Synthesis of tris(β-diketones) and study of their complexation with some transition metals

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New chelating ligands consisting of three β-diketone fragments, *viz.*, 1,3,5-tris[(acetylaceton-3-yl)methyl]benzene, 1,3,5-tris[(benzoylaceton-3-yl)methyl]benzene, and 1,3,5-tris[(dibenzoylmethan-1-yl)methyl]benzene, linked to each other through the mesitylene spacer were synthesized by the reaction of 1,3,5-tris(bromomethyl)benzene with the corresponding β-diketone sodium salt. The acidity of these compounds and their complexation properties were studied by pH-potentiometry in aqueous-ethanol solutions. Tris(β-diketones) form mononuclear complexes with lanthanide ions, whose stability increases in the series $La^{3+} < Gd^{3+} < Lu^{3+}$. 1,3,5-Tris[(acetylaceton-3-yl)methyl]benzene forms both mononuclear and polynuclear complexes with the Ni^{2+} and Cu^{2+} ions. The stability constants and selectivity of complex formation increase substantially with an increase in the degree of deprotonation of the ligands, thus indicating that all deprotonated chelate groups are involved in coordination with the metal ion. The replacement of the methyl groups by the phenyl substituents in the β-diketone fragments of the molecules affects substantially the composition and stability of the complexes formed.

Key words: β-diketones, pH-potentiometry, complex formation, lanthanide complexes, copper complexes, nickel complexes, stability constants, chelating agents.

β-Diketones are used for solving many tasks of organic, coordination, and other divisions of chemistry. One of the most practically important properties of these compounds is their ability to form chelate complexes of different structure with ions of many metals.[1,2] The development of extraction methods provided wide use of β-diketones for separation of elements with similar properties, for instance, actinides and lanthanides, and concentrating microadmixtures of elements.[3,4]

Practical significance of β-diketones induced the development of studies directed to syntheses of new representatives of the series of β-diketones,[5—9] which can be divided into two main groups. The first group includes studies of the synthesis of β-diketones with substituents of more complicated structure, whereas the second group concerns works on the synthesis of β-diketone derivatives in which one or both carbonyl oxygen atoms are substituted for the S or Se atoms, imine or amine groups optimal for binding of specified metal ions.

Another, qualitatively distinctive approach to the modification of the complexation properties of β-diketones is the synthesis of polytopic ligands[10] with three-dimensional architecture. The presence of several functional groups in a molecule can favor both an increase in the efficiency and selectivity of complex formation due to the "cooperative effect" and the creation of compounds with a new architecture. However, only restricted number of publications on polydentate compounds based on β-diketones are available in literature. Interest in these compounds has especially increased during recent several years due to the intensive development of supramolecular chemistry. Among relevant studies we can distinguish the works aimed at synthesizing the binuclear Cu^{2+} complexes,

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where the β-diketonate fragments in a molecule are linked through the *m*-xylylene and 2,7-naphthalenediyl-bismethylene spacers, and at studying their metal-receptor properties.[11—13] The binuclear V^{2+} and V^{3+} complexes were also synthesized from the ligand with the *m*-xylylene spacer, and they are promising catalysts of redox processes.[14]

The use of ligands with two spatially separated β-diketonate groups made it possible to create the coordination "host" polymers with architecture of "molecular shelves" of high strength and capacity.[15] Bis(β-diketones) with rigid phenylene and naphthalenediyl spacers were used to create metal-supramolecular structures with triangular (complexes with Cu^{2+} and Ni^{2+}) and tetrahedral (complexes with Ga^{3+} and Fe^{3+}) geometry.[16,17] Ligands with arylenedi(oxymethylene) and ethylenedioxide spacers were used for the synthesis of metallocryptands closed into a macrocycle by two Cu^{2+} or Ni^{2+} ions. An alkaline metal ion is also involved in complex formation exerting the template effect. This is indicated by its coordination with the oxygen atoms of the bridging and β-diketonate fragments.[18]

Intramolecular interactions between metal ions are known to affect strongly the magnetic, redox, and spectral properties of coordination compounds. This is confirmed by the data on the binuclear lanthanide (in particular, with Eu^{3+} ions) complexes of the series of bis(β-diketones) linked through arylene spacers, whose luminescence is substantially higher than that of their monoanalogs.[19,20]

