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Preparation and Crystal Structure of Bis(dibenzo-18-crown-6)-(tetrachlorocuprato(II)-Cl, Cl', Cl'', Cl''')dipotassium Diaqua(dibenzo-18-crown-6)potassium Dichlorocuprate(I)-dibenzo-18-crown-6

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Abstract—New mixed complex compound bis(dibenzo-18-crown-6)(tetrachlorocuprato(II)-Cl, Cl', Cl'', Cl''') dipotassium diaqua(dibenzo-18-crown-6)potassium dichlorocuprate(I)dibenzo-18-crown-6 $[(CuCl_4)[K(Db18C6)]_2]\cdot[K(Db18C6)(H_2O)_2]^+\cdot[CuCl_2]^-\cdot$Db18C6 was prepared and its structure was studied by the X-ray structural analysis. The structure was found to be disordered. The asymmetric part of its unit cell contains 1/4 of each of its four components. For a given $[CuCl_4]^{2-}$ anion its Cu^{2+} cation is disordered over two equally probable positions and its independent Cl atom is disordered over three positions differing by occupancy. In this structure two $[K(Db18C6)]^+$ fragment of the complex molecule and the complex cation $[K(Db18C6)(H_2O)_2]^+$ are of guest–*host* type with K^+ cation as the guest. In this structure the statistically disordered alternating cations and Db18C6 molecules form infinite chains. The statistically disordered $[CuCl_2]^-$ anions also form infinite chains.

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In this publication we describe the results of X-ray structural analysis of the crystals of new mixed complex compound bis(dibenzo-18-crown-6)(tetrachlorocuprato(II)(Cl, Cl', Cl'', Cl''')dipotassium diaqua (dibenzo-18-crown-6)potassium dichlorocurate(I) dibenzo-18-crown-6, $[(CuCl_4)[K(Db18C6)]_2]\cdot[K(Db18C6)\cdot(H_2O)_2]^+\cdot[CuCl_2]^-\cdot$Db18C6 (**I**). Such complex compounds have not been prepared before and have not been studied in respect to their structure: see Cambridge Structural Database [1].

We found that complex compound **I** has molecular-ionic structure; the structure of crystal is shown in the figure, the principal bond lengths and bond angles are listed in Tables 1 and 2.

As we established, the centrosymmetrical crystal structure of the complex compound **I** is randomly disordered. The asymmetric part of its cell contains 1/4 part of the complex molecule $[(CuCl_4)[K(Db18C6)]_2]$, 1/4 part of complex cation $[K(Db18C6)(H_2O)_2]^+$, 1/4 part of anion $[CuCl_2]^-$ and 1/4 part of molecule Db18C6. The K^+ cations and atoms of the Db18C6 crown-ligand related to these complex molecule and complex cation are denoted respectively by the letters a and b. As far as in the complex cation the occupancy of two positions of its K^b cation and O^{w1} and O^{w2} atoms of two water molecules equals 0.5 and occupancy of the positions of the atoms of its Db18C6 (b) crown ligand equals 1, hence in this position of unit cell is present either complex cation $[K(Db18C6)(H_2O)_2]^+$, or Db18C6 (b) molecule only with 50% probabilitiy.

In structure **I** the center of the complex molecule $[(CuCl_4)[K(Db18C6)]_2]$ is located in the point with coordinates (1/2,1/2, 0) and with point symmetry 2/*m*. Thus, this molecule (with accounting for disordering of its $[CuCl_4]^{2-}$ anion) has statistically averaged symmetry center, symmetry axis 2 and orthogonal to the latter symmetry plane *m* that includes the centers of the atoms K^a, O^{1a}, O^{10a} and $K^{a''}$, $O^{1a''}$, $O^{10a''}$. In this complex molecule the angle between the planes defined by three atoms Cu^1, Cl^1, $Cl^{1'}$ and K^a, Cl^1, $Cl^{1'}$ equals 143.0(2)°.

