Structure-colour Correlation Study in the Class of Preformed Acid Azo Chromium (1:1) Complex Dyes Resulted from the Same Coupling Component

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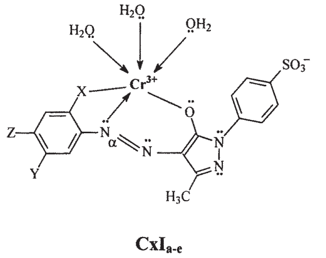
This paper aims to explain the variation of UV-Vis spectral parameters of preformated acid azo chromium (1:1) complex dyes resulted from the same coupling component, having benzene-azo-pyrazolone type structures, versus spectral parameters of (1:1) chromium complex of the metallizable azo dye: 2-aminophenol → 1-(4’-sulphophenyl)-3-methyl-5-pyrazolone acid, considered as the reference structure. Were taken into account the electronic effects (σ, π) of substituent. The purity and the molecular structure of these compounds were verified by means of thin layer chromatography, chromium analysis as well by spectral study in IR and UV-Vis ranges.

Keywords: complex, structure, substituent effects

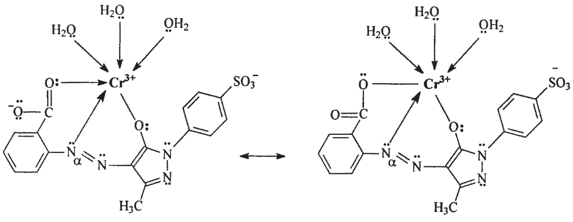
Preformed acid azo chromium (1:1) complex dyes are compounds containing one or two sulfonic groups in the molecule and shows the structure of ortho, ortho’-dihydroxyazo; ortho-hydroxy, ortho’-aminoazo; ortho-hydroxy, ortho’-carboxyazo or ortho, ortho’-diaminoazo, that were previously transformed into chromium (1:1) complex. Commercial products are known for Neolan (CIBA) and Palatine Fast (BASF) and serve to dye wool and some to leather dyeing - Erganil (BASF) type dyes. Respective complexes are very stable and do not decompose by heating in strongly acidic or basic solutions. They dye wool in strong acid bath. This paper aims to explain the variation of UV-Vis spectral parameters of preformed acid azo chromium (1:1) complex dyes resulted from the same coupling component compared to those of the (1:1) chromium complex of metallizable azo dye (A), considered as the reference structure, taking into account the electronic effects (σ, π) of the substituents. (A). 2-hydroxy-1-[1-(4’-sulphophenyl)-3-methyl-5-pyrazolone acid]-azo-benzene (IUPAC). For this we have synthesized a series of known dyes from the PALATINE FAST (BASF) range. They are part of the class of preformed acid azo chromium (1:1) complex dyes, having benzene-azo-pyrazolone type structures, which were purified and analyzed. From this series of dyes, those with the general structure **CxI**$_{a-e}$ were studied:



(1)

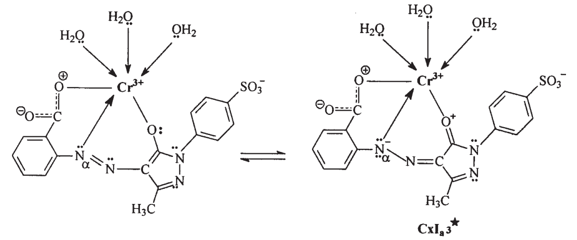
CxI$_{a-e}$

CxI$_a$ (CxI$_{a-e}$, when X=COO; Y=Z=H), **CxI**$_b$ (CxI$_{a-e}$, when X=O; Y=Z=H), **CxI**$_c$ (CxI$_{a-e}$, when X=O; Y=Cl; Z=H), **CxI**$_d$ (CxI$_{a-e}$, when X=O; Y=NO$_2$; Z=H) si **CxI**$_e$ (CxI$_{a-e}$, when X=O; Y=H; Z=NO$_2$). The chemical structures of compounds: **CxI**$_a$, **CxI**$_b$, **CxI**$_c$, **CxI**$_d$ **si CxI**$_e$, both in the ground and in the excited state are the next:



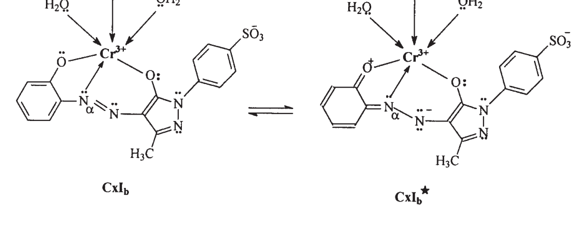
CxI$_a$1 CxI$_a$2

(2)



