An Unusual Structure of the Hydrated Sodium Chloride Complex of Cryptand [2.2.2]

N. Kent Dalley* [a], Krzysztof E. Krakowiak [b], Jerald S. Bradshaw [a], Xiaolan Kou [a] and Reed M. Izatt [a]

[a] Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, USA

[b] IBC Advanced Technologies, Inc., P.O. Box 98, American Fork, Utah 84003, USA

Received April 18, 1995

The solid state structure of the Na[2.2.2]Cl•3H_2O complex has the sodium ion displaced towards one of the cryptand nitrogens and the chloride and water molecules associated by hydrogen bonds to form a pseudo cube with two chloride ions at opposite corners of the cube and water oxygens at the other six corners.

J. Heterocyclic Chem., **32**, 1201 (1995).

Introduction.

The first alkali cation-[2.2.2]-cryptates reported in the early 1970s exhibit similar structures in the solid state [1] and illustrate interesting trends as a function of cation diameter. The common features of these compounds in which the anion is a small univalent species are that the metal ion and the nitrogen atoms lie on a 3-fold axis with the three triethyleneoxy branches linking the nitrogen atoms being related by the 3-fold symmetry. The anion lies on a different 3-fold axis. The host conformation changes corresponding to different cations are observed using several parameters including the N...N interatomic distance, the cation to donor atom interatomic distances and the torsion angles of the three-dimensional ligand. Examination of the M-O interatomic distances and the torsion angles of the host for the alkali cation-[2.2.2] cryptates indicates that the potassium-cryptate exists in a least strained state with the cation-donor atom distances being approximately equal to the sum of the radii of the cation and donor atoms and the torsion angles being approximately equal to the expected low energy values for O-C-C-O of 60° (*gauche*) and for C-O-C-C of 180° (*trans*) [1]. Cryptates of the other alkali metal ions illustrate expected conformational changes that the host makes in order to accommodate the smaller cation, Na^+, and the larger cations, Rb^+ and Cs^+. Cryptates of Li^+ with [2.2.2] do not form, probably because of the small radius of Li^+. It is apparent that Na^+ is also small for the [2.2.2] cavity as the Na-O (2.57 and 2.58Å) and Na-N (2.75 and 2.78Å) distances are longer than the sum of the radii of Na and O (2.42Å) and Na and N (2.52Å) [1,2]. Using the same reasoning, Rb^+ and Cs^+ are too large for the host. The cation size trend is also reflected in the N...N distances in the complexes which are 5.50, 5.75, 6.01 and 6.07Å [1] for the Na^+, K^+, Rb^+ and Cs^+ complexes, respectively. It is interesting that K^+, Rb^+ and Cs^+ lie at the midpoint of the line joining the two nitrogens but Na^+ is slightly displaced from that point.

The small displacment of Na^+ (0.03Å) from the center of the Na[2.2.2]I complex can be accounted for by the small radius of the cation. A similar small displacement was expected in the Na[2.2.2]Cl cryptate. However, a much greater displacement was found. We now report the solid state structure of Na[2.2.2]Cl•3H_2O in which the Na^+ is significantly displaced from the center of the host. The original purpose of this X-ray study was to verify that the product of the synthesis of [2.2.2] which was isolated by alumina chromatography [3] was the desired product. The crystallization of Na[2.2.2]Cl was not expected. The unsymmetrical position of the Na^+ and the role of the waters in the formation of an aggregate anion were also not expected but they are of interest.

Results and Discussion.

Figure 1 shows the conformation of the cation and the atom labels. The atomic positional and thermal parameters are listed in Table 1. Bond lengths and angles are contained in Table 2. The cryptate and the Cl^- lie on three fold axes. However, since the water is not on a three fold axis, there are three symmetry related waters for each Na[2.2.2]Cl unit. The formulation of the compound is

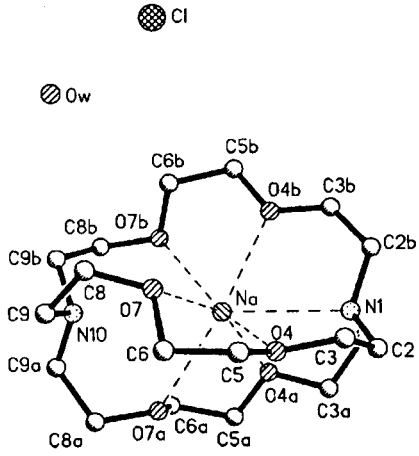


Figure 1. Conformation of Na[2.2.2]Cl•3H_2O with two of the symmetery related water molecules omitted for clarity.

