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Possible Role of Relativistic Effects in the Plasticity of the Coordination Geometry of Cadmium(II). A Voltammetric Study of the Stability of the Complexes of Cadmium(II) with 12-Crown-4,15-Crown-5 and 18-Crown-6 in Aqueous Solution and the Structures of [Cd(benzo-18-crown-6)(NCS)$_2$] and [K(18-crown-6)][Cd(SCN)$_3$]

James M. Harrington,[†] S. Bart Jones,[†] Peter H. White,[‡] and Robert D. Hancock*,[†]

Departments of Chemistry, University of North Carolina at Wilmington, Wilmington, North Carolina 28403, and University of North Carolina at Chapel Hill, Chapel Hill, North Carolina

A differential pulse voltammetric study of complexes of Cd(II) and Pb(II) with crown ethers is reported. Measured log K_1 values for Cd(II) with 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane), 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane), and 12-crown-4 (1,4,7,10-tetraoxacyclododecane) are respectively 2.53 (±0.06), 1.97 (±0.07), and 1.72 (±0.08) and for Pb(II) with 18-crown-6 is 4.17 (±0.03), all at 25 °C in 0.1 M LiNO$_3$. Cd(II) is smaller than is usually associated with strong bonding with crown ethers. The high log K_1 values for Cd^{2+} with crown ethers found here are discussed in terms of distortion of Cd(II) by relativistic effects. The resulting plasticity of the coordination geometry of the Cd(II) ion allows it to meet the metal ion size requirements of all the crown ethers, allowing high log K_1 values to occur. Crystal structures for [Cd(bz-18-crown-6)(SCN)$_2$] (**1**) (bz-18-crown-6 = benzo-1,4,7,10,13,16-hexaoxacyclooctadecane) and [K(18-crown-6)][Cd(SCN)$_3$] (**2**) are reported. **1** was triclinic, space group $P\bar{1}$, a = 8.5413(2), b = 10.0389(2), and c = 13.4644(2) Å, α = 94.424(1), β = 102.286(1), and γ = 93.236(1)°, Z = 2, and final R = 0.023. **2** was orthorhombic, space group $Cmc2_1$, a = 14.7309(3), b = 15.1647(3), and c = 10.6154(2) Å, Z = 4, and final R = 0.020. In **1**, the Cd occupies the cavity of the bz-18-crown-6 with long average Cd–O bond lengths of 2.65 Å and is N-bonded to the thiocyanates with short average Cd–N bonds of 2.12 Å. In [Cd(bz-18-crown-6)(SCN)$_2$], the linear coordination involving the Cd and the two N-bonded thiocyanate groups in **1** is discussed in terms of the role of relativistic effects in the tendency to linear coordination geometry in group 12 metal ions. In **2** Cd forms a polymeric structure involving thiocyanate bridges between Cd atoms and K$^+$ occupies the cavity of the crown ether. **2** highlights the fact that cadmium is almost never S-bonded to thiocyanate except in bridging thiocyanates.

Introduction

An important aspect of understanding the complexation of metal ions by crown ethers has been the determination of the formation constants[1] of these ligands with a large variety of metal ions. The earliest concept[2] that arose in terms of such understanding was the size-match selectivity hypothesis. In this intuitively attractive idea, the cavity of the macrocycle is of fixed size, and the macrocycle is quite rigid. The metal ions that fit the cavity most closely, for example K$^+$ with 18-crown-6, which has M–O bond lengths of 2.8–2.9 Å, then form the most stable complexes.[2] (See Figure 1 for the key to ligand abbreviations.) Subsequent work has shown[3] that the effect of cavity size is not the only, or usually even the most important, contributing factor to selectivity of crown ethers for metal ions on the basis of their size. Of prime importance is the fact that large metal ions form more stable complexes as part of five-membered chelate rings, while small metal ions form more stable complexes as part of six-

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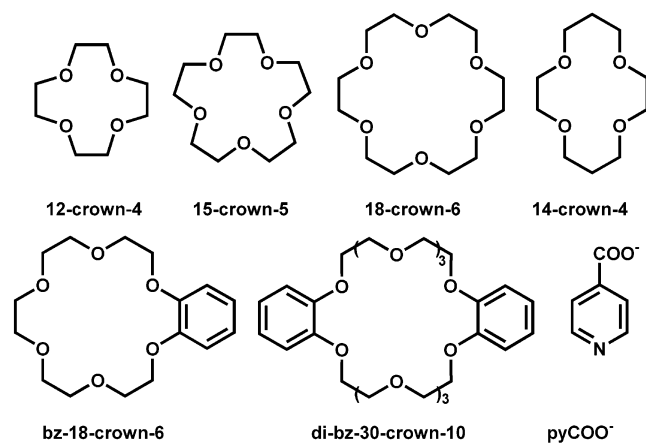
Figure 1. Ligands discussed in this paper.

Figure 2. Formation constants[1] of metal ions with the ligand 15-crown-5 as a function of ionic radius.[8] Log K_1 values are shown as bars whose height indicates the value of log K_1 for each metal ion. Note that, usually, as discussed in the text, metal ions with an ionic radius below 1.00 Å form only weak complexes with crown ethers such as 15-crown-5.[3,4]

