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Heavy Alkaline-Earth Polyether Carboxylates. The Crystal Structure of $\{Ca[OOC(CH_2)O(CH_2)_2]_2O(H_2O)_2\}_2$[1]

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Introduction

The search for reagents useful as precursors to group 2 oxide-based ceramic materials has witnessed unprecedented activity during the last decade.[2−5] Metal alkoxides and β-diketonate derivatives have been widely investigated for these purposes, although there has also been interest in complexes of noncyclic polyether alcohols and acids. For example, the monomeric polyether alkoxides $Ba[O(CH_2CH_2O)_nCH_3]_2$ ($n = 2, 3$) synthesized by Rees are liquid at room temperature,[6] and the "lariat" barium complex $Ba(RCOCHC(NR')Me)_2$ ($R = t$-Bu; $R' = (CH_2CH_2O)_2Me$) has been used with lead bis(dipivaloylmethanide) and water-saturated O_2 to deposit films of $BaPbO_3$.[7] Mixtures of barium and titanium methoxyethoxides ($M(OCH_2CH_2OCH_3)_n$; M = Ba ($n = 2$); M = Ti ($n = 4$)) have served as a source of $BaTiO_3$ ceramics via sol−gel methods.[8]

Although synthetic procedures for alkoxides can often be extended to carboxylates, fewer examples of polyether carboxylates with electron-poor metals are known. Pyruvic acid oxime complexes of titanium have been used to prepare anatase TiO_2 below 300 °C,[9] and Apblett has described viscous liquid polyether carboxylates of yttrium that can serve as precursors for Y_2O_3.[10] One might expect related complexes to be accessible with the group 2 metals, and we report here the synthesis and characterization of polyether carboxylates of the heavy alkaline-earth metals calcium, strontium, and barium.

Experimental Section

Materials. 2-(2-Methoxyethoxy)acetic acid (Hmeaa) and 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (Hmeeaa) were obtained commercially from Aldrich and were distilled prior to use. 3,6,9-Trioxaundecanedioic acid (Htodd) was used as received from Fluka. All of the compounds were formed by the reaction of the free acid with the appropriate metal hydroxides in deionized water. Details are given for the preparation of $Ca(meaa)_2(H_2O)_2$; the calcium derivatives of the other carboxylic acids were formed in the same way on a similar scale. The strontium and barium compounds were prepared analogously.

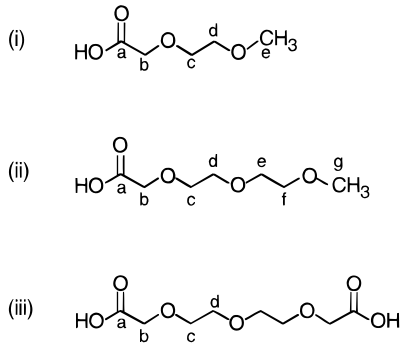

Figure 1. ^1H and ^{13}C NMR lettering designations for 2-(2-methoxyethoxy)acetic acid (meaa) (i), 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (meeaa) (ii), and 3,6,9-trioxaundecanedioic acid (todd) (iii).

Physical Measurements. Proton NMR spectra were obtained using Bruker NR-300 and AM-400 spectrometers at 300 and 400 MHz, respectively, and referenced to the residual proton resonances of either $CDCl_3$ (δ 7.24) or D_2O (δ 4.63). Carbon NMR spectra were obtained at 50.3 and 100.6 MHz on Bruker NR-200 and AM-400 instruments and were externally referenced. Where pertinent, DEPT pulse sequences were used for the unambiguous assignment of carbon resonances (see Figure 1 for assignment letters). Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. TGA measurements were performed on a TA Instruments Hi-Res 2950 thermogravimetric analyzer.

