Dedicated to Professor Vladimir Fedorov on the occasion of his 75th birthday

Binuclear Complexes with the "Chinese Lantern" Geometry as Intermediates in the Liquid-Phase Oxidation of Dibenzyl Ether with Atmospheric Oxygen in the Presence of Copper(II) Carboxylates

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Abstract—Reactions of copper(II) carboxylates with dibenzyl ether (DBE) gave binuclear complexes of the formula $Cu_2(\mu$ -OOCR)_4(DBE)_2 (R = Bu^{*I*}, Ph, and CF₃). The complexes were characterized by X-ray diffraction. The axial positions in the lantern-type dimer are occupied by the coordinated DBE molecules. The complexes seem to be analogs of intermediate catalysts for the oxidation of DBE with atmospheric oxygen in the presence of transition metal complexes. When stored in air, the complex $Cu_2(\mu$ -OOCPh)_4(DBE)_2 underwent oxidation into $Cu_2(\mu$ -OOCPh)_4(HOOCPh)_2, which was characterized by X-ray diffraction. The geometry of its framework is similar; the structure is stabilized by intramolecular H bonds between the axially oriented benzoic acid molecules and the adjacent bridging benzoate anions.

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Investigations of the main pathways of liquid-phase oxidation of dibenzyl ether (DBE) with atmospheric oxygen (hereafter, air) in the presence of metal complexes [1] are largely motivated by the need of catalytic methods for the recovery of DBE, which is a waste product in the large-capacity production of such chemicals as benzyl alcohol (BAlc), benzyl benzoate (BB), benzoic acid (BAc), and benzylcellulose [2–4]. In addition, DBE is a by-product in the preparation of benzyl-containing phenols, amides, amines, etc. [5–7]. Furthermore, because DBE is readily oxidizable and because its monohydroperoxide (HP) is fairly stable, the process under discussion can be regarded as a convenient model reaction for revealing the structural fac-

tors that influence the activity and selectivity of metalcomplex catalysts for liquid-phase oxidation of organic substrates containing an activated CH bond [1].

In the study of the catalytic properties of polynuclear carboxylates of 3d metals [8–15], particular emphasis has been placed on alternative pathways of the liquid-phase oxidation of DBE and the decomposition of HP, varying with the structure and composition of the starting metal complex and the reaction conditions.

It has been found that the oxidation of DBE with air in the presence of a metal complex (more than 250 complexes studied) follows the scheme:

$$PhCH_{2}OCH_{2}Ph \xrightarrow{O_{2}} PhCH(OOH)OCH_{2}Ph \xrightarrow{-H_{2}O} PhCHO \xrightarrow{O_{2}} 2PhCOOH \leftarrow BAld BAc O_{2}$$
(1)

$$DBE HP \xrightarrow{I \rightarrow PhCOOCH_{2}Ph \xrightarrow{O_{2}} PhCHO = BB BAld BAld } O_{2}$$
(1)

In this case, the dehydration of HP to BB usually proceeds at a rate of three to five times lower; when the conversion of DBE is less than 10-15%, the reaction sequence can be schematically represented as follows:

 $DBE \to HP \to 2BAld \to 2BAc.$ (2)

It has been also found that the activities of the complexes studied in each step of sequence (2) change in a similar way. Therefore, at a low conversion of DBE, the formation and dehydration of HP, as well as the oxidation of benzaldehyde (BAld) to BAc, can occur at the same "catalytic center" (metal center). According to the scheme proposed by us for alternative catalytic cycles of BAld formation, the terminal ligands in the starting complex (Cat) can be replaced by DBE and its coordinated (activated) molecule in the complex DBE \cdot Cat will be oxidized into HP with dioxygen coming from either the bulk or the complex DBE \cdot Cat \cdot O₂.

According to the kinetic data for the decomposition of HP in DBE oxidate in an inert atmosphere (when BB is the major product), the rate-limiting step of the process in the catalytic systems studied (Cat' that are derived from the starting metal complexes under the action of the components of the reaction mixture) is the formation of the intermediate complexes HP · Cat'. At the same time, the components of the oxidate (P) can also act as catalyst poisons by forming the complexes P · Cat'. We have also assumed that the observed differences in the properties of the complexes studied in the liquid-phase oxidation of DBE and in the decomposition of HP are due to a competition for the "catalytic center" between HP and dioxygen.

