Synthesis, structure and solid state polymerization of diaquabis(propynoato)magnesium

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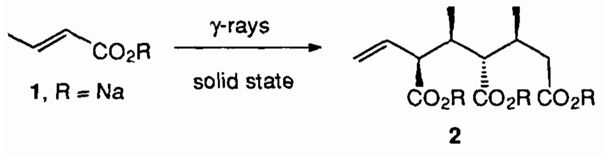
Abstract

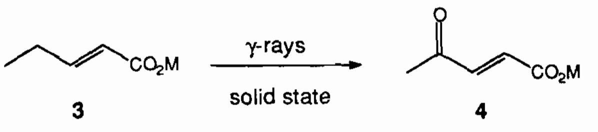
Upon irradiation with X-rays or ^{60}Co γ-rays, diaquabis(propynoato)magnesium (**5**) is converted to the corresponding deep brown polypropynoate. The crystal structure of **5** contains an infinite set of short contacts (3.698 Å) between nearly parallel acetylene moieties; the presence of such a chain is a requirement for a propynoate material to be sensitive to ionizing radiation. Crystals of **5**, $Mg(O_2CC{\equiv}CH)_2(OH_2)_2$, belong to the orthorhombic system, space group *Pbca*, $a=6.901(2)$, $b=16.134(3)$, $c=7.391(2)$ Å, $Z=4$. Full-matrix least-squares refinement of positional and displacement parameters for all atoms, using 888 data for which $|F_o| \leqslant 3.92\sigma(|F_o|)$ led to $R=0.035$; $R_w=0.049$.

Key words: Crystal structures; Solid state polymerization; Irradiation; Magnesium complexes; Propynoato complexes; Aqua complexes

Introduction

Metal complexes and salts containing α,β-unsaturated carboxylates as ligands often exhibit remarkable solid state reactivity. Thus, for example, we have shown that irradiation of solid sodium *trans*-2-butenoate **1** leads to trimer **2**, one of eight possible diastereomers [1]. This reaction is all the more remarkable since it is stereospecific, and trimer **2** cannot be prepared in solution. Another unusual reaction occurs when solid metal *trans*-2-pentenoates are irradiated in air. In this reaction, which is general for all metal pentenoates, the pentenoate moiety **3** undergoes a regiospecific oxidation to acetylacrylate **4** [2]. Irradiation of solid metal propynoates with ^{60}Co γ-rays leads readily to the corresponding polypropynoates [3]; the products of these irradiations are amorphous, oligomeric mixtures. While we have not yet observed unusual stereospecific and/or regiospecific effects in solid state alkynoate chemistry, these materials provide a fertile ground for studying structure–reactivity relationships in the solid reactant phases. It appears that factors such as the distance between reactive triple bonds, crystal lattice energy, and the absorption cross section of the materials for X- or γ-rays strongly influence the reactivity of metal propynoates [4–7]. By contrast, irradiation of solid 'all-organic' acetylenes does not lead to significant amounts of product [8–10]. Our work thus far indicates that all reactive metal-containing phases exhibit infinite chains of short acetylene–acetylene contacts. With a view to expanding our understanding of the solid state reactivity of metal propynoates, as well as establishing a database of structure–reactivity relationships for radiation-sensitive metal salts and complexes, we have prepared diaquabis(propynoato)magnesium (**5**), determined its crystal structure, and studied its behavior under γ-irradiation.





Experimental

$Mg(O_2CC{\equiv}CH)_2(OH_2)_2$ (5)

Single crystals of **5** were prepared by the slow addition of $Mg(OH)_2$ to 25 ml of ≈5 M aqueous propynoic

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acid to the phenolphthalein endpoint. A few additional drops of acid were added to dispel the color of the solution. The solution was filtered and allowed to evaporate in air; colorless acicular crystals were removed from larger masses in the evaporating dish. X-ray powder photography indicated that the larger masses and the acicular crystals were identical. The material is stable when heated in air, but darkens to a brown solid at temperatures near 250 °C. IR (KBr): 3594, 3381, 3250, 2097, 1645, 1623, 1404, 921, 782, 728, 689, 633, 586, 532 cm^{-1}.

X-ray structure determination

Preliminary Weissenberg and oscillation photographs, as well as polarized light microscopy indicated the crystal to be of good quality. The crystal was transferred to a Supper No. 455 goniometer and optically centered on a Syntex P2$_1$ diffractometer. Operations on the Syntex P2$_1$ diffractometer were performed as described previously [11,12]. The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering were included in the calculations [13]. Complete experimental detail is presented in Table 1, atomic coordinates in Table 2, and bond lengths and angles in Table 3.

