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Host–Guest Complexes of 18-Crown-6 with Neutral Molecules Possessing the Structure Element XH_2 (X = O, N, C)

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Abstract: The interaction of neutral molecules with the structure elements OH_2, NH_2, and CH_2 and 18-crown-6 was studied in solid and solution. Crystalline complexes were synthesized with H_2O, "activated" by $UO_2(NO_3)_2{\cdot}4H_2O$ or cyanoacetic acid, with molecules possessing NH_2 and CH_2. The solid complexes, studied by IR spectroscopy, showed interactions via XH···O hydrogen bonds to crown ether oxygen atoms and characteristic bands for the symmetry of the 18-crown-6 ring. X-ray structure analyses of selected complexes were conducted: 18-crown-6·$UO_2(NO_3)_2{\cdot}4H_2O$, 18-crown-6/cyanoacetic acid/water, 18-crown-6/2cyanamide, 18-crown-6/2(1-chloroethylsulfonamide), 18-crown-6/4(methyl 4-aminobenzoate), and 18-crown-6/adiponitrile. Complexes in solution were studied by ^1H NMR and ^{13}C NMR showing interaction via XH···O hydrogen bonds and changes of the crown ether ring flexibility by complexation.

Introduction

The discovery by Pedersen[1] of macrocyclic polyethers and the synthesis by Lehn[2] of corresponding amino polyethers has led to numerous investigations into the chemistry of these compounds. Primarily, interest has been devoted to understanding their complexing behavior toward ionic compounds, in particular, salts of alkali and alkaline earth as well as ammonium ions. Extensive reviews of this work are available.[3]

In contrast, Pedersen's observation[4] of complex formation between macrocyclic polyethers and neutral polar molecules has only recently attracted attention. The present work is addressed to these complexes.

In classifying complexes of neutral molecules and cyclic polyethers and amino polyethers, it is advantageous to use Cram's terminology of "host–guest complexes".[5]

1. Electrostatic Interactions as Mediators for Bonding in Polyether Complexes

Comparing the crystal structures of 18-crown-6 and its complexes with the thiocyanates of sodium, potassium, and cesium,[6] one finds a high degree of conformational flexibility for the crown ether which can thus adopt itself to changes in its environment. The most stable conformation of the crown ether has approximate D_{3d} symmetry with a polar cavity to accomodate the cation. Optimum conditions are found for the potassium complex in which the crown ether can be divided into six subunits. Each subunit can be assigned a dipole moment originating from the ether oxygens; a simple computation using the C–O group moment gives a value of ca. 1.3 D.[7]

The six noncoplanar dipoles are directed toward the interior of the ring, forming an inverse cavity to the electrostatic field of the cation (Figure 1). In this way, polar–dipolar interactions provide a satisfactory explanation for the complexation of "hard" alkali and ammonium ions which do not allow for any significant covalent bonding.

The effectiveness of ion–dipole interactions in the formation of alkali metal complexes raised the question of whether stable host–guest complexes of macrocyclic polyethers could also be obtained on the basis of weaker interactions, such as dipole–dipole forces. This possibility was indicated in work by Gokel et al.,[8] MacLachlan,[9] and Goldberg[10] while our investigations were in progress.

Table I. Aquo Complexes of Transition Metals

	ref	mp/°C
18-crown-6·$Mn(NO_3)_2{\cdot}6H_2O$	(I) 13, 14	109
18-crown-6·$Co(NO_3)_2{\cdot}6H_2O$	(II) 14, 15	121
18-crown-6·$Ni(NO_3)_2{\cdot}8H_2O$	(III) 14, 15	116
18-crown-6·$UO_2(NO_3)_2{\cdot}2H_2O$	(IV) 16, 17, 19	155
18-crown-6·$UO_2(NO_3)_2{\cdot}4H_2O$	(V) 18–20	147–150
18-crown-6·$Th(NO_3)_4{\cdot}3H_2O$	(VI) 17, 19	180

Such complexes appear suitable to probe two important questions, viz., (1) determination of parameters that influence complexation of nonspherical substrates by polyethers and (2) manifestation of structural complementarity that in other types of complexes is partially obscured by charge effects. The search for these complexes proved extremely fruitful. Reaction with crown ethers, in particular, 18-crown-6, is facile for those guest molecules possessing the following structural features: a hydrogen atom arrangement that is complementary to the crown ether and in which the hydrogens are rendered acidic by a neighboring polar group, a relatively large dipole moment, and a relatively low molecular mass. The complexes thus obtained can be characterized both in solution and as crystalline solids; structurally, they can be divided into three groups.

2. Complexes with Guest Molecules Containing the Structure Element OH_2

The simplest compound to fit the criteria outlined above is, of course, H_2O. While its dipole moment of 1.85 D[11] is not particularly large, its hydrogen bonding capacity is excellent. So far no stable binary complex of water and 18-crown-6 has been found.[12] It can be made to react, however, if the environment is such as to enhance dipole moment and acidity. Suitable conditions are interaction with transition metal cations and formation of structures exhibiting X···OH_2 hydrogen bonds. Table I shows

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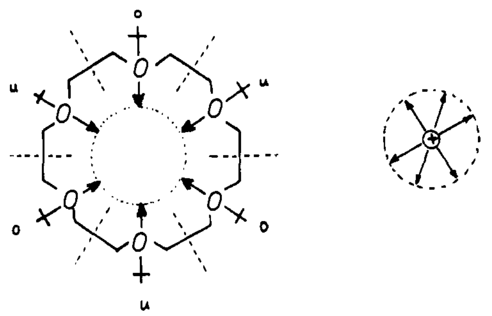

Figure 1. Electrostatic field of cation and inverse cavity of crown ether for D_{3d} symmetry.

the water-containing complexes obtained from ethereal solutions by reaction of 18-crown-6 with transition metal aquo complexes.

There are basic differences in properties between these complexes and alkali and alkaline earth complexes of polyethers: the transition metal complexes contain water; their solubility in nonpolar solvents is low and they are unstable in protic or highly dipolar aprotic solvents; they effect no anion activation; shifts to higher wavenumbers of OH valence bonds relative to the starting transition metal compound suggest participation in specific hydrogen bonds of water molecules incorporated in the polyether complex; their interpretation is further supported by ^{1}H NMR spectra (the water signals are shifted to low field and exhibit a significant temperative and concentration dependence indicative of hydrogen bonds); CH_2 rocking bonds at 960 cm^{-1} and C–C stretching at 835 cm^{-1} indicate D_{3d} symmetry for the crown ether (as in the K^+ complex); complexation also effects the ^{1}H NMR bonds of the crown ether which are shifted to lower field in benzene; analysis of nitrate IR bands reveals little or no change in the inner coordination sphere from the original simple complexes as these bands are practically unchanged in the crown ether complex (there is no indication of symmetry enhancement from C_{2v} to D_{3h}[17]); similar conclusions can be drawn from UV spectra.

These results essentially preclude a structure assignment of the classical[6] cation/crown ether complex type. This has been confirmed by X-ray diffraction analysis. Besides 18-crown-6·$UO_2(NO_3)_2·2H_2O$ which has been investigated by IR[17] and X-ray[16] analysis, another uranium complex, 18-crown-6·$UO_2(NO_3)_2·4H_2O$, has been characterized. An X-ray structure determination of the latter complex obtained from acetic acid or water gave results largely in agreement with the previous analysis of Eller and Pennemann.[18]

The inner coordination sphere of the uranyl cation remains unchanged on complexation. Although only the positions of the water oxygens were determined, distances and angles suggest that these are hydrogen-bonded to the crown ether oxygen atoms. In both complexes 18-crown-6 possesses approximate D_{3d} symmetry.

The same type of bonding is found in 18-crown-6·$Mn(NO_3)_2·6H_2O$.[13] Again, the crown ether has approximate D_{3d} symmetry and is bonded to the manganese cation via water molecules. In this case, two coordinated water ligands each participate in the crown ether linkage. In addition, there is a three-dimensional network of hydrogen bonds involving lattice water molecules. The remaining complexes listed in Table I probably possess similar structures of trans H_2O ligands linking crown ether and metal cations.

