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The chromate ion as a ligand. Physicochemical studies of nickel(II) chromate complexes with 2,2′-bipyridine

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Abstract

The preparation of two novel nickel chromate complexes with 2,2′-bipyridine is described. The results of thermal, spectral, magnetic and scanning microscopic studies are analyzed. The data show that the complexes are monomers with pseudooctahedral arrangement around the nickel ion. The coordination of the chromate ion has been found in one of the complexes. The TG–DTG–DTA data show that the thermal decomposition of the complexes occurs in two and three stages in air and four stages in He atmosphere. The decomposition of the complexes has been discussed and compared to that known for other metal chromate complexes with bpy. © 1998 Elsevier Science B.V.

Keywords: Chromate ion; Nickel chromate complexes; 2, 2′-bipyridine; Physiochemical studies

1. Introduction

One of the possible routs for the detoxication of the carcinogenic Cr(VI) species is the process of its complexation [1,2]. This could limit the reduction of Cr(VI) ion [1] a condition *sine qua non* for the mutagenicity of chromium [3], or even completely abolish it [4]. The *coordination model* of Cr(VI) genotoxicity was built on the physicochemical and biological studies of copper(II) chromate and dichromate complexes with 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) [1]. Recently, it has been supported with the studies on copper(II) complexes with imidazoles [4].

This paper presents the results of further investigation on (metal ion–bpy–chromate) system. We report here the syntheses and physicochemical studies (thermal decomposition, spectroscopy UV/Vis, IR, FIR, magnetic and scanning microscopy data) for two novel nickel chromate complexes with 2,2′-bipyridine (bpy).

2. Experimental

2.1. Preparation of the compounds

2.1.1. Green complex: [Ni bpy(H_2O)$_4$]CrO_4 **[A]**

A methanolic solution of 2,2′-bipyridine (47 cm^3, 0.75 M) was added dropwise upon stirring water solution of K_2CrO_4 (140 cm^3, 0.25 M). The yellow bipyridinium chromate precipitating upon the bpy addition disappears when 30 cm^3 out of 140 cm^3 of the nickel sulphate (chloride, nitrate) (0.25 M) was

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added. The color of the solution was brown, slightly turbid. The solution was allowed to stand 24 h and the resulting light green powder has been filtered and washed with water. The precipitate was dried for five days over silica gel, after that three extra days in the vacuum box and finally two days in the dry box at 40°C.

The green compound has been also obtained from $NiCl_2$ and Ni_2SO_4 in a similar way using Ni : bpy : Cr (1 : 2 : 1) proportions (Table 2).

2.1.2. *Red complex: [Nibpy$_2$ CrO$_4$]bpy 8H$_2$O* **[B]**

A methanolic solution of 2,2′-bipyridine (100 cm^3, 0.75 M) was added dropwise upon stirring to the same amount of 0.25 M K_2CrO_4 dissolved in water. The yellow precipitate which was appearing during the mixing of the reagents (approximately after adding 30 cm^3 of the bpy) was dissolving upon further adding of the ligand. This was mixed with the 90 cm^3 of the nickel(II) sulphate (chloride, nitride) solutions (0.25 M). The change of the color of the solution from yellow to light brown was observed upon the addition of the nickel salt. The mixture was allowed to stand for three days in the mother liquid. The solution was evaporated to approximately half of the initial volume and left to stand overnight. The obtained reddish brown crystals were recrystallized from hot water (60 cm^3), filtered, washed with water and dried in the desiccator over silica gel.

The red compound has been also obtained in a similar way from $Ni(NO_3)_2$ using 1 : 2 : 1 (Ni : b-py : Cr) proportions.

2.2. *Apparatus, methods and calculations*

The concentration of the metal ions was obtained using Perkin–Elmer 180 atomic absorption spectrophotometer and carbon, hydrogen and nitrogen analyses using modified Kupman method.

TG and DTA studies were carried out simultaneously using Paulik–Paulik–Erdey type derivatograph in dynamic air and helium atmosphere over the temperature range 293–1273 K at heating rates 2.5 deg min^{-1}. The sample weight was 200 mg. The X-ray patterns of the final residues were obtained on a DRON-2 diffractometer with Cu-K radiation lamp.

IR spectra were recorded on a Perkin–Elmer 180 (50–3500 cm^{-1}) spectrophotometer in KBr pellets. FIR spectra were obtained in Nujoll mulls sandwiched between polyethylene plates.

