Dipotassium(I) Cyclooctatetraenide–1-Methoxy-2-(2-methoxyethoxy)ethane

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Abstract. $K_2(C_8H_8).(CH_3OCH_2CH_2)_2O$, ($K_2COT$.diglyme), orthorhombic, *Pnma*, $a = 7.689$ (3), $b = 15.376$ (5), $c = 13.703$ (5) Å (from diffractometer data), $Z = 4$, $D_x = 1.30$ g cm^{-3}. The packing of the K$^+$ and COT^{2-} ions may be described as a zigzag chain of K_2COT units. This chain is in the direction of the *a* axis and is embedded in a diglyme environment. Only one potassium ion of each K_2COT unit is coordinated by the complexing ether, diglyme.

Introduction. The crystals were prepared under exclusion of air and water by slowly adding a mixture of diglyme and tetrahydrofuran (THF) (1:2) to a 0·8 mol K_2COT solution in THF. After one day single crystals separated out. The results of an elementary analysis are K, 24·60 (24·71), C, 52·82 (53·12) and H, 7·07 (7·01)%. (Values in parentheses are the calculated ones.) The crystals are very sensitive to air. Therefore they were mounted in paraffin (m.p. 42–44°C) in thin-walled glass capillaries under a He atmosphere. Unit-cell dimensions and intensities were obtained from a crystal of approximate dimensions $0.4 \times 0.3 \times 0.2$ mm, with a computer-controlled Nonius CAD-3 diffractometer (Cu Kα radiation, Ni-filtered, θ–2θ scan). Systematic absences were 0*kl* for $k + l$ odd, and *hk*0 for *h* odd. Space group *Pnma* or its acentric counterpart *Pn2$_1$a* are the only choices which are consistent with these conditions. The statistics of the *E* values (prepared for use in *MULTAN*) indicated the centrosymmetric space group *Pnma*. All intensities in two symmetry-related octants up to $\theta = 50°$ were measured. Averaging the symmetry-related reflexions gave 1071 unique observations. 9 reflexions were omitted because of a very large discrepancy between the individual measurements. Of the 1062 unique reflexions, 472 had a significant intensity [$I > 3\sigma_c(I)$, $\sigma_c(I)$ derived from counting statistics]. The intensity data were reduced to structure amplitudes by application of Lorentz and polarization factors. Values for $\sigma(F)$ were calculated according to the formula $\sigma(F) = [\sigma_c^2(F) + (0.05F_{obs})^2]^{1/2}$. The structure was determined by direct methods applying the program *MULTAN* (Germain, Main & Woolfson, 1971) and refined by full-matrix least-squares methods, with anisotropic thermal parameters. Hydrogen atoms were not included in the refinement or in the structure-factor calculation, because no trace of them appeared on a final difference map. The quantity minimized was $\sum w(|F_o| - K|F_c|)^2$ with $w = 1/\sigma^2(F)$. The final refinement resulted in a residual, *R*, of 0·099 for 472 reflexions. Final atomic parameters are given in Table 1. The atomic scattering factors used were those for K$^+$ (corrected for anomalous scattering $\Delta f'$), O and C as given in *International Tables for X-ray Crystallography* (1962).*

Discussion. As part of a programme carried out by the Department of Molecular Spectroscopy at this Uni-

Table 1. *Final atomic parameters* (*with e.s.d. in parentheses*)

