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Electron density studies on complexes of 18-crown-6

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Abstract - Electron density studies on 18 - crown - 6 x 2 cyanamide as well as 18 - crown-6 x KN_3 x H_2O show, that the chemistry of crownethers obviously is characterized by highly sophisticated electrostatic interactions, which can be formed as a consequence of a very symmetric and flexible arrangement of electron density. As a consequence the electrostatic interactions, which mainly describe the binding situation, are overlayed by dipole-dipole interactions and dispersive interactions respectively. Detailed measurements show, that strong polarisation effects in the lone pair region of the oxygens play an important role.

INTRODUCTION

The chemistry of crownethers and aminopolyethers is well known in the field of synthesis, behaviour and application. Nevertheless, there are several questions to be answered concerning their structural and bonding characteristics available from experimental data.
These are as follows:

- Are, indeed, the C-C bonds in potassium complexes of 18- crown- 6 shortened. If there are what the reasons are.
- What kind of forces are acting between the host and the guest in complexes like 18 - crown - 6 x 2 cyanamide?
- What kind of interactions between oxygen donors and the encapsulated cation are stabilizing the ionic complexes with alkaline cations?
- What type of interactions causes the "anion-activation" of these complexes in dipolar aprotic solvents?

In order to find more details in these structural aspects, X- ray and neutron diffraction measurements have been carried out on different types of 18 - crown- 6 complexes. The data were collected around 100 K for the cyanamide complex and the potassium azide complex.

THE C-C-BOND IN POTASSIUM-COMPLEXES OF 18-CROWN-6

The distance of a bond between two sp^3 hybridized carbon atoms is 153 pm obtained as an average value for single aliphatic bonds in crystal structures. In many alkaline complexes the average C- C - bond distance was found to be significantly smaller than 150 pm. In the low- temperature structure (100 K) of the uncomplexed ring distances of comparable magnitude (149.6 (3) pm) were observed. The same study showed that the bond shortening can only partly be attributed to the effect of thermal motion. The reason for this anomaly, often referred to as "macrocyclic effect", is remained to be unknown (ref. 1-6).

The crystal structure of 18-crown-6 x $KClO_4$ has lately been determined from X-ray data collected at 20 K. The extremely low temperature was maintained by a double stage closed-cycle helium cryostate mounted on an Eulerian cradle (ref. 7-9). The advantage of cooling the sample is demonstrated in Fig. 1, where the ORTEP plots of the molecules corresponding to 295 K (ref. 10,11) and 20 K, (ref. 20) structural data are compared. The probability ellipsoids representing the atomic thermal displacements are reduced dramatically for the 20 K structure. The molecular data obtained also show that the considerable shortening in the C-C bond distances (149.6(3) pm) are not only due to thermal effects.

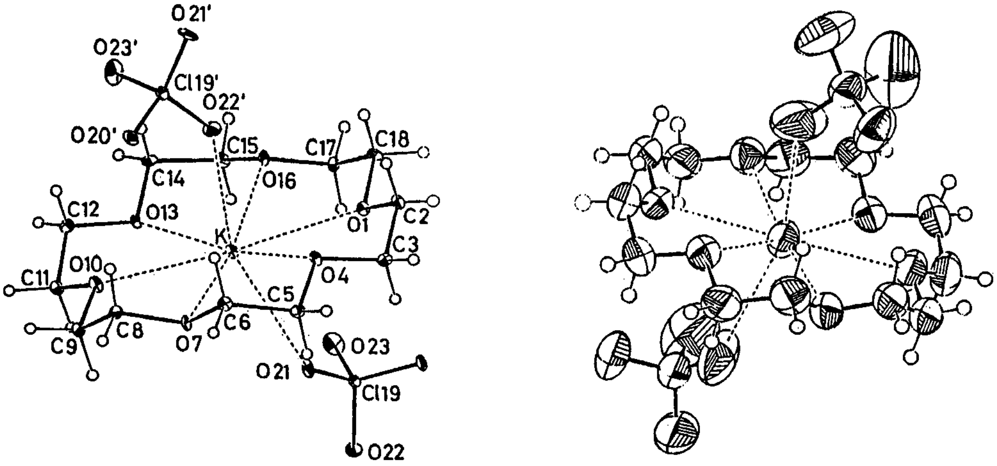

Fig. 1. X-ray-structure of 18-crown-6 x $KCLO_4$ at 295 K (right) and 20 K (left).

