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Thermal behaviour of metal complexes of two 5-nitroso-4-xyloxylamino pyrimidine derivatives with Co(II), Ni(II), Cu(II) and Ag(I) ions

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Abstract

The thermal behaviour of seven metal complexes of 2-methylthio-5-nitroso-6-oxo-4-xyloxylamino pyrimidine (**A**) and 1-methyl-2-methylthio-5-nitroso-6-oxo-4-xyloxylamino pyrimidine (**B**) with Co(II), Ni(II), Cu(II) and Ag(I) ions has been studied by thermogravimetric and differential scanning calorimetric techniques. IR spectroscopy was used in the identification of the intermediate and final products of the pyrolysis. The enthalpies of several of the processes were also calculated.

INTRODUCTION

Interest in the metal complexes of pyrimidine derivatives stems from the fact that they are widespread in living systems. Such studies are of interest in order to establish the role of metal ions in biological systems. Moreover, among pyrimidine derivatives, thiopyrimidine derivatives have found application as drugs, for instance, as anti-metabolites [1]; they also have anti-bacterial and anti-viral [2,3] properties, and anti-tumour and anti-thyroidal activities [4,5].

In addition, studies on these metal complexes are interesting for the development of tools for structural and functional investigations of biological molecules, a research area which has grown considerably in recent years [6,7].

In the present paper we describe the thermal behaviour of seven complexes obtained by reactions of two thyopyrimidine derivatives, 2-methylthio-5-nitroso-6-oxo-4-xylosylamino pyrimidine (**A**) and 1-methyl-2-methylthio-5-nitroso-6-oxo-4-xylosylamino pyrimidine (**B**), with Co(II), Ni(II),

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Cu(II) and Ag(I) metal ions. This study complements a series of previous papers, all devoted to the study of the reactivity of 4-glycosylaminopyrimidine derivatives with some metal ions [8–11].

EXPERIMENTAL

The two pyrimidine derivatives were prepared by a previously reported method [12] using analytical reagent grade chemicals.

The preparative methods for the isolated complexes $Co(\mathbf{A}^-)_2 4H_2O$, $Ni(\mathbf{A})_2(NO_3^-)_2 4H_2O$, $Cu(\mathbf{A}^-)(NO_3^-)2H_2O$, $Ag(\mathbf{A}^-)2.5H_2O$, $Ni(\mathbf{B})_2(NO_3^-)_2 4H_2O$, $Cu(\mathbf{B}^-)(NO_3^-)2H_2O$ and $Ag(\mathbf{B})(NO_3^-)H_2O$ have been described in a previous paper [11], also using analytical reagent grade chemicals. Their corresponding chemical analyses are summarized in Table 1.

The TG and DTG curves were obtained on a Mettler TG 50 thermobalance and the DSC curves on a Mettler DSC 20 differential scanning calorimeter, for which a static air atmosphere, heating rates of 10 or 20 °C min^{-1} and sample weights between 0.84 and 2.38 mg were used. The thermogravimetric curves were obtained under an oxygen flow rate of 100 ml min^{-1} using sample weights between 4.46 and 10.77 mg. The IR spectra of the residues from pyrolitic processes were recorded on a Perkin–Elmer 983 G spectrophotometer using KBr pellets for the 4000–250 cm^{-1} range and polyethylene pellets for the 600–180 cm^{-1} range.

RESULTS AND DISCUSSION

A schematic representation of compounds **A** and **B** is shown in Fig. 1.

The analytical, magnetic and spectral data of the seven complexes obtained suggest that when $\mathbf{A}^-$ or $\mathbf{B}^-$ anions are present in a complex molecule, their coordination to the metal ion occurs through the negatively

TABLE 1

Colour, analytical data (theoretical values in parentheses) and proposed formulae for the complexes