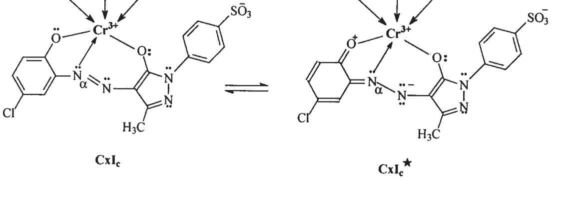
CxI$_a$3 CxI$_a$3*

(3)



CxI$_b$ CxI$_b$*

(4)



CxI$_c$ CxI$_c$*

(5)

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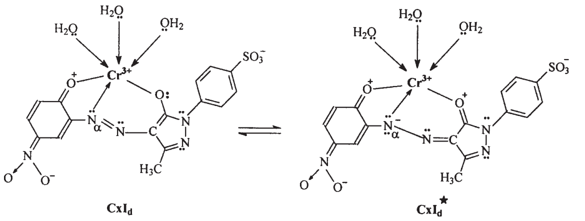
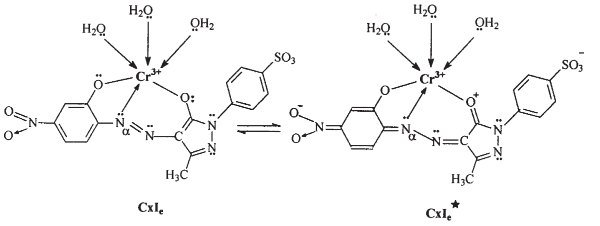


(6)



(7)

Experimental part

Materials

Diazotizing components: anthranilic acid (Ac.A), 2-aminophenol (2AF), 4-chloro-2-aminophenol (4ClAF), 4-nitro-2-aminophenol (4NAF), 5-nitro-2-aminophenol (5NAF).

Coupling components

1-(4'-sulfophenyl)-3-methyl-5-pyrazolone acid (FMPS).

The chromium (1:1) complex dyes of the following metallizable azo dyes resulted from the same coupling component were synthesized:

1) 2AF→ FMPS;
2) Ac.A→ FMPS;
3) 4ClAF→ FMPS;
4) 4NAF→ FMPS;
5) 5NAF→ FMPS.

The yields for the preparation of the studied acid azo chromium (1:1) complex dyes are 80-90%.

Equipment

IR spectra were measured with a FT IR –Jasco 6300 spectrophotometer, using KBr pellets and UV –Vis spectra were performed in distilled water with a UV / Vis / NIR spectrophotometer. Were used cells with 1 cm pathlength, working in the range dye concentrations of 1.75 -3.65 * 10-2 g / L in distilled water.

Synthesis

Chromium (1:1) complexes dyes (**CxI_{a-e}**) were synthesized according to the literature [1], from corresponding azo dyes by complexation with chromium, in a mixture of ethylene glycol-water at a volume ratio of solvent : water of between 1:2 ... 1:6, at 90 – 110°C temperatures , in 8-20 h, depending on the structure of the metallisable azo dye containing the sulphonic acid group in the coupling component.

Physico-chemical analysis

The final products were isolated from the reaction mass and then purified by recrystallization from absolute ethanol. For the solubilization of azo chromium (1:1) complex dyes a mixture of distilled water and ammonia was used. Standard concentrations of these dyes were determined by chemical analysis of reductive cleavage with VSO_4 [2] and have values between 98.5 to 99 % .

Purified compounds were subject to both spectrophotometric analysis (chromium content analysis) by atomic absorption spectrometry, with atomization in air -acetylene flame [3].

Purity determination of investigated dyes was carried out by using the thin layer chromatography method on silica gel on aluminum support by working with the eluent: n-BuOH: EtOH: sol. 25 % NH_3: Py = 4:1:3:2 (vol./vol.). For dissolving the samples of azo chromium (1:1) complex dyes was used as solvent, distilled water and ammonia. Spectral parameters determination of investigated dyes was carried out by using spectrophotometric method in IR and UV-Vis ranges.

Results and discussions

Colour development is known as a dynamic phenomenon and is equally dependent on the structure of a compound both in the ground and in the excited state . Our interpretations are based on the accepted premise in the literature , that the ground state of azo chromium(1:1) complex dyes are found in the form azo, while their excited state corresponds to hydrazono type structure. Azo-hydrazone tautomerism has been observed before and after metal-ion complexation [4].

