

## Cu(II) Crown–Tetraphenylporphyrinate: Molecular Structure and Evaluation of the Formation of Multinuclear Complexes with s–Metals

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Dedicated to our colleague, teacher and friend –  
professor A. T. Soldatenkov (December 1938 – October 2016),  
who has unexpectedly left us

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*A novel neutral complex of a crown-fused tetraphenylporphyrin was obtained and its structure determined by X-ray analysis. Quantum chemical calculations were performed to establish the possibility of exploiting its crown units for the formation of multinuclear complexes with cations of alkaline and alkaline earth metals.*

**Keywords:** Crown-porphyrins, multinuclear complexes, X-ray analysis, quantum chemical calculations.

## Краун–тетрафенилпорфирилат меди(II): молекулярное строение и оценка возможности получения многоядерных комплексов с s–металлами

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*Методом РСА было определено молекулярное строение краун–тетрафенилпорфирилата меди(II). Квантово-химическими расчётами произведена оценка возможности получения на его основе многоядерных комплексов с катионами s-металлов.*

**Ключевые слова:** Краун–порфирины, многоядерные комплексы, РСА, квантово-химические расчеты.

## Introduction

Multifunctional tetrapyrrolic ligands draw continuous interest of researchers in many areas. The pronounced optical properties of porphyrins, combined with their ability to form extremely stable metal complexes, make such compounds required in the production of chemical sensors<sup>[1]</sup> and other nano-scale devices.<sup>[2]</sup> Subunits that can act as auxiliary coordination sites, such as crown ethers, can further enhance the properties of such macromolecules. In our laboratory we continue to study fused crown-tetraphenylporphyrins.

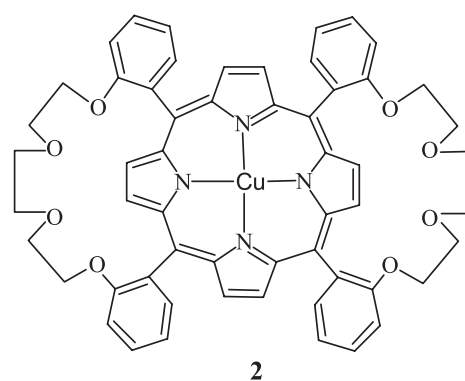
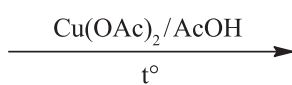
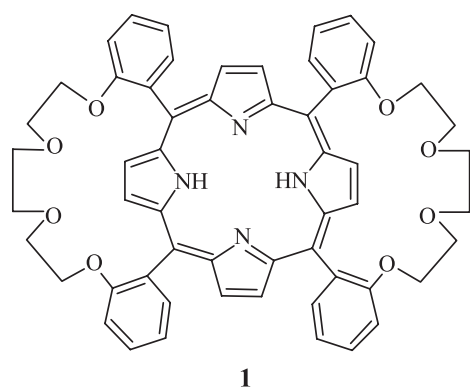
## Results and Discussion

The free porphyrinic ligand **1** was synthesized as described in literature.<sup>[3]</sup> Its copper complex **2** was prepared by heating a solution of the free crown-porphyrin in AcOH with excess copper(II) acetate followed by extraction with methylene chloride and chromatographic separation.

Complex **2** was characterized by single-crystal X-ray diffraction study. Its structure is shown in Figure 1 along with the atomic numbering scheme. Selected bond lengths and angles are listed in Table 1. The full geometrical parameters for **2** are available as supplementary material.

**Table 1.** Selected geometrical parameters (Å and deg). Symmetry transformations used to generate equivalent atoms: (a)  $-x+1, -y, -z+1$ .

