ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 1, pp. 52–56. © Pleiades Publishing, Ltd., 2009.
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Aquabis(dibenzo-18-crown-6)(tetrabromocuprato(II))dipotassium: Synthesis and Crystal Structure

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Received October 11, 2007

Abstract—The novel complex $[K(Db18C6)(H_2O)]^+[K(Db1)]^+(CuBr_4)^{2-}$ (**I**) was obtained. Its crystal structure (space group $P2_1/c$, $a = 17.970$ Å, $b = 29.838$ Å, $c = 9.074$ Å, $\beta = 103.11°$, $Z = 4$) was studied by X-ray diffraction analysis, solved by the direct method, and refined by the least-squares method in the anisotropic approximation to $R = 0.098$ from 6220 independent reflections (CAD-4 automated diffractometer, $\lambda MoK\alpha$). In both "guest–host" complex ions, the K^+ cation is in the cavity of the crown ligand Db18C6 and is coordinated by all its O atoms, as well as by a Br atom of the complex anion $[CuBr_4]^{2-}$ or the water O atom. The coordination of either K^+ cation is extended to a hexagonal bipyramid by a weak $K^+ \longrightarrow \pi(C\cdots C)$ bond to two C atoms of the benzene ring of the adjacent ligand Db18C6. In the crystal, the complex anions and cations are united into infinite double chains through the above contacts and the interion hydrogen bonds O–H···Br.

DOI: 10.1134/S1070328409010114

In this paper, we described the synthesis of and X-ray diffraction data for the crystals of the mixed complex aquabis(dibenzo-18-crown-6)(tetrabromocuprato(II))dipotassium, $[K(Db18C6)(H_2O)]^+[K(Db18C6)]^+(CuBr_4)^{2-}$ (**I**). Such "guest–host" complexes [1] with a metal complex as an anion remain poorly studied. The goal of this study was to obtain novel complexes of this type and examine their molecular and crystal structures.

EXPERIMENTAL

Synthesis of complex I. Powdered dibenzo-18-crown-6, crystalline KSCN, and crystalline $Cu(NO_3)_2 \cdot xH_2O$ were dissolved in aqueous 80% THF in the molar ratio 2 : 2 : 1. Concentrated aqueous HBr was added dropwise in some molar excess. The reaction mixture was allowed to evaporate at room temperature. After several days, well-edged (with bright faces) black opaque crystals of complex **I** formed on the bottom of the reaction vessel.