membered chelate rings.[4] Very small crown ethers such as 12-crown-4 cannot accommodate metal ions in their cavity, and the metal ion is coordinated above the plane of the oxygen donors. The selectivity of such small crown ethers is governed almost entirely by chelate ring size.[3] Contrary to a common misconception, repeated even in the Aldrich catalog,[5] 12-crown-4 displays no selectivity for the small Li^{+} ion relative to other metal ions and Li^{+} does not even have[1] a log K_1 in water with 12-crown-4 large enough to have been reported. As a small metal ion, it is not well complexed as part of the five-membered chelate rings it would form with 12-crown-4. Selectivity for Li^{+} is achieved with crown ethers such as 14-crown-4, with which it forms six-membered chelate rings,[4] favoring complexation with small metal ions. Very large macrocycles such as di-bz-30-crown-10 also effectively have no cavity and wrap around the metal ion rather like a tennis-ball seam.[6] Here again, cavity size effects are not expected to be important. Cavity size effects appear[3] to be important in 18-crown-6 but are also to some extent coincident with expectations from chelate ring size effects and are therefore not always readily distinguishable from them. 18-Crown-6 encircles metal ions of suitable size as the low-strain D_{3d} conformer. A metal ion such as K^{+} fits 18-crown-6 best,[2] with its K−O bond lengths of about 2.82−2.88 Å,[7] and these are the M−O bond lengths that will be expected[3] to give the best fit and, therefore, the thermodynamically most stable complexes with 18-crown-6. Cavity size effects may also control metal ion selectivity for 15-crown-5 complexes, although there are insufficient[1] log K_1 data in water to be sure of the latter.

Metal ions that complex strongly with crown ethers such as 18-crown-6, 15-crown-5, or 12-crown-4, are all large, with ionic radii in excess[4] of 1.0 Å. This fact is shown in Figure 2, where log K_1 values for 15-crown-5 complexes are indicated as a function of ionic radius.[8] Similar plots are
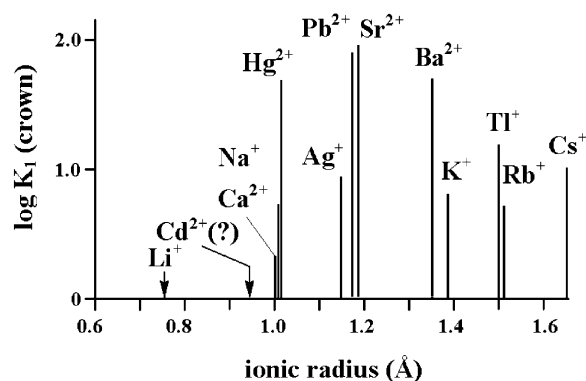
obtained for 18-crown-6 and 12-crown-4 complexes. As metal ion radius falls below 1.0 Å there is a rapid drop in log K_1 with crown ethers. Cadmium(II) is interesting because it has an ionic radius[8] of 0.95 Å but has, rather surprisingly, not been adequately studied[1] with crown ethers. One might expect, because of the somewhat small ionic radius, that log K_1 for Cd(II) with 18-crown-6 and 15-crown-5 would be low. Thus, Ca(II) with an ionic radius[8] of 1.00 Å has log K_1 with 18-crown-6 of[1] only 0.46, so that one might expect the smaller Cd(II) ion to form a complex of even lower stability. The only reports of formation constants for Cd(II) with 18-crown-6 are those of Luca et al.[9] and of Vasiliev et al.[10] Luca et al. employed polarography to determine an approximate value of log K_1 for Cd(II) with 18-crown-6 of about 2, which these authors indicated was only a rough value. This log K_1 for Cd(II) seems high at first sight, when compared with the low log K_1 value for Ca(II). There has been considerable success reported in the use of polarographic or voltammetric techniques for the study of complex formation in aqueous solution.[11−16] In this paper is reported a voltammetric and crystallographic study of complexes of Cd(II) with the crown ethers 12-crown-4, 15-crown-5, and 18-crown-6, which is aimed at determining accurate log K_1 values for these complexes. A rationale is provided for the unexpectedly high log K_1 values found for crown ethers with Cd^{2+} in terms of the structures of complexes of Cd(II), both reported here and in the literature. Neither the work of Luca et al. nor of Vasiliev et al. with Cd(II) and 18-crown-6 met the criteria for inclusion in the *Critical Stability Constants* database.[1] A voltammetric study of the Pb(II) complex with

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(7) There are 318 reports of structures containing the [K(18-crown-6)][+] complex cation in the CSD. Inspection of some of these suggests bond lengths in the range indicated. See also the structure of [K(18-crown-6)][Cd(SCN)$_3$] reported in this work.

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18-crown-6 is also reported as a validation of the voltammetric approach used here. (Note that the technique employed here is not here referred to as polarography, since in the strictest sense polarography utilizes a new Hg drop for each of the many points constituting the polarogram. In the present approach a single Hg drop is used to generate the entire "polarogram" and is thus more correctly referred to as voltammetry and the resulting trace of current as a function of potential as a "voltammogram").

Experimental Method

Materials. Cd(NO₃)₂·4H₂O (99.99%) was obtained from Fisher, and Pb(NO₃)₂ (99.99%) and LiNO₃ plus the crown ethers 12-crown-4 (98%), 15-crown-5 (98%), and 18-crown-6 (99%) were obtained from Aldrich. The materials were used as received to make up stock solutions. Metal ion solutions were standardized by usual procedures. The method used to produce crystals was adapted from a previous paper on the formation of crystals of crown ether/halide complexes with Cd(II).[17]

[Cd(bz-18-crown-6)(SCN)₂] (1). Crystals of **1** were formed by dissolving 0.23 g of bz-18-crown-6 in 25 mL of *n*-butanol with heating and allowing the solution to cool to room temperature. A 0.23 g amount of Cd(NO₃)₂ and 0.12 g of NaSCN were dissolved in 25 mL of deionized water, and the two solutions were mixed. Clear crystals formed at the interface of the two liquid phases and were collected after allowing 1 week for complete formation. Anal. Calcd for C₁₈H₂₄N₂S₂Cd: C, 39.96; H, 4.47; N, 5.17. Found: C, 39.18; H, 4.32; N, 5.44.

