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SYNTHESIS, SPECTRAL CHARACTERIZATION, THERMAL STUDIES AND STRUCTURE OF BIDENTATE AZO DYE Cr(III) COMPLEXES

BY

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Abstract. In this paper a two new complexes of Cr(III) and Acid red 44 azo dye were synthesized and characterized.

The structures of these metal complexes of Cr(III) were confirmed by elemental analysis, spectroscopic UV-Vis, IR, conductivity and pH-metric measurements. Also was investigates the thermostability by thermogravimetric analyses (TG-DTG). The X-ray powder diffraction reflects that azo dye complexes with Cr(III) are amorphous.

The octahedral geometry of the metal complexes of Cr(III) structures was confirmed by experimental data. The ligand coordinates through the azo dye nitrogen atom and hydroxyl oxygen atom after deprotonation, so the proposed structures indicates that Acid red 44 dye is a bidentate ligand.

Key words: Dye Acid red 44; ligand; complex compounds, Cr(III).

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1. Introduction

In this work a continuation of the authors research in this field is presented (Sibiescu & Vizitiu, 2015). The paper consists in the synthesis and the study of the obtained coordination compounds by the interaction of Cr(III) chloride with Acid red 44 dye. There are several areas where this compound can be found: in biology as protein stain, only slightly staining cellulose used in microscopy, in histology for staining fibrin in conjunction with MSB (Martius, Scarlet and Blue), also as food additive knows as E 126 and not at least in textile and leather industry, known as Ponceau 6R, for dyeing wool, silk and other materials as complex azo dyes (Kocaokutgen & Ozkinali, 2004).

The environmental impact of the natural processes purification of the wastewater resulting from azo dyes in textile industry, it be should take into account. So, this aspect is of high importance due to the fact that from the total quantity of textile dyes for leather and printing inks, loss amount of the dye is about 11% (Sibiescu *et al.*, 2010).

The new synthesized coordination compounds is included in the category of hexa-coordinated complexes where the central atom is octahedrically surrounded by nitrogen atom from azo group -N=N- and oxygen atom derived from hydroxyl group, after deprotonation, and molecules of water. This category of complexes have also applications in gravimetric determination of some transitional metals ions (Salkat *et al*., 2013; Sibiescu *et al*., 2010).

2. Experimental

The Acid red 44 dye (symbol HL) as ligand was complexed in aqueous solution with Cr(III) of chloride. Experiments were conducted using solutions of 10^{-2}M concentrations of $CrCl_3 \cdot 6H_2O$ – Merk and the Acid red 44 dye ligand – Fluka.

The molar ratio was found by pH measurements, UV-VIS spectroscopy, using the molar ratio methods and electric conductivity measurements using the continuous variation methods (Yoe & Jones, 1944). The spectroscopy measurements was made at λ_{max} = 518 nm at Spectrofotometer UV VIS- CARY 300 - Varian. The stability constants of these complexes were determinate by Turner Anderson and Harvey Mannig methods (Harvay & Manning, 1950).

The coordination compounds were obtained in melting mixture and by reaction in water solvent. For this purpose, stoichiometric quantities of the reagents were used: (a) 1 mole of Cr(III) of chloride and 1 mole HL dye; (b) 1 mole of Cr(III) of chloride and 2 mole HL dye, were maintained each of them (a) and (b) at room temperature. After forty minutes, when the reaction was completed, the obtained compounds were separated and washed by distilled water for three times. Finally the complex compounds were dried at 70°C temperature till constant weight. The obtained products were purple friable solids.

The infrared absorption spectra were recorded on solid samples in the 200-4000 cm^{-1} range employing the KBr pelleting method using an FTIR 660 Plus photometer. The changes in frequencies of chemical bonds of the new coordination compounds in the infrared absorption spectra confirmed their formation.

In order to studied the thermal stability and dynamic thermogravimetry of the new synthetized compounds it was used a Diamond TG/DTA derivatograph produced by Perkin Elmer – USA. The temperature of decomposition was up to 610°C and it was determined the reaction rates and the reaction mechanism. Also the values of kinetic parameters was determinate too (Chirilă *et al*., 2011; Freeman & Carrol, 1958; Yildiz *et al*., 2010).

