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Fluorinated lithium 1,3-diketonates as reagents to modify podands and crown-ethers

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Abstract

Fluorinated enaminoketones, a new type of ligands, bearing two independent coordination centers (polyether's and fluorinated enaminoketones fragments) have been obtained. The crystal structure of the Cu(II) complex of 1,5-*bis*-[2-(4′,4′,4′-trifluoro-1′-methyl-3′-oxo-but-1′-enylamino)-phenoxy]-3-oxapentane (**10**) has been elucidated by X-ray crystallography. The results obtained show that the complex **10** consists of two crystallographically independent molecules $C_{26}H_{24}CuF_6N_2O_5$ (**A** and **B**), and the metal atom in the complex **10** has four-coordinated arrangement, as a polyhedron with a distorted square with two nitrogen and two oxygen atoms located in corners.

Keywords: Fluorine-containing lithium 1,3-diketonates; Fluorine-containing enaminoketones; Crown-ethers; Podands; X-ray crystallography

1. Introduction

We have recently suggested a new version for the Claisen condensation of fluorinated alkyl carboxylates with methylketones [1]. We have found that use of lithium hydride as a condensing agent in saturated hydrocarbons as solvents enables one to prepare lithium salts of fluorinated 1,3-diketonates in high (80–90%) yields. They are precipitated from the reaction mixture like white powders and can be easily separated [2]. Treatment of lithium salts of fluorinated 1,3-diketonates with acids affords the corresponding fluoroalkylcontaining β-diketones [3].

Lithium 1,3-diketonates **1** are easily accessible, more convenient in handling and are more stable at storage than the corresponding 1,3-diketones. We have found that diketonates **1** can be used instead of the corresponding diketones in a variety of synthetic procedures without their additional purification. This allows one to simplify substantially many synthetic procedures. Indeed, lithium β-diketonates **1** proved to be appropriate reagents for the synthesis of β-diketones metal-chelates, β-hydroxyketones, regioisomeric enaminoketones (β-aminovinylketones), as well as a variety of fluorinated heterocycles (izoxazoles, pyrazoles, pyrimidines, 1,4-diazepines, pyrazines, etc.) [1–9].

Effective methods for the synthesis of regioisomeric fluorinated enaminoketones have been developed in our laboratory on the basis of fluorine-containing lithium 1,3-diketonates **1** [8]. Use of lithium diketonates **1** instead of the corresponding 1,3-diketones improved the reaction selectivity and yields of the targeted products due to elimination of some by-products formation and retro-decomposition processes [10].

The ability of enaminoketones to coordinate with a variety of ions (mainly transition metals) prompted us to design functionally modified representatives of this class bearing two or several independent coordination centers in one molecule. In this paper, we report on the synthesis of novel fluorinated enaminoketones as ligands bearing two coordination centers of different nature. It is worth noting that these compounds may not only be involved in heterocyclization reactions [4,11,12] which are widely used to obtain biologically active derivatives; they enhance penetration of such compounds through

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biological membranes due to the presence of both polyether's and fluorinated fragments [13,14].

The one Cu(II) complex of 1,5-*bis*-[2-(4′,4′,4′-trifluoro-1′-methyl-3′-oxo-but-1′-enylamino-)-phenoxy]-3-oxapentane has been obtained in a crystalline form, and its crystal structure was elucidated by X-ray crystallography.

2. Results and discussion

2.1. Synthesis of ligands

Enaminoketones **4** and **5** were obtained by condensation of **1** with 1,5-diamino-3-oxapentane **2** and 1,5-bis(2-amino)-phenoxy-3-oxapentane **3** in glacial acetic acid. Enaminoketones **8** and **9** were obtained by condensation of **1** with 4,5′- and 4,4′-diaminodibenzo-18-crown-6 ethers **6** and **7** under similar conditions (Scheme 1). Only one of two possible regioisomers was obtained, as evidenced by the only set of resonance signals in the ^{1}H and ^{19}F NMR spectra of the targeted products. The spectroscopic characteristics of compounds **4**, **5**, **8** and **9** correspond to those for enaminoketones with β-position of R^F and amino group. Indeed, the singlet of CH proton is observed in the ^{1}H NMR spectra at δ 5.50–5.90 ppm, while the resonance signals for regioisomeric aminovinylketones bearing the geminal amino and polyfluoroalkyl substituents are usually observed at δ 6.40–6.60 ppm. [8]. The chemical shifts of the CF_3-group in the ^{19}F NMR spectra of enaminoketones **4**, **5**, **8** and **9** are close to $\sim\delta$ 85 ppm and correspond to the fragment $CF_3C{=}O$ [15]. The results of X-ray diffraction analysis of compound **10** confirmed our conclusion concerning the regiochemistry of the reaction between lithium diketonates **1** and 1,5-bis(2-amino)phenoxy-3-oxapentane **3**.

