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Synthesis and Crystal Structure of Bis(2,2,2-Cryptand Potassium) Tetrakis(isocyanato)cuprate(II)

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Abstract—A new complex compound, bis(2,2,2-cryptand potassium) tetrakis(isocyanato)cuprate(II), $2[K(Crypt\text{-}222)]^+ [Cu(NCS)_4]^{2-}$ was prepared and its crystal structure was studied by X-ray structural analysis. The structure includes one symmetrically independent complex cation $[K(Crypt\text{-}222)]^+$ of a *guest–host* type and independent one half of $[Cu(NCS)_4]^{2-}$ anion. Through the center of the anion passes crystallographic symmetry axis 2, the approximate point symmetry of the anion is D_2, while the approximate point symmetry of the complex cation is D_3. The coordination polyhedron of the $[Cu(NCS)_4]^{2-}$ anion (four N atoms) conjugated with Cu^{2+} cation is a nonplanar square considerably screwed into a flattened tetrahedron. The K^+ cation (coordination number 8) of the complex cation $[K(Crypt\text{-}222)]^+$ is coordinated by all eight heteroatoms (6O + 2N) of the 2,2,2-cryptand ligand, and its coordination polyhedron can be described as bis-basecentered trigonal prism slightly screwed into an anti-prism.

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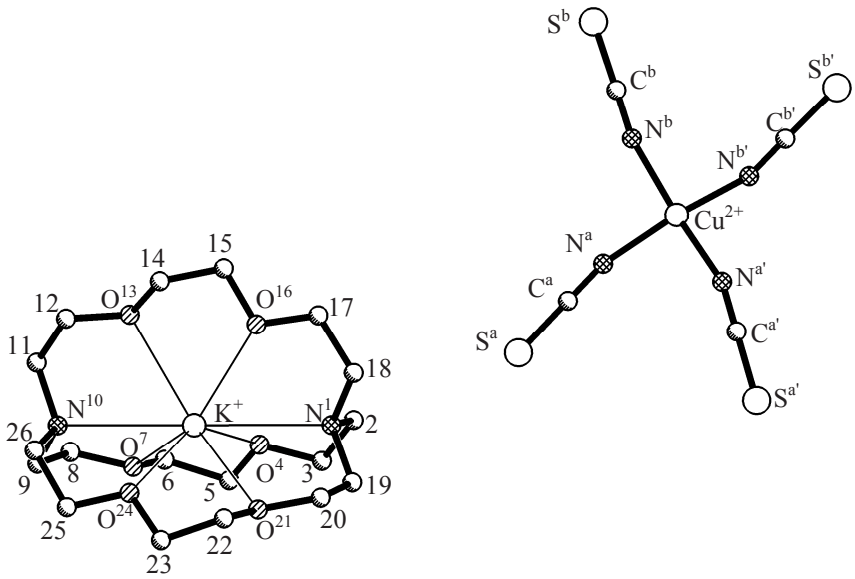
In this report we describe the results of X-ray structural analysis of a new complex compound bis (2,2,2-cryptand potassium) tetrakis(isothiocyanato)-cuprate(II), $2[K(Crypt\text{-}222)]^+ [Cu(NCS)_4]^{2-}$ (**I**), where $[K(Crypt\text{-}222)]^+$ is a complex cation of a *guest–host* type [1] whose bimacrocyclic ligand is 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (2,2,2-cryptand). Earlier such complex compounds containing any complex cation of the *guest–host* type and anion $[Cu(NCS)_4]^{2-}$ have never been synthesized and studied structurally.

We established (see Experimental) that the asymmetric part of the unit cell of crystals of compound **I** contained one individual complex cation and one half of individual anion $[Cu(NCS)_4]^{2-}$; through the center of the latter passed the crystallographic 2nd order symmetry axis. The molecular–ionic structure of compound **I** in crystal is shown in the figure. The bond lengths, principal bond and torsion angles are listed in Tables 1–3, respectively.