The diffuse reflectance, room and liquid nitrogen temperature absorption spectra were recorded in the wavenumber range of 12000–49000 cm^{-1} with a Hitachi Model 356 UV/Vis spectrophotometer connected to an IBM/PC computer.

The solid-state spectra were measured in Li_2CO_3 matrix (10% sample concentration). The absorption spectra were recorded in formamide solutions. The band positions were determined with the digital filter method [5,6]. The relations between crystal field parameters and transition energies have been calculated using computer program LFPOH based on the Perumareddi data [7].

Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant.

Scanning electron micrographs were made with Stereoscan 180 Cambridge apparatus.

3. Results and discussion

The scanning electron micrographs of the substrates **[A]** and **[B]** when magnified 3000 and 20 times, respectively, showed that under the condition of the experiment, **[A]** forms very small crystallites and **[B]** large crystals (Figs. 1 and 2). Attempts to grow single crystals are being undertaken, up to now, without success.

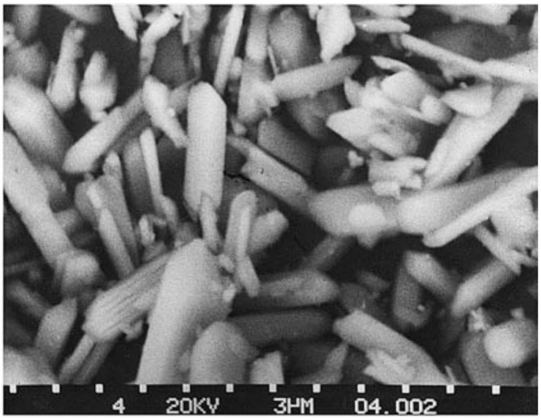

Fig. 1. Scanning electron micrograph of $[Nibpy(H_2O)_4]CrO_4$ **[A]** (magnification 3000 times).

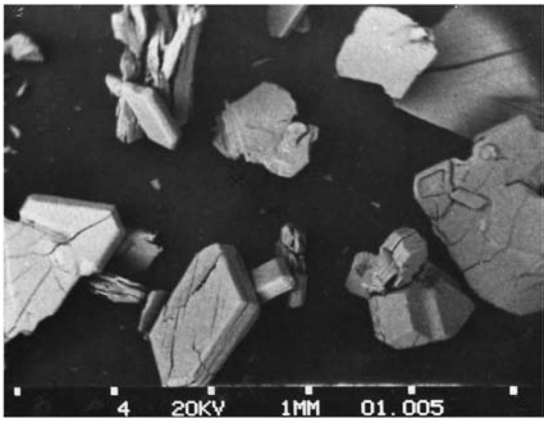

Fig. 2. Scanning electron micrograph of [Nibpy$_2$CrO$_4$]bpy 8H$_2$O [**B**] (magnification 20 times).

Table 1 presents the analyses of the spectra and the magnetic data. The temperature dependence of the magnetic susceptibility shows that the complexes are monomers [11]. The value of the effective moments are greater than the spin-only value of 2.83 BM which is expected for an orbital singlet ground state $^3A_{2g}$ in O_h symmetry for six-coordinate nickel(II) ion. Thus, in both complexes the nickel ion is situated in the pseudooctahedral environment. Table 2 shows the formulae of the isolating complexes depending upon the condition of the experiment and Table 3 the IR data (vide infra).

From the results presented in Table 2, we can conclude that among four candidates to be bound to the Ni(II) ion (i.e. bpy, water, the chromate and X ions ($X = Cl^-$, SO_4^{2-}, NO_3^-) the strongest one is the organic ligand. The most important factor determining the composition of the coordination sphere around Ni(II) ion is the amount of the organic ligand. For the M : L : Cr molar ratio being 1 : 3 : 1, in each case, we have observed the precipitation of **[B]** with total Ni : L ratio = 1 : 3. However, the IR data show that for some reasons, unlike in Nibpy$_3$SO$_4$ [18]

