



## CHARACTERIZATION BY VIBRATIONAL SPECTROSCOPY OF COORDINATION POLYMERS OBTAINED FROM $\text{Cu}^{\text{II}}$ , $\text{Ni}^{\text{II}}$ AND $\text{Zn}^{\text{II}}$ CYCLAM PERCHLORATE AND AMARANTH

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The coordination polymers  $[\{\text{Cu}^{\text{II}}(\text{cyclam})\}_3(\text{amaranth trianion})_2 \cdot 13\text{H}_2\text{O}\}_n$  (**5**),  $[\{\text{Ni}^{\text{II}}(\text{cyclam})\}_3(\text{amaranth trianion})_2 \cdot 4\text{H}_2\text{O}\}_n$  (**6**) and  $[\{\text{Zn}^{\text{II}}(\text{cyclam})\}_3(\text{amaranth trianion})_2 \cdot 14\text{H}_2\text{O}\}_n$  (**7**) (cyclam = 1,4,8,11-tetraazacyclotetra-decane) obtained by reaction of  $[\text{Cu}^{\text{II}}(\text{cyclam})](\text{ClO}_4)_2$ ,  $[\text{Ni}^{\text{II}}(\text{cyclam})](\text{ClO}_4)_2$  or  $[\text{Zn}^{\text{II}}(\text{cyclam})](\text{ClO}_4)_2$  with trisodium 2-hydroxy-1-(4-sulfonato-1-naphthylazo)naphthalen-3,6-disulfonate salt (amaranth) were analyzed by IR and Raman spectrometry.

### INTRODUCTION

In the field of coordination polymer/metal organic frameworks research, networks based on sulfonic organic compounds are less attractive due to the fact that sulfonate anion has a weak coordination force.<sup>1-3</sup> Weaker ligation coupled with a range of coordination modes has a great advantage because it makes possible the solid state dynamics, a very important property for coordination polymer chemistry.<sup>4-6</sup> The lack of regular inorganic assembles is not wholly detrimental because the new inorganic cluster can form *in situ* and the structure-directing role of the organic linker can be enhanced. In contrast to other materials sulfonate coordination polymers offer a much greater likelihood of forming polar pores.<sup>7</sup> The spherical ligating ability of the sulfonate group makes easier the coordination in three dimensions.

There are a few studies on supramolecular motifs of salts of various sulfonated azo dyes.<sup>8-12</sup> One difficulty in examining sulfonated dyes is that they exhibit generally poor crystal growth properties,

making single crystal diffraction studies difficult. Using synchrotron radiation, Kennedy and coworkers<sup>9</sup> succeeded to determine the first crystal structure of a red azo lake pigment. Another exception is 7-hydroxy-8-(phenylazo)-1,3-naphthalenedisulfonic acid (Orange G), the salts of which are found to grow as robust crystal. This has led to crystallographic characterization of Orange G dianion both with polyatomic organic cations<sup>13</sup> and as its Mg, Ca and Li salts.<sup>14</sup> Kennedy and coworkers<sup>12</sup> synthesized eight new structures of *s*-block metal compounds of Orange G, together with the structure of its Ag (I) complexes. These studies show that Orange G can make higher connectivity complexes and the sodium salt of this azo dye forms a 3-dimensional coordination polymer. In the solid state Orange G exists largely as ketohydrazone tautomer.

The utilization of macrocyclic complexes offers several advantages over free metal ions in the assembly of multidimensional coordination polymer networks because utilization of these complexes enables the control of the extending direction of networks, which simplify the network structures.<sup>15,16</sup>

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For preparation of sulfonated coordination polymers, metal-macrocylic complexes were seldom used, till now being known the following compounds, namely:  $[\text{Cd}(\text{cyclam})(1,5\text{-nds})]_2$  (1,5-nds = naphthalene-1,5-disulfonate),<sup>1,17</sup>  $[\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2](1,5\text{-nds}) \cdot 2\text{H}_2\text{O}$ ,<sup>2,18</sup>  $\text{Cu}(1,4,6,8,11\text{-pentaaza-13-methyl-6(1-phenylethyl-cyclotetradecane)})(\text{methanedisulfonate})$ ,<sup>1,19</sup>  $[\text{Cu}(\text{cyclam})(1,5\text{-nds})]_n$ ,<sup>18,20</sup>  $[\{\text{Ni}(\text{cyclam})\}(1,5\text{-nds})] \cdot 1/3(\text{H}_2\text{O})$   $[\text{Ni}(\text{cyclam})(1,5\text{-nds})]_n \cdot n\text{H}_2\text{O}$ ,<sup>1,18</sup>  $[\text{Cu}(\text{cyclam})(\text{PTMSO}_3)_2] \cdot 6\text{EtOH}$ <sup>21</sup> and  $[\text{Cu}(\text{cyclam})](\text{PTMSO}_3)_2$ <sup>21</sup> ( $\text{PTMSO}_3$ =polychlorotriphenylmethanesulfonate).

The different coordination modes observed in this series  $\text{Co}^{2+}/\mu^0$ ,  $\text{Ni}^{2+}/\mu^1$ ,  $\text{Cu}^{2+}/\mu^1$  and  $\text{Cd}^{2+}/\mu^2$  serve as examples to demonstrate that the coordination strength increases in the order  $\text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} < \text{Cd}^{2+}$ .

Taking into consideration the above mentioned advantages offered by using of metal-macrocylic complexes in the synthesis of the coordination polymers and the fact that azo dyes are able to coordinate electropositive metals, we prepared these kind of polymers using as ligand sulfonated

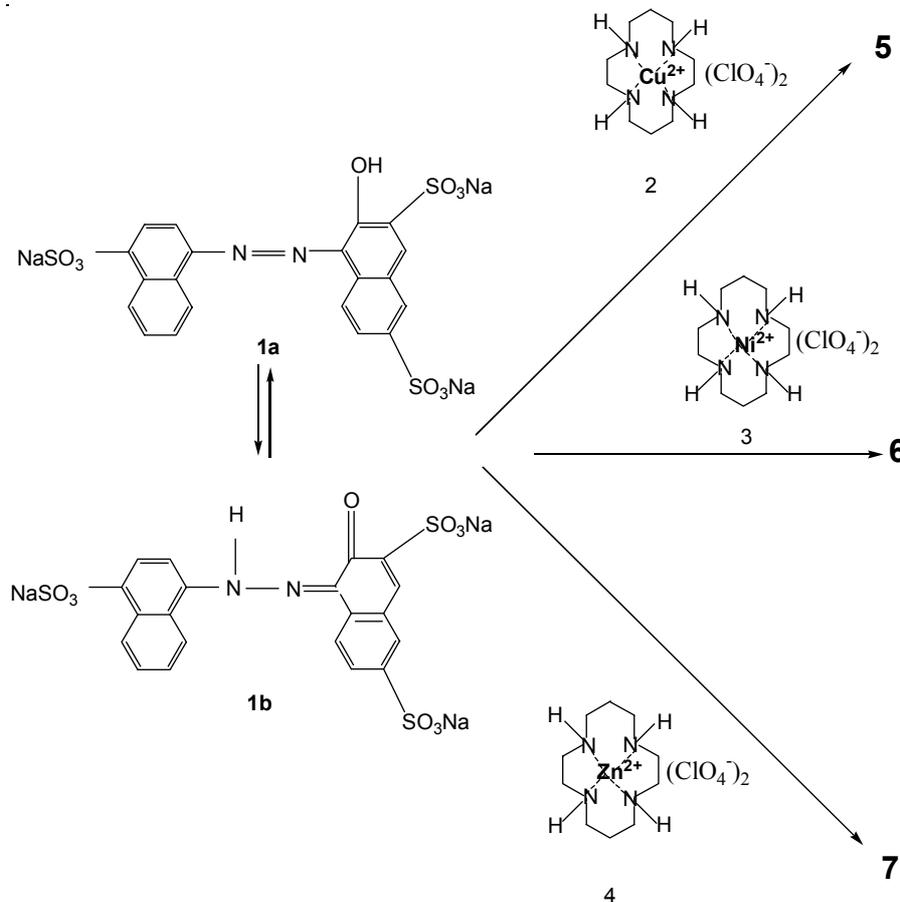
azo dye trisodium 2-hydroxy-1-(4-sulfonato-1-naphthylazo)naphthalene-3,6-disulfonate salt, and as metals  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$  and  $\text{Zn}$  complexed by 1,4,8,11-tetraazacyclotetradecane (cyclam).

