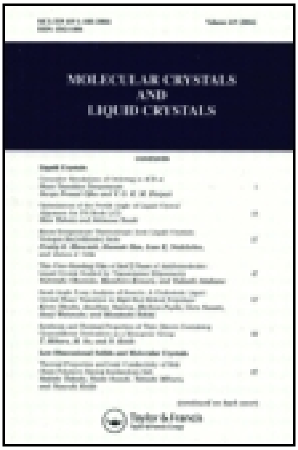

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Electronic Studies of The New 2:1 Cu(II) Complexes of 4-Arylazo-Pyrazol-5-one Dyes

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ELECTRONIC STUDIES OF THE NEW 2:1 Cu(II) COMPLEXES OF 4-ARYLAZO-PYRAZOL-5-ONE DYES

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The relationship between the solvatochromic behaviour of the 2:1 Cu(II)-complex with 1-(2′-benzthyazolyl)-3-methyl-4-azo(derivatives)-pyrazol-5-ones has studied.

The light fastness properties of the ligands and their 2:1 Cu(II) complexes with respect to the symmetry of the coordination polyhedra around Cu(II) cation, the electronic effects of the substituent groups of the ligands and the nature and polarity of the solvents were investigated and explained by means of the Molecular Orbital Theorys.

These complexes strongly absorb between 700–1100 nm which is the most favorable wavelength region for semiconductor laser optical recording dye medium.

Keywords: azo-dyes; coordination compounds of Cu(II); Cu(II) solvent equilibrium; IR; 4-azo-pyrazol-5-one; UV-VIS

1. INTRODUCTION

The chromatic dependence of the 2:1 Cu(II) complex dyes on the type of the coupling component, to pyrazol-5-one system and the stereochemistry of the coordination compounds has been studied in our paper.

The azo derivatives of the 4-substituted 1-(2′benzthyazolyl)-pyrazol-5-one have as auxochrome a ketone group.

The nature of the absorption bands between 700–1100 nm in these 2:1 Cu(II) complexes has been reported in this paper.

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The deepening of intensity of a chromogen by an auxochrome group is attributable to the conjugation of the free electrons in auxochrome with the π-electrons of the aryl ring [1].

A ketone group is a potentially reactive group and this reactivity is attributable to the mesomeric effects, which enhance the electron density on the oxygen atom of the ketone group.

Usually a ketone group may react with an amino group to form a Schiff base and such reactions are possible between ketone groups of an azo dye and the amino groups of the polypeptides of a protein, e.g. that of the wool keratine. There are many references in the literature to the chemical interactions between ketones or aldehides and wool [2–5].

If a ketone or an aldehide group is introduced into the structure of an azo dye [6] molecule, such a dye becomes capable to react with the functional groups of wool keratine or with the hydroxyl groups of cellulose, forming covalent bonds between these fibres. Our azo derivatives can be included into the reactive dyes.

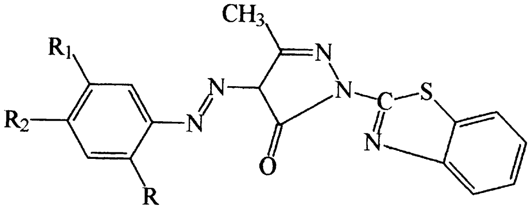
2. EXPERIMENTAL

UV-VIS measurements. The absorption spectra were recorded by means of a Shimadzu 2501 PC spectrophotometer at 296 K with an accuracy of 0.2 nm in 1 cm silica gels. The absorption of NP at λ_m in surfactant solutions obeys the Bougner-Lambert-Beer rule over the concentration range investigated.

3. RESULTS AND DISCUSSIONS

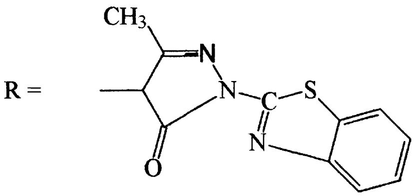
The synthesis and the characterization of the 2:1 Cu(II) complexes with 1-(2′-benzthyazolyl)-3-methyl-4-azo(derivatives)-pyrazol-5-one have been reported [7].

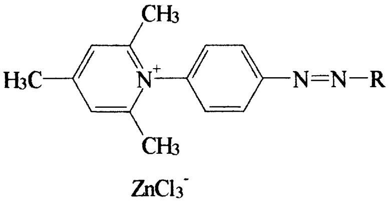
The general formula of the used azoderivatives as the ligands is given below:



(A)

where: R=COOH; R_1=R_2=H for the ligand (1); R=OH; R_1=NO_2; R_2=H for the ligand (2); R=OH; R_1=Cl; R_2=H for the ligand (3); R=R_1=H; R_2=NO_2 for the ligand (4); and (B):





where R is: the first for the ligand (5) and the second for the ligand (6).

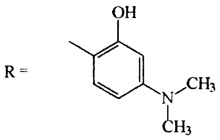


TABLE 1 Electronic Spectra of the 2:1 Cu(II) Complexes in Solvents with Different Polarity