Synthesis of $Ca(meaa)_2(H_2O)_2$. $Ca(OH)_2$ (0.437 g, 5.90 mmol) and Hmeaa (1.45 g, 10.8 mmol) were placed in a 125 mL Erlenmeyer flask. H_2O (50 mL) was added, and the mixture was stirred for 3 h. The product was obtained by rotary evaporation of the solution, leaving 1.73 g (93%, based on acid) of calcium bis[2-(2-methoxyethoxy)acetate] dihydrate$(H_2O)_2$ as a transparent, viscous oil. The product could be desolvated by placing it under vacuum (10^{-3} Torr, 6 h), producing a white flaky solid. Anal. Calcd for $C_{10}H_{18}CaO_8$: C, 39.21; H, 5.92; Ca, 13.08. Found: C, 38.50; H, 5.68; Ca, 13.10. ^1H NMR (D_2O): δ 3.77 (s, 2H, H_b); δ 3.47−3.49 (m, 2H, H_c); δ 3.43−3.45 (m, 2H, H_d); δ 3.18 (s, 3H, H_e). ^{13}C NMR ($CDCl_3$): δ 176.40 (C_a); δ 71.48 (C_b); δ 70.92 (C_c); δ 68.96 (C_d); δ 59.25 (C_e). Principal IR bands (KBr pellet, cm^{-1}): 3410 (br, $\nu(H_2O)$); 2927 (w); 2264 (w); 1706 (m); 1603 (s, $\nu_{asym}(CO_2)$); 1428 (m); 1327 (w); 1125 (m); 1086 (m); 904 (w); 846 (w).

Synthesis of $Ca(meeaa)_2(H_2O)$. $Ca(meeaa)_2(H_2O)$ was isolated in quantitative yield as a transparent, viscous oil. Anal. Calcd for $C_{14}H_{28}CaO_{11}$: C, 40.77; H, 6.84; Ca, 9.72. Found: C, 40.90; H, 6.58; Ca, 8.60. ^1H NMR (D_2O): δ 3.82 (s, 2H, H_b); δ 3.77−3.79 (m, 6H, H_c, H_d, H_e); δ 3.55−3.57 (m, 2H, H_f); δ 3.23 (s, 3H, H_g). ^{13}C NMR (D_2O)SPCLN δ 176.92 (C_a); δ 71.76 (C_b); δ 70.93 (C_c); δ 70.05 (C_d, C_e); δ 69.96 (C_f); δ 59.09 (C_g). Principal IR bands (KBr pellet, cm^{-1}): 3400 (br, $\nu(H_2O)$); 2924 (m); 2886 (m); 2328 (w); 1731 (w); 1600 (s, $\nu_{asym}(CO_2)$); 1427 (m); 1324 (m); 1248 (w); 1199 (w); 1120 (s); 1086 (s); 1027 (w); 943 (w); 904 (w); 847 (w); 711 (w); 667 (w); 604 (w); 497 (w).

Synthesis of $Ca(todd)(H_2O)_2$. $Ca(todd)(H_2O)_2$ was isolated in 98% yield as a white solid. Anal. Calcd for $C_8H_{16}CaO_9$: C, 32.43; H, 5.44; Ca, 13.53. Found: C, 32.20; H, 5.48; Ca, 13.56. ^1H NMR (D_2O): δ 3.94 (s, 4H, H_b); δ 3.65 (s, 8H, H_c, H_d). ^{13}C NMR (D_2O): δ 178.10 (C_a); δ 70.95 (C_b); δ 69.27 (C_c); δ 69.04 (C_d). Principal IR bands (KBr pellet, cm^{-1}): 3431 (br, $\nu(H_2O)$); 3264 (sh); 2925 (w); 2330 (w); 1594 (s, $\nu_{asym}(CO_2)$); 1433 (m); 1332 (m); 1255 (w); 1125 (m); 1115 (m); 1104 (m); 1069 (m); 906 (w); 697 (w); 605 (w); 490 (w).

X-ray Crystallography. A needle-shaped crystal of $Ca(todd)(H_2O)_2$ was grown from water. All measurements were performed on a Rigaku AFC6S diffractometer at Vanderbilt University with graphite-monochromated Mo Kα radiation. Pertinent crystal and data collection parameters for the study are given in Table 1. The space group $P2_1/n$ was uniquely determined from systematic absences. Data were reduced to a unique set of intensities and associated σ values in the usual manner. No correction for decay or absorption was necessary. The structure was solved using direct methods (SHELXS-86) and Fourier techniques.

