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New Binuclear Copper(II) Complex Based on 1,2-Bis(2-(4,4,4-trifluoro-1,3-dioxobutyl)phenoxyethane: Synthesis and Structure

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Abstract—New binuclear complex 1,2-bis[2-(4,4,4-trifluoro-1-hydroxy-3-oxobut-1-enyl)phenoxy]ethanedi(dimethylformamide)dicopper(II) is synthesized, and its structure is studied by X-ray diffraction (XRD) (CIF file CCDC no. 2179252). A crystal of the complex is formed by centrosymmetric $Cu_2L_2(DMF)_2$ molecules in which the coordination environment of each metallocenter is a distorted square pyramid, and the whole molecule is a metallomacrocycle containing the calixarene-like cavity. Its size is determined the distance between the Cu...Cu metallocenters (7.699 Å) and the distance between the planes of the opposite phenyl radicals in the *cis* position (8.200–8.323 Å). The cavity is a parallelogram. The carcass-type binuclear structure is formed due to an increase in the denticity of the ligand via the formation of the bis(triketone)-like structure that weakens the donor character of both functional groups of the β-diketone fragment.

Keywords: copper(II) complexes, triketone-like ligands, metallomacrocycles
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INTRODUCTION

Classical β-diketones and related ligands have been studied for more than 100 years, since their capability of chelating provides the formation of nontrivial and sometimes unexpected in structure coordination compounds. These ligands and their analogs are still of considerable interest leading to the substantial development of coordination chemistry [1, 2]. In addition, a combination of coordination chemistry of metals and supramolecular chemistry within several decades resulted in the preparation of metal-containing ensembles of an unusual range that often demonstrate unique properties [3]. In this case, the β-diketone component is attractive for the formation of metallosupramolecular structures [4, 5]. In the most part of cases, this fragment is involved in the formation of a six-membered chelate, and the square, square pyramidal, or octahedral coordination environment is formed depending on the metal, conditions, and chemical structure of the ligand [1, 3–7]. Since transition metal complexes with organic ligands play a significant role in biological processes [6], the synthetic copper(II) complexes are considered as promising antimicrobial agents [7], an alternative to anticancer platinum drugs [8] by the formation of heteroligand compounds with DNA molecules [9], and potential modulators of inflammatory and autoimmune reactions [10]. The chemical structure of the ligand affects the coordination compound structure and biological activity of the metal complex. In particular, fluorine and fluorine-containing substituents and diketo groups enhance the biological effect of organic compounds and their metal complexes retaining the square pyramidal or octahedral coordination environment [11]. Like phenols, β-diketones provide an antioxidant effect [12, 13], which is retained in the copper(II) complexes [14]. Chelating triketone-like ligands are derivatives of β-diketones and, hence, demonstrate a possibility of basically changing the structure of the coordination compound depending on the synthesis conditions [15], which makes it possible to synthesize from them metal complexes with both biological [16] and luminescence [17] activity. In these cases, a standard six-membered chelate with the predominant square pyramidal coordination environment of the metallocenter is formed, but the presence of additional donor atoms provides the conjugation of the chelates leading to a binuclear structure of coordination compounds.

This work continues to characterize the chelating properties of triketone-like ligands and their derivatives and is devoted to the development of the synthesis of the new binuclear copper(II) complex based on 1,2-bis(2-(4,4,4-trifluoro-1,3-dioxobutyl)phenoxy)ethane (H_2L).

Table 1. Crystallographic data and experimental and structure refinement parameters for complex **I**

Parameter	Value
Empirical formula	$C_{50}H_{42}N_2O_{14}F_{12}Cu_2$
FW	1249.93
Crystal system	Triclinic
Space group	$P\bar{1}$
Z	1
a, Å	11.2752(8)
b, Å	11.5169(10)
c, Å	13.2346(13)
α, deg	86.615(7)
β, deg	67.412(8)
γ, deg	70.645(7)
V, Å^3	1492.5(2)
ρ_{calc}, g/cm^3	1.391
μ, mm^{-1}	0.809
F(000)	634
Crystal sizes, mm	0.41 × 0.29 × 0.17
Data collection range over θ, deg	3.707 < θ < 30.493
Ranges of reflection indices	$-16 \le h \le 14$, $-16 \le k \le 15$, $-18 \le l \le 17$
Measured reflections	16843
Independent reflections	8138
Reflections with $I \ge 2\sigma(I)$	4071
Number of refined parameters	421
R_1 ($I > 2\sigma(I)$)	0.0993
wR_2 ($I > 2\sigma(I)$)	0.2474
R_1 (all reflections)	0.1670
wR_2 (all reflections)	0.3002
GOOF	1.064
Residual electron density (max/min), e/Å^3	1.176/−0.759