Complex	Colour	Analytical data (%)			
		C	H	N	Metal
$Co(\mathbf{A}^-)_2 4H_2O$	Orange	31.39 (31.29)	4.32 (4.43)	14.80 (14.60)	7.40 (7.70)
$Ni(\mathbf{A})_2(NO_3^-)_2 4H_2O$	Green	27.84 (26.94)	4.19 (4.04)	15.09 (15.71)	6.72 (6.59)
$Cu(\mathbf{A}^-)(NO_3^-)2H_2O$	Green	25.21 (25.07)	3.56 (3.55)	13.51 (14.63)	12.95 (13.25)
$Ag(\mathbf{A}^-)2.5H_2O$	Dark green	24.85 (25.53)	3.71 (3.83)	11.32 (11.91)	23.19 (22.95)
$Ni(\mathbf{B})_2(NO_3^-)_2 4H_2O$	Green	28.25 (28.73)	4.27 (4.35)	15.00 (15.23)	6.33 (6.39)
$Cu(\mathbf{B}^-)(NO_3^-)2H_2O$	Brown	26.34 (26.80)	3.82 (3.86)	13.95 (14.21)	12.62 (12.90)
$Ag(\mathbf{B})(NO_3^-)H_2O$	Green	26.97 (26.30)	3.39 (3.19)	13.52 (13.94)	21.10 (21.49)

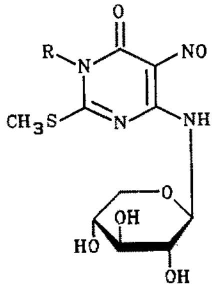

Fig. 1. Schematic representation of compounds **A** ($R = H$) and **B** ($R = CH_3$).

charged O atom of the 6-oxy group and the O atom of the C-5–NO group. However, when **A** or **B** are present in neutral molecular forms, the coordination occurs through the oxygen atom of the 6-oxo group and the N atom of the C-5–NO group for the two Ni(II) complexes studied, but through the sulphur atom in the case of the $Ag(\mathbf{B})(NO_3^-)$ complex. The inferred structures defined by the arrangement of the donor atoms around the metal ion were $[Co(\mathbf{A}^-)_2]4H_2O$ (tetrahedral), $[Ni(\mathbf{A})_2(H_2O)_2](NO_3^-)_2$-$2H_2O$ and $[Ni(\mathbf{B})_2(H_2O)_2](NO_3^-)_2 2H_2O$ (octahedral), $[Cu(\mathbf{A}^-)(H_2O)_2]$-$(NO_3^-)$ and $[Cu(\mathbf{B}^-)(H_2O)_2](NO_3^-)$ (tetrahedral), $[Ag(\mathbf{A}^-)]2.5H_2O$ (linear, dimeric) and $[Ag(\mathbf{B})](NO_3^-)H_2O$ (linear, polymeric).

The thermal behaviour of the compounds (**A** and **B**) used as ligands in the complexes under study have been previously reported [8].

The TG and DSC curves of **A** and **B** complexes are shown in Figs. 2 and 3 respectively. The data given in Table 2 were obtained from these curves.

The TG curves of the seven complexes show a first weight loss which finished at temperatures which vary between 120 °C in the case of the $[Cu(\mathbf{B}^-)(H_2O)_2](NO_3^-)$ complex and 160 °C for the $[Ni(\mathbf{A})_2(H_2O)_2]$-$(NO_3^-)_2 2H_2O$ complex. These weight losses are in concordance with the theoretical values calculated for the total dehydration of the complexes and are summarized in Table 2. The expected endothermic effects accompanying the dehydrations can be observed in the CDS plots of all the complexes. The unsymmetrical character of these endothermics in the case of the Ni(II) and Cu(II) complexes together with the analytical and magnetic data [11], suggest that two of the four water molecules present in each of these complexes are directly coordinated to the corresponding metal ion. This fact is also supported by the higher dehydration energies in the four complexes mentioned above. In contrast, the low dehydration energies for each mole of water in the cases of $[Co(\mathbf{A}^-)_2]4H_2O$, $[Ag(\mathbf{A}^-)]2.5H_2O$ and $[Ag(\mathbf{B})](NO_3^-)H_2O$, suggest that the water is probably not coordinated to the corresponding metal ions. In addition, dehydrated species from complexes with uncoordinated water are all unstable, whereas those complexes with coordinated water give rise to stable dehydrated species, as can be seen in the corresponding TG plots of $[Co(\mathbf{A}^-)_2]4H_2O$, $[Ag(\mathbf{A}^-)]2.5H_2O$