Recently [16], we have found that a reaction of the polymer complex [FeCl₂(NCMe)₂]_n with 3,5-dimethylpyrazole (HDmpz) yields a tetrahedral complex of the formula [Fe(HDmpz)₃Cl]Cl, which is oxidized with air in acetonitrile into the binuclear complex [Fe(HDmpz)₃Cl₂]₂(μ -O) (A). The same complex can be obtained by a reaction of FeCl₃ · 6H₂O with HDmpz. However, oxidation of complex A with air in a solution of DBE in CH₂Cl₂ gives the complex ((HDmpz)FeCl₂[η^2 -N,O-(Dmpz)C(O)H(Ph)] (B)) containing the coordinated tetrahedral intermediate in the condensation of HDmpz with BAld (Schemes 1 and 2).

The structures of the complexes under discussion were confirmed by X-ray diffraction data.

Note that complex B is the first example of intermediate complexes capable of forming from the products of the liquid-phase oxidation of DBE with air under the conditions of metal-complex catalysis.



The aforesaid results and assumptions served as a main prerequisite for revealing the possibility of isolation and identification of intermediate complexes in the 3*d*-metal carboxylate-catalyzed liquid-phase oxidation of DBE with air.

Here we describe the synthesis and structures of possible intermediates of the catalytic oxidation of DBE with air: the adducts of the formulas $Cu_2(\mu - OOCR)_4(DBE)_2$ (R = Bu^t, Ph, and CF₃) and $Cu_2(\mu - OOCPh)_4(BAc)_2$.

EXPERIMENTAL

Aqueous cupric acetate was used without further purification. Dibenzyl ether was purified by distillation in vacuo in an inert atmosphere as described in [16]. All manipulations involving the synthesis and isolation of the complexes were carried out under pure argon in dehydrated solvents, unless otherwise specified.

Synthesis of $Cu_2(\mu$ -OOCBu')₄(DBE)₂ (I). A. The complex $Cu_2(OOCBu')_4(NEt_3)_2$ (0.2 g, 0.27 mmol) was dissolved in dibenzyl ether (10 mL) and heated in air at 165°C for 0.5 h. The resulting homogeneous solution was slowly to room temperature while gradually cooling the oil bath. The blue-green crystals that formed were separated from the mother liquor by decantation, successively washed with cold benzene and hexane, and dried under argon. The yield of complex I was 0.038 g (15%).

B. Cupric pivalate (0.2 g, 0.75 mmol) was dissolved in acetonitrile (10 mL) and crystallized at -5° C. The small crystals that formed were separated from the faintly colored mother liquor by decantation. Then dehydrated DBE (10 mL) was added and the resulting suspension was stirred at 60°C to homogenization. The solution was kept at $+5^{\circ}$ C for 24 h. The bluegreen crystals that formed were separated from the mother liquor by decantation, successively washed with cold benzene and hexane, and dried under argon. The yield of complex I was 0.296 g (85%).

For $C_{48}H_{64}O_{10}Cu_2$ ($M = 928.07$)				
anal. calcd., %:	C, 62.12;	Н, 6.95.		
Found, %:	C, 61.85;	Н, 6.73.		

IR (cm⁻¹): 3071 w, 2554 w, 1715 w, 1677 s, 1608 m, 1583 m, 1569 m, 1497 w, 1452 m, 1471 m, 1404 m, 1320 m, 1271 s, 1178 m, 1070 m, 1052 s, 1000 w, 931 m, 842 w, 804 m, 705 s, 683 s, 667 m, 616 w.

Synthesis of $Cu_2(\mu$ -OOCPh)₄(DBE)₂ · DBE (II). Cupric benzoate (0.2 g, 0.65 mmol) was dissolved in acetonitrile (15 mL) and crystallized at -5° C. The small crystals that formed were separated from the faintly colored mother liquor by decantation. Then dehydrated DBE (10 mL) was added and the resulting suspension was stirred at 60°C to homogenization. The solution was kept at $+5^{\circ}$ C for 24 h. The bluegreen crystals that formed were separated from the mother liquor by decantation, successively washed

No. 3

2012

with cold benzene and hexane, and dried under argon. The yield of complex **II** was 0.314 g (80%).

