

The Structures of Alkalides and Electrides. II. Structure of Caesium Bis(15-Crown-5)* Electride

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Abstract. $\text{Cs}^+\text{C}_{20}\text{H}_{40}\text{O}_{10}\cdot\text{e}^-$, $M_r = 573.44$, triclinic, $P\bar{1}$, $a = 8.597$ (4), $b = 8.886$ (8), $c = 9.941$ (9) Å, $\alpha = 102.91$ (8), $\beta = 90.06$ (6), $\gamma = 97.74$ (6)°, $V = 733.1$ (11) Å³, $Z = 1$, $D_x = 1.30$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 12.9$ cm⁻¹, $F(000) = 295$, $T = 215$ (2) K, final $R = 0.024$ for 2587 [$I > 3\sigma(I)$] of 2595 unique reflections. The structure determination confirmed that this compound is an electride. Examination of the structure by computer simulation using an Evans & Sutherland PS-350 display system reveals a large cavity (approximate dimensions are larger than 4 Å) around the center of the unit cell (1/2, 1/2, 1/2). This cavity is the most likely site for the center of charge of the trapped electron which serves as the anion.

Introduction. The electride, $\text{Cs}^+(\text{15C5})_2\cdot\text{e}^-$ (15C5 = 15-crown-5), has some unusual magnetic properties (Dawes, 1986). The magnetic susceptibility of a sample that was quenched from room temperature to 5 K showed Curie–Weiss type behavior down to 2 K. However, when the sample was cooled gradually from 250 K to low temperatures it showed an anti-ferromagnetic transition with a Néel temperature of 4.2 K. Structure determination was undertaken to help understand these properties.

Experimental. Single crystals were obtained from a mixed dimethyl ether–diethyl ether solution by using temperature scanning. The procedures for single crystal handling and mounting have been described in a previous paper (Ward, Huang & Dye, 1988).

The crystal used for data collection was irregular in shape, dark grey in color, and had approximate dimensions 0.6 × 0.8 × 0.8 mm. The diffractometer was a Nicolet P3F using graphite-monochromated Mo $K\alpha$ radiation and a locally modified Nicolet LT-1 low-temperature system. Unit-cell parameters were determined by least squares from the setting angles of 15 reflections in the range $20 <$

$2\theta < 26^\circ$. Intensity data were collected with θ – 2θ scans at 8° min^{-1} (in 2θ) for $\sin\theta/\lambda < 0.5947 \text{ \AA}^{-1}$; reflection indices: $0 \leq h \leq 10$, $-10 \leq k \leq 10$, $-11 \leq l \leq 11$. A linear decay correction was based on the intensities of three monitored reflections (8.0% decrease in average intensity). An empirical absorption correction (DIFABS; Walker & Stuart, 1983) was applied with a transmission factor range of 0.879 to 1.000 on I . Reflection averaging led to $R_{\text{int}} = 1.4\%$ and 2595 unique data from 2783 reflections. Taking a data cut-off of $I > 3\sigma(I)$, there are 2587 observed and eight unobserved data. The structure was solved by direct methods. Full-matrix least-squares refinement was on F with non-H atoms refined anisotropically, H atoms were placed in calculated positions and refined isotropically, 223 total parameters, $w = 1.0$, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. After the final cycle of refinement, the maximum $\Delta/\sigma = 0.18$, $R = 0.024$, $wR = 0.027$, $S = 0.614$. The final difference-map peak heights ranged from -0.85 (5) to 0.68 (5) e Å⁻³. Scattering factors were from Cromer & Waber (1974) and f' and f'' from Cromer (1974). All computations were carried out with a VAX 11/750 computer using the SDP (Frenz, 1978) software system.

Discussion. The refined atomic coordinates and isotropic temperature factors are presented in Table 1; bond distances and angles are given in Table 2.† The molecular structure and the numbering of the atoms are shown in Fig. 1 and the stereographic packing diagram is shown in Fig. 2.

