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Solid-State Polymerization of Aquabis(3-butenoato)calcium

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Aquabis(3-butenoato)calcium, $Ca(C_4H_5O_2)_2(H_2O)$ (**1**), the monomeric precursor for a new solid-state polymerization reaction, was synthesized from 3-butenoic acid and calcium carbonate. Irradiation of solid **1** with ^{60}Co γ-rays (305 kGy dose) leads to high molecular weight calcium poly(3-butenoate), $\bar{M}_w = 400\,000$, in 97% yield. Prior to this report, solid-state reactivity was unknown for metal salts of β, γ-unsaturated carboxylic acids. An X-ray structure determination of **1** shows it to be a two-dimensional coordination polymer. The most outstanding feature of the crystal packing is a bilayer arrangement, leading to nearly parallel, reactive vinyl groups, with short $-C{=}C- \cdots -C{=}C-$ contacts of 3.73 and 3.90 Å along the crystallographic *b* direction. Crystal data for **1**: monoclinic, space group $P2_1/n$, $a = 5.9083(13)$, $b = 6.7877(18)$, $c = 27.927(10)$ Å; $\beta = 92.42(2)°$; $V = 1119.0(5)$ Å^3; $Z = 4$; $R = 0.091$, $R_w = 0.103$ for 464 data for which $I > 1.96\sigma(I)$.

Introduction

The solid-state reactivity of metal alkenoates containing terminal double bonds was first investigated by Morawetz and Rubin in 1962.[1] In this early, elegant study, it was observed that crystalline potassium acrylate, when exposed to 1−8 kGy ^{60}Co γ-rays, reacted to form potassium polyacrylate, with molecular weights in the range 100 000−400 000. The authors also noted that the potassium salt was much more reactive than the corresponding lithium and sodium salts, and, in a far-reaching statement, proposed that reactivity was controlled by the geometry of the crystal lattice. The crystal structure of potassium acrylate remains unknown to this date, but the observed orthorhombic unit cell, with $a = 20.5$, $b = 4.15$, and $c = 5.73$ Å, requires an infinite set of reactive centers at distances ≤ 4.15 Å. This value is consistent with the *topochemical postulate*, which requires that reactive groups capable of undergoing solid-state dimerization or polymerization be at distances ≤ 4.2 Å.[2−4] Following this early work, studies of the solid-state reactivity of various phases of calcium acrylate and barium methacrylate were carried out.[5−7] Later, crystal structures of calcium acrylate dihydrate,[8] anhydrous barium methacrylate,[9] and barium methacrylate monohydrate[10] were determined. However, the authors of these papers did not consider putative reaction pathways for polymerization using the detailed geometric information available from these determinations.

Our current research program seeks to discover and characterize new solid-state reactions involving metal salts and complexes of unsaturated carboxylate ligands.[11,12] When possible, we obtain detailed structural information on the reactants, with a view to establishing and extending geometric criteria for solid-state reactivity.[13,14] In recent studies of metal alkenoate solid-state chemistry, we have focused on α, β-unsaturated carboxylates substituted at the β-carbon atom. Upon exposure to ^{60}Co γ-rays, metal complexes and salts containing these enoates exhibit extraordinary solid-state reactivity; examples include the γ-ray-induced stereospecific trimerization of sodium *trans*-2-butenoate to give *one of eight* possible diastereoisomers[15] and the stereospecific cyclodimerization of calcium *trans*-2-butenoate to form *one of four* possible diastereoisomers.[16] Two outstanding features of alkenoate solid-state chemistry suggested further experiments. First,

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metal alkynoates and alkenoates exhibit widespread solid-state reactivity, whereas the corresponding “all-organic” salts are stable to ionizing radiation.[14,17] Second, many of these materials, particularly those containing metal atoms with small radii, crystallize in a bilayer motif.[18] A bilayer arrangement of unsaturated organic groups will foster the occurrence of parallel unsaturated groups, with short distances between the reactive centers.[18]

As an extension of the ideas just presented, one might expect activation and alignment of unsaturated centers in salts of the *less reactive* β,γ-unsaturated carboxylic acids. Before we began this study, solid-state reactivity was unknown for this class of compounds. We report here the synthesis, X-ray structure determination, and solid-state polymerization of aquabis(3-butenoato)calcium.