To find out about other reasons for this observation the bonding properties of the complexes mentioned above were aimed to be analyzed in terms of their experimental charge density distribution. The molecular electron density can be obtained from X-ray diffraction data directly, by X-X or X-N techniques or by leastsquares fitting of a model-predicted distribution to the observations (multipole refinement) (ref. 13-15). The former two methods lead to the thermally averaged density while the latter one makes it possible to extract the static distribution from the measured intensities.

EXPERIMENTAL ELECTRON DENSITY IN 18-CROWN-6 × 2 CYANAMIDE

Figure 2 shows the X-ray structure of the title compound (ref. 16).

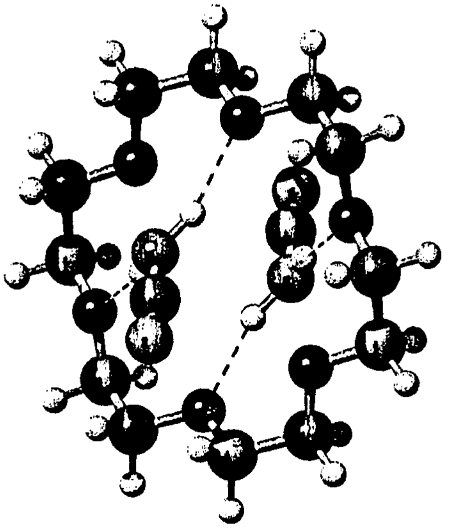

Fig. 2. X-ray-structure of 18 - crown - 6 x 2 cyanamide

The ring has a quasi D_{3d}- symmetry with "inverted" donors. The two cyanamide molecules are coordinated above and below the ring in such a way that hydrogen bonds can be formed and the dipoles can be compensated.
Figure 3 shows the dynamic electron deformation density (edd) in the mean plane of the crown:

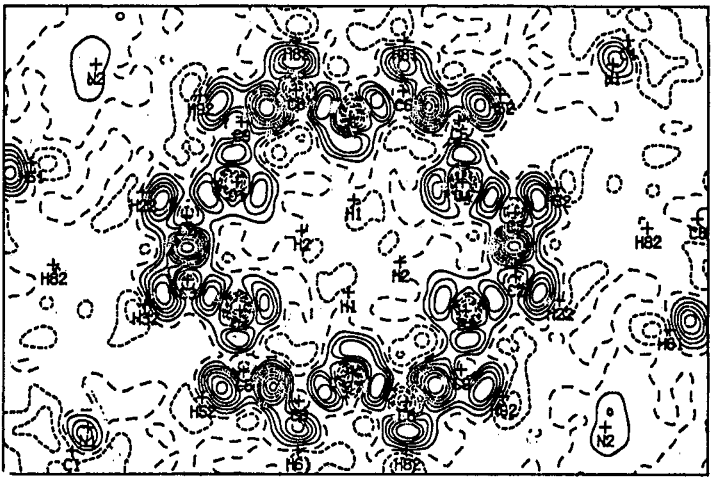

Fig. 3. Electron density distribution in 18 - crown- 6 x 2 cyanamide, obtained by x- n - technique, in the crown's mean plane.

Local maxima in the deformation density are clearly visible in the bonds and in the lone - pair regions of the oxygen atoms.
Additional features are:

- Different orientations and shapes of the lone- pair peaks.
- A high degree of overall symmetry in the edd contours.
- No charge accumulation in the middle of the ring.

