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A Hexanuclear Cobalt(III) Complex Containing the Pseudocubane Fragment $[Co_4(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2]$ in Its Metal Framework and a Solvated Dibenzyl Ether Molecule

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Abstract—Room-temperature oxidation of a mixture of the complex $(Co^{II})_3(\mu\text{-}OOCBu^t)_6(NEt_3)_2$ and dibenzyl ether (DBE) with atmospheric oxygen in dichloromethane–benzene (4 : 1) gave the hexanuclear complex $[(Co^{III})_6(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2(\mu\text{-}OOCBu^t)_9(OH)_2(HOOCBu^t)](HNEt_3) \cdot 0.5DBE \cdot C_6H_6$ (**I**) as the major reaction product. According to X-ray diffraction data, the metal framework of complex **I** contains the pseudocubane fragment $[Co_4(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2]$ linked with two "peripheral" cobalt(III) ions. The possibility of using complex **I** as an intermediate catalyst for liquid-phase oxidation of DBE as well as the conformational changes in the DBE molecule due to its adaptation to the metal complexes are discussed.

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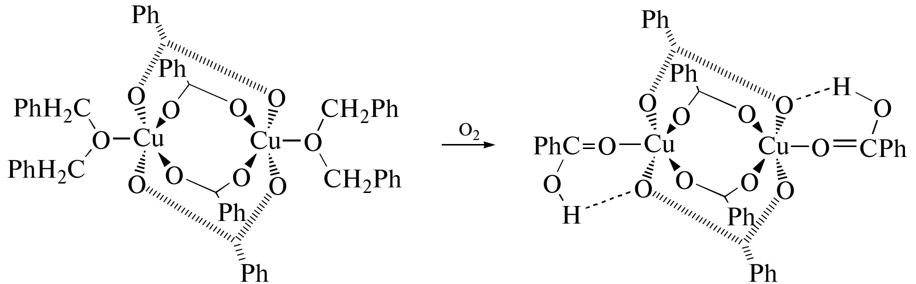
INTRODUCTION

For homogeneous metal complex catalysis, an original complex is known not to be often an "actual catalyst species." Such a species (or a few species when sequential, parallel, alternative, and other pathways are possible) can be generated from the components of a reaction mixture or from primary products (autocatalysis). In addition, special agents (modifiers or promoters) can be added both to facilitate the formation of an intermediate catalyst and prevent (or inhibit) its deactivation [1–5]. Obviously, the understanding of the mechanisms of the aforementioned processes is a key factor for the design of more efficient catalytic systems (specifically those with higher selectivity [6–10]).

Earlier [5, 11, 12], we have studied the influence of the composition and structure of various mono- and polynuclear, homo- and heteroligand carboxylate and pyrazolate 3*d*-metal complexes on their activity and selectivity in the liquid-phase oxidation of dibenzyl ether (DBE, a by-product of a number of large-capacity productions [13]) with atmospheric oxygen (hereafter, air).

We have demonstrated that at a relatively low (10–15%) conversion of DBE into a mixture of the corresponding monohydroperoxide (HP), benzaldehyde (BAld), and benzoic acid (BAc), the sequence of solventless transformations DBE → HP → 2Bald → 2BAc can occur on the same "catalytic center" (intermediate complex) passivated by reaction products. In addition, in the context of the schemes proposed for the catalytic cycles of DBE oxidation under the conditions studied, pre-coordination (activation) of DBE to the starting or intermediate complex (generated from the components of the reaction mixture) has been suggested as a key step [5].

Recently, such complexes of the formula $Cu_2(\mu\text{-}OOCR)_4(DBE)_2$ (R = Bu^t (**I**), Ph(**II**), and CF_3 (**III**)) have been obtained and identified by X-ray diffraction [14]. In these dinuclear carboxylates shaped like a "Chinese lantern", the DBE molecules are axial; the metal–metal distances largely depend on the substituent R in the carboxylate anion. Interestingly, benzoate complex **II** in air undergoes room-temperature oxidation into the complex $Cu_2(\mu\text{-}OOCPh)_4(HOOCPh)_2$ (**IV**). Its structure shows geometrically the same framework as that in the starting complex and is stabilized by strong intramolecular hydrogen bonds between the axially coordinated BAc molecules and the adjacent benzoate bridges (X-ray diffraction data) [14].