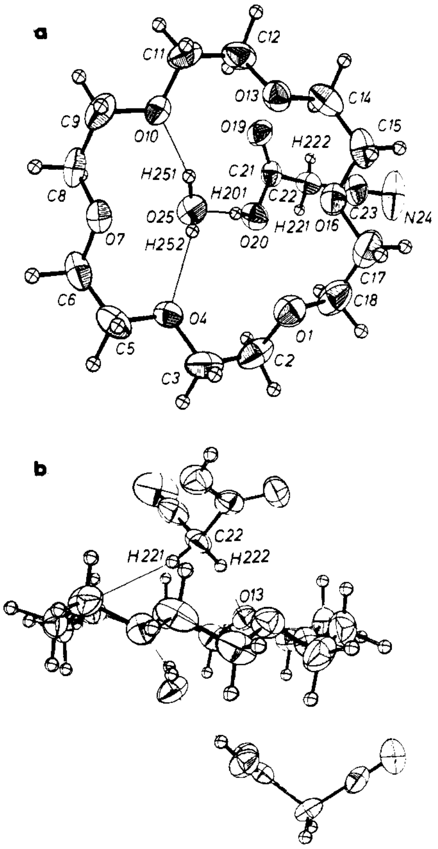

Figure 2. 18-Crown-6/cyanoacetic acid/water (VII): (a) view perpendicular to the crown ether plane; (b) view parallel to crown ether plane (including another, symmetry-related, cyanoacetic acid molecule).

Table II. Angles and Distances of the Hydrogen Bonds in 18-Crown-6/Cyanoacetic Acid/Water

atoms			distance/ pm 1-2	distance/ pm 1-3	angle/ deg 1-2-3
1	2	3			
O_{25}	H_{201}	O_{20}	180.4	259.5	
O_4	H_{252}	O_{25}	229.7	292.8	168.0
O_7	H_{252}	O_{25}	287.4	313.3	
O_7	H_{251}	O_{25}	283.9	313.3	
O_{10}	H_{251}	O_{25}	194.8	291.7	162.4
O_4	H_{221}	C_{22}	235.2		
O_7	H_{221}	C_{22}	251.4		144.2
O_{13}	H_{222}	C_{22}	252.9		151.6
O_{16}	H_{222}	C_{22}	296.2		
O_{19}	H_{222}	C_{22}	256.9		111.0
O_{20}	H_{221}	C_{22}	244.9		107.7

Table III. Least-Squares Plane

atoms	deviations from plane (pm)
O_1	19.29
O_4	−19.98
O_7	24.63
O_{10}	−29.04
O_{13}	27.70
O_{16}	−22.60

2.1. Structures with RXH···OH_2 Hydrogen Bonds. In analogy to water-containing transition metal/crown ether complexes, organic molecules with acidic OH groups give complexes of different stoichiometries that incorporate water. Vögtle and Müller[21] have described a number of complexes of 18-crown-6 and substituted phenols, dihydroxybenzenes, and oximes containing water molecules.

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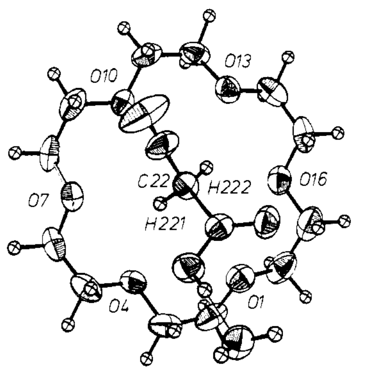


Figure 3. 8-Crown-6 cyanoacetic acid/water (view perpendicular to crown ether plane).

We have now investigated the reaction product of 18-crown-6 and cyanoacetic acid. From IR data, participation of the carboxyl group in hydrogen bonding and approximate D_{3d} symmetry of the crown ether can be inferred; in the ^1H NMR spectrum a slight downfield shift of the methylene protons of cyanoacetic acid is observed.[22] In order to obtain conclusive data we carried out an X-ray crystal structure analysis (Figure 2). Pertinent structural data are given in Tables II and III. A list of atomic coordinates and temperature factors as well as bond lengths and angles is available upon request (A.K.).

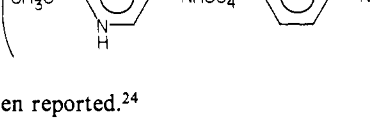
The crown ether possesses approximate D_{3d} symmetry. Below its plane a water molecule is hydrogen-bonded via $H_{251}\cdots O_{10}$ (194.8 pm) and $H_{252}\cdots O_4$ (229.7 pm) to the crown ether and via $H_{201}\cdots O_{25}$ (180.4 pm) to the carboxyl group of a cyanoacetic acid molecule. Interestingly, while the hydrogen bond angles with the crown ether oxygens are roughly equal (168.0°/162.4°), the distances are not.

Above the crown ether plane a molecule of cyanoacetic acid is bonded via its CH_2 group (Figure 3). The methylene group forms two bifurcated hydrogen bonds to crown ether oxygens, viz. $H_{221}\cdots O_7$ (251.4 pm)/$H_{221}\cdots O_4$ (275.2 pm), and $H_{222}\cdots O_{13}$ (253.0 pm)/$H_{222}\cdots O_{16}$ (296.0 pm), respectively. The last bond is certainly very weak and there is an adidtional interaction with a carboxyl oxygen, $H_{222}\cdots O_{19}$ (256.9 pm). The structure is thus composed of polymeric chains with sequence crown ether–water–cyanoacetic acid. Compared with the structures of the transition metal/water complexes of 18-crown-6, the CH_2 group of cyanoacetic acid has the same linking function as "activated" H_2O. Apparently it is immaterial whether activation is through coordinated metal cations or acidic organic molecules.

3. Complexes with Guest Molecules Having NH_2 as Structure Element

While comlexes with aliphatic amines have not been isolated, several are known with aromatic amines as well as amides. These are listed in Table IV. Common features of these compounds are: a prevalence of 1:2 stoichiometry (4-nitroaniline and methyl 4-aminobenzoate occur with two compositions, 1:1/1:2 and 1:1/1:4, respectively, whereas 2-methyl-2-(*n*-propyl)-1,3-propanediol dicarbamate, and bromoaniline form 1:1 complexes); they are sparely soluble in nonpolar solents and are unstable in protic or highly dipolar solvents; shifts to lower wavenumbers of IR NH valence bonds indicate hydrogen bonding; low-field shifts of NH hydrogens in ^1H NMR spectra show dependence on temperature and concentration characteristic of hydrogen bonding; crown ether IR bonds are in most cases consistent with approximate D_{3d} symmetry (CH_2 rock at 960 cm^{-1}, C–C stretch at 835 cm^{-1}); complexation is accompanied by a shift to lower field of the crown ether in the ^1H NMR spectrum in benzene.

