Crown Inclusion Compounds with 3,4-Diamino-1,2,5-Oxadiazole. X-ray Structures of Its 1:1 Inclusion Complexes with 15-Crown-5 and Benzo-15-crown-5 *

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Abstract

The X-ray crystal structures of two closely related molecular complexes of 15-crown-5 and benzo-15-crown-5 with 3,4-diamino-1,2,5-oxadiazole are reported (I and II). Both complexes are of 1:1 stoichiometry with the host–guest alternation in the infinite chains formed due to the unsymmetrical H-bonding patterns between the components. Crystals of I are monoclinic, \( P2_1/c \), \( a = 7.856(3) \), \( b = 12.994(1) \), \( c = 16.033(1) \) Å, \( \beta = 94.79(2) \)°, \( Z = 4 \), final R-factor is 0.0488. Crystals of II are orthorhombic, \( P2_12_12_1 \), \( a = 8.260(4) \), \( b = 15.692(5) \), \( c = 13.955(7) \) Å, \( Z = 4 \), final R-factor is 0.0522.

Introduction

Many complexes that incorporate 15-crown-5 and benzo-15-crown-5 ligands cover a wide range of over 30 metal cations as a search of the Cambridge Structural Database (version 5.19) [1] reveals. Both crowns form 1:1 complexes with Na\(^+\) [2] and 2:1 complexes with K\(^+\), Ba\(^{2+}\) [3–4], Ag\(^+\) [5] etc. For the transition elements two main types of complexes, with direct metal to crown interactions and those with the crown ether oxygens bound to the metal via a bridging water and OH···O hydrogen bonds [6] (second sphere coordination) have been reported. These two types have been also found in one structure [7], where each Li\(^+\) ion from the \([\text{Li}_2(\text{H}_2\text{O})_2(\text{benzo-15-crown-5})_3]^{2+}\) cation is coordinated to one benz-15-crown-5 and one water molecule, and, in their turn, each of the two water molecules is H-bonded to the third crown molecule. The area of host–guest complexes between 15-membered crown ethers and neutral H-donor molecules is not extensively studied due to the components being sterically or symmetry mismatched, resulting in subtle, unsymmetrical hydrogen bonding patterns. In the 1:1 complexes of 15-crown-5 and benzo-15-crown-5 with aminosulfuric acid the guest molecule exists in the zwitterionic form \(\text{NH}_3^+\text{SO}_3^-\) with well separated positively (\(\text{NH}_3^+\)) and negatively (\(\text{SO}_3^-\)) charged centers. In contrast to the 18-membered crown ether complexes [8], the cavity dimension of the 15-membered crown ring is not sufficient to accommodate the \(\text{NH}_3^+\) group. That is why only two of the \(\text{NH}_3^+\) hydrogens participate in \(\text{NH}_3^+\)···O host–guest contacts of the H-bond type in the same way as in the complexes \(\text{NH}_3\text{Cl}\text{O}_2\text{U}_2\text{Cl}_4\cdot\text{CH}_3\text{CN}\) and \(\text{NH}_3\text{ClO}_2\text{U}_2\text{Cl}_4\cdot\text{CH}_3\text{CN}\) [9] where the ammonium ion forms two hydrogen bonds with each crown entity.

No host–guest complex between a neutral organic molecule and 15-crown-5 has been described yet, while for benzo-15-crown-5 two complexes with dithiooxamide and thioacetamide as the guest have been reported. There the host–guest interactions are similar to those described for 18-crown-6 and the crystals of the 1:1 complex with the bifunctional thiooxamide consist of infinite chains of alternating host-guest molecules [10]. In the 1:2 complex with thioacetamide the host forms a distinct molecular entity with two molecules of the guest. In both structures the crown host is approached from both sides by two coordinating guest molecules, its oxygens being involved in one bifurcated and one simple hydrogen-bonding interaction on each face. In the ternary 1:1:1 complex between benzo-15-crown-5, 3,4-dinitrobenzoic acid and water [11], the water molecule is involved as a H-donor in the hydrogen bonding to three O atoms of the most flexible part of the crown (one single and

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Figure 1. Numbering scheme of the two host molecules (complexes I and II) and the guest molecule present in both complexes.

one bifurcated bond) and as an acceptor in a hydrogen bond with the carboxylic group of 3,4-dinitrobenzoic acid.

In earlier work [12] we have described the crystal structures of one ternary and one binary complex between the bifunctional diamine, 3,4-diamino-1,2,5-oxadiazole and 18-crown-6 and cis-anti-cis-dicyclohexano-18-crown-6. In the former complex the water molecule is inserted as ambifunctional hydrogen-bonding links (complementary mediator) between the NH-donor and the hexaoxa ring. In the latter binary complex both amine groups offer all of their protons for direct host–guest interactions.

The present contribution is confined to the structures of two new host–guest inclusion complexes of 15-crown-5 and benzo-15-crown-5 with the same guest, 3,4-diamino-1,2,5-oxadiazole, (complexes I and II). For 15-crown-5 it is the first example of a host–guest complex with a neutral organic molecule. Features of these complexes of interest to us include the number of crown oxygen atoms that participate in hydrogen bonding and the extent this hydrogen bonding influences the crown ether conformation.

Synthesis

Both complexes were prepared in a similar way. 1 mmol of the respective crown ether and 1 mmol of 3,4-diamino-1,2,5-oxadiazole were dissolved simultaneously in 10 mL of methanol at 65 °C. The crystals precipitated on cooling to 20 °C were separated and air-dried. Crystals suitable for X-ray crystallography were obtained by recrystallization from a 1:1 benzene:methanol mixture.

Complex I


Complex II