(II) **(IV)**

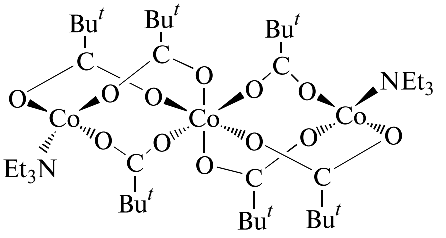
(1)

Note that the liquid-phase oxidation of DBE and the decomposition of its HP can be inhibited in an inert atmosphere by benzoic acid, which is the final (dead-end) product of the catalytic reaction under discussion [5, 15–20].

A room-temperature reaction of aqueous copper(II) acetate with 3,5-bis(trifluoromethyl)pyrazole, $[(CF_3)_2PzH]$, in chloroform in the presence of Et_3N yields the complex $[Cu_2(\mu\text{-}(CF_3)_2Pz)_2(\mu\text{-}OH_2)(OC(Me)OHNEt_3)(OH_2)(HCCl_3)(OOCMe)(\mu\text{-}OOCMe)]_2$. Heating of this complex with DBE in air at 180°C affords the unusual tetranuclear cluster $[Cu_4(\mu_4\text{-}OH)(\mu\text{-}(CF_3)_2Pz)_4(\mu\text{-}OOCPh)_2(\mu\text{-}OH)_2]^-$ $[(Et_3NH)^+(H_2O)(DBE)_2]$ (**V**), which contains two nonequivalent solvated DBE molecules in the crystal (Fig. 1) [21].

One of them (A) is hydrogen-bonded to the solvated water molecule, the second H atom and the O atom of which are bound to the bridging OH group and the proton of the cation $[HNEt_3]^+$, respectively. The second DBE molecule (B) is virtually inside the cavity $[(\mu_4\text{-}OH)(\mu\text{-}OOCPh)_2(\mu\text{-}(CF_3)_2Pz)_2]$ formed by the bridging ligands and shows Ph···Ph contacts with the phenyl group of one benzoate anion. It seems to be quite probable that such contacts are responsible for angles of 54.6° between the planes of the benzene rings and the plane $O(CH_2)_2$ in molecule B. In molecule A, these angles are nearly 90° and the geometry of the fragment OR_2 is ordinary for ethers.

A different sequence of transformations of DBE into BAld and BAc has been assumed in [11] for the liquid-phase oxidation of DBE with air at 70°C in the presence of tricobalt(II) hexapivalate (**VI**). We found it expedient to study this transformation at room temperature.



(VI)

Here we discuss the composition and structure of a product obtained by oxidation of complex **VI** in the presence of DBE. This product can be formulated as the hexanuclear complex $Co_6(\mu_4\text{-}O)_4(\mu\text{-}OOCBu^t)_9(OH)_2(HOOCBu^t)(HNEt_3)$ (**VII**), which crystallizes with a solvated DBE molecule. In addition, based on the X-ray diffraction data for complexes **I–III, V** and **VII**, we analyze conformational changes in the DBE molecule due to its adaptation to the above metal complexes.

EXPERIMENTAL

Aqueous copper acetate and pivalic acid (ACROS ORGANICS) were used as purchased. Dibenzyl ether was purified by distillation in vacuo in an inert atmosphere as described in [12].

IR spectra were recorded on a Nexus-Nicolet FTIR spectrophotometer in the 400–4000 cm^{-1} range by using frustrated total internal reflection from single crystals of test complexes.

