Coordination Polymers

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Threading Cesium Ions: Metal, Host, and Ligand Control in Supramolecular Coordination Chemistry**

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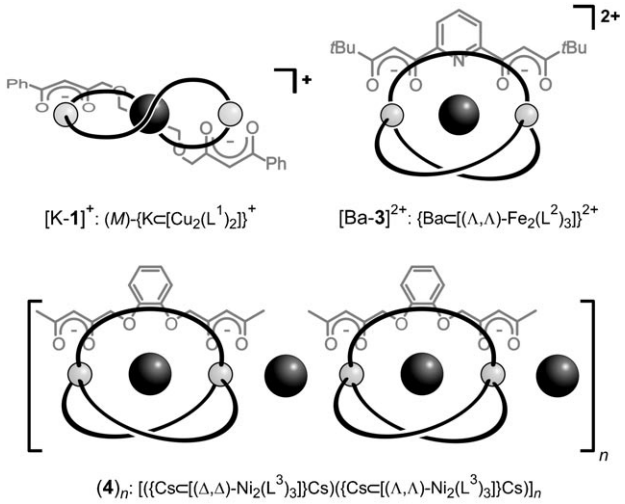
Dedicated to Professor Johann Gasteiger on the occasion of his 65th birthday

In earlier work we demonstrated that the bis-1,3-diketo dianion $(L^1)^{2-}$ is an excellent ligand for the complexation of copper(II) ions and, owing to the extra oxygen donors of the glycolate spacer, most suitable for the synthesis of racemic dinuclear double-stranded helicates (*P*/*M*)-{M⊂[$Cu_2(L^1)_2$-$(MeOH)_2$]}OAc (M-**1**, M = K^+, Rb^+, Cs^+; Scheme 1, top left).[1]

In contrast, reaction of the bis-1,3-diketo dianion $(L^2)^{2-}$ (H_2L^2 = **2**) with iron(III) chloride in the presence of alkali-, alkaline-earth-, or rare-earth-metal cations (M^{n+}) yields triple-stranded {2}-iron helicates/mesocates {M⊂[Fe_2-$(L^2)_3$]}[X]$_n$ (M-**3**, M = K^+, Sr^{2+}, Ba^{2+}, La^{3+}).[2–4] For example, the metallacryptate Ba-**3** is a racemic mixture with either (Δ,Δ)-*fac*- or (Λ,Λ)-*fac*-coordinated iron centers (Scheme 1, top right).[2] However, the two iron centers in *meso*-K-**3** [(Δ,Λ)-*fac*] have opposite configuration.[3] The mono-, di-, and trivalent guest cations are endohedrally encapsulated in the cavity of the bicyclic dinuclear host to give [M-**3**]$^{n+}$ and their charge is compensated by $[FeCl_4]^-$ or PF_6^- anions (X^-).

Interestingly, starting from hexacoordinate nickel(II) instead of tetra- or pentacoordinate copper(II) as well as the bis-1,3-diketo dianion $(L^3)^{2-}$ in the presence of cesium ions, we isolated the neutral {2}-metallacryptate [({Cs⊂[$Ni_2(L^3)_3$]}$Cs)_2$] (**4**) with (Δ,Δ)-*fac* and (Λ,Λ)-*fac* stereochemistry at the nickel centers. The *meso* building blocks **4** are self-complementary and aggregate along the external cesium ions



Scheme 1. The cation [K-**1**]$^+$ (top left), the dication [Ba-**3**]$^{2+}$ (top right), and the repeating unit in the 1D *meso*-polymer (**4**)$_n$ (bottom).

to yield the one-dimensional coordination polymer *meso*-[({Cs⊂[(Δ,Δ)-$Ni_2(L^3)_3$]}Cs)({Cs⊂[(Λ,Λ)-$Ni_2(L^3)_3$]}Cs)]$_n$ (**4**)$_n$ (Scheme 1, bottom).[1]