[K(18-crown-6)][Cd(SCN)₃] (2). Crystals of **2** were produced by dissolving 0.28 g of 18-crown-6 in 20 mL of *n*-butanol and 0.32 g of Cd(NO₃)₂ and 0.20 g of KSCN in 20 mL of deionized water. The two solutions were placed together in a beaker, and the resulting needlelike crystals, which formed rapidly at the interface, were collected after standing for 1 day. Anal. Calcd for C₁₅H₂₄N₃O₆S₃-KCd: C, 30.50; H, 4.10; N, 7.12. Found: C, 30.15; H, 4.17; N, 7.21.

Instrumentation. Voltammetric measurements were made with a Metrohm 663 polarograph, which was controlled by an EcoChemie PGStat 10 potentiostat and the general purpose electrochemical system (GPES) software by EcoChemie. A dropping mercury electrode set to the SMDE mode was used as the working electrode, a Ag/AgCl/KCl electrode was the reference electrode, and a glassy carbon rod was the auxiliary electrode. The readings were taken in a jacketed glass vessel with the temperature controlled to 25.0 ± 0.01 °C. pH was measured with a VWR SymPHony pH meter and a Corning glass electrode.

Voltammetry. For each titration, 50.0 mL of a solution of 5.00 × 10⁻⁵ M Cd²⁺ or Pb²⁺ in 0.1 M LiNO₃ was placed in the jacketed cell, and an *E°* reading was taken with a step potential of 0.001 95 V and a modulation amplitude of −0.025 05 V/s over the potential range of −0.4 to −1.8 V. Peaks were recorded in the differential pulse (DP) mode of the instrument. Additions of ligand were made, and voltammograms were recorded after each addition with the same step potential, modulation amplitude, and potential range. pH was also recorded after each addition to correct for hydrolysis if necessary. For the Cd(II) titration of 18-crown-6, there were two sets of readings taken, one with 23 additions at an addition size of 0.5 mL and 2 final additions of 390 µL and another of 30 additions with an addition size of 0.2 mL, both of 0.100 M solution of ligand. For Pb(II), two sets of readings with 18-crown-6 were performed,
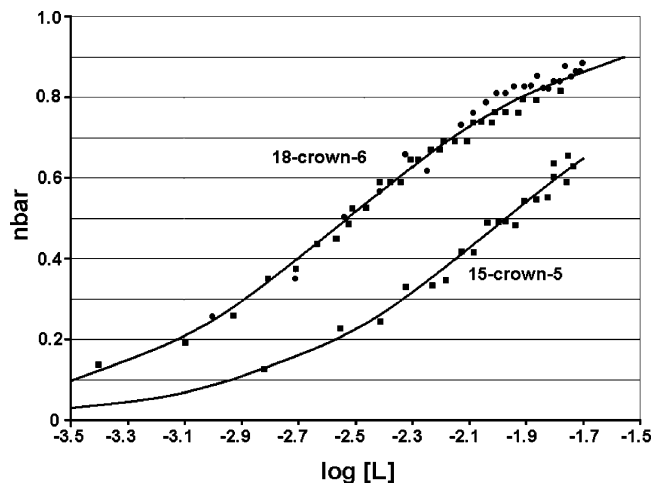
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Figure 3. Complex-formation curves of $\bar{n}$ versus log [L] (L = free ligand) for Cd(II) complexes of 18-crown-6 and 15-crown-5, as determined here from voltammetry. The solid lines are theoretical $\bar{n}$ versus log [L] formation curves for a system that contains only M and ML species in solution, calculated as described in the text from eq 5.

one with one addition of 0.200 mL and 24 additions of 0.100 mL of 0.1 M ligand and the other with 25 additions of 0.100 mL of 0.0100 M ligand. For Cd(II) with 15-crown-5, one titration was performed of four additions of 0.25 mL and 21 additions at an addition size of 0.5 mL of a 0.0505 M solution of ligand. For Cd-(II) with 12-crown-4, 25 additions of 0.2 mL were performed with a 0.101 M solution of ligand.

Calculation of Formation Constants. A single sharp peak was observed for solutions of the metal ions, which for Cd²⁺ occurred at −0.644 V and for Pb²⁺ at −0.448 V. These peaks began to move to more negative potentials as titration with the crown ligand proceeded, and no additional peaks appeared. This is typical of labile behavior in the electrochemical experiment.[11−16] From the shifts in peak positions a modified version[16] of the Lingane equation[18] was used to analyze the voltammetric data:

$$\Delta E_p = RT/nF \ln([I_i]/[I]) + RT/nF \ln([M_T]/[M_{Free}]) \quad (1)$$

ΔE_p is the potential change of the titration point relative to that for the metal ion alone and $[M_T]$ and $[M_{Free}]$ are the total metal ion and free metal ion concentration. I_i is the current for the metal ion peak with no ligand added, and I is the peak current for each ligand addition. For labile systems, I_i is equal to I, corrected for any dilution that may occur, so that eq 1 simplifies to

$$\Delta E_p = RT/nF \ln([M_T]/[M_{Free}]) \quad (2)$$

From the value of $[M_{Free}]$ calculated using eq 2 for each data point, the concentration of the complex [ML] was calculated as

$$[ML] = [M_T] - [M_{Free}] \quad (3)$$

The concentration of free ligand, [L], was calculated from the total ligand, $[L_T]$, as

$$[L] = [L_T] - [ML] \quad (4)$$

Values of $\bar{n}$, the ratio of the concentration of ligand bound to metal ion to total concentration of metal ion, were calculated as

$$\bar{n} = [ML]/[M_T] \quad (5)$$

In Figure 3 is shown a plot of $\bar{n}$ as a function of log [L] for the Cd(II) complexes of 18-crown-6 and 15-crown-5. The solid lines

