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Cryptates with Macrotricyclic Ligands. The Structure of the Sodium [3]-Cryptate $[(C_{32}H_{64}N_4O_{10})Na_2]I_2$

J. FISCHER, M. MELLINGER and R. WEISS[1]
Institut le Bel, Université Louis Pasteur, 67070 Strasbourg-Cédex, France

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The macrotricyclic ligand $C_{32}H_{64}N_4O_{10}$ forms with sodium iodide the 1:2 complex of the [3]-cryptate type, $(Na_2\subset L)I_2$ ($L = C_{32}H_{64}N_4O_{10}$). This compound crystallizes in space group $P2_1/c$ with $a = 8.726(4)$, $b = 10.114(7)$, $c = 24.422(11)$Å, $\beta = 103.89(4)^\circ$, $Z = 2$. The structure was determined from diffractometer data by the heavy atom method and refined by least-squares to $R(F) = 0.057$ for 1927 reflections. The structure consists of centrosymmetric cations $(Na_2\subset L)^{2+}$ and I^- anions; the sodium ions are accommodated inside the tricyclic ligand, with each bonded to two nitrogen and five oxygen atoms of L. The Na–N distances are 2.70(1) and 2.73(1) and the Na–O range from 2.39(1) to 2.48(1)Å. The iodide ions no longer interact with the sodium ions: all the $Na^+\cdots I^-$ separations exceed 5Å. The distance between the sodium ions inside L is 6.40 Å.

Introduction

Metal complexes with macrotricyclic ligands ([3]-cryptates) having a ligand to metal ratio of 1:2 and 1:3 have been synthesized recently [2]. N.m.r. studies and stability measurements indicate that in some cases two metal cations may be enclosed within the same ligand. In order to establish the molecular structure of such a dication [3]-cryptate and to study the relationship between conformation and complexation selectivity of the macrotricyclic ligand we have investigated the structure of the 1:2 complex $(Na_2\subset L)I_2$, L = tricyclic ligand $C_{32}H_{64}N_4O_{10}$ (Fig. 1).

Experimental

Suitable crystals of $(Na_2\subset L)I_2$ were prepared by slow evaporation of methanol–butanol solutions of L and NaI in the ratio 1:2. The complex is monoclinic with $a = 8.726(4)$, $b = 10.114(6)$, $c = 24.421(11)$Å, $\beta = 103.88(3)^\circ$; $V = 2092$ Å^3; $d_{obs} = 1.51$ g/cm^3, for $Z = 2$, $d_{calc} = 1.53$ g/cm^3, $\mu = 15.70$ cm^{-1}. Precession photographs showed systematic absences for h0l reflections with l odd and 0k0 reflections with k odd, indicating the space group $P2_1/c$.

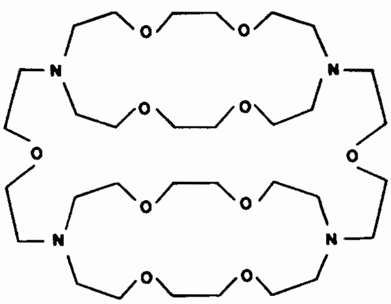

Fig. 1. (L) = $C_{32}H_{64}N_4O_{10}$.

The unit cell dimensions and their estimated standard deviations were obtained at room temperature (20 ± 2 °C) with MoKα radiation (λ = 0.70926 Å) using the method outlined by Busing for a four-circle diffractometer [3]. The experimental density was measured by flotation in a bromoform–carbon tetrachloride mixture.

A crystal was ground to a small sphere of 0.15 mm diameter, sealed in a Lindeman glass capillary and mounted on a rotation-free goniometer head [4]. All quantitative data were obtained from a Picker four-circle diffractometer controlled by a PDP-8/I computer, using graphite monochromated MoKα radiation. The monochromator was set at a 2θ angle of 11.68° (θ = 5.45°). The refined parameters listed above and the orientation matrix were obtained using standard routines supplied by Picker. Intensity data were collected using the θ–2θ scan technique with a scan range of 1.6° + tanθ and a scan rate of 2°/min. Stationary background counts (20 sec) were recorded at each end of the scan. Attenuators were used whenever the scan count exceeded 7000 counts/sec. The intensities of three standard reflections were monitored throughout the data collection at intervals of 70 measurements; their intensities show a mean loss of 12%, which was corrected during data reduction by use of a local program.

