The Fused Metallacrown Anion Na$_2${[Na$_{0.5}$[Ga(salicylhydroximate)]$_4$]$_2$(μ_2-OH)$_4$}$^-$ Is an Inorganic Analogue of a Cryptate

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We have previously demonstrated the structural analogy of the crown ethers[1] to a new class of metal clusters called metallacrowns.[2-8] Both molecular classes contain core structures with 9-, 12-, or 15-membered rings that include 3, 4, or 5 formally neutral oxygen donors to which metal ions can be coordinated. The previous metallacrowns, whether vacant,[2-4] with homometallic captured metals,[3,5] mixed valent,[3,6,7] or heterometallic,[3,8] were composed of a single metallacrown ring. Herein we demonstrate by presenting the X-ray structure[9] of Na[(Na(DMF)$_3$)$_2${[Na$_{0.5}$[Ga(SHI)]$_4$]$_2$(μ_2-OH)$_4$}], (**1**, {Na$_2$[Na{(12-MC$_{\mathrm{Ga^{3+}N(SHI)}}$-4)$_2(OH)_4$}]}$^-$) that metallacrowns can be fused together through bridging hydroxides to form bicyclic metallacrowns. Rigorously, this nanosize compound most closely resembles confacially linked crown ethers; however, conceptually the metallacrown can be likened to cryptates[1] by having a cavity that binds sodium. Another class of inorganic analogues of cryptates, based on a polyoxometalate framework, shows selectivity for lanthanides.[10]

The reaction of H$_3$SHI[3]:Ga(NO$_3$)$_3$:sodium trichloroacetate (NaTCA) (1:1:3) in DMF leads to isolation of **1**. An ORTEP diagram of **1** is shown as Figure 1. The 12-MC$_{\mathrm{Ga^{3+}N(SHI)}}$-4 core of **1** is similar to that of the previously characterized iron and manganese 12-MC-4 complexes,[3] with the Ga(III) internal ring separations of ≈4.6 Å and a cavity radius of 0.56 Å. The obvious differences include the square-pyramidal coordination of the Ga(III) ions and the bridging of metal ions from the two metallacrown rings across apical positions by hydroxide oxygen atoms (average Ga–OH = 1.91 Å). The separation of the Ga(III) across the hydroxide bridge is 3.54 Å. Three Na(I) ions are bound to the cluster, and a fourth is bound to solvent in the lattice. Two capping Na(I) are seven-coordinate by virtue of coordination by four metallacrown ring oxygens (average Na$_C$–O$_X$ = 2.52 Å) and three DMF oxygen atoms (average Na$_C$–O$_S$ = 2.39 Å). This is

