Synthesis and Characterization of Coordination Polymer with Humidity Sensor Properties Prepared from Cu^{II} Cyclam Perchlorate and Tartrazine

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Reaction of [Cu^{II} (cyclam)] $(ClO_4)_2$ with trisodium(4E)-5-oxo-1-(4-sulfonatophenyl)-4-[(4-sulfonatophenyl)hydrazono]-3-pyrazole carboxylate (tartrazine), in aqueous DMF yielded coordination polymer [{Cu(cyclam)}$_3$(trt)$_2$·6H$_2$O], characterized by powder X-ray diffraction, IR and Raman spectrometry is investigated. The study of humidity sensor properties of this coordination polymer recommends it for construction of electronic devices for humidity detection at tens of degree temperatures around the value of 0 °C.

Keywords: Coordination polymer, cyclam, azo-dye, humidity sensor properties

In literature only a few studies about the humidity sensor using organic semiconductors are presented. Thus, investigation related to the colorant orange (Orange Dye, OD) [1,2,] a p-type organic semiconductor and methyl red [3] using a cell formed from Ag/methyl red/Ag were tested for such applications. Unfortunately, these dyes are soluble in water and cannot be used to detect high concentration of water.

In return, nickel phtalocyanine, being insoluble in water and thermal stable, and allowing deposition in thin film by heat evaporation without dissociation, exhibits better humidity sensor properties [4-6]. Encouraged by these results we tried to see if coordination polymers with azo dyes may show such properties. From a few azo-dye polymers prepared by us [7], only one polymer, [{Cu(cyclam)}$_3$ (trt)$_2$· 6H$_2$O]$_n$ (**3**), that is nickel phthalocyanine practically insoluble in water, presented properties that recommend it for use as humidity sensor.

Experimental part

Materials and instruments

All chemicals were reagent grade obtained from commercial sources and used without purification. FTIR spectra of solid sample were recorded on a JASCO 610 instrument in KBr pellets. Backscattered powder Raman spectra were recorded at room temperature with a JASCO NRS 3300 spectrophotometer equipped with a CCD detector (-69 °C) using a 600 L mm^{-1} grating with spectral resolution 0.65 cm^{-1}. Calibration was based on the Si 521 cm^{-1} peak. Excitation was 100 mW at 756 nm. The incident laser beam (1m diameter at the sample surface) was focused through an Olympus microscope. Powder XRD patterns were obtained with a Bruker D8 Advance powder diffractometer at 40 kV and 40 mA, equipped with an incident beam Ge 111 monochromator using CuK radiation (λ =1.540598A°). The patterns were indexed using the Dicvol method [8]. Nyquist impedance spectra of the sample were recorded on an AUTOLAB 100 instrument with FRA2 interface and processing of the data were performed by means of NOVA 1.6 soft. Elemental analyses were performed with a THERMO FINNIGAN EA 1112HT O/H-N/C, instrument.

*Synthesis of [{Cu(cyclam)}$_3$(trt)$_2$6 H$_2$O]$_n$ (**3**)*

To a DMF (10 mL) solution of [Cu^{II} (cyclam)] $(ClO_4)_2$ (0.736g, 0.142 mmol) an aqueous solution (5 mL) of trisodium (4*E*)-5-oxo-1-(4-sulfonatophenyl)-4-[(4-sulfonatophenyl) hydrazono]-3-pyrazole carboxylate (*tartrazine*) (0.267 g, 0.5 mmol) was added dropwise. The solution was allowed to stand at room temperature for three days. The resulting precipitate 0.240 g (59%), was filtered and washed by sonication with methanol until the filtrate was colourless, and then with ether and dried at room temperature. Yield: 0.24 g, (59%). Anal. Calc. for $C_{62}H_{104}N_{20}O_{24}S_4Cu_3$; C, 40.64 %; H, 5.72 %; N, 10.37 %; Found: C, 40.45 %; H, 5.83 %; N. 15.38 %. IR (KBr) = 3229, 3168, 2935, 2873, 1690, 1597, 1630, 1597, 1554, 1475, 1338, 1293, 1220, 1190, 1143, 1032, 1009, 980, 964, 884, 859, 833, 764, 712, 691, 682, 645, 608, 567, 527,435. Raman (powder) ν = 1685, 1598, 1501, 1474, 1411, 1339, 1268, 1216, 1170, 1121, 1087, 1032, 867, 803, 764, 736, 711, 693, 633, 609, 511, 848, 424, 396, 346, 284, 262, 156.

