Silver Chloroacetate: Crystal Structure and Thermal Polymerization Mechanism

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The structure of silver chloroacetate was determined by single-crystal X-ray structure analysis. This represents the first salt of a monohalogenoacetic acid with a monovalent metal whose structure was determined with high precision. The salt undergoes a thermally induced solid-state polymerization to polyglycolide under elimination of silver chloride. A probable mechanism for a structure-determined reaction in the solid state is discussed.

Introduction

We have recently reported on the unusual solid-state polymerization in salts of halogenoacetic acids that leads to polyglycolide, the simplest polyester[1,2].

$$X{-}CH_2{-}COO^{-}\,{}^{+}M\ (s) \rightarrow 1/n\ [{-}CH_2{-}COO{-}]_n\ (s) + MX\ (s) \quad (1)$$

$X = Cl, Br, I;\ M = Na, K, Rb, NH_4$

The reaction is purely thermally induced. Only a few such polymerizations and oligomerizations in the solid state are known[3–10] in contrast to the well-studied photopolymerization and photooligomerization reactions[11–21]. We found that the polymerization reaction occurs in 7 out of 8 prepared halogenoacetates[2]. Various modern methods, among them thermal analysis, in situ X-ray powder diffractometry, scanning electron microscopy[1,2], in situ EXAFS[22,23] and in situ IR spectroscopy[24] were applied to study this reaction (which has, incidentally, been known for more than 140 years[25,26]). With none of these methods could a liquid intermediate be detected, therefore we assume that this reaction occurs entirely in the solid state. If this is the case, it is very likely that the crystal structure of the parent material, the halogenoacetate, plays a decisive role in the reaction pathway, i.e., that we have a topochemical reaction[11,12,16,20,27]. We report here the crystal structure of silver chloroacetate and discuss structural features that corroborate a solid-state polymerization reaction. The solid-state polymerization in silver chloroacetate was observed as early as 1881 by Beckurts and Otto[28].

Results and Discussion

The previously reported results on the thermochemical reactivity of halogenoacetates suffer from the fact the they could not be underpinned with structural data. Unfortunately, no structure of a salt of a monohalogenoacetic acid with a monovalent metal is reported in the literature, except for sodium fluoroacetate[29]. However, this structure was derived from film data of a small crystal that notably deteriorated under the influence of radiation. With 207 reflections, an R_1 value of 12.7% was obtained. The authors reported the difficulty in growing larger crystals. The structure of ammonium fluoroacetate is known[30], and the structure of ammonium chloroacetate was announced[31], but never published. According to our earlier studies, ammonium chloroacetates melts before elimination of ammonium chloride[2], therefore the structures of ammonium salts are probably not helpful in interpreting thermochemical data of alkali halogenoacetates.

A number of solvate crystal structures of the type $MOOC{-}CH_2{-}X \cdot n\ HOOC{-}CH_2{-}X$ has been solved and reported. However, these structural data are also not very helpful when the reactivity of pure halogenoacetates is discussed as these compounds usually melt before any elimination reaction occurs (see ref.[23] for a detailed study on rubidium bromoacetate · bromoacetic acid). Di- and trihalogenoacetates tend to decompose to ill-defined products[28]. Some structures of di- and trivalent cations with halogenoacetic acids are known; however, because we found that calcium chloroacetate does not polymerize[2], we suppose that these compounds have a different chemical reactivity. In any case, the crystal chemistry of higher-valent cations is likely to be very different from that of monovalent cations.

We report here the structure of silver chloroacetate, the first example of a compound for which a solid-state polymerization has been experimentally proven. In all other cases of a verified polymerizability, the structure is not known. On the other hand, in the cases with a known structure, nothing is known about the polymerizability.

Silver chloroacetate crystallizes as a dimer with two molecules in the asymmetric unit. The asymmetric unit is shown in Figure 1.

Two carboxy groups are bridged almost symmetrically by two silver atoms. The dimer adopts an almost planar structure, although the two O–Ag–O bonds are twisted. The position of the silver atoms between the two oxygen atoms is slightly asymmetric. In the second coordination shell of silver, an oxygen atom and a chlorine atom are coordinated, both by neighboring molecules (Figure 2).