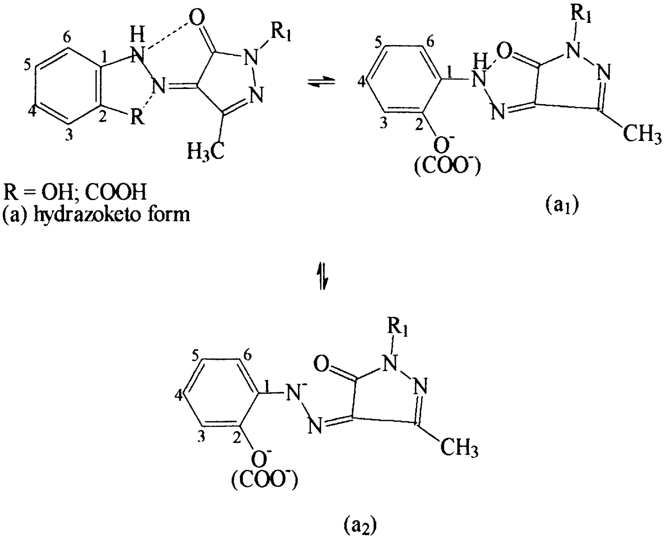
Compounds	DMSO*	AN*	DMF*	EtOH*	Dioxane
I	276(2,0194)	221(3,6407)	274(1,8425)	274(1,9425)	274(2,0030)
	418(1,6797)	274(1,9478)	418(1,6356)	415(1,9134)	416(0,6824)
		412(1,7075)			
II	283(1,4655)	290(1,4395)	279(1,4408)	290(1,4911)	280(1,5329)
	331(1,7014)	325(1,6353)	332(1,6907)	319(1,6469)	329(1,3696)
	491(1,1847)	484(1,0508)	491(1,1742)	477(1,1527)	489(1,1098)
III	281(1,8928)	279(1,8233)	281(1,8448)	280(1,7411)	280(1,8227)
	507(0,8998)	500(0,8084)	509(0,8405)	491(0,9290)	504(0,8420)
IV	329(0,4790)	328(0,52640	266(1,0801)	330(0,5064)	329(0,5063)
	412(0,5716)	407(0,8652)	329(0,5822)	410(0,8767)	410(0,7832)
	433(0,5325)	426(0,7583)	411(0,7804)	429(0,7530)	430(0,6908)
	492(0,4387)		431(0,7206)		
	520(0,4535)		488(0,3683)		
V	281(0,7035)	278(0,7059)	282(0,6957)	278(0,6575)	281(0,6744)
	303(0,6413)	302(0,6374)	403(0,4444)	379(0,3885)	397(0,4198)
	403(0,4428)	395(0,4514)			
VI	257(1,1416)	268(1,1211)	270(1,0414)	268(1,0966)	269(1,1100)
	268(1,1160)	476(1,4789)	477(1,3929)	472(1,4900)	472(1,3106)
	468(1,3017)				

*Dimethyle sulphoxide; acetonitrile; dimethyleformamide; ethylic alcohol; dioxane.

The azo derivatives (1), (2), (3) are terdentate and dibasic ligands having (ONO) potential donor atoms and give six-coordinated 2:1 Cu(II) complexes with a distorted-octahedral configuration and the azoderivatives (4), (5), (6) are bidentate and monobasic ligands having (ON) potential donor atoms and give four-coordinated 2:1 Cu(II) complexes with a distorted square-planar or tetrahedral configuration.

We studied the solvatochromic behaviour (Table 1) of the 2:1 Cu(II) complexes in solvents with different polarity. The behaviour of the ligands during the complexation is very different from a ligand to another. It had been reported [8] that 4-aryl-azo-pyrazol-5-ones are in a tautomeric equilibrium between the azoenol and the hydrazo keto forms.

The terdentate azo-pyrazol-5-one ligands (ONO) exhibit usually the following equilibrium [9]:



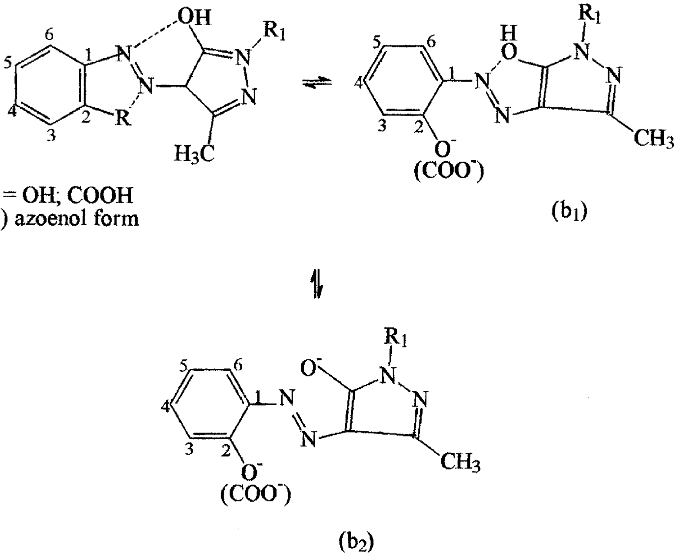
R = OH; COOH
(a) hydrazoketo form

(a_1)

(a_2)

The hydrazo keto form (a) shows a characteristic band [9] at 508 nm in different organic solvents and it is generally more dominant than the azophenol form (b). This band is shifted to higher wave lengths at around 517 nm in the form (a_1) and at around 520 nm in the form (a_2) during increasing of the polarity of the solvents.

The azophenol form (b) shows a characteristic band [9] at around 422.1 nm. This form is predominantely when there are in the 5-position of the aryl ring a strong electron withdrawing functional group.



R = OH; COOH
(b) azoenol form

(b1)

(b2)

The (π-π*) transition bands of the >C=O bond and of the N=N bond in the complex (II) are greater than those of the complex (I) with ~20 nm respectively 70 nm (Table 1) and an increasing in the polarity of the Cu–O bond (O ketonic oxygen) and Cu–N bond (N azo nitrogen) in this case is expected [12].

