

SECTION 3: FUNCTIONAL FRAMEWORKS

Structure and γ -Ray-Induced Solid-State Polymerization of Sodium Propynoate: Influence of Bilayer Formation on Solid-State ReactivityJ. D. Jaufmann, C. B. Case, R. B. Sandor, and Bruce M. Foxman¹

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Sodium propynoate, $\text{Na}(\text{O}_2\text{CC}\equiv\text{CH})$ **1**, was synthesized from propynoic acid and sodium hydroxide in methanol solution. Irradiation of solid **1** with ^{60}Co γ -rays (654 kGy dose) leads to an amorphous dark-colored acetylenic polymer in high yield. An X-ray structure determination of compound **1** shows that the sodium ion is five-coordinate, with a square-pyramidal geometry. The five-coordinate local moiety is part of an unusual two-dimensional polymer in the crystal *bc* plane. Crystal packing of the two-dimensional, solid-state polymers leads to a bilayer motif, and the relatively short metal–metal distance of 3.575 Å promotes close packing of the organic tails with parallel acetylene moieties and a very short $-\text{C}\equiv\text{C}-\cdots-\text{C}\equiv\text{C}-$ contact of 3.29 Å along the crystallographic *b* direction. Crystal data for **1**: orthorhombic, space group $Pna2_1$, $a = 19.837(6)$, $b = 3.575(1)$, and $c = 5.232(1)$ Å; $V = 371.0$ Å³; $Z = 4$; $R = 0.0262$; $R_w = 0.0327$ for 427 data for which $I > 1.96\sigma(I)$. © 2000 Academic Press

Key Words: solid-state polymerization; acetylenic polymer; coordination polymer; gamma-ray irradiation; bilayer structure.

INTRODUCTION

In order to “engineer,” or discover, a solid-state reaction, one needs to produce an extended solid-state array with correctly oriented reactive groups. In optimal cases, unique lattice-controlled reactions, such as dimerization, polymerization, etc., will be possible. With this in mind, we have been exploring the solid-state reactivity of metal salts and complexes of unsaturated carboxylates, including both alkenoates and alkynoates. Davydov and co-workers studied the solid-state reactivity of metal propynoates in the 1960’s and 1970’s (1). We proposed that insight into the structural chemistry surrounding the solid-state reactivity of mono-acetylenes might be gained by *designing* a reactive phase using the principles of the *topochemical postulate* (2). The postulate, as formulated by Cohen, Schmidt, and Hirshfeld (2), asserts that alkene systems capable of undergoing

photochemical solid-state dimerization or polymerization should be oriented in a parallel fashion, and that the unsaturated centers should lie within ca. 4.2 Å of one another. We inferred that such criteria might also apply to other solid-state reactions which occurred thermally or upon irradiation with X- or γ -rays. By using the Cambridge Structural Database (3) and the idea of *structure analogy* (4), we predicted that the crystal structure of a tetraaquabis(propynoato)metal(II) complex would contain extended arrays with short $-\text{C}\equiv\text{C}-\cdots-\text{C}\equiv\text{C}-$ contacts, and would react in the solid state (5). Upon irradiation with ^{60}Co γ -rays, crystals of tetraaquabis(propynoato)zinc change from colorless to black. The product is produced in an efficient manner and high yield; X-ray and NMR studies showed it to be an amorphous polypropynoate. Further important design criteria include selection of a metal salt or complex with a small radius and relatively low coordination number; crystallization of such a material should lead to a phase containing short contacts between unsaturated centers (6). In order to further explore this idea, we examined the structure and solid-state reactivity of sodium propynoate **1**. Of a limited set of salts studied by Davydov, the sodium salt was the most reactive material. In a larger group of materials studied in our laboratory, it remains at the top (7–11). In order to elucidate the reasons for the high reactivity, we have carried out a complete X-ray structure determination and study of the solid-state reactivity of **1**.

EXPERIMENTAL

Instrumentation. NMR spectra were recorded on a Varian XL-300 spectrometer. A Gammacell 220 Irradiator (Atomic Energy of Canada, Ltd.) equipped with a ^{60}Co source was used for all γ -irradiation experiments. X-ray powder diffraction, oscillation, and Weissenberg photographs were obtained using $\text{CuK}\alpha$ radiation, a Philips 12045B generator, and Supper Weissenberg and Debye-Scherer cameras.

