

both molecules the Mg—O(axial) distances are longer than the Mg—O(equatorial) distances to the O atoms on the same cyclohexane ring. O(5) and O(12) are on one side of an approximate plane containing O(1), O(16), O(23), O(26), O(29), and the water O is on the other side. This compares with the Mg(SCN)₂ complex with benzo-15-crown-5 which contains the five ether O atoms in an approximate plane, and an N from the anions on each side. The deviations of the five O atoms and of the Mg atom from the plane are all slightly larger in the present structure.

This shape of the molecule with five O atoms in a plane and two below is similar to those found in the analogous molecule with benzene rings instead of the cyclohexanes here (Herbert & Truter, 1980; Owen, 1981).

Bond lengths and angles in the ligand (I) are as expected for this class of compound. The torsion angles are close to the expected *±gauche* and *trans*, the largest deviations being O(5)—C(4)—C(3)—O(23), O(12)—C(13)—C(14)—O(29) and C(22)—O(1)—C(2)—C(3) (see Table 2).

Each water molecule is H-bonded to two perchlorate O atoms. Though the exact positions of the perchlorate O atoms must be in doubt in view of their large thermal parameters which indicate possible statistical disorder, the two molecules do seem to differ in their H-bonding schemes.* Molecule (1) shows fairly strong convention-

al single H bonds (O...O distances ~2.75 Å, angles at H ~173°). Molecule (2), however, has the perchlorates in different orientations (Fig. 2) and the H bonding is much weaker (O...O distances ~3.15 Å, angles at H again ~173°). There may be further interactions with a second O atom, though the geometry indicates this to be very weak.

The isomer of the ligand (I) is confirmed as that shown in Fig. 1, with both H atoms at the cyclohexane ring junctions on the same side of the molecule, and opposite to the O(23)—O(29) bridge.

There are no close contacts between molecules of note, and so the crystals are made up of equal numbers of discrete left- and right-handed molecules.

I thank Dr D. G. Parsons for the crystals, and the Royal Society for some equipment.

References

- HERBERT, J. A. & TRUTER, M. R. (1980). *J. Chem. Soc. Perkin Trans. 2*, pp. 1253–1258.
International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.2B. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1971). *ORTEP II*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
 OWEN, J. D. (1978). *J. Chem. Soc. Dalton Trans.* pp. 1418–1423.
 OWEN, J. D. (1981). *J. Chem. Soc. Perkin Trans. 2* pp. 12–18.
 OWEN, J. D. (1982). Crystallographic programs for the Prime 550 computer.
 PARSONS, D. G. (1982). Personal communication.
 SHELDRIK, G. M. (1976). *SHELX*. Programs for crystal structure determination. Univ. of Cambridge, England.

* Hydrogen-bonding parameters have been deposited. See deposition footnote.

Acta Cryst. (1983). **C39**, 582–584

Refinement of Potassium Tetrafluorophthalate, 2K⁺·C₈F₄O₄²⁻

BY D. S. SAKE GOWDA AND REUBEN RUDMAN

Department of Chemistry, Adelphi University, Garden City, NY 11530, USA

(Received 12 October 1982; accepted 25 January 1983)

Abstract. KTFP, $M_r = 314.3$, monoclinic, $P2_1/c$, $a = 7.133$ (2), $b = 10.825$ (3), $c = 7.114$ (2) Å, $\beta = 111.82$ (1)°, $V = 510.0$ Å³, $Z = 2$, $D_x = 2.047$ Mg m⁻³, Ni-filtered Cu K radiation, $\lambda K\alpha_1 = 1.54051$ Å, $\mu(\text{Cu } K\alpha) = 8.86$ mm⁻¹, $F(000) = 308$, 294 K, $R = 0.034$ for 836 reflections, starting with the positional parameters reported by Griffin, Yeung, LaPrade & Waugh [*J. Chem. Phys.* (1973), **59**, 777–783]. The average C—F intramolecular distance is 1.339 (3) Å, while the average intra- and shortest

intermolecular F...F distances are 2.702 (3) and 2.713 (2) Å, respectively. This refinement of KTFP corroborated the original choice of space group (in which the molecules are constrained to lie on twofold rotation axes) rather than the acentric space group *Pc*. The K⁺ ion is coordinated by one fluorine and six oxygen atoms; two of the oxygen atoms, from the same carboxyl group, are symmetrically arranged opposite the fluorine atom so as to form a pseudo-octahedral coordination.