Experimental Section

Fourier transform infrared (FTIR) spectra were recorded using a Perkin-Elmer Paragon 1000 spectrophotometer. The NMR spectra were recorded on a Varian XL-300 spectrometer. A Gammacell 220 Irradiation Chamber (Atomic Energy of Canada, Ltd.) equipped with a ^{60}Co source was used for γ-irradiation experiments. Molecular weight determinations were carried out on a locally constructed gel permeation chromatography (GPC) apparatus at the Max-Planck-Institut für Polymerforschung, Mainz (Millipore-Waters WISP710B sample changer; 590 pump; ERMA Optical Works detector ERC 7511; TosoHaas columns TSK 3000-, 5000-, and 6000-PWXL).

Aquabis(3-buenoato)calcium, $Ca(CH_2{=}CHCH_2CO_2)_2(H_2O)$ (1). Salt **1** was prepared by adding 3-butenoic acid (Aldrich, 0.835 mL, 9.51 mmol) to a stirred mixture of $CaCO_3$ (0.476 g, 4.76 mmol) in ≈50 mL of H_2O; CO_2 evolved immediately upon addition. The reaction mixture was stirred for 3 h, after which unreacted $CaCO_3$ was removed by filtration. The filtrate was allowed to evaporate in a fume hood (3−4 days) and the resulting **1** (0.977 g, 4.65 mmol, 97.7%) was dried in air for 1 day: IR (KBr) 3448, 3081, 2987, 1582, 1547, 993, 912 cm^{-1}; ^{1}H NMR (D_2O) δ 5.94 (1 H, ddt, $J = 14.2$, 10.2, 7.0 Hz), 5.13 (1 H, br d, $J = 14.2$ Hz), 5.10 (1 H, br d, $J = 10.2$ Hz), 2.97 (br d, 2 H, $J = 7.0$ Hz).

For growth of single crystals, ∼10 mg of **1** was dissolved in a minimal amount (3 mL) of H_2O and transferred to a 45 × 15 mm vial. The vial was placed in an Erlenmeyer flask containing acetone and sealed. After 3 days, long needles of **1** were obtained by vapor diffusion. The experimental density, measured by neutral buoyancy in hexanes/CCl_4, was 1.38(3) g/cm^3.

Irradiation of Complex 1. Samples of crystalline **1** (0.5 g) were placed in 2-dram glass vials, which were then purged with N_2 and sealed. The samples were irradiated with ^{60}Co γ-rays (254 Ci, nominal dose rate 212 Gy/h); doses varied from 10.2 to 305 kGy. At various times during the irradiation, a 0.2-g aliquot was removed from a sample vial, and that vial was not returned to the irradiator. Each sample was stirred for 2 d in 30 mL of MeOH; after filtration and washing, each sample was air-dried. The product was recovered by filtration and weighed; reactant was recovered to check mass balance. Inspection of ^{1}H NMR spectra revealed that this was an effective method for separation of monomer and polymeric product. Doses versus percent conversion for representative experiments: 10.2 kGy, 0.17%; 20.4 kGy, 1.9%; 40.7 kGy, 12%; 50.9 kGy, 16%; 61.1 kGy, 20%; 76.3 kGy, 23%; 102 kGy, 39%; 153 kGy, 61%; 305 kGy, 97%. Post-irradiation polymerization (60 °C, 1−5 d), after radiation doses ≤25 kGy, gave no significant improvement in conversion. Infrared (IR) spectra of the irradiated material showed a decrease in the intensity of the $H{-}C{=}C{-}$ bending modes (993, 912 cm^{-1}) with increasing exposure. For spectroscopic analysis, the polymer (10 mg) was dissolved in D_2O (1−1.5 mL) by using sonication for 3 h: ^{1}H NMR (D_2O) δ 1.9−2.2 (2 H, br d), 1.6−1.8 (1 H, br d), 1.1−1.5(2 H, br d). ^{13}C NMR (D_2O, dioxane internal standard, line broadening = 20) δ 183−185 (C), 67 (dioxane), 23.0−44.4 (CH_2, CH). Additionally, there was a small peak located at δ 0.8 (^{1}H NMR) which may be due to a methylene proton, as well as unidentified peaks in the δ 117−148 region (^{13}C NMR). Additional peaks below δ 25 in the ^{13}C NMR spectrum do not correspond to product and may be related to the methyl proton resonances at δ 0.8 in the ^{1}H NMR spectrum. The molecular weight was determined by size exclusion chromatography, using a 1:9 CH_3CN/H_2O mixture (0.03 M in NaH_2PO_4 and 0.15 M in NaCl; sample concentration, 1 g/L) as solvent, and poly(ethylene oxide) as standard. The molecular weight distribution was bimodal, with maxima at 10^5 and 10^6; $\bar{M}_w = 3.98 \times 10^5$; $\bar{M}_n = 7.90 \times 10^4$; $D = 5.04$.

