New enamine ligands derived from ethyl 2-ethoxymethylidene-3-oxo-3-polyfluoroalkylpropionates and *o*-phenylenediamine

Yu. S. Kudyakova, M. V. Goryaeva, Ya. V. Burgart, P. A. Slepukhin, and V. I. Saloutin*

I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences,
22/20 ul. S. Kovalevskoi/Akademicheskaya, 620041 Ekaterinburg, Russian Federation.
Fax: +7 (343) 374 5954. E-mail: saloutin@ios.uran.ru

Diethyl 2,2´-[1,2-phenylenebis(aminomethylidene)]bis(3-oxo-3-polyfluoroalkylpropionates) were synthesized by the condensation of a double excess of ethyl 2-ethoxymethylidene-3-oxo-3-polyfluoroalkylpropionates with *o*-phenylenediamine. The use of equimolar ratios of the starting reactants affords ethyl 2-[(2-aminophenyl)aminomethylidene]-3-oxo-3-polyfluoroalkylpropionates from which nonsymmetric biscondensation products were synthesized by the reaction with related reactants containing different polyfluoroalkyl substituent. The copper(II), nickel(II), and cobalt(II) complexes were obtained on the basis of new ligands.

Key words: β-keto acids, *o*-phenylenediamine, enamines, ligands, copper(II) complexes, nickel(II) complexes, cobalt(II) complexes, organofluorine compounds.

Interest in synthesis of metal complexes based on azomethine compounds is caused by their catalytic activity in polymerization reactions[1—3] and magnetic[4—7] and luminescence[8,9] properties. Non-fluorinated 2-ethoxymethylidene-1,3-dicarbonyl compounds in reactions with 1,2-diamines form biscondensation products at the ethoxymethylidene moiety[10—12] and related metal complexes.[13—16] It is possible to obtain monocondensation products[17—19] from which symmetric and asymmetric ligands[20] were synthesized, including the macrocyclic ligands[15,17—20] used in the synthesis of the metallocomplex compounds.[17—20] Schiff bases obtained by transformations of 2-ethoxymethylidene-3-oxo-3-fluoroalkylpropionates with different diamines can also serve as organic molecules forming the ligand shell. It is known[21] that the introduction of the fluorine atom into organic molecules changes their physicochemical properties, reactivity, biological activity and other characteristics caused by the presence of electronegative fluorine atoms and important in practical and theoretical aspects. However, published data on the participation of polyfluorinated analogs in similar polycondensation reactions are lacking.

In the present work, we studied the reactions of ethyl 2-ethoxymethylidene-3-oxo-3-polyfluoroalkylpropionates **1** with *o*-phenylenediamine with the purpose to synthesize new ligands and analyzed a possibility of the preparation of related metallocomplex compounds with a series of transition metals.

It was found that the reaction of compounds **1a—c** with 1 equiv. of *o*-phenylenediamine in diethyl ether at room temperature afforded the monoadducts, *viz.*, ethyl 2-[(2-aminophenyl)aminomethylidene]-3-fluoroalkyl-3-oxopropionates **2a—c**, as a result of the nucleophilic attack of the amino group at the ethoxymethylidene moiety (Scheme 1). The use of a double excess of esters **1a—c** results in the formation of symmetric products **3a—c** due to the condensation of two molecules of ester **1a—c** with one diamine molecule.

Monosubstitution products **2a—c** contain free NH_2 groups, which makes it possible to carry out their further transformations. The condensation of compounds **2a,c** with the corresponding substrates **1a,b** (see Scheme 1)

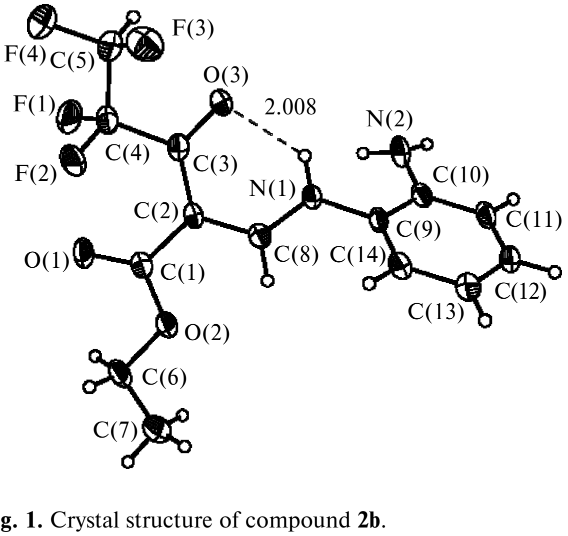
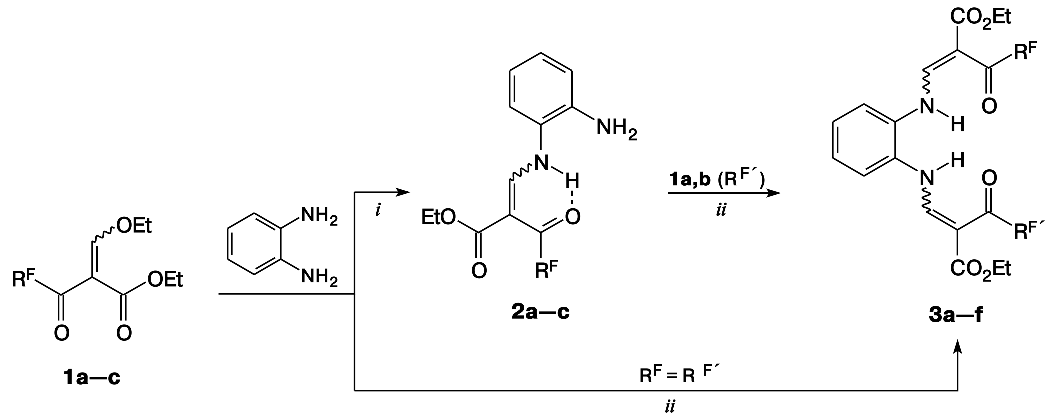


Fig. 1. Crystal structure of compound **2b**.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1544—1554, August, 2010.

Scheme 1



1: $R^F = CF_3$ (**a**), $(CF_2)_2H$ (**b**), C_3F_7 (**c**); **2:** $R^F = CF_3$ (**a**), $(CF_2)_2H$ (**b**), C_3F_7 (**c**); **3:** $R^F = R^{F'} = CF_3$ (**a**), $(CF_2)_2H$ (**b**), C_3F_7 (**c**); $R^F = CF_3$, $R^{F'} = (CF_2)_2H$ (**d**); $R^F = CF_3$, $R^{F'} = C_3F_7$ (**e**); $R^F = (CF_2)_2H$, $R^{F'} = C_3F_7$ (**f**)

Conditions: *i*. Et_2O, ~20 °C, 30 min; *ii*. Et_2O, ~20 °C, 4—5 h.

affords nonsymmetric tetradentate ligands **3d—f** containing two different polyfluorinated substituents.

The structures of synthesized compounds **2a—c** and **3a—f** were determined by IR spectroscopy, ^1H and ^{19}F NMR spectroscopy, and elemental analysis. The X-ray diffraction study was also carried out for ester **2b** (Fig. 1).

According to the X-ray diffraction data, ester **2b** exists in crystal as the *s-trans*,*s-cis*-conformer of the *E*-isomer of the aminoketone tautomer (see Fig. 1, Table 1). The molecule contains the intramolecular hydrogen bond O(3)...H(1)N(1), which is characterized by the following parameters: the intramolecular distance O(1)...H(1) is 2.00(8) Å, and the angles N(1)—H(1)...O(3) and C(3)—O(3)...H(1) are 131.52 and 101.79°. The main chelate moiety of the molecule has the approximately planar structure, because the maximum shifts of atoms from the hexagon H(1)N(1)C(8)C(2)C(3)O(3) are 0.06(4) Å (C(3) atom). The benzene moiety is turned out relative to the chelate unit: the dihedral angle between the H(1)N(1)C(8)C(2)C(3)O(3) planes and the benzene ring is 54.3°.

A comparative analysis of the IR spectra of compounds **2a—c** revealed no substantial differences between them.

Table 1. Selected bond lengths (*d*) and bond angles (ω) for compounds **2b** and **4b**

Parameter	Value
Bond length	*d*/Å
2b	
N(1)—C(8)	1.3229(17)
N(1)—C(9)	1.4279(18)
N(1)—H(1)	0.849(17)
O(1)—C(1)	1.2094(17)
C(1)—O(2)	1.3395(18)
C(1)—C(2)	1.473(2)
C(2)—C(8)	1.400(2)
C(2)—C(3)	1.428(2)
N(2)—C(10)	1.384(2)
O(3)—C(3)	1.2449(16)
C(3)—C(4)	1.544(2)
4b	
Cu(1)—O(1)	1.9213(14)
Cu(1)—N(1)	1.9504(15)
Cu(1)—N(2)	1.9855(17)
Cu(1)—Cl(2)	2.2541(6)
O(1)—C(9)	1.263(2)
N(1)—C(12)	1.289(2)
Bond length	*d*/Å
N(1)—C(1)	1.424(2
O(2)—C(7)	1.204(2)
C(7)—C(8)	1.484(3)
N(2)—C(2)	1.449(3)
C(9)—C(8)	1.383(3)
C(12)—C(8)	1.432(3)
C(1)—C(2)	1.392(3)
Angle	ω/deg
2b	
C(8)—N(1)—C(9)	124.02(14)
C(8)—N(1)—H(1)	116.6(10)
C(9)—N(1)—H(1)	119.1(10)
O(1)—C(1)—O(2)	122.55(13)
O(1)—C(1)—C(2)	125.04(14)
O(2)—C(1)—C(2)	112.32(12)
C(8)—C(2)—C(3)	119.00(12)
C(8)—C(2)—C(1)	118.70(14)
C(3)—C(2)—C(1)	122.30(13)
O(3)—C(3)—C(2)	122.89(13)
Angle	ω/deg
O(3)—C(3)—C(4)	113.10(13)
C(2)—C(3)—C(4)	123.92(12)
N(1)—C(8)—C(2)	126.30(15)
N(2)—C(10)—C(9)	120.30(13)
4b	
O(1)—Cu(1)—N(1)	92.04(6)
O(1)—Cu(1)—N(2)	176.38(7)
N(1)—Cu(1)—N(2)	85.31(6)
O(1)—Cu(1)—Cl(2)	90.19(5)
N(1)—Cu(1)—Cl(2)	175.31(5)
N(2)—Cu(1)—Cl(2)	92.63(5)
C(9)—O(1)—Cu(1)	127.28(14)
C(12)—N(1)—C(1)	122.57(16)
C(12)—N(1)—Cu(1)	125.09(14)
C(1)—N(1)—Cu(1)	112.31(12)
C(2)—N(2)—Cu(1)	109.38(12)
C(9)—C(8)—C(12)	121.65(17)
C(9)—C(8)—C(7)	121.86(18)

In each case, the presence of intense absorption bands of stretching vibrations corresponding to two carbonyl groups (1710—1697 and 1673—1647 cm^{-1}) and NH and NH_2 groups (3254—3177 cm^{-1}) also indicates that they exist are the *E*-isomer of the aminoketone tautomer stabilized by the intramolecular hydrogen bond between the oxygen atom of the polyfluoroacyl moiety and the hydrogen atom of the NH group.

