Russian Chemical Bulletin, International Edition, Vol. 58, No. 6, pp. 1241—1247, June, 2009

Synthesis and complexing ability of 2-(2-ethoxycarbonyl-3-oxo-3-polyfluoroalkylprop-1-enylamino) benzoic acids*

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The condensation of ethyl 2-ethoxymethylidene-3-oxo-3-polyfluoroalkylpropionates with 2-aminobenzoic acid occurs at the ethoxymethylidene substituent and gives 2-(2-ethoxycarbonyl-3-oxo-3-polyfluoroalkylprop-1-enylamino)benzoic acids. These compounds serve as new *O*,*N*,*O*-tridentate ligands capable of forming nickel(II) and copper(II) complexes.

Key words: 2-ethoxymethylidene-3-oxo-3-polyfluoroalkylpropionates, 2-aminobenzoic acid, ligands, nickel complexes, copper complexes, organofluorine compounds.

1,3-Dicarbonyl compounds and their amino derivatives are commonly recognized as templates for the formation of metal complexes.[1—5] The complexing ability of these compounds is responsible for various aspects of their practical use, including for the separation of mixtures of rare-earth metals, for the extraction fluorometric determination of elements, and as shift-reagents in NMR spectroscopy.[1,2] Metal chelates of 1,3-dicarbonyl compounds are used as antioxidants, lubricating oil additives, and catalysts for the oxidation, addition, and polymerization,[1,2] as well as for the preparation of metal oxide coatings, the introduction of metals into high-temperature superconducting films,[6,7] and the design of electroluminescent diodes.[8]

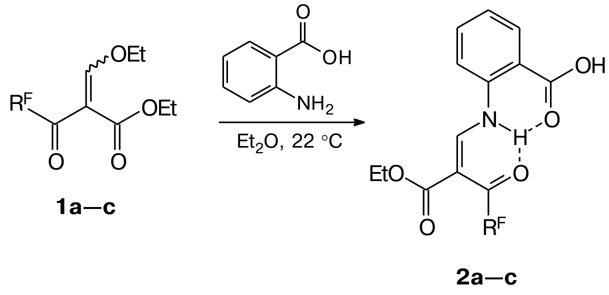
Nowadays, the design of multidentate ligands capable of forming coordination clusters and supramolecular structures assumes great importance.[9] Functionalized derivatives of 1,3-dicarbonyl compounds containing reactive groups, which assist in introducing additional coordination centers into the molecules, are convenient building blocks for this purpose. Readily accessible 2-alkoxymethylidene-3-oxoalkanoates can be used as such compounds. A series of mono-,[10] bi-,[11-13] tri-,[14] and hexadentate ligands were synthesized starting from nonfluorinated alkyl 2-ethoxymethylidene-3-oxoalkanoates.[15]

Previously, we have synthesized ethyl 2-ethoxymethylidene-3-oxo-3-polyfluoroalkylpropionates and used these compounds in the reactions with various monoamines to prepare ethyl 2-alkyl- and ethyl 2-(het)arylaminomethylidene-3-oxo-3-polyfluoroalkylpropionates.[16] It was found that the latter compounds, unlike nonfluorinated analogs,[10] do not form stable metal complexes.

In the present study, we used 2-aminobenzoic acid, whose carboxy group can serve as an additional coordination center, as the nucleophilic agent in the reactions with ethyl 2-ethoxymethylidene-3-oxo-3-fluoroalkylpropionates **1a—c**.

Thus, esters **1a—c** easily undergo the condensation with 2-aminobenzoic acid at the ethoxymethylidene substituent in diethyl ether at room temperature to form 2-(2-ethoxycarbonyl-3-oxo-3-polyfluoroalkylprop-1-enylamino)benzoic acids **2a—c** (Scheme 1). Products **2a—c** are crystalline compounds, which were isolated and purified by the crystallization from ethanol.

Scheme 1



$R^F = CF_3$ (**a**), $H(CF_2)_2$ (**b**), C_3F_7 (**c**).

The NH proton of acids **2a—c** is rather labile and can be involved in different tautomeric transformations, as well as in inter- and intramolecular hydrogen bonding. Due to this fact, acids **2a—c** can be involved in keto-enol

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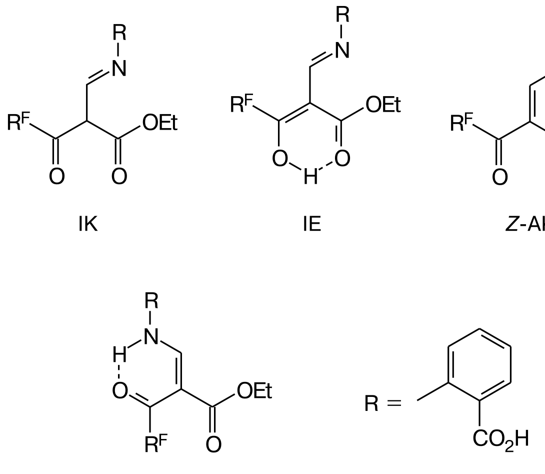
* Dedicated to Academician O. N. Chupakhin on the occasion of his 75th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1207—1212, June, 2009.

and amino-imino tautomerism and can exist as imino-ketone (IK), imino-enol (IE), and/or amino-ketone (AK) tautomers. In addition, the AK tautomer can exhibit *Z*,*E* isomerism resulting from different positions of the substituents with respect to the C=C bond. The *Z* isomer (*Z*-AK) is stabilized by an intramolecular hydrogen bond with the involvement of the ethoxycarbonyl substituent, whereas the *E* isomer (*E*-AK) is stabilized by an intramolecular hydrogen bond with the polyfluoroacyl fragment.



