$0 < l < 22$), 15138 unique reflections ($R_{int} = 0.095$ for equivalent reflections) of which 8318 were observed $[|F_o| > 4\sigma(F_o)]$. Two reference reflections were measured every 45 min and showed a total decrease in intensity of 15.3%. All intensities were corrected for this drift. Data were corrected for Lorentzian, polarization, and absorption effects[17] ($A^*_{min} = 2.916$, $A^*_{max} = 5.163$). The structure was solved by direct methods with the program MULTAN 87;[18] all other calculations were performed with the XTAL[19] system and ORTEP II[12] programs. Full-matrix least-squares refinements on F with weights of $w = 1/(\sigma2(Fo) + 0.0005\,F_o^2)$ gave final values $R = 0.125$ and $Rw = 0.128$ for 1460 variables and 8318 reflections. The five perchlorate ions and the four acetonitrile molecules were refined with 64 restraints on bond distances and angles. The remaining "half" perchlorate i was located in special position 4*c* and was fully disordered. Five atomic sites (of which two were in special position 4*e*) were observed for the water molecules and the half hydroxide anion. Two oxygen atoms of the perchlorate i, the carbon and nitrogen atoms of two acetonitrile molecules, and the five oxygen atoms of the water molecules were refined with isotropic displacement parameters (13 atoms), and all the other atoms (157) with anisotropic displacements parameters. The mean ratio of shift to error on the last cycle was 0.058. Hydrogen atoms were placed in calculated positions and included in F_c calculations. The final Fourier difference synthesis showed a maximum of $+1.44$ and a minimum of $-2.06\,e\,Å^{-3}$. Complex **1** is isostructural with $[LaFe(L^2)_3](ClO_4)_{0.5}(CF_3SO_3)_{4.5} \cdot CH_3CN \cdot 4H_2O$ and $[EuZn(L^2)_3](ClO_4)(CF_3SO_3)_4 \cdot 4CH_3CN$.[8] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100482. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code + (44)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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Crown Ethers, Double-Decker, and Sandwich Complexes: Cation-Mediated Formation of Metallatopomer Coronates**

Rolf W. Saalfrank,* Norbert Löw, Sabine Kareth, Verena Seitz, Frank Hampel, Dietmar Stalke, and Markus Teichert

Crown ethers, [2]cryptands, and [3]cryptands selectively complex alkali metal ions.[1] This discovery led to the construction of novel supramolecular architectures[2] capable of recognizing neutral as well as cationic or anionic substrates with formation of well-defined host–guest compounds. Recently we pointed out the structural analogy between coronates and cryptates[3] and their topologically equivalent metallacoronates and metallacryptates.[4] If one applies the knowledge of crown ethers to the chemistry of metallacrown ethers (MC),[5] the complexation of differently sized cations by metallacrown ethers should lead to metallacoronates of varying structures. Since the ionic radii of alkaline and alkaline earth metal cations differ significantly (whereas the diameter of the metallacrowns essentially does not change) the inclusion of small cations such as Na^+ or Ca^{2+} should lead to a metallacoronate with 1:1 stoichiometry, and, in contrast, encapsulation of the larger K^+ ions to a metallacrown ether sandwich complex (K^+:MC = 1:2).

Reaction of diethyl ketipinate[6] H_2L^1 with copper(II) acetate in the presence of calcium nitrate leads to green microcrystals of **1** (Scheme 1) after crystallization from tetrahydrofuran/diethyl ether. According to elemental analysis and FAB-MS data (FAB = fast atom bombardment, $m/e = 977$) **1** is a metallacoronate. Compound **1** is a neutral, trinuclear metal cluster (Figure 1), as determined by X-ray

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[+] Single-crystal X-ray analyses.