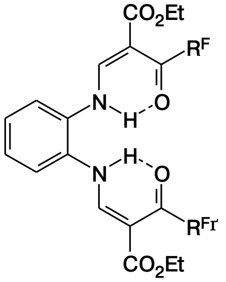
The IR spectrum of compound **2a** in a 3% solution of $CHCl_3$ exhibits a considerable broadening of absorption bands of vibrations of almost all characteristic groups.

It was established by ^{1}H and ^{19}F NMR spectroscopy that esters **2a—c** in a $CDCl_3$ solution exist as an equilibrium mixture of *Z*- and *E*-isomers. For example, the ^{1}H NMR spectra of compounds **2a—c** in $CDCl_3$ contains two sets of signals in which the signals of the NH- and CH-protons of the methylidene moiety are observed in the low-frequency region (δ_{CH} ~8.29—8.55, δ_{NH} ~11.14—12.18) as doublets with the spin-spin coupling constant (SSCC) ~14 Hz. The ^{19}F NMR spectra of compounds **2a—c** are also characterized by doubling of the resonance signals of the fluorine nuclei. The signals were assigned to the *Z*- or *E*-isomeric form according to the principles established earlier.[22] According to this, the shifts of the protons of the CH and NH groups are determining in the ^{1}H NMR spectra: for the *E*-isomer the signals of these groups are observed in a weaker field compared to the signals of the protons corresponding to the *Z*-isomer. In the ^{19}F spectra, the signals of the fluorine atoms of the α-CF_3 and α-CF_2 groups of the *Z* form are characterized by a more downfield shift compared to the corresponding signals of the fluorine atoms of the *E*-isomer.

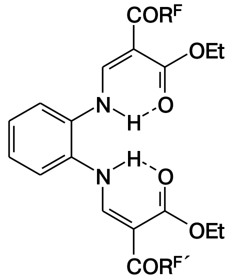
Easiness of isomerization of the C=C bonds in esters **2a—c** is due to the fact that, being neighbors of functional groups of different electronegativity, they are a part of the polarized push-pull conjugated system in which the rotation barrier about the C=C double bonds is substantially decreased.[23] We have earlier[22] found that the tendency to undergo isomerization of the *E*-isomer to a mixture of *Z*- and *E*-isomers upon dissolution is general for ethyl esters of 2-(R-aminomethylidene)-3-oxo-3-polyfluoroalkylpropionic acids (R is alkyl, aryl, or hetaryl).

The IR spectra of diesters **3a—f** contain two high-frequency absorption bands (1726—1698, 1703—1638 cm^{-1}) corresponding to vibrations of two different carbonyl groups and the broadened absorption band at 3210—3177 cm^{-1} caused by stretching vibrations of the NH group. These data indicate the existence of diesters **3a—f** as an aminoketone tautomer analogous to monosubstitution products **2a—c**.

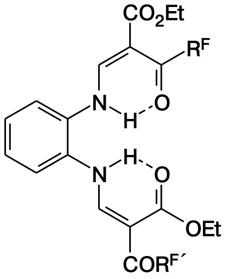
Three isomeric forms (*E*,*E*, *Z*,*Z*, and *E*,*Z*) are possible for symmetric diesters **3a—c** containing two C=C bonds, whereas four isomeric forms, *viz.*, *E*,*E*, *Z*,*Z*, *E*,*Z*, and *Z*,*E*, are possible for asymmetric diesters **3d—f** having two C=C bonds and two different fluorinated substituents.



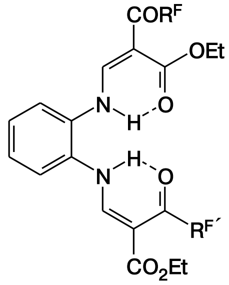
E,*E*



Z,*Z*



E,*Z*



Z,*E*

In fact, the ^{1}H and ^{19}F NMR spectra of compounds **3a—c** in $CDCl_3$ contain three sets of signals corresponding to the *E*,*E*-, *Z*,*Z*-, and *E*,*Z*-isomeric forms, whereas the spectra of compounds **3d—f** exhibit four sets corresponding to the *E*,*E*-, *E*,*Z*-, *Z*,*E*-, and *Z*,*Z* forms (see Experimental, Table 2). The signals were assigned to the *E*,*E*-, *E*,*Z*-, *Z*,*E*-, and *Z*,*Z* forms using the data obtained by us earlier.[22]

Based on the structure of ligands **2a—c**, one may assume that they are able to form metallocomplex compounds due to coordination involving the tridentate N_2O moiety. However, the treatment of ester **2b** with copper(II) and nickel(II) acetates gave no desirable metal complexes, unlike the transformations of the non-fluorinated analog.[17] Nevertheless, the use of copper(II) chloride made it possible to obtain complex **4b** (Scheme 2), being a crystalline dark green powder. The elemental analysis data for compound **4b** correspond to the composition CuLCl, where L is the monodeprotonated ligand. In its IR spectrum characteristic bands are the high-frequency absorption bands at 1708 cm^{-1} corresponding to vibrations of the carbonyl groups of the ester moiety, the bands at 1615 and 1593 cm^{-1} caused by vibrations of the C=O and C=C chelate node, and the absorption bands at 3282 and 3190 cm^{-1} corresponding to symmetric and antisymmetric stretching vibrations of the NH_2 group. A comparative analysis of the IR spectra of ligand **2b** and complex **4b** revealed their substantial differences. The absorption bands of the carbonyl group of the fluoroacyl substituent of complex **4b** are characterized by the shift to the low-frequency region compared to the analogous band

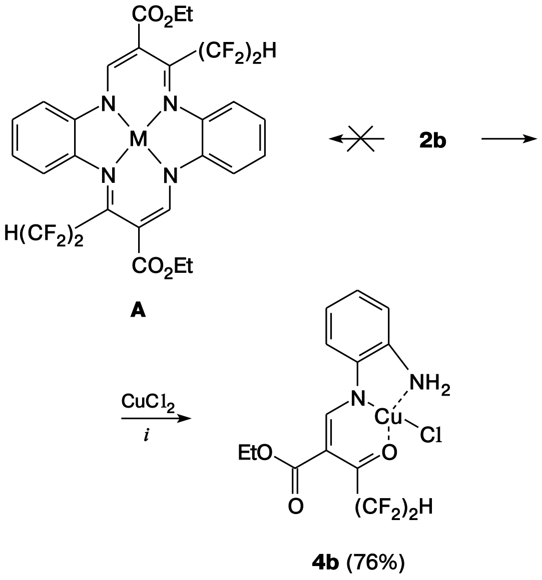
Table 2. Chemical shifts (δ) of the NH- and CH-protons of the *E*,*E*-, *Z*,*Z*-, *E*,*Z*-, and *Z*,*E*-isomers of compounds **3a—f** according to the data of ^{1}H NMR spectroscopy (in $CDCl_3$)

Compound	*E*,*E*	*Z*,*Z*	*E*,*Z*	*Z*,*E*
3a	8.51 (CH(*E*)); 12.15 (NH(*E*))	8.36 (CH(*Z*)); 11.58 (NH(*E*))	8.37 (CH(*Z*)); 8.51 (CH(*E*)); 11.59 (NH(*Z*)); 12.11 (NH(*E*))	—
3b	8.40 (CH(*E*)); 12.17 (NH(*E*))	8.29 (CH(*Z*)); 11.45 (NH(*E*))	8.29 (CH(*Z*); 8.40 (CH(*E*)); 11.46 (NH(*Z*)); 12.15 (NH(*E*))	—
3c	8.65 (CH(*E*)); 12.00 (NH(*E*))	8.42 (CH(*Z*)); 11.62 (NH(*E*))	8.43 (CH(*Z*)); 8.66 (CH(*E*)); 11.60 (NH(*Z*)); 12.01 (NH(*E*))	—
3d	8.40 (CH(*E*)); 8.50 (CH(*E*)); 12.15 (NH(*E*))	8.28 (CH(*Z*)); 8.35 (CH(*Z*)); 11.48 (NH(*E*))	8.36 (CH(*Z*)); 8.39 (CH(*E*)); 11.62 (NH(*Z*)); 12.11 (NH(*E*))	8.29 (CH(*Z*)); 8.49 (CH(*E*)); 11.43 (NH(*Z*)); 12.12 (NH(*E*))
3e	8.41 (CH(*E*)); 8.49 (CH(*E*)); 12.17 (NH(*E*))	8.22 (CH(*Z*)); 8.35 (CH(*Z*)); 12.02 (NH(*E*)); 12.17 (NH(*E*))	8.34 (CH(*Z*)); 8.41 (CH(*E*)); 11.60 (NH(*Z*)); 11.99 (NH(*E*))	8.22 (CH(*Z*)); 8.50 (CH(*E*)); 11.44 (NH(*Z*)); 12.10 (NH(*E*))
3f	8.39 (CH(*E*)); 8.40 (CH(*E*)); 11.45 (NH(*E*)); 11.48 (NH(*E*))	8.22 (CH(*Z*)); 8.29 (CH(*Z*)); 11.45 (NH(*E*)); 11.48 (NH(*E*))	8.28 (CH(*Z*)); 8.41 (CH(*E*)); 11.31 (NH(*Z*)); 12.03 (NH(*E*))	8.21 (CH(*Z*)); 8.38 (CH(*E*)); 11.34 (NH(*Z*)); 11.99 (NH(*E*))

of free ligand **2b**, and the vibrations of the ethoxycarbonyl group in ligand **2b** and in complex **4b** are observed in almost the same ranges. In addition, the IR spectra of metal complex **4b** are characterized by a decrease in the intensity of the absorption bands corresponding to stretching vibrations of the NH groups.

The steric structure of complex **4b** was studied by X-ray diffraction analysis (Fig. 2, see Table 1). According to the X-ray diffraction data, the copper(II) cation has a distorted planar square environment of two nitrogen atoms of the phenylenediamine moiety, the oxygen atom of the fluoroacyl group, and the chlorine atom. The maximum shifts from the plane of atoms surrounding the copper ion are 0.06(7) Å (N(1) atom). The maximum difference in the bond lengths forming the square environment of the Ni^{II} ion reaches 0.40(5) Å. As a result of the tridentate coordination of the ligand, two conjugated metal cycles, *viz*., five- and six-membered, are formed in the molecule. The crystal packing of complex **4b** is formed due to the formation of polymeric stacks with shortened intermolecular contacts between the copper and chlorine atoms of the adjacent molecules with the measured distances d(Cu(1)...Cl(2)[1.5 − x, −0.5 + y, 0.5 − z]) = = 3.030 Å and d(Cl(2)...Cu(1)[1.5 − x, −0.5 + y, 0.5 − z]) =

Scheme 2



Conditions: *i*. EtOH, b.p.

