Synthesis of New Metallomesogens Based on 3-Ketoesters

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Abstract—Ethyl 3-(4-hydroxyphenyl)-3-ketopropionate was synthesized by acylation of acetoacetic ester with 4-acetoxybenzoyl chloride, followed by cleavage of aroylacetoacetic ester and hydrolysis of the protecting acetate group. Further esterification of the phenol hydroxy group with 4-alkoxybenzoic acids resulted in the synthesis of mesogenic 3-aryl-3-keto ester used to produce copper(II) metallomesogenic complexes.

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Among many types of liquid-crystal compounds it is accepted to define a new class of mesomorphic metallocomplexes as metallomesogens [1–4]. Over the past 20 years an intensive research has been performed on the synthesis of metallomesogens and the study of their properties. This is due to the specific physical and chemical properties of metallomesogens that allow fundamental research of the liquid crystalline state of matter. Since recently, more studies were carried out to find the possibilities of practical application of metallomesogens. For example, metallomesogens were suggested as components of the optical glass with desired properties [4], components of liquid crystal mixtures for luminescent displays [5], and stationary phase in gas chromatography [6, 7].

To produce metallomesogens for application as ligands various 1,3-bifunctional organic compounds are often used [1-3]. For example, well-known ligands for coordination mesomorphic compounds are 1,3-diketones [1-5, 8, 9].

In carrying out targeted research on the synthesis of metallomesogenic complexes [10–12] and analyzing published data we noted that at present the metallomesogens based on 3-ketoesters remain unknown. These substances are structurally related to 1,3-diketones widely used as ligands in the preparation of metallomesogens. We believe that it is logical to expect the possibility of preparation of new types of metallomesogens on the basis of 3-ketoesters.

Previously we obtained homologous 3-(4-al-koxyphenyl)-3-ketopropionates, 3-(4'-pentylbiphenyl)-

3-ketopropanoates and the corresponding copper(II) complexes based on synthesized 3-aryl-3-ketoesters [13, 14] appropriate for testing this assumption. While determining the phase transition temperatures of the synthesized metallocomplexes we found that these compounds do not have the liquid crystal properties [14]. The absence of liquid crystal properties is most likely due to the insufficient number of rings in the hard scaffold of the molecules of these compounds.

The best way to increase the number of rings in the scaffold of mesogenic 3-ketoesters, in our opinion, is to synthesize 3-(4-benzoyloxyphenyl)-3-ketopropanoates. In the compounds of this type the benzene rings are bound with a bridging ester group. It is known that bridging groups in the hard scaffold of a metallomesogen molecule extend temperature limits of existence of the mesophase. This fact is known for many types of metallomesogenic complexes derived from 1,3-dicarbonyl chelating ligands [1–3, 10]. Therefore, we believed that a simultaneous increase in the number of rings and introduction of bridging groups in the mesogenic 3-ketoesters might improve the mesomorphic properties of the corresponding metallocomplexes.

For the synthesis of metallomesogenic complexes based on 3-aryl-3-ketoesters with bridging groups in the hard scaffold it seemed necessary to obtain the 3-(4-hydroxyphenyl)-3-oxopropanoic acid (**IV**), containing a free phenol hydroxy group. The starting compound was 4-acetoxybenzoic acid (**I**). The 4-acetoxybenzoyl chloride (**II**) obtained in the first stage from the acid I by treatment with thionyl chloride was used without purification for the acylation of ethyl acetoacetate. The reaction was carried out in the presence of magnesium chloride and pyridine [15]. The resulting (4-acetoxybenzoyl)acetoacetate (III) was subjected to cleavage by the action of aqueous ammonia in the presence of ammonium chloride. In these conditions not only the Hunsdiecker's splitting proceeded, but hydrolysis of acetate protecting group also occurred. This sequence of operations resulted in ethyl 3-(4-hydroxyphenyl)-3-oxopropanoate **IV** with a free phenol group in a total yield of 32%.