EXPERIMENTAL

All reagents (Sigma-Aldrich) were used as received. ^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer relative to TMS using $CDCl_3$ as the solvent. Elemental analysis was carried out on a Perkin Elmer CHN PE 2400 automated analyzer. FT-IR spectra were detected on a Spectrum Two spectrometer (Perkin Elmer) equipped with an attenuate total reflection (ATR) accessory with a diamond crystal.

Synthesis of H_2L [17]. A mixture of anhydrous tetrahydrofuran (16 mL), 1,2-bis(2-acetylphenoxy)ethane (0.5 g, 1.67 mmol), lithium hydride (27 mg, 3.35 mmol), and ethyl trifluoroacetate (0.42 mL, 3.35 mmol) was refluxed with stirring for 4 h. Then the mixture was cooled down, and hydrochloric acid (2 mL) and water (6 mL) were added. The mixture was stirred at room temperature for 15 min, and the solvent was evaporated on a rotary evaporator. The substance was recrystallized from chloroform. The yield was 95%. The product was a dark beige powder with T_m = 142–144°C.

For $C_{22}H_{16}O_6F_6$			
Anal. calcd., %	C, 53.89	H, 3.29	F, 23.25
Found, %	C, 54.03	H, 3.43	F, 23.10

IR (ν, cm^{-1}): 3394, 3162, 3075, 2960, 2879, 1601, 1491, 1453, 1289, 1251, 1230, 1203, 1169, 1144, 1112, 1069, 955, 936, 918, 813, 765, 750, 714, 646, 623, 611, 579.

^{1}H NMR (δ, ppm): 4.53 (2H, s, CH_2), 6.99 (1H, s, CH), 7.14 (1H, t, *J* = 7.6 Hz, γ-H), 7.57 (1H, m, *J* = 7.6 Hz, δ-H), 8.01 (1H, d, *J* = 7.1 Hz, H).

Synthesis of $[Cu_2L_2(DMF)_2]$ (I). Ligand H_2L (0.1 g, 0.204 mmol) was dissolved in methanol (4 mL) containing NaOH (16 mg, 0.4 mmol), and $Cu(CH_3COO)_2 \cdot H_2O$ (0.04 g, 0.200 mmol) was dissolved in water (4 mL). The resulting solutions were mixed together, and a turquoise precipitate was filtered off and dried at 20°C to a constant weight. The precipitate was dissolved in DMF (3 mL) and crystallized on slow solvent evaporating. The precipitate was filtered off and dried at 20°C to a constant weight. The yield was 92%.

For $C_{50}H_{42}N_2O_{14}F_{12}Cu_2$				
Anal. calcd., %	C, 48.04	H, 3.39	N, 2.24	F, 18.24
Found, %	C, 47.87	H, 3.21	N, 2.20	F, 18.10

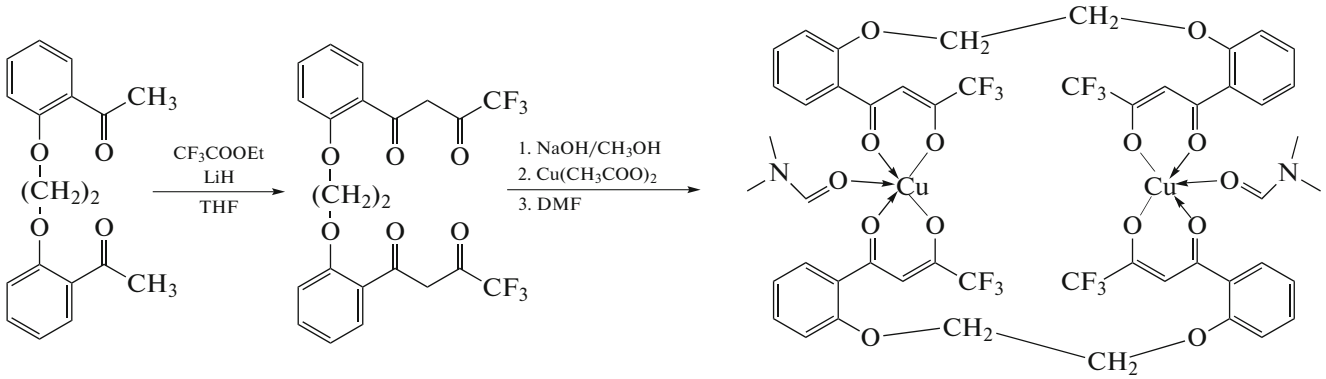
IR (ν, cm^{-1}): 2924, 2854, 1682, 1657, 1616, 1592, 1530, 1486, 1460, 1380, 1312, 1275, 1239, 1188, 1149, 1132, 1079, 1058, 1041, 952, 940, 807, 760, 720, 675, 663, 591, 565, 531, 431.

