Crystal Structure of Dicyclohexano-18-crown-6 Potassium 2-Nitrophenoxide

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Abstract. The first crystal structure of a potassium cation complex with dicyclohexano-18-crown-6 is reported. The potassium 2-nitrophenoxide complex of *syn-cis-syn* dicyclohexano-18-crown-6 crystallizes in the triclinic space group $P\bar{1}$ with cell constants $a = 8.604(2)$, $b = 10.772(4)$, $C = 16.123(5)$ Å, $\alpha = 73.86(3)°$, $\beta = 77.61(3)°$, $\gamma = 82.68(3)°$ and $Z = 2$ for $D_c = 1.31$ g cm^{-3}. Least-squares refinement based on 2742 observed reflections led to a final conventional R value of 0.040. Dicyclohexano-18-crown-6 has the shape of a saddle with the potassium cation sitting at the saddlepoint. The structure of the 2-nitrophenoxide anion is dominated by the quinoid resonance contributor. Because the complex is devoid of significant intercomplex interactions, it is a prototypical 1 : 1 : 1 complex.

Key words: crown ether, potassium, crystal structure, 2-nitrophenoxide.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82043 (26 pages).

1. Introduction

Since the discovery of crown ethers in 1967, [1] subsequent studies of their complexes have revolutionized the field of inclusion phenomena. Although dicyclohexano-18-crown-6 is a charter member of this class of compounds, to our amazement, we have not been able to find a crystal structure report of a potassium complex with it. In this paper, the crystal structure of the complex of potassium nitrophenoxide with *syn-cis-syn* dicyclohexano-18-crown-6 is described.

2. Experimental

2.1. SYNTHESIS

A mixture of 13.9 g (0.10 mole) 2-nitrophenol, 13.8 g (0.10 mole) anhydrous potassium carbonate and 50.0 ml anhydrous acetone was refluxed while stirring for 1 h, cooled to room temperature and filtered. The potassium 2-nitrophenoxide was separated from the precipitate with refluxing anhydrous acetone in a Soxhlet extractor until all of the color had been extracted from the contents of the thimble. The product crystallized from the extract as 17.3 g (97.7%)

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of bright-orange granules, which melted with decomposition at 282–286°C. Visible spectrum of an acetonitrile solution: λ_{max} 447 nm, ε_{max} 7,230.

To a stirred solution of 1.86 g (5.0 mmoles) of dicyclohexano-18-crown-6 (Parish Chemical Co., Orem UT) in 25.0 ml anhydrous acetone was added 0.89 g (5.0 mmoles) of the crude potassium 2-nitrophenoxide. When solution was complete, the mixture was heated to boiling and refluxed for 30 minutes, then cooled to room temperature. The volume of the solution was reduced to 10 ml in a rotary evaporator, yielding 0.74 g (26.9%) of yellow-orange crystals, m.p. 170–172°C. A suitable crystal for X-ray analysis could not be obtained. Anal. (Atlantic Microlab, Inc., Atlanta, Ga): Calcd. for $C_{26}H_{40}KNO_9$: C, 56.81; H, 7.33; N, 2.55. Found: C, 57.19; H, 7.19; N, 2.65.

Concentration of the mother liquor yielded an additional 0.90 g (32.7%) of crystals, m.p. 128–130°C. The sample for crystallographic analysis was crystallized from acetone/dichloromethane. Anal: Calcd. for $C_{26}H_{40}KNO_9$: C, 56.81; H, 7.33; N, 2.55. Found: C, 56.75; H, 7.34; N, 2.55.

Both products gave the same visible absorption spectra in acetonitrile solution: λ_{max} 448 nm, ε_{max} 7110.