## RESULTS AND DISCUSSION

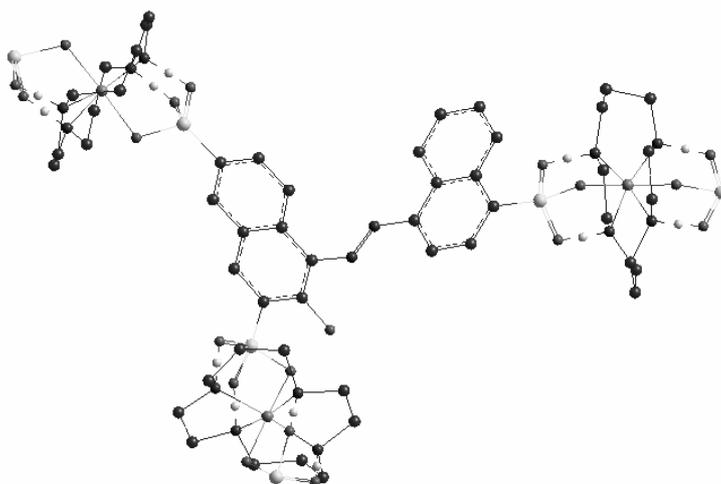
### 1. Synthesis

Reaction of  $[\text{Cu}^{\text{II}}(\text{cyclam})](\text{ClO}_4)_2$  (**2**),  $[\text{Ni}^{\text{II}}(\text{cyclam})](\text{ClO}_4)_2$  (**3**) or  $[\text{Zn}^{\text{II}}(\text{cyclam})](\text{ClO}_4)_2$  (**4**), dissolved in DMF, with trisodium 2-hydroxy-1-(4-sulfonato-1-naphthylazo)naphthalene-3,6-disulfonate salt (**1**), dissolved in water, generated coordination polymers  $[\{\text{Cu}^{\text{II}}(\text{cyclam})\}_3(\text{amaranth trianion})_2 \cdot 13\text{H}_2\text{O}]_n$  (**5**),  $[\{\text{Ni}^{\text{II}}(\text{cyclam})\}_3(\text{amaranth trianion})_2 \cdot 4\text{H}_2\text{O}]_n$  (**6**) and  $[\{\text{Zn}^{\text{II}}(\text{cyclam})\}_3(\text{amaranth trianion})_2 \cdot 14\text{H}_2\text{O}]_n$  (**7**) (see Scheme 1).

The coordination polymers **5-7** (see Scheme 2) were obtained by coordination of metal cyclamates by three  $\text{SO}_3^-$  groups of amaranth, in agreement with IR and Raman spectra, DSC-TGA and elemental analysis.



Scheme 1 – Synthesis of the coordination polymers **5-7**.



C= black, O= red, S= yellow, N= blue,  $Me^{2+}$  ( $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ) = green, H=white

Scheme 2 – Geometrically optimized structure of the monomeric unit coordination polymers 5-7.

## 2. Powder X-ray diffraction

The growth of the single-crystal in the case of compounds 5-7 failed so we characterized them,

from crystallographic point of view, by means of the powder XRD spectra (see Figs. 1-3).

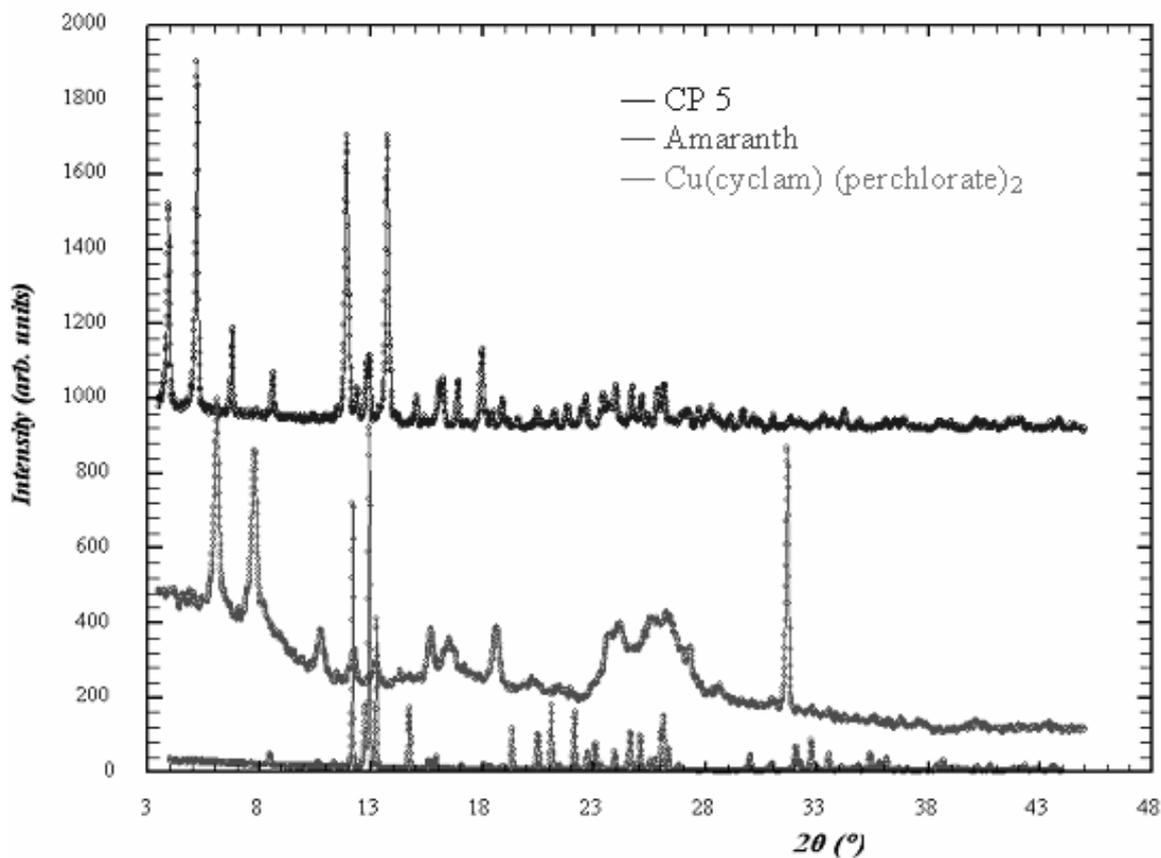


Fig. 1 – XRPD patterns for  $[Cu^{II}(cyclam)_3 (amaranth\ trianion)_2 \cdot 13H_2O]_n$  (5) and for the starting materials.