Solid state reactivity

Solid samples (350–600 mg) of **5** were ground to fine powders in an agate mortar, loaded into Pyrex tubes (1 × 15 cm), evacuated and sealed. The samples were irradiated with ^{60}Co γ-rays in a Gammacell 220 irradiator (Atomic Energy of Canada, Limited) at a nominal dose

TABLE 1. Data for the X-ray diffraction study of $Mg(O_2CC{\equiv}CH)_2(OH_2)_2$

Crystal data at 21(1) °C	
Crystal system	orthorhombic
Space group	*Pbca* (D_{2h}; No. 61)
a (Å)	6.901(2)
b (Å)	16.134(3)
c (Å)	7.391(2)
V (Å^3)	822.9(6)
Z	4
Crystal size (mm)	0.08 × 0.17 × 0.55
Formula weight	198.423
ρ_{obs}[a] (g cm^{-3})	1.56(2)
ρ_{calc} (g cm^{-3})	1.601
μ (Mo K$\bar{\alpha}$) (cm^{-1})	2.20
Cell constant determination	
12 pairs of $\pm(hkl)$ and refined 2θ, ω, χ values in the range $25 \leqslant \lvert 2\theta \rvert \leqslant 30°$ (λ(Mo K$\bar{\alpha}$) = 0.71073 Å)	
Measurement of intensity data	
Radiation	Mo K$\bar{\alpha}$, graphite monochromator
Reflections measured	$+h$, $+k$, $+l$ (to $2\theta = 60°$)
Scan type, speed (°/min)	θ–2θ, variable 1.95–3.91
Scan range (°)	symmetrical, $[1.8 + \Delta(\alpha_2 - \alpha_1)]$
No. reflections measured	1206, 1206 in unique set
Standard reflections, period 50	0 10 0, 002, 402; variation $\leqslant \pm 3\sigma(I)$ for each
Data reduction	as before[b]
Statistical information, R_s	0.024
Refinememt	
Refinement[c] data for which $F > 3.92\ \sigma(F)$	888
Weighting of reflections[c], p	0.035
Solution	Patterson, difference-Fourier
Refinement	full-matrix least-squares, with anisotropic displacement parameters for Mg, O and C atoms isotropic displacement parameters for H atoms secondary extinction parameter, 7.1(19) × 10^{-6}
R[d]	0.035
R_w[e]	0.049
SDU[f]	1.040
Final difference map (e$^-$/Å^3)	2 peaks, 0.24 near Mg other peaks random and $\leqslant 0.20$

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[a] Measured by neutral buoyancy in hexane/CCl$_4$. [b] Ref. 14; all computations in the present work were carried out using the SYNTEX XTL Structure Determination Package and the Enraf-Nonius MolEN Structure Determination Package. [c] Ref. 15. [d] $R_s = \Sigma\sigma(|F_o|)/\Sigma|F_o|$; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [e] $R_w = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$. [f] $SDU = \{\Sigma w[|F_o| - |F_c|]^2/(m - n)\}^{1/2}$ where m (= 888) is the number of observations and n (= 73) is the number of parameters.

TABLE 2. Atomic coordinates for $Mg(O_2CC{\equiv}CH)_2(OH_2)_2$[a,b]

Atom	x	y	z	B (Å^2)
Mg	0.000	0.000	0.000	1.68(1)
O(1)	0.1090(2)	−0.04372(8)	−0.2347(2)	2.69(3)
O(2)	0.2567(2)	−0.07796(7)	−0.4904(1)	2.10(2)
O(3)	0.1328(2)	−0.09513(8)	0.1434(2)	2.44(3)
C(1)	0.1333(2)	−0.08887(9)	−0.3681(2)	1.68(3)
C(2)	0.0112(2)	−0.1632(1)	−0.3870(2)	2.22(3)
C(3)	−0.0775(3)	−0.2250(1)	−0.4040(3)	3.24(4)
H(C3)	−0.146(4)	−0.275(2)	−0.418(4)	5.1(6)
H(O3A)	0.211(4)	−0.119(2)	0.078(4)	5.7(7)
H(O3B)	0.171(4)	−0.084(2)	0.236(5)	5.5(7)

