Spectroscopic and Theoretical Investigations of Complex Formation Of (3E,3'E)-7,7'-(Carbonylbis(Azanediyl))Bis(3-(2-(2-Hydroxyphenyl)Hydrazono)-4-Oxo-3,4-Dihydronaphthalene-2-Sulfonic Acid) with Metal Cations

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Abstract

A novel azo-dye was isolated by a diazo-coupling reaction and characterized by the elemental analysis, mass spectra, IR and UV-VIS spectroscopy. The processes of complex formation of H4L with some mono-, bis-, and trivalent metal cations were studied by spectrophotometric titration and theoretical modeling. The NBO effective charge calculations indicate a strong covalent character of the coordination bonds at complexation.

Keywords: Azodye; complex formation; UV-VIS spectroscopy; theoretical modeling, spatial and electronic structure.

Introduction

Azo compounds are usually intensely colored and resistant to different physical and chemical affections. Their good adhesive properties promote their application as dyes and pigments in a variety of fields including textile, polymer, and food industries, etc. [1, 2].

In fact, about half of the dyes in industrial use today are azo dyes [3, 4]. They are good complexing agents, and their metal complexes not only are used as dyes and pigments, but their thermal and optical properties provide their applications as optical recording media [5], toners [6] ink-jet printing [7], in non-linear and photoelectronics [8, 9], especially in optical information storage [10-13].

Introduction of one or two hydroxy-groups into the ortho- or para-positions of the aryl-substituents at the azo-group increases the complexing abilities of the organic dye and leads to the possibility of the proton migration that is reflected as the azo-hydrazone tautomerism and different ionization processes. Tautomeric and ionic forms can be easily distinguished by the position and intensity in the UV-VIS absorption bands [14]. Meanwhile, the introduction of several functional groups possessing violative protons into the composition of an azo-dye makes the spectral characteristics ambiguous. At the same time, the direct structure determination is in most times unavailable because of the high dispersity of azo-dyes. In this case, the only one possibility to assign the spectral changes at ionization or at complex formation with the corresponding tautomeric or ionic transformation of the organic species is quantum chemical modeling of the process.

In the presented paper, the spectroscopic studies of (3E,3'E)-7,7'-(carbonylbis(azanediyl))bis(3-(2-(2-hydroxyphenyl)hydrazono)-4-oxo-3,4-dihydronaphthalene-2-sulfonic acid) (H4L) (Scheme 1) and the processes of its complex formation with the transitional metal ions in different oxidation states by the UV-VIS spectrophotometric technique is discussed. The types of tautomeric equilibria at complex formation is studied by the theoretical B3LYP calculations.
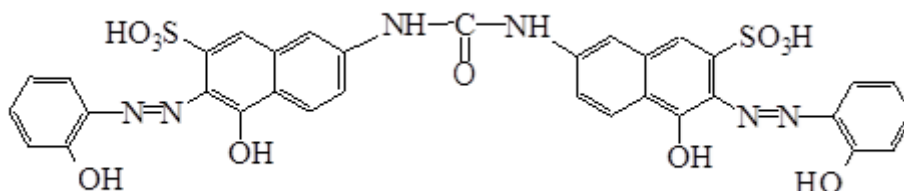
Scheme 1.

Experimental

Materials and methods

All the reagents from Acros Organics were of chemically pure grade.

C, H, and N elemental analysis was performed on a Varian 735–OES analyzer. The electrospray ionization (ESI) mass spectra were acquired on a Surveyor LCQ spectrometer. The FT-IR spectra were recorded in KBr pellets on a Perkin Elmer FT-IR 1650 spectrometer in the 4000-400 cm^{-1} region at the Shared Research and Educational Center of Physico-Chemical Studies of New Materials, Substances, and Catalytic Systems, PFUR. The UV-Visible spectra were measured using a Varian Cary 50 Scan spectrophotometer.

Spectrophotometric titration of solutions of H4L with the solutions of metal salts (AgNO$_3$; CuCl; CuCl$_2$; ZnCl$_2$; CrCl$_3$; FeCl$_3$) in water was carried out in neutral and alkaline media. Based on the results of titration, the saturation

curves were drawn for several wavelengths, and the metal-to-ligand ratios were calculated. The formation constants of metal complexes were determined by the procedure described by Beck & Nadypal [15].

Theoretical modeling

Quantum chemical modeling of molecular and electronic structures of H_4L, its anionic form, and complexes with metals was performed within the Density Functional Theory (DFT) using the hybride potential B3LYP [16] and a def2-SV(P) basis set [17] with the full geometry optimization. To analyze the electronic structure, the Natural Bonding Orbitals (NBO) approach was used [18]. All the calculations were performed with the Firefly 7.1.G software package [19].

