of nitrate by bromide.

A complete replacement of the coordinated $NO_3$ with solvent molecules is observed in DMF. This is evident from the molar conductivity data (Table 1) which are characteristic for an electrolyte of 2:1 type [7]. The position of a low-intensity band at about $14.2 \times 10^3$ $cm^{-1}$ in the reflectance spectra of $Cu(HL)_2(NO_3)_2$ is also in agreement with the X-ray analysis data on the octahedral configuration.

In contrast to this complex, the reflectance spectra of all other complexes (Table 2, Fig. 1) suggest the presence of the approximate group symmetry $D_{4h}$ [8]. This means that the coordination of the $Cu(HL)X_2$ complexes is realized by participation of both halide ions in addition to the chelate ligand. In the case of $Cu(HL)Cl_2$ this supposition is also confirmed by the corresponding molar conductivity data (Table 1).

However, the molar conductivity for $Cu(HL)Br_2$ indicates the presence of a 1:1 type of electrolyte in the given solvent [7], which is a direct consequence of the fact that the Cu–Cl bond is stronger than Cu–Br. As can be expected, the molar conductivity of the $CuL_2$ complex is the lowest, which is agreement with its non-electrolyte nature.

The effective magnetic moments of the bis(ligand) complexes (Table 1) have values which are characteristic of the magnetically isolated monomeric copper(II) compounds. In contrast, the $\mu_{eff}$ values for mono(ligand) complexes indicate that the neighbouring metal centres exhibit either direct or indirect (most probably via the halide ions) interactions.

## *Thermal behaviour*

The thermal decomposition of the investigated complexes, as well as of the ligand itself [2], was investigated by heating the substances in an air atmosphere to 1000°C. The results are presented in Table 3, and the respective TG, DTG and DTA curves for $Cu(HL)Cl_2$ and $CuL_2$ are shown in Figs. 2(a) and 2(b).

In the case of the mono(ligand) complexes $Cu(HL)Cl_2$ (Fig. 2(a)) and $Cu(HL)Br_2$, the first endothermic effect (Table 3) observed at 130 and 160°C corresponds to melting of the samples. The second endothermic effect corresponding to elimination of HX ($X = Cl, Br$) is observed at 230 and 220°C, respectively [9, 10]. On the basis of a comparison with thermal decomposition of the ligand itself [2], it can be supposed that the endothermic effects beginning at 230°C correspond to decomposition of the ligand moiety of the complex, in which the ligand undergoes an endothermic decomposition which is followed by oxidation of the ligand fragments by atmospheric oxygen. This is also confirmed by decomposition of the ligand itself in a nitrogen atmosphere [2]: the exothermic effect observed in the 380–680°C range on the DTA curve recorded for ligand decomposition in an air atmosphere appeared as an endothermic peak for the decomposition in a nitrogen atmosphere.

Decomposition of the bis(ligand) $Cu(HL)_2(NO_3)_2$ complex starts at 140°C (Table 4) with a very pronounced exothermic effect involving the loss of 66% of the total sample mass. This effect can be ascribed to simultaneous elimination of both the nitrate ions and the naphthalene ring [11], as well as to the beginning of elimination of the lighter part of the ligand, which is followed by oxidation of the ligand fragments by atmospheric oxygen.

The process of thermal decomposition of the bis(ligand) $Cu(HL)_2Cl_2$ complex begins with endothermic effects at 140 and 220°C corresponding to sample melting and elimination of the HCl molecule, respectively. Decomposition of the ligand moiety of the complex starts with the

