Asymmetric azomethine ligands based on 2-[(2-aminophenyl)aminomethylidene]-3-oxo-3-polyfluoroalkylpropionates and aldehydes

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

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

The condensation of ethyl 2-[(2-aminophenyl)aminomethylidene]-3-oxo-3-polyfluoroalkylpropionates with aldehydes (salicylaldehyde, furfural, and benzaldehyde) affords the corresponding azomethine derivatives exhibiting the complexing ability toward copper and nickel ions.

Key words: azomethines, aldehydes, ligands, nickel(π) complexes, copper(π) complexes, organofluorine compounds, X-ray diffraction study.

In recent years, transition metal chelate complexes have attracted considerable interest because they show promise for the design of versatile multifunctional materials. In this respect, metal complexes containing Schiff bases as the ligand shell deserve special attention because certain compounds belonging to this class have catalytic, 1-4anomalous magnetic, 5-8 and luminescence⁹ properties. Previously, 10 we have synthesized ethyl 2-[(2-aminophenyl)aminomethylidene]-3-oxo-3-polyfluoroalkylpropionates 1a-c by the condensation of ethyl 2-ethoxymethylidene-3-oxo-3-polyfluoroalkylpropionates with *o*-phenylenediamine. Compounds 1a-c are promising substrates for the synthesis of new ligands.

The aim of the present study was to examine the possibility of the formation of asymmetric ligands based on esters 1a-c in the reactions with aldehydes. Asymmetric ligands have attracted interest because the coordination units in metal complexes with these ligands can be substantially nonplanar, resulting in the appearance of paramagnetism.

For the preparation of the Schiff bases, we used salicylaldehyde having the chelating cavity, as well as benzaldehyde and furfural.

It was found that the reactions of compounds 1a-cwith salicylaldehyde under reflux in benzene in the presence of AcOH with azeotropic removal of water gave ethyl 2-{[2-(2-hydroxybenzylideneamino)phenyl]aminomethylidene}-3-oxo-3-polyfluoroalkylpropionates 2a-c(Scheme 1). Evidently, this transformation is accompanied by the formation the azomethine moiety between the



Scheme 1

i. C_6H_6 , AcOH, Δ , azeotropic reflux; *ii*. EtOH, Δ .

1, **2**: $R^{F} = CF_{3}$ (**a**), $(CF_{2})_{2}H$ (**b**), $C_{3}F_{7}$ (**c**) **3**: $R^{F} = CF_{3}$, M = Ni (**a**), Cu (**b**); $R^{F} = (CF_{2})_{2}H$, M = Ni (**c**), Cu (**d**); $R^{F} = C_{3}F_{7}$, M = Ni (**e**), Cu (**f**)

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aromatic amino group of compounds **1** and the carbonyl group of salicylaldehyde.

According to the ¹H and ¹⁹F NMR spectroscopic data, esters **2a**–**c** exist in solutions in CDCl₃ as mixtures of *E* and *Z* isomeric forms with respect to the C=C bond (see the Experimental section). The assignment of the signals of the *E* and *Z* isomers (Table 1) was made based on the principles, which we have revealed previously for a large range of 2-R-alkylaminomethylidene-3-oxo-3-polyfluoroalkylpropionates.¹¹ The *E*/*Z* isomer ratio for esters **1a**–**c** varies from case to case. However, it should be noted that the *E* isomer is the major species, and its percentage increases as the polyfluoroalkyl substituent grows longer (see Table 1). It should be noted that the ratio of the isomers in CDCl₃ is equal to that in DMSO-d₆.

As opposed to solutions, solid azomethines 2a-c exist as one isomer because the observed group of absorption bands in their IR spectra (two high-frequency absorption bands at 1716—1708 and 1694—1675 cm⁻¹ belonging to vibrations of two different carbonyl groups, an C=N stretching band at 1570—1562 cm⁻¹, and two broad absorption bands at 3221—3070 and 2790—2758 cm⁻¹ assigned to stretching vibrations of intramolecularly bonded NH and OH groups) corresponds to one isomer.

The structure of compound **2b** was additionally confirmed by X-ray diffraction data (Fig. 1, Table 2). In the crystal, this compound exists as the *s*-*cis*,*s*-*trans* conformer of the *E* isomer stabilized by two intramolecular hydrogen bonds. The hydrogen atom H(2) of the aminomethylidene moiety is involved in the intramolecular hydrogen bonding (N(2)-H(2)...O(1)) with the oxygen atom O(1) of the fluoroacyl substituent. The intramolecular N(2)-H(2)...O(1) hydrogen bond is characterized by the following parameters: the intramolecular distance (O(1)...H(2)) is 1.98(1) Å, (N(2)-H(2)), 0.84(1) Å; (N(2)...O(1)), 2.63(9) Å; the N(2)-H(2)...O(1) and C(16)-O(1)...H(2) angles are 134.7(1)° and 100.2(3)°, respectively). The second intramolecular hydrogen bond (O(2)-H(2A)...N(1)) occurs between the hydrogen atom



Fig. 1. Crystal structure of compound 2b.