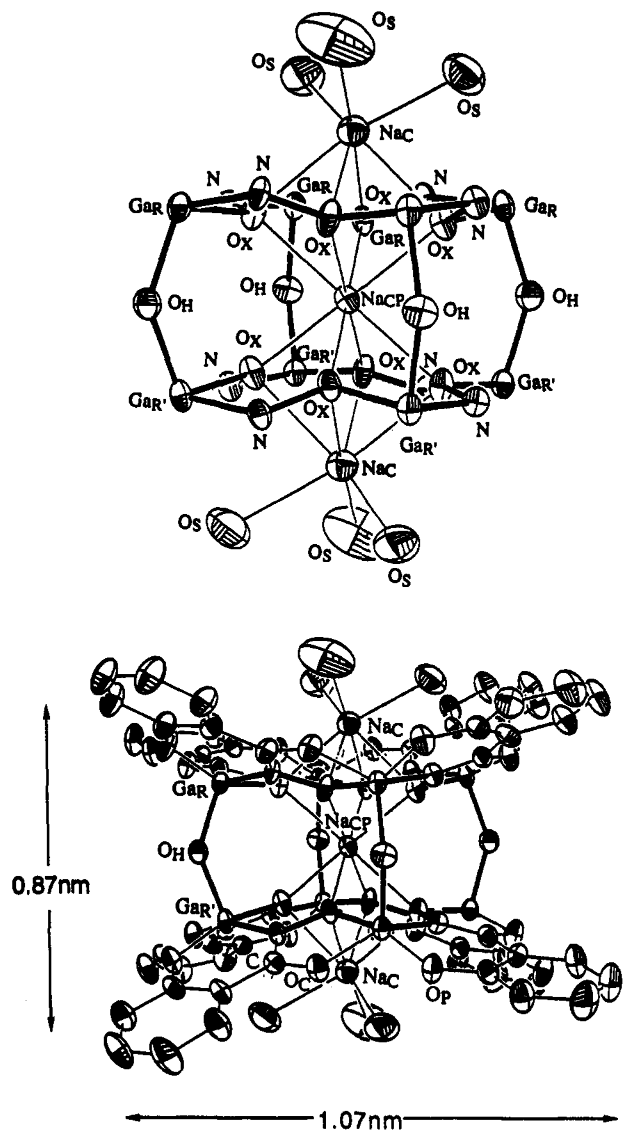

Figure 1. ORTEP diagram of Na$_2${[Na$_{0.5}$[Ga(SHI)]$_4$]$_2$(μ_2-OH)$_4$}$^-$ (**1**). Ga$_R$ and Ga$_{R'}$ are gallium atoms from different 12-MC-4 rings, and O$_H$ is a hydroxide bridging between gallium atoms. Selected averaged separations (Å) and angles (deg): Ga$_R$-Ga$_R$ = 4.64; Ga$_R$-Ga$_{R'}$ = 3.54; Ga$_R$-Na$_{CP}$ = 3.73; Ga$_R$-Na$_C$ = 3.60; Ga$_R$-O$_H$ = 1.91; Ga$_R$-O$_X$ = 1.90; Ga$_R$-O$_C$ = 1.95; Ga$_R$-O$_P$ = 1.87; Ga$_{R'}$-N = 1.99; Na$_{CP}$-O$_X$ = 2.43; Na$_C$-O$_X$ = 2.52; Na$_C$-O$_S$ = 2.39; Na$_{CP}$-O$_{OOP}$ = 1.66; Na$_C$-O$_{OOP}$ = 1.68; CS(MC) = 0.56; CS(MCp) = 1.07; BD = 2.62; N-Ga$_R$-O$_X$ = 83; Ga$_R$-O$_X$-N = 112; O$_X$-N-Ga$_R$ = 116. Abbreviations used: Ga$_R$ = *ring*(1) gallium; Ga$_{R'}$ = ring(2) gallium; Na$_{CP}$ = encapsulated sodium; Na$_C$ = capping sodium; O$_H$ = bridging hydroxide; O$_X$ = hydroximate oxygen; O$_C$ = hydroximate carbonyl oxygen; O$_P$ = phenolate oxygen; O$_S$ = solvent oxygen; Na$_{CP}$-O$_{OOP}$ = out-of-plane distance for encapsulated metal based on best least-squares plane for O$_X$ atoms; Na$_C$-O$_{OOP}$ = out-of-plane distance for capping metal based on best least-squares plane for the O$_X$ atoms; CS(MC) = cavity radius of 12-MC-4 ring; CS(MCp) = cavity radius of metallacryptate; BD = bite distance.

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(1) Bajaj, A. V.; Poonia, N. S. *Coord. Chem. Rev.* **1988,** *87,* 55. Dietrich, B. *J. Chem. Educ.* **1985,** *62,* 954. Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 89. Lehn, J.-M. *Structure and Bonding*; Springer-Verlag: New York, 1973; Vol. 16, p 1.

(2) H$_3$SHI is salicylhydroxamic acid. The nomenclature pattern for metallacrowns is M$'_{m'}$A$_a$[X-MC$_{\mathrm{M^{n+}H(L)}}$-Y] where X and Y indicate ring size and maximum number of oxygen donor atoms, MC specifies a metallacrown, M and n are the ring metal and its oxidation state, and H is the identity of the second heteroatom forming the metallacrown core. The ligand is specified by (L). There are m' captured metals (M$'$) bound to the ring oxygens and a bridging anions (A) spanning M and M$'$. Thus, Mn(OAc)$_2$[12-MC$_{\mathrm{Mn^{3+}N(SHI)}}$-4] indicates the core structure of 12-crown-4 with the carbon atoms replaced by Mn(III) and N atoms throughout the ring. An Mn(II) is captured, and there are two bridging acetates linking ring and captured metals. A vacant metallacrown is described by the VO^{3+} analogue 9-MC$_{\mathrm{VO^{3+}N(SHI)}}$-3. Additional descriptors of chirality for the ring and captured metal ions have been omitted in this definition. The proposed nomenclature for metallacryptates is M$''_{m''}$[M$'_{m'}${(X-MC$_{\mathrm{M^{n+}H(L)}}$-Y)$_2$(Z)$_z$}], where there are m' atoms of M$'$ in the metallacryptand cavity, m'' atoms of M$''$ capping the metallacryptate, and z atoms of Z forming the bridge between fused metallacrown ring metals. All other symbols are defined as for metallacrowns.

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(8) Lah, M. S.; Pecoraro, V. L. *Inorg. Chem.* **1991,** *30,* 878.

