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SOLVATOCHROMIC PROPERTIES OF AZO AND AZOMETHIN TRIDENTATE LIGANDS IN COORDINATIVE COMPOUNDS WITH [Er(ONO)] CHROMOPHORES

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The relationship between structure and solvatochromic properties of some tridendate organic ligands with (ONO) donor atoms belong to azo dyes *o, o` - dihydroxi azobenzene* $L^1H_2$, *1-(azo-β-naphtyl)-2-hydroxi-5-chlor-benzen* $L^2H_2$, and Schiff bases *o, o` - dihydroxi phenyl azomethin naphatalene* L^3H_2, *o,o`- hidroxy phenyl - carboxy azomethin naphatalene* L^4H_2 as well as the effects of Er^{3+} as [Er(ONO)] chromophore, on the organic moiety were investigated. The free organic ligands and their Er^{3+} complexes were prepared and characterized by elemental analysis, thermal gravimetry, UV/VIS and FTIR spectroscopy. The solvatochromic behaviour of the free organic ligands and their complexes were investigated by electronic spectra of their 10^{-4}-10^{-5} M solutions, in five different solvents. The solvatochromism was explained as a combination of the solvent polarity, nature and position of D/A couple and the size of the π conjugated system.

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Keywords: erbium complexes, azo-dyes complexes, azomethine complexes, solvatochromism

1 Introduction

The design and synthesis of robust chromophores as nonlinear optical materials have attracted much attention during the last decade. Azo and azomethine dyes are of particular interest because they can be readily prepared with a wide range of donor and acceptor groups. In addition due to the planarity of azo or azomethine bridge versus the non-planarity of stilbenes or other systems they will contribute to larger π electron transmission effects leading to higher optical activity of these materials in solutions[1, 2]. Moreover the metal-azo or metal-azomethine complexes' class have shown more promising optical storage characteristics and nonlinear optical activities [3, 4]. Representatives are lanthanide complexes with high yield in the absorbtion of the excitation energy and with high transfer rate to the metallic ion leading to the high luminiscence [5]. In addition, the optical nonlinearities are strongly dependent on couple ligand-metal [6] and in this respect they are directly related to the solvatochromism effects [7]. Therefore, each couple ligand-metal can be straitforwardly evaluated by solvatochromic proprieties to give a figure of merrit related to the optical nonliniarities. This study deals with the investigation of the solvatochromic properties of some ligands belonging to the azo dyes and Schiff bases series and their complexes with Er(III).

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2 Materials and methods

2.1. Materials

Solvents: dimethylsulphoxide, acetonitrile, dime-thylformamide, 1-butanol, ethanol, 1,4-dioxane;

Ligands: L^1H_2 : o, o`-dihydroxi azobenzene.

$Er(NO_3)3·6H_2O$, (all, analytical grade ,Sigma Aldrich)

2.2. Synthesis

The ligands – as prepared by the method reported elsewhere [8]: L^1H_2: o, o`-dihydroxi azobenzene $L^2H_2$: 1-(azo-β-naphtyl)-2-hydroxi-5-chlor-benzen, $L^3H_2$: o, o` - dihydroxi phenyl azomethin naphthalene; Schiff basesL^4H_2: o ,o`- hydroxy phenyl-carboxy azomethin naphthalene.

The erbium coordinative compounds synthesis: to a hot solution of ligand (0.6mM) in EtOH, it was added an ethanol solution of the metal nitrate (1.8mM). The mixture was stirred and refluxed for 1.5 h on a water bath until precipitation. The pH of the solution was adjusted with ammonia solution up to 7-7.5 during the reaction. The crystalline product was separated, filtered and washed with $EtOH/H_2O$ =1/2 (v/v).

Stable erbium compounds were isolated during the reaction of alcoholic solutions of o, o`-dihydroxi azobenzene (Er-$L^1H_2$), 1-(azo-β-naphtyl)-2-hydroxi-5-chlor-benzen (Er-$L^2H_2$), o, o`-dihydroxi phenyl azomethin naphatalene (Er-L^3H_2), o-carboxy phenyl- o`- hydroxi azomethin naphatalene (Er-L^4H_2.).