In structure **I** the $[CuCl_4]^{2-}$ anion of its complex molecule also would be of 2/*m* point symmetry with

Table 1. Principal bond lengths (d, Å) in structure **I**[a]

Bond	d	Bind	d
Cu^1–Cl^1	2.228(5)	Cu^1–$Cl^{1'}$	2.561(5)
Cu^1–Cl^{11}	1.845(7)	Cu^1–$Cl^{11'}$	2.179(7)
Cu^1–Cl^{12}	2.296(15)	Cu^1–$Cl^{12'}$	2.444(13)
K^a–Cl^1	3.260(4)	Cu^2–Cl^2	2.10(1)
K^a–Cl^{11}	3.256(9)	K^b–O^{w1}	2.676(6)
K^a–Cl^{12}	3.074(14)	K^b–O^{w2}	2.709(5)
K^a–O^{1a}	2.782(4)	K^b–O^{1b}	2.713(2)
K^a–O^{4a}	2.901(2)	K^b–O^{4b}	2.857(2)
K^a–O^{7a}	2.929(2)	K^b–O^{7b}	2.769(2)
K^a–O^{10a}	2.894(4)		

[a] In Tables 1, 2 and 3 are primed the transformed by symmetry basic position of atoms: (') $x, y, -z$; (") $1-x, 1-y, -z$; ("') $1-x, 1-y, z$; (`) $x, -y, 1/2-z$; (``) $1/2-x, 1/2-y, 1/2-z$.

Table 2. Principal bond angles (ω, deg) in structure **I**

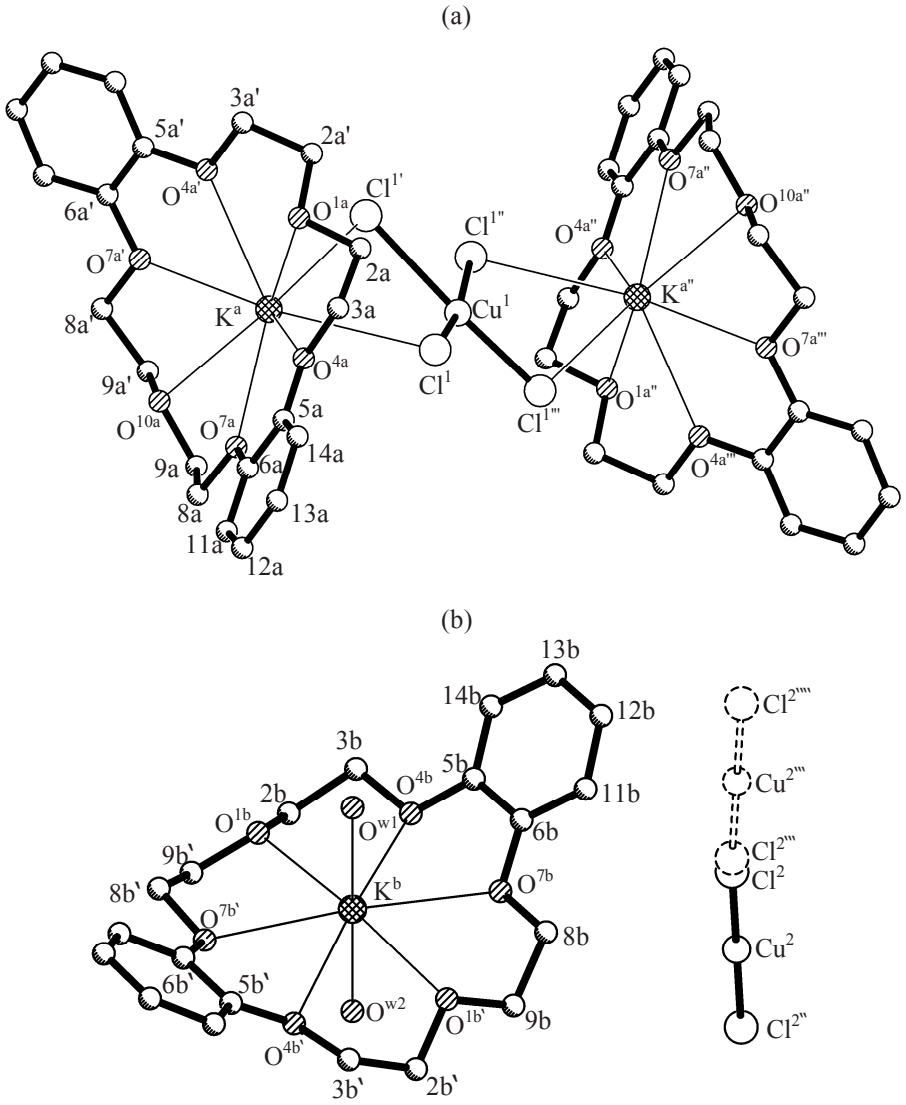
Angle	ω	Angle	ω
$Cl^1Cu^1Cl^{1'}$	89.0(2)	$Cl^1Cu^1Cl^{1'''}$	99.1(3)
$Cl^1Cu^1Cl^{1''}$	171.9(2)	$Cl^{1'}Cu^1Cl^{1''}$	82.9(3)
$Cu^1Cl^1K^a$	100.7(1)	$Cu^1Cl^{1'}K^a$	93.8(1)
$Cl^1K^aCl^{1'}$	62.2(1)	$O^{w1}K^bO^{w2}$	180
$Cl^1K^aO^{1a}$	90.4(1)	$O^{w1}K^bO^{1b}$	94.13(5)
$Cl^1K^aO^{4a}$	76.95(8)	$O^{w1}K^bO^{4b}$	95.19(5)
$Cl^1K^aO^{7a}$	91.40(9)	$O^{w1}K^bO^{7b}$	93.61(5)
$Cl^1K^aO^{10a}$	121.8(1)	$O^{w2}K^bO^{1b}$	85.87(5)
$Cl^1K^aO^{4a'}$	127.9(1)	$O^{w2}K^bO^{4b}$	84.81(5)
$Cl^1K^aO^{7a'}$	148.61(8)	$O^{w2}K^bO^{7b}$	86.39(5)
$O^{1a}K^aO^{4a}$	57.50(5)	$O^{1b}K^bO^{4b}$	61.19(5)
$O^{4a}K^aO^{7a}$	52.66(5)	$O^{4b}K^bO^{7b}$	55.05(5)
$O^{7a}K^aO^{10a}$	56.30(5)	$O^{7b}K^bO^{1b'}$	63.23(5)
$O^{1a}K^aO^{10a}$	141.7(1)	$O^{1b}K^bO^{1b'}$	171.7(1)
$O^{4a}K^aO^{7a'}$	134.41(8)	$O^{4b}K^bO^{4b'}$	169.62(9)
$Cl^2Cu^2Cl^{2''}$	180	$O^{7b}K^bO^{7b'}$	172.8(1)