XRD. Experimental data for complex **I** were obtained on an Xcalibur 3 automated diffractometer (CCD detector, MoK_α, graphite monochromator, T = 135(2) K). An absorption correction was applied analytically using the polyhedral crystal model [18]. The structure was solved and refined using the SHELX software [19]. All non-hydrogen atoms were solved by a direct method and refined in the anisotropic approximation. Hydrogen atoms were placed in geometrically calculated positions and included in refinement by the riding model with dependent thermal parameters. The crystallographic data and experimental and structure refinement characteristics are given in Table 1.

The atomic coordinates and thermal parameters were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2179252; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

As compared to classical β-diketones, the chelating ability of the mono- [4, 15] and bis(triketone)-like [17] ligands due to the presence of the third denticity of the non-carbonyl type favors the formation of a nontrivial coordination environment of the metallocenters. Ligand H_2L, exemplifying the bis(triketone)-like structure, was synthesized by the condensation of 1,2-bis(2-acetylphenoxy)ethane with ethyl trifluoroacetate via the previously developed method (Scheme 1) [17].



H_2L $Cu_2L_2(DMF)_2$ (**I**)

Scheme 1.

The reaction of ligand H_2L in the disodium form with copper(II) acetate in an aqueous-methanol solution followed by recrystallization from DMF affords the 1,2-bis[2-(4,4,4-trifluoro-1-hydroxy-3-oxobut-1-enyl)phenoxy]ethanedi(dimethylformamide)dicopper(II) complex (**I**), whose composition corresponds to the ratio Cu : L = 1 : 1 according to the elemental analysis data. The structure of complex **I** was determined by XRD.

In a crystal of complex **I** at the ratio Cu : L = 1 : 1 with the general formula $Cu_2L_2(DMF)_2$, the ligands and metallocenters form a centrosymmetric macrocyclic structure containing the calixarene-like cavity (Fig. 1). The triketonate fragments of the ligand molecule behave as independent chelating agents linked through the flexible chain fragment and coordinating two different copper ions. The coordination environment of each metallocenter is a distorted square pyramid (Fig. 1). The pyramid base is formed by the oxygen atoms of two β-dicarbonyl fragments of the adjacent ligands. The pyramid axis is occupied by the oxygen atom of the carbonyl group of the DMF molecule. The main characteristics of the coordination node are given in Table 2.