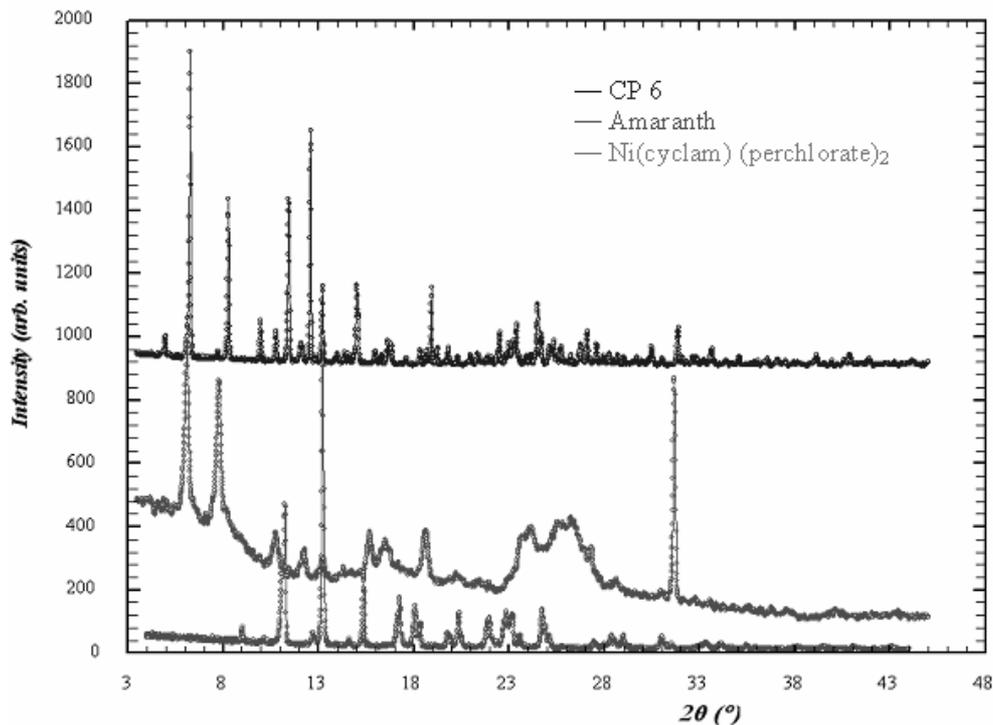


Fig. 2 – XRPD patterns for  $[\{\text{Ni}^{\text{II}}(\text{cyclam})\}_3(\text{amaranth trianion})_2 \cdot 4\text{H}_2\text{O}]_n$  (**6**) and for the starting materials.

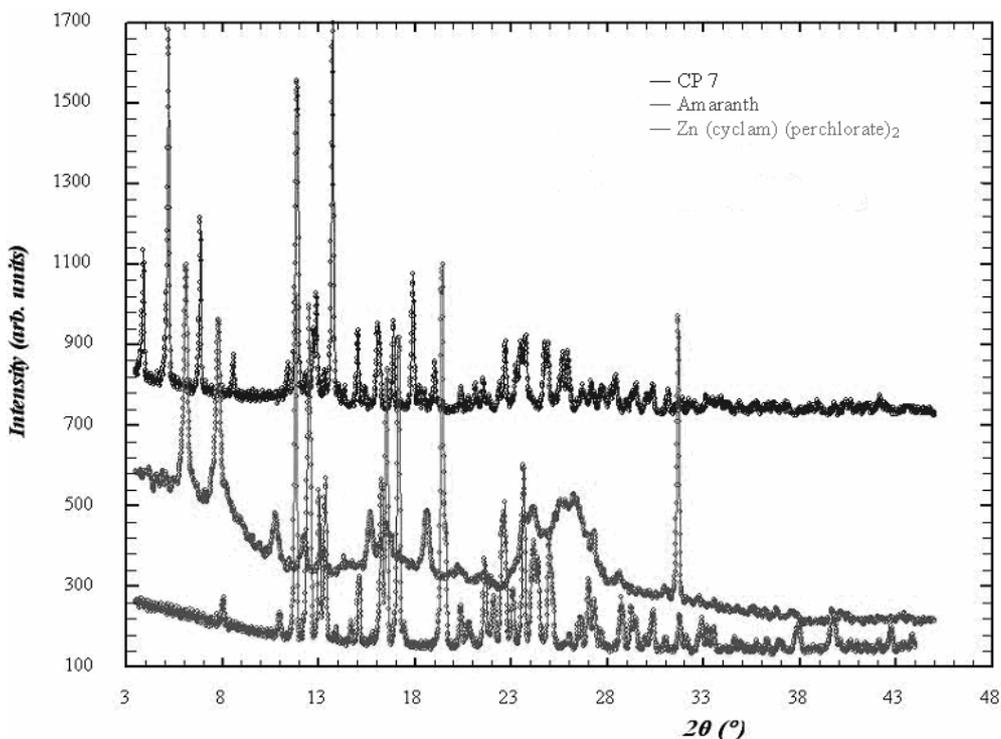


Fig. 3 – XRPD patterns for  $[\{\text{Zn}^{\text{II}}(\text{cyclam})\}_3(\text{amaranth trianion})_2 \cdot 14\text{H}_2\text{O}]_n$  (**7**) and for the starting materials.

The XRPD patterns of compounds **5-7** are completely different comparatively with those of the starting materials, proving the formation of new compounds.

Crystal data for coordination polymers **5-7**, obtained from powder XRD spectra are shown in Table 1.