The structure determination confirmed that the compound is an electride that contains only complexed cations, $\text{Cs}^+(\text{15C5})_2$, and undetected trapped

† Lists of structure factors and tables of anisotropic thermal parameters, least-squares planes, torsion angles, r.m.s. amplitudes of thermal vibration and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52971 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* 15-Crown-5: 1,4,7,10,13-pentaoxacyclopentadecane.

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Table 1. Positional and isotropic thermal parameters and their *e.s.d.*'s for caesium (15-crown-5)₂ electrider

	x	y	z	B(Å ²)
Cs1	0.000	0.000	0.000	2.837 (4)
O1	-0.1628 (2)	-0.1501 (2)	-0.2024 (2)	3.62 (4)
O4	0.1277 (2)	0.3223 (2)	-0.0605 (2)	4.13 (5)
O7	0.3425 (2)	0.0926 (2)	-0.1024 (2)	3.95 (4)
O10	0.1964 (2)	-0.2271 (2)	-0.1862 (2)	3.62 (4)
O13	-0.0214 (2)	-0.1137 (2)	-0.3396 (2)	3.60 (4)
C2	-0.1210 (4)	0.3157 (3)	-0.1679 (4)	4.41 (7)
C3	0.0534 (4)	0.3647 (4)	-0.1708 (4)	4.76 (7)
C5	0.2960 (4)	0.3554 (4)	-0.0546 (4)	4.96 (8)
C6	0.3732 (4)	0.2348 (4)	-0.1472 (4)	4.93 (8)
C8	0.4166 (4)	-0.0252 (4)	-0.1883 (4)	4.57 (7)
C9	0.3594 (4)	-0.1789 (4)	-0.1552 (4)	4.31 (7)
C11	0.1594 (4)	-0.2887 (3)	-0.3299 (3)	3.99 (7)
C12	-0.0081 (4)	-0.2742 (3)	-0.3558 (3)	4.14 (7)
C14	-0.1754 (4)	-0.0879 (4)	-0.3700 (3)	4.44 (7)
C15	-0.1766 (4)	0.0840 (4)	-0.3469 (3)	4.40 (7)
H2a	-0.160 (3)	0.349 (3)	-0.066 (3)	1.9 (6)
H2b	-0.178 (4)	0.357 (4)	-0.236 (3)	2.9 (8)
H3a	0.092 (4)	0.314 (4)	-0.263 (3)	2.8 (7)
H3b	0.072 (4)	0.479 (4)	-0.157 (4)	4.1 (9)
H5a	0.338 (4)	0.347 (4)	0.045 (3)	3.0 (8)
H5b	0.325 (4)	0.457 (4)	-0.092 (3)	3.1 (8)
H6a	0.326 (4)	0.227 (4)	-0.246 (4)	3.9 (9)
H6b	0.493 (4)	0.274 (4)	-0.138 (4)	3.8 (9)
H8a	0.535 (4)	-0.006 (4)	-0.167 (3)	3.1 (8)
H8b	0.392 (3)	-0.020 (3)	-0.286 (3)	1.8 (6)
H9a	0.420 (4)	-0.261 (4)	-0.203 (3)	2.4 (7)
H9b	0.375 (4)	-0.169 (3)	-0.049 (3)	2.1 (7)
H11a	0.182 (4)	-0.396 (4)	-0.354 (3)	2.5 (7)
H11b	0.230 (3)	-0.229 (3)	-0.385 (3)	1.7 (6)
H12a	-0.037 (4)	-0.326 (4)	-0.452 (3)	2.5 (7)
H12b	-0.081 (4)	-0.320 (4)	-0.291 (3)	2.5 (7)
H14a	-0.250 (4)	-0.133 (4)	-0.314 (3)	2.5 (7)
H14b	-0.204 (4)	-0.134 (4)	-0.461 (3)	3.1 (8)
H15a	-0.090 (4)	0.129 (3)	-0.393 (3)	2.1 (7)
H15b	-0.282 (4)	0.109 (4)	-0.382 (3)	2.9 (8)

H atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(8\pi^2/3)\sum_i U_i a_i^* a_i$.

