Complexation of Mercury(II) Compounds by Crown Ethers in Organic Media

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Abstract. Complexes between crown ethers having ring sizes of 15–24 atoms and 5 to 8 oxygens with HgX_2 species (X = Cl, I, CN, SCN) have been prepared and studied. Interactions of the substituents X bound to mercury with groups or fragments in the crown compound are essential in determining the characteristics and stability of the complexes formed. Complexes with crowns of 18C6 ring sizes are the most favourable except for HgX_2 compounds for which the size of X is larger than the macrocycle ring, as is the case for X = CF_3.

**Key words.** Crown ether, mercury(II) complexes.

1. Introduction

The interactions between crown ethers and related species with mercuric compounds have been a relatively unexplored subject. This is unfortunate if one considers the importance of Hg as a polluting agent and its toxicologic aspects for living creatures. The design of synthetic receptors which could scavenge this element from industrial wastes or even from biological fluids justifies a broader study of this field. In one of his first papers, Pedersen [1] described the formation of a complex between BD18C6 and $HgCl_2$. Given the donor atoms in the macrocycle and the characteristics of Hg^{2+}, a strong interaction between crown ethers and this cation is not to be expected [2]. In fact, the calculations reported by Izatt and coworkers [3] for association constants of mercury(II) compounds with crown ethers in water, showed, using $Hg(ClO_4)_2$, a very weak interaction between the cation and 15C5 (log K = 1.68). The interaction was stronger when the ligand possessed the 18C6 macroring (log K = 2.4–2.8). Accordingly, Takeda [4] found that the crown ether 15C5 did not extract Hg from an aqueous solution of mercury picrate to an organic phase (benzene), but the extraction was possible with 18C6 and DB18C6. The presence of nitrogen atoms in the macrocycle clearly favors the complexation of these species as has been shown for several macrocyclic polyamines and cryptands [2, 5–7]. Stable complexes between macroheterocycles containing sulfur atoms and Hg^{2+} have also been described [7b].

For ligands having nitrogen atoms, it is the number of these donor atoms which determines the stability of the complex with Hg^{2+}. For crown ethers, where every

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donor atom is oxygen, equilibrium constants are lower and such ligands do not seem to be very appropriate for the complexation of mercury cations. In addition, the size of the cavity is one of the essential factors in determining the stability of the complex. This factor would explain the weak interaction observed for 15C5 and Hg^{2+}, since the ionic radius of the cation (1.10 Å) [8a] is slightly larger than the cavity radius estimated for the crown ether (0.92 Å) [8b].
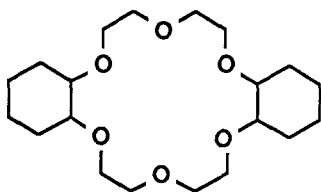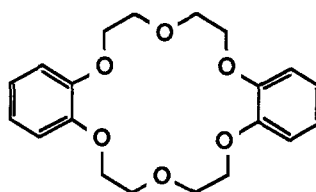
DC18C6   DB18C6
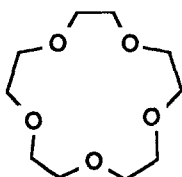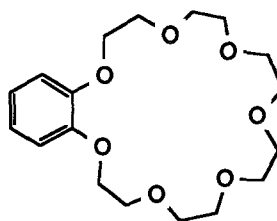
15C5   B21C7

The situation can be substantially modified in organic media. Transport experiments through organic liquid membranes have shown, for instance, how DC18C6 depresses the transport, with respect to free diffusion, by concentration of the complex into the organic phase [9]. An important factor we have to consider is the covalent character of the compounds HgX_2. Complexes of crown ethers with covalent HgX_2 compounds are likely to adopt rotaxane-like structures and accordingly possess some very particular characteristics. Thus, when estimating the critical ratio guest size/macrocycle size which permits the complex formation, it will be necessary to consider not only the ionic radius of the metal but also the size of the substituent X in HgX_2 which can become a limiting factor in some cases [10]. The steric volume of the substituent X as well as its characteristics has to play an essential role in determining the stability of the complex. In the same way, the complexation and decomplexation processes of crown ethers and covalent HgX_2 compounds follow a peculiar kinetic behavior, so that, in some cases, rate constants are up to 10^8 times lower than the usual values for such processes [11]. X-ray studies have confirmed the rotaxane-like structure for a few complexes of crown ethers with $HgCl_2$ [12], HgI_2 [13], $Hg(SCN)_2$ [14], $Hg(CN)_2$ and $Hg(CF_3)_2$ [15].

