

The Structures of Alkalides and Electrides. V. Structures of Caesium Bis(15-crown-5)* Kalide and Rubidium Bis(15-crown-5) Rubidide

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(Received 7 June 1989; accepted 12 February 1990)

Abstract. $\text{Cs}^+2(\text{C}_{10}\text{H}_{20}\text{O}_5)\cdot\text{K}^-$ (I), $M_r = 612.54$, monoclinic, $C2/m$, $a = 11.537$ (4), $b = 13.679$ (3), $c = 10.624$ (3) Å, $\beta = 90.12$ (2)°, $V = 1676.6$ (8) Å³, $Z = 2$, $D_x = 1.21$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 12.4$ cm⁻¹, $F(000) = 628$, $T = 213$ (2) K, final $R = 0.067$ for 1453 [$I > 3\sigma(I)$] of 1570 unique reflections. $\text{Rb}^+2(\text{C}_{10}\text{H}_{20}\text{O}_5)\cdot\text{Rb}^-$ (II), $M_r = 611.48$, monoclinic, $C2/m$, $a = 11.635$ (3), $b = 13.855$ (5), $c = 10.556$ (3) Å, $\beta = 88.82$ (2)°, $V = 1701.2$ (8) Å³, $Z = 2$, $D_x = 1.19$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 28.3$ cm⁻¹, $F(000) = 628$, $T = 222$ (2) K, final $R = 0.053$ for 1143 [$I > 3\sigma(I)$] of 2048 unique reflections. Both structures are isostructural with the natride, $\text{Rb}^+(15\text{C}5)_2\cdot\text{Na}^-$. The structures yield an average radius of 3.1 Å for both K^- and Rb^- .

Introduction. The crystal structures of several natrides and caesides have been determined and reported (Dawes, Fussa-Rydel, Ward, Huang & Dye, 1989; Huang, Ward, Kuchenmeister & Dye, 1987). It is of interest to determine the structures of two other types of alkalides, kalides and rubidides, and to estimate the sizes of K^- and Rb^- .

Experimental. Single crystals of both compounds were obtained by crystallization from mixed dimethyl ether-trimethylamine solutions by using temperature scanning. The procedures for single crystal handling and mounting have been described in a previous paper (Ward, Huang & Dye, 1988).

The crystals used for data collection for both compounds were rod shaped, dark grey in color, and had approximate dimensions $0.2 \times 0.4 \times 0.9$ mm (I) and $0.2 \times 0.4 \times 0.8$ mm (II). The diffractometer was a Nicolet P3F that used 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 24 reflections in the range $15 < 2\theta < 20^\circ$ (I) and 23 reflections in the range $20 < 2\theta < 25^\circ$ (II).

Intensity data were collected using θ - 2θ scans at 2° min^{-1} (I) and 4° min^{-1} (II) (in 2θ) to $\sin\theta/\lambda < 0.7041$ Å⁻¹ (I) and 0.6502 Å⁻¹ (II); reflection indices: $-16 \leq h \leq 16$, $-19 \leq k \leq 19$, $0 \leq l \leq 14$ (I) and $-15 \leq h \leq 15$, $-18 \leq k \leq 0$, $0 \leq l \leq 13$ (II). An anisotropic decay correction was based on the intensities of three monitor reflections [8.9% (I) and 6.5% (II) decrease in average intensity]. A numerical absorption correction based on measurement of indexed faces of the crystal was applied with transmission coefficients that ranged from 0.404 to 0.812 (I) and 0.150 to 0.326 (II) on I . Reflection averaging led to $R_{\text{int}} = 2.3\%$ and 1570 unique data from 4345 measured data (I) and $R_{\text{int}} = 4.3\%$ and 2048 unique data from 2154 measured reflections (II). Taking a data cut-off of $I > 3\sigma(I)$, there are 1453 observed and 117 unobserved data (I) and 1143 observed and 905 unobserved data (II). The structures were determined by direct methods (I) and then by isostructural coordinates (II). Hydrogen atoms were located by calculation. Full-matrix least-squares refinement was on F with non-H atoms refined anisotropically, H atoms isotropically (I) or restrained to ride on C's (II) (only the temperature factors were refined), 119 (I) and 87 (II) 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 $\Delta/\sigma = 0.13$, $R = 0.067$, $wR = 0.075$, $S = 1.459$ (I) and $\Delta/\sigma = 0.16$, $R = 0.053$, $wR = 0.050$, $S = 0.92$ (II). The final difference-map peak heights ranged from -0.57 (6) to 0.72 (6) e Å⁻³ (I) and from -0.27 (3) to 0.43 (3) e Å⁻³ (II). Scattering factors were from Cromer & Waber (1974) and f' and f'' from Cromer (1974) except those of the alkali-metal anions, which were from Dr David A. Liberman (Huang, Ward, Kuchenmeister & Dye, 1987, supplementary materials). All computations were carried out with a VAX 11/750 computer using the SDP (Frenz, 1978) software system.

