Preparation and Structure of Tris(acetylacetonato)silicon Dichloroargentate

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Dedicated to Prof. Ulrich Wannagat on the occasion of his 70th birthday

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Tris(acetylacetonato)silicon(IV) Cation, Dichloroargentate(I) Anion

The ionic compound $[Si(acac)_3][AgCl_2]\cdot CH_2Cl_2$ (**1**) was synthesized by reaction of $[Si(acac)_3][HCl_2]$ and silver acetate in dichloromethane. A single-crystal X-ray analysis shows that the cation has an octahedral tris-chelate structure and that the anion is a polymeric chain, composed of edge-sharing $AgCl_4$ tetrahedra.

In a search for anions yielding well crystallizing salts when combined with voluminous unipositive silicon complex cations such as $[Si(acac)_3]^+$ [1, 2] we expected halogenoargentate anions to be good candidates. The mononuclear $[AgI_3]^{2-}$ [3], the dinuclear $[Ag_2Cl_4]^{2-}$ [4] or the polynuclear $[AgCl_2]^-$ [5] are known to form from silver(I) halides in the presence of excess halide and to yield salts with a good crystallization tendency when combined with substituted ammonium cations.

The starting complex of our investigation was the salt $[Si(acac)_3][HCl_2]$ [1, 6]. The addition of powdered silver acetate to a solution of $[Si(acac)_3][HCl_2]$ in dichloromethane causes the formation of a silver chloride precipitate. In addition, needle-shaped colorless crystals of a not yet identified product form, when the reaction mixture is layered with an diethylether/pentane mixture. These crystals disappear, together with the AgCl, on standing of the reaction mixture within a few days. At the same time, the formation of well developed crystals of $[Si(acac)_3][AgCl_2]\cdot CH_2Cl_2$ (**1**) is observed. The crystals are stable in air for a limited time. They quantitatively loose solvent when heated to 85 °C.

The formation of **1** can be described as a two step process:

$$[Si(acac)_3][HCl_2] + AgCH_3COO \rightarrow [Si(acac)_3]^+ + Cl^- + AgCl + CH_3COOH$$

$$[Si(acac)_3]^+ + Cl^- + AgCl \xrightarrow{CH_2Cl_2} [Si(acac)_3][AgCl_2]\cdot CH_2Cl_2$$

The far infrared spectrum showed strong but poorly resolved absorption bands in the 100 to 200 cm^{-1} region. This is in accord with the presence of $[AgCl_2]^-$ chains with tetracoordinate silver atoms [7].

The results of an X-ray analysis are shown in Figures 1 and 2. The structural data for the cation agree within narrow limits with those of the $[Si(acac)_3]^+$ cation in its $TCNQ^-$ salt ($TCNQ^-$ = 7,7,8,8-tetracyano-p-quinodimethan radical anion) [2].

The C_3O_2 parts of the three chelate rings are nearly planar with deviations less than 0.02 Å from their respective best planes. The Si atom deviates by 0.44, 0.20, and 0.21 Å from these planes. Correspondingly, the A, B, and C chelate rings are folded by 21.2°, 9.8°, and 9.9° along their O–O axes. The complex cations are chiral. Since the space group is centrosymmetric, the crystal contains equal amounts of Λ and Δ complex cations.

The silver atoms in the linear polymeric macro anions are tetrahedrally coordinated. The $[AgCl_2]^-$ chains are parallel to each other, running along

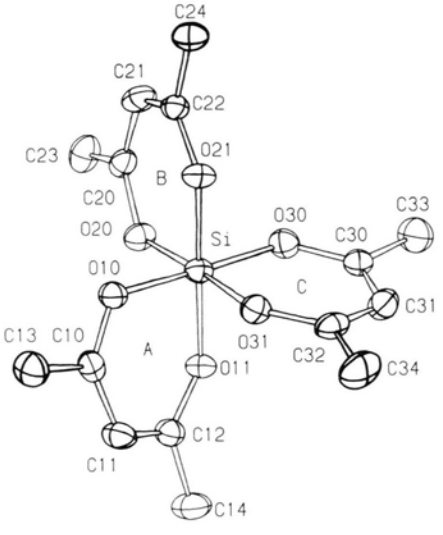

Fig. 1. The $[Si(acac)_3]^+$ cation. Selected bond lengths [Å] and angles [deg]: Si–O: 1.770 ± 0.004, O–C: 1.288 ± 0.003, C–C: 1.375 ± 0.007, C–C(methyl): 1.497 ± 0.007, O–Si–O: 93.8 ± 0.4, Si–O–C: 127.6 ± 0.8, O–C–C: 122.9 ± 0.2, C–C–C: 121.6 ± 0.4, C–C–C(methyl): 122.1 ± 0.4.