Results and discussions

Reaction of [Cu^{II}(cyclam]$(ClO_4)_2$ (**2**) with aqueous trisodium (4*E*)-5-oxo-1-(4-sulfonatophenyl)-4-[(4-sulfonatophenyl)hydrazono]-3-pyrazole carboxylate (tartrazine) (**1**) formed coordination polymer [{Cu(cyclam)}$_3$(trt)$_2$·6H$_2$O]$_n$ (**3**) (scheme 1).

The coordination polymer **3** consists of one-dimensional chains resulting from coordination of cyclam complexed metal by the SO_3 groups of tartrazine, in agreement with XRPD patterns, IR and Raman spectra and elemental analysis.

*X-ray powder diffraction studies of **3***

Sulfonated dyes, with a few exceptions, exhibit poor crystal growth making single crystal diffraction studies difficult [9]. In case of the compound **3,** growth of single crystal good for X-ray studies failed, so it was characterized, from crystallographic point of view, by means of powder XRD spectrum (fig. 1). The XRPD patterns for **3** are completely different comparatively with those of starting materials, demonstrating the formation of polymer **3**. Crystallographic data of **3** are shown in table 1.

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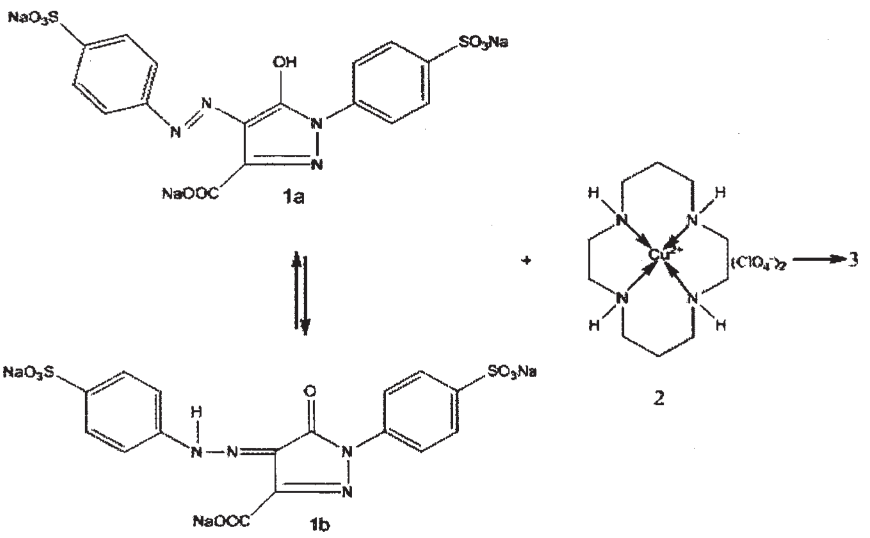

Scheme 1. Schematic representation of synthesis of coordination polymer **3**.

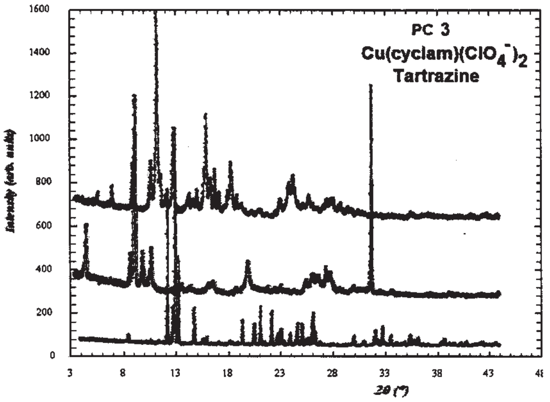

Fig. 1. XRPD patterns for **3** (up), **1** (middle) and **2** (down)

Table 1
CRYSTAL DATA FOR **3**

PC	Elementary lattice		Crystal system	Space group	Z	Volume Å^3	calc. g·cm^{-3}	det.* g·cm^{-3}
	Å	Grade						
3	a= 15.195(7) b= 19.730(2) c= 24.735(4)	α=β=γ=90	orthorhombic	Pna2$_1$	4	7416	1.520	1.485

*Density was determined by picnometer method

Raman and FTIR of ***3***

Because the changes in the electron density are relatively low at the carbon atoms to which sulfonic group are substituted [10] and the participation of sulfur d orbital in the conjugated system is very low, the contribution into C-S bond is practically negligible in aza dye compounds [11]. Due to this fact, the results obtained by Neica, in her dissertation thesis [12], in connection with identification of Raman spectrum vibrations of tartrazine can be applied in analysis of the similar spectrum of the coordination polymer **3** (table 2).

