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# Crystal Structure of the Potassium Salt of Chloranil

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The crystal structures of K$^+$(chloranil)$^-$ have been studied by X-ray diffraction. Several polymorphs were recognized, two of which ($\alpha$- and $\beta$-forms) grew into comparatively good crystals. The $\alpha$-form is orthorhombic, space group $P2_12_12_1$ with unit cell dimensions: $a=13.49$, $b=17.02$, $c=4.03$ Å. The $\beta$-form is orthorhombic, space group $P22_12$ with unit cell dimensions: $a=14.13$, $b=17.35$, $c=3.71$ Å. The structure of the $\alpha$-form was deduced from the Patterson synthesis and refined by the block-diagonal least-squares method. The final $R$ value was 0.13 for 146 observed reflections. Chloranil anions are stacked with equal intervals in the crystal, forming columns parallel to the c axis, the interplanar spacing being 3.47 Å. The electrostatic energy calculated by Evjen's method was about $-148$ kcal/mol, indicating that the structure is essentially ionic.

The magnetic, optical and electronic properties of chloranil anion radical (CA$^-$) salts of alkali metals[1–5] have been extensively studied in an effort to obtain information on the electronic structures of these radical salts. It is of interest that the absorption spectra of Li$^+$CA$^-$ and Na$^+$CA$^-$ greatly differ from those of K$^+$CA$^-$ and Rb$^+$CA$^-$. The two former salts show a strong intermolecular charge-transfer band in the near infrared region and a blue shifted band originating from the monomer band in the visible region, whereas the latter salts show a weak charge-transfer band in the

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[2] J. J. André and G. Weill, *ibid.*, **269**, 499 (1969).

[3] J. J. André and G. Weill, *Mol. Phys.*, **15**, 97 (1968).

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near infrared region and a band quite similar to the anion radical monomer band. This seems to indicate stronger charge-transfer interaction between the anion radicals in lithium and sodium salts than in potassium and rubidium salts. A knowledge of the crystal structure is highly desirable for understanding the difference between the electronic structures of these radical salts. The crystal of $K^+CA^-$ has been subjected to X-ray crystal analysis as a part of our systematic studies on the radical salts.

## Experimental

Dark green crystals of $K^+CA^-$ were grown from an acetone solution by the diffusion method according to Torrey and Hunter.[6] The shape of the crystals depends on the conditions of growing. Sometimes they are needle-like and sometimes platy. Several polymorphs were recognized from X-ray diffraction patterns, two of which (referred to as α- and β-forms) were orthorhombic and had comparatively good crystallinity. The structure of the α-form was determined in the present study. The cell dimensions and possible space groups were obtained from oscillation and Weissenberg photographs. Since the c axis is very short in both modifications, it is impossible to decide whether the systematic absences observed for 00*l* reflections were due to the space group symmetries of crystals or merely due to an accidental extinction. Important crystallographic data are given in Table 1. A crystal with the dimensions $0.04\times0.38\times0.15$ mm³ was used for the intensity measurements of the α-form. Equi-inclination Weissenberg photographs were taken around the b axis (0th to 7th layer) and around the c axis (0th and 1st layer), utilizing the multiple film technique with Cu*Kα* radiation. The intensities were estimated visually with a calibrated intensity scale. Accuracy of the measurements was bad, the diffraction spots being markedly diffuse owing to poor crystallinity of the specimen. In total, intensities of only 146 independent reflections could be collected. The usual Lorentz, polarization and spot shape corrections were applied, but no corrections were made for absorption.

TABLE 1. CRYSTALLOGRAPHIC DATA OF α- AND β-MODIFICATION OF $K^+CA^-$ CRYSTALS

| Chemical formula Crystal system | α<br>$KC_6O_2Cl_4$<br>Orthorhombic | β<br>$KC_6O_2Cl_4$<br>Orthorhombic |
|---|---|---|
| a | 13.49±0.02 Å | 14.13 Å |
| b | 17.02±0.01 | 17.35 |
| c | 4.03±0.01 | 3.71 |
| Space group | $P2_12_12_1$ | $P22_12$ |
| *Z* | 4 | 4 |
| $D_c$ | 2.04 g·cm⁻³ | 2.08 g·cm⁻³ |

## Structure Determination of the α-Form

Three-dimensional Patterson maps were synthesized. The space groups $P2_12_12_1$ and $P2_12_12$ can be distinguished by examining the peak distribution in the Patterson maps. The space group $P2_12_12_1$ was found to be the true space group of this crystal. The positions of chlorine atoms were derived from the Patterson maps with the aid of the known molecular structure of chloranil.[7] All the remaining atoms were located from successive Fourier and difference Fourier syntheses. The structure was refined by a block-diagonal least-squares program HBLS–IV due to Dr. Ashida, assigning anisotropic temperature factors to Cl and K atoms and isotropic temperature factors to all the remaining atoms. The weighting scheme used was $w=1.0$ for $F_0\geq20.0$ and $w=0.5$ otherwise. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[8] The final R-value was 0.13 for 146 observed reflections. The final atomic parameters are given in Table 2 with their standard deviations. The observed and calculated structure factors are compared in Table 3.

