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Triaqua(18-Crown-6)strontium Tetrachlorocuprate(II) Hemihydrate: Synthesis and Crystal Structure

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Abstract—The new complex $[Sr(18\text{-crown-}6)(H_2O)_3]^{2+}[CuCl_4]^{2-} \cdot 0.42H_2O$ was obtained; its crystal structure was determined by X-ray diffraction analysis: space group $P2_1$, $a = 10.305$ Å, $b = 13.570$ Å, $c = 17.566$ Å, $\beta = 98.23°$, $Z = 4$ (direct method, anisotropic full-matrix least-squares method, $R = 0.053$ from independent reflections; CAD-4 automated diffractometer, λMoK_α). The asymmetric part of the unit cell comprises two independent "guest–host" complex cations $[Sr(18\text{-crown-}6)(H_2O)_3]^{2+}$, two independent complex anions $[CuCl_4]^{2-}$, and a hydrate water molecule with a position population of 0.84(1).

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In this study, we obtained the new crystalline complex $[Sr(18\text{-crown-}6)(H_2O)_3]^{2+}[CuCl_4]^{2-} \cdot 0.42H_2O$ (**I**) and characterized it by X-ray diffraction analysis. The structures of similar complexes combining a "guest–host" complex cation of an alkaline-earth metal [1] and a complex anion of a transition metal have been poorly studied to date.

EXPERIMENTAL

Synthesis of complex I. Crystalline 18-crown-6, strontium chloride hydrate, and copper(II) chloride hydrate in the molar ratio 1 : 1 : 1 were dissolved in acetone–ethanol–water (3 : 2 : 1). The mixture was left at room temperature for evaporation. After several days, yellow-orange transparent crystals of complex **I** formed on the bottom and walls 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 CAD-4 automated diffractometer (MoK_α radiation, graphite monochromator). The crystals are monoclinic: $[Sr(C_{12}H_{24}O_6)(H_2O)_3]^{2+}[CuCl_4]^{2-} \cdot 0.42H_2O$, $M = 618.84$; space group $P2_1$, $a = 10.305(2)$, $b = 13.570(2)$, $c = 17.566(2)$ Å, $\beta = 98.23(1)°$, $V = 2431.1(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.691$ g/cm^3, $\mu(MoK_\alpha) = 35.47$ cm^{-1}.

The intensities of 5883 reflections from a single crystal $0.20 \times 0.36 \times 0.54$ mm were measured in the quadrant of reciprocal space ($2\theta \le 54°$, $\omega/2\theta$ scan mode). During the diffraction experiment, the crystal degraded substantially: the intensities of three control reflections diminished by, on average, a factor of four. The intensities of all reflections were corrected for degradation of the crystal and for absorption with the SHELXA program [2]. Absorption correction cannot be applied in an alternative, more accurate way because of the degradation of the crystal. After nine systematic absences were excluded and the intensities of 327 pairs of equivalent reflections $0kl$ and $0k\bar{l}$ ($R_{int} = 0.021$) were averaged, the number of independent reflections was 5547 ($F^2(hkl)$ and $\sigma(F^2)$).

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

In an intermediate step of the refinement, the highest peaks $\Delta\rho$ revealed from the difference electron-density map suggested orientational disorder of one independent anion $[CuCl_4]^{2-}$ (a) in structure **I**: each of its atoms in the unit cell occupies two positions (major and minor ones). The general populations of these positions and their coordinates and thermal parameters were then refined by the least-squares method.