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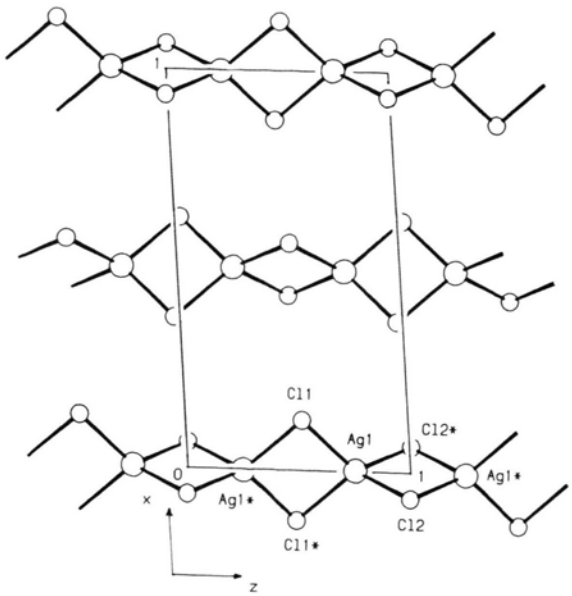

Fig. 2. Projection of the anionic part of the crystal structure of **1** along the y axis. Selected bond lengths [Å] and angles [deg]: Ag–Cl(1): 2.586, Ag–Cl(1)*: 2.689, Ag–Cl(2): 2.643, Ag–Ag*: 3.744, Cl(2)–Ag–Cl(1): 123.0.

the crystallographic z axis (Fig. 2). The same type of $[AgX_2]^-$ macro anions is found in $[N(CH_3)_4][AgCl_2]$ [5] and $[N(CH_3)_4][AgI_2]$ [8]. Interestingly, there also exists the dimeric $[Ag_2Cl_4]^{2-}$ anion containing Ag^+ in a distorted trigonal-planar coordination. This anion occurs in $[PPh_4]_2[Ag_2Cl_4]$ [4]. The data available so far for substituted ammonium and phosphonium haloargentates suggest that the nuclearity of the anions drops with increasing size of the cations. Evidently the $[Si(acac)_3]^+$ and $[N(CH_3)_4]^+$ cations are equivalent, concerning their preference to crystallize with polymeric $[AgCl_2]^-$ anions. The salts containing $(AgX_2^-)_n$ macro anions are the final products of the aggregation of AgX_2^- units. Consistent with their polymeric structure they are insoluble or of low solubility. From the fact that we isolated only **1**, we cannot conclude, however, that no mononuclear and/or polynuclear anions exist in solution.

Experimental

Preparation of tris(acetylacetonato)silicon dichloroargentate(I) (**1**)

240 mg of $[Si(acac)_3][HCl_2]$ (0.6 mmol), prepared according to ref. [6], were dissolved in 10 ml of dichloromethane and 100 mg silver acetate (0.6 mmol) were added. The suspension was stirred at room temperature for 4 h. Then it was layered with 15 ml of a diethylether/pentane (1 : 1) mixture. Needle-shaped colorless crystals of an unidentified reaction product grew overnight. During the next few days, these crystals dissolved together with most of the gray AgCl precipitate and the colorless prisms of **1** began to grow; yield of these crystals: 126 mg (41%). They are not soluble in any of the common solvents. Decomposition without melting occurs at about 200 °C.

IR (KBr, cm^{-1}): 3120 s, 3045 s, 2960 s, 2920 s, 1555 vs, 1420 s, 1385 s, 1340 s, 1310 s, 1190 w, 1030 s, 960 m, 840 w, 820 w, 650 w, 615 m, 540 m, 460 w. – Far IR (Nujol): 356 m, 344 m, 287 w, 220 ··· 100 s.

$C_{16}H_{23}AgCl_4O_6Si$ (589.1)
Found C 32.0 H 3.8 Ag 18.21 Cl 20.0 Si 4.66%,
Calcd C 32.6 H 3.9 Ag 18.31 Cl 24.1 Si 4.77%.

Table I. Atomic Parameter for **1**.

