A Quadruply Stranded, Alkaline Earth Metal Containing Helical Catenate: A Charge-Neutral Heterotopic Homodinuclear [2]Catenane**

Stephanie L. Castro, Oliver Just, and
William S. Rees, Jr.*

*Dedicated to Professor Dietmar Seyferth
on the occasion of his 70th birthday*

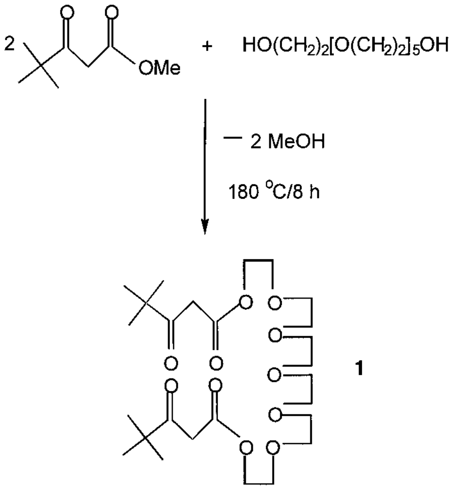
Organized supramolecular architectures such as catenates, helicates, and metallamacrocycles have long attracted considerable interest, both for their intrinsic aesthetic appeal and the challenge associated with their preparation. Successful synthetic strategies have often relied on templating effects of transition metal ions, π donor–acceptor interactions, or favorable hydrogen bonding.[1]

Employment of metals in the self-assembled formation of catenates is restricted, typically, to transition metal ions, whose preferred coordination geometry results in selective binding to specific sites of the ligand. In the formation of dinuclear catenates, segmental ligands often are employed, leading to heterodinuclear complexes in which each metal ion is attached to a portion of the ligand according to its stereochemical preferences.[2, 3] Due to the somewhat rigid coordination requirements of transition metals, metal ions will bind selectively to only one functionality present within the ligand. Moreover, metallamacrocycles with two distinct binding environments have been prepared to bind both hard and soft metal ions in the same molecule.[4, 5] In addition to being synthesized from neutral ligands by templated syntheses, such structures generate a high positive charge as their size increases.

As one component of an on-going research project related to coordination chemistry of alkaline earth metals, we examined ligands that would accommodate barium's high size-to-charge ratio. The reaction described here is completely self-templated, resulting in a charge-neutral species. Such helicates and catenanes are, if not unknown, very rare compositions.

The novel multidentate ligand 2,2,28,28-tetramethyl-3,5,25,27-tetraoxo-6,9,12,15,18,21,24-heptaoxanonacosane (**1**, see Scheme 1) consists of a hexaethylene glycol central segment with a β-ketoester functionality at each terminus. It possesses nine oxygen atoms with potential coordination capabilities (for steric reasons, the ester oxygen atoms are not considered as binding sites), and, following deprotonation, forms a dianionic ligand. Its structure and concept resemble the bis(β-diketone)-substituted oligoethylene glycol prepared by Kokube and co-workers,[4, 6] as well as the noncyclic crown ether arrangements of Vögtle et al.[7] Prior to the crystal structure resolution of the title compound, it was presumed that **1** would form a mononuclear complex with barium, in analogy to the reported noncyclic crown ether–rubidium structure of 1,20-bis(8-quinolyloxy)-3,6,9,12,15,18-hexaoxaicosane · RbI.[7] In this complex, the ligand wraps around the metal ion in a spiral fashion, giving rise to a mononuclear compound. The bis(β-diketone)oligoethylene glycol ligands of Kokube et al. form dinuclear metallamacrocycles, with a transition metal ion bound by the diketones to generate a "crown ether" pocket, which additionally encapsulates an alkali metal of the appropriate size. The crystal structure of the complex consisting of the dianion of 2,4,17,19-tetraoxo-6,9,12,15-tetraoxaicosane, copper(II). K^+(picrate)[6] shows a nearly planar arrangement of the diketonate oxygen atoms around the Cu^{II} ion, as well as a K^+ ion, which resides slightly off-center in the O_6 pseudo crown ether cavity formed by the oligoether section of the ligand.

The bis(ketoester) oligoether ligand **1** was prepared by a transesterification of hexaethylene glycol with two equivalents of methyl 4,4-dimethyl-3-oxopentanoate (Scheme 1). This procedure follows that of Kellogg et al.,[8] who previously reported the preparation of bis(ketoesters) of shorter glycols.