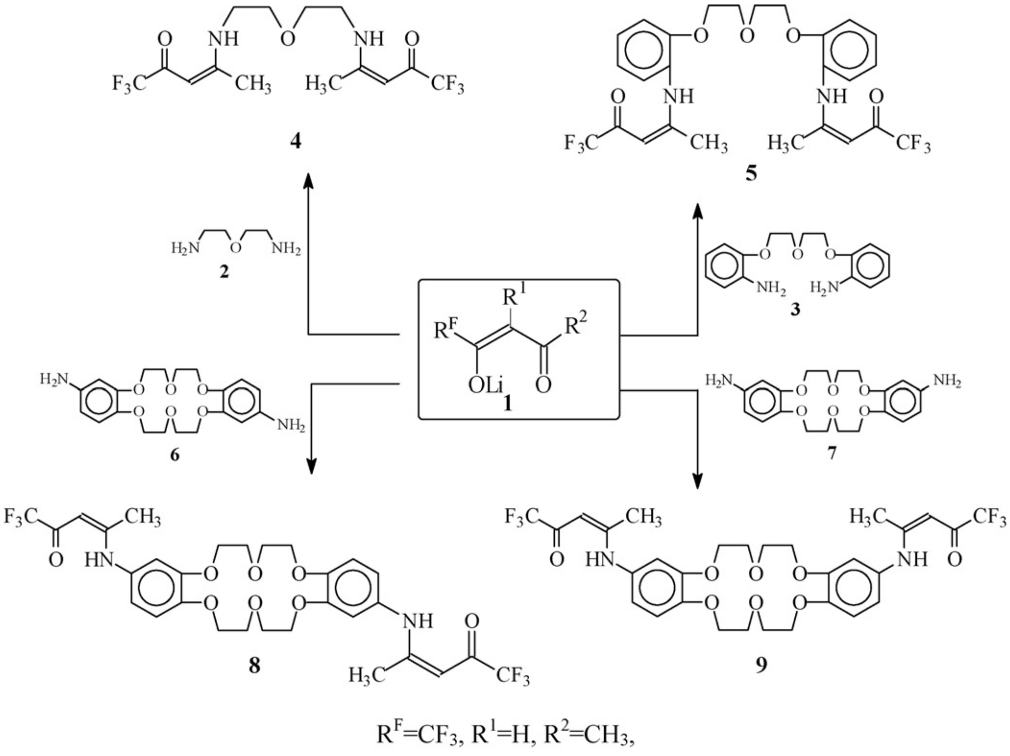
Besides that, we have previously reported that the formation of one or another isomer (or both regioisomeric enaminoketones) is determined by the nature of R^F, R^1 and R^2 groups in the starting lithium diketonates **1**, as well as a substituent in the amine group. If $R^1 = H$, $R^2 = Alk$ or $R^1 + R^2 = (CH_2)_3$, $(CH_2)_4$, the major condensation products are enaminoketones bearing the amino group in β-position to the carbonyl group, irrespectively of the length of the fluoroalkyl substituent ($CF_3 \cdots C_6F_{13}$ or $HCF_2 \cdots H(CF_2)_4$), and the nature of amine [8]. The regioselectivity of this reaction follows to the general rules found previously for the reactions of 1,3-diketones with ammonia, amines [10] or ammonium salts [16].

Complexes derived from the reactions of compounds **4**, **5**, **9** with nickel acetate were registered by TLC, however, attempts to isolate these complexes failed. A similar phenomenon has been described in previous papers [17,18].

The complex **10** was obtained by treatment of **5** with copper acetate and its molecular structure was elucidated by X-ray crystallography.

2.2. Crystal structure

The crystal structure of **10** is formed by two crystallographic independent molecules $C_{26}H_{24}CuF_6N_2O_5$ (Fig. 1). CuA, CuB, O(3A), O(3B) atoms are in the special position on the two-fold axis. The metal ion has tetra-coordination surrounding and its coordination polyhedron is a distorted square with [2N, 2O] atoms in its corners (Scheme 2).