3.1. Structure Element $PhNH_2$: Complexes with Derivatives of Aniline. Derivatives of aniline are important both preparatively and physiologically. Interactions between 18-crown-6 and 4-substituted anilines, first studied by Takayama et al.,[23] involved 4-aminobenzoic acid, 4-chloro- and 4-nitroaniline, as well as various sulfonamides carrying an NH_2 group in the 4 position. A crystalline 1:1 complex with sulfamethoxypyridazine



has also been reported.[24]

Table IV. Host–Guest Complexes of 18-Crown-6 and NH Acidic Substrates

functionality of the R-Ph-NH₂ group	guest molecule	mp/°C	stoichiometry host: guest
	aniline (VIII)	28	1:2[a]
	4-fluoroaniline (IX)	42–46	1:2
	4-chloroaniline (X)	66–68	1:2
	4-bromoaniline (XI)	32–36, 56–64	1:1
	4-iodoaniline (XII)	63–63	1:2
	4-cyanoaniline (XIII)	98–101	1:2
	4-nitroaniline (XIV)	102–107	1:2
	4-nitroaniline (XV)	83.5–85.5	1:1
	4-aminobenzoic acid (XVI)	150–151	1:2
	methyl 4-aminobenzoate (XVII)	58–60	1:4
	methyl 4-aminobenzoate (XVIII)	50–51	1:1
	ethyl 4-aminobenzoate (XIX)	72	1:2
	propyl 4-aminobenzoate (XX)	68–68	1:2
	2-aminobenzoic acid (XXI)	52–53	1:2
	methyl 2-aminobenzoate (XXII)	34–36	1:2
$R-NH_2$	cyanamide (XXIII)	93	1:2
$R-CONH_2$	ethyl carbamate (XXIV)	61	1:2
	2-chloropropionamide (XXV)	55–57	1:2
	2-bromopropionamide (XXVI)	74–76	1:2
	2-methyl-2-(*n*-propyl)-1,3-propanediol dicarbamate (XXVII)	86	1:1
$R-SO_2NH_2$	benzenesulfonamide (XXVIII)	92	1:2
	toluenesulfonamide (XXIX)	95	1:2
	1-chloroethylsulfonamide (XXX)	118	1:2

[a] The complex had a nonstoichiometric content of about 10% water.

Vögtle et al. prepared a number of 18-crown-6 complexes:[21] 3-nitroaniline (1:1 stoichiometry), 4-nitroaniline, 2,4-dinitroaniline, 4-nitro-2-hydroxyaniline, 2,6-diaminopyridine, and 4-nitro-1,2-phenylenediamine (1:2), pentafluoroaniline (3:2). The structure of the 1:2 complex of 18-crown-6 and 4-nitroaniline is similar to that of other 1:2 complexes, coordination being via the amino groups.[25] Except for disorder of one crown ether oxygen, the crown ether has approximate D_{3d} symmetry.

Weber and Sheldrick[26] determined the structure of 18-crown-6/2(2,4-dinitroaniline) which shows the commonly found overall C_i symmetry. Coordination is via NH_2 with two bifurcated hydrogen bonds. The crown ether itself possesses only C_i symmetry.

While the common stoichiometry is 1:2, 1:1 complexes stand out conspicuously. Since these substrates have only one primary amino group, the question arises as to the second coordination site. Possible groups would be OCH_3 (methyl 4-aminobenzoate) or Br (bromoaniline) which are known to coordinate in complexes of the dimethyl ester of acetylenedicarboxylic acid[10] and of BrCN and bromomalononitrile,[22] respectively. In the case of the 3- and 4-nitroaniline complexes charge-transfer interactions may also

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Table V. IR Bands of Complexes of 4-Nitroaniline (cm^{-1})

vibration	4-nitroaniline	18-crown-6/4-nitroaniline	18-crown-6/2(4-nitroaniline)
NH-stretching	3482 m	3428 m	3448 m
	3359 m	3359 m	3356 m
	3240 w	3275 w	3257 m
	3220 w	3254 m	3235 w
NH bending		1660 m	
	1655 sh	1655 sh	
	1633 s	1632 vw	1632 s
aromatic ring	1600 s	1604 *m*	1601 s
	1590 s	1581 m	1585 m
	1580 sh		

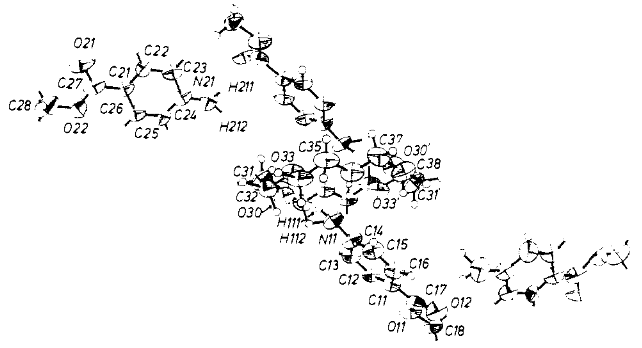

Figure 4. 18-Crown-6/4(methyl 4-aminobenzoate) (view parallel to crown ether plane).

have to be considered; they have been invoked for trinitrobenzene and various crown ethers.[27] A further important feature is the occurrence of two stoichiometries of complexes of 4-nitroaniline (1:1 and 1:2) and methyl 4-aminobenzoate (1:1 and 1:4). Such a phenomenon was first pointed out by Vgtle[21] in complexes of rubeanic acid. Depending on reaction time and temperature, the color of the solution changes from red to yellow as the stoichiometry of the complexes goes from 1:2 to 1:1.

We have begun a broad study of this phenomenon. Starting from the 1:2 complex with 4-nitroaniline, the choice of solvent determines which complex is obtained: in toluene, 1:2 stoichiometry is found [this compound probably corresponds to the one reported by Vögtle and Müller, even though its melting range is higher (102–107 vs. 89–97 °C)]; in ether, the lower melting 1:1 complex is obtained (mp 83.5–85.5 °C). The IR spectra of both complexes and of 4-nitroaniline are clearly distinguished, in particular as regards NH valence and deformation bands as well as aromatic bands. The different NH bands indicate varying NH–O hydrogen bonds, while the less pronounced changes in aromatic bands may be due to charge transfer from the aromatic π system to the crown ether or between 4-nitroaniline molecules. The relevant IR data are shown in Table V. We are currently conducting an X-ray analysis of 18-crown-6/4-nitroaniline which should, in conjunction with the previous structure determination of the 1:2 complex,[25] allow a concise picture of this system's structural capabilities.

In the case of complexes with methyl 4-aminobenzoate the stoichiometry is determined by how fast crystallization takes place. Fast recrystallization of the 1:1 complex leaves the stoichiometry unchanged, while crystallization over several weeks leads to the 1:4 complex. Both complexes differ in their melting points, viz., 50–51 and 58–60 °C, respectively.

To gain further insight into these unusual compositions X-ray structure analyses were undertaken; we report here the structure of 18-crown-6/4(methyl 4-aminobenzoate). The structure was solved by direct methods. Crystallographic data are given in the Experimental Section; Figure 4 shows the molecular geometry.

Table VI. Hydrogen Bond Distances

atoms		distance/pm	atoms		distance/pm
O_{33}	H_{111}	268	O_{21}	H_{381}	242
O_{33}	H_{112}	289	O_{12}	H_{221}	213
O_{30}	H_{111}	203	O_{12}	N_{21}	302
O_{30}	H_{112}	215			
O_{33}	N_{11}	309			
O_{36}	N_{11}	313			
O_{30}	N_{11}	304			

Table VII. Angles between Normals to Planes (deg)

plane 1–plane 2	47.23
plane 1–plane 3	136.17
plane 2–plane 3	121.21

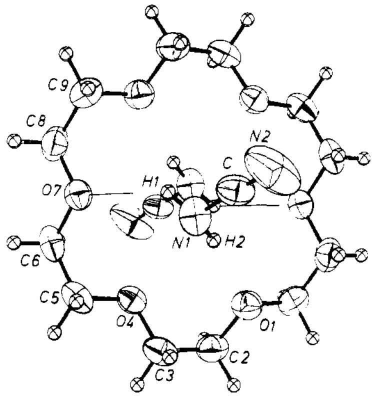

Figure 5. 18-Crown-6/2cyanamide (view perpendicular to the crown ether plane).

The structure is unusual. Two ester molecules are bonded via NH_2 to O_{30} and $O_{30'}$, respectively ($O_{30}\cdots H_{111}$ 203 pm, $O_{30}\cdots H_{112}$ 215 pm). The remaining two ester molecules are hydrogen-bonded via one amino hydrogen to the carbonyl oxygens of the ester molecules bound directly to the crown ether ($O_{12}\cdots H_{221}$ 213 pm). There is a further weak hydrogen bond (242 pm) from O_{21}, of the outer ester molecule to H_{381} of a symmetry-related crown ether. A list of hydrogen bond interactions is given in Table VI.