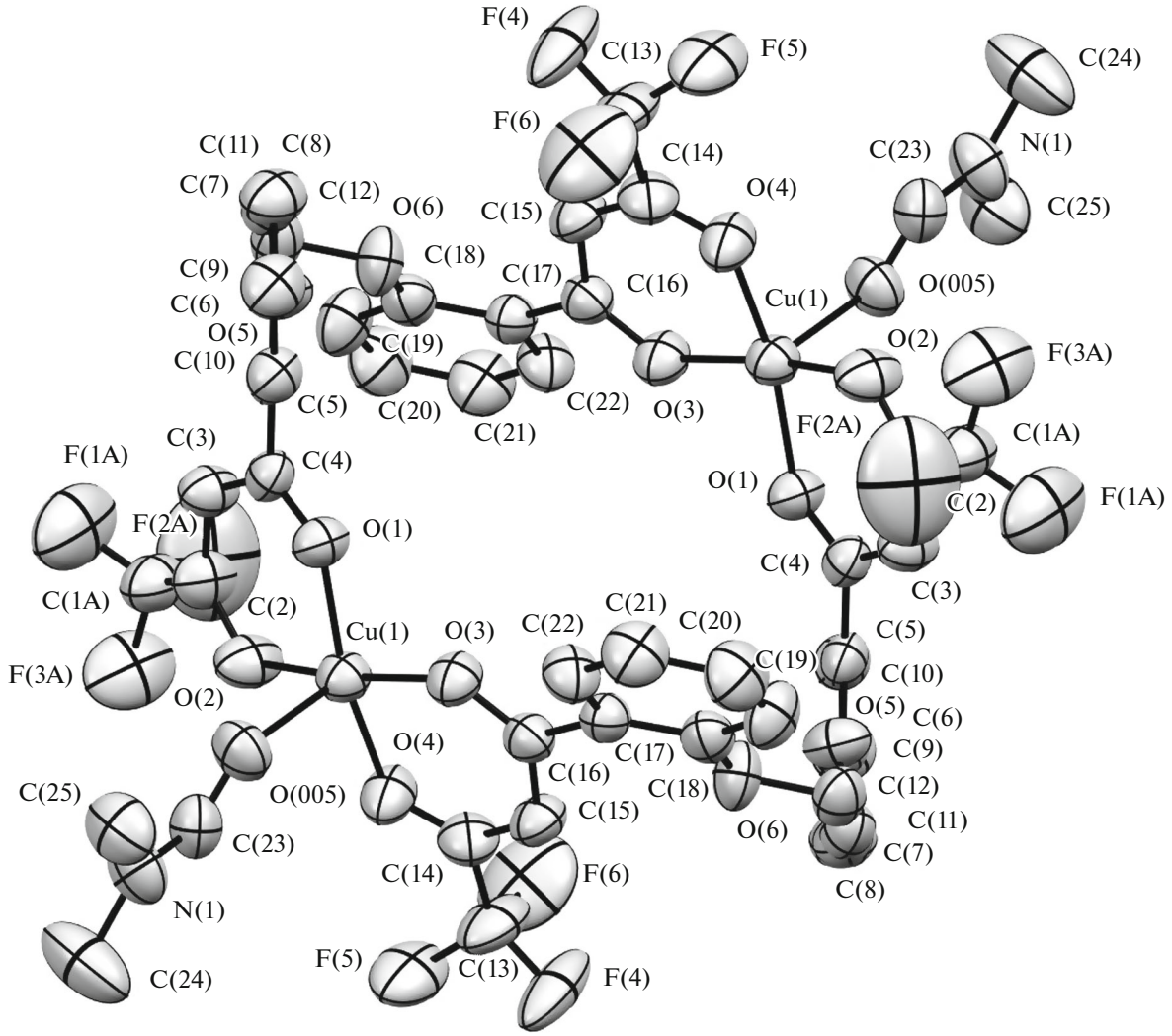
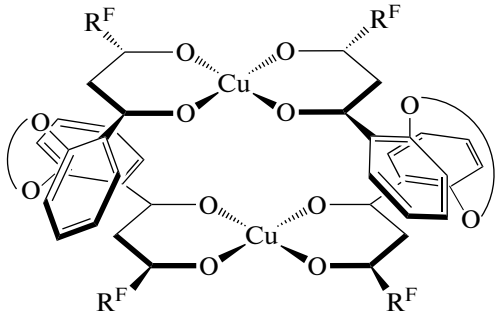


Fig. 1. Molecular structure of complex **I** in thermal ellipsoids of 50% probability. Hydrogen atoms are omitted.

Thus, each organic ligand L is bidentate with respect to the "own" copper atom (Fig. 1) to form two equatorial bonds. The oxygen atoms of the phenoxy groups are not involved in coordination. As a result, ligand L performs the tetradentate chelate (μ_2-bridging) function and forms two equivalent six-membered chelates of the CuOCCCO type.

In a crystal of complex **I**, the calixarene-like cavity in a conformation similar to "1,3-alternation" [20, 21] is formed by four phenyl radicals and two bases of coordination pyramids (Fig. 1, Scheme 2). The cavity size is determined by the distance between the metallocenters Cu...Cu (7.699 Å) and the distance between the planes of opposite phenyl radicals in the *cis* position (8.200–8.323 Å). The cavity is a parallelogram.



Scheme 2.

