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Quantum-Chemical Calculations of the Tautomeric Forms of Azo Derivatives of Acetylacetone and Determination of the Stability Constants of Their Complexes with Rare-Earth Metals

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Abstract—The effective atomic charges in the tautomeric forms (enol-azo, keto-azo, and hydrazo) of 3-(2-hydroxy-5-nitro-3-sulfophenylazo)pentane-2,4-dione (L^1), 3-(2-hydroxy-3,5-disulfophenylazo)pentane-2,4-dione (L^2), 3-(5-chloro-2-hydroxy-3-sulfophenylazo)pentane-2,4-dione (L^3), 3-(2-hydroxy-4-nitrophenylazo)pentane-2,4-dione (L^4), and 3-(2-hydroxyphenylazo)pentane-2,4-dione (L^5) were calculated by the Hückel method (MO LCAO). It was found that the hydrazo form is most reactive for *meta*- and *meta'*-substituted derivatives ($L^{1–3}$) and the keto-azo form is most reactive for *para*-substituted (L^4) and unsubstituted ones (L^5). The stability constants of complexes of rare-earth metals (La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) with $L^{1–5}$ determined by potentiometric titration decrease in the order: Lu > Yb > Tm > Er > Ho > Dy > Tb > Gd > Eu > Sm > Nd > Ce > La. Functionalization of the aromatic part of ligands L affected neither the rare-earth metal : L ratio (1 : 2) nor the above order of the stability constants.

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Tautomeric equilibrium of an organic reagent characterizes the reactivity of its functional groups. Determination of the reactivity of each tautomer of a reagent is important for understanding of the complexation mechanism. Tautomerism is responsible for the selectivity of a reagent, the character of its color reactions with chemical elements, and the stability and conditions of formation of its complexes. Thus, a study of the reactivities of the tautomers of a reagent is a necessary step in a further investigation of their complexation reactions. In addition, determination of the influence of substituents on the position of the tautomeric equilibrium and the effective atomic charges on reactive sites is of current interest for a study of the mechanism of action of organic reagents.

In this study, using the Hückel method (MO LCAO), we calculated the effective atomic charges in the tautomeric forms (enol-azo, keto-azo, and hydrazo) of 3-(2-hydroxy-5-nitro-3-sulfophenylazo)pentane-2,4-dione (**L[1]**), 3-(2-hydroxy-3,5-disulfophenylazo)pentane-2,4-dione (**L[2]**), 3-(5-chloro-2-hydroxy-3-sulfophenylazo)pentane-2,4-dione (**L[3]**), 3-(2-hydroxy-4-nitrophenylazo)pentane-2,4-dione (**L[4]**), and 3-(2-hydroxyphenylazo)pentane-2,4-dione (**L[5]**) and determined the stability constants of complexes of rare-earth metals (Ln) with $L^{1–5}$.

EXPERIMENTAL

Earlier, ligands $L^{1–5}$ have been prepared by azo coupling of diazotized *o*-aminophenol derivatives with acetylacetone in a weakly basic medium [1]. The individuality of the ligands was proved by IR and ^1H and ^{13}C NMR spectroscopy. Their purity was checked by electronic absorption spectroscopy in solution and by paper chromatography.

An initial solution of a rare-earth metal (c_{Ln} = 0.1 mol/l) was prepared by dissolving Ln or its oxide in dilute HCl (1 : 1, 20 ml) with slight heating as described in [2]. Ligands $L^{1–3}$ containing SO_3H groups are soluble in water; L^4 and L^5 are insoluble in water. That is why pH-metric titration of solutions of L and Ln was carried out at 25°C in water ($L^{1–3}$) and aqueous ethanol (3 : 7) ($L^{4, 5}$) with the Bates correction [3]. The volume of titrated solutions was 50 ml ($c_L = 2 \times 10^{-3}$ mol/l, $c_{Ln} = 1 \times 10^{-3}$ mol/l). The ionic strength of the solutions was maintained constant (I = 0.1) by adding a calculated amount of KCl. A 0.02 M KOH solution free of carbon dioxide served as a titrant. Solutions were stirred with a magnetic stirring bar. The pH values were measured on an I-130 ionometer with glass and flow silver-chloride electrodes.