(9) X-ray parameters for Na[Na$_2${[Na$_{0.5}$[Ga(salicylhydroximate)]$_4$]$_2$(μ_2-OH)$_4$}], **1**: Na$_4$Ga$_8$C$_{92}$H$_{126}$N$_{20}$O$_{43}$, 2850 g/mol, $P\bar{1}$; a = 14.654(3) Å; b = 14.819(5) Å; c = 16.441(4) Å; α = 99.05(2)°; β = 107.32(2)°; γ = 114.40(2)°; V = 2939(1) Å^3; Z = 1; ρ_{calcd} = 1.61 g/cm^3; ρ_{obs} = 1.62 g/cm^3; λ(Mo Kα) = 0.7107 Å; μ(Mo Kα) = 19.0 cm^{-1}; crystal dimensions 0.62 × 0.68 × 0.74 mm; largest residual 0.91 e/Å^3. The intensities of 10 864 unique reflections were measured between 0 $< 2\theta <$ 55° at room temperature on an R$\bar{3}$ diffractometer using Mo Kα radiation. The structure was solved by direct methods with SHELXTL-PLUS. Anisotropic thermal parameters were used for all non-hydrogen atoms. For 7777 data with $I > 3\sigma(I)$, the final R = 0.052, R_w = 0.053. Anal. Calcd for **1**: Ga, 19.57; Na, 3.23; C, 38.77; H, 4.46; N, 9.81. Found: Ga, 17.23; Na, 2.93; C, 38.54; H, 4.17; N, 9.75. ^{1}H NMR spectrum of **1** in DMF-d_7 gives clean resonances at 6.5 (quartet), 6.6 (doublet), 7.0 (sextet), and 7.8 (quartet) ppm.

(10) Fischer, J.; Ricard, L.; Weiss, R. *J. Am. Chem. Soc.* **1976,** *98,* 3050. Creaser, I.; Heckel, M. C.; Neitz, R. J.; Pope, M. T. *Inorg. Chem.* **1993,** *32,* 1573.

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the first example of binding a metal to a metallacrown ring structure without a bridging anion such as acetate, sulfate, or chloride assisting metal sequestration. The third Na(I) is found in the cavity formed by the $[(12\text{-MC}_{\text{Ga}^{3+}\text{N(SHI)}}\text{-}4)_2(\text{OH})_4]^{4-}$ unit. It is eight-coordinate with a square-prismatic polyhedron. This encapsulated sodium ion is displaced 1.66 Å above and below the best least-squares plane of oxygen atoms (average $\text{Na}_{\text{CP}}\text{–O}_{\text{X}}$ = 2.43 Å), while the other captured sodium ions are displaced from the ring by 1.68 Å. The cavity radius of the metallacryptate is 1.07 Å, which is ideal for sequestering Na(I) with a 1.18 Å radius.[11] For comparison, the 2.2.2 cryptand (log $K_{\text{Na}} = 3.9$) has a cavity radius[12] of 1.16 Å. The dimensions of the metallacryptate (based on phenyl ring carbons) are 1.07 nm × 1.07 nm × 0.87 nm (Figure 1), making this complex a true nanoparticle.

The solution speciation of the metallacryptate **1** was investigated by ESI-MS[13] and Ga-EXAFS.[14] The ESI-MS of **1** in CH_3CN has a molecular ion at 1895 *m/z* (base peak), with the only other significant peak, >10% of base, corresponding to $\text{Na}[\text{Na}\{12\text{-MC}_{\text{Ga}^{3+}\text{N(SHI)}}\text{-}4\}_2(\text{OH})_4]^{2-}$. The EXAFS spectra of **1** as a solid and in DMF or MeOH solutions (Figure 2a) give virtually identical data and are in agreement with the crystal structure. This includes the inter-ring $\text{Ga}_{\text{R}}\text{-Ga}_{\text{R}'}$ separation of 3.54 Å (peak at ≈3.1 Å in Figure 2a) that shows that the metallacrowns remain fused in solution. Addition of 4 equiv of acid to **1** in DMF (Figure 2b) disrupts the complex. This combination of Ga-EXAFS spectra and ESI-MS demonstrates convincingly that the complex not only has retained its general integrity in neutral solutions but also maintains an identical structure. These observations are consistent with the apparent stability[3,5,6,8] of other metallacrowns in DMF or acetonitrile. Thus, we conclude that the metallacryptate **1** retains its structure in neutral solutions.

Future studies with **1** and other metallacrowns are focused on further evaluating the pH dependence of the structural integrity of these materials in solution and determining the monovalent cation affinity of the complexes to test a functional analogy to the crown ethers. We also anticipate that the isostructural Fe(III) complex of **1** can be prepared, leading to paramagnetic particles of volume ≈ 1 nm³.