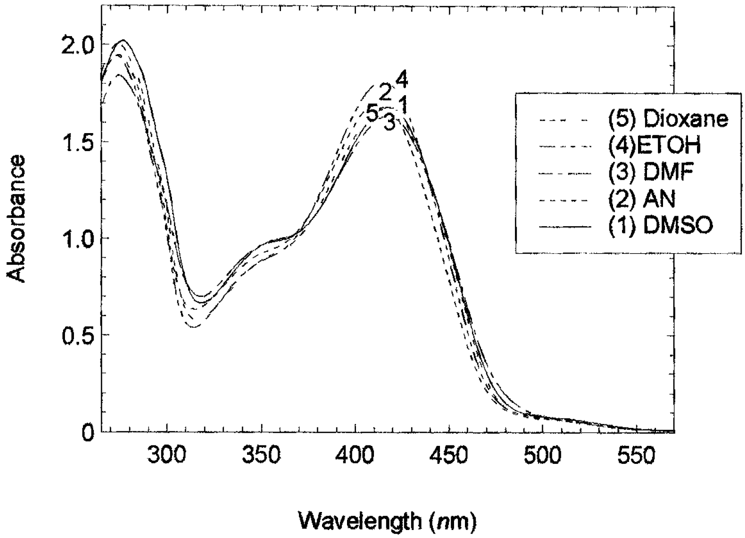


FIGURE 1(a) The electronic absorption spectra of the compund (I).

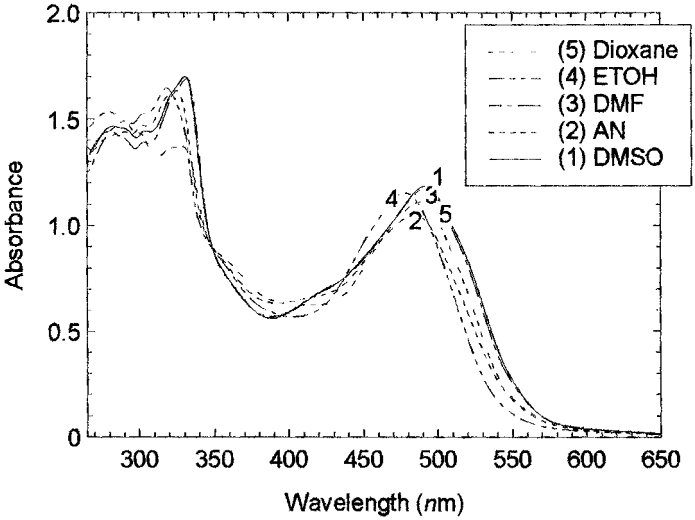


FIGURE 1(b) The electronic absorption spectra of the compund (II).

Well defined isosbestic points were observed (at 350 nm; 438 nm; in EtOH/DMF/AN and at 495 nm in EtOH/AN – Fig. 1(b)) studying the dependence of the electronic spectra of the complex (II) in the different solvents.

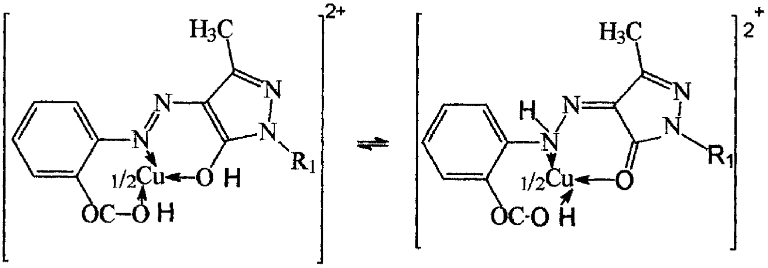
The band 438 nm is bathochromic shifted by the increasing of the polarity of the solvents, to 450 nm in the form (b_1) and to 470 nm in the form (b_2).

The 2:1 Cu(II) complex with the ligand (1) labeled with (I) exhibits characteristic azo bands at 412–418 nm and therefore the azophenol form of the ligand (1) during the complexation can be proposed. This is possible because in the ligand (1) there is not a substituent in the 5-position with an electron withdrawing property while in ortho position there is a –COOH group with a strong (–I, –E) character .

The characteristic band of the π-π^* transition in the ketonic group of the pyrazol ring exhibits at around 274 nm in a good agreement with a literature data [10] and it is inaffected by the solvent polarity. We explained this behaviour as a consequence of the implication of the oxygen atom in an ortho-condensed the chelate ring that caused a sterical hinderence to this oxygen atom in interaction with the molecules of the solvents.

It has been observed well defined isosbestic points (305 nm, 378 nm and 505 nm) studying the dependence of the visible spectra of the compound (I) in DMF/DMSO.

The bathochromic shift of the azo band to 505 nm shows the presence of the hydrazo keto form (a) of the ligand (1) in equilibrium with the azophenol form (b):



The bathochromic shifted of the azo band reveals that the ligand is attributed to dπ-pπ interaction between Cu(II) cation and the nitrogen donor atom which disturbs the π-electron system [11,12].