Table 1. Formation Constants for Cd(II), Pb(II), and Hg(II) with Crown Ethers[a]

metal ion	12-crown-4	15-crown-5	18-crown-6	ref
		log K_1		
Cd(II)	1.72(0.08)	1.97(0.07)	2.53(0.06)	this work
Pb(II)	2.00[b]	1.85[b]	4.17(0.03)[c,d]	this work, lit.[b]
Hg(II)		1.62	2.42	refs 1 and 19

[a] In 0.1 M LiNO$_3$ at 25.0 °C. Figures in parentheses are standard deviations of log K_1 values fitted to the voltammetric data. [b] Reference 1. [c] This work. [d] Reported[22] log K_1 with 18-crown-6 = 4.27.

on these plots are theoretical $\bar{n}$ versus log [L] curves calculated from

$$\bar{n} = K_1[L]/(1 + K_1(L)) \qquad (6)$$

where K_1 is the formation constant for the crown complex. Equation 6 assumes a simple system where the only metal-ion-containing species in solution are M$_{Free}$ and ML. The good fit observed for the experimental points to the theoretical $\bar{n}$ versus log [L] curves in Figure 3 suggests that this is an adequate model of the speciation in the Cd(II) solutions of crown ethers. The fact that $\bar{n}$ does not rise above 1.0 even for the 12-crown-4 complex eliminates the possibility of the presence of ML$_2$ species. Hydrolysis was negligible due to a fairly constant pH of 6.5, at which pH Cd^{2+} and Pb^{2+} are not significantly hydrolyzed.[1] Only $\bar{n}$ values between 0.2 and 0.8, where accuracy of calculation of log K_1 will be greatest, were used for calculating log K_1. The program EXCEL[19] was used for data storage, data handling, and the execution of all these calculations. The stability constants determined here are reported in Table 1.

Molecular Structure Determination. A Bruker SMART 1K diffractometer, using the ω scan mode was employed for crystal

screening, unit cell determination, and data collection. The structure was solved by direct methods and refined to convergence.[20] Some details of the structures are given in Table 2, and crystal coordinates and details of the structure determinations of **1** and **2** have been deposited with the CSD (Cambridge Structural Database).[21] Selections of bond lengths and angles for **1** and **2** are given in Tables 3 and 4.

Discussion

Stability Constants. The stability constants for Cd(II) and Pb(II) determined here are reported in Table 1, together with some literature values[1] for discussion purposes. The value of log K_1 for Pb(II) with 18-crown-6 of 4.17 determined here may be compared with the "best" value of 4.31 given in *Critical Stability Constants*[1] at an ionic strength of 0.1 Note that a slightly lower value of 4.27 has been reported[22] by researchers with wide experience in determining the thermodynamics of complexation of metal ions by crown ethers. Considering that the present work was carried out in 0.1 M LiNO$_3$, the Li$^+$ may at this high excess concentration bind very weakly with 18-crown-6, thereby lowering the measured log K_1 with Pb(II) slightly. The results for Pb(II) with 18-crown-6 give some confidence in the results for Cd(II) in Table 1. The good fit obtained between the experimental $\bar{n}$ versus log [L] curves in Figure 2 and the theoretical curves based on a simple model with only M and ML present, as implied in eq 6, gives one confidence that the analysis of complex formation here is correct. This model with only M and ML formed in solution is in line with all other studies[1] of the complexes of metal ions with the crowns studied here,

Table 2. Crystallographic Data for [Cd(bz-18-crown-6)(SCN)$_2$] (**1**) and [K(18-crown-6)][Cd(SCN)$_3$] (**2**)

	1	**2**
empirical formula	C$_{18}$H$_{24}$N$_2$S$_2$Cd	C$_{15}$H$_{24}$N$_3$O$_6$S$_3$CdK
M	540.91	590.04
T/K	173	173
cryst system	triclinic	orthorhombic
space group	$P1$	$Cmc2_1$
a/Å	8.5413(2)	14.7309(3)
b/Å	10.0389(2)	15.1647(3)
c/Å	13.4644(2)	10.6154(2)
α/deg	94.424(1)	90
β/deg	102.286(1)	90
γ/deg	93.236(1)	90
V/Å^3	1121.56(4)	2371.37(8)
Z	2	4
μ/mm^{-1}	1.20	1.40
reflcns collcd	6510	3471
indpndt reflcns	5771	3404
final R indices [$I \geq 2\sigma(I)$]	R1 = 0.021 wR2 = 0.25	R1 = 0.028, wR2 = 0.029
R indices (all data)	R1 = 0.023, wR2 = 0.028	R1 = 0.020 wR2 = 0.25

Table 3. Selection of Bond Lengths (Å) and Angles (deg) for **1** ([Cd(bz-18-crown-6)(SCN)$_2$])

			Bond Lengths			
Cd(1)−N(1)	2.1205(15)	Cd(1)−N(3)	2.1140(15)	Cd(1)−O(6)	2.6958(11)
Cd(1)−O(9)	2.6401(12)	Cd(1)−O(12)	2.5550(11)	Cd(1)−O(15)	2.6494(12)
Cd(1)−O(18)	2.6086(11)	Cd(1)−O(21)	2.7243(10)		
			Bond Angles			
N(1)−Cd(1)−N(3)	176.28(6)		N(1)−Cd(1)−O(6)	92.17(5)
N(1)−Cd(1)−O(9)	83.82(5)		N(1)−Cd(1)−O(12)	93.25(5)
N(1)−Cd(1)−O(15)	91.68(5)		N(1)−Cd(1)−O(18)	85.44(5)
N(1)−Cd(1)−O(21)	90.43(5)		N(3)−Cd(1)−O(9)	96.75(5)
N(3)−Cd(1)−O(12)	90.24(5)		Cd(1)−O(15)−C(14)	110.14(11)
N(3)−Cd(1)−O(15)	91.17(5)		Cd(1)−O(15)−C(16)	114.52(10)
N(3)−Cd(1)−O(18)	93.72(5)		N(3)−Cd(1)−O(21)	86.01(5)

