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SYNTHESIS, CHARACTERISATION AND THERMAL BEHAVIOUR OF SOME COMPLEXES WITH LIGANDS HAVING 1,3,4-THIADIAZOLE MOIETIES

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The investigations concerning the thermal behaviour of a series of Ni(II) and Cu(II) complexes of type $[\mathrm{MLCl_n}]\cdot m\mathrm{H_2O}$ ((**1**) M:Ni, L:L(1), n=1, m=2; (**2**) M:Cu, L:L(2), n=1, m=2; (**3**) M:Ni, L:L(3), n=2, m=0; (**4**) M:Cu, L:L(3), n=1, m=2) are presented in this paper. The ligands L(1)–L(3) have been synthesised by template condensation of 1,2-diaminoethane with formaldehyde and 2-amino-1,3,4-thiadiazole-5-thiole or 2-acetamino-1,3,4-thiadiazole-5-sulfonamide. The bonding and stereochemistry of the complexes have been characterised by IR, electronic and magnetic studies at room temperature. The thermal behaviour provided confirmation of the complex composition as well as the number and the nature of water molecules and the intervals of thermal stability. The different nature of the ligands and/or the metallic ions generates a different thermal behaviour for complexes. The complexes do not show biological activity against HIV virus.

Keywords: *formaldehyde, macrocyclic ligand, template, thermal stability, 1,3,4-thiadiazole moiety*

Introduction

There is much interest in synthesis and characterisation of complexes with heterocyclic ligands with particular attention focused on bioinorganic studies. It has been shown that the complexes with 1,3,4-thiadiazole derivatives are biologically active having fungicidal properties [1–5], inhibitory activity against carbonic anhydrase [6–11] as well as antibacterial activity [12–14]. Our studies concerning the thermal stability have evidenced that some complexes with 2-amino-1,3,4-thiadiazole-5-thiole could generate sulphides by thermal degradation [15, 16], behaviour evidenced also for other complexes that contain ligands with sulphur as donor [17, 18]. Moreover, in the last years much attention was focused on the synthesis of complexes with macrocyclic ligands bearing various heterocycles as substituents both at carbon and nitrogen atoms [19–22]. Such type of compounds besides having supplementary set donors, presents a high thermodynamic and kinetic stability [23] and there are very few studies concerning its thermal behaviour [24, 25].

On the basis of these considerations we have been synthesised complexes of Ni(II) and Cu(II) with ligands resulted by condensation of 1,2-diaminoethane, formaldehyde and heterocyclic derivatives: 2-amino-1,3,4-thiadiazole-5-thiole (HTDA) and, respectively, 5-acetamido-1,3,4-thiadiazole-2-sulfonamide (ATS). The complexes were formulated on the basis of analytical, spectral and magnetic data. The new complexes have been inactive against HIV virus. The thermal decomposition of these complexes was used in order to confirm the composition and also in order to obtain information about the interval of the thermal stability of these species.

Experimental

All reagents were of commercial analytical quality and have been used without further purification. Chemical analysis of carbon, nitrogen, sulphur and hydrogen has been performed using an EA 1110 analyzer. Nickel was determined gravimetrically using dimethylglyoxime and copper was determined volumetrically using thiosulfate method in the laboratories of Inorganic Chemistry Department.

IR spectra were recorded in KBr pellets with a Bio-Rad FTIR 135 spectrometer in the range 400–4000 $\mathrm{cm^{-1}}$. Electronic spectra by diffuse reflectance technique, with MgO as standard, were recorded in the range 380–1100 nm, on a VSU 2P-Zeiss Jena spectrometer. Magnetic measurements were done by Faraday’s method, at room temperature, using $\mathrm{Hg[Co(NCS)_4]}$ as standard. The molar magnetic susceptibilities were calculated and corrected for the atomic diamagnetism. EPR spectra were recorded on microcrystalline samples at room temperature with a

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Varian E-9 spectrometer. The field was calibrated using crystalline diphenylpicrylhydrazyl (*g*=2.0036).