In structure **I** all four (two independent) anion-ligands SCN^- of the complex anion $[Cu(NCS)_4]^{2-}$ coordinate its cation Cu^{2+} by isothiocyanate type, through N atoms. The coordination polyhedron of this cation Cu^{2+} (coordination number 4) is a nonplanar square considerably screwed into a flattened tetrahedron strongly oblate along the common diagonal between the bond angles $N^aCuN^{b'}$ and $N^{a'}CuN^b$ (see bond angles N–Cu–N in Table 2). In this $Cu(NCS)_4]^{2-}$ anion the average bond length of four Cu–N bonds equals 1.932(2) Å being noticeably below the sum of effective ion radius of Cu^{2+} cation (0.57 Å for coordination number 4) [2] and van der Waals radius of the nitrogen atom (1.50–1.55 Å [3, 4]) and also noticeably less than the sum of covalent radii of Cu and N (1.32 and 0.70 Å respectively [5]).

In compound **I** the structure of the two independent SCN^- anion-ligands of the anion $[Cu(NCS)_4]^{2-}$ is close to linear and the covalent bond lengths of S=C and N=C bonds are close to the average statistical values for the isocyanates, 1.620(22) and 1.149(17) Å respectively [6].

It is apparent that in the structure **I** the approximate point symmetry of anion $[Cu(NCS)_4]^{2-}$ is D_2, namely, besides the crystallographic axis *2* it has two approximately 2nd order symmetry axes orthogonal to the axis *2* and to each other. For more detailed description of this anion geometry we show deviations



Molecular–ionic structure of complex compound **I** in te crystal. Anion $[Cu(NCS)_4]^{2-}$ and complex cation $[K(Crypt\text{-}222)]^+$ are shown. The anion $[Cu(NCS)_4]^{2-}$ is located on the crystallographic axis *2*, its basic atoms multiplied by the axis *2* are primed. To avoid the figure overloading, the H atoms at the C atoms of the complex anion are omitted.

of its atoms from the mean-square plane of its four atoms N^a, N^b, $N^{a'}$ and $N^{b'}$, Å: Cu^{2+} 0 , N^a 0.409(2), N^b –0.405(2), $N^{a'}$ –0.409(2), $N^{b'}$ 0.405(2), C^a 0.368(4), C^b –0.365(4), S^a 0.320(4), and S^b –0.342(4).

For comparison, in the Cambridge Structural Database [7] (version before August, 2008) there are only five crystal structures (with complete data) that include the anion $[Cu(NCS)_4]^{2-}$ [8–12]. In three of these structures [8–10] the cation Cu^{2+} coordination polyhedron is an ideal planar square and in two [11, 12] is a screwed tetrahedron.

In the structure **I** the complex cation $[K(Crypt\text{-}222)]^+$ (whose cation K^+ is located in the cavity of the 2,2,2-cryptand-ligand) has approximatly 3rd order symmetry axis passing through its N^1, K^+ and N^{10} atoms, and three orthogonal to it approximatly 2-nd order symmetry axes passing respectively through the middles of the bonds C^5–C^6, C^{14}–C^{15}, and C^{22}–C^{23} and

Table 1. Bond lengths (*d*, Å) in the structure **I**

Bond	*d*	Bond	*d*	Bond	*d*	Bond	*d*
$Cu–N^a$	1.931(2)	$C^5–C^6$	1.487(3)	$K–O^{13}$	2.847(2)	$C^{15}–O^{16}$	1.420(2)
$Cu–N^b$	1.934(2)	$C^6–O^7$	1.418(2)	$K–O^{16}$	2.763(2)	$O^{16}–C^{17}$	1.416(2)
$S^a=C^a$	1.618(2)	$O^7–C^8$	1.417(2)	$K–O^{21}$	2.853(2)	$C^{17}–C^{18}$	1.504(2)
$S^b=C^b$	1.617(2)	$C^8–C^9$	1.497(3)	$K–O^{24}$	2.765(2)	$C^{19}–C^{20}$	1.491(3)
$N^a=C^a$	1.153(2)	$N^{10}–C^9$	1.469(2)	$N^1–C^{19}$	1.471(2)	$C^{20}–O^{21}$	1.418(2)
$N^b=C^b$	1.155(2)	$N^{10}–C^{11}$	1.467(2)	$N^1–C^{18}$	1.472(2)	$O^{21}–C^{22}$	1.420(2)
–	–	$N^{10}–C^{26}$	1.469(2)	$N^1–C^2$	1.470(2)	$C^{22}–C^{23}$	1.489(4)
$K–N^1$	2.998(2)	$C^{11}–C^{12}$	1.493(3)	$C^2–C^3$	1.498(3)	$C^{23}–O^{24}$	1.417(2)
$K–O^4$	2.846(2)	$C^{12}–O^{13}$	1.419(2)	$C^3–O^4$	1.414(2)	$O^{24}–C^{25}$	1.417(2)
$K–O^7$	2.835(2)	$O^{13}–C^{14}$	1.413(2)	$O^4–C^5$	1.417(2)	$C^{25}–C^{26}$	1.492(3)
$K–N^{10}$	2.985(2)	$C^{14}–C^{15}$	1.489(3)				

