Tetrahedron Letters,Vol.28,No.16,pp 1753-1756,1987 0040-4039/87 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

MOLECULAR STRUCTURES OF 4,13-DIAZA-18-CROWN-6 DERIVATIVES HAVING GLYCYL-GLYCINE SIDEARMS: TWO POTASSIUM IODIDE COMPLEXES

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Abstract. Solid state structures are presented for two crystalline K^+ complexes of N,N'-bis(methyl glycidylglycidino)-4,13-diaza-18-crown-6. The two different complexes co-crystallize and both structures are fully resolved. The sidearm-K^+ interactions differ in each but in both cases the proximal (amide) carbonyl participates in cation binding while the distal (ester) carbonyl does not.

The molecule valinomycin is remarkable for its structure and complexing ability. It possesses twelve alternating amino and hydroxyacids in a macroring containing 36 atoms. The chirality about the macroring alternates from D,D- to L,L- and back.[1] The molecule favors K^+ over Na^+ by a ratio of 51,000:10 or about 5000:1 in anhydrous methanol solution.[2] When complexation between K^+ and valinomycin occurs, only the six ester donor groups solvate the cation[3] while the amide residues participate in hydrogen bonding which helps retain the "tennis ball seam" conformation.[4] The lariat ethers[5] were designed to mimic valinomycin in the sense that they are flexible molecules which are still capable of forming capsular[6] complexes. Most of the early work on the lariat ethers was designed to conclusively demonstrate macroring and sidearm cooperativity in cation binding. The results of ammonium ion binding,[7] ^{13}C NMR relaxation time studies,[8] and studies utilizing lanthanide shift reagents[9] all confirmed this principle. In addition, we recently presented the results of an extensive effort to obtain solid state structures of these complexes.[10] We are currently involved in a major effort to diversify the structural types within this class.

The syntheses and cation binding properties of 4,13-diaza-18-crown-6 derivatives having $-CH_2-CO-NH-CHR-CO-OCH_3$ sidearms are described in the accompanying paper.[11] These compounds have several features analogous to those of valinomycin. First, they contain a cation-binding macroring. Second, they are flexible macrocycles. Third, four carbonyl donor groups are available in the sidearms for cation binding, and each sidearm alternates an amide carbonyl with an ester carbonyl group. We have prepared N,N'-bis(methyl glycidylglycino)-4,13-diaza-18-crown-6 (**1**, diaza-18-crown-6 sidearms are $CH_2CONHCH_2COOCH_3$), the simplest of these molecules, and successfully crystallized the K^+ complex. We present here the results of X-ray structure analysis for **1**•K^+I^-.

The KI complex of **1** (mp 42-43 °C, see preceding paper) crystallizes with equal numbers of two

independent complex cations; one contains a crystallographic twofold symmetry axis ($\mathbf{1}_2$) and one is centrosymmetric ($\mathbf{1}_c$). Stereoviews of both complexes are shown in Figure 1. The twofold symmetric complex has unprimed labels while those of the centrosymmetric complex are primed. In both complexes, the macroring is in a D_{3d} conformation with one sidearm above and one below the macroring. In the twofold symmetric complex, the potassium ion lies approximately on the line connecting the two macroring nitrogens as well as on a line connecting O1 and O2, but the O3-K-O3 angle is 157.4(1)°. In the centrosymmetric complex, the potassium lies on the inversion center, on all lines connecting donors with their symmetric counterparts. Because the iodide ions are not coordinated to the metal ions, K^+ is octacoordinated in both complexes.