The solid-state structures of acids **2a—c** were studied by IR spectroscopy and X-ray diffraction. Thus, the IR spectra of compounds **2a—c** show three groups of intense absorption bands at 1709—1702, 1691—1682, and 1663—1640 cm^{-1} assigned to the stretching vibrations of three nonequivalent carbonyl groups (CO_2Et, CO_2H, and $R^FC=O$, respectively) and intense absorption bands at 3150—3086 cm^{-1} corresponding to the stretching vibrations of NH and OH groups involved in hydrogen bonding.[17] The low-frequency shift of the absorption bands of the carbonyl groups is attributed to their conjugation with the C=C bond and the involvement of two of these groups in the formation of intramolecular hydrogen bonds with the NH group. These IR spectroscopic data are in better agreement with the AK isomers of acids **2a—c**, which was confirmed by the X-ray diffraction study of compound **2a** (Figs 1 and 2).

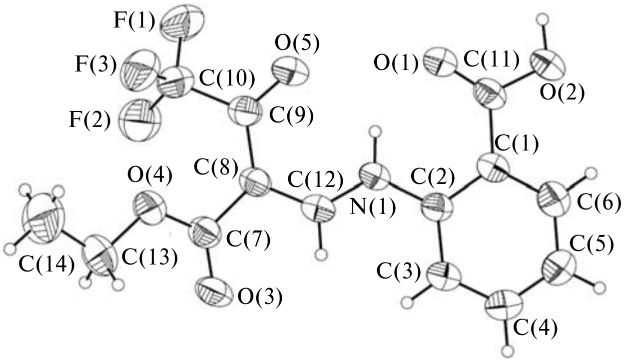


Fig. 1. Molecular structure of compound **2a** with displacement ellipsoids drawn at the 50% probability level.

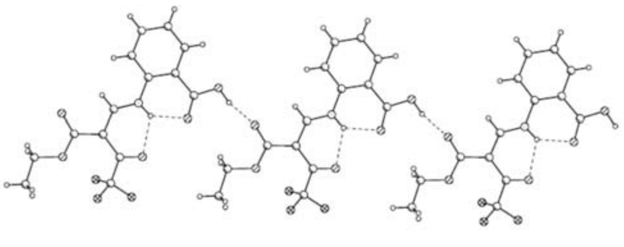


Fig. 2. Hydrogen bonds in the crystal structure of compound **2a** along the diagonal of the *ab* plane based on the X-ray diffraction data.

According to the X-ray diffraction data, acid **2a** exists in the crystal as the *s-cis*,*s-cis* conformer of the *E*-AK isomer with the trifluoromethyl and ethoxy substituents in adjacent positions. The NH hydrogen atom is involved in two intramolecular hydrogen bonds with the oxygen atom of the trifluoroacetyl substituent (N(1)—H(1)...O(5)) and the oxygen atom of the carboxy group (N(1)—H(1)...O(1)) (see Fig. 1, Table 1).

In the crystal structure, molecules **2a** form chains through strong intermolecular hydrogen bonds between the oxygen atom of the ethoxycarbonyl fragment of one molecule and the hydrogen atom of the carboxy group of another molecule O(2)—H(2)...O(3) #1 [$x + 1, y + 1, z$] (see Fig. 2, Table 1).

Then the structures of compounds **2a—c** were studied in a chloroform solution by IR and NMR spectroscopy.

In the IR spectra of compounds **2a—c** recorded in a 3% $CHCl_3$ solution, the absorption bands of virtually all characteristic groups are substantially broadened. This fact indicates that the acids undergo structural changes upon dissolution.

The ^{1}H NMR spectra of compounds **2a—c** measured in $CDCl_3$ show two sets of signals, the signals for the protons of the NH and CH= groups being observed at low field ($\delta_{CH} \approx 8.51$—8.72, $\delta_{NH} \approx 12.78$—13.60) as doublets with the spin-spin coupling constant of ~14 Hz. The ^{19}F NMR spectra of compounds **2a—c** are also characterized by the doubling of the resonances for the fluorine nuclei. It can

Table 1. Parameters of D—H...A hydrogen bonds in the crystal packing of compound **2a**

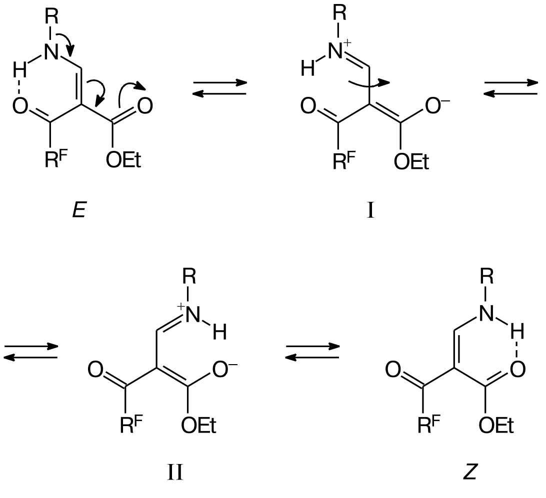
D—H...A	D—H	H...A	D—H...A /deg	D...A /Å
	Å			
N(1)—H(1)...O(1)	0.89(2)	1.93(2)	137.3(1.4)	2.656(2)
N(1)—H(1)...O(5)	0.89(2)	2.10(2)	124.4(1.4)	2.711(2)
O(2)—H(2)...O(3)$^{\#1}$	0.92(2)	1.75(2)	166.1(1.9)	2.648(2)

Note: The symmetry code$^{\#1}$: [$x + 1, y + 1, z$].

be concluded that in a chloroform solution, compounds **2a—c** exist as mixtures of *Z* and *E* isomers of the AK tautomer, as opposed to the solid state, in which only one isomeric form (*E*-AK) is observed.