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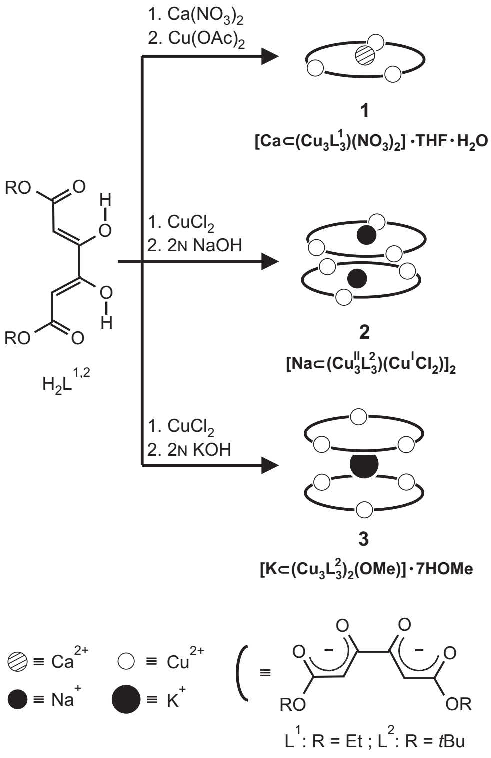

Scheme 1.

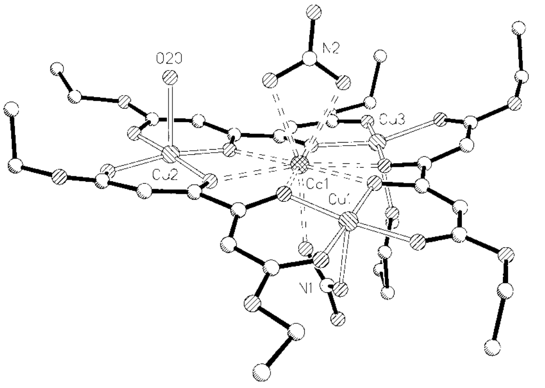

Figure 1. Molecular structure of **1**. Side view with counterion and coordinated solvent molecules; H atoms are omitted for clarity.

crystallographic analysis.[7] Formal replacement of the three copper(II) centers in the [15]metallacrown-6 system (15-MC-6) by ethylene bridges leads to the topologically equivalent crown ether [18]crown-6. The copper atoms are linked across the sides of the triangle through bis(bidentate) diethyl ketipinate dianions L^1, and each copper(II) ion is coordinated in a square-planar fashion to four oxygen atoms. Additional coordination of water, tetrahydrofuran, and nitrate leads to a square-pyramidal environment of O donors for each copper ion. The center of the resulting metallacoronand 15-MC-6 contains an encapsulated calcium ion, whose charge is compensated by two axially coordinated nitrate ions (Figure 1).

Double deprotonation of H_2L^2 by 2 N sodium hydroxide and reaction of the formed dianion with copper(II) chloride dihydrate also yields the metallacoronate **2** (FAB-MS data, $m/e = 898$; see Scheme 1), whose molecular structure was determined by X-ray crystallographic analysis (Figure 2).[8]

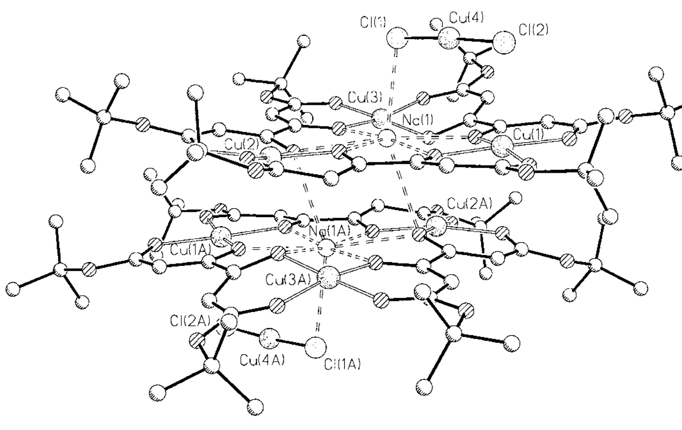

Figure 2. Molecular structure of dimer **2**. Side view; H atoms are omitted for clarity.