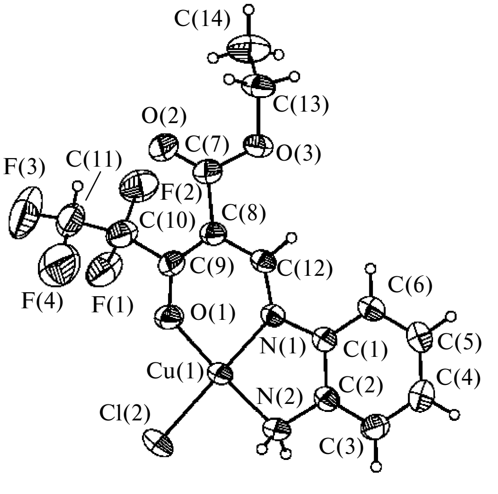


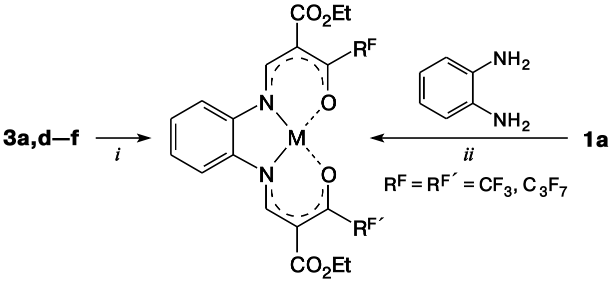
Fig. 2. Crystal structure of compound **4b**.

= 3.170 Å. In addition, the structure contains the intermolecular hydrogen bond between the hydrogen atom of the amino group and the oxygen atom of the fluoroacyl moiety of the adjacent molecule (N(2)—H(2A)...O(1) [$-x + 3/2$, $y - 1/2$, $-z + 1/2$]), which is characterized by the following parameters: d(N(2)—H) = 0.900 Å, d(H...O(1)) = 2.585(2) Å, d(N(2)...O(1)) = 3.432(2) Å, and ω(N(2)—H(2A)...O(1)) = 156.9(2)°.

Our further attempts to synthesize the N_4-tetradentate macrocyclic ligand from esters **2a—c** by analogy to the non-fluorinated derivatives[15,17—20] were unsuccessful: neither template nor direct syntheses did not allow us to obtained a macrocycle of the **A** type (see Scheme 2).

Upon the treatment with nickel(ii), cobalt(ii), and copper(ii) salts, compounds **3a,d—f** readily form metal complexes **5a—j** (Scheme 3). Symmetric chelates **5** can also be synthesized by the template method. Metal complex **5a** was synthesized on the nickel(ii) ion matrix from ester **1a** and *o*-phenylenediamine.

Scheme 3

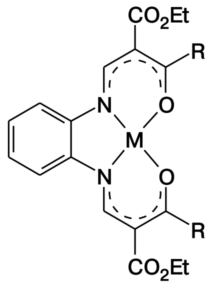


5a—j

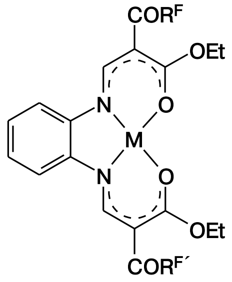
5: $R^F = R^{F'} = CF_3$, M = Ni (**a**), Co (**b**), Cu (**c**); $R^F = R^{F'} = C_3F_7$, M = Ni (**d**), Cu (**e**), Co (**f**); $R^F = CF_3$, $R^{F'} = C_3F_7$, M = Ni (**g**), Cu (**h**); $R^F = (CF_2)_2H$, $R^{F'} = C_3F_7$, M = Ni (**i**), Cu (**j**)

Conditions: *i*. EtOH, $M(OAc)_2$, Δ, 5 min; *ii*. EtOH, $Ni(OAc)_2$, ~20 °C, 2 days.

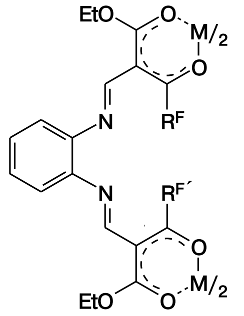
The structures of complexes **5** were determined by ^1H and ^{19}F NMR spectroscopy, IR spectroscopy, elemental analysis, and X-ray diffraction. In metal complexes **5a—j** coordination with the metal ion can occur by three different ways: due to the nitrogen atom and the oxygen atom at the fluoroalkyl substituent (structure **B**), involving the nitrogen atom and the oxygen atom of the ester group (structure **C**), or due to the oxygen atoms of the 1,3-dicarbonyl moiety (structure **D**).



B



C

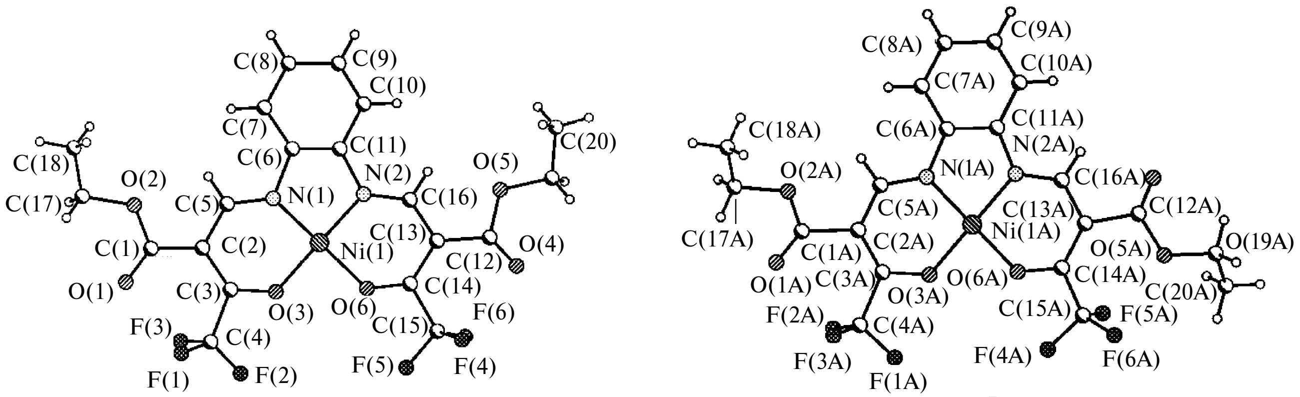


D

The IR spectra of compounds **5a—j** contain two high-frequency absorption bands at 1726—1698 cm^{-1} assigned to vibrations of the carbonyl groups, which may correspond to structures **B** and **C**. The ^1H and ^{19}F NMR spectra of nickel complexes **5a,d,g,i** detected in $CDCl_3$ solutions exhibit one set of signals. The ^{19}F NMR spectra of complexes **5a,d,g,i** contain a downfield shift of the signals of the α-fluorine atoms (δ_{CF_3} ~94 (**5a,d,g**), $\delta_{\alpha\text{-}CF_2}$ ~43 (**5d,i**), and $\delta_{\alpha\text{-}CF_2}$ ~51 (**5g,i**)) compared to analogous values for free ligands **3a,d—f** (δ_{CF_3} ~88—89 (**3a,d,e**), $\delta_{\alpha\text{-}CF_2}$ ~40—41 (**3d,f**), and $\delta_{\alpha\text{-}CF_2}$ ~48—49 (**3e,f**)), which is explained by the participation of the polyfluoroacyl groups in coordination with the nickel(ii) cation, which is observed in structure **B**.

Using the X-ray diffraction study, we determined the spatial structure of complexes **5a—j** for compounds **5a,d** as an example (Figs 3—6). The crystal packing of compound **5a** is formed by two crystallographically independent molecules (**I** and **Ia**) with different spatial orientations of one ethoxycarbonyl group (see Fig. 3).

The atoms of molecule **I** in compound **5a** are enumerated with figures, whereas the atoms of molecule **Ia** are designated with figures added by letter "A". The general organization of the chelate node (bond lengths, bond angles) of the both molecules is similar (Table 3). The atoms Ni(1)—N(1)—N(2)—O(6)—O(3) and Ni(1A)—N(1A)—N(2A)—O(6A)—O(3A) forming the chelate nodes of molecules **I** and **Ia** lie in almost the same plane (the shift from the root-mean-square plane is not more than 0.01(4) Å). The aryl and amino enone moieties are arranged in the same plane (the maximum deviation of the carbon atoms of the aryl substituent reaches 0.07(8) Å (C(10) and C(7A) atoms), whereas the shift of the amino enone substituent is 0.15(1) Å (C(2A) atom). The nickel atoms in molecules **I** and **Ia** have the coordination mode of a distorted square. A slight distortion of the chelate



I **Ia**

Fig. 3. General view of molecules **I** and **Ia** in compound **5a**.

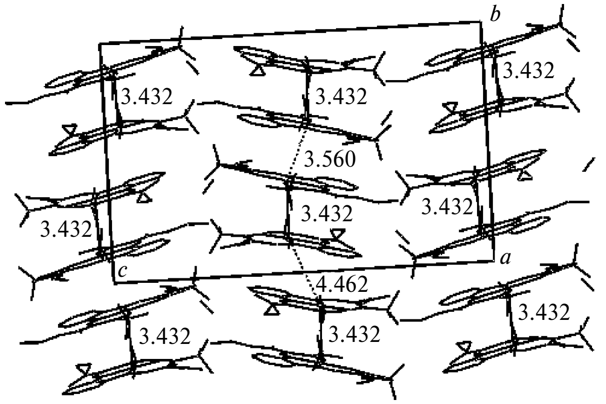


Fig. 4. Molecular packing along the *a* axis of molecules **5a** (hydrogen atoms are omitted).

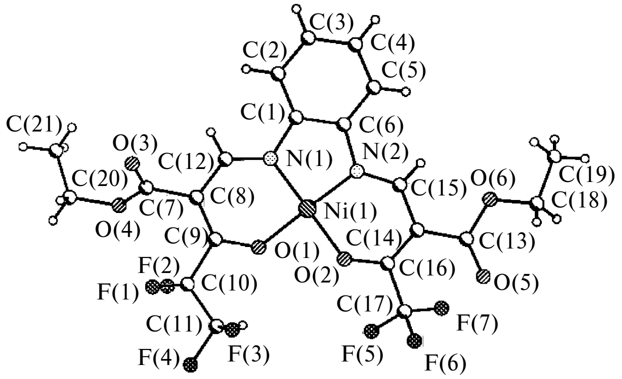


Fig. 5. General view of molecule **5d**.

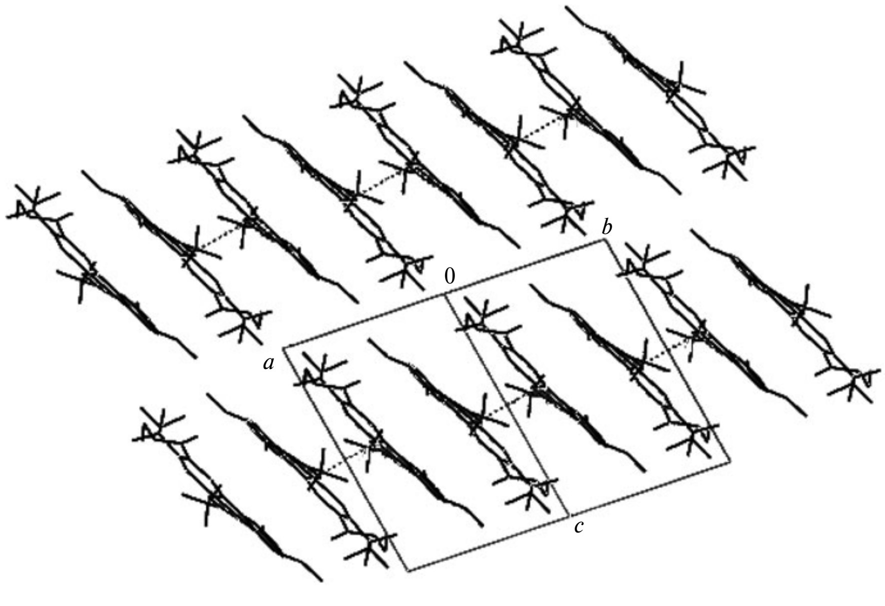


Fig. 6. Molecular packing along the vector *a* + *b* of molecules **5d** (hydrogen atoms are omitted).