## Description of Structure and Discussion

The structure viewed along the b and c axes is presented in Figs. 1(a) and (b), respectively. Chloranil anions are planar and stacked with equal intervals,

TABLE 2. FINAL POSITIONAL PARAMETERS AND THERMAL PARAMETERS FOR α-FORM WITH THEIR e.s.d.'s IN PARENTHESES
The temperature factor expression used was $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$

| | *x* | *y* | *z* | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| K | 0.405(3) | 0.364(2) | 0.732(9) | 0.034(5) | 0.003(1) | 0.139(35) | 0.001(3) | 0.001(14) | −0.013(9) |
| Cl(1) | 0.694(3) | 0.070(2) | −0.089(10) | 0.017(4) | 0.003(1) | 0.093(32) | −0.001(2) | −0.008(12) | 0.007(9) |
| Cl(2) | 0.616(3) | 0.248(2) | −0.087(12) | 0.018(4) | 0.002(1) | 0.168(46) | −0.001(2) | −0.012(16) | 0.014(10) |
| Cl(3) | 0.294(3) | 0.148(2) | 0.565(12) | 0.019(4) | 0.007(2) | 0.219(55) | 0.000(3) | −0.007(16) | −0.004(16) |
| Cl(4) | 0.382(3) | −0.024(2) | 0.593(13) | 0.025(5) | 0.004(2) | 0.148(46) | −0.002(3) | −0.020(16) | 0.013(10) |
| O(1) | 0.567(6) | −0.041(5) | 0.258(27) | 11(3) | | | | | |
| O(2) | 0.420(6) | 0.259(5) | 0.237(25) | 11(3) | | | | | |
| C(1) | 0.588(9) | 0.093(7) | 0.099(41) | 10(4) | | | | | |
| C(2) | 0.550(8) | 0.167(8) | 0.094(38) | 10(4) | | | | | |
| C(3) | 0.458(9) | 0.190(7) | 0.239(39) | 10(5) | isotropic thermal parameters (in Å²) | | | | |
| C(4) | 0.403(8) | 0.126(7) | 0.396(36) | 10(4) | | | | | |
| C(5) | 0.442(9) | 0.053(7) | 0.399(41) | 10(4) | | | | | |
| C(6) | 0.536(9) | 0.032(7) | 0.252(41) | 10(5) | | | | | |

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6) H. A. Torrey and W. H. Hunter, *J. Amer. Chem. Soc.*, **34**, 702 (1912).

7) Shirley. S. C. Chu, G. A. Jeffrey, and T. Sakurai, *Acta Crystallogr.*, **15**, 661 (1962).

8) International Tables for X-Ray Crystallography, Vol. III p. 202, (1962), Kynoch Press, Birmingham.