Our further studies on the supramolecular coordination chemistry of copper(II)[5] focused on the synthesis of oligonuclear complexes by self-assembly[6] with the 2,6-pyridinyl-bridged pentadentate ligand $(L^2)^{2-}$. To this end, we treated **2**[7] with calcium hydride and copper(II) acetate in methanol and isolated the metallacoronate **5** (Scheme 2). We characterized the molecular structure of **5** by X-ray crystallography[8–10] of crystals obtained by vapor diffusion of diethyl ether into a solution of **5** in methanol: **5**·4 MeOH is present in the crystal as a dinuclear copper(II) coronate, in which a calcium ion is encapsulated in the center, and two acetate ions act as counterions (Figure 1, top). The two crystallographically equivalent copper(II) ions of the idealized-C_{2h}-symmetric **5**[11] have tetragonal-pyramidal coordination geometry, each with two pairs of oxygen donors and one molecule of methanol.

In contrast, treatment of a solution of **2** in methanol with copper(II) acetate and cesium carbonate (in place of calcium hydride) does not yield a metallacoronate similar to **5**; instead, the larger cesium ion, which prefers a higher coordination number, functions as a template for the formation of the one-dimensional coordination polymer (**6**)$_n$ (Scheme 2). Crystals obtained by vapor diffusion of diethyl

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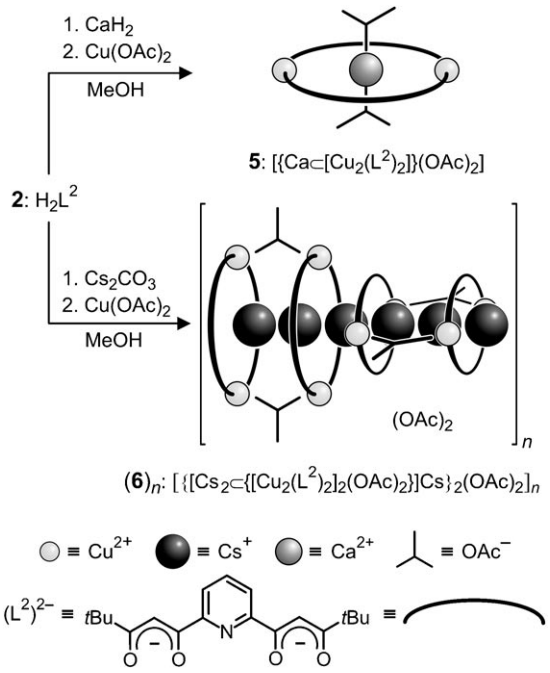

Scheme 2. Synthesis of metallacoronate **5** and 1D coordination polymer $(\mathbf{6})_n$ from copper(II) acetate and **2** with either CaH_2 or Cs_2CO_3 as base.