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Table 1. Crystallographic Data for Ca(todd)$(H_2O)_2$

formula: $C_{16}H_{32}Ca_2O_{18}$
fw = 592.6
$a = 7.975(2)$ Å
$b = 10.513(2)$ Å
$c = 14.711(2)$ Å
$\beta = 91.93(2)°$
$V = 1232.7(4)$ Å^3
$Z = 2$ (dimers/cell)
space group: $P2_1/n$ (No. 14)
$T = 20$ °C
$\lambda = 0.710\ 73$ Å
$\rho_{calcd} = 1.596$ g cm^{-3}
$\mu = 5.30$ cm^{-1}
R^a ($I > 3.0\sigma(I)$) = 0.066
$R_w{}^b$ ($I > 3.0\sigma(I)$) = 0.098

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o{}^2)]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Ca(todd)$(H_2O)_2$

atoms	distance	atoms	distance
Ca(1)···Ca(1)′	3.891(4)	O(3)−C(3)	1.41(1)
Ca(1)−O(1)	2.432(7)	O(4)−C(4)	1.42(1)
Ca(1)−O(1)′	2.449(7)	O(4)−C(5)	1.46(1)
Ca(1)−O(3)	2.457(7)	O(5)−C(6)	1.40(1)
Ca(1)−O(4)	2.625(7)	O(5)−C(7)	1.40(1)
Ca(1)−O(5)	2.459(8)	O(6)−C(8)	1.25(1)
Ca(1)−O(7)	2.430(7)	O(7)−C(8)	1.24(1)
Ca(1)−O(8)	2.405(7)	C(1)−C(2)	1.50(1)
Ca(1)−O(9)	2.463(7)	C(3)−C(4)	1.51(2)
O(1)−C(1)	1.27(1)	C(5)−C(6)	1.43(2)
O(2)−C(1)	1.24(1)	C(7)−C(8)	1.50(1)
O(3)−C(2)	1.44(1)		

atoms	angle	atoms	angle
Ca(1)−Ca(1)−O(7)	73.2(2)	O(7)−C(8)−C(7)	118.0(9)
Ca(1)−Ca(1)−O(8)	79.8(2)	O(4)−Ca(1)−O(5)	63.6(3)
Ca(1)−Ca(1)−O(9)	116.7(2)	O(5)−Ca(1)−O(7)	63.2(2)
O(1)−Ca(1)−O(1)′	74.3(2)	O(8)−Ca(1)−O(9)	78.4(2)
O(1)−Ca(1)−O(3)	64.0(2)	Ca(1)−O(1)−Ca(1)′	105.7(2)
O(1)−Ca(1)−O(7)	77.2(2)	Ca(1)−O(1)−C(1)	126.0(6)
O(1)−Ca(1)−O(8)	81.3(2)	Ca(1)−O(7)−C(8)	125.7(6)
O(3)−Ca(1)−O(4)	62.5(2)	O(1)−C(1)−O(2)	127(1)
O(6)−C(8)−O(7)	126(1)	O(1)−C(1)−C(2)	116.9(9)
O(6)−C(8)−C(7)	116.0(9)	O(2)−C(1)−C(2)	116.2(9)

All of the non-hydrogen atoms were refined isotropically. As not all of the hydrogen atoms were evident in difference Fourier maps, their positions were calculated using idealized geometries based on packing considerations and d(C−H) = 0.95 Å. One hydrogen on each coordinated water molecule was located, and its thermal parameters were refined. The positions of all hydrogens were fixed for the final cycles of refinement. A final difference map was featureless. Selected bond distances and angles are listed in Table 2.

Results and Discussion

Synthesis of Carboxylate Derivatives. Several different methods were attempted for the synthesis of the alkaline-earth derivatives of Hmeaa, Hmeeaa, and Htodd in nonaqueous media. The reaction of bis[(trimethylsilyl)amido]calcium[11] with the free acid in toluene did not cleanly lead to $Ca(O_2CR)_2$ products, nor did a metathetical synthesis using sodium 2-(2-methoxyethoxy)-acetate with either $CaCl_2$ or CaI_2. The reaction of $CaCO_3$ with the free acid in either methanol or THF was also ineffective.

The most successful route for the synthesis of the carboxylates was the reaction of the metal hydroxides and the free acids in deionized water (eq 1). All of the carboxylates were isolated in ≥85% yield on removal of the water.

$$\mathrm{Ae(OH)_2} + (2/n)\mathrm{R(CO_2H)}_n \xrightarrow{\mathrm{H_2O}} \mathrm{Ae(O_2CR)}_{2/n}\mathrm{(H_2O)}_m + 2\mathrm{H_2O} \quad (1)$$