Figure 4 gives more details, in terms of static edd, on the C- O bonds and the non- bonding deformation at O (4), which does not take part in a hydrogen bond.

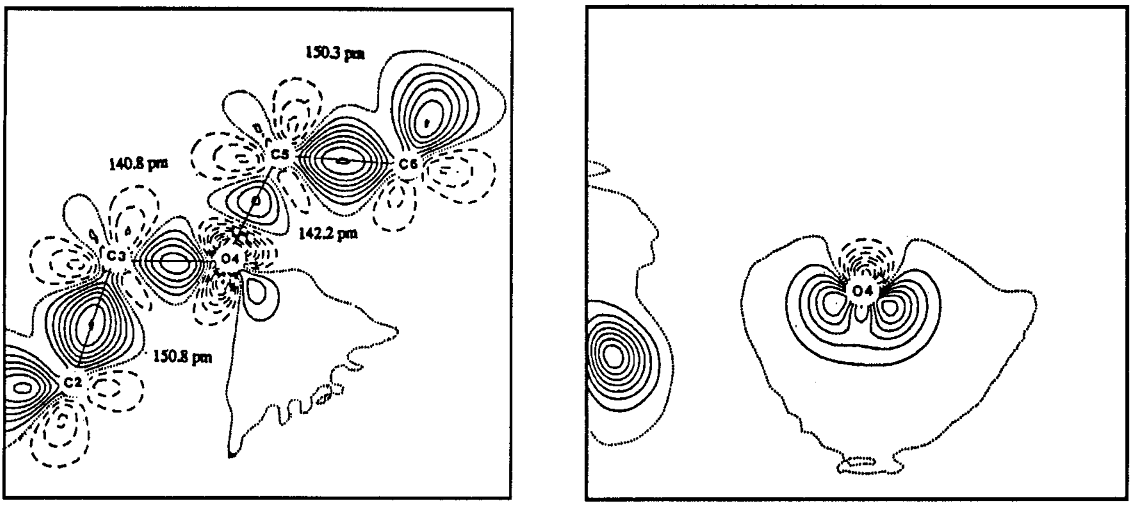

Fig. 4. Static model edd of 18 - crown- 6 x 2 cyanamide in the plane defined by the C (3) - O (4) - C (5) atoms (left) and in the plane bisecting that angle (right).

Two distinct maxima, assigned to sp^3 hybridized lone-pairs, can be seen for O(4) in the bisecting plane.

Figure 5 shows a different situation found for the C (18) - O (1) - C (2) unit.