 $R = C_3H_7$ (a), C_4H_9 (b), C_5H_{11} (c), C_6H_{13} (d), C_7H_{15} (e), C_8H_{17} (f), C_9H_{19} (g). DCC is *N*,*N*-dicyclohexylcarbodiimide, DMAP is *N*,*N*-dimethylaminopyridine.

The structure of compound IV was proved by the spectral data. The UV spectrum of this substance exhibits an absorption maximum at 283 nm, which corresponds to the absorption of substituted aromatic ring. The IR spectrum of this compound contains strong vibration bands of the O-H group in the region of 3000–3600 cm⁻¹ confirming the removal of the acetate protecting group in the reaction with aqueous ammonia. In the region of vibrations of the carbonyl group there are two strong bands at 1736 and 1673 cm^{-1} , which correspond to two C=O groups of the ketoester IV. At the successful splitting according to Hunsdiecker hydrolysis of phenol ester occurs, while the 3keto ester is not affected. This is confirmed by the fact that in the ¹H NMR spectrum of the ketoester IV there is no singlet of the acetyl group with intensity corresponding to three protons. At the same time, the proton signals of ethoxy group of the ethyl ester remains in the ¹H NMR spectrum: a triplet at δ 1.19 ppm and a quartet at δ 4.12 ppm.

In the ¹H NMR spectrum of compound **IV** there is a doublet of the aromatic ring protons and a two-proton singlet of C^2H_2 group at δ 3.00 ppm. These data confirm the 3-aryl-3-ketoester structure of compound **IV**.

Further we synthesized a series of esters, Va-Vg, by esterification of phenol IV with 4-alkoxybenzoic acids in the presence of dicyclohexylcarbodiimide and dimethylaminopyridine. The structure of benzoates Va-Vg was confirmed by spectral studies. In the IR spectra of all esters the characteristic vibration bands of the O-H are absent. The IR spectra of homologous esters contain three strong bands of the characteristic vibrations of the C=O groups, for compound Va at at 1730, 1689, and 1627 cm⁻¹. In the ¹H and ¹³C NMR spectra of the benzoates Va–Vg there are the signals of 3-aryl-3-ketoester fragment and the carboxylate residues (Table 1). According to the ¹H NMR spectra, the compounds Va–Vg are mixtures of tautomers with predominance of the keto form (4:1). Thus, for the enol forms of the compounds Va–Vg in the proton spectrum there is a characteristic singlet of the vinyl proton C²H at δ 5.82 ppm and a broad singlet of the proton of OH group at δ 12.65 ppm.

In the synthesis of metallomesogens with 1,3bifunctional ligands the process of complex formation with bivalent metals capable of forming flat square complexes is most often used. Such coordination ensures planarity of the chelate unit, which is important for obtaining substances with liquid crystal properties [1, 10, 11]. As complexing agents for the metallomesogens with 1,3-bifunctional ligands the ions of copper(II), nickel(II), palladium(II) and other metals were suggested [1-10].

We synthesized mesogenic complexes VIa–VIg containing bridging ester groups in the hard scaffold of molecules by the reaction of β -ketoesters Va–Vg with copper(II) acetate. The complexes are dark green crystalline substances, readily soluble in benzene, chloroform, ethyl acetate and sparingly soluble in alcohol. The structures of the synthesized compounds were confirmed by IR and UV spectra and elemental analysis (Table 2).

The UV absorption spectra of the complexes VIa– VIg contain an absorption maximum at 270-277 nm. The absorption maxima positions do not differ from those in the spectra of the initial β -ketoesters Va–Vg. Most likely, they correspond to the absorption of aromatic fragment of the ligand.

The IR spectra of compounds **VIa–VIg** contain the bands of stretching vibrations of the benzoate C=O bond at 1730-1720 cm⁻¹. The conjugated system of the bonds of the chelate ring induces a number of strong bands in the region of 1600-1460 cm⁻¹. Among other well-identifiable characteristic vibration bands in the IR spectra of chelates **VIa–VIg**, for example, vibration bands of C-H bonds of the aromatic and alkyl substituents in the region of 3100–2850 cm⁻¹ and C–O bonds at 1260–1160 cm⁻¹ can be specified. In the synthesis, isolation, and preparation of analytical samples of the copper(II) complexes **VIa–VIg** we used water and various alcohols. These agents are known [16, 17] to be sometimes included in the complex compounds. The lack of absorption bands of O–H in

the IR spectra of the synthesized compounds **VIa–VIg** indicates the absence of coordinated water or alcohol in these complexes. These data are consistent with the data of elemental analysis on the percentage of copper in the resulting complexes.