These complexes with a rotaxane-like structure have remained almost unknown. Complexes of crown ethers with aryldiazonium salts [16] show a partial arrangement of this class, but attempts to obtain true rotaxane structures from them by reaction with an amine to form an azocompound with the azo group passing through the macrocycle ring have failed [17], [18]. Some complexes with related characteristics have also been described for crown ethers and organometallic species [19–21].

In connection with our work on cooperative binding and transport of HgX_2 species [28] we were interested in the study of the complexation of $Hg(CN)_2$ and $Hg(SCN)_2$ by crown ethers in organic media and the factors affecting this interaction. In the present work we have studied the complexation of crown ethers with ring sizes of 15–24 atoms, having 5 to 8 oxygen atoms, with mercuric species HgX_2 as guests, X being: Cl, I, SCN or CN.

2. Experimental

2.1. PREPARATION AND CHARACTERIZATION OF THE COMPLEXES

Results obtained in the preparation of complexes of crown compounds with HgX_2 species (X = Cl, I, CN, SCN) are summarized in Table I. Benzocrown ethers were prepared as previously reported [22] as well as the biphenyl crown ethers BF19C5, DMBF19C5 and bis-BF19C5 [15] [23]. Diacetyl-DB18C6 was obtained from DB18C6 by treatment with $AcOH/P_2O_5/CH_3SO_3H$ [24]. Benzyloxymethyl-21C7 was synthesized according to the method described by Bartsch [25] and its hydrogenolysis in acidic media gave the hydroxymethyl-21C7 [26]. The other crown ethers were obtained from commercial sources.

PhCH₂OCH₂21C7   HOCH₂21C7
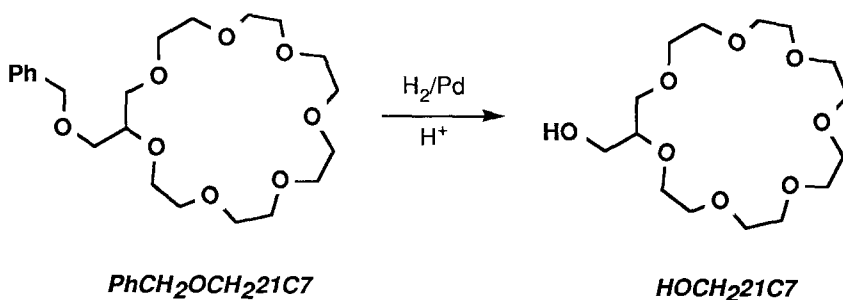
The preparation of complexes between crown ethers and mercuric compounds HgX_2 is as follows. The crown ether is dissolved in an apolar solvent ($CHCl_3$ or CH_2Cl_2) and the mercuric compound is added in a more polar solvent (acetone or methanol). For example, the preparation of $18C6\cdot Hg(SCN)_2$ involved the crown ether in chloroform and the $Hg(SCN)_2$ in methanol, using a ratio $HCCl_3/MeOH$ (4:1). The resulting solution was stirred at room temperature in the dark for 24 hours. The solvent was vacuum distilled and the residue was crystallized from a mixture of AcOEt/Acetone (1:1). Some of the complexes in Table I are described

Table I.   Complexes between crown ethers and mercuric species.[a]

Crown ether	Mercuric salt	Yield %	Melting point (°C)
18C6	$Hg(SCN)_2$	35	267.0 d (AcOEt/Acetone 1:1)
	$Hg(CN)_2$	58	310.0 d (Acetone/MeOH 1:1)
	$HgCl_2$	86	274.9 d (MeOH)
	HgI_2	39	220.6 d (Acetone/MeOH 1:1)
B18C6	$Hg(SCN)_2$	48	161.5 d (AcOEt)
	$Hg(CN)_2$	95	198.2 d (Acetone)
	$HgCl_2$	15	209.1 d (AcOEt)
	HgI_2	6	152.7 d (AcOEt)
DC18C6	$Hg(SCN)_2$	77	211 d (MeOH)
	$Hg(CN)_2$	69	270 d (MeOH)
DB18C6	$Hg(SCN)_2$	42	244 d (MeOH)
	$Hg(CN)_2$	77	275 d (MeOH)
	$HgCl_2$	85	271 d (MeOH)
	HgI_2	36	175 d (Acetone/MeOH 2:1)
diacetyl--DB18C6	$Hg(SCN)_2$	56	174 ± 1 d (AcOEt/MeOH)
	$Hg(CN)_2$	54	255 ± 1 d (AcOEt/MeOH 4:1)
BF19C5	$Hg(SCN)_2$	26	205 ± 3 d (AcOEt)
DMBF19C5	$Hg(SCN)_2$	58	165 ± 1 d (AcOEt)
bis-BF19C5	$Hg(SCN)_2$	38	167 ± 2 d (AcOEt)
	$Hg(CN)_2$	40	190 ± 1 d (AcOEt)
21C7	$Hg(CN)_2$	87	260 ± 1 d (AcOEt)
	$Hg(SCN)_2$	–	oil
$HOCH_2$21C7	$Hg(SCN)_2$	–	oil
$PhCH_2OCH_2$21C7	$Hg(CN)_2$	–	oil
	$Hg(SCN)_2$	–	oil
B21C7	$Hg(SCN)_2$	–	oil
	$Hg(CN)_2$	32	148 ± 1 d (AcOEt)
DB24C8	$Hg(SCN)_2$	76	115 ± 1 d (MeOH)
	$Hg(CN)_2$	90	157 ± 1 d (MeOH)