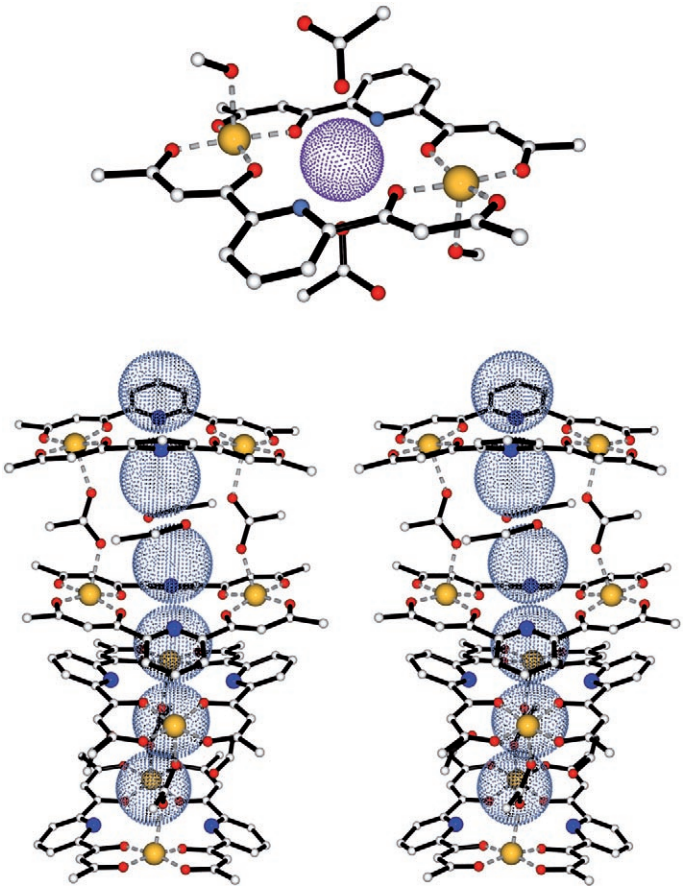

Figure 1. Top: Molecular structure of the metallacoronate **5**·4 MeOH. Bottom: Stereoview of the dicationic repeating unit of $(\mathbf{6}\cdot 10\,EtOH\cdot 2\,H_2O)_n$. C white, Ca purple (dotted), Cs blue (dotted), Cu gold, O red, N blue. *t*Bu groups, hydrogen atoms, noncoordinating solvent molecules, and the OAc^- counterions are omitted for clarity.

ether into a solution of **6** in ethanol were subjected to X-ray crystal structure analysis.[10,12–14] The analysis showed that $(\mathbf{6}\cdot 10\,EtOH\cdot 2\,H_2O)_n$ is composed of dicationic components $[\{[(Cs\cdot EtOH)_2\subset\{[Cu_2(L^2)_2]_2(OAc)_2\}]Cs\}_2]^{2+}$ and acetate ions as counterions. The acetate ions are located close to the 1D coordination polymer in the crystal lattice together with solvent molecules. The individual modules are composed of two concave $\{Cu_2(L^2)_2\}$ metallacoronands linked by two bidentate acetate ions, which results in a tetragonal-pyramidal coordination environment of the four copper ions. Endohedral encapsulation of two cesium ions and two molecules of ethanol into the thus formed container $\{[Cu_2(L^2)_2]_2(OAc)_2\}$ then gives the cryptate $[(Cs\cdot EtOH)_2\subset\{[Cu_2(L^2)_2]_2(OAc)_2\}]$ with C_i molecular symmetry. Exohedral coordination of a further cesium ion to the cryptate generates the self-complementary unit $\{[(Cs\cdot EtOH)_2\subset\{[Cu_2(L^2)_2]_2(OAc)_2\}]Cs\}^+$. Linkage of these building blocks alternately rotated by 90° finally affords the dicationic monomer $[\{[(Cs\cdot EtOH)_2\subset\{[Cu_2(L^2)_2]_2(OAc)_2\}]Cs\}_2]^{2+}$ of the one-dimensional coordination polymer $(\mathbf{6}\cdot 10\,EtOH\cdot 2\,H_2O)_n$ (Figure 1, bottom).[15]

An interesting feature of $(\mathbf{6}\cdot 10\,EtOH\cdot 2\,H_2O)_n$ is the formal encapsulation of a cesium acetate dimer between the two concave $\{Cu_2(L^2)_2\}$ metallacoronands. This cesium–cesium distance amounts to $d_{Cs\text{-}Cs} = 3.75$ Å, which is even shorter than the cesium–cesium distances in the 3D network of crystalline cesium acetate itself ($d_{Cs\text{-}Cs} = 3.98$ and 3.91 Å).[16] Most notably, the *exo*/*endo*-cesium distances ($d_{Cs\text{-}Cs} = 3.71$ Å) in dicationic monomer $[\{[(Cs_{endo}\cdot EtOH)_2\subset\{[Cu_2(L^2)_2]_2(OAc)_2\}]Cs_{exo}\}_2]^{2+}$ are even shorter than twice the ionic radii of 12-coordinate cesium ions ($r_{ionic} = 1.88$ Å).[17] To the best of our knowledge, the interatomic distances of the cesium cations in $(\mathbf{6}\cdot 10\,EtOH\cdot 2\,H_2O)_n$ are the shortest measured so far.[18]

In conclusion, we have developed a convenient route for the template-mediated self-assembly of the metallacoronate **5**. Furthermore, exchange of the small alkaline-earth-metal ion Ca^{2+} by the large alkali-metal ion Cs^+ allowed the synthesis of the one-dimensional coordination polymer $(\mathbf{6})_n$. The most striking characteristic of $(\mathbf{6})_n$ is its chain of cesium ions with interatomic distances shorter than twice their ionic radii.