Mesomorphic properties of the synthesized compounds. Investigation of phase transitions in the synthesized compounds showed that the β -ketoesters **Va–Vg** are characterized by the mesomorphism. These compounds form mainly the monotropic smectic phase. We found the existence in benzoate **Vf** of a thermotropic smectic phase A, in benzoate **Va**, a monotropic nematic phase. The formation of mesophases by two-ring mesogens with different 1,3-bifunctional groups has been found previously [18, 19]. The liquid-crystalline state in these materials is likely stabilized due to the formation of additional quasi-cycle with involvement of the 1,3-bifunctional group [18, 19].

In the study of phase transitions of the synthesized chelates **VIa–VIg** we found that for compounds **VIa** and **VIb** only the transition to isotropic liquid phase is typical. Increasing the number of carbon atoms in the alkoxide chain of the mesogenic molecules led to stabilization of complexes **VIc–VIg** in liquid crystal-line state. Moreover, these compounds are characterized by the formation of a nematic phase. This fact is quite important, as most of the known columnar metallomesogens are characterized by smectic mesomorphism [1–3], which largely limits their application.

As mentioned above, the copper(II) complexes with 3-(4-alkoxyphenyl)-3-ketoester and 3-(4-pentylbiphenyl)-3-ketoesters [14] do not form liquid crystal phases. The introduction of an additional benzene ring and the bridging of the ester group in the rigid scaffold of the molecule increases mesogenic ability of the chelating 3-ketoesters **VIb–VIg**, which affects positively the mesomorphic properties of the corresponding metallocomplexes.

Thus, we established that the mesogenic 3-ketoesters can be used as chelating ligands in the preparation of metallomesogens.

EXPERIMENTAL

IR spectra were recorded in the region of 400-4000 cm⁻¹ from tablets with potassium bromide on a Nicolet FTIR Nexus spectrometer, UV spectra from ethanol solutions were taken on a Specord M500 spectro-photometer. NMR spectra were recorded on a Bruker

