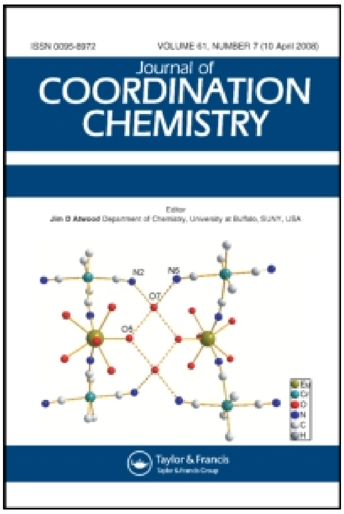

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SYNTHESES AND STRUCTURES OF SIX COMPOUNDS THAT CONTAIN THE SODIUM ANION

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SYNTHESES AND STRUCTURES OF SIX COMPOUNDS THAT CONTAIN THE SODIUM ANION

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Crystal structures have been obtained for the sodide (IUPAC, *natride*) salts, K^+(12-crown-4)$_2$-Na^- (I), Na^+(cryptand[2.2.1])Na^-(II), Rb^+(18-crown-6)$Na^- \cdot CH_3NH_2$ (III), K^+(18-crown-6) $Na^- \cdot 2(CH_3NH_2) \cdot 3$(18-crown-6)(IV), Cs^+(cryptand[3.2.2])Na^-(V), and $(Li^+)_2$(TMPAND)$_2$-$(Na^-)_2 \cdot (CH_3NH_2)$(VI), in which TMPAND is 5,12,17-trimethyl-1,5,9,12,17-pentaazabicyclo [7.5.5] nonadecane). The synthesis, handling and crystal growth techniques are described and the properties and structures are compared with those of other alkalides.

Keywords: Alkalide; electride; crown ether; cryptand; sodide; aza-cryptand

INTRODUCTION

The structures and some properties of 22 salts that contain alkali metal *anions* (*alkalides*) have been published.[1–9] In all cases, the counter-cation is complexed by one or more crown ether or cryptand molecules or their aza-analogues. In some structures the coordination of the cation is completed by incorporating solvent or the alkali metal anion in the primary coordination layer.[3,8] Related to the alkalides are *electrides* in which trapped electrons serve as the anions.[10] The crystal structures of five electrides have been published.[4,11–13,32] In three cases, their structures are very similar to those of corresponding alkalides, with "X-ray empty" cavities in place of alkali metal anions. Theoretical and experimental evidence suggest that the

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* Corresponding author.

bulk of the "excess" electron density in electrides resides in these cavities and in the interconnecting channels.[14]

Except for the thermal instability of alkali metal solutions and of alkalides and electrides, the synthesis methods are straightforward.[15] The alkali metal (or metals) and complexant are first co-dissolved in a primary amine such as methylamine ($MeNH_2$) or in dimethyl ether (Me_2O) in the correct stoichiometric proportions. In the case of alkalides that contain only one of the alkali metals, excess metal can be used since the solution process stops when all of the complexant is tied up by the cations and an equal concentration of alkali metal anion is present. It is more difficult to synthesize pure electrides since the equilibrium

$$2e^-_{solv} + M^+L_n \leftrightarrow M^- + nL \qquad (1)$$

(in which L is the complexant) can produce alkali metal anions that often co-crystallize with the electride. It should be noted that Li^- has never been observed, either in solution or in the solid state, presumably because of the strong solvation/complexation of Li^+. Also of importance is the tendency of reaction 1 to lie to the right when sodium is present. The sodium metal anion, Na^-, is thermodynamically favored so that the equilibrium constant for reaction 1 is four or five orders of magnitude larger for sodium than for other alkali metals.

After formation of a solution in $MeNH_2$ or Me_2O of stoichiometry $M^+L_n \cdot M'^-$, in which M and M′ may be the same or different metals, a less polar co-solvent, such as diethyl ether (Et_2O) or trimethylamine (Me_3N) is added to reduce the solubility and to provide a saturated solution. Crystals are then grown by either slow cooling or slow evaporation of the more volatile $MeNH_2$ or Me_2O. Details of the synthetic methods and of handling and mounting of the crystals for structure determination have been described elsewhere.[1,15–18]

Crystalline alkalides are ionic solids in which the complexed alkali cations have normal structures and the anions are large alkali metal anions; their radii are about 2.7, 3.1, 3.2 and 3.5 Å for Na^-, K^-, Rb^-, and Cs^-, respectively. The structures tend to be dominated by close-packing of the larger complexed cations (except that cesides have large enough anions to open the cation packing). Because the complexed cations have various sizes and shapes, a wide array of packing geometries is encountered.

Alkalides and electrides are thermodynamically unstable to irreversible decomposition, in which the complexant is reduced by M^- or e^-.[19,20] Thus, it is necessary to keep them cold (below ≈240 K) at all times. They also react readily with air and moisture so that anaerobic handling is required. The strong reducing power of alkalides and electrides severely limits the solvents in which they can be studied and from which they can be crystallized. Protic solvents (except certain amines), ketones, aromatic solvents, amides, fluorinated or other halogen-containing solvents, any solvents that freeze above 240 K, *etc.*, must be avoided. Difficulties in crystal growth often introduce defects and/or disorder. In mixed complexant structures, the inherent incompatibility of the symmetry of different ring structures results in disorder.[9]

EXPERIMENTAL

Sources and purification methods for solvents, complexants and alkali metals have been described previously as have the procedures used for crystal growth and handling.[1,15–18] All syntheses used vacuum-line methods and modified H-cells with rigorous exclusion of air and moisture. Transfers to the Nicolet P3F diffractometer were made in a stream of cold, boil-off nitrogen to prevent decomposition. The software methods SDP[21] (I, II and III), TEXAN[22] (IV and V) and SHELXL-93[23] (VI) were used for data handling and refinement. Direct methods were used to solve the structures.

RESULTS AND DISCUSSION

Structure I: Potassium Bis(12-crown-4) Sodide: $KNaC_{16}H_{32}O_8$

The crown ether 12-crown-4 (12C4) is the smallest available commercially. The small, compact ring size yields relatively weak complexation of alkali metal cations. Attempts to prepare crystalline sodides with complexed Li^+ or Na^+ and to synthesize electrides were unsuccessful. The compounds $Rb^+(12C4)_2Na^-$ and $Cs^+(12C4)_2Na^-$ were synthesized and characterized by analysis and ^{23}Na NMR,[24] but no crystal structures were obtained at that time. Mixed sandwich complexation of K^+ and Rb^+ by one 18-crown-6 (18C6) molecule and one 12C4 molecule yielded six crystalline alkalides.[9] The title compound (I) is stable in both $MeNH_2$ and Me_2O. However when Et_2O was added as a co-solvent, the alkali metals were released by decomplexation. It was necessary, therefore, to grow crystals from Me_2O by slow cooling.