Table 1
Analyses (%) of compounds and magnetic moments

Compound		Ni	Cr	C	H	N	μ (BM)
[A] [Nibpy(H$_2$O)$_4$]CrO$_4$	Theory	14.56	12.90	29.81	4.00	6.95	3.41 ($T = 78$ K)
	Found	15.20	13.39	30.18	3.52	6.30	3.48 ($T = 297$ K)
[B] [Nibpy$_2$CrO$_4$]bpy8H$_2$O	Theory	7.45	6.60	45.76	5.12	10.67	3.37 ($T = 78$ K)
	Found	8.10	6.63	46.02	5.11	11.59	3.38 ($T = 297$ K)

Table 2
The condition of the experiment, i.e. the nickel(II) salts, the molar ratios of the reagents and the resulting solid products (in compound **[B]** the water of crystallization has been omitted)

Ni : bpy : Cr(VI)	NiSO$_4$	NiCl$_2$	Ni(NO$_3$)$_2$
1 : 1 : 1	[Ni(H$_2$O)$_4$bpy]CrO$_4$ **[A]**	[Ni(H$_2$O)$_4$bpy]CrO$_4$ **[A]**	[Ni(H$_2$O)$_4$bpy]CrO$_4$ **[A]**
1 : 2 : 1	[Ni(H$_2$O)$_4$bpy]CrO$_4$ **[A]**	[Ni(H$_2$O)$_4$bpy]CrO$_4$ **[A]**	[Nibpy$_2$(CrO$_4$)]bpy **[B]**
1 : 3 : 1	[Nibpy$_2$(CrO$_4$)]bpy **[B]**	[Nibpy$_2$(CrO$_4$)]bpy **[B]**	[Nibpy$_2$(CrO$_4$)]bpy **[B]**

Table 3
The important bands (cm^{-1}) in the IR and FIR spectra for nickel(II) chromate complexes with bpy

Compound	ν_1	ν_2	ν_3	ν_4	ν_{Ni-N}	$\nu_{asNiOCr}$
[A]	825_{ms}	305	876_{vs} 894_{s}sh 906_{s}	330_{w} 352_{ms} 365_{w}	240_{s} 268_{vs}	
[B]	814_{w}		880_{vs} 895_{s} 906_{s}	363_{s} 384_{w}	262_{ms} 288_{vs}	778_{vs}

Note: s – strong; ms – medium strong; vs – very strong; w – weak; sh – shoulder.

and $Nibpy_3Cl_2$ $C_6H_4O_6$ [19] one bpy molecule is out of the coordination sphere and at the same time the chromate ion is coordinated to the nickel(II) ion. It seems to be a stronger ligand than the sulphate ion and/or water.

For the 1 : 2 : 1 M : L : Cr we observe ‘the competition’ between the chromate ion and water molecules. Besides the organic ligand, in this competition the counter anions i.e. sulphate, chloride and nitrate seem to play a key role. The sulphate and chloride seem to favor water molecules to be coordinated whereas the nitrate anions promotes the chromate anion. For the 1 : 1 : 1 ratio, in each case, the chromate ion is out of the coordination sphere.

Such results indicate that for the chromate ion to be coordinated to the nickel ion there must be:

- the appropriate concentration of the organic ligand
- the nitrate rather than chloride or sulphate anions must be present.

4. Spectral studies

4.1. Infrared spectra

Table 3 shows the band positions assigned to the Cr–O vibrations in the nickel chromate complexes with bpy. The analysis of the spectra in the region of the Cr–O activity show that the chromate ion in these complexes is bound in a different way. In contrast to **[A]**, the **[B]** compound shows both splittings of the bands and the appearing of very strong, new band at 778 cm^{-1}. The latter is the most characteristic feature of the chromates coordination to the metal ion [8]. It is associated with the M–O–Cr bridge or ring [8]. The ν_{as} mode is very strong and was found to be approximately at 770 cm^{-1} in various chromate complexes [8].