Scheme 1.

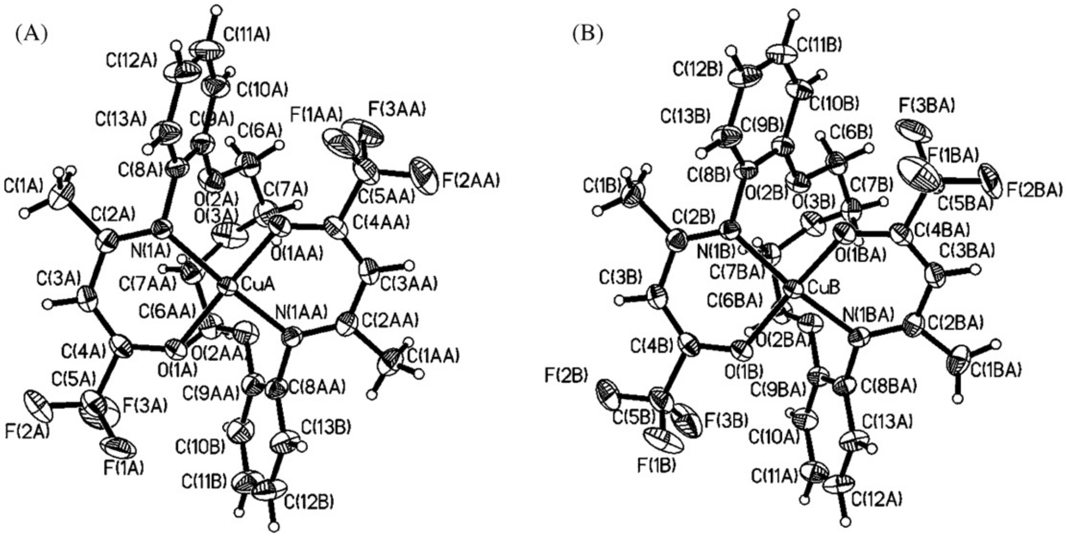
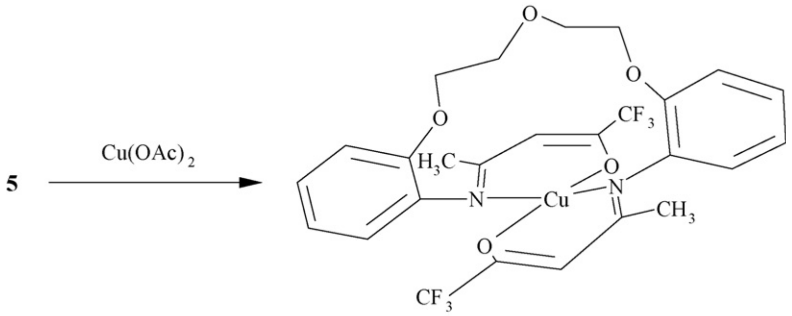


Fig. 1. Designations of atoms in molecule $C_{26}H_{24}CuF_6N_2O_5$: (A) molecule A and (B) molecule B.



10

Scheme 2.

The coordination sites of the bidentate ligand form two slightly puckered six-membered chelate rings in the *trans*-configuration. Another feature of this complex is that β-aminovinylketone fragments appear to be in a rare iminoenol form [19]. Indeed, it follows from the crystallographic data (Table 1) that bond lengths of the chelate fragments are equal to 1.351 Å for $C_{(2)}{=}N_{(1)}$, 1.427 Å for $C_{(2)}–C_{(3)}$, 1.351 Å for $C_{(3)}{=}C_{(4)}$ and 1.276 Å for $C_{(4)}–O_{(1)}$. Values of bond lengths $Cu–O_{(1)}$ and $Cu–N_{(1)}$ proved to be 1.906 and 2.004 Å, respectively.