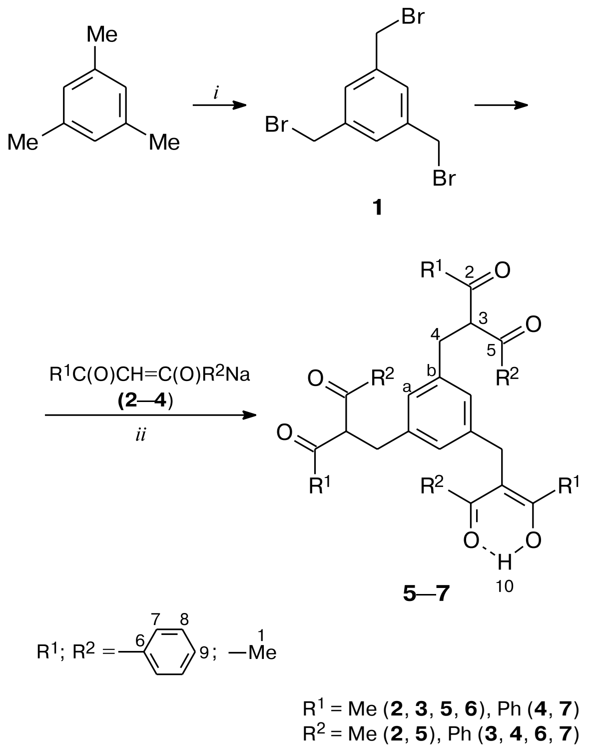
The works on the synthesis of tris-[21] and tetrakis(β-diketones)[22] and studies of their catalytic properties should be mentioned. Publications on these poly(β-diketones) are virtually lacking, because, most likely, their syntheses are difficult.

We have also reported earlier the synthesis of 1,3-bis(acetylacetonyloxy)- and 1,3-bis(benzoylacetonyloxy)benzenes and studies of the effect of their ditopic structure on the complexation properties toward the lanthanide ions.[23] A substantial increase in the stability and selectivity of complex formation with an increase in the degree of deprotonation of the ligands was found. Continuing this work, we synthesized new tris(β-diketones) and present the results of studies of their structures, acidic properties, and ability to complex formation with the lanthanide ions (La^{3+}, Gd^{3+}, Lu^{3+}), Ni^{2+}, and Cu^{2+}.

Results and Discussion

Synthesis of ligands. To synthesize tris(β-diketones), we used the modified method of nucleophilic substitution described for 1,4-bis[(acetylaceton-3-yl)methyl]benzene[24] and applied later for the synthesis of similar *meta*-isomers.[12] According to a previously described procedure,[12] β-diketone was added to potassium *tert*-butoxide in boiling *tert*-butyl alcohol, and then bis(bromomethyl)benzene and KI were added. However, when a considerable excess of β-diketone over bis(bromomethyl)benzene was used, a problem of purification of the target products from the initial β-diketone appeared.[12] Therefore, we developed a modified procedure in which the preliminarily prepared β-diketone sodium salt and its reaction with 1,3,5-tris(bromomethyl)benzene (**1**) was carried out in the absence of KI in a higher-boiling solvent dioxane instead of *tert*-butyl alcohol. This favored a substantial shortening of the reaction duration (from 1 day and more to 3 h) and obtaining more pure compounds.

Scheme 1

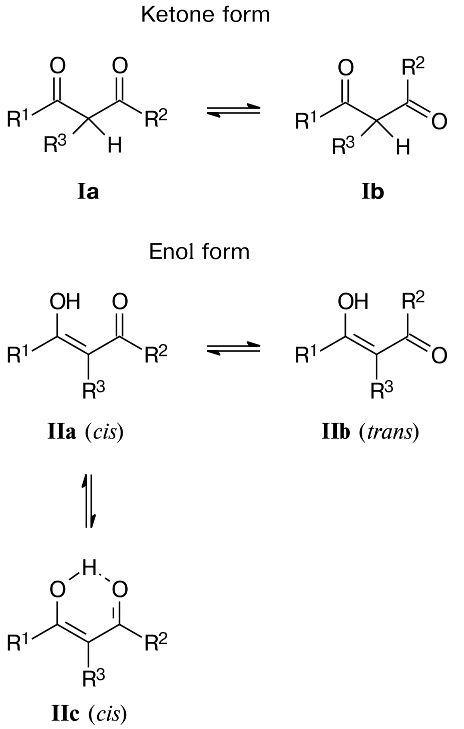


Reagents and conditions: *i*. NBS, AIBN/HCO_2Me, 14 h, 20 °C. *ii*. Dioxane, Δ, 3 h.

The compositions and structures of tris(β-diketones) **5—7** were confirmed by the data of elemental analysis, MALDI-TOF mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy, and IR spectroscopy.

Spectral and structural features of compounds 5—7. Diketones can exist as keto-enol tautometers (I and II), whereas enols can have *cis*- or *trans*-configuration (Scheme 2). Enols of β-diketones that exist in the *cis*-form (IIa) can additionally be stabilized due to the formation of a strong intramolecular form (IIc).[25] IR and NMR spectroscopic methods are very informative for determining structural features of these compounds.