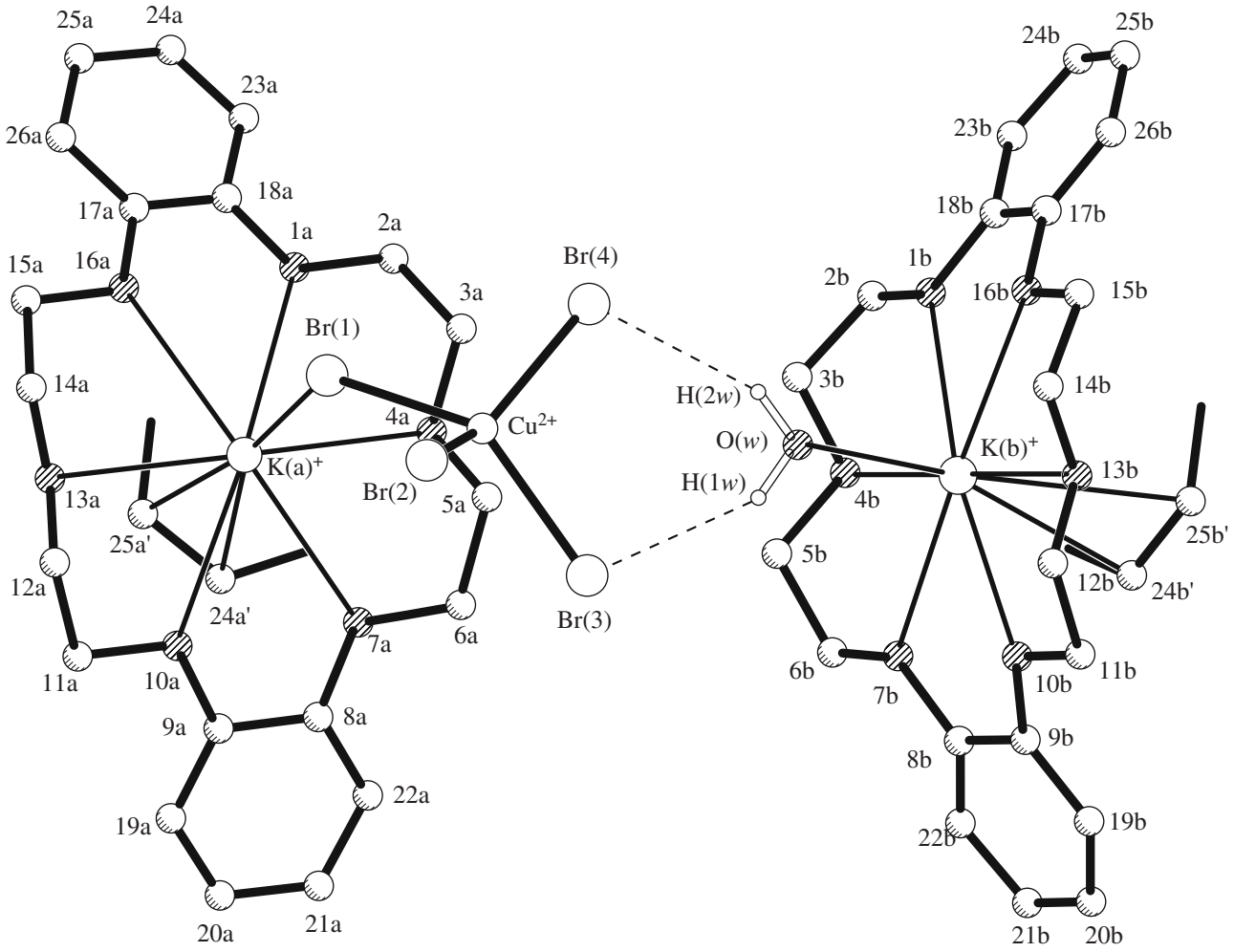
X-ray diffraction analysis. The unit cell parameters of the crystal and a three-dimensional set of reflection intensities were obtained on an Enraf-Nonius CAD4 automated diffractometer (MoK_α radiation, graphite monochromator). The crystals of complex **I** are monoclinic: $[K(Db18C6)(H_2O)]^+[K(Db18C6)](CuBr_4)$ (M = 1200.18); space group $P2_1/c$, a = 17.970(4) Å, b = 29.838(8) Å, c = 9.074(3) Å, β = 103.11(3)°, V = 4739(3) Å^3, Z = 4, ρ_{calcd} = 1.682 g/cm^3, $\mu(MoK_\alpha)$ = 40.68 cm^{-1}).

The intensities of 6850 reflections were measured in the quadrant of reciprocal space $2\theta \le 45°$, $\omega/2\theta$ scan mode) for a single crystal $0.08 \times 0.20 \times 0.68$ mm. The absorption correction was applied by a semiempirical method [2]. After 163 systematic absences were excluded and the intensities of 467 pairs of equivalent reflections $hk0$ and $\bar{h}k0$ (R_{int} = 0.043) were averaged, the number of independent $F^2(hkl)$ and $\sigma(F^2)$ reflections was 6220.

Structure **I** was solved by the direct method (SHELXS-97) [3] and refined on F^2 by the full-matrix least-squares method (SHELXL-97) [3] in the anisotropic approximation for non-hydrogen atoms. Almost all independent reflections (including very weak ones with $I < 2\sigma(I)$) were used in the refinement, except for some reflections with highly discrepant measured and calculated F^2 values.

When solving and initially refining structure **I**, we unambiguously demonstrated that the ligand $[CuBr_4]^{2-}$ in the complex anion $[K(CuBr_4)(Db18C6)]^-$ (**A**) and the water molecule in the complex cation $[K(Db18C6)(H_2O)]^+$ (**B**) are mutually randomly disordered and each of their atoms occupies two positions in the unit cell: main and secondary ones (see below). The general populations of these positions were then refined by introducing an additional variable parameter [3].