Comp. no.	R	Yield, %	Phase transition temperature, °C ^a	UV spectrum, λ _{max} , nm	IR spectrum, v, cm ⁻¹	¹ H NMR spectrum, δ, ppm (<i>J</i> , Hz) ^b	¹³ C NMR spectrum, δ, ppm
Va	C ₃ H ₇	73	Cr 71 I (I 65 N 55 SmA 50 Cr)	270	3077, 2965, 2930, 2871 (C–H), 1730, 1689, 1627 (C=O), 1606, 1576, 1505 (C=C _{arom})	1.04 t (3H, CH ₃ , <i>J</i> 7), 1.82 sextet (2H, CH ₂ , <i>J</i> 7), 4.02 t (2H, O <u>CH₂C₂H₅, <i>J</i> 7), 1.21 t (3H, CH₃, <i>J</i> 7) 4.15 q (2H, O<u>CH₂CH₃, <i>J</i> 7), 4.03 s (2H, C²H₂), 7.04 d (2H, Ar, <i>J</i> 9), 7.36 d (2H, Ar, <i>J</i> 9), 8.04 d (2H, Ar, <i>J</i> 9), 8.12 d (2H, Ar, <i>J</i> 9)</u></u>	10.60, 14.23 (CH ₃); 22.96 (CH ₂); 46.06 ($C^{2}H_{2}$ ketone); 61.37, 70.19 (OCH ₂); 87.58 (= $C^{2}H$, enol) 114.94, 121.97, 122.70, 128.03, 130.69, 132.86, 134.61, 155.85 (C_{arom}); 164.31, 164.39, 168.00, 191.95 (C =O, C^{3} , ketone, enol)
Vb	C ₄ H ₉	91	Cr 85 I (I 77 SmA 57 Cr)	270	3118, 3061, 2921, 2870, 2854 (C–H), 1727, 1685, 1627 (C=O), 1608, 1580, 1514 (C=C _{arom})	0.99 t (3H, CH ₃ , <i>J</i> 7) 1.50 sextet (2H, CH ₂ , <i>J</i> 7), 1.79 quintet (2H, CH ₂ , <i>J</i> 7), 4.07 t (2H, O <u>CH₂</u> C ₃ H ₇ , <i>J</i> 7), 1.21 t (3H, CH ₃), 4.15 q (2H, O <u>CH₂</u> CH ₃ , <i>J</i> 7), 4.04 s (2H, C ² H ₂), 7.04 d (2H, Ar, <i>J</i> 9), 7.36 d (2H, Ar, <i>J</i> 9), 8.04 d (2H, Ar, <i>J</i> 9), 8.12 d (2H, Ar, <i>J</i> 9)	14.00, 14.23 (CH ₃); 19.72, 31.73 (CH ₂); 46.08 (C ² H ₂ , ketone); 61.41, 68.48 (OCH ₂); 87.61 (=C ² H, enol); 114.98, 121.96, 122.72, 128.05, 130.71, 132.87, 134.62, 155.87 (C _{arom}); 164.36, 164.44, 168.07, 192.05 (C=O, C ³ , ketone, enol)
Vc	C ₅ H ₁₁	73	Cr 84 I (I 76 SmC 70 Cr)	271	3113, 3062, 2955, 2871 (C–H), 1728, 1647, 1619 (C=O), 1607, 1579, 1513 (C=C _{arom})	0.94 t (3H, CH ₃ , J 7), 1.36– 1.50 м (4H, CH ₂), 1.81 quintet (2H, CH ₂ , J 7), 4.06 t (2H, O <u>CH₂C₄H₉, J 7), 1.21 t (3H, CH₃, J 7), 4.15 q (2H, OCH₂CH₃), 4.03 s (2H, C²H₂), 7.03 d (2H, Ar, J 9), 7.36 d (2H, Ar, J 9), 8.04 d (2H, Ar, J 9), 8.12 d (2H, Ar, J 9)</u>	14.20, 14.23 (CH ₃); 22.97, 28.74, 29.38 (CH ₂); 46.07 (C ² H ₂ , ketone); 61.38, 68.74 (OCH ₂); 88.01 (=C ² H, enol); 114.95, 121.99, 122.70, 128.05, 130.70, 132.88, 134.64, 155.86 (C _{arom}); 164.32, 164.41, 167.99, 191.94 (C=O, C ³ , ketone, enol)
VΓ	C ₆ H ₁₃	70	Cr 92 I (I 87 SmA 68 Cr)	276	3111, 3060, 2931, 2869 (C–H), 1728, 1685, 1620 (C=O), 1607, 1579, 1513 (C=C _{arom})	0.92 t (3H, CH ₃ , J 7), 1.30– 1.40 M (4H, CH ₂), 1.48 quintet (2H, CH ₂ , J 7), 1.80 quintet (2H, CH ₂ , J 7), 4.06 t (2H, OCH ₂ C ₅ H ₁₁ , J 7), 1.21 t (3H, CH ₃ , J 7), 4.15 q (2H, OCH ₂ CH ₃ , J 7), 4.04 s (2H, C ² H ₂), 7.03 d (2H, Ar, J 9), 7.36 d (2H, Ar, J 9), 8.04 d (2H, Ar, J 9), 8.12 d (2H, Ar, J 9)	14.22 (CH ₃); 23.13, 26.26, 29.65, 32.16 (CH ₂); 46.07 (C ² H ₂ , ketone); 61.40, 68.76 (OCH ₂); 87.60 (=C ² H, enol); 114.96, 121.95, 122.72, 128.05, 130.71, 132.87, 134.62, 155.86 (C _{arom}); 164.35, 164.42, 168.05, 192.03 (C=O, C ³ , ketone, enol)

Table 1. Physicochemical characteristics of 3-ketoesters Va-Vg

Table 1. (Contd.)