Table 1. Data for the X-ray Diffraction Study of 1[a]

parameter	value
chemical formula	**1**, $Ca(C_4H_5O_2)_2(H_2O)$
a, Å	5.9083(13)
b, Å	6.7877(18)
c, Å	27.927(10)
β, deg	92.42(2)
V, Å^3	1119.0(5)
Z	4
formula wt	226.246
space group	$P2_1/n$ [C^5_{2h}; no. 14]
T, °C	21(1)
λ (Mo$K\bar{\alpha}$), Å	0.71073
ρ_{obs}, g cm^{-3}	1.38(3)
ρ_{calc}, g cm^{-3}	1.355
μ, cm^{-1} (Mo$K\bar{\alpha}$)	5.40
transmission factors	0.954−0.998
R	0.0911
R_w	0.103

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$.

X-ray Structure Determination of 1. Single crystals of **1** were grown by the diffusion technique just described. Most crystals were extremely thin, often curved in shape, and/or easily deformed. After many trials, a more suitable crystal was found and mounted on a glass fiber. Because earlier experiments indicated that crystals decomposed rapidly under CuKα irradiation, the crystal was transferred to an Enraf-Nonius CAD4-Turbo diffractometer equipped with MoKα radiation. Data were collected using the Enraf-Nonius EXPRESS program.[19] Inspection of the standard reflections indicated that no decomposition had occurred during data collection. The crystal had poor diffraction quality, with no observable reflections at $2\theta > 41°$. After data reduction, 464 reflections with $I > 1.96\sigma(I)$ were used in structure solution and refinement.[20,21] The structure was solved by using the Patterson function and successive difference Fourier syntheses. Because of the paucity and poor quality of the data, refinement was carried out using restraints. The C−C distances and C−C−C angles were restrained to be at normal values with esd values of 0.05 and 0.5° Å, respectively, and the isotropic displacement parameters of the vinyl C atoms were restrained to increase monotonically.[21−23] This method was highly pre-

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Table 2. Atomic Coordinates for 1[a,b]

Atom	x	y	z	B (Å^2)
Ca(1)	0.8223(6)	0.0150(7)	−0.28171(12)	0.0280
O(1)	1.0978(18)	0.018(2)	−0.3393(4)	0.041(3)
O(2)	1.443(2)	0.039(2)	−0.3084(4)	0.047(4)
O(3)	0.661(2)	−0.1462(19)	−0.2086(4)	0.029(4)
O(4)	0.712(3)	0.175(2)	−0.2029(5)	0.042(5)
O(5)	1.153(2)	−0.0655(19)	−0.2326(5)	0.047(4)
C(1)	1.304(3)	0.014(4)	−0.3441(6)	0.046(5)
C(2)	1.410(6)	−0.078(5)	−0.3864(13)	0.134(12)
C(3)	1.246(8)	−0.094(7)	−0.4246(9)	0.200(13)
C(4)	1.228(11)	0.046(9)	−0.4572(18)	0.275(14)
C(5)	0.655(3)	0.019(4)	−0.1852(5)	0.035(4)
C(6)	0.528(5)	0.024(6)	−0.1395(11)	0.136(11)
C(7)	0.642(9)	−0.099(6)	−0.1048(8)	0.195(12)
C(8)	0.672(11)	−0.034(9)	−0.0570(14)	0.269(14)

[a] Atoms refined using anisotropic displacement parameters are given in the form of the isotropic equivalent displacement parameter defined as: $1.33[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma B_{12} + ac\cos\beta B_{13} + bc\cos\alpha B_{23}]$. [b] Numbers in parentheses in this and following tables are estimated standard deviations (esds) to the least significant digit.

