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Crystal structure of cyclooctatetraenylpotassium, $C_8H_8K_2 \cdot (OC_4H_8)_3$

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Abstract

Crystals of $C_8H_8K_2 \cdot 3THF$ were prepared by the reaction of cyclooctatetraene with metallic potassium in tetrahydrofuran (THF). X-ray diffraction data were collected on a four-circle diffractometer at $-80\,^\circ C$. The compound crystallizes in the triclinic space group $P\bar{1}$ with a 10.263(3), b 13.157(4), c 9.443(3) Å, α 87.51(2), β 115.93(2), γ 76.81(2)°, $Z = 2$. The structure was solved by heavy-atom methods and refined by least-squares to a final R value of 0.051. The cyclooctatetraene with crystallographic centre of symmetry is planar and bonded on either side to two equivalent K^+ ions. The adjacent non-equivalent K^+ ions are connected by two oxygen bridges from THF molecules, and are catenated.

Introduction

In organometallic chemistry the studies of π-complexes are interesting. For π-complexes of unsaturated hydrocarbon groups with alkali metals a number of structural studies have been carried out on organolithium and organosodium systems [1–4] but fewer on organopotassium systems. Up to now the crystal structure of cyclooctatetraenylpotassium has not been reported, even though it is widely used as a reagent for the synthesis of transition metal cyclooctatetraenyl complexes.

In the known cyclooctatetraene (COT) complexes of lanthanide and actinide metals [5–7] the cyclooctatetraene behaves as a $(COT)^{2-}$ anion having ten π-electrons and its complexes have proved to be sandwich compounds analogous to ferrocene. Because alkali metals are different from f-block transition metals in electronic structure and oxidation state, it can be inferred that structure of the COT complexes of alkali metals would be different from those of f-block transition

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metals. We have prepared the extremely air-sensitive crystals of cyclooctatetraenylpotassium and have determined its crystal structure at low temperature.

Experimental

Preparation of the crystal

Cyclooctatetraene was dissolved in tetrahydrofuran (THF). To this solution was added metallic K under an atmosphere of nitrogen and the reaction was carried out at room temperature. When the resulting solution was cooled, we obtained crystals of the complex of cyclooctatetraenylpotassium with THF molecules.

Determination of crystal structure

The crystals are extremely air- and temperature-sensitive and can explode on contact with air, so were kept in a dry and cold nitrogen atmosphere. A crystal of dimensions 0.3 × 0.2 × 0.3 mm was selected for the study.

Intensity data were collected on a Nicolet four-circle diffractometer with an LT-1 low temperature device at about $-80\,^{\circ}\mathrm{C}$, using graphite-monochromated Mo-K_α radiation. The ω scan mode, scan speeds of between 4.88 to 29.3°/min and scan range of 1.1° were used. The intensity of one check reflection was measured after every 68 reflections. A total of 3308 reflections were collected within the range $3^{\circ} < 2\theta < 46^{\circ}$, of which 2084 reflections with $I > 2.5\sigma(I)$ were considered observed. No obvious changes were observed in the check reflection intensities, thus that the crystal was stable during data collection. The intensities were corrected for Lorentz and polarization factors, but not for absorption. The crystal data are listed in Table 1.

The crystal structure was solved by the heavy-atom method. The coordinates of the two K atoms from the Patterson analysis were used to calculate the Fourier map. Successive Fourier syntheses gave the coordinates of all non-hydrogen atoms.

The atomic coordinates and anisotropic temperature factors for all non-hydrogen atoms were refined by block diagonal least squares. The eight hydrogen atoms of the COT anion were located on a difference Fourier map. The hydrogen atoms of THF were not found, owing to the strong thermal vibration of atoms in THF, and their coordinates were calculated according to theoretical models. Further refinements led to final convergence at $R = 0.051$ and $R_w = 0.054$.

All calculations were performed on an Eclipse S/140 computer using SHELXTL programs.

Table 1

Crystal data

$C_8H_8K_2\cdot(OC_4H_8)_3$	M.W. 398.7
Triclinic system	Space group $P\bar{1}$
a 10.263(3) Å	b 13.157(4) Å
c 9.443(3) Å	α 87.51(2)°
β 114.93(2)°	γ 76.81(2)°
V 1111.6 Å^3	$Z = 2$
D_c 1.19 g cm^{-3}	μ 4.4 cm^{-1} (Mo-K_α $\lambda = 0.71069$ Å)

Results and discussion

The coordinates and equivalent isotropic temperature factors of non-hydrogen atoms are listed in Table 2. Bond distances and bond angles are given in Tables 3 and 4.