Generally, the splittings in the 770–1000 cm^{-1} absorption region (i.e. the region of the Cr–O stretching mode vibrations) seem to be explicable only in

Table 4
Electronic spectra (cm^{-1}) resolved under digital filtration 250/20/100 (see the text) and crystal field parameters for the complexes. (The values in the parentheses are obtained from the calculation)

Compound	Diff. reflectance spectra	Room temp. formamide solution	Liquid nitrogen temperature [a]	Assign
A	(9600)	(9700)	(9900)	d–d
	15600	16200	16300	d–d
	21300	22200	22300	Cr–O
	24900	27000	26800	Cr–O
	26200sh	29400	27700	d–d
	32500	33500		Ligand
	34400	34800		Ligand
	38400	35800sh		Cr–O
	41900br			Ligand
Mean values for Dq and B: Dq = 980 cm^{-1}; B = 970)				
B	(1220)	(1084)	(1250)	d–d
	18300	14400?	19100	
		15400?		d–d
		17400		
	22700	21800	22200	Cr–O
	26000	27000	26800	Cr–O
	28000sh	28400sh	28300sh	d–d
	32400	33250		L
	34500	34450		L
	39500	40770		Cr–O
	41400br	41070		L
Mean values for Dq = 1180 cm^{-1} and B = 720				

[a] Liquid nitrogen measurements were made only for the visible part of the spectra.

terms of the coordinated CrO_4 group [8–10]. In **[B]** this coordination is seen mainly through Ni–Cr–O vibration. If this is the case, as it has been found elsewhere [14,23] the various function of the organic ligand can be proposed **[B]**, i.e. the coordinating and non-coordinating one. On the basis of the elemental analysis, the arguments given above as well as electronic spectral data (Table 4 vide infra) we propose the formula $[Nibpy(H_2O)_4]CrO_4$ and $[Nibpy_2CrO_4]bpy\ 8H_2O$ for **[A]** and **[B]**, respectively.

4.2. Electronic spectra

A considerable number of Ni(II) complexes with bpy have been reported so far [11,12]. Literature data point to a wide variety of Ni(II)–bpy complexes of the mono-, bis- and tris-type, respectively [12].

The band maxima resolved with the digital filter method of both compounds together with the spectroscopic parameters 10Dq and B are presented in Table 4. The d–d bands in the electronic reflectance, solution and low-temperature spectra and magnetic moments indicate that the nickel(II) ion is in a pseudooctahedral environment. The very detailed analysis of the electronic spectra will be published separately [20]. The spectra are formed by the spin-allowed d–d transitions from $^3A_{2g}$ to $^3T_{2g}$, T_{1g} and $T_{1g}(P)$ states, respectively.

Both the ligand field splitting parameter and values of the Racah parameter B are between the pure $Ni(H_2O)_6^{2+}$ ($10Dq = 8500\ cm^{-1}$, $B = 881\ cm^{-1}$) [13] and $Ni(bpy)_3^{2+}$ ($10Dq = 12790\ cm^{-1}$, $B = 710\ cm^{-1}$) values [12]. The respective values for the green complex are higher than for hexaaquanickel(II) ion whereas for the red one are lower than tris bpy nickel(II) ion (Table 4). These results support the IR data for the existence of the $[NiO_4N_2]$ and $[NiO_2N_4]$ chromophores in the **[A]** and **[B]** complexes, respectively. It is well known [14] that bpy can exist both in inner and outer coordination spheres. Our results support the foundings of Czakis et al. [14] who observed that in some Ni(II) complexes with 2,4′-bpy the nitrate anions are non-coordinating and some of the organic ligand are outside the coordination sphere.

The nephelauxetic parameters 0.93 **[A]** and 0.69 **[B]** are in the range of pseudooctahedral Ni(II) complexes [13].

5. Thermal studies

The TG, DTG and DTA curves for both complexes are given in Figs. 3–6 and the data characteristic of the thermal decomposition processes are collected in Tables 5 and 6. Whereas the thermolysis of nickel(II) bpy complexes in a vacuum results in stoichiometric products [22], the thermal decomposition of these complexes in air or inert atmosphere proceeds often through the non-stoichiometric products [15].

5.1. $[Nibpy(H_2O)_4]CrO_4$ **[A]**

The DTA curve in air indicate two main energetic effect which occur in the range 25–235 and 235–425°C, respectively. Both are well determined. The