2.3Characterizations

The elemental analyses: Carlo Erba EA 1108 equipment for total carbon, nitrogen and hydrogen content. IR spectra: Perkin Elmer SPECTRUM 100 spectrometer, universal ATR accessory, in the range 550-4000 cm^{-1}, resolution of 4 cm^{-1}, 16 scans. Thermal analysis: equipment, Netzsch 409. TG/ DTG and DTA recorded in the range 25^0C - 600^0C, 10 $K.min^{-1}$ heating rate. Measurements were performed in static air atmosphere, using Pt-Rh crucible.

UV-VIS spectroscopy: Shimadzu 2501 spectrophotometer at 296 K with, resolution 0.2 nm. The structures of the ligands and Er-ligands were designed and optimized using Hyperchem software.

The solvatocromism behaviour was investigated for solution at concentration of 2.5×10^{-4} M in polar solvents: dimethylsulphoxide (DMSO), acetonitrile (AN), dimethylformamide (DMF), ethanol (EtOH), 1,4- dioxane (Diox).

3 Results and discussion

The elemental analysis data showed a good agreement of experimental and theoretical values related to the chemical composition of the ligands and Er-complexes (Table 1 and 2). The mass loss in thermal decomposition of the Er-complexes, occurs first of all between 100–150°C, resulting in 5.57% (for Er- L^1H_2), 4.42%(Er- L^2H_2), 4.84%(Er- L^3H_2), 4.50% (Er- L^4H_2), which corresponds to two molecules of coordinated water in each complex Therefore in the table 2, x=2 H_2O molecules. Each erbium complex obeys the Bougner-Lambert-Beer rule as reported elsewhere [9], and the values m=1 and n=2 (table 2) were established.

Table 1. Elemental analysis of calculated and experimental values of organic ligands

Compound	Calculated (%)			Experimental (%)		
	C	H	N	C	H	N
L^1H_2:$C_{12}H_{10}N_2O_2$	67.28	4.60	13.08	66.88	3.92	13.88
L^2H_2: $C_{16}H_{11}N_2ClO_2$	64.10	3.67	9.34	63.93	4.07	9.54
L^3H_2: $C_{17}H_{13}NO_2$	77.56	4.94	5.32	78.00	4.54	5.73
L^4H_2: $C_{18}H_{13}NO_3$	74.22	4.46	4.81	73.82	4.16	4.22

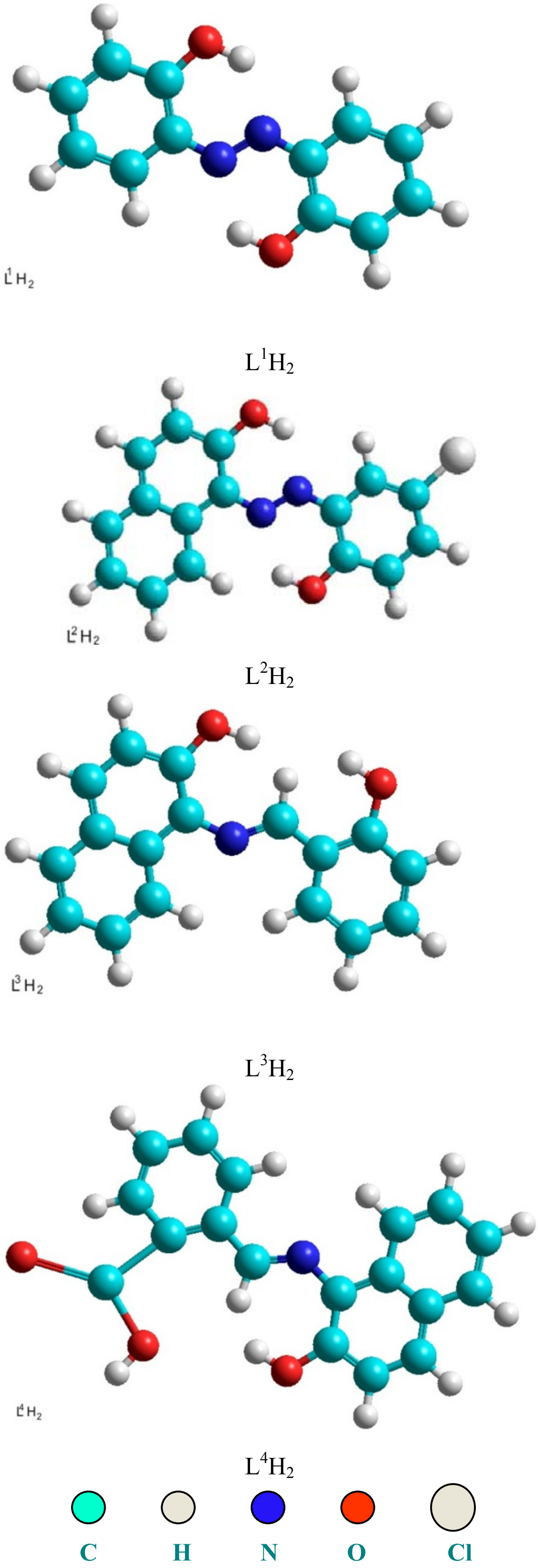
Table 2. Elemental analysis of calculated and experimental values of erbium coordinated complexes.