Scheme 2



The IR spectra (Fig. 1) of compounds **5**—**7** are characterized by absorption bands at 3000—3100 cm^{-1} (ν(=CH)); 3000—2800 cm^{-1} ((ν(CH), ν(CH_2), and ν(Me)); 1750—1650 cm^{-1} (ν(C=O)); at ~1450, 1500, and 1600 cm^{-1} (ν(Ph)); 1100—1400 cm^{-1} (ν_{as}(CCC)) and 1050—900 (ν_s(CCC)). In addition, the spectra of compounds **6** and **7** exhibit intense absorption bands in an interval of 800—650 cm^{-1} assigned to the absorption of the monosubstituted phenyl fragments: γ(=CH) and δ(Ph).[26]

For all the three β-diketones, the bands assigned to the ν(C=O) vibrations are doublet: 1727 and 1699 cm^{-1} for **5**, 1716 and 1674 cm^{-1} for **6**, and 1695 and 1668 cm^{-1} for **7**. The frequencies of these vibrations decrease with an increase in the number of aromatic substituents in the β-diketone fragments due to conjugation with the π-systems of these substituents, which agrees with published data.[26] The doublet character of the keto-carbonyl bands, which are almost the same in intensity, is caused, most likely, by syn- and antiphase stretching vibrations of the carbonyl groups in the β-diketone fragments.[27]

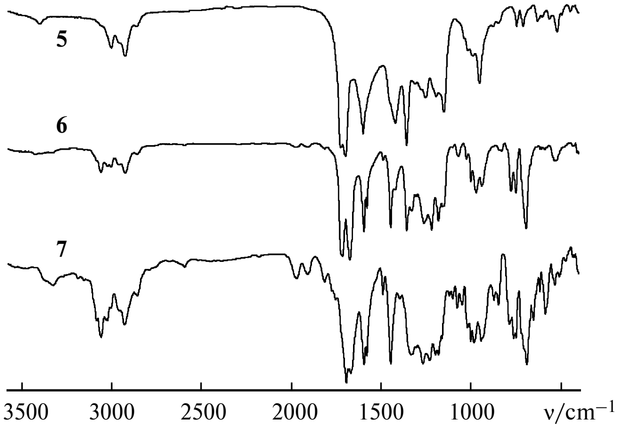


Fig. 1. IR spectra of compounds **5**—**7**.

At the same time, in the IR spectrum of compound **5**, unlike those of compounds **6** and **7**, the absorption band at ~1600 cm^{-1}, which exhibits stretching vibrations of multiple bands of the aromatic rings and enol structures ν(C=O) and ν(C=C),[26,27] is broadened and the whole spectrum is diffuse (the peaks are less distinct). This indicates the presence of considerable amounts of enol forms along with ketone forms. The stretching vibrations ν(OH) are detected as a broad diffuse base of the ν(CH) lines in the interval 2400—3300 cm^{-1} with an uncertain maximum, which is characteristic of enol structures.[26,27] The presence of some amounts of enol forms cannot be excluded for compounds **6** and **7**, because the properties described for them can be disguised by strong stretching vibrations ν(C=O) and ν(Ph) that are observed at the corresponding frequencies and characteristic of keto structures.

It is known that an increased content of the enol form is observed in inert solvents due to the formation of an intramolecular hydrogen bond.[25] Indeed, the chemical shifts of protons of the OH groups (~16—17 ppm, Table 1) observed in the ^{1}H NMR spectra of solutions of compounds **5**—**7** in $CDCl_3$ indicate that their molecules contain a strong intramolecular hydrogen bond. At the same time, according to the ^{1}H NMR spectral data, tris(β-diketones) **5**—**7** exist predominantly in the keto form in solutions. For instance, for compound **5** the fraction of the enol form is ~35%, whereas the replacement of one of the methyl groups by the phenyl group in the β-diketone fragments decreases the content of the enol form to 5% in compound **6**, while it is virtually absent (<0.3%) in the case of hexaphenyl derivative **7**. An inverse dependence could be expected, because in β-diketones with aromatic substituents the fraction of the enol form usually increases due to an additional stabilization caused by the formation of a single π-electron system of conjugation between the phenyl substituent and six-membered ring of the enol tautomer.[25] This did not occur, most likely, due to steric hindrance induced by the adjacent β-diketone fragments in these compounds that prevent this stabilization.