X-ray diffraction studies were carried out on a Bruker SMART Apex II automated diffractometer equipped with a CCD detector (MoK_α radiation, graphite monochromator, $\lambda = 0.71073$ Å, ω scan mode) according to a standard procedure. The structures were calculated with the SHELXTL PLUS program package (PC version) and refined with the SHELXTL-97 program [22, 23]. The crystallographic parameters and the data collection and refinement statistics are summarized in Table 1. The comprehensive tables of the atomic coordinates, bond lengths, and bond angles in structures **VIII** and **IX** have been deposited with the Cambridge Crystallographic Data Collection (nos. 957851 and 957852, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Synthesis of complex VII · 0.5 DBE · C_6H_6 (VIII). Dibenzyl ether (0.5 mL, 3.0 mmol) was added to a violet solution of complex **VI** (0.2 g, 0.27 mmol) in dichloromethane–benzene (4 : 1, 10 mL). Air was bubbled through the resulting solution at room temperature for 2 h. The solution was left in an open flask at room temperature for 48 h. The precipitate that formed as green large prisms was separated from the mother liquor by decantation, washed successively with cold benzene and hexane, and dried under argon. The yield was 0.038 g (67%).

Table 1. Crystallographic parameters and the data collection and refinement statistics for structures **VII** · 0.5DBE · C_6H_6 (**VIII**) and DBE (**IX**)

Parameter	Value	
	VIII	**IX**
Empirical formula	$C_{71}H_{129}NO_{28.5}Co_6$	$C_{14}H_{14}O$
M	1806.33	198.25
Temperature, K	173(2)	173(2)
Color	Brown-green	Colorless
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
Unit cell parameters		
a, Å	27.9565(10)	5.645(3)
b, Å	24.4020(9)	7.533(3)
c, Å	28.4295(10)	26.105(12)
α, deg	90	90
β, deg	112.9060(10)	90
V, Å^3	17865.1(11)	1110.0(9)
Z	8	4
ρ_{calcd}, mg/m^3	1.343	1.186
μ, mm^{-1}	1.160	0.073
F(000)	7616	424
Crystal dimensions, mm	0.14 × 0.12 × 0.10	0.12 × 0.10 × 0.008
θ scan range, deg	1.84–28.00	2.81–27.97
Ranges of h, k, and l indices	$-36 \le h \le 36$, $-31 \le k \le 32$, $-37 \le l \le 37$	$-7 \le h \le 7$, $-9 \le k \le 9$, $-34 \le l \le 34$
Number of measured reflections	180952	10246
Number of unique reflections (R_{int})	42670 (0.1027)	2597 (0.0996)
GOOF	1.015	1.033
R ($I > 2\sigma(I)$)	$R_1 = 0.0701$, $wR_2 = 0.1737$	$R_1 = 0.0535$, $wR_2 = 0.1240$
R (for all reflections)	$R_1 = 0.1449$, $wR_2 = 0.2178$	$R_1 = 0.0650$, $wR_2 = 0.1315$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	2.575/–1.026	0.187/–0.208

IR (KBr, ν, cm^{-1}): 3375 m br, 2960 s, 2929 w, 2902 w, 2871 w, 1650 w, 1574 s, 1483 s, 1457 w, 1471 s, 1360 s, 1289 m, 1225 m, 1201 w, 1124 w, 937 w, 897 m, 867 m, 783 m, 765 w, 641 w, 610 s, 525 w, 433 w.

For $C_{61}H_{119}O_{29.5}Co_6$ (powder)		
anal. calcd., %:	C, 43.65;	H, 7.09.
Found, %:	C, 43.60;	H, 7.01.

Synthesis of single crystals of dibenzyl ether (IX). Dibenzyl ether (2 mL) was mixed with heptane (5 mL) and kept in a refrigerator at –10°C for 48 h. The large crystals (immediately melting at room temperature) that formed were transferred, together with the mother liquor, to a frozen Petri dish placed on thawing ice. A single crystal was glued on a goniometric head and transferred as quickly as possible to a flow of evaporating liquid nitrogen.