Quantum-chemical calculations of the tautomeric forms of azo derivatives of acetylacetone. Reactions of metal ions with organic reagents (azo derivatives of β-diketones, L) mainly occur through the

Table 1. Sum of the effective charges on the electron-donating atoms

L	L^1	L^2	L^3	L^4	L^5
Enol-azo (I)	–1.546	–1.255	–1.601	–1.726	–3.219
Keto-azo (II)	–1.864	–1.652	–1.922	–2.666	–3.430
Hydrazo (III)	–1.963	–1.735	–2.021	–2.647	–3.255

electronic periphery, which makes it important to study their electronic structures. To determine the reactivities of tautomers L and the specific character of deprotonation of their functional groups, we performed quantum-chemical calculations using the Hückel method (MO LCAO) [4–8]. The Hückel method involves a π-electron approximation: the molecular orbitals are written as a linear combination of the atomic orbitals of π-electrons ($2p_z$ orbitals of the C, O, and N atoms, etc.):

$$\varphi_1 = \sum_{q=1}^{m} C_{q_i}\chi_q(2p_z), \quad (1)$$

where C_{q_i} are unknown coefficients determined by solving a system of equations in the simple version of MO LCAO:

$$\sum_q (H_{pq} - ES_{pq})C_{q_i} = 0, \quad p = \overline{1, m}, \quad (2)$$

where the following definitions are introduced:

$$H_{pq} = \int \chi_p^* \hat{H} \chi_q \mathrm{d}V, \quad (3)$$

$$S_{pq} = \int \chi_p^* \chi_q \mathrm{d}V. \quad (4)$$

The H_{pq} values are the matrix elements of the effective Hamiltonian for a π-electron moving in an effective field with no regard to other π-electrons; S_{pq} are the overlap integrals for the atomic orbitals χ_p and χ_q. The system of equations (2) has nontrivial solutions if the determinant of the coefficients C_{q_i} is zero:

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots & H_{1n} - ES_{1m} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots & H_{2n} - ES_{2m} \\ \hline H_{m1} - ES_{m1} & H_{m2} - ES_{m2} & \dots & H_{mn} - ES_{mn} \end{bmatrix} = 0. \quad (5)$$

Opening of this determinant leads to an m-order equation with respect to E. Solution of this equation gives m real roots $E_1, E_2, \dots, E_m$ called the orbital energies of the molecule in the π- electron approximation. Each of these roots E_i is substituted into Eq. (2) to determine the ratios of the coefficients C_{q_i} and the numerical values of these coefficients are found from the normalization condition for the molecular orbitals φ_i:

$$\int U_1^* U_i \mathrm{d}V = \int |U_i|^2 \mathrm{d}V = \sum_{qq'} C_{q_i}^* C_{q_i'} S_{qq'} = 1^*. \quad (6)$$

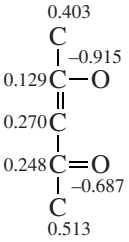
Thus, for solution of the system of equations (2) (i.e., for determination of the orbital energies E_i and the corresponding sets of coefficients C_{q_i}), one must know numerical H_{pq} and S_{pq} values. However, H_{pq} values cannot be calculated exactly because the explicit expression for the operator $\hat{H}$ is unknown. In the Hückel method, H_{pq} and S_{pq} are estimated from the Hückel approximations [6].

The numerical values of coefficients C_{q_i} allow one to determine the effective charge q_A (au) of an atom A in the molecule according to the MO method by the formula [8]:

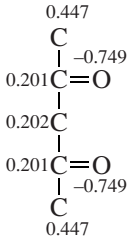
$$q_A = n_A^0 - \sum_i n_i \sum_{q \in A} |C_{q_i}|^2, \quad (7)$$

where n_A^0 is the positive charge of the nuclear core of the atom A (in the Hückel method, $n_A^0 = 1$ for all atoms), n_i is the number of electrons in the ith molecular orbital; summation for i is performed over the occupied molecular orbitals. We designed a program for Hückel computations and determined the numerical values of coefficients C_{q_i} in Eq. (1). Using formula (7), we calculated the effective atomic charges for all molecules under study and constructed their molecular diagrams. The results obtained are presented in scheme and in Table 1.