For $C_{70}H_{62}O_{11}Cu_2$ (<i>M</i> = 1206.28)				
anal. calcd., %:	C, 69.69;	H, 5.18.		
Found, %:	C, 69.50;	H, 4.99.		

IR (cm⁻¹): 3571 w, 3064 w, 1593 m, 1548 s, 1494 w, 1417 s, 1360 w, 1312 w, 1270 w, 1207 w, 1094 m, 1064 m, 1027 m, 952 w, 806 w, 737 m, 695 s, 607 w.

Synthesis of Cu₂(μ -OOCCF₃)₄(DBE)₂ (III). Aqueous cupric acetate (0.2 g, 1 mmol) was dissolved in boiling trifluoroacetic acid (5 mL) and allowed to cool to room temperature in the bath. The precipitate that formed was dissolved at 80°C in acetonitrile (10 mL) and kept in a refrigerator at -5° C. The resulting fine crystalline product was separated from the mother liquor by decantation. Then dehydrated DBE (10 mL) was added and the resulting suspension was stirred in air at 60°C to homogenization. The solution was kept at $+5^{\circ}$ C for 24 h. The blue-green crystals that formed were separated from the mother liquor by decantation, successively washed with cold benzene and hexane, and dried under argon. The yield of complex III was 0.209 g (45%).

For $Cu_2C_{32}H_{28}O_{10}F_{12}$ (<i>M</i> = 975.66)				
anal. calcd., %:	C, 41.43;	H, 3.04.		
Found, %:	C, 41.28;	H, 2.89.		

IR (cm⁻¹): 1648, 1575 s, 1534 s, 1496 w, 1470 w, 1414 m, 1357 w, 1196 s, 1150 s, 1034 w, 1022 m, 951 w, 878 w, 857 m, 793 m, 746 m, 732 s, 694 s, 621 w, 601 w.

Synthesis of $Cu_2(\mu$ -OOCPh)₄[OC(OH)Ph]₂ (IV). The flask with the mother liquor of complex II was filled with air, sealed, and kept at room temperature for a month. The large green crystals that formed over the solution were isolated mechanically.

For $Cu_2C_{42}H_{32}O_{12}$ ($M = 855.76$)				
anal. calcd., %:	C, 58.95;	Н, 3.77.		
Found, %:	C, 58.79;	Н, 3.60.		

IR (cm⁻¹): 3030 w, 2911 w, 2659 w, 2549 w, 1718 w, 1676 m, 1609 m, 1601 w, 1583 w, 1568 m, 1500 w, 1452 w, 1386 s, 1318 m, 1273 m, 1212 w, 1178 w, 1164 w, 1145 w, 1125 w, 1097 w, 1070 m, 1025 m, 1001 w, 945 w, 930 w, 853 m, 842 w, 833 w, 819 w, 805 w, 725 m, 709 s, 693 s, 681 s, 659 m, 617 w.

IR spectra were recorded on a Nexus-Nicolet FTIR spectrophotometer in the 400–4000 cm⁻¹ range by using frustrated total internal reflection from a single crystal of a test complex.

X-ray diffraction study was carried out on a Bruker SMART Apex II automated diffractometer equipped with a CCD detector (Mo K_{α} radiation, graphite monochromator, ω scan mode). The structures of the complexes were calculated with the SHELXTL PLUS program package (PC version) and refined with the SHELXTL-97 program [17, 18]. Crystallographic parameters and the data collection and refinement statistics are summarized in table. The comprehensive tables of the atomic coordinates, bond lengths, and bond angles in structures **I**–**IV** have been deposited with the Cambridge Crystallographic Data Collection (nos. 856456–856459; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data request/cif).

RESULTS AND DISCUSSION

Dissolution of the complex $Cu_2(\mu-OOCBu')_4(NEt_3)_2$ in DBE followed by heating in air to 165°C and by slow cooling to room temperature gave complex I in a rather low yield (15%). However, when the starting adducts contained more labile terminal ligands (acetonitrile) than triethylamine, the yields of the complexes $Cu_2(\mu-OOCR)_4(DBE)_2$ (I–III) were noticeably higher (45–85%) even under milder conditions (60°C).