Compound	Calculated (%)				Experimental (%)			
	C	H	N	Er	C	H	N	Er
Er- L^1H_2: $NH_4[Er_m(C_{24}H_{28}N_5O_6)_n](H_2O)_x$	44.35	4.31	10.78	25.76	45.01	3.99	10.18	25.86
Er- L^2H_2: $NH_4[Er_m(C_{32}H_{30}N_5Cl_2O_6)_n](H_2O)_x$	46.92	3.66	8.55	20.44	46.22	3.06	8.15	20.62
Er- L^3H_2: $NH_4[Er_m(C_{34}H_{34}N_3O_6)_n](H_2O)_x$	54.59	4.54	5.62	22.38	55.09	4.14	5.88	22.78
Er- L^4H_2: $NH_4[Er_m(C_{36}H_{34}N_3O_8)_n](H_2O)_x$	53.77	4.23	5.22	20.82	54.07	3.99	5.83	21.02

Table 3. Assignments of the characteristic bands in organic compounds.

	Group frequencies (cm^{-1})					
Compound	**-N=N-**		**δ O-H phenol**		**Ar-Cl**	
L^1H_2	1574	-	1189	1201	-	
$NH_4[Er(L^1)_2(H_2O)_2]$	1575	1595	1192	1201	-	
L^2H_2	1597	1613	1250	1404	1150	
$NH_4[Er(L^2)_2(H_2O)_2]$	1596	1614	1240	1411	1150	
	-C=N-		**δ O-H phenol**		**(OCO$^-$)-salts**	
L^3H_2	1589	1611	1317	1328		
$NH_4[Er(L^3)_2(H_2O)_2]$	1586	1602;1618	1318	-		
L^4H_2	1584	1600	1239	1270	1618	1632
$NH_4[Er(L^4)_2(H_2O)_2]$	1585	1603	1257	1287	1618	-

The donors groups (-N=N-, -CH=N- and OH phenolic) were assigned by FT-IR spectroscopy (table 3), for each compound. The bands of the free azo dyes at 1575 and 1613 cm^{-1} and of δ C-O phenol centred on 1400 cm^{-1}, underwent a change in intensities, while the δ C-O phenol bands around 1250 cm^{-1} are negative shifted with ~ 10-15 cm^{-1} in erbium-ligand complexes, indicating that the hydroxylic oxygen and the nitrogen of the azo group were coordinated to Er^{3+}. For the Schiff bases, the specific bands at 1600 cm^{-1} for νC=N; 1260 -1180 cm^{-1} for δ C-OH phenol and 1630 cm^{-1} for (OCO^-) in the salts, were assigned. These bands underwent changes in intensities after complexation indicating the group contribution to the coordination with erbium. [10,11]. Infrared spectra of all the Er-complexes showed also broad weak or medium intensity bands at 3240-3125 cm^{-1} assigned to ν OH of the water molecules. Based on elemental analysis, TG and FT-IR the following chemical structures for ligands and Er-complexes were proposed and optimized by Hyperchem software (Figure 1 and Figure 2). The planarity of the aromatic rings was confirmed by the structure modelling that shows Cs Point Group symmetry for all molecules. In all ligands the ground state corresponds to trans arrangement of the ortho, ortho` donor groups (OH, OH) and (OH, COOH), respectively, as expected.