In structure **I**, the positions of almost all H atoms were determined from the difference electron-density map. Then, all the H atoms of two independent ligands 18-crown-6 (a and b) were located geometrically: their coordinates and isotropic thermal parameters were calculated in the riding model [2] during the refinement. The coordinates of 12 hydrogen atoms of six coordinated water molecules and two underpopulated positions H(1*w*) and H(2*w*) of the hydrate water molecule were refined under loose geometrical constraints of the DFIX type [2] for short interatomic distances of these atoms. The refined general populations of the O(*w*),

Table 1. Selected bond lengths and angles in structure **I***

Bond	d(a), Å	d(b), Å	Bond	d(a), Å	d(b), Å
Cu–Cl(1)	2.245(2)	2.253(2)	Sr–O(7)	2.673(3)	2.710(4)
Cu–Cl(2)	2.280(2)	2.267(2)	Sr–O(10)	2.699(3)	2.702(4)
Cu–Cl(3)	2.245(2)	2.251(2)	Sr–O(13)	2.672(3)	2.692(4)
Cu–Cl(4)	2.244(2)	2.220(2)	Sr–O(16)	2.690(3)	2.725(4)
			Sr–O(*w*1)	2.583(4)	2.592(4)
Sr–O(1)	2.700(3)	2.684(4)	Sr–O(*w*2)	2.603(3)	2.591(4)
Sr–O(4)	2.690(3)	2.708(4)	Sr–O(*w*3)	2.577(4)	2.499(4)
Angle	**ω(a), deg**	**ω(b), deg**	**Angle**	**ω(a), deg**	**ω(b), deg**
Cl(1)CuCl(2)	127.93(9)	136.14(7)	O(1)SrO(10)	171.6(1)	177.9(1)
Cl(1)CuCl(3)	100.36(8)	96.34(7)	O(4)SrO(13)	158.4(1)	157.2(1)
Cl(1)CuCl(4)	97.96(8)	97.04(7)	O(7)SrO(16)	135.4(1)	133.3(1)
Cl(2)CuCl(3)	102.01(9)	99.54(7)	O(1)SrO(*w*3)	90.6(1)	90.9(2)
Cl(2)CuCl(4)	101.32(6)	96.72(6)	O(4)SrO(*w*3)	76.2(1)	78.5(2)
Cl(3)CuCl(4)	131.26(9)	139.57(8)	O(7)SrO(*w*3)	68.8(1)	65.8(1)
O(1)SrO(16)	61.9(1)	60.4(1)	O(10)SrO(*w*3)	97.8(1)	91.2(2)
O(1)SrO(4)	61.9(1)	61.4(1)	O(13)SrO(*w*3)	82.2(1)	78.7(2)
O(4)SrO(7)	61.1(1)	60.0(1)	O(16)SrO(*w*3)	66.7(1)	67.6(1)
O(7)SrO(10)	61.3(1)	60.8(1)	O(*w*1)SrO(*w*2)	70.8(1)	72.1(1)
O(10)SrO(13)	61.8(1)	61.9(1)	O(*w*1)SrO(*w*3)	144.2(1)	143.5(2)
O(13)SrO(16)	60.7(1)	59.9(1)	O(*w*2)SrO(*w*3)	145.0(1)	143.9(2)

* The letters a and b at the chemical symbols and the ordinal numbers of the atoms are omitted for brevity and given in the column headings; for brevity, the bond lengths and angles are listed only for the major orientation of the disordered anion $[CuCl_4]^{2-}$ (a).

H(1*w*), and H(2*w*) atoms of the hydrate water molecule were somewhat lower than unity.

For enantiomorphous crystal **I**, we also refined the isotropic extinction coefficient $g = 0.0013(2)$ [2] and the Flack parameter $\chi = 0.002(5)$ [3]. In the final cycle of the refinement, the absolute differences for all 562 variable parameters of structure **I** were less than 0.001σ.

Final residuals are $R = 0.031$ and $wR_2 = 0.055$ for 4050 reflections with $I \geq 2\sigma(I)$ and $R = 0.053$ and $wR_2 = 0.068$ for all independent reflections; the goodness-of-fit ratio S is 0.96 (for the definitions of wR_2 and S, see [2]). In the final difference electron-density map: $-0.34 < \Delta\rho < 0.33$ e Å^{-3}. The f curves used and the corresponding corrections for anomalous dispersion ($\Delta f'$ and $\Delta f''$) were taken from [4].

Selected bond lengths and angles are given in Table 1. Atomic coordinates and other parameters for structure **I** have been deposited with the Cambridge Crystallographic Data Collection (no. 692478; deposit@ccdc.cam.ac.uk).