The characterization of the compounds with Cr(III) and Acid red 44 dye was completed by the investigation with X-ray diffraction for the crystallinity degree too. The diffractograms were recorded at Bruker D8 Advan CE difractometer with a nickel filter, copper anode in the 2θ = 2-60° range, at room temperature (Seatle, 1997; Flondor *et al*., 2007; Freeman & Carrol, 1958).

3. Results and Discussions

For an easier writing the Acid red 44 dye ("HL") was noted as it follows (Fig. 1):

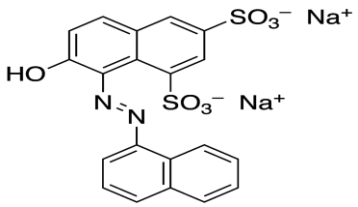


Fig. 1 − The structure of the Acid red 44 dye.

The methods, specified above, have revealed that in aqueous solution there are presence two complexes, one of them at 1:1 ratio (pH = 5.1) and the other one at 1:2 (pH = 6.8). The higher stability of the second complex is showed by experimental data: Kst = $1.2 \cdot 10^5$ for Cr-L (1:1) complex and Kst = $8.6 \cdot 10^7$ for Cr-L (1:2) complex. The results of the chemical analysis are in concordance with theoretical values with an errors + or – 0.5 % (Table 1).

Table 1

The Chemical Analysis of the Studied Complex Compounds

Compounds	C%		H%		N%		Cr%	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
$CrLCl_2 \cdot 4H_2O$	34.38	34.46	1.68	1.72	4.04	4.02	7.47	7.46
$CrL_2Cl \cdot 2H_2O$	44.12	44.02	2.01	2.20	5.01	5.13	4.57	4.76

From the results of the chemical analysis and the reactant rate, the following chemical reactions (1) and (2) were established for the syntheses of the both complex compounds:

$$CrCl_3 + HL + 4H_2O \rightarrow CrLCl_2 \cdot 4H_2O + HCl \quad (1)$$

$$CrCl_3 + 2HL + 2H_2O \rightarrow CrL_2Cl \cdot 2H_2O + 2HCl \quad (2)$$

The absorption peaks of the nitrogen atom from azo group -N=N- , of the aromatic group, of the $–SO_2$, and of the -OH group, from orto- position, were carefully analyzed.

The spectra obtained were almost similar to those of the free dye. The only difference is revealed from the participation of the above mentioned groups in the coordinate bonding. The corresponding vibration frequencies are lower than for the free dye (Mahmoud *et al*, 2016; Flondor *et al.*, 2007).

The frequencies of the azo group ($\gamma_{-N=N-}$ = 1417-1562 cm^{-1}) are modified after complexion that explains the involvement of the group in the coordination process, naming "internal complex" the compounds (Table 2).

Table 2

The Vibration Frequencies of Some Specifics Groups of the Studies Compounds

Nr. crt.	Compound	γ_{OH}	$\gamma_{-N=N-}$	γ_{asSO2}	γ_{simSO2}	γ_{arom}	γ_{Cr-N}	γ_{Cr-O}
1.	H L	3390	1598-1442	1189	1490	1198-1138	–	–
2.	$CrLCl \cdot 4H_2O$	3387	1562-1417	1189	1490	1148-1098	499	455
3.	$CrHL_2 \cdot 2H_2O$	3384	1562-1417	1189	1490	1143-1098	493	445

From the thermal decomposition process of the studied complex compounds it follows that this process takes place in several stages, according to the recorded derivatograms during this process (Table 3).

The coordination water is evaporated from the beginning in the first step of decomposition process for the both compounds. In the second step the weaker chemical bonds of the studied complex compounds are broken. Finally, Cr_2O_3, the solid product, are obtained. There were not analyzed the resulted gaseous products. The gaseous compounds resulted from the thermal decomposition have to pass through a smaller layer of deposed solids, as the decomposition reaction advances.

The Freeman-Carroll was the method used for calculate the reaction order from the thermal decomposition (Freeman & Carrol, 1958). From both decomposition steps, the values for the reaction order were ranged between 0.50-0.99.

This is in according to the reference literature (Ben-Saber *et al.*, 2005; Flondor *et al.*, 2007).The values of the reaction order for this decomposition reaction, should be no more than 1 and no less than 0.

It was obtain an increasing value for the reaction order, very close to 1, on account of dispersion degree of the system.

The reaction order is not influenced by the resistance of the solid reaction products in the thermal decomposition reactions, where the gaseous products pass through monomolecular layers (Chirilă *et al.*, 2011).