location of its central atom Cu^1 (Cu^{2+} cation) exactly in the point (1/2, 1/2, 0) and would have ideal square-planar coordination by four Cl atoms. However, such ideal coordination commonly is not inherent to $[CuCl_4]^{2-}$ anion, and in structure **I** it is disordered relatively to the point (1/2,1/2, 0). Its Cu^1 is deviated noticeably from this point by ±0.237(5) Å while remains on the 2 axis being split into two close positions with the occupancy 0.5, and its independent chlorine atom turned to be disordered over three positions, Cl^1, Cl^{11}, and Cl^{12} , with occupancies 0.48(1), 0.33(1), and 0.19(1), respectively and with the following distances: $Cl^1\cdots Cl^{11}$ 1.09(3), $Cl^1\cdots Cl^{12}$ 2.35(3), and $Cl^{11}\cdots Cl^{12}$ 1.34(3) Å .

In structure **I** in the disordered $[CuCl_4]^{2-}$ anion the coordination polyhedrons of its Cu^{2+} cation (for the different sets of positions of its disordered Cl atoms and their equivalents by symmetry) are strongly screwed squares or flattened tetrahedrons with a significant dummy disproportionated (due to its disordering) Cu^1–Cl bond lengths and respective Cl–Cu^1–Cl bond angles. In this $[CuCl_4]^{2-}$ anion the average bond length of all disordered Cu^1–Cl bonds equals 2.24±0.18 Å being a bit less than the sum of the Cu^{2+} cation ef-fective ion radius (0.57 Å for coordination number 4) [2] and van der Waals radius of Cl atom (1.75–1.80 Å [3, 4]) and a bit less than the sum of covalent radii of Cu (1.28 Å) and Cl (1.02 Å) [5].