Angles within the NH_2 groups appear to be very small (H_{112}–N_{11}–H_{111} 45 (9)° and H_{112}–N_{21}–H_{211} 67 (9)°); however, owing to the size of the asymmetric unit, hydrogen positions could not be determined accurately, and consequently a discussion of hydrogen bond angles does not seem meaningful. The coordinates of the phenyl, methyl, and methylene hydrogens have been calculated.

The symmetry of the crown ether approximates to D_{3d}. To describe the orientation of the ester molecules relative to each other and to the crown ether it is advantageous to relate to the normals to the phenyl planes (plane 2, C_{11}–C_{16}; plane 3, C_{21}–C_{26}) and the least-squares plane of the crown ether oxygens (plane 1) (Table VII).

The structure of 18-crown-6/2(4-aminobenzoic acid) is of particular interest because of the physiological importance of 4-aminobenzoic acid as a simple receptor model. Preliminary results of an X-ray structure investigation show the crystals to be monoclinic; the asymmetric unit contains three molecules in space group $P2_1/n$. Weissenberg and precession photographs revealed a superstructure containing an orthorhombic substructure. (We thank Dr. A. Gieren for carrying out these investigations.) Solution of the structure will require significant effort and has not been successful thus far.

3.2. Structure Element R–NH$_2$: 18-Crown-6/2cyanamide. According to the criteria for the selection of guest molecules (section 1), cyanamide, with dipole moment of 3.8 D and molecular mass 112, appears to be a prime choice. The ^1H NMR spectrum of cyanamide in $CDCl_3$ shows no NH signals. These are observed, however, in the complex, narrowing and shifting to lower field

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Table VIII. NH Stretching Bands of 2-Chloropropionamide (cm^{-1})

2-chloro-propionamide	18-crown-6/ 2(2-chloro-propionamide)
	3435 m
3340 s	3340 m
	3295 w
	3218 w
3170 s	3100 vw

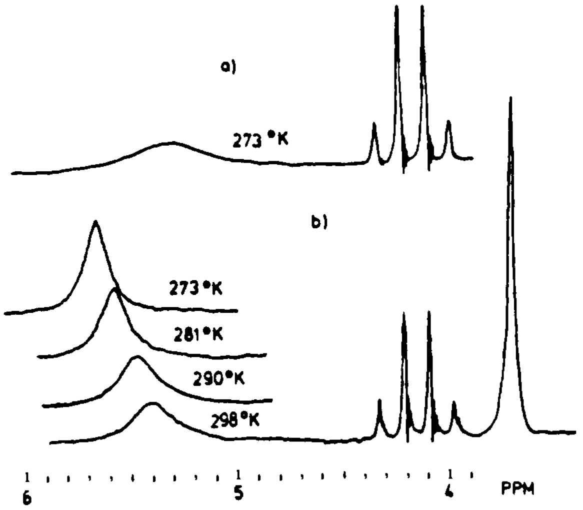

Figure 6. ^1H NMR spectra in $CDCl_3$: (a) ethyl carbamates at 0 °C; (b) ethyl carbamate complex of 18-crown-6.

with decreasing temperature. Their position depends on concentration. Both observations suggest participation of the NH_2 group in hydrogen bonding to the crown ether.

The IR spectrum displays a significant shift of the NH stretching mode to lower wavenumbers (3260–3200 cm^{-1}) and a smaller shift to higher wavenumbers of the in-plane NH_2 bending mode (1585–1605 cm^{-1}). The bands at 960 and 835 cm^{-1} are characteristic of approximate D_{3d} symmetry of the crown ether.

Figure 5 shows the results of an X-ray crystal structure determination. Atomic coordinates and bonds lengths and angles of the crown ether are available upon request (A.K.). Geometric data of the hydrogen bonds are given in Table XII.

The two cyanamide molecules are attached above and below the crown ether via hydrogen bonds (to O_1 and O_7) that differ considerably in distances and angles. The NH_2 planes are almost perpendicular to the crown ether plane, while the N_1–C–N_2 axis is inclined to this plane. Again, the symmetry of 18-crown-6 approximates to D_{3d}; the complex has overall symmetry C_i.

3.3. Structure Element RCO_2NH_2: Complexes with Carboxyl Amides. The NH_2 hydrogens of carboxyl amides are rendered more acidic owing to the inductive effect of the neighboring carbonyl group so that they also should be disposed to react with 18-crown-6. Table IV lists the complexes investigated in our work. Analogous complexes with acetamide, thioacetamide, benzamide, 4-nitrobenzamide, and phenyl carbamate have been reported by Vögtle and Müller.[21,28] With the exception of 2-methyl-2-(*n*-propyl)-1,3-propanediol dicarbamate which uses both NH_2 groups for coordination, forming a polymeric 1:1 structure, all of our complexes possess 1:2 composition.

From IR spectra D_{3d} symmetry can be inferred for the crown ether (bands at 960 and 835 cm^{-1}). Formation of NH···O hydrogen bonds is reflected by splitting and shift to higher wavenumbers of NH bands between 3500 and 3000 cm^{-1}. This is exemplified for the 2-chloropropionamide complex (Table VIII). Temperature and concentration dependence of the ^1H NMR spectra is typical of hydrogen bond interactions. With increasing dilution, the signal of the ethyl carbamate complex gives way to that of uncomplexed ethyl carbamate (Figure 6). The NH signal is shifted to lower field on complexation with concurrent narrowing. A further low-field shift occurs with decreasing temperature.

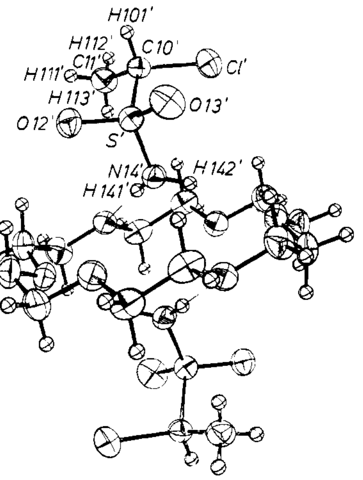

Figure 7. 18-Crown-6/2(1-chloroethylsulfonamide) (view nearly parallel to crown ether plane).

2-Chloro- and 2-bromopropionamide are chiral molecules. A racemate of a chiral uncharged compound could conceivably yield two different types of complex with the crown ether coordinating either two identical or opposite enantiomers.

C_i symmetry which is found in all host–guest complexes (except with cyanoacetic acid/water) can only be attained, however, for the isomer (*RS*)-18-crown-6 since only in this case can dipole moments be balanced. It is reasonable to assume that this form is more stable than either *RR* or *SS* complexes. Using equal amounts of enantiomers of a suitable neutral chiral substrate, only (*RS*)-18-crown-6 should be formed.

In order to show that *RS* complex is indeed favored, a 58:42 mixture of (*R*/*S*)-2-bromopropionamide was allowed to react with successive portions of 18-crown-6; after each portion the rotation of the precipitated complex was measured. During the course of the reaction the specific rotation increased from 2.1 to 5.2°/g, while a specific rotation of 2.7°/g would be expected if there were no change in enantiomer ratio.

A crystal structure analysis of (*RS*)-18-crown-6/2-(2-bromopropionamide) is in progress. An *RS* complex has been confirmed in the case of chiral sulfonamides (section 3.4.). The *RS* isomer is thus preferentially formed in the solid owing to its greater stability. We are presently investigating potential applications of this effect for enantiomer separation as well as the possibility of obtaining complexes with only one kind of isomer.

3.4. Structure Element $R–SO_2NH_2$: Complexes with Sulfonamides. In sulfonamides the acidity of NH_2 protons is enhanced by the neighboring SO_2 group. ^1H NMR spectra of 18-crown-6/2(1-chloroethylsulfonamide) (this complex contains a chiral aliphatic sulfonamide) show the usual features of NH_2 hydrogen bond formation (low-field shift of NH_2 signal in the complex; further shift to lower field and peak narrowing with decreasing temperature). This is also borne out in the vibrational spectra: the bands at 3380 and 3280 cm^{-1} of the sulfonamide appear at 3342, 3240, and 3093 cm^{-1} in the complex.