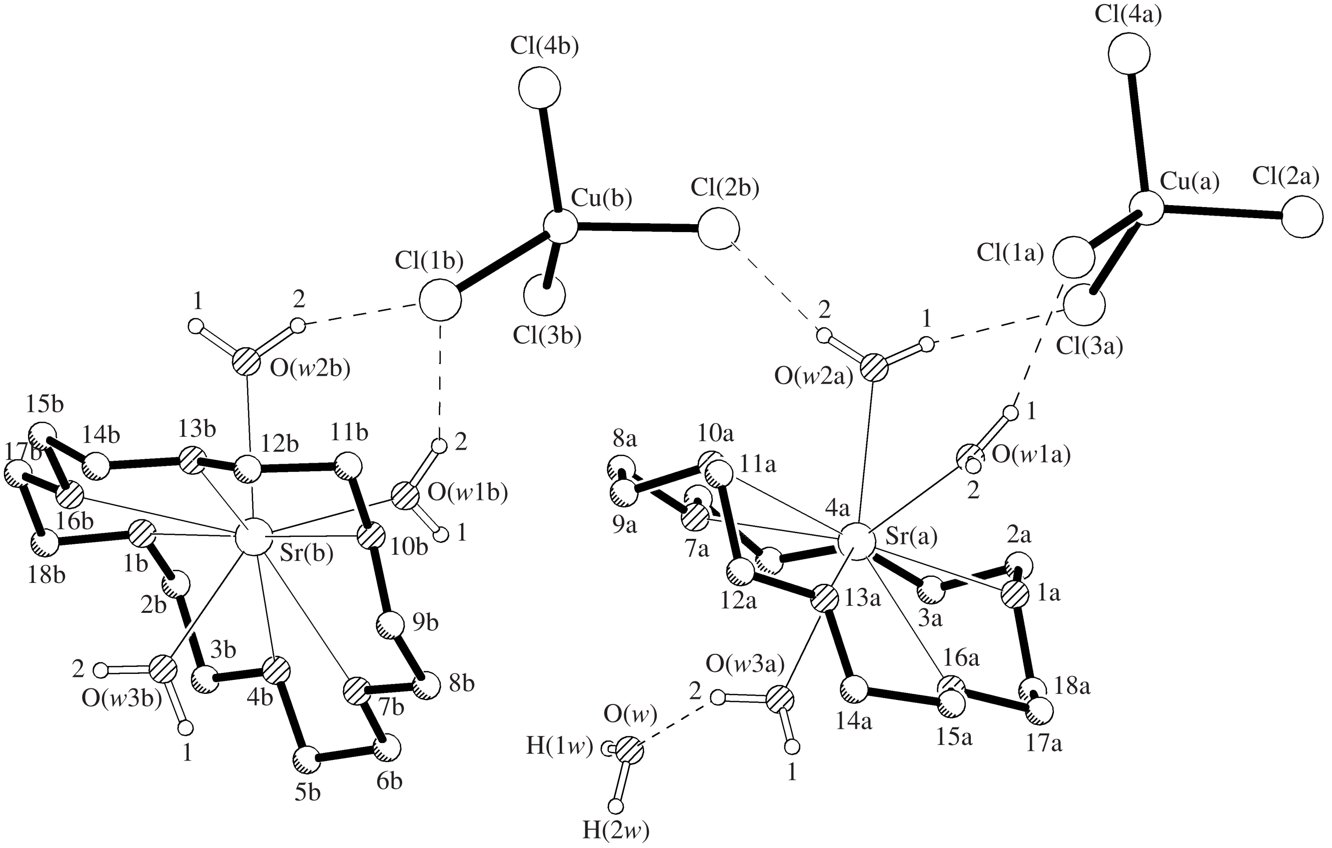
RESULTS AND DISCUSSION

Crystal structure **I** consists of two symmetrically independent "guest–host" complex cations $[Sr(18\text{-crown-}6)(H_2O)_3]^{2+}$ (a and b), two independent complex anions $[CuCl_4]^{2-}$ (a and b), and a hydrate water molecule with a position population of 0.84(1). Crystal structure **I** is shown in figure.