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Sodium Propynoate (1). Pulverized sodium hydroxide (1.0 g, 25 mmol) was dissolved in 75 mL of CH₃OH. The resultant solution was cooled to 10°C, and propynoic acid (1.75 g, 25 mmol) added with stirring. The CH₃OH was evaporated under a hood at room temperature, and the solid was air-dried. ¹³C NMR (D₂O, acetone internal standard) δ 158 (C), 78.2 (C), 69.5 (CH); IR major features 3280, 2100 cm⁻¹. Care was taken at all times to avoid unnecessary exposure to light. A platelike crystal suitable for diffraction studies was obtained by slow evaporation of a concentrated methanol solution of **1** on a flat glass plate.

Irradiation of Salt 1. Samples of crystalline **1** (5–10 g) were placed in Pyrex ampoules, which were then evacuated and sealed. The samples were irradiated with ⁶⁰Co γ-rays (nominal dose rate 1.3 kGy/h); doses varied from 218 to 872 kGy. At various times during the irradiation a sample was removed from the irradiator, and remaining monomer was removed by extraction with MeOH; after filtration and washing each sample was air-dried. The insoluble product was recovered by filtration and weighed; reactant was recovered to check mass balance. Inspection of ¹H NMR spectra revealed that this was an effective method for separation of monomer and polymeric product. Doses vs percent conversion for representative experiments: 218 kGy, 43.0%; 436 kGy, 63.4%; 654 kGy, 74.9%; 872 kGy, 75.3%. IR spectra of the irradiated material showed a strong decrease in the intensity of the –C≡C– stretching mode (2100 cm⁻¹) with increasing exposure. ¹H NMR (D₂O) δ 5.9–7.2 (1 H, m); ¹³C NMR (D₂O) δ 175.2 (C), 137.6 (C), 129.8 (CH). Additionally, there was a small peak located at δ 160 (¹³C NMR) which may be due to an impurity, or correspond to an end-group signal. A classical bromine titration (12) was carried out in order to obtain the degree of unsaturation in the polymerized product. An ≈ 0.11 M bromine/KBr solution was prepared and standardized with a standard Na₂S₂O₃ solution before each use. The degree of unsaturation found using the titration was 1.00 ± 0.05, consistent with one double bond per repeat unit. Owing to many technical difficulties, it was not possible to obtain high-quality molecular weight information for these water-soluble polyelectrolytes. Results of a preliminary GPC analysis of the molecular weight indicate a trimodal distribution, with the highest fraction having an \bar{M}_w near 8000, and two further fractions with lower molecular weights. A complete study of molecular weight distribution, as well as its dependence on conversion, will be the subject of a later study. Single crystals and powdered samples became colored, with increasing intensity, as the irradiation proceeded. At no stage was phase separation observed. X-ray powder diffraction studies as well as oscillation and Weissenberg photographs at various stages of irradiation, either as the “intact mixed crystals” or as separated product, indicated that the product appeared as an amorphous phase. No new single-

TABLE 1
Crystal Data for Na(O₂CC≡CH)^a

| | |
|---|--|
| Chemical formula | 1 , C ₃ H ₃ O ₂ Na |
| <i>a</i> , Å | 19.837(6) |
| <i>b</i> , Å | 3.575(1) |
| <i>c</i> , Å | 5.232(2) |
| <i>V</i> , Å ³ | 371.0 |
| <i>Z</i> | 4 |
| Formula wt | 92.03 |
| Space group | <i>Pna</i> 2 ₁ [<i>C</i> ₂ ^v ; No. 33] |
| <i>T</i> , °C | 21(1) |
| λ , Å | 0.71073, graphite monochromator |
| ρ_{calc} ; ρ_{obs} , g-cm ⁻³ | 1.647; 1.62(1) |
| μ , mm ⁻¹ | 0.22 |
| Absorption correction | Empirical, trans. factors 0.84–0.98 |
| Data collection | + <i>h</i> , + <i>k</i> , + <i>l</i> (to 2 θ = 27.5°) |
| Reflections measured | 477; 427 with <i>I</i> > 1.96 σ (<i>I</i>) |
| <i>R</i> | 0.0262 |
| <i>R</i> _w | 0.0327 |
| <i>S</i> | 1.086 |