RESULTS AND DISCUSSION

According to X-ray diffraction data, the unit cell of complex **VII** in structure **VIII** (Figs. 2, 3; Tables 1, 2) contains two independent molecules with close geometries. In the central pseudocubane fragment $Co_4(\mu_3\text{-}O)_4$, the cobalt(III) atoms make up a tetrahedron at short nonbinding distances from each other (Co···Co 2.6982(8)–2.8702(9) Å). Apparently, this is due to the contracting effect of the bridging O atoms that center

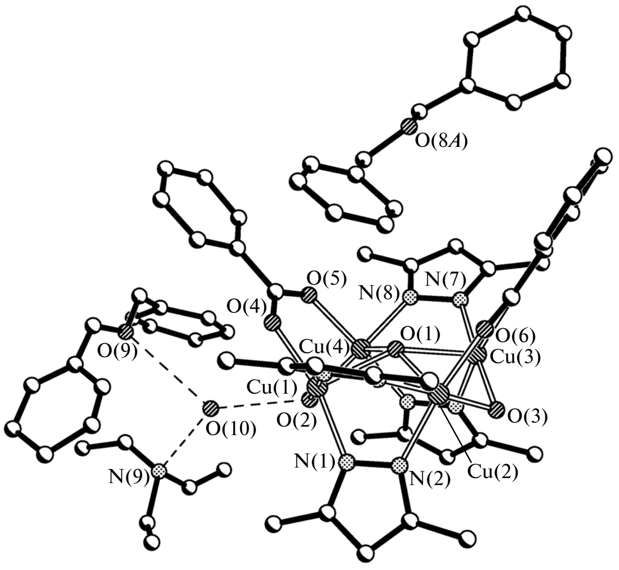


Fig. 1. Fragment of the crystal packing of complex **V**. The F_3C substituents in the pyrazole rings are omitted.

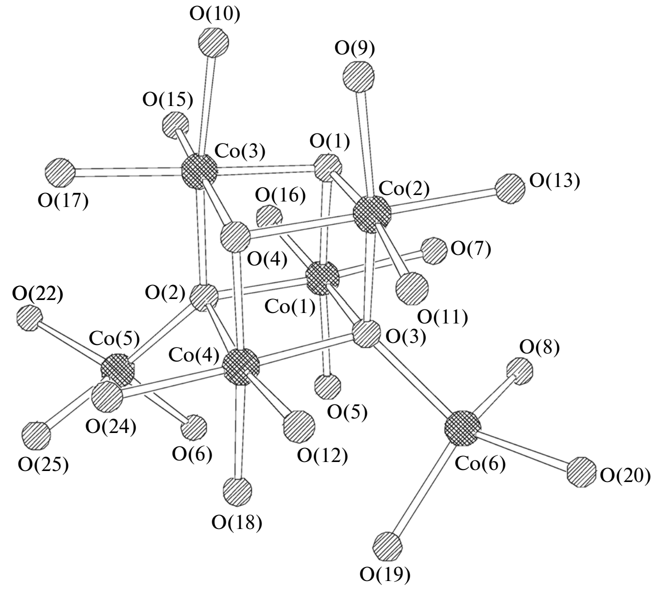


Fig. 2. Metal framework of structure **VII**.