Cu1—N1	1.966(4)	C3—C4	1.410(7)
Cu1—N2	1.954(4)	C4—C5	1.379(7)
N1—C1	1.353(6)	C5—C28 <sup>a</sup>	1.368(7)
N1—C4	1.356(6)	C1—C24	1.369(7)
N2—C25	1.369(6)	C24—C25	1.368(7)
N2—C28	1.355(6)	C25—C26	1.408(7)
C1—C2	1.415(7)	C26—C27	1.333(7)
C2—C3	1.336(7)	C27—C28	1.421(7)
N1—Cu1—N2	90.06(16)	C25—N2—C28	105.0(4)
Cu1—N1—C1	127.2(3)	N1—C1—C24	126.1(4)
Cu1—N1—C4	127.2(3)	N1—C4—C5	125.3(4)
Cu1—N2—C25	127.6(3)	C1—C24—C25	123.7(4)
Cu1—N2—C28	127.5(3)	C4—C5—C28 <sup>a</sup>	123.4(5)
C1—N1—C4	105.1(4)	N2—C25—C24	125.3(4)
N2—C28—C5 <sup>a</sup>	126.2(4)		



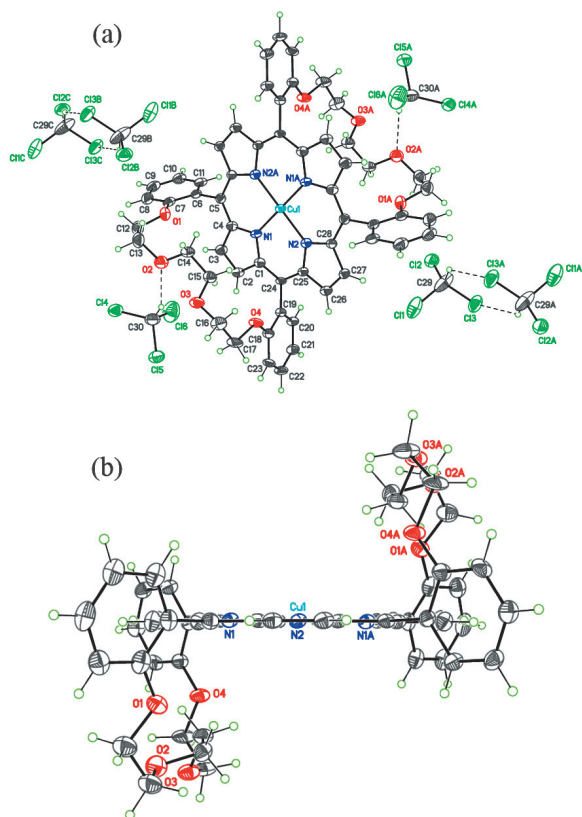
The molecule of **2** possesses the intrinsic  $C_i$  symmetry. The central porphyrin core is virtually planar (rms deviation is 0.010 Å). The copper(II) atom is surrounded by the four nitrogen atoms of the porphyrin fragment in a square-planar mode (Figure 1a). The Cu—N distances (1.966(4) and 1.954(4) Å, Table 1) are amongst the shortest ones within the related Cu-porphyrinate complexes.<sup>[4]</sup> The complex studied represents a rare example of Cu-porphyrinate derivatives containing the planar Cu-porphyrin fragment with such short Cu—N bond lengths. Only three recently reported complexes (metal-metalloporphyrin framework) display analogous conformation of Cu-porphyrin core.<sup>[5]</sup> The lengths of the C—N and C—C bonds flanking the porphyrin cavity are essentially delocalized (Table 1).

The crown ether substituents at *meso*-carbon atoms of the porphyrin core are *anti*-periplanar relative to the porphyrin plane (Figure 1b). Their spatial conformation is *t-g-g-t-g-t-g-g-t* (*t* – *trans*; *g* – *gauche*). Remarkably, it is almost identical to that of the free ligand described by us previously.<sup>[3]</sup> However, the size of internal cavity of these substituents in copper(II) complex **2** is slightly smaller than in the free ligand. It is clear demonstrated by the N...O distances between their heteroatoms (4.235(6), 4.355(6), 4.690(6) and 4.960(6) Å in **2** and 4.224(4), 4.501(4), 4.725(4) and 5.024(4) Å in the free ligand).