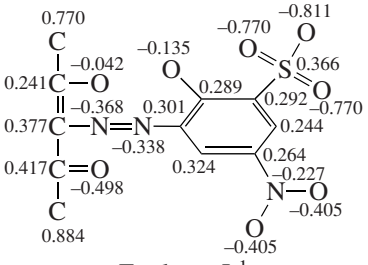
Determination of the stability constants of the complexes. The dissociation constants of reagents L^{1-5} were calculated by the Schwarzenbach equation [1] from potentiometric data: $pK_1 = 5.71 \pm 0.01$, $pK_2 = 8.84 \pm 0.01$ (L^1); $pK_1 = 6.03 \pm 0.03$, $pK_2 = 9.78 \pm 0.06$ (L^2); $pK_1 = 6.28 \pm 0.01$, $pK_2 = 10.14 \pm 0.01$ (L^3); $pK_1 = 6.35 \pm 0.04$, $pK_2 = 10.22 \pm 0.04$ (L^4); $pK_1 = 6.50 \pm 0.01$, $pK_2 = 10.41 \pm 0.01$ (L^5). It can be seen that functionalization of the molecules into different positions with respect to the azo group increases their acid properties and the pK values of the reagents can correlate with the inductive constants of the substituents. Based on our quantum-chemical calculations, one can assume that pK_1 characterizes the deprotonation of the *ortho*-OH group in the aromatic part of the molecule, while pK_2 characterizes the deprotonation of the hydrazone form (=N–NH–).



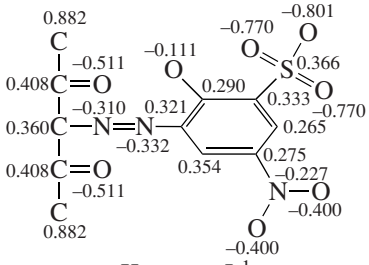
Enol



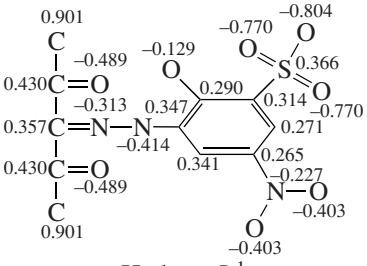
Keton



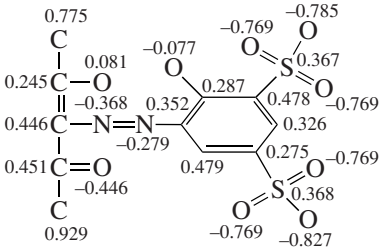
Enol-azo L^1



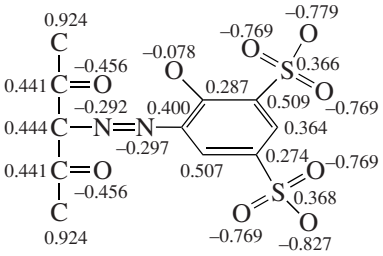
Keto-azo L^1



Hydrazo L^1



Enol-azo L^2



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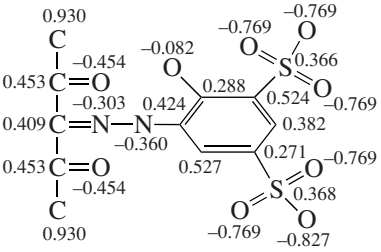
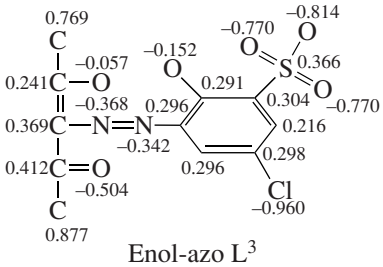
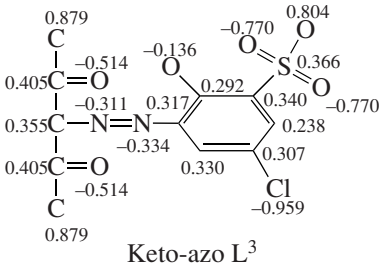