Synthesis and characterization of (3E,3'E)-7,7'-(carbonylbis(azanediyl))bis(3-(2-(2-hydroxyphenyl)hydrazono)-4-oxo-3,4-dihydronaphthalene-2-sulfonic acid) (H₄L)

Synthesis of (H₄L was performed by a traditional azo-coupling reaction under standard conditions (**Scheme 2**).
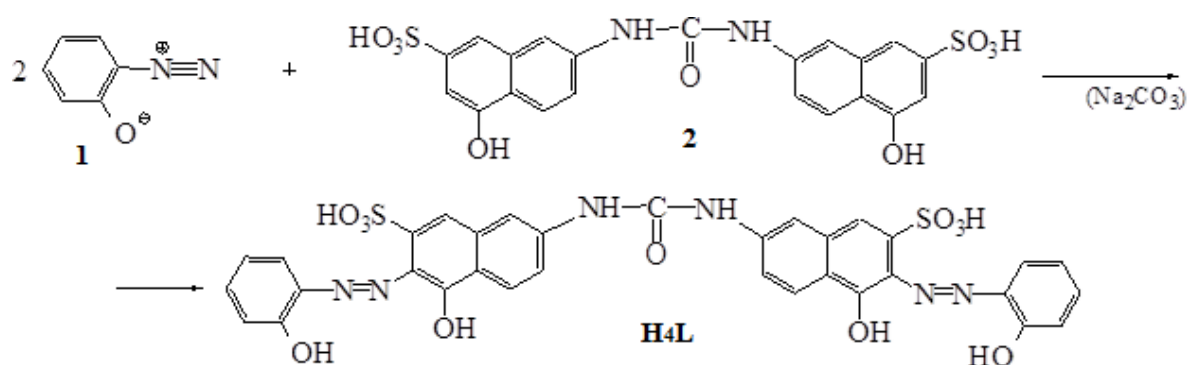
Scheme 2.

Diazotation

5.4.g (0.05 mol) of *o*-aminophenol was mixed at stirring with 60 ml of distilled water and 8.2 ml of 36% HCl. The absorbent carbon (0.5 g) was added to the brown colored solution, stirred for 5 min., and then filtered off. The obtained colorless solution was cooled till 2-3°C, and slowly mixed within 15 min. with 17.25 ml of $NaNO_2$ solution (C 200 g·l^{-1}). The obtained transparent solution of **1** was stirred at 2-3°C for more 30 min., and then the pH was adjusted to 2-3 with 5% solution of Na_2CO_3.

Azo-coupling

12.6 g (0.025 mol) of **2** was mixed with 1.6 g (0.04 mol) of NaOH, heated till 70°C, and stirred for 5-10 min. until the full dissolution. The solution was then cooled till 20°C and mixed dropwise with the previously prepared solution of **1** at intensive stirring. The reaction mixture was kept under stirring for 4 hours more. The precipitated azo-dye H₄L is filtered off, washed with 50 ml of the distilled water, and dried under vacuum until the constant mass. Yield 15 g (80.6%).

Elemental analysis, calc. (found), %: C – 53.22 (53.14); H – 3.22 (3.56); N – 11.29 (11.13); S – 8.60 (8.8.48). MS (m/e, M+) 744. IR (KBr), cm^{-1}: 3350 – 3200 (OH + NH); 3068(CH ar); 1713 (C=O); 1400 (N=N). UV–Vis (water), nm (log ε): 519.0 (4.23); 259.9 (4.45).

Results and Discussion

Spectrophotometric titration

The electronic absorption spectrum of an aqueous solution of H_4L is characterized by the two wide none-resolved absorption bands with the maxima at 519.0 (log ε 4.23) and 259.9 (log ε 4.45) nm and a shoulder at 452.1 nm (**Fig. 1**).

At addition of transition metal cations (Ag^+, Cu^+, Cu^{2+}, Zn^{2+}, Fe^{3+}, Cr^{3+}), the position of an absorption band in the visible region of the spectrum slightly shifts to longer wavelengths (**Table 1**), and the shoulder at 452.1 nm tends to decrease its intensity. In the case of trivalent metals such as Cr^{3+} and Fe^{3+}, the shoulder at around 580 nm appears in the UV-VIS spectrum (**Fig. 1a**). The intensity of the high wavelength absorption band increases in the case of mono- and divalent metal cations addition (**Fig. 1b, c**) and decreases for Fe^{3+} and Cr^{3+}.