Table 3. Selected Bond Lengths (Å) and Angles (°) for 1[a]

Ca(1)−O(1)	2.337(11)	O(3)−C(5)	1.30(3)
Ca(1)−O(2)[a]	2.336(13)	O(4)−C(5)	1.22(3)
Ca(1)−O(3)	2.537(13)	C(1)−C(2)	1.50(4)
Ca(1)−O(3)[b]	2.318(15)	C(2)−C(3)	1.42(4)
Ca(1)−O(4)	2.562(14)	C(3)−C(4)	1.32(4)
Ca(1)−O(4)[c]	2.356(15)	C(5)−C(6)	1.51(4)
Ca(1)−O(5)	2.403(13)	C(6)−C(7)	1.43(4)
O(1)−C(1)	1.233(19)	C(7)−C(8)	1.41(4)
O(2)−C(1)	1.276(19)		
O(1)−Ca(1)−O(2)[a]	117.8(4)	O(1)−Ca(1)−O(5)	79.7(4)
O(1)−Ca(1)−O(3)	148.6(5)	O(2)[a]−Ca(1)−O(5)	160.7(4)
O(2)[a]−Ca(1)−O(3)	84.2(4)	O(3)−Ca(1)−O(5)	76.6(4)
O(1)−Ca(1)−O(3)[b]	82.9(5)	O(3)[b]−Ca(1)−O(5)	104.7(5)
O(2)[a]−Ca(1)−O(3)	86.5(5)	O(4)−Ca(1)−O(5)	80.6(5)
O(3)−Ca(1)−O(3)[b]	122.7(4)	O(4)[c]−Ca(1)−O(5)	86.8(5)
O(1)−Ca(1)−O(4)	142.9(5)	Ca(1)−O(1)−C(1)	142.7(11)
O(2)[a]−Ca(1)−O(4)	88.3(5)	Ca(1)−O(2)[a]−C(1)[a]	144.9(11)
O(3)−Ca(1)−O(4)	51.2(4)	Ca(1)−O(3)−Ca(1)[c]	108.3(5)
O(3)[b]−Ca(1)−O(4)	72.2(4)	Ca(1)−O(3)−C(5)	92.9(10)
O(1)−Ca(1)−O(4)[c]	86.6(5)	Ca(1)−O(3)[b]−C(5)[b]	156.6(11)
O(2)[a]−Ca(1)−O(4)[c]	86.3(5)	Ca(1)−O(4)−Ca(1)[b]	106.4(6)
O(3)−Ca(1)−O(4)[c]	72.0(4)	Ca(1)−O(4)−C(5)	93.8(11)
O(3)[b]−Ca(1)−O(4)[c]	162.7(4)	Ca(1)−O(4)[c]−C(5)[c]	153.9(13)
O(4)−Ca(1)−O(4)[c]	123.3(4)		

[a] Symmetry operations: a: [$x - 1, y, z$]; b: [$3/2 - x, y + 1/2, -z - 1/2$]; c: [$3/2 - x, y - 1/2, -z - 1/2$].

ferred over the less-desirable option of fixing all or some parameters of "misbehaving" atoms at coordinates obtained from difference maps. Details of the restraints are available as Supporting Information. Final refinement of positional and isotropic displacement parameters for all atoms (anisotropic displacement parameters for Ca, total of 62 parameters) led to $R = 0.091$ and $R_w = 0.103$. Although the structure determination is not of high quality, the coordination of the calcium ion as well as the packing of the complex have been clearly established. All drawings were made using the Oxford University program CAMERON.[23b] Crystal data are presented in Table 1, atomic coordinates in Table 2, and selected bond lengths and angles in Table 3. A complete report is available as Supporting Information and/or a CIF file.

Results and Discussion

Molecular Structure of Complex 1. The local environment of a single, seven-coordinate calcium ion is shown in Figure 1. The donor atoms arise from two crystallographically independent carboxylates (I: C1→ C4, O1, and O2; II: C5→ C8, O3, and O4) as well as additional I and II moieties that are symmetry related.