Acidic and complexation properties of tris(β-diketones). The constants of stepped deprotonation pK_i for compounds **5**—**7** described by equilibria (1) and (2) and pK of acetylacetone (**8**), benzoylacetone (**9**),

Table 1. Parameters of the ^{1}H and ^{13}C NMR spectra (CDCl$_3$, δ, J/Hz) for the keto form* of compounds **5**—**7**

Atom	**5**		**6**		**7**	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
a	6.5—6.8	124—129	6.8—6.9 (6.77)	128.2 (127.2)	6.98	128.1
b		139.0 (140.9)		138.8 (141.0)		139.9
1	2.1—2.2 (2.0—2.1)	30.0 (23.2)	2.0—2.1 (1.99)	28.3 (25.3)		
2		203.2 (191.8)		202.5 (183.3)		195.3
3	3.9—4.0	69.9 (108.1)	4.58—4.68	64.0 (96.7)	5.28 (t, J = 7.1)	58.7
4	3.0—3.2 (3.5—3.7)	34.0 (32.9)	3.10—3.20 (3.53—3.57)	34.0 (33.5)	3.27 (d, J = 7.1) (3.85)	34.9
5				195.3 (193.3)		
6				138.8		135.9
7			7.8—7.9	128.8	7.78 (d, J = 7.8)	128.9
8			7.35—7.48	128.6	7.34 (t, J = 8.2)	128.6
9			7.5—7.6	133.3	7.47 (t, J = 7.0)	133.5
10	(16.7—16.8)		(17.0; 16.1)		(17.1; 16.8)	

* The values for the enol forms if any are given in parentheses.

and dibenzoylmethane (**10**) determined under similar conditions by pH-metric titration are presented in Table 2.

$$H_3L \rightleftharpoons H_2L^- + H^+, \quad (1)$$

$$H_2L^- \rightleftharpoons L^{2-} + 2\,H^+. \quad (2)$$

The replacement of the methyl substituent by the phenyl group in the β-diketone fragments in the series of compounds **5**—**7** decreases the acidity of the first proton, which agrees with the indicated above decrease in the fraction of the enol form. The substitution of one hydrogen atom in the methylene group of β-diketone for any substituent R usually also results in a sharp decrease in the acidity, which is caused by both steric hindrance and a decrease in the mobility of the second proton of the methylene group and, hence, an insignificant degree of enolization of β-diketone.[25] However, the deprotonation constants of tris(β-diketones) **5**—**7** and their monoanalogs **8**—**10** by the first step have the same order. In the case of compound **5**, even a slight increase in acidity compared to that of compound **8** is observed. Further two protons are abstracted. For compounds **5** and **6**, the acidity constant increases, on the average, by one order of magnitude. At the same time, for compound **7** this constant almost coincides with the average value of the second and third acidity constants (pK_1 ≈ p$K_{2,3}$/2), indicating the absence of a mutual effect on the acid-base properties of the β-diketone fragments in this compound. As a whole, this can indicate the stabilization of the monoanion formed in compounds **5** and **6** due to the formation of an intramolecular hydrogen bond decreasing pK_1, whereas the bulky substituents in compound **7** prevent, most likely, its formation.

Table 2. Values of pK_i for compounds **5**—**10**

Compound	pK_1	p$K_{2,3}$
5	9.37±0.04	21.02±0.04
6	9.97±0.05	22.63±0.1
7	10.34±0.07	20.58±0.1
8	9.47±0.03*	
9	9.56±0.03*	
10	9.68±0.08	

* Data in Ref. 23.

The addition of the lanthanide ions in the lanthanide ion to ligand mole ratios equal to 0.5 : 1, 1 : 1, and 2 : 1 considerably shifts the equilibrium of tris(β-diketones) to the deprotonated forms. The curves of pH-metric titration of ligands **5**—**7** in the presence of the lanthanide ions are much lower (Fig. 2) and indicate complex formation in solutions. The stability constants (logβ) of the complexes of β-diketones **5**—**7** calculated from the

