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NOTE

A STRUCTURAL STUDY OF THE SILVER PERCHLORATE 1,5-HEXADIENE COMPLEX $2\,AgClO_4 \cdot 3\,C_6H_{10}$

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A bidimensional X-ray examination was undertaken in order to study the molecular structure of crystalline silver perchlorate 1,5-hexadiene complex, the stoichiometry of which is strikingly different in respect to that of 1:1 complexes formed by $AgClO_4$ with 1,7-octadiene and 1,9-decadiene[1].

The study of the structure of $2\,AgClO_4 \cdot 3\,C_6H_{10}$ complex appeared interesting also because the IR examination of this crystalline complex shows that all the double bonds of 1,5-hexadiene are interacting with Ag^+ ions[1].

EXPERIMENTAL

The crystalline $2\,AgClO_4 \cdot 3\,C_6H_{10}$ complex was prepared by Bressan *et al.*[1]. Crystals are thermally stable (m.p. 105°) unless they are exposed prolongedly to light and air. Crystals are approximately rod shaped and the direction of elongation generally corresponds to the axis labelled as *b*. They were cut, when necessary, in order to be rod-shaped also in other directions and were sealed in Lindemann glass capillaries. The X-ray examination was performed in a Weissenberg camera using Cu-$K\alpha$ radiation.

The *b* and *c* projections of the unit cell were investigated. The intensities of reflections, evaluated by visual estimation, were corrected by the usual angular factors and the absorption was taken into account in the approximation of a cylindrical shape of crystals.

RESULTS AND DISCUSSION

The unit cell of $2\,AgClO_4 \cdot 3\,C_6H_{10}$ is monoclinic; its parameters are:

$$a = 13.39 \pm 0.04\ \text{Å};\quad b = 13.05 \pm 0.04\ \text{Å};\quad c = 7.22 \pm 0.03\ \text{Å}$$
$$\gamma = 98°;\quad Z = 4\,AgClO_4 \cdot 6\,C_6H_{10};\quad D_c = 1.76\ \text{g/cm}^3$$

The systematic absence of the $(hk0)$ reflections when $k \neq 2n$ and of the $(00l)$ reflections when $l \neq 2n$ indicates that the space group is $P2_1/b$. Four of the six molecules of 1,5-hexadiene contained in the unit cell must be in general positions [1,5-hexadiene (I)] while the remaining two [1,5-hexadiene (II)] must be placed on symmetry centres.

From Patterson projections on (010) and (001) the x, y, z coordinates of Ag and Cl atoms were obtained. The signs of almost all the (*h*0*l*) and of most of the (*hk*0) reflections are thus obtained.

From successive Fourier projections and trial calculations on (010) and (001), it was possible to define, to a fairly good approximation, the positions of the C atoms of the diolefin molecules having the following best trial conformations:

1,5-Hexadiene (I)	1,5-Hexadiene (II)
$\widehat{(\overline{C_1C_2C_3})\quad(\overline{C_2C_3C_4})} \approx -130°$	$\widehat{(\overline{C_{9'}C_{8'}C_{7'}})\quad(\overline{C_{8'}C_{7'}C_7})} \approx -110°$
$\widehat{(\overline{C_2C_3C_4})\quad(\overline{C_3C_4C_5})} \approx 70°$	$\widehat{(\overline{C_{8'}C_{7'}C_7})\quad(\overline{C_{7'}C_7C_8})} \approx 180°$
$\widehat{(\overline{C_3C_4C_5})\quad(\overline{C_4C_5C_6})} \approx -130°$	$\widehat{(\overline{C_{7'}C_7C_8})\quad(\overline{C_7C_8C_9})} \approx 110°$

The bond lengths and valence angles here assumed are:

$$\text{C–C} = 1.54\ \text{Å};\ \text{C=C} = 1.34\ \text{Å};\ \measuredangle\,\text{C–C–C} = 112°40';\ \measuredangle\,\text{C=C–C} = 125°$$

Fig. 1 shows the projection on 001 of the crystal structure of the silver perchlorate 1,5-hexadiene complex. Both double bonds of the hexadiene (I) molecule