The theoretical calculation [13] showed that the azo distance for tartrazine molecule is 127.1 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 [14]. The bond length between nitrogen and C of pyrazole ring, with OH substituent is 136.5 pm, which is shorter then that between azo N and the C of the phenyl ring 142.1 pm [15,16]. The elongation of the bond length supports the charge delocalization from pyrazole ring and the localization at the azo bond [17 - 19]. The calculated C=C bond lengths of the pyrazole ring vary from 140.2 to 140.5, which is between the length of a C-C single bond (154.0 pm) and that of a C=C double bond (134.0 pm) [13,20].

Similarly, the calculated C=N bond length from pyrazole ring vary from 135.0 pm to 137.7 pm, lengths which are also intermediate between those for a C-N single bond (148.0 pm) and C=N double bond (128.0 pm) [13,21]. The calculated data suggest an extended π delocalization over the pyrazole system [22,23]. Due to this density electron donation a decreasing of the bond order of the azo group and lengthening of the bond take place, indicating the presence of NH tautomer in solid tartrazine. This electronic delocalization take also place and in coordination polymers, where the tartrazine trianion is coordinated by transitional metals, and the NH tautomer is present in the solid form (*vide infra*).

For analysis of the IR spectra of **3** (table 3) we have taken into consideration theoretical calculations of these spectra of other azo dyes from literature [24 - 27].

The difference between symmetric and asymmetric vibrations of the carboxylate groups in the case of compound **3** is 216 cm^{-1} and only 83 cm^{-1} for tartrazine (Na$_3$trt), difference which sustains a monodentate coordination mode [28]. N=N stretching vibration, due to its symmetry, has a very characteristic band in the Raman spectroscopy but is difficult to be observed in the IR spectrum. The change of N=N bond length in the molecule which has two non-equivalent C-N parts (*vide supra*) produces a modification in the dipole moment. Due to this

Table 2
RAMAN SPECTRUM OF COMPOUND **3**

v, cm^{-1}	*Signal assigned to*
1558 s	C=C symmetrical stretching mode of pyrazole +quadrant stretching mode of the phenyl ring contribution + C-H bending mode of OH group
1501s, 1474m, 1411 w	C=C pyrazole bending mode+ N=N bending mode + C-=H bending mode of phenyl ring
1399 s	Azo group stretching mode(C-N=N-C) + symmetrical stretching of COOH group
1268 vw	Bending mode of N-N=C-C$_{carboxylic}$ from pyrazole ring
1216 m	C-H torsion mode of both phenyl rings + N=C-C$_{carboxylic}$ bending mode + stretching mode of C$_{phenyl}$-N and C$_{pyrazole}$-N(N belong to azo group)
1121 s	Out of plane C-H deformation of phenyl rings
1087s	Phenyl bending mode bonded by nitrogen of pyrazole ring
1032s	Phenyl bonded by azo group bending mode + N=N asymmetrical mode + C- SO_3^- symmetrical stretching mode
867 vw	Out of plane deformation of both phenyl rings + bending modes of OH and COOH groups
803 vw	Bending mode of SO_3^- substituted on phenyl on phenyl moiety bonded by pyrazole
764 vw	Bending mode of SO_3^- from phenyl moiety bonded by azo group + out of plane C-H deformation of phenyl group bonded by azo group
712 vw	Bending mode of SO_3^- groups
693 ms	Out of plane CH deformation of pyrazole ring
634 ms	Out of plane deformation of phenyl rings
609 ms	Pyrazole bending + out of plane CH deformation of the phenyl rings
511 vw	Wagging mode of SO_3^- substituted on phenyl moiety bonded to pyrazole + out of plane CX-H deformation of phenyl and of pyrazole rings

w=weak, s=strong, m=medium, v=very

Table 3
IR SPECTRUM OF COMPOUND **3**

v, cm^{-1}	*Signal assigned to*	*Reference*
3229 ms, 3168 ms	N-H stretching	25
2935 ms	CH_2 asymmetric stretching	25
2893 ms	CH_2 symmetric stretching	25
1554 s	COO^- asymmetric vibration	25
1475 s	OH in plane bending deformation	24
1450 s, 1380 s	N=N group stretching mode	29
1338 s	COO^- symmetric vibration	25
1293,w	C-N stretching mode	34
1220 s (sh)	N=N stretching vibration	32,33
1200 s,1130 s	C-N stretching vibration	30,31
1190 s	SO_3 asymmetric stretching vibrations + C-N stretching mode + C-H in plane bending	11
1033 s	SO_3 symmetric stretching vibrations	24
1009 vs	C-N=N-C cromophore stretching vibrations	24
764 w, 691 s	SO_3 symmetric bending vibrations	26
711 ms	OH out of plane bending vibrations	24
527 w,435 w	SO_3 wagging vibration	26