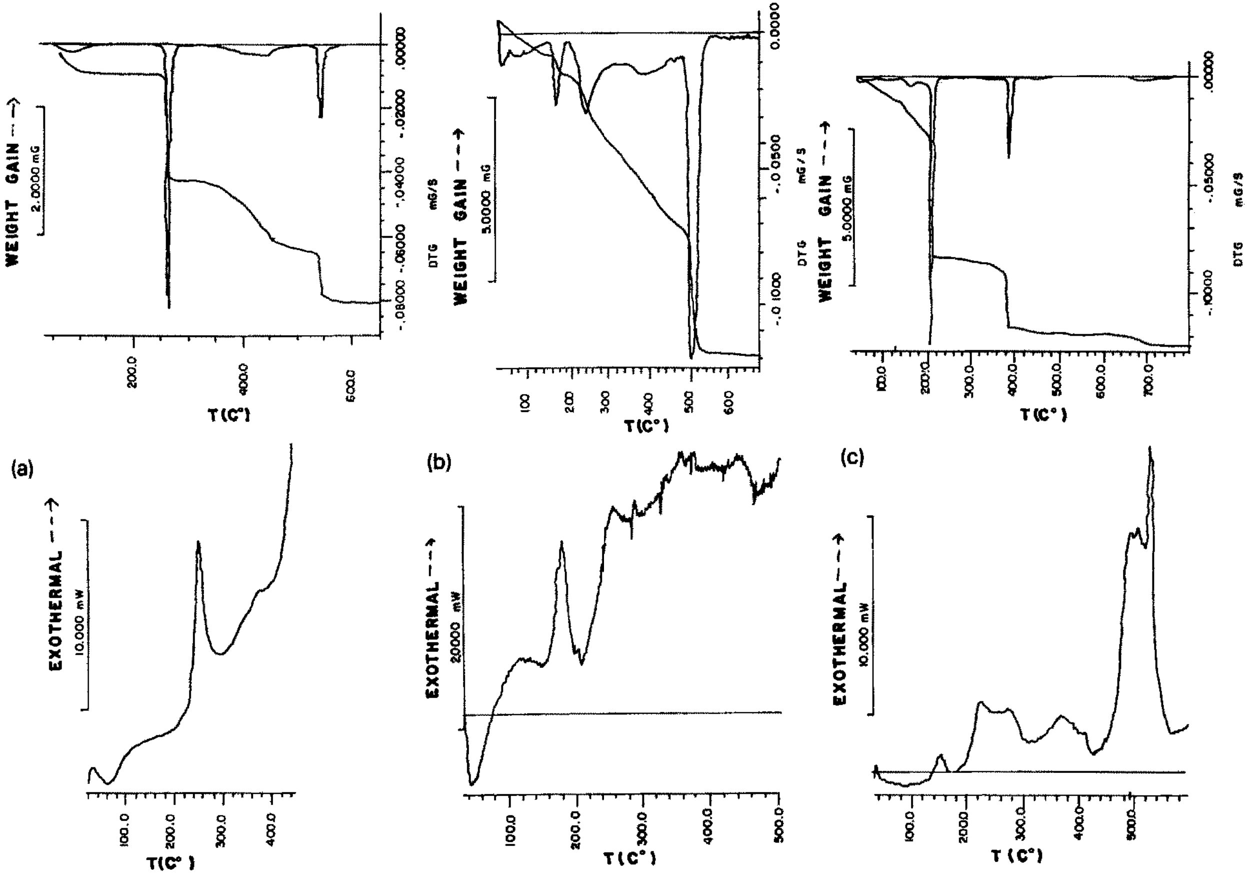

Fig. 2. TG and DSC curves of (a) $[Co(A^-)_2]4H_2O$; (b) $[Ni(A)_2(H_2O)_2](NO_3^-)_2 2H_2O$; (c) $[Cu(A^-)(H_2O)_2](NO_3^-)$; (d) $[Ag(A^-)]2.5H_2O$.

