Structure of the Potassium Salt of *p*-Chloranil, Solvated with Acetone

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Abstract

Crystals of the salt $K^+ . C_6Cl_4O_2^-$, solvated with acetone in the crystal lattice, are monoclinic, space group $P2_1/c$, with $a = 11\cdot121$ (6), $b = 16\cdot880$ (8), $c = 7\cdot203$ (4) Å, $\beta = 105\cdot9$ (1)°, $Z = 4$. Intensity data were collected on a four-circle diffractometer with Mo $K\bar{\alpha}$ radiation. The structure was solved by direct methods and refined by full-matrix least squares to a final conventional R value of $0\cdot087$ for the 1195 observed reflections with $I \geq 3\sigma(I)$. The quinoid ring adopts a shallow chair conformation with the chlorine atoms significantly displaced from its mean plane. Chloranil anions are alternately stacked ($3\cdot384$ and $3\cdot761$ Å), approximately along the c axis, to form columns, with the molecular planes almost parallel to each other. Between the columns there are channels running along the c axis, in which acetone molecules are accommodated.

Introduction

The alkaline salts of *p*-chloranil (CA) are almost unique among organic free-radical salts in that they are able to crystallize by incorporating solvent molecules (Hiroma & Kuroda, 1974; Sugano, Ohta & Kuroda, 1975). The physical properties of the crystalline solvated forms are strikingly different from those of the solvent-free form. For instance, the hydration process of the potassium salt of chloranil (KCA) results in an increase of the electronic absorption band attributed to the charge-transfer interaction among radicals (Hiroma & Kuroda, 1974) and in a decrease of the spin paramagnetism (Hiroma & Kuroda, 1974; Sugano, Ohta & Kuroda, 1975). Furthermore, organic solvents like acetone can enter into the crystal lattice of KCA to form solvent-containing crystals characterized by a low paramagnetic susceptibility (Hiroma & Kuroda, 1974).

It has also been shown (Bozio, Girlando & Pecile, 1977) that the infrared spectra of both the hydrate and acetone-containing forms display strong bands, in addition to those proper to the solvent molecules, which are absent in the room-temperature spectrum of solvent-free KCA and are attributable to a vibronic effect. Changes of the physical properties quite similar to those mentioned above have been found to occur when the solvent-free form of KCA is cooled below the phase-transition temperature (220 K) (Sugano, Ohta & Kuroda, 1975; Bozio, Girlando & Pecile, 1977; André & Weill, 1971).

The crystal structure of the polymorphic *a* form of KCA at room temperature has been reported (Konno, Kobayashi, Marumo & Saito, 1973). It is orthorhombic, space group $P2_12_12_1$, with unit-cell dimensions: $a = 13\cdot49$, $b = 17\cdot02$, $c = 4\cdot03$ Å. CA anions are stacked at equal intervals forming columns parallel to the c axis, the interplanar spacing being $3\cdot47$ Å. The crystal structure of the low-temperature phase of solvent-free KCA and those of the solvated forms have not yet been reported.

In the absence of this fundamental information, it has been widely assumed (Hiroma & Kuroda, 1974; Sugano, Ohta & Kuroda, 1975; Bozio, Girlando & Pecile, 1977; André & Weill, 1971; Hiroma & Kuroda, 1973) that the structural change responsible for the strong variation of physical properties observed on going from the high-temperature to the low-temperature phase of KCA, or to the solvated forms, is a change from regular stacks of CA anions to dimerized ones characterized by alternating interplanar distances.

In view of the interesting behaviour of solvent-containing forms of KCA and of their similarity to the low-temperature phase of solvent-free KCA we have decided to perform crystal structure analyses of this series of salts in order to elucidate the role of the crystal structure in determining their physical properties. In the present paper we report the crystal and molecular structure of the KCA salt solvated with acetone.

Experimental

Crystals of the KCA salt solvated with acetone were obtained by slow diffusion of KI and CA acetone solutions using the crystal-growth apparatus described by Pott & Kommandeur (1967). As the crystals gradually lose acetone, the crystals to be subjected to X-ray analysis were mounted in quartz capillaries; a few drops of acetone were placed at each end of the capillary which was then sealed with a high-vacuum wax.