w=weak, s=strong, m=medium, v=very, sh=shoulder effect the N=N stretching mode became active in the IR and has a medium intensity. Oliveira and coworker [26] predicted for the NH isomer, quite intense bands at 1554, 1324, and at 1294 cm^{-1}. The first absorption was assigned as a combined mode including δNH, νCO, νC=N, βCH vibrations, and the other two bands are attributed to δNH, νN-H, βCH, νCC modes. All of these vibrations are characteristic for keto-hydrazo isomer and may be used as fingerprints in the IR spectrum. Oliveira observed experimentally, in the case of azo dye Ponceau 4R, only two bands at 1495 and at 1221 cm^{-1}. In the IR spectra of compound **3** these vibrations were identified, as strong bands, at 1597 cm^{-1} and at 1221cm^{-1} (sh). The bands from 1220-1223 cm^{-1} range are mixed with azo stretching vibrations (*vide supra*). As in case of Raman spectra, the IR vibrations are mixed with vibrations produced by phenyl and pyrazole rings [35,36].

Study of humidity sensor properties of ***3***

The pastille of polymer $[\{Cu(cyclam)\}_3(trt)_2{\cdot}6H_2O]_n$ **3** was obtained, at a pressure of 100 atm. with a device commonly used in IR and Raman preparation of samples, in cylindrical form with a diameter of 10 mm and thickness of 0.3 mm. After this treatment there were no structural changes observed in the structure of the polymer **3**. This fact was confirmed by analyses of X diffraction, IR and Raman spectra. In order to measure conductivity properties of this polymer (accepting a priori that it shows isotropy in volume phase of the pastille) the variation of the pastille resistance with temperature in -130 ˚C +19 ˚C temperature range, in direct current (DC) regime was studied. On circular surfaces of the pastille, the wires Cu conductors with low specific resistance were glue to Ag conductive paste (fig. 2). After this stage the socked remained in the oven at room temperature for 72 h. This time was needed to achieve the strengthening of the connections to avoid a massive migration of Ag ions in the substrate structure. Resistance and temperature measurements were made using an electronic multimeter UT60 connected to computer. We have to specify that the temperature sensor was attached to the sample pellet at the interface metal (Ag) / organic compound.

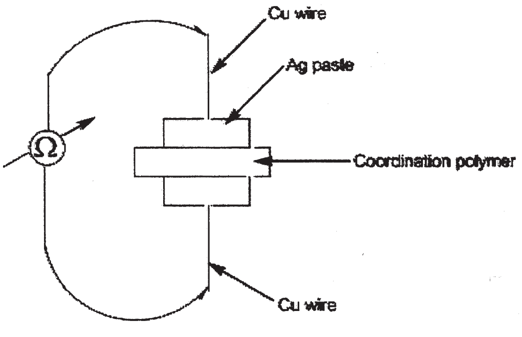

Fig. 2. Scheme of the circuit prepared for measuring conductivity properties of **3**

The sample was initially immersed in liquid nitrogen and then extracted from it and exposed to the laboratory atmosphere. No connections damage or cracks in the sample were observed. In the preliminary determinations, in the absence of the thermostability at low temperatures, the experiments pursued the temperature modification in the course of time on contact surface of the sample and the variation in time of the sample resistance in the immersion and in the laboratory atmosphere. From these data the dependence of sample resistance function of the temperature were configured. Analyzing the temperature / time dependence (fig. 3) it is noticed that there is a rapid temperature change of the interface metal / organic compound, immediately after drawing of the sample from liquid nitrogen and exposure to laboratory atmosphere, time in which this change occurs, although is short, does not affect the sample. The phenomenon is reversible during the sample immersion in the liquid nitrogen. Sample undergoes a dramatic resistance change of the value from 150 MΩ to 1.98 MΩ in the interval in which the transition temperature of liquid nitrogen to the laboratory environment take place, initial (12 s), after that follows a relatively slow growth (500 s) of the sample resistance up to the value of 60 MΩ followed by a quick return (15 s) to the value of 150 MΩ (fig. 4).