Table 1

Crystal data for the coordination polymers 5-7

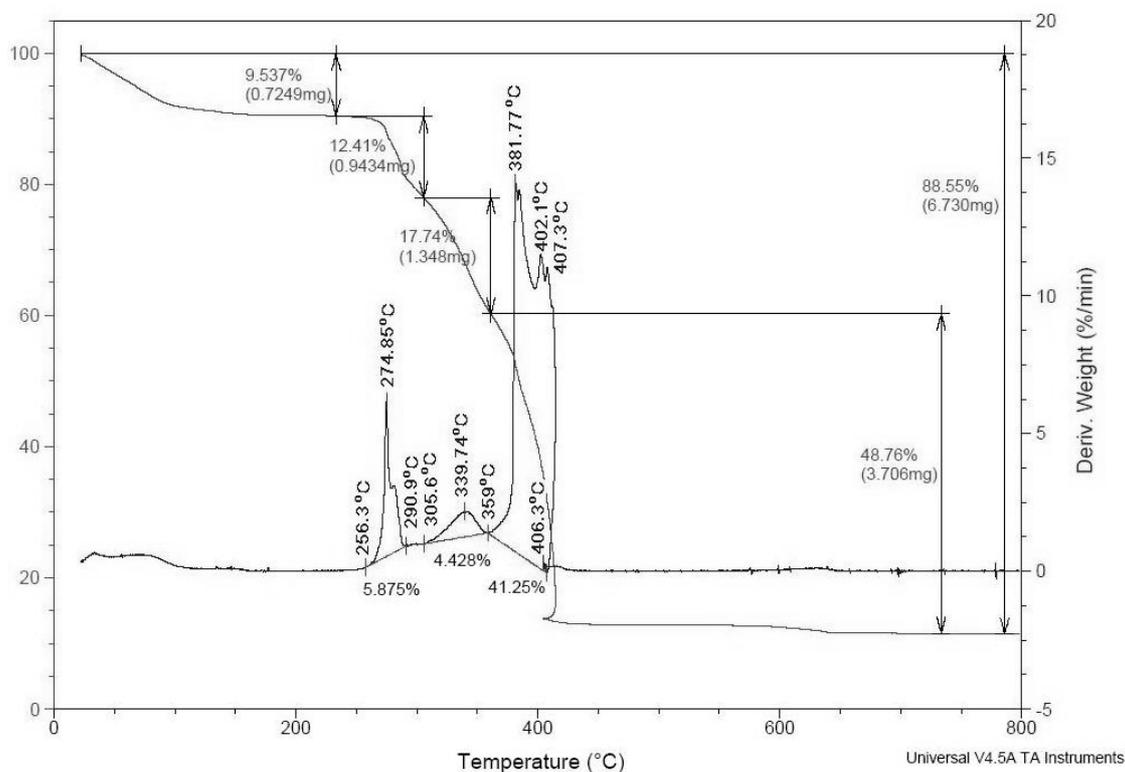
Compound	Elementary lattice		Crystal system	Space group	Z	Volume Å <sup>3</sup>	$\rho_{\text{calc.}}$ g·cm <sup>-3</sup>	$\rho_{\text{det.}}$ * g·cm <sup>-3</sup>
	Å	Degree						
5	a = 8.149 b = 44.448 c = 25.825	$\alpha=\beta=\gamma=90$	orthorhombic	Pbca	8	9350	2.656	2.499
6	a = 17.699 b = 8.542 c = 28.12	$\beta=93.96$ $\alpha=\gamma=90$	monoclinic	P2/c	4	4240	2.906	2.832
7	a = 8.224 b = 44.618 c = 25.549	$\alpha=\beta=\gamma=90$	orthorhombic	Pbca	8	9374	2.657	2.533

\*Density was determined by picnometer method

### 3. Thermal gravimetric analysis

Thermal gravimetric analysis of compounds 5-7 are shown in Figs. 4-6. Thermogravimetric analysis (TGA) curves for 5 (see Fig. 4) showed a loss of solvent at a relatively low temperature. On further heating a few consecutive weight losses were observed in 274.85-407.30 °C range corresponding to amaranth trianion and macrocyclic ligand decomposition. Differential

scanning calorimetry (DSC) indicates that compound 5 undergoes the first decomposition in 256.30-290.90 °C range centred at 272.85 °C, the second one in 305.60-356.0 °C range centered at 339.64 °C, and a multiple one, very exothermic, in 359.00-406.30 °C range at 381.77, 384.27, 402.10 and 407.30 °C. Finally, the CuO residue (observed 14.46%, calculated 12.38%) remained above 407.30 °C.

Fig. 4 – DSC-TGA curves for  $[\{\text{Cu}^{\text{II}}(\text{cyclam})\}_3(\text{amaranth trianion})_2 \cdot 13\text{H}_2\text{O}\}_n$  (5).

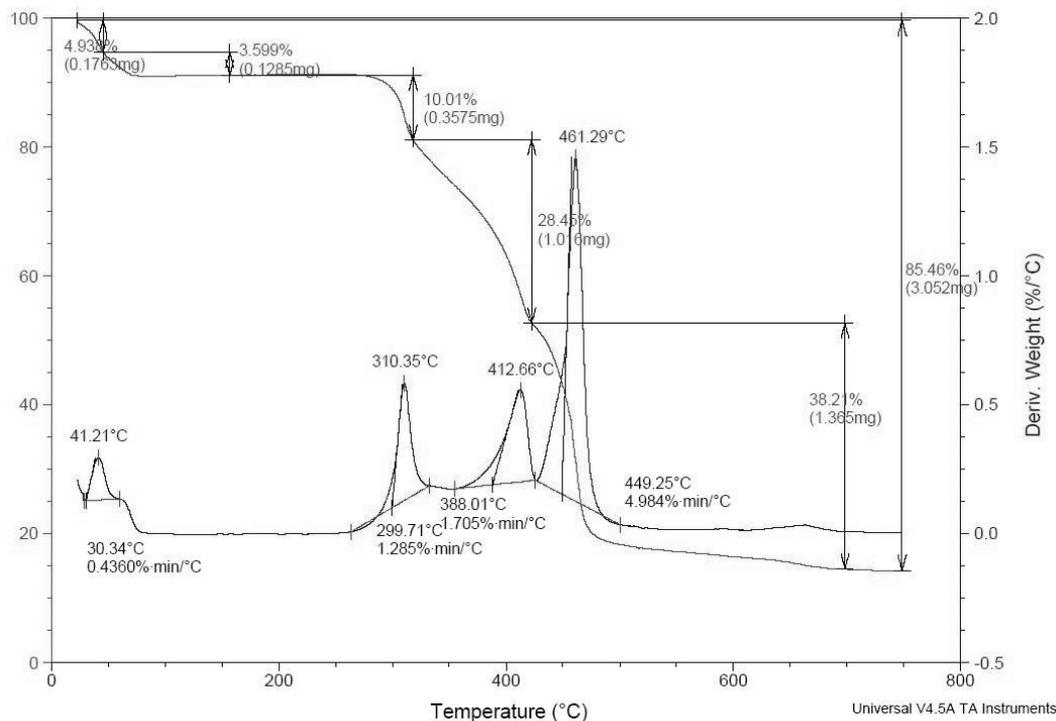


Fig. 5 – DSC-TGA curves for  $\{[\text{Ni}^{\text{II}}(\text{cyclam})]_3(\text{amaranth trianion})_2 \cdot 4\text{H}_2\text{O}\}_n$  (**6**).