Chemical Properties. The colorless calcium and strontium derivatives of Hmeaa (Ae(meaa)$_2$(H$_2$O)$_n$; Ae = Ca (n = 2); Sr (n = 4)) and Hmeeaa (Ae(meeaa)$_2$(H$_2$O)$_n$; Ae = Ca (n = 1); Sr (n = 7)) form extremely viscous liquid derivatives that can be drawn into long fibers; the slightly yellow barium compounds (Ba(meaa)$_2$(H$_2$O)$_5$, Ba(meeaa)$_2$(H$_2$O)$_2$) are much less viscous. The amount of water associated with the compounds can easily be changed by placing them under vacuum; reduction of the water content is accompanied by transformation of the oils into hygroscopic solids. The solids return to their initial oily state if exposed to the atmosphere for more than 24 h. All six monocarboxylates are highly soluble in a range of solvents including H_2O, methanol, acetone, THF, $CHCl_3$, and CH_2Cl_2; the degree of hydration has little effect on solubility. The three Hmeeaa derivatives are also soluble in aromatic solvents.

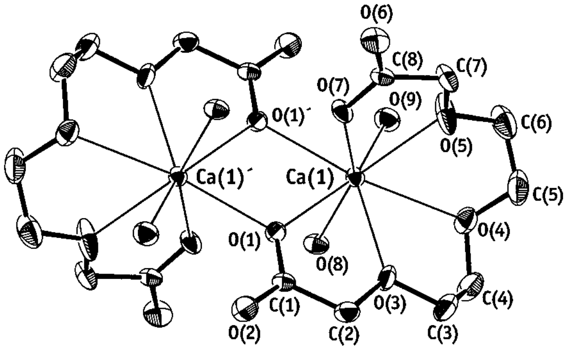

Figure 2. ORTEP diagram of the non-hydrogen atoms of Ca(todd)-(H$_2$O)$_2$, giving the numbering scheme used in the tables. Thermal ellipsoids are shown at the 35% level.

Unlike the carboxylates prepared from the Hmeaa and Hmeeaa, the calcium, strontium, and barium derivatives of the dicarboxylic 3,6,9-trioxaundecanedioic acid (Ae(todd)$_2$(H$_2$O)$_n$; Ae = Ca, Sr (n = 2); Ba (n = 4)) are solids at room temperature and display little solubility in solvents less polar than H_2O and methanol.

Thermal Gravimetric Analysis. The polyether carboxylates were examined with TGA under air, and all were found to undergo initial loss of water followed by stepwise decomposition of the ligands. The residual mass left by the Ae(meaa)$_2$(H$_2$O)$_n$ and (Ae(meeaa)$_2$(H$_2$O)$_n$ derivatives on heating to ~900 °C corresponded to the formation of the metal oxides. In the case of the Ae(todd)(H$_2$O)$_n$ complexes, the Sr and Ba derivatives converted cleanly to the carbonates (confirmed by powder XRD); the Ca salt left a mixture of CaO and $CaCO_3$. This behavior is consistent with the greater thermal stability of the carbonates of the larger group 2 metals.[12]

Structure of Ca(todd)(H$_2$O)$_2$. Of the three Ae(todd)(H$_2$O)$_n$ complexes, only the calcium compound provided crystals suitable for X-ray diffraction study. In the solid state, Ca(todd)-(H$_2$O)$_2$ forms a centrosymmetric dinuclear unit in which the carboxylates are twisted into fan-like shapes in an "open crown" arrangement. All of the ether oxygen atoms and both ends of the carboxylates are coordinated to the calcium centers, although one CO_2 group spans the metals through O(1) (μ_2, η^1) and the other is bound in an η^1 fashion through O(7) (Figure 2). Two water molecules are present on each calcium, raising the coordination number to 8 and generating a distorted dodecahedral geometry around the metals. Although a number of calcium dicarboxylate crystal structures are known,[13−17] in none

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of these are both carboxylate groups bound to the same metal; the arrangement found in Ca(todd)$(H_2O)_2$ is undoubtedly dictated by the additional sites for coordination provided by the polyether backbone.

The twisting in the $[todd]^{2-}$ ligand is evident in the 78° angle between the two five-membered chelate rings defined by Ca(1)−O(1)−C(1)−C(2)−O(3) and Ca(1)−O(7)−C(8)−C(7)−O(5). With the exception of the somewhat longer Ca(1)−O(4) distance at 2.625(7) Å, the Ca−O(carboxylate) and Ca−O(ether) bonds fall in a comparatively narrow range from 2.430(7) to 2.459(8) Å (Table 2); this illustrates the geometric constraints that the relatively strong Ca−O(ether) bonds exert on the structure. These calcium−oxygen distances compare favorably with the Ca−O(ether) contacts in the eight-coordinate calcium complex benzo-15-crown-5-Ca$(NCS)_2$−MeOH (av = 2.53 Å),[18] values consistent with the crown-like environment.

