Complexes of Mercury(II) Cyanide with Crown Ethers in Dimethylsulfoxide

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Abstract

The complexation of mercury(II) cyanide with macrocyclic ligands 15-crown-5, 18-crown-6 and dibenzo-24-crown-8 in dimethylsulfoxide was studied using [199]Hg NMR measurements. No significant complexation with 15-crown-5 was observed. The stability constants K_s for 1 : 1 complexes with two other ligands were determined and found to be similar, in contrary to the results reported in nitrobenzene. Solvent effects on K_s values obtained are discussed in comparison with the literature data. The X-ray crystal structure of $Hg(CN)_2 \cdot 18$-crown-6 was also determined.

Introduction

The stability and the stoichiometry of the crown ether complexes depends on a number of factors, among them first of all on the match between the diameter of the cation and the cavity size of the ligand [1–5], the degree of flexibility of the ligand [4–7], the number and the nature of heteroatoms and substituent groups in the ring [3–5, 8] as well as solvent properties [3–5, 9, 10]. For small crown ethers with rigid rings the effect of the cavity size is predominant and in aprotic solvents (when there is no hydrogen bonding to ligands [11]) the order of stability constants K_s for the same cation and different ligands was found, in general, to be solvent independent [9, 10]. On the other hand, different behaviour can be expected taking into account different slopes of the linear decrease of log K_s for various ligands with the solvent donor number DN [2, 3, 9–12]. In the present study, it is shown that the differentiating effect of the cavity size on stability constants reported in the literature for complexes of mercury(II) with 18-crown-6 and dibenzo-24-crown-8 in less basic solvents is strongly diminished in dimethylsulfoxide (DMSO).

The complexation of mercury(II) with crown ethers and other macrocyclic ligands has sparked considerable interest recently [13, 14], largely because of the search for the application of solvent extraction of those complexes to control and remove mercury, a highly dangerous element, from industrial waste streams. Some of those complexes involve covalent compounds of mercury instead of lone cations. Complexes of macrocyclic polyethers with non-ionic mercury molecules, in particular with certain organomercurials as $Hg(CF_3)_2$ and with $Hg(CN)_2$ were also widely explored [15–18] as simple models for allosteric effects found in enzymology and a rotaxane-like structure of the above complexes was supported by crystallography [16, 19]. However, the knowledge of factors affecting stability constants for complexes with simple cations and with covalent molecules is still very incomplete.

Experimental

Anhydrous DMSO (99.8%, Sigma-Aldrich) and *N,N*-dimethylformamide (DMF, Uvasol grade, Merck), $Hg(CN)_2$ (p.a., POCh), and three crown ethers (all >98%, Merck) were used as received. Solutions for measurements contained 0.1 M mercury salt and varying concentrations of crown ethers.

[199]Hg NMR measurements were made on a Varian UNITY-Plus 200 MHz spectrometer at 35.7679 MHz and the temperature of 300 K. The sealed 4-mm o.d. solution samples were fit into standard 5-mm o.d. thin-walled NMR tubes (Wilmad 528-PP) with liquid benzene-d_6 in the annular space. Benzene-d_6 was used for the lock system and [199]Hg signal of $Hg(CN)_2$ in DMSO as the external reference standard. For the same DMSO solvent of samples the bulk diamagnetic susceptibility corrections was neglected (for the highest concentration of crown ether its volume corresponds only to 0.09% of the sample volume). Only one averaged signal of [199]Hg was observed in DMSO. The stability constants for 1 : 1 complexes were calculated from the variation of the chemical shift with the [ligand]/[mercury(II)] mole ratio according to the method of Popov et al. [9, 20] using a similar computer program for the fitting of experimental points to the theoretical equation.