Anti-HIV tests were performed by adding the DMSO solutions with various concentrations of complexes to cell culture medium, T4 lymphocytes and then HIV-1. Cultures were incubated at 37°C in a 5% carbon dioxide atmosphere for six days. To the incubated cultures was then added the tetrazolium salt; the formazan color development was analysed spectrophotometrically. Complexes-treated virus-infected cells were compared with complexes-treated non-infected cells as well as with other appropriate controls (untreated infected and untreated non-infected cells, complexes-containing wells without cells) on the same plate.

The heating curves (TG, DTA and DTG) were recorded in a static air atmosphere using a MOM Hungary, Paulik–Paulik–Erdey derivatograph type with a sample mass of ca. 50 mg over the temperature range 20–1000°C, using a heating rate of 10°C min^{-1}.

Synthesis of the complexes

Compound [NiL(1)Cl]·2H_2O (**1**)

To a suspension of nickel(II) chloride (1 mmole, 0.237 g), HTDA (2 mmoles, 0.266 g) and 1,2-diaminoethane (2 mmoles, 0.13 mL) in 100 mL methanol was added dropwise 1 mL triethylamine and 10 mL formaldehyde (37%). The reaction mixture was refluxed 24 h until a green-brownish compound was formed. The microcrystalline product was filtered off, washed with EtOH, Et_2O and air-dried. Analysis, found: Ni, 10.68; C, 25.88; Cl, 6.58; H, 4.45; N, 24.90; S, 22.83%; mass loss until 120°C, 6.39%; $NiC_{12}ClH_{25}N_{10}O_2S_4$ requires: Ni, 10.41; C, 25.57; Cl, 6.29; H, 4.47; N, 24.84; S, 22.75%; mass loss until 120°C, 6.39%.

IR (KBr pellet), cm^{-1}: ν_{OH}, 3420m, sh; ν_{NH}, 3260s, br; $\nu_{as(CH_2)}$, 2938m; $\nu_{s(CH_2)}$, 2880m, 2860m; TI ($\delta_{NH}\nu_{C=N}$ +δ_{CH}), 1650m, 1600sh; δ_{NH_2}, 1540m; $\nu_{sC=N}$, 1450m; TII (δ_{NH}+δ_{CH}+$\nu_{C=N}$+$\nu_{C=S}$), 1365s, 1360s; $\nu_{C_{heterocyclic}-N}$, 1280w, 1265w; $\nu_{C_{aliphatic}-N}$, 1185m; TIII ($\nu_{C=N}$+$\nu_{C=S}$), 1045s; ν_{N-N}, 960m; ρ_{CH_2}, 780m; TIV ($\nu_{C=S}$), 710m; $\nu_{as(C-S-C)}$, 640w; $\nu_{s(C-S-C)}$, 608w, ν_{Ni-N}, 440w.

Compound [CuL(2)Cl]·2H_2O (**2**)

To a suspension of copper(II) chloride (1 mmole, 0.170 g), HTDA (2 mmoles, 0.266 g) and 1,2-diaminoethane (2 mmoles, 0.13 mL) in 100 mL methanol was added dropwise 1 mL triethylamine and 10 mL formaldehyde (37%). The reaction mixture was refluxed 24 h until a green-brownish compound was formed. The microcrystalline product was filtered off, washed with EtOH, Et_2O and air-dried. Analysis, found: Cu, 15.49; C, 23.38; Cl, 8.75; H, 5.60; N, 23.82; S, 15.64; mass loss until 120°C, 8.58%; $CuC_8ClH_{23}N_7O_2S_2$ requires: Cu, 15.41; C, 23.30; Cl, 8.62; H, 5.62; N, 23.77; S, 15.55; mass loss until 120°C, 8.74%.