Atom	x	y	z	U_{eq}
Anion				
Ag	1.00218(3)	.00041(2)	.75140(5)	.051(1)
Cl(1)	.12520(8)	.03330(6)	.52416(15)	.047(1)
Cl(2)	.93494(9)	.07079(5)	.99161(15)	.044(1)
Cation				
Si	.47274(9)	.18478(5)	.04433(16)	.035(1)
O(10)	.4247(2)	.2532(1)	−.0247(4)	.040(2)
O(11)	.5008(2)	.2076(1)	.2685(4)	.038(2)
O(20)	.3552(2)	.1626(1)	.1098(4)	.041(2)
O(21)	.4481(2)	.1616(1)	−.1785(4)	.043(2)
O(30)	.5187(2)	.1152(1)	.1094(4)	.042(2)
O(31)	.5905(2)	.2098(1)	−.0133(4)	.042(2)
C(10)	.4496(3)	.3024(2)	.0462(7)	.043(3)
C(11)	.4968(4)	.3078(2)	.2152(6)	.049(3)
C(12)	.5153(3)	.2598(2)	.3244(6)	.043(3)
C(13)	.4214(4)	.3548(2)	−.0652(7)	.058(3)
C(14)	.5530(4)	.2653(2)	.5153(7)	.061(4)
C(20)	.2905(3)	.1292(2)	.0244(6)	.039(3)
C(21)	.2977(3)	.1129(2)	−.1498(7)	.047(3)
C(22)	.3749(3)	.1302(2)	−.2460(6)	.039(3)
C(23)	.2075(3)	.1098(2)	.1298(7)	.055(3)
C(24)	.3805(4)	.1135(2)	−.4381(6)	.055(3)
C(30)	.6100(3)	.0982(2)	.1325(6)	.043(3)
C(31)	.6895(4)	.1323(2)	.0965(7)	.050(3)
C(32)	.6771(3)	.1863(2)	.0238(6)	.046(3)
C(33)	.6239(4)	.0378(2)	.2023(7)	.062(4)
C(34)	.7646(4)	.2233(3)	−.0194(8)	.074(4)
Solvent				
Cl(1A)	.62073(14)	.01715(8)	.72746(24)	.088(1)
Cl(1B)	.67435(14)	.12978(8)	.59826(23)	.088(1)
C(1A)	.7210(4)	.0622(3)	.6797(8)	.075(4)

X-ray crystallography

A crystal (size 0.6, 0.6, 0.5 mm) was mounted on a glass fibre and coated with lacquer. X-ray data were collected on a Philips PW 1100 instrument (MoKα radiation, λ = 0.71069 Å, graphite monochromator, room temperature, 2θ range 4° to 40°). Crystal data: M_r = 589.1, monoclinic, $P2_1/n$ (No. 14), a = 13.414(2), b = 23.074(4), c = 7.519(1) Å, β = 94.77(2)°, V = 2319.2 Å^3, Z = 4, d_o = 1.66, d_c = 1.687 g·cm^{-3}, F(000) = 1184 e, μ = 12.9 cm^{-1}. Intensity data: 4509 reflections measured, 4216 unique reflections, 3594 reflections considered as observed ($I > 1.0\sigma(I)$). The structure was solved by direct methods (WXMY program [9]). At a later stage, hydrogen atoms were included (U = 0.08 Å^2) for the F_c calculations, but were not refined. Refinement [10] with anisotropic temperature factors for the heavy atoms gave R = 0.052, $R_w(F)$ = 0.0485, 253 parameters, ϱ_{max} = 0.65 e·Å^{-3}. Atomic coordinates are listed in Table I. Further details concerning the crystal structure analysis are available upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2 (FRG), by quoting the depository number CSD-55607, the names of the authors, and the journal citation.

[1] W. Dilthey, Chem. Ber. **36,** 923 (1903).
[2] K. Ueyama, G. Matsubayashi, I. Shimohara, and T. Tanaka, J. Chem. Res. (M) **1985,** 801.
[3] G. A. Bowmaker, G. R. Clark, D. A. Rogers, A. Camus, and N. Marsich, J. Chem. Soc. Dalton Trans. **1984,** 37.
[4] G. Helgesson and S. Jagner, J. Chem. Soc. Dalton Trans. **1988,** 2117.
[5] G. Helgesson, M. Josefsson, and S. Jagner, Acta Crystallogr. Sect. C, **44,** 1729 (1988).
[6] R. F. Riley, R. West, and R. Barbarin, Inorg. Synth. **7,** 30 (1963).
[7] G. L. Bottger and A. L. Geddes, Spectrochim. Acta, Part A, **23,** 1551 (1967).
[8] K. Peters, H. G. von Schnering, W. Ott, and H.-M. Seidenspinner, Acta Crystallogr. Sect. C, **40,** 789 (1984).
[9] T. Debaerdemaeker, Z. Kristallogr. submitted for publication.
[10] G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, England (1976).