Table 4. Selection of Bond Lengths (Å) and Angles (deg) for **2** ([K(18-crown-6)][Cd(SCN)₃])

Bond Lengths					
Cd(1)-S(1)	2.7103(7)	Cd(1)-S(2)	2.7457(5)	Cd(1)-N(2)	2.2640(23)
Cd(1)-N(4)	2.3331(18)	K(1)-S(2)	3.5821(7)	K(1)-O(5)	2.8287(24)
K(1)-O(8)	2.8662(15)	K(1)-O(11)	2.8849(15)	K(1)-O(14)	2.9210(24)

Bond Angles			
S(1)−Cd(1)−S(2)	83.943(14)	S(1)−Cd(1)−N(2)	176.30(6)
S(1)−Cd(1)−N(4)	90.35(4)	S(2)−Cd(1)−N(2)	93.45(4)
S(2)−Cd(1)−N(4)	92.71(5)	N(2)−Cd(1)−N(4)	92.39(6)
N(2)−Cd(1)−N(4)a	92.39(6)	S(2)−K(1)−O(5)	90.95(4)
S(2)−K(1)−O(8)	75.80(3)	O(5)−K(1)−O(8)	58.83(4)

where only M and ML were found in aqueous solution.[1] These constants are also, like the log K_1 values reported in Table 1, usually reported[1] in concentrations rather than activities, most commonly at an ionic strength of 0.1.

The stability constants found here were somewhat higher than would be expected for Cd²⁺ ($r^+ = 0.95$ Å[8]) in terms of the fact, mentioned in the Introduction, that metal ions with r^+ less than 1.0 Å do not tend to form strong complexes with crown ethers, at least those crown ethers that form only five-membered chelate rings.[3,4] The log K_1 values in Table 1 show a small range of variation for the Cd(II) complexes, which is evident in comparison with the Pb(II) complexes. It would seem that Cd(II) is not very sensitive to the range of cavity size evidenced in passing from 12-crown-4 to 15-crown-5 and then 18-crown-6. The Cd²⁺ ion forms more stable complexes with crown ethers than does Hg²⁺, which has[8] an r^+ of 1.02 Å, which would seem to suit Hg²⁺ better for complexing with crown ethers, requiring as they do[3,4] an ionic radius in excess of 1.0 Å.

Cd−L Bond Lengths and Their Plasticity. A possible explanation for the unexpectedly high log K_1 values, and lesser sensitivity to cavity size of Cd(II) with crown ethers, may be found in examining the structures[21] of Cd(II) complexes with crown ethers. The structure of [Cd(bz-18-crown-6)(NCS)₂] (**1**) determined here is shown in Figure 4. There are several points of interest. First, the axial Cd−N bonds are very short, averaging 2.12 Å. Second, the equatorial Cd−O bonds to the O-donors of the crown are long, averaging 2.65 Å. These bond lengths should be compared with average Cd−O bonds of 2.39 ± 0.02 Å in eight-coordinate complexes such as the [Cd(12-crown-4)₂] complex,[23] which shows no signs of bond length distortion. The third point is the conformation of the macrocyclic ring in **1**, which is not like the D_{3d} conformer found in low-strain[3] complexes of 18-crown-6, as discussed below. The distortion of the coordination geometry of **1** resembles the structures of Hg(II) complexes of 18-crown-6, where there are very short axial bonds to Hg(II) and long Hg−O bonds to the O-donors of the crown ethers. In the structure[24] of [Hg(18-

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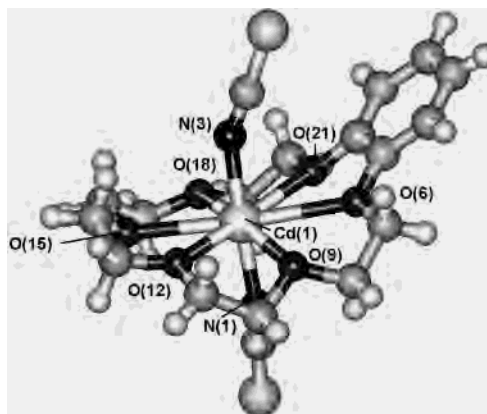(24) Hazell, A. *Acta Crystallogr., Sect. C* **1988**, *44*, 88.

Figure 4. Structure of **1**, the [Cd(bz-18-crown-6)(SCN)₂] complex, showing the numbering scheme for Cd and its donor atoms and the N-bonded thiocyanates coordinated to Cd(II). N(1) and N(3) are the N-donors from the N-bonded SCN⁻ groups.

crown-6)Cl₂], the Hg−Cl bonds are very short at 2.30 Å and the Hg−O bonds are very long at 2.85 Å. The Hg−X bonds in such complexes are[24] only about 0.1 Å longer than is found in the corresponding gas-phase X−Hg−X molecules (X = Cl, Br, I). This type of distortion toward what is effectively linear coordination geometry for the X−Hg−X portion of [Hg(18-crown-6)X₂] complexes has been attributed[25] to relativistic effects.[26] It would seem that the same type of distortion might be occurring in **1**. Relativistic effects greatly lower the energy of the valence shell s orbital next in energy to a filled d-orbital in heavy d¹⁰ metal ions. This leads to a tendency to sp hybridization and the formation of more covalent M−L bonds. This effect is at a maximum at Au(I) but is still significant[26] at the row above in the periodic table, at Ag(I). Thus, Cd(II) might be expected to show distortions toward linear two-coordination, which effects are paramount[26] for Au(I) and Hg(II). In situations not involving crown ethers, this distortion toward linear two-coordination is generally not obvious for Cd(II). One sign of this tendency may be tentatively identified in complexes of the [Cd-(amine)₂(H₂O)₄] type with unidentate amine ligands. There are some 30 examples[21] of Cd(II) complexes of this type, if a variety of unidentate O-donors other than water is included. These complexes always have the amines trans to each other, which it seems plausible to liken to the structures of Hg(II) complexes, and relate to relativistic effects. In contrast, in 71 examples[21] of Zn(II) complexes with unidentate ligands forming 2N,4O donor sets, the two N donors are sometimes