Metallacoronate **2** is a dimer of two $[Na \subset (Cu_3L^2_3)(CuCl_2)]$ building blocks. The monomer is composed of a $[Cu_3L^2_3]$ metallacrown with a sodium ion, which is η^6 coordinated to all oxygen atoms in the inner ring and located at the center. The counterion of the $[Na \subset (Cu_3L^2_3)]^+$ cation is a $(CuCl_2)^-$ ion[9] which coordinates to the encapsulated sodium ion through a chlorine atom. The tendency for eightfold coordination around Na$^+$ ions is the driving force for dimerization. The linkage of the coronates to give the dimer **2** is accomplished by coordination of one ring oxygen to the neighboring sodium center. This leads to a minor mutual deformation of the monomeric building blocks.

Whereas encapsulation of the small cations Na$^+$ and Ca^{2+} leads to host–guest systems of 1:1 stoichiometry, double deprotonation of di-*tert*-butyl ketipinate H_2L^2 with 2 N potassium hydroxide and reaction with copper(II) chloride dihydrate affords the metallacrown ether sandwich complex **3** with 2:1 stoichiometry ($m/e = 2125$; see Scheme 1). X-ray crystallographic analysis[10] reveals that **3** is constructed of two neutral trimetallacrown-6 building blocks that are rotated relative to each other by 60° (Figure 3). The sandwichlike linkage results from a crystallographically disordered potassium ion between the two metallacrowns. The counterion of $[K \subset (Cu_3L^2_3)_2]^+$ of **3** is a methoxide ion which is bound to the encapsulated

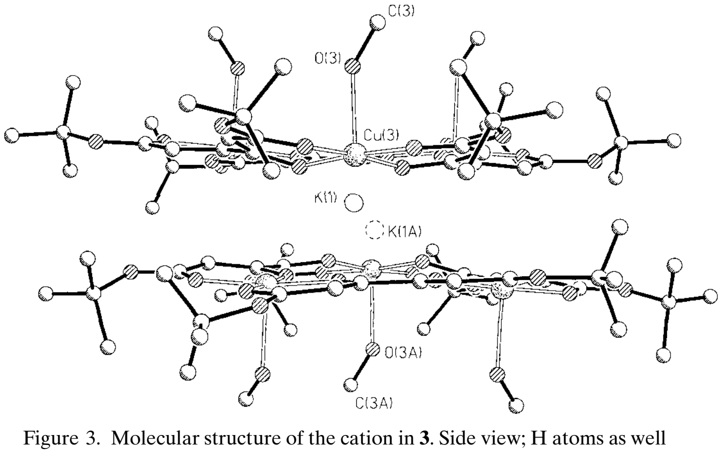

Figure 3. Molecular structure of the cation in **3**. Side view; H atoms as well as the methoxide and methanol molecules coordinated to potassium are omitted for clarity.

potassium ion; methanol is coordinated to the opposite sides (not shown). The coordination spheres of the six copper centers are saturated by methanol molecules, and, thus, each Cu^{2+} ion is surrounded by O donors in a tetragonal-pyramidal fashion.

As with organocrown ethers, the size of the cation (Na^+, Ca^{2+}, or K^+) determines whether metallacoronates (**1** and **2**) or a metallacrown ether sandwich complex (**3**) are formed in the case of metallacrown ethers $[Cu_3L_3]$ ($L = L^1, L^2$).

Experimental Section

1: A solution of copper(II) acetate monohydrate (200 mg, 1 mmol) in methanol (50 mL) was added dropwise to a mixture of H_2L^1 (230 mg, 1.0 mmol) and calcium nitrate tetrahydrate (475 mg, 2 mmol) in methanol (50 mL). The dark green solution was stirred for one hour and then concentrated to 10 mL. To achieve complete precipitation of the product, water (200 mL) was added. The product was filtered, washed with water, and dried under vacuum (oil pump). Yield of dark green crystals from tetrahydrofuran/diethyl ether: 320 mg (85%); decomp above 127 °C; IR ($CHBr_3$): $\tilde{\nu} = 2960$ (CH), 1614 ($C\overset{\cdots}{-}O$), 1524 cm^{-1} ($C{=}C$); FAB-MS (3-nitrobenzyl alcohol (*m*-NBA) matrix): m/z (%) = 977 (100, $[Ca \subset (Cu_3L^1_3)NO_3]^+$); correct elemental analysis.