Scheme 1. Synthetic route leading to the bis(ketoester) oligoether ligand **1**.

Complex **2** became accessible through treatment of a slurry of $Ba(NH_2)_2$ in toluene with one equivalent of **1**. The NMR spectrum of **2** shows a shift in the α-H resonance from $\delta = 3.54$ to $\delta = 4.67$, consistent with the deprotonation of the ketoester. Accordingly, the ethylene resonances have become broad multiplets, which indicates a loss of symmetry in the ligand as well as the presence of diastereotopic protons. X-ray quality single crystals of **2** were grown by a slow evaporation of a solution in $CHCl_3$/benzene. The molecular structure of **2** (Figure 1), determined by X-ray diffraction, exhibits several unique features. The two ligands bind through their terminal ketoester functionalities to one barium atom each, forming

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[*] Prof. Dr. W. S. Rees, Jr., Dr. S. L. Castro, Dr. O. Just
School of Chemistry and Biochemistry and
School of Materials Science and Engineering and
Molecular Design Institute
Georgia Institute of Technology
Atlanta, GA 30332-0400 (USA)
Fax: (+1) 404-894-1144
E-mail: will.rees@chemistry.gatech.edu

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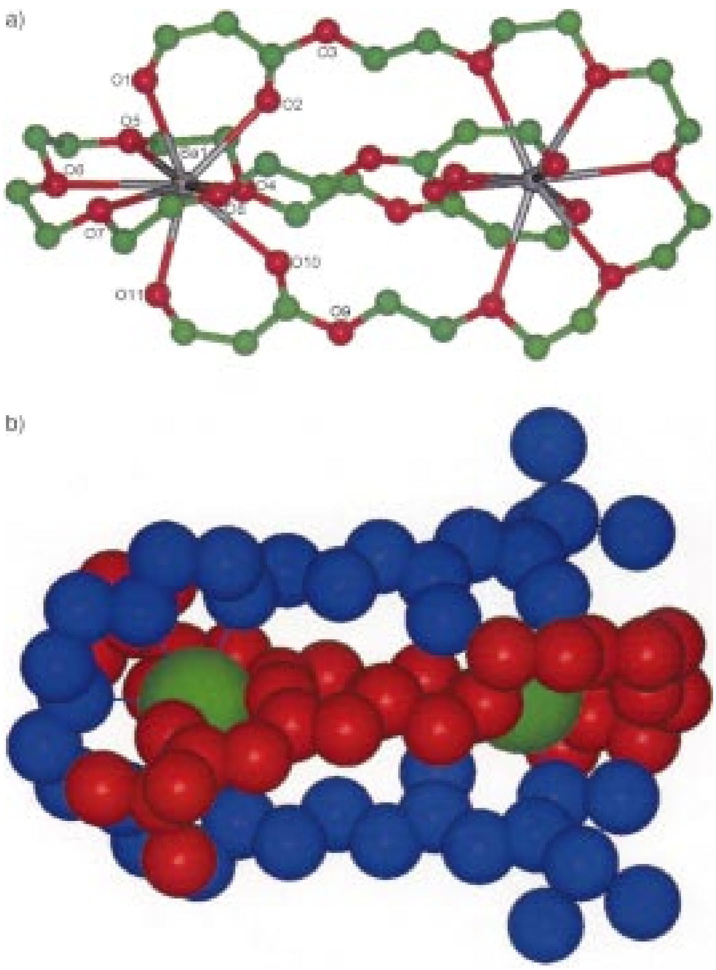

Figure 1. a) An ORTEP plot representation (gray: barium, green: carbon, red: oxygen) and b) a space-filling model of **2** (green: barium, red: one ligand, blue: the second ligand). All *t*Bu groups have been omitted for clarity. Selected interatomic distances [Å]: Ba1-O1 2.639(9), Ba1-O2 2.693(7), Ba1-O4 2.926(7), Ba1-O5 2.934(7), Ba1-O6 2.968(7), Ba1-O7 2.919(8), Ba1-O8 3.016(8), Ba1-O10 2.786(8), Ba1-O11 2.615(7).

two interlocked metallamacrocycles. The [2]catenate contains two nine-coordinate barium cores bound by four oxygen atoms stemming from two ketoester groups of one ligand, and additionally encapsulated by five oxygen atoms from the polyether chain of the second ligand. The complex displays idealized C_2 symmetry, with the C_2 rotational axis bisecting the Ba1–Ba1A vector. Average Ba–O$_{keto}$ interatomic distances of 2.627 Å (O1, O11) are slightly shorter than the corresponding distances for the Ba–O$_{ester}$ interactions (O2, O10: 2.740 Å). Both barium atoms reside in the center of the crown ether like pocket, interacting with five oxygen atoms of the polyether chain with Ba–O interatomic distances ranging from 2.919 to 3.016 Å. Furthermore, the catenate **2** exhibits a most unusual left-handed helical twist (25.9(4)°).