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

Angle[a]	ω	Angle	ω	Angle[a]	ω	Angle	ω
N^aCuN^b	93.4(1)	$O^{16}KO^{21}$	94.65(5)	O^4KO^{13}	120.87(5)	$N^{10}C^{11}C^{12}$	114.2(2)
$N^aCuN^{a'}$	91.3(1)	$O^{16}KO^{24}$	117.18(6)	O^4KO^{16}	99.28(5)	$C^{11}C^{12}O^{13}$	110.1(2)
$N^aCuN^{b'}$	155.7(1)	$O^{21}KO^{24}$	60.60(5)	O^4KO^{21}	99.22(5)	$C^{12}O^{13}C^{14}$	110.8(2)
$N^bCuN^{b'}$	92.1(2)	$C^{19}N^1C^{18}$	110.1(2)	O^4KO^{24}	138.41(5)	$O^{13}C^{14}C^{15}$	109.1(2)
CuN^aC^a	159.1(2)	$C^{19}N^1C^2$	111.0(2)	O^7KN^{10}	60.65(5)	$C^{14}C^{15}O^{16}$	109.5(2)
CuN^bC^b	159.7(2)	$C^{18}N^1C^2$	109.3(2)	O^7KO^{13}	100.02(5)	$C^{15}O^{16}C^{17}$	112.4(2)
$S^aC^aN^a$	179.6(3)	$N^1C^2C^3$	114.7(2)	O^7KO^{16}	139.99(5)	$O^{16}C^{17}C^{18}$	109.1(2)
$S^bC^bN^b$	178.5(2)	$C^2C^3O^4$	110.1(2)	O^7KO^{21}	120.32(5)	$C^{17}C^{18}N^1$	113.3(2)
N^1KO^4	60.68(5)	$C^3O^4C^5$	111.2(2)	O^7KO^{24}	97.93(5)	$N^1C^{19}C^{20}$	114.1(2)
N^1KO^7	118.75(5)	$O^4C^5C^6$	110.3(2)	$N^{10}KO^{13}$	60.69(5)	$C^{19}C^{20}O^{21}$	109.3(2)
N^1KN^{10}	179.37(5)	$C^5C^6O^7$	109.9(2)	$N^{10}KO^{16}$	120.05(5)	$C^{20}O^{21}C^{22}$	112.1(2)
N^1KO^{13}	119.47(5)	$C^6O^7C^8$	110.8(2)	$N^{10}KO^{21}$	120.01(5)	$O^{21}C^{22}C^{23}$	110.1(2)
N^1KO^{16}	60.22(5)	$O^7C^8C^9$	109.8(2)	$N^{10}KO^{24}$	60.18(5)	$C^{22}C^{23}O^{24}$	109.1(2)
N^1KO^{21}	60.39(5)	$C^8C^9N^{10}$	114.3(2)	$O^{13}KO^{16}$	60.22(5)	$C^{23}O^{24}C^{25}$	112.6(2)
N^1KO^{24}	120.29(5)	$C^9N^{10}C^{11}$	111.4(2)	$O^{13}KO^{21}$	134.26(5)	$O^{24}C^{25}C^{26}$	108.7(2)
O^4KO^7	59.11(4)	$C^9N^{10}C^{26}$	109.8(2)	$O^{13}KO^{24}$	95.54(5)	$C^{25}C^{26}N^{10}$	114.1(2)
O^4KN^{10}	118.69(5)	$C^{11}N^{10}C^{26}$	109.7(2)				

[a] The symmetrically transformed ($-x$, y, $1/2 - z$) basic atoms of the anion $[Cu(NCS)_4]^{2-}$ are primed.