In structure **I**, the positions of all H atoms of the crown ligands *A* and *B* were located geometrically:



Structure of the complex $[K(Db18C6)(H_2O)][K(CuBr_4)(Db18C6)]$ (**I**). The secondary atomic positions in the mutually randomly disordered anion $[CuBr_4]^{2-}$ and water molecule, as well as the H atoms in two crown ligands Db18C6, are omitted for clarity. The carbon atoms of the neighboring crown ligands that extend the coordination polyhedra of the cations K^+(a) and K^+(b) to bipyramids are primed. Hydrogen bonds are indicated with dashed lines.

their coordinates and isotropic thermal parameters were calculated in the rider model [3] during the refinement. The underpopulated positions H(1*w*) and H(2*w*) of the hydrogen atoms in the disordered water molecule were objectively located from an electron-density difference map in the intermediate step of the anisotropic refinement of structure **I**. The fixed coordinates determined from this difference map were used in further calculations of the positions H(1*w*) and H(2*w*).

For the exposed crystal of complex **I**, we also refined the isotropic extinction coefficient: g = 0.00050(8) [3]. In the final cycle of the refinement, the absolute differences for all 592 variable parameters were less than 0.001σ. The final coordinates and equivalent isotropic thermal parameters are given in Table 1.

The final residuals are $R = 0.047$ and $wR_2 = 0.080$ for 3200 reflections with $I \geq 2\sigma(I)$ and $R = 0.098$ and $wR_2 = 0.135$ for all reflections; the goodness-of-fit ratio S is 0.90 (for the definitions of wR_2 and S, see [3]). In the final electron-density difference map: $-0.27 < \Delta\rho < 0.30$ e Å^{-3}. The used f curves and the corresponding corrections for anomalous dispersion (f' and f'') were taken from [4].

RESULTS AND DISCUSSION

As noted above, crystal structure **I** consists of two independent complex ions $[K(CuBr_4)(Db18C6)]^-$ (*A*) and $[K(Db18C6)(H_2O)]^+$ (*B*) of the "guest–host" type [1]. Their structures are shown in figure; selected bond lengths and angles are given in Table 2.

In the crystal of complex **I**, the probability of the main position is 72.8%. In this position, the anion $[CuBr_4]^{2-}$ is near the cation K^+(a), coordinating it through Br(1), and the water molecule is near the cation K^+(b), coordinating it through O(*w*). As mentioned above, the anion $[CuBr_4]^{2-}$ and the water molecule in

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10$) for crystal structure **I***