A crystal with dimensions 0.4 × 0.4 × 0.6 mm was selected and mounted on the diffractometer. In the refinement, hydrogen atoms were located by calculation and refined isotropically. The crystallographic and refinement data for all of the structures described in this paper are given in Table I. Bond distances and bond angles as well as other crystal data for this structure and others can be found in the Supplemental Materials. The positions and thermal parameters of the atoms in compound I are given in Table II. Normal potassium–oxygen distances from 2.739 to 2.779 Å were obtained for the complexed cation. The structure of the $K^+(12C4)_2$ unit is virtually identical to that in a tris-cyclodextrin clathrate[25] except that in the latter structure the K^+–O distances are 0.1–0.2 Å longer. The potassium cation is 1.9 Å from the plane of four oxygens of each ring. Figures 1 and 2 show the single molecule and the stereoview, respectively.

Structure II: Sodium (Cryptand[2.2.1]) Sodide: $Na_2C_{16}H_{32}O_5N_2$

Cryptand[2.2.1] (C221) has the optimal cavity size for Na^+ and is the only other alkalide or electride besides $Na^+(C222)Na^-$ to contain the complexed sodium cation. Attempts to synthesize mixed alkalides, $Na^+L_nM^-$, in which M^- is another alkali metal anion, invariably yield the more stable sodide instead, and attempts to form electrides such as $Na^+(C222)e^-$ also yield the Na^- species. The thermodynamics of formation of $Na^+(C221)Na^-$ from sodium metal and the complexant has been studied electrochemically.[26]

Dimethyl ether and diethyl ether were used for crystallization and the slow evaporation method was used to get good single crystals. The solubility of $Na^+(C221)Na^-$ in Me_2O is much greater than that of $Na^+(C222)Na^-$, which has only limited solubility. Table III shows the positional and thermal parameters of the atoms. The bond distances between the sodium cation and the oxygen atoms range from 2.366 to 2.487 Å. Single molecule and the stereodrawing are shown in Figures 3 and 4.

Once again, the structure of the complexed cation is essentially the same as that in conventional salts such as $Na^+(C221)SCN^-$,[27] with Na^+ completely encapsulated in the cryptand. The Na^+–O distances in the sodide range from 2.37 to 2.60 Å, while in the thiocyanate salt they are between 2.45 and 2.52 Å. As is common in alkalides, the anion, Na^-, is surrounded by hydrogens of the complexant. The closest distance to adjacent hydrogens is 3.95 Å and the average distance to the neighboring hydrogens is 4.1 Å. Assuming a hydrogen van der Waals radius of 1.2 Å yields a minimum contact distance of 2.75 Å and an average Na^- "radius" of 2.9 Å.

TABLE I Crystallographic and refinement data for $K^+(12C4)_2Na^-$(I), $Na^+(C221)Na^-$(II), $Rb^+(18C6)Na^- \cdot CH_3NH_2$(III), $K^+(18C6)Na^- \cdot 2(CH_3NH_2) \cdot 3(18C6)$(IV), $Cs^+(C322)Na^-$(V) and $(Li^+)_2(TMPAND)_2(Na^-)_2 \cdot CH_3NH_2$(VI)

	I	*II*	*III*	*IV*	*V*	*VI*
Space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$R\bar{3}$	$P2_1/n$	Pc
Cell parameters						
a, Å	11.0527(25)	8.4976(36)	8.3919(61)	18.4033(42)	12.2637(22)	9.2280(36)
b, Å	15.3311(34)	13.0383(59)	12.4835(84)	18.4033(42)	17.0657(39)	15.3977(59)
c, Å	15.3115(36)	22.9368(93)	22.037(15)	17.111(15)	15.6607(42)	16.0970(67)
β°	93.59(2)	94.567(34)			111.106(17)	93.293(32)
z	4	4	4	6	4	2
Crystal dimensions, mm	0.4 × 0.4 × 0.6	0.3 × 0.3 × 0.4	0.8 × 0.8 × 1.1	0.4 × 0.4 × 0.6	0.2 × 0.2 × 0.2	1.0 × 1.0 × 1.2
Scan type	ω	ω	ω	ω	ω	ω
Maximum 2θ	55°	50°	55°	115°(Cu)	50°	115°(Cu)
Temperature, K	213	210	200	180	170	175
No. of reflections collected	6406	7259	3154	5148	5850	9635
No. of unique reflections	5949	3740	3018	1564	5428	3315
No. of reflections used in refinement. with $F_0^2 > 3\sigma(F_0^2)$	3311	1955	1427	1471	1932	3251
No. of variables	364	355	316	187	233	673
R	0.045	0.030	0.037	0.055	0.071	0.070
R_w	0.040	0.035	0.037	0.054	0.045	0.197*
High peak in final diffraction map, e/Å^3	0.29	0.10	0.40	0.25	0.18	0.41

*refinement on F^2.

TABLE II Positional parameters and their estimated standard deviations for $K^+(12C4)_2$ Na^- (I)

Atom	*x*	*y*	*z*	*B*(*A*2)
K^+	−0.00375(5)	0.24205(4)	0.51658(4)	4.15(1)
Na^-	0.5036(1)	0.5392(1)	0.25341(9)	6.86(3)
O1	−0.1239(2)	0.0844(1)	0.5275(1)	4.31(4)
O4	−0.0829(2)	0.1593(1)	0.3634(1)	4.50(4)
O7	−0.1907(2)	0.3163(1)	0.4169(1)	4.96(4)
O10	−0.2337(2)	0.2407(1)	0.5799(1)	4.89(4)
O13	0.2267(2)	0.1816(1)	0.5590(1)	5.04(4)
O16	0.1906(2)	0.3262(1)	0.4465(1)	4.83(4)
O19	0.0552(2)	0.4083(1)	0.5746(1)	4.95(4)
O22	0.0907(2)	0.2623(1)	0.6861(1)	5.38(5)
C2	−0.1727(3)	0.0452(2)	0.4495(2)	5.78(8)
C3	−0.0927(3)	0.0666(2)	0.3796(2)	5.89(8)
C5	−0.1823(3)	0.1958(2)	0.3141(2)	5.81(8)
C6	−0.1807(3)	0.2909(2)	0.3269(2)	6.12(8)
C8	−0.3096(3)	0.3120(2)	0.4447(2)	5.92(8)
C9	−0.3014(3)	0.3140(2)	0.5410(2)	6.10(8)
C11	−0.2981(3)	0.1618(2)	0.5804(2)	5.90(8)
C12	−0.2098(3)	0.0898(2)	0.5956(2)	5.80(7)
C14	0.3064(3)	0.2031(2)	0.4906(2)	5.34(7)
C15	0.3092(3)	0.2996(2)	0.4729(2)	5.69(8)
C17	0.1713(3)	0.4192(2)	0.4516(2)	5.41(7)
C18	0.1577(3)	0.4494(2)	0.5435(2)	5.53(8)
C20	0.0504(3)	0.4119(2)	0.6683(2)	5.35(7)
C21	0.1293(3)	0.3450(2)	0.7146(2)	5.72(8)
C23	0.1797(3)	0.1946(2)	0.7054(2)	5.97(8)
C24	0.2790(3)	0.1961(2)	0.6441(2)	6.25(8)