While absorptions at 950–960 and 835 cm^{-1} are characteristic of D_{3d} symmetry of the crown ether, there are, however, additional bands at 964, 919, and 844 cm^{-1} that might indicate lower symmetry; e.g., the 844-cm^{-1} band is also present in arylsulfonamide complexes (see below) in which the crown ether assumes C_i symmetry.

Figure 7 shows the result of an X-ray crystal structure; atomic coordinates, temperature factors, and crown ether bond lengths and angles are available upon request (A.K.). Details of hydrogen bonding are given in Table IX. The overall molecular symmetry is C_i, while the crown ether is approximately D_{3d}.

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(28) Vögtle, F.; Müller, W. M. *Naturwissenschaften* **1980**, *67*, 255.

Table IX. Hydrogen Bonds in 18-Crown-6/2(1-Chloroethylsulfonamide)

atoms 1 2 3	distance/pm 2···3	angle/deg 1–2···3
$N_{14}-H_{141}\cdots O_1$	230.0	166.8
$N_{14}-H_{141}\cdots O_4$	292.7	
$N_{14}-H_{141}\cdots O'_7$	308.4	
$N_{14}-H_{142}\cdots O_7$	222.0	169.2
$N_{14}-H_{142}\cdots O_4$	278.5	

The chloroethylsulfonamide ligands on both sides of the crown ether are coordinated via NH···O hydrogen bonds. The strongest interactions are found for $H_{141}\cdots O_1$ (230.0 pm) and $H_{142}\cdots O_7$ (222.0 pm) which are also similar in their angles (166.8°/169.2°). Other comparatively short contacts are $H_{141}\cdots O_4$ (292.7 pm), $H_{141}\cdots O_7$ (308.4 pm), and $H_{142}\cdots O_4$ (278.5 pm); it is questionable if these can be classified as hydrogen bonds. On the other hand, in a polyfunctional system the overall stability may well be increased significantly by a sum of small contributions.

Overall C_i symmetry requires the presence of one *R* and one *S* enantiomer in each complex unit. It is further evident that the complex possesses no dipole moment. Its formation from a racemic mixture implies a greater stability of the crystalline *RS* form than either *RR* or *SS* isomers. Since physical and chemical properties are the same for both enantiomers, any difference must result from symmetry (section 3.3).

Benzene- and toluenesulfonamide have a larger dipole moment (5.0–5.1 D) and a larger molecular mass than cyanamide. These compounds yield the crystalline 1:2 complexes 18-crown-6/2-benzenesulfonamide and 18-crown-6/2toluenesulfonamide. Complexation leads to ^1H NMR signals of NH_2 protons at lower field that are significantly narrowed.

Vibrational spectra are inconclusive as to the conformation of the crown ether. We therefore determined the crystal structure of 18-crown-6/2benzenesulfonamide.[29] The complex exhibits the usual C_i geometry; both amino hydrogens form bonds to opposite crown ether oxygens, $H_{101}\cdots O_4$ (233.7 pm) and $H_{102}\cdots O_4$ (199.4 pm). However, in contrast to the usual D_{3d} symmetry 18-crown-6 adopts only C_i symmetry in the benzenesulfonamide complex. Torsion angles around C–C bonds are close to 65°; this compares with four angles of 180° in 18-crown-6, reflecting its conformational flexibility in changing structural and electronic environments.

4. Structure Element CH_2

Historically the starting point for the investigation of complexes of 18-crown-6 with CH acids as substrates has been Gokel's observation[8] that on dissolution of 18-crown-6 in acetonitrile a crystalline solid of variable stoichiometry precipitates, the components of which can be recovered in vacuo. The authors suggested utilization of this effect for the purification of 18-crown-6.

At about the same time MacLachlan investigated complexes of 18-crown-6 with 2acetonitrile, 2acetonitrile-d_3, 2nitromethane, and acetic anhydride.[9] From single-crystal Raman data he inferred D_{3d} symmetry of the crown ether. Boer et al.[9] attempted an X-ray structure determination of 18-crown-6/2nitromethane which yielded space group and lattice constants and confirmed the D_{3d} symmetry of the crown ether.

We have attempted to react 18-crown-6 with compounds leaving activated CH_2 groups. The kind of activation necessary in this case may be appreciated by reference to the $O{-}C(CN)_2$ analogy.[30] This implies similar reactivity for $H_2O{-}H_2NCN{-}H_2C(CN)_2$. Consequently, we tried out primarily substrates derived from malononitrile (Table X).

With the exception of 18-crown-6/cyanoacetic acid/water (section 2.2), the usual 1:2 or 1:1 compositions are found. Also, other characteristics of host–guest complexes with OH and NH acidic substrates are typically observed here: IR bands at 960 and 835 cm^{-1} indicate approximate D_{3d} symmetry of the crown ether; shifts in CH stretching bands suggest participation of CH_2 groups in hydrogen bonding; the crown ether ^1H NMR signal is shifted to lower field in benzene; effects of complexation can be seen very clearly in measurements of ^{13}C spin–lattice relaxation which provide information about changes in crown ether flexibility. Table XI contains values of T_1 for 18-crown-6 and its complexes with malononitrile and potassium acetate.

Table X. Complexes with Guest Molecules Containing the Structure Element $-CH_2$

guest molecule	mp/°C	stoichiometry host:guest
malononitrile[22] (XXXI)	138	1:2
chloroacetonitrile[22] (XXXII)	78	1:2
cyanacetic acid/water[22] (XXXIII)	77	1:1:1
acetonitrile[22] (XXXIV)	77	1:2[a]
nitromethane[22] (XXXV)	107–115	1:2[a]
glutaronitrile[22] (XXXVI)	54	1:1
adiponitrile[22] (XXXVII)	56	1:1

[a] Not stoichiometric.

Table XI. ^{13}C Spin-Lattice Relaxation Measurements[a]

	C_1	Me_4Si/ppm	T_1	T_1(uncompl./T_1(compl.
18-crown-6	1	72.5	1.98	
18-crown-6/2 malononitrile	1	71.4	0.69	2.87
18-crown-6 potassium acetate	1	71.1	0.69	2.87

[a] Shifts are relative to Me_4Si in $CDCl_3$.

The constraint imposed on crown ether flexibility by complexation with malononitrile in chloroform is the same as for bonding of potassium ion under comparable conditions, this suggesting a close structural resemblance. ^1H NMR signals of CH_2 groups show concentration- and temperature-dependent shifts to lower field that are typical for hydrogen bonds. However, in the complexes with acetonitrile and nitromethane (1:1.6–1.8 stoichiometry), these shifts are nonsignificant. Together with the variable composition and the relatively high volatility of the substrates it indicates rather weak host–guest interactions.

We have therefore concentrated further work on the reactivity of aliphatic dinitriles. A more detailed picture of structure and bonding could be obtained from X-ray crystallographic analysis of the complexes 18-crown-6/2malononitrile, 18-crown-6/cyanoacetic acid/water (section 2.2.), and 18-crown-6/adiponitrile.

In the 2malononitrile complex the crown ether has approximate D_{3d} symmetry; the malononitrile ligands are hydrogen bonded to opposite oxygen atoms of 18-crown-6.[31]

Hydrogen bond distances are comparable to those in other CH–O bridged compounds.[32] It is noteworthy that beside the short $H_{101}{-}O_1$ bond (223 pm) another weaker interaction exists between H_{102} and O_1 (265 pm) making the hydrogen atoms distinguishable. The symmetry of malononitrile is thereby lowered to C_s from C_{2v}. Very significantly, the distance between C_{10} and O_4 (318 pm) is substantially smaller than the sum of the van der Waals radii (340 pm), implying a stabilizing interaction of the dipole–dipole type. A similarly short C–O distance has been reported by Goldberg for the complex of 18-crown-6 with the dimethyl ester of acetylenedicarboxylic acid.[10] It may also be noted that the malononitrile dipoles are oriented almost perpendicular (ca. 9° inclined) to the plane of 18-crown-6 with their positive poles toward the center of the crown ether void.