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

TABLE 3. Bond lengths (Å) angles (°) for $Mg(O_2CC{\equiv}CH)_2(OH_2)_2$

Bond lengths			
Mg–O(1)	2.018(1)	O(3)–H(O3A)	0.82(3)
Mg–O(2)	2.099(1)	O(3)–H(O3B)	0.75(4)
Mg–O(3)	2.078(1)	C(1)–C(2)	1.473(2)
O(1)–C(1)	1.237(2)	C(2)–C(3)	1.176(3)
O(2)–C(1)	1.255(2)	C(3)–H(C3)	0.94(3)
Bond angles			
O(1)–Mg–O(2)	86.59(5)	Mg–O(3)–H(O3A)	110(2)
O(1)–Mg–O(2)	93.41(5)	Mg–O(3)–H(O3B)	117.(2)
O(1)–Mg–O(3)	90.91(5)	H(O3A)–O(3)–H(O3B)	114.(3)
O(1)–Mg–O(3)	89.09(5)	O(1)–C(1)–O(2)	125.7(1)
O(2)–Mg–O(3)	94.16(5)	O(1)–C(1)–C(2)	118.5(1)
O(2)–Mg–O(3)	85.84(5)	O(2)–C(1)–C(2)	115.7(1)
Mg–O(1)–C(1)	160.3(1)	C(1)–C(2)–C(3)	176.5(2)
Mg–O(2)–C(1)	130.7(1)	C(2)–C(3)–H(C3)	179.(2)

rate of 2.3 MRad/day. After irradiation each sample was extracted with 100 ml methanol under reflux to remove residual monomer, leaving the polymeric product as an insoluble brown solid. Tests for material balance (the sum of the weights of recovered reactant and insoluble product) indicated that no weight loss had occurred; this and elemental analyses showed that no CO_2 or H_2O had been lost in the irradiation. No melting or charring of the product occurs at temperatures below 250 °C. The $-C{\equiv}C-$ stretching frequency at 2097 cm^{-1} was absent in the insoluble solid; further information on the constitution of the polymeric product (e.g. appearance of a $-C{=}C-$ peak) was not available using IR spectroscopy owing to the poor definition and extreme broadening of all absorptions in the spectrum of the polymer. Owing to the lack of solubility in all solvents tested, no NMR spectra were obtained. The solid product was amorphous to X-rays. The degree of conversion reaches about 20% after about 20 MRad irradiation; further irradiation results in insignificant increases in yield of product (6.9 Mrad, 9.1%; 16.1 MRad, 18%; 32.2 MRad, 21%; 48.3 MRad, 22%). It should be noted, however, that yields are quantitative based on conversion. Evaporation of the methanol solution gives **5**; X-ray powder photography shows this material to be identical to the original reactant phase.

Results and discussion

The molecular structure of the title complex is shown in Fig. 1; the magnesium ion has crystallographically-imposed $\bar{1}$ symmetry, and resides at the center of a nearly regular octahedron (Table 3). The six-coordinate environment is generated by oxygen atoms from four separate symmetry-related propynoate ligands and two inversion-related water molecules. The propynoate ligands each bridge to four other Mg complexes in a *syn–anti* fashion (Mg–O(1)–C(1), 160.3(1)°; Mg–O(2) –C(1), 130.7(1)°, see Fig. 2). All bridging occurs in the

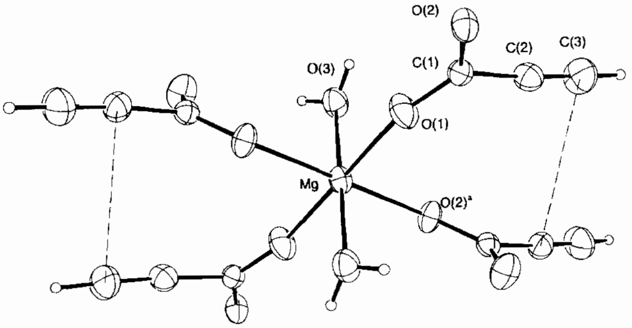

Fig. 1. Molecular structure of $Mg(O_2CC{\equiv}CH)_2(OH_2)_2$, showing 50% probability ellipsoids for atoms refined by using anisotropic displacement parameters. Dashed lines show contacts of 3.698 Å between nearly parallel propynoates.

