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CRYSTAL STRUCTURE OF THE CRYPTAND [3.3.3] - POTASSIUM IODIDE COMPLEX: A LARGE COORDINATION NUMBER FOR POTASSIUM ION

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Abstract. Cryptand [3.3.3] was prepared by a one-step process from 2 moles of 1,11-diiodo-3,6,9-trioxaundecane and 1 mole of 1,11-diamino-3,6,9-trioxaundecane in acetonitrile using potassium carbonate as the base. An X-ray crystal study of the KI-[3.3.3] complex shows that all cryptand donor atoms are directed towards the encapsulated K^+ . The K^+ ion is not midway between the two nitrogen atoms, but is 3.15 Å from one nitrogen and 3.37 Å from the other. The X-ray structure strongly suggests that potassium is coordinated by eleven donor atoms.

INTRODUCTION

Cryptands, particularly [2.2.2] and smaller, are useful complexing agents for metal cations.¹ Usually these three dimensional ligands complex a metal ion with the cation located at or near the center of the cavity and all the oxygen and nitrogen donor atoms participating in cation-donor atom interactions. Larger cryptands have been synthesized but because their cavities are large compared to the size of the cations, and their flexibility is large compared to that of the smaller cryptands, they are not good complexing agents.¹ Few structural or thermodynamic studies of these large ligands and their complexes have been performed. The largest cryptand complex studied by the X-ray diffraction method has been a $Ba(SCN)_2$ complex with [3.2.2].²⁻⁵ While there are many studies of the interaction of cations with the smaller cryptands,⁶⁻¹⁰ only one study of the interactions of the larger cryptands has been reported.¹¹ The large cryptands do not interact strongly with cations as compared to the smaller cryptands.^{12,13} We now report the preparation, crystallization and crystal structure of the KI complex of [3.3.3]. The structural study of this complex gives important information regarding the complexation of cations by large hosts and the organization of a large host by a relatively small cation. In addition, this complex is one of a few examples of a K^+ -complex in which the coordination number of K^+ is so large. The possible coordination number of a cation with this ligand is eleven. Even though the K-donor atom interatomic distances are significantly longer than found in complexes with smaller coordination numbers, it is likely that the coordination number of K^+ is eleven. Truter has pointed out that for alkali metal ion-polycyclic ether complexes, the maximum coordination number is usually observed.¹⁴ This results in M-donor atom interatomic distances that are longer than expected.

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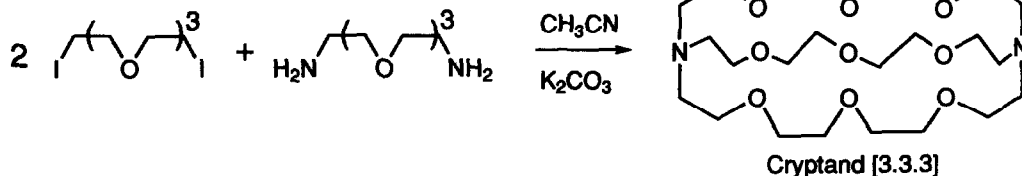
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RESULTS AND DISCUSSION

Cryptand [3.3.3] was prepared using a one-step process^{15,16} by treating 2 moles of 1,11-diiodo-3,6,9-trioxaundecane with one mole of 1,11-diamino-3,6,9-trioxaundecane as shown in Scheme I. It is interesting that when this material was chromatographed on alumina using a non-polar solvent, the potassium iodide complex of [3.3.3] was isolated. Treatment of the complex with a polar solvent on silica gel gave the free cryptand. The potassium iodide complex was carefully crystallized to give crystals suitable for X-ray crystal analysis.

Scheme 1. Preparation of Cryptand [3.3.3]



A computer drawing of the crystal structure of KI-[3.3.3] complex is shown in Figure 1. The positional and thermal parameters of the atoms are listed in Table 1. The figure shows that K^+ does organize the host to the extent that all the donor atoms are directed towards the K^+ . The molecule contains a 3-fold crystallographic axis with the nitrogen atoms of the ligand, the K^+ and the I lying on that axis. There is disorder in the carbon and oxygen chains which join the nitrogens. It was possible to resolve the disorder for C3 and O7 but some disorder exists that could not be resolved. The figure contains only the disordered atoms C3 and O7 in the more populated sites, (0.75), and in the discussion of complexation of K^+ by the ligand, only those atoms will be considered. As mentioned above, all of the donor atoms point into the cavity and the donor atom-C-C-donor atom torsion angles are as expected for complexation in these ligands with their absolute values ranging from 58° to 65° . The torsion angles are listed in Figure 1. Computer drawing of KI-[3.3.3] complex. Disordered atoms in less populated sites, C3' and O7' and hydrogen atoms are omitted for clarity.