H(2A) and the nitrogen atom N(1) of the salicylideneimine moiety; the intramolecular distance (N(1)...H(2A)) is 1.89(3) Å, (O(2)-H(2A)), 0.82(1) Å; (N(1)...O(2)), 2.62(1) Å; the O(2)-H(2A)...N(1) and C(7)-N(1)...H(2A) angles are 147.0(5)° and 96.8(3)°, respectively). The dihedral angle between the planes of the salicylideneimine (O(2)C(9)C(8)C(7)) and aminoenone (C(1)N(2)C(19)C(15)) moieties is 63.95°.

It should be noted that molecule **2b** contains two disordered groups (tetrafluoroethyl and ethoxycarbonyl). The occupancies of the positions of the C(14A) and O(3A) atoms and the atoms of the disordered perfluoroalkyl group were refined based on the independent thermal parameters. The occupancies of the positions of the C(20), C(21), C(20A), and C(21A) atoms were taken to be equal to 0.5. The thermal ellipsoids of the C(20), C(20A) and C(17), C(17A) atoms were forced to be equal.

It was shown that esters $2\mathbf{a} - \mathbf{c}$ act as tetradentate N₂O₂ ligands, which readily form metal complexes $3\mathbf{a} - \mathbf{f}$ upon treatment with nickel(II) and copper(II) salts (see Scheme 1).

Com- pound	RF	δ				Content	
		СН		NH		(%)	
		E	Z	E	Z	E	Ζ
2a	CF ₃	8.67	8.53	12.43	11.75	66	34
2b	$(CF_2)_2H$	8.57	8.47	12.42	11.56	80	20
2c	C_3F_7	8.41	8.56	11.62	12.30	86	14
4	$(CF_2)_2H$	8.73	8.58	12.82	11.67	70	30
5	$(CF_2)_2H$	8.64	8.54	12.99	11.66	69	31

Table 1. The NH and CH shifts of the protons of the *E* and *Z* isomers of compounds 2a-c, 4, and 5 in ¹H NMR spectra

Note. The ¹H NMR spectra of compounds 2a-c and 5 were recorded in CDCl₃; of compound 4, in DMSO-d₆.

Bond	d∕Å	Angle	ω/deg
N(1)-C(7)	1.280(2)	C(7) - N(1) - C(2)	120.2(18)
N(1) - C(2)	1.415(2)	C(19) - C(15) - C(16)	119.9(2)
O(2) - C(9)	1.350(2)	C(19) - C(15) - C(14)	118.9(2)
C(15)-C(19)	1.381(3)	C(16) - C(15) - C(14)	121.2(2)
C(15)-C(16)	1.412(3)	C(19) - N(2) - C(1)	127.6(2)
C(15)-C(14)	1.460(3)	C(3) - C(2) - N(1)	122.6(2)
N(2)-C(19)	1.321(2)	C(1) - C(2) - N(1)	118.3(2)
N(2) - C(1)	1.406(2)	C(6) - C(1) - N(2)	123.0(2)
O(1) - C(16)	1.232(2)	N(2) - C(1) - C(2)	117.5(2)
C(2) - C(1)	1.397(3)	N(1) - C(7) - C(8)	123.1(19)
O(3)-C(14)	1.211(3)	C(9) - C(8) - C(7)	121.4(19)
		O(2) - C(9) - C(10)	118.2(2)
		O(1) - C(16) - C(15)	123.9(2)
		N(2) - C(19) - C(15)	125.5(2)

Table 2. Selected bond lengths (*d*) and bond angles (ω) for compound **2b**

The structures of complexes 3a-f were determined by ¹H and ¹⁹F NMR spectroscopy, IR spectroscopy, elemental analysis, and X-ray diffraction.

Unlike the free ligands, complexes 3a-f are characterized by one high-frequency absorption band at 1725–1700 cm⁻¹ belonging to vibrations of one carbonyl group and by the absence of absorption bands in the region characteristic of NH and OH stretching vibrations (see the Experimental section). The ¹H and ¹⁹F NMR spectra of nickel complexes 3a,c,e measured in CDCl₃ show one set of signals. It should be noted that the signals for the α -fluorine atoms in the ¹⁹F NMR spectra of these complexes are shifted downfield compared to the corresponding signals of free ligands 2a-c, which is indicative of the

involvement of the polyfluoroacyl group in the formation of the chelate unit.

