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Synthesis, structure and solid-state polymerization of dimethyl(propynoato)thallium ☆

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Abstract

The structure of acetatodimethylthallium **2** has been used as a model in an attempt to predict and 'engineer' a phase of dimethyl(propynoato)thallium **3** which would be reactive in the solid state. Upon irradiation with X-rays or ^{60}Co γ-rays, **3** is indeed converted to the corresponding deep-brown polypropynoate. The crystal structure of **3** contains, as expected, an infinite set of short contacts (3.454 Å) between acetylene moieties; the presence of such a chain is a requirement for a propynoate material to be sensitive to ionizing radiation. However, the crystal structures of **2** and **3** are quite different owing to subtle changes in C–H···O hydrogen bonding. Crystals of **3**, $(CH_3)_2Tl(O_2CC{\equiv}CH)$, belong to the orthorhombic system, space group *Pnma*, $a=7.316(4)$, $b=11.268(6)$, $c=9.033(5)$ Å; $Z=4$. Full-matrix least-squares refinement of positional and displacement parameters for all nonhydrogen atoms, using 338 data for which $|F_o|>3.92\sigma(|F_o|)$, led to $R=0.059$ and $R_w=0.068$.

Keywords: Polymerization; Crystal structures; Thallium complexes; Alkyl complexes; Carboxylato complexes

1. Introduction

The structural chemical literature may serve as a predictive database for the design and/or discovery of new solid-state reactions. Several years ago, during a search for solid phases containing molecules with short distances between reactive unsaturated centers, we considered the packing of molecules in crystalline bis(acetato)tetraaquanickel(II) **1** [1]. In that structure there was a short C···C ($CH_3\cdots CH_3$) contact of about 4.0 Å, as well as parallel C–C bonds between pairs of molecules. These parameters are reminiscent of those proposed by Cohen et al. [2] as the topochemical postulate: in polymerizing systems, a suitable contact of about 4 Å between neighboring molecules in the crystal is a necessary condition for the initial dimerization step which must precede chain propagation [2b]. We hypothesized that, given proposed similarities in the packing of acetate and a selected unsaturated carboxylate, synthesis of the analogous tetraaquabis(carboxylato)metal(II) complexes would yield phases capable of undergoing solid-state reactions upon irradiation. We chose propynoate as a suitable target molecule, and synthesized the analogous zinc, nickel and cobalt complexes. These isomorphous phases had a structure very similar to that of **1**, complete with a set of parallel acetylene–acetylene contacts in the range 3.5–4.0 Å. Upon irradiation with ^{60}Co γ-rays, the solid materials polymerize to the analogous polypropynoates; the products are amorphous oligomeric mixtures [3–5].

While the solid-state irradiation of metal alkenoates often proceeds with unusual stereospecific and/or regiospecific effects [6,7], such phenomena are absent in solid-state alkynoate chemistry. Nonetheless, these materials provide a useful database for the study of structure–reactivity (and other) relationships in the solid reactant phases. The extant evidence indicates that factors such as the distance between reactive triple bonds, the crystal lattice energy and the absorption cross section of the materials for X-rays or γ-rays strongly influence the reactivity of metal propynoates [4,5,8–10]. On the other hand, irradiation of solid 'all-organic' acetylenes produces no significant product [11–14]. Our work to date indicates that all reactive metal-containing phases exhibit infinite chains of short acetylene–acetylene contacts; however, the angle between acetylene moieties in the reactant crystal may deviate significantly from 0° or 180° [9].

☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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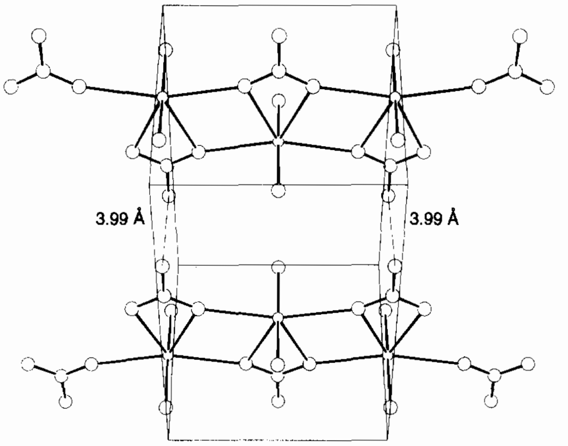

Fig. 1. View of the packing of coordination polymers in 2 showing short C···C (CH_3···CH_3) contacts (*a* axis is horizontal; dashed lines are nearly parallel to *c*).

We surmised that the availability of a suitable neutral heavy-metal organometallic derivative would allow us to explore further the reactivity of a highly absorbing species in a molecular crystal with a comparatively low lattice energy. We also hoped to open a window to the solid-state reaction behavior of organometallic compounds. The question of how to approach an entry to an organometallic derivative was solved, as before, by consideration of the structures of organometallic acetate derivatives. A literature search using the Cambridge Structural Database [15] indicated that the structure of the coordination polymer, acetatodimethylthallium **2** [16], contained an infinite series of short C···C (CH_3···CH_3) contacts (3.99 Å) between the acetate methyl groups, as shown in Fig. 1. By analogy with our earlier studies of **1**, we hoped that dimethyl(propynoato)thallium **3** would have a crystal structure similar to that of **1** and might undergo a solid-state polymerization reaction upon irradiation with ^{60}Co γ-rays. This paper reports the synthesis, structure and solid-state reaction behavior of **3**.

2. Experimental

2.1. Instrumentation

Melting points were determined on a Laboratory Devices Mel-Temp apparatus and are uncorrected. IR spectra were recorded using a Perkin-Elmer 683 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-300 (300 MHz) spectrometer. Chemical shifts are given in parts per million downfield from 3-(trimethylsilyl)-1-propane sulfonic acid sodium salt. The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. A Gammacell 220 irradiator (Atomic Energy of Canada, Ltd.) equipped with a ^{60}Co source was used for all γ-irradiation experiments. The nominal activity of the source during these experiments was 0.0403 Mrad/h.

2.2. Dimethylthallium iodide

The procedure of Gilman and Jones [17] was used for the preparation of dimethylthallium iodide. Pyridine was used for recrystallization.

2.3. Dimethyl(propynoato)thallium (3)

3.01 g (8.30 mmol) of recrystallized dimethylthallium iodide was stirred with 1.01 g (4.15 mmol) of silver oxide in 70 ml water for 2 h [18]. The resulting basic solution was filtered through sintered glass and neutralized with 0.58 g (8.30 mmol) of propynoic acid (neat). The volume of solution was decreased to 20 ml under reduced pressure, and the remaining solvent was evaporated over a two day period to afford **3** (2.40 g, 7.91 mmol, 95.3%): m.p. 182–184 °C. IR (KBr): 3263, 3190, 2080, 1585, 1342, 885, 775 cm^{-1}. ^{1}H NMR (D_2O) δ: 4.88, 3.15 (1H, s), 1.19 (6H, d, $^2J(^1H-^{205}Tl)=396$ Hz).

2.4. Dimethyl(polypropynoato)thallium (4)

Dimethyl(propynoato)thallium (4.62 g, 15.2 mmol) was irradiated (^{60}Co γ-rays; 19.5 Mrad) in the Gammacell 220. The resulting dark-amber powder was stirred with anhydrous ethanol (20 ml) to give a clear solution with remaining undissolved material. The filtrate was concentrated under reduced pressure to give 3.76 g of **3** as a white powder: m.p. 182–184 °C; IR and NMR identical to **3**. The insoluble material was isolated by filtration, washed with anhydrous ethanol (3×10 ml) and dried in vacuo over $CaSO_4$ to give **4** (0.85 g, 18.4%); m.p. 215 °C dec. IR (KBr): 2922, 1545, 1380, 855, 795. ^{1}H NMR (D_2O) δ: 4.85, broad envelope between 7.0 and 5.5 with a peak at 5.85, 1.11 (6H, d, $^2J(^1H-^{205}Tl)=399$ Hz). Doses versus percent conversion for other experiments: 7.15 Mrad, 3.24%; 13.8 Mrad, 11.8%; 24.5 Mrad, 22.9%; 33.7 Mrad, 25.7%.