[a]All compounds gave the expected combustion analysis for 1:1 complexes.

as oils. For those cases, crystalline compounds could not be obtained with any of the solvents tried.

In Table II, the chemical shifts observed for 18C6 and DC18C6 and their complexes with HgX_2 species are summarized. Similar trends are found for the other ligands studied. Data obtained permit us to consider that chemical shifts in the ^1H NMR for crown ethers and their complexes with HgX_2 compounds are mainly affected by factors related to the characteristics of the substituents X bound to mercury, as well as to the structure of the ligand, especially the presence of aromatic rings, the nature of the substituents and the symmetry and rigidity of the system. Because of these factors the changes in the ^1H NMR of crown ethers which proceed upon complexation with HgX_2 species cannot be easily predicted. The most general trend observed for complexation of metal cations is a downfield shift [27]. However, for the complexes we have studied, there are cases where aliphatic

Table II.   Chemical shifts for 18C6 and DB18C6 and their complexes with HgX_2 species in $CDCl_3$.

Compound	Chemical shifts (ppm, δ)				
	18C6	DB18C6			
Free ligand	3.67	4.01–4.05	4.16–4.19	6.89	6.9
CE·Hg(CN)$_2$	3.66	4.07–4.08	4.20–4.22	6.84–6.88	6.90–6.95
CE·HgCl$_2$	3.66	4.11–4.12	4.21–4.24	6.82–6.86	6.88–6.93
CE·Hg(SCN)$_2$	3.68	4.10–4.16	4.23–4.29	6.85–6.93	6.94–7.01
CE·HgI$_2$	3.61	4.01–4.07	4.14–4.20	6.79–6.89	6.89–6.97

Table III.   Some characteristic infrared bands for the complexes 18C6·HgX_2(cm^{-1}).

18C6 free	18C6. Hg(SCN)$_2$	18C6. Hg(CN)$_2$	18C6. HgCl$_2$	18C6. HgI$_2$
1354	1348	1347	1347	1344
1107	1096	1099	1100	1103
	296	423	345	234

protons experience a downfield shift (as is the case for complexes of DB18C6 with $Hg(CN)_2$ or $HgCl_2$), but for some others an upfield shift is observed (for instance in 18C6·$Hg(CN)_2$, 21C7·$Hg(CN)_2$ or B18C6·$Hg(SCN)_2$). The substituents X bound to mercury (especially the ones with higher electron densities) and their steric and electronic interactions with macrocycle substituents (for example, aromatic groups) play an essential role in determining such behavior.

Infrared spectroscopy was one of the first methods used for the characterization of complexes with crown ethers [1]. The binding of the oxygens in the macrocycle with the mercury guest is reflected in the C—O stretching bands and in vibrations corresponding to methylene groups which are affected by the binding of the vicinal oxygens. In our case, the infrared characterization of complex formation was important in connection with transport experiments using polymer-bound crown ethers [28]. In general, small shifts to lower frequencies can be observed for bands in the region $800-1400$ cm^{-1}, as well as variations in the intensity and shape of the

Table IV.   Frequencies for -SCN bands in the complexes CE·Hg(SCN)$_2$ (KBr Pellets).