Table 1

Atomic Positional Coordinates (x10⁴) and Equivalent Isotropic Displacement Coefficients (Å² x 10³) for the Cryptate

	x	y	z	U(eq) [a]
Na	6667	3333	4032(2)	46(1)
Cl	0	0	2680(2)	86(1)
N1	6667	3333	6546(3)	35(1)
C2	7505(3)	2775(3)	6946(2)	44(1)
H2A	7330	2532	7781	43(7) [b]
H2B	8435	3462	6872	43(8) [b]
C3	7287(3)	1569(3)	6227(2)	44(1)
H3A	6370	856	6320	44(8) [b]
H3B	7873	1251	6504	32(7) [b]
O4	7549(2)	1949(2)	4991(2)	41(1)
C5	7552(3)	903(3)	4292(2)	46(2)
H5A	6780	48	4491	42(8) [b]
H5B	8352	859	4461	44(8) [b]
C6	7503(3)	1192(3)	2986(3)	45(2)
H6A	7588	554	2487	35(7) [b]
H6B	8233	2080	2804	53(9) [b]
O7	6238(2)	1133(2)	2766(2)	44(1)
C8	5848(3)	917(3)	1531(3)	48(2)
H8A	4927	711	1470	51(9) [b]
H8B	5895	151	1242	34(7) [b]
C9	6701(3)	2123(3)	739(2)	45(2)
H9A	6399	1924	-81	46(8) [b]
H9B	7616	2308	769	26(6) [b]
N10	6667	3333	1130(3)	40(1)
Ow	1985(3)	-292(3)	824(2)	84(2)
H1	1394	-740	277	77(13) [b]
H2	1551	23	1266	149(2) [b]

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] Isotropic U value.

$[Na(C_{18}H_{36}N_2O_4)]$ Cl•3H_2O. The most significant structural feature of the cryptate is the large displacement of the Na^+ (0.216 Å) from the midpoint of the line joining N1 and N10. The Na-donor atom interatomic distances are shown in Table 3. These data show that the Na^+ is also significantly closer to O4 than to O7. The torsion angles for the ligand are listed in Table 4. There is one torsion angle, C6-O7-C8-C9, which deviates significantly from the expected *trans* value while the other values are normal. While the chloride ions do not interact with the Na^+,

Table 2

Bond Length and Angles for the Cryptate

1	2	3	1-2Å	1-2-3°
C2	N1	C2A	1.462(4)	111.2(2)
N1	C2	C3		113.3(2)
C2	C3	O4	1.503(5)	108.6(2)
C3	O4	C5	1.427(3)	110.8(2)
O4	C5	C6	1.428(4)	109.0(3)
C5	C6	O7	1.495(4)	107.6(3)
C6	O7	C8	1.436(5)	113.1(2)
O7	C8	C9	1.426(3)	113.5(2)
C8	C9	N10	1.512(4)	112.3(3)
C9	N10	C9A	1.470(4)	111.6(2)

Table 3

Interatomic Distances Between Na^+ and Donor Atoms of the Ligand

1	2	1-2Å
Na	N1	2.792(4)
Na	O4	2.502(3)
Na	O7	2.705(2)
Na	N10	3.223(4)

they are rather close to the cryptate. This will be discussed later. Each chloride is hydrogen bonded to three symmetry related waters through one hydrogen of each water. The second hydrogen of each water is hydrogen bonded to a water molecule of another $Cl(H_2O)_3^-$ unit which is related to the first unit by a center of symmetry. The resulting large water-chloride anion is shown in Figure 2. Hydrogen bond data are listed in Table 5.