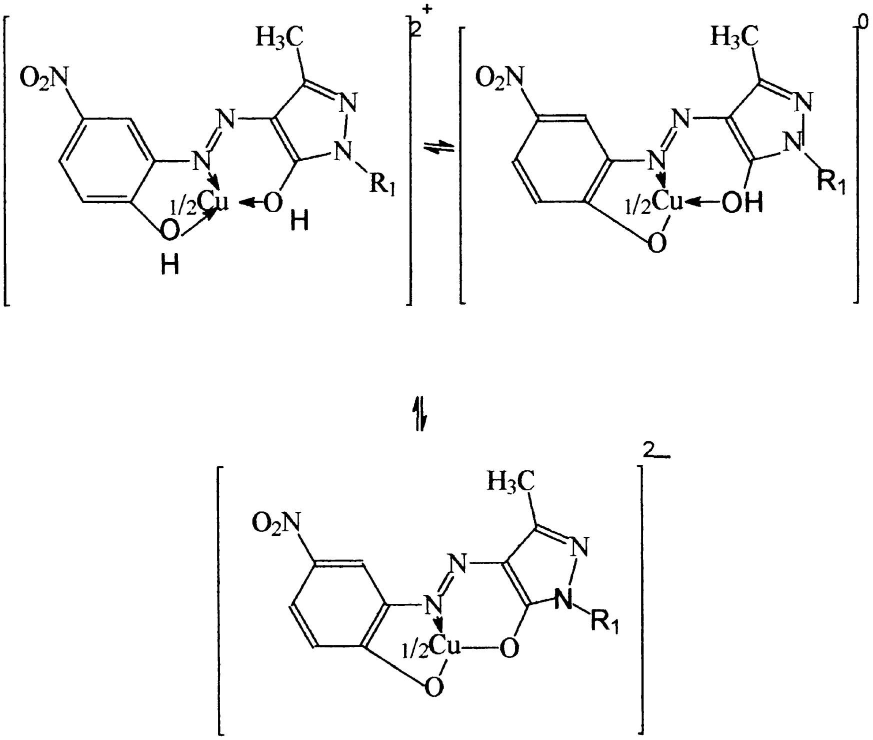
The isosbestic points at 305 nm and 378 nm correspond to a red shift of the π-π^* transition of the >C=O bond and of the heterocyclic ring owing to an increasing of the polarity of the Cu—O bond (O, ketonic oxygen) in the same time with the increasing of the polarity of the solvents.

In the ligand (2) of the 2:1 Cu(II) complex (II) the aromatic ring is 5-substituted with a NO_2 group. According with the literature data [9] the ligand bands around (≈ 477–489) nm suggest that this ligand coordinates in an azophenolic form (b_1). This behavior of this ligand is caused by the (—I, —E) of the NO_2 group. The powerful resonance effects of the NO_2 group involves the d-electrons of the central metal and therefore the resonating system is stabilized, the polarizability of the π electron system increases and a bathochromic displacement of the visible absorption is possible.

The band at 438 nm corresponds to a blue shift of the $\pi \rightarrow \pi^*$ transition within the —N=N— group and it is suitable for an azophenolic form of the type (b). The band at around 495 nm corresponds to a red shift of the azo band and it is suitable for an azophenolic form of the type (b_2). In this case there is probably an equilibrium among the three azophenolic forms.

In the complex (II) the red shift of the $\pi \rightarrow \pi^*$ transition assigned to the heterocyclic ring from around 322 nm to 350 nm shows an increasing of the polarity within the Cu—O coordinative bond.

The 2:1 Cu(II) complex (III) with the ligand (3) exhibits a band at around 280 nm (Table 1) corresponding to the π-π^* transition of the >C=O bond of the pyrazolonic ring comparable with that of the complex(II) and a band at around 500 nm corresponding to a hydrazoketo [9] form of the coordinated ligand (3) within the complex. This is probably due to the electronic effect (−I, +E) of the chlorine in the 5 position of the aryl ring that stabilized the hydrazoketo form of the ligand during the complexation.



These bands are weakly affected by the polarity of the solvents excepting EtOH where the blue shift from 500 nm to 491 nm appears. The band at 491 nm is probably owing to the presence of the azophenolic form caused by the protic solvent [14].

In the case of this complex the electronic spectra (Fig. 1(c)) also present three well defined isosbestic points at 295 nm in DMSO, and at 320 nm, 440 nm in EtOH/DMF.

The blue shift from ~500 nm to 440 nm certifies an equilibrium between hydrazoketo form (a) and an azo phenolic form of the type (b_1). The red shift of the >C=O band from ~280 nm to around 295 nm and the shift of the heterocyclic ring band at around 320 nm denotes an increasing in the polarity of the Cu−O bond and an ionic character of this coordinative bond [11] caused probably by the protonation of the oxygen. The following equilibrium is possible:

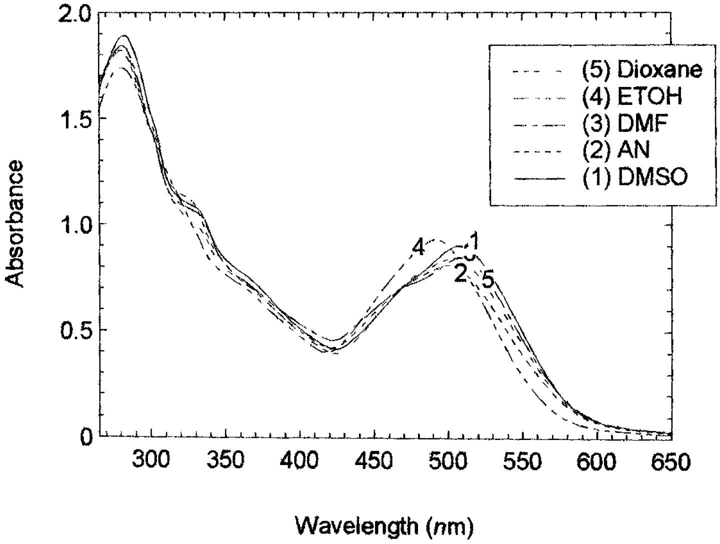
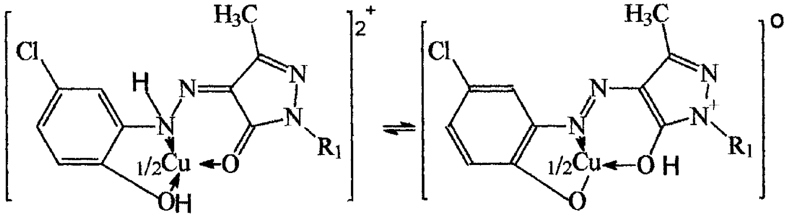
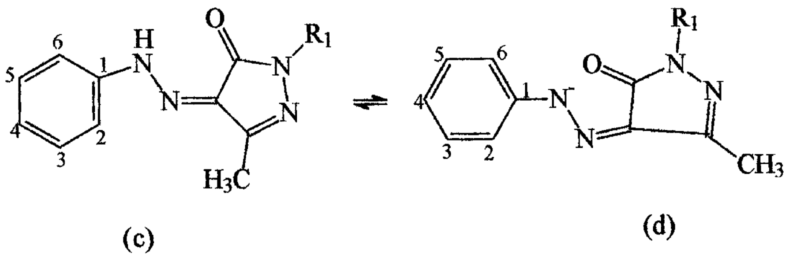