A standard deviation was assigned to each measured intensity using the expression

TABLE I. Atomic coordinates and β_{ij} with their esd's. Temperature factors are in the form $\exp -[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$.

I	0.24991(8)	0.01670(5)	0.12730(2)	0.0310(1)	0.01578(7)	0.00314(1)	0.00296(8)	0.00117(2)	0.00100(2)
Na	0.2263(2)	0.0136(2)	0.3861(1)	0.0142(4)	0.0100(2)	0.0018(5)	0.0008(2)	0.0015(1)	-0.00009(8)
N(1)	0.1782(8)	-0.2082(6)	0.3236(2)	0.018(1)	0.0130(7)	0.0026(1)	-0.0001(7)	0.0017(3)	-0.0012(2)
C(1)	0.292(1)	-0.205(1)	0.2877(4)	0.032(2)	0.018(1)	0.0034(2)	0.0000(1)	0.0044(6)	-0.0024(4)
C(2)	0.449(1)	-0.154(1)	0.3173(5)	0.023(1)	0.016(1)	0.0035(2)	-0.0000(1)	0.0052(5)	-0.0022(4)
O(1)	0.438(6)	-0.0206(5)	0.3359(2)	0.0167(8)	0.0136(5)	0.0025(1)	0.0002(5)	0.0018(2)	0.0002(2)
O(3)	0.409(1)	0.079(1)	0.2920(4)	0.021(1)	0.022(1)	0.0025(2)	0.001(1)	0.0033(4)	0.0017(4)
C(4)	0.416(1)	0.208(1)	0.3174(4)	0.017(1)	0.018(1)	0.0035(2)	-0.003(2)	0.0017(5)	0.0027(4)
O(2)	0.295(1)	0.214(1)	0.3454(5)	0.040(1)	0.0102(1)	0.0034(1)	0.0004(8)	0.0050(4)	0.0008(2)
C(5)	0.269(2)	0.330(1)	0.3710(7)	0.125(7)	0.012(1)	0.0058(5)	-0.006(2)	0.010(1)	-0.0012(7)
C(6)	0.320(2)	0.332(1)	0.4293(6)	0.074(5)	0.010(1)	0.0043(3)	0.012(6)	-0.009(1)	-0.0023(4)
N(2)	0.314(1)	0.2103(9)	0.4638(3)	0.020(1)	0.022(1)	0.0027(1)	0.005(1)	-0.0013(4)	-0.0008(3)
C(7)	0.209(1)	0.180(2)	0.5020(7)	0.039(3)	0.047(3)	0.0036(3)	0.001(2)	0.0048(8)	-0.0063(9)
C(8)	0.039(1)	0.177(1)	0.4719(5)	0.040(4)	0.028(2)	0.0052(4)	-0.008(2)	0.008(1)	-0.0039(8)
O(3)	0.017(1)	0.083(1)	0.4270(5)	0.024(1)	0.0183(1)	0.0034(1)	0.0006(8)	0.0042(3)	-0.0010(3)
C(9)	⊖0.136(1)	0.106(1)	0.3870(5)	0.018(1)	0.023(1)	0.0048(3)	0.004(1)	0.0052(6)	0.0020(6)
C(10)	-0.138(1)	-0.016(1)	0.3524(5)	0.020(1)	0.038(3)	0.0056(4)	-0.007(1)	0.0048(8)	-0.0027(8)
O(4)	-0.032(1)	0.011(1)	0.3173(5)	0.0140(8)	0.0162(7)	0.0034(1)	-0.0002(6)	0.0001(2)	0.0006(2)
C(11)	-0.0042(1)	-0.078(1)	0.2712(5)	0.024(1)	0.021(1)	0.0028(2)	-0.003(1)	-0.0016(5)	-0.0004(4)
C(12)	0.015(1)	-0.211(1)	0.2904(4)	0.021(1)	0.017(1)	0.0034(2)	-0.005(1)	-0.0003(5)	-0.0027(4)
C(13)	0.206(1)	-0.318(1)	0.3633(5)	0.031(2)	0.009(8)	0.0039(2)	0.0002(2)	0.0030(6)	-0.0001(3)
C(14)	0.173(1)	-0.2812(9)	0.4177(4)	0.024(1)	0.013(1)	0.0034(2)	-0.002(1)	0.0020(5)	0.0011(4)
O(5)	0.2760(7)	-0.1821(6)	0.4473(2)	0.0197(9)	0.0153(7)	0.0028(1)	0.012(7)	0.0000(3)	0.0017(2)
C(15)	0.618(1)	0.198(1)	0.4982(5)	0.036(3)	0.060(5)	0.011(1)	-0.07(3)	-0.001(1)	0.021(2)
C(16)	0.458(1)	0.208(1)	0.5099(5)	0.040(3)	0.049(4)	0.0083(7)	-0.08(3)	-0.002(1)	0.015(1)