2.5. X-ray structure determination of 3

Preliminary Weissenberg and oscillation photographs, as well as polarized light microscopy, indicated the crystal to be of acceptable quality. Operations on the Syntex $P2_1$ diffractometer were performed as described previously [19,20]. The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering were included in the calculations [21]. Refinement using anisotropic displacement parameters for all nonhydrogen atoms was suggested in part by features on electron density difference maps. The hydrogen atom attached to the β-carbon atom of the propynoate moiety was included as a fixed contribution to F_c; methyl hydrogen atoms were not located and were not included in the refinement. Complete experimental detail is presented in Table 1, atomic coordinates in Table 2, and bond lengths and angles in Table 3. Given the values of the displacement parameters, it would have been desirable to repeat the structure determination at low temperature. However, low temperature facilities were not available. Nonetheless, the packing and general features of the structure are firmly established by this study.

3. Results and discussion

Dimethylthallium iodide was prepared according to the procedure of Gilman and Jones [17]. Vigorous stirring of dimethylthallium iodide with silver oxide in water was used to prepare an aqueous solution of dimethylthallium hydroxide [18] which was then neutralized with neat propynoic acid to form dimethyl(propynoato)thallium(III) **3**. Filtration and subsequent evaporation of the resulting solution gave colorless needles of **3**.

An X-ray structure determination of **3** shows that the complex is an infinite coordination polymer (Fig. 2). The dominant feature of the molecular structure, as seen in other $(CH_3)_2Tl$ chelates [16], is the short, nearly linear pair of $Tl–CH_3$ bonds (Tl–C, 2.16(4) Å; C–Tl–C, 174(1)°). The coordination polymer has crystallographically imposed *m* symmetry; all atoms except the methyl carbon atom (C4) lie in the mirror plane. Each thallium atom has a square-pyramidal geometry (Fig. 2), and is bonded to two methyl carbon atoms and three oxygen atoms. One oxygen atom of the propynoate ligand is bound to two thallium atoms and the other to one thallium atom. The doubly coordinated oxygen atom O1 bridges thallium atoms unsymmetrically with Tl–O distances of 2.39(2) and 2.65(2) Å, and a Tl–O1–Tl angle of 123.4(9)°. The singly coordinated oxygen atom O2 has a significantly greater Tl–O distance of 2.76(2) Å, as well as an unusually large Tl–O–C angle of 170.(2)°. The coordination polymer is similar

Table 1
Data for the X-ray diffraction study of $[(CH_3)_2Tl(O_2CC{\equiv}CH)]$

Crystal data at 21(1) °C
Crystal system: orthorhombic
Space group: *Pnma* (D_{2h}^{16}; No. 62)
$a = 7.316(4)$ Å
$b = 11.268(6)$ Å
$c = 9.033(5)$ Å
$V = 744.7(12)$ Å^3
$Z = 4$
Crystal size: 0.40×0.25×0.15 mm
Formula weight: 303.48
ρ_{obs} [a] $= 2.68(2)$ g cm^{-3}
$\rho_{calc} = 2.707$ g cm^{-3}
$\mu = 218.4$ cm^{-1} (Mo K$\bar{\alpha}$)
Cell constant determination: 6 pairs of ±(*hkl*) and refined 2θ, ω, χ values in the range $21 \leq |2\theta| \leq 26°$ (λ(Mo K$\bar{\alpha}$) = 0.71073 Å)