Being similar to that in known COT complexes of *f*-block transition metals, the COT in the present structure behaves as a dianion, (COT)$^{2-}$. The rings of (COT)$^{2-}$ are planar with the largest deviation by carbon atoms from the least-squares plane of 0.005 Å. The C–C–C angles of the rings are all 135°, which is consistent with the interior angles of a regular octagon. The C–C bond distances range from 1.39 to 1.42 Å. The average C–C bond distances are 1.407 Å in ring 1 and 1.403 Å in ring 2 and are close to the normal aromatic C–C bond length and thus different from the single bond length of 1.48 Å and from the bond length of the double bond of 1.34 Å in the cyclooctatetraene molecule. These facts indicate the aromaticity of (COT)$^{2-}$. The planes of rings 1 and 2 are at the crystallographic centres of symmetry at $(0, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2})$, respectively, and intersect at an angle of 100.7°. Each ring is bonded to two equivalent K$^+$ ions which are linked by the symmetry centre on both sides to form a bipyramid that is different from the sandwich complexes of *f*-block transition metals with COT. There are two K$^+$ ions in an asymmetric unit to give two independent bipyramidal molecules, (COT)K$_2$.

Table 2

Coordinates ($\times 10^4$) and equivalent temperature factors (Å$^2 \times 10^3$) for the non-hydrogen atoms

Atom	*x*	*y*	*z*	*U*
K(1)	587(1)	1589(1)	4873(1)	46(1)
K(2)	1889(1)	3890(1)	4537(1)	42(1)
C(1)	439(5)	−345(3)	3354(5)	42(2)
C(2)	1687(5)	−707(3)	4833(5)	42(2)
C(3)	1946(5)	−656(3)	6422(5)	43(2)
C(4)	1056(5)	−220(3)	7157(5)	42(2)
C(5)	211(6)	6118(4)	3976(7)	52(3)
C(6)	1166(5)	5924(4)	5626(7)	53(3)
C(7)	1417(5)	5176(4)	6878(5)	49(2)
C(8)	847(5)	4339(4)	7056(5)	50(2)
O(1)	3464(3)	1923(2)	6419(4)	55(2)
C(11)	4691(6)	1221(5)	6369(7)	84(3)
C(12)	5944(8)	1101(9)	7883(9)	222(7)
C(13)	5408(6)	1641(8)	8897(8)	186(6)
C(14)	3828(6)	1902(6)	8042(6)	100(4)
O(2)	1102(5)	2478(3)	2419(4)	76(2)
C(21)	−221(11)	2934(6)	1045(7)	189(6)
C(22)	−362(7)	2303(5)	−151(6)	97(4)
C(23)	1096(8)	1628(6)	328(6)	120(4)
C(24)	1984(6)	1649(4)	2004(6)	68(3)
O(3)	3955(5)	4023(4)	3583(6)	116(3)
C(31)	4972(7)	3340(5)	3194(9)	104(4)
C(32)	4810(8)	3849(6)	1659(7)	104(4)
C(33)	4310(8)	4978(6)	1733(8)	101(4)
C(34)	3532(11)	5029(6)	2658(12)	191(8)

Table 3

Bond distances (Å)