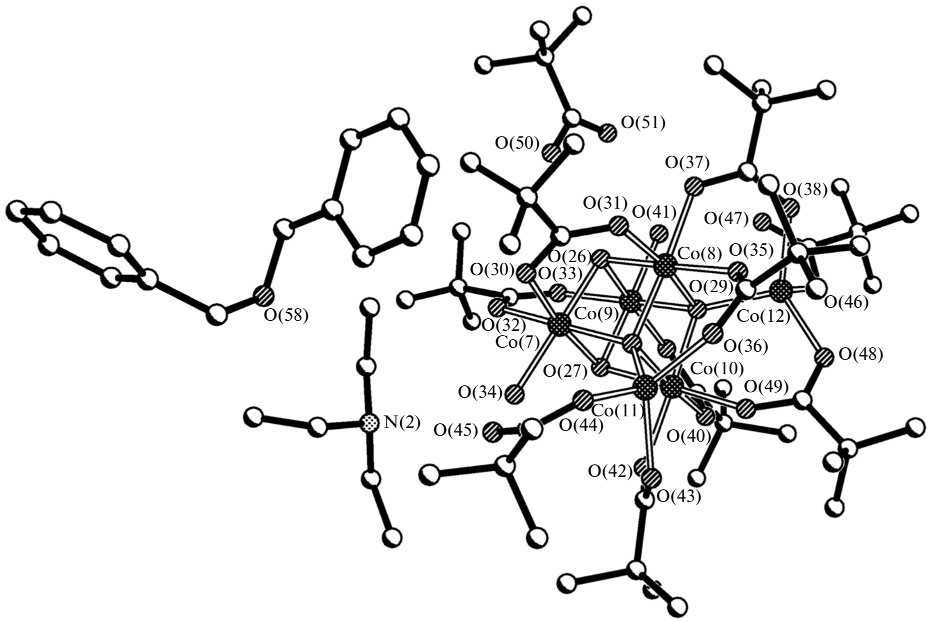


Fig. 3. Structure **VII** (one of two independent molecules is shown only).

each face Co_3. The Co–O bond lengths (1.847(2)–1.906 Å) are characteristic of cobalt(III) compounds [24–31]. The bridging O atoms shared by two faces of the tetrahedron are additionally bound to two peripheral cobalt atoms (Co–O, 1.938(2)–1.950(2) Å), thus forming the metal framework Co_6.

Either peripheral cobalt atom is additionally coordinated by three O atoms (Figs. 2, 3). Two of them belong to two bridging pivalate anions linked with the Co(1) and Co(4) atoms (Co–O, 1.909(3)–1.965(3) Å); the third O atom comes from the terminal pivalate anion (Co–O, 1.943(3) and 1.945(3) Å). The two other cobalt atoms of the fragment Co_4O_4 that are not involved in this coordination are also linked by bridging pivalate ligands in the pairs Co(2)···Co(4) and Co(3)···Co(1) (Co–O, 1.898(3) and 1.946(3) Å; 1.912(3) and 1.926(3) Å, respectively). The Co(2) and Co(3) atoms are also bridged by a pivalate anion (Co–O, 1.917(3) and 1.920(3) Å). In addition, either of these Co atoms is coordinated by the terminal OH group

Table 2. Selected bond lengths in structure **VIII**

Bond	*d*, Å	Bond	*d*, Å
Co(1)–O(1)	1.856(3)	Co(1)–O(2)	1.877(3)
Co(1)–O(3)	1.906(3)	Co(1)–O(7)	1.907(3)
Co(1)–O(16)	1.910(3)	Co(1)–O(5)	1.921(3)
Co(1)–Co(3)	2.7018(9)	Co(1)–Co(4)	2.8214(9)
Co(1)–Co(2)	2.8520(9)	Co(2)–O(4)	1.851(3)
Co(2)–O(1)	1.873(3)	Co(2)–O(3)	1.896(3)
Co(2)–O(9)	1.914(3)	Co(2)–O(13)	1.928(3)
Co(2)–O(11)	1.946(3)	Co(2)–Co(4)	2.7068(9)
Co(2)–Co(3)	2.7170(9)	Co(3)–O(1)	1.845(3)
Co(3)–O(4)	1.866(3)	Co(3)–O(2)	1.899(3)
Co(3)–O(10)	1.916(3)	Co(3)–O(15)	1.922(3)
Co(3)–O(17)	1.944(3)	Co(3)–Co(4)	2.8650(9)
Co(5)–O(22)	1.940(4)	Co(5)–O(2)	1.949(3)
Co(5)–O(6)	1.954(4)	Co(5)–O(25)	1.959(4)
Co(4)–O(4)	1.851(3)	Co(4)–O(3)	1.884(3)
Co(4)–O(12)	1.896(3)	Co(4)–O(2)	1.903(3)
Co(4)–O(18)	1.918(3)	Co(4)–O(24)	1.921(3)
Co(6)–O(3)	1.935(3)	Co(6)–O(20)	1.941(4)
Co(6)–O(19)	1.961(3)	Co(6)–O(8)	1.963(4)
Co(7)–O(26)	1.838(3)	Co(7)–O(27)	1.874(4)
Co(7)–O(28)	1.898(3)	Co(7)–O(32)	1.920(4)
Co(7)–O(34)	1.928(4)	Co(7)–O(30)	1.937(4)
Co(7)–Co(8)	2.6974(10)	Co(7)–Co(9)	2.7108(10)
Co(7)–Co(10)	2.8673(10)	Co(8)–O(26)	1.863(3)
Co(8)–O(28)	1.887(3)	Co(8)–O(29)	1.907(4)
Co(8)–O(31)	1.909(4)	Co(8)–O(37)	1.914(4)
Co(8)–O(35)	1.935(4)	Co(8)–Co(10)	2.8252(11)
Co(8)–Co(9)	2.8687(10)	Co(9)–O(27)	1.835(4)
Co(9)–O(26)	1.868(4)	Co(9)–O(29)	1.901(4)
Co(9)–O(33)	1.928(4)	Co(9)–O(41)	1.937(4)
Co(9)–O(39)	1.938(4)	Co(9)–Co(10)	2.7137(10)
Co(10)–O(27)	1.870(4)	Co(10)–O(29)	1.877(4)
Co(10)–O(28)	1.908(4)	Co(10)–O(40)	1.916(4)
Co(10)–O(42)	1.929(4)	Co(10)–O(49)	1.931(4)
Co(11)–O(28)	1.938(3)	Co(11)–O(44)	1.945(4)
Co(11)–O(36)	1.956(4)	Co(11)–O(43)	1.959(4)
Co(12)–O(46)	1.922(4)	Co(12)–O(29)	1.943(4)
Co(12)–O(38)	1.944(5)	Co(12)–O(48)	1.946(4)