In structure **I**, in the complex molecule and cation the halves of their Db18C6 (a and b) crown ligands are symmetrically independent because Db18C6 (a) ligand has a symmetry plane coinciding with the crystallographic *m* plane and Db18C6 (b) ligand (molecule) has the symmetry axis 2 coinciding with the crystallographic one and passing through the centers of the atoms O^{w1}, K^b and O^{w2}. Therewith, the Db18C6 (a) ligand has also approximate symmetry axis 2 and another symmetry plane and Db18C6 (b) ligand (molecule) has also two approximate symmetry planes. With accounting for these approximate symmetry elements, these Db18C6 (a) ligand and Db18C6 (b) ligand (molecue) are of approximately C_{2v} symmetry. The same approximate C_{2v} symmetry in structure **I** have two $[K(Db18C6)]^+$ fragments of the complex molecule and the whole complex cation $[K(Db18C6)(H_2O)_2]^+$.

In structure **I** two mutually symmetric $[K(Db18C6)]^+$ fragments of the complex molecule and the complex cation itself are of *guest–host* type [6]: each of their K^a and K^b cations is located in the cavity



Molecular-ionic structure of complex compound **I** in crystal: (a) fragment $\{(CuCl_4)[K(Db18C6)]_2\}$ and (b) fragment $[K(Db18C6)\cdot(H_2O)_2]^+\cdot[CuCl_2]^-$ Db18C6. In (a) the less occupied positions of Cl atoms and the second position of $Cu^{1'}$ atom in the central disordered $[CuCl_4]^{2-}$ anion are omitted to make the picture more clear. In (b) the occupancy factor of positions of the statistically disordered atoms Cu^{2}, Cl^{2}, $Cl^{2``}$ and K^b, O^{w1}, O^{w2} equals 0.5. In (a) and (b) the H atoms in the Db18C6 crown-ligands are omitted. The transformed by symmetry basic positions of atoms are primed (see footnote to Table 1).

of the corresponding Db18C6 (a or b) crown ligand and is coordinated by all its six O atoms, and in addition the cation K^a is coordinated at one side by two chlorine atoms of the $[CuCl_4]^{2-}$ anion and cation K^b is coordinated on the opposite sides by the atoms O^{w1} and O^{w2} of two water molecules. Thus, the coordination polyhedron of K^a cation (coordination number 8) is a screwed hexagonal pyramid split into two apexes at two chlorine atoms. The coordination tetrahedron of the K^b cation (coordination number 8) is a screwed hexagonal bipyramid with two opposite apexes at the atoms O^{w1} and O^{w2}.

In structure **I** the average bond length of all disordered K^a–Cl bonds of $\{(CuCl_4)[K(Db18C6)]_2\}$ molecule equals 3.23±0.05 Å being a bit shorter than the sum of effective ion radius of K^+ cation (1.51 Å for coordination number 8) [2] and the above mentioned van der Waals radius of chlorine atom, while the average bond length of all K^a–O_{Db18C6} coordination bonds equals 2.89 ± 0.04 Å being a bit shorter than the sum of the ion radius of K^+ cation and van der Waals radius of oxygen atom (1.40–1.52 Å [3, 4]). In the complex cation $[K(Db18C6)(H_2O)_2]^+$ the average bond length of K^b–O_{Db18C6} coordination bonds equals 2.78±0.05 Å, and

the average length of two axial K^b–O^{w1} and K^b–O^{w2} 269 ±0.02 Å coordination bonds are by ~0.1 Å less.

In structure **I** the cation K^a of the $[K(Db18C6)]^+$ fragment of the complex molecule deviates from the mean square plane of the six O atoms of the Db18C6 (a) ligand by 1.063(2) Å to the side of two chlorine atoms of $[CuCl_4]^{2-}$ anion coordinating the K^a cation. In the complex cation $[K(Db18C6)(H_2O)_2]^+$ its K^b cation deviates a bit from the mean square plane of six O atoms of Db18C6 (b) ligand by 0.209(2) Å to the atom O^{w1} and to the direction of bending of two benzene rings of Db18C6 (b) ligand. The greater deviation of K^a cation as compared with K^b corresponds to a larger (by ~0.1 Å) average bond length K^a–O_{Db18C6} as compared with average K^b–O_{Db18C6} bond length (as considered above).