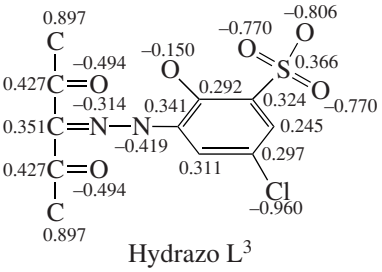
Hydrazo L^2



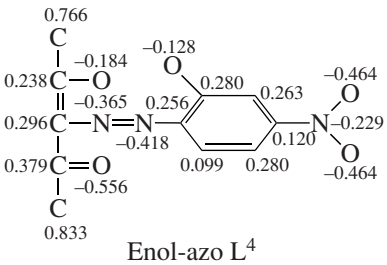
Enol-azo L^3



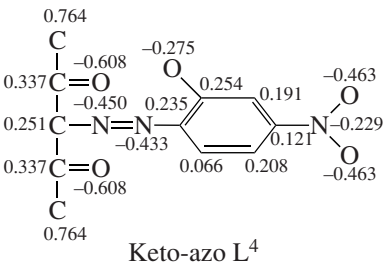
Keto-azo L^3



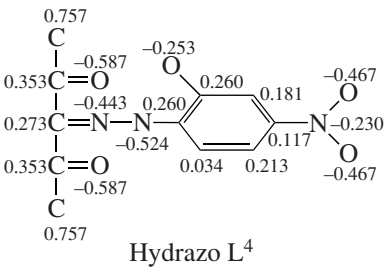
Hydrazo L^3



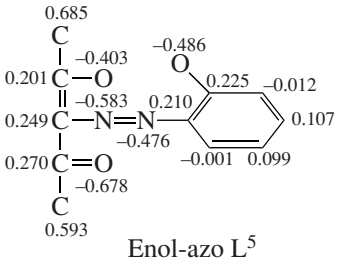
Enol-azo L^4



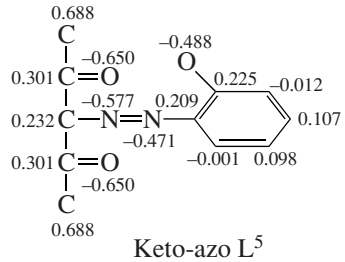
Keto-azo L^4



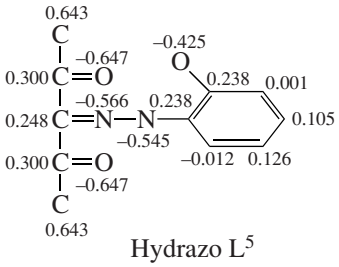
Hydrazo L^4



Enol-azo L^5



Keto-azo L^5



Hydrazo L^5

Scheme.

We determined the step stability constants by using the Bjerrum technique [9, 10]:

$$[L] = \frac{(2-m)c_{H_2L} - [H^+] + [OH^-]}{[H^+]K_1 + 2[H^+]^2K_1K_2},$$

$$\alpha_{L(H)} = 1 + [H^+]K_1 + [H^+]^2K_1K_2,$$

$$\bar{n} = \frac{c_L - [L]\alpha_{L(H)}}{c_{Ln}},$$

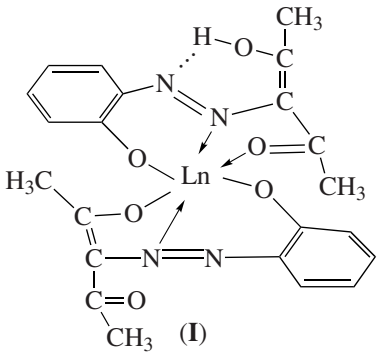
where $c_L = 2 \times 10^{-3}$ mol/l, $c_{Ln} = 1 \times 10^{-3}$ mol/l, Ln : H_2L = 1 : 2; K_1 and K_2 are the protonation constants of the reagent and m is the neutralization point.

We plotted $\bar{n}$ versus pL. The reciprocal concentrations of the ligands ($-\log L = pL$) at $\bar{n} = 0.5$ and 1.5 equal the logarithms of the step stability constants $\log K_1$ and $\log K_2$, respectively. To determine the exact values of the stability constants ($\log\beta_1 = \log K_1$; $\log\beta_2 = \log K_1 + \log K_2$), the potentiometric data were processed by the least-squares method [11] and are given in Table 2.