The isobestic points observed at spectrophotometric titration indicate the existence of the equilibrium processes of complex formation of H_4L with the metal cations. With the help of the saturation curves (plot of the intensity of the absorption at a given wavelength *vs* the amount of the metal salt added to the solution of H_4L), the composition of the complexes and their formation constants were calculated and presented in the **Table 1**. As it is evident, the stability of the complexes increases as the following series: $CrL < FeL < Zn_2L < Cu_2L < Cu_4L < Ag_4L$. The composition of the complexes depends on the oxidation state of the metal cation.

Table 1. UV-VIS characteristics (λ_{max}, log ε), complex composition (x), and formation constants (K_f) of some metal complexes of H_4L (the mean deviation did not exceed 10%)

M^{n+}	x in M_xL	λ_{max}, nm	log ε*	K_f
-	-	519.0	4.23	-
Ag^+	4	526.8	4.40	$5.57 \cdot 10^{17}$
Cu^+	4	525.9	4.21	$2.66 \cdot 10^{17}$
Cu^{2+}	2	527.0	4.35	$3.16 \cdot 10^{9}$
Zn^{2+}	2	520.0	4.40	$2.88 \cdot 10^{9}$
Fe^{3+}	1	524.0	4.20	$1.21 \cdot 10^{5}$
Cr^{3+}	1	525.7	4.25	$9.90 \cdot 10^{4}$

* The log ε values of the complexes were calculated from the saturation curves with respect to the partial dissociation of the compounds at the equilibrium point.
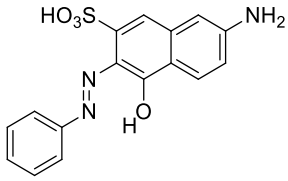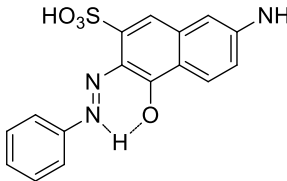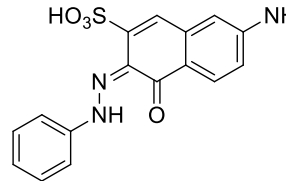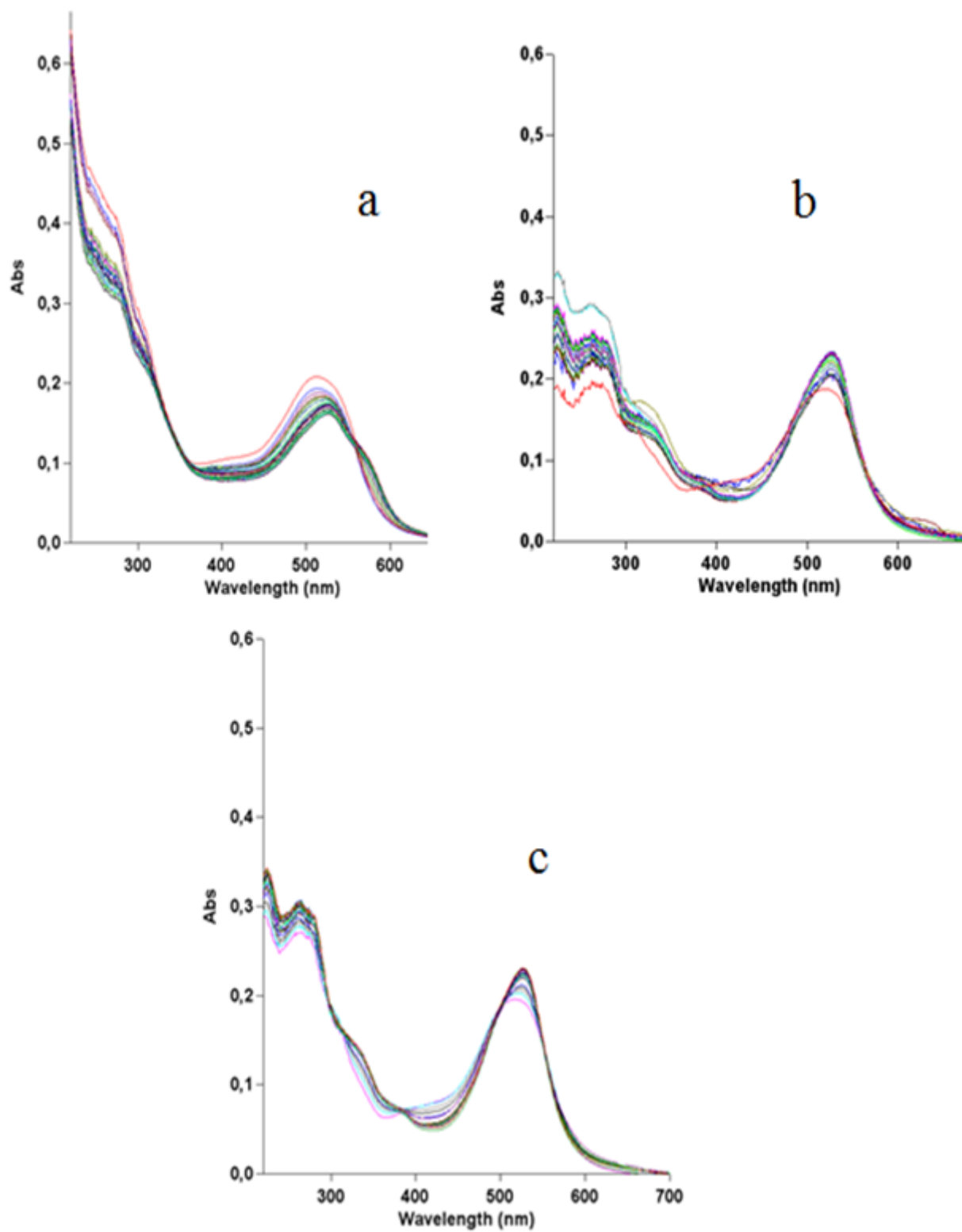
Fig. 1. Changes in the UV-VIS absorption spectra of an aqueous solution of H4L (1) at a stepwise addition of CrCl₃ (a); CuCl₂ (b), and AgNO₃ (c)