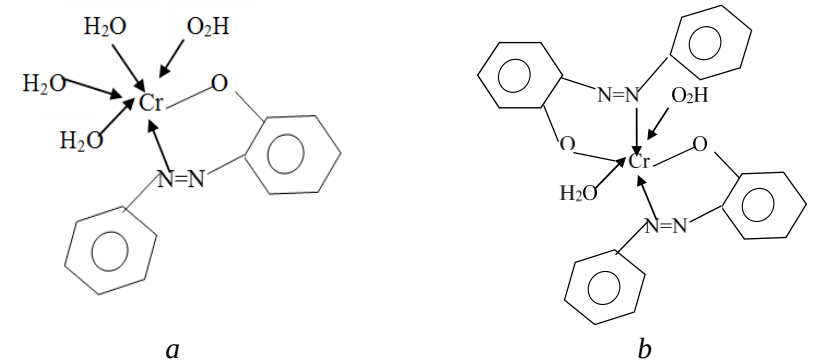
Table 3

The Characteristic Temperatures of Thermal Decomposition Stages, the Values of the Reaction Order and Activation Energies of the Corresponding (KJ/mol) for the Studied Complex Compounds Complex compound

Compounds	Stage I				Stage II				Stage III			
	Ti [^{o}C]	Tf [^{o}C]	n	E	Ti [^{o}C]	Tf [^{o}C]	n	E	Ti [^{o}C]	Tf [^{o}C]	n	E
$CrLCl{\cdot}4H_2O$	82	293	0.93	69	300	398	0.50	200	399	600	–	–
$CrHL_2{\cdot}2H_2O$	98	306	0.96	75	310	521	0.99	121	530	610	–	–

X-ray diffractograms have shown that the new synthesized compounds have an amorphous structure.

Based on the experimental and theoretical data the following structures was proposed (Figs. 2*a* and 2*b*):



a *b*

Fig. 2 − The proposed structures of the complex ions corresponding to the coordination compounds: $CrLCl_2{\cdot}4H_2O$ (*a*) and $CrL_2Cl{\cdot}2H_2O$ (*b*).

4. Conclusions

In this paper, the study of formation and stability in aqueous medium of two new complex compounds of Cr(III), derived from the interaction between

$CrCl_3$ and Acid red 44 dye, in molar ratio central atom Cr(III): ligand = 1:1 and 1:2 is presented.

The methods applied for study are specific for research in solution of complex compounds: elemental chemical analysis, UV-VIS and IR spectrophotometry, conductometry, pH-metry, XRD spectroscopy, and the thermal stability.

The new coordination compounds synthesized by the interaction of Cr(III) with Acid red 44 dye is included in the category of hexa-coordinated complexes and it was established that the most stable complex is $CrL_2Cl{\cdot}2H_2O$.

The both new compounds have a thermal stability to about 390°C. Based on the experimental and theoretical data the proposed structures indicates that Acid red 44 dye is a bidentate ligand.

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SINTEZA, CARACTERIZAREA SPECTRALĂ, STUDIUL TERMIC ŞI STRUCTURA UNOR COMPLECŞI AI Cr(III) CU UN COLORANT AZOIC BIDENTAT

(Rezumat)

În această lucrare se continuă cercetările cu privire la sinteza, caracterizarea şi stabilirea structurii unor complecşi cu liganzi din clasa coloranţilor azoici.

Mai concret au fost obţinuţi doi noi complecşi în urma interacţiunii colorantului Roşu Acid 44 cu cationul de Cr(III).

Structurile noilor complecşi sintetizaţi în raport molar de 1:1 şi 1:2 au fost stabilite cu ajutorul următoarelor analize: analiza elementală, conductometrie, pH-metrie, spectroscopie UV-VIS, FTIR şi XRD.

De asemenea s-a efectuat şi descompunerea termică a celor doi noi complecşi până la o temperatură de aproximativ 600°C, din care s-au obţinut informaţii cu privire la stabilitatea termică.

Analizând şi coroborând toate datele experimentale s-au propus două structuri ale complecşilor sintetizaţi din care reiese că ligandul este bidentat iar atomul central este hexacoordinat. O altă concluzie finală este aceea că ambii compuşi sunt stabili termic până în jurul temperaturii de 100°C şi au o structură amorfă.