Structure III: Rubidium (18-crown-6) Sodide·Methylamine: $RbNaC_{13}H_{31}O_6N$

This compound was synthesized in $MeNH_2$ and crystallized by slowly cooling a solution that contained the co-solvent Et_2O. The red-bronze colored crystals were harvested after pumping to $\sim 10^{-5}$ torr at ~ 200 K. Surprisingly, one $MeNH_2$ molecule per cation was retained in the structure even after this evacuation. Since the size of Rb^+ is slightly larger than the hole of the 18C6 ring, the cation is displaced about 1.0 Å above the ring plane. The distances between Rb^+ and oxygen atoms of the ring range from 2.84 to 3.04 Å. The coordination environment of Rb^+ consists of the six oxygen atoms of the 18C6 ring, the anion, Na^-, and one molecule of $MeNH_2$ with an Rb^+ to N distance of 3.00 Å. This structure is different from that of $Rb^+(18C6)Rb^-$ in which Rb^+ and Rb^- are in contact but there are no solvent molecules in the structure.[3] In the present case, the smaller size of Na^- permits coordination of Rb^+ to both a methylamine molecule and a Na^- ion, both of which are on the same side of the $Rb^+(18C6)$ species.

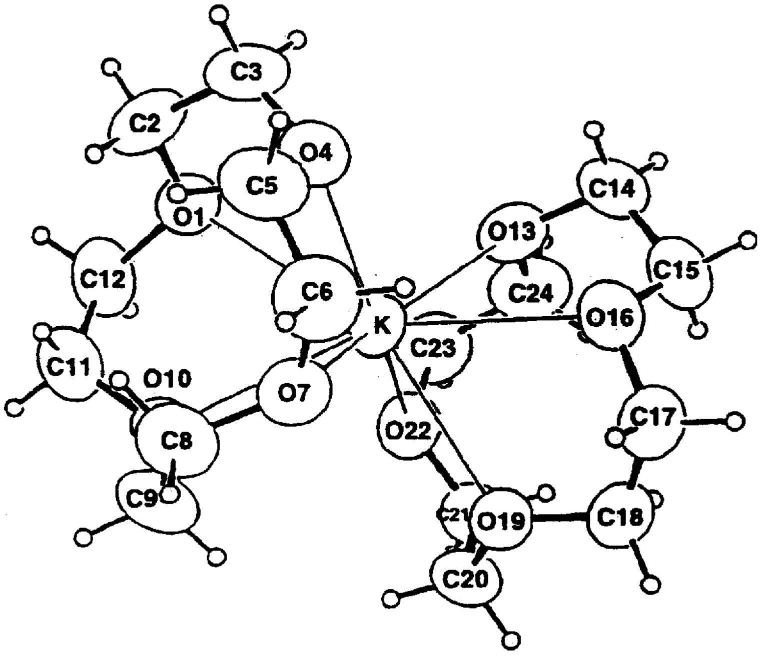

FIGURE 1 Single molecule view of the complexed cation in $K^+(12\text{-crown-}4)_2Na^-$(I). Thermal Ellipsoids in this and other figures are at the 50% level.

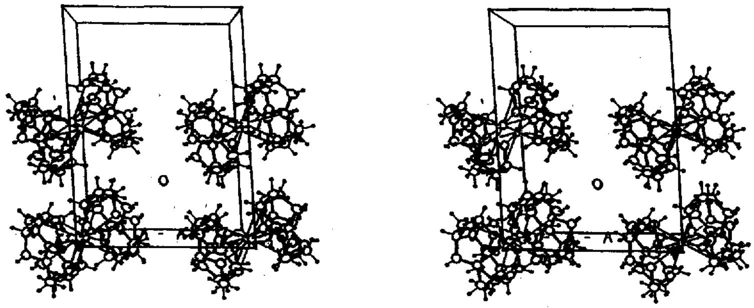

FIGURE 2 Stereoview of the unit cell of $K^+(12\text{-crown-}4)_2Na^-$.

The distance between Rb^+ and Na^- is only 4.57 Å, which is only slightly larger than the sum of the radii (4.2–4.4 Å) indicating the formation of a contact ion-pair. The positional data and thermal parameters are given in Table IV. Single molecule and stereo drawings are shown in Figures 5 and 6, respectively.

TABLE III Positional parameters and their estimated standard deviations for Na^+(C221)Na^- (II)

Atom	*x*	*y*	*z*	*B*(*A*2)
Na^+	0.4527(1)	0.72519(7)	0.41419(4)	3.27(2)
Na^-	0.0791(2)	0.7282(1)	0.17797(5)	7.21(3)
O4	0.6691(2)	0.7029(1)	0.34835(6)	3.80(4)
O7	0.4372(2)	0.5578(1)	0.36617(6)	4.10(4)
O13	0.4822(2)	0.6567(1)	0.51493(6)	4.22(4)
O16	0.5746(2)	0.8518(1)	0.48490(7)	3.87(4)
O21	0.2218(2)	0.8145(1)	0.37927(7)	4.62(4)
N1	0.5230(2)	0.8987(2)	0.36338(8)	3.81(5)
N10	0.2010(2)	0.6244(2)	0.43769(9)	4.41(5)
C2	0.6471(3)	0.8787(2)	0.3239(1)	4.49(6)
C3	0.6380(3)	0.7714(2)	0.2999(1)	4.63(6)
C5	0.6816(3)	0.5979(2)	0.3308(1)	4.47(6)
C6	0.5247(3)	0.5489(2)	0.3162(1)	4.51(7)
C8	0.2803(3)	0.5185(2)	0.3566(1)	4.86(7)
C9	0.2088(3)	0.5195(2)	0.4144(1)	5.19(7)
C11	0.2002(3)	0.6247(2)	0.5015(1)	5.19(7)
C12	0.3554(3)	0.5940(2)	0.5324(1)	5.23(7)
C14	0.5363(4)	0.7300(2)	0.5578(1)	4.99(7)
C15	0.6543(3)	0.7969(2)	0.5323(1)	4.72(7)
C17	0.6732(3)	0.9229(2)	0.4582(1)	4.71(7)
C18	0.5759(3)	0.9732(2)	0.4085(1)	4.80(7)
C19	0.3765(3)	0.9321(2)	0.3303(1)	5.18(7)
C20	0.2339(3)	0.9200(2)	0.3641(1)	5.48(7)
C22	0.0867(3)	0.7935(2)	0.4100(1)	5.64(7)
C23	0.0634(3)	0.6794(3)	0.4101(1)	5.79(8)