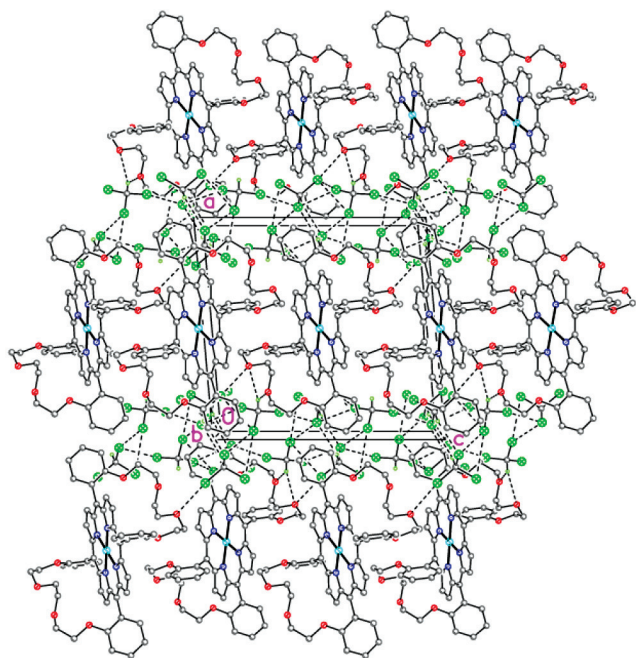
Apparently, this fact is explained by the presence of chloroform solvate molecules in the crystal of **2** which form the H-bonded associates with the Cu-porphyrin molecules by the C—H...O hydrogen bonds (Figure 1a, Table 2). Interestingly, the other chloroform solvate molecules in the crystal of **2** form centrosymmetric dimers by the weak C—H...Cl hydrogen bonds (Figure 1a, Table 2). The associates are bound to each other *via* the intermolecular non-valent attractive Cl...Cl interactions (Cl1...Cl4 [1-*x*, 1-*y*, 1-*z*] 3.551(3) Å, Cl1...Cl5 [1-*x*, 1-*y*, 1-*z*] 3.521(4) Å, Cl2...Cl4 [-1+*x*, *y*, *z*] 3.483(3) Å, Cl3...Cl4 [-1+*x*, *y*, *z*] 3.337(3), Cl3...Cl5 [1-*x*, 1-*y*, 1-*z*] 3.520(4) Å, Cl3...Cl4 [1-*x*, 0.5+*y*, 0.5-*z*] 3.211(4) Å) (Figure 2).

**Table 2.** Intermolecular hydrogen bonds (Å and deg.) for **2**·3CHCl<sub>3</sub>. D – proton donor; A – proton acceptor; Symmetry transformations used to generate equivalent atoms: (b)  $-x, -y+1, -z+1$ ; (c)  $x, -y-1/2, z-3/2$ .

D*—H...A*	d(D—H)	d(H...A)	d(D...A)	∠(D—H...A)
C29—H29...Cl3 <sup>b</sup>	1.00	2.79	3.544(4)	132
C30—H30...O2 <sup>c</sup>	1.00	2.09	2.925(5)	140



**Figure 1.** (a) Molecular structure of complex  $2 \cdot 3\text{CHCl}_3$  (50% ellipsoids), the intermolecular  $\text{C—H}\cdots\text{O}$  and  $\text{C—H}\cdots\text{Cl}$  hydrogen bonds are drawn by dashed lines; the H-bonded dimers formed by one of the two crystallographically independent chloroform molecules are shown additionally; (b) the projection of complex **2** along the porphyrin plane.