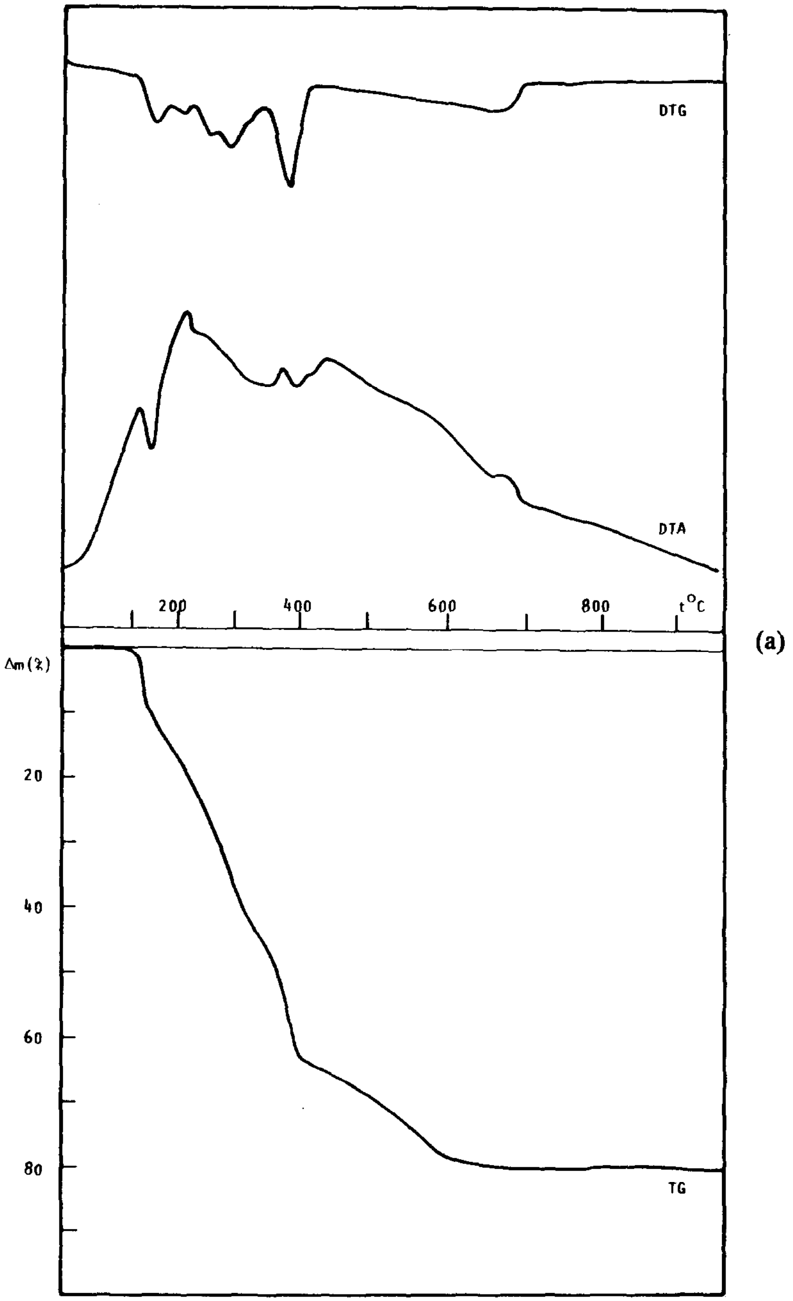


Fig. 2. TG, DTG and DTA curves of $Cu(HL)Cl_2$ (a) and $CuL_2$ (b) complexes.

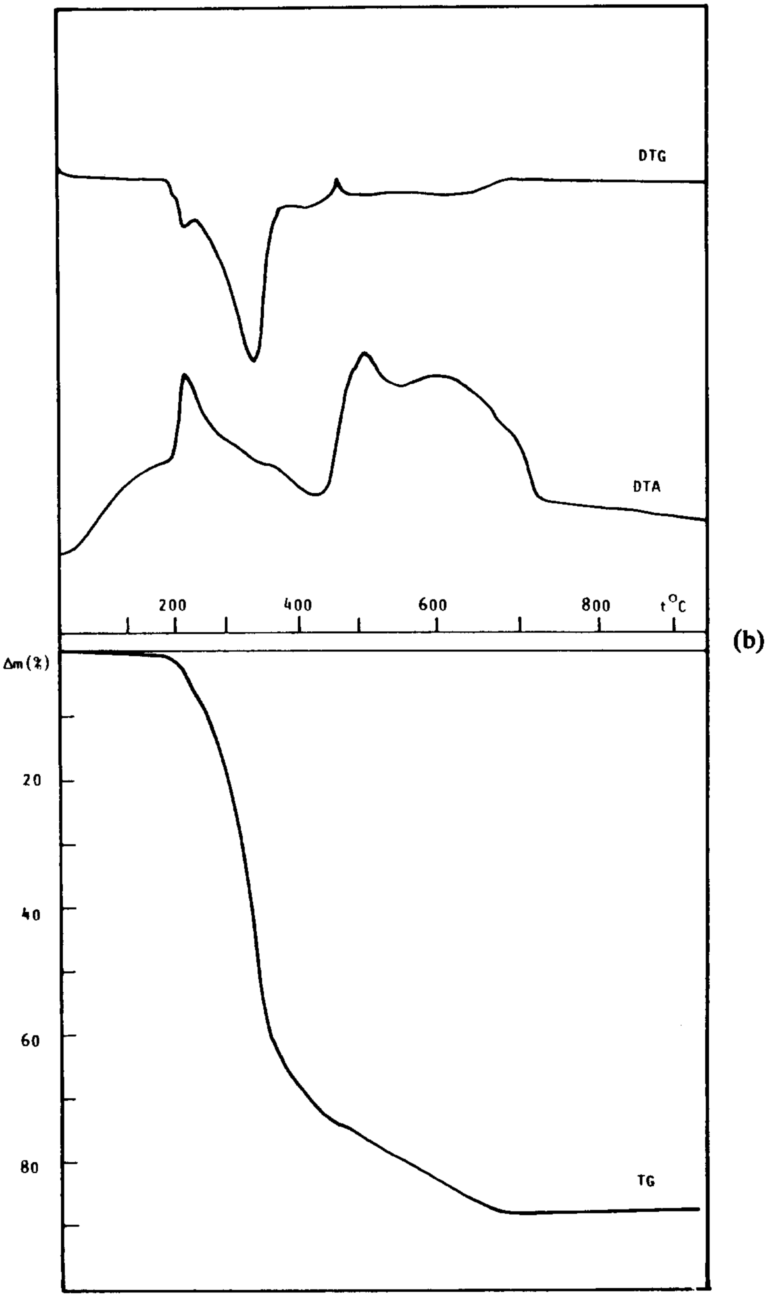


Fig. 2. (continued)