^a $R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$; $R_w = \{\sum w [|F_o| - |F_c|]^2 / \sum w |F_o|^2\}^{1/2}$; $S = \{\sum w [|F_o| - |F_c|]^2 / (m - n)\}^{1/2}$, where *m* (=427) is the number of observations and *n* (=60) is the number of parameters.

crystal diffraction maxima or powder diffraction lines were observed at early, intermediate or late stages of conversion.

X-Ray Structure Determination. A suitable crystal was mounted on a Pyrex fiber affixed to a brass pin, transferred to a Supper No. 455 goniometer, and optically centered on a Syntex P2₁ diffractometer. Operations were performed as described previously (13). The structure was solved using the heavy-atom method; preliminary computational work was carried out using the Enraf-Nonius MolEN software package (14). Final refinement was carried out using the Oxford University CRYSTALS package (15); drawings were produced using CAMERON (16) and ChemRay (17). At the conclusion of least-squares refinement of positional and anisotropic displacement parameters for all nonhydrogen atoms (isotropic displacement parameters for H atoms), *R* = 0.0262 and *R*_w = 0.0327. A summary of experimental detail is presented in Table 1, atomic coordinates in Table 2,

TABLE 2
Atomic Coordinates for Na(O₂CC≡CH)^a

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} |
|-------|---------------|-----------|-----------|------------------------|
| Na(1) | 0.05665(4) | 0.2135(2) | 0.2501(3) | 0.0303 |
| O(1) | – 0.05321(7) | 0.2688(4) | 0.4309(5) | 0.0346 |
| O(2) | – 0.0887(1) | 0.2795(4) | 0.0269(4) | 0.0375 |
| C(1) | – 0.09560(9) | 0.3349(5) | 0.2584(5) | 0.0249 |
| C(2) | – 0.15959(11) | 0.5016(6) | 0.3459(5) | 0.0320 |
| C(3) | – 0.21020(14) | 0.6311(8) | 0.4194(7) | 0.0506 |
| H(3) | – 0.251(3) | 0.761(11) | 0.483(9) | 0.098(16) |

TABLE 3
Selected Bond Lengths and Angles for Na(O₂CC≡CH)

| | | | |
|--|-----------|---|------------|
| Na(1)–O(1) | 2.384(2) | O(1)–C(1) | 1.256(3) |
| Na(1)–O(1) ^a | 2.402(2) | O(2)–C(1) | 1.235(3) |
| Na(1)–O(1) ^b | 2.494(2) | C(1)–C(2) | 1.475(3) |
| Na(1)–O(2) ^c | 2.368(2) | C(2)–C(3) | 1.170(3) |
| Na(1)–O(2) ^d | 2.405(2) | C(3)–H(3) | 0.99(5) |
| | | | |
| O(1)–Na(1)–O(1) ^a | 108.03(5) | Na(1) ^c –O(1)–Na(1) ^d | 93.80(7) |
| O(1)–Na(1)–O(1) ^b | 100.32(5) | Na(1)–O(1)–C(1) | 110.04(17) |
| O(1) ^a –Na(1)–O(1) | 93.80(7) | Na(1) ^c –O(1)–C(1) | 128.00(12) |
| O(1)–Na(1)–O(2) ^c | 93.69(7) | Na(1) ^d –O(1)–C(1) | 108.87(13) |
| O(1) ^a –Na(1)–O(2) | 84.18(7) | Na(1) ^a –O(2)–Na(1) ^b | 97.00(7) |
| O(1) ^b –Na(1)–O(2) | 165.77(8) | Na(1) ^a –O(2)–C(1) | 138.51(14) |
| O(1)–Na(1)–O(2) ^d | 86.56(6) | Na(1) ^b –O(2)–C(1) | 119.94(13) |
| O(1) ^a –Na(1)–O(2) ^d | 165.30(8) | O(1)–C(1)–O(2) | 126.9(2) |
| O(1) ^b –Na(1)–O(2) ^d | 81.45(6) | O(1)–C(1)–C(2) | 115.4(2) |
| O(2) ^c –Na(1)–O(2) ^d | 97.00(7) | O(2)–C(1)–C(2) | 117.7(2) |
| Na(1)–O(1)–Na(1) ^c | 104.02(6) | C(1)–C(2)–C(3) | 178.8(3) |
| Na(1)–O(1)–Na(1) ^d | 110.63(6) | C(2)–C(3)–H(3) | 175.2(25) |