Note that the yields of complexes I–III correlate with the basicities of the corresponding carboxylate anions in the starting complexes: $Bu'CO_2^- > PhCO_2^- > F_3CCO_2^-$.

According to X-ray diffraction data, complexes I– III (Figs. 1–3) are traditional lantern-type dimers with a short nonbonding metal–metal distance dependent on the substituent R in the bridging carboxylate anions: the Cu···Cu distance in the complex with the pivalate anion (2.5692(7) Å) is somewhat shorter than those in the case of the electron-withdrawing benzoate and trifluoroacetate anions (Cu···Cu 2.5813(8) and 2.6882(18) Å, respectively), while the Cu–O bond lengths do not differ greatly (1.929(3)– 1.976(5) Å).

Doromotor	Value			
Farameter	Ι	II	III	IV
Temperature, K	120(2)	100(2)	150(2)	100(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\overline{1}$	<i>P</i> 2 ₁	C2/c	$P2_1/n$
Unit cell parameters				
<i>a</i> , Å	11.5242(16)	10.4206(15)	10.310(4)	10.6181(11)
<i>b</i> , Å	11.7479(16)	27.226(4)	20.876(8)	11.6145(12)
<i>c</i> , Å	19.439(3)	10.6230(15)	18.768(8)	15.1774(16)
α, deg	98.900(2)	90	90	90
β, deg	106.403(2)	106.172(2)	93.657(7)	91.219(2)
γ, deg	101.476(2)	90	90	90
$V, Å^3$	2411.1(6)	2894.6(7)	4031(3)	1871.3(3)
Ζ	2	2	4	2
$\rho_{calcd}, mg/m^3$	1.278	1.384	1.608	1.519
μ , mm ⁻¹	0.935	0.799	1.164	1.203
<i>F</i> (000)	980	1256	1960	876
Crystal dimensions, mm	$0.14 \times 0.12 \times 0.10$	$0.14 \times 0.12 \times 0.10$	$0.18 \times 0.16 \times 0.14$	$0.16 \times 0.14 \times 0.12$
θ scan range, deg	1.82-26.00	2.42-26.00	2.17-26.99	2.68 - 27.00
Ranges of h , k , and l indices	$-14 \le h \le 14,$ $-14 \le k \le 14,$ $-23 \le l \le 23$	$-12 \le h \le 12, -33 \le k \le 33, -13 \le l \le 13$	$-13 \le h \le 13, -24 \le k \le 26, -23 \le l \le 22$	$-13 \le h \le 13, \\ -14 \le k \le 14, \\ -19 \le l \le 19$
Number of measured re- flections	21461	25773	12245	17180
Number of independent reflections	9435 ($R_{\rm int} = 0.0921$)	11267 ($R_{\rm int} = 0.0778$)	4334 ($R_{\rm int} = 0.0797$)	4012 ($R_{\rm int} = 0.0752$)
GOOF	0.951	0.965	1.127	0.975
$R(I > 2\sigma(I))^*$	$R_1 = 0.0487,$ $wR_2 = 0.0804$	$R_1 = 0.0525,$ $wR_2 = 0.0756$	$R_1 = 0.0849,$ $wR_2 = 0.2022$	$ R_1 = 0.0517, \\ wR_2 = 0.1110 $
<i>R</i> (for all reflections)	$R_1 = 0.1089,$ $wR_2 = 0.0946$	$R_1 = 0.0979,$ $wR_2 = 0.0896$	$R_1 = 0.1629,$ $wR_2 = 0.2504$	$R_1 = 0.0998,$ $wR_2 = 0.1330$
$\Delta \rho_{\rm max} / \Delta \rho_{\rm min}$, $e { m A}^{-3}$	1.421/-0.970	0.294/-0.349	0.966/-1.160	0.771/-0.518
* $R_1 = \Sigma F_0 - F_c /\Sigma F_0 ; wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2\}^{1/2}.$				

Crystallographic parameters and the data collection and refinement statistics for structures I-IV