K(1)–C(1)	2.937(6)	K(1)–C(1′) [a]	2.978(5)
K(1)–C(2)	2.936(6)	K(1)–C(2′) [a]	2.983(4)
K(1)–C(3)	2.944(5)	K(1)–C(3′) [a]	2.972(4)
K(1)–C(4)	2.954(5)	K(1)–C(4′) [a]	2.950(5)
K(1)–O(1)	2.839(3)	K(1)–O(2)	2.846(5)
K(2)–C(5)	2.938(4)	K(2)–C(5′) [a]	3.029(7)
K(2)–C(6)	2.958(5)	K(2)–C(6′) [a]	3.025(6)
K(2)–C(7)	2.973(5)	K(2)–C(7′) [a]	2.989(4)
K(2)–C(8)	3.021(6)	K(2)–C(8′) [a]	2.954(4)
K(2)–O(1)	2.781(3)	K(2)–O(2)	2.783(4)
K(2)–O(3)	2.665(6)	C(1)–C(2)	1.406(5)
C(2)–C(3)	1.417(7)	C(3)–C(4)	1.406(8)
C(4)–C(1′) [a]	1.401(6)	C(5)–C(6)	1.421(7)
C(6)–C(7)	1.400(8)	C(7)–C(8)	1.394(8)
C(8)–C(5′) [a]	1.395(7)	O(1)–C(11)	1.401(7)
C(11)–C(12)	1.435(8)	C(12)–C(13)	1.431(13)
C(13)–C(14)	1.421(8)	C(14)–O(1)	1.413(7)
O(2)–C(21)	1.400(7)	C(21)–C(22)	1.409(10)
C(22)–C(23)	1.422(10)	C(23)–C(24)	1.461(7)
C(24)–O(2)	1.431(7)	O(3)–C(31)	1.399(9)
C(31)–C(32)	1.496(11)	C(32)–C(33)	1.472(11)
C(33)–C(34)	1.404(17)	C(34)–O(3)	1.422(10)

[a] The value for the primed atom was obtained by applying the centrosymmetric operation to the unprimed atom.

Table 4

Main bond angles (°)

O(1)–K(1)–O(2)	74.8(1)	O(1)–K(2)–O(2)	76.7(1)
O(1)–K(2)–O(3)	95.2(1)	O(2)–K(2)–O(3)	87.1(2)
K(1)–O(1)–K(2)	80.4(1)	K(1)–O(1)–C(11)	119.7(3)
K(1)–O(1)–C(14)	107.9(3)	K(2)–O(1)–C(11)	125.8(4)
K(2)–O(1)–C(14)	115.2(3)	C(11)–O(1)–C(14)	105.5(4)
K(1)–O(2)–K(2)	80.3(1)	K(1)–O(2)–C(21)	112.7(5)
K(1)–O(2)–C(24)	108.4(3)	K(2)–O(2)–C(21)	112.8(4)
K(2)–O(2)–C(24)	131.7(3)	C(21)–O(2)–C(24)	107.1(4)
K(2)–O(3)–C(31)	137.5(4)	K(2)–O(3)–C(34)	109.8(6)
C(31)–O(3)–C(34)	107.1(7)	C(4′)–C(1)–C(2)	134.9(5)
C(1)–C(2)–C(3)	134.7(5)	C(2)–C(3)–C(4)	134.6(4)
C(3)–C(4)–C(1′)	135.8(4)	C(8′)–C(5)–C(6)	135.5(5)
C(5)–C(6)–C(7)	133.7(5)	C(6)–C(7)–C(8)	136.2(4)
C(7)–C(8)–C(5′)	134.6(4)	O(1)–C(11)–C(12)	107.1(6)
C(11)–C(12)–C(13)	107.8(6)	C(12)–C(13)–C(14)	104.6(6)
C(13)–C(14)–O(1)	107.8(6)	O(2)–C(21)–C(22)	110.6(6)
C(21)–C(22)–C(23)	105.1(6)	C(22)–C(23)–C(24)	108.2(6)
C(23)–C(24)–O(2)	106.0(4)	O(3)–C(31)–C(32)	106.9(5)
C(31)–C(32)–C(33)	101.7(6)	C(32)–C(33)–C(34)	105.7(7)
C(33)–C(34)–O(3)	109.4(7)		

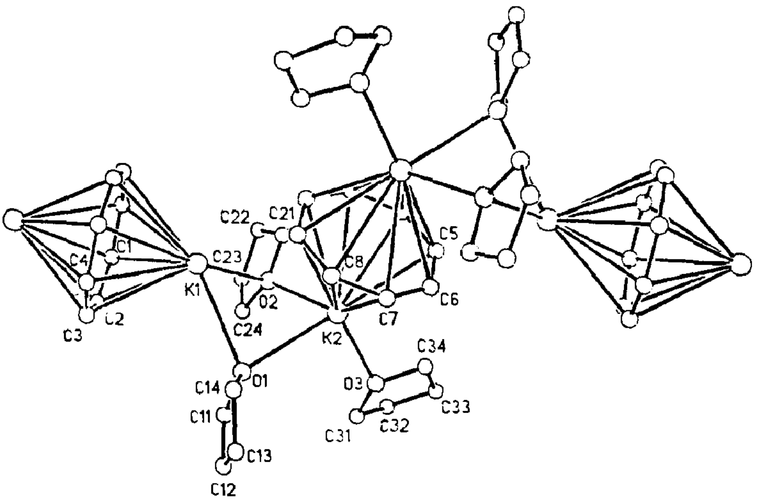

Fig. 1. Structure of $(C_8H_8)K_2 \cdot 3THF$.