The crystal of complex **I** contains a branched network of intermolecular bonds due to weak interactions between the hydrogen atoms of the methyl group of the DMF molecule, the oxygen atom of the trifluoroacetyl radical (C–H...O, H...O 2.604 Å; C–H

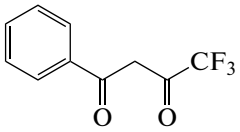
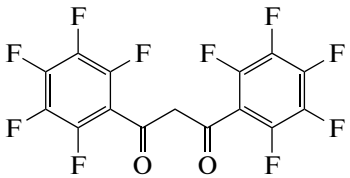
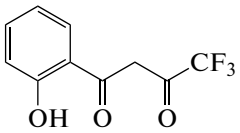
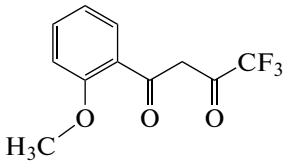
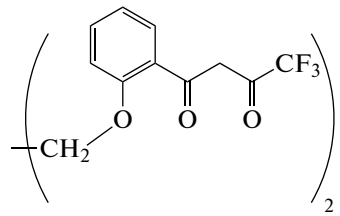
Table 2. Selected bond lengths (Å) and bond angles (deg) in the coordination node of complex **I**

Bond	*d*, Å	Angle	ω, deg
Cu(1)–O(1)	1.946(4)	O(2)Cu(1)O(1)	92.45(16)
Cu(1)–O(2)	1.945(4)	O(3)Cu(1)O(1)	85.60(15)
Cu(1)–O(3)	1.940(4)	O(4)Cu(1)O(1)	166.27(18)
Cu(1)–O(4)	1.936(4)	O(3)Cu(1)O(2)	169.68(19)
Cu(1)–O(005)	2.177(4)	O(1)Cu(1)O(005)	96.45(17)

0.960 Å, angle C–H...O 160°), and the fluorine atom of the ligand of another molecule of complex **I** (C–H...F, H...F 2.453 Å; C–H 0.960 Å, angle C–H...F 155°). The molecules of complex **I** between each other form four weak intermolecular bonds between the hydrogen atom of the aromatic ring and the fluorine atom of the ligand in the adjacent molecule of the complex (C–H...F, H...F 2.661 Å; C–H 0.930 Å, angle C–H...F 144°).

A comparative analysis of Cu–O bond lengths in the series of the copper(II) complexes based on the 3-benzoyl-1,1,1-trifluoroacetone derivatives shows (Table 3) that an increase in the denticity of the latter by the introduction of oxygen-containing functional groups results in a decrease in the donor character of both functional groups of the β-diketone fragment, since the bond lengths increase. This favors the formation of the binuclear structure in the case of 1,1,1-tri-

Table 3. Characterization of the copper(II) complexes in the series of the 3-benzoyl-1,1,1-trifluoroacetone derivatives

Formula of ligand	Bond length, Å			References
	$Cu–O_{enolate}$	$Cu–O_{carbonyl}$		
		of ligand	of DMF	
	1.9033(12)	1.9095(14)		[22]
	1.9063(8)	1.9236(7)		[23]
	1.915(4)	1.950(4) 1.966(4)	2.314(4)	[4]
	1.9199(16) 1.9356(15)	1.9258(15) 1.9313(16)	2.2471(17)	[15]
	1.936(4) 1.945(4)	1.940(4) 1.946(4)	2.177(4)	This work

fluoro-4-(2-hydroxyphenyl)butanedione-2,4 [4]. In the case of 1,1,1-trifluoro-4-(2-methoxyphenyl)-butanedione-2,4 [15], weak donor properties transform, in fact, the triketone-like ligand into β-diketone, but an increase in its denticity via bis(triketone)-like structure formation again weakens the donor character of both functional groups of the β-diketone fragment, providing the formation of the binuclear structure: complex **I**.

To conclude, this study confirms the earlier formulated regularity in the series of the β-alanine derivatives [2, 24]: an increase in the denticity of the ligand and steric hindrances of donor atoms favors the formation of oligonuclear coordination compounds. Indeed, this regularity is also confirmed in the β-diketone series for the copper(II) complexes based on the 3-benzoyl-1,1,1-trifluoroacetone derivatives, which demonstrates a synthetic possibility of the simple purposeful variation of the ligand structure for the synthesis of complicated coordination structures.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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