2 and **3**: General procedure: Aqueous sodium or potassium hydroxide (2 mL, 2 N) was added dropwise to a solution containing copper(II) chloride dihydrate (171 mg, 1.0 mmol) and H_2L^2 (286 mg, 1.0 mmol) in methanol (100 mL). To achieve complete precipitation of the products, water (200 mL) was added. The products were filtered, washed with water, and dried under vacuum (oil pump).

2: Yield of dark green crystals from chloroform/diethyl ether: 220 mg (55%); decomp above 230 °C; IR ($CHBr_3$): $\tilde{\nu} = 2950$ (CH), 1640, 1590 ($C\overset{\cdots}{-}O$), 1540 cm^{-1} ($C{=}C$); FAB-MS (*m*-NBA): m/z (%) = 898 (100, $[Na \subset (Cu_3L^2_3)]^+$); correct elemental analysis.

3: Yield of dark green crystals from methanol: 280 mg (73%); decomp above 180 °C; IR ($CHBr_3$): $\tilde{\nu} = 3300$ (OH), 2970 (CH), 1655, 1600 ($C\overset{\cdots}{-}O$), 15750 cm^{-1} ($C{=}C$); FAB-MS (*m*-NBA): m/z (%) = 2125 (30, $[K \subset (Cu_3L^2_3)_2]^+$), 1082 (95, $[K \subset (Cu_3L^2_3)_2]^+$); correct elemental analysis.

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[7] **1**: $C_{34}H_{46}CaCu_3N_2O_{26}$, $M = 1129.45$, triclinic, space group P, $a = 1204.9(2)$, $b = 1359.59(12)$, $c = 1449.58(8)$ pm, $\alpha = 92.057(6)$, $\beta = 105.35(9)$, $\gamma = 96.83(1)^\circ$, $V = 2268.1(4)$ Å^3, $\rho_{calcd} = 1.651\ g\,cm^{-3}$, $Z = 2$, crystal dimensions $0.15 \times 0.2 \times 0.3\ mm^3$. Enraf-Nonius Mach3 diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm), $T = 200(2)$ K, graphite monochromator, scan range: $4.8 < 2\theta < 50.0^\circ$. Of 7982 measured reflections, 7982 were independent and 5777 with $I > 2\sigma(I)$. The structure was solved by direct methods using SHELXS-96 and refined with all data (356 parameters) by full-matrix least squares on F^2 using SHELXL93 (G. M. Sheldrick, Göttingen, **1993**). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed in idealized positions with a riding model. Final R values: $R1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.0377$ for $I > 2\sigma(I)$ and $wR2 = \Sigma w|(F_o^2 - F_c^2)^2|/\Sigma w(F_o^2)^2)^{0.5} = 0.1040$ (all data); min./max. residual electron density: $-0.646/0.659\ e\,Å^{-3}$.[15]