0		Vield	Phase transition	IIV spectrum	IR spectrum	¹ H NMR spectrum & ppm	¹³ C NMR spectrum
Comp.	R	0/0	temperature °C ^a	λ nm	$v \text{ cm}^{-1}$	$(I \text{ Hz})^{b}$	δ npm
110.		/0	temperature, e	romax, min	v, em	(0,112)	o, ppm
Ve	C_7H_{15}	82	Cr 95 I	270	3120, 3062, 2956,	0.93 t (3H, CH ₃ , <i>J</i> 7), 1.33–	14.26 (CH ₃); 23.14,
			(I 89 SmA 83 Cr)		2944, 2925, 2856	1.45 м (6Н, СН ₂), 1.50	26.56, 29.65, 29.69,
					(C–H), 1728, 1648,	quintet (2H, CH ₂ , <i>J</i> 7), 1.83	32.38 (CH ₂); 46.06
					1621 (C=O), 1606,	quintet (2H, CH ₂ , <i>J</i> 7), 4.08	$(C^2H_2, \text{ ketone}); 61.36,$
					1580, 1513	t (2H, O <u>CH</u> ₂ C ₆ H ₁₃ , <i>J</i> 7),	68.75 (OCH ₂); 87.58
					(C=C _{arom})	1.23 t (3H, CH ₃ , <i>J</i> 7), 4.17	$(=C^{2}H, enol); 114.94,$
						q (2H, OCH ₂ CH ₃ , <i>J</i> 7), 4.05	121.96, 122.70, 128.03,
						s (2H, C ² H ₂), 7.05 d (2H,	130.69, 132.85, 134.61,
						Ar, J9), 7.38 d (2H, Ar, J	155.85 (Carom); 164.30,
						9), 8.06 d (2H, Ar, <i>J</i> 9),	164.40, 167.98, 191.93
						8.14 d (2H, Ar, J9)	$(C=O, C^3, ketone, enol)$
Vf	C_8H_{17}	82	Cr 87 SmA 92 I	270	3113, 3062, 2955,	0.90 t (3H, CH ₃ , J7), 1.25-	14.23, 14.27 (CH ₃);
					2871 (С-Н), 1728,	1.43 м (8Н, СН ₂), 1.48	23.17, 26.61, 29.70,
					1647, 1619 (C=O),	quintet (2H, CH ₂ , J7), 1.80	29.84, 29.95, 32.41
					1607, 1579, 1513	quintet (2H, CH ₂ , J7), 4.06	(CH ₂); 46.07 (C ² H ₂ ,
					(C=C _{arom})	t (2H, O <u>CH</u> ₂ C ₇ H ₁₅ , <i>J</i> 7),	ketone); 61.36, 68.75
						1.21 t (3H, CH ₃ , J7), 4.15	(OCH ₂); 87.58 (=C ² H,
						q (2H, OCH ₂ CH ₃ , <i>J</i> 7), 4.03	enol); 114.94, 121.97,
						s (2H, C ² H ₂), 7.03 d (2H,	122.70, 128.03, 130.69,
						Ar, J9), 7.36 d (2H, Ar, J	132.86, 134.63, 155.85
						9), 8.04 d (2H, Ar, <i>J</i> 9),	(Carom); 164.30, 164.40,
						8.12 d (2H, Ar, J 9)	167.98, 191.93 (C=O,
							C ³ , ketone, enol)
Vg	C_9H_{19}	75	Cr 101 I	270	3106, 3061, 2921,	0.89 t (3H, CH ₃ , J7), 1.25-	14.23, 14.28 (CH ₃);
			(I 97 SmA 72 Cr)		2853 (С-Н), 1727,	1.40 м (10Н, СН ₂), 1.48	23.17, 26.59, 29.70,
					1684, 1630 (C=O),	quintet (2H, CH ₂ , J7), 1.80	29.84, 29.98, 30.13,
					1609, 1580, 1514	quintet (2H, CH ₂ , J7), 4.06	32.45 (CH ₂); 46.07
					(C=C _{arom})	t (2H, O <u>CH</u> ₂ C ₈ H ₁₇ , <i>J</i> 7),	(C ² H ₂ , ketone); 61.36,
						1.21 t (3H, CH ₃), 4.15 q	68.75 (OCH ₂); 87.58
						(2H, OCH ₂ CH ₃ , <i>J</i> 7), 4.03 s	(=C ² H, enol); 114.95,
						(2H, C ² H ₂), 7.03 d (2H, Ar,	121.99, 122.69, 128.03,
						J 9), 7.36 d (2H, Ar, J 9),	130.69, 132.86, 134.63,
						8.04 d (2H, Ar, J 9), 8.12 d	155.86 (Carom); 164.30,
						(2H, Ar, <i>J</i> 9)	164.41, 167.97, 191.91
							$(C=O, C^3, ketone, enol)$