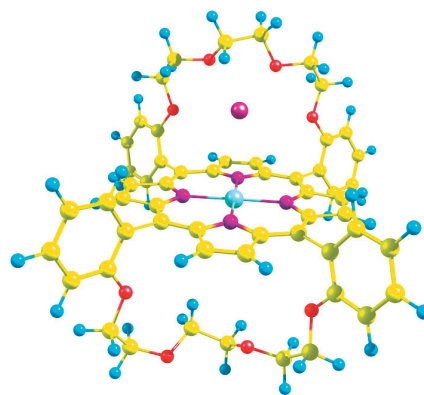


**Figure 2.** Crystal structure of complex  $2 \cdot 3\text{CHCl}_3$ , the intermolecular  $\text{C—H}\cdots\text{O}$  and  $\text{C—H}\cdots\text{Cl}$  hydrogen bonds as well as secondary  $\text{Cl}\cdots\text{Cl}$  interactions are drawn by dashed lines.

Utilization of the crown coordination sites of macroheterocycle **1** would be very interesting as it would result in the formation of multinuclear complexes. Obviously, alkaline, alkaline earth metal and ammonia type cations have the highest affinity to oxygen atoms of the ligand. In order to evaluate the best candidates for complexation we started a series of quantum chemistry calculations. The first results demonstrate that the Cu(II) derivative of **1** further can react with alkaline and alkaline earth metal cations (M) with the formation of multinuclear complexes with the O–M distances being almost the same as in simple crown complexes. The calculated O–M bond lengths for the binuclear complexes with  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are given in Table 3, with the experimental O–Na distances with simple crowns<sup>[6]</sup> for comparison. The optimized geometry for the binuclear complex of **2** with  $\text{Na}^+$  is shown in Figure 3.

**Table 3.** The calculated O–Me distances for binuclear complexes of **2** with *s*-metals and literature data for some Na-crown complexes.

Ligand	<i>s</i> -Metal cation	O–M bond, Å
( <b>2</b> )	$\text{Li}^+$	2.09, 2.12, 2.99, 3.44
( <b>2</b> )	$\text{Na}^+$	2.43, 2.47, 2.93, 3.13
( <b>2</b> )	$\text{K}^+$	2.69, 2.80, 2.93, 3.07
( <b>2</b> )	$\text{Mg}^{2+}$	2.14, 2.18, 2.23, 2.35,
( <b>2</b> )	$\text{Ca}^{2+}$	2.51, 2.52, 2.59, 2.62
[dibenzo-18-crown-6]	$\text{Na}^+$	2.76
12-crown-4	$\text{Na}^+$	2.45 (in $\text{Na}[12\text{-crown-4}]_2$ sandwich)



**Figure 3.** Molecular model of a binuclear  $\text{Na}^+[\text{Cu-crownTPP}]$  complex according to quantum chemical calculations.

It should be noted that our preliminary calculations were performed without the correction for solvation effects, as it would be too time-consuming for such large molecular systems. However in further research we will refine the results by employing a solvation model. Calculations for tri-nuclear complexes as well as experimental studies in solutions are also planned.

## Conclusions

The presence of crown ether units in the structure of crown-porphyrin **1** should alter its properties, as new coordi-

nation sites are introduced. Though its Cu(II) porphyrinate **2** behaves similarly to the simpler CuTPP, it yet has some differences in the structure of the tetrapyrrolic core in the crystalline state and probably in solutions, due to the electron-donating nature of the crown oxygen atoms that allows to form hydrogen bonds and coordination bonds with various cations. Quantum chemical calculations show that stable complexes with alkaline and alkaline earth metals can be formed thus resulting in the conversion of **2** into bi- or even trinuclear complexes.

## Experimental

### Materials and Equipment

Dichloromethane, acetic acid, and copper(II) acetate of analytical grade were from Khimmed company and were used without further purification. Boron trifluoride etherate, triethylamine, Oxone, pyrrole and basic  $\text{Al}_2\text{O}_3$  for chromatography were from Alfa Aesar. Pyrrole was passed through a short plug of  $\text{Al}_2\text{O}_3$  prior to use. LCMS analysis was performed on a Shimadzu Prominence LC-2020 system equipped with a diode array detector and a mass spectrometer (ESI ionization mode). Elemental analysis was made on a Eurovector-EA3000 automated analyzer. UV-vis spectra were recorded on a Varian Cary 50 instrument.