Indeed, deviation of Cu(A) atom from the least-squares plane of the coordination node N(1A)–N(1AA)–O(1A)–O(1AA) is 0.04 Å in molecule **A**, whereas deviation of Cu(B) atom from the plane N(1B)–N(1BB)–O(1B)–O(1BB) is 0.05 Å in case of molecule **B**. The dihedral angle between the least-squares planes of molecule **A** Cu(A)–N(1A)–C(2A)–C(3A)–C(4A)–O(1A) and Cu(A)–N(1AA)–C(2AA)–C(3AA)–C(4AA)–O(1AA) is 18.7°, while the same dihedral angle in molecule **B** is equal to 26°. The dihedral angle between the plane of the coordination metal node Cu(A)–N(1A)–N(1AA)–O(1A)–O(1AA) and the plane of the chelate N–(1A)–C(2A)–C(3A)–C(4A)–O(1A) in **A** is 9.4°, while the same dihedral angle in **B** proved to be 13.4°.

Unusual behavior of the second coordination center of the polyether moiety should be noted. While two oxygen atoms are

Table 1
Crystal data and structure refinement for $C_{26}H_{24}CuF_6N_2O_5$

Empirical formula	$C_{26}H_{24}CuF_6N_2O_5$
Formula weight	622.01
Crystal system	Rhombic
Space group	*Iba*2
a (Å)	16.330(3)
b (Å)	21.888(4)
c (Å)	15.164(3)
α (°)	90
β (°)	90
γ (°)	90
U (Å^3)	5420.1(2)
Z	**8**
λ (Å)	0.71073
Calculated density (g/cm^3)	1.52
Absorption coefficient (μ, mm^{-1})	0.886
Reflections collected	4039
Reflections unique	4039
Reflections with $[F_0 > 4\sigma(F_0)]$	2766
Parameters	420
Theta range for data collection $(2\theta)_{\max}$ (°)	59.94
Limiting indices	$0 \leq h \leq 22$ $0 \leq k \leq 30$ $0 \leq l \leq 21$
Final R indices ($F_0 > 4\sigma(F_0)$)	0.034

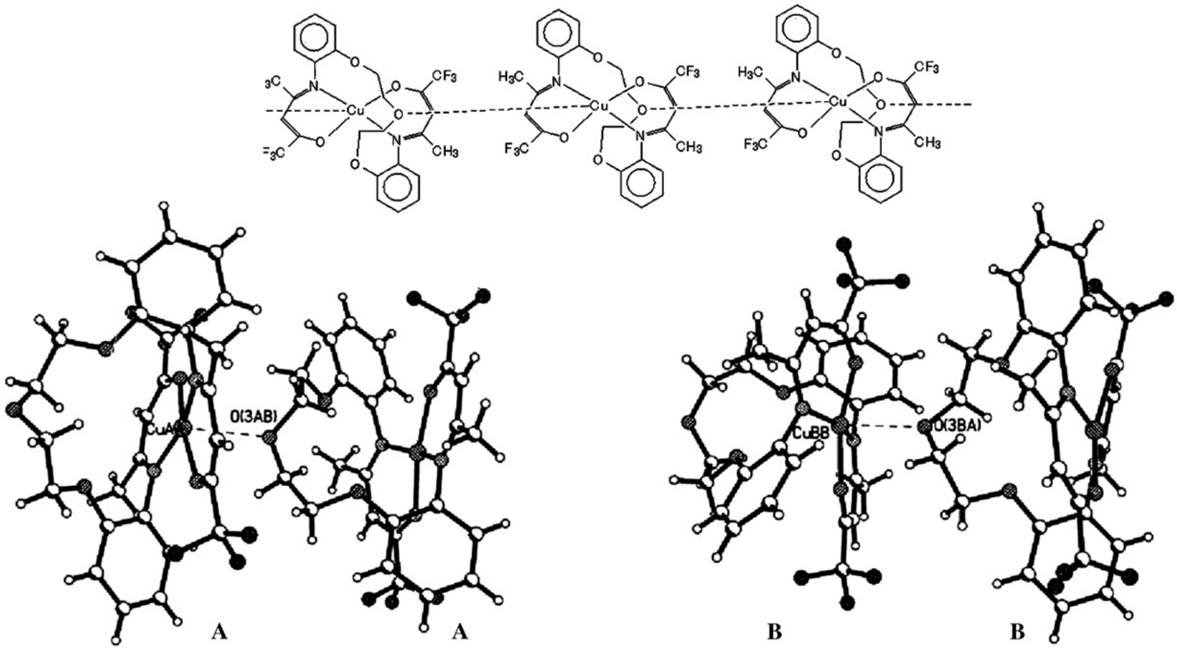


Fig. 2. Intermolecular van der Waals Cu···O interactions in complex **10**.

orientated towards the copper ion within the molecule, the central oxygen atom of the polyether chain is coordinated with a copper ion of the neighboring molecule (Fig. 2). It is due to shorter intermolecular distances Cu–O 2.698(5) Å for Cu(AA)–O(3AB) and 2.622(4) Å for Cu(BB)–O(3BA), in comparison with the sum of van der Waals's radiuses for Cu and O atoms which is equal to 3.19 Å [20].