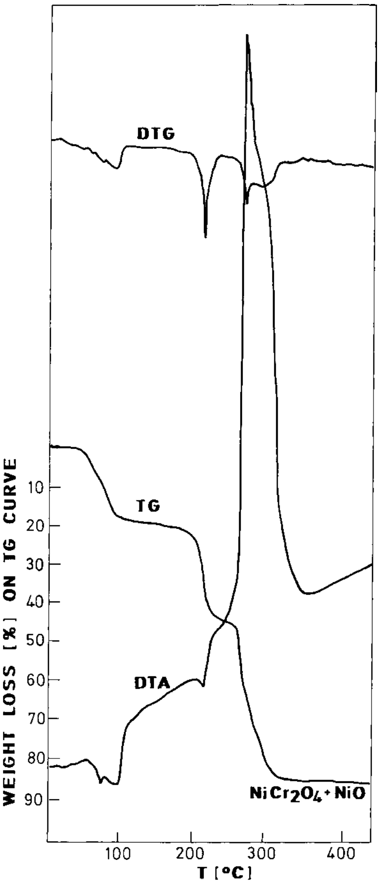

Fig. 3. TG, DTG and DTA traces for $[Nibpy(H_2O)_4]CrO_4$ [A] in air.

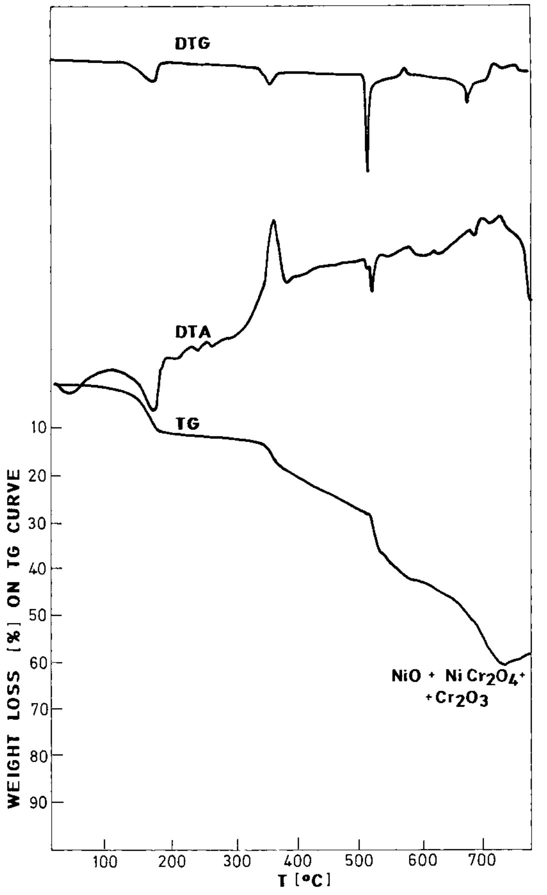

Fig. 4. TG, DTG and DTA traces for [Nibpy$(H_2O)_4$]CrO_4 [**A**] in inert atmosphere.

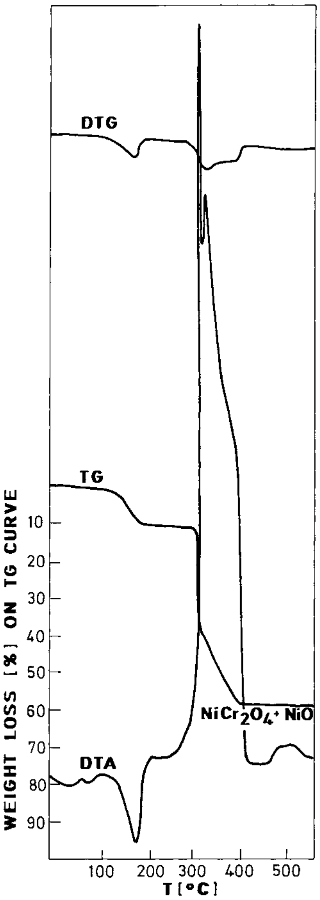

Fig. 5. TG, DTG and DTA traces for [Nibpy$_2$$CrO_4$]bpy [**B**] in air.

first one is endothermic and the second one is very high and exothermic in character. The latter one splits, so it is evidently composed of more than one effect.

In the first step the molecule loses two water molecules. The next step is composed with the loses of the remaining water and the decomposition of the bpy and the reduction of chromium(VI). The final products obtained is a mixture of NiO and $NiCr_2O_4$. Fig. 7 shows the grains of $NiCr_2O_4$ covered with 'dust' of NiO. (Pure nickel chromite can be obtained from a double salt $(NH_4)_2Ni(CrO_4)_2$ pyrolysis at 1200°C [22]).