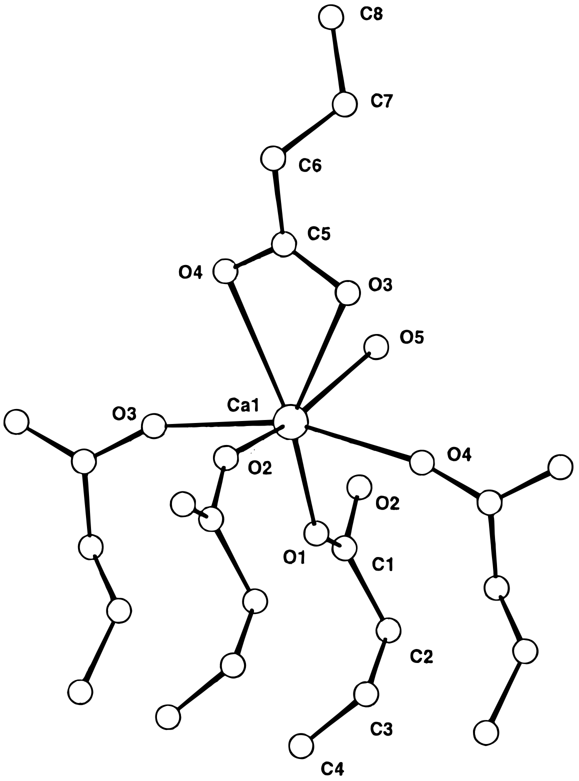

Figure 1. Molecular structure of **1**, showing the coordination of a single calcium ion. Ligands in the asymmetric unit are *fully* labeled; symmetry-related, bridging ligands (see text) are labeled only at the donor atoms.

Thus, carboxylate II provides, through chelation, a pair of O atoms (O3 and O4), whereas symmetry-related molecules of II provide two additional atoms (O3: $3/2 - x, y + 1/2, -z - 1/2$; and O4: $3/2 - x, y - 1/2, -z - 1/2$). Two more carboxylate O atoms (O1; and O2: $x - 1, y, z$) and a water oxygen atom (O5) complete the seven-coordinate complex. Distances from Ca to O range from 2.336 to 2.562 Å, which is near the ranges observed for other seven-coordinate calcium carboxylate salts [$Ca(CH_3COO)_2(H_2O)$, 2.301−2.503 Å, and $Ca(CH_3COO)_2(CH_3COOH)(H_2O)$, 2.352−2.524 Å].[24,25] Other bond distances and angles are normal.

The extensive bridging by carboxylate ligands leads to a two-dimensional coordination polymer based on the calcium complex. The nature of the polymer and bridging is revealed in Figures 2 and 3, which present views of the coordination polymer projected down the crystallographic *b* and *a* axes, respectively. Figure 2 shows that *syn, anti*-bridging by carboxylate I connects complexes along the *a* axis. Similarly, Figure 3 depicts chelation of carboxylate II, with interconnection of calcium complexes along the *b* axis via *anti, anti*-bridging.

Crystal Packing; Solid-State Reactivity. In addition to aiding our understanding of the bridging modes

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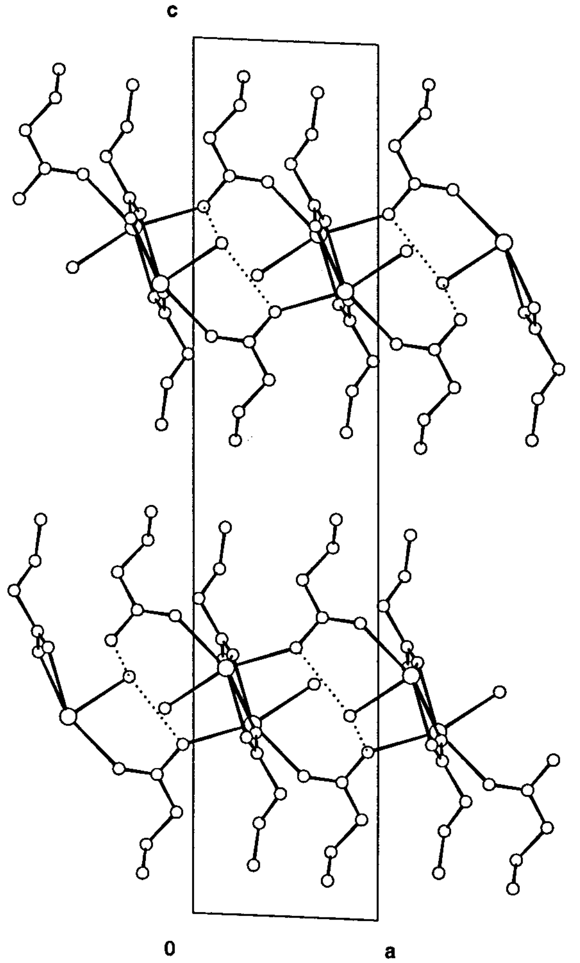