The structure of complex **3d** was additionally confirmed by X-ray diffraction data (Fig. 2). The X-ray diffraction study showed that the copper(II) cation in complex **3d** is in the distorted square coordination environment formed by two nitrogen atoms (N(1) and N(2)) of the phenylenediamine moiety, the oxygen atom (O(1)) of the fluoroacyl group, and the oxygen atom (O(4)) of the salicylideneimine moiety. The distortion was caused by a slight difference in the lengths of the sides of the square N(1)-N(2)-O(1)-O(4) (the maximum difference between the sides N(2)-O(4) and N(2)-N(1) is 0.209 Å).

Molecule **3d** has an approximately planar conformation. The deviations of the atoms Cu-N(1)-N(2)--O(4)-O(1), which form the chelate unit of the molecule, from its mean plane are at most 0.02(4) Å. The salicylideneimine and amino enone moieties lie in the same plane (the maximum deviations of the carbon atoms of the salicylideneimine moiety are 0.29(7) (C(21)) and 0.28(4) Å (C(20)); the maximum deviations of the carbon atoms of the aminoenone moiety are 0.22(0) (C(12)) and 0.20(8) Å (C(16)).

The tetradentate coordination of the ligand results in the formation of three fused metallacycles (two six-membered rings and one five-membered ring). The chelate unit is characterized by the strong delocalization of the electron density in the six-membered metallacycles, which is reflected in the equalization of the Cu-X (X = N, O), C-X (X = N, O), and C-C bond lengths of the metallacycles (Table 3). Thus, the measured difference in the C-C bond lengths in the metallacycles is at most 0.04 Å, the difference in the C-O and C-N bond lengths is 0.03 Å,



Fig. 2. Molecular structure of compound 3d.

Parameter	Value	Parameter	Value	Parameter	Value
Bond	d/Å	Bond	d∕Å	Angle	ω/deg
Cu(1) - O(4)	1.8783(16)	C(1)—C(2)	1.478(3)	C(6) - N(1) - Cu(1)	125.96(16)
Cu(1) - N(1)	1.9247(19)	C(14) - C(9)	1.399(3)	C(9) - N(1) - Cu(1)	113.43(14)
Cu(1) - N(2)	1.9419(18)	C(3) - C(2)	1.397(3)	C(15)-N(2)-C(14)	122.50(2)
Cu(1) - O(1)	1.9434(14)		ω/deg	C(15) - N(2) - Cu(1)	124.77(17)
O(3) - C(1)	1.345(3)	Angle		C(14) - N(2) - Cu(1)	112.60(15)
O(4) - C(17)	1.455(3)	O(4) - Cu(1) - N(1)	177.91(8)	N(1) - C(6) - C(2)	127.0(2)
O(2) - C(1)	1.211(2)	O(4) - Cu(1) - N(2)	94.39(8)	O(2) - C(1) - O(3)	123.0(2)
O(1) - C(3)	1.267(3)	N(1) - Cu(1) - N(2)	84.27(8)	C(9) - C(14) - N(2)	115.2(2)
N(1) - C(6)	1.301(3)	O(4) - Cu(1) - O(1)	89.81(6)	C(13) - C(14) - N(2)	125.9(2)
N(1) - C(9)	1.426(3)	N(1)-Cu(1)-O(1)	91.55(7)	O(1) - C(3) - C(2)	126.0(2)
N(2) - C(15)	1.289(3)	N(2)-Cu(1)-O(1)	175.75(8)	C(14) - C(9) - N(1)	114.5(2)
N(2) - C(14)	1.423(3)	C(1) - O(3) - C(7)	118.84(16)	C(10) - C(9) - N(1)	125.7(2)
C(16)-C(15)	1.419(3)	C(17) - O(4) - Cu(1)	127.29(15)	O(4) - C(17) - C(16)	124.2(2)
C(16) - C(17)	1.437(3)	C(3) - O(1) - Cu(1)	128.10(15)	C(3) - C(2) - C(6)	121.3(2)
C(6)–C(2)	1.415(3)	C(6) - N(1) - C(9)	120.50(2)	N(2)-C(15)-C(16)	125.8(2)

Table 3. Selected bond lengths (d) and bond angles (ω) for compound 3d

and the differences in the Cu–X bond lengths (X = N, O) is 0.06 Å. Hence, it is impossible to determine whether the chelate fragment is in the iminoenol or amino enone form.

In the crystal packing of complex 3d, the translationally related molecules stack with the mean interplanar distances of 3.152 and 3.162 Å (Fig. 3). The unit cell contains two centrosymmetrically related molecules with the interatomic Cu...Cu distance of 3.58 Å. To extend the range of azomethines, we performed the condensation of ester **1b** with other aldehydes (benzaldehyde and furfural) and obtained Schiff bases **4** and **5**, respectively (Scheme 2). These transformations require less time compared to the reactions with salicylaldehyde, the condensation with benzaldehyde occurring easily in the absence of the catalyst (acetic acid).