As shown in Fig. 3, molecules of compound **10** is packed in crystal structure one above other.

3. Experimental

3.1. Measurements and apparatus

Spectroscopic studies and elemental analysis have been made in the Center for Joint Use of Equipments ''Spectroscopy and Analysis of Organic Compounds'' (Ekaterinburg, Russia).

IR spectra were obtained on a Perkin-Elmer ''Spectrum One'' spectrometer in nujol suspension. The frequencies are given in

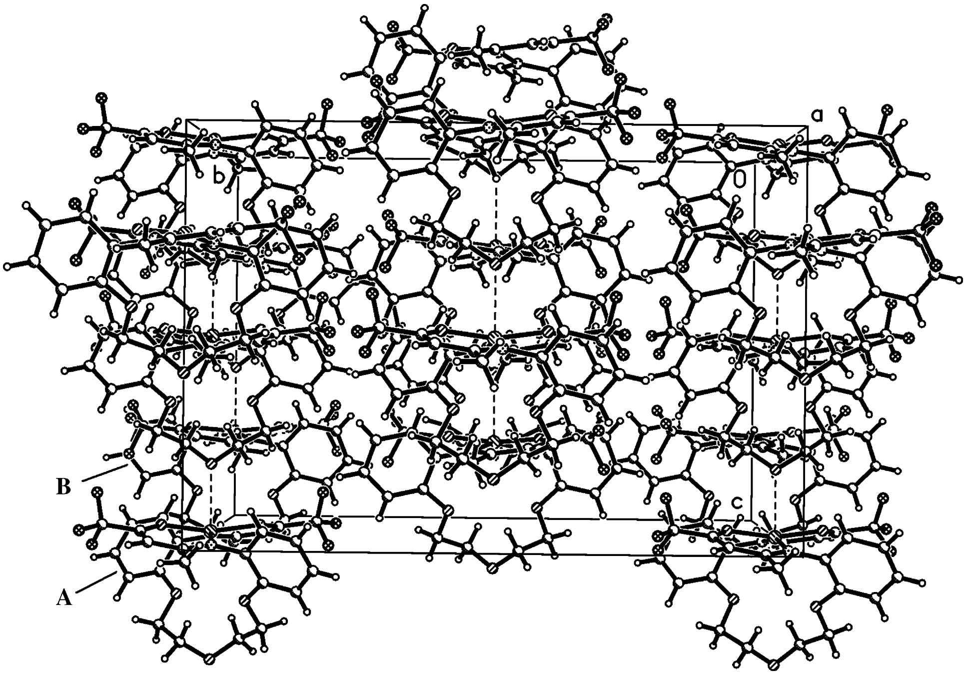


Fig. 3. The crystal structure of $C_{26}H_{24}CuF_6N_2O_5$.