Symmetry operations: ^a4₅₅₄: $-x, -y, z - 1/2$, ^b4₅₆₄: $-x, 1 - y, z - 1/2$, ^c4₅₅₅: $-x, -y, z + 1/2$, ^d4₅₆₅: $-x, 1 - y, z + 1/2$.

and bond lengths and angles in Table 3. Tables of atomic coordinates, anisotropic displacement parameters, all bond lengths and angles, and observed and calculated structure factors are available from the authors as a CIF file.

RESULTS AND DISCUSSION

The square-pyramidal coordination environment of a single sodium ion is shown in Fig. 1. Along the left and right

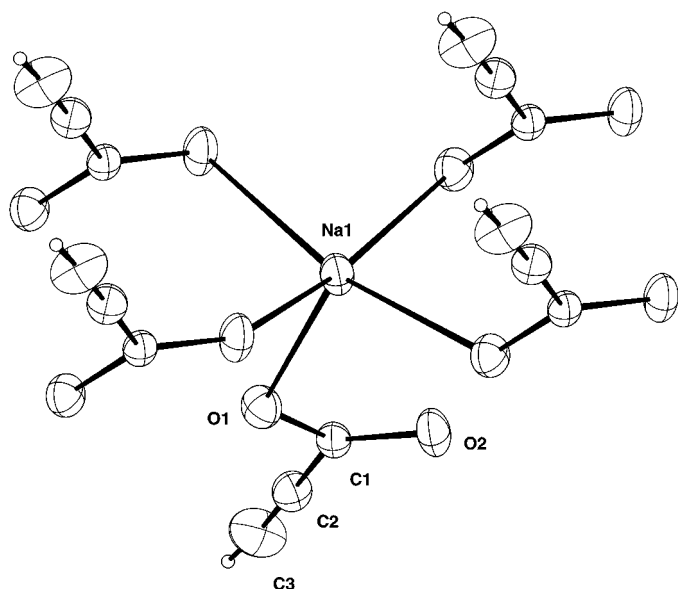


FIG. 1. Coordination environment of a single sodium ion in Na(O₂CC≡CH) **1**, showing labeling scheme and 40% probability ellipsoids.

edges of the basal plane of the square pyramid, the oxygen atoms (and the propynoate ligands) are related by a unit translation along the *b* direction (3.575 Å). Square-pyramidal geometry has not been previously observed for simple sodium carboxylate salts (or other simple Na-containing structures), although it certainly occurs in more complex structures, such as *N*-chloro-*N*-sodiotoluene-*p*-toluenesulfonamide **2** (18). The Na–O distances (2.37–2.49 Å) are slightly longer than those in **2**. The square-pyramidal unit is part of an extended two-dimensional “coordination polymer”, based on a five-coordinate Na⁺ ion and carboxylate bridging (19). Figure 2 shows part of the extended two-dimensional polymer; carboxylate tails point directly away from the two parallel sheets containing sodium ions. Within each of the two parallel sheets, sodium ions are related by unit translations along *b* (3.575 Å) and *c* (5.232 Å). Sodium ions in the upper and lower sheet in Fig. 2 (alternatively, the *bases* of interconnected square pyramids) are related by the 2₁ screw axis ($-x, -y, z + 1/2$) and appropriate translations. From a ligation point of view, carboxylate oxygen atom O(1) is formally four-coordinate and bridges to *three* sodium ions (two in the same plane, connecting basal vertices of the square pyramid, and one in the plane below). Oxygen atom O(2) is three-coordinate, and bridges to two other sodium ions in the same plane, again connecting basal vertices of the square pyramids (see Fig. 3 for a view of a single plane). The single coordination plane shown in Fig. 3 has two very unusual features. First, the “horizontal” Na–Na distance in Fig. 3 corresponds to a unit translation along *b*, 3.575 Å. The relatively short distance requires that the carboxylate–carboxylate distances also be 3.575 Å. Along with the two-dimensional nature of the coordination polymer, this *requires* the formation of a bilayer, with close-packed organic moieties along the *b* direction. Second, the tilting of the propynoates at an angle of 31° to the sodium-rich plane leads to a short contact of 3.29 Å between α and β' carbon atoms, as shown in Figs. 3 and 4. Figure 4 also shows that the overall packing of the coordination polymers occurs in a bilayer motif. Such arrangements often lead to reactive phases when unsaturated carboxylates are involved (4). Further, the bilayer motif, as well as two-dimensional coordination polymer formation, are dominant factors in the packing and assembly of metal carboxylate complexes and salts with three or more carbon atoms (20). The short contacts between C2 and C3 are also shown in a van der Waals representation in Fig. 5. There is no evidence for C–H \cdots O hydrogen bonding in this structure, either by inspection of the appropriate distances and angles, or the \equiv C–H stretching frequency, 3280 cm⁻¹, which is essentially unshifted from the solution value (21).