The center $[Ca(1)-O(1)]_2$ core displays nearly equal Ca(1)−O(1) and Ca(1)−O(1)′ bond lengths of 2.432(7) and 2.449(7) Å, respectively. The two calcium atoms lie within 0.14 Å of the plane of the associated carboxylate groups, an arrangement that is typical for calcium carboxylates.[19] The C(8)−O(6) and C(8)−O(7) bond lengths in the η^1-carboxylate group are equal at 1.24(1) and 1.25(1) Å, respectively. In the η^2 group, the O(1)−C(1) bond length is only marginally longer than the O(2)−C(1) distance (1.27(1) and 1.24(1) Å, respectively); this reflects the higher coordination number around O(1).

The effect of hydrogen bonding between the dinuclear units is apparent in the close contacts between the water and carbonyl oxygen atoms of adjacent units (Figure 3). The O(6) carbonyl oxygen is 2.74(1) Å from both O(8)′ and O(9)′ (related by the transformation ($^1/_2 + x$, $^1/_2 - y$, $^1/_2 + z$). One hydrogen atom located on O(8) is 1.77(1) Å from O(6)′ in an adjacent dimer, forming an O(8)···H···O(6)′ angle of 146°. Although extended arrays of the dinuclear units do exist in the crystal, they are unlike the layers of Ca ions, carboxylate groups, and water molecules that are typically found in metal dicarboxylate structures.[13] Evidence for weak intramolecular hydrogen bonding is provided by the close contact (2.67(1) Å) between the O(2)′ carbonyl oxygen and the O(9) water oxygen (related by the inversion center); one hydrogen atom located on O(9) is 2.40(1) Å from O(2)′.

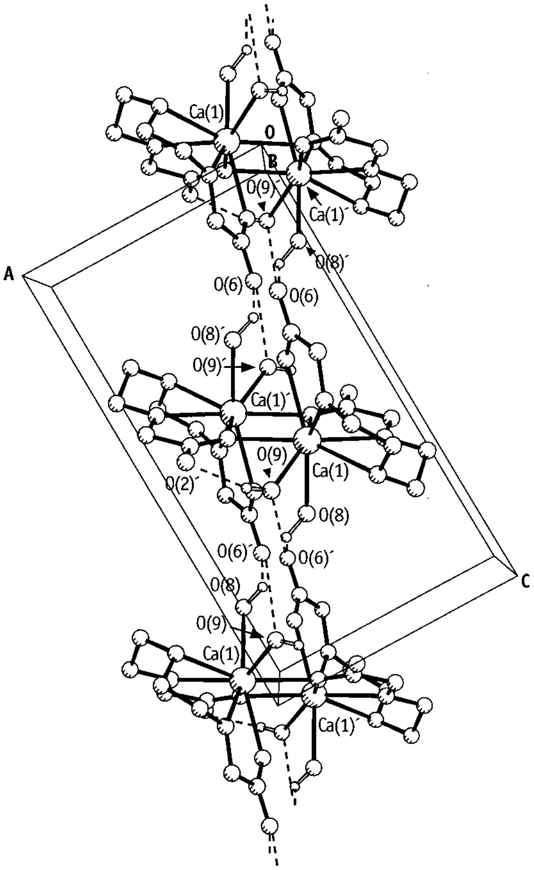

Figure 3. Portion of the packing diagram of Ca$(todd)_2(H_2O)_2$; the primed and unprimed intermolecular contacts are related by the transformation $^1/_2 + x$, $^1/_2 - y$, $^1/_2 + z$.

In summary, we have found that, depending on whether a mono- or dicarboxylic acid is involved, polyether carboxylates of the heavy group 2 elements display a considerable range of physical properties. The drive to coordinate both the carboxylate and the ether oxygens in Ca(todd)$(H_2O)_2$ produces a novel coordination environment that may exist in related $[todd]^{2-}$ and other dicarboxylate derivatives. Depending on the metal and carboxylate involved, the salts described here have been found to function as precursors to metal oxides and/or carbonates.

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Supporting Information Available: Details of the synthesis of the strontium and barium carboxylates and tables of fractional coordinates, bond distances and angles, and anisotropic thermal parameters for Ca(todd)$(H_2O)_2$ (6 pages). Ordering information is given on any current masthead page.

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