IR (KBr pellet), cm^{-1}: ν_{OH}, 3480m, sh; $\nu_{as(NH_2)}$, 3420s; $\nu_{s(NH_2)}$, 3240m, br; $\nu_{as(CH_2)}$, 2925m; $\nu_{s(CH_2)}$, 2870m, 2860m; TI, 1650m, 1610m; δ_{NH_2}, 1560s; $\nu_{s(C=N)}$, 1450s; TII, 1360s; $\nu_{C_{heterocyclic}-N}$, 1275m, 1250w; $\nu_{C_{aliphatic}-N}$, 1110m, 1080w; TIII, 1045s; ν_{N-N}, 965w; ρ_{CH_2}, 780m; TIV, 730w; $\nu_{as(C-S-C)}$, 650w; $\nu_{s(C-S-C)}$, 610w; ν_{Ni-N}, 455w.

Compound [NiL(3)Cl_2] (**3**)

To a suspension of nickel(II) chloride (1 mmole, 0.237 g), ATS (2 mmoles, 0.266 g) and 1,2-diaminoethane (2 mmoles, 0.13 mL) in 100 mL methanol was added dropwise 1 mL triethylamine and 10 mL formaldehyde (37%). The reaction mixture was refluxed 24 h until a green-brownish compound was formed. The microcrystalline product was filtered off, washed with EtOH, Et_2O and air-dried. Analysis, found: Ni, 9.02; C, 22.11; Cl, 10.92; H, 3.63; N, 25.46; S, 19.62%; $NiC_{12}Cl_2H_{24}N_{12}O_4S_4$ requires: Ni, 8.92; C, 21.90; Cl, 10.77; H, 3.68; N, 25.53; S, 19.48%.

IR (KBr pellet), cm^{-1}: ν_{NH}, 3300s, br; $\nu_{as(CH_2)}$, 2970m, 2935m; $\nu_{s(CH_2)}$, 2880m; δ_{NH}, 1640s,1600m; δ_{NH_2}, 1520m; $\nu_{C=N}$, 1450s, 1410m, 1380s,1360s; $\nu_{as(SO_2)}$, 1330m, 1310m; $\nu_{s(C-N)}$, 1280s; ν_{S-N}, 930m; ρ_{NH}, 820m; ρ_{CH_2}, 780w, 660m; ν_{Ni-N}, 405w.

Compound [CuL(3)Cl_2]·4H_2O (**4**)

To a suspension of nickel(II) chloride (1 mmole, 0.237 g), ATS (2 mmoles, 0.266 g) and 1,2-diaminoethane (2 mmoles, 0.13 mL) in 100 mL methanol was added dropwise 1 mL triethylamine and 10 mL formaldehyde (37%). The reaction mixture was refluxed 24 h until a green-brownish compound was formed. The microcrystalline product was filtered off, washed with EtOH, Et_2O and air-dried. Analysis, found: Cu, 8.69; C, 19.66; Cl, 9.73; H, 4.35; N, 22.89; S, 17.84; mass loss until 120°C, 9.86%; $CuC_{12}Cl_2H_{32}N_{12}O_8S_4$ requires: Cu, 8.64; C, 19.61; Cl, 9.65; H, 4.39; N, 22.86; S, 17.44; mass loss until 120°C, 9.80%.

IR (KBr pellet), cm^{-1}: ν_{OH}, 3420m; ν_{NH}, 3200s, br; $\nu_{as(CH_2)}$, 2960m; $\nu_{s(CH_2)}$, 2890m; δ_{NH}, 1670s,1630m; δ_{NH_2}, 1460m; $\nu_{C=N}$, 1450s, 1370s; $\nu_{as(SO_2)}$, 1320m, 1300m; $\nu_{s(C-N)}$, 1260s, 1180s; ν_{S-N}, 950m, 935m; ρ_{NH}, 910m, 880m, 840m; ρ_{CH_2}, 780w, 660m; ν_{Cu-N}, 460w, 410w.