The IR spectra of compounds **4** and **5** show characteristic absorption bands of two carbonyl groups of the ester



Scheme 2

i. C_6H_6 , Δ , azeotropic reflux; *ii*. $CuCl_2$.



Fig. 3. Packing of molecules 3d along the b axis (hydrogen atoms are not shown).

and fluoroacyl groups and the C=N, C=C, and NH stretching vibrations.

Like esters 2a-c, compounds 4 and 5 exist in solution as mixtures of *E* and *Z* isomers, as was confirmed by their ¹H and ¹⁹F NMR spectra (see Table 1).

Based on the structures of esters 4 and 5, it can be suggested that they can bind transition metal cations to form metal complexes with complex structures. However, the reactions of compounds 4 and 5 with copper(II) and nickel(II) acetates afforded unstable complexes, which we failed to isolate and characterize. The reactions of ligands 4 and 5 with copper(II) chloride gave the same complex 6. Previously, we have synthesized this chelate by the chelation of starting ester 1b with copper(II) chloride.¹⁰ Apparently, ligands 4 and 5 are unstable under the conditions used for the synthesis of the complexes and undergo the hydrolytic cleavage of the C=N bond. The high stability of salicylidene derivatives 2a-c is apparently attributed to the involvement of the OH group in the formation of the coordination unit.

Therefore, we showed that the modification of esters 1a-c with various aldehydes is an efficient route to new asymmetric azomethine ligands. In this respect, aldehydes containing additional functional groups capable of forming complexes hold the most promise.

Experimental

The IR spectra were recorded on a Perkin Elmer Spectrum One diffuse-reflectance Fourier-transform infrared spectrometer (400–4000 cm⁻¹). The ¹H and ¹⁹F NMR spectra were measured on a Bruker DRX-400 spectrometer (400 MHz) using SiMe₄ and C₆F₆ as the internal standards, respectively. The elemental analysis was performed on a Carlo Erba CHNS-O EA 1108 elemental analyzer. The course of the reactions was monitored by TLC on Alugram Sil G/UV₂₅₄ plates.

The single-crystal X-ray diffraction study of compounds 2b and 3d was carried out on a Xcalibur 3 diffractometer at 295(2) K $(\omega/2\theta$ -scanning technique, Mo-K α radiation, graphite monochromator, CCD detector). The crystal structures were solved by direct methods followed by calculations of Fourier maps with the use of the SHELXS-97 program package and then refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms with the use of the SHELXL-97 program package.¹² The hydrogen atoms were positioned geometrically and refined using the riding model. The X-ray diffraction data collection and structure refinement statistics for compounds 2b and 3d are given in Tables 2-4. The complete crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC 753055 and 753056, respectively) and can be obtained, free of charge, on application to www.ccdc.cam.ac.uk/conts/retrieving.html (12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis of azomethines 2a-c (general procedure). A mixture of ester 1a-c (0.005 mol), salicylaldehyde (0.005 mol), and glacial acetic acid (1 mL) in benzene (30 mL) was refluxed with azeotropic removal of water for 7 days. Then the reaction mixture was concentrated, and the precipitate was crystallized from ethanol.

Ethyl 4,4,4-trifluoro-2-{[2-(2-hydroxybenzylideneamino)phenyl]aminomethylidene}-3-oxobutanoate (2a). The yield was 1.36 g (67%), m.p. 119–120 °C. IR, v/cm⁻¹: 3070 (NH); 2985 (CH str.); 2790 (OH); 1716 (CO₂Et); 1694 (COR^F); 1620 (C=C); 1590, 1563 (C=N, NH); 1247–1159 (C-F). ¹H NMR (CDCl₃), $\delta, E, Z: 1.33$ (br.t, 3 H, OCH₂CH₃, J=7.1 Hz); 6.98–7.47 (m, 8 H, 2 C₆H₄); 8.68 (s, 1 H, CH=N); 11.91 (br.s, 1 H, OH); *E* (66%): 4.29 (q, 2 H, OCH₂CH₃, J=7.1 Hz); 8.67 (d, 1 H, CH=C, J=14.0 Hz); 12.43 (br.d, 1 H, NH, J=14.0 Hz); *Z* (34%): 4.35 (q, 2 H, OCH₂CH₃, J=7.1 Hz); 8.53 (d, 1 H, CH=C, J=14.0 Hz); 11.75 (br.d, 1 H, NH, J=14.0 Hz). ¹⁹F NMR (DMSO-d₆), $\delta,$ *E* (66%): 89.21 (s, 3 F, CF₃); *Z* (34%): 89.91 (s, 3 F, CF₃). Found (%): C, 59.19; H, 4.22; F, 14.01; N, 7.03. C₂₀H₁₇F₃N₂O₄. Calculated (%): C, 59.11; H, 4.22; F, 14.13; N, 6.89.