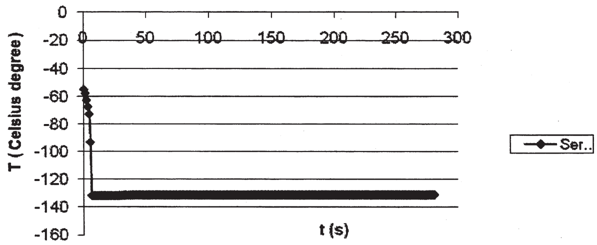

Fig. 3. Temperature-time dependences of the sample

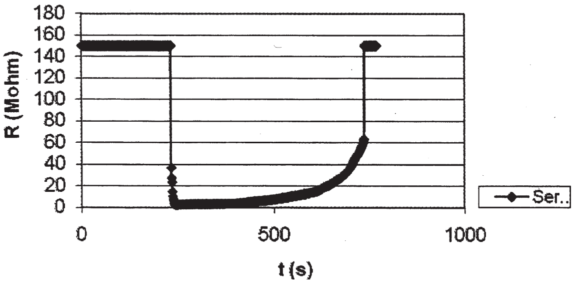

Fig. 4. Variations of the sample resistance function of time

Dramatic changes of the resistance occur between (-10°C, +20°C) around the value of 0°C, and 18°C, respectively, the characteristic of the resistance-temperature having a step function form in the first temperature range (fig. 5). Experimental visual inspection of the sample, revealed the occurrence of condenses, that in our opinion would be, probable, due to the presence of the moisture in the laboratory atmosphere. In usually way, the sample conductivity at room temperature can be explained by concerted contribution given by the resistance of organic compound crystallites and that of the intercrystallite barriers. Evidently, resistance of the barriers at the level of crystallite contacts has a much higher value than that of the crystallites, fact that explain the high resistance of the sample in direct current (DC) measurements.

Dramatic changes of the resistance around the value of 0°C might be due to the fact that resistance of intercrystallite barriers is much lowered due to the presence of water molecules. Conductivity of the sample results thus from variation of the temperature and of intercrystallite barriers resistance (variation managed by humidity).

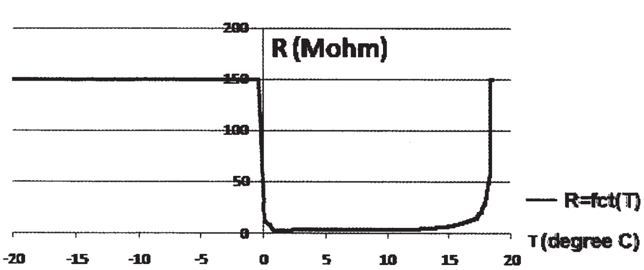

Fig. 5. Variations of the sample resistance function of temperature

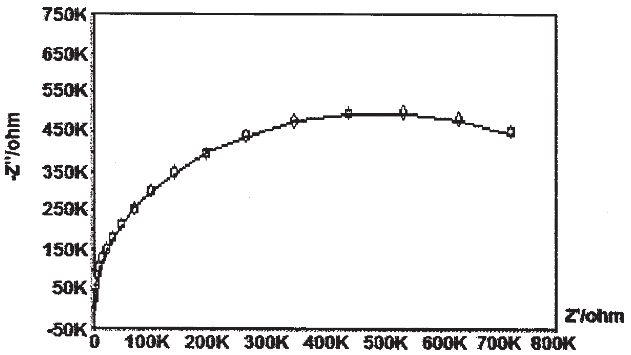

Fig. 6. Impedance spectrum $-Z_{im}$ (-Z") function of Z_{re} (Z') for the proposed circuit of the sample

Electrical properties of the sample in AC regime were determined by means of Nyquist (Cole-Cole plot) impedance spectra (fig. 6). The frequency range covered was between 10 kHz-0.1 Hz, for an alternative signal with 0.01 V amplitude at laboratory temperature (293 K). The best circuit to analyze the sample was made from the following elements: R_1, the resistance of the ohmic contacts of the pastille made from analyzed compound, series with a parallel circuit R_2C, R_2, which in the laboratory temperature conditions, is an equivalent resistance of the polymer, made from nanocrystallites resistance and intercrystalites barriers resistance and C which express, in its turn, an equivalent capacity of the analyzed sample (ohmic contacts, pastille).

The measured values were: $R_1 = 99.7\Omega$ error 0.22%; $R_2 = 0.997$ MΩ error 0.55%; C=0.998μF error 0.15%. The difference in probe resistance (see R_2 value) between DC and AC experiments results from temperature changes in the case of DC signal and the type of circuit analyzed in AC signal. Step-type behaviour of the sample resistance to the temperature changes, in the mentioned interval in DC experiment and R_2 sample resistance in AC experiment, could serve to construction of some functional electronic devices for humidity detection.

Conclusions

The coordination polymer $[\{Cu(cyclam)\}_3(trt)_2 \cdot 6H_2O]_n$ (**3**) was prepared and characterized by means of IR, Raman spectra, and elemental analysis. The study of humidity sensor properties of **3,** recommend it for construction of electronic devices for humidity detection at tens of degree temperatures around the value of 0°C.

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