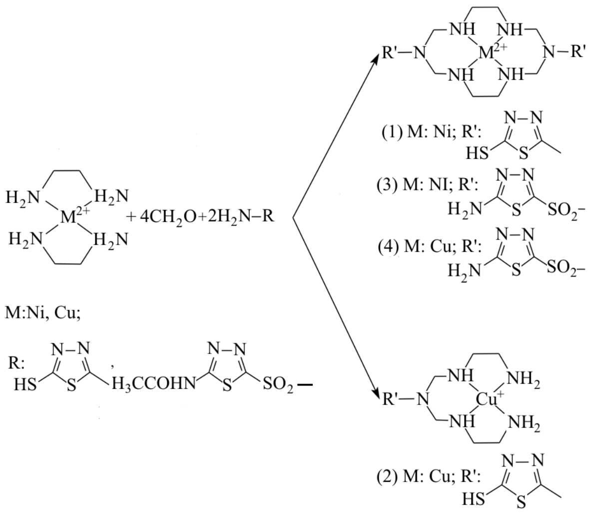
Results and discussion

Synthesis and physico-chemical characterisation of the complexes

The template condensation reaction of aliphatic polyamines with various nucleophiles and formaldehyde are the subject of many studies. Using this method there were synthesised a great number of unsaturated polyaza macrocyclic or acyclic compounds containing $–N–CH_2–N–$ linkages [19]. We have synthesised ligands containing 1,3,4-thiadiazole residues by condensation of 1,2-diaminoethane, formaldehyde and 2-amino-1,3,4-thiadiazole-5-thiole (HTDA), respectively, 5-acetamido-1,3,4-thiadiazole-2-sulfonamide (ATS) in presence of Ni(II) or Cu(II). The synthesis has been performed in order to obtain azamacrocyclic complexes bearing 1,3,4-thiadiazole moieties as part of the ligand superstructure. The presence of the supplementary coordinating groups offers the possibility of the generation homo- or heteropolynuclear species. Detailed studies of these behaviours will be the subject of other reports.

The one-pot reaction (Scheme 1) of excess formaldehyde with 1:1:1 molar mixture of nickel(II) or copper(II) chloride, 1,2-diaminoethane and 2-amino-1,3,4-thiadiazole-5-thiole (HTDA), respectively, 2-acetamido-1,3,4-thiadiazole-5-sulfonamide (ATS) in an alkaline medium produced the following species $[MLCl_n]\cdot mH_2O$ ((**1**) M:Ni, L:L(1), n=1, m=2; (**2**) M:Cu, L:L(2), n=1, m=2; (**3**) M:Ni, L:L(3), n=2, m=0; (**4**) M:Cu, L:L(3), n=1, m=2) (Scheme 1).

All the complexes are polycrystalline solids soluble in dimethyl sulfoxide and N,N-dimethylformamide. As the electronic spectra in solution indicated, the hexaazamacrocyclic complexes, with two non-coordinated tertiary amine nitrogens are stable in aqueous acidic solution for a long period like other cyclic aminoalkanes.



Scheme 1

The major IR spectral features of complexes presented at experimental part indicate that in the spectra of complexes appear the characteristic bands of 1,3,4-thiadiazole moieties [26, 27].

The bands corresponding to the combined vibration modes of the thioamide moiety are significantly splitted and shifted in the spectra of the complexes (**1**) and (**2**). In the range characteristic for the TI vibrations, the spectra of the complexes display two components, both shifted towards higher wavenumbers in comparison with both HTDA and its sodium salt. In the same sense are shifted the bands associated to TII and TIII while those associated with TIV are shifted towards lower wavenumbers.

The bands due to secondary amide group are absent in spectra of complexes [29, 30]. This information suggests that the hydrolysis of acetamide group occurs in the case of complexes (**3**) and (**4**) during the condensation processes. For these complexes in the range characteristic for the $\nu_{as(SO_2)}$, $\nu_{C=N}$ and, respectively, $\nu_{S–N}$ vibrations [31], the spectra of the complexes display two components and was also observed the shift of the band associated with $\nu_{s(SO_2)}$ towards higher wavenumbers. All these modifications indicate the involvement of the thiadiazole derivatives in condensation.

The infrared spectra of the compounds exhibit vibration from only secondary and not primary amines, except for complex (**2**) for which do appear two large bands at 3420 and 3240 cm^{-1}.