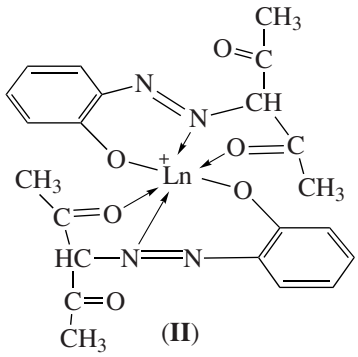
RESULTS AND DISCUSSION

It can be seen in the molecular diagrams of tautomeric forms L^{1-5} that the reactivities of the corresponding tautomers decrease and the reactive sites change when passing from acetylacetone to its azo derivatives. With an increase in the electron-donating properties of the substituent that is *meta* to the azo group, the absolute effective charges on the O atoms in the *ortho*-positions become lower. On functionalization (L^{1-3}), the sum of the absolute effective charges on the atoms in the reactive sites increases when passing from the enol-azo through keto-azo to hydrazo form. However, the order is different for L^4 and L^5: keto-azo > hydrazo > enol-azo (Table 2).

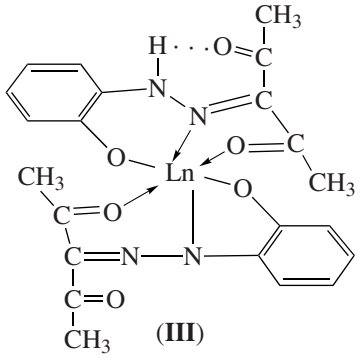
These results show that functionalization of a molecule into different positions with respect to the azo group can serve as a tool for regulation of the reactivity of the tautomer. Thus, based on our molecular diagrams of ligands L, we can suggest more than 15 structures for a Ln–L complex. The most likely structures are as follows:



(**I**)



(**II**)



(**III**)

It was found experimentally that Ln complexes with azo derivatives of acetylacetone, which contain no OH group *ortho* to the azo group, are colorless (no color effect was observed upon the complexation). The functions of formation show that some of the proposed structures are impossible. It follows from the molecular diagrams that the N and O atoms in the tautomers of L bear the great π-electron densities ($^{0.081\ -0.403}_{O-O}$ enol, $^{-0.368\ -0.583}_{N-N}$ azo, $^{-0.077\ -0.486}_{O-O}$ aromatic enol-azo, $^{-0.456\ -0.650}_{O-O}$ ketone, $^{-0.292\ -0.577}_{N-N}$ azo, $^{-0.078\ -0.488}_{O-O}$ aromatic keto-azo, $^{-0.454\ -0.647}_{O-O}$ ketone, $^{-0.360\ -0.545}_{N-N}$ hydrazo, and $^{-0.082\ -0.425}_{O-O}$ aromatic hydrazo), which corresponds to structures **I–III**. With regard to the sum of the π-electron density, one can believe that structure **III** is most likely for L^{1-3} and that structure **II** is most likely for $L^{4,5}$.

From the potentiometric data, we found that the stability constants of the Ln–L complexes decrease in the following order (Table 2):

L^{1-5}: Lu > Yb > Tm > Er > Ho > Dy > Tb > Gd > Eu > Sm > Nd > Ce > La.

Apparently, the character of changing stability of the Ln–L complexes is associated with hydrolysis of ions [13], the ionic radius and electronic configuration of Ln, and the nature of L (shift of tautomeric equilibrium). A comparison of the stability constants of the complexes with L^{1-5} shows that functionalization of the aromatic part of the molecule does not change the order of the stability of the complexes, complexes with L^5 being more stable. This is due to the lower negative inductive effect of the H atom in L^5 compared to the introduced functional group in L^{1-4}. In addition, ligands L^4 and L^5 are insoluble in water (unlike sulfo-containing ligands L^{1-3}) and the stability constants of their

Table 2. Logarithms of stability constants of the complexes with L and acetylacetone