When sodium propynoate is irradiated with ⁶⁰Co γ -rays, the initially colorless material changes from colorless to yellow, orange, red, brown, and finally a dark brown-black solid. As the irradiation proceeds, the –C≡C– stretching

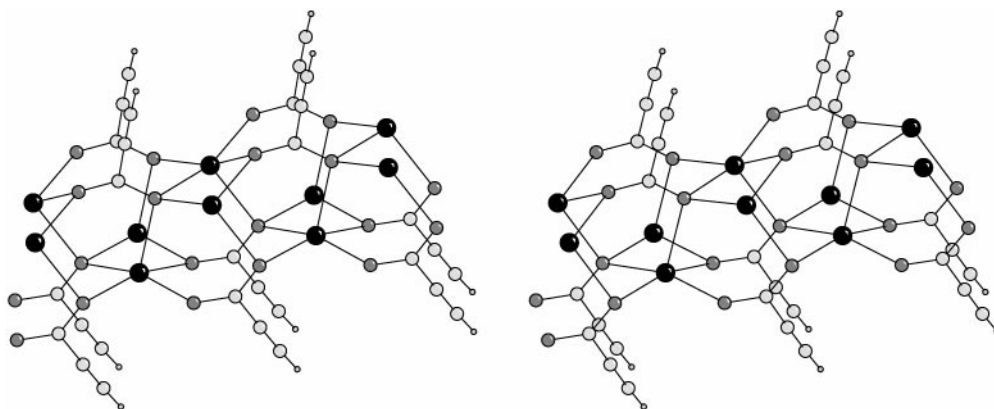


FIG. 2. Stereoview of the two-dimensional coordination polymer in **1**, showing the two layers of Na ions, carboxylate tails approximately normal to the coordination plane, and four-coordinate O(1) atoms. In Figs. 2, 3, and 4, Na ions are shown as large dark spheres, O atoms as small dark spheres, and C atoms as gray spheres.

frequency loses intensity, indicating the likely formation of a polypropynoate. Single crystals darken in color upon irradiation. The product crystal is a brown-black pseudomorph, with the polymeric product present as an amorphous

phase. Only the X-ray diffraction pattern of the reactant is observed throughout the conversion. Maximum conversion, 75%, is reached at ca. 650 kGy; presumably, the crystal lattice is significantly disordered at this point, precluding further reaction. The resultant polypropynoate is water-soluble, and in D_2O the NMR spectra (1H δ 5.9–7.2; ^{13}C δ 175.2, 137.6, 129.8) are consistent with polypropynoate (5, 7–10) or substituted polyacetylene spectra (22). The product is a substituted polyacetylene, likely a mixture of isomers, with a trimodal molecular weight distribution (maximum $\bar{M}_w \approx 8000$), and properties consistent with those described by Davydov (1). While solid metal propynoates apparently may not be employed to produce stereoregular polymers or oligomers, their study provides an excellent database of structure–reactivity relationships as well as an elucidation of the factors that affect X- and γ -ray-induced processes in solids. Further, the variation in sensitivity to γ -ray exposure makes the *reactants*, rather than the products, excellent candidates for development as dosimeters (23).