Table 1. *Crystal data*

$K^+.C_6Cl_4O_2^-.C_3H_6O$	$V = 1300.4$ Å^3
$M_r = 343.05$	Space group $P2_1/c$
$\lambda(\text{Mo } K\alpha) = 0.7107$ Å	$Z = 4$
$a = 11.121$ (6) Å	$D_c = 1.752$ Mg m^{-3}
$b = 16.880$ (8)	$\mu(\text{Mo } K\alpha) = 1.208$ mm^{-1}
$c = 7.203$ (4)	$F(000) = 684e$
$\beta = 105.9$ (1)°	

The crystal data, obtained from single-crystal diffractometry, are given in Table 1. The intensities were collected from a crystal $0.30 \times 0.30 \times 0.05$ mm on a Philips PW 1100 four-circle diffractometer operating in the $\theta/2\theta$ scan mode (scan width = $1.1°$, scan speed = $0.04°$ s^{-1}), with Mo $K\bar{\alpha}$ radiation monochromatized by a graphite crystal. 1537 independent reflections up to $\theta = 25°$ were measured, of which 1195 had intensities greater than three times their standard deviations (σ), σ being calculated from the counting statistics of the measurements. During the data collection three standard reflections were measured every 60 min to check the stability of the crystal and electronics. The fall in their intensities reached about 18%, as a result of acetone loss from the crystal. Intensities were corrected for Lorentz and polarization effects and were converted to an absolute scale by Wilson's method. Absorption and extinction corrections were ignored.

Structure determination and refinement

The positional parameters of all non-hydrogen atoms were determined by direct methods. Normalized structure factors were calculated and the 150 reflections with $|E(hkl)| \geq 1.40$ were used in the phasing program *MULTAN* (Germain, Main & Woolfson, 1971). An E map was calculated and the structural solution was evident. The conventional R value was 0.21. The refinement of the structure parameters was carried out by full-matrix least-squares analysis, allowing the atoms to vibrate anisotropically. The correction for the real and imaginary parts of the anomalous dispersion was applied to Cl and K only (*International Tables for X-ray Crystallography*, 1974a).

The final R value for the 1195 observed reflections with $I \geq 3\sigma(I)$ was 0.087. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1$. The calculations were carried out on the Cyber 76 computer of the Centro di Calcolo Inter-Universitario Italia Nord Orientale with the *SHELX* 76 system of computing programs (Sheldrick, 1976). All scattering factors were those of *International Tables for X-ray Crystallography* (1974b).*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34433 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Intramolecular bond distances (Å) and angles (°), with e.s.d.'s in parentheses, for the CA$^-$ anion and the acetone molecule*

Cl(1)–C(2)	1.71 (1)	C(1)–C(2)–C(3)	123 (1)
Cl(2)–C(3)	1.70 (1)	C(1)–C(2)–Cl(1)	116 (1)
Cl(3)–C(5)	1.70 (1)	Cl(1)–C(2)–C(3)	120 (1)
Cl(4)–C(6)	1.70 (1)	C(2)–C(3)–C(4)	122 (1)
O(1)–C(1)	1.25 (2)	C(2)–C(3)–Cl(2)	123 (1)
O(2)–C(4)	1.26 (2)	Cl(2)–C(3)–C(4)	115 (1)
C(1)–C(2)	1.44 (2)	C(3)–C(4)–C(5)	116 (1)
C(2)–C(3)	1.36 (2)	C(3)–C(4)–O(2)	123 (1)
C(3)–C(4)	1.43 (2)	O(2)–C(4)–C(5)	121 (1)
C(4)–C(5)	1.44 (2)	C(4)–C(5)–C(6)	122 (1)
C(5)–C(6)	1.38 (2)	C(4)–C(5)–Cl(3)	118 (1)
C(6)–C(1)	1.44 (2)	Cl(3)–C(5)–C(6)	121 (1)
		C(5)–C(6)–Cl(4)	122 (1)
C(A1)–O(A)	1.24 (2)	C(5)–C(6)–C(1)	122 (1)
C(A1)–C(A2)	1.54 (2)	Cl(4)–C(6)–C(1)	116 (1)
C(A1)–C(A3)	1.51 (2)	C(6)–C(1)–C(2)	115 (1)
		C(6)–C(1)–O(1)	123 (1)
		O(1)–C(1)–C(2)	122 (1)
		O(A)–C(A1)–C(A2)	117 (1)
		O(A)–C(A1)–C(A3)	120 (1)
		C(A2)–C(A1)–C(A3)	122 (1)