Measurement of intensity data
Radiation: Mo K$\bar{\alpha}$, graphite monochromator
Reflections measured: $+h$, $+k$, $+l$ ($3 \leq 2\theta \leq 45°$)
Scan type, speed: ω, variable, 1.95–3.91° min^{-1}
Scan range: 1°, with 1° offset in ω for background measurement
No. of reflections measured: 514
Standard reflections: 004, 040, 400; period: 70; variation: $\leq \pm 3\sigma(I)$ for each
Absorption correction: empirical, normalized transmission factors 0.626–1.000
Data reduction: as before [b]

Refinement
Refinement [c], with 338 data for which $I > 1.96\sigma(I)$
Weighting of reflections: as before [c], $p = 0.08$
Solution: Patterson, difference-Fourier
Refinement [d]: full-matrix least-squares with:
    anisotropic displacement parameters for Tl, C and O atoms
    isotropic displacement parameters for fixed H atom
    $R = 0.0585$; $R_w = 0.0684$; $SDU = 1.328$
    R (structure factor calcn. with all 514 reflections) = 0.104
Final difference map: peaks of 0.92 to 2.24 e Å^{-3} centered around Tl; other peaks random and in range −1.2 to +0.85 e Å^{-3}

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[a] Measured by neutral buoyancy in 1,1-diiodomethane/carbon tetrachloride.

[b] Ref. [22]. All computations in the present work were carried out using the Enraf-Nonius MolEN structure determination package.

[c] Ref. [23]. [d] $R_{av} = \Sigma|I - I_{av}|/\Sigma I$; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$. $SDU = \{\Sigma w[|F_o| - |F_c|]^2/(m - n)\}^{1/2}$ where m (=338) is the number of observations and n (=46) is the number of parameters.

Table 2
Atomic coordinates for $[(CH_3)_2Tl(O_2CC{\equiv}CH)]$ [a,b]

Atom	x	y	z	B (Å^2)
Tl	0.2371(2)	0.250	0.1109(1)	5.94(3)
O1	0.595(3)	0.250	0.150(2)	8.8(9)
O2	0.868(3)	0.250	0.049(2)	8.6(9)
C1	0.706(4)	0.250	0.046(3)	4.1(7)
C2	0.614(5)	0.250	−0.107(3)	7.(1)
C3	0.537(4)	0.250	−0.223(3)	9.(2)
C4	0.233(3)	0.441(4)	0.098(3)	11.(1)
H1	0.475	0.250	−0.315	12.2

[a] Atoms refined using anisotropic displacement parameters 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 table are e.s.d.s in the least significant digit.

to that observed in **2**; however, in **2** the O atoms are equivalent, leading to a distorted six-coordinate environment around Tl (Fig. 1). Each acetate ligand bridges in both *anti–anti* and *anti–syn* fashions to give an infinite, linear coordination polymer [16]. A more closely related mode of carboxylate ligand coordination exists in the structure of the dimeric compound di-μ-pentafluorobenzoatobis-[bis(pentafluorophenyl)-(triphenylphosphineoxide)thallium(III)] [24]. The pentafluorobenzoate ligands are unsymmetrically chelated to the thallium atoms (Tl–O 2.389(7) and 2.531(6) Å). One of the oxygen atoms of the pentafluorobenzoate ligand bridges two thallium atoms (Tl–O 2.531(6), 2.789(6) Å); the Tl–O–Tl angle is 109.3°. As in the structure of **3**, the long 2.789 Å Tl–O distance is associated with a large Tl–O–C angle of 161.1(5)°. However, in **3** the long Tl–O distance is associated with the non-bridging oxygen atom.