Table 3. Selected bond lengths (*d*) and bond angles (ω) for compounds **5a** and **5d**

Parameter	**5a**	
	I	**Ia**
Bond length	*d*/Å	
Ni(1)—N(1)	1.807(3)	1.823(3)
Ni(1)—N(2)	1.822(4)	1.839(3)
Ni(1)—O(6)	1.824(3)	1.817(3)
Ni(1)—O(3)	1.841(3)	1.817(3)
N(1)—C(5)	1.299(5)	1.318(5)
N(1)—C(6)	1.431(5)	1.421(5)
N(2)—C(16)	1.286(5)	1.316(5)
N(2)—C(11)	1.419(5)	1.406(5)
C(6)—C(11)	1.369(6)	1.384(6)
O(3)—C(3)	1.252(5)	1.262(5)
O(6)—C(14)	1.269(5)	1.277(5)
C(13)—C(14)	1.394(6)	1.368(6)
C(13)—C(16)	1.403(6)	1.395(6)
C(2)—C(3)	1.384(6)	1.369(6)
C(2)—C(5)	1.405(6)	1.399(6)
C(1)—O(1)	1.177(5)	1.185(6)
O(4)—C(12)	1.169(5)	1.179(6)
C(1)—C(2)	1.485(6)	1.503(6)
C(12)—C(13)	1.485(6)	1.485(6)
Angle	ω/deg	
N(1)—Ni(1)—N(2)	86.86(16)	86.41(16)
O(6)—Ni(1)—O(3)	87.14(13)	85.07(13)
N(2)—Ni(1)—O(6)	93.12(15)	94.51(15)
N(1)—Ni(1)—O(3)	92.87(15)	93.99(14)
C(5)—N(1)—Ni(1)	127.0(3)	126.2(3)
C(16)—N(2)—Ni(1)	126.8(3)	124.1(3)
C(6)—N(1)—Ni(1)	113.9(3)	113.4(3)
C(11)—N(2)—Ni(1)	112.7(3)	114.0(3)
C(3)—O(3)—Ni(1)	129.7(3)	128.8(3)
C(14)—O(6)—Ni(1)	129.6(3)	128.6(3)
C(14)—C(13)—C(16)	119.6(4)	120.3(4)
C(3)—C(2)—C(5)	119.6(4)	121.9(4)

Parameter	**5d**
Bond length	*d*/Å
Ni(1)—N(1)	1.8403(19)
Ni(1)—N(2)	1.8315(19)
Ni(1)—O(2)	1.8395(17)
Ni(1)—O(1)	1.8398(16)
N(1)—C(12)	1.300(3)
N(1)—C(1)	1.421(3)
N(2)—C(15)	1.302(3)
N(2)—C(6)	1.426(3)
C(6)—C(1)	1.393(3)
O(1)—C(9)	1.281(3)
O(2)—C(16)	1.266(3)
C(16)—C(14)	1.386(3)
C(15)—C(14)	1.423(3)
C(8)—C(9)	1.378(3)
C(8)—C(12)	1.410(3)
O(3)—C(7)	1.197(3)
O(5)—C(13)	1.195(3)
C(8)—C(7)	1.490(4)
C(14)—C(13)	1.476(3)
Angle	ω/deg
N(2)—Ni(1)—N(1)	86.61(8)
O(2)—Ni(1)—O(1)	85.38(7)
N(2)—Ni(1)—O(2)	93.69(8)
O(1)—Ni(1)—N(1)	94.30(8)
C(12)—N(1)—Ni(1)	125.28(18)
C(15)—N(2)—Ni(1)	125.75(17)
C(1)—N(1)—Ni(1)	113.29(14)
C(6)—N(2)—Ni(1)	113.15(15)
C(16)—O(2)—Ni(1)	128.28(16)
C(9)—O(1)—Ni(1)	127.82(16)
C(9)—C(8)—C(12)	120.7(2)
C(16)—C(14)—C(15)	119.2(2)

node is due to non-equivalency of the bonds that form the square. The chelate node is characterized by the strong delocalization of the electron density of the six-membered metallocycles, which is observed in the equalization of groups of the Ni—X bond lengths (X = N, O), C—X (X = N, O) and the C—C bond lengths of the metallocycle (see Table 3). In particular, the measured difference in the C—C bond length in the metallocycle does not exceed 0.04 Å, whereas that in the C—O and C—N bond lengths is 0.03 Å. It is impossible to choose unambiguously between the imino enol and amino enone forms of the chelate moiety. At the same time, the C—CO_2Et and N—Ar bond lengths close to standard values for ordinary bonds indicate the absence of a considerable conjugation between these moieties and the electron system of six-membered metallocycles.

The molecular packing of **5a** is formed by zigzag alternation of stacks of molecules **I** and **Ia** with the interplanar distance 3.43 Å (see Fig. 4), which suggests intermolecular contacts inside the stack. The cavities between the stacks are occupied by acetonitrile molecules. The packing in the stack can be described by the alternation of the Ni—Ni-bonded dimers of molecules **I** and **Ia** in the sequence —**I**—**I**—**Ia**—**Ia**— in such a way that the Ni—Ni distance in the stack varies from 3.43 Å for Ni(1)—Ni(1A) to 3.56 Å for Ni(1)—Ni(1) and 4.46 Å for Ni(1A)—Ni(1A).

According to the X-ray diffraction data, the spatial structure of molecules of nonsymmetric complex **5d** (see Fig. 5) resembles the structure of symmetric metal complex **5a** (see Fig. 3). The molecule is slightly convex, the dihedral angle between the planes Ni(1)N(1)C(1)C(6)-N(2) and Ni(1)O(1)C(9)C(8)C(12)N(1) is 4.5°, that between Ni(1)N(1)C(1)C(6)N(2) and Ni(1)O(2)C(14)-C(15)C(16)N(2) is 7.1°, and the angle between the Ni(1)O(2)C(14)C(15)C(16)N(2) and Ni(1)O(1)C(9)-C(8)C(12)N(1) planes is 10.7°. The deviation of the particular atoms of the chelate cycles from the root-mean square plane that passes through these cycles reaches 0.2 Å. The coordination mode of the nickel atom is a distorted square. The distortions made by nonequivalence of the substituted are insignificant and compared with the distortions observed for compound **5a** (see Table 3).

The molecular packing is formed by splay stacks of molecules, and centrosymmetric Ni—Ni-bonded dimers with of interplanar distance of 3.45(6) Å can be distinguished inside the stacks, where the interplanar distance between the dimers is somewhat longer, being 3.52 Å (see Fig. 6).

Thus, we showed a possibility of preparing tri- and tetradentate ligands **2** and **3** based on the reactions of ethyl 2-ethoxymethylidene-3-oxo-3-polyfluoroalkylpropionates **1** with *o*-phenylenediamine. Depending on the ratio of the reactants, one can synthesize products of both mono- and disubstitution, being tri- or tetradentate ligands **2** and **3**, respectively. Metal complexes **4** of the composition (L = H)CuCl and complexes **5** of the composition (L = 2H)M (M = Ni^{II}, Cu^{II}, Co^{II}) were synthesized from tridentate ligands **2** and tetradentate ligands **3**, respectively. The spatial structure of the synthesized complexes was studied by X-ray diffraction analysis.

Experimental

Melting points were measured in open capillaries with a Stuart SMP3 apparatus for melting temperature determination. IR diffuse reflectance spectra were recorded on a Perkin—Elmer Spectrum One FTIR spectrometer (suspension with Nujol). NMR spectra were obtained on a Bruker DRX-400 spectrometer (^{1}H, 400 MHz, relative to Me$_4$Si; ^{19}F, 376 MHz, relative to C$_6$F$_6$) (solutions in CDCl$_3$). Elemental analysis was carried out with a Perkin—Elmer PE 2400 series II CHNS-O elemental analyzer. The reaction course 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 earlier.[22]

The X-ray diffraction studies of compounds **2b**, **4b**, and **5a,d** were performed on an Xcalibur 3 diffractometer equipped with a CCD detector (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, 295(2) K (120(2) K for **2b**), ω scan mode, scan increment 1°, time of frame measurement 20 s). A fragment of the red

Table 4. Crystallographic data and parameters of X-ray experiment for compounds **2b**, **4b**, and **5a,d**

Parameter	**2b**	**4b**	**5a**	**5d**
Molecular formula	$C_{14}H_{14}F_4N_2O_3$	$C_{14}H_{13}ClCuF_4N_2O_3$	$C_{42}H_{35}F_{12}N_5Ni_2O_{12}$	$C_{21}H_{17}F_7N_2NiO_6$
Molecular weight	334.27	432.25	1147.17	585.08
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*C*2/*c*	*P*2$_1$/*n*	*P*2$_1$/*n*	*P*-1
a/Å	14.2258(19)	14.8456(12)	14.4067(12)	8.9249(14)
b/Å	10.9485(15)	6.1422(6)	14.1185(8)	11.3653(16)
c/Å	18.883(3)	19.5709(19)	22.458(3)	13.0296(17)
α/deg	90	90	90	97.183(11)
β/deg	96.250(11)	110.895(8)	90.030(9)	107.600(13)
γ/deg	90	90	90	111.082(14)
Volume/Å^3	2923.5(7)	1667.2(3)	4567.9(7)	1134.1(3)
Z	8	4	4	2
d_{calc}/g cm^{-3}	1.519	1.722	1.668	1.713
μ/mm^{-1}	0.140	1.528	0.941	0.955
F(000)	1376	868	2328	592
Scan angle, θ/deg	3.09 < θ < 26.37	2.94 < θ < 26.38	2.71 < θ < 26.36	2.80 < θ < 26.37
Number of collected reflections	5218	5580	26028	9923
Number of independent reflections	2965 (R_{int} = 0.0231)	3341 (R_{int} = 0.0147)	9055 (R_{int} = 0.0934)	4617 (R_{int} = 0.0240)
Number of reflections with $I > 2\sigma(I)$	1916	2345	4564	2899
Collection completeness (%) (for θ/deg)	98.9% (26.37)	97.8% (26.00)	97.3% (26.00)	99.4% (26.37)
Number of calculated parameters	220	226	658	334
Goodness-of-fit *S* on F^2	1.006	1.001	1.001	1.001
R_1 [$I > 2\sigma(I)$]	0.0335	0.0273	0.0566	0.0366
wR_2 [$I > 2\sigma(I)$]	0.0755	0.0672	0.1278	0.0778
R_1 (for all reflections)	0.0573	0.0454	0.1144	0.0672
wR_2 (for all reflections)	0.0787	0.0714	0.1394	0.0822
Residual electron density /e · Å^3, ρ_{max}/ρ_{min}	0.211/–0.179	0.286/–0.338	0.584/–0.368	0.730/–0.235

filament crystal 0.29S0.15S0.06 mm in size was used for the study of compound **5a**, and a fragment of the red filament crystal 0.22S0.13S0.06 mm in size was used for studying compound **5d**. An absorption correction was applied analytically by the polyhedral crystal model.[24] The structure was solved by a direct method using the SHELXS97 program[25] and refined using the SHELXL97 program[26] by the least-squares method in the anisotropic full-matrix approximation for non-hydrogen atoms. Hydrogen atoms were added to the geometrically calculated positions and included into refinement in the isotropic approximation with the dependent thermal parameters in the riding model. The main parameters of structural experiments are given in Table 4. The bond lengths and bond angles characterizing compounds **2b** and **4b** are listed in Table 1, and those for compound **5a,d** are presented in Table 3.