The spectra in the characteristic ranges for water show a large band about 3400 cm^{-1} assigned to ν_{OH} stretching vibrations [32]. The new bands, observed in 400–460 region are assignable to $\nu_{M–N}$ vibrations [32].

The diffuse-reflectance spectra of complexes (**1**) and (**3**) in the VIS-near-IR region show the bands, as is usually observed for Ni(II) in complexes with pseudooctahedral surrounding [33]. The two-absorption bands spin allowed are shown in Table 1 together with the corresponding assignments and the crystal field parameters. The distortion from a regular octahedron, associated with the different nature of ligands and/or donor atoms, generated the broad aspect of these bands. The average values of crystal field parameter falling in range 9000–9500 cm^{-1}, are consistent with the presence of chlorine as donor beside nitrogen, atoms that generate a weak field.

The electronic spectrum of Cu(II) complexes (**4**) shows a broad band centred at 16130 and a shoulder at higher energies, which agree with an octahedral geometry [33, 34].

The Ni(II) complexes exhibit at room temperature magnetic moments close to the spin only value indicating the absence of magnetic interaction between paramagnetic ions in this condition [34]. Both copper com-

Table 1 Absorption maxima (cm^{-1}), assignments, crystal field parameters and magnetic moments for complexes (**1**)–(**4**)

Complex	Absorption maxima/cm^{-1}	Assignments	B/cm^{-1}	β	μ_{eff}/μ_B
[NiL(1)Cl]·2H$_2$O (**1**)	(25520)* 14990 9150	$^3A_2\rightarrow{}^3T_2$ $^3A_2\rightarrow{}^3T_1(F)$ $^3A_2\rightarrow{}^3T_1(P)$	871	0.84	3.20
[CuL(2)Cl]·2H$_2$O (**2**)	>26315	CT			0
[NiL(3)Cl$_2$] (**3**)	(26687)* 15625 9524	$^3A_2\rightarrow{}^3T_2$ $^3A_2\rightarrow{}^3T_1(F)$ $^3A_2\rightarrow{}^3T_1(P)$	916	0.88	3.15
[CuL(3)Cl$_2$]·4H$_2$O (**4**)	26315 18518 16130	CT $d_{xz},d_{yz}\rightarrow d_{x2-y2}$ $d_{xy}\rightarrow d_{x2-y2}$			1.75

*the calculated values with König equations [35].

pounds are EPR silent suggesting for complex (**4**) the possibility of dimerisation and the appearance of an antiferromagnetic coupling between paramagnetic ions mediated by the thiadiazole moieties that could act as bridge. This behaviour is also according to the smaller value of the magnetic moment at room temperature. Complex (**2**) is diamagnetic, which means that 2-amino-1,3,4-thiadiazole-5-thiole reduced Cu(II) during the condensation processes. Such behaviour has already been observed for similar thiole derivatives [28, 37–39].

The complexes were tested in vitro for the anti-HIV activity but it was not evidenced any significant activity. This behaviour could be assigned either to degeneration or rapid metabolisation of the complexes in the cultures conditions.

Thermal behaviour of the complexes

Thermal behaviour of complexes was investigated by thermal gravimetric analysis (TG) and the final residues were examined by X-ray diffraction on powder. The intermediate products formed during thermolysis were not possible to identify because the steps were not distinct, except for the anhydrous complexes formed after the first decomposition step of complexes (**1**), (**2**) and (**4**).

According to the observed mass losses, the following degradation scheme might be proposed for complex (**1**):

$$[Ni(C_{12}H_{18}N_{10}S_4)Cl]\cdot 2H_2O\rightarrow[Ni(C_{12}H_{18}N_{10}S_4)Cl]\rightarrow$$
$$\rightarrow[Ni(C_2H_2N_2S_2)Cl]\rightarrow NiO_{0.5}Cl\rightarrow NiO$$

The first step in the curve (Fig. 1) occurred in the temperature range 50–160°C (the maximum decomposition rate corresponds to 80°C according to DTG curve) with an endothermic effect. This step corresponds to distinct loss of two water molecules. The anhydrous complex suffers two degradation processes that could not be well separated. The empirical formula [Ni(C$_2$H$_2$N$_2$S$_2$)Cl] was tentatively proposed for the intermediate resulted at 305°C according to the mass loss (Table 2). The product formed, after these steps, is a mixture of nickel(II) chloride and oxide, the total transformation in oxide being made at 600°C.

