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, $K^+(C222).e^-$ (monoclinic, $C2/c$) (Huang et $al.$, 1988). The Na^- anions are isolated from each other with a shortest separation of 8·2 Å to the four nearest anions. The cation $K^+(C222)$ has twofold symmetry and is essentially the same as that in the salt, $K^+(C222).I^-$ (Moras, Metz & Weiss, 1972). Thus, as with all other natrides studied to date, 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 K^-, Rb^- and Cs^- (Huang, Ward & Dye, 1989; Huang, Ward, Kuchenmeister & Dye, 1987).

The size of Na^- in this structure is estimated from the Na^-—H distances. The minimum radius is 2·5 Å

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* 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 Li^+(tmtcy*)-[Li^+(dmtcy†)$^-$.CH₃NH₂]Na$^-$

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Abstract. μ-(1,4-Dimethyl-1,4,7-triazacyclononamido)(methylamine)(1,4,7-trimethyl-1,4,7-triazacyclononane)dilithium natride, [$Li_2(C_8H_{18}N_3)(CH_5N)(C_9H_{21}N_3)]^+.Na^-$, $M_r = 395·47$, orthorhombic, $Pbca$, $a = 25·271$ (8), $b = 10·904$ (3), $c = 21·566$ (6) Å, $V = 5942·1$ (7) Å³, $Z = 8$, $D_x = 0·884$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·6$ cm^{-1}, $F(000) = 1744$, $T = 203$ (4) K, final $R = 0·078$ for 650 [$I >$ $3\sigma(I)$] of 2779 unique reflections. The structure contains a mixed unit of Li^+(tmtcy) and Li^+(dmtcy$^-$) along with the natride Na^-. The coordination number is four for both Li^+ cations. The existence of the negative amide group is confirmed by the shorter distances between its nitrogen and two Li^+ ions (1·89 and 1·97 Å compared to 2·05 to 2·15 Å for the other six Li^+—N distances).

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

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* tmtcy: 1,4,7-trimethyl-1,4,7-triazacyclononane.
† dmtcy: 1,4-dimethyl-1,4,7-triazacyclononane.
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Table 1. *Positional and isotropic thermal parameters and their e.s.d.'s for* $Li^+(tmtcy)[Li^+(dmtcy^-).CH_3NH_2].Na^-$

	x	y	z	$B(Å^2)$
Na1	0·5999 (3)	0·6300 (8)	0·6043 (5)	8·8 (3)
N1	0·3412 (4)	0·719 (1)	0·6417 (6)	2·4 (3)
N4	0·3157 (5)	0·809 (1)	0·5160 (6)	3·6 (4)
N7	0·3901 (6)	0·938 (1)	0·5924 (6)	4·8 (4)
N13	0·3180 (6)	0·508 (2)	0·7641 (6)	6·0 (4)
N16	0·3841 (5)	0·414 (1)	0·6698 (6)	4·0 (4)
N19	0·4259 (5)	0·572 (1)	0·7616 (8)	5·7 (4)
N25	0·4442 (5)	0·673 (1)	0·5184 (6)	4·5 (4)
C2	0·2925 (6)	0·694 (2)	0·6125 (7)	3·9 (5)*
C3	0·2735 (7)	0·782 (2)	0·5627 (8)	5·1 (5)*
C5	0·3260 (7)	0·939 (2)	0·5067 (8)	5·8 (5)*
C6	0·3447 (7)	1·004 (2)	0·5617 (8)	6·2 (6)*
C8	0·3862 (7)	0·919 (2)	0·6584 (7)	4·5 (4)*
C9	0·3408 (6)	0·836 (1)	0·6765 (7)	3·6 (4)*
C11	0·3055 (7)	0·744 (2)	0·4589 (8)	5·6 (5)*
C12	0·4392 (7)	1·005 (2)	0·5774 (9)	6·0 (6)*
C14	0·3091 (9)	0·384 (2)	0·736 (1)	9·0 (7)*
C15	0·3494 (8)	0·336 (2)	0·7017 (9)	8·3 (7)*
C17	0·4409 (8)	0·408 (2)	0·687 (1)	9·2 (7)*
C18	0·4552 (8)	0·464 (2)	0·743 (1)	8·3 (7)*
C20	0·3952 (8)	0·560 (2)	0·8209 (9)	8·1 (6)*
C21	0·3481 (8)	0·502 (2)	0·818 (1)	9·6 (8)*
C22	0·2682 (8)	0·571 (2)	0·7763 (9)	8·4 (7)*
C23	0·3780 (8)	0·392 (2)	0·6036 (8)	7·0 (6)*
C24	0·4606 (7)	0·671 (2)	0·7643 (9)	6·7 (6)*
C26	0·4638 (7)	0·746 (2)	0·4664 (9)	6·2 (6)*
Li	0·364 (1)	0·590 (3)	0·694 (1)	3·5 (8)*
Li2	0·382 (1)	0·757 (3)	0·566 (1)	3·3 (7)*

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33})$. N1, N4, N7, C2, C3, C5, C6, C8, C9, C11 and C12 belong to dmtcy. N13, N16, N19, C14, C15, C17, C18, C20, C21, C22, C23 and C24 belong to tmtcy. N25 and C26 belong to the methylamine.