Experimental Section

General Procedure: Ligand H_2L^2 (**2**) (331 mg, 1.00 mmol) was added in one batch under nitrogen to a colorless suspension of CaH_2 or Cs_2CO_3 (2 mmol)[19] in dry MeOH (50 mL). The mixture was stirred at 20 °C for 1 h, during which time the color changed to yellow. Copper(II) acetate monohydrate (200 mg, 1.00 mmol) was then added, and the dark-green suspension was stirred for further 16 h at 20 °C. The suspension was filtered, the solvent was removed, and the remaining green crude reaction product was dried under vacuum (oil pump).

5: 84 mg of CaH_2; yield: 348 mg (65%) green crystals of **5**·4 MeOH after fractional crystallization from MeOH by vapor diffusion of diethyl ether, suitable for X-ray structure determination; m.p. > 202–203 °C (decomp.); IR (neat): $\tilde{\nu}$ = 2966, 2867, 1571, 1559, 1509, 1360, 1304, 1273, 1225, 1192, 1142, 1109, 996, 955, 895, 789 cm^{-1}; FAB-MS (3-nitrobenzyl alcohol matrix (*m*-NBA)): *m*/*z* (%): 1826 (1) $[2M-OAc]^+$, 1766 (1) $[2M-2OAc]^+$, 1709 (2) $[2M-3OAc]^+$, 1651 (2) $[2M-4OAc]^+$, 1588 (3) $[2M-4OAc-Cu]^+$, 1195 (10) $[M-2OAc+L+Ca]^+$, 993 (9), 978 (15), 883 (100) $[M-OAc]^+$, 824 (16) $[M-2OAc]^+$, 698 (79) $[M-2OAc-2Cu]^+$, 641 (9) $[M-2OAc-2Cu-C_4H_9]^+$; elemental analysis (%) calcd for $C_{42}H_{52}CaCu_2N_2O_{12}\cdot H_2O$ (960.18): C 52.44, H 5.66, N 2.91; found: C 52.23, H 5.50, N 2.87.[20]

$(\mathbf{6})_n$: 652 mg of Cs_2CO_3; yield: 234 mg (39%) green needles of $(\mathbf{6}\cdot 10\ EtOH\cdot 2\ H_2O)_n$ after fractional crystallization from EtOH by vapor diffusion of diethyl ether, suitable for X-ray structure determination; m.p. > 197–199 °C (decomp.); IR ($CHBr_3$): $\tilde{\nu}$ = 2962, 2869, 1595, 1574, 1556, 1514, 1444, 1424, 1392, 1361, 1297, 1265, 1112, 1048, 1025, 994, 955, 891, 777 cm^{-1}; FAB-MS (*m*-NBA): *m*/*z* (%): 1902 (1) $[M-Cu-3OAc]^+$, 1834 (2) $[M-Cs-3OAc]^+$, 1703 (12) $[M-2Cs-3OAc]^+$, 1050 (4) $[M-Cs-2Cu-2L-3OAc]^+$, 917 (100) $[M-2Cs-2Cu-2L-3OAc]^+$, 807 (7) $[Na\subset Cu_2L_2]^+$ (Na^+ from the matrix); elemental analysis (%) calcd for $C_{82}H_{101}Cs_3Cu_4N_4O_{22}\cdot 3H_2O$ (2201.64): C 44.73, H 4.90, N 2.54; found: C 44.61, H 4.94, N 2.56.[20]