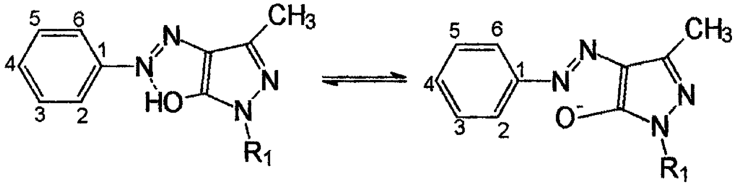
FIGURE 1(c) The electronic absorption spectra of the compund (III).



The bidentate azo pyrazol-5-one (ON) ligands coordinate in general in one of the hydrazoketo forms (c) or (d) with a specific band in the range 488.6 nm and 550 nm respectively [12].



The azophenolic forms (e) and (f) of these ligands can be present too, at a lower wave length (~424 nm and ~460 nm respectively) than the hydrazo keto forms [9].



(e) (f)

The results obtained for the complexes (IV), (V), (VI) with the bidentate azo ligands (4), (5), (6) were explained according to the possible equilibriums (c), (d), (e), (f).

The 2:1 Cu(II) complex (IV) exhibits (Table 1) a hydrazo keto forme (d) of the ligand (4) in DMSO at 520 nm and a hydrazo keto forme (c) of the ligand (4) in DMF at 488 nm. In the other solvents with a different polarity the ligand (4) shows a constant band at around (~430 nm) corresponding to the azophenolic form (e).

There are many isosbestic points (Fig. 1(d)) of the complex (IV) in the electronic absorption spectra, but only three of them are well-defined: at 341 nm in (DMSO/AN/DIOXAN); at 388 nm in (DMF/EtOH); at 460 nm in (AN/EtOH).

The wave lengths 341 nm and 388 nm denote a bathochromic displacement of the band corresponds to the (C=O) bond involved in the (Cu←O=) coordinative bond. We suggest an equilibrium between (c) and

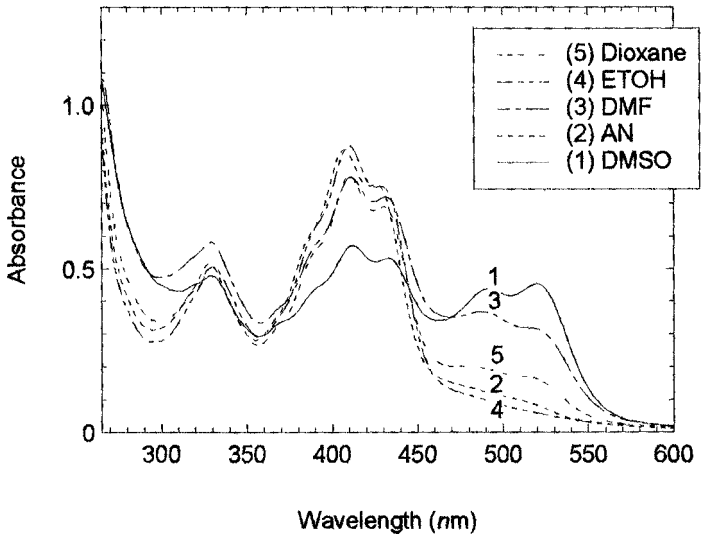
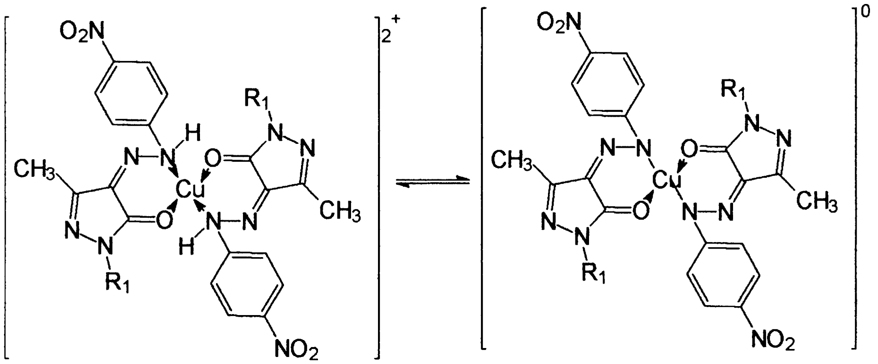
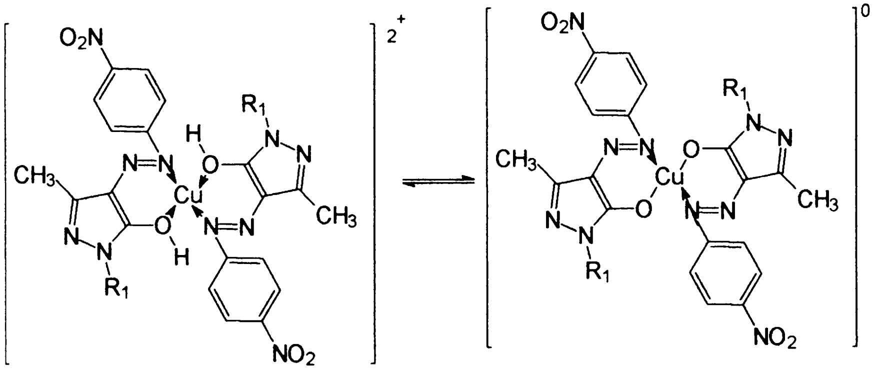


FIGURE 1(d) The electronic absorption spectra of the compund (IV).