Table 2
Bond lengths (Å) and angles (°) for $C_{26}H_{24}CuF_6N_2O_5$

CuA–O(1A)	1.906(2)	C(5B)-F(1B)	1.301(6)
CuA-N(1A)	2.004(2)	B)–F(3B)	1.314(5)
O(1A)–C(4A)	1.276(3)	C(6B)–C(7B)	1.502(4)
O(2A)–C(9A)	1.366(3)	C(8B)–C(13B)	1.383(4)
O(2A)–C(6A)	1.437(4)	C(8B)–C(9B)	1.386(4)
O(3A)–C(7A)	1.402(4)	C(9B)–C(10B)	1.381(4)
N(1A)–C(2A)	1.309(4)	C(10B)–C(11B)	1.379(4)
N(1A)–C(8A)	1.444(3)	C(11B)–C(12B)	1.367(5)
C(1A)–C(2A)	1.496(4)	C(12B)–C(13B)	1.391(4)
C(2A)–C(3A)	1.427(4)	O(1A)–CuA–O(1AA)	169.5(2)
C(3A)–C(4A)	1.351(4)	O(1A)–CuA–N(1AA)	88.91(9)
C(4A)–C(5A)	1.511(4)	O(1A)–CuA–N(1A)	92.42(9)
C(5A)–F(1A)	1.291(6)	N(1AA)–CuA–N(1A)	165.4(2)
C(5A)–F(2A)	1.305(6)	C(4A)–O(1A)–CuA	125.7(2)
C(5A)–F(3A)	1.341(7)	C(9A)–O(2A)–C(6A)	118.3(2)
C(6A)–C(7A)	1.498(5)	C(7AA)–O(3A)–C(7A)	116.8(4)
C(8A)–C(9A)	1.382(4)	C(2A)–N(1A)–C(8A)	116.8(2)
C(8A)–C(13A)	1.382(4)	C(2A)–N(1A)–CuA	125.8(2)
C(9A)–C(10A)	1.384(4)	C(8A)–N(1A)–CuA	117.1(2)
C(10A)–C(11A)	1.380(5)	N(1A)–C(2A)–C(3A)	122.2(3)
C(11A)–C(12A)	1.367(5)	N(1A)–C(2A)–C(1A)	122.5(3)
C(12A)–C(13A)	1.392(4)	C(3A)–C(2A)–C(1A)	115.3(3)
CuB–O(1B)	1.914(2)	C(4A)–C(3A)–C(2A)	125.0(3)
CuB–N(1B)	2.009(2)	O(1A)–C(4A)–C(3A)	128.8(3)
O(1B)–C(4B)	1.279(3)	O(1A)–C(4A)–C(5A)	112.3(3)
O(2B)–C(9B)	1.367(3)	C(3A)–C(4A)–C(5A)	118.9(3)
O(2B)–C(6B)	1.435(4)	F(1A)–C(5A)–F(2A)	108.0(5)
O(3B)–C(7B)	1.414(4)	F(1A)–C(5A)–F(3A)	105.4(5)
N(1B)–C(2B)	1.307(4)	F(2A)–C(5A)–F(3A)	105.3(5)
N(1B)–C(8B)	1.439(3)	F(1A)–C(5A)–C(4A)	114.1(4)
C(1B)–C(2B)	1.505(4)	F(2A)–C(5A)–C(4A)	114.2(4)
C(2B)–C(3B)	1.427(4)	F(3A)–C(5A)–C(4A)	109.2(4)
C(3B)–C(4B)	1.349(4)	O(2A)–C(6A)–C(7A)	108.3(3)
C(4B)–C(5B)	1.519(4)	O(3A)–C(7A)–C(6A)	115.3(3)
C(9A)–C(8A)–C(13A)	119.9(3)	C(13B)–C(8B)–C(9B)	119.7(2)
C(9A)–C(8A)–N(1A)	119.0(3)	C(13B)–C(8B)–N(1B)	121.6(3)
C(13A)–C(8A)–N(1A)	121.1(3)	C(9B)–C(8B)–N(1B)	118.6(2)
O(2A)–C(9A)–C(8A)	114.9(2)	O(2B)–C(9B)–C(10B)	125.4(3)
O(2A)–C(9A)–C(10A)	125.3(3)	O(2B)–C(9B)–C(8B)	114.6(2)
C(8A)–C(9A)–C(10A)	119.8(3)	C(10B)–C(9B)–C(8B)	119.9(3)
C(11A)–C(10A)–C(9A)	120.0(3)	C(11B)–C(10B)–C(9B)	120.0(3)
C(12A)–C(11A)–C(10A)	120.5(3)	C(12B)–C(11B)–C(10B)	120.5(3)
C(11A)–C(12A)–C(13A)	119.8(4)	C(11B)–C(12B)–C(13B)	119.9(3)
C(8A)–C(13A)–C(12A)	120.0(3)	C(8B)–C(13B)–C(12B)	119.9(3)
O(1B)–CuB–O(1BA)	164.7(2)		
O(1B)–CuB–N(1BA)	90.11(9)		
O(1B)–CuB–N(1B)	92.53(8)		
N(1BA)–CuB–N(1B)	160.1(2)		
C(4B)–O(1B)–CuB	125.3(2)		
C(9B)–O(2B)–C(6B)	118.9(2)		
C(7BA)–O(3B)–C(7B)	117.4(4)		
C(2B)–N(1B)–C(8B)	117.7(2)		
C(2B)–N(1B)–CuB	125.5(2)		
C(8B)–N(1B)–CuB	116.6(2)		
N(1B)–C(2B)–C(3B)	122.5(3)		
N(1B)–C(2B)–C(1B)	122.8(3)		
C(3B)–C(2B)–C(1B)	114.7(3)		
C(4B)–C(3B)–C(2B)	125.3(3)		
O(1B)–C(4B)–C(3B)	128.7(2)		
O(1B)–C(4B)–C(5B)	112.3(3)		
C(3B)–C(4B)–C(5B)	118.9(3)		
F(1B)–C(5B)–F(2B)	107.2(5)		
F(1B)–C(5B)–F(3B)	105.9(4)		
F(2B)–C(5B)–F(3B)	105.5(4)		
F(1B)–C(5B)–C(4B)	112.3(4)		
F(2B)–C(5B)–C(4B)	113.4(4)		
F(3B)–C(5B)–C(4B)	111.9(3)		
O(2B)–C(6B)–C(7B)	108.2(3)		
O(3B)–C(7B)–C(6B)	114.8(3)		