Table 3. Selected bond lengths and bond angles in structure **IX**

Bond	*d*, Å	Bond	*d*, Å
O(1)–C(8)	1.405(2)	O(1)–C(1)	1.417(2)
C(1)–C(2)	1.497(3)	C(2)–C(7)	1.397(3)
C(2)–C(3)	1.399(3)	C(3)–C(4)	1.385(3)
C(4)–C(5)	1.381(3)	C(5)–C(6)	1.386(3)
C(6)–C(7)	1.381(3)	C(8)–C(9)	1.500(3)
C(9)–C(14)	1.391(3)	C(9)–C(10)	1.394(3)
C(10)–C(11)	1.380(3)	C(11)–C(12)	1.391(3)
C(12)–C(13)	1.382(3)	C(13)–C(14)	1.389(3)
Angle	ω, deg	Angle	ω, deg
C(8)O(1)C(1)	112.48(14)	O(1)C(1)C(2)	110.40(15)
C(7)C(2)C(3)	118.43(18)	C(7)C(2)C(1)	121.64(16)
C(3)C(2)C(1)	119.93(17)	C(4)C(3)C(2)	120.8(2)
C(5)C(4)C(3)	120.2(2)	C(4)C(5)C(6)	119.5(2)
C(7)C(6)C(5)	120.8(2)	C(6)C(7)C(2)	120.30(18)
O(1)C(8)C(9)	111.19(15)	C(14)C(9)C(10)	118.93(17)
C(14)C(9)C(8)	121.92(16)	C(10)C(9)C(8)	119.15(16)
C(11)C(10)C(9)	120.83(18)	C(10)C(11)C(12)	119.95(19)
C(13)C(12)C(11)	119.63(19)	C(12)C(13)C(14)	120.51(19)
C(13)C(14)C(9)	120.15(18)		

(Co–O, 1.925(3) and 1.939(3) Å). As a result, the polynuclear complex is a monoanion with a distorted tetrahedral environment for either peripheral Co(III) atom and with a distorted octahedral environment for each Co(III) atom of the pseudocubane fragment. In complex **VII**, the triethylammonium cation serves as a counterion. Its H atom shows contacts with one of the OH groups (N···O 3.110(4) Å) and with the O atom of the terminal pivalate anion (N···O 3.344(5) Å). The H atom of the same OH group is linked by a short hydrogen bond with the O atom of solvated pivalic acid (O···O 2.587(4) Å), which in turn is hydrogen-bonded to the μ_3-O atom (O···O 2.559(3) Å).