Ethyl 4,4,5,5-tetrafluoro-2-{[2-(2-hydroxybenzylideneamino)phenyl]aminomethylidene}-3-oxopentanoate (2b). The

Compound	2b	3d
Formula	$C_{21}H_{18}F_4N_2O_4$	$C_{21}H_{16}CuF_4N_2O_4$
Molecular weight	438.37	499.90
Crystal system	Triclinic	Triclinic
T/K	295(2)	120(2)
Space group	$P\overline{1}$	$P\overline{1}$
Unit cell parameters		
a/Å	5.8264(11)	7.6646(9)
<i>b</i> /Å	8.5505(11)	9.8476(10)
c/Å	21.110(4))	13.9529(14)
α/deg	83.829(12)	98.895(8)
β/deg	82.306(15)	95.542(9)
γ/deg	77.267(14)	108.303(9)
$V/Å^3$	1013.3(3)	975.93(18)
Ζ	2	2
$d_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.437	1.701
μ/mm^{-1}	0.124	1.190
F(000)	452	506
θ/deg	$3.01 < \theta < 26.37$	$2.96 < \theta < 28.28$
Total number of reflections	4394	5394
Number of independent reflections	4002	4645
R _{int}	0.0283	0.0328
Number of reflections with $I > 2\sigma(I)$	1610	2744
Completeness of data set (%)	96.7	97.1
(for θ /deg)	(26.00)	(26.00)
Number of calculated parameters	330	289
Goodness of fit S based on F^2	1.003	0.996
$R_1 (I \ge 2\sigma(I))$	0.0601	0.0355
$wR_2 (I \ge 2\sigma(I))$	0.1501	0.0563
R_1 (based on all reflections)	0.1399	0.0672
wR_2 (based on all data)	0.1657	0.0581
$\rho_{\text{max}}/\rho_{\text{min}} (e \cdot \text{\AA}^{-3})$	0.468/-0.293	0.542/-0.392

Table 4. Crystallographic parameters and the X-ray diffraction data collection and structure refinement statistics for compounds 2b and 3d

yield was 1.49 g (68%), m.p. 137–138 °C. IR, v/cm^{-1} : 3080 (NH); 2991 (C-H str.); 2775 (OH); 1710 (CO₂Et); 1693 (COR^F); 1637, 1608, 1562 (C=C, NH, C=N); 1311–1086 (C-F). ¹H NMR (CDCl₃), δ, E, Z: 6.98, 7.10, 7.23, and 7.28-7.47 (all m, 8 H, 2 C₆H₄); E (80%): 1.32 (t, 3 H, OCH_2CH_3 , J = 7.1 Hz); 4.28 (q, 2 H, OCH_2CH_3 , J = 7.1 Hz); 6.65 (tt, 1 H, H(CF₂)₂, J= 53.3 Hz, J = 5.8 Hz); 8.57 (d, 1 H, CH=C, J = 14.0 Hz); 8.67 (s, 1 H, CH=N); 12.42 (br.d, 1 H, NH, J = 14.0 Hz); Z(20%): 1.33 (t, 3 H, OCH₂<u>CH₃</u>, J = 7.1 Hz); 4.36 (q, 2 H, OCH_2CH_3 , J = 7.1 Hz); 6.38 (tt, 1 H, $H(CF_2)_2$, *J* = 53.3 Hz, *J* = 5.8 Hz); 8.47 (d, 1 H, CH=C, *J* = 14.1 Hz); 8.68 (s, 1 H, CH=N); 11.56 (br.d, 1 H, NH, J = 14.1 Hz). ¹⁹F NMR (CDCl₃), δ : *E* (80%): 23.37 (dm, 2 F, α -CF₂, *J* = 53.5 Hz); 39.70 (dm, 2 F, β -CF₂, J = 56.4 Hz); Z (20%): 22.29 (dm, 2 F, α -CF₂, J = 53.2 Hz); 41.25 (dm, 2 F, β -CF₂H, J = 56.4 Hz). Found (%): C, 57.71; H, 4.24; F, 14.42; N, 6.40. C₂₁H₁₈F₄N₂O₄. Calculated (%): C, 57.54; H, 4.14; F, 14.60; N, 6.39.