This paper is a continuation of the paper: "Structure-colour correlation study in the class of complexable monoazo dyes"]5]. The structure of the studied azo chromium (1:1) complex dyes resulted from the same coupling component was proved by spectrophotometric (chromium content analysis) and FTIR analysis and the purity was proved by thin layer chromatography on silica gel on aluminum support.

Chromatographic analysis

In table 1, the chromatography revealed us that the approached way, allowed to obtain uniform products.

- Spectroscopic analysis

In table 2, is presented the chromium content analysis by atomic absorption spectroscopy with atomization in air-acetylene flame. This is an instrumental analysis method based on the wavelength radiation absorption

Table 1

PRESENTATION OF R_f (RETENTION FACTOR) VALUES IN THIN LAYER CHROMATOGRAPHY OF ACID AZO CHROMIUM (1:1) COMPLEX DYES OF CxI_{a-e} TYPE

Chromium (1:1) complex dye	**CxI_d**	**CxI_a**	**CxI_b**	**CxI_c**	**CxI_e**
(1) X	O	COO	O	O	O
(4) Y	NO_2	H	H	Cl	H
(5) Z	H	H	H	H	NO_2
R_f	0.52	0.61	0.53	0.52	0.53

Table 2

CHROMIUM CONTENT ANALYSIS BY ATOMIC ABSOPTION SPECTROSCOPY OF ACID AZO CHROMIUM (1:1) COMPLEX DYES of CxI_{a-e} TYPE

Chromium (1:1) complex dye		**CxI_d**	**CxI_a**	**CxI_b**	**CxI_c**	**CxI_e**
(1) X		O	COO	O	O	O
(4) Y		NO_2	H	H	Cl	H
(5) Z		H	H	H	H	NO_2
Molecular weight (M)		523	506	476	511.5	523
Cr%	**Calc.**	9.9	10.3	10.9	10.2	9.9
	Exp.	9.5	9.8	10.5	9.7	9.3

Determinations attest a good agreement between the real and the assigned structures.

No.	Vibration nature	CxI_c	CxI_d
1	**Deformation vibration γ_{OH} (cm^{-1})**	3450 (i)	3450 (i)
2	**Aromatic ring deformation vibration $\gamma_{C=C}$ (cm^{-1})**	1590-1630 (i)	1590-1630 (i)
3	**Valence vibration $\nu^s_{S=O}$ (cm^{-1})**	1150-1250 (i)	1150-1250 (i)
4	**Valence vibration $\nu^{as}_{S=O}$ (cm^{-1})**	1040 (i)	1040 (i)
5	**Valence vibration at 5-membered heterocycles**	1590 (m) 1490 (m) 1400 (m)	1590 (m) 1490 (m) 1400 (m)
6	**Deformation vibration of 1,2,4-tri-substituted benzene ring γ_{C-H} (cm^{-1})**	805-825 (i) 870-885 (i)	805-825 (i) 870-885 (i)
7	**Mono-substituted aromatic ring deformation vibration γ_{C-H} (cm^{-1})**	735-765(i) 685-710 (i)	735-765(i) 685-710 (i)
8	**Valence vibration ν^s_{C-Cl} (cm^{-1})**	630-680 (i)	-
9	**Valence vibration ν^s_{NO2} (cm^{-1})**	-	1320-1360 (i)
10	**Valence vibration ν^{as}_{NO2} (cm^{-1})**	-	1465-1570 (i)
11	**Valence deformation γ_{C-H} (cm^{-1})**	-	832-868 (s)

in which: (i) = intense band; (m) = medium band; (s) = weak band.

Table 3
IR SPECTRAL ANALYSIS OF ACID AZO CHROMIUM (1:1) COMPLEX DYES, CxI_c AND CxI_d

(1:1) Complex Dye	CxI_d	CxI_a	CxI_b	CxI_c	CxI_e
(1) X	O	COO	O	O	O
(4) Y	NO_2	H	H	Cl	H
(5) Z	H	H	H	H	NO_2
λ_{max}(nm)	422.3 (yellow)	423 (yellow)	473.5 (orange)	482.6 (yellowish red)	514 (ruby)
ε_{max}* 10^{-3} M^{-1}cm^{-1}	6.95	11.2	18.1	13.3	7.7
Conc.*10^2 g/L	2.92	2.56	2.62	3.62	3.41
$\Delta\lambda_{max}$ (nm)	-51.2	-50.5	0	+9.1	+40.9
$\Delta\varepsilon_{max}$* 10^{-3} M^{-1}cm^{-1}	-11.5	-6.9	0	-4.8	-10.4

Table 4
(UV-Vis) SPECTRAL ANALYSIS OF ACID AZO CHROMIUM (1:1) COMPLEX DYES OF CxI_{a-e} TYPE

characteristic to each element; for chromium atom λ_{Cr} = 357.9 nm.