Atom	*x*	*y*	*z*	U_{equiv}, Å^2	Atom	*x*	*y*	*z*	U_{equiv}, Å^2
Cu	2781.8(8)	6016.6(4)	–359(1)	58.3(4)	Cu "	2159(2)	6025(1)	–188(4)	78(1)
Br(1)	4054.6(7)	6294.9(5)	–179(2)	81.0(5)	Br(1")	916(3)	6272(2)	–42(6)	111(2)
Br(2)	2794(1)	5451(1)	–2174(3)	79.7(7)	Br(2")	2432(4)	5582(3)	2040(7)	125(3)
Br(3)	2166(1)	5602(1)	1295(3)	112.9(9)	Br(3")	2665(4)	5506(3)	–1752(7)	116(3)
Br(4)	2136.9(9)	6718.0(5)	–399(2)	99.8(6)	Br(4")	2608(3)	6703(1)	–1107(5)	110(2)
O(*w*)	588(7)	6224(4)	565(16)	152(6)	O(*w*")	4179(14)	6175(9)	623(27)	137(1)
H(1*w*)	862	5972	808	170	H(2*w*)	889	6438	306	170
K(a)	5222.0(8)	6498.7(4)	3014(2)	65.9(5)	K(b)	–289.9(8)	6473.6(5)	2333(2)	80.0(5)
O(1a)	4943(2)	7391(1)	2387(4)	59(1)	O(1b)	36(2)	7348(1)	1859(4)	65(1)
C(2a)	4321(3)	7582(2)	2926(6)	69(2)	C(2b)	681(3)	7536(2)	2915(6)	76(2)
C(3a)	3736(3)	7225(2)	2934(6)	70(2)	C(3b)	1252(3)	7171(2)	3427(7)	78(2)
O(4a)	4046(2)	6886(1)	3995(4)	63(1)	O(4b)	939(2)	6846(1)	4250(5)	68(1)
C(5a)	3529(3)	6523(2)	3877(7)	77(2)	C(5b)	1456(3)	6483(2)	4699(7)	75(2)
C(6a)	3845(3)	6185(2)	5078(7)	84(2)	C(6b)	1115(3)	6172(2)	5676(6)	84(2)
O(7a)	4526(2)	5997(1)	4782(4)	72(1)	O(7b)	435(2)	5980(1)	4763(4)	75(1)
C(8a)	4928(3)	5697(2)	5809(6)	79(2)	C(8b)	24(3)	5693(2)	5462(6)	70(2)
C(9a)	5596(3)	5530(2)	5464(5)	78(2)	C(9b)	–647(3)	5527(2)	4539(5)	71(2)
O(10a)	5750(2)	5690(1)	4155(5)	78(1)	O(10b)	–795(2)	5666(1)	3059(5)	78(1)
C(11a)	6374(3)	5494(2)	3640(6)	77(2)	C(11b)	–1464(3)	5488(2)	2060(6)	94(3)
C(12a)	6334(3)	5663(2)	2068(6)	73(2)	C(12b)	–1479(4)	5642(2)	478(6)	91(2)
O(13a)	6487(2)	6131(1)	2136(4)	64(1)	O(13b)	–1569(2)	6113(1)	402(5)	71(1)
C(14a)	6431(3)	6303(2)	657(6)	65(2)	C(14b)	–1538(3)	6277(2)	–1048(6)	77(2)
C(15a)	6598(3)	6795(2)	766(6)	59(2)	C(15b)	–1679(3)	6770(2)	–1115(6)	64(2)
O(16a)	6004(2)	7011(1)	1324(4)	62(1)	O(16b)	–1070(2)	6987(1)	–73(5)	67(1)
C(17a)	6045(3)	7471(1)	1446(6)	53(2)	C(17b)	–1097(3)	7445(1)	25(6)	56(2)
C(18a)	5475(2)	7674(1)	2033(5)	51(2)	C(18b)	–501(2)	7640(2)	1090(5)	55(2)
C(19a)	6047(3)	5232(2)	6438(7)	91(3)	C(19b)	–1101(3)	5236(2)	5129(7)	93(3)
C(20a)	5848(4)	5104(2)	7760(8)	122(4)	C(20b)	–901(4)	5116(3)	6641(8)	124(4)
C(21a)	5182(4)	5260(2)	8083(7)	111(4)	C(21b)	–241(4)	5279(3)	7554(6)	122(4)
C(22a)	4730(3)	5563(2)	7122(6)	94(3)	C(22b)	227(3)	5566(2)	6961(6)	94(3)
C(23a)	5472(3)	8136(2)	2194(6)	68(2)	C(23b)	–493(3)	8098(2)	1302(6)	63(2)
C(24a)	6034(3)	8392(2)	1793(7)	73(2)	C(24b)	–1068(4)	8362(2)	466(7)	81(2)
C(25a)	6577(3)	8194(2)	1162(7)	76(2)	C(25b)	–1646(3)	8171(2)	–612(7)	83(2)
C(26a)	6586(3)	7733(2)	994(6)	64(2)	C(26b)	–1666(3)	7713(2)	–814(6)	74(2)

* The U_{equiv} values for the non-hydrogen atoms were calculated as one third of the trace of the orthogonalized tensor U_{ij}. The occupancy factors of the disordered atoms are 0.728(2) for Cu, Br(1), Br(2), Br(3), Br(4), O(*w*), H(1*w*), and H(2*w*) and 0.272(2) for Cu", Br(1"), Br(2"), Br(3"), Br(4"), and O(*w*"). The parameters of the secondary position O(*w*") were refined in the isotropic approximation.