Table 4

Torsion Angles in the Cryptate

1	2	3	4	1-2-3-4(°)
C2A	N1	C2	C3	-159.6(2)
C2B	N1	C2	C3	75.9(4)
N1	C2	C3	O4	57.5(3)
C2	C3	O4	C5	171.4(3)
C3	O4	C5	C6	166.8(2)
O4	C5	C6	O7	-64.3(3)
C5	C6	O7	C8	-159.2(2)
C6	O7	C8	C9	-70.9(4)
O7	C8	C9	N10	-58.3(4)
C8	C9	N10	C9A	155.4(3)
C8	C9	N10	C9B	-78.8(4)

The unexpected presence of the waters in the crystal of the Na[2.2.2]Cl complex results in the formation of a multiatom divalent anion. This aggregate (see Figure 2) consists of eight nonhydrogen atoms which form a pseudo cube approximately 3.1 x 3.1 x 3.1 Å. The atoms are not held together by covalent bonds, but the hydrogen bonds give the polyhedron structural integrity.

It is not unusual for the Na^+ to be significantly displaced from the center of [2.2.2] when the anion consists of several atoms. There are several examples of this in the literature because when studying the structures of complex anions, Na[2.2.2]$^+$ is often the cation of choice. When Na^+ is encapsulated in a three dimensional cape, it

Table 5

Hydrogen Bond Data for the Hydrated Anion

D	H	A	H...AÅ	D...AÅ	D-H...Å deg
OW	H1	OW sym	2.22	3.063	167
OW	H2	Cl	2.360	3.207	158

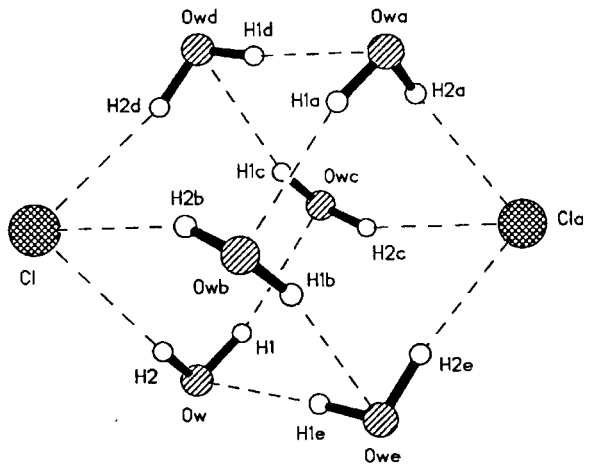


Figure 2. The pseudo-cubic $Cl_2(H_2O)_6^{2-}$ aggregate ion.

will not distort the anion of interest. Table 6 lists representatives of these structures. In some, the cryptate lies on a three-fold axis. However, some cations are distorted so much by the large anions that they lose their three-fold symmetry.

The complexes listed in Table 6 show that in the presence of large multi-atom anions, the complex cation is often distorted. The distortion is usually attributed to the strain of the host caused by complexing a guest significantly smaller than its cavity [4,7]. However, it should be noted that while Na^+ is not exactly at the center of the host in the Na[2.2.2]I complex, the donor atoms are arranged essentially symmetrically about the cation (see Table 6). This suggests that cation radius is not the only factor causing unsymmetric complexation. The large multiatom anions in the compounds listed in Table 6 do not interact with the Na^+ but they do approach the cryptand which suggests packing forces are also a factor in distorting the host. The chloride ions in the title compound are approximately 7 Å from the Na^+. However, water molecules of the aggregate anion do approach C9 atoms of the ligand. The OW-H92 interatomic distance is 3.08 Å. It is significant that the only unusual torsion angle in the ligand is the C6-O7-C8-C9 torsion angle which is –70.9° rather than the expected *trans* value (see Table 4). These atoms join N10, the nitrogen farthest from the Na^+. Evidence supporting the role of packing forces in the distortion of these cryptates is found in reference [4] which contains structures of four crystallographically different cryptates. The complex cation which has the shortest Na^+-anion distance (6.01 Å and 0.44° shorter than any other similar interaction) is the most distorted cation while the other three are more normal [4].