Determinations attest a good agreement between the real and the assigned structures.

IR spectrophotometric analysis

The studied chromium (1:1) complexes dyes were characterized by IR spectra and the characteristic peaks for **CxI_c** and **CxI_d** are given in table 3. IR spectroscopy is not used to detect the azo groups (-N = N-), because having a non-polar character, these do not give intense and specific bands; their existence is found as small absorption bands in the spectral region 1400-1450 cm^{-1}. At **CxI_d**, specific vibrations of 5-membered heterocycles are covered by the valence vibrations characteristic to aromatic nitro-compounds.

IR spectra highlight the main characteristic bands of the chromatable azo dyes corresponding to the studied chromium (1:1) complexes dyes, except that in the spectral region of 800-1000 cm^{-1} in the complexes a series of the bands associated to water molecules, strongly coordinated in an aqueous complex are appearing. These bands increase in intensity when O-Cr bond very strong and water molecules are forming strong H bonds with the neighboring atoms. It also found stretching and bending absorptions at approx. 3400 and 1600 cm^{-1}, characteristically to water molecules. Complexes containing water, decrease the vibration valence ν_{H2O} with 30-40 cm^{-1} and δ_{H2O} increase with 20-30 cm^{-1}. The characteristic band Cr-O vibration bond newly formed, which ought to be reflected in the IR spectrum of all studied chromium (1:1) complexes dyes could not be clearly attributed, even when chrome-disalicylate acid was used as a reference structure. This is due to the presence of a large number of bands in the region 600-800 cm^{-1}, where we would have expected to find this band.

Is also worth mentioning that in this region 620 -700 cm^{-1} the characteristic band of ν^s_{C-Cl} stretching vibration is found. Determinations attest a good agreement between the real and the assigned structures.

UV-Vis spectrophotometric analysis

Table 4, presents the (UV-Vis) spectral data on the behavior of **CxI_{a-e}** type dyes, in aqueous solutions.

λ_{max} – represents the maximum absorption wavelength value of chromium (1:1) complex dye;

ε_{max}*10^{-3} – represent the molar extinction coefficient value of investigated chromium (1:1) complex dye* 10^{-3}, by respecting the Lambert-Beer law;

$\Delta\lambda_{max}$ – represents the difference between the maximum absorption wavelength value of investigated chromium (1:1) complex dye and that of the chromium (1:1) complex dye, considered as the reference structure, CxI_b;

$\Delta\varepsilon_{max}$*10^{-3} – represents the difference between the molar extinction coefficient of the investigated chromium (1:1) complex dye*10^{-3} and that of the chromium (1:1) complex dye*10^{-3}, considered as the reference structure, CxI_b .

UV-Vis spectral data interpretation

Correlating the spectral parameters given in table 3, with azo structures, results the following findings:

- Replacing of -O- phenolic atom from **CxI_b** dye structure with -COO$^-$ group, is giving rise a strong hypsochromic and hypochromic shift in the Vis spectrum.

Hypsochromic effect appearance is explained both by electronegativity increasing of –O- phenolic atom and $N_{\ddot{U}}$ atom (from azo group) and by steric effect due to the presence of the -COO- group in ortho position to $N_{\ddot{U}}$ atom. Electronegativity increasing of -O-phenolic atom is due to the formation of coordinative covalent bond O:→ Cr at **CxI_a1** resonance structure, which opposes to the migration direction of electron density from left to right, to azo group. This link show a pronounced polar character compared to O-Cr link from **CxI_b** dye, that shows covalent character. **CxI_a** dye can be represented by **CxI_a1, CxI_a2** azo resonance and mesomere **CxI_a3** structures. Steric effect which appears between -COO$^-$ group and $N_{\dot{\alpha}}$ atom causes -COO$^-$ group rotation around C-C link , leading to its conjugation interruption with the benzene ring. So this group acts only through its σ attractive effect to $N_{\dot{\alpha}}$ atom . Because -COO$^-$

group is not involved in conjugation with the benzene ring , this opposes to the migration direction of electron density from left to right byπ acceptor and σ attractive effect. These effects increases N_α atom electronegativity, disfavoring N:→ Cr coordinative covalent bond formation. At **CxI_a** dye, the transition from the ground state molecule (**CxI_a3**) in the excited (**CxI_a3^***) occurs by moving electrons from right to left, from -O- pyrazolone atom to azo group.