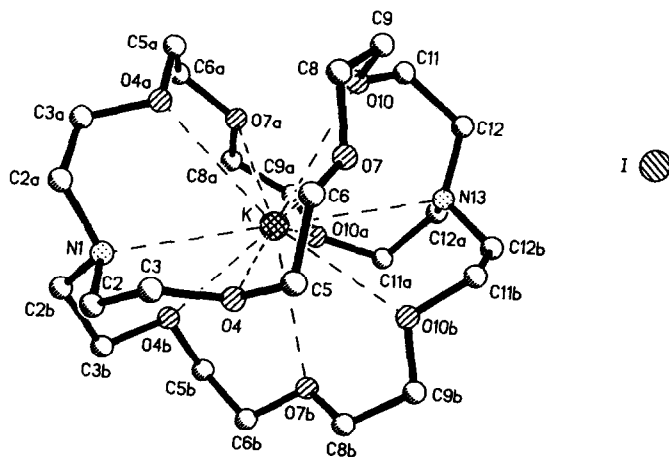


TABLE 1. Atomic Positional Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for the Cryptand

	<u>x</u>	<u>y</u>	<u>z</u>	<u>U(eq)^a</u>
K	0	0	5018(5)	46(1)
I	0	0	0	52(1)
N1	0	0	6992(10)	51(2)
C2	1034(10)	1071(9)	7346(6)	71(2)
H2A	1697	942	7295	80 ^b
H2B	929	1157	7931	80 ^b
C3	1339(14)	2202(8)	6910(5)	71(2)
H3A	2034	2838	7167	80 ^b
H3B	700	2366	6973	80 ^b
O4	1614(6)	2152(5)	6054(4)	51(2)
C5	1889(12)	3224(9)	5652(7)	93(2)
H5A	2406	3387	5180	80 ^b
H5B	2313	3856	6046	80 ^b
C6	866(9)	3348(8)	5405(7)	74(2)
H6A	1178	4087	5108	80 ^b
H6B	464	3409	5890	80 ^b
O7	163(7)	2528(10)	4794(7)	71(2)
C8	-1007(9)	2290(12)	4696(7)	72(2)
H8A	-933	3059	4633	80 ^b
H8B	-1511	1920	5171	80 ^b
C9	-1601(10)	1579(9)	3977(7)	57(2)
H9A	-1202	2007	3479	80 ^b
H9B	-2401	1435	3964	80 ^b
O10	-1632(6)	481(6)	3993(4)	50(2)
C11	-1927(10)	-125(11)	3223(9)	75(2)
H11A	-2435	105	2945	80 ^b
H11B	-2393	-971	3300	80 ^b
C12	-928(9)	208(11)	2646(6)	61(2)
H12A	-579	1019	2465	80 ^b
H12B	-1277	-283	2162	80 ^b
N13	0	0	2905(8)	33(2)
C3'	2013(12)	1812(16)	6761(9)	27(2) ^b
O7'	-205(12)	2304(12)	5282(11)	45(2) ^b

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

Table 2. The fact that several C—C—O—C torsion angles deviate significantly from the expected trans ($\sim 180^\circ$) value is evidence of the large flexibility of [3.3.3]. Because the cavity of [3.3.3] is so much larger than that of [2.2.2] and other smaller cryptands, K-O and K-N distances are much larger than the similar values found in the KI-[2.2.2] complex which range from 2.78 Å to 2.88 Å.³ In the KI-[3.3.3] complex, K-O distances range from 3.01 Å to 3.20 Å while the K⁺ ion is 3.15 Å from N1 and 3.37 Å from N13. The K-donor atom distances are found in Table 3. The average C-C and C-O distances are not unusual being 1.46(2) Å and 1.41(1) Å, respectively (Table 4).