Table 2. Bond distances (Å) and angles (°) for caesium (15-crown-5)₂ electrider

Cs1—O1	3.080 (2)	O7—C8	1.418 (4)
Cs1—O4	3.114 (2)	O10—C9	1.422 (3)
Cs1—O7	3.179 (2)	O10—C11	1.429 (3)
Cs1—O10	3.099 (2)	O13—C12	1.419 (4)
Cs1—O13	3.298 (2)	O13—C14	1.417 (4)
O1—C2	1.430 (3)	C2—C3	1.506 (5)
O1—C15	1.424 (3)	C5—C6	1.480 (5)
O4—C3	1.414 (4)	C8—C9	1.495 (5)
O4—C5	1.436 (4)	C11—C12	1.490 (5)
O7—C6	1.424 (4)	C14—C15	1.495 (5)
O1—Cs1—O4	56.40 (5)	C6—O7—C8	110.5 (3)
O1—Cs1—O7	93.94 (5)	Cs1—O10—C9	110.4 (2)
O1—Cs1—O10	104.37 (5)	Cs1—O10—C11	122.5 (2)
O1—Cs1—O13	53.15 (5)	C9—O10—C11	113.9 (2)
O4—Cs1—O7	54.80 (5)	Cs1—O13—C12	100.3 (2)
O4—Cs1—O10	103.47 (5)	Cs1—O13—C14	101.8 (2)
O4—Cs1—O13	83.39 (5)	C12—O13—C14	112.7 (2)
O7—Cs1—O10	54.67 (5)	O1—C2—C3	112.6 (3)
O7—Cs1—O13	74.03 (5)	O4—C3—C2	108.9 (3)
O10—Cs1—O13	52.49 (5)	O4—C5—C6	113.6 (2)
Cs1—O1—C2	110.5 (2)	O7—C6—C5	109.2 (3)
Cs1—O1—C15	122.3 (2)	O7—C8—C9	109.3 (3)
C2—O1—C15	114.1 (3)	O10—C9—C8	112.8 (3)
Cs1—O4—C3	116.7 (2)	O10—C11—C12	108.1 (2)
Cs1—O4—C5	113.7 (2)	O13—C12—C11	108.3 (2)
C3—O4—C5	115.0 (3)	O13—C14—C15	108.2 (2)
Cs1—O7—C6	117.8 (2)	O1—C15—C14	108.7 (3)
Cs1—O7—C8	118.5 (2)		

electrons. The Cs⁺—O distances in the sandwich cation are 3.080 to 3.298 Å with an average value of 3.154 Å which is normal for caesium-crown ether

complexes. Examination of the structure by computer simulation using an Evans & Sutherland PS-350 display system reveals a large cavity at the center of the unit cell (1/2, 1/2, 1/2). This cavity is the most likely site for the center of charge of the trapped electron which serves as the anion. The distances between the center (1/2, 1/2, 1/2) and the nearest H atoms are 3.25, 3.36, 3.57, 3.76 and 3.80 Å. Taking 1.2 Å as the van der Waals radius of the H atom we estimate that the cavity radius is 2.0 Å minimum and 2.35 Å when averaged over the nearest 10 H atoms. This compares with the cavity radius in the electrider Cs⁺(18C6)₂e⁻ (Dawes, Ward, Huang & Dye, 1986), which is 2.1 Å minimum and 2.4 Å average. Thus, the cavity sizes are almost the same. The distances between cavities are 8.597, 8.886 and 9.941 Å along the *a*, *b* and *c* axes respectively. These distances in Cs⁺(18C6)₂e⁻ are 8.68, 10.27 and 10.27 Å. The cavities in Cs⁺(15C5)₂e⁻ are closer than those in Cs⁺(18C6)₂e⁻, the distances are more

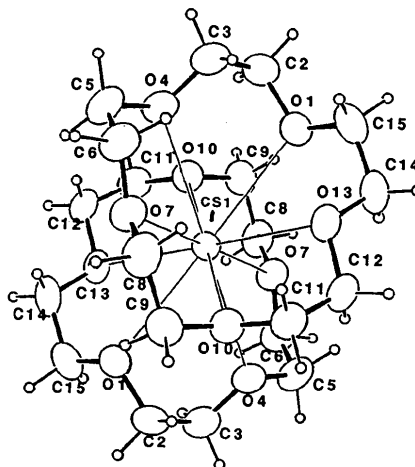


Fig. 1. The molecular structure and numbering of the atoms for Cs⁺(15-crown-5)₂e⁻ [ORTEP (Johnson, 1965), 50% probability ellipsoids].