*Atoms refined isotropically.

Tehan, 1974; Tehan, Barnett & Dye, 1974), more than 30 alkalides have been synthesized. They all have the same feature in that for all alkali-metal cations complexed by crown ethers, cryptands or their analogs, the aza crowns, the counterions are alkali-metal anions. It came as a surprise, therefore, when a different type of crystal structure was determined for the crystals obtained from the Li–tmtcy–Na system which we had believed were crystals of $Li^+(tmtcy)_2.Na^-$. The structure was found to contain a mixed unit of $Li^+(tmtcy)$ and $Li^+(dmtcy^-).CH_3NH_2$ along with the natride Na^- (CH_3NH_2 was introduced during the synthesis as a solvent to dissolve the metals and the complexant). It was determined later that the complexant tmtcy contained some dmtcy as an impurity.

Experimental. Single crystals were obtained by recrystallization from a mixed dimethyl ether–diethyl ether solution using slow solvent evaporation at 195 K. The polycrystalline sample was obtained by dissolving Li, Na and the complexant in methylamine and then evaporating the solvent. The procedures for single crystal handling and mounting have been described in a previous paper (Ward,

Table 2. *Bond distances* (Å) *and angles* (°) *for* $Li^+(tmtcy)[Li^+(dmtcy^-).CH_3NH_2].Na^-$ *with e.s.d.'s in parentheses*

N1—C2	1·411 (10)	N16—C15	1·405 (12)
N1—C9	1·476 (9)	N16—C17	1·482 (13)
N1—Li	1·89 (2)	N16—C23	1·458 (11)
N1—Li2	1·97 (2)	N16—Li	2·05 (2)
N4—C3	1·495 (10)	N19—C18	1·453 (12)
N4—C5	1·456 (11)	N19—C20	1·502 (12)
N4—C11	1·443 (10)	N19—C24	1·392 (10)
N4—Li2	2·06 (2)	N19—Li	2·15 (2)
N7—C6	1·505 (11)	N25—C26	1·462 (10)
N7—C8	1·442 (10)	N25—Li2	2·09 (2)
N7—C12	1·475 (10)	C2—C3	1·520 (11)
N7—Li2	2·07 (2)	C5—C6	1·459 (12)
N13—C14	1·492 (13)	C8—C9	1·513 (11)
N13—C21	1·382 (13)	C14—C15	1·367 (14)
N13—C22	1·456 (11)	C17—C18	1·408 (14)
N13—Li	2·10 (2)	C20—C21	1·349 (14)
C2—N1—C9	112·9 (7)	C18—N19—C24	108·8 (8)
C2—N1—Li	112·5 (7)	C18—N19—Li	104·9 (8)
C2—N1—Li2	97·0 (7)	C20—N19—C24	111·0 (10)
C9—N1—Li	109·9 (7)	C20—N19—Li	102·1 (7)
C9—N1—Li2	104·2 (7)	C24—N19—Li	114·9 (8)
Li—N1—Li2	119·7 (7)	C26—N25—Li2	113·2 (7)
C3—N4—C5	114·1 (8)	N1—C2—C3	117·8 (8)
C3—N4—C11	110·7 (7)	N4—C3—C2	112·0 (8)
C3—N4—Li2	99·9 (7)	N4—C5—C6	115·0 (10)
C5—N4—C11	113·2 (9)	N7—C6—C5	112·0 (9)
C5—N4—Li2	101·1 (8)	N7—C8—C9	113·3 (8)
C11—N4—Li2	117·1 (8)	N1—C9—C8	112·2 (8)
C6—N7—C8	116·8 (9)	N13—C14—C15	117·0 (10)
C6—N7—C12	108·2 (7)	N16—C15—C14	120·0 (10)
C6—N7—Li2	104·6 (7)	N16—C17—C18	116·0 (10)
C8—N7—C12	110·3 (8)	N19—C18—C17	117·0 (10)
C8—N7—Li2	97·2 (7)	N19—C20—C21	117·0 (10)
C12—N7—Li2	119·9 (8)	N13—C21—C20	121·0 (10)
C14—N13—C21	112·0 (10)	N1—Li—N13	125·4 (8)
C14—N13—C22	112·0 (10)	N1—Li—N16	128·3 (8)
C14—N13—Li	100·2 (8)	N1—Li—N19	133·5 (9)
C21—N13—C22	110·0 (10)	N13—Li—N16	85·7 (8)
C21—N13—Li	108·4 (9)	N13—Li—N19	82·9 (7)
C22—N13—Li	113·9 (8)	N16—Li—N19	84·7 (7)
C15—N16—C17	117·0 (10)	N1—Li2—N4	94·2 (7)
C15—N16—C23	108·2 (9)	N1—Li2—N7	91·4 (7)
C15—N16—Li	106·6 (8)	N1—Li2—N25	134·7 (9)
C17—N16—C23	109·6 (9)	N4—Li2—N7	88·2 (7)
C17—N16—Li	103·1 (8)	N4—Li2—N25	118·4 (8)
C23—N16—Li	112·3 (8)	N7—Li2—N25	118·2 (8)
C18—N19—C20	115·0 (10)		