The displacement of the cation towards one of the nitrogen atoms is unusual but has been noted in several cryptand complexes with large multi-atom anions¹⁷ and also, somewhat surprisingly, in a NaCl-[2.2.2]·H₂O complex.¹⁸ The weak K⁺-donor atom interactions, which are indicated by the large donor atom interatomic distances, are a result of the large flexible ligand with eleven donor atoms. Apparently a lower energy structure results when there are the maximum donor atom-K⁺ interactions even if they are weak, rather than when there are fewer but stronger K⁺-donor atom interactions. This is in agreement with the findings of Truter.¹⁴ The disorder of some atoms of the cryptand is due to the weak interactions between the cation and the donor atoms. The K⁺-donor atom attractive forces are not strong enough to completely organize the ligand into a rigid molecule such as the K⁺-[2.2.2] complex ion and so allows more than one conformation of the ligand to exist.

It is possible to evaluate the coordination of a metal ion by considering cation-donor atom interatomic distances and also by considering the relationship of the cavity of a ligand versus the size of the metal ion. Using either approach, the radii of the cation and donor atoms are a function of the coordination number of the cation. Both Shannon¹⁹ and Baur²⁰ attempted to obtain these values and have published radii of metal ions and donor atoms as a function of the type of coordination. Neither author considered eleven coordinate complexes so interpolated

TABLE 2. Torsion Angles in the KI-[3.3.3] Complex

<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>1-2-3-4(°)</u>
C2A	N1	C2	C3	-82(2)
C2B	N1	C2	C3	165(1)
N1	C2	C3	O4	-60(2)
C2	C3	O4	C5	180(1)
C3	O4	C5	C6	-80(1)
O4	C5	C6	O7	-65(1)
C5	C6	O7	C8	160(1)
C6	O7	C8	C9	171(1)
O7	C8	C9	O10	58(1)
C8	C9	O10	C11	-165(1)
C9	O10	C11	C12	86(2)
O10	C11	C12	N13	62(2)
C11	C12	N13	C12A	91(2)
C11	C12	N13	C12B	-142(1)

or extrapolated values must be used. Extrapolations of donor atom radii were made by extending the work of Fronczek and Gandour.²¹ Using these methods the radii for eleven coordinated K^+ is about 1.63\AA ¹⁹ while the radii for oxide and nitride are 1.45\AA and 1.60\AA ²⁰ respectively. Using these values the K–O and K–N interatomic distances of 3.05\AA and 3.20\AA compare favorable with those distances obtained in this study (see Table 3).

The second method to evaluate the coordination of a metal ion in a complex is to examine the relationship between the size of the guest-ion radius of the cavity²¹ and the size of the cation. Using the values for the radii of oxide and nitride discussed above, the guest-ion radius of the cavity of [3.3.3] is 1.61\AA . This compares well with the radius of the eleven coordinated K^+ which is about 1.63\AA . Other features of the structure which support a coordination number of eleven are the fact that all donor atoms are directed into the cavity and that the donor atom- K^+ -donor atom angles are approximately nearly equivalent ranging from 54.1° to 56.7° . It is of interest that the donor atom- K^+ -donor atom angles in a nine coordinated K^+ -diptychand compound also have values of about 56° .²²

In summary, the K^+ is coordinated by eleven donor atoms. This is shown (1) by the organization of the ligand by the cation, (2) by comparing the K^+ -donor atom distances found with those expected considering the coordination number of the cation, and (3) by comparing the cation size with the guest-ion radius of the cavity. It is also apparent from the long K^+ -donor atom distance and the disorder of the ligand that [3.3.3] does not form strong complexes with cations, a fact established earlier by Lehn and Sauvage.¹¹

TABLE 3. Interatomic Distances Between K^+ and the Ligand Donor Atoms

<u>1</u>	<u>2</u>	<u>1-2(Å)</u>
K	N1	3.15(2)
K	O4	3.01(1)
K	O7	3.20(1)
K	O7'	3.16(2)
K	O10	2.98(1)
K	N13	3.37(1)

EXPERIMENTAL

Preparation of Cryptand [3.3.3]. A mixture of 0.96 g (5 mmol) of 3,6,9-trioxa-1,11-undecanediamine (Texaco), 4.35 g (10.5 mmol) of 1,11-diiodo-3,6,9-trioxaundecane (prepared from the dichloro compound and NaI in acetone) and 15 g of K_2CO_3 was stirred at reflux temperature in 200 mL of CH_3CN for 72 h. The mixture was cooled and filtered and the residue was washed with 50 mL of CH_2Cl_2 . The filtrate was evaporated and the residue was mixed with 100 mL of THF/ethanol:50/1. After mixing for 2 h, the mixture was filtered to give 1.24 g (40%) of solid [3.3.3]-KI; mp $193-194^\circ C$; 1H NMR (δ): 2.6 (m, 12 H), 3.57 (t, 12 H), 3.65 (s, m, 24 H); ^{13}C NMR: 54.15, 67.11,