Discussion. The refined atomic coordinates and the isotropic temperature factors are presented in Table 1 (I) and Table 2 (II); bond distances and bond

* 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 kalide

	x	y	z	B (Å ²)
Cs1	0.500	0.000	0.500	5.43 (2)
K1	0.500	0.500	0.000	5.87 (9)
O1	0.4754 (7)	0.000	0.2033 (8)	5.8 (2)
O4	0.5141 (5)	-0.1790 (4)	0.3301 (5)	5.7 (1)
O7	0.7271 (5)	-0.1056 (4)	0.4388 (6)	6.7 (1)
C2	0.4117 (8)	-0.0877 (7)	0.1790 (8)	6.4 (2)
C3	0.4872 (9)	-0.1710 (7)	0.204 (1)	7.5 (3)
C5	0.614 (1)	-0.2347 (6)	0.3558 (9)	7.8 (3)
C6	0.7228 (8)	-0.1789 (8)	0.347 (1)	8.8 (3)
C8a	0.828 (1)	-0.031 (1)	0.470 (2)	5.8 (4)
C8b	0.819 (1)	0.055 (1)	0.384 (2)	6.4 (4)
H2a	0.391 (6)	-0.073 (5)	0.110 (7)	3 (2)*
H2b	0.369 (6)	-0.075 (5)	0.237 (7)	4 (2)*
H3a	0.461 (6)	-0.218 (6)	0.179 (7)	4 (2)*
H3b	0.543 (4)	-0.154 (4)	0.167 (4)	1 (1)*
H5a	0.600 (6)	-0.288 (5)	0.314 (6)	3 (2)*
H5b	0.605 (5)	-0.239 (4)	0.420 (5)	1 (1)*
H6a	0.778 (6)	-0.209 (5)	0.345 (6)	3 (2)*
H6b	0.734 (6)	-0.153 (6)	0.284 (7)	4 (2)*
H8aa	0.902	-0.061	0.465	8.7*
H8ab	0.816	-0.008	0.554	8.7*
H8ba	0.802	0.033	0.301	8.7*
H8bb	0.888	0.091	0.384	8.7*

Notes: (1) Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $B_{eq} = \frac{1}{3}\pi^2[U_{22} + (U_{11} + U_{33} + 2U_{13}\cos\beta)/\sin^2\beta]$. (2) Starred atoms were refined isotropically. (3) C8a and C8b are disordered with 0.5 occupancy; correspondingly atoms H8aa, H8ab, H8ba and H8bb have 0.5 occupancy.

angles are given in Table 3.* The molecular structures and the numbering of the atoms are shown in Fig. 1 (I) and Fig. 2 (II) and the stereographic packing diagrams are shown in Fig. 3 (I) and Fig. 4 (II). These two compounds are isostructural with another alkali, $Rb^+(15C5)_2Na^-$ (Dawes *et al.*, 1989) as expected.

In both structures the atom C8 was found to be disordered and was modeled as two half-occupancy atoms C8a and C8b. The H atoms bonded to them were also half-occupancy and were constrained to ride on the C atoms.