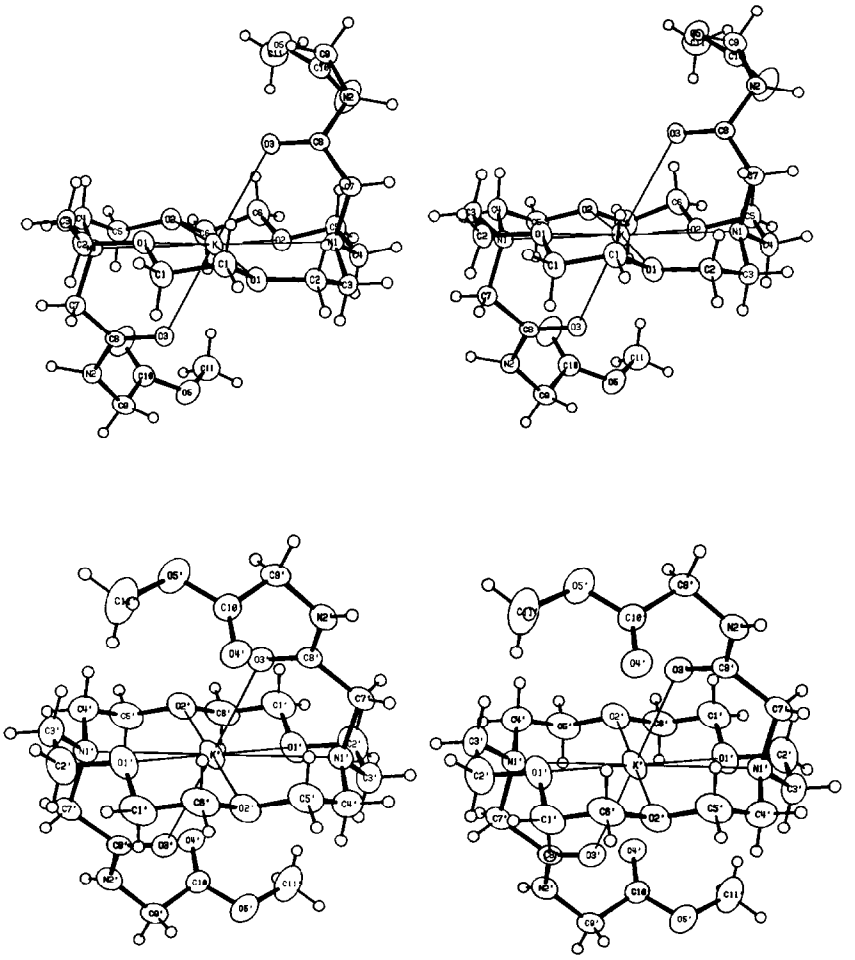

Figure 1. Stereoviews of $\mathbf{1}_2$ (top) and $\mathbf{1}_c$ (bottom).

The most significant differences between the two complexes are observed in the sidearms. As viewed in Figure 1, both sidearms in the twofold symmetric complex coil to the back. In the centrosymmetric complex, the sidearm on the bottom coils to the back while the sidearm on top coils to the front. The biggest difference is the potassium donor distance: K-O3, 2.841(3) Å vs. K'-O3', 2.638(3) Å. Consequently, the centrosymmetric complex has a smaller cavity (R = 1.375 Å) than the twofold symmetric complex (R = 1.411 Å). The angles for complexation by the amide carbonyl are similar: K-O3-C8, 121.0(2)° vs. K'-O3'-C8', 125.8(2)°. The potassium ion does not lie in the plane of the carbonyl in either complex. For the twofold symmetric complex, the torsion angle K-O3-C8-C7 is -18.0° and the metal ion lies on the si face of both carbonyl groups. On the other hand, in the centrosymmetric complex, the metal ion is farther out of plane; K'-O3'-C8'-C7' is 32.0°, and is located on the si face of one carbonyl and on the re face of the other. Except for the sign changes in the torsion angles of the peptide sidearms, only C3-N1-C7-C8 differs greatly: -137.3° in the centrosymmetric complex; -157.5° in the twofold symmetric complex.

The crystallization of the two independent complexes of different symmetry points out the difference in chirality in the complexed form. The twofold symmetric complex is chiral and both enantiomers are present, while the centrosymmetric complex is achiral. This phenomenon is likened to the situation where there is no stereoselectivity in the formation of diastereomers of which one diastereomer is a meso compound.

The complexes exhibit a topography similar to that observed for the related 18-membered macrocyclic BiBLE having 2-oxabutyl sidearms[10] and to that observed by others for the complexation of copper ion with carboxylatomethyl sidearms.[13] This anti binding, one arm on top and the other on the bottom, is probably the preferred topography for cations with radii equal to or larger than that of K^+. The only exception thus far observed is the cryptate-like topography of the potassium complex of the BiBLE having 2-hydroxyethyl sidearms.[10]

The poorer binding of potassium cation to **1** than to BiBLEs having ethereal or hydroxylic oxygens as donors on the sidearms is not apparent from the crystal structures. This may be due to conformational factors and there is a possibility of intramolecular hydrogen bonding from the amide nitrogens to the oxygen atoms of the macroring. We hope to report the crystal structure of uncomplexed **1** in the near future.

Acknowledgments. We warmly thank the NIH for grants (GM-29150, GM-31846, GM-36262) which supported this work.

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