TGA curves for **6** (see Fig. 5) showed a first weight loss of solvent at temperature below 30 °C and the second loss at 41.21 °C corresponding to the loss of four guest water molecules. DSC shows that **6** loses these water molecules at 30,43–61.32 °C, centered at 41.21 °C, the host being stable

up to 310.35 °C, and then three consecutive weight losses were observed in 310.35–461.29 °C range with the loss of amaranth trianion and macrocyclic ligand. Finally the NiO residue (observed 14.54%, calculated 11.11%) remained above 461.29 °C.

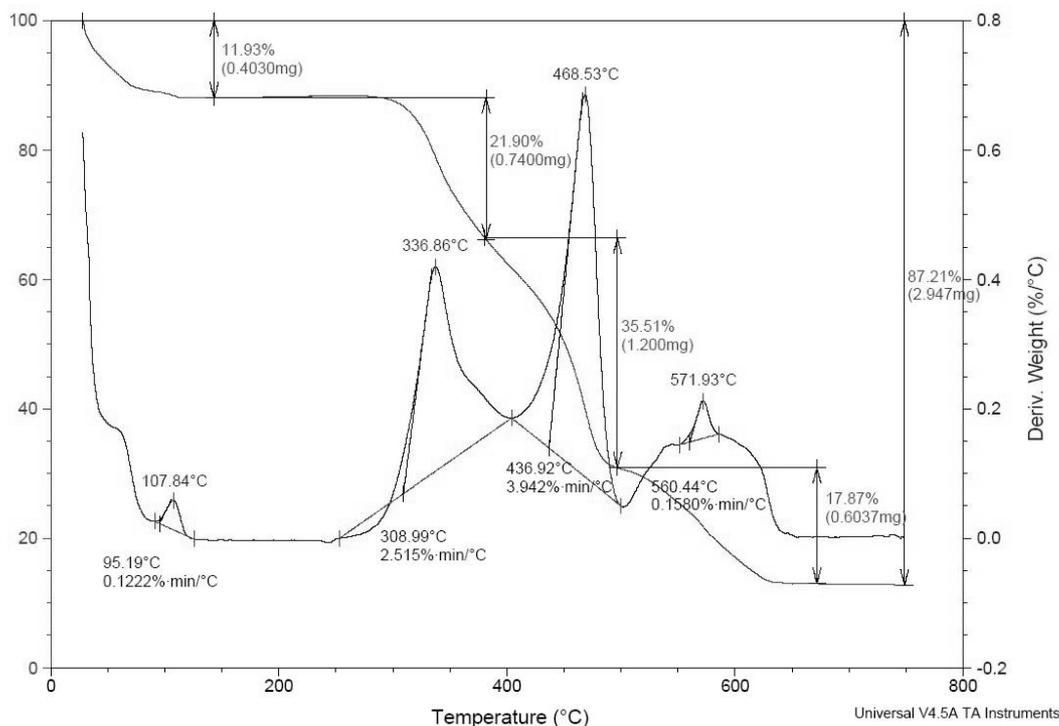


Fig. 6 – DSC-TGA curves for  $\{[\text{Zn}^{\text{II}}(\text{cyclam})]_3(\text{amaranth trianion})_2 \cdot 14\text{H}_2\text{O}\}_n$  (**7**).

TGA curves for **7** (see Fig. 6) showed a first weight loss of guest water molecules at 107.84 °C corresponding to the loss of 14 guest water molecules. DSC indicates that **7** loses these water molecules at 95.19–119.35 °C, centered at 107.84 °C. On the further heating, three consecutive weight losses were observed in 336.38–591.93 °C range corresponding to amaranth trianion and macrocyclic ligand decomposition. Finally the ZnO residue (observed 12.79%, calculated 11.51%) remained above 591.38 °C.

#### 4. Vibrational spectral analysis

##### 4.1. Vibrations attributed to cyclam moiety

The infrared spectrum (see Fig. 7) displays two medium strength bands at 3207, 3167 cm<sup>-1</sup> for **5**, 3214, 3172 cm<sup>-1</sup> for **6** and 3230 cm<sup>-1</sup> for **7** corresponding to the N-H stretching, two medium strength bands at 2923 cm<sup>-1</sup> and 2870 cm<sup>-1</sup> for **5** at 2926 cm<sup>-1</sup> and 2860 cm<sup>-1</sup> for **6** and at 2925 cm<sup>-1</sup> and 2868 cm<sup>-1</sup> for **7** corresponding to CH<sub>2</sub>

asymmetric and symmetric stretching, respectively, and a medium strength CH<sub>2</sub> deformation band at 1490 cm<sup>-1</sup> for **5**, shoulder at 1482 cm<sup>-1</sup> for **6** and shoulder at 1477 cm<sup>-1</sup> for **7**.<sup>22</sup>

##### 4.2. Hydroxyl vibrations

In the IR spectrum of amaranth the broad intense band at 3436 cm<sup>-1</sup> is attributed to hydrogen bonded OH vibrations.<sup>23</sup> In the case of compounds **5-7** a broad intense band appears at 3436, 3446 and 3446 cm<sup>-1</sup> (nujol). The in-plane OH deformation vibration appears in the IR as strong band at 1496 cm<sup>-1</sup> for **5** at 1493 cm<sup>-1</sup> for **6** and at 1495 for **7** corresponding to in-plane-bending vibration of OH group.<sup>23</sup>

The OH out-of plane deformation vibration in IR lies in the region 290–320 cm<sup>-1</sup> for free OH and in the region 517–717 cm<sup>-1</sup> for associated OH.<sup>24</sup> The medium strong band at 740 cm<sup>-1</sup> for **5**, at 762 cm<sup>-1</sup> for **6** and 761 cm<sup>-1</sup> for **7** in the IR spectra corresponds to out-of-plane bending mode of hydroxyl vibrations.<sup>23</sup>

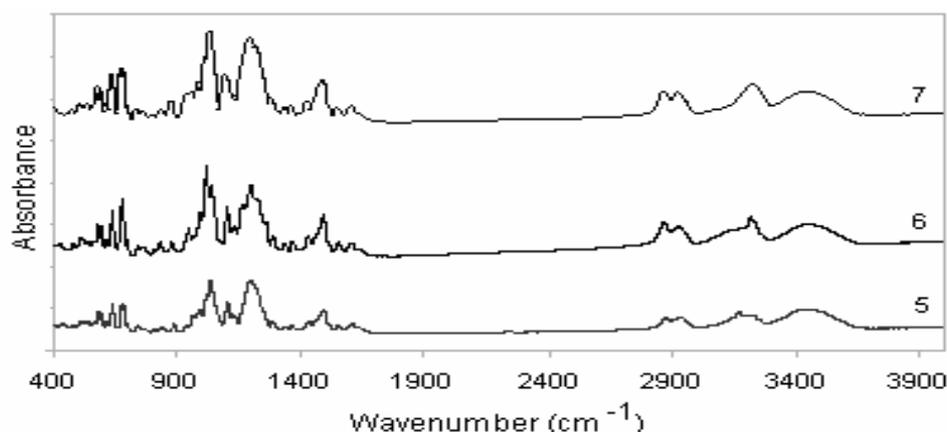


Fig. 7 – Experimental infrared spectra recorded in solid state of compounds **5-7**.