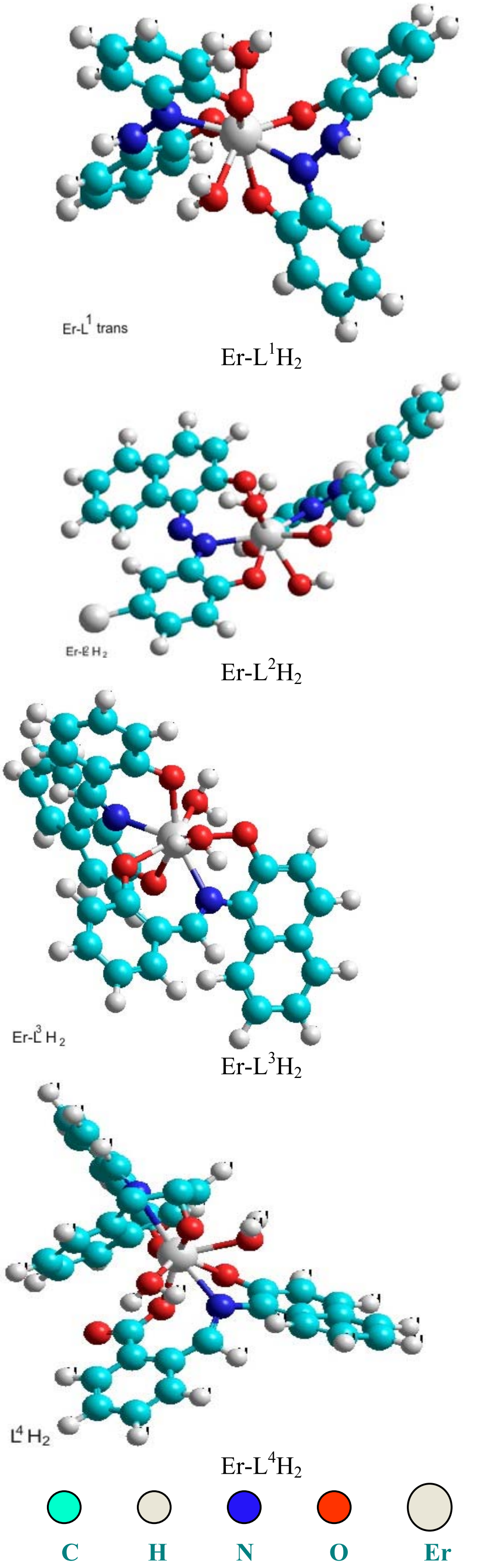
L^1H_2

L^2H_2

L^3H_2

L^4H_2

Fig. 1 The chemical structures of ligands



Er-L^1H_2

Er-L^2H_2

Er-L^3H_2

Er-L^4H_2

Fig. 2 The chemical structures of Er-ligands complexes

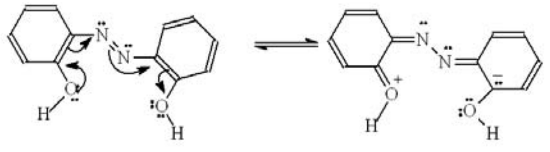
Table 4. λ_{max} (nm) and the molar extinction coefficients, [lgε (L mol^{-1} cm^{-1})] of the charge transfer bands for the free ligands.