In conclusion, conjugation decreasing, polar character increasing of $O^{\delta+}\rightarrow$ Cr bond from **CxI_a3** mesomere structure, compared to **CxI_b** structure and disfavoring N:→ Cr coordinative-covalent bond formation, leads to decreasing of dye molecule planarity, so by default absorption intensity decreasing resulting in a strong hypochromic effect .

- Introduction of -Cl atom into **CxI_b** dye structure in para position to -O-phenolic atom, is giving rise a small bathochomic shift, in the visible spectrum.

The explanation is that -Cl atom acts by strong σ attractive effect, reducing the electron density in the benzene ring, in meta and para position. Compared with **CxI_b** dye, this effect causes on the one hand electron-donor capacity increasing of -O-phenolic- atom engaged in conjugation with azo group (through its non-bonding electrons from the orbital $2p_z$), on the other hand determines the electron-donor capacity decreasing of N_α atom, that is disfavoring N:→ Cr coordinative-covalent bond formation, explaining the hypochromic shift by decreasing of the dye molecule planarity.

At **CxI_b** and **CxI_c** dyes, molecule transition from the ground state to the excited state (**CxI_b^***, **CxI_c^***) takes place by moving electrons from left to right, from -O-phenolic atom to azo group.

- Introduction of $–NO_2$ group into CxI_b dye structure in para-position to -O-phenolic atom, is giving rise to a strong hypsocromic and hypochromic shift, in Vis spectrum.

The explanation is that $-NO_2$ group situated in this position causes a strong π acceptor effect, which leads to the appearance in the ground state of dye molecule of azo-quinone-imine structure (CxI_d),. This structure leads to conjugation decreasing along the dye molecule and bond polarity increasing of O^+-Cr, which gets a strong ionic character, explaining the strong hypsochromic shift.

The molecule transition from the ground state (CxI_d) in the excited state (CxI_d^*) occurs by moving electrons from right to left, from -O-pyrazolone atom to azo group. These two effects cause the molecule dye planarity decreasing, implicitly absorption intensity decreasing, which explains the strong hypochromic effect. Replacing of –Cl atom by $–NO_2$ group into CxI_c dye structure, is giving rise to a strong hypsochromic and hypochromic shift: $\Delta\lambda_{max}$ = -60.3 nm, $\Delta\varepsilon_{max}*10^{-3}$ = -6.35, which is due to conjugation decreasing and ionic nature of O^+-Cr bond.

- Introduction of $-NO_2$ group into CxI_b dye structure in para-position to azo group, is giving rise to a strong bathochromic and hypochromic shift.

The explanation is that the $-NO_2$ group situated in this position causes a strong π acceptor effect, which leads to electron-donating ability increasing of -O-pyrazolone atom, so conjugation extending along the azo dye molecule. The molecule transition from the ground state (CxI_e) in the excited state (CxI_e^*) occurs by moving electrons from right to left, from -O-pyrazolone atom to azo group with $-NO_2$ group involvement.

Changing the position of $-NO_2$ group to azo group from meta to para position, is giving rise to a very strong bathochromic shift: $\Delta\lambda_{max}$ = 92.1 nm, which is explained by conjugation extending along the azo chromium (1:1) complex dye molecule.

Conclusions

A number of preformed acid azo chromium (1:1) complex dyes, having benzene-azo-pyrazolone type structures, with a sulphonic group in the coupling component, have been synthesized by methods described in the literature (2-7 structures). The structure of the synthesized compounds was confirmed by spectrophotometric analysis and their purity was confirmed by thin layer chromatography. These chromium (1:1) complex dyes were characterized by IR, UV-Vis spectral analysis. Determinations attest a good agreement between the real and the assigned structures.

This paper has explained the variation of UV-Vis spectral parameters of preformed acid azo chromium (1:1) complex dyes, having benzene-azo-pyrazolone type structures, resulted from the same coupling component, depending on the nature and position of substituent in the diazotation component, taking into account the electronic effects (σ, π) of the substituent.

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References

1. RUSE, M., ALIFANTI, C., PINTEA, A., TATARU, S., Rev. Chim. (Bucharest), **50**, no. 5, 1999, p.362
2. VOYKSNER, D. R., STRAUB, R., KEEVER, T.J., FREEMAN, H.S., HSU, W.N., Environ Sci. Technol., 27, (8), 1993, p.1665-1667
3. J.W. ROBINSON, "Atomic Spectroscopy", 2nd-ed., Marcel Dekker, Inc., Academic Press, New York, 1996, p.65
4. HU, B., WANG, G, HUANG, W., Dyes and Pigments, 91, 2011, p.105-111
5. RUSE, M., TARABASANU-MIHAILA, C., BERCU, C., Industria Textila, 50, (2), 1999, p.107-111

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