Unlike other solid propynoates, the sodium salt is extremely sensitive to room light, and becomes pink to red in less than an hour. The two major factors that affect solid-state reactivity of monoacetylenes are (a) the distance and orientation of the acetylene moieties, and (b) the absorption cross section of the material for γ -rays (5, 7–11). The orientation of the monoacetylenes is of lesser importance than it is in the solid-state polymerization of diacetylenes (24). For example, solid-state polymerization of propynoates occurs even when the groups at ≈ 4.0 Å are nearly orthogonal to one another (8). With regard to the absorption cross section criterion, in an all-light-atom phase such as sodium propynoate, with parallel acetylene groups, distance must be the most important factor. In the present case the distance between potentially reactive acetylenes is 3.29 Å, a very short contact ≈ 0.1 Å less than a van der Waals

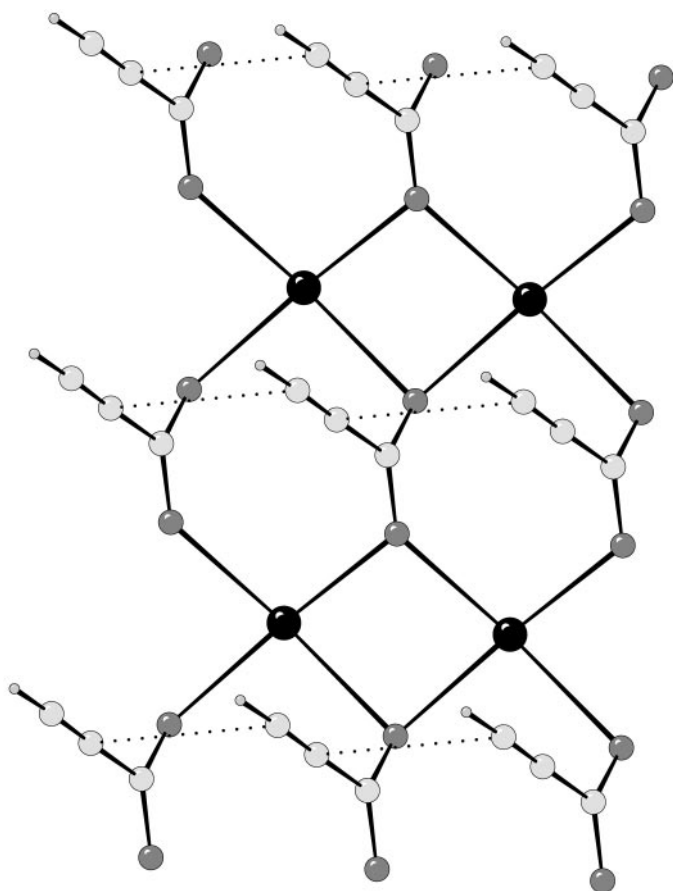


FIG. 3. View of the top layer of Na ions and associated propynoate ligands. Dotted lines show contacts between C2...C3 [0, -1, 0] of 3.29 Å.