Table 6

Some Examples of Distorted $Na[2.2.2]^+$ Cations

Complex	Na-X range (Å)	Reference
$(Na[2.2.2])_4Sb_9$ [a]	Na-N 2.90-2.93 Na-O 2.47-3.30	[4]
$(Na[2.2.2])_2As_2Se_2$ [b]	Na-N 2.81-3.18 Na-O 2.48-2.51	[5]
$(Na[2.2.2])_2Pb_5$ [c]	Na-N 2.66-3.23 Na-O 2.48-2.66	[6]
$Na[2.2.2]Sn_5$ (1)	Na-N 2.91-3.01 Na-O 2.56-2.65	[6]
(2)	Na-N 2.66-3.43 Na-O 2.43-2.63	[6]
$(Na[2.2.2])_3Sb_7$ [c,d]	Na-N 2.83-2.94 Na-O 2.40-2.71	[7]
$Na[2.2.2]\ [CO_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO_2)]$	Na-N 2.665-2.957 Na-O 2.558-2.674	[8]
$(Na[2.2.2])_2\ [Fe_2(CO)_6(\mu_2\text{-}PPh_2)]$	Na-N 2.693-3.142 Na-O 2.497-2.748	[9]
$Na[2.2.2]Cl{\cdot}3H_2O$ [c]	Na-N 2.792-3.223 Na-O 2.502-2.705	this paper
Na[2.2.2]I [c]	Na-N 2.722-2.782 Na-O 2.566-2.582	[2]

[a] Data given for only the most distorted cation. [b] Only 5 Na-O distances listed in paper. [c] Cation lies on 3-fold axis. [d] Data given for only one of the similar cations.

Table 7

Summary of the Crystal Data and Experimental Conditions

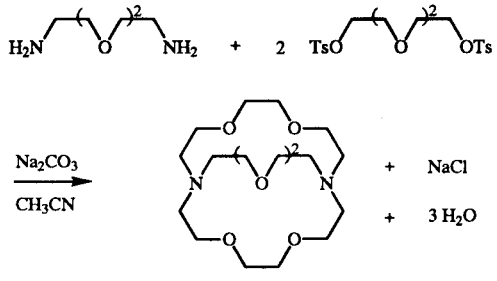
Formula	$[Na(C_{18}H_{36}N_2O_6)]Cl{\cdot}3H_2O$
Formula weight	489
F(000)	528
Crystal Size, mm	0.26 x 0.30 x 0.32
μ, mm^{-1}	0.19
Space group	$P\bar{3}$
Crystal system	Trigonal
a,Å	11.444(3)Å
c,Å	11.106(3)Å
Volume, $Å^3$	1254.2
Z	2
Density, calc. Mg/m^2	1.295
2θ range, deg	4.0 to 55.0
Independent data	1938
Observed data	1043 ($F>6.0\ \sigma(F)$)
Data/parameter ratio	9.5:1
R	4.63%
R_w	5.59%
Weighting Scheme	$w^{-1} = \sigma(F)^2 + 0.0003F^2$
Extinction Correction	$X = 0.0038(9)$, where $F^* = F[1 + 0.002XF^2/\sin(2\theta)]^{-1/4}$
Goodness of fit	1.96
Largest peak in difference map $eÅ^{-3}$	0.43
Largest hole in difference map $eÅ^{-3}$	-0.30

Finally, if packing forces are important in distorting the solid state cryptate, the distortions should not be present when the complex is in solution. In fact, the interactions between the Na^+ and the donor atoms of [2.2.2] would be similar and therefore, in the solution state, the conformation of [2.2.2] in the complex should be similar to the uncomplexed [2.2.2] molecule in the solution state. This is the case

as the ^{13}C nmr spectra of [2.2.2] and the title compound in the solution state are similar in that no additional signals for carbon atoms were observed in the spectrum of the complex.