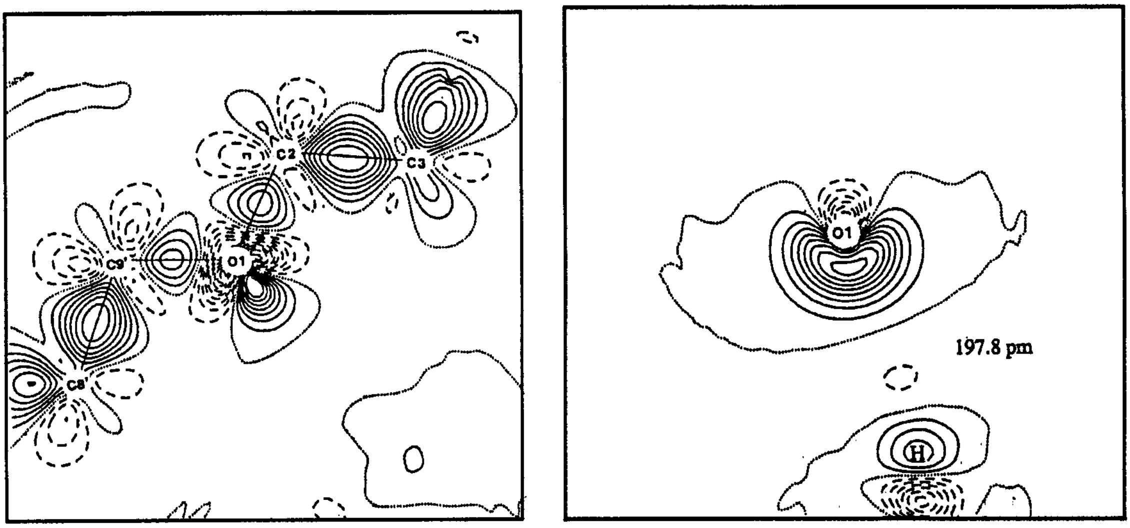

Fig. 5. Static model edd of 18-crown-6 x 2 cyanamide in the C(18) - O(1) - C(2) - plane (left) and perpendicular to it (right).

O (1) is the acceptor of a hydrogen bond. Consequently only one continuous lobe appears in the bisecting plane, indicating a polarization effect due to the proton of the guest partner. No charge accumulation is found between the oxygen and hydrogen atoms, as figure 6 shows in more detail.

This could indicate that the electrostatic interaction, as expected on energetic basis is the main contribution to the contact.

The commonly accepted description of the nature of hydrogen bonds17), covalent $n - \sigma^*$ = interactions between oxygen and hydrogen is in contrast to this result. The accuracy of the method used here is 1 contourline. It is therefore not allowed, to exclude covalent interactions on a charge - range of 0,1 $e/Å^3$, as used for $n - \sigma^*$ = interactions.

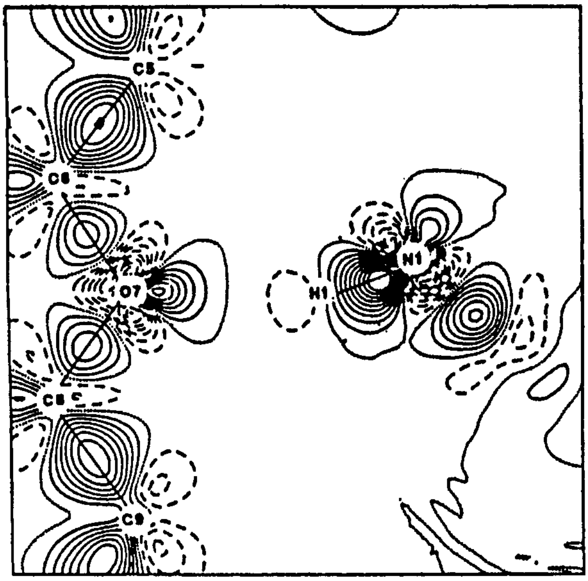

Fig. 6. Static model edd in the O(7) - H(1) - N(1) - plane of 18-crown - 6 x 2 cyanamide.

More important seems to us, that the analysis of the dipole-dipole interactions, in terms of dipole moments calculated from the multipole populations, revealed that the asymetries in the crown are induced by the electric field of the cyanamide molecule and contribute to the stability of the host-guest complex.

EXPERIMENTAL ELECTRON DENSITY IN 18-CROWN-6 × KN_3 × H_2O

Figure 7 shows the structure of the title complex.

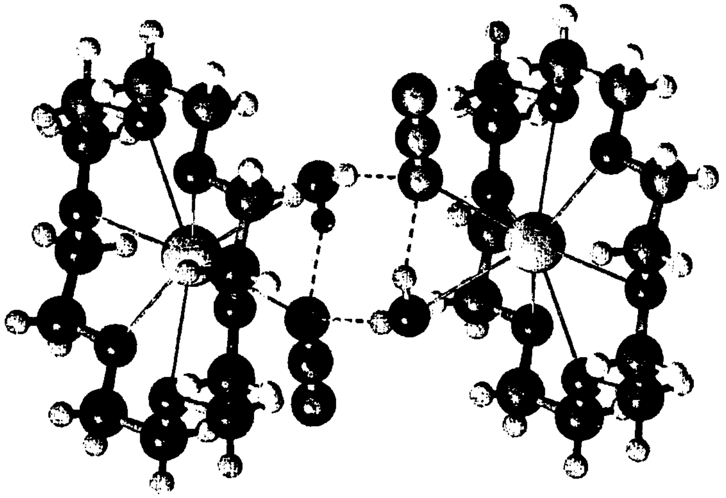

Fig. 7. X-ray structure of 18 - crown - 6 x 2 KN_3 x H_2O

The crown again has a quasi D_{3d} - symmetry with "inverted" oxygen donors.