In structure **I** the average bond lengths in the Db18C6 (a) ligand and Db18C6 (b) ligand (molecule) are: 1.416(2) Å for the O^1–C^2 and C^9–O bonds; 1.430(2) Å for C^3–O^4 and O^7–C^8 bonds; 1.375(2) Å for O^4–C^5 and C^6–O^7 bonds; 1.488(3) Å for C^2–C^3 and C^8–C^9 bonds; 1.380(7) Å for the C–C bonds in the benzene rings of Db18C6. These average bond lengths are close to the statistically average values for the ligand (molecule) Db18C6. In structure **I** the C–O–C bond angles at the O^1 and O^{10a} atoms of these ligands are a bit larger than ideal tetrahedron angle 109.5°, while at the atoms O^4 and O^7 they are rather closer to 120° than to 109.5°.

In structure **I** the molecules of Db18C6 (a) ligand and Db18C6 (b) ligand are in the most widespread *butterfly* conformation of such compound, when all the intercyclic torsion angles O–CH_2 –CH_2–O are close to ±65° (*gauche* type), two torsion angles O^{4a}–C^{5a}–C^{6a}–O^{7a} (or O^{4b}–C^{5b}–C^{6b}–O^{7b}) and similar by symmetry are close to 0° (of *cis* type) while all other endocyclic torsion angles except those including benzene rings fall to the range 180 ± 10° (of *trans* type), see Table 3. In these ligands and the ligand-molecule Db18C6 [(a) and (b)] their benzene rings are planar within deviation ±0.007(2) Å over their six C atoms. The angle between mean square planes of two benzene rings in each such ligand and ligand-molecule Db18C6 (a and b) equals 120.1(1)° (a) and 106.6(1)° (b).

In structure **I** the anion $[CuCl_2]^-$ is linear, and the half-occupied position of its central Cu^2 atom (Cu^{1+} cation) is located at the inversion center *i* (1/4,1/4,1/4) while the anion axis is parallel to the crystallographic *x* axis. The multiplied due to symmetry $[CuCl_2]^-$ anions in structure **I** form infinite chains directed along the *x* azis. The chain increment $a/2$ = 4.45 Å being almost equal to the length of one $[CuCl_2]^-$ anion. Therefore in such chain the $[CuCl_2]^-$ anions are randomly disordered, namely, they are located in every other place that explains their total occupancy equal to 0.5.

Table 3. Principal torsion angles (τ, deg) in the crown-ligands Db18C6 in structure **I**

Angle	τ	Angle	τ
$C^{2a'}O^{1a}C^{2a}C^{3a}$	171.2(2)	$C^{9b'}O^{1b}C^{2b}C^{3b}$	176.8(2)
$O^{1a}C^{2a}C^{3a}O^{4a}$	61.9(4)	$O^{1b}C^{2b}C^{3b}O^{4b}$	66.3(3)
$C^{2a}C^{3a}O^{4a}C^{5a}$	175.7(3)	$C^{2b}C^{3b}O^{4b}C^{5b}$	–173.0(2)
$C^{3a}O^{4a}C^{5a}C^{6a}$	177.3(3)	$C^{3b}O^{4b}C^{5b}C^{6b}$	170.0(2)
$O^{4a}C^{5a}C^{6a}O^{7a}$	–0.3(3)	$O^{4b}C^{5b}C^{6b}O^{7b}$	0.8(2)
$C^{5a}C^{6a}O^{7a}C^{8a}$	–178.3(2)	$C^{5b}C^{6b}O^{7b}C^{8b}$	–175.0(2)
$C^{6a}O^{7a}C^{8a}C^{9a}$	–175.1(2)	$C^{6b}O^{7b}C^{8b}C^{9b}$	177.4(2)
$O^{7a}C^{8a}C^{9a}O^{10a}$	–63.6(4)	$O^{7b}C^{8b}C^{9b}O^{1b'}$	–68.0(3)
$C^{8a}C^{9a}O^{10a}C^{9a'}$	–173.9(2)	$C^{8b}C^{9b}O^{1b'}C^{2b'}$	–176.9(2)

In the crystal structure of **I** the complex molecules $[(CuCl_4)[K(Db18C6)]_2]$ are individual, that is, have van der Waals contacts only with neighboring molecules, while complex cations $[K(Db18C6)(H_2O)_2]^+$ and alternative free molecules Db18C6 (b) are statistically disordered, they alternate with each other to form the infinite chains along the direction of *x* axis (infinite along the line drawn through the centers of their O^{w1}, K^b, and O^{w2} atoms of half occupancy). These chains are formed by the intermolecular hydrogen bonds O^w–H···O_{Db18C6} between the ligand water molecules in the complex cations with ether O atoms in the Db18C6 (b) molecule.