In order to study the influence of intervening chain length in α,ω "bifunctional" ligand molecules, we carried out an X-ray

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(29) Knöchel, A.; Kopf, J.; Oehler, J.; Rudolph, G. *J. Chem. Soc., Chem. Commun.* **1978**, 595.

(30) Grimm, H. G. *Z. Elektrochem. Angew. Phys. Chem.* **1925**, *31*, 474.

(31) Kaufmann, R.; Knöchel, A.; Kopf, J.; Oehler, J.; Rudolph, G. *Chem. Ber.* **1977**, *110*, 2249.

(32) Vinogradov, S. N.; Linnell, R. H. "Hydrogen Bonding"; Van Nostrand-Reinhold: New York, 1971.

Table XII. Hydrogen Bonding in Crystalline Complexes[29,31]

guest	hydrogen bonds	O atoms	distance/pm	angles/deg	symmetry of 18-crown-6	stoichiometry
malononitrile	2 simple CH-O	O1	223.5	157.8	D_{3d}	1:2
		O1′	269.4			
adiponitrile	2 simple CH-O	O2	257.5	123.4	D_{3d}	1:1
		O8	242.7	146.8		
cyanamide	2 simple NH-O	O1	210.8	169.9	D_{3d}	1:2
		O7	234.3	138.5		
benzenesulfonamide	2 simple NH-O	O4	199.4	170.1	C_i	1:2
		O4′	233.7			
1-chloroethylsulfonamide	2 simple NH-O	O1	230.0	166.8	D_{3d}	1:2
		O7	222.0	169.2		
methyl 4-aminobenzoate	2 simple NH-O to the same O	O30	203		D_{3d}	1:4
		O30	215			
cyanoacetic acid/water	2 simple OH-O	O4	229.7	168.0	D_{3d}	1:1:1
		O10	194.8	162.4		
	2 bifurcated CH-O	O7	251.4	144.2		
		O13	252.9	151.6		
	hydrogen bond to a carbonyl O	O19	256.9	111.0		
		O20	244.9	107.7		

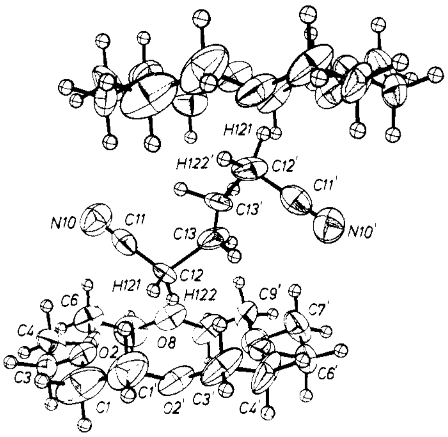

Figure 8. 18-Crown-6/adiponitrile (view parallel to crown ether plane; to get a clearer spatial perspective, another crown ether molecule has been included).

analysis of the 1:1 complex 18-crown-6/adiponitrile. Because of disorder in the adiponitrile molecule the structure could only be refined to $R = 0.148$; however, the salient features can be discerned (Figure 8, Table XII). Atomic coordinates and temperature factors are available upon request (A.K.).

In contrast to the crystallographic C_i symmetry exhibited by the other complexes discussed in this paper, 18-crown-6/adiponitrile possesses two C_2 axes, viz., one axis in the crown ether plane bisecting the C_1–$C_{1'}$ and C_9–$C_{9'}$ bonds, the other bisecting the line C_{13}–$C_{13'}$. Again, the symmetry of the crown ether approximates to D_{3d}.

Adiponitrile is bifunctional; its outer CH_2 groups each coordinate to a crown ether molecule. The crystal lattice is thus composed of polymer chains of alternating crown ether and adiponitriles moieties. Bonding to the crown ether is via both hydrogens, H_{121}–O_2 (257.5 pm) and H_{122}–O_8 (242.7 pm), with less difference in bond lengths than is found in the malononitrile complex. In particular, the interaction between H_{122} and O_8 is stronger for adiponitrile. The inner CH_2 groups are not coordinated and act only as spacers. The structure is similar to that of 18-crown-6/dimethyl acetylenedicarboxylate[10] in which both methyl groups form simple hydrogen bonds to opposite oxygens of the crown ether.

Unlike the other complexes there are two different structure elements present in 18-crown-6/cyanoacetic acid/water. Its features have been discussed in section 2.2.

5. Discussion

Crown ethers, most notably 18-crown-6, are capable of forming host–guest complexes with neutral polar substrates possessing a suitable hydrogen atom arrangement. The variability of these complexes appears to be greater than that of host–guest complexes involving metal cations, but additional parameters are necessary for a comprehensive understanding of their properties. In the interpretation of IR and X-ray data one has to be careful to remember that these reflect solid-state properties that may not necessarily correlate well with solution data as obtained, e.g., from NMR spectroscopy.

5.1. Conformation and Symmetry of the Crown Ether. The crown ether adopts a conformation that allows optimum host–guest interaction, thereby departing from its free-state C_i symmetry. In most cases this preferred symmetry is approximate by D_{3d}, although it is C_i in the 1:1 complexes with benzenesulfonamide, 2,4-dinitroaniline,[26] and guadinium nitrate[33] and the 1:5 complex with urea.[34] The different conformation in these complexes cannot be due to peculiarities of a structure element, since it is observed for three elements which in the majority of cases lead to D_{3d} symmetry. This means that in addition to the geometry of the complexing group there must be other molecular properties influencing the conformation of the crown ether.

5.2. Structural Properties of the Substrate. Comparing complexes with structure elements OH_2, NH_2, and CH_2 with regard to stoichiometry different groups can be recognized. They can all be derived from complexes with the 1:2 composition. In 1:2 host–guest complexes the guest molecules are coordinated above and below the plane of the crown ether subject to certain symmetry requirements; the crown ether may be looked upon as a matrix. High overall symmetry appears to be crucial. Thus, it has not been possible to obtain any "mixed" complexes; either no reaction took place or complete substitution occurred. From this a relative stability order can be derived: H_2N-CN > CN-CH_2-CN > CN-$(CH_2)_2$-CN ≳ CN-$(CH)_2$-CN > H_2N-SO_2-Bz > Cl-C-H_2-CN > CN$(CH_2)_3$-CN ≳ CN$(CH_2)_4$-CN ≳ CH_3CN. 1:1 complexes, in general, form polymeric chains in the crystal lattice; the guest molecules act "bifunctionally". This possibility exists for substrate molecules possessing two XH_2 groups, both of which can coordinate. In this sense, metal cations having at least two H_2O or NH_3 ligands must be viewed as single substrate molecules. The structure of the polymeric chains of metal ions and crown ethers is most clearly illustrated in the complex $UO_2(NO_3)_2 \cdot 2H_2O \cdot$18-crown-6.[1,16,17]

For substrates having NH_2 or CH_2 groups, it is apparently essential for the coordinating groups to be spaced far enough apart. Polymeric 1:1 chains with 18-crown-6 are found with 2-methyl-2-(*n*-propyl)-1,3-propanediol dicarbamate, glutaronitrile,

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(33) Bandy, J. A.; Truter, M. R.; Wingfield, J. N.; Lamb, J. D. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1025.

(34) Harkema, S.; van Hummel, G. J.; Daasvatn, K.; Reinhoudt, D. N. *J. Chem. Soc., Chem. Commun.* **1981**, 368.

adiponitrile, dimethyl sulfate,[28] and dimethyl acetylenedicarboxylate.[10] It appears that a minimum distance between crown ether units must be maintained below which repulsive forces would otherwise become dominant (in all cases, distances between crown ether planes are larger than $\sim$600 pm). Without sufficient spacing between the functional groups a 1:2 composition becomes more favorable in which either only one group coordinates (e.g., dimethyl sulfone)[35] or both groups establish a common bonding scheme (e.g., succinonitrile).[36]

An exception to the postulated symmetry requirement seems to be provided by the complex 18-crown-6/cyanoacetic acid/water. It must be noted, however, that the carboxyl group in spite of its acidic hydrogen does not interact directly with the crown ether, but rather by way of an intermittent water molecule.