cm^{-1}. The ^{1}H, ^{19}F spectra were recorded by using a Bruker DRX-400 spectrometer [400 MHz (^{1}H), 376 MHz (^{19}F)], solvent $CDCl_3$, the internal standard—TMS for ^{1}H and C_6F_6 for ^{19}F.

3.2. Synthesis of ligands

Compounds **1**–**3**, **6**, **7** were described earlier [2,21,22]. A course of the reaction was controlled by TLC (Silufol UV-254, eluent—$CHCl_3$, water solutions of copper acetate was used for display of plates).

*3.2.1. 1,5-Bis-(4′,4′,4′-trifluoro-1′-methyl-3′-oxo-but-1′-enylamino)-3-oxapentane (**4**)*

A mixture of (1.75 g, 11 mmol) **1** and (0.57 g, 5.5 mmol) **2** in a glacial AcOH was maintained at room temperature until disappearance of the starting compounds (the TLC control). The reaction mixture was poured out into water. The precipitate was filtered off and recrystallized from a mixture of chloroform and hexene 1:10, to give 1.4 g of a white powder **4** in 68% yield, mp 101–102 °C. Found: C, 44.70; H, 4.88; F, 29.79; N, 7.44. Calc. for $C_{14}H_{18}F_6N_2O_3$: C, 44.69; H, 4.82; F, 30.29; N, 7.45. IR (nujol suspension, cm^{-1}): 1065, 1099, 1124, 1184 (C–O–C), 1591 (C=C), 1625 (C=O), 3182 (NH). The ^{1}H NMR ($CDCl_3$): δ 2.11 (s, 3H, Me); 3.55–3.59 (m, 2H, O–CH_2), 3.69–3.71 (m, 2H, O-CH_2), 5.34 (s, 1H, =CH–); 11.24 (br. s, 1H, NH). The ^{19}F NMR ($CDCl_3$): δ 85.01 (s, CF_3).

*3.2.2. 1,5-Bis-[2-(4′,4′,4′-trifluoro-1′-methyl-3′-oxo-but-1′-enylamino)phenoxy]-3-oxapentane (**5**)*

Similarly from (0.28 g, 1.8 mmol) **1** and (0.2 g, 0.88 mmol) 1,5-bis-(aminophenoxy)-3-oxopentane (**3**) was obtained 0.4 g of **5**, as light-yellow powder, 83% yield, mp 76 °C. Found: C, 55.90; H, 3.65; F, 19.78; N, 4.86. Calc. for $C_{26}H_{20}F_6N_2O_5$: C, 56.32; H, 3.64; F, 20.56; N, 5.05. IR (nujol suspension, cm^{-1}): 1035, 1060, 1117, 1242 (C–O–C), 1576 (C=C), 1615 (C=O), NH). The ^{1}H NMR ($CDCl_3$): δ 3.08 (s, 3H, Me); 3.93–3.95 (m, 2H, O–CH_2), 4.16–4.18 (m, 2H, O-CH_2), 5.49 (s, 1H, =CH–); 6.95–7.28 (m, 4H, Ar), 12.40 (br. s, 1H, NH). The ^{19}F NMR ($CDCl_3$): δ 85.08 (s, CF_3).