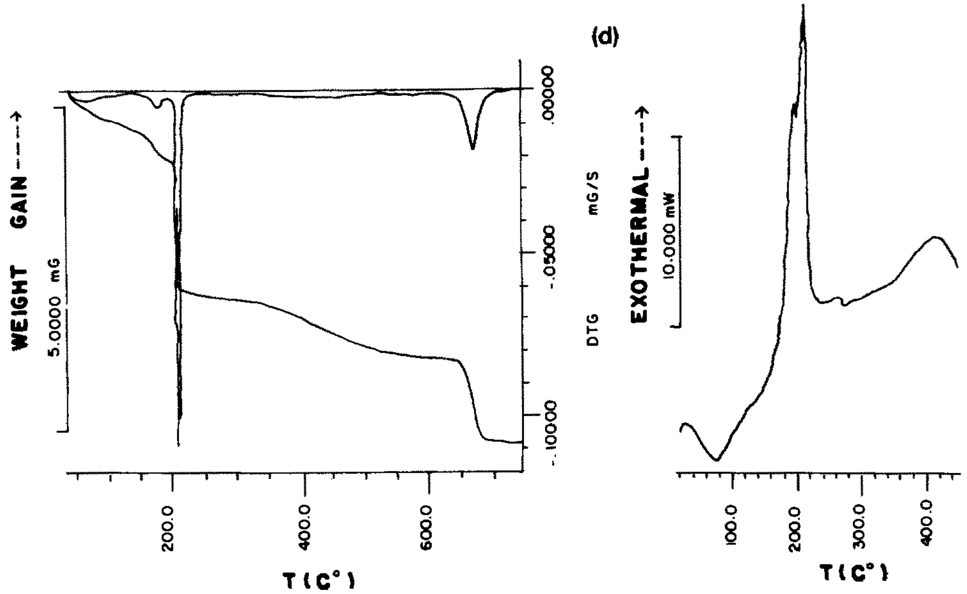

Fig. 2. (continued).

and [Ag(**B**)](NO_3^-)H_2O. Moreover, it is apparent that none of the complexes have a clear melting point, as can be seen in Figs. 2 and 3.

The complexes with uncoordinated NO_3^- ions, i.e. all except [Co(A^-)$_2$]$4H_2O$ and [Ag(A^-)]$2.5H_2O$, start their pyrolytic decomposition at lower temperatures (120–150 ° C) than those without NO_3^- ions in their stoichiometries, which decompose at 260 ° C in the case of [Co(A^-)$_2$]$4H_2O$ and at 215 ° C in the case of [Ag(A^-)]$2.5H_2O$. This suggests that the pyrolytic decomposition continues in the former complexes with elimination of the free nitrate group.

In three of the nitrate complexes, [Ni(A)$_2$(H_2O)$_2$](NO_3^-)$_2$$2H_2O$, [Cu($A^-$)($H_2O$)$_2$]($NO_3^-$) and [Cu($B^-$)($H_2O$)$_2$]($NO_3^-$), this effect seems to be differentiated in the corresponding TG curves by a second slight weight loss which overlaps with a third abrupt one, corresponding to the continuation of the pyrolysis; this prevents the corresponding weight loss to be determined, except in the case of the [Cu(B^-)(H_2O)$_2$](NO_3^-) complex where the found and calculated accumulated weight losses are in good agreement.

The IR spectra of samples of the three above complexes heated to the final temperature of this TG effect, show clearly the loss of the strong, sharp band corresponding to free NO_3^- groups. The loss of the nitrate groups in these three complexes is accompanied by exothermic effects in their DSC plots whose calculated enthalpies must be viewed with caution because these effects overlap with an adjacent exothermic corresponding to the continuation of the pyrolytic decomposition.

TABLE 2

Thermoanalytical data of the metal complexes

Complex	Process	Temperature [a] (°C)	ΔH (kJ mol^{-1})	Accumulated weight loss		Residue	
				Found	Calculated	Found	Calculated
$[Co(A^-)]4H_2O$	$-4H_2O$	53 (endo)	61	9.70	9.41	10.08	10.44
	−Xylose	260 (exo)	– [b]	44.97	44.18		
	−Pyrolysis	380 (exo)	– [b]	–	–		
$[Ni(A)_2(H_2O)_2](NO_3^-)_2 2H_2O$	$-4H_2O$	51 (endo)	152.6	6.72	6.59	8.55	8.38
	$-2NO_3^-$	179 (exo)	131.3 [b]	–	–		
	−Pyrolysis	280 (exo)	– [b]	–	–		
		373 (exo)	– [b]	–	–		
$[Cu(A^-)(H_2O)_2](NO_3^-)$	$-2H_2O$	65 (endo) [b]	– [b]	7.47	7.51	16.21	16.59
	$-NO_3^-$	152 (exo)	42.8	– [b]	– [b]		
	−Xylose	220 (exo)	– [b]	50.01	48.17		
	−Pyrolysis	280 (exo)	– [b]	–	–		
		370 (exo)	– [b]	–	–		
		500 (exo)	– [b]	–	–		