Table 3. Observed and calculated structure factors for α-form

| $h$ | $k$ | $F_o$ | $F_c$ | $h$ | $k$ | $F_o$ | $F_c$ | $h$ | $k$ | $F_o$ | $F_c$ | $h$ | $k$ | $F_o$ | $F_c$ | $h$ | $k$ | $F_o$ | $F_c$ | $h$ | $k$ | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $l=0$ | | | | 6 | 3 | 20 | 29 | 1 | 9 | 17 | 11 | 9 | 1 | 16 | 5 | 4 | 5 | 27 | 32 | 5 | 1 | 20 | 14 |
| 2 | 0 | 54 | 56 | 7 | 3 | 22 | 25 | 2 | 9 | 18 | 10 | 0 | 2 | 50 | 52 | 0 | 6 | 36 | 41 | 1 | 2 | 29 | 31 |
| 4 | 0 | 91 | 86 | 0 | 4 | 8 | 4 | 6 | 9 | 32 | 34 | 1 | 2 | 75 | 74 | 1 | 6 | 24 | 21 | 3 | 2 | 17 | 21 |
| 6 | 0 | 54 | 55 | 2 | 4 | 44 | 45 | 0 | 10 | 95 | 91 | 2 | 2 | 64 | 65 | 2 | 6 | 16 | 28 | 4 | 2 | 42 | 34 |
| 8 | 0 | 21 | 22 | 4 | 4 | 44 | 43 | 1 | 10 | 58 | 51 | 4 | 2 | 24 | 30 | 4 | 6 | 23 | 22 | 6 | 2 | 22 | 15 |
| 10 | 0 | 21 | 12 | 8 | 4 | 19 | 17 | 3 | 10 | 19 | 28 | 5 | 2 | 15 | 15 | 1 | 8 | 44 | 41 | 7 | 2 | 24 | 11 |
| 1 | 1 | 10 | 13 | 1 | 5 | 59 | 54 | 3 | 11 | 30 | 26 | 6 | 2 | 21 | 19 | 2 | 8 | 29 | 27 | 4 | 3 | 35 | 25 |
| 2 | 1 | 15 | 18 | 2 | 5 | 144 | 136 | 3 | 12 | 31 | 32 | 9 | 2 | 14 | 12 | 2 | 9 | 25 | 27 | 5 | 3 | 30 | 22 |
| 3 | 1 | 11 | 16 | 4 | 5 | 52 | 50 | 2 | 13 | 47 | 53 | 1 | 3 | 32 | 39 | 4 | 9 | 37 | 33 | 3 | 4 | 33 | 32 |
| 4 | 1 | 17 | 22 | 5 | 5 | 13 | 14 | 2 | 14 | 19 | 22 | 2 | 3 | 64 | 67 | 1 | 10 | 34 | 37 | 4 | 4 | 30 | 26 |
| 5 | 1 | 27 | 26 | 6 | 5 | 14 | 12 | $l=1$ | | | | 3 | 3 | 42 | 49 | 2 | 10 | 30 | 29 | 0 | 5 | 40 | 31 |
| 6 | 1 | 27 | 32 | 8 | 5 | 18 | 19 | 2 | 0 | 149 | 158 | 4 | 3 | 48 | 44 | 1 | 12 | 35 | 31 | 1 | 5 | 44 | 34 |
| 7 | 1 | 17 | 20 | 0 | 6 | 24 | 16 | 3 | 0 | 94 | 94 | 5 | 3 | 36 | 34 | $l=2$ | | | | 3 | 5 | 34 | 31 |
| 8 | 1 | 10 | 9 | 3 | 6 | 20 | 20 | 4 | 0 | 16 | 12 | 6 | 3 | 16 | 22 | 1 | 0 | 40 | 58 | 1 | 6 | 34 | 30 |
| 9 | 1 | 11 | 9 | 1 | 7 | 66 | 66 | 5 | 0 | 10 | 7 | 7 | 3 | 21 | 16 | 2 | 0 | 33 | 36 | $l=3$ | | | |
| 0 | 2 | 13 | 26 | 3 | 7 | 50 | 46 | 8 | 0 | 18 | 20 | 0 | 4 | 16 | 24 | 3 | 0 | 14 | 7 | 3 | 0 | 15 | 17 |
| 1 | 2 | 40 | 35 | 5 | 7 | 19 | 16 | 9 | 0 | 19 | 16 | 1 | 4 | 32 | 31 | 4 | 0 | 11 | 1 | 5 | 0 | 12 | 9 |
| 3 | 2 | 35 | 35 | 0 | 8 | 58 | 58 | 0 | 1 | 35 | 38 | 2 | 4 | 17 | 16 | 5 | 0 | 22 | 20 | 0 | 2 | 21 | 16 |
| 5 | 2 | 60 | 69 | 1 | 8 | 31 | 35 | 1 | 1 | 22 | 25 | 6 | 4 | 30 | 33 | 6 | 0 | 16 | 9 | 1 | 4 | 33 | 23 |
| 7 | 2 | 25 | 27 | 2 | 8 | 18 | 21 | 2 | 1 | 20 | 25 | 7 | 4 | 22 | 24 | 11 | 0 | 14 | 66 | 5 | 4 | 27 | 19 |
| 2 | 3 | 21 | 25 | 3 | 8 | 23 | 22 | 3 | 1 | 20 | 19 | 0 | 5 | 113 | 113 | 1 | 1 | 22 | 18 | | | | |
| 3 | 3 | 98 | 87 | 4 | 8 | 61 | 57 | 4 | 1 | 31 | 35 | 1 | 5 | 83 | 89 | 2 | 1 | 38 | 39 | | | | |
| 4 | 3 | 32 | 36 | 5 | 8 | 35 | 35 | 5 | 1 | 19 | 24 | 2 | 5 | 50 | 55 | 3 | 1 | 30 | 33 | | | | |
| 5 | 3 | 19 | 23 | 6 | 8 | 25 | 23 | 8 | 1 | 13 | 7 | 3 | 5 | 52 | 56 | 4 | 1 | 20 | 14 | | | | |