Compound	SCN band (cm^{-1})
Free	2050
18C6	2125
DC18C6	2123
B18C6	2120
DB18C6	2126
bis-BF19C5	2133
BF19C5	2128
DMBF19C5	2129
DB24C8	2106

same bands and the presence of X—Hg—X bands in the low frequency region [12b–14]. This is illustrated in Table III for complexes of 18C6. The most prominent difference is observed in complexes formed with $Hg(SCN)_2$, as shown in Table IV. The —SCN band for the uncomplexed mercuric compound appears at about $2050 \, cm^{-1}$, but for most complexes such a band is observed at 2120–$2130 \, cm^{-1}$. For crown ethers with larger ring sizes, the band in the complex can be shifted to frequencies similar to the ones for the free species.

3. Results and Discussion

3.1. STABILITY OF COMPLEXES BETWEEN CROWN ETHERS AND HgX$_2$ SPECIES

When studying factors which determine the stability of complexes between crown ethers and different guests, especially metallic cations, the fit between the cavity size in the macrocycle and the size of the guest is considered essential. For complexes with HgX_2 compounds, Rebek and coworkers have shown the fundamental role of the size of the substituent X in the formation of the complexes. In this way, they found that $Hg(CF_3)_2$ did not form stable complexes with crown ethers having ring sizes of 19 atoms or less [23], even though the cavity size of a 18 membered ring, e.g. 18C6, (≈ 1.45 Å [8b]) should have been big enough to accommodate a Hg^{2+} ion (ionic radius = 1.16 Å [8a]). For these cases, the size of the CF_3 group (radius ≈ 2.0 Å) does not permit the formation of the complex. However, this mercuric compound was complexed by larger macrocycles such as BF20C6, BP20C6, BF22C6, 21C7, etc. (cavity radius 1.9–2.2 Å) [11, 15].

The rotaxane-like structure of the complexes formed by crown ethers and Hg(II) species is responsible for this behavior. The formation of these complexes requires that one of the X groups bound to the Hg passes through the macrocycle cavity. For that process to occur, the size of the cavity has to be larger than the steric volume of the X group, which can be clearly bigger than that of the Hg^{2+} cation. The very slow rate constants observed for some of the complexation and decomplexation processes with these guests can also be explained by the former considerations. In general, complexation of crown ethers with inorganic and organic cations is fast, with rate constants of the order of 10^6 [29]. However, the rate constant for the complexation of $Hg(CN)_2$ by 18C6 is about $10^{-2} \, M^{-1} \, s^{-1}$ and the rate constant for decomplexation of $Hg(CF_3)_2$ from its complex with 21C7 is even smaller, in the range of 10^{-4} [11]. When the size of the ring is large enough, rate constants are usually higher and can be compared with the ones found for other guests. The requirement for the substituent bound to the mercury to pass through the macrocycle ring, implies the existence of a highly organized transition state. The interaction between atoms and groups in the macrocycle with the substituent X in HgX_2 causes the slowness of the related processes.

These characteristics make the calculation of the association constants difficult. Only for a few cases, could the exact values be determined by NMR techniques (Table V). For 18 membered rings, the affinity seems to be very high and the processes are very slow. A minimum value was assigned based on kinetic data. It is likely that the value would be higher than the one listed in Table V.