Table 3. *Atomic coordinates with their e.s.d.'s in parentheses*

	x	y	z
Cl(1)	0.7707 (4)	0.4809 (3)	0.0999 (8)
Cl(2)	0.9096 (4)	0.6452 (2)	0.1809 (8)
Cl(3)	1.3419 (4)	0.4956 (2)	0.4657 (7)
Cl(4)	1.2041 (4)	0.3319 (2)	0.3933 (8)
O(1)	0.9362 (9)	0.3473 (5)	0.234 (1)
O(2)	1.1732 (9)	0.6296 (5)	0.367 (1)
C(1)	0.992 (1)	0.4122 (7)	0.263 (2)
C(2)	0.927 (1)	0.4863 (8)	0.218 (2)
C(3)	0.986 (1)	0.5576 (7)	0.244 (2)
C(4)	1.117 (1)	0.5641 (7)	0.337 (2)
C(5)	1.184 (1)	0.4907 (7)	0.383 (2)
C(6)	1.124 (1)	0.4186 (7)	0.350 (2)
K	0.1701 (3)	0.7411 (2)	0.0851 (5)
O(A)	0.6363 (9)	0.2137 (6)	0.582 (2)
C(A1)	0.546 (1)	0.1683 (8)	0.537 (3)
C(A2)	0.479 (2)	0.149 (1)	0.694 (3)
C(A3)	0.503 (2)	0.135 (1)	0.336 (3)

Results and discussion

The geometries of the CA$^-$ anion and of the acetone molecule are shown in Table 2, where bond lengths and valence angles, not corrected for changes due to thermal vibration, are marked. The final structural parameters with the e.s.d.'s of all non-hydrogen atoms are listed in Table 3. Least-squares planes (with the dihedral angle) are given in Table 4.

Deviations from planarity are observed in the CA$^-$ anion. The ring adopts a shallow chair conformation with the chlorine atoms significantly displaced from the mean plane through the C_6 ring. With regard to the
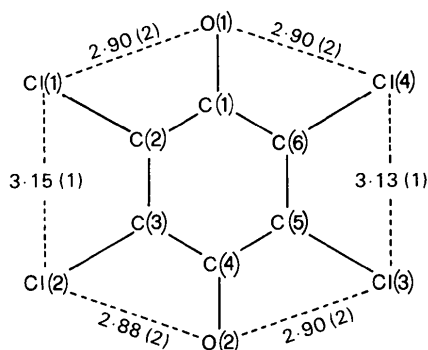
Fig. 1. Intramolecular non-bonded distances (Å) in the CA⁻ anion.

Fig. 2. Coordination about the K^+ cation and nearest-neighbour overlap within a column of CA⁻ anions.

Table 4. *Deviations* (Å) *of the atoms from some least-squares planes*

The equations of the planes are in the form $PX + QY + RZ = S$ in orthogonal Å space with X parallel to a, Z perpendicular to a in the *ac* plane, and Y perpendicular to the *ac* plane. Asterisks indicate atoms not used in the plane calculations.

Plane A: $-0.4217X + 0.0325Y + 0.9061Z = -2.5533$

C(1)	−0.005 (15)	C(4)	0.023 (15)
C(2)	0.020 (15)	C(5)	−0.010 (15)
C(3)	−0.029 (15)	C(6)	0.001 (15)
Cl(1)*	−0.088 (7)	Cl(3)*	−0.158 (7)
Cl(2)*	−0.073 (7)	Cl(4)*	−0.116 (7)
O(1)*	0.014 (11)	O(2)*	0.004 (11)

Plane B: $-0.5479X + 0.7838Y − 0.2926Z = -1.6021$

O(A)	0.002 (12)	C(A1)	−0.005 (16)
C(A2)	0.002 (16)	C(A3)	0.002 (16)

The dihedral angle between planes A and B is 89.5°.

planarity of the anion, it was noticed (van Weperen & Visser, 1972) that the chloro derivatives of *p*-benzo-quinone also have a tendency to be non-planar, the O and Cl atoms substituted at neighbouring atoms being alternately above and below the best plane through the C atoms.

The intramolecular non-bonded distances (Fig. 1) agree well with those observed in tetrachloro-*p*-benzo-quinone (chloranil) and are appreciably shorter than the sums of the van der Waals radii (1.8, 1.4 and 1.7 Å for Cl, O and C respectively; Nyburg, 1961). There-fore, the non-planarity of the CA⁻ anion may be ascribed to steric interaction between the substituents.