(d) forms of the ligand (4) because only the hydrazoketo shape contains the (C=O) bond. On the other hand we can conclude that the hydrazoketo form depends on the polarity of the solvent.



A bathochromic shift of the azophenolic band from 430 nm to 460 nm corresponds to the equilibrium between (e) and (f) in the azophenolic forms of the coordinated ligand (4) within the complex (IV) according to the literature data [9].



The 2:1 Cu(II) complex (V) exhibits an azophenolic form (e) at ~379–403 nm of the ligand opposite to the literature data [9–11] for a 4-substituted position of the ligand with a strong withdrawing cationic group.

This is probably due to the contribution of the Cu^{2+} coordinated to the azophenolic protonated oxygen of the ligand that balances the two anions $[ZnCl_3]^-$. These anions rested uncompensated out of the partially electronic saturated heterocyclic cationic nitrogen.

This is the only complex of the series with a negative solvatochromy (Table 1) of the azo band.

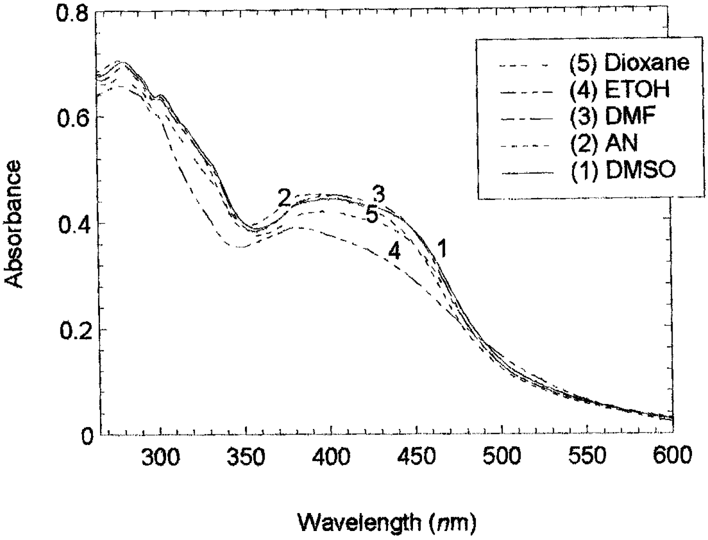


FIGURE 1(e) The electronic absorption spectra of the compund (V).

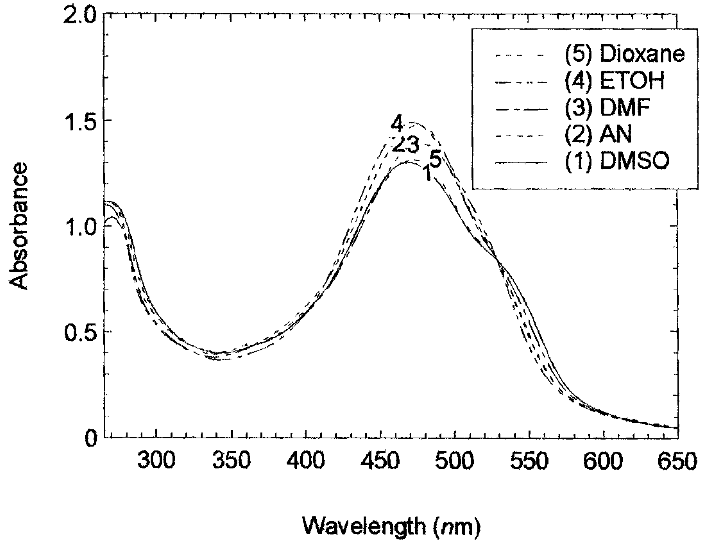
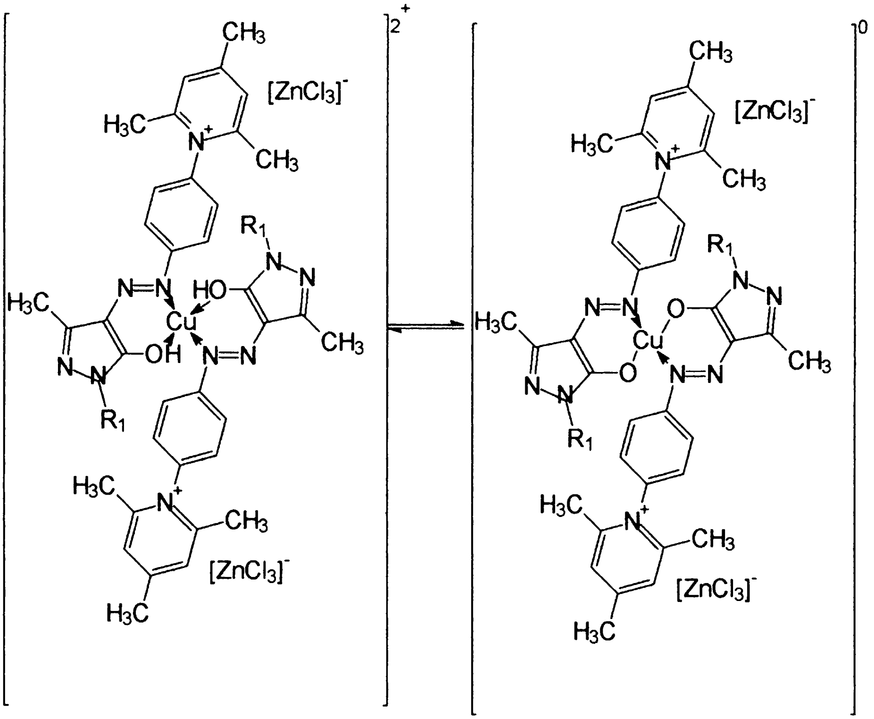


FIGURE 1(f) The electronic absorption spectra of the compund (VI).