BF19C5

DMBF19C5

BP20C6

BP19C5

bis-BF19C5
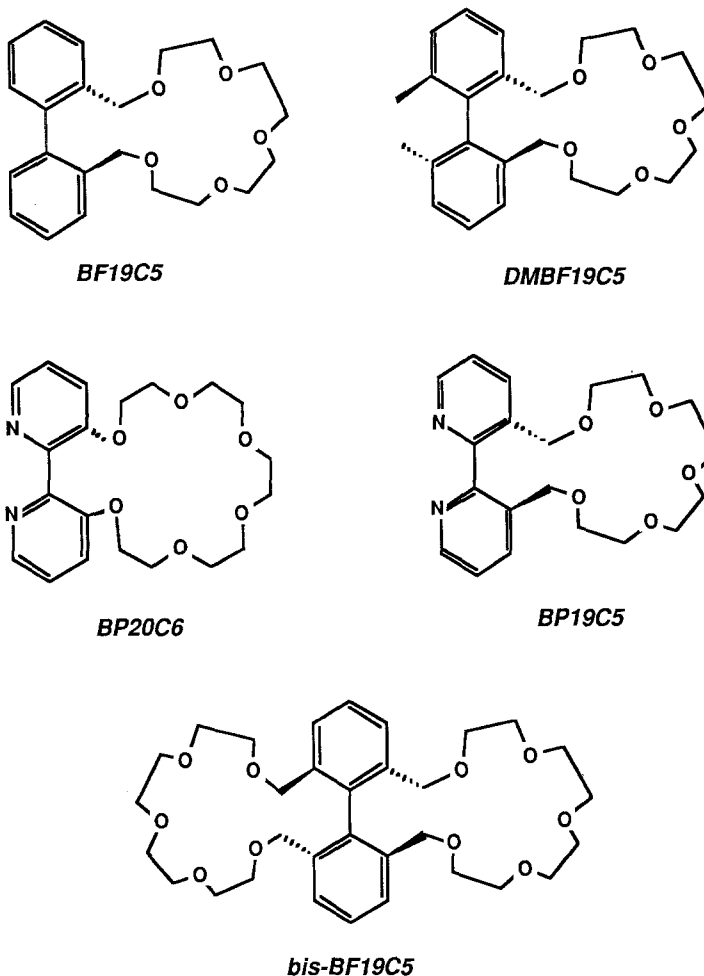
The formation of crystalline complexes is considered indicative of the existence of a favorable association constant between the host and the guest [1]. No definite crystalline complexes could be obtained for HgX_2 and 15C5 or B15C5. Complexes with crown ethers with 18 atoms in the ring (18C6, DB18C6, etc.) as well as with 21C7 are well defined crystalline solids, but the complexation of crown ethers having biphenyl or bipyridyl moieties affords waxy solids which can be crystallized only with difficulty. A similar situation was observed for B21C7 and $Hg(CN)_2$ or $Hg(SCN)_2$, especially for the latter, where an oil was formed which could not be crystallized. For complexes of $HOCH_2$21C7 and $PhCH_2$21C7 only oily products were always obtained. For some of the oily products, the Hg(II) compound eventually precipitates out.

We believe that the decomposition points of the complexes give information on the relative stabilities in related complexes, and they can be used as additional data to establish the trends in the variations of the association constants. Figure 1a shows the decomposition points of complexes formed by $Hg(CN)_2$ and $Hg(SCN)_2$

Table V.   Calculated values for K_a in the complexes $CE \cdot HgX_2$.

