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Structure of Potassium 4,5-Dichloro-2-cyano-3,6-dioxo-1,4-cyclohexadienolate (KDDQH), $C_7Cl_2NO_3^-.K^+$

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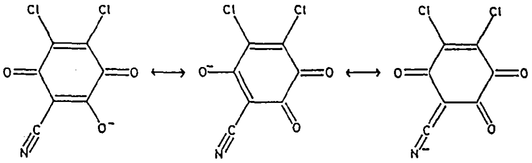
Abstract. $M_r = 256\cdot1$, tetragonal, $I4_1/a$, $a = 20\cdot611\,(2)$, $c = 8\cdot3990\,(6)$ Å, $V = 3568\cdot0\,(6)$ Å^3, $Z = 16$, $D_x = 1\cdot907$ Mg m^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0\cdot71069$ Å, $\mu = 1\cdot158$ mm^{-1}, $F(000) = 2016$, room temperature, $R = 0\cdot030$ for 2313 unique reflections. The anions form isolated dimers with a parallel interplanar distance of 3·206 Å.

Introduction. It is known that alkali-metal$^+$ (except Li$^+$).TCNQ$^-$ and K$^+$.chloranil$^-$ radical salts undergo a spin Peierls transition. This is due to the instability of the lattice distortion in the uniform linear chains of anion radicals at low temperature (Vegter, Himba & Kommandeur, 1969; Andre & Weill, 1971). 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) shows electrical and optical properties similar to those of the chloranil and TCNQ radical salts (Iida, 1971; Mayerle & Torrance, 1981). These salts are suitable materials for charge density distribution studies of the anion radicals. The present paper reports the crystal structure and charge density analysis of K$^+$.DDQH$^-$.

Experimental. Red rectangular plates grown by slow evaporation of a mixture of equimolar methanol solutions of KI and DDQ at room temperature. Crystals shown by the crystal structure analysis to be KDDQH, not KDDQ. Experimental data are given in Table 1. Structure solved by heavy-atom methods and refined on F by the full-matrix least-squares program *RADIEL* (Coppens, Guru-Row, Leung, Stevens, Becker & Yang, 1979). Atomic scattering factors of Cl, O and N atoms divided into those from core and valence electrons. Population of the valence-shell density of these atoms refined. Net charge on DDQH$^-$ anion constrained to be −1. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974); correction for anomalous dispersion. No correction for secondary extinction.

Discussion. The atomic parameters are given in Table 2.† A projection of the structure along the c axis is shown in Fig. 1. Two centrosymmetrically related anions form isolated dimers in parallel planes with an interplanar distance of 3·206 (15) Å. No linear chain stacking was found, in contrast to the structures observed in the K$^+$.TCNQ$^-$ and K$^+$.chloranil$^-$ salts (Konno, Ishii & Saito, 1977; Konno, Kobayashi, Marumo & Saito, 1973; Zanotti & Del Pra, 1980). Short contacts between adjacent dimers are found only between Cl(1) and Cl(2) with a distance of 3·370 (1) Å (Table 3). The K$^+$ ion is coordinated by five O atoms of three anions and one N atom of the cyano group of the other anion (see Table 3) in a distorted bipyramid. Fig. 2 shows the geometry of the DDQH$^-$ anion. The anion is expected to resonate among three structures.



The C—C bond distances in the anion calculated from these amounts of double-bond character (Pauling, 1960) are in agreement with the observed values. The double-bond distance of 1·210 (2) Å observed for C(4)—O(2) and those of 1·231 (2) and 1·238 (2) Å for C(1)—O(1) and C(5)—O(3) with two-thirds double-bond character are significantly shorter than the corresponding values of 1·225 and 1·255 Å calculated from the mean bond distances of 1·225 Å for the C=O double bond and 1·320 Å for the C—OH single bond observed in 1,4-benzoquinone (Trotter, 1960), tetrahydroxy-1,4-benzoquinone (Klug, 1965) and chloranilic acid (Andersen, 1967*a*,*b*). These bond shortenings are consistent with the negative charge of *ca* −0·30 e residing on the O atoms (see Table 1). The

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38921 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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C—Cl distances of 1·704 (2) and 1·711 (2) Å are in good agreement with the values observed in chloranil and some related molecules (Chu, Jeffrey & Sakurai, 1962; van Weperen & Visser, 1972; Rees, 1970) and in the DDQ molecule (Zanotti, Bardi & Del Pra, 1980). The DDQH$^-$ anion is slightly distorted to a $_{1}^{4}\beta$ boat conformation. The two Cl atoms bend away in opposite directions from the counterpart anion of the dimer owing to the repulsion between Cl atoms and the CN group and O(3) (see Fig. 2*a*). On a difference density map in the plane of the anion, peaks with maximum heights of 0·3—0·4 e Å^{-3} are found between six C—C bonds of the benzene ring and of 0·24 e Å^{-3} in the C—C bond of the cyano group.