The wave length ~400 nm of the azo linkage N=N corresponds to a non-polar azophenolic form and according to the literature data [9–11], a covalent character of the Cu–N bond is expected. The electronic absorption spectra exhibit at 480 nm an isosbestic points.

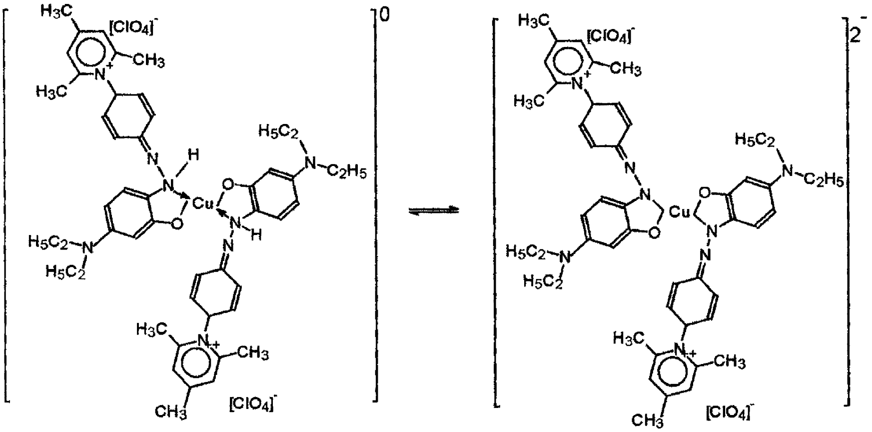
The band at 480 nm was assigned to an azophenolic form (f) of the ligand where the deprotonation of the oxygen involved in the coordination bond is possible owing to an interaction with the solvent. Taking into account all these considerations we propose the following equilibrium:



In each case the R_1 substituent is the benzthyazolyl rest.

The 2:1 Cu(II) complex (VI) exhibits in all solvents a band at ~470 nm which corresponds to a hydrazo keto form (c) of the coordinated ligand (6) according to the literature data [8]. The electronic absorption spectra show two well-defined isosbestic points at 528 nm and 538 nm (Table 1), (Fig. 1(f)).

Both of them correspond to a polarized hydrazoketo form (d) and it is possible the following equilibrium.



These complexes strongly absorb between 600–1100 nm which is the most favorable wave length region for semiconductor laser optical recording medium.

The bands correspond to the d–d transitions were assigned according to the literature data [15–17].

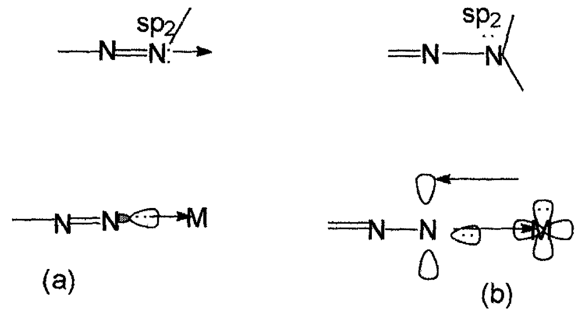
These bands are sharp and very intense for the complexes with a high distorted coordination polyhedra.

The solvatochromic behavior involves a change of the donor properties of the nitrogen atom of the azo group.

Consequently because of the azoderivates belong to the weak field ligands [18] we suggest for the nitrogen donor atom sp^2 hybridized involved in the Cu–N linkage a σ-donor character diagramme (a) in the azophenolic form of the ligand and a σ-donor and π-acceptor character diagramme (b) in the hydrazo keto form of the ligand (Fig. 2).

TABLE 2 The d-d Absorption Bands of the Complexes

Compounds	Bands λ_{max} (nm)	Assignments
I, II, III	900	$z^2 \rightarrow x^2 - y^2$
Distorted O_h	574	$xz, yz \rightarrow x^2 - y^2$
symmetry	938; 1000	$xy \rightarrow x^2 - y^2$
IV	1000	$z^2 \rightarrow x^2 - y^2$
Distorted D_{4h} to	699	$xz, yz \rightarrow x^2 - y^2$
D_{2h} symmetry	800	$xy \rightarrow x^2 - y^2$
V, VI	714	$z^2 \rightarrow xy$
Distorted $T_d$to	600	$xz \rightarrow xy$
D_{2d}symmetry	555	$yz \rightarrow xy$
	625	$x^2 - y^2 \rightarrow xy$



the azophenolic form the hydrazo keto form

FIGURE 2 The donor function of the nitrogene atom of the azo group of the ligands (a) the azophenolic form of the ligands (σ-donor character of the N atom) (b) the hydrazo keto form of the ligands (σ-donor and π-acceptor character of the N atom).

It is expected that these changes of the donor properties of the nitrogen atom to be a very important factor in modifying the diagramme of the molecular orbitals of the complexes.

On the other hand we had found an interesting correlation between the energy consumed in the excitation (E_{ex}) of the π-electron system of the N=N bond to its antibonding π^*-orbital (the light fastness property) and the symmetry of the coordinated polyhedra around the central metal cation (Table 3).