It is known that compounds containing functional groups at the double bond, which are responsible for the polarization of this bond or its involvement in the conjugation system, have a substantially lower barrier to rotation about the C=C bond.[18,19] This is particularly typical of enamino ketones, the so-called push-pull olefins, which contain electron-withdrawing substituents on one side and electron-donating substituents on another side. In these compounds, the formally double C=C bond has a partial single-bond character due to the electron delocalization. As a result, the barrier to rotation about the double bond is substantially lower than that in normal olefins.[18] In the case under consideration, the crystallization affords apparently only the conformational *E* isomer, which is partially isomerized to the *Z* isomer upon dissolution. Presumably, the isomerization occurs through the resonance structures I and II (Scheme 2).

Scheme 2



R = 2-$C_6H_4CO_2H$

The assignment of the *Z* and *E* isomers in the ^{1}H NMR spectra of compounds **2a—c** was made based on the data obtained previously for esters of 2-alkyl-, 2-aryl-, and 2-hetarylaminomethylidene-3-oxo-3-polyfluoroalkylpropionic acids,[16] according to which the CH and NH protons of the *E* isomer are observed at lower field compared to the corresponding protons of the *Z* isomer. The large shifts δ_{NH} for the *E* isomer are indicative of a stronger intramolecular hydrogen bond in this isomer and, consequently, of the higher stability of the *E* isomer.

Based on the analysis of the ^{19}F NMR spectroscopic data for 2-alkyl-, 2-aryl-, and 2-hetarylaminomethylidene-3-oxo-3-polyfluoroalkylpropionates,[16] the signals of the CF_3 and α-CF_2 groups of the *Z* isomer containing the free polyfluoroacyl group are characterized by a downfield shift with respect to the corresponding signals of the hydrogen-bonded polyfluoroacyl group in the *E* isomer. Thus, the ^{19}F NMR spectrum of compound **2a** recorded in $CDCl_3$ shows a signal of the trifluoromethyl group at δ 89.79 assigned to the *Z* isomer and a signal at δ 88.91 assigned to the *E* isomer. The similar assignment was made for compounds **2b,c**.

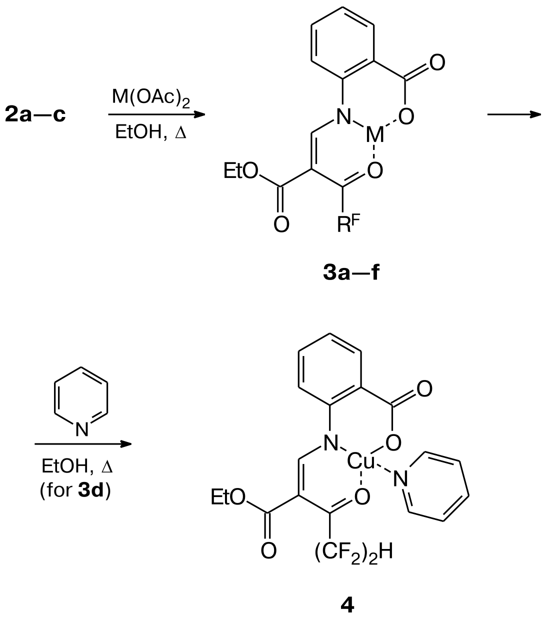
Table 2. Content of the *Z* and *E* isomers in solutions of compounds **2a—c** in $CDCl_3$ according to the NMR

Compound	R^F	Content (%)	
		E	*Z*
2a	CF_3	62	38
2b	$(CF_2)_2H$	60	40
2c	C_3F_7	53	47

Therefore, we showed that compounds **2a—c** exist in a $CDCl_3$ solution as mixtures of *Z* and *E* isomers, with the more stable *E* isomer predominating (Table 2). An increase in the length of the polyfluoroalkyl substituent leads to an increase in the percentage of the *Z* isomer.

We investigated the complexing ability of acids **2a—c** with respect to transition metal cations. The structures of these compounds suggest that they can form metal complexes through the coordination with the involvement of the *O*,*N*,*O*-tridentate fragment and the salt formation at the carboxy substituent.

Scheme 3



3: R^F = CF_3, M = Ni (**a**), Cu (**b**); R^F = $(CF_2)_2H$, M = Ni (**c**), Cu (**d**); R^F = C_3F_7, M = Ni (**e**), Cu (**f**).

The treatment of acids **2a—c** with nickel(II) and copper(II) salts afforded compounds **3a—f** (Scheme 3).

The elemental analysis data for compounds **3a—f** dried at 60 °C correspond to the composition ML • H_2O, where L is the dideprotonated ligand. The elemental analysis data obtained after careful drying of compounds **3** at 170—180 °C are consistent with the composition ML.

A comparative analysis of the IR spectra of ligands **2a—c** and complexes **3a—f** revealed substantial differences in the absorption band regions corresponding to the vibrations of the carbonyl group of the acidic fragment. Thus, the band of the carbonyl group of the carboxy substituent in ligands **2** is observed at 1663—1640 cm^{-1}, whereas the absorption of the carbonyl groups of complexes **3** is manifested at 1589—1583 cm^{-1}, which is indicative of their carboxylate nature. The vibrations of the ethoxycarbonyl group in ligands **2** and complexes **3** are observed in almost the same regions (1709—1702 cm^{-1}). The absorption bands of the carbonyl groups of the polyfluoroacyl moieties in complexes **3** are characterized by small low-frequency shifts (1690—1680 cm^{-1}) compared to the corresponding bands of free ligands **2** (1691—1682 cm^{-1}). The IR spectra of completely dried compounds **3a—f** show also broadened absorption bands in the 3460—3128 cm^{-1} region corresponding to the stretching vibrations of the hydroxy groups of a coordinated water molecule. The difficulties in eliminating water from complexes **3a—f** are apparently attributed to the fact that the coordination number 4 is most typical of the divalent copper cation, and the water molecule is required for the saturation of the copper coordination sphere.