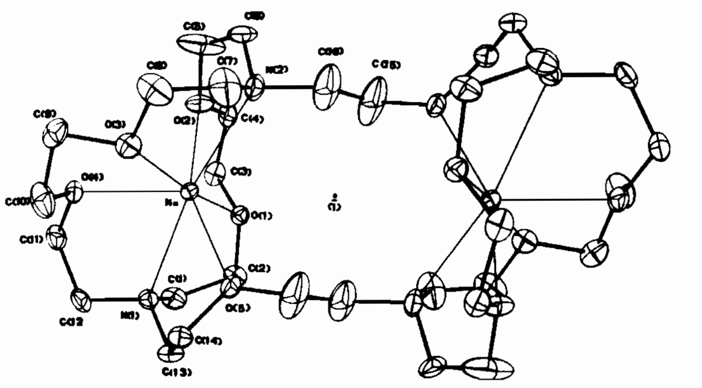

Figure 2. The $(Na_2 \subset L)^{2+}$ cation and the numbering scheme used.

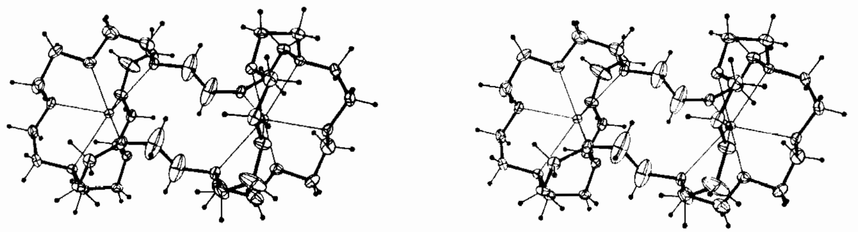

Figure 3. Stereoscopic view of the $(Na_2 \subset L)^{2+}$ cations.

TABLE II. Bond lengths (Å) in $[Na_2\subset L]I_2$ with esd's.

N(1)–C(1)	1.474(16)Å
C(1)–C(2)	1.486(17)
C(2)–O(1)	1.437(13)
O(1)–C(3)	1.452(12)
C(3)–C(4)	1.435(16)
C(4)–O(2)	1.391(18)
O(2)–C(5)	1.374(21)
C(5)–C(6)	1.485(23)
C(6)–N(2)	1.503(15)
N(2)–C(7)	1.490(20)
C(7)–C(8)	1.490(20)
C(8)–O(3)	1.429(17)
O(3)–C(9)	1.477(16)
C(9)–C(10)	1.500(18)
C(10)–O(4)	1.436(20)
O(4)–C(11)	1.433(17)
C(11)–C(12)	1.479(16)
C(12)–N(1)	1.461(11)
N(1)–C(13)	1.463(13)
C(13)–C(14)	1.473(17)
C(14)–O(5)	1.418(11)
O(5)–C(15)	1.433(12)
C(15)–C(16)	1.498(20)
C(16)–N(2)	1.471(13)
Na–O(1)	2.476(6)
Na–O(2)	2.399(13)
Na–O(3)	2.385(14)
Na–O(4)	2.471(12)
Na–O(5')	2.456(6)
Na–N(1)	2.690(7)
Na–N(2)	2.729(9)

