

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) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.06$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 2.3$  cm<sup>-1</sup>,  $F(000) = 2592$ ,  $T = 206$  (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,  $\text{Na}^-$ , does not form dimers,  $\text{Na}_2^{2-}$ , or chains as are seen in some  $\text{K}^-$ ,  $\text{Rb}^-$  and  $\text{Cs}^-$  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,  $\text{Na}_2^{2-}$  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  $\theta$ - $2\theta$  scans at  $2^\circ \text{ min}^{-1}$  (in  $2\theta$ ) to  $\sin\theta/\lambda < 0.5951$  Å<sup>-1</sup>; 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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Table 1. Positional and isotropic thermal parameters and their *e.s.d.*'s for  $K^+$  (cryptand[2.2.2]). $Na^-$ 

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
K1	0.000	0.000	0.000	2.447 (9)
Na1	0.000	0.000	0.4151 (1)	6.41 (4)
O4	-0.0007 (1)	0.09556 (6)	0.0989 (1)	4.00 (3)
O7	-0.1552 (1)	0.04284 (6)	0.0677 (1)	3.85 (3)
O13	0.06218 (9)	0.04014 (6)	-0.1801 (1)	2.97 (3)
N1	0.1544 (1)	0.06749 (7)	-0.0041 (2)	3.33 (4)
C2	0.1485 (2)	0.10556 (9)	0.0771 (2)	4.44 (5)
C3	0.0643 (2)	0.13368 (9)	0.0834 (2)	4.33 (5)
C5	-0.0800 (2)	0.1207 (1)	0.1173 (2)	4.68 (6)
C6	-0.1438 (2)	0.0792 (1)	0.1457 (2)	4.80 (6)
C8	-0.2226 (2)	0.0064 (1)	0.0884 (2)	4.59 (6)
C9	-0.2300 (1)	-0.03334 (9)	0.0088 (2)	4.31 (5)
C11	0.1605 (1)	0.09597 (9)	-0.0963 (2)	3.95 (5)
C12	0.1457 (1)	0.06197 (9)	-0.1840 (2)	3.84 (5)
C14	0.0458 (1)	0.00877 (9)	-0.2633 (2)	3.49 (5)
H2a	0.196 (2)	0.133 (1)	0.074 (2)	2.7 (6)*
H2b	0.157 (1)	0.0848 (9)	0.134 (2)	1.3 (5)*
H3a	0.066 (2)	0.1558 (9)	0.144 (2)	2.5 (6)*
H3b	0.051 (1)	0.1562 (8)	0.023 (2)	1.0 (5)*
H5a	-0.101 (1)	0.1427 (8)	0.057 (2)	1.6 (5)*
H5b	-0.073 (1)	0.1455 (8)	0.168 (2)	1.6 (5)*
H6a	-0.126 (1)	0.0602 (9)	0.205 (2)	1.8 (5)*
H6b	-0.197 (2)	0.095 (1)	0.155 (2)	3.7 (7)*
H8a	-0.277 (1)	0.0258 (9)	0.095 (2)	1.7 (5)*
H8b	-0.211 (1)	-0.0102 (8)	0.151 (2)	1.1 (5)*
H9a	-0.236 (1)	-0.0137 (8)	-0.053 (2)	1.0 (5)*
H9b	-0.283 (1)	-0.0561 (9)	0.021 (2)	1.6 (5)*
H11a	0.215 (1)	0.1138 (9)	-0.107 (2)	1.7 (5)*
H11b	0.117 (1)	0.1218 (8)	-0.093 (2)	0.8 (4)*
H12a	0.151 (1)	0.0837 (8)	-0.241 (2)	1.1 (5)*
H12b	0.189 (1)	0.0341 (9)	-0.190 (2)	1.7 (5)*
H14a	0.085 (1)	-0.0222 (8)	-0.263 (2)	1.0 (4)*
H14b	0.053 (1)	0.0303 (8)	-0.327 (2)	0.9 (5)*

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:  $B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33})$ .

\*Atoms refined isotropically.