DTA curve in helium indicates three well resolved peaks and the fourth one without unequivocal energetic character. The first (20–235°C) and the third (425–570°C) peaks are endothermic, while the second (235–425°C) is exothermic. In the first step the complex loses a part of water molecule. In the second one both the remaining water and partial deamination takes place. On further heating (III step) the next portion of bpy is eliminated. The last step is connected with the loss of the remaining organic molecule together with the final decomposition of the complex. The X-ray diffraction points to the mixture of NiO, Cr_2O_3 and $NiCr_2O_4$. The decomposition and the oxidation of the organic ligand are at cost of the chromate oxygens.

5.2. *[Nibpy$_2$$CrO_4$]bpy 8$H_2O$* [**B**]

The thermoanalytical data obtained show that the thermal decomposition of [**B**] proceeds in three and

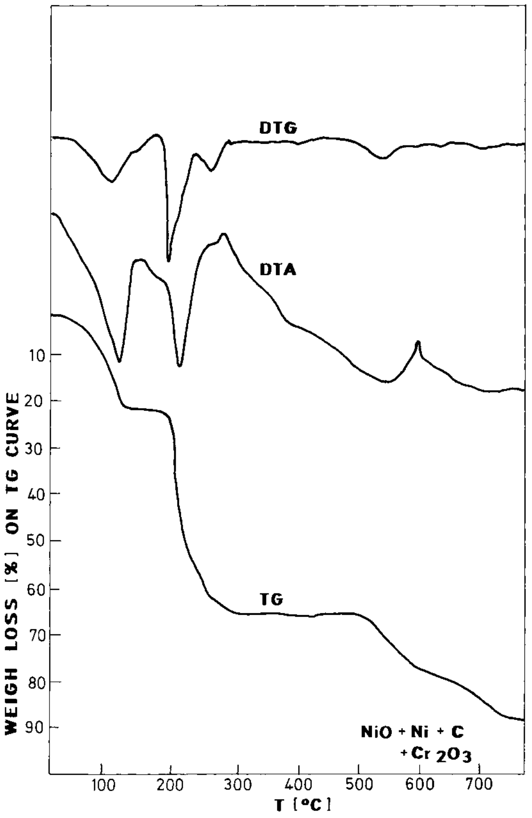

Fig. 6. TG, DTG and DTA traces for [Nibpy$_2$CrO$_4$]bpy [**B**] in inert atmosphere.

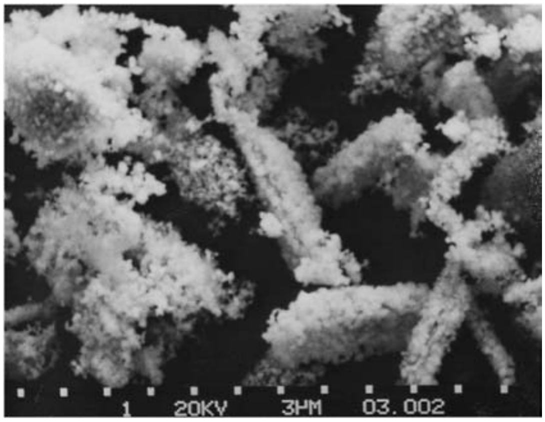

Fig. 7. Scanning electron micrograph of NiCr$_2$O$_4$ and NiO – final residue of [**A**] and [**B**] decomposition in air.

four stages in air and inert atmosphere, respectively. In air the complex loses all water molecules in the first stage (25–160°C). In the second step the deamination of bpy molecule outside coordination sphere takes place. Finally, the asymmetric exothermic DTA peak show on the deamination along with the redox process resulting in the formation of NiO + NiCr$_2$O$_4$ mixture.

In argon atmosphere the third step, i.e. the decomposition of Nibpy$_2$CrO$_4$ is evidently divided into formation of the non-stoichiometric [Nibpy$_{1.4}$CrO$_4$]

Table 5
Thermal decomposition of green nickel chromate complex with 2,2′-bpy [**A**]