A similar situation may be operative in the formation of 18-crown-6/4-bromoaniline through participation of bromine in bonding to the crown ether, although confirmation by crystal structure analysis is still lacking. In this context, it is noteworthy that BrCN and 18-crown-6 form a nonstoichiometric complex.[22]

With methyl 4-aminobenzoate 1:1 and 1:4 complexes of 18-crown-6 have been isolated. Since the X-ray investigation of the 1:1 complex is not yet conducted interpretations are tentative. In the case of 1:1 stoichiometry it is conceivable that in addition to NH_2 the ester methyl group may coordinate (as in 18-crown-6/dimethyl acetylenedicarboxylate). In the 1:4 complex, additional substrate molecules are coordinated to the primary 1:2 host-guest moiety via NH-O bridges to the primary ester host molecules; similar secondary bonding is found in the 1:5 complexes of 18-crown-6 with urea,[34] and rubeanic acid.[21] In all of these cases the influence of crystallization parameters is obvious and shows the importance of lattice forces in the formation of a particular structure type. Analogous considerations should be valid for the 4-aminobenzoic acid complex. The lattice shows a superstructure which is likely to be due to hydrogen bonds between carboxyl groups. For 4-nitroaniline, see section 3.1.

5.3. Overall System of Interactions. Several bonding types and effects are operative in the formation and stability of host-guest complexes. The very important $X—H\cdots O$ interactions between substrates and crown ether oxygens are evident from IR and ^1H NMR spectra as well as crystal-structure determinations. In all complexes discussed here both XH_2 hydrogens take part in coordination, although different schemes are observed (Table XII).

For steric reasons interaction with two crown ether oxygens on the side adjacent to the guest molecule (e.g., O1, O7) is generally favored (complexes with cyanamide and chloroethylsulfonamide).

Interaction in complexes with hydrated metal salts and with malononitrile is with the oxygens related by the center of inversion which are thus above (O1) and below (O1′) the crown ether plane. The same pattern is found on the benzenesulfonamide complex; in it, bond distances are 20–30 pm shorter, indicating stronger bonds, and the crown ether has C_i symmetry (see above).

An unusual bonding scheme is present in 18-crown-6/cyanoacetic acid/water. The CH_2 group forms bifurcated bonds to O7 and O13 (crown ether), and O19 and O20 (carboxyl), respectively, with distances between 245 and 257 pm. In several cases distances in the range 270–300 pm are observed between XH_2 hydrogens of guest molecules and other oxygens of the crown ether; these interactions are certainly very weak, and it is debatable whether they are significant. However, in a polyfunctional bonding system with several relatively weak interactions, overall stability may critically depend on seemingly insignificant contributions.

It is impossible at the present time to quantify the extent of stabilization imported by hydrogen bonds toward overall bonding energy of host-guest complexes. Qualitatively it appears reasonable to assume an increase in importance $CH_2 < NH_2 < OH_2$. This implies that for CH acidic substrates other forms of interaction should predominate. The correlation between $NH\cdots O$ distance and angle postulated by Weber and Sheldrick[26] from an analysis of the 2,4-dinitroaniline complex finds some support in the present investigation. It appears that a shorter hydrogen bond leads to a larger bonding angle.

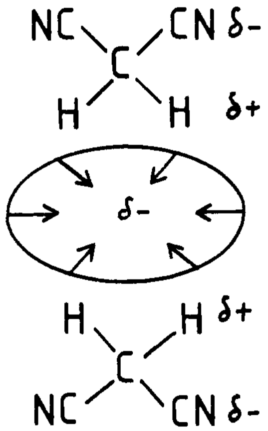

Figure 9. Electrostatic model of 18-crown-6/2malononitrile on the basis of dipole–dipole interactions.

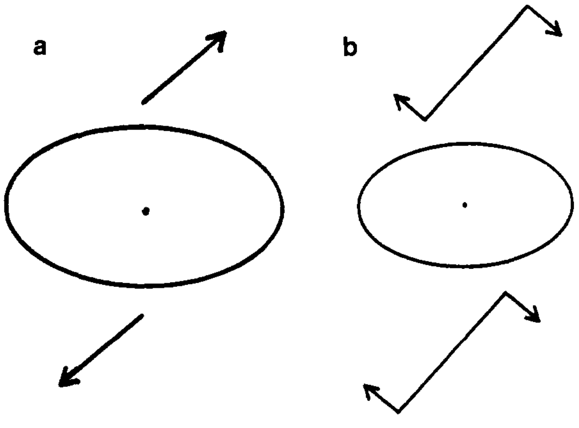

Figure 10. Possible arrangements of dipole compensation in host-guest complexes with overall C_i symmetry for 1:2 (a) and 1:1 stoichiometry (b).

For dipole–dipole interactions apparently almost ideal conditions are found in the complexes of 18-crown-6 with malononitrile and related compounds. In the solid state the substrate molecules are oriented much like the electrostatic model predicts (Figure 9); the deviation is only slight (9°) and extensive dipole–dipole forces may operate. At the same time, this arrangement also facilitates a favorable interaction between the acidic CH_2 protons and crown ether oxygens. In this case, the requirements of both bonding systems tend to supplement each other, resulting in a very favorable host-guest complementarity and large complex stability.

Most systems, regardless of relative importance of hydrogen bonding and dipole forces, possess C_i symmetry with a center of inversion in the plane of the crown ether. Attainment of overall C_i symmetry allows compensation of guest molecule dipole moments (Figure 10). The limits of the dipole interaction concept are evident in the case of 18-crown-6/cyanoacetic acid/water. The complex is the only example known to date in which 18-crown-6 coordinates two different entities. Although charge distribution in the substrates may be such as to allow a certain compensation of dipoles, it is more likely that complete compensation is possible only over larger lattice segments.

The strongest suggestion comes from reactions of 18-crown-6 with racemates of chiral amides (2-bromopropionamide, 1-chloroethylsulfonamide) in which only the *R*/*S* complex is formed, i.e., a complex having C_i symmetry and no dipole moment. A further approach lies in attempting to single out the contribution of hydrogen bonding in various complexes. Corresponding to proton acidity this should decrease in the order $OH_2 > NH_2 > CH_2$ and should therefore be least for CH acidic substrates which

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[35] Bandy, J. A.; Truter, M. R.; Vögtle, F. *Acta Crystallogr., Sect. B* **1981**, *37*, 1568.

[36] Bachmann, K.; von Deuten, K.; Dickel, M.; Frank, J.; Knöchel, A.; Kopf, J.; Rudolph, G., in preparation.