The cation is nearly in the center of the ring, but 79 pm far from the mean plane of the oxygen atoms. Figure 8 shows the deformation density distribution in the mean plane of the crown.

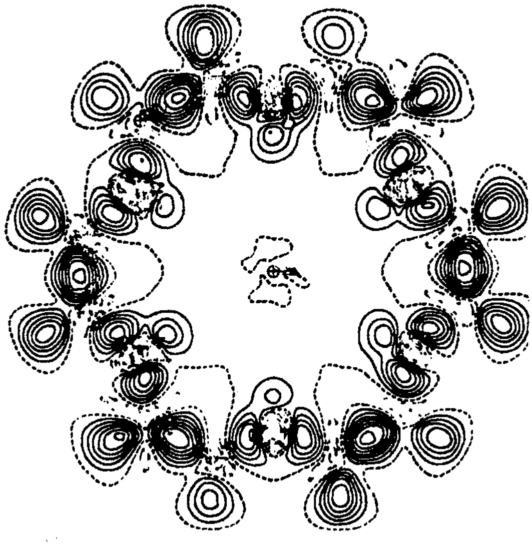

Fig. 8. Charge density ditribution in the meanplane of 18 - Crown - 6 x 2 KN_3 x H_2O

The highly symmetrical deformation pattern is very similar to that found for the neutral complex. In Fig. 9 the nonbonded deformation density of two oxygen atoms (O(1) and O(4), situated above and below the ring's mean plane, are seen.

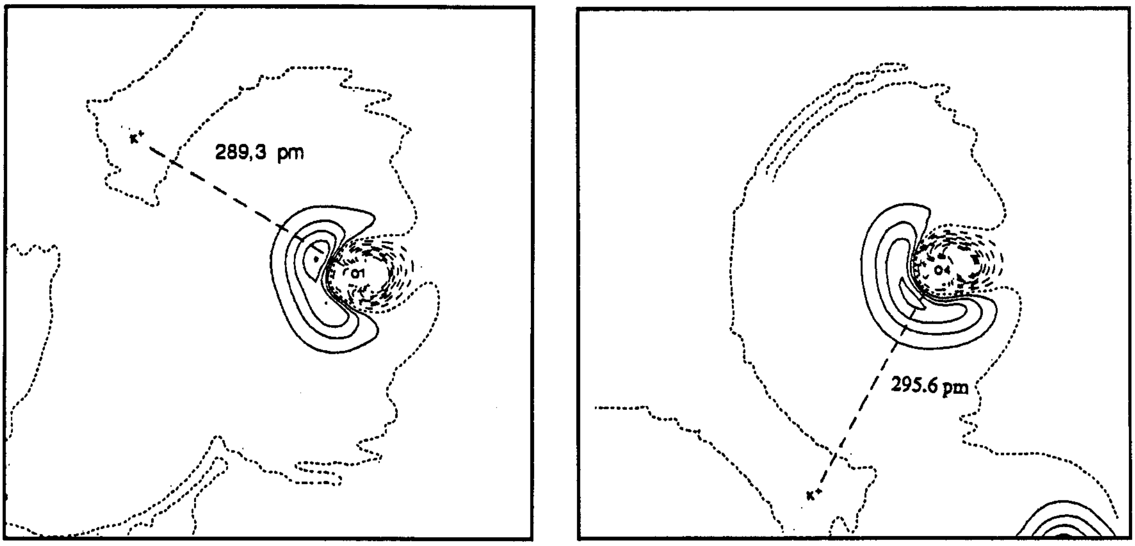

Fig. 9. Static model edd of 18-crown-6 x 2 KN_3 x H_2O in the bisecting planes of C(18) - O(1) - C(2) (left) and C(3) - O(4) - C(5) (right)