[8] **2**: $C_{84}H_{120}Cl_4Cu_8Na_2O_{36}$, $M = 2401.88$, triclinic, space group $P\bar{1}$, $a = 12.091(1)$, $b = 14.705(1)$, $c = 17.005(2)$ Å, $\alpha = 105.03(2)$, $\beta = 98.73(2)$, $\gamma = 92.52(2)^\circ$, $V = 2875.2(5)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.525\ g\,cm^{-3}$, $F(000) = 1350$, $\lambda = 0.71073$ Å, $T = 193$ K, $\mu(Mo_{K\alpha}) = 1.763\ mm^{-1}$, min./max. transmission: 0.703/0.768, crystal dimensions $0.30 \times 0.30 \times 0.25\ mm^3$, $3.88^\circ \leq 2\theta \leq 52.90^\circ$. Of 28414 measured reflections, 11697 were independent ($R_{int} = 0.0200$) and employed in the structure refinement of 695 parameters with 69 restraints. Final R values: $R1 = 0.0293$ ($I > 2\sigma(I)$) and $wR2 = 0.0709$ (all data); min./max. residual electron density: $-358/437\ e\,nm^{-3}$. Crystallographic data for **2** and **3** were collected on a Stoe-Siemens-Huber four circle diffractometer with Siemens CCD area detector by using φ and ω scans on a shock-cooled crystal in an oil drop.[11] Data were integrated with the program SAINT. For all data a semiempirical absorption correction was applied. The structures were solved by direct methods[12] and refined on F^2 by the least-squares method.[13] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included with a riding model. All disordered components were refined anisotropically with the assistance of distance and ADP restraints.[14]

[9] The $[CuCl_2]^-$ counterion is presumably produced by reduction of $CuCl_2$ by the solvent methanol.

[10] **3**: $C_{92}H_{151}Cu_6KO_{44}$, $M = 2381.56$, triclinic, space group $P\bar{1}$, $a = 14.304(2)$, $b = 14.966(4)$, $c = 17.076(2)$ Å, $\alpha = 99.39(2)$, $\beta = 111.36(2)$, $\gamma = 104.56(2)^\circ$, $V = 3160.8(10)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.336\ g\,cm^{-3}$, $F(000) = 1338$, $\lambda = 0.71073$ Å, $T = 193$ K, $\mu(Mo_{K\alpha}) = 1.107\ mm^{-1}$, min./max. transmission: 0.671/0.738, crystal dimensions $0.55 \times 0.50 \times 0.45\ mm^3$, $5.32^\circ \leq 2\theta \leq 50.00^\circ$. Of 29889 measured reflections, 10442 were independent ($R_{int} = 0.0578$) and employed in the structure refinement of 770 parameters with 75 restraints. Final R values are $R1 = 0.0655$ ($I > 2\sigma(I)$) and $wR2 = 0.1755$ (all data); min./max. residual electron density: $-991/989\ e\,nm^{-3}$. The potassium ion in **3** is disordered

around an inversion center with occupancies of 0.50. The carbon atom of one coordinated methanol molecule is disordered over two sites (0.74:0.26). The carbon atom of the methoxide ion is disordered over three sites (0.38:0.31:0.31). The asymmetric unit is occupied by one methanol solvent molecule and four partially occupied and one disordered water molecule (0.68:0.32). The hydrogen atoms of the hydroxyl groups and the methoxide ion could not be located in the difference fourier synthesis.[14]

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[14] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-100739 (**1**) and 100744 (**2**, **3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code +(44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk). Red-green stereo presentations of **1**–**3** are available on the WWW under http://www.organik.uni-erlangen.de/saalfrank/index.html.

Evidence for C–H···O Hydrogen Bond Assisted Recognition of a Pyrimidine Base in the Parallel DNA Triple-Helical Motif**

Judith Marfurt and Christian Leumann*

The structural and energetic influence of nonconventional C–H···O hydrogen bonds on molecular recognition has become a focus of interest. Whereas a large body of structural data evidences their importance in molecular recognition of small molecules in the crystalline state,[1] only limited experimental data is available on their contribution to biomolecular recognition in solution.[2] C–H···O hydrogen bonds have only recently begun to be used as design elements for directing intermolecular organization of small organic molecules (crystal engineering).[1, 3] Their use as a designer element for biomolecular complexation is virtually unexplored.

We recently reported on the selective recognition of G–C base pairs in DNA duplexes by parallel complementary oligodeoxynucleotides containing the unnatural nucleoside 7-(2′-deoxy-β-D-ribofuranosyl)hypoxanthine (^{7}H).[4] Although only one conventional N–H···N hydrogen bond between ^{7}H and G can be formed, the ^{7}H · G–C base triple (Figure 1) has the same stability as the canonical $\underline{C}^+$ · G–C base triple ($\underline{C}$ = 5-methyl deoxycytidine) at pH 7.0, in which the base of the third strand is bound through two conventional hydrogen bonds to the purine base of the Watson–Crick duplex. Since precise structural data were lacking, we empirically attributed the extra stability to the presence of one or two C–H···O hydrogen bonds flanking the conventional hydrogen bond of the third-strand base.