Unfortunately, we failed to interpret the ^{1}H NMR spectra of complexes **3a—f** because of a strong broadening of the signals. In addition, we failed to grow crystals of complexes **3a—f** suitable for X-ray diffraction.

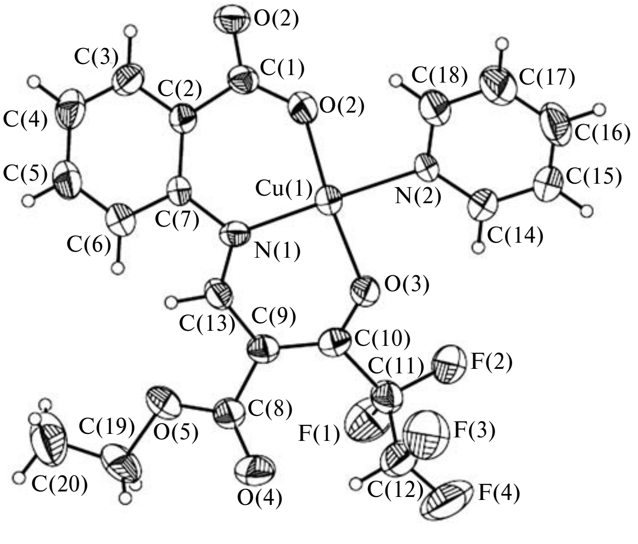


Fig. 3. Molecular structure of compound **4** with displacement ellipsoids drawn at the 50% probability level.

Table 3. Selected geometric parameters of the coordination unit in the crystal packing of compound **4**

Bond	*d*/Å	Angle	ω/deg
Cu(1)—O(1)	1.925(3)	O(1)—Cu(1)—O(3)	147.52(14)
Cu(1)—N(1)	1.935(4)	N(1)—Cu(1)—N(2)	177.77(19)
Cu(1)—O(3)	1.942(2)	O(1)—Cu(1)—N(1)	91.46(12)
Cu(1)—N(2)	2.014(3)	N(1)—Cu(1)—O(3)	90.11(14)
Cu(1)—O(2)$^{\#1}$	2.219(3)	O(1)—Cu(1)—N(2)	90.33(12)
O(3)—C(10)	1.259(4)	O(3)—Cu(1)—N(2)	89.08(14)
C(9)—C(10)	1.393(5)	O(1)—Cu(1)—O(2)$^{\#1}$	104.60(11)
C(9)—C(13)	1.420(5)	N(1)—Cu(1)—O(2)$^{\#1}$	88.81(12)
N(1)—C(13)	1.297(5)	O(3)—Cu(1)—O(2)$^{\#1}$	107.87(14)
O(1)—C(1)	1.274(4)	N(2)—Cu(1)—O(2)$^{\#1}$	89.46(13)
		C(13)—N(1)—Cu(1)	125.2(3)
		C(7)—N(1)—Cu(1)	117.6(3)
		C(10)—O(3)—Cu(1)	129.7(3)
		C(1)—O(1)—Cu(1)	127.6(2)
		C(10)—C(9)—C(13)	120.0(4)
		C(14)—N(2)—Cu(1)	124.6(3)
		C(18)—N(2)-Cu(1)	117.4(3)

Note: The symmetry code$^{\#1}$: [$^{\#1}$ *x*, −*y*, *z* + 1/2], $^{\#2}$: [*x*, −*y*, *z* − 1/2].

To confirm the structures of products **3a—f**, we synthesized complex **4** from compound **3d** and pyridine (see Scheme 3). The X-ray diffraction study of complex **4** showed that the molecule contains a tridentate unit, in which the copper(II) cation is coordinated by the hydroxy oxygen atom, the nitrogen atom of the aminobenzoic fragment, and the oxygen atom of the fluoroacyl substituent (Fig. 3). The saturation of the coordination sphere of the copper(II) cation is achieved as a result of coordination by the nitrogen atom of pyridine serving as a coligand. The coordination environment of the copper(II)

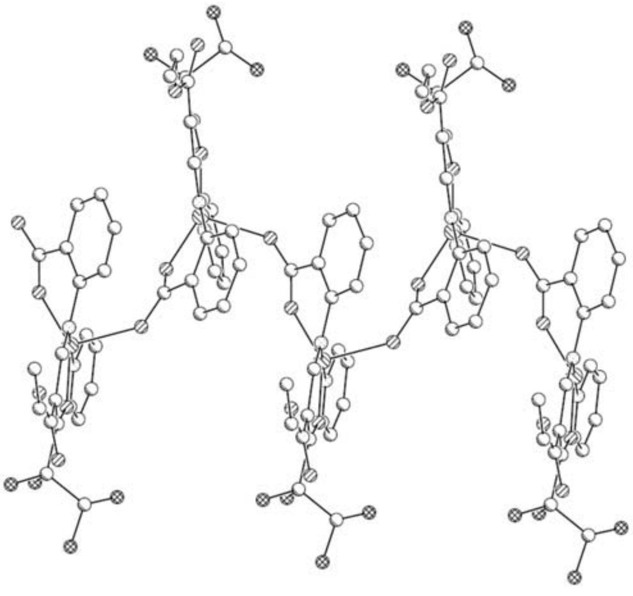


Fig. 4. Molecular packing of compound **4** along the *c* axis.

atom can be described as a distorted square pyramid, whose apical position is occupied by the oxygen atom O(2) #1 [x, $-y$, $z + 1/2$] of the adjacent molecule. The dihedral angle between the planes of the O(1)—Cu(1)—N(1) and O(3)—Cu(1)—N(1) fragments is 32.46°. The chelate ring at the tetrafluoroethyl substituent is characterized by a high degree of electron density delocalization, which is reflected in an essential equalization of the pairs of the C(9)—C(13), C(9)—C(10) and O(3)—C(10), N(1)—C(13) bond lengths. Principal geometric parameters of the coordination unit are presented in Table 3.