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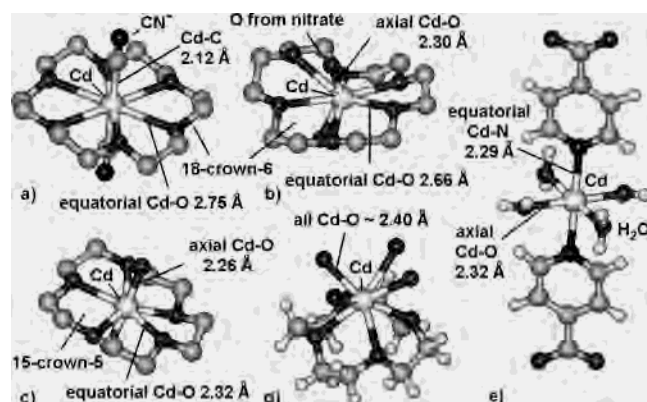(26) Koltsoyannis, N. *J. Chem. Soc., Dalton Trans.* **1997**, 1.

Figure 5. Plasticity of the coordination geometry of Cd(II). (a) The complex[29] [Cd(18-crown-6)(CN)$_2$] is shown, with short axial Cd−C bonds brought about by relativistic effects[26] with concomitant long equatorial Cd−O bonds to the O-donors of 18-crown-6. (b) The ionic binding of O-donors from nitrates on the axial sites of Cd(II) in [Cd(18-crown-6)-(NO$_3$)$_2$][33] is much less able to produce short Cd−O bonds, with much less accompanying lengthening of the Cd−O equatorial bonds to 18-crown-6, which thus has a buckled ++−++− conformation to accommodate the shorter Cd−O bond lengths. (c) The [Cd(15-crown-5)(H$_2$O)$_2$] cation,[30] where Cd(II) shows very short overall Cd−O bond lengths which enables it to reside in the small cavity of 15-crown-5. (d) The undistorted eight-coordinate [Cd(12-crown-4)(NO$_3$)$_2$] complex, which shows fairly regular geometry with all Cd−O bond lengths very close to 2.40 Å. (e) The complex [Cd(pyCOO)$_2$-(H$_2$O)$_4$], which has[27] trans nitrogen donors and slightly shortened Cd−N bonds, which may be evidence for relativistic effects, as discussed in the text.

cis to each other. The shortening of the Cd−N bonds is also present in these complexes, although very small. Thus, typically, as is seen for [Cd(pyCOO)$_2$(H$_2$O)$_4$] in Figure 5, the Cd−N bonds average[27] 2.31 Å, while the Cd−O bonds average 2.34 Å. Since Cd−O bonds would normally be[25] some 0.06 Å shorter than Cd−N bonds, this represents a distortion toward shorter axial bonds here of some 0.09 Å. In contrast, in the Zn(II) analog,[28] where relativistic effects would be expected to be much less,[26] the two Zn−N bonds at 2.16 Å are longer than the Zn−O bonds at 2.10 Å, as is normally found. Figure 4 shows that this type of distortion can become almost as extreme as in the Hg(II) complexes with 18-crown-6. In fact, with more covalently bound axial groups, the distortion of the Cd(II) can become even more extreme, as seen for[29] [Cd(18-crown-6)(CN)$_2$] in Figure 5. Here the Cd−O bonds have been extended out to 2.75 Å. In contrast, some distortion in the opposite sense is possible, as in [Cd(15-crown-5)(H$_2$O)$_2$]$^{2+}$. Here the Cd−O bonds to the O-donors of 15-crown-5 average[30] only 2.32 Å, while the Cd−O bonds to the axial waters average 2.26 Å, as seen in Figure 5. The shorter Cd−O bonds overall may reflect the seven-coordination of Cd(II) in the latter complex, as opposed to eight-coordination in 18-crown-6 complexes of Cd(II).

Figure 5 shows that Cd(II) is capable of considerable plasticity in the lengths of its bonds. It appears able to expand its equatorial Cd−O bonds from undistorted lengths of 2.40

Å out to the bond lengths of 2.7−2.9 Å needed[3] to fit the cavity of 18-crown-6. Cd(II) can also contract its M−O bond lengths to the 2.29 Å needed[3] to fit the cavity of 15-crown-5. 12-Crown-4 effectively has no cavity, and metal ions are coordinated to it above the plane, as seen[31] in Figure 5, where undistorted Cd−O bond lengths of 2.40 Å are appropriate.[3] As discussed above, Cd(II) shows an unusual ability to complex almost equally strongly with 12-crown-4, 15-crown-5, and 18-crown-6, in the face of the very different metal ion size requirements of these crown ethers. It seems reasonable to attribute the ability of Cd(II) to complex strongly with all three crown ethers to its ability to alter its equatorial M−O bond lengths. It seems likely that this ability is due to relativistic effects. Support for this suggestion is seen in that the similarly sized Ca(II) ion shows[21] little ability in the structures of its complexes with these crowns to alter Ca−O bond lengths to meet their metal ion size requirements. Relativistic effects are at a minimum in group 1 and 2 of the periodic table.[26] Thus, in all 15-crown-5 structures, Ca(II) coordinates to the crown lying well above the plane of the O-donors, with normal Ca−O bond lengths of about 2.5 Å, and does not appear able to contract its M−O bond lengths to coordinate to 15-crown-5 lying in the plane of the macrocycle. Ca(II) also does not appear[21] able to adapt to the size requirements of the cavity of 18-crown-6.