Theoretical modeling

The H_4L molecule contains six violative protons two of which belong to the SO_3H fragments and are fully ionized in the solutions.

To study the possibility of azo-hydrazone transformations of the molecule, the model H_2L^1 fragment was optimized. The structure of its azo- and hydrazo-forms as well as the transitional state and their relative energies are presented in the **Table 2**. As it is evident, the hydrazo H_2L^1 isomer is 22.0 kJ mol^{-1} more stable than the azo-isomer. A small value of the transition energy from azo- to hydrazo-isomer (4.5 kJ mol^{-1}) indicates the possibility of tautomeric transformations under different conditions.

	H_2L^1 azo	H_2L^1 transitional	H_2L^1 hydrazo
Molecule			
ΔE_{tot}, kJ mol^{-1}	0	+4,5	-22,0
ΔE_{tot}, kJ mol^{-1}	+ 22,0	+ 26,5	0

Taking in consideration the predominant hydrazo-structure, the geometries of four possible conformers and isomers of H_4L with the ionized SO_3H groups were optimized by the DFT method, and their relative energies were calculated (**Fig. 2**).

As it is evident, the conformer **a** with *anti-anti* positions of two sulfo-groups is 8.9 kJ mol^{-1} more stable than the conformer **b** with the *cyn-anti* configuration. The stability of the *cyn-cyn* hydrazo isomer **c** and *anti-anti* azo isomer **d** are 29.5 and 34.5 kJ mol^{-1} less stable than the **a** isomer, respectively.

The H_4L^{2-} dianion is planar. It is stabilized by intramolecular hydrogen bonds (O1···H(N2) 1.788 Å) (**Fig. 3**). The DFT calculated maxima of the long wave absorption bands in the UV-VIS spectra and the corresponding oscillator forces are in a good accordance with the experimental UV-VIS spectra (**Table 3**).

Table 3. Theoretical (TDDFT) bond lengths λ (nm) and oscillator forces *f* of the long wave UV-VIS absorption spectra of H_4L^{2-}, $Zn_2L(H_2O)_2$, and $Cu_4L(H_2O)_2$ in comparison with the experimental data

Molecule	λ, nm (*f*)	λ$_{max}$, nm (*log ε*)
H_4L	481 (0.90), 453 (0.14), 421 (0.55), 356 (0.16)	519.0 (4.23)
$Zn_2L(H_2O)_2$	517 (0.10), 482 (0.74), 468 (0.33), 453 (0.13)	520.0 (4.40)
$Cu_4L(H_2O)_2$	634 (0.22), 474 (0.23)	525.9 (4.21)

a (0 kJ mol^{-1})

b (+ 8,9 kJ mol^{-1})