Table 2. Bond distances (Å) and angles (°) for  $K^+$  (cryptand[2.2.2]). $Na^-$  with *e.s.d.*'s in parentheses

K1—O4	2.773 (2)	O13—C14	1.420 (3)
K1—O7	2.835 (2)	N1—C2	1.480 (3)
K1—O13	2.860 (2)	N1—C11	1.466 (3)
K1—N1	2.973 (2)	N1—C9'	1.482 (2)
O4—C3	1.422 (3)	C2—C3	1.509 (4)
O4—C5	1.426 (3)	C5—C6	1.506 (4)
O7—C6	1.427 (3)	C8—C9	1.493 (4)
O7—C8	1.434 (3)	C11—C12	1.504 (4)
O13—C12	1.429 (3)	C14—C14'	1.511 (2)
O4—K1—O7	60.14 (5)	K1—O7—C6	112.7 (1)
O4—K1—O13	97.00 (5)	K1—O7—C8	117.4 (1)
O4—K1—O4'	120.95 (3)	C6—O7—C8	110.8 (2)
O4—K1—O7'	99.92 (4)	K1—O13—C12	119.1 (1)
O4—K1—O13'	137.35 (4)	K1—O13—C14	116.4 (1)
O4—K1—N1	60.91 (5)	C12—O13—C14	110.6 (2)
O4—K1—N1'	120.33 (4)	K1—N1—C2	107.8 (1)
O7—K1—O13	116.61 (4)	K1—N1—C11	110.5 (1)
O7—K1—O7'	141.46 (4)	K1—N1—C9'	108.8 (1)
O7—K1—O13'	97.24 (3)	C2—N1—C11	110.2 (2)
O7—K1—N1	119.67 (5)	C2—N1—C9'	109.7 (2)
O7—K1—N1'	61.16 (3)	C11—N1—C9'	109.7 (2)
O13—K1—O4'	137.36 (3)	N1—C2—C3	113.9 (2)
O13—K1—O13'	59.07 (3)	O4—C3—C2	108.9 (2)
O13—K1—N1	59.97 (5)	O4—C5—C6	108.8 (2)
O13—K1—N1'	117.87 (3)	O7—C6—C5	109.6 (2)
O4'—K1—O13'	97.01 (4)	O7—C8—C9	110.0 (2)
O4'—K1—N1	120.32 (4)	C8—C9—N1'	114.6 (2)
N1—K1—N1'	177.82 (4)	N1—C11—C12	114.2 (2)
K1—O4—C3	120.8 (1)	O13—C12—C11	109.4 (2)
K1—O4—C5	118.6 (1)	O13—C14—C14'	109.7 (2)
C3—O4—C5	110.9 (2)		

'Indicates an atom at  $-x, -y, z$ .

data cut-off of  $I > 3\sigma(I)$ , there were 1198 observed and 77 unobserved data. The structure was solved by the Patterson method. H atoms were located by calculation. Full-matrix least-squares refinement was on *F* with non-H atoms refined anisotropically, H atoms isotropically, 200 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  $\Delta/\sigma = 0.10$ ,  $R = 0.021$ ,  $wR = 0.021$ ,  $S = 0.38$ . The final difference-map peak heights ranged from  $-0.02$  (1) to  $0.03$  (1)  $e \text{ \AA}^{-3}$ . Scattering factors were from Cromer & Waber (1974) and  $f'$  and  $f''$  from Cromer (1974) except that of the sodium anion which was from Dr David A. Liberman (Huang, Ward, Kuchenmeister & Dye, 1987, supplementary materials). All computations were carried out with a VAX 11/750 computer with the *SDP* (Frenz, 1978) software system.

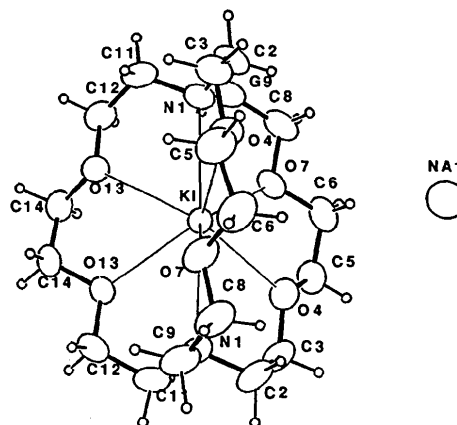


Fig. 1. The molecular structure and numbering of the atoms for potassium cryptand[2.2.2] natride [ORTEP (Johnson, 1965), 50% probability ellipsoids].