The estimated standard deviations are those obtained from the least-squares refinement. The expression used for the anisotropic thermal parameters is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	X/a	Y/b	Z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K(1)	0·2959 (7)	−0·25	0·7496 (5)	0·0120 (10)	0·0112 (5)	0·0059 (4)		0·0002 (7)	
K(2)	0·3046 (7)	−0·25	0·3999 (4)	0·0165 (11)	0·0033 (3)	0·0058 (4)		−0·0000 (6)	
C(1)	0·518 (2)	−0·203 (1)	0·579 (1)	0·016 (3)	0·008 (1)	0·006 (1)	−0·002 (2)	0·002 (2)	−0·001 (1)
C(2)	0·386 (3)	−0·139 (1)	0·580 (1)	0·021 (4)	0·006 (1)	0·006 (1)	−0·002 (2)	0·001 (3)	−0·000 (1)
C(3)	0·205 (3)	−0·140 (1)	0·578 (2)	0·021 (4)	0·008 (1)	0·008 (2)	0·001 (2)	0·002 (3)	0·000 (1)
C(4)	0·080 (2)	−0·205 (1)	0·576 (1)	0·010 (3)	0·007 (1)	0·006 (1)	0·002 (1)	0·001 (2)	−0·001 (1)
C(5)	0·279 (3)	−0·171 (1)	0·153 (2)	0·027 (5)	0·007 (1)	0·008 (1)	−0·006 (2)	0·001 (3)	0·001 (1)
C(6)	0·190 (3)	−0·092 (1)	0·197 (2)	0·027 (5)	0·005 (1)	0·009 (2)	0·000 (2)	−0·004 (3)	−0·000 (1)
C(7)	0·189 (3)	−0·013 (1)	0·345 (2)	0·035 (5)	0·003 (1)	0·017 (2)	0·002 (2)	0·005 (4)	−0·002 (1)
O(1)	0·194 (2)	−0·25	0·192 (1)	0·011 (3)	0·006 (1)	0·007 (1)		−0·000 (1)	
O(2)	0·233 (1)	−0·094 (1)	0·299 (1)	0·017 (3)	0·005 (1)	0·010 (1)	−0·000 (1)	−0·000 (1)	0·001 (1)

versity for the study of alkali-metal aromatic radical ion pairs, single crystals of K_2COT stabilized by the complexing ethers THF, diglyme and triglyme [1,2-bis-(2-methoxyethoxy)ethane] and single crystals of Rb_2COT stabilized by diglyme were prepared. Since these crystals were not as sensitive to air as earlier prepared alkali-biphenyl crystals (Canters, Klaassen & de Boer, 1970), we first succeeded in solving the crystal structure of K_2COT stabilized by diglyme. A crystal structure analysis of sodium-biphenyl stabilized by triglyme is in progress.

The structure of K_2COT.diglyme is illustrated in Figs. 1 and 2. The potassium ions lie on a crystallographic mirror plane, whereas the COT ring and the diglyme molecule lie perpendicular to this plane. Thus the asymmetric unit consists of only half of the COT ring atoms and half of the diglyme atoms. The structure may be described as consisting of K_2COT units that are packed in an electrostatically favourable way, forming a zigzag chain in the direction of the a axis. This column of K_2COT units is surrounded by diglyme molecules in such a way that the potassium ions outside the column [K(2) in Fig. 1] are coordinated by the diglyme, whereas the potassium ions inside the column [K(1) in Fig. 1] are coordinated by COT^{2-} rings. In a K_2COT unit the average K–C distance is 2·98 (2) Å for K(1) and 3·05 (2) Å for K(2).

The shortest K–C distances of potassium ion K(1) to the COT rings of two other K_2COT units are 3·26 (2) Å and 3·31 (2) Å for the distances K(1')–C(1) and K(1')–C(4) respectively (Fig. 1). The diglyme molecule has normal bond distances and angles, which are summarized along with the distances concerning the coordination of potassium ion K(2) in Table 2. As can be seen the K(2) ion is on one side coordinated by four oxygen atoms and on the other side shielded by one COT dianion. It may be compared with the glymated fluorenylpotassium contact ion pairs, studied by Smid (1972).

The cyclooctatetraene dianion is planar and has an average C–C bond length of $1·40 \pm 0·02$ Å. A weighted

least-squares plane through the C atoms of the COT ring ($0·0139X + 0·0Y - 1·0Z + 7·89$ Å $= 0$) has all of the atoms of the ring within $0·01 \pm 0·01$ Å of the plane. Bond lengths and angles for the COT ring together with the distances concerning the coordination of potassium ion K(1) are summarized in Table 3.

Table 3. *Bond lengths and angles for the COT ring*

Single prime indicates screw-axis related atom $(\frac{1}{2}+x, y, \frac{1}{2}-z)$. Double prime indicates mirror-related atom $(x, \frac{1}{2}-y, z)$.