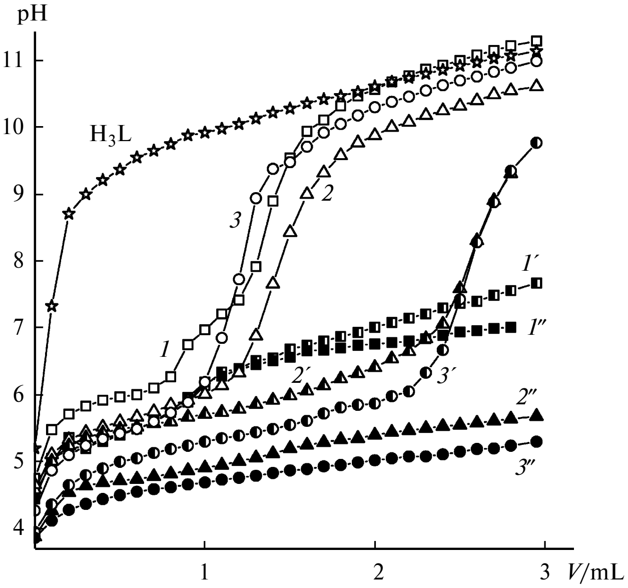


Fig. 2. Curves of pH-metric titration of compound **5** in the absence (H$_3$L) and presence of Ln^{3+}: La^{3+} (*1*, *1*′, *1*″), Gd^{3+} (*2*, *2*′, *2*″), and Lu^{3+} (*3*, *3*′, *3*″) at the Ln^{3+} to ligand mole ratios 0.5 : 1, 1 : 1, and 2 : 1, respectively.

Table 3. Stability constants (logβ, β/L mol^{-1}) of the complexes of β-diketones **5**—**7** $\{([H_{3-k/m}L]^{k/m-})_m(Me^{p+})_n\}^{pn-k}$ formed in the $H_3L - Me^{p+}$ system

Me^{p+}	*m*	*n*	*k*	logβ			$\Delta log\beta_{Ln/La}$		
				5	**6**	**7**	**5**	**6**	**7**
La^{3+}	1	1	1	6.3±0.07	6.9±0.07	6.54±0.07			
	1	1	2	—	—	10.0±0.13			
	1	1	3	14.1±0.12	15.9±0.09	13.12±0.06			
	2	1	3	17.9±0.2	18.7±0.2	17.54±0.12			
	2	1	4	—	—	20.1±0.3			
	2	1	5	—	—	20.1±0.3			
Gd^{3+}	1	1	2	—	—	12.2±0.12			2.2
	1	1	3	15.7±0.16	18.6±0.12	16.22±0.06	1.6	1.7	3.1
	2	1	3	17.7±0.2	20.44±0.16	—	−0.2	−0.2	
	2	1	5	—	—	20.4±0.4			0.3
Lu^{3+}	1	1	1	6.8±0.06	7.5±0.04	—	0.5	0.6	
	1	1	3	17.3±0.16	19.6±0.16	17.78±0.04	3.2	3.7	4.66
	2	1	3	19.6±0.25	20.3±0.24	—	1.7	1.6	
	2	1	5	—	—	22.9±0.5			2.8
Ni^{2+}	1	1	1	5.5±0.04	5.1±0.2	—			
	1	1	2	8.24±0.05	8.7±0.2	9.7±0.1			
	1	2	3	14.63±0.05	15.8±0.1	—			
Cu^{2+}	1	1	1	8.76±0.04	*	*			
	1	1	2	13.63±0.1					
	2	3	6	44.8±0.16					

* The constants were not determined because of precipitation in the system.

above data and described by equilibrium (3) are given in Table 3.

$$mH_3L + nLn^{3+} \rightleftharpoons \{([H_{3-k/m}L]^{k/m-})_m(Me^{p+})_n\}^{pn-k} + kH^+, \qquad (3)$$

where H_3L is ligand **3**—**5**, and Me^{p+} is the metal ion.

According to Eq. (3), stoichiometry of the $\{([H_{3-k/m}L]^{k/m-})_m(Me^{p+})_n\}^{pn-k}$ complexes that formed was designated by indices *m*, *n*, *k*, where *m* is the number of reacting $[H_{3-k}L]^{k-}$ anions of the ligand, *n* is the number of cations, *p* is the cation charge, and *k* is the number of abstracting protons.

Under the concentration conditions studied, ligands **5**—**7** are characterized by the formation of neutral complexes with the lanthanide ions (La^{3+}, Gd^{3+}, Lu^{3+}) with stoichiometry $m = 1$, $n = 1$, $k = 3$. In the case of the complex with ligand **6**, the stability constant is maximum, exceeding the stability constants of similar complexes with ligands **5** and **7** by 2—3 orders of magnitude. This increase in stability correlates with the decrease in the dissociation constant of compound **6** ($pK_{1-3} = 32.6\pm0.15$) as compared to those for compounds **5** ($pK_{1-3} = 30.39\pm0.08$) and **7** ($pK_{1-3} = 30.92\pm0.17$) (see Table 3). The remarkable increase in the stability of the complex with $m = 1$, $n = 1$, $k = 3$ as compared to that with $m = 1$, $n = 1$, $k = 1$—2 suggests that all the three diketonate fragments act as donor groups toward the lanthanide ions.