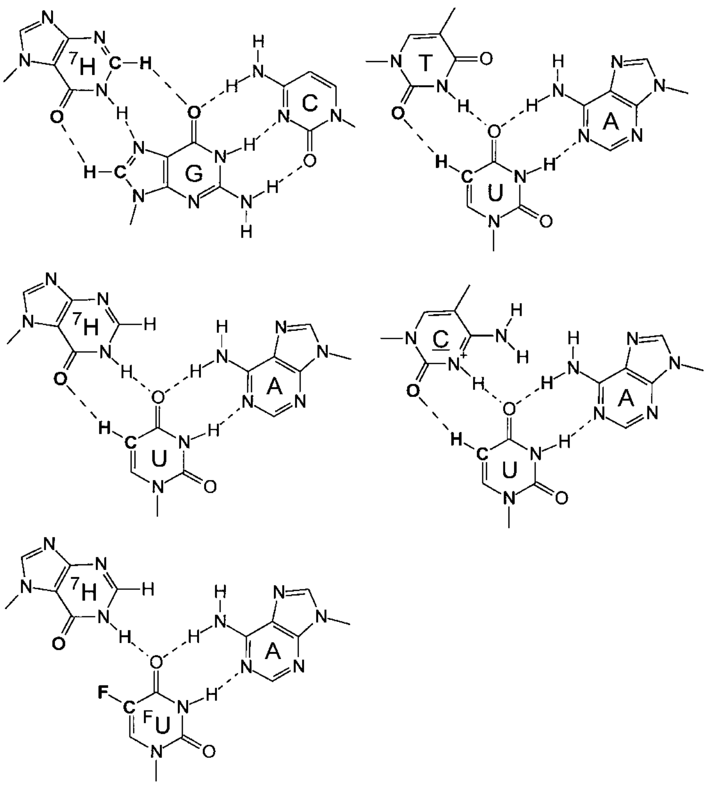

Figure 1. Experimentally investigated base triples in the parallel triple-helical binding motif.

To explore whether such weak electrostatic interactions can be further exploited for the recognition of DNA duplexes by oligonucleotides, we investigated the recognition of pyrimidine bases by considering such C–H···O hydrogen bonds. Specifically we investigated the interaction of a deoxyuridine unit in a DNA duplex with a ^{7}H unit in the third strand (Figure 1).

The DNA target duplexes **1** as well as the third-strand oligonucletides **2** (Figure 2) were synthesized by standard phosphoramidite chemistry from commercially available and recently described DNA building blocks.[4] The binding efficiency of the third strands to the target duplex was

1 5'-GCTAAAAAGA**X**AGAGAGATCG
CGATTTTTCT**Y**TCTCTCTAGC-5'

2 5'-TTTTT$\underline{C}$T**Z**T$\underline{C}$T$\underline{C}$T$\underline{C}$T

Z	X Y	G C	dU A	d^{F}U A	T A
$\underline{C}$		37.7 (-3.0)	24.2 (0)	18.5 (2.1)	17.9 (1.1)
^{7}H		40.0 (-3.4)	30.0 (-0.8)	24.0 (0.3)	18.2 (1.7)
T		---	27.7 (-0.7)	19.5 (1.9)	16.9 (2.0)

Figure 2. Top: Sequences of the target duplexes **1** and third strands **2**; bottom: T_m values [°C] for third-strand dissociation from UV melting curves (λ = 260 nm) and (in parentheses) ΔG values [kcal mol^{-1}] for triplex formation at 25 °C. Total single-strand concentration: 1.6 μM. Buffer: 10 mM sodium cacodylate, 100 mM NaCl, 0.25 mM spermine, pH 7.0.

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