Table XIII. Crystal and Data-Collection Parameters for 18-Crown-6 Complex

	18-crown-6/ cyanacetic acid/water	18-crown-6/ 2cyanamide	18-crown-6/2(1-chloroethylsulfonamide)	18-crown-6/ adiponitrile	18-crown-6·UO_2 $(NO_3)_2 \cdot 4H_2O$	18-crown-6/2(4-aminobenzoic acid)	18-crown-6/ 4(methyl 4-aminobenzoate)
formula	$C_{15}H_{29}NO_9$	$C_{14}H_{28}N_4O_6$	$C_{16}H_{36}Cl_2N_2O_{10}S_2$	$C_{18}H_{32}N_2O_6$	$C_{12}H_{32}UN_2O_{18}$	$C_{26}H_{38}N_2O_{10}$	$C_{44}H_{60}N_4O_{14}$
formula wt	367.4	348.4	551.5	372.5	730.4	538.5	869.52
crystal system	monoclinic p	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic p	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$Pnn2(C_{2v}^{10}$; no. 34)	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Z	4	2	2	2	1	12	4
D_{calcd}/g cm^{-3}	1.23	1.22	1.43	1.16	1.90	1.21	1.25
$V/\times 10^9$ pm^3	1.9833	0.9508	1.2803	1.06285	0.63957	8.8405	4.62770
a/pm	105.8 (2)	828.8 (3)	1056.3 (4)	753.8	757.2	1049.1 (8)	1818.2
b/pm	1709.5 (5)	1446.9 (4)	1106.9 (5)	1039.3	782.4	1779.9 (17)	1212.5
c/pm	1161.6 (3)	801.8 (4)	1109.2 (3)	1356.6	1135.3	4735.0 (42)	2123.6
α/deg	90	90	90	90	97.45	90	90
β/deg	96.79 (2)	98.57 (3)	99.19 (3)	90.0	105.84	90.89 (7)	98.77
γ/deg	90	90	90	90	92.30	90	90
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα/Cu Kα	Mo Kα
fract. angle/deg	$2 < 2\theta < 45$	$1 < 2\theta < 50$	$2 < 2\theta < 54$				
F(000)	792	376	584	404	354	3456	1936
no. of refl							
meas	1554	1898	2267		2389		1919
indep. refl		1689		990	2263		
R	0.043	0.050	0.034	0.148	0.0927		0.112
R_w	0.022 ($1554 \geqslant 3\sigma$)	0.025	0.031 ($2267 \geqslant 3\sigma$)		0.1059		

accordingly should be most sensitive to dipolar forces.

An analysis of the synthetic work involving CH acidic substrates reveals that 1:2 host–guest complexes apparently are obtained only for those potential guest molecules that possess a permanent dipole moment and, correspondingly, belong to symmetry groups C_n or C_{nv}. In contrast, substances like dimethyl malonate or methoxy- and phenylacetonitrile do not react. Although they possess the proper structure elements and acidity, they have no well-defined symmetry due to unhindered rotation. Such symmetry restrictions are not applicable to NH acidic substrates, as evidenced by the reactivity of amides. Apparently, hydrogen bonding is much stronger here. The influence of charge-transfer interactions is a subject of our present investigations, the results of which will be published later on.

A quantitative assessment of the various contributions toward complex stability is not feasible at the present time. In particular, lattice forces are very likely to play a significant role in the solid state as shown by the existence of variable stoichiometries for a number of host–guest combinations. It is not surprising then that in a homologous series of guest molecules having the same structure elements and comparable dipole moments and acidity there is an upper limit in size for complex formation. Thus, complexes with alkyl 4-aminobenzoates are formed only with methyl, ethyl, and propyl esters. In solution, a correlation between complex stability constants and substrate properties such as dipole moment or acidity is conceivable; at the present time, however, reliable data of these constants are lacking.

6. Experimental Section

The substances used were commercially available or were synthesized by known methods. They were recrystallized or redestilled if necessary. NMR measurements were performed on a Bruker WH 90 spectrometer. For the X-ray structure analyses the following programs were used: MULTAN,[37] SHEL X,[38] XANADU,[39] ORTEP.[40] The calculations were performed with the TR 440 computer at the University of Hamburg. Table XIII shows important data of the crystal-structure determination of the investigated 18-crown-6 complexes.

Preparation of the Complexes. A concentrated solution of dry 18-crown-6 in dry ether was added to a stoichiometric amount respectively excess (XXXII) of a boiling saturated solution of the XH_2 compound in dry ether or ether/acetonitrile mixtures (XXV, XXX). The precipitates formed immediately (I–III, XIII, XIV, XVI), after several hours (XXIII, XXIV, XXVII, XXXII) at room temperature, after days (VIII, XI, XVII, XIX–XXII, XXV, XXVI, XXX), or even weeks (XII) at -18 °C; some formed after addition of petroleum ether until the solution became cloudy and cooling to -18 °C for days (IX, X). The precipitates were usually recrystallized from dry ether. Some complexes were recrystallized from mixtures ether/acetonitrile (I–III, XXX), from petroleum ether (XXII), from mixtures ether/petroleum ether (XXI), or from toluene (XIV). Complex XVII formed when the mother liquor from recrystallization of XVIII was evaporated very slowly over a period of three months. Complex V was prepared in glacial acetic acid or H_2O nanopure.

The following complexes had to be prepared under N_2: I–III, VIII, XI, XX, XXI. The stoichiometry of the complexes was determined by elementary analysis. Experimental details and analytical data are available at request.

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Registry No. IV, 87206-07-3; VIII, 87157-04-8; IX, 87157-05-9; X, 87157-06-0; XI, 87157-07-1; XII, 87157-08-2; XIII, 87157-09-3; XIV, 78957-10-5; XV, 70402-12-9; XVI, 87157-10-6; XVII, 87157-11-7;

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Polymer-Immobilized Complexes of Platinum(II): Their Precursors and Preparation Studied by High-Resolution Solid-State ^{31}P NMR Using Magic-Angle Spinning Techniques

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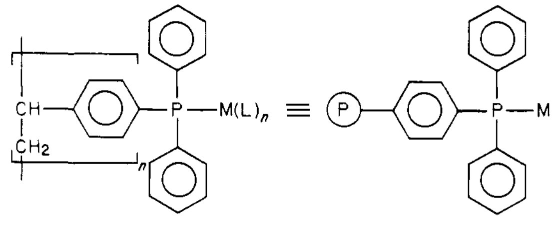
Abstract: Solid-state ^{31}P NMR employing high-power proton decoupling, cross-polarization, and magic-angle spinning has been used to characterize various polymer-immobilized phosphine ligands and their platinum complexes. The reduction of polymer (polystyrene cross-linked with divinylbenzene) bound phosphine oxide, to tertiary phosphine, was monitored by these solid-state ^{31}P NMR techniques. The immobilization of a platinum complex, through reaction with the immobilized tertiary phosphine ligands, and the success of an alternate preparation of such a system were also monitored by this NMR method. To demonstrate the versatility of the NMR technique, platinum complexes were coordinated to 4-poly(vinyl)pyridine, through the pyridine nitrogen, and the outcome of this process was elucidated from the solid-state ^{31}P spectra of triphenylphosphine ligands that were coordinated to the platinum but were not part of the polymer support.

In recent years there has been a great deal of research on polymer-immobilized transition-metal catalysts. In many cases these catalysts involve a cross-linked (with 2–20% divinylbenzene), insoluble polystyrene backbone linked to a previously homogeneous transition-metal catalyst through a phosphorus ligand on the polymer (**1**).



1, M = metal centre; L = ligand

These "heterogenized" catalysts offer the advantages of insoluble heterogeneous catalysts, such as ease of separation, but still retain the high selectivity of homogeneous catalysts. The fixed position of the catalyst on the polymer may also impart greater site isolation and, in some cases, this can drastically increase the activity of the catalyst. Extensive study has been done on the preparation of these systems, and their activity, selectivity, and other properties have been well documented. A number of general reviews that delineate the state of the art in these areas have been published,[2-8] but as yet little success has been achieved in determining either their general structure or the structure at the active site. Such techniques as elemental analysis, microprobe analysis,[9] Fourier transform infrared spectroscopy (FTIR),[10] X-ray photoelectron spectroscopy (ESCA),[11] ESR,[12,13] and photoacoustic spectroscopy[14] have been employed with varying degrees of success. In principle, ^{31}P NMR spectroscopy is an attractive technique with which to investigate these species. The high abundance of ^{31}P (100%, $I = {}^1/_2$) and the generation of metal–^{31}P couplings (for $I = {}^1/_2$ metals, such as ^{103}Rh and ^{195}Pt) make this method highly sensitive and extremely elucidative for studies of homogeneous solutions of transition-metal complexes. The application of this technique, however, to polymer-immobilized systems has met with only limited success. Recent high-resolution solution ^{31}P NMR, on solvent-swollen polymers, by Grubbs et al.[15] reports that a signal observed for an uncoordinated immobilized phosphorus group subsequently disappeared upon coordination to a rhodium complex (with no new peaks appearing). Other related work has been reported by Naaktgeboren et al.[16,17] A general explanation[18] of

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