An interesting point is the lower amount of lengthening of the Cd−O bonds in **1** than in [Cd(18-crown-6)(CN)$_2$].[29] One would expect[25] greater distortion toward linearity and greater shortening of the axial Cd−X bonds in complexes of this type. The conformation of the Bz-18-crown-6 ring in **1** is not, as noted above, the usual D_{3d} type of conformation found in complexes of 18-crown-6 with metal ions[7] such as K$^+$ (Figure 5) which fit the cavity of 18-crown-6 well. Rather, it is of the ++−++− type, which is that found[3] in 18-crown-6 complexes of metal ions such as Bi(III)[32] that have M−O bond lengths of Bi−O = 2.54−2.62 Å that are too short for the cavity of 18-crown-6 and which conformer is best fitted[3] by metal ions with M−O bond lengths of about 2.5 Å. (The ++−++− designation indicates whether the lone pair on the O-donor atom of the crown, which lone pair is not bonded to the metal ion, lies above or below the plane of the macrocycle. In this convention, the D_{3d} conformer would be +−+−+−.) One would surmise that the N-bonded NCS$^−$ ligand is not covalent enough in its bonding to distort the Cd(II) out to the bond lengths of 2.8 Å required for the D_{3d} conformer. In support of this idea of the role of increased covalence in the axial bonds producing lengthening of the equatorial Cd−O bonds, it is found[33] that in [Cd(18-crown-6)(NO$_3$)$_2$], with the expected ionicity of the Cd−O bonds to the O-donors of the axial nitrates, the ++−++− conformer is adopted, and the equatorial Cd−O bonds are similar in length[33] to those in **1** at 2.66 Å. Following this idea[25] of the covalence in the Cd−O bond

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being important for lengthening the equatorial M−O bonds, it is found that with Zn(II), with highly covalent bonding in the [Zn(18-crown-6)R$_2$] complexes, with R = ethyl,[34] phenyl,[35] or iodomethyl,[36] very short axial Zn−C bonds occur, with long Zn−O bonds to the O-donors of 18-crown-6 of about 2.85 Å. More typically, with chloride and H$_2$O occupying the axial sites on Zn(II), the Zn(II) is coordinated in one side of the cavity of 18-crown-6, by only three Zn−O bonds to the crown.[37] Note that with alkyl substituents on the axial sites, even Mg(II) can coordinate[34] with the D_{3d} conformer of 18-crown-6, with long Mg−O bonds of 2.78 Å and Mg−C bonds of 2.10 Å. Cd(II) is better able to achieve the covalent bonding leading to linear coordination geometry, which is probably attributable to relativistic effects. Cd(II) can therefore achieve this type of structure with ligands of anything but the lowest level of covalence in the axial Cd−X bonds. Thus even with X = Cl,[17] Br,[24] or I[24] short Cd−X bonds result, with the D_{3d} type of structure. Some idea of where bonds to axial groups in 18-crown-6 complexes fall in the range of extent of covalence versus ionicity is given by[38] the ionicity parameters (H_B) for unidentate ligands:

Ligand:	H$_2$O	NCS$^-$	NH$_3$	Cl$^-$	Br$^-$	I$^-$	SCN$^-$	CN$^-$	(alkyl)
		(N-bonded)					(S-bonded)		
H_B (Ionicity):	0.0	-0.082	-0.088	-0.10	-0.108	-0.122	-0.128	-0.148	<-0.15

(← increasing ionicity vs. increasing covalence in M-L bond →)

It should be noted that density functional theory calculations have supported[39] quantitative aspects of the model of bonding in aqueous solution from which the above H_B parameters are derived.

The order of decreasing ionicity in M−L bonds indicated by the H_B parameters suggests that the level of ionicity in the Cd−OH$_2$ and Cd−NCS bonds is too high to distort the axial Cd−L bonds to the point where the equatorial Cd−O bonds can extend out to the bond lengths required to allow the D_{3d} conformer to be observed in the 18-crown-6 complexes. In Mg(II) and Zn(II) complexes of 18-crown-6, only alkyl groups give sufficiently covalent axial M−L bonds to allow for the formation of the D_{3d} conformer, with long M−O bonds to the crown. In contrast, Hg(II) forms M−L bonds of such high covalence[38] that with all axial groups the D_{3d} conformer is formed, with very short axial bonds.[21] A possible reason for the lower stability of crown complexes of Hg(II) than of Cd(II), noted in Table 1, may be that the covalence in the linear X−Hg−X portion of the crown complex is so high that the residual charge on Hg(II) is too low to provide much positive charge to form interactions with the O-donors of 18-crown-6.
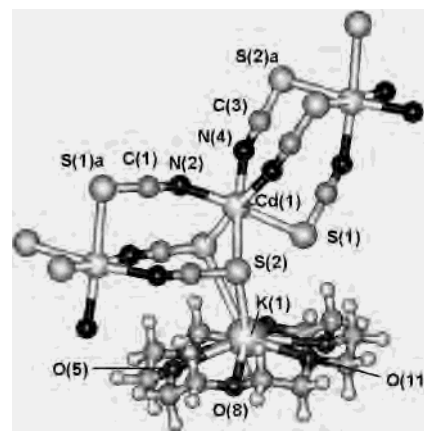
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Figure 6. Structure of [K(18-crown-6)][Cd(SCN)$_3$] (**2**), showing one [K(18-crown-6)]$^+$ cation bound to a pair of sulfurs from the ([Cd(SCN)$_3$]$^-$)$_n$ polymer. The Cd is held in the polymer by three bridging thiocyanates, giving the Cd(II) an S3,N3 donor set.