As shown in Fig. 3, the sheets of planar coordination polymer are linked by C–H···O hydrogen bonds (C3···O2[$x-\frac{1}{2}, y, -z-\frac{1}{2}$], 3.199 Å; C–H···O, 171.8°). The C–H···O hydrogen bonds also lead to an infinite zigzag arrangement of C2···C3[$\frac{1}{2}+x, y, -\frac{1}{2}-z$]···C2[$x-\frac{1}{2}, y, -\frac{1}{2}-z$] short acetylene contacts of 3.454 Å. Clearly, the presence of strong C–H···O hydrogen bonding has led to a significant difference between packing of the chains in **2** (Fig. 1) and **3** (Figs. 3 and 4). A further lesson may be learned from a closer examination of the structures of **2** and **3**. It appears likely that weak hydrogen bonds influence the packing in **2**. In the acetato polymer, there is a pertinent short distance (3.35 Å) between the carboxylate oxygen atom and a methyl carbon atom (related by [$\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$]) attached to Tl; the C–O···C_{methyl} angle is 136.5°. A significant consequence of these differences in hydrogen bonding and packing is that while the chain of $CH_3\cdots CH_3$ contacts in the acetato polymer is perpendicular to the polymer sheet (Fig. 1), the chains of C2···C3′···C2″ acetylenic contacts occur between coplanar sheets of the propynoato polymer (Fig. 4).

Upon exposure to ^{60}Co γ-radiation, solid **3** develops a dark-orange color, similar to the color change observed for the solid-state polymerization of other metal propynoates [4,5,8–10]. As the irradiation proceeds, there is a concomitant loss in intensity of the $-C{\equiv}C-$ stretching mode at 2080 cm^{-1}, indicating the likely formation of a polypropynoate. Conversion to product occurs linearly with dose of ^{60}Co γ-radiation in the range of approximately 7 to 21 Mrad, with a slower rate at both the onset of reaction and at doses above 21 Mrad. Yields of about 26% are obtained after 34 Mrad doses. The

Table 3
Bond lengths (Å) and angles (°) for $[(CH_3)_2Tl(O_2CC{\equiv}CH)]$

Atom 1	Atom 2	Distance		Atom 1	Atom 2	Distance	
Tl	O1	2.65(2)		O1	C1	1.24(4)	
Tl	O1 [a]	2.39(2)		O2	C1	1.19(3)	
Tl	O2 [b]	2.76(2)		C1	C2	1.54(4)	
Tl	C4	2.16(4)		C2	C3	1.18(4)	
Atom 1	**Atom 2**	**Atom 3**	**Angle**	**Atom 1**	**Atom 2**	**Atom 3**	**Angle**
O1	Tl	O1 [a]	107.9(7)	Tl	O1	C1	123.(2)
O1	Tl	O2 [b]	176.1(6)	Tl	O1 [a]	C1 [a]	114.(2)
O1	Tl	C4	91.3(7)	Tl	O2 [b]	C1 [b]	170.(2)
O1 [a]	Tl	O2 [b]	76.0(7)	O1	C1	O2	129.(3)
O1 [a]	Tl	C4	92.4(8)	O1	C1	C2	114.(3)
O2 [b]	Tl	C4	88.5(7)	O2	C1	C2	117.(3)
C4	Tl	C4 [c]	174.(1)	C1	C2	C3	177.(3)
Tl	O1	Tl [a]	123.4(9)				

[a] Symmetry operator: ($x-\frac{1}{2}, y, \frac{1}{2}-z$).

[b] Symmetry operator: ($x-1, y, z$).

[c] Symmetry operator: ($x, \frac{1}{2}-y, z$).

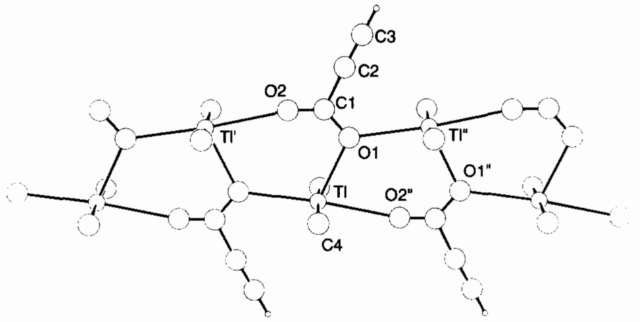

Fig. 2. View of the coordination polymer in 3 showing labeling scheme and square-pyramidal coordination of thallium.