To estimate the sizes of the anions, K^- and Rb^- , we take 1.2 Å as the van der Waals radius of the H atom. From the distances between the anions and the nearest H atoms we estimated that the minimum radii are 2.77 Å for K^- and 2.64 Å for Rb^- and the average radii are 3.1 Å for K^- and 3.1 Å for Rb^- [compared with Na^- , 2.35–2.60 Å as the minimum and 2.64–2.89 Å as the average (Huang, Ward & Dye, 1989), and with Cs^- , 3.1–3.2 Å as the minimum

* 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 53050 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Positional and isotropic thermal parameters and their e.s.d.'s for rubidium (15-crown-5)₂ rubidide

	x	y	z	B (Å ²)
Rb1	0.500	0.000	0.500	4.68 (2)
Rb2	0.500	0.500	0.000	9.63 (5)
O1	0.4703 (6)	0.0000	0.2112 (6)	7.9 (2)
O4	0.5127 (4)	-0.1756 (3)	0.3353 (4)	8.1 (1)
O7	0.7210 (4)	-0.1041 (3)	0.4454 (5)	8.7 (1)
C2	0.4084 (6)	-0.0855 (5)	0.1857 (6)	8.2 (2)
C3	0.4878 (7)	-0.1665 (5)	0.2058 (6)	9.2 (2)
C5	0.6128 (6)	-0.2293 (5)	0.3633 (8)	10.2 (2)
C6	0.7201 (6)	-0.1749 (6)	0.3492 (8)	11.2 (2)
C8a	0.8077	-0.0468	0.3984	8.4 (4)*
C8b	0.8124	0.0390	0.4778	8.1 (4)*
H2a	0.3789	-0.0853	0.1038	5 (1)*
H2b	0.3467	-0.0915	0.2483	7 (2)*
H3a	0.4561	-0.2250	0.1766	6 (2)*
H3b	0.5568	-0.1522	0.1567	5 (1)*
H5a	0.6174	-0.2824	0.3063	9 (2)*
H5b	0.6074	-0.2524	0.4481	7 (2)*
H6a	0.7851	-0.2159	0.3525	7 (2)*
H6b	0.7217	-0.1435	0.2690	9 (2)*
H8aa	0.7995	-0.0393	0.3051	2 (2)*
H8ab	0.8902	-0.0891	0.3847	4 (3)*
H8ba	0.8923	0.0443	0.4388	3 (2)*
H8bb	0.8170	-0.0070	0.5447	2 (1)*

Notes: (1) Starred atoms were refined isotropically. (2) Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $B_{eq} = \frac{1}{3}\pi^2[U_{22} + (U_{11} + U_{33} + 2U_{13}\cos\beta)/\sin^2\beta]$. (3) C8a and C8b are disordered with 0.5 occupancy; correspondingly atoms H8aa, H8ab, H8ba and H8bb have 0.5 occupancy.

Table 3. Bond distances (Å) and bond angles (°) for caesium (15-crown-5)₂ kalide and rubidium (15-crown-5)₂ rubidide

Numbers in parentheses are e.s.d.'s in the least significant digits.

	(I)	(II)
Cs1/Rb1—O1	3.171 (8)	3.075 (6)
Cs1/Rb1—O4	3.056 (5)	2.992 (4)
Cs1/Rb1—O7	3.078 (5)	2.994 (4)
O1—C2	1.436 (10)	1.415 (7)
O4—C3	1.383 (12)	1.408 (8)
O4—C5	1.418 (12)	1.418 (9)
O7—C6	1.400 (12)	1.411 (9)
O7—C8a	1.593 (14)	1.368
O7—C8b	1.403	1.441
C2—C3	1.463 (13)	1.473 (10)
C5—C6	1.476 (14)	1.463 (10)
C8a—C8b	1.50 (2)	1.458
O1—Cs1/Rb1—O4	54.2 (1)	55.2 (8)
O1—Cs1/Rb1—O7	82.1 (2)	85.6 (1)
O4—Cs1/Rb1—O4 ⁱ	107.0	108.8
O4—Cs1/Rb1—O7	56.5 (2)	57.6 (1)
O4—Cs1/Rb1—O7 ⁱ	101.9	104.4
O7—Cs1/Rb1—O7 ⁱ	56.2	57.6
Cs1/Rb1—O1—C2	103.0 (5)	104.8 (4)
Cs1/Rb1—O4—C3	120.0 (5)	118.9 (4)
Cs1/Rb1—O4—C5	111.4 (5)	109.7 (4)
Cs1/Rb1—O7—C6	117.2 (5)	117.0 (4)
Cs1/Rb1—O7—C8a	106.3 (5)	114.5 (3)
C2—O1—C2 ⁱ	114.0	113.6
C3—O4—C5	114.4 (7)	115.8 (5)
C6—O7—C8a	129.3 (8)	99.1
C6—O7—C8b ⁱ	95.4	128.4
O1—C2—C3	108.4 (8)	106.7 (6)
O4—C3—C2	111.8 (8)	110.5 (6)
O4—C5—C6	114.0 (8)	114.3 (6)
O7—C6—C5	111.1 (8)	107.7 (6)
O7—C8a—C8b	109. (1)	107.5

Symmetry code: (i) $x, -y, z$.