Table 1. *Experimental data*

Diffractometer: Rigaku automated four-circle diffractometer
Radiation: Mo $K\alpha$
Monochromator: graphite
Crystal dimensions: 0·24 × 0·24 × 0·22 mm
Faces: (001), (00$\bar{1}$), (1$\bar{1}$0), ($\bar{1}$10), ($\bar{1}\bar{1}$0), (230)
Transmission factors (Busing & Levy, 1957): 0·878–0·899
Number of reflections used in refinement of cell constants: 32 ($16° < \theta < 24°$)
$2\theta_{\max}$: 65°
Number of symmetry-related reflections measured in four octants of reciprocal space (hkl, $k\bar{h}l$, $\bar{k}hl$, $\bar{h}\bar{k}l$): 12 904
Number of unique reflections used in structure refinements: 2313
Number of unobserved reflections: 882
Standard reflections: three after every 50 reflections (decay less than 2%)
Number of parameters refined: 133
R_{int}: 0·021 R: 0·030 S: 1·94
w: 1·0 wR: 0·032 $(\Delta/\sigma)_{\max}$: 0·2

Table 2. *Positional parameters* (× 10^5) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{\text{eq}} = \frac{8\pi^2}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2 × 10^2)
K	26528 (2)	13991 (2)	70439 (5)	269 (1)
Cl(1)	10245 (3)	18915 (3)	53754 (7)	371 (1)
Cl(2)	6630 (3)	31048 (3)	32494 (7)	345 (1)
O(1)	20409 (7)	11110 (7)	40492 (18)	289 (4)
O(2)	15087 (7)	31844 (7)	4630 (18)	294 (4)
O(3)	23950 (8)	23299 (7)	−5978 (17)	300 (4)
N	30741 (11)	8483 (11)	6325 (28)	423 (6)
C(1)	19257 (9)	15693 (9)	31535 (22)	213 (4)
C(2)	14137 (9)	20542 (9)	36305 (22)	222 (4)
C(3)	12652 (9)	25717 (9)	27467 (23)	217 (4)
C(4)	16159 (9)	27055 (9)	12529 (22)	204 (4)
C(5)	21258 (9)	22120 (9)	6874 (22)	208 (4)
C(6)	22477 (9)	16758 (9)	16706 (22)	211 (4)
C(7)	27045 (10)	12064 (10)	11343 (25)	264 (5)

The charge density distribution of the DDQH$^-$ anion is Cl(1) = 0·21 (6), Cl(2) = 0·05 (6), O(1) = −0·29 (4), O(2) = −0·29 (5), O(3) = −0·34 (4) and N = −0·34 (5) e (Coppens, Guru-Row, Leung, Stevens, Becker & Yang, 1979).

Table 3. *Selected intermolecular distances* (Å)

K—O(1$^{\text{i}}$)	2·876 (2)	K—O(3$^{\text{ii}}$)	2·889 (2)
K—O(1$^{\text{i}}$)	2·798 (2)	K—O(3$^{\text{iii}}$)	2·808 (2)
K—O(2$^{\text{ii}}$)	2·856 (2)	K—N$^{\text{iv}}$	2·826 (2)
Cl(2)···Cl(1$^{\text{v}}$)	3·370 (1)		

Symmetry code: (i) $\frac{1}{4}+y, \frac{1}{4}-x, \frac{1}{4}+z$; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$; (iii) $x, y, 1+z$; (iv) $\frac{1}{4}-y, -\frac{1}{4}+x, \frac{3}{4}+z$; (v) $\frac{1}{4}-y, \frac{1}{4}+x, \frac{1}{4}-z$.

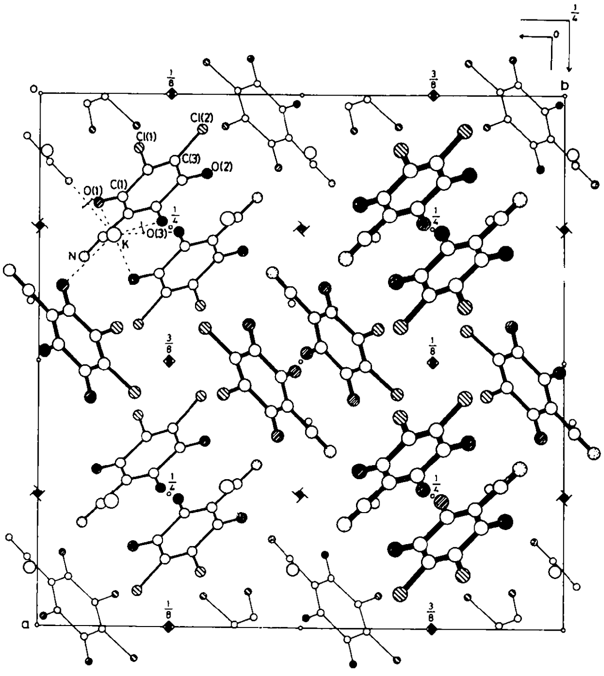

Fig. 1. Projection of the structure along the *c* axis.