The crystal packing of complex **4** consists of polymeric chains formed as a result of the additional coordination of the copper ion by the oxygen atom of the carboxylate group of the adjacent molecule (Fig. 4).

To sum up, we have performed reactions of fluoroalkylated 2-ethoxymethylidene-3-oxo esters **1** with 2-aminobenzoic acid giving new *O*,*N*,*O*-tridentate ligands capable of coordinating transition metal cations.

Experimental

The melting points were measured in open capillaries on a Stuart SMP3 melting-point apparatus. The diffuse reflectance IR spectra were recorded on a Perkin Elmer Spectrum One Fourier-transform IR spectrometer in the 400—4000 cm^{-1} region. The NMR spectra were measured on Bruker DRX-400 spectrometers (400 MHz for ^{1}H and 376 MHz for ^{19}F) with $SiMe_4$ and C_6F_6 as the internal standard for ^{1}H and ^{19}F NMR, respectively. The chemical shifts and the spin-spin coupling constants were measured with an accuracy of 0.01 ppm and 0.1 Hz, respectively. The elemental analysis was carried out on an automated Perkin Elmer PE-2400 series II CHNS-O elemental analyzer. The course of the reactions was monitored by TLC on Sorbfil PTSKh-AF-V-UF plates.

The starting ethyl 2-ethoxymethylidene-3-oxo-3-polyfluoroalkylpropionates **1a—c** were synthesized according to a procedure described previously.[16]

Single crystals of compound **2c** were obtained by crystallization from ethanol, $C_{14}H_{12}F_3NO_5$, M = 331.25, triclinic crystals, space group $P\bar{1}$, a = 7.2980(5) Å, b = 8.9895(6) Å, c = = 11.4924(7) Å, α = 93.665(5)°, β = 90.261(5)°, γ = 105.204(6)°, V = 725.91(8) Å^3, Z = 2, d_{calc} = 1.515 g cm^{-3}, μ(Mo-Kα) = = 0.139 cm^{-1}, F(000) = 340. A total of 7061 reflections were measured on a Xcalibur 3 diffractometer at 295(2) K (ω/2θ scanning technique, Mo-K$_\alpha$ radiation, graphite monochromator, CCD detector), 3437 independent reflections (R_{int} = 0.0250), 1910 reflections with $F_o > 4\sigma(F_o)$. The structure was solved by direct methods and refined by the least-squares method with the use of the SHELXL-97 program package[20] to R_1 = 0.0378, wR_2 = 0.0813, and GOOF = 1.002 (based on reflections with $I > 2\sigma(I)$).

Single crystals of compound **4** were obtained by crystallization from ethanol, $C_{20}H_{16}F_4N_2O_5Cu$, M = 503.89, monoclinic crystals, space group Cc, a = 15.4178(16) Å, b = 17.493(2) Å, c = 9.3890(10) Å, α = 90.00°, β = 103.885(10)°, γ = 90.00°, V = 2009.5(4) Å^3, Z = 4, d_{calc} = 1.666 g cm^{-3}, μ(Mo-Kα) = = 1.160 cm^{-1}, F(000) = 1020. A total of 4938 reflections were measured on a Xcalibur 3 diffractometer at 295(2) K (ω/2θ scanning technique, Mo-K$_\alpha$ radiation, graphite monochromator, CCD detector), 2870 independent reflections (R_{int} = 0.0290), 1948 reflections with $F_o > 4\sigma(F_o)$. The analytical absorption correction was applied using a multifaceted crystal model. The structure was solved by direct methods and refined by the least-squares method with the use of the SHELXL-97 program package[20] to R_1 = 0.0295, wR_2 = 0.0470, and GOOF = 1.002 (based on reflections with $I > 2\sigma(I)$).

The complete crystallographic data for compounds **2c** and **4** were deposited with the Cambridge Crystallographic Data Centre (CCDC 720575 and CCDC 720576) and can be obtained, free of charge, on application to www.ccdc.cam.ac.uk/conts/retrieving.html (orwww.ccdc.cam.ac.uk/conts/retrieving.html CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Reaction of ethyl 2-ethoxymethylidene-3-oxo-3-polyfluoroalkylpropionates 1 with 2-aminobenzoic acid (general procedure). A mixture of ester **1** (4 mmol) and 2-aminobenzoic acid (4 mmol) in Et_2O (10 mL) was stirred at room temperature for 2—4 h. Then the reaction mixture was concentrated, and the precipitate that formed was crystallized from ethanol and dried.