Coordination of potassium ion K(1)

COT	Distance	COT	Angle
C(1)–C(1'')	1·46 (3) Å	C(1'')–C(1)–C(2)	134 (2)°
C(1)–C(2)	1·41 (3)	C(1)—C(2)–C(3)	135 (2)
C(2)–C(3)	1·39 (3)	C(2)—C(3)–C(4)	135 (2)
C(3)–C(4)	1·38 (3)	C(3)—C(4)–C(4'')	136 (2)
C(4)–C(4'')	1·38 (3)		

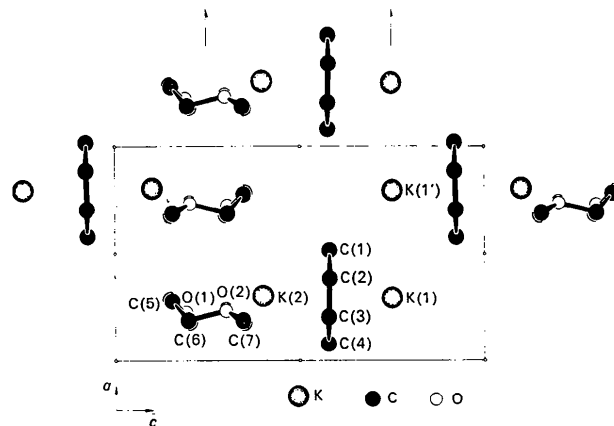| K–COT	Distance
K(1)–C(1)	2·98 (2) Å
K(1)–C(2)	2·97 (2)
K(1)–C(3)	2·98 (2)
K(1)–C(4)	2·98 (2)
K(1')–C(1)	3·26 (2)
K(1')–C(4)	3·31 (2)

Fig. 1. Projection along **b** of the structure lying between $y = 0$ and $\frac{1}{2}$. The upper half of the cell contents are related by the centres of symmetry (small circles) and have been omitted for clarity. There is a mirror plane at $y = \frac{1}{4}$.

Table 2. *Bond lengths and angles for the diglyme molecule*

Oxygen atom O(1) is on the mirror plane and C(7) is the methyl carbon atom. Single prime indicates screw-axis related atom $(\frac{1}{2}+x, y, \frac{1}{2}-z)$. Double prime indicates mirror related atom $(x, \frac{1}{2}-y, z)$.

Coordination of potassium ion K(2)

Diglyme	Distance	Diglyme	Angle
O(1)–C(5)	1·47 (2) Å	C(5'')–O(1)–C(5)	111 (2)°
C(5)–C(6)	1·52 (3)	O(1)—C(5)–C(6)	108 (2)
C(6)–O(2)	1·45 (3)	C(5)—C(6)–O(2)	105 (2)
O(2)–C(7)	1·44 (2)	C(6)--O(2)–C(7)	111 (2)

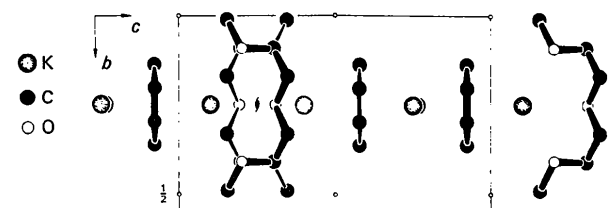| K–diglyme	Distance Å	K–COT	Distance
K(2)–O(1)	2·97 (2)	K(2)–C(1)	3·04 (2) Å
K(2)–O(2)	2·82 (2)	K(2)–C(2)	3·06 (2)
K(2)–O(1')	3·25 (2)	K(2)–C(3)	3·06 (2)
		K(2)–C(4)	3·05 (2)

Fig. 2. Projection of the structure along the a axis. Small circles indicate inversion centres. A mirror plane lies perpendicular to the plane of projection, at $y = \frac{1}{4}$.

It is noteworthy that in contrast to the single crystals of bis(tetramethylethylenediamine)lithium(I) naphthalenide (Brooks, Wendell & Stucky, 1972) in which we detected an e.p.r. signal probably due to the presence of a small amount of the mononegative ion of naphthalene, we were unable to detect an e.p.r. signal in the alkali COT single crystals, even after ultraviolet irradiation at low temperature: a common technique for removing electrons from radicals in solution or in a glass.