69.27, 69.42; MS: 509; MS(CI): 510. This material proved to be the KI complex of [3.3.3] as determined by the X-ray analysis. Pure [3.3.3] was isolated after silica gel chromatography using CH₃OH/NH₄OH:10/1 as the eluant. The ¹H NMR spectrum of pure [3.3.3] was the same as that reported.²³

TABLE 4. Bond Lengths and Angles for the KI-[3.3.3] Complex

<u>1</u>	<u>2</u>	<u>3</u>	<u>1-2 (Å)</u>	<u>1-3 (deg)</u>
C2	N1	C2A	1.48(1)	106.4(8)
N1	C2	C3		114.7(10)
N1	C2	C3'		116.8(10)
C2	C3	O4	1.49(2)	110.7(10)
C3	O4	C5	1.42(1)	109.7(9)
C3'	O4	C5	1.40(2)	136.7(9)
O4	C5	C6	1.41(1)	115.7(9)
C5	C6	O7	1.47(2)	112.8(11)
C5	C6	O7'		116.7(12)
C6	O7	O8	1.40(1)	118.1(12)
O7	C8	C9	1.40(2)	114.0(12)
O7'	C8	C9	1.40(2)	134.7(16)
C8	C9	O10	1.43(2)	111.9(11)
C9	O10	C11	1.41(2)	114.5(10)
O10	C11	C12	1.40(2)	115.4(8)
C11	C12	N13	1.47(2)	118.0(10)
C12	N13	C12A	1.42(2)	112.0(6)
C2	C3'	O4	1.48(2)	112.3(12)
C6	O7'	C8	1.39(1)	119.0(14)

X-ray Determination. Crystal data and intensity data were obtained using a Siemens R3m/V automated diffractometer utilizing Mo K α ($\lambda = 0.71073\text{Å}$) radiation. The lattice parameters and orientation matrix were calculated using a least-squares procedure involving 25 carefully centered reflections. Intensity data were obtained using a variable speed 2θ - θ scanning procedure. A summary of the experimental procedures and the single crystal data is found in Table 5.

The trial model of the compound was obtained using direct methods. The E-map gave positions for all the non-hydrogen atoms. As expected, the molecule lies on a three-fold axis. Two of the atoms, C3 and O7, were clearly disordered and it was possible to resolve the disorder using difference maps. The atoms in the more populated sites,

C3 and O7, were assigned population parameters of 0.75 based on the magnitude of peaks in the difference maps while C3' and O7' were assigned population parameters of 0.25. The C11 - C12 bond length suggested disorder in that portion of the molecule, but it was not possible to resolve that disorder. Positions for hydrogen atoms bonded to the carbon atoms (except for C3') were calculated and a riding model was used in the refinement process. All non-hydrogen atoms were refined anisotropically with the exceptions of C3' and O7' which were refined isotropically. Weights based on counting statistics were applied to the data. Atomic scattering factors were obtained from volume IV of The International Tables for X-ray Crystallography.²⁴ All programs used in solving, refining and displaying the molecule are contained in the program package SHELXTL-PLUS.²⁵

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TABLE 5. Crystal Data and Experimental Conditions Summary

Formula	[K(C ₂₄ H ₄₈ N ₂ O ₉)] ⁺ I ⁻
Formula weight	674.6
F(000)	1050
Crystal size, mm	0.12 x 0.32 x 0.40
μ , (mm ⁻¹)	1.21
Space group	R3
Crystal system	Rhombohedral
a, Å	12.994(2)
c, Å	15.966(2)
V, Å ³	2338.4
Z	3
D _x , g/cc	1.437
2 θ range, deg.	4.0 to 50.0
Independent data	1011 (R _{int} = 2.31%)
Observed data	952 (F > 4.0 σ (F))
Data/parameter ratio	7.9:1
R	0.048
R _w	0.074
Weighting scheme	w ⁻¹ = σ^2 (F) + 0.0064F ²
Goodness of fit	0.90
Largest peaks in difference map, eÅ ⁻³	0.80, -0.57

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