$$\sigma(I) = [C + (t_c/t_b)^2 (B_1 + B_2) + (pI)^2]^{1/2}$$

where C is the scan count, B_1 and B_2 are background counts, t_c and t_b are respectively scan and background times, and p is an empirical coefficient of the net count I [5]. The factor p was given an initial value of 0.05. A total of 5721 independent reflections was recorded in the range $2\theta < 60°$. Only 1927 of these had $I > 3\sigma(I)$ and were retained. No absorption corrections were applied in view of the small crystal dimensions and linear absorption coefficient.

A three-dimensional Patterson map readily yielded the position of the iodide ions. The R factor at this stage was 0.53. A Fourier map computed using these positions revealed the coordinates of all other non-hydrogen atoms.

In all structure factor calculations, the atomic scattering factors used were those tabulated by Moore [6] using Pepinsky's modifications. The effects of anomalous dispersion were included for the I^- anions and Na^+ cations; the values of $\Delta f'$ and $\Delta f''$ are those given in the "International Tables for X-ray Crystallography" [7]. Atomic coordinates and individual anisotropic thermal parameters were refined by full-matrix least-squares using the program SFLS-5 [8]. In all least-squares computations, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The weight w was taken as $1/\sigma^2(F_o)$. A p value of 0.08 was used in the last cycles of refinement. The refinement converged to a discrepancy factor $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ equal to 0.057 and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ equal to 0.064. The standard deviation of a unit weight observation was 1.2.

A Fourier difference map computed at this stage revealed electron density concentration close to the calculated positions for hydrogen atoms (C–H: 1 Å, C–C–H: 109.5°) which were then fixed in these calculated positions with isotropic temperature factors derived from the expression $B_H = 1.6\ B_C - 2.0$ [9]. No other peaks higher than $0.4 e Å^{-3}$ were detected. All computations were carried out on a Univac 1108 computer. Other programs used were ORTEP for drawings [10] and local programs for Fourier calculations.

Results and Discussion

The crystal structure of $Na_2\subset L)I_2$ consists of complex cations $(Na_2\subset L)^{2+}$ and iodide ions I^-. The geometry of the centrosymmetric cations together with the numbering system used for the independent atoms is shown in Figure 2. The positional and thermal parameters are given in Table I. A stereoscopic view of $(Na_2\subset L)^{2+}$ is shown in Figure 3.

Two sodium cations are completely enclosed within the ligand L. Each metal ion interacts with seven heteroatoms of L, two nitrogens and five oxygens. Ligand L may be considered as formed by two diazatetraoxacyclooctadecane rings (22) linked together by two $-CH_2-CH_2-O-CH_2-CH_2-$ chains. The two nitrogen atoms and four of the five oxygen atoms interacting with one sodium ion belong to one (22) cycle. The fifth oxygen atom linked to sodium belongs to one of the two other chains. The (22) macrocycle is itself able to form complexes with alkali metal cations as well as transition metal ions [11].

The coordination polyhedron of the Na^+ ions has an irregular shape as is often observed in complexes or inclusion compounds of alkali metal cations. It is most conveniently described as a distorted capped trigonal prism, formed by N(1), O(1), O(5), N(2), O(2) and O(3). The O(1) O(2) O(3) N(1) face of the trigonal prism is capped by O(4).