Structure IV: Potassium (18-crown-6) Sodide·2 Methylamine·3(18-crown-6): $KNaC_{50}H_{106}O_{24}N_2$

This sodide was crystallized from a mixture of $MeNH_2$, Et_2O and Me_2O by slow cooling and the crystals were harvested while still damp with solvent. Because K^+ is just the right size to fit into the hole in the 18C6 ring, we expected the cation to be at the center. This proved to be the case, with K^+ coordinated to six oxygens of the crown ether at a distance of 2.79 Å and to two nitrogens of $MeNH_2$ with a K^+–N distance of 2.89 Å. The bonding between the potassium cation and the nitrogen atoms of $MeNH_2$ is not strong. Evacuation under high vacuum at low temperature results in lattice collapse and the crystals were destroyed. The space group is $R\bar{3}$ with Na^- at 8.56 Å from K^+ on the three-fold inversion axis. The big surprise was the presence of six free 18-crown-6 molecules around each complexed K^+, each one shared by two complexed potassium cations. This structure is similar to that of the lithium-based sodide, Li^+(18C6)Na^-·2$MeNH_2$·3(18C6), which also has three free crown ethers per Li^+, with similar placement and the

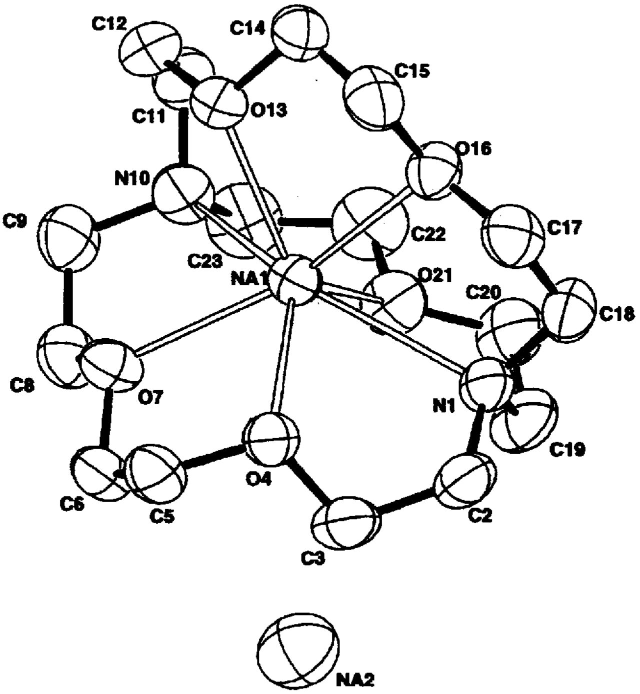

FIGURE 3 Single molecule view of Na$^+$(cryptand[2.2.1])Na$^-$(II), that shows both the complexed Na$^+$ (Na 1) and the anion, Na$^-$ (Na 2).

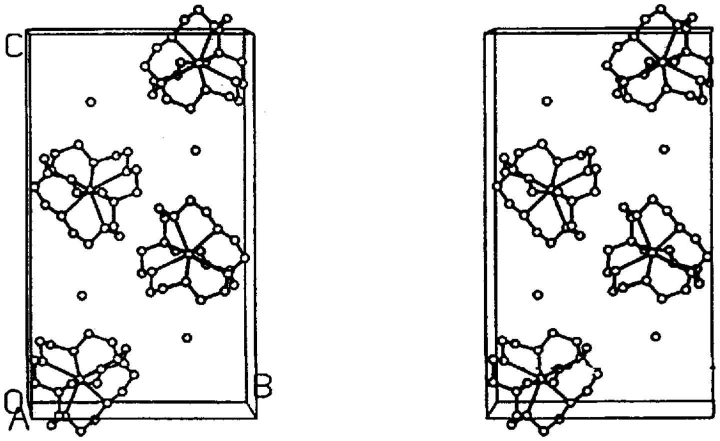

FIGURE 4 Stereoview of the unit cell of Na$^+$(cryptand[2.2.1])Na$^-$.

TABLE IV Positional parameters and their estimated standard deviations for $Rb^+(18C6)Na^-\cdot CH_3NH_2$(III)

Atom	*x*	*y*	*z*	*B*(*A*2)
Rb	0.2527(1)	0.41238(5)	0.60542(3)	3.39(1)
Na	0.3309(5)	0.7628(3)	0.6570(2)	7.4(1)
O1	0.5062(6)	0.2798(4)	0.5578(2)	3.5(1)
O4	0.4055(6)	0.4522(3)	0.4825(2)	3.5(1)
O7	0.1360(6)	0.5653(4)	0.5195(2)	4.4(1)
O10	−0.0976(6)	0.4667(4)	0.5881(2)	4.5(1)
O13	0.0016(6)	0.2931(4)	0.6601(2)	4.7(1)
O16	0.2755(6)	0.1765(4)	0.6271(2)	3.8(1)
N101	0.366(1)	0.4412(6)	0.7335(3)	8.0(2)
C2	0.5760(9)	0.3054(5)	0.5005(3)	3.9(2)
C3	0.5676(9)	0.4243(6)	0.4910(3)	4.0(2)
C5	0.391(1)	0.5657(6)	0.4755(3)	4.6(2)
C6	0.2187(9)	0.5931(6)	0.4651(3)	4.8(2)
C8	−0.024(1)	0.6014(6)	0.5190(4)	5.1(2)
C9	−0.096(1)	0.5788(6)	0.5786(4)	5.4(2)
C11	−0.171(1)	0.4357(8)	0.6431(4)	5.8(2)
C12	−0.1619(9)	0.3204(8)	0.6515(4)	6.0(2)
C14	0.023(1)	0.1839(7)	0.6754(3)	6.2(2)
C15	0.195(1)	0.1598(6)	0.6838(3)	5.2(2)
C17	0.436(1)	0.1497(6)	0.6306(3)	4.2(2)
C18	0.5124(9)	0.1702(5)	0.5700(3)	3.9(2)
C102	0.235(1)	0.4473(8)	0.7724(4)	10.7(3)