The light fastness property is higher for the compounds having λ_{max} at shorter wavelengths and a higher excitation energy (E_{ex}) [14].

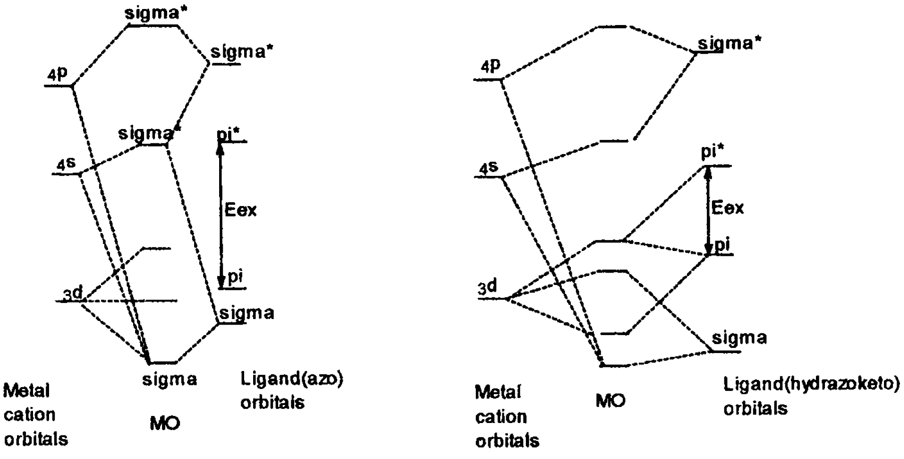
TABLE 3 Fastness Properties of the 2:1 Cu(II) Complexes and the Excitation Energies of –N=N– Linkage

	λ_{max} (nm)					E_{ex}(eV)				
Compounds	DMSO	AN	DMF	ETOH	DIOX	DMSO	AN	DMF	ETOH	DIOX
I	418	412	418	415	416	2.97	3.01	2.97	2.99	2.98
II	491	484	491	477	489	2.53	2.56	2.53	2.60	2.54
III	507	500	509	491	504	2.45	2.48	2.44	2.53	2.46
IV	520	426	488	429	430	2.38	2.91	2.54	2.89	2.88
V	403	395	403	379	397	3.08	3.14	3.08	3.27	3.12
VI	468	476	477	472	472	2.65	2.60	2.60	2.63	2.63

We explained the light fastness properties of the distorted O_h complexes (I, II, III) by using the diagram of the molecular orbitals of a ML_6 complex (Fig. 3) [13].

In our case the diagramme (1) corresponds to nitrogen atom of the keto-form and the diagramme (2) corresponds to the nitrogen atom of the hydrazoketo-form. These diagrammes are in a good agreement with the data of the Table 3 and with the electronic effects within the organic molecule of the ligand.

The octahedral complexes (I) and (II) have the different light fastnest properties owing to the different electronic effects in the molecules of the ligands. The experimental results show that $-NO_2$ group in the 5-position of the aromatic ring causes a decrease of the (E_{ex}) (Fig. 3) owing to its withdrawing electronic effect. The light fastnest property of the complexe (III) with the ligand in the hydrazo keto form was explained on the basis of the distorted symmetry around Cu(II) cation O_h to D_{4h} when the molecular bonding orbitals t_{2g} of the complexes are splitted into e_g, b_{2g} orbitals of the D_{4h} symmetry that have a metallic character while the energetically higher lying antibonding $t_{2g}{}^*$ and $e_g{}^*$, $b_{2g}{}^*$ have essentially a ligand character and produce an increasing in the π_L energy, and in the $\triangle = 10$ Dq value and in the light fastness property is high comparable with the complexes (I, II).



(1) (2)

FIGURE 3 The diagrames of the molecular orbitals of a ML_6 complex with a σ-donor atom (1) and a σ-donor and π-acceptor atom (2).

The E(ex) is greater in D_{4h} complexe (IV) than in the Oh complexes because of the energy of the $\pi_L{}^*$ in the D_{4h} complexes is increased by the antibonding orbitals $a_{2u}{}^*$ (π^*) , and $\triangle(D_{4h}) > \triangle(O_h)$ [13] and the D_{4h} complex (IV) has better light fastness property than the distorted O_h complex (III) (Table 3).

The light fastness properties of the distorted T_d(V, VI) complexes were explained on the bases of the properties of the t_2 orbitals that can participate both in the σ-bonding and in the π-bonding molecular orbitals and cause a diminuation of the π_L energy and an increasing of the $\pi_L{}^*$ energy. Therefore, an increasing of the (E_{ex}) takes place [13].

Indeed, the complex (V) with the tetrahedral symmetry around the Cu(II) cation and in a keto form of the ligand has a high light fastnest property comparable with the light fastnest property of the T_d complex (VI) in a hydrazoketo form. The complex (VI) can be placed between (III) and (IV) complexes because the molecular orbitals t_2 have a ligand character and cause a decrease of the π_L energy during $t_2{}^*$ antibonding orbitals weakly increase the $\pi_L{}^*$ energy [13].

CONCLUSIONS

In this paper we have dealt with the investigation of the solvatochromic properties of a series of the six Cu(II) complexes with a different azo-derivatives as ligands. The solvatochromic properties were colligated with the light fastness properties of these complexes. In our case we have found that the light fastness properties obey the following order

- keto form > hydrazoketo form
- D_{4h} > distorted $O_h > O_h > T_d$

and we have explained this order on the basis of the diagrammes of the molecular orbitals of the complexes.

We have concluded that the light fastness properties depend on the following factors; the polarity of the solvent that affects the donor character of the nitrogen atom of the azo group, the nature of the ligands (bi or three-dentate), the symmetry around the metallic cation.

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