$[Ag(\mathbf{A}^-)]2.5H_2O$	$-2.5H_2O$	77 (endo)	29	9.81	9.57	23.19	22.95
	$-$Xylose	200 (exo)	183	28.84	28.36		
	$-$Pyrolysis	260 (exo)	–[b]	–	–		
		410 (exo)	–[b]	–	–		
$[Ni(\mathbf{B})_2(H_2O)_2](NO_3^-)_2 2H_2O$	$-4H_2O$	107 (endo)	153[b]	7.40	7.84	8.05	8.06
	$-$(Xylose + $2NO_3^-$)	164 (exo)	341	48.90	50.29		
	$-$Pyrolysis	244 (exo)	–[b]	–	–		
		403 (exo)	–[b]	–	–		
$[Cu(\mathbf{B}^-)(H_2O)_2](NO_3^-)$	$-2H_2O$	57 (endo)	138	7.29	7.30	15.80	16.15
	$-NO_3^-$	151 (exo)	69	18.79	19.88		
	$-$Pyrolysis	204 (exo)	–[b]	–	–		
		363 (exo)	–[b]	–	–		
		504 (exo)	–[b]	–	–		
$[Ag(\mathbf{B})](NO_3^-)H_2O$	$-H_2O$	44 (endo)	27	4. 03	3.50	21.10	20.74
	$-$(Xylose + NO_3^-)	163 (exo)	268	42.53	41.01		
	$-$Pyrolysis	458 (exo)	–[b]	–	–		

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[a] Measured at the peak.

[b] Overlaps with an adjacent exothermic effect.