##### 4.3. Azo chromophoric group (-C=N=N-C-) vibrations

N=N stretching vibration, due to its symmetry, has a very characteristic and intensive band in the Raman spectrum but is difficult to observe in the IR spectrum. The change of N=N bond length in the molecule which has two unequivalent C-N parts, because just one naphthalene ring is substituted with OH group, produces a modification in the dipole moment. Due to this effect the N=N stretching mode became active in IR and has a medium intensity. The band occurring between 1450 cm<sup>-1</sup> and 1380 cm<sup>-1</sup> corresponds to the stretching mode of an azo-compound.<sup>25</sup> C-N

stretching vibrations of azo-compounds appear in the 1200–1130 cm<sup>-1</sup> region (IR).<sup>26,27</sup> Substituents on conjugated naphthalene groups influence both the peak wave number and intensity.<sup>23</sup> The intense band observed at 1364 cm<sup>-1</sup> for **5**, at 1365 cm<sup>-1</sup> for **6** and at 1363 cm<sup>-1</sup> for **7** in the Raman spectrum (see Fig. 8) and the weak band at 1366 cm<sup>-1</sup> for **5**, at 1368 cm<sup>-1</sup> for **6** and at 1366 cm<sup>-1</sup> for **7** in the IR spectrum can be attributed to the azo stretching vibrations. This large downshift of these vibrations can be explained by a greater conjugation and by a  $\pi$ -electron delocalization.<sup>28</sup> The theoretical calculation<sup>23</sup> showed that the azo distance for amaranth molecule is 129.1 pm. The calculated

N=N bond distance is 124.5-125.0 pm for OH tautomer whereas the N-N bond distance for NH isomer is 130.0 pm.<sup>29</sup> The bond length between nitrogen and naphthalene ring with OH substituent is 139.8 pm, which is shorter than that between N and the naphthalene ring without OH substituent 142.1 pm.<sup>29a</sup> These calculations show that a  $\pi$ -electron delocalization over the naphthyl azo system takes place, delocalization which is responsible for the nonlinearity of the molecule.<sup>30</sup> By comparison of these data we can observe that the azo distance in amaranth is appreciably elongated. This elongation can be explained by the fact that hydroxyl group can donate some electron density via naphthalene ring substituted with this group into the  $\pi^*$  orbital of the azo moiety. Due to this density electron donation a decreasing of the bond order of the azo group and lengthening of this bond takes place, indicating the presence of NH tautomer **1b** (see Scheme 1) in the solid form. This affirmation is sustained by a recent paper of Oliveira and coworkers.<sup>29a</sup> Analyzing the overall profile of the calculated IR spectra they noted that the NH and OH structures of trisodium 2-hydroxy-1-(4-sulfonato-1-naphthylazo)-naphthalene-6,8-disulfonate (azo-dye E124) show similar band profile, with the main difference found in the region between 1600 and 1200  $\text{cm}^{-1}$ . For the NH isomer, intense bands are predicted at 1554 (assigned as a combined mode including  $\delta\text{NH}$ ,  $\nu\text{CO}$ ,  $\nu\text{C}=\text{N}$ ,  $\beta\text{CH}$  vibrations), 1324 and 1294  $\text{cm}^{-1}$  (attributed to  $\delta\text{NH}$ ,  $\nu\text{N-H}$ ,  $\beta\text{CH}$ ,  $\nu\text{CC}$  modes). All of these vibrations are characteristic to NH isomer and may be used as fingerprints in the IR spectrum. Experimentally, the corresponding absorptions are

observed at 1495 and 1221  $\text{cm}^{-1}$  in the case of azo-dye E124. In the Raman spectrum, which is more sensitive to the tautomeric forms than the IR, three bands were observed around 1574, 1515 and 1364  $\text{cm}^{-1}$ , assigned to  $\delta\text{NH}$ ,  $\nu\text{C}=\text{O}$ ,  $\nu\text{C}=\text{N}$  and  $\nu\text{CC}$ , respectively. These bands are predicted only for the NH species at 1606, 1554 and 1375  $\text{cm}^{-1}$ . For polymer **5** the corresponding vibrations of NH tautomer appears as a band at 1496  $\text{cm}^{-1}$  and as shoulder at 1222  $\text{cm}^{-1}$ (IR) and at 1570, 1513 and 1364  $\text{cm}^{-1}$ (Raman). For polymer **6** these signal appear at 1493  $\text{cm}^{-1}$  (band) and 1367  $\text{cm}^{-1}$  (shoulder) (IR) and at 1570, 1512 and 1365  $\text{cm}^{-1}$  (Raman). For polymer **7** these bands can be observed at 1495  $\text{cm}^{-1}$  and at 1221  $\text{cm}^{-1}$  (IR) and at 1569, 1513 and 1363  $\text{cm}^{-1}$ (Raman). These bands are mixed with other kinds of vibrations, especially with naphthalene rings stretching or in-plane-bending vibration of OH group, as has been stated above.

The above mentioned IR and Raman data sustain the presence of NH form in solid state in polymers **5-7**. The medium intensity band at 1284  $\text{cm}^{-1}$  for **5**, at 1288  $\text{cm}^{-1}$  for **6** and at 1284  $\text{cm}^{-1}$  for **7** in the IR, the weak band at 1285  $\text{cm}^{-1}$  for **5**, at 1283  $\text{cm}^{-1}$  for **6** and at 1281  $\text{cm}^{-1}$  for **7** in the Raman originate from the stretching mode of C-N group connected to naphthalene ring substituted with OH group and the naphthalene ring unsubstituted with OH group.<sup>22</sup> The (C-N=N-C) chromophore gives a very intense band at 1222 (sh)  $\text{cm}^{-1}$  for **5**, at 1224  $\text{cm}^{-1}$  for **6** and at 1221  $\text{cm}^{-1}$  for **7** in the IR, corresponding to the asymmetric stretching of this group, mixed with vibrations corresponding to NH tautomer.<sup>23, 29a</sup>

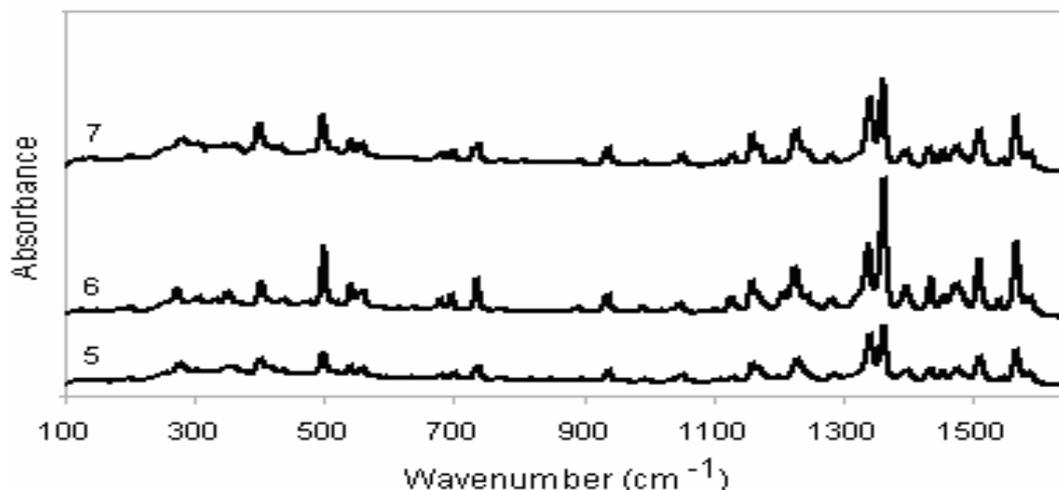


Fig. 8 – Experimental Raman spectra recorded in solid state of compounds **5-7**.