In the crystal structure of **I** there are very short interatomic contacts that are absent in the real crystal structure. All the atoms involved formally in these contacts are statistically disordered and occupancy of their positions equals 0.5. Actually in each such contact (between a pair of atomic positions) the occupancy of one position is 1 and another is 0.

EXPERIMENTAL

The complex compound **I** was synthesized as follows. Powdered crown ether dibenzo-18-crown-6, crystalline potassium chloride KCl, and copper(II) chloride hydrate $CuCl_2 \cdot xH_2O$ were mixed and

dissolved in 80 % aqueous tetrahydrofuran in the mole ratio 4:3:2, and the mixture was left for evaporation at room temperature. Few days later on the vessel bottom and walls appeared transparent yellow crystals of the complex compound **I**. The results of the synthesis are somewhat unexpected due to the presence in the final compound **I** of dichlorocopper(I) anions appearing probably due to the partial hydrolysis of the parent copper(II) chloride hydrate.

For the X-ray structural analysis the crystal unit cell parameters and three-dimensional array of reflexes intensity were registered on an automatic difractometer Enraf-Nonius CAD-4 (MoK_α-radiation, graphite monochromator). The crystals **I** are orthorombic: $[(CuCl_4)\cdot[K(C_{20}H_{24}O_6)]_2]\cdot[K(C_{20}H_{24}O_6)(H_2O)_2]^+\cdot[CuCl_2]^-\cdot C_{20}H_{24}O_6$, M = 1934.68; a = 8.900(2), b = 28.230(6), c = 35.940(8) Å, V = 9030(3) Å^3, Z 4, d_{calc} = 1.423 g cm^{-3}, μ(MoK_α) = 8.60 cm^{-1}, space group *Ibam* (no. 72).

Intensities of 4438 reflexes ($h + k + l = 2n$, $2\theta \le 50°$) were measured in the reciprocal space octant by the method of $\omega/2\theta$-scanning from the single crystal of the size $0.14 \times 0.45 \times 0.90$ mm. The intensities of the reflexes were then corrected for extinction by semi-empirical method [7], and after exclusion of 370 systematically extinguished reflexes the working array of the measured $F^2(hkl)$ and $\sigma(F^2)$ consisted of 4068 independent reflexes.

Structure of **I** was solved by the direct method with the SHELXS-97 program [8] and refined by full-matrix least square method relatively to F^2 with the SHELXL-97 program [8] in approximation of anisotropic thermal vibrations for all non-hydrogen atoms. For the structure refinement were used almost all the reflexes in the working array [including even very weak ones with $I < 2\sigma(I)$] with exclusion of only a few reflexes with bad fit of measured and calculated F^2 values.

At the refinement of the structure of **I** it was unequivocally established that its K^b cation and two respective ligand water molecules as well as $[CuCl_2]^-$ anion were disordered with occupancy of positions equal to 0.5. Therefore we failed to elucidate position of the H atoms in the ligand water molecules.

Positions of all independent H atoms in the Db18C6 (a) ligand and in the Db18C6 (b) ligand (molecule) are localized objectively in the Fourier synthesis of differential electron density in the intermediate step of anisotropic refinement of structure **I**. In further calculations these H atoms were defined geometrically, their coordinates and isotropic thermal parameters were calculated using *rider* model [8] in the procedure of refinement of structure **I** by the least square method.

In the last cycle of the full-matrix refinement the absolute shifts of all 309 varied parameters of structure **I** were less than 0.001σ. The final R-factors are: $R1$ 0.043 and $wR2$ 0.103 over 2035 observed reflexes with $I \ge 2\sigma(I)$; $R1$ 0.098 and $wR2$ 0.150 over all 4068 measured independent reflexes; the adjustment quality factor S = 0.90 (definition of wR_2 and S values is given in the Manual [8]). In the final Fourier synthesis of differential electron density $-0.18 < \Delta\rho < 0.23$ eÅ^{-3}.

The final coordinates and thermal parameters of the atoms in structure **I** as well as the complete tables of its bond lengths, bond and torsion angles and other parameters are deposited to the Cambridge Structural Database [1] as a cif-file, deposit no. 714893.

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