2.2. X-RAY DATA COLLECTION AND STRUCTURE SOLUTION

Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo$K\alpha$ radiation (λ = 0.71073 Å) and a graphite monochromator, by ω-2θ scans designed to yield equal relative precision for all observed data, subject to a maximum scan time. Cell dimensions were obtained from a least-squares fit to the setting angles of 25 reflections having $11.0° < \theta < 12.0°$. One hemisphere of data was collected; angular limits and other experimental parameters are listed in Table I. Data reduction included corrections for background, Lorentz, and polarization effects. Absorption effects were insignificant. Data having $I > 3\sigma(I)$ were considered observed and used in the refinement.

The structure was solved by direct methods using MULTAN [2] and refined by full-matrix least squares based of F with weights $w = \sigma^{-2}(F_0)$, using the Enraf-Nonius SDP [3]. Scattering factors were those of Cromer and Waber [4] with anomalous coefficients of Cromer [5]. Nonhydrogen atoms were treated anisotropically. Hydrogen atoms were located by difference maps and included as fixed contributions. Final R factors and residual electron density are given in Table I.

Table I. Crystal data and data collection parameters

Formula	$C_{26}H_{40}NO_9K$	$F(000)$	588
f_w	549.7	cryst. size, mm	0.16 × 0.28 × 0.32
cryst. system	Triclinic	θ limits, deg	1–25
space group	$P\bar{1}$	scan rates, deg min^{-1}	0.39–4.0
a, Å	8.604(2)	precision, $I/\sigma(I)$	50
b, Å	10.772(4)	max. scan time, s	120
c, Å	16.123(5)	unique data	4929
α, deg	73.86(3)	observed data	2742
β, deg	77.61(3)	variables	335
γ, deg	82.68(3)	B for H atoms, Å^2	5.0
V, Å^3	1398.3(9)	R	0.040
Z	2	R (all data)	0.117
D, g cm^{-3}	1.306	R_w	0.044
T, deg	22–24	GOF	1.72
μ, cm^{-1}	2.36	max residual, e Å^{-3}	0.37

3. Results and Discussion

The atomic positional parameters are given in Table II. Selected torsion angles are presented in Table III. Tables of hydrogen atom coordinates, anisotropic thermal parameters, distances and angles, and structure factors are in the Supplementary Material. The structure with all atoms is shown in Figure 1, while a skeletal drawing that emphasizes the arrangement of donor atoms about the potassium cation is presented in Figure 2.

Table II.   Atomic positional parameters for nonhydrogen atoms

Atom	x	y	z	Atom	x	y	z
K	0.60141(8)	0.42958(6)	0.79794(4)	C(13)	0.6597(5)	0.2131(3)	0.6650(2)
O(1)	0.6829(2)	0.2546(2)	0.9510(1)	C(14)	0.6996(5)	0.1152(3)	0.7438(2)
O(2)	0.3695(2)	0.3641(2)	0.9559(1)	C(15)	0.8105(4)	0.0929(3)	0.8713(2)
O(3)	0.3387(2)	0.6121(2)	0.8425(1)	C(16)	0.9697(4)	0.0190(3)	0.8481(2)
O(4)	0.3887(2)	0.5549(2)	0.6819(1)	C(17)	1.1053(5)	0.1075(4)	0.8102(2)
O(5)	0.5236(3)	0.2927(2)	0.6895(1)	C(18)	1.1161(4)	0.1886(3)	0.8703(2)
O(6)	0.7584(3)	0.1782(2)	0.7962(1)	C(19)	0.9595(4)	0.2640(3)	0.8926(2)
C(1)	0.5496(4)	0.1876(3)	1.0019(2)	C(20)	0.8242(4)	0.1753(3)	0.9313(2)
C(2)	0.4219(4)	0.2813(3)	1.0312(2)	O(1A)	0.8362(3)	0.4896(2)	0.6628(1)
C(3)	0.2521(4)	0.4610(3)	0.9770(2)	O(2A)	0.8169(3)	0.6071(2)	0.7906(1)
C(4)	0.2059(4)	0.5455(3)	0.8944(2)	O(3A)	0.8752(3)	0.8048(2)	0.7537(2)
C(5)	0.3056(3)	0.7099(3)	0.7667(2)	N(1A)	0.8479(3)	0.7085(2)	0.7337(2)
C(6)	0.4487(4)	0.7886(3)	0.7336(2)	C(1A)	0.8492(4)	0.6022(3)	0.6150(2)
C(7)	0.4348(4)	0.8940(3)	0.6494(2)	C(2A)	0.8533(3)	0.7164(3)	0.6438(2)
C(8)	0.4040(4)	0.8358(3)	0.5799(2)	C(3A)	0.8670(4)	0.8388(3)	0.5846(3)
C(9)	0.2571(4)	0.7624(3)	0.6133(2)	C(4A)	0.8787(4)	0.8551(4)	0.4980(3)
C(10)	0.2667(3)	0.6545(3)	0.6973(2)	C(5A)	0.8781(5)	0.7460(5)	0.4675(2)
C(11)	0.3418(4)	0.4696(3)	0.6403(2)	C(6A)	0.8644(5)	0.6286(4)	0.5215(2)
C(12)	0.4807(4)	0.3833(3)	0.6140(2)				