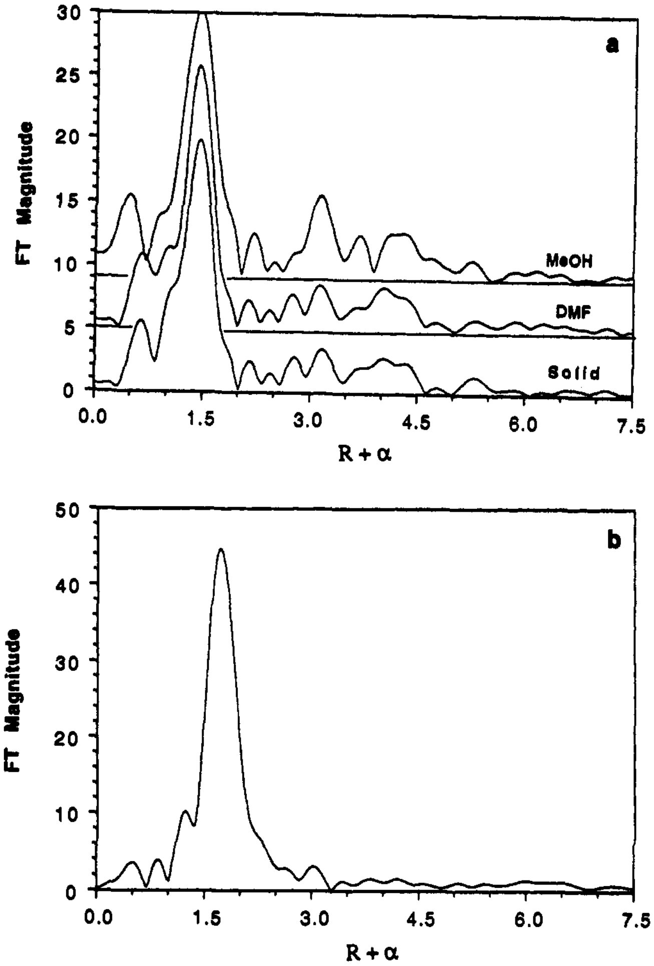

Figure 2. Fourier transforms of the k^3 weighted EXAFS over the range $k = 2.0\text{–}12.5$ of $\text{Na}_2\{[\text{Na}_{0.5}[\text{Ga(SHI)}]_4]_2(\mu_2\text{-OH})_4\}^-$ (**1**). (a) Solid at 40 K; in DMF at 40 K; in MeOH at 10 K. The greater intensity of the $\text{Ga}_{\text{R}}\text{-Ga}_{\text{R}'}$ peak at $R + \alpha = 3.1$ Å for the MeOH data is due to reduced thermal vibrations at lower temperature. (b) in DMF with 4 equiv of HCl added.

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Supplementary Material Available: Tables of fractional atomic positions, anisotropic thermal parameters of all non-hydrogen atoms, and a complete set of bond distances and bond angles for **1**; Figure 3, a complete numbering scheme for all atoms; Figure 4, the ESI-MS of **1** in CH_3CN; Figure 5, the EXAFS data of the solid and solution samples of **1** (18 pages); observed and calculated structure factors for **1** (38 pages). Ordering information is given on any current masthead page.

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(11) For eight-coordinate sodium from: Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(12) The cavity size of the 2.2.2 cryptand was calculated on the basis of the coordinates for the X-ray structure of Ca(2.2.2) cryptate (Metz, P. B.; Moras, D.; Weiss, R. *Acta Crystallogr.* **1973**, *B29*, 1377) using 1.36 Å as the radius for the oxygen atoms.

(13) The Electrospray Ionization Mass Spectrum (ESI-MS) was collected on a Vestec quadrupole mass spectrometer with a repeller voltage of 20 V.

(14) The solid sample was prepared as a finely ground powder in BN supported on Kapton tape. A portion of the solid was dissolved in DMF, with and without 4 equiv of HCl or MeOH (10 mM in 1), loaded into a Lucite cuvette with Kapton windows, and quickly frozen in liquid nitrogen. X-ray absorption spectra were measured at the National Synchrotron Light Source beamline X9A using a Si[111] crystal monochromator with a post monochromator mirror for harmonic rejection; and at the Stanford Synchrotron Radiation Laboratory beamline VII-3 employing a 50% detuned Si[220] double crystal monochromator. Data for the solid and DMF solution were measured in transmission mode, with the sample held at ca. 40 K using a Displex cryostat. The methanol and HCl samples were held at 10 K in an Oxford cryostat and measured by fluorescence.