(2*E*)-2-(2-Ethoxycarbonyl-4,4,4-trifluoro-3-oxobut-1-enylamino)benzoic acid (2a). The yield was 0.98 g (74%), m.p. 175—176 °C. IR, ν/cm^{-1}: 3150 (NH); 2999 (C—H); 1704 (CO_2Et); 1682 (COR^F); 1640 (CO_2H); 1609, 1579 (C=C, NH); 1206—1145 (C—F). ^{1}H NMR ($CDCl_3$), δ, *E* isomer (62%): 1.36 (t, 3 H, $OCH_2C\underline{H}_3$, ^{3}J = 7.2 Hz); 4.33 (q, 2 H, $O\underline{CH}_2CH_3$, ^{3}J = 7.2 Hz); 7.34 (ddd, 1 H, H(4´), $^{3}J_{\mathrm{H(4'),H(3')}}$ = 7.9 Hz, $^{3}J_{\mathrm{H(4')-H(5')}}$ = 7.7 Hz, $^{4}J_{\mathrm{H(4')-H(6')}}$ = 1.0 Hz); 7.55 (dd, 1 H, H(6´), $^{3}J_{\mathrm{H(6'),H(5')}}$ = 8.4 Hz, $^{4}J_{\mathrm{H(6')-H(4')}}$ = 1.0 Hz); 7.70 (ddd, 1 H, H(5´), $^{3}J_{\mathrm{H(5'),H(6')}}$ = 8.4 Hz, $^{3}J_{\mathrm{(5'),H(4')}}$ = 7.7 Hz, $^{4}J_{\mathrm{H(5'),H(3')}}$ = 1.5 Hz); 8.24 (dd, 1 H, H(3´), $^{3}J_{\mathrm{H(3'),H(4')}}$ = 7.9 Hz, $^{4}J_{\mathrm{H(3'),H(5')}}$ = 1.5 Hz); 8.72 (d, 1 H, CH, ^{3}J = 13.9 Hz); 13.60 (d, 1 H, NH, ^{3}J = 13.9 Hz); 13.87 (br.s, 1 H, OH); *Z* isomer (38%): 1.38 (t, 3 H, $OCH_2\underline{CH}_3$, ^{3}J = = 7.1 Hz); 4.40 (q, 2 H, $O\underline{CH}_2CH_3$, ^{3}J = 7.1 Hz); 7.30 (ddd, 1 H, H(4´), $^{3}J_{\mathrm{H(4'),H(3')}}$ = 8.0 Hz, $^{3}J_{\mathrm{H(4'),H(5')}}$ = 7.6 Hz, $^{4}J_{\mathrm{H(4'),H(6')}}$ = = 1.0 Hz); 7.48 (dd, 1 H, H(6´), $^{3}J_{\mathrm{H(6')-H(5')}}$ = 8.5 Hz, $^{4}J_{\mathrm{H(6')-H(4')}}$ = 1.0 Hz); 7.69 (ddd, 1 H, H(5´), $^{3}J_{\mathrm{H(5'),H(6')}}$ = = 8.5 Hz, $^{3}J_{\mathrm{(5'),H(4')}}$ = 7.6 Hz, $^{4}J_{\mathrm{H(5'),H(3')}}$ = 1.5 Hz); 8.22 (dd, 1 H, H(3´), $^{3}J_{\mathrm{H(3'),H(4')}}$ = 8.0 Hz, $^{4}J_{\mathrm{H(3'),H(5')}}$ = 1.5 Hz); 8.55 (d, 1 H, CH, ^{3}J = 13.8 Hz); 13.03 (d, 1 H, NH, ^{3}J = 13.8 Hz); 13.87 (br.s, 1 H, OH). ^{19}F NMR ($CDCl_3$), δ, *E* isomer (62%): 88.91 (s, CF_3); *Z* isomer (38%): 89.79 (s, CF_3). Found (%): C, 50.72; H, 3.58; F, 17.13; N, 4.17. $C_{14}H_{12}F_3NO_5$. Calculated (%): C, 50.76; H, 3.65; F, 17.21; N, 4.23.

(2*E*)-2-(2-Ethoxycarbonyl-4,4,5,5-tetrafluoro-3-oxopent-1-enylamino)benzoic acid (2b). The yield was 1.13 g (78%), m.p. 183—185 °C. IR, ν/cm^{-1}: 3150, 3086 (NH); 2986 (C—H); 1709 (CO_2Et); 1692 (COR^F); 1656 (CO_2H); 1608, 1585, 1569 (C=C, NH); 1233—1079 (C—F). ^{1}H NMR ($(CD_3)_2SO$), δ, *E* isomer (61%): 1.29 (t, 3 H, $OCH_2\underline{CH}_3$, ^{3}J = 7.1 Hz); 4.23 (q, 2 H, $O\underline{CH}_2CH_3$, ^{3}J = 7.1 Hz); 6.99 (tt, 1 H, $\underline{H}(CF_2)_2$, $^{2}J_{\mathrm{H,F}}$ = = 52.7 Hz, $^{3}J_{\mathrm{H-F}}$ = 5.7 Hz); 7.38 (br.t, 1 H, H(4´), $^{3}J_{\mathrm{H(4'),H(3')}}$ = = $J_{\mathrm{H(4'),H(5')}}$ = 7.7 Hz); 7.74 (ddd, 1 H, H(5´), $^{3}J_{\mathrm{H(5'),H(6')}}$ = = 8.2 Hz, $^{3}J_{\mathrm{(5'),H(4')}}$ = 7.7 Hz, $^{4}J_{\mathrm{H(5'),H(3')}}$ = 1.4 Hz); 7.83 (br.d, 1 H, H(6´), $^{3}J_{\mathrm{H(6'),H(5')}}$ = 8.2 Hz); 8.04 (dd, 1 H, H(3´), $^{3}J_{\mathrm{H(3'),H(4')}}$ = 7.7 Hz, $^{4}J_{\mathrm{H(3'),H(5')}}$ = 1.4 Hz); 8.65 (d, 1 H, CH, ^{3}J = 14.0 Hz); 13.57 (d, 1 H, NH, ^{3}J = 14.0 Hz); 13.90 (br.s, 1 H, OH); *Z* isomer (39%): 1.31 (t, 3 H, $OCH_2\underline{CH}_3$, ^{3}J = 7.1 Hz); 4.33 (q, 2 H, $O\underline{CH}_2CH_3$, ^{3}J = 7.1 Hz); 6.88 (tt, 1 H, $H(CF_2)_2$,