Host	Guest	Solvent	$K_{eq.}$ (M^{-1})	Method	
18C6	$Hg(CN)_2$	acetone/$CDCl_3$ 1 : 0.8	$> 10^4$	^1H NMR	
DB18C6	,,	,,	$> 10^4$	,,	
DMBF19C5	,,	acetone/C_6D_6 1 : 1	13	,,	[15]
bis-BF19C5	,,	,,	$K_1^i = 11$	,,	,,
			$K_2^i = 110$		
BF19C5	$Hg(SCN)_2$	MeOH	197	,,	[28]
DMBF19C5	,,	,,	172	,,	,,
bis-BF19C5	,,	,,	$K_1^i = 156$	,,	,,
			$K_2^i = 632$	,,	,,
BF20C6	$Hg(CF_3)_2$	$CDCl_3$	1700	^{19}F NMR	[11]
BP20C6	,,	,,	200	,,	,,
21C7	$Hg(CN)_2$	acetone/$CDCl_3$ 1 : 0,8	1.5×10^3	^1H NMR	
BF22C6	$Hg(CF_3)_2$	acetone/C_6D_6 1 : 1	450	^{19}F NMR	[10]
DMBF22C6	,,	,,	150	,,	,,
BP22C6	,,	,,	700	,,	,,
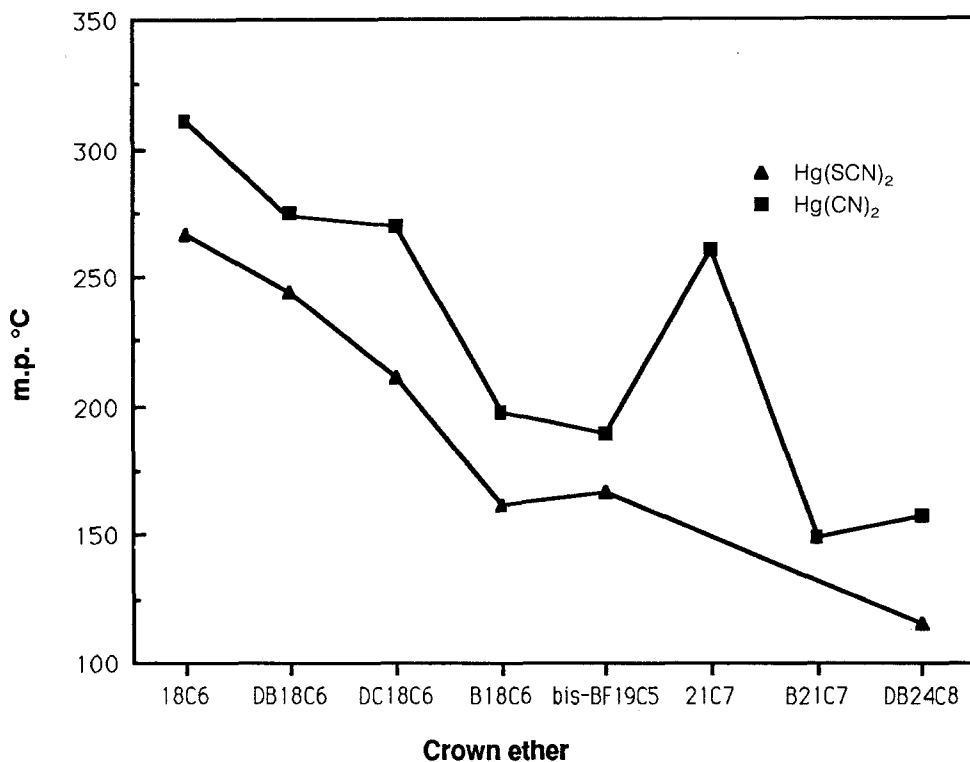
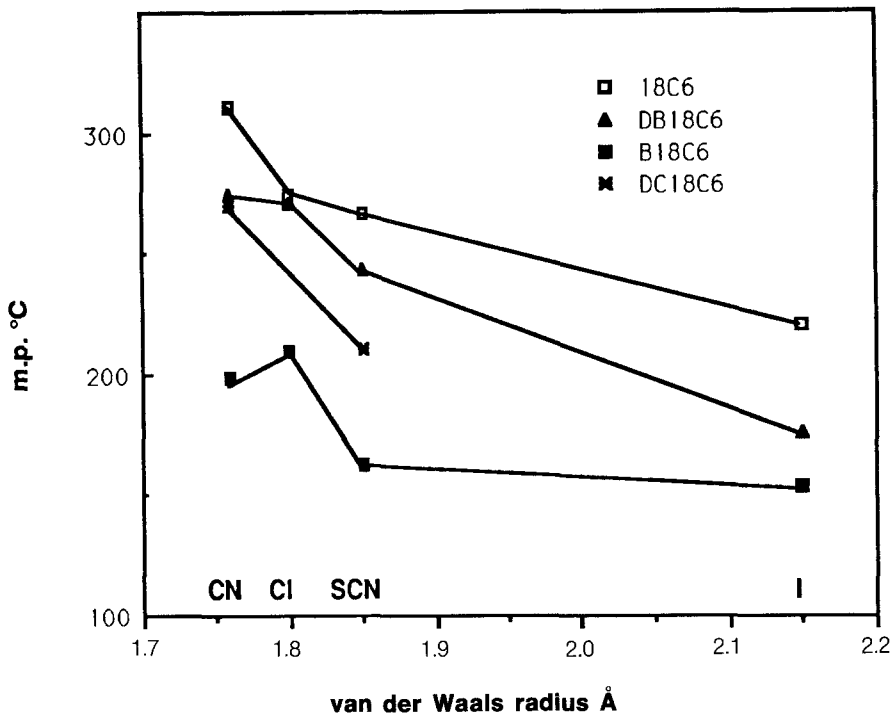Fig. 1a   m.ps. of $Hg(SCN)_2$ and $Hg(CN)_2$ complexes with crown ethers.

Fig. 1b   m.ps. of HgX_2 complexes with crown ethers having ring sizes of 18 members.

with crown ethers of different classes. Figure 1b represents the variation in the decomposition point of complexes formed by crown ethers with ring sizes of 18 members, when the size of the substituent is changed. For that, the van der Waals radius of the atom directly bound to Hg was chosen as the representative parameter for the size of the X group, the order being I > SCN > Cl > CN.

Analysis of both graphs shows some trends. First, it is clear that the stability of the complexes increases when the size of X in HgX_2 decreases. This is in agreement with the former observation that $Hg(CN)_2$ was able to displace $Hg(CF_3)_2$ from its complexes with several crown ethers [11], [15] (see experiments 16–19 in Table VII). If we consider the structure of the macrocycle, Figure 1a shows the trend is lower stability for larger macrocycles. Also the symmetry of the ligand plays an important role. The most symmetric crown ethers form the most stable complexes, and the presence of substituents or groups which alter the symmetry of the macrocycle and/or introduce additional steric factors (which will produce unfavourable interactions with the X groups) lead to destabilization of the complex. In this sense, the presence of benzo groups in benzo or dibenzo ethers is not favorable (relative to the unsubstituted crown ether) as it also decreases the basicity of some of the oxygen donor atoms.