c (+ 29,5 kJ mol^{-1})
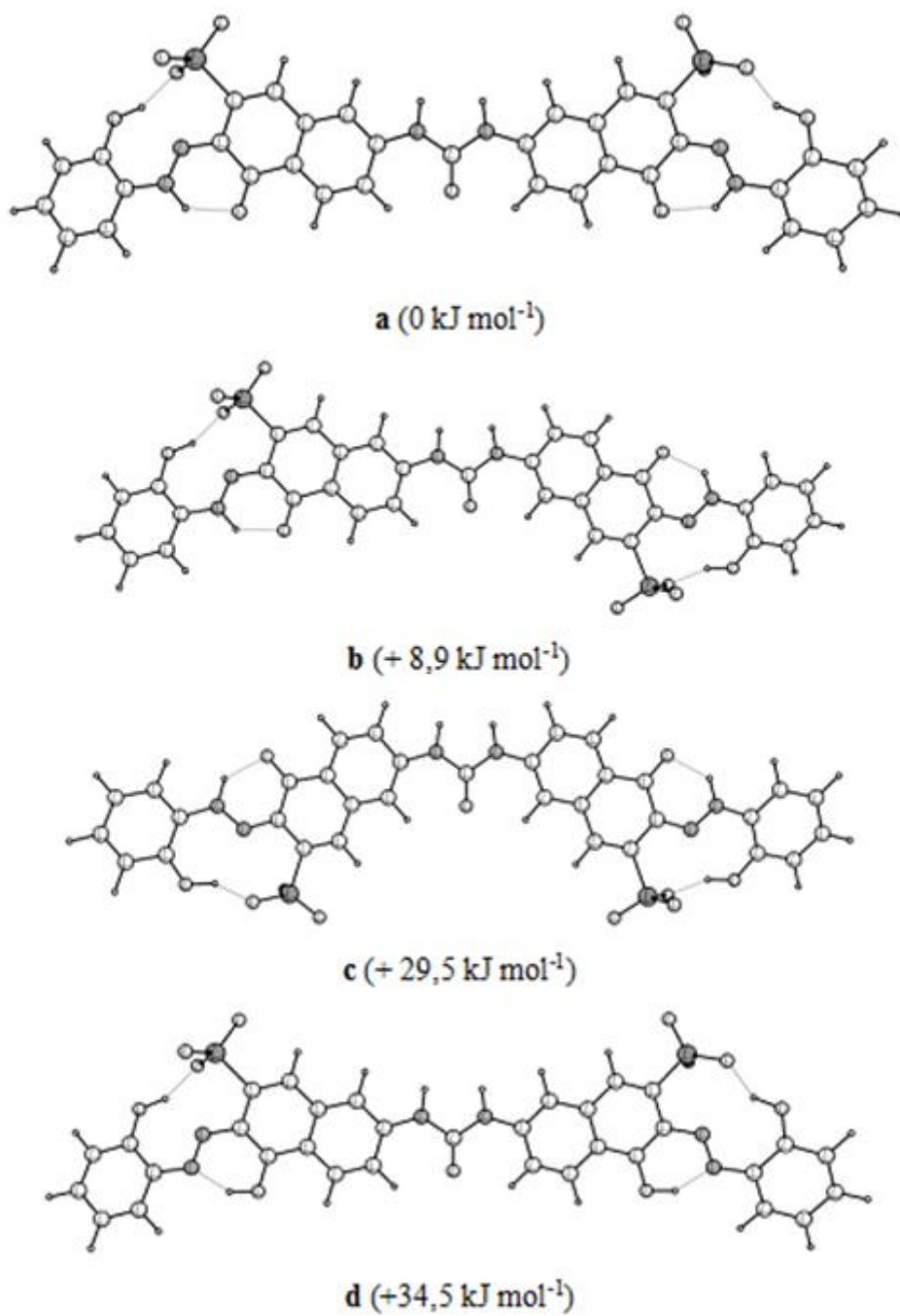
d (+34,5 kJ mol^{-1})

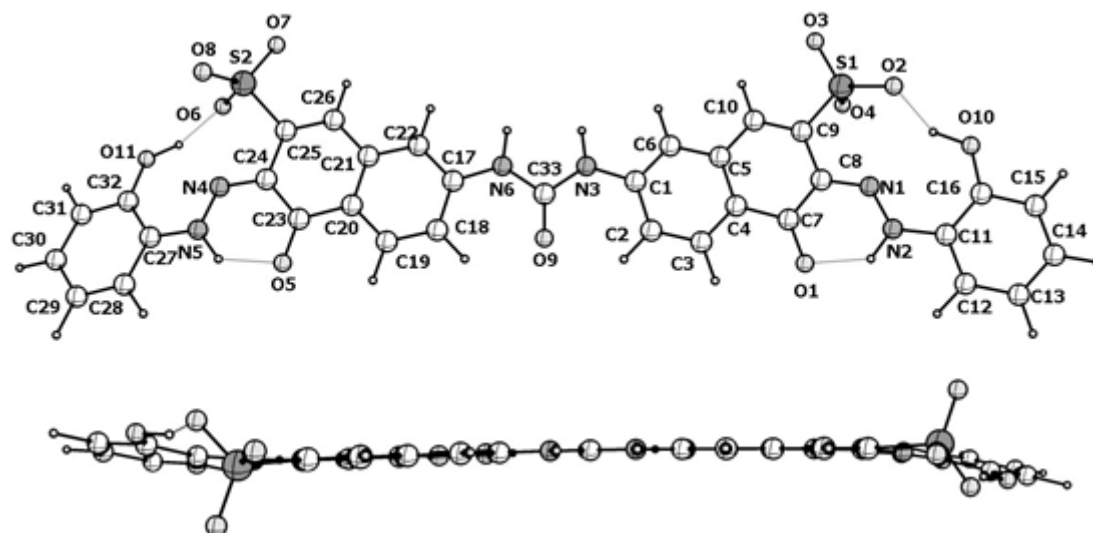**Fig. 2**. Geometry optimization of some isomers of H$_4$L and their relative energies