Table III.   Torsion angles (°) around the macroring

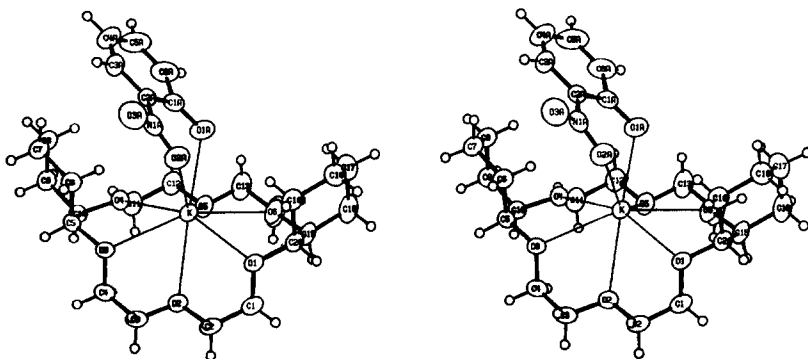| Atoms	Angle
O(1)—C(1)—C(2)—O(2)	65.1
C(1)—C(2)—O(2)—C(3)	−177.3
C(2)—O(2)—C(3)—C(4)	178.7
O(2)—C(3)—C(4)—O(3)	−65.2
C(3)—C(4)—O(3)—C(5)	−171.9
C(4)—O(3)—C(5)—C(10)	−69.1
O(3)—C(5)—C(10)—O(4)	−49.8
C(5)—C(10)—O(4)—C(11)	161.5
C(10)—O(4)—C(11)—C(12)	171.0
O(4)—C(11)—C(12)—O(5)	70.8
C(11)—C(12)—O(5)—C(13)	−177.9
C(12)—O(5)—C(13)—C(14)	−177.6
O(5)—C(13)—C(14)—O(6)	−70.1
C(13)—C(14)—O(6)—C(15)	−176.2
C(14)—O(6)—C(15)—C(20)	−164.5
O(6)—C(15)—C(20)—O(1)	53.1
C(15)—C(20)—O(1)—C(1)	66.7
C(20)—O(1)—C(1)—C(2)	169.5

Fig. 1. Stereodrawing of the potassium 2-nitrophenoxide complex of *syn-cis-syn* dicyclohexano-18-crown-6.
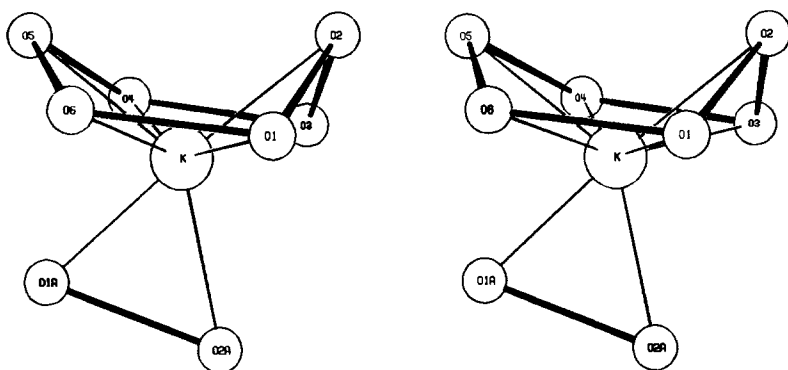