^a Here and hereinafter Cr is crystal phase; N is nematic phase; SmA, SmC are smectic phase of A or C type; *I* is isotropic liquid phase. In parentheses the type of phase transitions and temperature of monotropic transitions are given. ^b Proton signals given correspond to the keto form of 1,3-dicarbonyl compound Va–Vg.

Avance 500 instrument (operating frequency 500.13 MHz for ¹H and 125.75 MHz for ¹³C) from solutions in deuterodioxane. Chemical shifts are given relative to TMS as internal reference. The reaction course and purity of the compounds was monitored by TLC on Merck Kieselgel 60 F254 plates. The melting points and phase transitions were determined on a heating

bench connected to the polarizing microscope. Determining the mesophase type was performed by comparing the observed textures with appropriate references [20]

Ethyl 3-(4-hydroxyphenyl)-3-oxopropanoate (IV). To a heterogeneous mixture of 12.10 g (0.127 mol) of

Comp. no.	R	Yield, %	Phase transition temperature, °C ^a	UV spectrum, λ_{max} , nm	IR spectrum, v, cm ⁻¹	Found Cu, %/ Calculated Cu, %
VIa	C ₃ H ₇	84.5	Cr 218 I (decomp.)	276	3074, 2977, 2933, 2878 (C–H), 1730 (C=O, ester), 1604, 1575, 1538, 1510, 1497 (C=O, C=C, C=C _{arom}), 1166, 1197, 1267 (C–O)	8.00/7.92
VIb	C ₄ H ₉	80	Cr 219 I (decomp.)	270	2958, 2931, 2872 (C–H), 1728, (C=O, ester), 1604, 1575, 1542, 1510, 1498 (C=O, C=C, C=C _{arom}), 1164, 1199, 1268 (C–O)	8.07/7.65
VIc	C_5H_{11}	93	Cr 223 I (I 166 N 151 Cr)	271	3072, 2960, 2942, 2871 (C–H), 1724 (C=O, ester), 1606, 1577, 1545, 1512, 1498 (C=O, C=C, C=C _{arom}), 1163, 1199, 1261 (C–O)	7.37/7.40
VId	C ₆ H ₁₃	85	Cr 209 N 220 I	270	2929, 2862 (C–H), 1725 (C=O, ester), 1606, 1577, 1541, 1514, 1497 (C=O, C=C, C=C _{arom}), 1162, 1196, 1263 (C–O)	7.33/7.17
VIe	C ₇ H ₁₅	91	Cr 196 N 211 I	277	3066, 2936, 2865 (CH), 1732 (C=O, ester), 1603, 1580, 1569, 1531, 1511, 1494 (C=O, C=C, C=C _{arom}), 1162, 1194, 1257 (C-O)	6.84/6.95
VIf	C_8H_{17}	84	Cr 179 N 203 I	270	2924, 2856 (C–H), 1726 (C=O, ester), 1605, 1580, 1531, 1510, 1495 (C=O, C=C, C=C _{arom}), 1162, 1193, 1258 (C–O)	7.21/6.74
VIg	C9H19	88	Cr 173 N 196 I	269	2923, 2851 (C–H), 1721 (C=O, ester), 1605, 1576, 1534, 1513, 1497 (C=O, C=C, C=C _{arom}), 1165, 1199, 1257 (C–O)	6.64/6.55