Introduction. The structure of KTFP was reported by Griffin, Yeung, LaPrade & Waugh (1973). As the aim of that report was primarily for the purpose of determining the ^{19}F chemical shielding tensors, only the molecular structure was described. The environment about the K^+ ions was not given and the interatomic distances and angles were not as accurate as similar values determined recently for the tetrahalophthalic anhydride (TXPA) (Sake Gowda & Rudman, 1982*a,b*) and tetrafluorophthalic acid (TFAC) (Sake Gowda & Rudman, 1983) compounds. Furthermore, it was also noted that the structure had been refined in the centrosymmetric space group $P2/c$ with both molecules in the unit cell constrained to lie on twofold rotation axes. The fact that the systematic absences observed in KTFP are also consistent with acentric Pc (which does not require a molecular twofold axis) was not discussed. Although Griffin *et al.* noted that the observed NMR spectrum is consistent with only two unique C—F distances, molecular distortions of the type noted in the TXPA compounds (symmetrically equivalent bond lengths and angles, with small deviations from planarity) would be sufficient to lower the crystallographic symmetry but would not necessarily be noticeable in the NMR spectrum.

Experimental. KTFP from TFAC dissolved in aqueous KOH, white prisms, $0.10 \times 0.10 \times 0.25$ mm, Syntex $P2_1$ -F diffractometer, lattice parameters from 17 reflections ($27 < 2\theta < 56^\circ$), data collection: 1661 ($h, \pm k, \pm l$ with $2\theta < 115^\circ$, $h, k, \pm l$ with $115 < 2\theta < 130^\circ$) automatic recentering every 633 reflections, with 3 standard reflections (002, 210, 031) every 102 reflections (3.1% variation), 874 independent, 836 used in full-matrix least-squares refinement using positional parameters of Griffin *et al.* (1973) as starting parameters [38 reflections not used included 33 with $I < 2\sigma(I)$, one measured improperly due to beam-stop interference and four excluded from final stages of refinement due to extinction effects], L_p and empirical absorption (7 ψ -scan curves) applied, decay corrections not needed, anisotropic refinement in both $P2/c$ (and Pc) based on F , final cycle: 82 (161) parameters, R and R_w (defined in Sake Gowda & Rudman, 1982*a*) 0.034 (0.027) and 0.056 (0.037), $S = 3.171$ (2.203), $w^{-1} = \sigma^2(F) + (0.015 F_o)^2$, $\sigma(F) = \sigma(F^2)/(2F)$, $\sigma(F^2)$ based on counting statistics [$R = 0.034$ (0.027), $R_w = 0.056$ (0.037) for all unique data]; final ΔF map featureless, lattice parameters calculated with CELREF (Adelphi University Library of Crystallographic Programs), all other calculations done with the Syntex XTL programs, which utilize atomic scattering functions (f) based on the analytical expressions found in *International Tables for X-ray Crystallography* (1974); f for K^+ , F, O, and C used.

Discussion. Refinement in acentric Pc , in which the starting parameters were adjusted so as to destroy

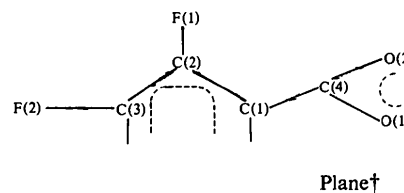
initially the twofold symmetry, converged to atomic positions not significantly different from those obtained using the centrosymmetric space group $P2/c$.* In addition, an analysis of the X-ray intensity distribution statistics was in agreement with a centrosymmetric structure and the piezoelectric test of a single crystal of KTFP was negative.

Our results corroborate the reported structure of KTFP and are in good agreement with the positional parameters reported previously (Table 1). The average C—F bond length (Table 2) [1.339 (3) Å] is similar to that found in TFAC (Sake Gowda & Rudman, 1983) [1.335 (2) Å] and perfluorobiphenyl (Gleason & Britton, 1976) [1.339 (2) Å]. The tetrafluorobenzene moiety (plane A) is planar within an estimated standard deviation of 0.003 Å, while the carboxyl carbon atom lies 0.068 (2) Å off plane A , with both carboxyl groups nearly perpendicular to this plane (Table 1). This differs from the configuration in TFAC, in which the two crystallographically independent carboxyl groups are inclined at angles of 81 and 14° to the benzene ring.