The apical position in the tetragonal-pyramidal environment of each Cu(II) atom copper in the binuclear complex are occupied by the O atoms of the coordinated DBE molecule. The corresponding Cu-O bond lengths also vary with the substituent in the carboxylate anion (2.178(3) and 2.196(3) Å for R =Bu' and 2.107(6) and 2.146(6) Å for $R = CF_3$). In complex II, the Cu– O_{DBE} bonds are longer (2.219(3) and 2.204(3) Å) than those in complexes I and III. Apparently, this is due to contacts between the benzene rings of the coordinated DBE molecules (Fig. 4) and the phenyl substituents of the bridging

benzoate anions (angle Ph_{C(2)-C(7)}/Ph_{C(51)-C(58)} 2.1°, $CPh_{C(2)-C(7)}\cdots CPh_{C(51)-C(58)}$ 3.415(7)-3.481(7) Å; angle $Ph_{C(9)-C(14)}/Ph_{C(30)-C(35)}$ 6.1°, $CPh_{C(9)-C(14)}$... $CPh_{C(30)-C(35)}$ 3.509(7)–3.538(7) Å). The crystal unit cell of complex II contains a solvate DBE molecule, which is out of contact with other molecules in the unit cell; this DBE molecule is geometrically similar to the coordinated DBE molecules (in II: O(11)-C, 1.417(5) and 1.442(5) Å; O(9)-C, 1.441(5) and 1.454(5) Å; O(10)–C, 1.433(5) and 1.444(5) Å; in **III**: O(5)-C, 1.452(7) Å; O(6)-C, 1.424(7) Å; in I:

Vol. 38 RUSSIAN JOURNAL OF COORDINATION CHEMISTRY



Fig. 1. Structure @I with atomic thermal displacement ellipsoids (30% probability). Selected bond lengths and bond angles: Cu(1)…Cu(2), 2.5692(7) Å; Cu(1)-O(1), 1.939(3) Å; Cu(1)-O(3), 1.973(3) Å; Cu(1)-O(5), 1.942(3) Å; Cu(1)-O(7), 1.974(3) Å; Cu(2)-O(2), 1.975(3) Å; Cu(2)-O(4), 1.929(3) Å; Cu(2)-O(6), 1.972(3) Å; Cu(2)-O(8), 1.932(3) Å; Cu(1)-O(9), 2.196(3) Å; Cu(2)-O(10), 2.178(3) Å; O(1)Cu(1)Cu(2), 86.58(8)°; O(3)Cu(1)Cu(2), 84.25(8)°; O(5)Cu(1)Cu(2), 86.15(8)°; O(7)Cu(1)Cu(2), 82.49(8)°; O(9)Cu(1)Cu(2), 176.09(7)°; O(2)Cu(2)Cu(1), 83.05(8)°; O(4)Cu(2)Cu(1), 85.37(8)°; O(6)Cu(2)Cu(1), 83.51(8)°; O(8)Cu(2)Cu(1), 87.15(8)°; O(10)Cu(2)Cu(1), 177.97(7)°.

O(9)–C, 1.431(6) and 1.443(6) Å; O(10)–C, 1.435(6) and 1.444(6) Å).

As noted above, air exposure of the reaction mixture containing complex II at room temperature for a month results in the formation of green single crystals of complex IV. According to X-ray diffraction data (Fig. 5), the latter is also a binuclear lantern-type dimer with two axially coordinated BAc molecules (Cu···Cu 2.5996(9) Å; Cu(1)–O(1), 1.944(3) Å; Cu(1)–O(2), 1.991(3) Å; Cu(1)–O(3), 2.179(3) Å; Cu(1) - O(5), 1.951(3) Å; Cu(1) - O(6), 1.950(3) Å). The Cu-O(2) bond is slightly longer than the other metal-oxygen bonds in the tetrabridged dimer, probably because of the hydrogen bonding between the carboxyl groups of BAc (Cu-O, 2.179(3) Å) and the O(2) and O(2A) atoms of the corresponding bridging benzoate anions (O···O 2.715(4), H-O 1.78 Å). As a result, the coordinated BAc molecules are coplanar with the fragment $Cu_2(\mu$ -OOCPh)₂.