The thermal degradation of the compound (**2**) begins at 50°C (Fig. 2). Within the temperature interval 50–115°C the water molecules are lost in a well definite, endothermic step; the temperature range corresponding to the lost indicates their nature as crystallisation water. This behaviour supports the formulation [CuL(2)]Cl·1.5H$_2$O for the compound that was proposed on the basis of analytical and spectral data. The next exothermic step of the thermal degradation that occurs between 115–385°C, corresponds to minimum two processes, as the DTG and DTA curves indicate. The empirical formula [Cu(C$_2$H$_2$N$_2$S$_2$)Cl] was also proposed for the intermediate resulted at 385°C according to the mass loss (Table 2). Such behaviour was also observed for other complexes with 1,3,4-thiadiazole derivatives [40]. In the next step accompanied by a strong exothermic effect, until 535°C,

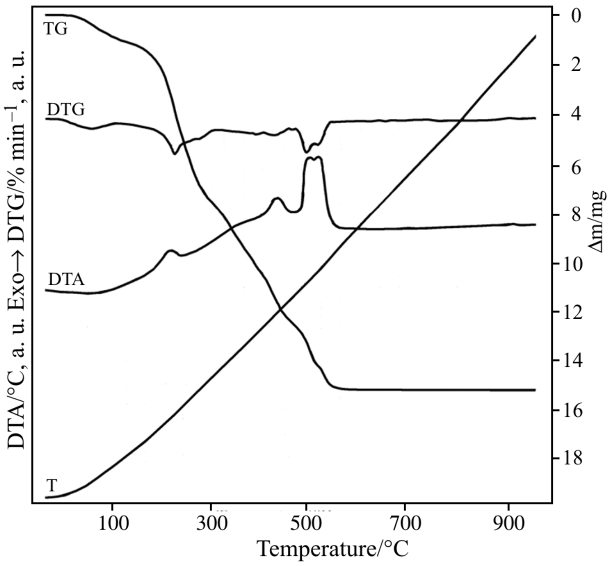


Fig. 1 TG, DTG and DTA curves of (**1**) (sample mass: 17.4 mg)

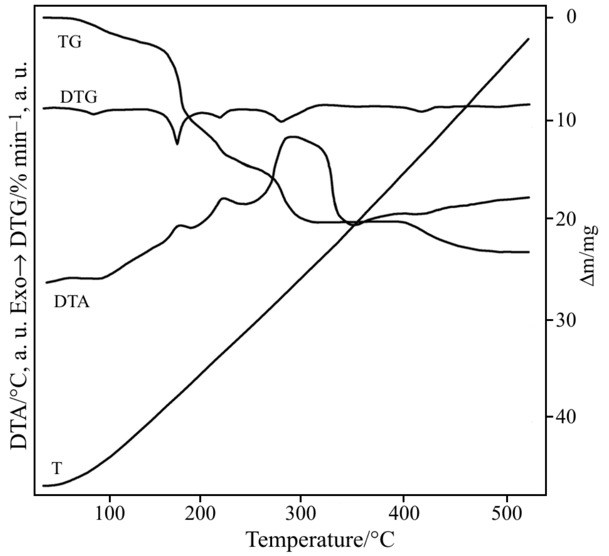


Fig. 2 TG, DTG and DTA curves of (**2**) (sample mass: 30.0 mg)

occurs the oxidation of the organic component that leads to a mixture of copper(II) sulphate and oxide. The final residue at 900°C is copper(II) oxide.