Figure 2. View of the crystal structure down the *b* axis. Dotted lines indicate the O2···O5···O2^a hydrogen bonds (not all are shown to improve clarity).

adopted by the carboxylate ligands, Figures 2 and 3 also clearly show the most important feature of the packing of the two-dimensional coordination polymer. As in other metal carboxylate phases, the organic chains segregate into a hydrophobic layer. In this case and others, these layers meet one another, creating a bilayer motif (see Figures 2 and 3). In the crystal structure of triaquabis(*trans*-2-pentenoato)calcium, one-dimensional coordination polymers are alternately connected by hydrogen bonds in a hydrophilic layer and hydrophobic interactions in a layer similar to that observed here.[18] In the present structure, the "layers" correspond to the hydrophobic tails of the butenoates and the central, metal-bridged area of the coordination polymer. Figure 2 shows that the two halves of the layer are also connected by pairs of hydrogen bonds between the coordinated water and two carboxylate oxygen atoms. Although protons were not located, the following data support the presence of hydrogen bonds: O5···O2^a[x,y,z], 2.87 Å; O5···O2^b[$5/2 - x, y - 1/2, -z - 3/2$], 2.99 Å; O2^a–O5–O2^b, 129.5°.

Inspection of Figure 3 reveals sets of short –C=C– ··· –C=C– contacts along the *b* axis. These contacts occur, left-to-right at the top of the diagram, between C4···C7, 3.73 Å; C8···C3, 3.90 Å, and repeat infinitely. The chain of infinite contacts is generated by the operation [$3/2 - x$, $y + 1/2$, $-z - 1/2$]. The short distances are associated with interplanar angles (for respective vinyl group planes) of 22.3°. The topochemical postulate asserts that solid-state polymerization should occur if reactive groups are parallel and separated by distances ≤4.2 Å.[2–4] The data presented here fit the criteria of the topochemical postulate well.

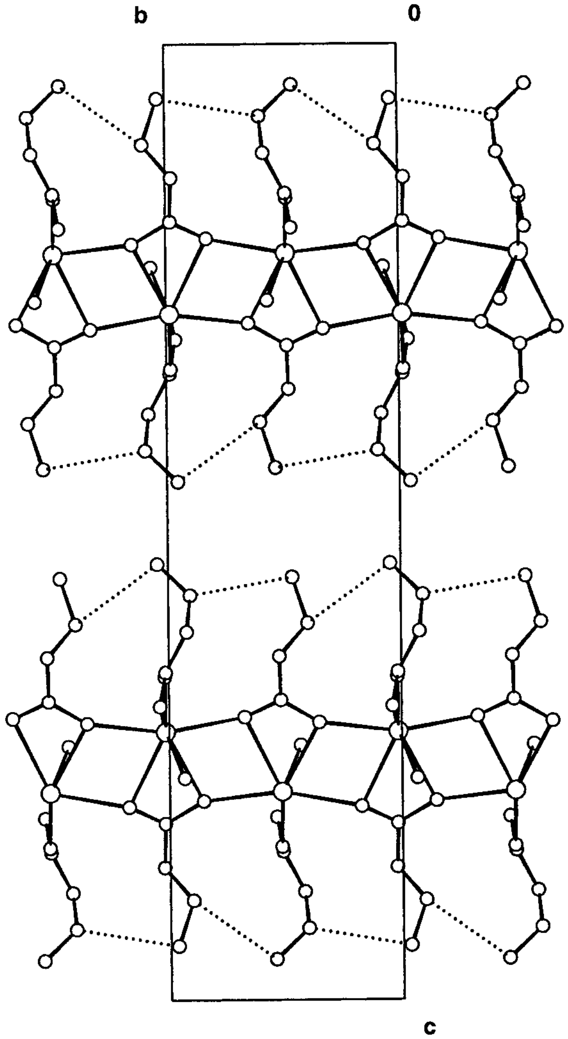

Figure 3. View of the crystal structure down the *a* axis. Dotted lines indicate the putative reaction pathway for polymerization.