For a twofold excess of the ligand, the predominant neutral complex has the composition $m = 2$, $n = 1$, $k = 3$. The stability of the complex of this type with ligand **6** also exceeds the stability of similar complexes with ligands **5** and **7** by ~1—2 orders of magnitude. However, the logβ values of the 1 : 2 complexes increases less considerably with an increase in the degree of deprotonation. For instance, for compound **7**, on going from the La^{3+} complexes with the composition $m = 2$, $n = 1$, $k = 3$ to the complex with $m = 2$, $n = 1$, $k = 4$, the stability increases only by 2.5 logarithmic units. The further deprotonation of the ligands on going to the complex with $m = 2$, $n = 1$, $k = 5$ exerts no effect on the logβ value. This indicates that the deprotonation of the β-diketone fragment does not result, in this case, in the formation of an additional coordination bond with the lanthanide ion.

The formation of a neutral complex particle with three ligands ($m = 3$, $n = 1$, $k = 3$), which is typical of the lanthanide ion complexes with mono-β-diketones,[25] could be expected. However, the results of processing the data of pH-metric titration obtained even in a threefold excess of ligand **5** did not confirm the formation of complexes with this composition.

The stability constants of the complexes β increase in the series $La^{3+} < Gd^{3+} < Lu^{3+}$ (see Table 3). The selectivity of complex formation ($\Delta log\beta_{Ln/La} = log\beta_{Ln} - log\beta_{La}$) increases noticeably on going from compounds **5** and **6** to compound **7**. An increase in the degree of deprotona-

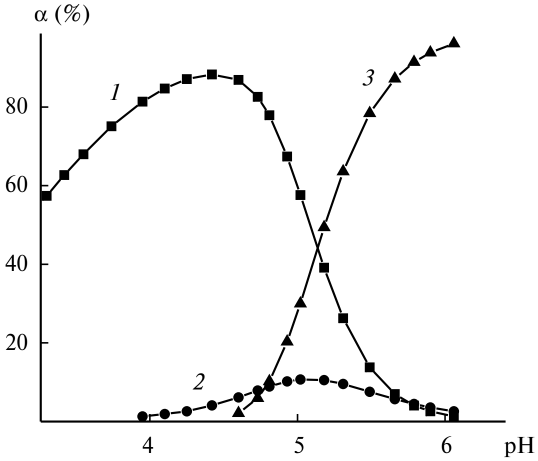


Fig. 3. Plots of the degree of accumulation of the complex forms *vs.* pH for a system of ligand **5** and Cu^{2+} taken in the 1 : 2 ratio. Complex forms: $m = 1, n = 1, k = 1$ (*1*); $m = 1, n = 1, k = 2$ (*2*); $m = 2, n = 3, k = 6$ (*3*).

tion (k) of the complexes also enhances the selectivity. Among all the tris(β-diketones) studied, the maximum selectivity is observed for the formation of neutral complexes with $m = 1$, $n = 1$, $k = 3$, in particular, for the complex of β-diketone **7** with Lu^{3+}, whose $\Delta\log\beta_{Ln/La}$ is 4.66.

The composition and stability constants were determined by pH-metric titration for the Ni^{2+} complexes with all the tris(β-diketones) synthesized. In the case of the Cu^{2+} ion, the complex was synthesized only with ligand **5**, whereas precipitates were formed in the presence of ligands **6** or **7**. The stability constants of the complexes with Ni^{2+} ($m = 1, n = 1, k = 1$ and $m = 1, n = 1, k = 2$) are by approximately 1—2 orders of magnitude lower than the corresponding constants for the complexes with the lanthanides. It is of interest that binuclear complexes ($m = 1$, $n = 2$, $k = 3$) were formed with an increase in the degree of deprotonation of the ligands, whereas coordination of only one metal ion was observed for the lanthanide ions in the whole pH range studied. The increase in the volume of substituents on going from ligands **5** and **6** to compound **7** prevents the formation of a binuclear complex.

The study of complex formation with the Cu^{2+} ion in an aqueous solution found only three complex particles, two of which are neutral (see Table 3). The plots of the degree of their accumulation *vs.* pH are shown in Fig. 3. Their stability is much higher than that in the case of similar in composition complexes with the Ln^{3+} and Ni^{2+} ions. The accumulation of the complexes also increases with an increase in ligand deprotonation in the complex ($m = 1$, $n = 1$), indicating coordination of the both β-diketonate fragments to the metal ion.

When the metal ion concentration and pH increase, a neutral complex particle containing three metal ions ($m = 2$, $n = 3$, $k = 6$) is accumulated instead of the binuclear particle ($m = 1$, $n = 2$, $k = 3$) found for Ni^{2+}. The shape of the calculated model of the structure of this complex is a cylindrical capsule 8.6 Å in diameter (nonbonding distance 7.7 Å) and ~8.1 Å in height (Fig. 4).