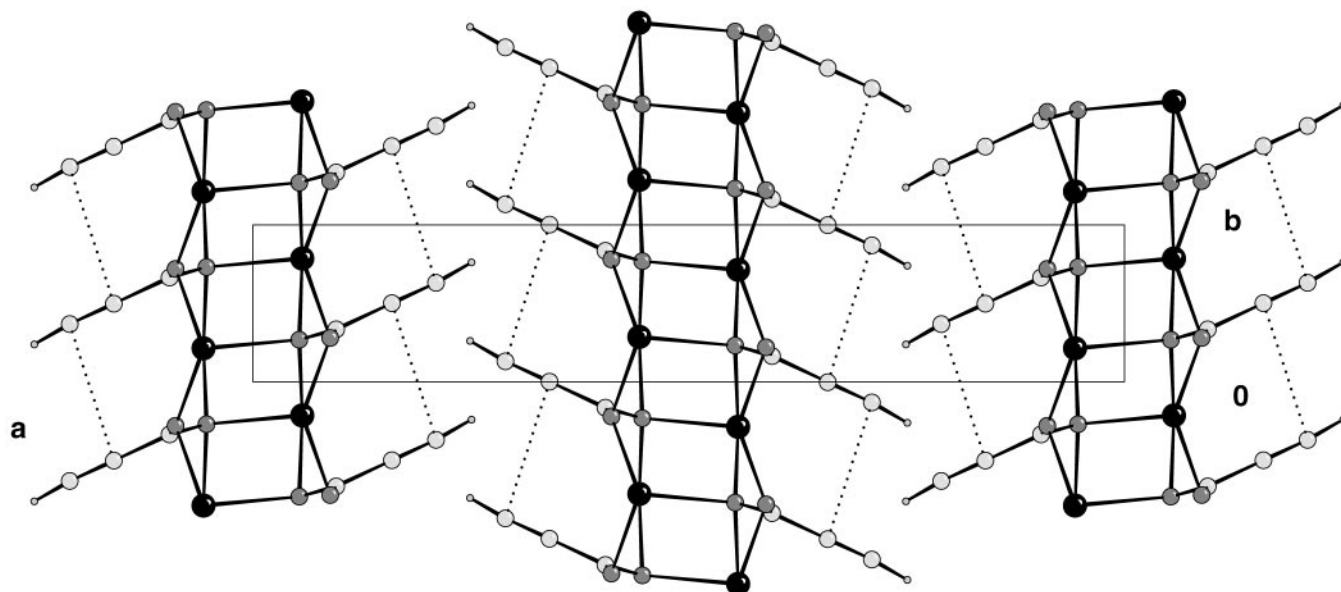


FIG. 4. View of the crystal structure of **1** along the c axis, showing the bilayer motif and the short $C2 \cdots C3$ $[0, -1, 0]$ contacts of 3.29 \AA .

separation (Fig. 5). Why does such a short contact arise in this case? A two-dimensional coordination polymer, generated by metal carboxylate interactions, including carboxylate bridging, serves as a bifunctional template (4). The first function of such a template is to generate a bilayer structure. Second, for compact structures with low coordination numbers (such as one might find with a sodium ion), the metal–metal distance and the carboxylate–carboxylate distance within the bilayer will be in the vicinity of 3.5 \AA , near the van der Waals separation for the unsaturated ligands, which will be close-packed and suitably positioned to undergo a solid-state reaction. Sodium *trans*-2-butenate, which has a 3.47 \AA lattice repeat distance and undergoes a stereospecific γ -ray-induced trimerization reac-

tion, likely packs in a bilayer structure (25). Presumably, other sodium-containing phases, as well as phases containing other small cations, will exhibit unusual solid-state reactivity. The preparation and study of such materials is currently in progress in our laboratories.

ACKNOWLEDGMENTS

We thank the National Science Foundation (DMR-9629994) for the partial support of this research, and Professor B. B. Snider for helpful discussions.

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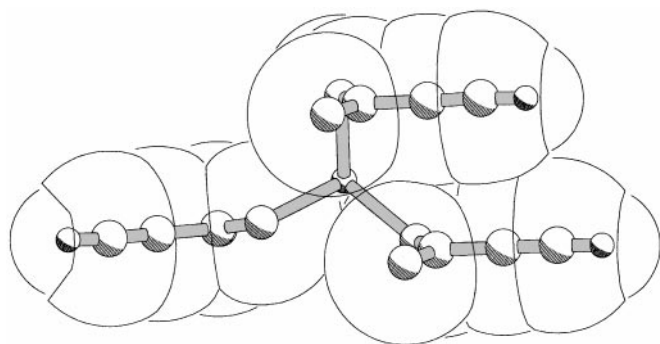


FIG. 5. A single Na ion, with three coordinated propenoate groups. The two groups at the right are related by a unit translation along b . Van der Waals spheres of enclosure show $C2$ and $C3$ $[0, -1, 0]$ in contact.

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