	Ligands- λ_{max} (nm), [lgε (L mol^{-1} cm^{-1})]			
Solvents	L^2H_2	L^4H_2	L^3H_2	L^1H_2
DMSO	596 [4.111]	449, 472 [4.018, 4.080]	443, 467 [4.073, 4.059]	399 [4.130]
DMF	559 [4.173]	447, 468 [3.985, 3.968]	440, 460 [2.993, 2.965]	399 [4.011]
AN	429 [4.154]	441, 464 [3.908, 3.898]	438, 458 [3.838, 3.820]	395 [4.078]
EtOH	502 [4.188]	448, 468 [4.097, 4.069]	441, 461 [3.860, 3.834]	395 [4.080]
Diox	495 [4.165]	445, 466 [3.949, 3.934]	442, 460 [3.768, 3.765]	397 [4.085]

After coordination the symmetry of the molecules has changed. The Er^{3+} cation is eight coordinated in all compounds as a complex anion with chiral C_1 symmetry.

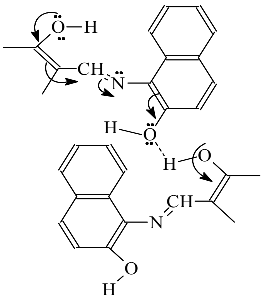
The solvatocromic behaviour was studied in solvents corresponding to the following equilibrium:NH_4 [Er $(L)_2(H_2O)_2$]+Solvent→ $NH_4{}^+$/Solvent+[Er $(L)_2(H_2O)_2$] $^-$ / Solvent In further discussions we refer only to the complex anions [Er $(L)_2(H_2O)_2$] $^-$.The wavelengths of the charge transfer bands were selected for each compound in all solvents, presented in Table 4. The charge transfer (CT) takes place between mesomeric structures as result of the interactions with the solvent. In consequence the solvatocromism is strongly dependent on the CT [12]. The C_s symmetry of the ligand molecules, the nature of π conjugated system, p-π and π – π interactions, are responsible for the solvatochromic behaviour of the compounds. Donor (D) and acceptor (A), were the two –OH groups in the L^1H_2, L^2H_2, L^3H_2 ligands and –OH, respectively –COOH in the L^4H_2 ligand. The π conjugated system were phenyl rings in L^1H_2 and naphtyl combined with phenyl rings in (L^2H_2, L^3H_2, L^4H_2) bonded through azo –N=N- in (L^1H_2, L^2H_2) and azomethin (CH=N) groups in (L^3H_2, L^4H_2). The symmetry point group C_s was related to the presence of the dipole momentum, the different behaviour of the free ligands versus solvent polarity and also depended on the nature of p-π and π – π interactions. Thus the L^1H_2 ligand was invariant toward the changing of the solvent polarity. This behaviour corresponded to a D-π-A system with a reversible solvatochromism which included a combination of two valence bond forms namely neutral $(L^1H_2)_n$ and zwitterionic forms $(L^1H_2)_z$ in the ground state:

$$D\text{-}\pi\text{-}A \leftrightarrow {}^{+}D\text{-}\pi\text{-}A^{-}$$

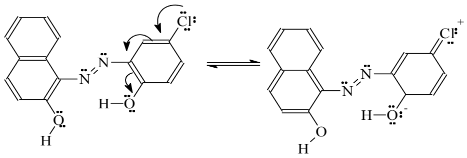


$(L^1H_2)_n$ $(L^1H_2)_z$

The ligands L^3H_2, L^4H_2 exhibited a slight batochromic shift of the bands associated to the CT in all solvents. This shift was associated with the enlargement of the π conjugated system from the naphthalene rings. Although the wavelength of the corresponding CT band of each solvent was slightly red shifted, it remained relatively constant with solvent polarity like CT band of the L^1H_2 ligand. We concluded that the reversible solvatochromism of the L^3H_2, L^4H_2 ligands was a consequence of the non-axial position of the D/A groups related to the linkage functions –N=N-, -CH=N-. Supplementary, the L^3H_2, and L^4H_2 ligands showed a splitting of the CT band especially in the DMSO and DMF solvents. The literature data suggested that when two molecules aggregate to form a dimmer, the ground state remains unaffected but the excited state was split due to the dipole-dipole interactions of the molecules arranged in different orientations [13]. The dimmer formation was possible for the Schiff bases ligands due to their trans-cis isomerism [14], and we formulated bellow the hydrogen bonding in dimmer aggregates.