#### 4.4. Sulfonate group vibrations

Asymmetric vibrations of  $\text{SO}_3^-$  group of sulfonic acid salts usually occur in the IR at 1250–1140  $\text{cm}^{-1}$ .<sup>25</sup> The band due to the symmetric stretching vibration is sharper and occurs at 1130–1080  $\text{cm}^{-1}$ .  $\text{SO}_3^-$  symmetric deformation modes give strong bands in the 550–660  $\text{cm}^{-1}$  region (IR).<sup>31,32</sup> The sulfonic group does not affect the conjugated system irrespective of the substitution position in the naphthalene rings. Changes in the electron density are relatively low at the carbon atoms to which sulfonic group are substituted.<sup>33</sup> The participation of sulfur d orbitals in the conjugated system is very low, and the  $\pi$  contribution into C-S bond is practically negligible.<sup>22</sup> The asymmetric stretching mode of  $\text{SO}_3^-$  is mixed with C-N stretching, C-H in-plane-bending<sup>22</sup> giving a very broad band at 1198  $\text{cm}^{-1}$  (for **5** and **6**) and at 1199  $\text{cm}^{-1}$  (for **7**) in the IR spectrum. The very intense band at 1037  $\text{cm}^{-1}$  (for **5**), at 1039  $\text{cm}^{-1}$  (for **6**) and at 1037  $\text{cm}^{-1}$  (for **7**) in the IR and medium intense at 1051  $\text{cm}^{-1}$  (for **5**), at 1048  $\text{cm}^{-1}$  (for **6**) and at 1053 (for **7**) in the Raman can be attributed to symmetric stretching vibrations of  $\text{SO}_3^-$  group, vibrations that are mixed with naphthalene ring deformations.<sup>23</sup>  $\text{SO}_3^-$  symmetric bending vibrations are coupled with out-of-plane bending vibrations or with naphthalene ring deformations giving a intense bands at 683 and 638  $\text{cm}^{-1}$  (for **5**), at 678 and 637  $\text{cm}^{-1}$  (for **6**) and at 683 and 638  $\text{cm}^{-1}$  (for **7**) in the IR. The medium intense IR bands at 508  $\text{cm}^{-1}$  (for **5**), at 507  $\text{cm}^{-1}$  (for **6**) and at 507  $\text{cm}^{-1}$  (for **7**) and weak bands at 477  $\text{cm}^{-1}$  (for **5**), at 479  $\text{cm}^{-1}$  (for **6**) and at 477  $\text{cm}^{-1}$  (for **7**) correspond to  $\text{SO}_3^-$  wagging vibrations. Weak bands at 350, 332  $\text{cm}^{-1}$  (for **5**), at 351, 334  $\text{cm}^{-1}$  (for **6**) and at 362, 336  $\text{cm}^{-1}$  (for **7**) in the Raman are assigned to  $\text{SO}_3^-$  rocking vibrations which are mixed with torsion vibrations of both naphthalene rings and azo group.

#### 4.5. Naphthalene ring vibrations

Naphthalene ring vibrations make a major contribution in the IR and Raman spectra. Naphthalene ring stretching vibrations are expected in the region 1580–1300  $\text{cm}^{-1}$  whereas naphthalene CH bending modes give rise to bands in the region 1230–970  $\text{cm}^{-1}$ .<sup>34</sup> These vibrations are mixed with in-plane-bending vibration of OH group, coupled with C-N stretching vibration or with  $\text{SO}_3^-$  vibrations.

## EXPERIMENTAL

### 1. General

All chemical utilized in this investigation were obtained from commercial sources, were reagent grade, and were used without further purification. Distilled water was used for all procedures. Infrared spectra of solid samples were recorded on FTIR spectrometer JASCO 610 in KBr pellets. The Raman spectra were recorded in powder at room temperature with a JASCO NRS 3300 spectrophotometer in a backscattering arrangement and equipped with a CCD detector (-69 °C) using a 600  $\text{lmm}^{-1}$  grating with spectral resolution 0.65  $\text{cm}^{-1}$ . The incident laser beam (1  $\mu\text{m}^2$  diameter at the sample surface) was focused through an Olympus microscope, and the Raman calibration was achieved by using the Si 521  $\text{cm}^{-1}$  peak. Excitation was 100 mW at 758 nm. Thermogravimetric analysis (TGA) studies were performed in air (100  $\text{mL}\cdot\text{min}^{-1}$ ) by using a STD Q 600 TA instrument, over the temperature domain of 25–750 °C and a heating rate of 5 °C $\cdot\text{min}^{-1}$ . The powder X-ray diffraction patterns were obtained with a Bruker D8 Advance powder diffractometer working at 40 kV and 40 mA, using  $\text{CuK}\alpha_1$  wavelength ( $\lambda = 1.540598 \text{ \AA}$ ) equipped with an incident beam Ge 111 monochromator. The powder diffraction patterns for resulting compounds were indexed using Dicvol method.<sup>35</sup> The elemental analysis of the prepared polymers were performed by a EA 1112H T O/H-N/C, THERMO FINNIGAU instrument.

**2. Experimental procedure for preparation of  $\{[\text{Cu}^{\text{II}}(\text{cyclam})][\text{amaranth trianion}]\}_n$  (**5**),  $\{[\text{Ni}^{\text{II}}(\text{cyclam})][\text{amaranth trianion}](\text{H}_2\text{O})_4\}_n$  (**6**) and  $\{[\text{Ni}^{\text{II}}(\text{cyclam})][\text{amaranth trianion}](\text{H}_2\text{O})_4\}_n$  (**7**)**  
 $[\text{Cu}^{\text{II}}(\text{cyclam})](\text{ClO}_4)_2$  (**2**),  $[\text{Ni}^{\text{II}}(\text{cyclam})](\text{ClO}_4)_2$  (**3**) and  $[\text{Zn}^{\text{II}}(\text{cyclam})](\text{ClO}_4)_2$  (**4**) were prepared according to the published procedures.<sup>36–38</sup>

Caution: The perchlorate salts used in this study are potentially explosive and should be handled in small quantities.