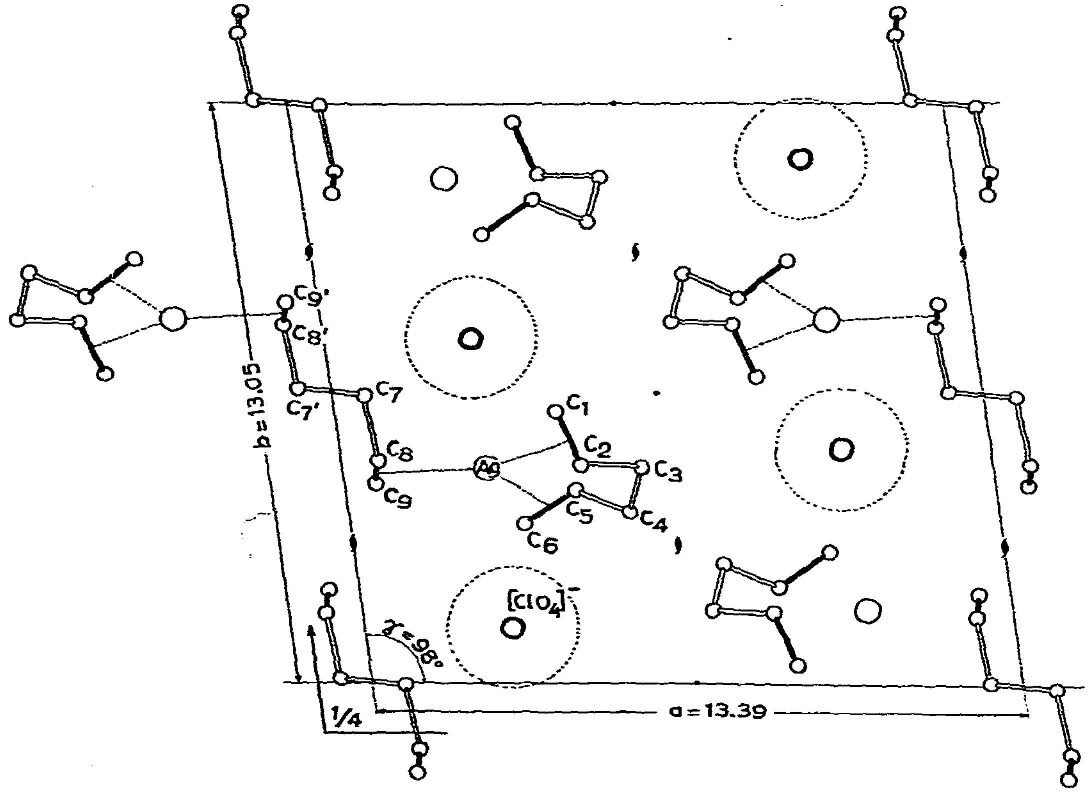

Fig. 1. Projection along the *c* axis of the structure of the silver perchlorate 1,5-hexadiene complex.

are π-bonded to the same Ag^+ ion, whereas the double bonds of the hexadiene (II) molecule are π-bonded to two different Ag^+ ions. The coordination of the C=C double bonds around each Ag^+ ion was found to be a deformed trigonal coordination with distances between Ag^+ and the centres of the double bonds of ~2.4 Å.

The coordination distances Ag–C are analogous to those found for the silver perchlorate benzene complex[2], for the silver nitrate cyclooctatetraene complex[3] and for the silver nitrate *cis,cis,cis*-1,4,7-cyclonoatriene complex[4].

The atomic coordinates of Ag, Cl and C atoms are reported in Table 1.

TABLE 1

ATOMIC COORDINATES OF Ag, Cl AND C ATOMS

Atom	*x/a*	*y/b*	*z/c*
Ag	0.2188	0.3683	0.2500
Cl	0.224	0.096	0.538
C_1	0.340	0.468	0.477
C_2	0.366	0.377	0.439
C_3	0.459	0.375	0.307
C_4	0.431	0.294	0.155
C_5	0.353	0.334	0.024
C_6	0.268	0.271	0.985
C_7	0.050	0.493	0.445
C_8	0.058	0.380	0.410
C_9	0.049	0.342	0.239

The introduction of the carbon atoms in the structure factors calculations improves the reliability factor *R*, which lowers from 24% and 22% (*R* calculated with Ag and Cl atoms only) to 21% and 15% (*R* calculated with Ag, Cl and C atoms) respectively for the (001) and the (010) projection. The thermal factor, *B*, was assumed isotropic and equal to 6.4 Å^2 for both projections.

On the contrary, it was not possible to establish a set of coordinates for the oxygen atoms that could decidedly lower the reliability factor *R*.

It is however significant that the *R* factor improves if the ClO_4^- ions are considered freely rotating around the Cl^- atoms. A check of the interatomic distances between atoms of different molecular ions shows that they reach reasonable values (lowest C–C distance: 3.6 Å).

The most interesting feature of the crystal structure of this complex lies in the presence of binuclear ions $[Ag_2(C_6H_{10})_3]^{2+}$. These ions seem to be present also in the solutions of the complex. The IR spectra of the ethyl alcohol solutions of $2\,AgClO_4 \cdot 3\,C_6H_{10}$ in fact do not show the absorption band at 1643–1645 cm^{-1} corresponding to the C=C stretching of free 1,5-hexadiene molecules, whereas one absorption band is present at 1576 cm^{-1}, which is very near to the two peculiar bands of the crystalline complex (1598 cm^{-1} and 1586 cm^{-1})[1].

With our X-ray data and the limitations of a bidimensional analysis, no further refinement of the crystal structure of this complex is possible. The signs of the structure factors when calculated with Ag and Cl only in respect to the calculation in which carbon atoms are also included, do not vary. Furthermore many atoms overlap in both electron density projections, and the thermal factor *B* has a high value.

In our opinion, the binuclear ion model of the silver perchlorate 1,5-hexadiene complex and its approximate stereochemistry is substantially proved by this work. No tridimensional refinement of the structure of this complex will be undertaken.

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