According to X-ray diffraction data at 100 K, the geometry of complex **IV** is almost identical with its room-temperature geometry [19].

In contrast to lantern-type dimers in which hydrogen bonding (like that in complex IV) activates the axially coordinated organic molecules [20-23], the coordinated benzoic acid in complex IV, which is the final (deadlock) product of the catalytic oxidation of DBE with air, will most likely decrease the effective concentration of catalytic intermediates such as, e.g., complexes I–III.

It should be emphasized that although lantern-type copper(II) complexes containing weak O-donors in the axial position are well studied [24-30], complexes I–III we characterized here are the first examples of stable transition metal complexes with dibenzyl ether.

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Fig. 2. Structure **II** with atomic thermal displacement ellipsoids (50% probability). Selected bond lengths and bond angles: Cu(1)…Cu(2), 2.5813(8) Å; Cu(1)–O(1), 1.948(3) Å; Cu(1)–O(3), 1.947(3) Å; Cu(1)–O(5), 1.960(4) Å; Cu(1)–O(7), 1.953(3) Å; Cu(1)–O(9), 2.204(3) Å; Cu(2)–O(2), 1.941(3) Å; Cu(2)–O(4), 1.952(3) Å; Cu(2)–O(6), 1.959(4) Å; Cu(2)–O(8), 1.961(3) Å; Cu(2)–O(10), 2.219(3) Å; O(1)Cu(1)Cu(2), 81.69(11)°; O(3)Cu(1)Cu(2), 87.11(11)°; O(7)Cu(1)Cu(2), 82.70(10)°; O(5)Cu(1)Cu(2), 86.89(11)°; O(9)Cu(1)Cu(2), 174.81(9)°; O(2)Cu(2)Cu(1), 87.88(11)°; O(4)Cu(2)Cu(1), 82.90(11)°; O(6)Cu(2)Cu(1), 83.02(11)°; O(8)Cu(2)Cu(1), 87.44(11)°; O(10)Cu(2)Cu(1), 175.22(9)°.



Fig. 3. Structure **III** with atomic thermal displacement ellipsoids (30% probability). Selected bond lengths and bond angles: Cu(1)–Cu(2), 2.6882(18) Å; Cu(1)–O(1), 1.967(6) Å; Cu(1)–O(1A), 1.967(6) Å; Cu(1)–O(3), 1.960(5) Å; Cu(1)–O(3A), 1.960(5) Å; Cu(1)–O(5), 2.107(6) Å; Cu(2)–O(2), 1.966(5) Å; Cu(2)–O(2A), 1.966(5) Å; Cu(2)–O(4), 1.976(5) Å; Cu(2)–O(4A), 1.976(5) Å; Cu(2)–O(6), 2.146(5) Å; O(1)Cu(1)Cu(2), 82.73(16)°; O(1A)Cu(1)Cu(2), 82.73(16)°; O(3A)Cu(1)Cu(2), 84.64(14)°; O(5)Cu(1)Cu(2), 180.0°; O(2)Cu(2)Cu(1), 83.98(13)°; O(2A)Cu(2)Cu(1), 82.53(12)°; O(4A)Cu(2)Cu(1), 82.53(12)°; O(6)Cu(2)Cu(1), 180.0°.

RUSSIAN JOURNAL OF COORDINATION CHEMISTRY Vol. 38 No. 3 2012



Fig. 4. Fragment of the packing of structure II.



Fig. 5. Structure **IV**. Selected bond lengths and bond angles: Cu(1)…Cu(1*A*), 2.5996(9) Å; Cu(1)–O(1), 1.944(3) Å; Cu(1)–O(2), 1.991(3) Å; Cu(1)–O(3), 2.179(3) Å; Cu(1)–O(5), 1.951(3) Å; Cu(1)–O(6), 1.950(3) Å; O(1)Cu(1)Cu(1*A*), 85.50(8)°; O(2)Cu(1)Cu(1*A*), 83.83(8)°; O(3)Cu(1)Cu(1*A*), 174.55(8)°; O(5)Cu(1)Cu(1*A*), 83.60(8)°; O(6)Cu(1)Cu(1*A*), 85.77(8)°.

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