TABLE 3

TG analysis of octahedral Cu(II) complexes with HL and L

| Effect | Fragment eliminated | Cu(HL)$Cl_2$ | | | Cu(HL)$Br_2$ | | | Cu$L_2$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $T$ (°C) | $\Delta m_{exp}$ (%) | $\Delta m_{calc}$ (%) | $T$ (°C) | $\Delta m_{exp}$ (%) | $\Delta m_{calc}$ (%) | $T$ (°C) | $\Delta m_{exp}$ (%) | $\Delta m_{calc}$ (%) |
| Endo | $CH_2{=}CH_2 + 2CO - O_2$ | 130 | 13 | 14.1 | 160 | | | | | |
| Endo | Melting | | | | | | | | | |
| Exo | $2(CH_2{=}CH_2)$ | | | | | | | 200 | 11.0 | 10.8 |
| Endo | $2HX^a$ | 230 | 20 | 20.1 | 220 | 24.0 | 23.8 | | | |
| Exo | $2(CH_2{=}CH_2 + CO)$ | | | | 220–390 | 16.5 | 16.5 | | | |
| Exo | $NH_3 + NO - O$ | 380 | 9 | 8.6 | | | | | | |
| Exo | Naphthalene ring | 400–610 | 35 | 35.1 | | | | 290–380 | 49.0 | 49.2 |
| Exo | Naphthalene ring $+ 2(NH_3 + NO - O + CO)$ | | | | 390–760 | 50.0 | 50.3 | | | |
| Exo | $2(NH_3 + NO - O + CO + CO_2 - O_2)$ | | | | | | | 380–460 | 27.5 | 27.5 |
| Residue | CuO | | 22 | 22.1 | | 9.5 | 9.4 | | 12.5 | 12.5 |

TABLE 4

TC analyses of octahedral Cu(II) complexes with HL and L

| Effect | Fragment eliminated | $Cu(HL)_2Cl_2$ | | | $Cu(HL)_2(NO_3)_2$ | | |
|---|---|---|---|---|---|---|---|
| | | $T$ (°C) | $\Delta m_{exp}$ (%) | $\Delta m_{calc}$ (%) | $T$ (°C) | $\Delta m_{exp}$ (%) | $\Delta m_{calc}$ (%) |
| Endo | Melting | 140 | | | | | |
| Exo | Naphthalene ring + $2(NO_3 + CH_2{=}CH_2)$ | | | | 140 | 66.0 | 65.3 |
| Endo | 2HCl | 220 | 12.5 | 12.7 | | | |
| Exo | 2CO | | | | 240 | 8.7 | 8.5 |
| Exo | $2(CH_2{=}CH_2) + 2CO$ | 220–340 | 19.5 | 19.0 | | | |
| Exo | $2CO - O_2$ | | | | 320 | 3.5 | 3.74 |
| Exo | $2(NH_3 + NO - O)$ | | | | 320–620 | 11.0 | 12.4 |
| Exo | Naphthalene ring + $2(NH_3 + NO - O - CO)$ | 340–700 | 58.0 | 57.7 | | | |
| Residue | CuO | | 11.0 | 10.8 | | 12.0 | 12.4 |

decomposition of the lighter part of the ligand, observed as an endothermic effect, and is completed at 700°C (Table 4).

In the case of the $CuL_2$ (Table 3, Fig. 2(b)), the process of thermal decomposition is analogous to the decomposition of the ligand itself. An X-ray diffraction analysis of the residue obtained in thermal decomposition of all the complexes showed that CuO was formed as the final product.

## REFERENCES

1 D.Ž. Obadović, A.F. Petrović, V.M. Leovac and S.Yu. Chundak, J. Phys.: Condens. Matter., 2 (1990) 3611.
2 D.Ž. Obadović, D.M. Petrović, V.M. Leovac and S.Yu. Chundak, J. Therm. Anal., 36 (1990) 99.
3 P. Kubelka and F. Munk, Z. Tech. Phys., 12 (1931) 593.
4 Yu.Ya. Kharitonov, R.I. Machokhoshvili, N.B. Genevanova and R.N. Shchelkov, Zh. Neorg. Khim., 19 (1974) 1124.
5 S.Yu. Chundak, V.M. Leovac, D.Ž. Obadović and D.M. Petrović, Transition Met. Chem., 11 (1986) 308.
6 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley–Interscience, New York, 1986.
7 W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.
8 D.M. Petrović, V.M. Leovac and S. Lukić, Z. Kristallogr., 31 (1986) 168.
9 J. Zsako, G. Liptau and C. Varhelyi, J. Therm. Anal., 31 (1986) 1027.
10 E. Jona, M. Jamnicky and M. Žemlička, J. Therm. Anal., 30 (1985) 913.
11 A.J. Chacko and G. Papameswaren, J. Therm. Anal., 29 (1984) 3.