Fig. 2. Skeletal drawing of complex. K—O distances in Å: O(1), 2.820(2); O(2), 2.854(2); O(3), 2.907(2); O(4), 2.847(2); O(5), 2.804(2); O(6), 2.873(2); O(1A), 2.628(2); O(2A), 2.792(2).

The complex shown in Figure 1 is the *syn-cis-syn* isomer of dicyclohexano-18-crown-6, which has the shape of a saddle; the potassium cation sits at the saddlepoint. Hughes and Truter [6] have compared the structural features of dicyclohexano-18-crown-6 metal ion complexes. The *syn-cis-syn* isomer is seen in five of the seven reported. [6–11] As shown in Figure 2, the donor atoms are arranged in a boat conformation, which corresponds to form 3 in the Hughes and Truter analysis [6]. The more typical arrangement of macroring donor atoms in potassium complexes of eighteen-membered coronands is the chair conformation or D_{3d} conformation, although the boat conformation is seen in potassium cation complexes of cryptands and a bibrachial lariat ether [12]. The metal cation is located below the bottom of the boat, displaced towards the nitrophenoxide ion. A similar phenomenon is seen in the potassium thiocyanate complex of 221 cryptand [13]. The two cyclohexano rings are on the same side of the macroring as the metal ion and the counterion. The shortest C···C distance between these rings is C(6) to C(19), 6.95 Å. Because the oxygens attached to these rings occupy the bottom of the boat, the cyclohexano rings serve as side stabilizers, providing a hydrophobic shield on the sides of the metal ion between the donors of the macroring and the donors of the counterion.

The potassium cation is octacoordinated with six donors from the macroring and two donors from the nitrophenoxide. The phenoxide oxygen is the closest metal-donor contact, 2.628 Å. The next closest, 2.792 Å, is an oxygen on the nitro group. The metal-donor distances

to the macroring's oxygens range from 2.804 to 2.907 Å, mean 2.85 Å. The cavity size, R[13], of the crown ether is 1.45 Å, a value more typical for potassium complexes of lariat ethers than crowns [12].

The nitrophenoxide ion has some statistically significant differences in distances when compared to other potassium 2-nitrophenoxide complexes [14,15], as well as to the un-complexed phenol [16]. The O(1A)—C(1A) distance is 1.247(3) Å, which is considerably shorter than that of other complexes (1.281(5) Å [15] and 1.298(5) Å [14]), as well as the phenol (1.337(7) Å [16]). The only other metal complex of 2-nitrophenoxide with such a short C—O distance (1.241(6) Å) is the sodium *bis*(1,10-phenanthroline) complex [17]. The K—O(1A) distance, 2.628(2) Å, reported here is also shorter than any reported previously. What distinguishes the 2-nitrophenoxide ligand in this structure from others [14,15,17,18] is that it is only associated with one potassium cation. The shortest intercomplex contact is between O(3A) and C(16), 3.356 Å. As discussed previously [10,11,13], the quinoid form strongly contributes to the structure of 2-nitrophenoxide. This contribution is quite exagger-ated in our structure in that C(5A)—C(6A) and C(3A)—C(4A) are significantly short, 1.324(6) and 1.340(5) Å, respectively.

In summary, the structure reveals very strong interactions between the potassium cation and the donor atoms of the crown as well as those of the counterion. Because it is devoid of significant intercomplex interactions, it is a prototypical 1 : 1 : 1 complex.

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