Table 2. Selected bond lengths and angles in structure **I***

Bond	*d*, Å	*d*", Å	Bond	*d*(a), Å	*d*(b), Å
Cu–Br(1)	2.404(2)	2.385(5)	K–X	3.226(2)	2.601(7)
Cu–Br(2)	2.362(3)	2.373(6)	K–O(1)	2.744(4)	2.729(4)
Cu–Br(3)	2.402(3)	2.413(6)	K–O(4)	2.729(4)	2.719(4)
Cu–Br(4)	2.389(2)	2.397(5)	K–O(7)	2.700(4)	2.725(4)
Angle	ω, deg	ω", deg	K–O(10)	2.712(4)	2.708(4)
Br(1)CuBr(2)	97.8(1)	98.1(3)	K–O(13)	2.797(4)	2.772(4)
Br(1)CuBr(3)	134.6(1)	135.6(3)	K–O(16)	2.764(4)	2.773(4)
Br(1)CuBr(4)	98.6(1)	98.7(3)	K–C(24)'	3.424(6)	3.476(7)
Br(2)CuBr(3)	98.4(1)	96.4(3)	K–C(25)'	3.432(6)	3.550(7)
Br(2)CuBr(4)	134.2(1)	138.2(3)			
Br(3)CuBr(4)	99.8(1)	97.8(3)			
CuBr(1)K(a/b)	122.75(7)	145.1(2)			

* The double prime or the letters a and b at the chemical symbol or the number of the atom are omitted for brevity and given in the column headings; X = Br(1) in A and O(*w*) in B. The primed atoms are obtained from the basic atoms (C(24a), C(25a), C(24b), and C(25b)) by the symmetry operation: *x*, 3/2 – *y*, 1/2 + *z*.

the crystal of complex **I** are randomly disordered over two interchangeable positions with populations of 0.728(2) and 0.272(2) (in tables and in text, secondary positions of their atoms are marked with a double prime). Thus, complex **I** can have another structure (27.2% probability). In that structure, the anion $[CuBr_4]^{2-}$ is near the cation K^+(b), coordinating it through Br(1"), and the water molecule is near the cation K^+(a), coordinating it through O(*w*").

The coordination polyhedron of the Cu^{2+} cation in the anion $[CuBr_4]^{2-}$ disordered in two positions can be described as a tetrahedron strongly flattened along the shared diagonal between the bond angles Br(1)CuBr(3) and Br(2)CuBr(4) (or between Br(1")Cu"Br(3") and Br(2")Cu"Br(4")). The average Cu–Br bond length in complex **I** (2.390 ± 0.013 Å) is somewhat shorter than the sum of the effective radius of the Cu^{2+} cation (0.57 Å for C.N. 4) [5] and the van der Waals radius of the Br atom (1.85–1.95 Å) [6, 7] and than the sum of the covalent radii of the Cu (1.28 Å) and Br atoms (1.14 Å) [8].

The orientation of the disordered anion $[CuBr_4]^{2-}$ in complex **I** can be characterized by the following torsion angles: Br(3)–Cu–Br(1)–K(a) (–24.2(2)°), Cu–Br(1)–K(a)–O(7a) (19.5(1)°), Br(2")–Cu"–Br(1")–K(b) (24.6(5)°), and Cu"–Br(1")–K(b)–O(7b) (–18.6(4)°). In subsequent discussion of the geometrical structure of complex ions *A* and *B* in the crystal, we will consider only the main positions (population 0.728) of the atoms of the anion $[CuBr_4]^{2-}$ and the water molecule.

In structure **I**, the cation K^+(a) or K^+(b) in the complex ions *A* and *B* are in the cavity of the corresponding crown ligand Db18C6 and coordinated by all its six O atoms. The cation K^+(a) is also coordinated by the Br(1) atom of the anion $[CuBr_4]^{2-}$ and the cation K^+(b), by the O(*w*) atom of the water molecule. In addition, on the opposite side of the averaged plane of the 18-membered macrocycle of the ligand Db18C6, the cation K^+(a) or K^+(b) is weakly bound to two atoms (C(24a') and C(25a') or C(24b') and C(25b')) of one of the benzene rings of the ligand Db18C6 of the adjacent complex ion *A* or *B*; the primed C atoms were obtained from the basic ones via the symmetry operation: *x*, 3/2 – *y*, 1/2 + *z*.