^2J = 52.4 Hz, ^2J = 5.6 Hz); 7.32 (br.t, 1 H, H(4´), $^3J_{\mathrm{H}(4'),\mathrm{H}(3')} = J_{\mathrm{H}(4'),\mathrm{H}(5')}$ = 7.6 Hz); 7.69 (ddd, 1 H, H(5´), $^3J_{\mathrm{H}(5'),\mathrm{H}(6')}$ = 8.5 Hz, $^3J_{(5'),\mathrm{H}(4')}$ = 7.6 Hz, $^4J_{\mathrm{H}(5'),\mathrm{H}(3')}$ = 1.4 Hz); 7.78 (br.d, 1 H, H(6´), $^3J_{\mathrm{H}(6'),\mathrm{H}(5')}$= 8.5 Hz); 8.03 (dd, 1 H, H(3´), $^3J_{\mathrm{H}(3'),\mathrm{H}(4')}$ = 7.6 Hz, $^4J_{\mathrm{H}(3')-\mathrm{H}(5')}$ = 1.4 Hz); 8.51 (d, 1 H, CH, ^3J = 14.2 Hz); 12.78 (d, 1 H, NH, ^3J = 14.2 Hz); 13.90 (br.s, 1 H, OH). ^{19}F NMR ($(CD_3)_2SO$), δ, *E* isomer (61%): 25.21 (dt, 2 F, CF_2H, *J* = 52.7 Hz, *J* = 8.0 Hz); 41.46 (m, 2 F, CF_2); *Z* isomer (39%): 24.48 (dt, 2 F, CF_2H, *J* = 52.4 Hz, *J* = 8.2 Hz); 42.24 (m, 2 F, CF_2). Found (%): C, 49.52; H, 3.57; F, 20.75; N, 3.77. $C_{15}H_{13}F_4NO_5$. Calculated (%): C, 49.60; H, 3.61; F, 20.92; N, 3.86.

(2*E*)-2-(2-Ethoxycarbonyl-4,4,5,5,6,6,6-heptafluoro-3-oxohex-1-enylamino)benzoic acid (2c). The yield was 1.19 g (69%), m.p. 155—156 °C. IR, ν/cm^{-1}: 3120, 3107 (NH); 2995 (C—H); 1702 (CO_2Et); 1691 (COR^F); 1663 (CO_2H), 1650, 1607, 1573 (C=C, NH); 1241—1126 (C—F). ^{1}H NMR ($CDCl_3$), δ: 1.27 (br.t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.0 Hz); 8.04 (br.d, 1 H, H(3´), $^3J_{\mathrm{H}(3'),\mathrm{H}(4')}$ = 7.7 Hz); 13.92 (br.s, 1 H, OH); *E* isomer (53%): 4.21 (q, 2 H, $O\underline{CH_2}CH_3$, ^3J = 7.2 Hz); 7.38 (br.t, 1 H, H(4´), $^3J_{\mathrm{H}(4'),\mathrm{H}(3')} = {}^3J_{\mathrm{H}(4'),\mathrm{H}(5')}$ = 7.7 Hz); 7.73 (ddd, 1 H, H(5´), $^3J_{\mathrm{H}(5'),\mathrm{H}(6')}$ = 8.2 Hz, $^3J_{\mathrm{H}(5'),\mathrm{H}(4')}$ = 7.7 Hz); 7.85 (br.d, 1 H, H(6´), $^3J_{\mathrm{H}(6'),\mathrm{H}(5')}$ = 8.2 Hz); 8.66 (d, 1 H, CH, ^3J = 14.2 Hz); 13.53 (d, 1 H, NH, ^3J = 14.2 Hz); *Z* isomer (47%): 4.30 (q, 2 H, $O\underline{CH_2}CH_3$, ^3J = 7.1 Hz); 7.33 (br.t, 1 H, H(4´), $^3J_{\mathrm{H}(4'),\mathrm{H}(3')} = {}^3J_{\mathrm{H}(4'),\mathrm{H}(5')}$ = 7.7 Hz); 7.70 (ddd, 1 H, H(5´), $^3J_{\mathrm{H}(5'),\mathrm{H}(6')}$ = 8.2 Hz, $^3J_{\mathrm{H}(5'),\mathrm{H}(4')}$ = 7.7 Hz, $^4J_{\mathrm{H}(5'),\mathrm{H}(3')}$ = 1.4 Hz); 7.80 (br.d, 1 H, H(6´), $^3J_{\mathrm{H}(6'),\mathrm{H}(5')}$ = 8.2 Hz); 8.51 (d, 1 H, CH, ^3J = 14.2 Hz); 12.83 (d, 1 H, NH, ^3J = 14.2 Hz). ^{19}F NMR ($(CD_3)_2SO$), δ, *E* isomer (53%): 39.66 (m, 2 F, CF_2); 49.71 (m, 2 F, CF_2); 82.99 (t, 2 F, CF_3, *J* = 9.2 Hz); *Z* isomer (47%): 39.18 (m, 2 F, CF_2); 50.09 (m, 2 F, CF_2); 42.24 (m, 2 F, CF_2); 82.96 (t, 2 F, CF_3, *J* = 9.5 Hz). Found (%): C, 44.54; H, 2.79; F, 30.65; N, 3.15. $C_{16}H_{12}F_7NO_5$. Calculated (%): C, 44.56; H, 2.80; F, 30.84; N, 3.25.