Table 2. Physicochemical characteristics of metallocomplexes VIa-VIg

magnesium chloride and 14.6 ml (0.115 mol) of ethyl acetoacetate in 270 ml of methylene chloride at cooling to 5°C under vigorous stirring was added dropwise 10.0 ml of pyridine. The resulting reaction mixture was stirred with cooling in ice bath for 40 min. Then a solution of acetoxybenzoyl chloride II, prepared from 20.67 g (0.115 mol) of 4-atcetoxybenzoic acid I and an excess of thionyl chloride, in 40 ml of methylene chloride was added dropwise. The reaction mixture was stirred for 2.5 h with cooling in ice bath, left overnight at room temperature and then diluted with 250 ml of water. The organic layer was separated, the aqueous layer was extracted with methylene chloride. The combined organic extracts were washed with water. Methylene chloride was distilled off under a reduced pressure. The residue containing aroylacetoacetic ether III was dissolved in 100 ml of ethanol. To this solution 30 ml of water, 30 ml of 25% ammonia solution, and 8.06 g (0.151 mol) of

ammonium chloride was added. The reaction mixture was kept at room temperature for 4 h and then treated in succession with 30 ml of concentrated hydrochloric acid and 100 ml of water. Organic compound was repeatedly extracted with toluene. The toluene solution was washed with water and then passed through a column with alumina. Eluting with toluene separated most of the impurities (TLC control). The main product was isolated eluting with ethyl acetate and petroleum ether (1:3). The resulting solution was further purified by boiling with activated charcoal. After removal of the solvent in vacuo 7.6 g of oily β -ketoester IV was obtained, yield 32%. UV spectrum (λ_{max} , nm): 283. IR spectrum, v, cm⁻¹ (the film between KBr plates): 3000-3600 br (OH), 2983, 2940 (C-H), 1736, 1673 (C=O), 1604, 1583, 1515 (C=Sar.). ¹H NMR spectrum, δ, ppm: 1.19 t (3H, J7 Hz, CH₃), 3.00 s (2H, COCH₂CO), 4.12 q (2H, J 7 Hz, OCH₂), 6.81 d (2H, J 8.5 Hz), 7.84 d (2H, J 8.5 Hz), aromatic protons.

Ethyl 3-[4-(4'-propoxy)benzoyloxyphenyl]-3-oxopropanoate (Va). To a mixture of 0.52 g (2.89 mmol) of 4-propoxybenzoate, 0.55 g (2.64 mmol) of phenol IV, and 0.60 g (2.91 mmol) of N,N'-dicyclo-hexylcarbodiimide in 20 ml of methylene chloride was added in a catalytic amount N,N-dimethylaminopyridine. The reaction mixture was stirred for 25 h. The precipitate of dicyclohexylurea was removed by filtration through a layer of aluminum oxide, the sorbent was then washed additionally with methylene chloride. The combined filtrate was recrystallized from 2propanol. The yield of ester Va 0.66 g (73%).

Compound **Vb–Vg** were obtained by similar procedure. The properties of esters **Va–Vg** are shown in Table 1.

Copper(II) bis-{1-ethoxy-3-[4'-(4"-propyloxybenzovl)phenvl|propane-1,3-dionate} (VIa). To a solution of 0.203 g (0.549 mmol) of β -ketoester Va in 10 ml of 2-propanol under reflux while stirring was added 0.075 g (0.375 mmol) of copper(II) acetate monohydrate. The stirring under reflux was continued for 20 min, then 5 ml of water was added. After 15 min, the dilution with water (10 ml) was repeated, and the mixture was stirred under reflux for 10 min. The precipitated complex compound was filtered off, washed successively with 2-propanol, a mixture of 2propanol and water (1:1), and then with water. After drying in air and in a vacuum 0.186 g of compound VIa was obtained. Yield 84.5%. To obtain an analytical sample the material was recrystallized from a mixture of chloroform and 2-propanol.

Compounds **VIc–VIg** were obtained by similar procedure. Properties of chelates **VIa–VIg** are shown in Table 2.

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