The L^2H_2 ligand was different in behaviour both in the increasing of the wavelength of CT band with the increasing of the solvent polarity and in the larger red shift (in each solvent of ~ 100 – 150 nm) as compared with the other ligands. To explain this solvatochromic behaviour we analysed D-π-A system. The donor D (Cl) atom and the acceptor A (OH) group lied axially in para, position of benzene ring, while azo –N=N- function assured the planarity of the aromatic rings and the dynamic motion of the π electrons. The β naphtol hydroxyl group increased the push-pull motion by its withdrawing capacity.



The L^2H_2 ligand showed a discontinuity in the increasing of the CT wavelength only in acetonitrile solvent AN. We explained this aspect as a possible exchange of protons between the –OH group and the nitrogen atom of acetonitrile CH_3-CN. Lanthanides generally adopt the Ln^{3+} oxidation state with simple molecules, and form coordinative bonds with an ionic character [15]. Only asymmetric molecules of Er^{3+} complexes, without inversion centre, exhibit solvatochromic behaviour. Supplementary the electrostatic interactions Er-organic moiety increase the polarity of the organic ligands by the push-pull motion of electrons in the π conjugated skeleton. Thorough examination of our complexes (table 5 and 6) revealed interesting aspects and positive solvatochromism as compared with the free ligand, in all solvents due to our coordinative sphere involved in the solvatochromic phenomena.

The complex NH_4 $[Er(L^1)_2 (H_2O)_2]$ of the ligand L^1H_2 showed a positive solvatochromism with a red shift as compared with the free ligand in all solvents as a result of the C_1 symmetry and the zwitterionic form of the de-protonated organic moiety. The second azo dye complex NH_4 $[Er(L^2)_2 (H_2O)_2]$ showed a red shift as well as a positive solvatochromism against the free ligand only in AN, EtOH and DIOX solvents while in DMSO and DMF solvents a slight blue shift of the CT band was present.

Table 5. Wavelengths, λ_{max} (nm) of the charge transfer bands of the free ligands LH_2 and $NH_4[Er(L)_2 (H_2O)_2$] complexes in various solvents.

	Solvents- λ_{max} (nm)				
Complexes	**DMSO**	**DMF**	**AN**	**EtOH**	**Diox**
L^1H_2	399	399	395	395	397
Er-L^1	503	429	434	396	397
L^2H_2	596	559	429	502	495
Er-L^2	551	492	528	509	498
L^3H_2	443, 467	440, 460	438, 458	441, 461	442, 460
Er-L^3	441, 461	397, 416	396, 416	450, 484	457, 484
L^4H_2	449, 472	447, 468	441, 464	448, 468	445, 466
Er-L^4	445	438	426	448, 468	445, 466

Where
NH_4 $[Er(L^1)_2 (H_2O)_2$]=Er-L^1
NH_4 $[Er(L^2)_2 (H_2O)_2$]=Er-L^2
NH_4 $[Er(L^3)_2 (H_2O)_2$]=Er-L^3
NH_4 $[Er(L^4)_2 (H_2O)_2$]=Er-L^4

Table 6. Wavelengths, λ_{max} (nm), and molar extinction coefficients, [lgε] (L mol^{-1} cm^{-1}), of the charge transfer bands of the NH_4 [Er(L)$_2$ (H_2O)$_2$] complexes in various solvents