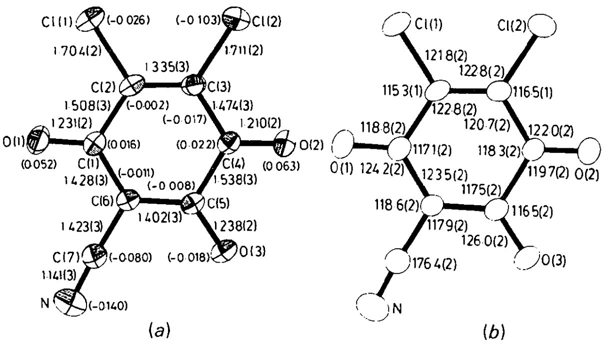

Fig. 2. Geometry of the DDQH$^-$ anion. (*a*) Bond lengths (Å) and out-of-plane displacements (Å) of atoms from the least-squares plane through the six atoms of the cyclohexadiene ring in the anion. The equation of the plane is $0{\cdot}6987X + 0{\cdot}05246Y + 0{\cdot}4864Z = 5{\cdot}7422$. (*b*) Bond angles (°).

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The Sodium Picrate Benzo-15-crown-5 Complex,* $Na^+.C_6H_2N_3O_7^-.C_{14}H_{20}O_5$

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Abstract. $M_r = 519{\cdot}40$, monoclinic, $P2_1/n$, $a = 11{\cdot}125\,(3)$, $b = 13{\cdot}555\,(4)$, $c = 14{\cdot}924\,(5)$ Å, $\beta = 93{\cdot}40\,(2)°$, $V = 2247\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}536$ g cm^{-3}, $\lambda(\text{Mo }K\alpha_1) = 0{\cdot}70926$ Å, $\mu(\text{Mo }K\alpha) = 0{\cdot}975$ cm^{-1}, $F(000) = 270$, $T = 296$ K, $R = 0{\cdot}061$ for 2786 $[I > 2\sigma(I)]$ of 6588 total unique data. The structural analysis reveals that the Na^+ ion is coordinated to all five crown oxygens [Na—O 2·400 (3) to 2·501 (3) Å] as well as to the phenoxide [Na—O 2·350 (3) Å] and an *ortho* nitro oxygen [Na—O 2·510 (3) Å] of the anion. The Na^+ ion lies out of the cavity of the crown toward the picrate by 0·900 (1) Å.

Introduction. *In vitro* conditions which favor the encapsulation of different alkali and alkaline-earth cations by the macrocyclic ligand benzo-15-crown-5 (B15C5) while the cation is subjected to an anionic effect of diverse organic charge neutralizers [*e.g.* picrate (pic), or 3,5-dinitrobenzoate (3,5-DNB)] have been investigated by one of the authors (NSP) for a number of years. The ultimate aim of this research is to throw some light on the chemical principles which control the hitherto undiscovered mechanism of discrimination of Na^+–K^+ and Mg^{2+}–Ca^{2+} pairs by the cell membrane in biological systems (Williams, 1970).

Earlier X-ray structural work on B15C5 complexes of some alkali and alkaline-earth picrates showed that cations with a higher charge density, Ca^{2+} (Bhagwat, Manohar & Poonia, 1980*a*) and Li^+ (Bhagwat, Manohar & Poonia, 1980*b*), prefer direct bonding with the anion and the solvent (water) molecules while the macrocyclic ligand is hydrogen-bonded to the water molecules in the coordination sphere of the cation. A larger cation, Ba^{2+}, is cooordinated to the anion, the solvent molecule, as well as to the macrocycle (Venkatasubramanian, Poonia, Hackert, Clinger & Ernst, 1983). With a fairly low charge density, K^+ forms charge-separated sandwich complexes $K^+(B15C5)_2$ in which the weakly nucleophilic counterion I^- is separated from the cation by the ligand (Mallinson & Truter, 1972) and in which the strongly chelating picrate anion does not interact with the cation (Bhagwat, Manohar & Poonia, 1981). It was of interest to us to determine whether the Na^+ ion in the $Na^+(B15C5)$ complex is bonded uniquely to the crown ether (as K^+), to the crown ether as well as to the counterion (as Ba^{2+}), or whether there is no direct bonding between the cation and crown ether (as for Li^+ and Ca^{2+}). This led us to undertake the X-ray structural analysis of the complex $Na^+pic^-(B15C5)$.

Experimental. Equimolar amounts (0·04 *M* each) of sodium picrate and B15C5 (Aldrich) were disolved in warm ethanol. The crystalline complex (m.p. 426 K) was obtained upon cooling the solution. It is interesting

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* (6,7,9,10,12,13,15,16-Octahydro-5,8,11,14,17-pentaoxabenzocyclopentadecene)(2,4,6-trinitrophenolato)sodium.

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