As can be seen from Table 3, the distances from K(1) to carbons of the ring are in the range 2.936 to 2.983 Å with a mean of 2.957 Å while those from K(2) to carbons are in the range 2.938 to 3.029 Å with a mean of 2.986 Å. The distance of K(1) and K(2) to the centre of the planes are 2.32 and 2.36 Å, respectively. These results reflect more-ionic K–C bonding, as is expected. The vector from the K atom to the centre of the plane deviates from the normal to the plane by 0.9° for K(1) and 1.9° for K(2), thus accounting for the difference between the distances of K–C and K–C′.

It is noteworthy that $(COT)K_2 \cdot 3THF$ and $Na(C_5H_5) \cdot TMEDA$ [4] have the same chain structure but differ mode in the way in which the metals are connected to unsaturated hydrocarbon groups. There are no –M–U–M–U– chains (M = metal, U = unsaturated hydrocarbon group) in $(COT)K_2 \cdot 3THF$, that is, potassium does not bond to two COT dianions in a bridging mode, but each COT is part of a $(COT)K_2$ molecule. The adjacent $(COT)K_2$ are connected by two K–O–K bridges (via the O from THF) to form a chain structure along b, as shown in Fig. 1. This is probably why the crystal is very unstable.

The angle between planes of the two oxygen bridges is 106.9°. Two different sets of K–O bridging bond distances are observed, averaging K(1)–O 2.843(4) Å and K(2)–O 2.782(1) Å, which indicates the comparative weakness of the K(1)–O bridge. This difference probably originates in the stronger bonding between K(1) and COT as well as the Van der Waals contacts of K(1) with the atoms of neighbouring COT (K(1)–C(5′) 3.295(5) Å, K(1)–C(6′) 3.260(5) Å). By contrast, the bonding between K(2) and COT is somewhat weak, for not only is K(2) bonded to the bridging THF molecule, but also to a terminal THF.

Figure 2 shows a projection of the structure onto the plane that is formed by the potassium atoms. The skeleton of the structure is a puckered chain of potassium atoms, in which two centrosymmetric K atoms are bridged by a COT and two of the non-symmetric K atoms are bridged by the oxygen atoms in the THF molecules. There are two crystallographically distinct K–K–K angles, viz. 172.3° and 92.2°,

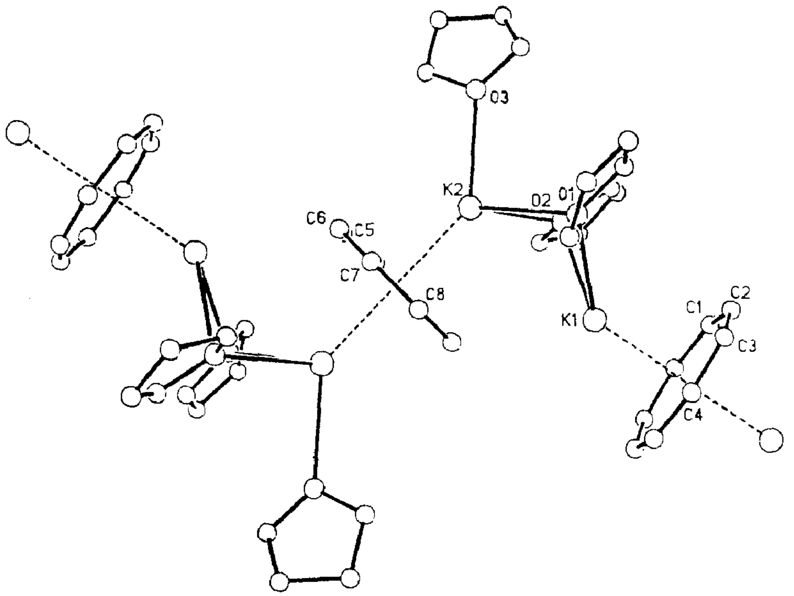

Fig. 2. Projection of structure on the plane of K atoms.

which are noticeably different from those in the nearly tetrahedral orientation in structure of $Na(C_5H_5) \cdot TMEDA$.

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