The addition of three equivalents of KOH (pH = 6.1) with respect to tris(β-diketone) at the metal to ligand ratio 2 : 1 resulted in the precipitation of a neutral complex. The elemental analysis data correspond to the composition of a trinuclear complex similar to that existing in solution. Nevertheless, the low solubility of the complex indicates its polymeric character. Probably, the increase in the degree of accumulation of this complex and the complete deprotonation of ligand **5** in solution upon the addition of about three equivalents of KOH induce the disproportionation of the trinuclear complexes leading to the precipitation of polymeric complexes.

Thus, synthesized tris(β-diketones) **5**—**7** in the solid state and in solutions exist predominantly in the keto form. They form with the lanthanide ions the mono- and bis-β-diketonate complexes, whose stability increases with an increase in the number of lanthanide

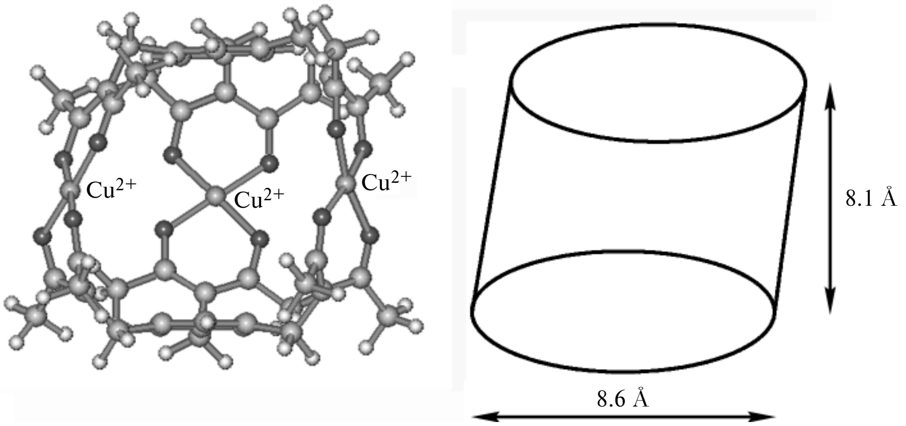


Fig. 4. Model of the structure of the neutral trinuclear Cu^{2+} complex with two tris(β-diketonates) **5** optimized by the semiempirical method (PM3).

($La^{3+} < Gd^{3+} < Lu^{3+}$). The replacement of the both methyl substituents by the phenyl groups in the β-diketonate ligands decreases the stability of the complexes and increases the selectivity in the series La^{3+}, Gd^{3+}, and Lu^{3+}, which is probably caused by steric hindrance for the formation of a coordination site. The Ni^{2+} and Cu^{2+} ions form, in addition to mononuclear complexes, bi- and trinuclear complexes involving one and two ligands, respectively. The increase in the degree of deprotonation of tris(β-diketones) substantially increases the stability constants of the complexes and selectivity of complex formation.

Experimental

Bidistilled water was used, and EtOH was additionally purified according to a standard procedure.[28] 1,4-Dioxane and toluene were purified by distillation over metallic sodium, and acetylacetone was distilled. Commercial reagents (KOH, lanthanide chlorides, $CuCl_2$, mesitylene, *N*-bromosuccinimide, azoisobutyronitrile, methyl formate, benzoyl acetone, dibenzoylmethane, and metallic sodium) were used as received. 1,3,5-Tris(bromomethyl)benzene (**1**) was synthesized by a described procedure.[29] Sodium salts of β-diketones **2**—**4** were synthesized by the addition of equimolar amounts of the corresponding β-diketone to a suspension of metallic sodium, and after stirring at 40 °C for 3 h the precipitate formed was decanted from residues of unreacted sodium, washed with diethyl ether, and dried *in vacuo*.

General procedure of synthesis of tris(β-diketones) (5—7). A mixture of sodium salt of β-diketone (18.6 mmol) and 1,3,5-tris(bromomethyl)benzene (2.12 g, 6 mmol) in anhydrous dioxane (100 mL) was refluxed with stirring for 3 h under argon. The reaction mixture was filtered, and the solvent was distilled off from the filtrate *in vacuo*. The residue was dissolved in CH_2Cl_2 and washed several times with water. The organic layer was separated, dried with $MgSO_4$, and concentrated. Solvent residues were removed at 80 °C *in vacuo*.

1,3,5-Tris(2-acetyl-3-oxobut-1-yl)benzene (5) was synthesized in a yield of 1.84 g (74%) as a viscous oil. Found (%): C, 69.89; H, 7.45. $C_{24}H_{30}O_6$. Calculated (%): C, 69.54; H, 7.30. MALDI-TOF mass spectrum, *m/z*: 416 $[M + H]^+$, 438 $[M + Na]^+$, 455 $[M + K]^+$.