Ln	*i*	$\log\beta_i$						Ionic radius of Ln, nm [12]
		L^1	L^2	L^3	L^4	L^5	Acac* [9]	
La	1	6.23 ± 0.04	6.27 ± 0.04	6.32 ± 0.05	6.40 ± 0.07	6.52 ± 0.01	4.96	0.1061
	2	12.71 ± 0.03	12.73 ± 0.05	12.77 ± 0.04	12.84 ± 0.05	12.95 ± 0.03	8.41	
	3						10.91	
Ce	1	6.47 ± 0.01	6.53 ± 0.04	6.60 ± 0.04	6.69 ± 0.04	6.82 ± 0.05	5.30	0.1034
	2	12.93 ± 0.07	12.97 ± 0.06	13.03 ± 0.07	13.11 ± 0.02	13.23 ± 0.03	9.40	
	3						12.60	
Nd	1	6.71 ± 0.04	6.75 ± 0.07	6.83 ± 0.05	6.94 ± 0.06	7.06 ± 0.02	5.3	0.0995
	2	13.17 ± 0.02	13.22 ± 0.03	13.29 ± 0.06	13.38 ± 0.03	13.50 ± 0.04	9.27	
	3						12.65	
Sm	1	7.18 ±0.04	7.25 ± 0.04	7.35 ± 0.06	7.46 ± 0.05	7.61 ± 0.07	5.59	0.0964
	2	13.53 ± 0.06	13.59 ± 0.06	13.68 ± 0.03	13.78 ± 0.03	13.91 ± 0.05	10.05	
	3						12.95	
Eu	1	7.52 ± 0.05	7.60 ± 0.04	7.73 ± 0.04	7.86 ± 0.04	8.04 ± 0.05	5.87	0.0950
	2	13.87 ± 0.03	13.94 ± 0.03	14.06 ± 0.02	14.17 ± 0.08	14.32 ± 0.03	10.35	
	3						13.64	
Gd	1	7.60 ± 0.05	7.69 ± 0.05	7.84 ± 0.06	8.01 ± 0.04	8.20 ± 0.04	5.90	0.0938
	2	13.93 ± 0.03	14.01 ± 0.03	14.14 ± 0.03	14.26 ± 0.03	14.43 ± 0.03	10.38	
	3						13.79	
Tb	1	7.75 ± 0.04	7.86 ± 0.05	8.02 ± 0.04	8.19 ± 0.04	8.50 ± 0.01	6.02	0.0923
	2	14.07 ± 0.04	14.16 ± 0.02	14.31 ± 0.02	14.45 ± 0.03	14.74 ± 0.02	10.63	
	3						14.04	
Dy	1	7.78 ± 0.04	7.90 ± 0.02	8.08 ± 0.05	8.26 ± 0.04	8.57 ± 0.04	6.03	0.0908
	2	14.09 ± 0.03	14.19 ± 0.03	14.36 ± 0.07	14.52 ± 0.05	14.83 ± 0.03	10.70	
	3						14.04	
Ho	1	7.83 ± 0.01	7.96 ± 0.05	8.15 ± 0.04	8.38 ± 0.04	8.75 ± 0.04	6.05	0.0894
	2	14.13 ± 0.03	14.24 ± 0.03	14.43 ± 0.07	14.61 ± 0.03	14.94 ± 0.05	10.73	
	3						14.13	
Er	1	7.92 ± 0.02	8.06 ± 0.04	8.29 ± 0.04	8.55 ± 0.05	8.88 ± 0.05	6.09	0.0881
	2	14.21 ± 0.03	14.33 ± 0.06	14.54 ± 0.03	14.76 ± 0.03	15.04 ± 0.03	10.85	
	3						14.33	
Tm	1	8.11 ± 0.02	8.17 ± 0.04	8.42 ± 0.06	8.70 ± 0.07	9.21 ± 0.06	5.99	0.0869
	2	14.40 ± 0.01	14.53 ± 0.02	14.75 ± 0.07	14.99 ± 0.03	15.41 ± 0.07	10.67	
	3						14.05	
Yb	1	8.37 ± 0.04	8.53 ± 0.04	8.80 ± 0.05	9.11 ± 0.04	9.57 ± 0.06	6.23	0.0858
	2	14.68 ± 0.05	14.82 ± 0.03	15.07 ± 0.04	15.33 ± 0.07	15.78 ± 0.01	11.00	
	3						14.63	
Lu	1	8.45 ± 0.04	8.64 ± 0.04	8.86 ± 0.04	9.17 ± 0.06	9.65 ± 0.04	6.18	0.0848
	2	14.77 ± 0.05	14.92 ± 0.03	15.18 ± 0.05	15.51 ± 0.08	16.03 ± 0.03	11.04	
	3						13.90	

* Acetylacetone.