Bond distances and bond angles within the $(Na_2\subset L)^{2+}$ cation are given in Tables II and III. The Na–N distances of 2.70(1) and 2.73(1)Å are in the range of those reported for the sodium [2]-cryptates,

TABLE III. Bond angles (°) in $[Na_2{\subset}L]I_2$ with esd's.

N(1)–C(1)–C(2)	113.28(0.92)°
C(1)–C(2)–O(1)	110.87(0.88)
C(2)–O(1)–C(3)	115.81(0.85)
O(1)–C(3)–C(4)	109.35(0.75)
C(3)–C(4)–O(2)	106.91(0.99)
C(4)–O(2)–C(5)	119.54(1.42)
O(2)–C(5)–C(6)	115.79(1.62)
C(5)–C(6)–N(2)	121.06(1.45)
C(6)–N(2)–C(7)	129.05(1.28)
N(2)–C(7)–C(8)	112.60(1.11)
C(7)–C(8)–O(3)	109.00(1.25)
C(8)–O(3)–C(9)	109.26(1.14)
O(3)–C(9)–C(10)	97.18(1.06)
C(9)–C(10)–O(4)	104.42(1.11)
C(10)–O(4)–C(11)	114.71(1.16)
O(4)–C(11)–C(12)	112.38(1.07)
C(11)–C(12)–N(1)	111.28(0.88)
C(12)–N(1)–C(13)	109.54(0.88)
N(1)–C(13)–C(14)	111.19(0.87)
C(13)–C(14)–O(5)	114.17(0.87)
C(14)–O(5)–C′(15)	125.28(0.92)
N(2)–C(16)–C(15)	121.26(1.03)
C(16)–C(15)–O′(5)	104.62(0.91)
C(13)–N(1)–C(1)	112.16(0.93)
C(12)–N(1)–C(1)	112.15(0.86)
C(6)–N(2)–C(16)	107.69(1.08)
C(7)–N(2)–C(16)	99.16(1.05)

(Na⊂222)I [12] and (Na⊂222)Na [13] where (222) represents the bicyclic ligand diazahexaoxobicyclo-octadecane.

The metal oxygen distances, which range from 2.39(1) to 2.48(1)Å with a mean value of 2.44(1)Å are comparable to those reported for several sodium polyether complexes [14]. These distances are smaller than those found in the [2] cryptate cation $(Na{\subset}222)^+$ [12, 13], in which the Na–O bonds have a mean value of 2.58(2)Å.

It has been shown recently that the cavity size strongly affects the stability constant of the cryptate. The optimal cation for a bicyclic ligand is the one which gives rise to metal–oxygen and metal–nitrogen distances very close to the sum of the ionic radius of the cation, and the Van der Waals radius of oxygen or nitrogen [15] (2.40 and 2.50 Å for $Na^+\cdots O$ and $Na^+\cdots N$ respectively [16]). The Na–O distances found in $(Na_2{\subset}L)^{2+}$, thus indicate that L is able to adopt a conformation presenting two cavities which are better adapted for the sodium cation than is the cavity in the bicyclic ligand (222).

An examination of the dihedral angles of the C–C bonds linking together the oxygen and nitrogen atoms interacting with one sodium cation leads to the same conclusion (see Table IV). In $(Na_2{\subset}L)^{2+}$, only the dihedral angle of C(5)–C(6) has a value (–34.3°) distinctly different from 60°. The mean value of the dihedral angles for the other three C–C bonds is 62.4°. In contrast the mean value of the C–C dihedral angles in $(Na{\subset}222)^+$ is 48° [12, 13].

TABLE IV. Dihedral angles (°) in $[Na_2{\subset}L]I_2$ with esd's. Primed atoms are related to their equivalent non primed by the center of symmetry at (1/2 0 1/2).