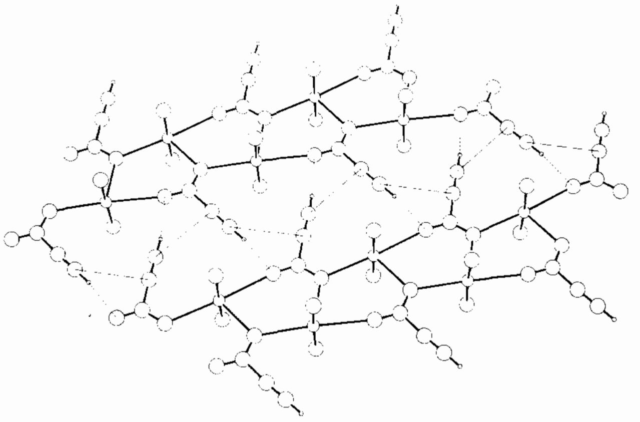

Fig. 3. View of two coordination polymers in 3 showing C–H···O hydrogen bonds and short acetylene–acetylene contacts of 3.454 Å.

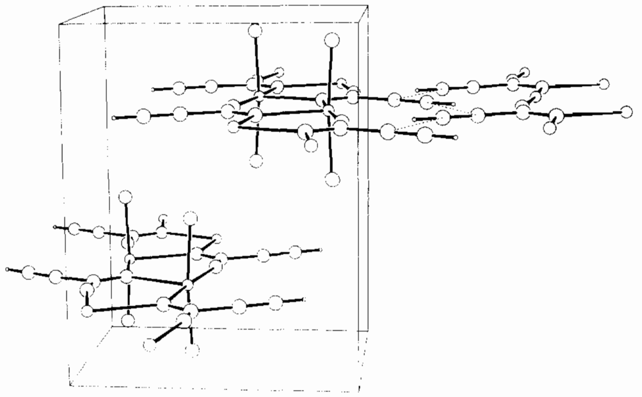

Fig. 4. View of the packing of coordination polymers in 3 showing short acetylene–acetylene contacts (*b* axis is vertical, *c* axis is horizontal).

product is isolated after removal of reactant by extraction with absolute ethanol. The product is soluble in water, and in D_2O the ^1H and ^{13}C NMR spectra consist of broad resonances (^1H δ: 5.5–7.0; ^{13}C δ: 175–186, 120–155) which are in the expected regions for a polypropynoate or substituted polyacetylene [4,5,8,9,25]. The resonances were too poorly resolved to allow assignment of possible stereochemistry of the product(s). The sensitivity of the compound to ionizing radiation is consistent with the presence of an infinite chain of short $-C{\equiv}C-\cdots-C{\equiv}C-$ contacts (3.454 Å); while these contacts are between acetylene moieties in the same crystallographic plane, the acetylene units deviate by 54.4° from parallelism (Fig. 4). As mentioned in the Introduction, the criterion of parallelism is not an important one for the solid-state reactivity of monoacetylenes [9].

In conclusion, we attempted to use the structural literature, namely, the structure of acetatodimethylthallium **2**, to engineer a reactive phase of dimethyl(propynoato)thallium **3**. The resultant material indeed shows high reactivity under γ-irradiation, and has, as we had anticipated, a set of infinite, short acetylene–acetylene contacts. However, the crystal structures of **2** (Fig. 1) and **3** (Fig. 4) are quite different owing to subtle differences in C–H···O hydrogen bonding. We expect that, e.g., the crystal structure of 2-butynoato(dimethyl)thallium **5**, where the acetylenic C–H···O hydrogen bond is not possible, might more closely resemble that of **2**. Accordingly, we are examining the structure–reactivity relationships for **5** and other thallium compounds of similar stoichiometry.

4. Supplementary material

Tables of anisotropic displacement parameters as well as observed and calculated structure amplitudes are available from the authors.

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