* Details of the data collection and structure refinement, and tables of anisotropic thermal parameters, observed *vs* calculated structure factors, distances and angles about K^+ , ORTEP diagrams of the TFP^- anion and the $\text{F}\cdots\text{F}$ distances, and a stereoview of the packing within the unit cell have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38348 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters for KTFP given in fractional coordinates ($\times 10^5$ for K^+ ; $\times 10^4$ for F, O, C)

The deviations of the atoms from the least-squares planes ($\times 10^3$ Å) are also shown, as are the $B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} \rho_i^* \rho_j^* a_i^* a_j^*$. The e.s.d.'s are in parentheses.



| | x | y | z | A | B | B_{eq} (Å ²) |
|------|-----------|-----------|----------|---------|--------|----------------------------|
| K | 23610 (8) | 11450 (5) | 2979 (8) | | | 2.29 |
| F(1) | 1360 (3) | 5899 (2) | -570 (3) | 1 (2) | | 3.86 |
| F(2) | 3160 (3) | 3747 (1) | 982 (3) | 2 (2) | | 3.13 |
| O(1) | 1688 (3) | 8655 (2) | 1259 (3) | | -1 (2) | 2.80 |
| O(2) | 3646 (3) | 8696 (2) | -569 (3) | | -1 (2) | 2.76 |
| C(1) | 4065 (3) | 7036 (2) | 1703 (3) | 5 (2) | -1 (2) | 1.95 |
| C(2) | 3149 (4) | 5925 (2) | 966 (4) | -11 (3) | | 2.40 |
| C(3) | 4063 (4) | 4811 (2) | 1740 (4) | -1 (3) | | 2.41 |
| C(4) | 3037 (3) | 8225 (2) | 719 (3) | 67 (2)‡ | 4 (2) | 2.07 |

† Equation of plane A : $0.7532x - 0.0075y - 0.6577z = 1.0423$.
Equation of plane B : $-0.4506x - 0.5264y - 0.7210z = -5.9227$.
Angle between plane A and plane B : 82.0° .

‡ Not included in calculation of least-squares plane.

Table 2. *Interatomic distances (Å) and angles (°) in KTFP*

The primed atoms are the symmetry-related atoms within the anion; the atoms identified by superscripts are described in Fig. 1.

(a) TFP anion

| | | | |
|--------------|-----------|-----------------|-----------|
| F(1)—C(2) | 1.337 (3) | C(2)—C(1)—C(4) | 119.1 (2) |
| F(2)—C(3) | 1.332 (3) | C(2)—C(1)—C(1)' | 119.1 (2) |
| O(1)—C(4) | 1.252 (3) | C(4)—C(1)—C(1)' | 121.9 (2) |
| O(2)—C(4) | 1.258 (3) | C(1)—C(2)—F(1) | 120.3 (2) |
| C(1)—C(2) | 1.375 (3) | C(1)—C(2)—C(3) | 121.5 (2) |
| C(2)—C(3) | 1.384 (3) | F(1)—C(2)—C(3) | 118.1 (2) |
| C(3)—C(3)' | 1.372 (4) | C(2)—C(3)—C(3)' | 119.4 (2) |
| C(1)—C(1)' | 1.393 (3) | C(2)—C(3)—F(2) | 120.5 (2) |
| C(1)—C(4) | 1.518 (3) | F(2)—C(3)—C(3)' | 120.1 (2) |
| F(1)...F(2) | 2.690 (2) | C(1)—C(4)—O(1) | 118.0 (2) |
| F(2)...F(2)' | 2.709 (3) | C(1)—C(4)—O(2) | 116.2 (2) |
| | | O(1)—C(4)—O(2) | 125.9 (2) |

(b) K⁺ coordination sphere

| K ⁺ to | | K ⁺ to | | K ⁺ to | |
|-------------------|-----------|-------------------|-----------|-------------------|-----------|
| F(2) | 2.880 (2) | O(1) ^b | 2.690 (2) | O(1) ^c | 2.740 (2) |
| O(1) ^a | 2.865 (2) | O(2) ^b | 2.741 (2) | O(2) ^c | 2.788 (2) |
| O(2) ^a | 2.944 (2) | | | | |