In the crystal **I**, one independent anion $[CuCl_4]^{2-}$ (a) is reorientationally disordered over two (major and minor) positions with populations of 0.887(3) and 0.113(3), respectively (the minor positions are marked with a prime). Selected distances between the major and minor positions are Cu(a)···Cu(a)' 0.690(9) Å, Cl(1a)···Cl(1a)' 0.58(1) Å, Cl(2a)···Cl(4a)' 0.69(1) Å, and Cl(3a)···Cl(3a)' 0.54(1) Å.

In structure **I**, the coordination polyhedron of the Cu^{2+} cation in either anion $[CuCl_4]^{2-}$ (a or b) can be described as a tetrahedron strongly flattened along the shared diagonal between the bond angles Cl(1)CuCl(2) and Cl(3)CuCl(4). In both anions (with no regard to the minor orientation of the anion a), the average Cu–Cl bond length (2.25 ± 0.01 Å) is somewhat shorter than the sum of the ionic radius of the Cu^{2+} cation (0.57 Å for CN 4) [5] and the van der Waals radius of the Cl atom (1.75–1.80 Å) [6, 7] and is slightly shorter than the sum of the covalent radii of the Cu(1.28 Å) and Cl atoms (1.02 Å) [8].

In complex **I**, the Sr(a) or Sr(b) cation in two structurally similar complex cations [Sr(18-crown-



Crystal structure of complex **I**. The minor (poorly populated) positions of the atoms in the disordered anion $[CuCl_4]^{2-}$ (a) and the H atoms in two 18-crown-6 ligands (a and b) are omitted for clarity. Hydrogen bonds are indicated with dashed lines.

$6)(H_2O)_3]^{2+}$ (a and b) is in the center of the cavity of the corresponding ligand 18-crown-6 (a or b) and is coordinated by all its six O atoms and three O atoms of three water molecules. The coordination polyhedron of the Sr(a) and Sr(b) cations (CN 9) is a strongly distorted hexagonal bipyramid with an equatorial plane made up of all the six O atoms of 18-crown-6; the one vertex is bifurcate (the O(*w*1a) and O(*w*2a) atoms or the O(*w*1b) and O(*w*2b) atoms) and the other vertex is single (O(*w*3a) or O(*w*3b)).

In structure **I**, the average $Sr–O_{crown}$ (2.695 ± 0.012 Å) and Sr–O(*w*) bond lengths (2.574 ± 0.025 Å) in two complex cations a and b are slightly or appreciably shorter than the sum of the ionic radius of the Sr^{2+} cation (1.31 Å for CN 9) [5] and the van der Waals radius of the O atom (1.40–1.52 Å) [6, 7]. On average, the Sr–O(*w*) bond is noticeably (by 0.121 Å) shorter than the $Sr–O_{crown}$ bond.

In structure **I**, the Sr(a) or Sr(b) cation in the corresponding complex cation deviates appreciably from the root-mean-square plane of the six O atoms of 18-crown-6: by 0.441(1) or 0.520(2) Å toward the O(*w*1a) and O(*w*2a) atoms (or toward the O(*w*1b) and O(*w*2b) atoms). The angle between these root-mean-square planes of two 18-crown-6 ligands (a and b) is 33.64(9)°.

In complex **I**, the average O–C and C–C bond lengths in two 18-crown-6 ligands (a and b) are 1.420(4) and 1.492(5) Å. The average O–C bond length is somewhat shorter than the statistical mean for the fragments $C\#–O–CH_2–C\#$ (1.426(11) Å) and the average C–C bond length is appreciably shorter than the statistical mean for the fragments $C\#–CH_2–CH_2–C\#$ (1.524(14) Å) [9]. Such a shortening of the endocyclic C–C bonds has been found in 18-crown-6 ligands and molecule [1, 10]. In complex **I**, all the bond angles COC in the crown ligands (a and b) are slightly greater, while the angles OCC are slightly smaller or greater, than an ideal tetrahedral angle of 109.5°.