Ethyl 4,4,5,5,6,6,6-heptafluoro-2-{[2-(2-hydroxybenzylideneamino)phenyl]aminomethylidene}-3-oxohexanoate (2c). The yield was 1.82 g (72%), m.p. 108–109 °C. IR, ν/cm^{-1} : 3221 (NH); 3069 (CH str.); 2758 (OH); 1708 (CO₂Et); 1675 (COR^F); 1644, 1608, 1570 (C=N, C=C, NH); 1290–1101 (C-F). ¹H NMR (CDCl₃), δ , *E*, *Z*: 6.99, 7.10, 7.23, and 7.28–7.47 (all m, 8 H, 2 C₆H₄); *E* (86%): 1.32 (t, 3 H, OCH₂CH₃, *J*=7.1 Hz); 4.35 (q, 2 H, O<u>CH₂CH₃</u>, *J* = 7.1 Hz); 8.40 (d, 1 H, CH=C, *J* = 14.0 Hz); 8.68 (s, 1 H, CH=N); 11.62 (br.d, 1 H, NH, *J*= 14.0 Hz); *Z* (14%): 1.31 (t, 3 H, OCH₂CH₃, *J* = 7.1 Hz); 4.28 (q, 2 H, O<u>CH₂CH₃</u>, *J* = 7.1 Hz); 8.56 (d, 1 H, CH=C, *J* = 14.0 Hz); 8.67 (s, 1 H, CH=N); 12.30 (br.d, 1 H, NH, *J* = 14.0 Hz). ¹⁹F NMR (DMSO-d₆), 8: *E* (86%): 37.55 (m, 2 F, β-CF₂); 49.02 (m, 2 F, α-CF₂); 81.62 (t, 3 F, γ-CF₃, *J* = 9.7 Hz); *Z* (14%): 38.20 (m, 2 F, β-CF₂); 48.35 (m, 2 F, α-CF₂); 81.72 (t, 3 F, γ-CF₃, *J* = 9.7 Hz). Found (%): C, 51.47; H, 3.40; F, 26.16; N, 5.84. C₂₂H₁₇F₇N₂O₄. Calculated (%): C, 52.18; H, 3.38; F, 26.26; N, 5.53.

Synthesis of metal complexes (3a-f) (general procedure). A mixture of ester 2a-c (0.002 mol) and metal(II) acetate (0.003 mol) in ethanol (10 mL) was refluxed with stirring. The precipitate that formed upon cooling was filtered off and crystal-lized from ethanol.

(2-Ethoxycarbonyl-4,4,4-trifluoro-1-{[2-(2-oxidobenzylideneamino)phenyl]aminato}-3-oxobut-1-ene)nickel(II) (3a). The yield was 0.61 g (75%), m.p. 203–204 °C. IR, v/cm⁻¹: 2982 (CH str.); 1720 (CO₂Et); 1606, 1581 (C=O, C=C); 1521 (C=N); 1282–1042 (C–F). ¹H NMR (CDCl₃), δ : 1.36 (t, 3 H, OCH₂<u>CH</u>₃, J = 7.1 Hz); 4.31 (q, 2 H, O<u>CH</u>₂CH₃, J = 7.1 Hz); 6.69, 7.07, 7.60, 7.72, 7.24, and 7.33 (all m, 8 H, 2 C_6H_4); 8.17 (s, 1 H, CH); 8.45 (s, 1 H, CH). ¹⁹F NMR (CDCl₃), δ : 94.25 (s, 3 F, CF₃). Found (%): C, 51.56; H, 3.57; N, 6.13; F, 11.92. $C_{20}H_{15}F_3N_2O_4Ni$. Calculated (%): C, 51.88; H, 3.27; F, 12.31; N, 6.05.

(2-Ethoxycarbonyl-4,4,4-trifluoro-1-{[2-(2-oxidobenzylideneamino)phenyl]aminato}-3-oxobut-1-ene)copper(11) (3b). The yield was 0.61 g (65%), m.p. 216–217 °C. IR, v/cm⁻¹: 3076, 2989 (CH str.); 1725 (CO₂Et); 1607, 1583 (C=O, C=C, 1532 (C=N); 1273–1125 (C–F). Found (%): C, 50.99; H, 3.02; F, 11.98; N, 5.75. $C_{20}H_{16}F_{3}N_{2}O_{4}Cu$. Calculated (%): C, 51.34; H, 3.23; F, 12.18; N, 5.99.

(2-Ethoxycarbonyl-4,4,5,5-tetrafluoro-1-{[2-(2-oxidobenzylideneamino)phenyl]aminato}-3-oxopent-1-ene)nickel(II) (3c). The yield was 0.72 g (73%), m.p. 218–220 °C. IR, v/cm⁻¹: 2991 (CH str.); 1710 (CO₂Et); 1606, 1584 (C=O, C=C); 1525 (C=N); 1288–1092 (C–F). ¹H NMR (CDCl₃), 8: 1.37 (t, 3 H, OCH₂<u>CH₃</u>, J = 7.1 Hz); 4.31 (q, 2 H, O<u>CH₂CH₃</u>, J = 7.1 Hz); 6.58 (tt, 1 H, H(CF₂)₂, J = 53.5 Hz, J = 5.7 Hz); 6.66, 6.96, 7.54, 7.69, 7.22, and 7.46 (all m, 8 H, 2 C₆H₄); 8.14 (s, 1 H, CH); 8.28 (s, 1 H, CH). ¹⁹F NMR (CDCl₃), 8: 23.4 (dm, 2 F, α-CF₂, J = 53.4 Hz); 48.66 (m, 2 F, β-CF₂). Found (%): C, 51.17; H, 3.18; F, 15.42; N, 5.76. C₂₁H₁₆F₄N₂O₄Ni. Calculated (%): C, 50.95; H, 3.26; F, 15.35; N, 5.66.