Thus, the coordination polyhedron of the cation K^+(a) or K^+(b) in the complex ions *A* and *B*, is a distorted hexagonal bipyramid with Br(1) as one vertex and with C(24a') and C(25a') as the other, bifurcated vertex (in *A*) or with O(*w*) as one vertex and with C(24b') and C(25b') as the other, bifurcated vertex (in *B*).

The average $K–O_{crown}$ bond length (2.74 ± 0.03 Å) in the complex ions *A* and *B* is appreciably shorter than the sum of the effective radius of the K^+ cation (1.51 *A* for C.N. 8) [5] and the van der Waals radius of the O atom (1.40–1.52 Å) [6, 7]; the K(b)–O(*w*) bond length in the complex cation *B* is substantially shorter (2.601(7) Å). In the complex anion *A*, the K(a)–Br(1) bond length (3.226(2) Å) is also noticeably shorter than the sum of the radius of the K^+ cation and the van der Waals radius of the Br atom mentioned above.

The weak contacts K(a)–C(24a'), K(a)–C(25a'), K(b)–C(24b'), and K(b)–C(25b') in complex **I** are of the $K^+ \longrightarrow \pi(C\cdots C)$ type. They are nearly perpendicular to the plane of the benzene ring. Similar $K^+ \longrightarrow \pi(C\cdots C)$ contacts have been found in other structures [9, 10]. In the complex ions *A* and *B*, the lengths of these weak K–C' contacts are longer by 0.11–0.34 Å than the sum of the aforementioned radius of the K^+ cat-

ion and the van der Waals radius of the C atom (1.70–1.80 Å) [7, 11].

The cation K^+(a) or K^+(b) in the complex ions *A* and *B* slightly deviates from the root-mean-square plane of six O atoms of the corresponding ligand Db18C6 (by 0.150(2) Å toward Br(1) or by 0.109(2) Å toward O(*w*)). The angle between the root-mean-square planes of the ligand *A* and *B* is 105.42(6)°.

In structure **I**, both ligands Db18C6 (*A* and *B*) are in the butterfly conformation with approximate symmetry C_{2v}. In this conformation, all endocyclic torsion angles O–CH_2–CH_2–O (*gauche*-type) are close to ±65°, two torsion angles O(7)C(8)C(9)O(10) and O(16)C(17)C(18)O(1) (*cis*-type) approximate to 0°, and all the other endocyclic torsion angles outside the benzene rings (*trans*-type) are 180° ± 10°. The angles between the root-mean-square planes of two benzene rings are 123.0(2)° and 119.5(2)° for ligands *A* and *B*, respectively.

Two complex ions *A* and *B* are linked by a pair of the interion hydrogen bonds O(*w*)–H(1*w*)···Br(3) and O(*w*)–H(2*w*)···Br(4) (see figure). The corresponding interatomic distances are O(*w*)–H(*w*) 0.90 Å, H(1*w*)···Br(3) 2.54 Å, H(2*w*)···Br(4) 2.61 Å, O(*w*)···Br(3) 3.33(1) Å, and O(*w*)…Br(4) 3.43(1) Å; the angles O(*w*)–H(1*w*)···Br(3)] and O(w)–H(2w)···Br(4) are 147° and 153°, respectively. The probability of these H-bonds is 72.8% because all the involved atomic positions are 0.728 populated. Since the anion $[CuBr_4]^{2-}$ and the water molecule are mutually disordered, crystal structure **I** contains similar alternative H-bonds: O(*w*")–H···Br(3") and O(*w*")–H···Br(4") (27.2% probability).

In the crystal **I**, the complex ions *A* and *B* multiplied by planes *z* are united through the aforementioned unusual weak contacts K(a)–C(24a'), K(a)–C(25a'), K(b)–C(24b'), and K(b)–C(25b') into infinite chains along axis *z*, each chain consisting of ions of only one type (*A* or *B*). Two adjacent dissimilar chains are held together by the aforesaid interion hydrogen bonds to form an infinite double chain containing both complex ions *A* and *B*.

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