Compound **2** is a rare example of a quadruply stranded helicate;[9] another example is $[Co_5(\mu_5\text{-tpda})_4(NCS)_2]$,[10] a linear, pentanuclear transition metal complex. Oligo(multidentate) ligands can complex with two or more identical metal ions, hence forming a variety of homonuclear architectures, such as double and triple helices. In addition, the employment of multidentate ligands possessing designed different binding sites allows for the preparation of heteronuclear metal complexes. In general, however, it is difficult to prepare homodinuclear complexes from such ligands, as a consequence of the somewhat rigid coordination requirements of most metal ions. One example of a homodinuclear helicate displaying metal ions in different coordination environments is made up of four- and two-coordinate Cu^{I} ions.[11] The lanthanide complex $(HH)_2(HT)\text{-}[Ln_2(L)_3]^{6+}$ (HT = head to tail; HH = head to head; L = 2-{6-[1-(3,5-dimethoxybenzyl)-1H-benzimidazol-2-yl]-pyridin-2-yl}-1,1′-dimethyl-5,5′-methylene-2′-(5-methylpyridin-2-yl)bis[1H-benzimidazole]) constitutes, to date, the only reported example of a homonuclear heterotopic triple helicate.[12] Increased coordinative flexibility of Ba^{2+} permits coordination to the pseudo crown ether portion of the designed catenand as well as to both of the anionic ketoester terminal moieties, making complex **2** a rare example of a heterotopic, homodinuclear catenate.

The first organometallic catenane, published in 1993 by Gruter et al.,[13] consisted of two interlocking crown ether and diarylalkyl rings surrounding a magnesium ion. The NMR evidence suggested an equilibrium between the interlocking ring structure and a second, noncatenated structure, in which the crown ether is bound to the magnesium in a side-on fashion. However, no crystal structures were available for these compounds. Since the first magnesium complex in 1993, no other alkaline earth containing catenates have been reported. To the best of our knowledge, complex **2**, therefore, also represents the first crystallographically characterized catenate containing a Group 2 element.

Experimental Section

1: Methyl 4,4-dimethyl-3-oxopentanoate (10 g, 63 mmol) and hexaethylene glycol (8.92 g, 31.0 mmol) were heated at 180 °C for 8 h under stirring. Subsequently, the formed methanol was removed by distillation and the residue was treated with benzene. The organic solution then was washed with brine, saturated Na_2CO_3, and water and dried over $MgSO_4$. Following solvent evaporation, **1** was isolated as a colorless and viscous liquid. Yield 11.16 g (67 %). Elemental analysis calcd for $C_{26}H_{46}O_{11}$: C 58.41, H 8.67; found: C 58.12, H 8.67; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 4.24$ (t, 8H; CH$_2$), 3.67 (t, 8H; CH$_2$), 3.60 (s, 16H; CH$_2$), 3.59 (s, 16H; CH$_2$), 3.54 (s, 4H; CH), 1.12 (s, 36H; CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 208.21$, 168.01, 70.67, 69.03, 64.33, 63.19, 44.78, 43.87, 27.46, 26.11.

2: Barium metal (0.365 g, 2.65 mmol) in 50 mL of toluene was dissolved in liquid ammonia at −78 °C. After excess NH_3 was allowed to evaporate at ambient temperature, the slurry in toluene was refluxed and then degassed under argon. Compound **1** (1.42 g, 2.65 mmol) was added through a syringe to the off-white slurry, which initially turned white, and then milky gray. The release of a small amount of heat and gas was registered. The mixture was stirred overnight at ambient temperature and then filtered to separate a white powder from a pale yellow solution. Following refluxing in toluene, the formed colorless microcrystalline powder was filtered, washed with hexane, and dried under vacuum. X-ray quality crystals were formed as small thin needles by slow evaporation of a solution in $CHCl_3$/benzene (1/2) under a stream of argon. Yield 1.73 g (49 %). C,H analysis calcd for $Ba_2O_{22}C_{52}H_{88}$: C 42.16, H 5.66; found: C 43.2, H 5.2; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 4.67$ (s, 4H; CH), 4.21 (m, 16H; CH$_2$), 3.87–3.55 (m, 32H; CH$_2$), 1.07 (s, 36H; CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 25ûC): $\delta =$ 196.77, 170.81, 75.33, 70.98, 59.53, 40.32, 28.98.