	Ligands- λ_{max} (nm), [lgε (L mol^{-1} cm^{-1})]			
Solvents	**Er-L^2**	**Er-L^1**	**Er-L^4**	**Er-L^3**
DMSO	551 [4.471]	503 [4.440]	445 [4.377]	441, 461 [4.254, 4.352]
DMF	492 [4.467]	429 [4.467]	438 [4.354]	397, 416 [4.203, 4.164]
AN	528 [4.383]	434 [4.361]	426 [4.433]	396, 416 [4.184, 4.143]
EtOH	509 [4.457]	396 [4.531]	448, 468 [4.497, 4.470]	450, 484 [4.340, 4,330]
Diox	498 [4.527]	397 [4.509]	445, 466 [4.397, 4.379]	457, 484 [4.285, 4.278]

The blue shift might be assigned to the interaction of solvents with the coordination sphere of the complex [16], due to the donor capacity of DMSO and DMF solvents [17] and we considered the following possible equilibrium:

$[Er(ONO)_2(H_2O)_2]^- + nDMF \rightarrow [Er(ONO)_2(H_2O)_2(DMF)_n]^-$

$[Er(ONO)_2(H_2O)_2]+nDMSO \rightarrow [Er(ONO)_2(H_2O)_2(DMSO)_n]^-$

A possible explanation of the blue shift of the CT band in the mentioned solvents was the change of the C_1 symmetry from $[Er(ONO)_2(H_2O)_2]^-$ to $[Er(ONO)_2(H_2O)_2(DMF)_n]^-$. Any increasing in symmetry induced a decreasing in the dipole momentum. In the series of the Schiff bases ligands, L^3H_2, L^4H_2, the corresponding complexes NH_4 $[Er(L^2)_2(H_2O)_2]$, NH_4 $[Er(L^2)_2(H_2O)_2]$ do not exhibit a sensitive dependence of the CT bands with the solvent polarity but a slight red shift of the CT band against the free ligands.

The discontinuity in the red shift of the CT band for all ligands after the complexation were analysed by comparing the two groups –N=N- and –CH=N- involved in the bridge between the aromatic rings as well as in the π electrons motion. In addition the involving of the nitrogen atom in the coordinative bond Er-N by its lone pair electrons was taken into account. We assumed that the π conjugated system was more disturbed by –CH=N- bridge than –N=N- bridge, because the lone pair electrons of the second azo nitrogen maintained unaffected π delocalization in the D-π-A system. This hypothesis agreed with the experimental data and corresponds to a decrease of polarity of the Schiff bases after the complexation by breaking off the D- π-A system in the azomethine bridge.

The wavelength of the charge transfer CT band related to the solvent polarity ordered the complexes with the positive solvatochromic behaviour as follows:
$NH_4[Er(L^2)_2(H_2O)_2]>NH_4[Er(L^1)_2(H_2O)_2]>NH_4$ $[Er(L^4)_2(H_2O)_2]$ > NH_4 $[Er(L^3)_2(H_2O)_2]$, while the ligands variation was different $L_2H_2 > L_4H_2 > L_3H_2 > L_1H_2$. These differences in the wavelength of the CT band were explained only on the bases of the relationship structure and properties. The solvatochromic behaviour of the free ligands depended on the nature (L^4H_2 (D/A=OH/COOH) > L^3H_2 (D/A=OH/OH) and the position of D/A couple (LH_2 axially couple works better than the others), the size of the π conjugated system ($L_4H_2 > L_3H_2 > L_1H_2$). The complexes solvatochromy depends on the π delocalization degree (delocaliziation in azo dyes complexes is greater than in the Schiff base complexes), and also on the size of the π conjugated system (L_2 H_2 > L_1 H_2 and L_4 H_2 > L_3 H_2).

4. Conclusions

Organic ligands with D-π-A systems belonging to azo dyes and Schiff bases usually show a batochromic solvatochromy with the solvent polarity. They might have or not available atoms in coordinating metallic cations or might use or not even D/A couple in the coordination bonds with the metal. These aspects had to be taken into account in their coordinative compounds simultaneously with the nature of the coordinative bond and the nature of the metallic cation. Surely in all cases the complexation provided a large red shift of the CT bands excepting the supplementary interactions between the solute-solvent. If the solvent possesses a donor capacity it would coordinates to metallic cation by penetrating the coordination sphere.

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