The full array of crystallographic data for compounds **2b**, **4b**, and **5a,d** was deposited with the Cambridge Crystallographic Data Centre (CCDC Nos 772 368, 751 317, 751 318, and 751 319, respectively) and is available at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Ethyl 2-[*N*-(2-aminophenyl)aminomethylidene]-3-oxo-4,4,4-trifluorobutanoate (2a). A mixture of ester **1a** (0.96 g, 4 mmol) and *o*-phenylenediamine (0.43 g, 4 mmol) in diethyl ether (10 mL) was stirred for 30 min at ~20 °C. Then the reaction mixture was evaporated, and the oil formed was triturated in hexane until precipitation. The yield was 1.08 g (89%), yellow powder, m.p. 76—78 °C. IR, ν/cm^{-1}: 3454, 3346 (NH_2); 3196 (ν(NH)); 3047, 2981 (C—H); 1710 (CO_2Et); 1647 (C=O); 1625, 1595, 1577 (C=C, δ(NH)); 1182—1011 (C—F). ^1H NMR, δ: *E* + *Z*: 7.10—7.19 (m, 3 H, CH, NH_2); 6.85—6.92 (m, 3 H, C_6H_4); *E* (66%): 1.34 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.2 Hz); 4.29 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.2 Hz); 8.55 (d, 1 H, CH, ^3J = 13.9 Hz); 12.13 (d, 1 H, NH, ^3J = 13.9 Hz); *Z* (34%): 1.37 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.1 Hz); 4.33 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.1 Hz); 8.40 (d, 1 H, CH, ^3J = 13.9 Hz); 11.29 (d, 1 H, NH, ^3J = 13.9 Hz). ^{19}F NMR, δ: *E* (66%): 89.13 (s, 3 F, CF_3); *Z* (34%): 90.04 (s, 3 F, CF_3). Found (%): C, 51.73; H, 4.17; F, 19.05; N, 9.02. $C_{13}H_{13}F_3N_2O_3$. Calculated (%): C, 51.66; H, 4.34; F, 18.86; N, 9.27.

Ethyl 2-[*N*-(2-aminophenyl)aminomethylidene]-3-oxo-4,4,5,5,6,6,6-heptafluorohexanoate (2b) was synthesized similarly to compound **2a** from ester **1b** (1.09 g, 4 mmol). The yield was 1.22 g (91%), yellow powder, m.p. 89—90 °C. IR, ν/cm^{-1}: 3459, 3360 (NH_2); 3200, 3177 (ν(NH)); 3023, 2982 (C—H); 1707 (CO_2Et); 1673 (C=O); 1629, 1604, 1588 (C=C, δ(NH)); 1245—1079 (C—F). ^1H NMR, δ: *E* + *Z*: 6.87—6.94 (m, 3 H, C_6H_4); 7.10—7.19 (m, 3 H, CH, NH_2); *E* (72%): 1.34 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.1 Hz); 4.28 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.1 Hz); 6.73 (tt, 2 H, 2 $(CF_2)_2H$, ^2J = 53.8 Hz, ^3J = 5.8 Hz); 8.46 (d, 1 H, CH, ^3J = 13.7 Hz); 12.18 (d, 1 H, NH, ^3J = 13.7 Hz); *Z* (28%): 1.37 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.1 Hz); 4.32 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.1 Hz); 6.36 (tt, 2 H, 2 $(CF_2)_2H$, ^2J = 53.2 Hz, ^3J = 5.8 Hz); 8.34 (d, 1 H, CH, ^3J = 13.9 Hz); 11.14 (d, 1 H, NH, ^3J = 13.9 Hz). ^{19}F NMR, δ: *E* (72%): 24.18 (dm, 2 F, CF_2H, ^2J = 53.2 Hz); 39.75 (m, 2 F, CF_2); *Z* (28%): 22.05 (dm, 2 F, CF_2H, ^2J = 53.8 Hz); 41.38 (m, 2 F, CF_2). Found (%): C, 50.19; H, 4.18; F, 22.60; N, 8.29. $C_{14}H_{14}F_4N_2O_3$. Calculated (%): C, 50.30; H, 4.22; F, 22.73; N, 8.38.

Ethyl 2-[*N*-(2-aminophenyl)aminomethylidene]-3-oxo-4,4,5,5,6,6,6-heptafluorohexanoate (2c) was synthesized similarly to compound **2a** from **1c** (1.36 g, 4 mmol). The yield was 1.38 g (86%), yellow powder, m.p. 69—70 °C. IR, ν/cm^{-1}: 3410, 3346 (NH_2); 3254 (ν(NH)); 3054, 2989 (C—H); 1697 (CO_2Et); 1649 (C=O); 1639, 1623, 1568 (C=C, δ(NH)); 1228—1130 (C—F). ^1H NMR, δ: *E* + *Z*: 7.11—7.19 (m, 3 H, CH, NH_2); 6.84—6.92 (m, 3 H, C_6H_4); *E* (56%): 1.33 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.1 Hz); 4.29 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.1 Hz); 8.45 (d, 1 H, CH, ^3J = 13.8 Hz); 11.99 (d, 1 H, NH, ^3J = 13.8 Hz); *Z* (44%): 1.36 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.1 Hz); 4.33 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.1 Hz); 8.29 (d, 1 H, CH, ^3J = 13.8 Hz); 11.16 (d, 1 H, NH, ^3J = 13.8 Hz). ^{19}F NMR, δ: *E* (56%): 38.34 (m, 2 F, β-CF_2); 48.66 (m, 2 F, α-CF_2); 81.51 (t, 3 F, CF_3, *J* = 9.9 Hz); *Z* (44%): 37.51 (m, 2 F, β-CF_2); 49.25 (m, 2 F, α-CF_2); 81.68 (t, 3 F, CF_3, *J* = 9.5 Hz). Found (%): C, 44.97; H, 3.11; F, 33.12; N, 6.94. $C_{15}H_{13}F_7N_2O_3$. Calculated (%): C, 44.79; H, 3.26; F, 33.06; N, 6.96.

Diethyl 2,2´-[1,2-phenylenebis(aminomethylidene)]bis(4,4,4-trifluoro-3-oxobutanoate) (3a). A mixture of ester **1a** (1.20 g, 5 mmol) and *o*-phenylenediamine (0.27 g, 2.5 mmol) in diethyl ether (20 mL) was stirred for 3 h at ~20 °C. Then the reaction mixture was concentrated, and the precipitate formed was filtered off, washed with hexane, and recrystallized from ethanol. The yield was 1.39 g (56%), light yellow powder, m.p. 117—119 °C. IR, ν/cm^{-1}: 3196 (ν(NH)); 2971, 2959 (C—H); 1724 (CO_2Et); 1698 (C=O); 1651, 1628, 1607, 1583 (C=C, δ(NH)); 1279—1130 (C—F). ^1H NMR, δ: all isomers: 7.39—7.46 (m, 4 H, C_6H_4); *E,E* (28%): 1.33 (t, 6 H, 2 $OCH_2C\underline{H}_3$, ^3J = 7.2 Hz); 4.28 (q, 4 H, 2 $OC\underline{H}_2CH_3$, ^3J = 7.2 Hz); 8.51 (d, 2 H, 2 CH, ^3J = 13.3 Hz); 12.15 (br.d, 2 H, 2 NH, ^3J = 13.3 Hz); *E,Z* (54%): 1.36, 1.33 (both t, 3 H each, 2 $OCH_2C\underline{H}_3$, ^3J = 7.2 Hz); 4.29, 4.32 (both q, 2 H each, 2 $OC\underline{H}_2CH_3$, ^3J = 7.2 Hz); 8.36, 8.51 (both d, 1 H each, 2 CH, ^3J = 13.3 Hz); 11.59, 12.11 (both d, 1 H each, 2 NH, ^3J = 13.3 Hz); *Z,Z* (18%): 1.36 (t, 6 H, 2 $OCH_2C\underline{H}_3$, ^3J = 7.2 Hz); 4.32 (q, 4 H, 2 $OC\underline{H}_2CH_3$, ^3J = 7.2 Hz); 8.36 (d, 2 H, 2 CH, ^3J = 13.3 Hz); 11.59 (br.d, 2 H, 2 NH, ^3J = 13.3 Hz). ^{19}F NMR, δ: *E,E* (28%): 88.92 (s, 2 CF_3); *E,Z* (54%): 88.95, 89.73 (both s, 2 CF_3); *Z,Z* (18%): 89.79 (s, 2 CF_3). Found (%): C, 48.35; H, 3.43; F, 22.76; N, 5.64. $C_{20}H_{18}F_6N_2O_6$. Calculated (%): C, 48.40; H, 3.66; F, 22.96; N, 5.64.

Diethyl 2,2´-[1,2-phenylenebis(aminomethylidene)]bis-(4,4,5,5-tetrafluoro-3-oxopentanoate) (3b) was synthesized similarly to compound **3a** from ester **1b** (1.36 g, 5 mmol). The yield was 1.82 g (65%), cream-colored powder, m.p. 133—135 °C. IR, ν/cm^{-1}: 3206 (ν(NH)); 3009, 2958 (C—H); 1698 (CO_2Et); 1638 (C=O); 1619, 1588, 1545 (C=C, δ(NH)); 1266—1079 (C—F). ^1H NMR, δ: all isomers: 7.44—7.36 (m, 4 H, C_6H_4); *E,E* (30%): 1.35 (t, 6 H, 2 $OCH_2C\underline{H}_3$, ^3J = 7.2 Hz); 4.30 (q, 4 H, 2 $OC\underline{H}_2CH_3$, ^3J = 7.2 Hz); 6.59 (tt, 2 H, 2 $H(CF_2)_2$, ^2J = 53.5 Hz, ^3J = 5.87 Hz); 8.40 (d, 2 H, 2 CH, ^3J = 13.1 Hz); 12.17 (br.d, 2 H, 2 NH, ^3J = 13.1 Hz); *E,Z* (52%): 1.35, 1.36 (both t, 3 H each, 2 $OCH_2C\underline{H}_3$, ^3J = 7.0 Hz); 4.30, 4.34 (both q, 2 H each, 2 $OC\underline{H}_2CH_3$, ^3J = 7.2 Hz); 6.34, 6.67 (both tt, 1 H each, 2 $H(CF_2)_2$, ^2J = 53.0 Hz, ^3J = 5.87 Hz); 8.29, 8.40 (both d, 1 H each, 2 CH, ^3J = 13.1 Hz); 11.45, 12.15 (both br.d, 1 H each, 2 NH, ^3J = 13.1 Hz); *Z,Z* (18%): 1.36 (t, 6 H, 2 $OCH_2C\underline{H}_3$, ^3J = 7.2 Hz); 4.34 (q, 4 H, 2 $OC\underline{H}_2CH_3$, ^3J = 7.2 Hz); 6.34 (tt, 2 H, 2 $H(CF_2)_2$, ^2J = 53.5 Hz, ^3J = 5.87 Hz);

8.29 (d, 2 H, 2 CH, ^3J = 13.1 Hz); 11.45 (br.d, 2 H, 2 NH, ^3J = 13.1 Hz). ^{19}F NMR, δ: *E,E* (30%): 23.45 (dt, 4 F, 2 HCF$_2$, ^2J = 53.4 Hz, ^3J = 7.9 Hz); 39.54 (m, 4 F, 2 CF$_2$); *E,Z* (52%): 22.24 (dm, 2 F, HCF$_2$, ^2J = 53.1 Hz); 23.89 (dt, 2 F, HCF$_2$, ^2J = 53.4 Hz, ^3J = 7.9 Hz); 39.64 (m, 2 F, CF$_2$); 41.33 (m, 2 F, CF$_2$); *Z,Z* (18%): 22.19 (dm, 4 F, 2 HCF$_2$, ^2J = 52.9 Hz); 41.33 (m, 4 F, 2 CF$_2$). Found (%): C, 47.32; H, 3.43; F, 27.21; N, 4.89. $C_{22}H_{20}F_8N_2O_6$. Calculated (%): C, 47.15; H, 3.60; F, 27.12; N, 5.00.