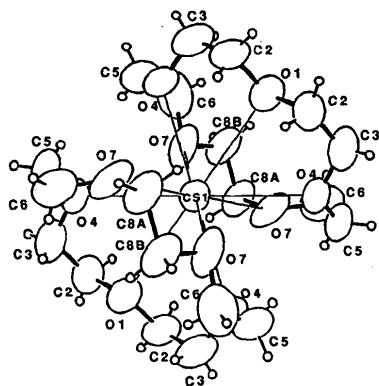


Fig. 1. The molecular structure and the numbering of the atoms of caesium bis(15-crown-5) kalide (I) [ORTEP (Johnson, 1965), 50% probability ellipsoids].

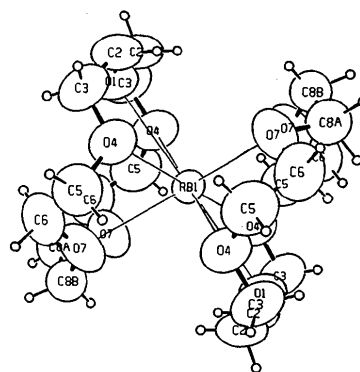


Fig. 2. The molecular structure and the numbering of the atoms of rubidium bis(15-crown-5) rubidide (II) [ORTEP (Johnson, 1965), 50% probability ellipsoids].

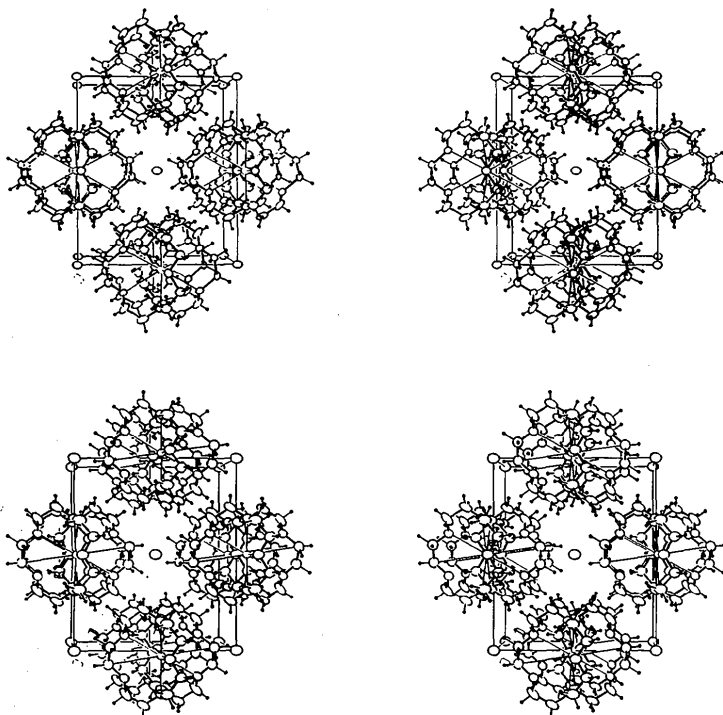


Fig. 3. Stereographic packing diagram of caesium bis(15-crown-5) kalide (I) [ORTEP (Johnson, 1965), 20% probability ellipsoids]. The b axis is vertical, the a axis is horizontal and the c axis is normal to the paper.

Fig. 4. Stereographic packing diagram of rubidium bis(15-crown-5) rubidide (II) [ORTEP (Johnson, 1965), 20% probability ellipsoids]. The b axis is vertical, the a axis is horizontal and the c axis is normal to the paper.

and 3.5 Å as the average (Huang *et al.*, 1987)]. Since alkali-metal anions are highly polarizable and H atoms may penetrate into the outer electron density, the estimated sizes may vary from compound to compound. From the structures of kalides and rubidides that we have determined, however, it appears that the sizes of K^- and Rb^- are very similar.

We acknowledge the support of National Science Foundation (grant DMR 87-14751). The X-ray diffractometer system was provided by NSF grant CHE-84-03823.