Upon exposure to ^{60}Co γ-rays, **1** undergoes a solid-state polymerization reaction. Based on the diffraction pattern of irradiated crystals, the product appears as an amorphous phase. Early indications of this reaction were provided by the gradual disappearance of the H–C=C– bending modes (993, 912 cm^{-1}) in the IR spectrum. At radiation doses >20 kGy, conversion to polymer occurs in a nearly linear fashion, with complete conversion at ~300 kGy. The product is isolated after removal of unreacted **1** by extraction with methanol. Figure 4 depicts the ^{1}H and ^{13}C NMR spectra, measured in D$_2$O, of the isolated product. Both spectra indicate that there is a small amount of side products. By analogy with the ^{1}H and ^{13}C NMR spectra of atactic polypropylene and the expected shifts due to a carboxy

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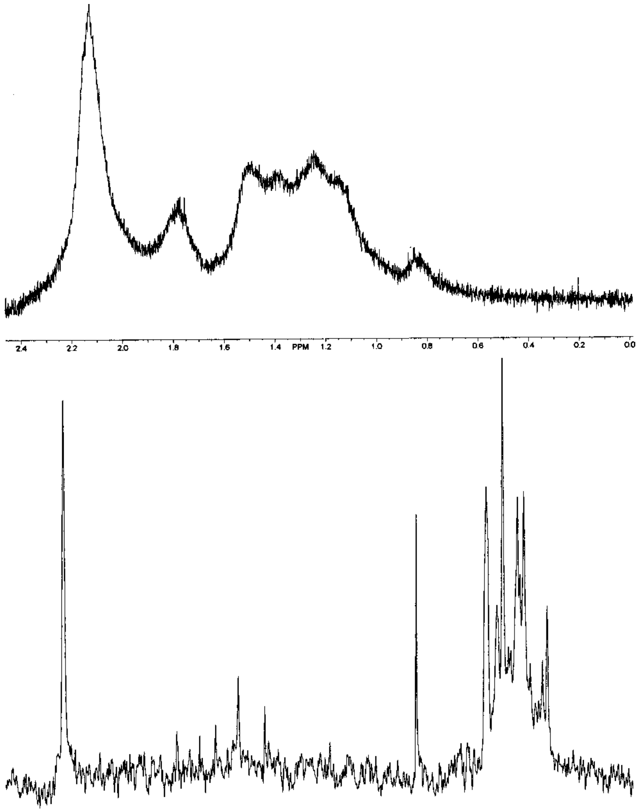

Figure 4. The ^{1}H (top) and ^{13}C (bottom) NMR spectra of calcium poly(3-butenoate).

group, the structure of the polymer can be assigned as atactic calcium poly(3-butenoate).[26] The molecular weight, $\bar{M}_w$ of ~400 000 is similar to that observed for the solid-state polymerization of potassium acrylate.[1] The bimodal distribution may arise from lower molecular weight polymer being produced at higher degrees of conversion, as previously observed for γ-irradiation of solid potassium acrylate.[1] 3-Butenoic acid may also be polymerized by ^{60}Co γ-irradiation of solutions or the neat liquid.[27−29] However, spectral or molecular weight information is not available.

In conclusion, we have synthesized and structurally characterized the monomeric precursor for a new solid-state polymerization reaction. The tendency of hydrophobic organic groups to aggregate in a bilayer motif leads to a highly reactive phase. The *steering effect* of such groups should be given serious consideration in "crystal engineering" of metal-containing phases that will undergo a solid-state reaction, consistent with the principles of the topochemical postulate. Given the observed greater sensitivity of the reactant to the more readily absorbed CuKα X-rays (compared with MoKα), the proposal that, during irradiation, the metal contributes to radical formation (perhaps by a secondary emission process) seems likely.[14] Finally, irradiation of solid **1** leads quantitatively to high molecular weight calcium poly(3-butenoate).

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Supporting Information Available: Tables of anisotropic displacement parameters, and all bond lengths and angles, a list of restraints, and complete CIF file (6 pages); observed and calculated structure amplitudes (3 pages). Ordering information is given on any current masthead page.

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