Synthesis of complexes 3a—f (general procedure). A mixture of acid **2a—c** (2 mmol) and nickel (or copper) acetate (2 mmol) in ethanol (10 mL) was refluxed for 30 min. Then the reaction mixture was poured into water (20 mL). In the case of compounds **3b,d,f**, the precipitate that formed was filtered off and crystallized from ethanol. Products **3a,c,e** were extracted with chloroform, the extracts were concentrated, and the products were isolated by column chromatography using chloroform as the eluent.

2-(2-Ethoxycarbonyl-4,4,4-trifluoro-3-oxobut-1-enylaminato)benzoatonickel(II) (3a). The yield was 1.05 g (90%), m.p. 167—168 °C. IR, ν/cm^{-1}: 2987 (C—H); 1702 (CO_2Et); 1680 (COR^F); 1644, 1638, 1610, (C=C, NH); 1589 (COO$^-$); 1275—1162 (C—O, C—F). Found (%): C, 43.26; H, 2.58; F, 14.60; N, 3.56. $C_{14}H_{10}F_3NO_5Ni$. Calculated (%): C, 43.35; H, 2.60; F, 14.69; N, 3.61.

2-(2-Ethoxycarbonyl-4,4,4-trifluoro-3-oxobut-1-enylaminato)benzoatocopper(II) (3b). The yield was 1.12 g (95%), m.p. 280—282 °C. IR, ν/cm^{-1}: 3074, 2985 (C—H); 1708 (CO_2Et); 1681 (COR^F); 1607 (C=C); 1583 (COO$^-$); 1242—1160 (C—O, C—F). Found (%): C, 42.78; H, 2.51; F, 14.40; N, 3.53. $C_{14}H_{10}F_3NO_5Cu$. Calculated (%): C, 42.81; H, 2.57; F, 14.51; N, 3.57.

2-(2-Ethoxycarbonyl-4,4,5,5-tetrafluoro-3-oxopent-1-enylaminato)benzoatonickel(II) (3c). The yield was 1.17 g (93%), m.p. 178—179 °C. IR, ν/cm^{-1}: 3938, 2921 (C—H); 1709 (CO_2Et); 1682 (COR^F); 1656, 1645 (C=C); 1588 (COO$^-$); 1259—1080 (C—O, C—F). Found (%): C, 42.87; H, 2.58; F, 18.07; N, 3.29. $C_{15}H_{11}F_4NO_5Ni$. Calculated (%): C, 42.90; H, 2.64; F, 18.10; N, 3.34.

2-(2-Ethoxycarbonyl-4,4,5,5-tetrafluoro-3-oxopent-1-enylaminato)benzoatocopper(II) (3d). The yield was 1.13 g (89%), m.p. 197—199 °C. IR, ν/cm^{-1}: 3071, 2985 (C—H); 1708 (CO_2Et); 1685 (COR^F); 1617 (C=C); 1585 (COO$^-$); 1227—1096 (C—O, C—F). Found (%): C, 42.41; H, 2.60; F, 17.88; N, 3.20. $C_{15}H_{11}F_4NO_5Cu$. Calculated (%): C, 42.41; H, 2.61; F, 17.89; N, 3.30.

2-(2-Ethoxycarbonyl-4,4,5,5,6,6,6-heptafluoro-3-oxohex-1-enylaminato)benzoatonickel(II) (3e). The yield was 1.24 g (85%), t.decomp. 310—315 °C. IR, ν/cm^{-1}: 2985 (C—H); 1704 (CO_2Et); 1688 (COR^F); 1637 (C=C); 1590 (COO$^-$); 1225—1117 (C—O, C—F). Found (%): C, 39.25; H, 2.03; F, 27.18; N, 2.90. $C_{16}H_{10}F_7NO_5Ni$. Calculated (%): C, 39.38; H, 2.07; F, 27.25; N, 2.87.

2-(2-Ethoxycarbonyl-4,4,5,5,6,6,6-heptafluoro-3-oxohex-1-enylaminato)benzoatocopper(II) (3f). The yield was 1.21 g (82%), m.p. 188—189 °C. IR, ν/cm^{-1}: 3075, 2986 (C—H); 1702 (CO_2Et); 1690 (COR^F); 1651 (C=C); 1584 (COO$^-$); 1216—1119 (C—O, C—F). Found (%): C, 38.95; H, 2.00; F, 26.88; N, 23.78. $C_{16}H_{10}F_7NO_5Cu$. Calculated (%): C, 39.00; H, 2.05; F, 26.99; N, 2.84.

Pyridine[2-(2-ethoxycarbonyl-4,4,5,5-tetrafluoro-3-oxopent-1-enylaminato)benzoato]copper(II) (4). A mixture of complex **3d** (0.5 mmol) and pyridine (0.5 mmol) in ethanol (10 mL) was refluxed for 2 h. Then the reaction mixture was concentrated. The crystals that formed were filtered off. The yield was 0.24 g (94%), m.p. 234—235 °C. IR, ν/cm^{-1}: 3091, 2990 (C—H); 1703 br. (CO_2Et, COR^F); 1627, 1607 (C=C); 1586 (COO$^-$); 1220—1096 (C—O, C—F). Found (%): C, 47.52; H, 3.13; F, 14.98; N, 5.45. $C_{20}H_{16}F_4N_2O_5Cu$. Calculated (%): C, 47.67; H, 3.20; F, 15.08; N, 5.56.

This study was financially supported by the Council on Grants of the President of the Russian Federation (Program for State Support of Leading Scientific Schools of the Russian Federation, Grant NSh-3758.2008.3).

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Received March 25, 2009;
in revised form April 23, 2009