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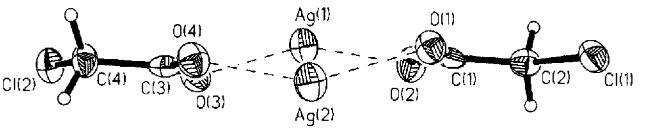
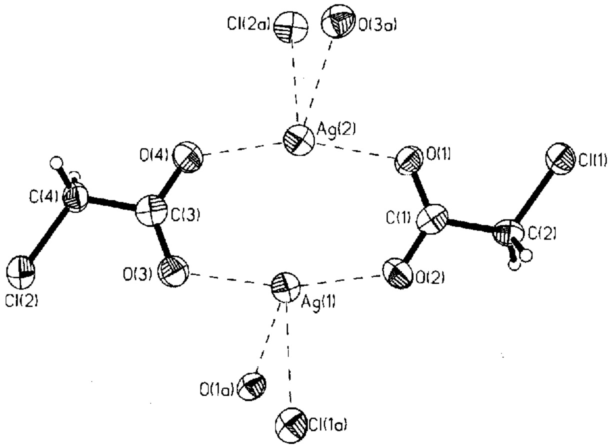
Figure 1. The dimeric unit in silver chloroacetate; two silver ions are bridging the carboxy groups; an almost planar structure is assumed[a]



[a] Selected bond lengths [Å] and angles [Å]: Ag1–O2 = Ag2–O4 2.247(5), Ag1–O3 = Ag1–O2 2.306(14), C–C 1.522(7), C–O 1.262(3), Ag–Ag 2.921(3), C–Cl 1.790(7); O–Ag–O 150.0(5), O–C–O 126.0(3), C–C–Cl 115.2(4), C1–O1–Ag2 = C3–O3–Ag1 115.5(4), C1–O2–Ag1 = C3–O4–Ag2 128.4(4).

Figure 2. The silver ion is coordinated twofold by the two oxygen atoms and in the second coordination sphere by one chlorine atom and one oxygen atom from neighboring molecules[a]



[a] Selected bond lengths [Å]: Ag1–O1a = Ag2–O3a 2.528(4), Ag1–Cl1a = Ag2–Cl2a 2.903(3).

Figure 3. The packing of the silver chloroacetate molecules in the crystals viewed on the *y*-*z* plane; the molecules are arranged in stacks in a herringbone arrangement

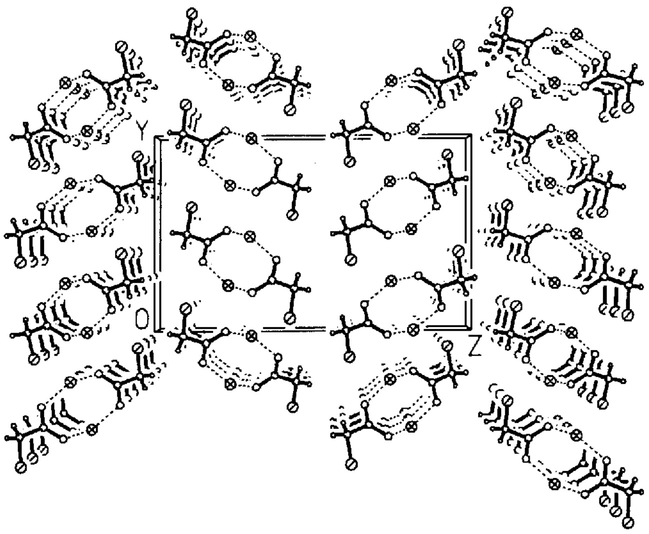
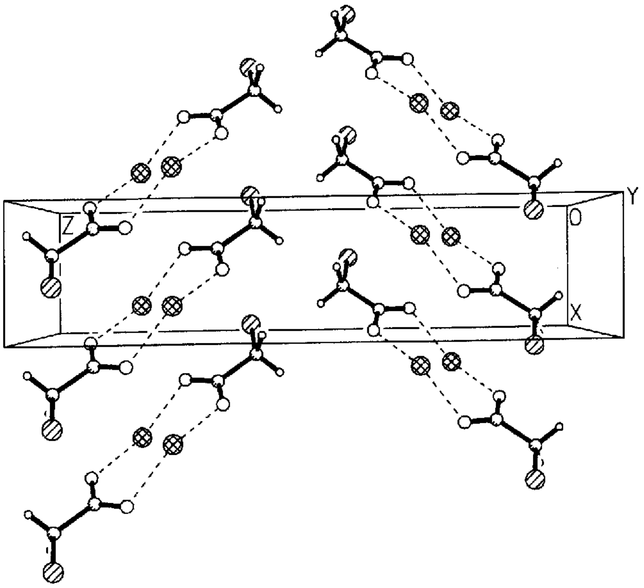


Figure 4. Packing of the silver chloroacetate molecules viewed on the *x*-*z* plane; the stacks are tilted with respect to the *y*-*z* plane