Fig. 3. Molecular structure and atomic numeration of H_4L^{2-} anion (DFT calculations)

The composition of the complexes of H_4L with mono- and divalent metals (Cu^+ and Zn^{2+}) for the theoretical modeling was chosen in accordance with their composition in the solutions derived from the spectrophotometric titration.

In the $Zn_2L(H_2O)_2$ molecule, H_4L acts as bis(tridentate) tetraanionic ligand (**Fig. 4**). The spatial structure of the coordination polyhedron of $Zn2+$ is determined by the tendency to a tetrahedral coordination and the planarity of the organic molecule. As the result, the O1-Zn2-O1 is found to be 164°, and the N2-Zn2-O(H2O) angle is 146°. Thus, the coordination polyhedron of $Zn2+$ can be described as a distorted tetrahedron. The two sulfo-groups are not involved in coordination with the zinc atoms, and the organic specie maintains its planarity.
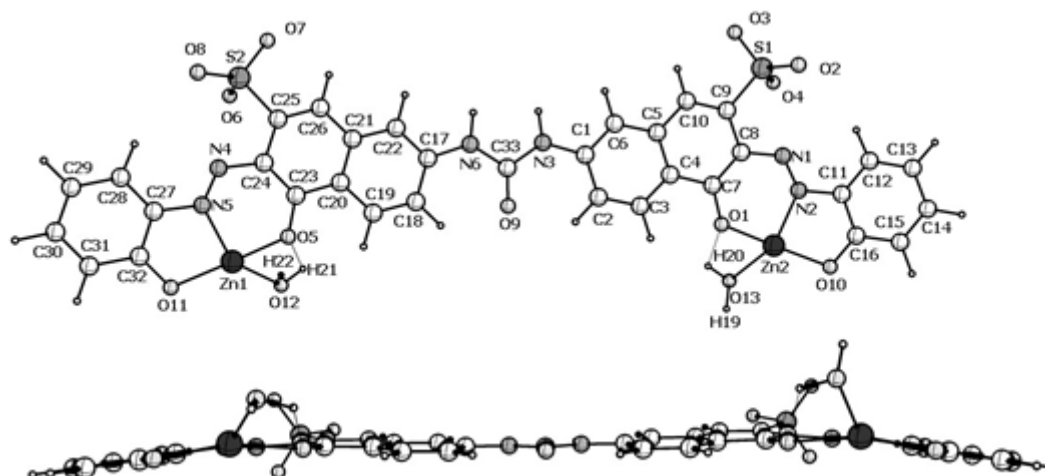

Fig. 4. Molecular structure of $Zn_2L(H_2O)_2$ (DFT calculations)