Crystals of $Hg(CN)_2 \cdot 18$-crown-6 were prepared by mixing the methanol solutions of both compounds at room temperature. The crystal structure was determined on a KUMA KM4CCD κ-axis diffractometer applying a graphite-monochromated MoKα radiation. The species was positioned at 62.25 mm from the KM4CCD camera; 600 frames were measured at 1.0° intervals with a counting time

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of 25 sec. The data were also corrected for Lorentz and polarization effects, as well as absorption correction [21]. Data reduction and analysis were carried out using the KUMA Diffraction (Wroclaw) programs. The structure was solved by the direct methods [22] and refined using a SHELXL computer program [23]. The refinement was based on F^2 for all reflections, except those with strongly negative F^2 values. Weighted R factors, wR, and all goodness-of-fit S values are based on the F^2 parameters. Conventional R factors are based on F with F set to zero for negative F^2. The $F_0^2 > 2s(F_0^2)$ criterion was used only for the calculation of R factors and is not relevant to the choice of reflections for refinement. The R factors based on F^2 were about twice as large as those based on F. All hydrogen atoms placed in the calculated positions and their thermal parameters were refined isotropically. Scattering factors were taken from literature (Tables 6.1.1.4 and 4.2.4.2 in the [24]). X-ray measurements were carried out in the Crystallography Unit of the Faculty of Chemistry, Warsaw University.

Results and discussion

Stability constants for complexes of mercury(II) with 18-crown-6 were reported only in nitrobenzene (PhNO$_2$) [12], acetonitrile (ACN) [12, 25] and water [26]. Unfortunately, we found that for a number of other solvents (including methanol, acetone, DMF, and tetrahydrofuran) the 1 : 1 complex precipitates relatively quickly after mixing the solutions of the crown ether and Hg(CN)$_2$ at room temperature, and therefore NMR measurements in those solvents were not possible.

Crystal structure of Hg(CN)$_2$·18-crown-6

The 1 : 1 stoichiometry of Hg(CN)$_2$ complexes with 18-crown-6 was confirmed and the crystal structure was determined by the X-ray diffraction. The summary of data collection and structure solution is given in Table 1. The structure of Hg(CN)$_2$·18-crown-6 is shown in Figure 1 with the numbering scheme. The metal coordination is hexagonal bipyramidal with cyano groups coordinated in the axial positions and 18-crown-6 in the equatorial plane, in the same manner as was established for crystals of the Hg(CN)$_2$·18-crown-6 monohydrate [19] and of HgCl$_2$·18-crown-6 [27]. The mercury atom is bound to all six oxygen atoms as found in similar complexes [19, 27] and the structure of the crown ring is also similar. However, two different O···Hg distances were found, equal to 2.745(2) Å and 2.894(2) Å, whereas for monohydrate complex all O···Hg distances have exactly the same length 2.838(2) Å [19] and all oxygen atoms are symmetry equivalent giving the pseudo rotaxane structure. Thus, for Hg(CN)$_2$·18-crown-6 the crystal system is trigonal with the space group R3, whereas for monohydrate Hg(CN)$_2$ and HgCl$_2$ complexes it is rhombohedral, R3⟨over bar⟩. Both Hg···C distances to carbon atoms in CN groups are also different (1.91(2) Å and 2.12(2) Å) whereas they are the same (2.047(4) Å) for monohydrate [19] involving a water

Table 1. Crystal data and structure refinement for Hg(CN)$_2$·18-crown-6 complex

Empirical formula	C$_{14}$H$_{24}$HgN$_2$O$_6$
Formula weight	516.94
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	trigonal, R3
Unit cell dimensions:	
a	11.590(2) Å
b	11.590(2) Å
c	12.225(2) Å
α	90°
β	90°
γ	120°
Volume	1422.2(4) Å^3
Z, Calculated density	3, 1.811 Mg/m^3
Absorption coefficient	8.145 mm^{-1}
$F(000)$	750
Crystal size	0.25 × 0.18 × 0.16 mm
Theta range for data collection	3.52 to 28.62°
Index ranges:	
h_{max}, h_{min}	15, −14
k_{max}, k_{min}	15, −15
l_{max}, l_{min}	16, −16
Reflections collected/unique	4444/1535 [R(int) = 0.0400]
Absorption correction	numerical
Max and min transmission	0.4467 and 0.2459
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	1534/1/72
Goodness-of-fit on F^2	0.960
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0304, wR2 = 0.0447
R indices (all data)	R1 = 0.0392, wR2 = 0.0486
Absolute structure parameter	0.00
Extinction coefficient	0.00141(12)
Largest diff. peak and hole	0.461 and −1.192 e A^{-3}