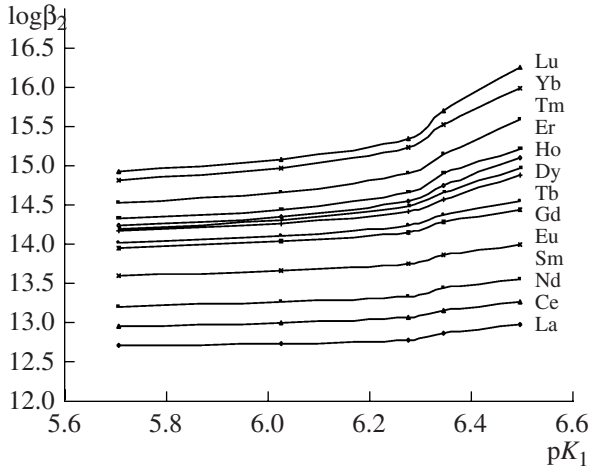


Fig. 1. Plots of $\log\beta_2$ vs. $f(pK_1)$.

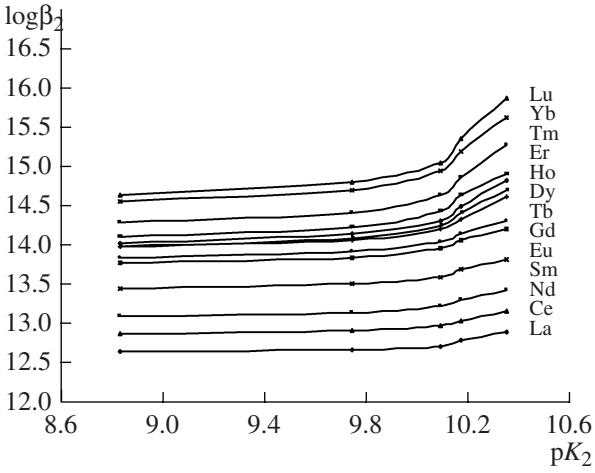


Fig. 2. Plots of $\log\beta_2$ vs. $f(pK_2)$.

complexes determined in aqueous ethanol are overestimated. Nevertheless, it is evident that the introduced functional groups affect the stability of the resulting complexes and the complexes with L^5 are more stable than those with L^4. The stability constants of the complexes increase monotonically (Table 2) when passing from L^1 to L^5, while the sum of the effective atomic charges on the reactive sites changes in a nonmonotonic way (Table 1). However, we found a correlation between the stability constants and the sum of the effective atomic charges: with an increase in the absolute value of the latter, the stability constants of the complexes increase (except for those with L^2). Apparently, the deviation from this correlation is due to the O_3H group that is *meta* to the azo group. The influence of the electron-withdrawing properties of the introduced functional group on the stability of the complex can be illustrated with the plots $\log\beta_2 = f(pK_1)$ and $\log\beta_2 = f(pK_2)$ shown in Figs. 1 and 2.

The character of both plots is similar; with an increase in the basic properties of L, the corresponding complexes become more stable (Figs. 1, 2). It can be seen that the reagents under discussion form more stable complexes with Lu(III), probably because of the electronic configuration and the ionic radius of lutetium(III).

Our calculations showed that the function of formation $\bar{n}$ of the complexes studied vary in the range $0 < \bar{n} \leq 2$, in contrast to their values in Ln acetylacetonates ($0 < \bar{n} \leq 3$) (Table 2). One can conclude that the functionalization of acetylacetone changes its reactive sites. Apparently, a change in the ratio of the components in the complexes when passing from Ln acetylacetonates to Ln complexes with azo derivatives of acetylacetone is due to steric hindrances and the reactivity of the tautomeric forms of the reagents.

The Ln complexes with L are more stable than those with acetylacetone (Table 2). Therefore, the analytical scope of ligands L can be predicted to be wide.

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