The observed length of the C—Cl bonds, which is significantly shorter than the sum of the single-bond covalent radii, 1.742 Å (Pauling, 1960), agrees with values from tetrachloro-*p*-benzoquinone, a chloranil–1,5-diaminonaphthalene complex, chloroethylenes and other aromatic compounds (van Weperen & Visser, 1972; Tamura & Ogawa, 1977; Chu, Jeffrey & Sakurai, 1962). The e.s.d.'s of the remaining bond
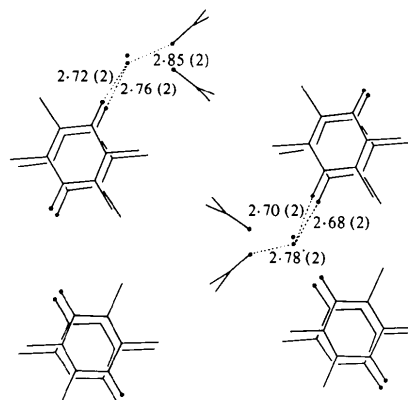
lengths and angles are rather high; thus it may not be appropriate to discuss bonds and angles in detail and to compare their values with those observed in tetra-chloro-*p*-benzoquinone (van Weperen & Visser, 1972), in the chloranil–1,5-diaminonaphthalene complex (Tamura & Ogawa, 1977) and in other chloranil molecular complexes (Prout & Tickle, 1973, and references therein).

The molecule of acetone, which is planar within experimental error and makes an angle of 89.5° with the mean plane through the C_6 ring of the CA⁻ anion, exhibits bonds and angles as expected for this kind of molecule.

The coordination of the K^+ cation is illustrated in Fig. 2. The K^+ ion lies approximately at the centre of a triangle formed by three O atoms. Two belong to neighbouring CA⁻ anions, while the third is from the acetone. This coordination of the K^+ cation is unusual and also differs markedly from that found in the crystal structure of the KCA solvent-free salt (Konno, Kobayashi, Marumo & Saito, 1973). The K⋯O distances are in the range 2.68–2.85 Å. Similar values have been found in the crystal structure of the KCA solvent-free salt (Konno, Kobayashi, Marumo & Saito, 1973). They agree with the sum of the ionic radius of K^+ (1.30 Å; Pauling, 1960) and the van der Waals radius of the O atom.

Crystal packing

The crystal structure of the KCA salt, solvated with acetone, viewed down b is presented in Fig. 3, while a perspective drawing of the crystal packing is shown in Fig. 4. Chloranil anions form columns along the *c* axis; in these, CA⁻ anions are stacked alternately (3.384 and 3.761 Å) with their molecular planes almost parallel to each other. These columns are held together by K^+ ions. Between these anionic columns
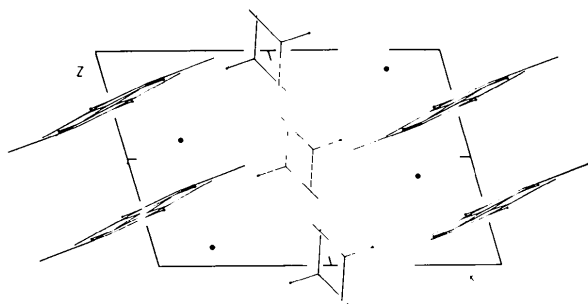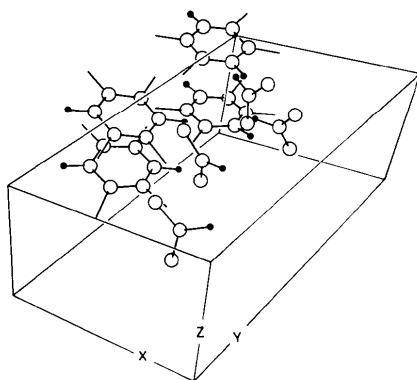
Fig. 3. The crystal structure viewed down **b**.

Fig. 4. Perspective drawing of the crystal packing (K⁺ cations are omitted).

channels run along the *c* axis. Each channel is surrounded by four columns composed of CA⁻. It is in these channels that the acetone molecules are accommodated. Since the CA⁻ anions are tilted at about 9° with respect to **c**, an anion does not fall exactly upon the adjacent one in the same column when the structure is viewed perpendicular to the molecular plane.

In addition, we wish to point out that this packing is different from that found in the crystal structure of the KCA solvent-free salt, where CA⁻ anions are stacked at equal intervals (3·47 Å) and the overlap between two adjacent CA⁻ anions within a column is rather small.

It is worthwhile noting that the structural differences between the KCA solvent-free salt and the KCA salts solvated with acetone, namely the equal/alternate stacking and the amount of overlap between adjacent CA⁻ anions within the same column, can well explain the differences in their physical properties.

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