Another approach, also in a qualitative sense, is to establish the relative order of association constants in these complexes through direct exchange experiments. Different experiments of this class were carried out by allowing the exchange between a complex $CE \cdot HgX_2$ and another crown ether (CE') or another HgX'_2

Table VI.   Direct exchange experiments $L_1 \cdot HgX_2 + L_2 \rightleftharpoons L_1 + L_2 \cdot HgX_2$

Experiment	HgX_2	L_1	L_2	Predominant complex
1	$Hg(CN)_2$	18C6	DB18C6	a
2	,,	21C7	,,	$DB18C6 \cdot Hg(CN)_2$
3	,,	L21C7[b]	,,	,,
4	,,	21C7	18C6	$18C6 \cdot Hg(CN)_2$
5	,,	bis-BF19C5	DB18C6	$DB18C6 \cdot Hg(CN)_2$
6	,,	,,	21C7	$21C7 \cdot Hg(CN)_2$
7	$Hg(CF_3)_2$	BF20C6	,,	$21C7 \cdot Hg(CF_3)_2$
8	,,	DMBF22C6	,,	,,
9	$Hg(SCN)_2$	DB18C6	P-DB18C6	a
10	,,	DC18C6	"	$P\text{-}DB18C6 \cdot Hg(SCN)_2$[c]
11	,,	BF19C5	,,	,,
12	,,	bis-BF19C5	,,	,,
13	,,	DB24C8	,,	d
14	,,	DB18C6	P-21C7	$DB18C6 \cdot Hg(SCN)_2$
15	,,	BF19C5	,,	$BF19C5 \cdot Hg(SCN)_2$[e]

[a]No modification of the initial situation after two months. [b]$L21C7 = PhCH_2OCH_221C7$.
[c]$K_{DB18C6} \geqslant K_{DC18C6}$. [d]$K_{P\text{-}DB18C6} \geqslant 60 K_{DB24C8}$. [e]$K_{BF19C5} \geqslant K_{L21C7}$

species (Tables VI and VII). In general, for every exchange study, two separate experiments were performed; one starting with one of the two possible complexes (for instance $CE \cdot HgX_2$ and $CE' \cdot HgX_2$) and adding, in similar conditions, the other competitive species (CE' or CE for the same example) and following the evolution of both systems at identical periods of time. Usually, after periods of time of about 1 month, appreciable variations from the initial position are only observable for one of the two equilibria, being indicative of a larger association constant for the complex which is being formed.

For experiments 1–6, ^1H NMR was used to follow the shift in the position of the equilibria, and ^{19}F NMR was used for 7, 8 and 16–19. In experiments 9–15, where polymer-bound DB18C6 [28] and 21C7 [30] crown ethers were used, the equilibration of the system was monitored by infrared spectroscopy. In these cases, $Hg(SCN)_2$ was used as the guest, and the SCN band when complexed (≈ 2130 cm^{-1}) permits observation of the formation of the polymeric complex. The intensity ratio between this band and one characteristic for the polymeric backbone (the C—H bands at ≈ 2778–3122 cm^{-1}) represents a measure of the complexation degree for the polymer-bound crown ether. Combustion analysis of different samples allows one to establish a quantitative relationship between the value of the

Table VII.   Direct exchange experiments $L \cdot HgX_2 + HgY_2 \rightleftharpoons HgX_2 + L \cdot HgY_2$

Experiment	L	HgX_2	HgY_2	Predominant complex
16	BF20C6	$Hg(CF_3)_2$	$Hg(CN)_2$	$BF20C6 \cdot Hg(CN)_2$
17	BP20C6	,,	,,	$BP20C6 \cdot Hg(CN)_2$
18	21C7	,,	,,	$21C7 \cdot Hg(CN)_2$
19	BF22C6	,,	,,	$BF22C6 \cdot Hg(CN)_2$

relative intensity and the complexation degree [28]. A quantitative approach to the values for association constants through direct exchange experiments is difficult because of the sluggishness of some of the processes for complexation and decomplexation, so that the final points for the equilibria are not accurately known.