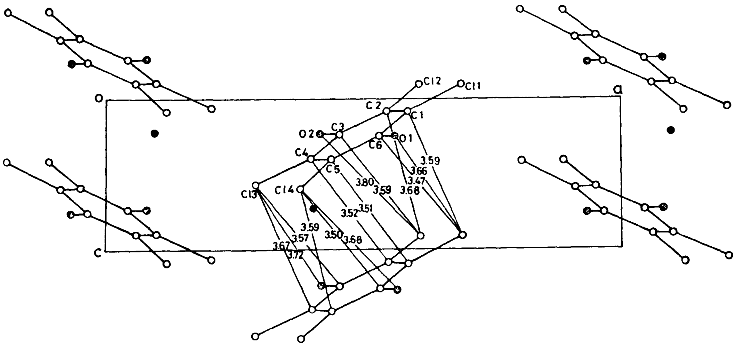

Fig. 1(a). Projection of the structure of α-form along the b axis.

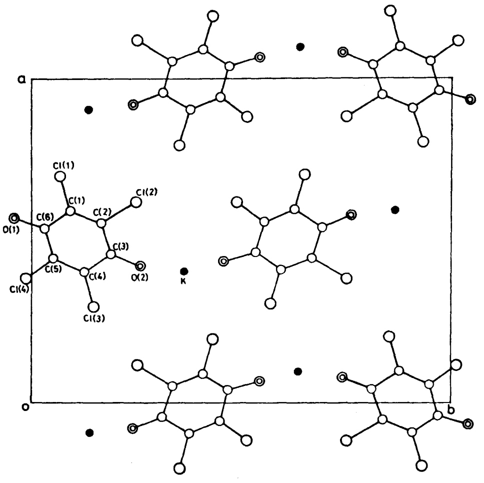

Fig. 1(b). Projection of the structure of α-form along the c axis.

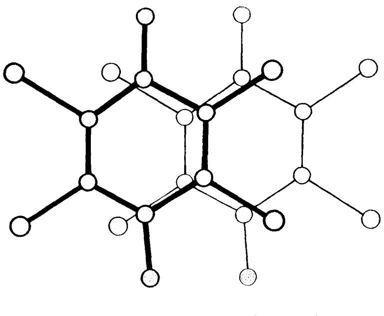

Fig. 2. Nearest-neighbor packing within the column of CA⁻ anions. Direction of view is perpendicular to the molecular plane.

forming columns parallel to the c axis. These columns are held together through K$^+$ ions. Since chloranil anions are inclined at an angle of 30° with respect to (001), an anion does not fall exactly upon the adjacent one in the same column when the structure is viewed perpendicularly to the molecular plane (Fig. 2). The least-squares plane through the atoms of anion is

$$0.468x + 0.190y + 0.863z = 4.35$$

where $x$, $y$, and $z$ are coordinates in Å units referred to the crystal axes a, b, and c, respectively. The interplanar spacing is 3.47 Å. Intermolecular atomic distances are given in Fig. 1(a). Bond distances and angles within an anion are shown in Fig. 3. Since the number of observable reflections is small, the

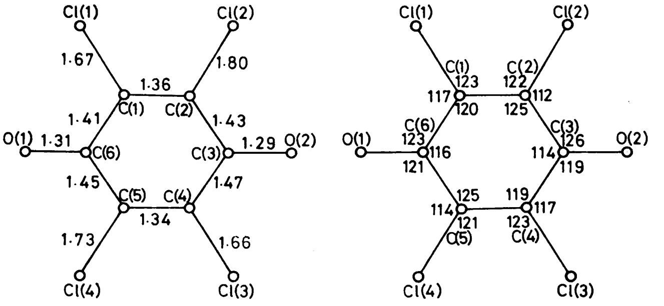

Fig. 3. Bond lengths(Å) and bond angles(degrees) within CA⁻ anion.

estimated standard deviations are extremely large: 0.22 Å for C–C, 0.19 Å for C–O, 0.16 Å for C–Cl. Thus it may not be practicable to discuss the interatomic distances and bond angles in detail. The average distances of chemically equivalent bonds are 1.35 Å for C=C, 1.44 Å for C–C, and 1.30 Å for C–O. Bond distances of C=C, C–C, and C–O in a chloranil anion were deduced by Iida[9] from infrared absorption spectra to be 1.37, 1.45, and 1.31 Å, respectively. The observed values of C=C, C–C, and C–O are in good accordance with these values. The $K^+$ ion lies at the center of a rectangle formed by two O(1) and two O(2) atoms related by *c* translation, respectively. The K–O distances are in the range 2.58—2.68 Å (Fig. 1(b)).