N(1)–C(1)–C(2)–O(1)	– 60.63(0.71)°
O(1)–C(3)–C(4)–O(2)	– 63.06(0.65)
O(2)–C(5)–C(6)–N(2)	– 34.28(1.36)
N(2)–C(7)–C(8)–O(3)	56.60(0.92)
O(3)–C(9)–C(10)–O(4)	– 76.74(0.68)
O(4)–C(11)–C(12)–N(1)	– 57.93(0.75)
N(1)–C(13)–C(14)–O(5)	– 64.53(0.69)
N(2)–C(16)–C(15)–O′(5)	–172.99(0.53)
C(12)–N(1)–C(1)–C(2)	159.24(0.54)
C(13)–N(1)–C(1)–C(2)	– 77.00(0.67)
C(14)–C(13)–N(1)–C(1)	143.87(0.54)
C(14)–C(13)–N(1)–C(12)	– 90.91(0.61)
C(13)–N(1)–C(12)–C(11)	152.44(0.54)
C(1)–N(1)–C(12)–C(11)	– 82.35(0.62)
C(7)–C(8)–O(3)–C(9)	–163.27(0.68)
C(5)–C(6)–N(2)–C(16)	140.87(0.88)
C(6)–N(2)–C(7)–C(8)	61.82(1.07)
C(16)–N(2)–C(7)–C(8)	177.89(0.72)
C(6)–N(2)–C(16)–C(15)	– 62.81(0.81)
C(7)–N(2)–C(16)–C(15)	164.26(0.72)
C(1)–C(2)–O(1)–C(3)	– 72.96(0.66)
C(2)–O(1)–C(3)–C(4)	–174.15(0.50)
C(3)–C(4)–O(2)–C(5)	–176.23(0.78)
C(4)–O(2)–C(5)–C(6)	–104.51(1.04)
C(5)–C(6)–N(2)–C(7)	–109.37(1.05)
C(7)–O(3)–C(8)–C(10)	–170.40(0.61)
C(9)–C(1)–O(4)–C(11)	–166.06(0.64)
C(10)–O(4)–C(11)–C(12)	– 68.41(0.83)
C(16)–C(15)–O′(5)–C′(14)	–105.61(0.47)
C(13)–C(14)–O(5)–C′(15)	–118.52(0.52)

TABLE V. Selected C–H•••H–C distances (Å) in $[(Na_2{\subset}L)]I_2$ showing inaccessibility of the crypt.

H1C2–H2C16	2.74 Å
H1C2–HIC16	2.79
H1C7–H1C15	2.44
H1C7–H1C9	2.66
H1C7–H1C10	3.00
HIC8–H1C14	2.50
H1C8–H1C10	3.00
H2C14–H2C15	2.27
H1C15–H2C16	2.67
HIC16–H2CI3	2.72
H1C16–H1C2	2.79

It is worth noting that despite the more suitable cavities for Na^+ in $(Na_2{\subset}L)^{2+}$, the stability of this cation and the selectivity of the tricyclic ligand L are less marked compared with the [2]-cryptate cation $(Na{\subset}222)^+$ and bicyclic ligand (222) respectively [17, 18]. As the two cavities of L are not independent of each other, ligand L is not as rigid as ligand (222) and

TABLE VI. I•••H and C–H•••H–C packing distances (Å) in [Na_2CL]I_2 (less than 3.50 Å). Roman numbers refer to equivalent positions as listed in "International Tables for X-ray Crystallography".

I•••H2C7	3.28 Å	(III)
I•••H1C12	3.42	(IV)
I•••H1C2	3.49	(IV)
H1C1•••H1C3	2.64	(IV)
H1C1•••H1C11	3.17	(IV)
H1C1•••H2C9	3.32	(IV)
H1C1•••H2C4	3.36	(IV)
H1C1•••H2C10	3.37	(IV)
H2C1•••H2C9	3.24	(IV)
H1C2•••H2C4	2.28	(IV)
H2C2•••H1C3	3.09	(IV)
H2C2•••H1C4	3.49	(IV)
H1C3•••H1C1	2.64	(IV)
H2C9•••H2C12	3.10	(IV)
H2C2•••H1C12	3.15	(IV)
H2C3•••H1C12	3.15	(IV)
H2C4•••H1C11	2.54	(IV)
H2C4•••H1C12	3.42	(IV)
H2C4•••H2C10	3.42	(IV)
H2C4•••H2C12	3.49	(IV)
H1C5•••H1C11	2.59	(IV)
H1C5•••H2C11	3.38	(IV)
H2C5•••H1C11	2.72	(IV)
H2C5•••H2C11	2.85	(IV)
H2C5•••H2C12	3.11	(IV)
H2C9•••H2C12	3.38	(IV)
H1C11•••H1C13	3.04	(IV)
H1C11•••H2C12	3.43	(IV)
H2C11•••H2C12	2.76	(IV)
H2C11•••H2C13	2.77	(IV)
H2C11•••H1C12	3.32	(IV)