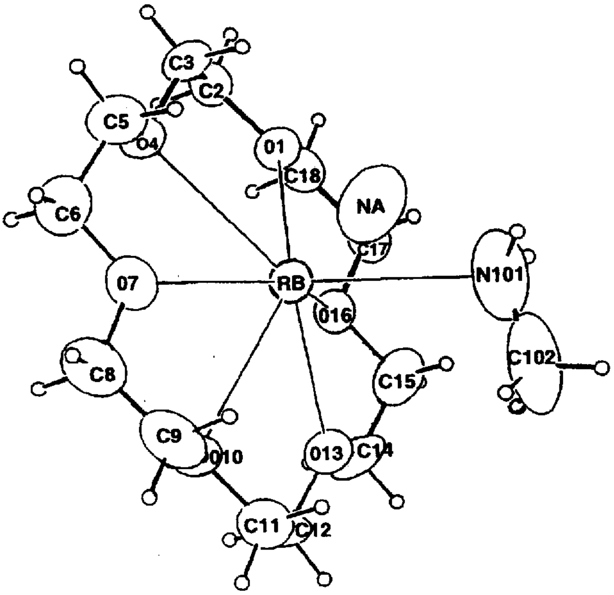

FIGURE 5 Single molecule view of the complexed cation in Rb^+(18-crown-6)-$Na^-\cdot CH_3NH_2$(III).

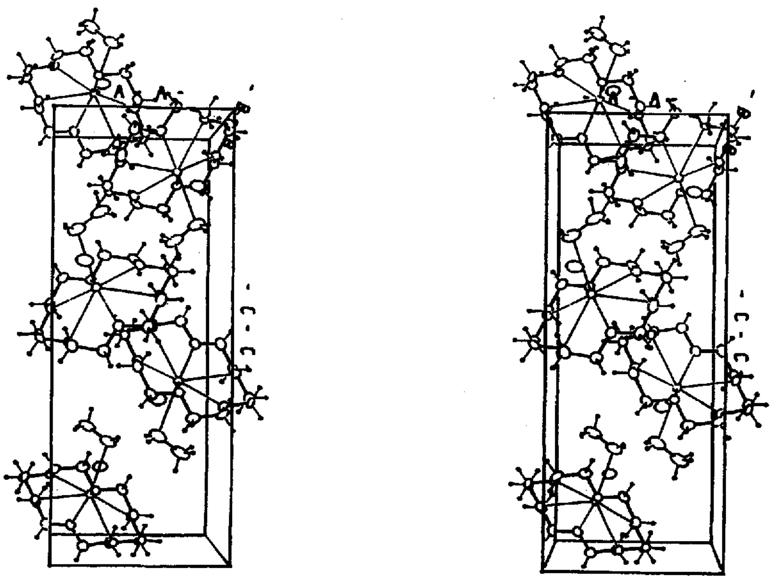

FIGURE 6 Stereoview of the unit cell of Rb^+(18-crown-6) $Na^- \cdot CH_3NH_2$.

sharing of each between two complexed Li^+ ions.[8] In the lithium case, there is evidence that Li^+ is off-center and dynamically jumping from site to site inside the ring.[28] The positional and thermal parameters are listed in Table V. Figure 7 shows the complexed central K^+18C6 unit and one of the six equivalent free 18C6 molecules in the structure. Figure 8 shows the stereoview of the unit cell.

Structure V: Cesium (Cryptand[3.2.2]) Sodide: $CsNaC_{20}H_{40}O_7N_2$

The complexant, C322 was synthesized and purified in our lab. This sodide compound was first reported in 1982.[29] The structure determination was not possible until recently when enough complexant was synthesized.

The complexant C322 should provide a better fit for the cesium cation than C222 because of its larger cavity size. In the structure of $Cs^+(C222)Cs^{-2}$ the Cs–O distances (2.89–2.99 Å) are significantly shorter than the normal Cs–O distances in other cesium complex cations such as that in $Cs^+(18C6)SCN^-$, in which the mean Cs–O distance is 3.15 Å.[30] The structure of the present compound confirms the "looser" fit of Cs^+ in the cryptand cavity. The cation–oxygen distances range from 3.12 to 3.32 Å,

TABLE V Positional parameters and their estimated standard deviations for $K^+(18C6)Na^-\cdot 2(CH_3NH_2)\cdot 3(18C6)(IV)$

Atom	*x*	*y*	*z*	*B(eq)*
K^+	0	0	0.5000	2.54(5)
Na^-	0	0	0	5.3(1)
O(1)	−0.0194(1)	0.1403(1)	0.5123(1)	3.2(1)
O(11)	0.0320(2)	0.4052(2)	0.3992(2)	4.0(1)
O(14)	0.2454(2)	0.4505(2)	0.4112(1)	4.0(1)
O(17)	0.3444(2)	0.3751(2)	0.4078(1)	3.9(1)
N(21)	0.0520(7)	0.0238(7)	0.3398(6)	3.5(4)*
C(2)	0.0452(2)	0.2120(2)	0.4732(2)	3.5(2)
C(3)	0.1285(2)	0.2287(2)	0.5054(3)	3.4(2)
C(12)	0.1103(2)	0.4162(2)	0.3717(2)	3.5(2)
C(13)	0.1709(3)	0.4475(3)	0.4393(2)	3.6(2)
C(15)	0.3061(3)	0.4654(3)	0.4709(2)	4.0(2)
C(16)	0.3764(3)	0.4585(3)	0.4347(2)	4.1(2)
C(18)	−0.0691(3)	0.3008(3)	0.3062(3)	4.1(2)
C(19)	−0.0277(3)	0.3891(3)	0.3391(3)	4.1(2)
C(22)	0.002(2)	0.030(1)	0.301(1)	6.5(7)*

*multiplicity = 0.3333.