In the $Cu_4L(H_2O)_2$ complex, H_4L can be described as a bis(bidentate)-bis(tridentate) ligand (**Fig. 5**). Two o-phenol fragments are turned by 180° comparing with their position in the Zn-complex. Two Cu^+ an N-atom of the azo-group, an O atom of the deprotonated hydroxy-group and one O atom of the sulfo-group surround cations to form a distorted triangular coordination mode. The Cu4-O2(SO₃) bond length (1.913 Å) does not differ a lot from that of the Cu4-O10(OH) distance (1.891 Å), and the Cu4-N bond length is significantly longer (2.261 Å). This type of coordination mode leads to the distortion of H_4L planarity in $Cu_4L(H_2O)_2$.
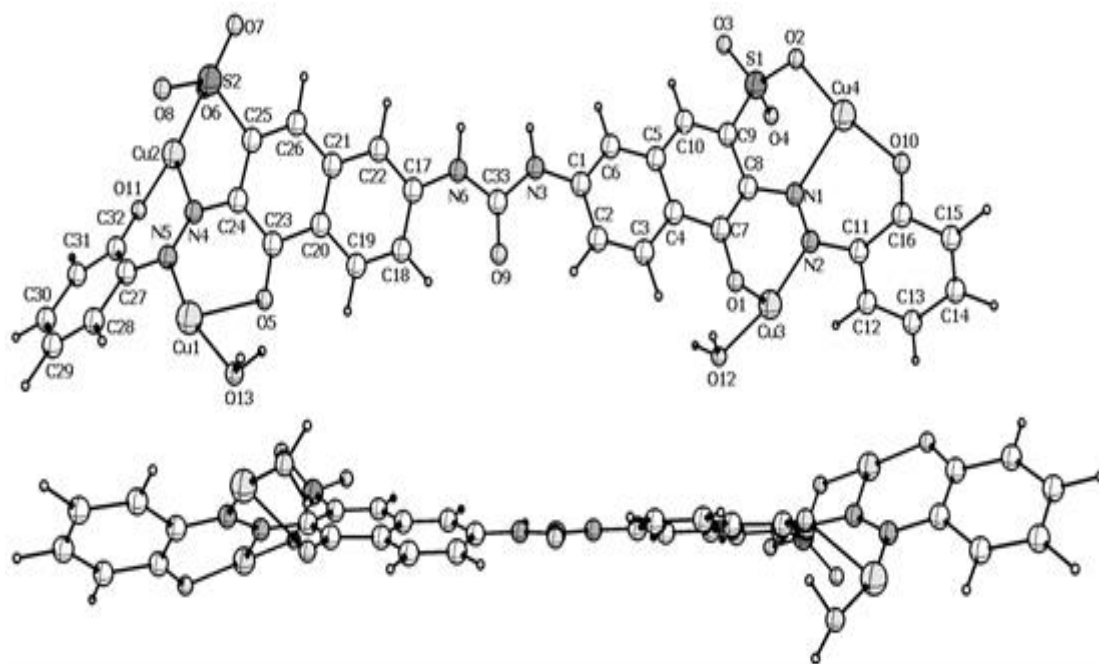
Fig. 5. Molecular structure of $Cu_4L(H_2O)_2$ (DFT calculations)

Another two Cu^+ cations in $Cu_4L(H_2O)_2$ undergo a traditional coordination mode involving an O atom of a quinolone fragments (Cu3-O1 2.174 Å), N atom of the azo-group (Cu3-N2 1.940 Å), and a water molecule (Cu3-O(H_2O) 2.019 Å).

In whole, the bond lengths of H_4L do not change a lot at complexation with the metal cations.

The NBO calculation of the atomic charges (**Table 4**) indicates a strong covalent character of the coordination bonds in $Zn_2L(H_2O)_2$ and electron transition from the organic ligand to the metal cation. The Zn effective charge was calculated as +1.559. Together with this, the electron density on the donating atoms (O1, N2, O10) significantly increases: for O1 from -0.667 to -0.913; for N2 from -0.306 to -0.477; and for O10 from -0.701 до -0.899. That is the feature of conjugated systems: at coordination, the electron density is shifted to the metal ion from the molecule in whole, and not only from the donating fragments.

The analogues electron redistribution at complexation is found for $Cu_4L(H_2O)_2$. The effective charges of the two non-equivalently coordinated Cu atoms are calculated as +0.743 and +0.781 for Cu3 and Cu4, respectively. The electron density on the donating O1, N2, N1, and O10 atoms increases to a less extent than in the case of $Zn_2L(H_2O)_2$. That may be due to a less charge of a Cu^+ cation compared with the Zn^{2+} cation. In total, the charge values indicate a significant income of a covalent component into the ligand -to-metal coordinate bond.

Table 4. NBO calculation of the atomic charges in H_4L, $Zn_2L(H_2O)_2$, and $Cu_4L(H_2O)_2$. Atomic numeration as in **Fig. 3-5**