**2.1. Preparation of  $\{[\text{Cu}^{\text{II}}(\text{cyclam})]_3(\text{amaranth trianion})_2 \cdot 13\text{H}_2\text{O}\}_n$  (**5**)** To a DMF (10 mL) solution of  $[\text{Cu}^{\text{II}}(\text{cyclam})](\text{ClO}_4)_2$  (0.738 g, 0.142 mmol) was added dropwise an aqueous solution (5 mL) of trisodium 2-hydroxy-1-(4-sulfonato-1-naphthylazo)naphthalene-3,6-disulfonate salt (amaranth) (0.320 g, 0.5 mmol). The resulted solution was allowed to stand at room temperature for a 24 h. The resulted red precipitate (0.600 g) was filtered, washed with methanol, ether and then by sonication with methanol until the washed solution was colorless and with ether and dried at room temperature. The precipitate is insoluble in organic solvents. Anal. Calc. for  $\text{C}_{70}\text{H}_{120}\text{N}_{16}\text{O}_{33}\text{S}_6\text{Cu}_3$ : C, 40.08; H, 5.77; N, 10.69. Found: C, 40.19; H, 5.96; N, 10.98. IR (KBr,  $\text{cm}^{-1}$ ): 3207ms, 3167ms, 2932ms, 2870ms, 1610w, 1551w, 1496s, 1490sh ms, 1432 w, 1366w, 1338vw, 1284ms, 1222 shs, 1198 vs, 1122 ms, 1104w, 1037vs, 1019 vs, 990ms, 964ms, 937w, 885w, 836vw, 808vw, 740ms, 699w, 723vw, 687s, 682s, 672s, 638s, 614w, 593ms, 581ms, 538w, 518w, 507vw, 477vw, 439vw, 405vw Raman (powder,  $\text{cm}^{-1}$ ): 1570s, 1513s, 1478 ms, 1437ms, 1399ms, 1364vs, 1343 vs, 1285w, 1230s, 1161s, 1128vw, 1051w, 992vw, 938ms, 845vw, 811vw, 779vw, 741ms, 701w, 683w, 633vw, 562w, 541w, 500s, 46vw, 402ms, 350w, 332w, 279ms, 200vw, 126vw, 57 s.

**2.2. Synthesis of  $\{[\text{Ni}^{\text{II}}(\text{cyclam})]_3(\text{amaranth trianion})_2 \cdot 4\text{H}_2\text{O}\}_n$  (**6**)** To a DMF (10 mL) solution of  $[\text{Ni}^{\text{II}}(\text{cyclam})](\text{ClO}_4)_2$  (0.650g, 1.42 mmol) was added dropwise an aqueous solution (5 mL) of trisodium 2-hydroxy-

1-(4-sulfonato-1-naphthylazo)naphthalene-3,6-disulfonate salt (amaranth) (0.320g, 0.5 mmol). The resulted solution was allowed to stand at room temperature for three weeks. The resulted red precipitate (0.460 g) was filtered, and purified by sonication with methanol until the washed solution was colorless and then with ether and dried at room temperature. The precipitate is insoluble in organic solvents. Anal.Calc. for  $C_{70}H_{102}N_{16}O_{24}S_6Ni_3$ : C, 43.79; H, 5.35; N, 11.67. Found: C, 43.92; H, 5.80; N, 11.50. IR (KBr,  $cm^{-1}$ ): 3214ms, 3172ms, 2926ms, 2860ms, 1607w, 1555w, 1493s, 1482shms, 1431 w, 1368w, 1288w, 1260ms, 1224shs, 1198s, 1166s, 1132ms, 1102s, 1075w, 1039s, 1018vs, 992ms, 947w, 877w, 831vw, 762w, 739vw, 698w, 678s, 637s, 611w, 593ms, 580ms, 564vw, 541 vw, 508w, 479vw, 426vw. Raman (powder,  $cm^{-1}$ ): 1570s, 1543w, 1512ms, 1476ms, 1437ms, 1399ms, 1365vs, 1341s, 1283vw, 1227 ms, 1160ms, 1127w, 1102w, 1048w, 990w, 937w, 739ms, 699m, 637vw, 593w, 543w, 501s, 476vw, 438vw, 403w, 351w, 334 vw, 305vw, 274w, 200 vw, 120vw, 55 s.

**2.3. Synthesis of  $\{[Zn^{II}(\text{cyclam})]_3(\text{amaranth trianion})_2 \cdot 14H_2O\}_n$  (7).** To a DMF (10 mL) solution of  $[Zn^{II}(\text{cyclam})](ClO_4)_2$  (0.658g, 0.142 mmol) was added dropwise an aqueous solution (5 mL) of trisodium 2-hydroxy-1-(4-sulfonato-1-naphthylazo)naphthalene-3,6-disulfonate salt (amaranth). The resulted solution was allowed to stand at room temperature for two weeks. The resulted red precipitate (0.380 g) was filtered and purified as was described for **6**. The precipitate is insoluble in organic solvents and in water. Anal.Calc. for  $C_{70}H_{112}N_{16}O_{34}S_6Zn_3$ : C, 39.65; H, 5.80; N, 10.57. Found C, 40.00; H, 5.40; N, 10.42. IR (KBr,  $cm^{-1}$ ): 3230ms, 2924ms, 2868ms, 1609w, 1552w, 1495s, 1477shms, 1432 w, 1368w, 1338w, 1284w, 1221ssh, 1198v s, 1135w, 1097s, 1037vs, 1019s, 991ms, 960w, 940w, 878w, 834vw, 803 vw, 761w, 740vw, 699w, 683s, 672 s, 638s, 615w, 593ms, 580ms, 537vw, 507w, 477vw. Raman (powder,  $cm^{-1}$ ): 1560s, 1543w, 1513ms, 1478ms, 1435ms, 1399ms, 1363vs, 1343s, 1281w, 1229 ms, 1197vw, 1161ms, 1129w, 1053w, 991w, 938ms, 892vw, 805vw, 773vw, 741ms, 701w, 690 vw, 543w, 500 s, 434vw, 401s, 362vw, 336vw, 280 w, 201vw, 143vw, 58s.

## CONCLUSIONS

In conclusion we succeeded to characterize by IR and Raman spectrometry the polymer obtained by coordination of  $[Cu^{II}(\text{cyclam})](ClO_4)_2$  (**2**),  $[Ni^{II}(\text{cyclam})](ClO_4)_2$  (**3**) and of  $[Zn^{II}(\text{cyclam})](ClO_4)_2$  (**4**) by amaranth (**1**). The structures of these polymers were also sustained by thermogravimetric and elemental analysis.

One of the differences between small model dyes and the larger, more complex colorants consist in adoption of the keto-hydrazone form rather than the simple azo form.<sup>11</sup> As has been stated above the sulfonic group does not affect the conjugated system irrespective of the substitution position in the naphthalene ring and changes in the electron density are relatively low at the carbon atoms to which sulfonic group are substituted. Due

to this lack of interaction between sulfonic group and the naphthalene ring the coordination of  $Cu^{II}$ ,  $Ni^{II}$  or  $Zn^{II}$  cyclam complexes by amaranth does not influence the  $\pi$  electron delocalization in coordination polymers and, as IR and Raman spectra show, the NH tautomer is also present.

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