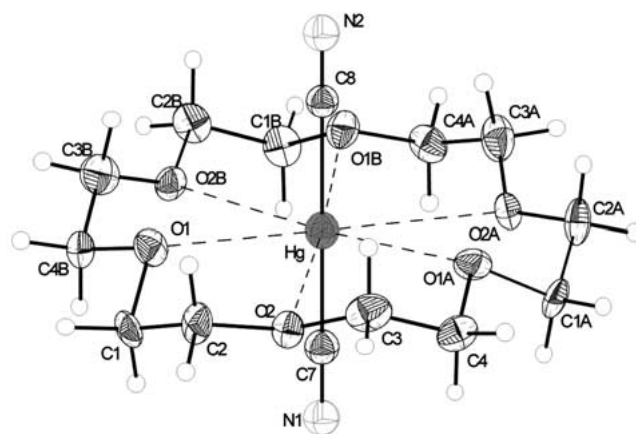molecule connecting the nitrogen atoms of both CN groups through hydrogen bonds.

Figure 1. ORTEP drawing of the molecular structure of Hg(CN)$_2$·18-crown-6 showing the atom numbering scheme.
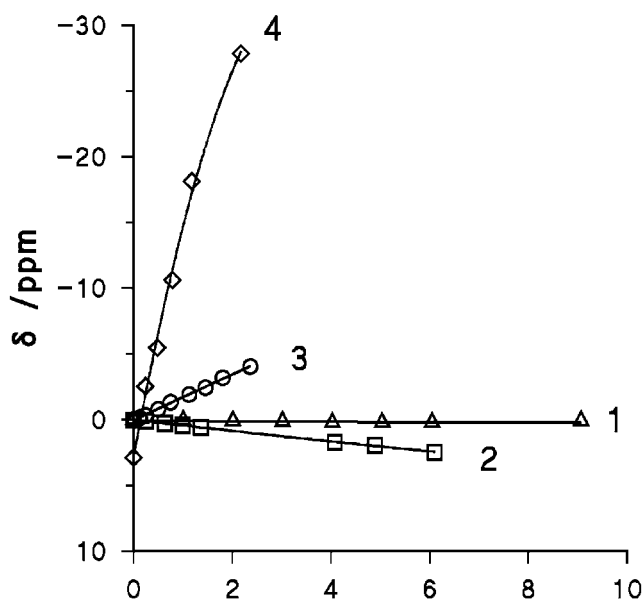
Figure 2. ^{199}Hg chemical shifts as a function of [ligand]/[mercury(II)] mole ratio for: 1, 15-crown-5 in DMSO; 2, 18-crown-6 in DMSO; 3, dibenzo-24-crown-8 in DMSO; 4, dibenzo-24-crown-8 in DMF.

Table 2. Stability constants (K_s in dm^3 mol^{-1}) for complexes of mercury(II) cyanide with crown ethers at 300 K

Ligand	Solvent	Log K_s
18-crown-6	DMSO	-0.8 ± 0.3
dibenzo-24-crown-8	DMSO	-0.4 ± 0.2
dibenzo-24-crown-8	DMF	0.6 ± 0.2

Stability constants in DMSO and DMF

Solutions of complexes between mercury(II) cyanide and crown ethers under investigation in DMSO were stable enough for NMR measurements and for dibenzo-24-crown-8 the measurements could be performed in DMF as well. Variations in ^{199}Hg chemical shifts with the ligand/mercury mole ratio for all ligands studied: 15-crown-5, 18-crown-6 and dibenzo-24-crown-8 (the last one in both solvents) are illustrated in Figure 2. There is no significant change in the ^{199}Hg chemical shift in the presence of 15-crown-5 (the maximum shift is only 0.213 ppm) indicating no significant complexation. No complexation was also detected for mercury(II) cations with that ligand in DMF using differential pulse polarography [12] and for Hg(CN)$_2$ with 15-crown-5 in mixtures of acetone and benzene or chloroform using ^{1}H NMR measurements [18]. In nitrobenzene [12] and water [26] a smaller stability of Hg^{2+}·15-crown-5 complex was reported in comparison with those formed with 18-crown-6 due to a smaller cavity size of 15-crown-5 (1.7–2.2 Å diameter [1,28]).