Here, similarily to O(1) and O(7) in the neutral complex, only one lone-pair lobe is found with a charge buildup in the direction of the cation. This density deformation indicates that the oxygen atoms are considerably polarized by the electric field of the potassium ion. The lone-pair density of oxygen atoms to which the potassium cation is coordinated in the enthalpy - controlled complex appears to be very similar to the nonbonded density of those oxygens, which are donors in hydrogen bonds (Figure 5). The analogy in the valence deformations might indicate the common electrostatic nature of the different types of interactions considered.

This qualitative statement is also supported by the deformation density of the azide ion as calculated in the K- N(19) - N(20)-plane (Fig. 10).

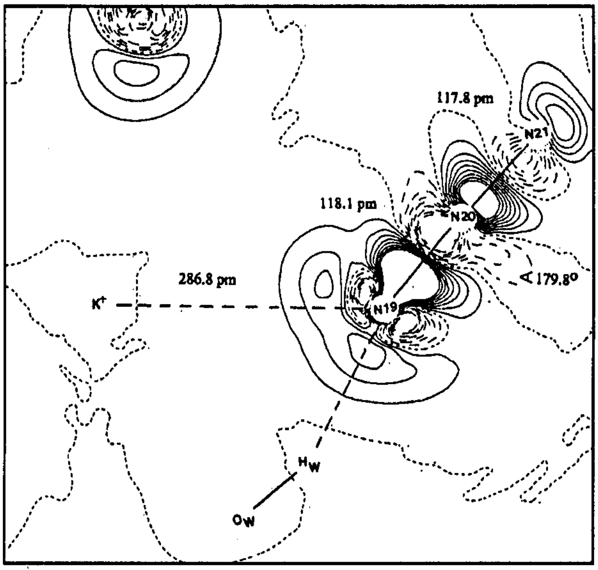

Fig. 10. Static model edd of 18-crown-6 x 2 KN_3 x H_2O in the K^+-$[N\text{-}N\text{-}N]^-$- plane

Here, the difference in the lone-pair density of the two terminal nitrogen atoms is clearly visible. The non-bonded electrons of N(19) are affected by the cation as well as by the protons of the water molecules. As a result, the symmetric lone-pair density, characteristic for the terminal atoms in the isolated azide molecule, is not preserved. It splits into regions, where extra charge is localized.
For a more detailed evaluation of the "anionactivation" one needs to study the electron density of alkaline complexes with different anions. This is the direction of our further research.
It is important to note that the greatest stability is found for complexes with "soft", highly polarizable anions. This indicates that besides the electrostatic interactions observed, dispersive forces also play an important role.

CONCLUSION

The structure and the chemical behavior of the crownether complexes are strongly affected by electrostatic and dipole-dipole interactions between the host and the guest. These forces cause observable changes in the molecular geometry, as well as in the local features of the deformation electron density.
The C- C bond density in the ring is almost perfectly transferable from one crown compound to the other. This is not true for the C- O bonds, as the valence deformation at the oxygen atoms was found to be strongly affected by secondary forces.
The N-H ...O hydrogen bonds in the neutral complex lead to extra charge concentration in the lone-pair region of the participating oxygen atoms in the direction of the proton. The analysis of the partial dipole moments reveals that the differences in the polarization of the C- O bonds are induced by the electric field of the cyanamide molecule.
The non- bonding region of the deformation ED at the oxygen atoms in the potassium complex is very similar in appearance to that obtained for the oxygens being involved in hydrogen bonds. These continguous lobes, with the maxima situated nearly on the O...K^+ internuclear vectors, are likely to be formed due to the electrostatic interaction between the atoms considered.

Acknowledgement

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