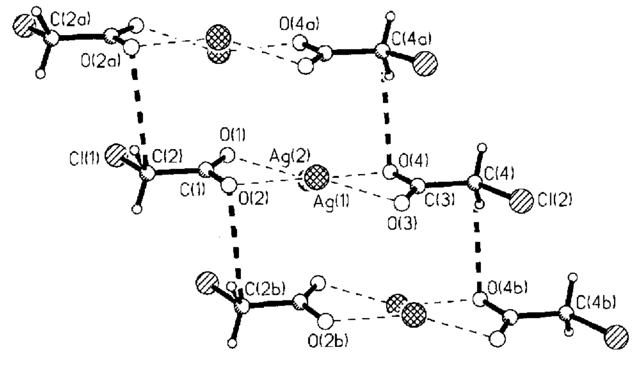
A very similar structure was reported for silver oxalate where two silver cations are bridging two carboxy groups. The divalent nature of oxalic acid leads to long polymeric chains[32]. The distance between the silver atoms in silver chloroacetate is only 2.921 Å. The corresponding values for silver oxalate is 2.945 Å. Both are small values, compared to that in elemental silver (2.8894 Å)[33]

The packing of the dimers in stacks is displayed in Figure 3. Viewed on the *y*-*z* plane, a herringbone arrangement of the single stacks is assumed. Visible is the small distance between silver ions and chlorine atoms in molecules of neighboring stacks. We assume that the short distance of 2.903 Å favors the elimination of silver chloride during the solid-state polymerization reaction. The distance between silver cations and chlorine anions in silver chloride is 2.775 Å[33], which indicates that a considerable attraction should already exist in silver chloroacetate. A distance of 2.56 Å was found in sodium fluoroacetate[29], a value close to the Na–F distance in sodium fluoride (2.317 Å[33]). As far as we know, it has not been determined whether sodium fluoroacetate undergoes thermally induced polymerization.

A projection on the *x*-*z* plane demonstrates that the molecules in different stacks are not arranged in parallel (Figure 4). Neighboring stacks are alternatively tilted against the *y*-*z* plane. In this representation, a possible mechanism for the reaction can be derived.

This mechanism will be demonstrated for three adjacent parallel molecules (Figure 5; slightly tilted projection). We assume that the polymerization occurs in each stack, parallel to the *x* axis. Each silver ion is also coordinated by a chlorine atom from a neighboring chain (not shown) at a distance of 2.903 Å (not shown in Figure 5). This proximity leads to elimination of silver chloride. The ions can leave the site of the reaction through the channels left by the silver ions and chlorine atoms (*x* direction, see Figure 3). The polymerization occurs through the formation of a covalent bond between an oxygen atom of a carboxy group and a carbon atom of a neighboring methylene group

Figure 5. Selection of three adjacent molecules in a stack, and the interactions between carbon and oxygen atoms that could lead to newly formed bonds; two parallel polyglycolide chains are formed in each stack; note that atoms O1a, O3a, Cl1a and Cl2a are labeled differently than in Figure 2



(C2a), as indicated in Figure 5 by dashed bonds. This would involve a shortening of the distance between carbon (e.g. C4a) and oxygen (e.g. O4) atoms from 3.250 Å to approximately 1.43 Å (for a typical C–O bond)[33] during the polymerization. This could partly be accomplished by rotation of the carboxy group around the C3–C4 bond. The magnitude of the angle C3–O4–C4a and the corresponding others is between 94 and 96°. One may speculate that elimination of silver chloride and nucleophilic attack of the oxygen atom at the carbon atom occur simultaneously, leading to a rapid polymerization along the stacks.

Each stack of silver chloroacetate dimers would result in two parallel chains of polyglycolide. Earlier studies on the single-crystal structure of polyglycolide fibers by Chatani et al.[34] reported a chain-like structure of the carboxylate groups that agrees well with the above assumption. The proposed mechanism appears consistent with the classical "topochemical principle" by Schmidt et al. where a proximity of neighboring groups as well as only small movement of reacting groups is postulated[27].

We reported the distinct micromorphology of the formed reaction product[1–2]. The eliminated metal halide is deposited as small cubes ($r \approx 1$ μm) in the polyglycolide matrix. On an atomic-length scale, this requires extensive diffusion of the formed silver chloride. This is remarkable as the reaction occurs smoothly at the considerably low temperature of 134.0°C (onset temperature from DSC; 5 K min^{-1}), driven by its highly negative reaction enthalpy ($\Delta H_r = -64.2$ kJ mol^{-1})[2]. One may speculate that the diffusion of silver and chlorine ions is facilitated by the open tunnels that are formed between the polymerizing carboxylate groups (parallel to the x axis, see Figure 3).

In fact, we have found earlier by in situ X-ray powder diffraction on sodium chloroacetate[2] that the formation of metal halide is delayed compared to the consumption of the halogenoacetate. This delay indicates that a certain time period is required to form larger crystals of metal halide, apparently due to the ions traveling in the crystal. The delay was not observed in an ex situ X-ray diffraction study on sodium chloroacetate[1], a fact that we ascribe to recrystallization of the small sodium chloride crystallites during storage of the aliquots, induced possibly by the surrounding atmospheric water.