1,3,5-Tris(2-acetyl-2-benzoylethyl)benzene (6) was isolated in a yield of 3.10 g (86%) as a viscous oil. Found (%): C, 77.84; H, 6.43. $C_{39}H_{36}O_6$. Calculated (%): C, 77.98; H, 6.04. MALDI-TOF mass spectrum, *m/z*: 624 $[M + Na]^+$, 640 $[M + K]^+$.

1,3,5-Tris(2,2-dibenzoylethyl)benzene (7) was isolated in a yield of 3.82 g (81%) as a solid, m.p. 65 °C. Found (%): C, 81.95; H, 6.36. $C_{54}H_{42}O_6$. Calculated (%): C, 82.42; H, 5.38. MALDI-TOF mass spectrum, *m/z*: 810 $[M + Na]^+$, 826 $[M + K]^+$.

Investigation methods. ^1H NMR spectra were recorded on a Bruker Avance 600 instrument with a working frequency of 600 MHz, and chemical shifts in the δ scale were measured using Me_4Si as internal standard. IR spectra (see Fig. 1) were obtained for compounds in thin layer between KBr plates on a FT-IR Vector-22 spectrometer (Bruker) with a resolution ability of 4 cm^{-1} and accumulation of 16 scans. The geometry of the model of the Cu^{2+} complex structure was optimized by the semiempirical method (PM3)[30] incorporated into the HyperChem7.03 program package.[31]

pH-Metric titration. Titration was carried out with a solution of KOH ($1.36 \cdot 10^{-2}$ mol L^{-1}) in an H_2O—EtOH (80 vol.%.) mixture on an I-130 instrument with the measurement accuracy to 0.05 pH unit at 40±1 °C. To determine acidity in the H_2O—EtOH (80 wt.%) mixture, a known procedure[32,33] was used, according to which the ionomer was tuned by standard buffer solutions in water and the electrode was preliminarily kept for 1 day in the H_2O—EtOH (80 vol.%) mixture for measurements of pH of aqueous-organic solutions. The pH values of aqueous-organic solvents were determined from the equation

$$pH = pH_{exp} - \Delta pH,$$

where pH_{exp} is the value measured in a mixed solvent, and ΔpH reflects the difference in activity of protons in aqueous and aqueous-organic solutions.

The ΔpH values were determined by measuring pH of solutions with different HCl concentrations in a mixed solvent (pH_{w+s}) and in water (pH_w) using the following equation:

$$\Delta pH = pH_{w+s} - pH_w.$$

Solutions were titrated at the lanthanide ion to ligand mole ratios 1 : 1 and 1 : 2 in the range of pH = 2.5—8, and for the free ligand this range was extended to pH 12 at the ligand concentrations $2 \cdot 10^{-3}$ and $4 \cdot 10^{-3}$ mol L^{-1}. The choice of the composition of the mixed solvent, concentrations used, and temperature of the medium during titration was caused by necessity to provide satisfactory solubility of the initial components and reaction products.

Experimental data were processed using the CPESSP program.[34] The mathematical model represented a set of Eqs (1), (2), and (3). The dissociation and complexation constants ($\beta_{i...q}$) corresponding to the minimum of the Fischer functional (Eq. (4)) were determined by the iteration procedure using the CPESSP program. Reliability of the model was estimated from the Fischer criterion (Eq. (5))

$$F = \sum\left[(\tilde{n}_{exp} - \tilde{n}_{calc})w_m\right]^2, \quad (4)$$

$$F_{min} < F\sigma^2(N - 2k), \quad (5)$$

where $\tilde{n}_{exp}$ and $\tilde{n}_{calc}$ are the experimental and theoretically calculated values of the Bjerrum function, N is the number of experimental points, k is the number of approached equilibria, w_m is the root-mean-square error for the mth experimental point, and σ^2 is the root-mean-square deviation.

The model that adequately describes experimental data under certain concentration conditions (ligand concentration $2 \cdot 10^{-3}$ mol L^{-1}, metal to ligand concentration ratio 1 : 1 and 1 : 2) was checked under different concentration conditions (ligand concentration $4 \cdot 10^{-3}$ mol L^{-1}, metal to ligand concentration ratios 1 : 1 and 1 : 2). This verification made it possible to refine stoichiometry of the formed complexes, in particular, to choose between the complexes with $m = 1$, $n = 1$ and $m = 2$, $n = 2$ or those with $m = 1$, $n = 1$ and $m = 2$, $n = 1$.

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