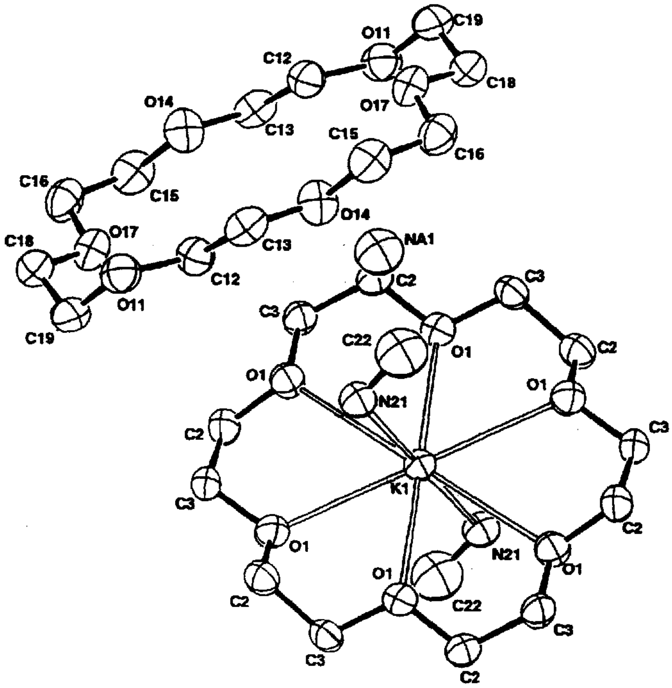

FIGURE 7 Single molecule view of the complexed cation and one of the "free" crown ether molecules in K^+(18-crown-6) $Na^-\cdot 2(CH_3NH_2)\cdot 3$(18-crown-6)(IV).

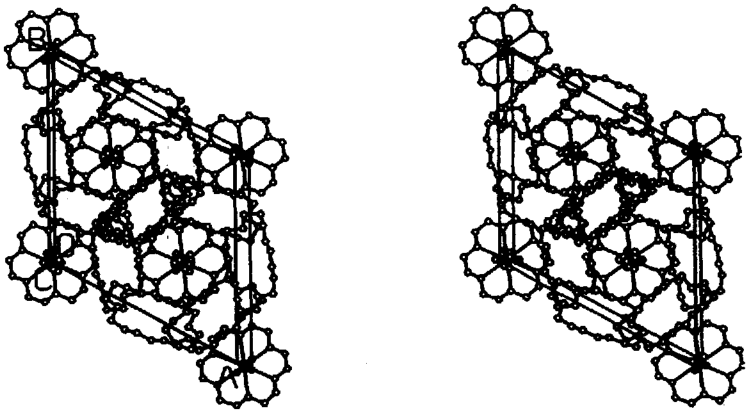

FIGURE 8 Stereoview of the unit cell in K^+(18-crown-6) $Na^-\cdot 2(CH_3NH_2)\cdot 3$(18-crown-6).

with an average distance of 3.17 Å, close to the value in "normal" complexed Cs^+.

The crystals were recrystallized from Me_2O-Et_2O solution by using the slow cooling method. The compound crystallized in the monoclinic space group $P2_1/n$. In the refinement several atoms were disordered and one carbon atom was refined isotropically to prevent a "non-positive-definite" situation. The positional and thermal parameters are given in Table VI. Single molecule and stereodrawings are shown in Figures 9 and 10, respectively.

Structure VI: [Lithium (TMPAND) Sodide]$_2$·Methylamine: $Li_2Na_2C_{35}H_{79}N_{11}$

This compound is the first alkalide with an azacage complexant that is similar to a cryptand. Each nitrogen in the "arms" of the complexant was methylated to avoid the presence of reactive H atoms that would be present in a secondary amine. Replacement of ether oxygens by this tertiary amine group greatly enhances stability.[5,31] There is, however, some problem with the slow encapsulation of Li^+ within the azacage. It was necessary to allow the solutions, first in $MeNH_2$ then in a Me_2O/Me_3N mixture to stand for several hours at −40°C or higher to ensure complexation. The synthesis and properties have been described in detail elsewhere.[31] In this structure the lithium cation is encapsulated within the complexant molecule.

TABLE VI Positional parameters and their estimated standard deviations for $Cs^+(C322)Na^-(V)$

Atom	*x*	*y*	*z*	*B(eq)*
Cs	0.2394(1)	0.10937(9)	0.48491(9)	2.73(4)
Na	0.2769(9)	0.1185(7)	0.0334(6)	7.4(5)
O(4)	0.183(1)	−0.0670(8)	0.5203(9)	3.7(7)
O(7)	0.052(1)	−0.0103(9)	0.336(1)	3.9(7)
O(10)	0.084(1)	0.139(1)	0.281(1)	7(1)
O(16)	0.263(1)	0.2880(9)	0.550(1)	5.3(8)
O(19)	0.204(1)	0.1756(7)	0.662(1)	3.8(7)
O(24)	0.502(1)	0.0920(8)	0.6116(8)	3.6(7)
O(27)	0.452(1)	0.1499(7)	0.429(1)	4.7(7)
N(1)	0.324(1)	0.026(1)	0.687(1)	3.0(8)
N(13)	0.258(1)	0.265(1)	0.362(1)	4.4(9)
C(2)	0.311(2)	−0.058(1)	0.679(1)	4(1)
C(3)	0.197(2)	−0.090(1)	0.612(1)	4(1)
C(5)	0.083(2)	−0.101(2)	0.465(2)	5(1)
C(6)	0.073(2)	−0.092(1)	0.364(2)	6(1)
C(8)	0.054(2)	0.005(2)	0.251(1)	5(2)
C(9)	0.014(2)	0.087(2)	0.222(2)	6(1)
C(11A)	0.0495	0.2253	0.2648	8(1)*
C(11B)	0.0748	0.2088	0.2218	6(1)*
C(12A)	0.1196	0.2657	0.2821	6(1)*
C(12B)	0.1604	0.2642	0.2507	5(1)*
C(14A)	0.2853	0.3409	0.4034	5(1)*
C(14B)	0.2173	0.3403	0.3961	3.1(9)*
C(15A)	0.3126	0.3495	0.5040	3.1(9)*
C(15B)	0.2385	0.3520	0.4848	5(1)*
C(17)	0.173(2)	0.298(1)	0.572(2)	6(1)
C(18)	0.190(2)	0.257(1)	0.662(1)	4.7(5)*
C(20)	0.254(3)	0.140(1)	0.750(2)	4(1)
C(21)	0.257(2)	0.054(1)	0.741(2)	4(1)
C(22)	0.450(2)	0.042(1)	0.738(1)	4(1)
C(23)	0.525(2)	0.034(1)	0.679(1)	4(1)
C(25)	0.585(2)	0.096(2)	0.565(2)	5(1)
C(26)	0.563(2)	0.163(1)	0.505(2)	6(1)
C(28A)	0.4481	0.2127	0.3646	5(1)*
C(28B)	0.4080	0.1866	0.3290	8(1)*
C(29A)	0.3859	0.2766	0.3602	4(1)*
C(29B)	0.3396	0.2491	0.3140	8(1)*

*atoms refined isotropically.