Diethyl 2,2´-[1,2-phenylenebis(aminomethylidene)]bis(4,4,5,5,6,6,6-heptafluoro-3-oxopentanoate) (3c) was synthesized similarly to compound **3a** from **1c** (1.70 g, 5 mmol). The yield was 1.43 g (72%), milk-white powder, m.p. 140—142 °C. IR, ν/cm^{-1}: 3210 (ν(NH)); 3015, 2953 (C—H); 1710 (CO$_2$Et); 1660 (C=O); 1621, 1580 (C=C, δ(NH)); 1269—1057 (C—F). ^{1}H NMR, δ: all isomers: 7.40—7.43 (m, 4 H, C$_6$H$_4$); *E,E* (35%): 1.31 (t, 6 H, 2 $OCH_2C\underline{H}_3$, ^3J = 7.1 Hz); 4.27 (q, 4 H, 2 $OC\underline{H}_2CH_3$, ^3J = 7.1 Hz); 8.65 (d, 2 H, 2 CH, ^3J = 13.3 Hz); 12.00 (br.d, 2 H, 2 NH, ^3J = 13.3 Hz); *E,Z* (45%): 1.35, 1.32 (both t, 3 H each, 2 $OCH_2C\underline{H}_3$, ^3J =7.1 Hz); 4.29, 4.34 (both q, 2 H each, 2 $OC\underline{H}_2CH_3$, *J* = 7.1); 8.65, 8.42 (both d, 1 H each, 2 CH, ^3J = 13.3 Hz); 11.60, 12.00 (both d, 1 H each, 2 NH, ^3J = 13.3 Hz); *Z,Z* (20%): 1.35 (t, 6 H, 2 $OCH_2C\underline{H}_3$, ^3J = 7.1 Hz); 4.34 (q, 4 H, 2 $OC\underline{H}_2CH_3$, ^3J = 7.1 Hz); 8.42 (d, 2 H, 2 CH, ^3J = 13.3 Hz); 11.60 (br.d, 2 H, 2 NH, ^3J = 13.3 Hz). ^{19}F NMR, δ: *E,E* (35%): 38.31 (m, 4 F, 2 β-CF$_2$); 48.44 (m, 4 F, 2 α-CF$_2$); 81.52 (t, 6 F, 2 CF$_3$, ^3J = 9.8 Hz); *E,Z* (45%): 37.55, 38.31 (both m, 2 F each, 2 β-CF$_2$); 48.44, 48.93 (both m, 2 F each, 2 α-CF$_2$); 81.52, 81.63 (both t, 3 F each, 2 CF$_3$, ^3J = 9.8 Hz); *Z,Z* (20%): 37.55 (m, 4 F, 2 β-CF$_2$); 48.93 (m, 4 F, 2 α-CF$_2$); 81.65 (t, 6 F, 2 CF$_3$, ^3J = 9.8 Hz). Found (%): C, 36.22; H, 2.23; F, 33.45; N, 3.50. $C_{24}H_{18}F_{14}N_2O_6$. Calculated (%): C, 36.37; H, 2.27; F, 33.58; N, 3.54.

Ethyl 2-({2-[*N*-(2-ethoxycarbonyl-3-oxo-3,3,3-trifluorobut-1-en-1-yl)amino]phenyl}aminomethylidene)-3-oxo-4,4,5,5-tetrafluoropentanoate (3d). A mixture of ester **2a** (0.91 g, 3 mmol) and ester **1b** (0.82 g, 3 mmol) in diethyl ether (15 mL) was stirred for 4 h at ~20 °C. Then the reaction mixture was evaporated, and the precipitate that formed was filtered off and recrystallized from hexane. The yield was 0.95 g (60%), milk-white powder, m.p. 115—118 °C. IR, ν/cm^{-1}: 3205 (ν(NH)); 3030, 2994 (C—H); 1726 (CO$_2$Et); 1700 (C=O); 1619, 1594, 1553 (C=C, δ(NH)); 1222—1027 (C—F). ^{1}H NMR, δ: all isomers: 1.33—1.39 (m, 6 H, 2 $OCH_2C\underline{H}_3$); 4.38—4.27 (m, 4 H, 2 $OC\underline{H}_2CH_3$); 7.32—7.45 (m, 4 H, C$_6$H$_4$); *E,E* (25%): 6.60 (tt, 1 H, (CF$_2$)$_2$H, ^2J = 53.5 Hz, ^3J = 5.8 Hz); 8.40 (d, 1 H, CH, ^3J = 13.1 Hz); 8.50 (d, 1 H, CH, ^3J = 13.1 Hz); 12.15 (br.d, 2 H, 2 NH, ^3J = 13.1 Hz); *Z,Z* (20%): 6.34 (tt, 1 H, (CF$_2$)$_2$H, ^2J= 52.9 Hz, ^3J = 5.8 Hz); 8.28 (d, 1 H, CH, ^3J = 13.2 Hz); 8.35 (d, 1 H, CH, ^3J = 13.2 Hz); 11.33 (d, 1 H, NH, ^3J = 13.2 Hz); 11.48 (d, 1 H, NH, ^3J = 13.2 Hz); *E,Z* (30%): 6.66 (tt, 1 H, (CF$_2$)$_2$H, ^2J = 53.7 Hz, ^3J = 6.0 Hz); 8.36 (d, 1 H, CH, ^3J = 13.3 Hz); 8.39 (d, 1 H, CH, ^3J = 13.3 Hz); 11.62 (d, 1 H, NH, ^3J = 13.3 Hz); 12.11 (d, 1 H, NH, ^3J = 13.3 Hz); *Z,E* (25%): 6.33 (tt, 1 H, (CF$_2$)$_2$H, ^2J = 53.3 Hz, ^3J = 6.0 Hz); 8.29 (d, 1 H, CH, ^3J = 13.2 Hz); 8.49 (d, 1 H, CH, ^3J= 13.2 Hz); 11.43 (d, 1 H, NH, ^3J = 13.2 Hz); 12.12 (d, 1 H, NH, ^3J = 13.2 Hz). ^{19}F NMR, δ: *E,E* (25%): 23.54 (dt, 2 F, HCF$_2$, ^2J = 53.5 Hz, ^3J = 7.7 Hz); 39.58 (m, 2 F, CF$_2$); 88.89 (s, 3 F, CF$_3$); *Z,Z* (20%): 22.16 (dm, 2 F, HCF$_2$, ^2J = 53.2 Hz); 41.34 (m, 2 F, CF$_2$); 89.78 (s, 3 F, CF$_3$); *E,Z* (30%): 23.88 (dt, 2 F, HCF$_2$, ^2J = 53.6 Hz, ^3J = 7.9 Hz); 39.63 (m, 2 F, CF$_2$); 89.71 (s, 3 F, CF$_3$); *Z,E* (25%): 22.21 (dm, 2 F, HCF$_2$, ^2J = 53.1 Hz); 41.29 (m, 2 F, CF$_2$); 88.87 (s, 3 F, CF$_3$). Found (%): C, 47.72; H, 3.50; F, 25.43; N, 5.62. $C_{21}H_{19}F_7N_2O_6$. Calculated (%): C, 47.74; H, 3.62; F, 25.17; N, 5.30.

Ethyl 2-({2-[*N*-(2-ethoxycarbonyl-3-oxo-3,3,3-trifluorobut-1-en-1-yl)amino]phenyl}aminomethylidene)-3-oxo-4,4,5,5,5,6,6,6-heptafluorohexanoate (3e) was synthesized similarly to compound **3d** from ester **2c** (1.21 g, 3 mmol) and ester **1a** (0.72 g, 3 mmol). The yield was 1.13 g (63%), milk-white powder, m.p. 80—83 °C. IR, ν/cm^{-1}: 3207 (ν(NH)); 3043, 2989 (C—H); 1699 (CO$_2$Et); 1659 (C=O); 1633, 1586, 1562 (C=C, δ(NH)); 1230—1119 (C—F). ^{1}H NMR, δ: all isomers: 1.31—1.39 (m, 6 H, $OCH_2C\underline{H}_3$); 4.28—4.73 (m, 4 H, $OC\underline{H}_2CH_3$); 7.30—7.45 (m, 4 H, C$_6$H$_4$); *E,E* (19%): 8.41 (d, 1 H, CH, ^3J = 13.2 Hz); 8.49 (d, 1 H, CH, ^3J = 13.2 Hz); 12.02 (d, 1 H, NH, ^3J = 13.2 Hz); 12.17 (d, 1 H, NH, ^3J = 13.2 Hz); *Z,Z* (20%): 8.22 (d, 1 H, CH, ^3J = 13.1 Hz); 8.35 (d, 1 H, CH, ^3J = 13.3 Hz); 11.34 (d, 1 H, NH, ^3J = 13.3 Hz); 11.64 (d, 1 H, NH, ^3J = 13.1 Hz); *E,Z* (25%): 8.34 (d, 1 H, CH, ^3J = 13.2 Hz); 8.41 (d, 1 H, CH, ^3J = 13.2 Hz); 11.60 (d, 1 H, NH, ^3J = 13.2 Hz); 11.99 (d, 1 H, NH, ^3J = 13.2 Hz); *Z,E* (36%): 8.22 (d, 1 H, CH, ^3J = 13.1 Hz); 8.50 (d, 1 H, CH, ^3J = 13.1 Hz); 11.44 (1 H, NH, ^3J = 13.1 Hz); 12.10 (d, 1 H, NH, ^3J = 13.1 Hz). ^{19}F NMR, δ: *E,E* (19%): 38.09 (m, 2 F, β-CF$_2$); 48.26 (m, 2 F, α-CF$_2$); 81.64 (t, 3 F, CF$_3$, ^3J = 9.9 Hz); 88.73 (s, 3 F, CF$_3$); *Z,Z* (20%): 37.47 (m, 2 F, β-CF$_2$); 48.95 (m, 2 F, α-CF$_2$); 81.59 (t, 3 F, CF$_3$, ^3J = 9.6 Hz); 89.71 (s, 3 F, CF$_3$); *E,Z* (25%): 38.02 (m, 2 F, β-CF$_2$); 48.18 (m, 2 F, α-CF$_2$); 81.61 (t, 3 F, CF$_3$, ^3J = 9.8 Hz); 89.79 (s, 3 F, CF$_3$); *Z,E* (36%): 37.46 (m, 2 F, β-CF$_2$); 48.89 (m, 2 F, α-CF$_2$); 81.60 (t, 3 F, CF$_3$, ^3J = 9.6 Hz); 88.89 (s, 3 F, CF$_3$). Found (%): C, 44.41; H, 3.03; F, 31.75; N, 4.70. $C_{22}H_{18}F_{10}N_2O_6$. Calculated (%): C, 44.31; H, 3.04; F, 31.86; N, 4.70.