Crystal data for **2** ($Ba_2O_{22}C_{52}H_{88}$): $M_r = 1339.918$, crystal dimensions $0.340 \times 0.136 \times 0.102$ mm, orthorhombic, space group $P2_12_12$, $a = 19.4469(3)$, $b = 19.5347(2)$, $c = 8.2529(2)$ Å; $V = 3135.19(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.419\ \text{g cm}^{-3}$, Siemens SMART CCD diffractometer, $1.48 < \theta < 25.00°$, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), ω scans, $T = 173(2)$ K; of 16334 measured reflections, 6519 were independent and 5518 observed with $I > 2\sigma(I)$, $-25 < h < 24$, $-25 < k < 24$, $-6 < l < 10$; $R_1 = 0.0659$, $wR_2 = 0.1503$, GOF = 1.258 for 373 parameters, $\Delta\rho_{max} = 2.335$ e Å^{-3}. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentzian and polarization corrections and absorption correction SADABS were applied, $\mu = 1.318$ mm^{-1}, min./max. transmission 0.6627/0.8773. The coordinates of the hydrogen atoms were calculated in SHELXL using an appropriate riding model with varied thermal parameters. 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-136903. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Copper Chalcogenolate Complexes as Precursors to Ternary Nanoclusters: Synthesis and Characterization of $[Hg_{15}Cu_{20}S_{25}(nPr_3P)_{18}]$[**]

Diem T. T. Tran, Nicholas J. Taylor, and
John F. Corrigan[*]

The chemistry and physics of binary semiconductor nanoclusters and colloids have been the focus of much attention due to the interesting electronic properties displayed by these nanometer sized "Q-particles".[1] The use of bis-silylated reagents $E(SiMe_3)_2$ (E = S, Se, Te) as a chalcogen source has led to the synthesis of near monodisperse XII-XVI particles [2] and a wealth of structural chemistry in copper chalcogenide complexes including the nanocluster $[Cu_{146}Se_{73}(PPh_3)_{30}]$.[3] It has also been shown that the monosilylated chalcogen reagents $RESiMe_3$ and $ArESiMe_3$ can yield mixed metal–chalcogenide–chalcogenolate complexes via subsequent chalcogen–carbon bond cleavage of the first formed metal–chalcogenolate cluster complexes.[4]

The importance of ternary semiconductor solids [5] prompts us to develop a general route into related nanometer sized ternary clusters.[1a] Brennan and co-workers have recently described the formation of ternary lanthanide-chalcogenolates [6] and Kanatzidis et al. have illustrated the utility of molecular copper–indium chalcogenolates for the generation of ternary solids.[7] We are developing suitable reagents for ternary nanocluster synthesis by targeting the reactive metal–silylchalcogenolate complexes $[L_nM{-}ESiMe_3]$, which can be used as a source of "metallachalcogenolate" (metal chalcogenide, $M{-}E^-$) fragments for the synthesis of polynuclear complexes of the type $[L_n(M'ME)_x]$.

Despite the propensity for chalcogenolate ligands to adopt bridging coordination modes, terminal coordination can be promoted by using bulky substituents about the chalcogen center [8] or by restricting the number of vacant coordination sites about the metal.[9] Herein we describe the synthesis of the tetrahedral copper–chalcogenolate complexes $[(nPr_3P)_3Cu\text{-}ESiMe_3]$ (**1a**, E = S; **1b**, E = Se; **1c**, E = Te) and demonstrate their utility in ternary nanocluster synthesis with the formation of $[Hg_{15}Cu_{20}S_{25}(nPr_3P)_{18}]$ **2** in high yield.

When CuOAc is treated with four equivalents of nPr_3P and one equivalent of $E(SiMe_3)_2$ at −40 °C, complexes **1a**–**c** are

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[*] Prof. Dr. J. F. Corrigan, D. T. T. Tran
Department of Chemistry
The University of Western Ontario
London, ON N6A 5B7 (Canada)
Fax: (+1) 519-661-3022
E-mail: corrigan@uwo.ca

Dr. N. J. Taylor
Department of Chemistry
The University of Waterloo
Waterloo, ON N2L 3G1 (Canada)

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