EXPERIMENTAL

The $Na[2.2.2]Cl \cdot 3H_2O$ complex was isolated during the one-step synthesis [3] of [2.2.2] using sodium carbonate as the base/template in acetonitrile according to the following reaction.



1,8-Diamino-3,6-dioxaoctane (1.48 g, 0.01 mole), 9.25 g (0.021 mole) of triethylene glycol ditosylate and 20 g of sodium carbonate were stirred under reflux in 250 ml of acetonitrile for 6 days. The solvent was evaporated and 100 ml of dichloromethane was added. This mixture was filtered and the solvent was evaporated. The residue was chromatographed on 120 g of activated alumina (Aldrich, Brockmann I, neutral, 150 mesh) using acetonitrile/ethanol, 50/1 as the eluant to give 2.4 g of solid, mp 89°-92°; ^1H nmr: δ 1.8 (s, 6 H, disappeared in deuterium oxide), 2.7 (t, 12 H), 3.7 (m, 24 H); ^{13}C nmr: δ 53.3, 68.1, 69.1. This solid complex was chromatographed on silica gel using methanol/ammonium hydroxide, 50/1, 20/1, 10/1 as the eluants to give free cryptand [2.2.2]; ^{13}C nmr: δ 56.7, 70.3, 71.4.

A suitable crystal of the sodium complex was mounted on a Siemens R3m/V automated diffractometer which utilized Mo-Kα radiation (λ = 0.71073 Å). Crystal data and the orientation matrix for the solid were obtained using a least squares procedure involving several carefully centered reflections. The crystal data along with structure determination data are included in Table 7. Single crystal intensity data were collected using a θ-2θ scan mode. The trial structure was obtained using direct methods and refined using a full-matrix least-squares procedure. As expected, the complex was oriented about a three fold axis with the nitrogens and the cation on the axis. The Cl^- was located on another three fold axis and did not interact with the complex cation. Difference maps indicated that the structure contained a water of solvation located near the Cl^- but not on a three fold axis. Positions for hydrogen atoms of the ligand were calculated and refined using a riding model for the hydrogens. The water hydrogens were located in a difference map and were allowed to ride on the water oxygen in the refinement. Non-hydrogen atoms were refined anisotropically while hydrogen atoms were refined isotropically. The programs used in the solution, refinement and display of the structure are contained in the SHELXTL-PLUS™ program package [10]. Atomic scattering factors are those found in the International Tables of X-ray Crystallography [11].

Acknowledgement.

This work was supported by U.S. Department of Energy, Chemical Sciences Division, Office of Basic Energy Sciences, Contract No. DE-FGO2-86ER 13463.

REFERENCES AND NOTES

[1] M. Dobler, Ionophores and their Structures, John Wiley and Sons, New York, 1981 Chapter 8, pp 177-197.

[2] P. D. Moras and R. L. Weiss, *Acta Crystallogr.*, **B29**, 396 (1973).

[3] K. E. Krakowiak, P. A. Krakowiak and J. S. Bradshaw, *Tetrahedron Letters*, **34**, 777 (1993).

[4] J. D. Corbett and P. A. Edwards, *J. Am. Chem. Soc.*, **99**, 3313 (1977).

[5] C. H. Belin and M. M. Charbonnel, *Inorg. Chem.*, **21**, 504 (1982).

[6] P. A. Edwards and J. D. Corbett, *Inorg. Chem.*, **16**, 903 (1977).

[7] D. G. Adolphson, J. D. Corbett and D. J. Merryman, *J. Am. Chem. Soc.*, **98**, 7234 (1976).

[8] L. M. Cirjak, R. E. Ginsburg and L. F. Dahl, *Inorg. Chem.*, **21**, 940 (1982).

[9] R. E. Ginsburg, R. K. Rothrock, R. G. Finke, J. P. Collman and L. F. Dahl, *J. Am. Chem. Soc.*, **101**, 6550 (1979).

[10] G. M. Sheldrick, SHELXTL-PLUS™, Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, 1990.

[11] J. A. Ibers and W. C. Hamilton, eds, International Tables for X-ray Crystallography, Vol **4**, Kynoch Press, Birmingham, England, 1974, p 89.