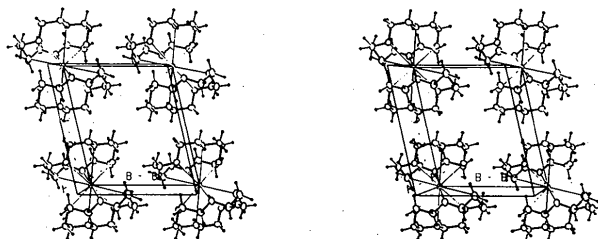


Fig. 2. Stereographic packing diagram for Cs⁺(15-crown-5)₂e⁻ [ORTEP (Johnson, 1965), 20% probability ellipsoids]. The *c* axis is vertical, the *b* axis is horizontal and the *a* axis is normal to the paper.

uniform and there is only one molecule per unit cell. All of these factors may contribute to the observation of antiferromagnetism at low temperatures for $\text{Cs}^+(\text{15C5})_2\text{e}^-$ but not for $\text{Cs}^+(\text{18C6})_2\text{e}^-$ (down to about 2 K).

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The Structures of Alkalides and Electrides. III. Structure of Potassium Cryptand[2.2.2]* Natride†

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Abstract. $\text{K}^+\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6\text{Na}^-$, $M_r = 438.59$, orthorhombic, *Fdd2*, $a = 15.769$ (7), $b = 25.245$ (7), $c = 13.818$ (13) Å, $V = 5501$ (3) Å³, $Z = 8$, $D_x = 1.06$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 2.3$ cm⁻¹, $F(000) = 2592$, $T = 206$ (4) K, final $R = 0.021$ for 1198 [$I > 3\sigma(I)$] of 1275 unique reflections. The structure is completely different from that of the corresponding electride, $\text{K}^+(\text{C222})\text{e}^-$, which shows evidence of paired electrons. This is additional evidence that the natride ion, Na^- , does not form dimers, Na_2^{2-} , or chains as are seen in some K^- , Rb^- and Cs^- crystals.

Introduction. After the structure of the electride $\text{K}^+(\text{C222})\text{e}^-$ was determined and its magnetic properties were interpreted by invoking electron spin pairing (Huang, Faber, Moeggenborg, Ward & Dye, 1988; Ward, Huang & Dye, 1988), it was predicted that the structure of the corresponding natride, $\text{K}^+(\text{C222})\text{Na}^-$, would be different from that of the electride since it was felt that dimers, Na_2^{2-} would

not form. Therefore, the structure of the natride was determined to compare it with that of the electride and with corresponding kalides and rubidides.

Experimental. Single crystals were obtained by crystallization from a mixed dimethyl ether-trimethylamine solution by using temperature scanning. The procedures for single crystal handling and mounting have been described in a previous paper (Ward *et al.*, 1988).

The crystal used for data collection was rod shaped, dark grey in color, and had approximate dimensions $0.4 \times 0.5 \times 0.8$ mm. The diffractometer was a Nicolet P3F using graphite-monochromated $\text{Mo K}\alpha$ radiation and a locally modified Nicolet LT-1 low-temperature system. Unit-cell parameters were determined by least squares from the setting angles of 16 reflections in the range $15 < 2\theta < 20^\circ$. Intensity data were collected using θ - 2θ scans at 2° min^{-1} (in 2θ) to $\sin\theta/\lambda < 0.5951$ Å⁻¹; reflection indices: $0 \leq h \leq 16$, $0 \leq k \leq 18$, $-30 \leq l \leq 30$; an anisotropic decay correction was based on the intensities of three monitored reflections. A numerical absorption correction based on measurement of indexed faces of the crystal was applied with a

* 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

† Natride and kalide are IUPAC (1990) recommended names.

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