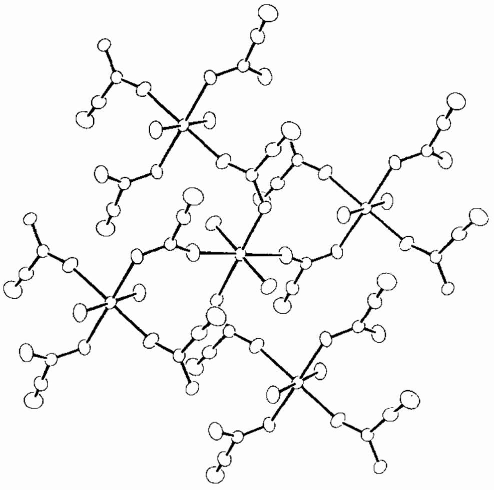

Fig. 2. A view of the two-dimensional coordination polymer in $Mg(O_2CC{\equiv}CH)_2(OH_2)_2$.

ac plane of the crystal structure, and links octahedral complexes to form a two-dimensional coordination polymer, a portion of which is shown in Fig. 2. The Mg–O distances (Table 3) are near the values found in the two forms of diaquabis(formato)magnesium (2.048–2.108 Å) [16, 17]. However, the Mg–O(1) distance, 2.018(1) Å, is significantly shorter; as described below, this O(1) carboxylate oxygen atom does not participate in hydrogen bonding. In the monoclinic modification [16] of the formate, the two independent complexes, each having crystallographic $\bar{1}$ symmetry, exhibit sixfold coordination through (i) six bridging formate groups, and (ii) two bridging formate groups and four water molecules, respectively. In like manner to **5**, the orthorhombic phase also crystallizes in space group *Pbca* [17] and, at the molecular level, has a single Mg ion with crystallographic $\bar{1}$ symmetry, two water molecules and four bridging formate groups. However, in this phase the *syn,anti*-bridging arrangement has more regular Mg–O–C angles (126.1(7), 133.7(8)°).

The crystal structure (Fig. 3) consists of sheets of two-dimensional coordination polymers in the *ac* planes. Strong hydrogen bonds link monomer units within the two-dimensional coordination polymer (O(2)···H(O3B)–O(3) [x, y, $z-1$], O···O, 2.852 Å, O···H–O, 168°). The two-dimensional sheets are interconnected by a weak C–H···O hydrogen bond [18] (C(3)–H(C3)···O(2) [$\frac{1}{2}+x$, $-\frac{1}{2}-y$, $-1-z$], C···O, 3.468 Å, C–H···O, 163°, ν(C–H) 3250 cm^{-1}) and a weak interaction between the other water H atom and the center of the triple bond (O3–H(O3A)···C$_{cent}$ [$\frac{1}{2}+x$, y, $-\frac{1}{2}-z$]), O···C, 3.35 Å, O–H···C, 176°). By contrast, in the orthorhombic phase of diaquabis(formato)magnesium, the two-dimensional layers are interlinked by strong hydrogen bonds between coordinated water and two formate groups in the next layer [17].

As observed in solid state polymerization of other metal propynoates, solid **5** first develops a yellow, then deep brown color upon X- or γ-irradiation. Loss of intensity in the –C≡C– stretching mode indicates the probable formation of a polypropynoate [5–7]. However, lack of solubility precludes further characterization at this time. We have previously shown that, for a solid state reaction to occur, orientational (i.e. angular) requirements appear to be considerably less important than the presence of a set of infinite, short ($\leqslant$4.2 Å) contacts between propynoate moieties [7]. Figure 4 shows an infinite chain of short –C≡C–···–C≡C–···–C≡C– contacts between nearly parallel propynoates (3.698 Å, C(2)–C(3) [$\frac{1}{2}+x$, y, $-\frac{1}{2}-z$]). An additional chain of short contacts at 3.701 Å (C(2)–C(3) [$\frac{1}{2}+x$, $-\frac{1}{2}-y$, $-1-z$]) is not shown. This material is less reactive than the other propynoates studied thus far [4–7], and conversion occurs to a lower extent than in other related materials. This may arise, in part, from the expected lower absorption cross section of **5** for X- or γ-rays. Further work, including solid state NMR studies and the determination of other structures, will help to provide a greater understanding of the factors