Huang & Dye, 1988). Under the microscope the majority of the crystals were found to be long needles with a reddish color. The crystal picked for study was diamond shaped, dark grey in color, and had approximate dimensions $0·2 \times 0·2 \times 0·4$ 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 24 reflections in the range $15 < 2\theta < 20°$. Intensity data were collected with θ–2θ scans at 2° min^{-1} (in 2θ) to $\sin\theta/\lambda < 0·4816$ Å^{-1}; reflection indices: $0 \le h \le 24$, $0 \le k \le 10$, $-20 \le l \le 0$; a linear decay correction was based on the intensities of three monitor reflections (0·2% decrease in average intensity). An empirical absorption correction (ψ scan) was applied with a transmis-

sion coefficient range of 0·904 to 0·969. Taking a data cut-off of $I > 3\sigma(I)$, there were 650 observed and 2129 unobserved data. The structure was solved by direct methods. H atoms were located by calculation. Because the crystal was small and there was some frost on the crystal during data collection, the background was relatively high and many reflections were too weak to be observed. The full-matrix least-squares refinement was on F with heavy atoms (Na and N) refined anisotropically, Li and C atoms isotropically, H atoms were constrained to ride on the carbons or nitrogens to which they are bonded (only the temperature factors were refined), 153 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 $\Delta/\sigma = 0·00$, $R = 0·078$, $wR = 0·080$, $S = 5·25$ [least-squares refinement with a cut-off of $I > 2\sigma(I)$ resulted in a much higher R factor (0·124)]. The final difference-map peak heights ranged from $-0·19$ (3) to 0·22 (3) e Å^{-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 using the *SDP* (Frenz, 1978) software system.
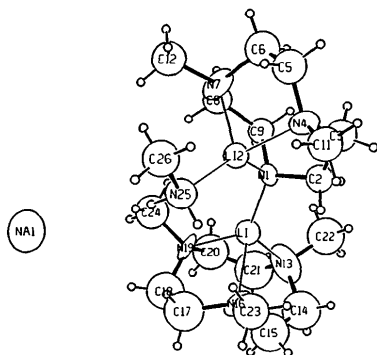

Fig. 1. The molecular structure and the numbering of the atoms for $Li^+(tmtcy)[Li^+(dmtcy^-).CH_3NH_2].Na^-$ [*ORTEP* (Johnson, 1965), 50% probability ellipsoids].
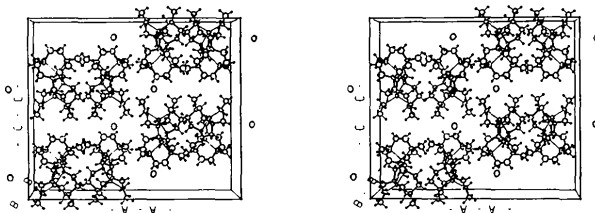
Fig. 2. Stereographic packing diagram for $Li^+(tmtcy)$-$[Li^+(dmtcy^-).CH_3NH_2].Na^-$ [*ORTEP* (Johnson, 1965), 20% probability ellipsoids]. The c axis is vertical, the a axis is horizontal and the b axis is normal to the paper.

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 numbering of the atoms are shown in Fig. 1 and the stereographic packing diagram is shown in Fig. 2.

Both Li^+ cations have coordination numbers of four. One is coordinated by three nitrogens from the molecule of tmtcy and by atom N1 (the N^-) of the $dmtcy^-$ ion. The second Li^+ is coordinated by N1, the other two nitrogens of dmtcy, and the fourth coordination is from the nitrogen of the methylamine molecule. Atom N1 of dmtcy forms a bridge between the two lithium cations and the bond distances between N1 and the two lithiums are shorter than the other six Li^+—N bonds [1·89 (2), 1·97 (2) Å compared to 2·05 (2) to 2·15 (2) Å]. In the structure the distances between the Na^- ion and the surrounding atoms (the nearest are H atoms) are: 3·47 Å minimum and 4·03 Å average for 12 nearest H atoms indicating an effective radius of 2·8 Å for Na^-. These distances are normal for natrides. Research is under way to determine the properites of this new compound (NMR, DSC *etc.*).

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* Lists of structure factors and tables of positional and isotropic thermal parmaters for the H atoms, anisotropic thermal parameters, torsion angles, least-squares planes and r.m.s. amplitudes of thermal vibration have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52962 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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