The structure does not contain dimeric $CA^-$ anions, and the overlap between two adjacent $CA^-$ anions in the column is rather small as shown in Fig. 2. This is in line with the spectroscopic study of this anion radical salt in crystals.

Electrostatic interactions seem to play the most important role in this anion radical salt. For the sake of confirmation, the electrostatic energy was calculated by Evjen's procedure.[10] The structure was divided into electrically neutral shells in the form of a rhombus as indicated in Fig. 4, which shows the structure of the α-form viewed along the a axis. Centers of $CA^-$ anions drawn with solid lines are at the same level as $K^+$ ions with solid circles, while those drawn with broken lines are shifted by $a/2$ with respect to those drawn with solid lines. The charge of $CA^-$ anion was assumed to be located equally at the two oxygen atoms. This assumption was supported by the theoretical calculation by Giacometti.[11] The electrostatic energy of $K^+$ ions and anions in each shell was calculated in the usual way. The summation of the energy converged quickly, giving a value of −148 kcal/mol. This amounts to 3/4 of the electrostatic energy of NaCl crystal and is much greater than the contributions of the van der Waals energy, charge-transfer energy, *etc.* The arrangement of K and O atoms appears to be determined mainly by electrostatic energy. When positions of two O atoms in a $CA^-$ anion are fixed in the structure, freedom of rotation remains around the line joining the two O atoms for the anion molecule. The optimum orientation of the anion molecule was estimated for the α-form by adopting the following form for the potential energy *V* due to the van der Waals and repulsive forces.

$$V=\sum_i\sum_j\left(\frac{a_{ij}\exp(-b_{ij}r_{ij})}{r_{ij}^{d_{ij}}}-\frac{c_{ij}}{r_{ij}^{6}}\right)$$

where $r_{ij}$ is the distance between the *i*-th atom in a $CA^-$ molecule and the *j*-th atom in the neighboring molecules, and $a_{ij}$, $b_{ij}$, $c_{ij}$, and $d_{ij}$ are the constants depending on atomic species, the values tabulated by De Santis *et al.*[12] being given. The summation for *i* is taken over all atoms in the $CA^-$ molecule under consideration and that for *j* is taken over atoms in all the 16 neighboring molecules. During the calculation, the shape of the molecule and the symmetry of the crystal were conserved. The structure was calculated to be most stable when the molecular plane makes an angle of 34° with the (001) plane as illustrated in Fig. 5. This is in good agreement with the experimental value of 30°.

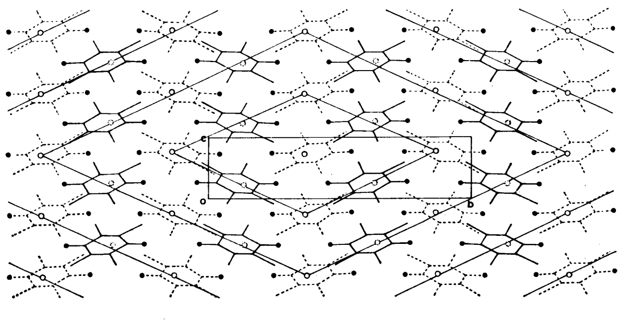

Fig. 4. Projection of the structure of α-form along the a axis, showing scheme for dividing the electrically neutral shells. Oxgen atoms are indicated by black circles.

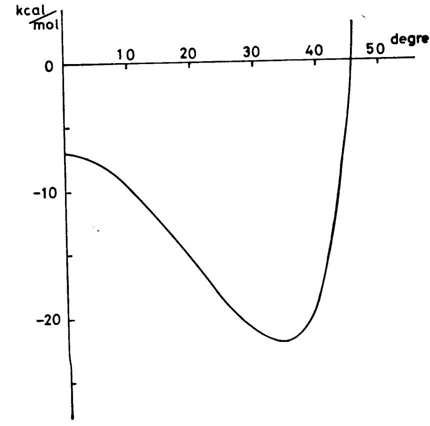

Fig. 5. Variation of non-bonded interaction energy with the change in rotation of the $CA^-$ anion.

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[10] H. M. Evjen, *Phys. Rev.*, **39**, 675 (1932).

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