The asymmetric unit has two lithium complexes and one $MeNH_2$ molecule (filling void space but not coordinated to Li^+). The Li^+–N distances within the cage range from 2.00 to 2.26 Å except for one nitrogen (N10) which has a Li2–N10 distance of 2.60 Å. One of the Na^- ions has an anomalously low thermal factor (0.0012). To avoid a "non-positive-definite" thermal parameter for this anion, SHELXL-93 software was used in the refinement. The appropriate data for this structure are given in Table VII while Figures 11 and 12 show the single molecule and stereopacking, respectively.

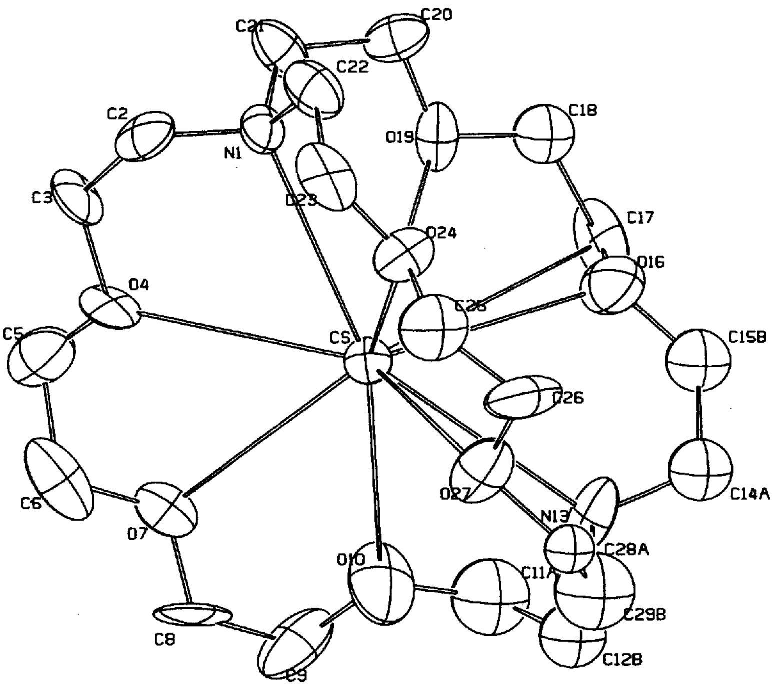

FIGURE 9 Single molecule view of the complexed cation in Cs$^+$(cryptand [3.2.2])Na$^-$(V).

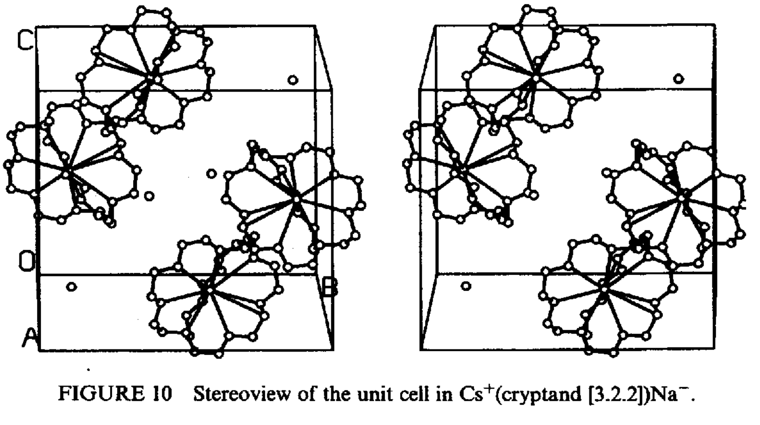

FIGURE 10 Stereoview of the unit cell in Cs$^+$(cryptand [3.2.2])Na$^-$.

TABLE VII Positional parameters and their estimated standard deviations for $(Li^+)_2(TMPAND)_2(Na^-)_2\cdot CH_3NH_2$ (VI)