All other curves shown in Figure 2 indicate a significant complexation and confirm the possibility for the determination of stability constants for 1 : 1 complexes. The K_s values obtained (with standard deviations of the mean value) are

given in Table 2. Before discussing those results it can be added that the use of the chemical shift observed in the presence of 15-crown-5 as an approximate correction for the bulk diamagnetic susceptibility results in the same stability constants within the experimental error, e.g. for 18-crown-6 after correction log $K_s = -0.7 \pm 0.2\%$.

Stability constants found in DMSO for both ligands are similar (Table 2), contrary to the results reported in nitrobenzene [12] where stability of the complex of mercury(II) cations (generated by the anodic oxidation of mercury electrode) with 18-crown-6 is substantially higher than those with dibenzo-24-crown-8. Moreover, the literature result is in full agreement with the expectation [28] that efficient complexation can occur if the ratio of the metal ion diameter to the crown cavity diameter falls within the range 0.75–0.90, whereas it is 0.74–0.92 and <0.6 for complexes with 18-crown-6 and dibenzo-24-crown-8, respectively (assuming mercury(II) ion size 2.38 Å [4] and cavity diameters 2.6–3.2 Å for 18-crown-6 [1, 28, 29] and >4 Å for dibenzo-24-crown-8 [28]). However, for complexes with non-ionic HgX$_2$ (X = Cl, CN, CF$_3$) of the pseudo-rotaxane structure, as described in the previous section for crystals of Hg(CN)$_2$·18-crown-6 and found previously for other similar complexes [16, 19, 29], the relative size of the substituent X, which has to pass through the macrocyclic ring, in respect of the cavity diameter is also important. Moreover, some 60 times slower kinetics for the complexation of Hg(CN)$_2$ with dibenzo-18-crown-6 than that with 18-crown-6 found in mixtures of acetone with chloroform not only indicates that the step of macrocycle rearrangement is slow [18] but also points to the pseudo-rotaxane structure of the complex in solutions, similar to those established for crystals. The same structure of HgX$_2$ complexes was considered in recent studies of the solvent extraction using crown ethers [13]. Thus, in order to explain the results obtained in DMSO a comparison of other data obtained for complexes with mercury(II) cation alone and with the non-ionic molecule should be analysed at first.

The stability constants obtained in this work as well as the values reported in the literature for mercury(II) ions and three crown ethers of interest in various solvents against the solvent donor number DN are plotted in Figure 3. In all the cases reasonable linear dependences are found, despite the fact that data in PhNO$_2$ and ACN (obtained from anodic oxidation of mercury [12, 25]) and in water (obtained for completely dissociated mercury(II) perchlorate) refer to complexes with the bare mercury(II) cations and our data in DMSO refer to molecular complex of Hg(CN)$_2$·18-crown-6. This means that the same solvent donor ability for solvation/desolvation of cations determines the solvent effect on the stability of all kinds of complexes under consideration.