Ethyl 2-({2-[*N*-(2-ethoxycarbonyl-3-oxo-4,4,5,5-tetrafluoropent-1-en-1-yl)amino]phenyl}aminomethylidene)-3-oxo-4,4,5,5,5,6,6,6-heptafluorohexanoate (3f) was synthesized similarly to compound **3d** from ester **2c** (1.21 g, 3 mmol) and ester **1b** (0.82 g, 3 mmol). The yield was 1.23 g (65%), milk-white powder, m.p. 98—100 °C. IR, ν/cm^{-1}: 3177 (ν(NH)); 3004, 2984 (C—H); 1725 (CO$_2$Et); 1703 (C=O); 1631, 1546, 1517 (C=C, δ(NH)); 1263—1084 (C—F). ^{1}H NMR, δ: all isomers: 1.31—1.39 (m, 6 H, 2 $OCH_2C\underline{H}_3$); 4.27—4.38 (m, 4 H, 2 $OC\underline{H}_2CH_3$); 7.32—7.44 (m, 4 H, C$_6$H$_4$); *E,E* (30%): 6.66 (tt, 1 H, H(CF$_2$)$_2$, ^2J = 53.8 Hz, ^3J = 5.6 Hz); 8.39 (d, 1 H, CH, ^3J = 13.1 Hz); 8.40 (d, 1 H, CH, ^3J = 13.1 Hz); 12.20 (d, 1 H, NH, ^3J = 13.1 Hz); 12.15 (d, 1 H, NH, ^3J = 13.1 Hz); *Z,Z* (29%): 6.34 (tt, 1 H, CF$_2$H, ^2J = 53.0 Hz, ^3J = 6.0 Hz); 8.22 (d, 1 H, CH, ^3J = 13.0 Hz); 8.29 (d, 1 H, CH, ^3J = 13.1 Hz); 11.45 (d, 1 H, NH, ^3J = 13.0 Hz); 11.48 (d, 1 H, NH, ^3J = 13.1 Hz); *E,Z* (15%): 6.58 (tt, 1 H, H(CF$_2$)$_2$, ^2J= 53.6 Hz, ^3J = 6.0 Hz); 8.21 (d, 1 H, CH, ^3J = 12.9 Hz); 8.38 (d, 1 H, CH, ^3J = 13.0 Hz); 11.34 (1 H, NH, ^3J = 13.0 Hz); 11.99 (1 H, NH, ^3J = 12.9 Hz); *Z,E* (26%): 6.59 (tt, 1 H, H(CF$_2$)$_2$, ^2J = 53.1 Hz, ^3J = 6.0 Hz); 8.28 (d, 1 H, CH, ^3J = 13.2 Hz); 8.41 (d, 1 H, CH, ^3J = 13.1 Hz); 11.31 (1 H, NH, ^3J = 13.1 Hz); 12.03 (1 H, NH, ^3J = 13.2 Hz). ^{19}F NMR, δ: *Z,Z* (29%): 22.34 (dm, 2 F, $HC\underline{F}_2CF_2$, ^2J = 53.0 Hz); 37.98 (m, 2 F, β-CF$_2$); 41.36 (m, 2 F, $HCF_2C\underline{F}_2$); 48.18 (m, 2 F, α-CF$_2$); 81.61 (t, 3 F, CF$_3$, ^3J = 9.8 Hz); *Z,E* (26%): 22.18 (dm, 2 F, $HC\underline{F}_2CF_2$, ^2J = 53.1 Hz); 38.10 (m, 2 F, β-CF$_2$); 41.32 (m, 2 F, $HCF_2C\underline{F}_2$); 48.27 (m, 2 F, α-CF$_2$); 81.59 (t, 3 F, CF$_3$, ^3J = 9.2 Hz); *E,E* (30%): 23.88 (dt, 2 F, $HC\underline{F}_2CF_2$, ^3J = 53.8 Hz); 37.47 (m, 2 F, β-CF$_2$); 39.63 (m, 2 F, $HCF_2C\underline{F}_2$); 48.89 (m, 2 F, α-CF$_2$);

81.60 (t, 3 F, CF_3, ^3J = 9.9 Hz); *E,Z* (15%): 23.89 (dt, 2 F, $HC\underline{F}_2CF_2$, ^2J = 53.6 Hz); 37.45 (m, 2 F, β-CF_2); 39.54 (m, 2 F, $HCF_2C\underline{F}_2$); 48.94 (м, 2 F, α-CF_2); 81.58 (t, 3 F, CF_3, ^3J = 9.9 Hz). Found (%): C, 44.25; H, 3.17; F, 33.57; N, 4.62. $C_{23}H_{19}F_{11}N_2O_6$. Calculated (%): C, 43.96; H, 3.05; F 33.26; N, 4.46.

Chloro{ethyl 2-[(2-aminophenyl)aminatomethylidene]-3-oxo-4,4,5,5-tetrafluoropentanoate}copper(II) (4b). A mixture of ester **2b** (0.67 g, 0.002 mol) and copper(II) chloride (0.40 g, 0.003 mol) in ethanol (10 mL) was refluxed with stirring for 2 h, and the precipitate formed was filtered off and recrystallized from ethanol. The yield was 0.69 g (80%), dark green powder, m.p. 205—207 °C. IR, ν/cm^{-1}: 3093—2943 (ν(C—H)), 1704 (CO_2Et), 1660 (COR^F), 1615 (C=N), 1591 (C=C), 1292—1058 (C—F). Found (%): C, 39.11; H, 2.95; N, 6.50; F, 17.65. $C_{14}H_{13}ClCuF_4N_2O_3$. Calculated (%): C, 38.90; H, 3.03; N, 6.48; F, 17.58.

Synthesis of metal complexes 5 (general procedure). ***A.*** A mixture of compound **3** (2 mmol) and nickel(II) acetate (copper(II) or cobalt(II)) (2 mmol) in ethanol (30 mL) was refluxed for 5 min. The hot mixture was then filtered, the filtrate was cooled down, and the precipitate formed was filtered off and recrystallized from ethanol.

B. A mixture of ester **1** (4 mmol), *o*-phenylenediamine (2 mmol), and nickel(II) acetate (2 mmol) in ethanol (30 mL) was stirred for 2 days at ~20 °C. The precipitate formed was filtered off and recrystallized from ethanol.

1,1´-(1,2-Phenylenebisaminato)bis(3-oxo-4,4,4-trifluoro-2-ethoxycarbonylbut-1-ene)nickel(II) (5a). The yield by method *A* was 0.94 g (85%), The yield by method *B* was 0.70 g (64%), red-orange crystals, m.p. 166—168 °C. IR, ν/cm^{-1}: 2957, 2932 (C—H); 1699 (CO_2Et, C=O); 1607, 1584 (C=C); 1287—1154 (C—F). ^{1}H NMR, δ: 1.36 (t, 6 H, 2 $OCH_2C\underline{H}_3$, ^3J = 7.0 Hz); 4.32 (q, 4 H, 2 $OC\underline{H}_2CH_3$, ^3J = 7.0 Hz); 7.25 (m, 2 H, C_6H_4); 7.63 (m, 2 H, C_6H_4); 8.43 (s, 2 H, 2 CH). ^{19}F NMR, δ: 94.04 (s, CF_3). Found (%): C, 43.46; H, 2.74; F, 20.53; N, 5.05. $C_{20}H_{16}F_6N_2NiO_6$. Calculated (%): C, 43.44; H, 2.92; F, 20.60; N, 5.07.

1,1´-(1,2-Phenylenebisaminato)bis(3-oxo-4,4,4-trifluoro-2-ethoxycarbonylbut-1-ene)cobalt(II) (5b). The yield by method *A* was 0.82 g (75%), orange powder, m.p. 176—178 °C. IR, ν/cm^{-1}: 2984, 2939 (C—H); 1725 (CO_2Et); 1703 (C=O); 1607, 1582 (C=C); 1276—1103 (C—F). Found (%): C, 43.72; H, 2.84; F, 20.42; N, 4.83. $C_{20}H_{16}CoF_6N_2O_6$. Calculated (%): C, 43.42; H, 2.91; F, 20.60; N, 5.06.

1,1´-(1,2-Phenylenebisaminato)bis(3-oxo-4,4,4-trifluoro-2-ethoxycarbonylbut-1-ene)copper(II) (5c). The yield by method *A* was 0.76 g (68%), brown powder, m.p. 170—175 °C. IR, ν/cm^{-1}: 2959, 2925 (C—H); 1726 (CO_2Et); 1709 (C=O); 1611, 1583 (C=C); 1281—1130 (C—F). Found (%): C, 42.97; H, 2.80; F, 20.15; N, 5.10. $C_{20}H_{16}CuF_6N_2O_6$. Calculated (%): C, 43.06; H, 2.89; F, 20.43; N, 5.02.

1,1´-(1,2-Phenylenebisaminato)bis(3-oxo-4,4,5,5,6,6,6-heptafluoro-2-ethoxycarbonylhex-1-ene)nickel(II) (5d). The yield by method *B* was 1.19 g (79%), dark red crystals, m.p. 212—214 °C. IR, ν/cm^{-1}: 2965, 2945 (C—H); 1727 br (CO_2Et, C=O); 1605, 1583 (C=C); 1225—1122 (C—F). ^{1}H NMR, δ: 1.34 (t, 6 H, 2 $OCH_2C\underline{H}_3$, ^3J = 7.2 Hz); 4.31 (q, 4 H, 2 $OC\underline{H}_2CH_3$, ^3J = 7.2 Hz); 7.24 (m, 2 H, C_6H_4); 7.64 (m, 2 H, C_6H_4); 8.30 (s, 2 H, 2 CH). ^{19}F NMR, δ: 38.10 (m, 4 F, 2 CF_2); 51.48 (m, 4 F, 2 CF_2); 81.43 (t, 6 F, 2 CF_3). Found (%): C, 38.32; H, 1.98; F, 34.86; N, 3.37. $C_{26}H_{16}F_{14}N_2NiO_6$. Calculated (%): C, 38.28; H, 2.14; F, 35.32; N, 3.72.