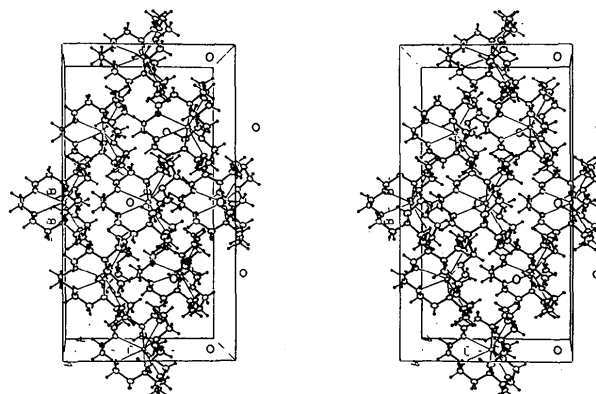


Fig. 2. Stereographic packing diagram for potassium cryptand[2.2.2] natride [ORTEP (Johnson, 1965), 20% probability ellipsoids]. The *b* axis is vertical, the *a* axis is horizontal and the *c* axis is normal to the paper.

transmission coefficient range of 0.889 to 0.928. Reflection averaging led to 1275 unique data and  $R_{int} = 1.2\%$  for 2764 total measured reflections. Taking a

**Discussion.** The refined atomic coordinates and the 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.

As expected, the natride has a completely different structure from the electride,  $\text{K}^+(\text{C222})\text{e}^-$  (monoclinic,  $C2/c$ ) (Huang *et al.*, 1988). The  $\text{Na}^-$  anions are isolated from each other with a shortest separation of 8.2 Å to the four nearest anions. The cation  $\text{K}^+(\text{C222})$  has twofold symmetry and is essentially the same as that in the salt,  $\text{K}^+(\text{C222})\text{I}^-$  (Moras, Metz & Weiss, 1972). Thus, as with all other natrides studied to date,  $\text{Na}^-$  does not exist as pairs, but rather as isolated anions. This contrasts with the existence of pairs and/or chains of anions with certain salts of  $\text{K}^-$ ,  $\text{Rb}^-$  and  $\text{Cs}^-$  (Huang, Ward & Dye, 1989; Huang, Ward, Kuchenmeister & Dye, 1987).

The size of  $\text{Na}^-$  in this structure is estimated from the  $\text{Na}^-$ —H distances. The minimum radius is 2.5 Å

\* Lists of structure factors and tables of anisotropic thermal parameters, 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 52974 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and the average (over 14 H's) is 2.7 Å. These radii are similar to other natrides (Huang *et al.*, 1989).

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## The Structures of Alkalides and Electrides. IV. Structure of $\text{Li}^+(\text{tmctcy}^*)$ - $[\text{Li}^+(\text{dmctcy}^\dagger)]^-\cdot\text{CH}_3\text{NH}_2[\text{Na}^-]$

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**Abstract.**  $\mu$ -(1,4-Dimethyl-1,4,7-triazacyclononamido)(methylamine)(1,4,7-trimethyl-1,4,7-triazacyclononane)dilithium natride,  $[\text{Li}_2(\text{C}_8\text{H}_{18}\text{N}_3)(\text{CH}_3\text{N})(\text{C}_9\text{H}_{21}\text{N}_3)]^+\cdot\text{Na}^-$ ,  $M_r = 395.47$ , orthorhombic, *Pbca*,  $a = 25.271$  (8),  $b = 10.904$  (3),  $c = 21.566$  (6) Å,  $V = 5942.1$  (7) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 0.884$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.6$  cm<sup>-1</sup>,  $F(000) = 1744$ ,  $T = 203$  (4) K, final  $R = 0.078$  for 650  $[I >$

$3\sigma(I)]$  of 2779 unique reflections. The structure contains a mixed unit of  $\text{Li}^+(\text{tmctcy})$  and  $\text{Li}^+(\text{dmctcy}^-)$  along with the natride  $\text{Na}^-$ . The coordination number is four for both  $\text{Li}^+$  cations. The existence of the negative amide group is confirmed by the shorter distances between its nitrogen and two  $\text{Li}^+$  ions (1.89 and 1.97 Å compared to 2.05 to 2.15 Å for the other six  $\text{Li}^+$ —N distances).

\* tmctcy: 1,4,7-trimethyl-1,4,7-triazacyclononane.

† dmctcy: 1,4-dimethyl-1,4,7-triazacyclononane.

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**Introduction.** Since the first alkalide,  $\text{Na}^+(\text{C222})\cdot\text{Na}^-$ , was synthesized and its structure was determined (Dye, Ceraso, Lok, Barnett &