Atom	H_4L	$Zn_2L(H_2O)_2$	$Cu_4L(H_2O)_2$	Atom	H_4L	$Zn_2L(H_2O)_2$	$Cu_4L(H_2O)_2$
O9	-0.662	-0.670	-0.667	O4	-0.973	-0.986	-0.963
C33	+0.882	+0.880	+0.879	N1	-0.189	-0.141	-0.278
N3	-0.639	-0.639	-0.644	N2	-0.306	-0.477	-0.333
C1	+0.191	+0.183	+0.177	H(N2)	+0.414	-	-
C2	-0.262	-0.261	-0.255	C11	+0.088	+0.062	+0.052
C3	-0.148	-0.166	-0.171	C12	-0.231	-0.195	-0.206
C4	-0.148	-0.134	-0.132	C13	-0.264	-0.263	-0.288
C5	-0.022	-0.021	-0.037	C14	-0.226	-0.212	-0.209
C6	-0.240	-0.237	-0.236	C15	-0.265	-0.298	-0.288
C7	+0.489	+0.433	+0,417	C16	+0.369	+0.368	+0.415
C8	+0.055	+0.046	+0.022	O10	-0.701	-0.899	-0.777
C9	-0.237	-0.218	-0.254	H(O10)	+0,538	-	-
C10	-0.239	-0.246	-0.241	Zn2	-	+1.559	-
O1	-0.667	-0.913	-0.838	O(H2O)	-	-0.952	-
S1	+2.366	+2.353	+2.346	Cu3	-	-	+0.743
O2	-1.012	-0.985	-1.050	Cu4	-	-	+0.781
O3	-0.988	-1.009	-0.969	O(H2O)	-	-	-0.952

Conclusions

A new azo-dye, 3E,3'E)-7,7'-(carbonylbis(azanediyl))bis(3-(2-(2-hydroxyphenyl)hydrazono)-4-oxo-3,4-dihydronaphthalene-2-sulfonic acid) (H_4L) was isolated and characterized by elemental analysis and spectral methods. Based on the spectrophotometric titration techniques, the formation of the metal complexes of the composition M_4L (M = Ag^+, Cu^+); M_2L (M = Cu^{2+}, Zn^{2+}), and ML (M = Cr^{3+}, Fe^{3+}) is established in the aqueous solutions. The formation constants of the complexes can be arranged as the following series: CrL < FeL < Zn_2L < Cu_2L < Cu_4L < Ag_4L. The theoretical DFT modeling indicates that the organic ligand exists in the planar *anti-anti* hydrazo isomer and depending on the composition of the complexes coordinates the metal cations in bis(tridentate) or bis(tridentate) bis(bidentate) coordination modes. The NBO effective charge calculations indicate a strong covalent character of the coordination bonds.

References

1. Elgemeie, G.E.H., Maher, H.H., Heba, M. Pigment & Resin Technology 30, 2001, p. 210.

2. Koh, J., Greaves, A.J. Dyes and Pigments, 50, 2001, p. 117.

3. Robert, T.M., Robert, N.B., Bhattacharjee, S.K. Organic Chemistry, 6th edition, New Delhi. Pearson Prentice Hall, 2011.

4. Zollinger, H. Color Chemistry. Syntheses, Properties, Application of Organic Dyes and Pigments, Third revised edition, Wiley-VCH, 2003.

5. Samieh, F., Ahmad, M.T., Hooshang, H., Hojatollah, K. ARKIVOC XIV, 2008, p. 115.

6. Kirkan, B., Gup, R. Turkey Journal of Chemistry, 32, 2008, p. 9.

7. Gregory, P.D., Waring, R., Hallas, G. The Chemistry and Application of Dyes, Plenum Press, London, 1990.

8. Katz, H.E., Singer, K.D., Sohn, J.E., Dirk, C.W., King, L.A., Gordon, H.M. Journal of the American Chemical Society, 109, 1987, p. 6561.

9. Li, X., Wu, Y., Gu, D., Gan, F. Dyes and Pigments, 86, 2010, p. 182.

10. Wang, S., Shen, S., Xu, H. Dyes and Pigments, 44, 2000, p. 195.

11. Gan, F.X., Hou, L.S., Wang, G.B., Liu, H.Y. Materials Science Engineering, B76, 2000, p. 63.

12. Chen, Y.Q., Wu, D.H., Gu, F.X. Dyes and Pigments, 76, 2008, p. 624.

13. Li, X.Y., Wu, Y.Q. Gu, D.H., Gan, F.X. Materials Science Engineering, B158, 2009, p. 53.

14. The Chemistry of Dyes - Azo Dyes / University of Bristol, School of Chemistry–URL: http://www.chm.bris.ac.uk/webprojects2002/price/azo.htm

15. Beck, M.T., Nadypal, I. Chemistry of complex equilibria, Akad. Kiado, Budapest, 1989.

16. Becke, A.D. Journal of Chemical Physics, 98, 1993, p. 5648.

17. Schaefer, A., Huber, C., Ahlrichs, R. Journal of Chemical Physics, 100, 1994, p. 5829.

18. Glendening, E.D., Badenhoop, J.K., Reed, A.E. "NBO 5.G," Theoretical Chemistry Institute, University of Wisconsin, Madison, W I, 2004 http://www.chem.wisc.edu/~nbo5

19. Granovsky, A. "Firefly version 7.1.G," http://classic.chem.msu.su/gran/firefly/index.html.