The TG, DTG and DTA curves corresponding to the complex (**3**) heating in static air atmosphere, in the 20–1000°C temperature range, are presented in Fig. 3. The complex (**3**) was isolated from reaction medium as anhydrous species as it is also confirmed by the thermal degradation that begins at 255°C. The thermal degradation occurs in three steps in the temperature range 255–730°C. In the first two endothermic steps the thiadiazole residues are lost together with one of the sulfoxide fragment. The endothermic effects could be associated with the molecular rearrangements that accompanied the covalent bonds cleavage. The third step, an exothermic and complex one, corresponds to the organic residue pyrolise and nickel(II) sulphate generation, as indicates the chemical analysis and IR spectrum.

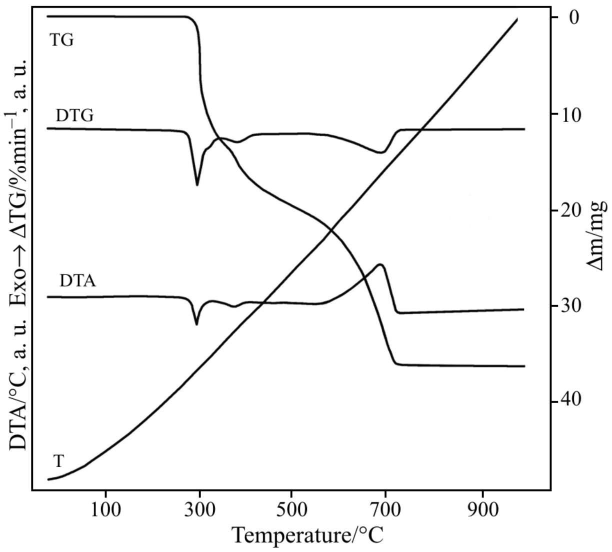


Fig. 3 TG, DTG and DTA curves of (**3**) (sample mass: 47.7 mg)

On the basis of TG curve, the following degradation scheme might be proposed for complex (**4**):

$$[\mathrm{Cu}(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{N}_{12}\mathrm{O}_4\mathrm{S}_4)\mathrm{Cl}_2]\cdot 4\mathrm{H}_2\mathrm{O}\rightarrow$$
$$\rightarrow[\mathrm{Cu}(\mathrm{C}_{12}\mathrm{H}_{24}\mathrm{N}_{12}\mathrm{O}_4\mathrm{S}_4)\mathrm{Cl}_2]\rightarrow$$
$$\rightarrow[\mathrm{Cu}(\mathrm{C}_8\mathrm{H}_{22}\mathrm{N}_6)\mathrm{Cl}_2]\rightarrow\mathrm{CuO}$$

Within the temperature range 50–150°C the crystallisation water molecules are lost in a well definite, endothermic step. In the next exothermic step, between 170–280°C, the thermal degradation of anhydrous complex occurs in minimum two processes, as the DTG and DTA curves indicate. The empirical formula $[\mathrm{Cu}(\mathrm{C}_8\mathrm{H}_{22}\mathrm{N}_6)\mathrm{Cl}_2]$ proposed for the intermediate resulted at 280°C according to the mass loss (Table 2) corresponds to the oxidative degradation of the two sulphonamide residues. In the next step accompanied by a strong exothermic effect, until 620°C, occurs the oxidation of the residual macrocyclic ligand with the formation of copper(II) oxide.

Conclusions

The nickel(II) and copper(II) complexes with ligands resulted in one-pot condensation of 1,2-diaminoethane, formaldehyde and heterocyclic derivatives 2-amino-1,3,4-thiadiazole-5-thiole (HTDA) or 2-acetamido-1,3,4-thiadiazole-5-sulfonamide (ATS) have been synthesised.

The bond and stereochemistry were characterised by means of IR, electronic and EPR spectroscopy. The proposed stereochemistries are according to the magnetic moment at room temperature.

Thermal decomposition of complexes gave the possibility to establish the number and nature of water molecule, the composition of complexes and also the intervals of thermal stability. During the thermal degradation it was not observed the formation of sulphide species as intermediates. The different thermal behaviour of the complexes could be associated with the different nature of the ligands and/or the metallic ions.

In order to confirm the nature of final residues the chemical analysis, IR spectra and X-ray diffractograms were used.

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