{1-[*N*-(3-Oxo-3,3,3-trifluoro-2-ethoxycarbonylbut-1-en-1-yl)aminato]-2-[*N*-(3-oxo-4,4,5,5-tetrafluoro-2-ethoxycarbonylpent-1-en-1-yl)aminato]benzene}nickel(II) (5e). The yield by method *A* was 2.19 g (75%), red crystals, m.p. 163—164 °C. IR, ν/cm^{-1}: 3075, 3017, 2986 (C—H); 1726 (CO_2Et); 1701 (C=O); 1606, 1584 (C=C, NH); 1300—1045 (C—F). ^{1}H NMR, δ: 1.36 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.1 Hz); 1.37 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.1 Hz); 4.32 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.1 Hz); 4.33 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.1 Hz); 6.41 (tt, 1 H, $H(CF_2)_2$, $^2J_{H,F}$ = 53.4 Hz, $^3J_{H,F}$ = 5.5 Hz); 7.24—7.25 (m, 2 H, C_6H_4); 7.63—7.66 (m, 2 H, C_6H_4); 8.35 (s, 1 H, CH); 8.44 (s, 1 H, CH). ^{19}F NMR, δ: 23.02 (dm, 2 F, HCF_2, $^2J_{F,H}$ = 53.4 Hz); 42.90 (m, 2 F, CF_2); 93.85 (s, 3 F, CF_3). Found (%): C, 43.21; H, 3.23; F, 23.01; N, 4.62. $C_{21}H_{17}F_7N_2NiO_6$. Calculated (%): C, 43.11; H, 2.93; F, 22.73; N, 4.79.

{1-[*N*-(3-Oxo-3,3,3-trifluoro-2-ethoxycarbonylbut-1-en-1-yl)aminato]-2-[*N*-(3-oxo-4,4,5,5-tetrafluoro-2-ethoxycarbonylpent-1-en-1-yl)aminato]benzene}copper(II) (5f). The yield by method *B* was 2.05 g (70%), dark green powder, m.p. 160—162 °C. IR, ν/cm^{-1}: 2997, 2909 (C—H); 1708 br (CO_2Et, C=O); 1605, 1584 (C=C, NH); 1238—1093 (C—F). Found (%): C, 43.08, H, 3.00; N, 4.57; F, 23.01. $C_{21}H_{17}CuF_7N_2O_6$. Calculated (%): C, 42.76; H, 2.90; N, 4.75; F, 22.54.

{1-[*N*-(3-Oxo-3,3,3-trifluoro-2-ethoxycarbonylbut-1-en-1-yl)aminato]-2-[*N*-(3-oxo-4,4,5,5,6,6,6-heptafluoro-2-ethoxycarbonylhex-1-en-1-yl)aminato]benzene}nickel(II) (5g). The yield by method *A* was 2.12 g (65%), dark red crystals, m.p. 160—162 °C. IR, ν/cm^{-1}: 3074, 2992, 2948 (C—H); 1723 br (CO_2Et, C=O); 1604, 1581 (C=C, NH); 1220—1044 (C—F). ^{1}H NMR, δ: 1.34 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.1 Hz); 1.36 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.1 Hz); 4.31 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.1 Hz); 4.32 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.1 Hz); 7.24—7.26 (m, 2 H, C_6H_4); 7.63—7.67 (m, 2 H, C_6H_4); 8.29 (s, 1 H, CH); 8.43 (s, 1 H, CH). ^{19}F NMR, δ: 38.37 (m, 2 F, CF_2); 51.49 (m, 2 F, CF_2); 82.00 (t, 3 F, CF_3, ^3J = 9.5 Hz); 93.69 (s, 3 F, CF_3). Found (%): C, 40.63; H, 2.35; F, 29.27; N, 4.17. $C_{22}H_{16}F_{10}N_2NiO_6$. Calculated (%): C, 40.46; H, 2.47; F, 29.09; N, 4.29.

{1-[*N*-(3-Oxo-3,3,3-trifluoro-2-ethoxycarbonylbut-1-en-1-yl)aminato]-2-[*N*-(3-oxo-4,4,5,5,6,6,6-heptafluoro-2-ethoxycarbonylhex-1-en-1-yl)aminato]benzene}copper(II) (5h). The yield by method *B* was 2.24 g (68%), dark green powder, m.p. 185—187 °C. IR, ν/cm^{-1}: 3064, 2986, 2943 (C—H); 1720 (CO_2Et); 1703 (C=O); 1603, 1583 (C=C); 1270—1125 (C—F). Found (%): C, 40.25; H, 2.58; F, 29.01; N, 4.47. $C_{22}H_{16}CuF_{10}N_2O_6$. Calculated (%): C, 40.16; H, 2.45; F, 28.88; N, 4.26.

{1-[*N*-(3-Oxo-3,3,3-trifluoro-2-ethoxycarbonylbut-1-en-1-yl)aminato]-2-[*N*-(3-oxo-4,4,5,5,6,6,6-heptafluoro-2-ethoxycarbonylhex-1-en-1-yl)aminato]benzene}nickel(II) (5i). The yield by method *A* was 2.37 g (72%), dark red powder, m.p. 178—180 °C. IR, ν/cm^{-1}: 2986, 2945 (C—H); 1721 br (CO_2Et, C=O); 1602, 1582 (C=C); 1281—1055 (C—F). ^{1}H NMR, δ: 1.34 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.1 Hz); 1.37 (t, 3 H, $OCH_2C\underline{H}_3$, ^3J = 7.1 Hz); 4.32 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.1 Hz); 4.33 (q, 2 H, $OC\underline{H}_2CH_3$, ^3J = 7.1 Hz); 6.31 (tt, 1 H, $H(CF_2)_2$, $^2J_{H,F}$ = 53.1 Hz, $^3J_{H,F}$ = = 5.7 Hz); 7.24—7.26 (m, 2 H, C_6H_4); 7.63—7.67 (m, 2 H, C_6H_4); 8.30 (s, 1 H, CH); 8.34 (s, 1 H, CH). ^{19}F NMR, δ: 22.49 (dm, 2 F, HCF_2, $^2J_{F,H}$ = 53.1 Hz); 38.13 (m, 2 F, CF_2); 42.74 (m, 2 F, CF_2); 51.43 (m, 2 F, CF_2); 81.56 (t, 3 F, CF_3, $^2J = 9.9$ Hz). Found (%): C, 40.30, H, 2.70; F, 29.85; N, 4.06. $C_{23}H_{17}F_{11}N_2NiO_6$. Calculated (%): C, 40.32; H, 2.50; F, 30.05; N, 4.09.

{1-[*N*-(3-Oxo-4,4,5,5-tetrafluoro-2-ethoxycarbonylpent-1-en-1-yl)aminato]-2-[*N*-(3-oxo-4,4,5,5,6,6,6-heptafluoro-2-ethoxycarbonylhex-1-en-1-yl)aminato]benzene}copper(II) (5j). The yield by method *B* was 2.38 g (69%), dark green powder, m.p. 195—197 °C. IR, ν/cm^{-1}: 2987, 2945 (C—H); 1722 br (CO_2Et, C=O); 1602, 1584 (C=C); 1277—1193 (C—F). Found (%): C, 39.62; H, 2.73; F, 29.85; N, 3.85. $C_{23}H_{17}CuF_{11}N_2O_6$. Calculated (%): C, 40.04; H, 2.48; F, 30.19; N, 4.06.

This work was financially supported by the Presidium of the Ural Branch of the Russian Academy of Sciences (Program No. 09-P-3-1013) and the Russian Foundation for Basic Research (Project No. 10-03-96017).

References

1. K. C. Gupta, A. K. Sutar, *Coord. Chem. Rev.*, 2008, **252**, 1420.
2. A. D. Garnovskii, I. S. Vasil´chenko, *Usp. Khim.*, 2002, **71**, 1064 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2002, **71**].
3. S. S. Ivanchev, *Usp. Khim.*, 2007, **76**, 669 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2007, **76**].
4. V. I. Ovcharenko, R. Z. Sagdeev, *Usp. Khim.*, 1999, **68**, 381 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1999, **68**].
5. J. A. Real, A. B. Gaspar, V. Niel, M. C. Munoz, *Coord. Chem. Rev.*, 2003, **236**, 121.
6. P. Chaudhuri, *Coord. Chem. Rev.*, 2003, **243**, 143.
7. V. T. Kalinnikov, Yu. V. Rakitin, V. M. Novotortsev, *Usp. Khim.*, 2003, **72**, 1123 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2003, **72**].
8. A. V. Metelitsa, A. S. Burlov, S. O. Bezuglyi, I. G. Borodkina, V. A. Bren´, A. D. Garnovskii, V. I. Minkin, *Koord. Khim.*, 2006, **32**, 894 [*Russ. Coord. Chem.* (*Engl. Transl.*), 2006, **32**].
9. K. Mueller, U. Schert, *Organic Light-Emitting Devices*, Wiley-VCH, New York, 2006.
10. L. Wolf, E.-G. Jäger, *Z. Anorg. Allg. Chem.*, 1966, **346**, 76.
11. E.-G. Jäger, *Z. Chem.*, 1968, **8**, 470.
12. E.-G. Jäger, K. Schuhmann, H. Görls, *Inorg. Chim. Acta*, 1997, **255**, 295.
13. E.-G. Jäger, G. Schlenvoigt, B. Kirchhof, M. Rudolph, K. Müller, *Z. Anorg. Allg. Chem.*, 1982, **485**, 173.
14. B. Weber, H. Rudolph, E.-G. Jäger, *Inorg. Chim. Acta*, 2002, **337**, 247.
15. B. Weber, I. Käpplinger, H. Görls, E.-G. Jäger, *Eur. J. Inorg. Chem.*, 2005, 2794.
16. M. Mukoyama, T. Nagata, T. Yamada, S. Imagawa, Patent 06,247,993 (Japan); *Chem. Abstrs*, 1995, **123**, 186919t.
17. E.-G. Jäger, D. Seidel, *Z. Chem.*, 1983, **23**, 31.
18. E.-G. Jäger, D. Seidel, *Z. Chem.*, 1985, **25**, 28.
19. K. Müller, D. Schade, *Z. Chem.*, 1986, **26**, 139.
20. K. Müller, D. Seidel, E.-G. Jäger, *Z. Anorg. Allg. Chem.*, 1988, **561**, 38.
21. W. R. Dolbier, Jr., *J. Fluor. Chem.*, 2005, **126**, 157.
22. M. V. Pryadeina, Ya. V. Burgart, V. I. Saloutin, P. A. Slepukhin, O. N. Kazheva, G. V. Shilov, O. A. D´yachenko, O. N. Chupakhin, *Zh. Org. Khim.*, 2007, **43**, 945 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2007, **43**, 945].
23. V. M. Potapov, *Stereokhimiya* [*Stereochemistry*], Khimiya, Moscow, 1988, 263 pp. (in Russian).
24. R. C. Clark, J. S. Reid, *Acta Crystallogr.*, 1995, **A51**, 887.
25. G. M. Sheldrick, *SHELXS-97*, *Program for the Solution of Crystal Structure*, University of Göttingen, Göttingen, Germany, 1997.
26. G. M. Sheldrick, *SHELXL-97*, *Program for the Refinement of Crystal Structure*, University of Göttingen, Göttingen, Germany, 1997.

Received October 21, 2009;
in revised form April 9, 2010