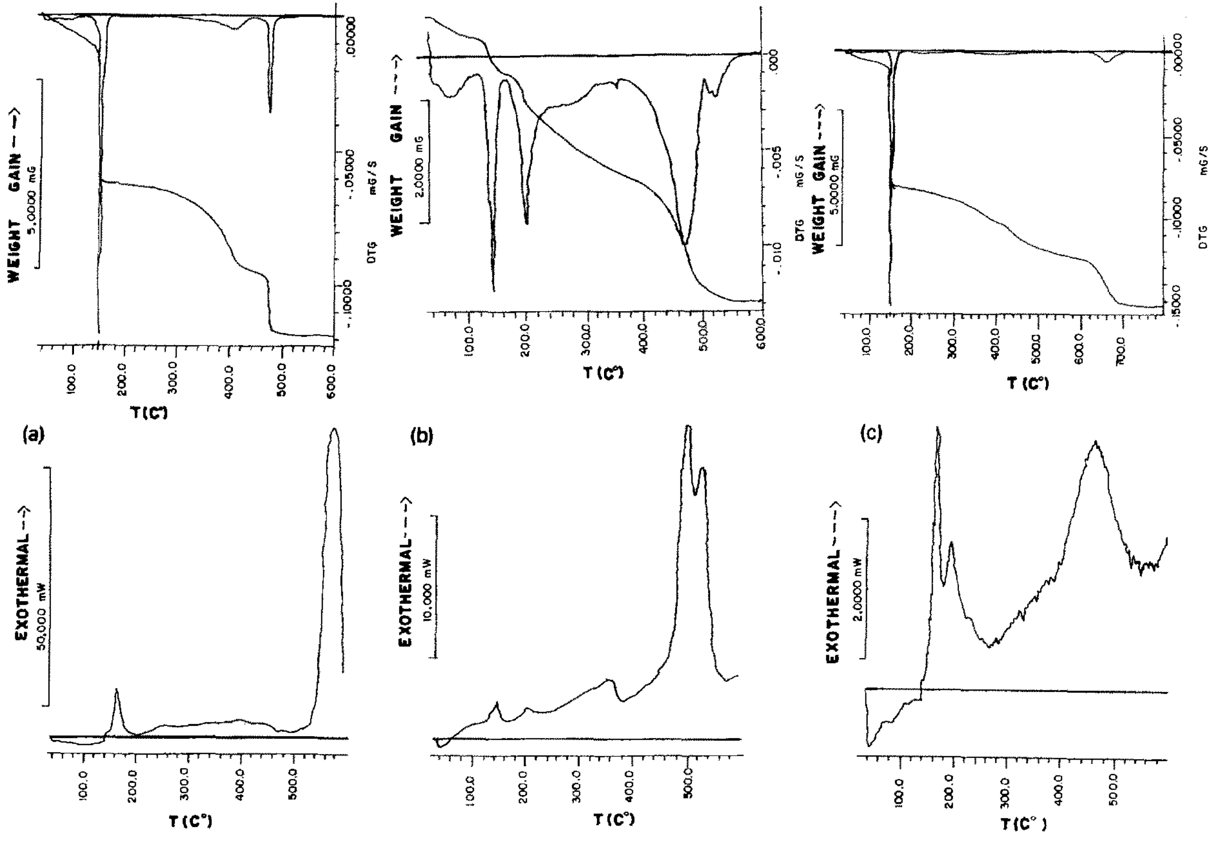

Fig. 3. TG and DSC curves of (a) $[Ni(\mathbf{B})_2(H_2O)_2](NO_3^-)_2 2H_2O$; (b) $[Cu(\mathbf{B}^-)(H_2O)_2](NO_3^-)$; (c) $[Ag(\mathbf{B})](NO_3^-)H_2O$.

Five of the seven complexes, all except $[Ni(A)_2(H_2O)_2](NO_3^-)_2 2H_2O$ and $[Cu(B^-)(H_2O)_2](NO_3^-)$, have characteristic abrupt weight losses in their TG plots when their pyrolytic decomposition continues after the dehydration. In all of their CSD diagrams a sharp exothermic effect accompanies the referred weight loss. In the case of $[Cu(A^-)(H_2O)_2](NO_3^-)$ this abrupt weight loss overlaps with the previous effect corresponding to the loss of the NO_3^- group, and two exothermics are clearly differentiated in its CSD diagram. The similarity of this effect in all of the five complexes under study suggests similar pyrolytic processes.

In order to clarify the nature of these processes, we have calculated the theoretical weight losses which correspond to the loss of the sugar residue for $[Co(A^-)_2 4H_2O$, $[Ag(A^-)]2.5H_2O$ and $[Cu(A^-)(H_2O)_2](NO_3^-)$, and those corresponding to the theoretical loss of nitrate group and sugar residue altogether for $[Ni(B)_2(H_2O)_2](NO_3^-)_2 2H_2O$ and $[Ag(B)](NO_3^-)H_2O$ (see Table 2). The very good agreement between those calculated values and the measured weight losses suggests the mentioned effects correspond to the loss of the sugar moiety. The species resulting from this loss of xylose are stable over a wide range of temperature (50–100 ° C), as reflected in the TG curves by the existence of broad plateau after the weight loss effect under discussion, then it was possible to record the IR spectra of the solid residues obtained after heating of the referred five complexes up to the corresponding plateau temperatures. All these spectra clearly show the loss of the (NO_3^-) group and the $\nu(C-C)$ and $\nu(C-O)$ bands corresponding to the sugar residue. In contrast, all the characteristic $\nu(C=C)$ and $\nu(C=N)$ bands of the pyrimidine moiety, together with those corresponding to the exocyclic substituents of the pyrimidine, remain practically unaltered.

The pyrolytic decomposition of the stable species formed after loss of xylose, can be divided into two steps. The first consisting of a slowly uninterrupted weight loss, followed by a second in which an abrupt weight loss is observed (in the case of the $[Cu(A^-)(H_2O)_2](NO_3^-)$ complex a third slow weight loss take place). The final residues were characterized by IR spectroscopy. The residues were Co_3O_4 from Co(II) complex ($T = 600$ ° C), NiO from $[Ni(B)_2(H_2O)_2](NO_3^-)_2 2H_2O$ complex ($T = 550$ ° C), CuO from $[Cu(A^-)(H_2O)_2](NO_3^-)$ complex ($T = 740$ ° C) and Ag from the two Ag(I) complexes ($T = 750$ ° C in both cases).

The two remaining complexes, namely $[Ni(A)_2(H_2O)_2](NO_3^-)_2 2H_2O$ and $[Cu(B^-)(H_2O)_2](NO_3^-)$, continue their pyrolytic decompositions uninterruptedly after dehydration, which is followed by the loss of the nitrate groups in both complexes, as mentioned above. After the loss of the nitrate groups, the pyrolytic decomposition continues without formation of stable intermediate species up to final temperatures of 600 ° C, in the case of $[Ni(A)_2(H_2O)_2](NO_3^-)_2 2H_2O$ and 750 ° C in the case of $[Cu(B^-)(H_2O)_2](NO_3^-)$, when the residues were NiO and CuO, respectively, as confirmed by IR spectroscopy.

The accumulated weight losses found for the final residues of the seven complexes are in very good agreement with the values calculated from the formulae, as can be seen in Table 2.

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