In structure **I**, both 18-crown-6 ligands (a and b) have an approximate axis *2* passing through the center of the cavity of the perpendicularly averaged plane of the 18-membered macroheterocycle. The conformations of both crown ligands are mirror images of each other: all the endocyclic torsion τ angles $O–CH_2–CH_2–O$ are close to ±60° (of the *gauche* type) and most of the τ angles $CH_2–O–CH_2–CH_2$ are 180° ± 12° (of the *trans* type); only two of the latter (C(18a)O(1a)C(2a)C(3a) and C(9a)O(10a)C(11a)C(12a) in the ligand a and C(18b)O(1b)C(2b)C(3b) and C(9b)O(10b)C(11b)C(12b)

Table 2. Geometrical parameters of the inter-ion (intermolecular) hydrogen bonds in crystal structure **I***

H bond O–H···Z	Distance, Å			Angle O–H···Z, deg
	O–H	H···Z	O···Z	
O(*w*1a)–H(1)···Cl(1a)	0.90(3)	2.42(3)	3.233(4)	150(3)
O(*w*1a)–H(2)···Cl(3b)^{i}	0.90(3)	2.46(3)	3.317(4)	159(3)
O(*w*2a)–H(1)···Cl(3a)	0.90(3)	2.42(3)	3.299(5)	167(3)
O(*w*2a)–H(2)···Cl(2b)	0.90(3)	2.45(3)	3.331(4)	165(3)
O(*w*3a)–H(1)···Cl(2b)^{ii}	0.90(3)	2.54(3)	3.387(4)	156(3)
O(*w*3a)–H(2)···O(*w*)	0.90(3)	2.16(3)	2.859(6)	134(3)
O(*w*1b)–H(1)···Cl(1a)^{iii}	0.90(3)	2.45(3)	3.322(5)	164(3)
O(*w*1b)–H(2)···Cl(1b)	0.90(3)	2.65(3)	3.411(5)	143(2)
O(*w*2b)–H(1)···Cl(2a)^{iv}	0.90(3)	2.41(3)	3.290(4)	164(4)
O(*w*2b)–H(2)···Cl(1b)	0.90(3)	2.40(3)	3.155(4)	141(3)
O(*w*3b)–H(1)···Cl(2a)^{v}	0.90(3)	2.42(3)	3.203(4)	145(3)
O(*w*3b)–H(2)···Cl(4a)^{v}	0.90(3)	2.39(3)	3.037(5)	129(3)
O(*w*)–H(1*w*)···Cl(4a)^{iii}	0.90(3)	2.62(3)	3.421(5)	148(4)
O(*w*)–H(2*w*)···Cl(3b)^{ii}	0.90(3)	2.55(3)	3.437(6)	167(5)

* The symmetry operation codes are ^{i} $-x, 1/2 + y, -z$; ^{ii} $1 + x, y, z$; ^{iii} $-x, -1/2 + y, -z$; ^{iv} $x, y, 1 + z$; ^{v} $1 + x, y, 1 + z$.

in the ligand b approximate in absolute value to or are somewhat greater than 80° (of the *gauche* type).

Thus, in structure **I**, two O–C and C–C bonds meet at the C(2a) and C(11a) atoms (or the C(2b) and C(11b) atoms) of the crown ligand a (or b) with the *gauche*-torsion angles C–O–C–C and O–C–C–O (of the same sign). Such a conformation of the 18-crown-6 molecules and ligands is called biangular [11] and differs vastly from the most prevalent conformation (for these compounds) with the approximate or exact symmetry D_{3d}.

As mentioned above, the asymmetric part of the unit cell of crystal structure **I** contains an independent hydrate water molecule with a position population of 0.84(1). Apparently, the considerable degradation of the crystal of complex **I** noticed in the Experimental part is due to slow "escape" of these molecules from this crystal (the volume of its unit cell insignificantly diminishes during the exposure).

Crystal structure **I** contains inter-ion (intermolecular) hydrogen bonds involving all H atoms of all water molecules (Table 2). These bonds make an infinite three-dimensional framework.

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