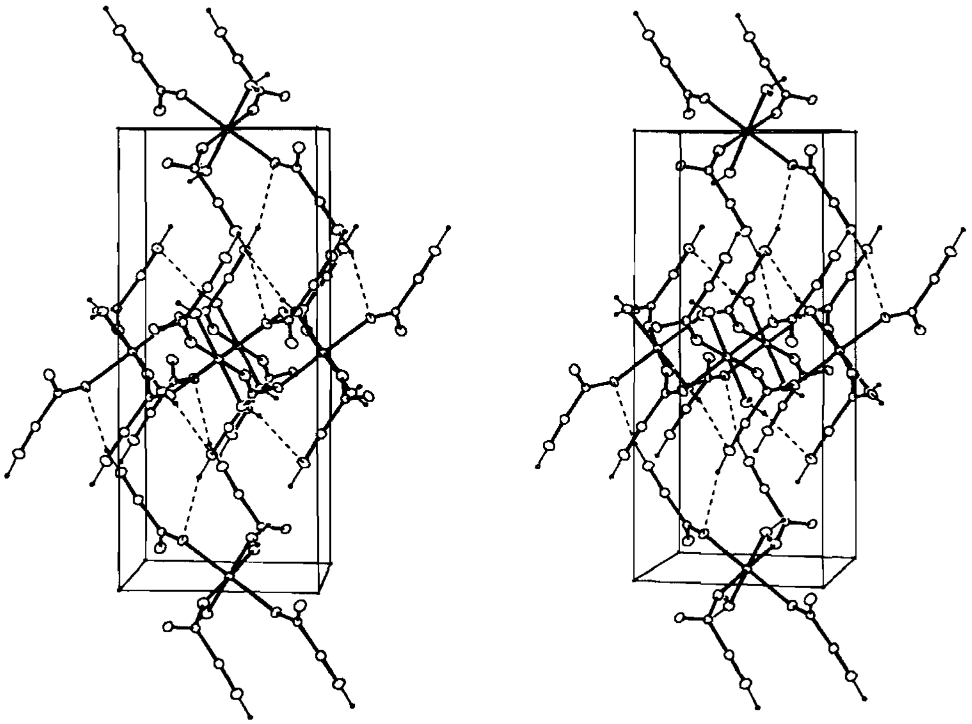

Fig. 3. Stereo view of the unit cell of **5** (*a* horizontal, *b* vertical), with hydrogen bonds shown as dashed lines.

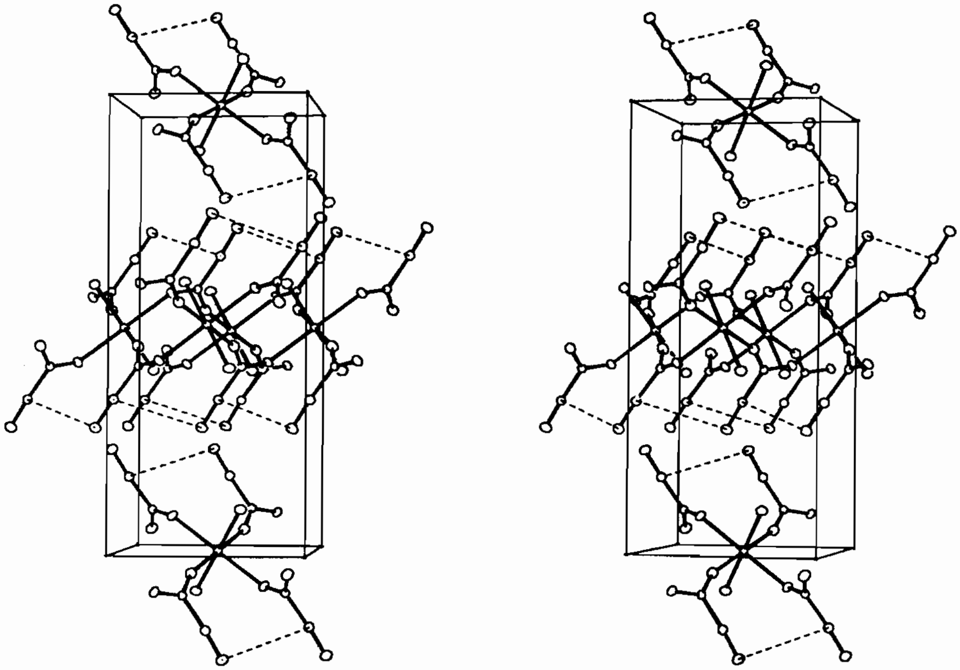

Fig. 4. Stereo view of the unit cell of 5 (*a* horizontal, *b* vertical), showing short contacts (3.698 Å) between nearly parallel acetylene moieties.

which influence the radiation sensitivity of solid metal propynoates.

Supplementary material

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

Acknowledgements

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