For experiment 3, starting from the complex $PhOCH_2OCH_221C7 \cdot Hg(CN)_2$ and DB18C6, it was observed that after a period of 73 days 78% of the $Hg(CN)_2$ had passed to the DB18C6, but equilibrium had not been reached. When the starting point was $DB18C6 \cdot Hg(CN)_2$ and $PhOCH_2OCH_221C7$, no variation could be observed after a similar period of time. Exchange processes for crown ethers which form stronger complexes than $PhCH_2OCH_221C7$ are still slower and, in general, periods of some months are required before significant changes are observed from the initial situation. For experiments 1 and 9, no appreciable exchange was observed even after two months of contact. However, for experiment 10 (initial complex $DC18C6 \cdot Hg(SCN)_2$), a significant transfer was observed, after that time, from DC18C6 to DB18C6.

In general, we can conclude that association constants are larger for crown ethers with smaller ring sizes, at least if the cavity permits the passage of the substituent X through it. In this sense, the association constant for $18C6 \cdot Hg(CN)_2$ is clearly larger than the one for $21C7 \cdot Hg(CN)_2$. This fact can be explained by considering that for larger macrocycles, in a planar conformation, oxygens atoms will not be as close to the central Hg atom, and the interaction will not be as strong as for macrocycles with smaller rings. The approach of some of the oxygen atoms to the Hg, in the larger macrocycles, requires the deformation of some parts of the ring, resulting in unfavorable steric interactions between the X groups of the mercuric compound and the fragment of the crown ether which is distorted out of the coplanar system formed by donor atoms around the Hg atom. Steric hindrance is even more important for non symmetrical crown ethers, having side chains or big substituents. Accordingly, association constants for complexes formed between crown ethers with ring sizes of 21C7 and HgX_2 species decrease in the order:

$$K_{21C7} > K_{B21C7} > K_{L21C7}.$$

$PhCH_2OCH_221C7$ (L21C7) possesses most of these unfavorable factors and its K_a values for complexation of HgX_2 species are expected to be very low. It is significant that in the exchange experiment between $L21C7 \cdot Hg(CN)_2$ and DB18C6, the variation in the concentration of DB18C6 and $DB18C6 \cdot Hg(CN)_2$ follows a second order rate law (first order in DB18C6 and first order in $Hg(CN)_2$) where it can be considered that

$$[Hg(CN)_2]_t = [L21C7 \cdot Hg(CN)_2]_o - [DB18C6Hg(CN)_2]_t,$$

and that would represent $K_a = 0$ for L21C7. The correlation factor is greater than 0.99 and the rate constant calculated in this way ($k = 3.02 \times 10^{-4} \, M^{-1} \, s^{-1}$) is in good agreement with the value obtained in $CDCl_3$ for complexation of DB18C6 with $Hg(CN)_2 (k = 2.75 \times 10^{-4} \, M^{-1} \, s^{-1})$ [11].

Similar destabilizing factors can be found for 18C6 rings. Experiment 10 confirms how the presence of cyclohexane rings, with important steric requirements, is reflected in a value of the association constant with $Hg(CN)_2$ being much lower than for crown ethers DB18C6 or 18C6.

The former unfavorable factors have to be important for biphenyl and bipyridyl systems for which low association constants can be predicted, as is experimentally observed. The important steric volume of biphenyl and bipyridyl groups prevents their accommodation coplanar with the macrocycle ring. These factors are clearly seen in the complex of dimethylbiphenyl22C6 and bistrifluormethylmercury, for which the X-ray structure exists [15]. One observes an important deformation of the crown ether, with not all the oxygens being coplanar. Only 5 of the oxygens are situated in a plane at a distance (2.8–3.12 Å) which permits the interaction with the Hg (compare with data in References 12–14). The sixth oxygen, a benzylic one, is out of the plane by 1.1 Å and is situated 3.45 Å from the Hg, the interaction being not important. These data, as well as experiments in Table VI (experiments 5–8 and 11, 12, 15) confirm the former hypothesis.

4. Conclusions

Interactions of crown ethers with covalent mercury(II) compounds in organic media can be important and crystalline complexes have been obtained for a variety of hosts. Because of the nature of the mechanism proposed for the complexation process [11] a limiting factor in the formation of the complexes is the size of the groups X in HgX_2 which have to pass through the macrocycle ring. The structure of the HgX_2 compound is essentially retained after complexation [12–15] and thus, the nature of the X group determines the stability of the complexes. For a given host, the stability of the crown·HgX_2 complex increases when the size of X decreases. For a given guest, a lower stability is found for larger macrocycles, for unsymmetric rings and for crowns having additional substituents. Unfavorable interactions between X groups and substituents or fragments of the crown ether would explain the observed trends. In general, the most stable complexes are formed for crown ethers having 18C6 rings except for HgX_2 compounds with an X substituent which cannot pass through the macrocycle ring.

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