The linear decrease of the stability constant with the solvent DN value is well established for many complexes with macrocyclic polyether ligands [2, 3, 9–12], and was usually discussed in terms of the competition between the solvent and the ligand for the cation: the cation desolvation is easier in less basic solvents. The positive partial charge on the mercury atom in HgX$_2$ molecules is not surprising if one compares the Mulliken group electronegativities for
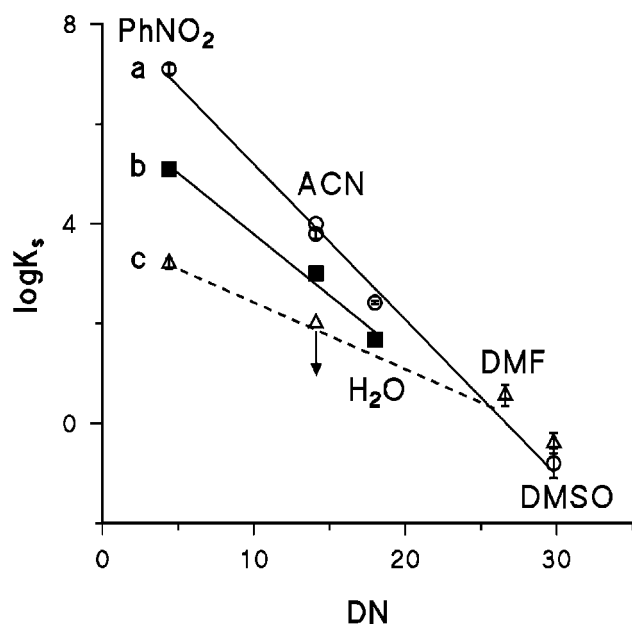
Figure 3. Stability constants for the complex formation between mercury(II) and crown ethers as a function of solvent donor number. Ligands (correlation coefficients *r* of lines shown are given in brackets): (a) 18-crown-6 ($r = 0.998$); (b) 15-crown-5 ($r = 0.994$); (c) dibenzo-24-crown-8 ($r = 0.990$). Data in nitobenzene ($PhNO_2$) from [12], in acetonitrile (ACN) from [12, 25] and in water from [26]; only upper limit of K_s for dibenzo-24-crown-8 complex in ACN was found.

CN and CF$_3$ (equal to 3.32 and 3.47 eV, respectively [30]) with the electronegativity of the mercury atom in the diagonal configuration equal to 1.81 eV [30]. The suggested decrease of the stability constant of a complex including non-ionic HgX_2 molecule with the increase in the solvent DN can also be supported by the observed 44 times decrease in K_s values for the complex of $Hg(CF_3)_2$ with the 20-membered ring ligand after changing toluene to the 50% mixture of acetone–benzene [15]. However, the effect of cation desolvation should not be dependent on the ligand nature. On the other hand, it is evident that slopes of the lines shown in Figure 3 decrease in the order of 18-crown-6 > 15-crown-5 > dibenzo-24-crown-8.

In general, the solvation of a ligand, a cation or a molecule, and a complex should be considered in order to explain solvent dependences shown in Figure 3. Specific interactions of crown ethers with solvent molecules resulting in the formation of 1 : 1 and/or 1 : 2 complexes were well documented [31] and for some of them the stability constants were determined. The formation of hydrogen bonding by solvent molecules with the oxygen atoms of the crown ether was established, in particular for 1 : 2 complexes forming crystals [31]. All the above studies indicated that the complexes stability does not depend on DN and thus, the solvation of ligand molecules is not manifested in linear plots shown in Figure 3. Then, different slopes of plots in Figure 3 can be explained in our opinion taking into account two processes depending on the solvent DN: desolvation of the reactant cation and solvation of the product complex. Both processes change in the opposite direction with the donor numbers resulting in different slopes in Figure 3

and, as a consequence, in the various differences of stability constants for two ligands in less and more basic solvents. Moreover, it is highly probable that the effect of the complex solvation is weaker in the case of 18-crown-6 when cation is well fitted to the cavity size than for dibenzo-24-crown-8 when a stronger solvation is possible because a greater cavity size allow an easier access of solvent molecules to the cation. The stronger complex solvation with the greatest ligand can be also related to the more conformational changes of the dibenzo24-crown-8 molecule in order to accommodate the cavity to the smaller cation size [8, 19, 32]. The above reasons can account for the increase of the complex solvation in the order of 18-crown-6 < dibenzo-24-crown-8 which nicely explains the order of slopes shown in Figure 3.

Supplementary data

Crystallographic data for the investigated structure have been deposited with the Cambridge Crystallographic Data Centre (deposition number CCDC 203892).

Acknowledgement

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