Reaction	Temperature range (°C)	Decomposition stage	DTA peak	Weight loss (%)	Found Calcd.
[**A**] in air:					
[Nibpy(H$_2$O)$_4$]CrO$_4$					
↓	23–235	I	Endo	10.20	8.94
[Nibpy(H$_2$O)$_2$]CrO$_4$					
↓	235–425	II	Exo	46.90	47.70
NiCr$_2$O$_4$ + NiO					
[**A**] in inert atmosphere:					
[Nibpy(H$_2$O)$_4$]CrO$_4$					
↓	20–235	I	Endo	10.52	11.17
[Nibpy(H$_2$O$_{1.5}$]CrO$_4$					
↓	235–425	II	Exo	10.57	10.52
[Ni(bpy)$_{0.9}$]CrO$_4$					
↓	425–570	III	Endo	19.64	19.38
[Ni(bpy)$_{0.4}$]CrO$_4$					
↓	570–715	IV	Exo	18.15	15.50
NiO + NiCr$_2$O$_4$ + Cr$_2$O$_3$					

Table 6
Thermal decomposition of red nickel chromate complex with 2,2′-bpy **[B]**

Reaction	Temperature range (°C)	Decomposition stage	DTA	Weight loss (%)	Found Calcd.
[B] in air					
$[\mathrm{Nibpy_2CrO_4}]\mathrm{bpy}\ 8\mathrm{H_2O}$					
↓	25–160	I	Endo	19.02	18.30
$[\mathrm{Nibpy_2CrO_4}]\mathrm{bpy}$					
↓	160–250	II	Endo	23.25	19.84
$[\mathrm{Nibpy_2CrO_4}]$					
↓	250–345	III	Exo	40.36	39.67
$\mathrm{NiCr_2O_4} + \mathrm{NiO}$					
[B] in inert atmosphere:					
$[\mathrm{Nibpy_2CrO_4}]\mathrm{bpy}\ 8\mathrm{H_2O}$					
↓	20–115	I	Endo	16.03	16.01
$[\mathrm{Nibpy_2CrO_4}]\mathrm{bpy}\ \mathrm{H_2O}$					
↓	215–250	II	Endo	22.27	22.13
$[\mathrm{Nibpy_2CrO_4}]$					
↓	250–330	III	Exo	11.46	11.90
$[\mathrm{Ni(bpy)_{1,4}CrO_4}]$					
↓	560–830	IV	Exo	—	15.46
$[\mathrm{NiO} + \mathrm{Ni} + \mathrm{C} + \mathrm{Cr_2O_3}]$					

and its decomposition into the mixture of $\mathrm{NiO} + \mathrm{Ni} + \mathrm{C} + \mathrm{Cr_2O_3}$.

5.2.1. *Thermal decomposition of the metal chromate complexes with bpy. (M- Ag(I), Cu(II) and Ni(II))*

Despite some differences in the chemical composition in air of the final products at 1000°C, i.e. $\mathrm{Ag} + \mathrm{Cr_2O_3}$ for $\mathrm{Ag_2bpy_2CrO_4}$ [15]; $\mathrm{Cu(I)CrO_2}$ for $[\mathrm{Cubpy_2Cl}]_2\mathrm{CrO_4}$[16] and $\mathrm{NiO} + \mathrm{NiCr_2O_4}$ for the complexes obtained in this work, the mechanism of the decomposition reveals some common feature for all the complexes. On the literature data and the results of this work the process of the thermal decomposition in air of the metal chromate complexes with bpy can be divided into two or three steps:

– the water loses (if the complex possesses it) (100–200°C)
– the decomposition of the organic part of the molecule with the formation of the stoichiometric or non-stoichiometric intermediate (200–400°C)
– the final loses of the rest of the organic fragment which accompanies the chromium(VI) reduction and the formation of the metal chromites (400–1000°C) (for the silver complexes). The metachromite $\mathrm{AgCrO_2}$ formed at 260–450°C decomposes into mixture $\mathrm{Ag} + \mathrm{Cr_2O_3}$ at higher temperatures [15,21].

The final products for nickel complexes (i.e the mixture of metal oxide and corresponding metal chromite) are in accordance with the results obtained for the thermal decomposition of the zinc and cadmium chromates [17].

The situation in inert atmosphere is different. The mechanisms are more complicated and more sensitive toward the metal ion, the amount of the organic ligand and the physical conditions. For example in the case of silver complexes the products was dependent upon the heating rate showing even the presence of substrate at 1000°C [15]. Evidently, the redox processes have been operating in the wide temperature range.

5.3. *Conclusion*

A synthetic method has been successfully employed to obtain two Ni(II) chromate complexes with bpy. The coordination of the chromate ion in **[B]** significantly influences the spectral characteristics and the decomposition schemes especially in inert atmosphere.

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