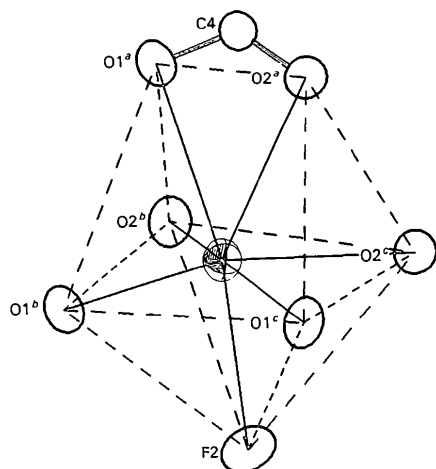


Fig. 1. Seven-coordination sphere around the K⁺ ion. K—O and K—F distances are given in Table 2; other distances and angles are found in the Supplementary Material. The symmetry-related positions are: carboxyl group [O(1)^a—C(4)—O(2)^a]: $x, y-1, z$; O(1)^b: $-x, 1-y, -z$; O(2)^b: $x, 1-y, 1/2+z$; O(1)^c: $x, 1-y, z-1/2$; O(2)^c: $1-x, 1-y, -z$.

There are four idealized seven-coordination models: pentagonal bipyramid (PB), capped trigonal prism (CTP), capped octahedron (CAOC), and tetragonal base-trigonal base (TB) (King, 1973; Britton & Dunitz, 1973; Drew, 1977). The coordination about the K⁺ ion (six oxygen and one fluorine, representing five different tetrafluorophthalate ions, Fig. 1) does not fit any of them. The O(1)^a—O(2)^a direction is nearly perpendicular (89.11°) to the O(1)^b—O(2)^b direction thus ruling out a distorted PB. The CTP and TB structures

are obviously not present, as the K⁺ ion lies in the plane defined by O(1)^b, O(1)^c, O(2)^b, O(2)^c.

If the O(1)^a—O(2)^a direction were tilted such that, e.g., F(2), K⁺, and O(1)^a were linear a CAOC would result. However, since the oxygen atoms of the single carboxyl group are symmetrically arranged about the F(2)—K⁺ axis and are separated by only 2.230 (3) Å [which is significantly shorter than the other interatomic distances (>3.4 Å) found in the coordination sphere] the coordination about K⁺ is more realistically described as octahedral coordination with one of the corners 'split' into two, thus forming a pseudo-octahedral coordination sphere. If one uses the average of the two oxygen positional coordinates as the position of the 'unsplit' atom, O(12), then the angle formed by O(12), K⁺, and F(2) is 164.4°.

Whereas the F(2) atoms participate in the potassium coordination sphere, the F(1) atoms participate in a short F...F intermolecular distance. In KTFP, the average intramolecular F...F non-bonded distance is 2.702 (3) Å, while the shortest intermolecular F...F distance is 2.713 (2) Å between F(1) atoms on adjacent molecules (related by the twofold axis). Both these distances are considerably shorter than double the fluorine van der Waals radius (1.47 Å) given by Bondi (1964), but just equal the distance calculated using Pauling's (1960) van der Waals radius (1.35 Å). Thus, the intramolecular and intermolecular F...F distances in KTFP are nearly equal, with the F(1) atoms which are all interrelated by the twofold rotation axis lying along a straight line extended through the crystal.

The authors thank Frank Dacol of the IBM Thomas J. Watson Laboratories for running the piezoelectric test. This research was supported by the National Science Foundation, Grant DMR 78-25865.

References

- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
 BRITTON, D. & DUNITZ, J. D. (1973). *Acta Cryst.* **A29**, 362–371.
 DREW, M. G. B. (1977). *Prog. Inorg. Chem.* **23**, 67–210.
 GLEASON, W. B. & BRITTON, D. (1976). *Cryst. Struct. Commun.* **5**, 483–488.
 GRIFFIN, R. G., YEUNG, H.-N., LAPRADE, M. D. & WAUGH, J. S. (1973). *J. Chem. Phys.* **59**, 777–783.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 KING, R. B. (1973). *J. Am. Chem. Soc.* **91**, 7211–7216.
 PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Cornell Univ. Press.
 SAKE GOWDA, D. S. & RUDMAN, R. (1982a). *Acta Cryst.* **B38**, 2842–2845.
 SAKE GOWDA, D. S. & RUDMAN, R. (1982b). *J. Phys. Chem.* **86**, 4356–4360.
 SAKE GOWDA, D. S. & RUDMAN, R. (1983). *Acta Cryst.* **C39**, 250–253.