In conclusion, the observed crystal structure of silver chloroacetate supports the assumption of a polymerization in the solid state. The elimination reaction is favored by a short distance between the silver ions and the chlorine atoms and also by a short distance between neighboring carboxylate groups. Polymerization occurs along stacks of dimeric units.

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Experimental Section

Growing of Single Crystals of Silver Chloroacetate: A single crystal of silver chloroacetate was grown by a gel method[35,36]. A 1 M aqueous solution of chloroacetic acid was mixed with ethanol and tetraethyl orthosilicate in the volume ratio of 7:3:1. One volume of triethylamine is added. Gelation occurs overnight. A 0.5 M aqueous

Table 1. Crystallographic data for silver chloroacetate

Formula	$C_2H_2AgClO_2$
M_w	201.36 g mol^{-1}
Crystal system	orthorhombic
Space group	$Pbc2_1$ (Int. Tables No. 29)
a / Å	4.198(2)
b / Å	10.988(11)
c / Å	18.015(18)
V / Å^3	831.0(12)
ρ_{calc}	3.219
Z	4
μ(Mo-Kα) / Å	0.71073
Crystal size / mm^3	0.1 · 0.2 · 0.6
T / K	293(2)
Measured reflections	2196
Unique reflections	1119
Observed reflections	1072
No. of parameters	111
R_{int}	0.059
R_1 (all reflections)	0.042
Observed criterion	$I > 2\sigma(I)$
Flack parameter	0.01(11)
wR_2 (all reflections)	0.1102

Table 2. Fractional atomic coordinates (· 10^4) and equivalent isotropic displacement parameters [Å^2] $[U_{eq} = (1/3)\, \Sigma_i \Sigma_j U_{ij} \cdot a_i^* \cdot a_j^* \cdot a_i \cdot a_j]$

	x	y	z	U(eq)
Ag1	2451(2)	4835(1)	3078(1)	42(1)
Ag2	2516(1)	2415(1)	2406(1)	41(1)
Cl1	-5956(4)	945(2)	4330(2)	36(1)
Cl2	10806(5)	6333(2)	1157(2)	42(1)
O1	-1816(14)	2117(6)	3185(4)	35(1)
O2	-221(17)	3678(4)	3900(4)	43(2)
O3	6742(16)	5139(5)	2313(4)	38(1)
O4	5132(14)	3588(4)	1591(4)	39(1)
C1	-1795(19)	2720(8)	3778(5)	31(2)
C2	-3741(19)	2331(6)	4446(5)	32(2)
C3	6692(20)	4546(6)	1709(5)	32(2)
C4	8654(20)	4948(7)	1037(5)	35(2)

solution of silver nitrate is placed above the gel. After 7 d, suitable crystals of silver chloroacetate were found in the gel.

X-ray Crystallographic Study: One colorless crystal was studied at room temperature with an Enraf-Nonius CAD4 four-circle single-crystal diffractometer (Mo-K_α radiation, graphite monochromator) in the range of $2.26° \leq \Theta \leq 27.60°$ [$-2 \leq h \leq 5$, $-2 \leq k \leq 14$, $-2 \leq l \leq 23$; $F(000) = 752$; $\mu(\text{Mo-}k_\alpha) = 5.321\ \text{mm}^{-1}$]. The structure was solved with SHELXS-86[37] and refined by the full-matrix, least-squares method of SHELXL-93[38] (nonhydrogen atoms anisotropic, hydrogen atoms isotropic with a "riding" model). An empirical absorption correction with the program DIFABS was performed[39]. Since silver chloroacetate crystallizes in a polar space group, polar axis constraints were applied by the method of Flack and Schwarzenbach[40,41]. Table 1 summarizes some details on the crystal structure and its determination[42]. Table 2 gives atomic coordinates and equivalent isotropic displacement parameters. The largest peaks in the final difference map were found at $x = 0.7462$, $y = 0.2863$, $z = 0.2400$ (2.28 e Å^{-3}); $x = -0.2465$, $y = 0.4382$, $z = 0.3100$ (2.13 e Å^{-3}); $x = 0.2472$, $y = 0.6955$, $z = 0.2400$ (1.96 e Å^{-3}) and $x = -0.2469$, $y = 0.5310$, $z = 0.3100$ (1.93 e Å^{-3}). They were attributed to some stacking disorder. However, our attempts to refine the structure under this assumption were not successful.

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[42] Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@chemcrys.cam.ac.uk], on quoting the deposition number CCDC-100023.

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