(2-Ethoxycarbonyl-4,4,5,5-tetrafluoro-1-{[2-(2-oxidobenzyl-ideneamino)phenyl]aminato}-3-oxopent-1-ene)copper(II) (3d). The yield was 0.69 g (69%), m.p. 215–216 °C. IR, v/cm⁻¹: 2988 (CH str.); 1700 br. (CO₂Et); 1609, 1582 (C=O, C=C); 1521 (C=N); 1228–1168 (C–F). Found (%): C, 50.15; H, 3.26; N, 5.48; F, 15.42. $C_{21}H_{16}F_4N_2O_4Cu$. Calculated (%): C, 50.45; H, 3.23; F, 15.20; N, 5.60.

(2-Ethoxycarbonyl-4,4,5,5,6,6,6-heptafluoro-1-{[2-(2-oxidobenzylideneamino)phenyl]aminato}-3-oxohex-1-ene)nickel(II) (3e). The yield was 0.79 g (70%), m.p. 193—194 °C. IR, v/cm⁻¹: 3060, 2984 (CH str.); 1703 (CO₂Et); 1605, 1580 (C=O, C=C); 1519 (C=N); 1218—1118 (C-F). ¹H NMR (CDCl₃), &: 1.34 (t, 3 H, OCH₂CH₃, J = 7.1 Hz); 4.30 (q, 2 H, OCH₂CH₃, J = 7.1 Hz); 6.69, 7.06, 7.62, 7.72, and 7.29 (all m, 4 H, 2 C₆H₄); 8.18 (s, 1 H, CH); 8.35 (s, 1 H, CH). ¹⁹F NMR (CDCl₃), &: 38.75 (m, 2 F, β-CF₂); 51.51 (m, 2 F, α-CF₂); 81.91 (t, 3 F, CF₃, J = 9.8 Hz). Found (%): C, 46.62; H, 2.59; F, 23.42; N, 4.66. C₂₂H₁₅F₇N₂O₄Ni. Calculated (%): C, 46.93; H, 2.69; F, 23.62; N, 4.98.

(2-Ethoxycarbonyl-4,4,5,5,6,6,6-heptafluoro-1-{[2-(2-oxidobenzylideneamino)phenyl]aminato}-3-oxohex-1-ene)copper(II) (3f). The yield was 0.77 g (68%), m.p. 159–161 °C. IR, v/cm⁻¹: 3071, 2986 (CH str.); 1705 (CO₂Et); 1605, 1581 (C=O, C=C); 1524 (C=N); 1281–1095 (C-F). Found (%): C, 46.23; H, 2.96; F, 23.50; N, 4.66. $C_{22}H_{15}F_7N_2O_4Cu$. Calculated (%): C, 46.53; H, 2.66; F, 23.42; N, 4.93.

Ethyl 2-{[2-(benzylideneamino)phenyl]aminomethylidene}-4,4,5,5-tetrafluoro-3-oxopentanoate (4). A mixture of ester 1b (3.34 g, 0.01 mol) and benzaldehyde (1.06 g, 0.01 mol) was refluxed in benzene (30 mL) with azeotropic removal of water for 30 h. Then the reaction mixture was concentrated, and the residue was dissolved in diethyl ether (15 mL). Hexane (40 mL) was added to the reaction solution, and the precipitate that formed was filtered off and recrystallized from ethanol. The yield was 2.63 g (62%), m.p. 109–111 °C. IR, v/cm⁻¹: 3170, 3114 (NH); 2979, 2932, 2905 (C–H str.); 1717 (CO₂Et); 1697 (COR^F); 1633, 1622, 1597, 1586 (C=N, NH, C=C); 1317–1097 (C–F). ¹H NMR (CDCl₃), δ , *E*, *Z*: 7.22–7.56 and 8.10–8.16 (all m, 9 H, C₆H₅, C₆H₄); 8.66 (s, 1 H, CH=N); *E* (69%): 1.35 (t, 3 H, OCH₂<u>CH₃</u>, *J* = 7.1 Hz); 4.30 (q, 2 H, O<u>CH₂</u>CH₃, *J* = 7.1 Hz); 6.69 (tt, 1 H, H(CF₂)₂, *J* = 53.7 Hz, *J* = 5.8 Hz); 8.64 (d, 1 H, CH=C, *J* = 14.6 Hz); 12.99 (br.d, 1 H, NH, *J* = 14.6 Hz); *Z* (31%): 1.37 (t, 3 H, OCH₂<u>CH₃</u>, *J* = 7.1 Hz); 4.39 (q, 2 H, O<u>CH₂</u>CH₃, *J* = 7.1 Hz); 6.39 (tt, 1 H, H(CF₂)₂, *J*=53.7 Hz, *J* = 5.8 Hz); 8.54 (d, 1 H, CH=C, *J* = 14.6 Hz); 11.67 (br.d, 1 H, NH, *J* = 13.9 Hz). ¹⁹F NMR (CDCl₃), $\delta : E$ (69%): 23.64 (dm, 2 F, CF₂H, *J*=53.7 Hz); 41.24 (m, 2 F, CF₂H). Found (%): C, 59.84; H, 4.05; F, 18.05; N, 6.48. C₂₁H₁₈F₄N₂O₃. Calculated (%): C, 59.72; H, 4.30; F, 17.99; N, 6.63.