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The Crystal Structures of the Molecular Complexes between Benzidine and 7,7,8,8-Tetracyano-p-quinodimethane. II. The Benzidine–TCNQ Solvent-Free Complex

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Abstract. Monoclinic, $C2/m$, $a=12\cdot231$ (2), $b=12\cdot679$ (4), $c=6\cdot477$ (8) Å, $\beta=94\cdot84$ (1)°, $C_{12}H_{12}N_2 \cdot C_{12}H_4N_4$, $Z=2$, $D_x=1\cdot33$, $D_m=1\cdot32$ g cm^{-3}. Crystals were grown from a chloroform solution. BD and TCNQ are alternately stacked along the c axis to form mixed molecular columns. The structure within these columns is the same as that found in crystals of the BD–TCNQ complex containing dichloromethane [Ikemoto, Chikaishi, Yakushi & Kuroda (1972). *Acta Cryst.* B**28**, 3502–3506], but, instead of forming a channelled structure as observed in the latter complex, the molecular columns are closely packed.

Introduction. Preliminary cell constants and space group were determined from Weissenberg and precession photographs. Since the systematic absence is $h+k=2n+1$ for general reflexions, the space group is either $C2/m$, $C2$ or Cm. The precise cell constants and intensity data were measured on a Rigaku four-circle automatic diffractometer using monochromated

Mo $K\alpha$ radiation. 1163 independent reflexions in the range $2\theta \leq 55°$ were measured. Of these reflexions 425 were three times as large as their standard deviations. No absorption correction was made, since the absorption effect is small ($R\mu \leq 0\cdot05$).

The structure was solved by the Patterson method. It was refined by the block-diagonal least-squares method assuming the space group $C2/m$. The final R value was $0\cdot082$. The weighting scheme was as follows: $w=1/[\sigma^2(F_o)+(cF_o)^2]^{1/2}$, where σ is the standard deviation estimated from the counting statistics and c is the parameter which stands for the other types of error (Grant, Killean & Lawrence, 1969). The value of c was determined to be $0\cdot06$ after a few least-squares calculations. The least-squares refinements in the space group
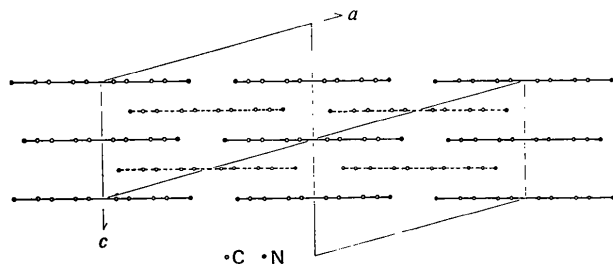

Fig. 1. Projection of the molecular arrangement onto the (010) plane. Molecules with centres at $y=0$ are shown by solid lines, those lying at $y=\frac{1}{2}$ are indicated by broken lines.

Table 1. *Atomic parameters*

(a) Atomic coordinates in fractions of cell edges and their standard deviations (in 10^{-3} Å)

BD

	x	y	z
C(1)	0·3016 (10)	0·0 (0)	0·1497 (10)
C(2)	0·2425 (6)	0·0935 (8)	0·1159 (7)
C(3)	0·1254 (7)	0·0930 (7)	0·0596 (7)
C(4)	0·0632 (9)	0·0 (0)	0·0300 (9)
N(1)	0·4182 (10)	0·0 (0)	0·2048 (12)
H(1)	0·449 (78)	0·059 (68)	0·183 (79)
H(2)	0·289 (68)	0·154 (68)	0·153 (64)
H(3)	0·089 (62)	0·155 (61)	0·055 (60)

TCNQ

	x	y	z
C(5)	0·3020 (6)	0·0950 (7)	0·6469 (6)
C(6)	0·2357 (9)	0·0 (0)	0·6090 (9)
C(7)	0·1197 (9)	0·0 (0)	0·5558 (9)
C(8)	0·0569 (6)	0·0971 (6)	0·5270 (6)
N(2)	0·3607 (6)	0·1662 (6)	0·6739 (7)
H(8)	0·101 (60)	0·158 (60)	0·528 (58)