Cd(II) Bonding to Thiocyanate. A puzzle is why Cd(II) has not produced S-bonded SCN$^-$ in **1**. It is particularly surprising that reported structures[21] show that Cd(II) is almost never S-bonded to SCN$^-$, except for bridging SCN$^-$ (Cd−N=C=S−Cd) groups, in light of the fact that Cd(II) is classified as "soft" in the Pearson HSAB classification.[40] A single example[41] has one N-bonded and one S-bonded thiocyanate, with the latter not bridging. Otherwise, S-bonded thiocyanates are always bridging, as is found for **2** here (Figure 6). Problems were experienced in attempts to grow crystals of [Cd(18-crown-6)(SCN)$_2$], hence the use of bz-18-crown-6 in the synthesis of **1**, which it was thought might contain S-bonded Cd(II) because of relativistic effects discussed above. In using KSCN in an attempt to grow crystals of the l8-crown-6 complex, **2** was obtained with K$^+$ occupying the cavity of 18-crown-6. The K$^+$ in **2** has fairly long K−O bond lengths of 2.88 Å, associated with the fact that the K$^+$ lies well above the plane of the O-donors of the crown. In that position K$^+$ binds on the side that rises above the plane of the crown to two S-donors from SCN$^-$ groups, with very long K−S bonds of 3.58 Å. These SCN$^-$ groups S-bonded to K$^+$ also bridge between pairs of Cd(II) ions as part of the ([Cd(SCN)$_3$]$^-$)$_n$ polymer. As is usual in this type of situation, an approximately D_{3d} conformation for 18-crown-6 is found[7] for virtually all complexes of ligands of the 18-crown-6 type with K$^+$, even when the K$^+$ lies out of the plane of the O-donors, as frequently happens when K$^+$ is coordinated to strongly binding axial donors on one side of the K$^+$ only. This is the case with **2,** as seen in Figure 6. The polymeric structure for the Cd(II) in **2** has bridging SCN$^-$ groups and occurs in two other reported structures.[42,43] Each Cd(II) has an approximately octahedral geometry, with three S-donors and three N-donors coordinated to faces of the Cd(II) octahedron. In the structure, the linear ([Cd(SCN)$_3$]$^-$)$_n$ polymer is surrounded by six columns of

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[K(18-crown-6)]$^+$, bound to the ([Cd(SCN)$_3$]$^-$)$_n$ polymer by the long K$-$S bonds noted above. The [K(18-crown-6)]$^+$ cations are held to each other only by van der Waals forces between 18-crown-6 groups.

The surprising reluctance of Cd(II) to S-bond with SCN$^-$ in view of its soft designation[40] in the HSAB classification is not so surprising if one realizes that the factors controlling preferences in aqueous solution are not[38] simply the one-dimensional continuum from hard to soft implied by the HSAB classification. Rather, in aqueous solution, in addition to the ionicity/covalence parameters implied by hard$-$soft scales for Lewis acids, there is a second dimension that leads, in fact, to the failure of attempts[38] to make the HSAB principle quantitative. This second dimension is that of the reduction of charge on the Lewis acid by binding to the ligand.[38] In water, this leads to energetically unfavorable desolvation of the Lewis acid. This second effect accounts for the numerous small deficiencies of the HSAB classification that become apparent on detailed analysis of acid$-$base behavior in aqueous solution. One such deficiency is apparent here. Cd(II) is classified as soft but is scarcely ever S-bonded to nonbridging SCN$^-$. Pb(II) and Bi(III) are classified as "intermediate" but form numerous complexes[15] that are S-bonded to the soft donor atom of nonbridging SCN$^-$. This is understandable in terms of energetically unfavorable desolvation effects[38] in Cd(II) on bonding to "soft" donor atoms such as S, which are much less important in Pb(II) and Bi(III).

Relativistic Effects. The relativistic effects that seem to be responsible for distortion of the coordination geometry of Cd(II) appear to respond to the covalence of the axial bonds to Cd(II). It seems possible that the binding of more covalent ligands to the axial sites on [Cd(18-crown-6)-(H$_2$O)$_2$]$^{2+}$ would lead to expansion of the equatorial bonds

to 18-crown-6 and a release of steric strain. One might thus find anomalously large binding constants of ligands such as I$^-$ to the axial sites on [Cd(18-crown-6)(H$_2$O)$_2$]$^{2+}$, driven by release of steric strain on extension of the equatorial Cd$-$O bonds, which possibility we are currently exploring.

Conclusions. The following conclusions are suggested by this study:

(1) Cd(II) forms stable complexes with the crown ethers 12-crown-4, 15-crown-5, and 18-crown-6, with a remarkable ability of the Cd(II) to bind strongly to these crowns of very different sizes. (2) Crystal structures of Cd(II) with crowns, reported here and elsewhere,[21] show how Cd(II) has a unique ability to adjust its Cd$-$O bond lengths to meet the requirements of the above crowns, which may possibly explain the ability of Cd(II) to complex strongly with all of these crowns. (3) Cd(II) may owe its ability to change Cd$-$O bond lengths to relativistic effects, which cause distortion of the Cd(II) toward what is effectively linear coordination geometry, with short axial bonds and long equatorial Cd$-$O bonds. (4) More covalent axial groups cause greater distortion of the Cd(II) coordination geometry.

This study has reinforced previous studies[11$-$15] using polarographic techniques that demonstrate the power of such electrochemical approaches for studying metal ion complexes in solution. The present aim is to extend these techniques to the study of metal ions in biological situations, where the ability to operate at very low total metal ion concentrations may prove invaluable.