Atom	*x*	*y*	*z*	*U(eq)**
Na1	0.6962(4)	0.4741(2)	0.5858(2)	0.0687(10)
Na2	0.2094(2)	0.03362(8)	0.85625(9)	0.0066(4)
Li1	0.7184(12)	0.1332(7)	0.3233(6)	0.035(2)
Li2	1.1982(14)	0.3562(7)	0.8596(8)	0.044(2)
N1	0.9958(6)	0.3070(4)	0.8396(3)	0.0355(12)
N4	1.2011(6)	0.3071(4)	0.9889(3)	0.0396(13)
N7	1.4050(6)	0.3166(4)	0.8600(3)	0.0358(12)
N10	1.2041(6)	0.2970(3)	0.7085(3)	0.0377(13)
N16	1.1974(7)	0.4859(3)	0.8483(3)	0.0396(13)
N23	0.8510(6)	0.1484(4)	0.2197(3)	0.0352(12)
N26	0.7068(6)	−0.0028(4)	0.2871(3)	0.0359(12)
N29	0.6882(6)	0.0885(4)	0.4465(3)	0.0431(14)
N32	0.9067(6)	0.2043(4)	0.3879(3)	0.0392(13)
N38	0.5300(6)	0.1996(4)	0.2898(3)	0.0363(12)
N45	0.2268(13)	0.0295(8)	0.6107(6)	0.105(4)
C2	0.9599(8)	0.2779(6)	0.9232(4)	0.042(2)
C3	1.0925(9)	0.2396(5)	0.9708(4)	0.042(2)
C5	1.3474(9)	0.2698(6)	1.0031(4)	0.045(2)
C6	1.4177(9)	0.2461(5)	0.9209(4)	0.044(2)
C8	1.4475(8)	0.2855(5)	0.7780(4)	0.042(2)
C9	1.3223(9)	0.2383(5)	0.7324(4)	0.041(2)
C11	1.0621(8)	0.2540(5)	0.7002(4)	0.042(2)
C12	0.9978(8)	0.2330(5)	0.7813(4)	0.0384(15)
C13	0.8929(8)	0.3742(5)	0.8082(5)	0.043(2)
C14	0.9280(9)	0.4650(5)	0.8391(5)	0.049(2)
C15	1.0644(10)	0.5037(5)	0.8014(5)	0.052(2)
C17	1.3241(10)	0.4985(6)	0.7956(5)	0.051(2)
C18	1.4715(9)	0.4760(5)	0.8361(5)	0.049(2)
C19	1.4891(8)	0.3943(5)	0.8898(4)	0.042(2)
C20	1.1667(11)	0.3572(6)	1.0611(5)	0.053(2)
C21	1.2327(11)	0.3402(6)	0.6292(4)	0.052(2)
C22	1.2114(12)	0.5452(6)	0.9223(6)	0.057(2)
C24	0.8334(8)	0.0660(5)	0.1739(4)	0.041(2)
C25	0.8320(8)	−0.0103(5)	0.2338(4)	0.0378(14)
C27	0.7313(9)	−0.0468(4)	0.3678(4)	0.042(2)
C28	0.6424(10)	−0.0024(5)	0.4321(4)	0.046(2)
C30	0.8342(9)	0.0940(7)	0.4910(4)	0.053(2)
C31	0.9536(9)	0.1265(6)	0.4360(5)	0.050(2)
C33	1.0127(9)	0.2237(6)	0.3247(5)	0.049(2)
C34	1.0024(7)	0.1580(5)	0.2537(4)	0.0379(15)
C35	0.8093(9)	0.2235(5)	0.1661(4)	0.046(2)
C36	0.6484(8)	0.2410(6)	0.1576(4)	0.047(2)
C37	0.5823(9)	0.2710(5)	0.2379(5)	0.047(2)
C39	0.4841(10)	0.2377(5)	0.3696(5)	0.048(2)
C40	0.4484(9)	0.1689(6)	0.4344(5)	0.053(2)
C41	0.5778(10)	0.1380(6)	0.4901(4)	0.054(2)
C42	0.5724(10)	−0.0347(5)	0.2438(5)	0.047(2)
C43	0.8987(13)	0.2801(6)	0.4419(6)	0.063(2)
C44	0.4020(8)	0.1611(6)	0.2474(5)	0.047(2)
C46	0.2851(20)	−0.0398(7)	0.5680(6)	0.107(5)

*calculated based on U's.

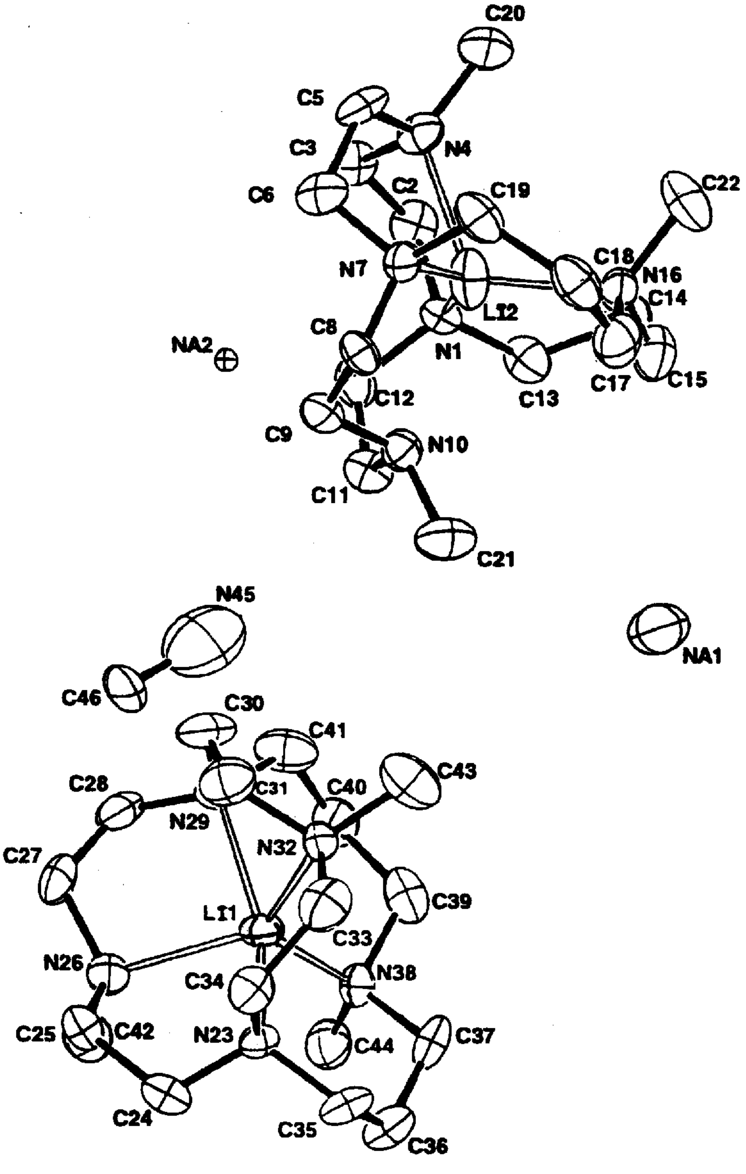

FIGURE 11 View of the two (non-equivalent) complexed lithium cations and Na⁻ ions and the "free" methylamine molecule in $(Li^+)_2(TMPAND)_2(Na^-)_2 \cdot CH_3NH_2$(VI).

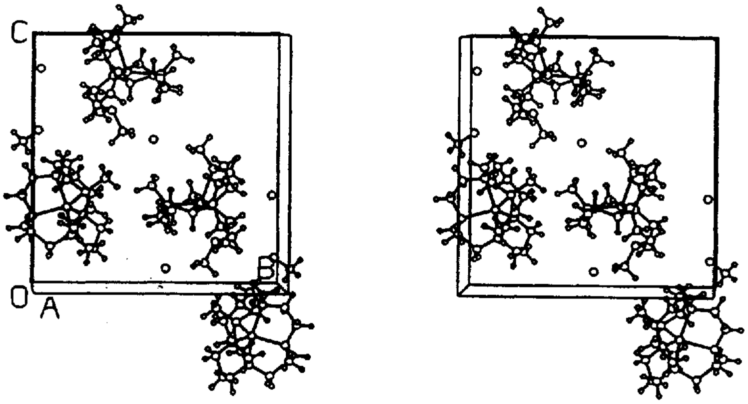

FIGURE 12 Stereoview of the unit cell in $(Li^+)_2(TMPAND)_2(Na^-)_2 \cdot CH_3NH_2$.

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