*3.2.3. 4,5′-Di-(4,4,4-trifluoro-1-methyl-3-oxo-but-1-enylamino)-dibenzo-18-crown-6 (**8**)*

Similarly from (0.12 g, 0.77 mmol) **1** and (0.3 g, 77 mmol) 4,5′-diaminodibenzo-18-crown-6 (**6**) was obtained 0.6 g of **8** as yellow powder, 91% yield, mp 201–202 °C. Found: C, 54.47; H, 4.91; F, 17.21; N, 4.15. Calc. for $C_{30}H_{32}F_6N_2O_8$: C, 54.38; H, 4.87; F, 17.20; N, 4.23. IR (nujol suspension, cm^{-1}): 1119, 1142, 1181, 1243 (C–O–C), 1578 (C=C), 1612 (C=O), 2917, 2961 (NH). The ^{1}H NMR ($CDCl_3$): δ 2.05 (s, 3H, Me); 4.02–4.03 (m, 4H, CH_2), 4.12–4.19 (m, 4H, CH_2), 5.51 (s, 1H, =CH–); 6.64–6.85 (m, 3H, Ar), 12.46 (br. s, 1H, NH). The ^{19}F NMR ($CDCl_3$): δ 85.00 (s, CF_3).

*3.2.4. 4,4′-Di-(4,4,4-trifluoro-1-methyl-3-oxo-but-1-enylamino)-dibenzo-18-crown-6 (**9**)*

Similarly from (0.34 g, 2 mmol) **1** and (0.41 g, 1 mmol) 4,4′-diaminodibenzo-18-crown-6 (**7**) was obtained 0.6 g of **9** as yellow powder, 91% yield, mp 170–171 °C. Found: C, 54.17; H, 4.89; F, 17.26; N, 4.04. Calc. for $C_{30}H_{32}F_6N_2O_8$: C, 54.38; H, 4.87; F, 17.20; N, 4.23. IR (nujol suspension, cm^{-1}): 1244, 1133, 1084, 1057 (C–O–C), 1582 (C=C), 1615 (C=O), 3440, 3560, 3628 (NH). The ^{1}H NMR ($CDCl_3$): δ 3.08 (s, 3H, Me); 4.01–4.18 (m, 16H, CH_2), 4.12–4.19 (m, 4H, CH_2), 5.51 (s, 1H, =CH–); 6.95–7.28 (m, 4H, Ar), 12.46 (br. s, 1H, NH). The ^{19}F NMR ($CDCl_3$): δ 85.00 (s, CF_3).

*3.3. Synthesis of the complex **10***

A solution of (0.1 g, 0.18 mmol) **5** and (0.035 g, 0.18 mmol) copper acetate was stirred in 10 ml ethanol for 2 h. The solvent was evaporated and residue was filtered off and recrystallized from a mixture of chloroform and hexane (1:10) to give 0.009 g of **10** as green needles in 82% yield, mp 190–191 °C. Found: C, 50.44; H, 3.98; F, 18.42; N, 4.56. Calc. for $C_{26}H_{24}F_6N_2O_5Cu$: C, 50.21; H, 3.89; F, 18.35; N, 4.50. IR (nujol suspension, cm^{-1}): 1146, 1117, 1255, 1240 (C–O–C), 1611 (C=N), 3066, 1531, 1495, 745 (C=C), 2961, 2935, 2852 (CH_2–CH_2).

*3.4. X-ray crystallography study of compound **10***

The X-ray experimental data were obtained at room temperature by using a four-circle Enraf-Nonius CAD-4 diffractometer ($\omega/2\theta$-scanning, Mo Kα radiation, graphite monochromator). The crystal structure was solved by direct methods with the subsequent Fourier-synthesis using the SHELXS-97 program [23]. The structure was refined in the anisotropic full-matrix approximation for all non-hydrogen atoms with the SHELXL-97 program [23]. Coordinates of hydrogen atoms were calculated. Fluoroalkyl groups disorder on two positions with population densities 0.6 and 0.4, 0.7 and 0.3 for fluorine atoms of fluoroalkyl groups of different molecules correspondingly.

Crystallographic data including bond lengths and torsion angles are given in Tables 1 and 2.

Crystallographic data (excluding structure factors) for the structures presented in this paper have been deposited in the Cambridge Crystallographic Data Centre, as supplementary publication nos. CCDC 636273. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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