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Acta Cryst. (1990). **C46**, 1841–1843

Structure of Bicyclophtalocyaninatochloroniobium(IV)

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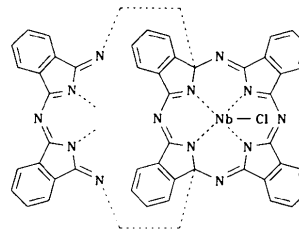
(Received 17 June 1989; accepted 23 January 1990)

Abstract. Chloro{12,28-[3-(3-isoindolylimino)-1,1'-isoindolediylidenediamino]niobium(IV), $[\text{Nb}(\text{Cl})(\text{C}_{48}\text{H}_{24}\text{N}_{13})]$, $M_r = 911.17$, monoclinic, $C2/c$, $a = 22.899$ (3), $b = 10.436$ (2), $c = 18.539$ (2) Å, $\beta = 123.09^\circ$, $V = 3711.8$ Å³, $Z = 4$, $D_x = 1.630$ g cm⁻³, $\text{Cu } K\alpha$, $\lambda = 1.54184$ Å, $\mu = 38.4$ cm⁻¹, $F(000) = 1844$, $T = 291$ K. Final R value is 0.033 for 2443 independent reflections with $I \geq 3\sigma(I)$ and 287 refined parameters. The bicyclophtalocyaninato ligand is composed of six isoindole units forming a trigonal prism with its six N donor atoms. The Cl ligand completes the coordination of the Nb atom to a monocapped trigonal prism. The complex has the symmetry C_2 with the Cl, Nb and one of the N atoms of the bicyclophtalocyaninato ligand lying on the twofold axis.

Introduction. Niobium and tantalum show a pronounced tendency towards the coordination number seven. In the case of phthalocyaninato complexes this leads to the formation of compounds like PcMCl_3 ($M = \text{Nb, Ta}$; $\text{H}_2\text{Pc} = \text{phthalocyanine}$) (Gingl & Strähle, 1988) or $[(\text{PcNb})_2\text{O}_2\text{Br}]^+$ (Gingl & Strähle, 1989) with monocapped trigonal prismatic coordination or with a coordination polyhedron characterized as square base-trigonal cap (Muetterties & Wright, 1967).

The preferred coordination number seven presumably also explains the formation of the bicyclophtalocyaninato ligand (see scheme) by template reaction at the Nb atom. $\text{NbCl}(\text{C}_{48}\text{H}_{24}\text{N}_{13})$ is obtained besides tris(2-cyanophenyl)-1,3,5-triazine as a byproduct with the synthesis of PcNbCl_3 from NbOCl_3 and phthalodinitrile. Similar bicyclophtalocyaninato complexes were proposed as precursors for the synthesis of cobalt and copper phthalocyanine (Baumann, Bienert, Rösch,

Vollmann & Wolf, 1956; Perkins & Whelen, 1957; Barnhart & Skiles, 1956).



Experimental. A yellow-green needle of approximate dimensions $0.4 \times 0.1 \times 0.05$ mm was used for the determination of the lattice parameters and the data collection on a single-crystal diffractometer (Enraf-Nonius CAD-4, graphite monochromator, $\text{Cu } K\alpha$ radiation). Accurate values of the lattice constants were obtained from 25 reflections with $11.4 < \theta < 31.8^\circ$. 2831 independent intensity data for $5 \leq \theta \leq 61^\circ$, index range $-25 \leq h \leq 25$, $0 \leq k \leq 11$, $0 \leq l \leq 21$, ω/θ scans; three orientation and three intensity control reflections monitored periodically, no significant variation; intensities were corrected for Lorentz and polarization effects, no absorption correction.

The structure was solved by the Patterson method, which revealed the Nb atom, and subsequent tangent expansion (Sheldrick, 1986). All H atoms were located in a difference electron density map and included in the structure-factor calculation but not refined. Full-matrix least-squares refinement [on F^2 's, unit weights for all 2443 reflections with $I > 3\sigma(I)$] with anisotropic temperature parameters for all non-H atoms converged at $R = 0.033$ ($wR = 0.038$). Maximum shift $\Delta/\sigma = 0.01$, largest peaks in the final difference Fourier map, $+1.5$ and -1.2 e Å⁻³. Atomic scattering factors, f' and f'' from *Internation-*

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