It should be emphasized that the reaction under discussion predominantly gives a hexanuclear complex, in contrast to oxidation of violet cobalt pivalate (obtained by fusion of cobalt acetate with pivalic acid) with air in THF [32]. That oxidation yields the complex $[Co_6(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_2(OH)_2(\mu\text{-}OOCBu^t)_9]^+(OOCBu^t)^-$ (structurally similar to complex **VII**) and the product of its transformations $Co_{14}(\mu_5\text{-}O)_2(\mu_3\text{-}O)_2(\mu_3\text{-}OH)_{12}(OH)_4(\mu\text{-}OOCBu^t)_8(OOCBu^t)_{10}$.

As mentioned above, the unit cell of complex **VIII** in the crystal contains 0.5 solvated DBE molecule and

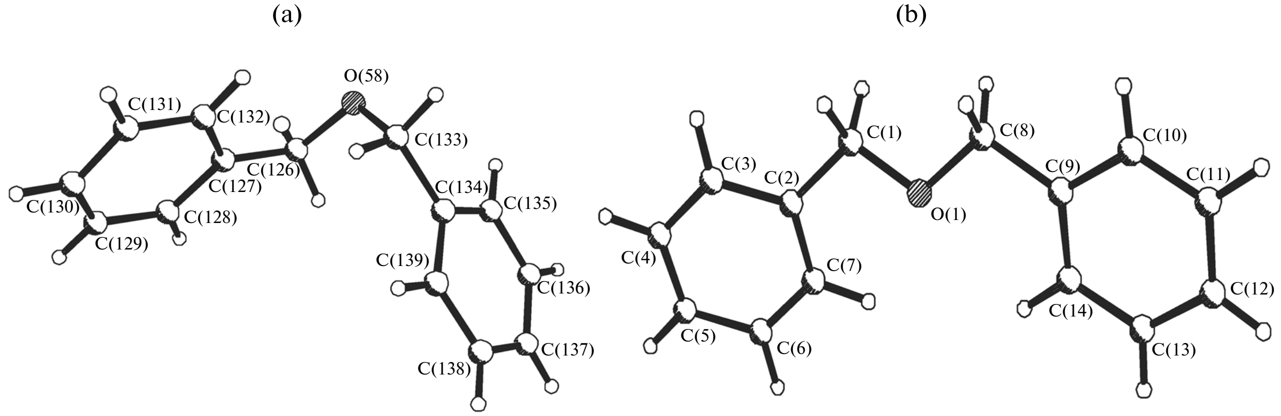


Fig. 4. Conformations of the DBE molecule in (a) the unit cell of the crystal of complex **VIII** and (b) a single crystal of DBE.

a disordered benzene molecule, both showing no strong contacts. In this complex, the DBE molecule adopts a twist conformation (Fig. 4a) and has bond lengths characteristics of ethers (Table 3).

At the same time, the DBE molecule in the single crystal **IX** is nearly planar (Fig. 4b), which is evident from the corresponding dihedral angles (Table 4); contacts between DBE molecules are virtually absent.

Table 4. Geometrical parameters of the dibenzyl ether molecule in the crystals of complexes **I–III**, **V**, and **VIII**

Com-pound		Bond lengths, Å		Dihedral angles, deg			Comment
		O–CH_2	H_2C–Ph	OCH_2C_{Ph}/OCH_2C_{Ph}	OCH_2C_{Ph}/Ph	Ph/Ph	
I		1.435(4)–1.444(4)	1.496(5)–1.500(5)	72.2 76.2	56.9, 53.2 63.6, 57.7	19.4 9.0	Ligand
II		1.424(7)–1.452(7)	1.498(9)–1.508(9)	77.2 79.5	56.5, 56.5 65.4, 65.4	10.6 1.6	Ligand
III	A	1.433(6)–1.454(6)	1.505(7)–1.514(8)	71.5 73.6	68.7, 99.4 63.2, 96.9	24.7 20.5	Ligand, Ph···Ph contacts with $PhCOO^-$
	B	1.417(7)–1.442(7)	1.490(7)–1.496(8)	59.1	99.00 47.7	86.4	Solvate
V	A	1.32(3)–1.42(3)	1.24(3)–1.37(3)	10.8	93.8 91.0	73.8	H-Bonded solvate
	B	1.40(3)–1.43(3)	1.37(3)–1.42(3)	7.0	60.5 52.2	52.8	Solvate
VII		1.393(11)–1.433(11)	1.487(13)–1.487(12)	77.5	8.2 50.0	64.2	Solvate
DBE		1.407(3)–1.418(2)	1.497(3)–1.501(3)	6.0	9.6 16.5	2.8	Single crystal