Table 3. Pricipal torsion angles (τ, deg) in structure **I**

Angle	τ	Angle	τ	Angle	τ	Angle	τ
$C^{19}N^1C^2C^3$	73.4(3)	$C^{14}C^{15}O^{16}C^{17}$	–178.6(2)	$C^8C^9N^{10}C^{11}$	72.6(3)	$C^{20}O^{21}C^{22}C^{23}$	–171.2(2)
$C^{18}N^1C^2C^3$	–165.0(2)	$C^{15}O^{16}C^{17}C^{18}$	164.5(2)	$C^8C^9N^{10}C^{26}$	–165.5(2)	$O^{21}C^{22}C^{23}O^{24}$	–65.4(3)
$N^1C^2C^3O^4$	63.8(3)	$O^{16}C^{17}C^{18}N^1$	61.4(3)	$C^9N^{10}C^{11}C^{12}$	–168.1(2)	$C^{22}C^{23}O^{24}C^{25}$	–173.1(2)
$C^2C^3O^4C^5$	176.3(2)	$C^{17}C^{18}N^1C^2$	77.6(3)	$C^{26}N^{10}C^{11}C^{12}$	70.0(3)	$C^{23}O^{24}C^{25}C^{26}$	167.5(2)
$C^3O^4C^5C^6$	–176.4(2)	$C^{17}C^{18}N^1C^{19}$	–160.3(2)	$N^{10}C^{11}C^{12}O^{13}$	64.5(3)	$O^{24}C^{25}C^{26}N^{10}$	61.2(3)
$O^4C^5C^6O^7$	–60.5(3)	$C^2N^1C^{19}C^{20}$	–167.1(2)	$C^{11}C^{12}O^{13}C^{14}$	–170.2(2)	$C^{25}C^{26}N^{10}C^9$	73.9(3)
$C^5C^6O^7C^8$	–175.5(2)	$C^{18}N^1C^{19}C^{20}$	71.8(3)	$C^{12}O^{13}C^{14}C^{15}$	–169.9(2)	$C^{25}C^{26}N^{10}C^{11}$	–163.3(2)
$C^6O^7C^8C^9$	176.2(2)	$N^1C^{19}C^{20}O^{21}$	65.6(3)	$O^{13}C^{14}C^{15}O^{16}$	–64.5(3)		
$O^7C^8C^9N^{10}$	63.7(3)	$C^{19}C^{20}O^{21}C^{22}$	–174.2(2)				

cation K^+. Therefore the approximate point symmetry of this complex cation is D_3.

In the structure **I** the cation K^+ of the complex cation $[K(Crypt\text{-}222)]^+$ is coordinated by all eight heteroatoms (6O + 2N) of the 2,2,2-cryptand ligand. The coordination polyhedron of the cation K^+ (coordination number 8) can be described as a bisbase-centered trigonal prism slightly screwed into the antiprism. Two bases of this prism are defined by two sets of three atoms, O^4, O^{16}, O^{21} and O^7, O^{13}, O^{24}, while the atoms N^1 and N^{10} are base-centering points of this prism.

In the structure **I** the average bond length of two coordination bonds of the complex cation $[K(Crypt-222)]^+$, K–N 2.992±0.007 Å, is a bit less than the sum of the effective ion radius of the cation K^+ (1.51 Å for the coordination number 8) [2] and van der Waals radius of the nitrogen atom (1.50–1.55 Å), while the average bond length of six coordination bonds K–O 2.818 ± 0.036 Å is noticeably less than the sum of the same ion radius of K^+ cation and van der Waals radius of the oxygen atom (1.40–1.52 Å) [3, 4].

The 2,2,2-cryptand ligand in the structure **I** has the same approximate D_3 symmetry as the complex cation, and its covalent bonds are of the following approximate bond lengths, Å: N–C 1.470(2), O–C 1.417(2) and C–C 1.493(4). These average bond lengths are almost the same or a bit larger or less than the respective average statistical values: N(sp^3)–C(sp^3) 1.469(14) Å for pyramidal fragments N(–C)$_3$, O–C(sp^3) 1.426(11) Å for the fragments C#–O–CH_2–C#, and C(sp^3)–C(sp^3) 1.524(14) Å for the fragments C#–CH_2–CH_2–C# [13]. The effective shortening of intracyclic C–C bonds like this is well known for crown ethers [14].