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[8] Crystal data for **5**·4 MeOH: $C_{46}H_{68}CaCu_2N_2O_{16}$, M = 1072.18 g mol^{-1}; crystal dimensions 0.35 × 0.20 × 0.15 mm^3; triclinic, space group $P\bar{1}$, a = 10.5377(3), b = 10.6617(2), c = 12.7741(3) Å, α = 96.925(1), β = 111.918(1), γ = 97.001(2)°, V = 1299.83(5) Å^3; Z = 1; $F(000)$ = 564, ρ_{calcd} = 1.370 g cm^{-3}; Nonius-KappaCCD diffractometer, $Mo_{K\alpha}$ radiation (λ = 0.71073 Å); T = 173(2) K; graphite monochromator; θ range 1.96° < θ < 25.05°; section of the reciprocal lattice: $-12 \le h \le 12$, $-12 \le k \le 12$, $-15 \le l \le 15$. Absorption correction: empirical (scalepack); of 8710 measured reflections, 4567 were independent and 4258 had $I > 2\sigma(I)$; linear absorption coefficient 0.983 mm^{-1}. The structure was solved by direct methods using SHELXS-97 and refinement was performed with all data (305 parameters) by full-matrix least-squares procedures on F^2 using SHELXL97;[9] all non-hydrogen atoms were refined anisotropically; R_1 = 0.0434 for $I > 2\sigma(I)$ and wR_2 = 0.1212 (all data); largest peak (0.742 e Å^{-3}) and hole (−0.756 e Å^{-3}).[9,10]
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[12] X-ray diffraction analysis of crystals of $(\mathbf{6})_n$ obtained from vapor diffusion of diethyl ether in a solution in MeOH revealed the formation of the same one-dimensional coordination polymer, but the poor data set did not allow complete refinement.
[13] Crystal data for $(\mathbf{6}\cdot 10\ EtOH\cdot 2\ H_2O)_n$: $C_{46}H_{66.5}Cs_{1.5}Cu_2N_2O_{14}$, M = 1197.96 g mol^{-1}; crystal dimensions 0.24 × 0.05 × 0.03 mm^3; monoclinic, space group $C2/c$, a = 19.908(2), b = 26.293(2), c = 22.112(3) Å, β = 112.79(1)°, V = 10671(2) Å^3; Z = 8; $F(000)$ = 4872, ρ_{calcd} = 1.491 g cm^{-3}; Nonius-KappaCCD diffractometer, $Mo_{K\alpha}$ radiation (λ = 0.71073 Å); T = 100(2) K; graphite monochromator; θ range 3.42° < θ < 26.37°; section of the reciprocal lattice: $-24 \le h \le 22$, $-31 \le k \le 32$, $-27 \le l \le 27$. A semiempirical absorption correction based on multiple scans was applied (SADABS 2.06;[21] T_{min} = 0.833, T_{max} = 0.833); of 52722 measured reflections, 10882 were independent and 6879 had $I > 2\sigma(I)$; linear absorption coefficient 1.866 mm^{-1}. The structure was solved by direct methods using SHELXTL NT 6.12 and refinement was performed with all data (703 parameters) by full-matrix least-squares on F^2 using SHELXTL NT 6.12.[14] All non-hydrogen atoms were refined anisotropically; R_1 = 0.0515 for $I > 2\sigma(I)$ and wR_2 = 0.1154 (all data); largest peak (0.833 e Å^{-3}) and hole (−0.955 e Å^{-3}).[14,21] Some of the solvent molecules partially coordinated to the Cs cations are disordered, thus resulting in large anisotropic displacement parameters. Attempts to reduce the strong anisotropy of these displacement parameters by applying a split model did not lead to reasonable results. A number of restraints (DFIX, SAME, SADI, SIMU) were applied in the treatment of the disorder.

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[19] Reaction of copper(II) acetate with **2** in methanol in the absence of the cited alkali-metal or alkaline-earth-metal ions yielded only polymeric material, which was insoluble in standard solvents.[5]
[20] Crystals of **5**·4 MeOH and (**6**·10 EtOH·2 H_2O)$_n$ lose solvent on prolonged exposure to the atmosphere. The powder formed was dried for 12 h under reduced pressure (10^{-4} mbar) at 35–40 °C and then subjected to elemental analysis.
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