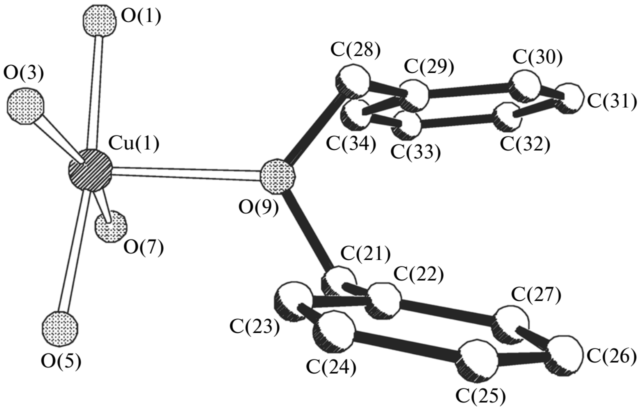


Fig. 5. Conformation of the coordinated DBE molecule in complexes **I–III** [14].

Note that when DBE is coordinated by copper(II) atoms in complexes **I–III** (Fig. 5), the O–C and C–C bonds lengths remain characteristic of ethers (Table 4); however, the values of the dihedral angles suggest nearly parallel orientation of the benzene rings of DBE.

The lengthening of the O–CH_2 bonds in the DBE molecule (Table 5) is virtually independent of the substituent R in the carboxylate anions of complexes **I–III** ($d \sim 0.03$ Å). However, one can see the following trend for the H_2C–Ph bonds: $Bu^t < Ph \ll CF_3$. At the same time, these bonds are substantially shortened in solvated DBE molecules (Table 5), especially in the H-bonded molecule **V**(A) ($d = -0.188$ Å); in this molecule, the O–CH_2 bond is also shortened. On the whole, the H_2C–Ph bond lengths are very sensitive to the type of nonvalent contacts of solvated DBE molecules in the crystals of the complexes studied.

Apparently, complex **VII** that forms upon the room-temperature oxidation of the starting complex **VI** with air in the presence of DBE and contains the tetraoxopseudocubane fragment $[(Co^{III})_4(\mu_3\text{-}O)_2(\mu_4\text{-}O)_2]$ can act as an intermediate catalyst for liquid-phase oxidation of DBE because it is known that cubane complexes with the metal framework $[(Co^{III})_4(\mu_3\text{-}O)_4]$ efficiently promote the oxidation of alkylbenzenes with air and the oxidation of benzyl alcohols with *tert*-butyl peroxide [26–28]. Data on the geometrical parameters of the coordinated and solvated DBE molecules in the complexes studied can be of its own value for modeling the elementary steps of activation of ethers and related compounds under the conditions of metal complex catalysis.

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Table 5. Selected bond length changes for the DBE molecule in the crystals of complexes **I–III**, **V**, and **VIII**

Compound		Averaged bond lengths (d, Å)				Comment**
		O–CH_2	d*	H_2C–Ph	d*	
DBE		1.413		1.498		Crystal
I		1.440	0.027	1.498	0.001	Ligand
II		1.438	0.026	1.503	0.005	Ligand
III	A	1.444	0.031	1.509	0.011	Ligand, Ph···Ph
	B	1.430	0.017	1.493	–0.006	Solvate
V	A	1.370	–0.043	1.305	–0.188	H-Bonded solvate
	B	1.415	0.003	1.395	–0.104	Solvate
VIII		1.413	0.001	1.487	–0.012	Solvate

* $d = d - d_{DBE}$.

** See also Table 4.

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