In the structure **I** the average bond angles in the 2,2,2-cryptand ligand are as follows: C–N–C 110.2(6)°, C–O–C 111.7(7)°, N–C–C 114.1(3)°, and O–C–C 109.6(6)°.

The 2,2,2-cryptand ligand conformation in the structure **I** can be completely characterized by the torsion angles τ in Table 3. As seen, all the τ angles of X–C–C–Y fragments (X, Y = N, O) are of *gauche* type and close to ±63°, among the all τ angles in C–N–C–C fragments a half is of *gauche* type (near 73°), and a half of trans type (close to –165°), and the τ angles in C–O–C–C fragment are of *trans* type in the range of 180 ± 15°.

In the crystal structure **I** all the short interatomic interionic contacts are close to or a bit shorter than the sum of respective atomic van der Waals radii.

EXPERIMENTAL

The complex compound **I** was synthesized as follows. In a mixture acetone–ethanol–water 2:3:1 was dissolved a crystalline 2,2,2-cryptand, potassium thiocyanate KSCN, and copper(II) thiocyanate $Cu(SCN)_2$ in the mole ratio 2:2:1, and the solution was left for evaporation at room temperature. After several days at the vessel bottom precipitated dark green (almost black) single crystals of complex **I**.

For the X-ray structural analysis the unit cell parameters of the crystal and three-dimensional set of reflexes intensity were registered on an automatic diffractometer Enraf-Nonius CAD-4 (MoK_α-radiation, graphite monochromator). The crystals **I** are monoclinic: $2[K(C_{18}H_{36}N_2O_6)]^+ [Cu(NCS)_4]^{2-}$, M 1127.04, a 20.940(3), b 13.815(3), c 21.620(4) Å, β 117.46(2)°, V 5550(2) Å^3, Z 4, d_{calc} 1.349 g cm^{-3}, μ(MoK_α) 7.54 cm^{-1}, space group $C2/c$.

The intensities of 5263 reflexes ($h + k = 2n$; $2\theta \leq 50$) were measured in the quadrant of reciprocal space by ω/2θ-scanning of the single crystal of the size 0.13×0.36×0.43 mm. The intensities of reflexes were then corrected for extinction by semiempirical method [15], and after exclusion of 237 systematically extinguished reflexes and averaging the intensity in 144 pairs of equivalent reflexes 0kl and 0$k\bar{l}$ (R_{int} = 0.023) the working array of the measured $F^2(hkl)$ and $\sigma(F^2)$ consisted of 4882 independent reflexes.

Structure of **I** was solved by the direct method with the SHELXS-97 program [16] and refined by theb full-matrix least-squares method (on F^2) with the SHELXL-97 program [16] in the approximation of anisotropic thermal vibrations for all nonhydrogen atoms. For the structure refinement were used almost all the reflexes in the working array [including even very weak with $I < 2\sigma(I)$] with exclusion of only few reflexes with a bad fit of measured and calculated F^2 values.

All hydrogen atoms in the structure **I** in the 2,2,2-cryptand ligand were localized objectively in the Fourier synthesis of differential electron density at the intermediate step of anisotropic refinement. Then all H atoms in the cryptand ligand were placed geometrically and their coordinates were refined using the *rider* model [16] in the procedure of refinement of structure **I** by the least-squares method; for the H atoms only their individual isotropic thermal parameters were refined.

For the exposed single crystal **I** by the least-squares method the coefficient of isotropic extinction, g = 0.00025(5) was also refined [16]. In the final cycle of the full-matrix refinement the absolute shifts of all 340 varied parameters of structure **I** were less than 0.001σ.

The final characteristics of the structure **I** refinement are as follows: $R1$ = 0.035 and $wR2$ = 0.076 over all 3220 observed reflexes with $I \geq 2\sigma(I)$; $R1$ = 0.066 and $wR2$ = 0.091 over all 4882 independent measured reflexes; the adjustment quality factor S = 0.99

(definitions for *wR*2 and *S* values are given in the manual [16]). In the final Fourier synthesis of differential electron density: $-0.20 < \Delta\rho < 0.18$ eÅ^{-3}.

Final coordinates and the thermal parameters of the atoms in the structure **I** as well as the complete tables of bond lengths, bond angles and other parameters are deposited as cif-file to the Cambridge Structural database, deposit no. 703460.

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