Ethyl 4,4,5,5-tetrafluoro-2-{[2-(2-furylmethylideneamino)phenyl]aminomethylidene}-3-oxopentanoate (5). A mixture of ester 1b (3.34 g, 0.01 mol), furfural (0.97 g, 0.01 mol), and glacial acetic acid (1 mL) was refluxed in benzene (30 mL) with azeotropic removal of water for 40 h. Then the reaction mixture was concentrated. The precipitate that formed was filtered off and recrystallized from ethanol. The yield was 2.84 g (69%), m.p. 116–117 °C. IR, v/cm⁻¹: 3108 (NH); 2982, 2939, 2874 (C-H str.); 1699 (CO₂Et); 1654 (COR^F); 1623, 1605, 1589, 1578, 1562 (C=N, NH, C=C), 1283–1077 (C-F). ¹H NMR (DMSO-d₆), δ, E, Z: 6.79–6.81 (m, 1 H, C₄H₃O); 7.32–7.39 (m, 4 H, C_6H_4); *E* (70%): 1.29 (t, 3 H, OCH₂<u>CH₃</u>, *J* = 7.1 Hz); 4.23 (q, 2 H, OCH_2CH_3 , J = 7.1 Hz); 7.01 (tt, 1 H, $H(CF_2)_2$, J = 52.6 Hz, J = 6.2 Hz); 7.57 (dd, 1 H, C₄H₃O, J = 7.8 Hz, J = 1.3 Hz; 7.78 (dd, 1 H, C₄H₃O, J = 7.8 Hz, J = 1.3 Hz); 8.07 $(br.d, 1 H, C_4H_3O, J=1.5 Hz); 8.73 (s, 1 H, CH=N); 8.74 (d, 1 H, CH=$ CH=C, J = 14.8 Hz); 12.82 (br.d, 1 H, NH, J = 14.8 Hz); Z (30%): 1.28 (t, 3 H, OCH₂<u>CH₃</u>, J = 7.1 Hz); 4.34 (q, 2 H, OCH_2CH_3 , J = 7.1 Hz); 6.87 (tt, 1 H, H(CF₂)₂, J = 52.6 Hz, J = 6.2 Hz; 7.54 (dd, 1 H, C₄H₃O, J = 7.9 Hz, J = 1.3 Hz); 7.71 (dd, 1 H, C_4H_3O , J = 7.9 Hz, J = 1.3 Hz); 8.05 (br.d, 1 H, $C_4H_3O, J = 1.5 Hz$; 8.70 (s, 1 H, CH=N); 8.58 (d, 1 H, CH=C, J = 14.8 Hz); 11.67 (br.d, 1 H, NH, J = 14.8). ¹⁹F NMR $(DMSO-d_6)$, δ : *E* (70%): 25.41 (dm, 2 F, CF₂H, *J* = 52.6 Hz); 41.71 (m, 2 F, CF₂); Z(30%): 24.24 (dm, 2 F, CF₂H, J= 52.6 Hz); 42.31 (m, 2 F, CF₂H). Found (%): C, 55.55; H, 3.75; F, 18.36; N, 6.81. C₁₉H₁₆F₄N₂O₄. Calculated (%): C, 55.34; H, 3.91; F, 18.43; N, 6.79.

Chloro[1-(2-aminophenylaminato)-2-ethoxycarbonyl-4,4,5,5-tetrafluoro-3-oxopent-1-ene]copper(II) (6). A mixture of compound 4 or 5 (0.002 mol) and copper(II) chloride (0.40 g, 0.003 mol) in ethanol (10 mL) was refluxed with stirring for 2 h. The precipitate that formed was filtered off and recrystallized from ethanol. The yield was 0.69 g (80% based on ester 4) and 0.73 g (81% based on ester 5), a dark-green powder, m.p. $205-207 \,^{\circ}C$ (cf. lit. data¹⁰).

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