the macrobicyclic effect is therefore probably much weaker in L.

The separation between the two sodium ions accommodated within L is 6.40(2)Å. This relatively large distance is accompanied by a dihedral angle of 173° about the C(6)–C(15) bond which with its centrosymmetric counterpart holds together the two parts of L containing one metal ion each.

The space between the two metal ions is not accessible in the present conformation as is shown by the C–H•••H–C contacts (see Table V).

As in most of the monovalent but not in the divalent metal [2]-cryptates for which the structures are known, the anions in (Na_2CL)I_2 no longer interact with the metal cations. All the $Na^+ \cdots I^-$ separations exceed 5 Å.

The other structural features of this [3]-cryptate do not differ from those found in the structures of the [2]-cryptates [15]. The mean values for the C–C, C–O and C–N bonds are 1.480(19), 1.428(26). 1.477(15)Å. The shortest packing separations are given in Table VI.

References

1 Author to whom the correspondence should be addressed.

2 J. M. Lehn, J. Simon and J. Wagner, *Angew. Chem., 85,* 622 (1973). *Angew. Chem. Internat. Edit., 12,* 599 (1973).

3 W. R. Busing in "Crystallographic Computing", F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p. 319.

4 In order to improve the stability of the crystal mounting, a special head, comprising only three translations, is used currently in this lab., following an original design of W. Peter, E.T.H., Zürich, private communication.

5 O. W. R. Cornfield, R. J. Doedens and J. A. Ibers, *Inorg. Chem., 6,* 197 (1967).

6 F. M. Moore, *Acta Crystallogr., 16,* 1139 (1963) and V. Vand, P. F. Eiland and R. Pepinsky, *ibid., 10,* 303 (1957).

7 "International Tables for X-ray Crystallography", Vol. III, The Kynoch Press, Birmingham, England, 1962, p. 215.

8 C. T. Prewitt, a FORTRAN IV full-matrix crystallographic least-squares program, SFLS-5, 1966.

9 P. Goldstein, K. Seftaud and K. N. Trueblood, *Acta Crystallogr., B24,* 778 (1968).

10 C. K. Johnson, Program ORTEP-II, ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tenn. 1965.

11 M. Herceg and R. Weiss, *Bull. Soc. Chim. de France, 2,* 549 (1972).

12 D. Moras and R. Weiss, *Acta Crystallogr., B29,* 396 (1973).

13 F. J. Tehan, B. L. Barnett and J. L. Dye, *J. Am. Chem. Soc., 76,* 7203 (1974).

14 M. R. Truter, *Structure and Bonding, 16,* 71 (1973) and references therein.

15 D. Moras, B. Metz and R. Weiss, *Acta Crystallogr., B29,* 383 (1973); *B29,* 388 (1973); *B29,* 396 (1973); *B29,* 1059 (1973).

16 R. D. Schannon and C. T. Prewitt, *Acta Crystallogr. B25,* 303 (1969).

17 J. Chemey, J. M. Lehn, J. P. Sauvage and M. E. Stubbs, *Chem. Comm.,* 1100 (1972).

18 J. M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc., 97,* 6700 (1975).

19 "International Tables for X-ray Crystallography", Vol. I, The Kynoch Press, Birmingham, England, 1969, p. 99.