Quantum chemical calculations were performed in Priroda software<sup>[9]</sup> (ver 14) using DFT theory with the PBE functional and internal 3z basis set.

### Synthesis

The free ligand **1** was obtained by a previously published procedure. Its Cu(II) derivative was prepared by stirring 70 mg (0.08 mmol) of the free porphyrin **1** and 100 mg (0.5 mmol) of copper acetate monohydrate in 30 mL of acetic acid at 70 °C. After 5 hours the reaction mixture was cooled, diluted with water and extracted with dichloromethane (3×40 mL). The combined extracts were washed with dilute sodium bicarbonate and water, dried with  $\text{Na}_2\text{SO}_4$  and evaporated. The residue was subjected to column chromatography on  $\text{Al}_2\text{O}_3$ . Yield 70 mg (91 %). Found: C 69.65, H 5.08, N 5.92 %.  $\text{C}_{56}\text{H}_{48}\text{N}_4\text{O}_8\text{Cu}$  requires: C 69.44, H 5.00, N 5.78 %.  $m/z$  (ESI) (%) 968 (100)  $[(\text{M}+\text{H})^+]$ . Single crystals of **2** were grown by slow evaporation from chloroform.

### X-Ray Structure Determination (Synchrotron Experiment)

The purple prismatic crystal of  $2\cdot 3\text{CHCl}_3$  ( $\text{C}_{59}\text{H}_{51}\text{N}_4\text{O}_8\text{Cl}_3\text{Cu}$ ,  $M=1326.62$ ) is monoclinic, space group  $\text{P2}_1/\text{c}$ , at  $T=100$  K:  $a=15.820(3)$  Å,  $b=10.970(2)$  Å,  $c=16.450(3)$  Å,  $\beta=94.96(3)^\circ$ ,  $V=2844.1(10)$  Å<sup>3</sup>,  $Z=2$  (complex occupies a special position on the inversion center),  $d_{\text{calc}}=1.549$  g/cm<sup>3</sup>,  $F(000)=1358$ ,  $\mu=2.137$  mm<sup>-1</sup>. X-Ray diffraction data were collected on the 'Belok' beamline ( $\lambda=0.98670$  Å) of the National Research Center 'Kurchatov Institute' (Moscow, Russian Federation) using a MAR CCD detector. A total of 720 images (23559 reflections, 3523 independent reflections,  $R_{\text{int}}=0.063$ ) were collected using an oscillation range of  $1.0^\circ$  and two vertical detector positions of 0 and  $15^\circ$  ( $\varphi$  scan mode,  $2\theta_{\text{max}}=72.6^\circ$ ) and corrected for absorption ( $T_{\text{min}}=0.707$ ;  $T_{\text{max}}=0.787$ ).<sup>[7]</sup> The data were integrated using the utility iMOSFLM in CCP4 program.<sup>[8]</sup> The structure was determined by direct methods and refined by full-matrix least squares technique on  $F^2$  with anisotropic displacement parameters for non-hydrogen atoms. The crystal of **2** contained two solvate chloroform molecules with the total occupancy of 0.75 each. The hydrogen atoms were placed in calculated positions and refined

within riding model with fixed isotropic displacement parameters [ $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$ ]. The final divergence factors were  $R_1=0.0776$  for 3346 independent reflections with  $I>2\sigma(I)$  and  $wR_2=0.2067$  for all independent reflections,  $S=1.067$ . The calculations were carried out using the SHELXTL program.<sup>[10]</sup>

Crystallographic data for  $2\cdot 3\text{CHCl}_3$  have been deposited with the Cambridge Crystallographic Data Center, CCDC 1409587.

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