deviations maybe from reactant–reactant and reactant–solvent interactions, which the model does not address. There is a correlation between large negative entropies and weak donor solvents. This work is being extended with the study of cross-reactions with the $Cr(CNdipp)_6^{2+}$ complex.

Acknowledgment. We are pleased to acknowledge the technical assistance of Don Appel with the NMR measurements and discussions with Profs. Harold Dodgen and John Hunt and Dr. Karl Kirchner. This work was supported by the National Science Foundation and by the Boeing Co. through funds for the purchase of the Nicolet NMR instrument.

Supplementary Material Available: Tables of reactant concentrations, temperatures, chemical shift values, and line widths (Tables 1 and 2a–f) (7 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Interactions in Aqueous Solution at 25 °C of Palladium(II) and Mercury(II) with 1,4-Dithia-18-crown-6 and 1,10-Dithia-18-crown-6. A Thermodynamic, Spectral, and X-ray Crystallographic Study

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log *K*, ΔH, and ΔS values for the interactions of Hg(II) and Pd(II) with 1,4-dithia-18-crown-6 (1,4-$T_2$18C6) and 1,10-dithia-18-crown-6 (1,10-$T_2$18C6) were determined in aqueous solution at 25 °C by polarography and competitive calorimetry. The reaction stoichiometries of either metal ion with 1,4-$T_2$18C6 and 1,10-$T_2$18C6 are 1:2 and 1:1, respectively. The formation of both metal complexes of 1,10-$T_2$18C6 is favored by both ΔH and ΔS, while that of both metal complexes of 1,4-$T_2$18C6 is favored by ΔH only. The thermodynamic results have been interpreted in terms of ligand field stabilization energy (LFSE), charge-transfer, and macrocyclic effects. The UV/vis absorption spectra of Pd(II) complexes with both crown thioethers in 0.5 M HNO_3 show that LFSE and charge-transfer effects make large contributions to the formation of the very stable complex $Pd(1,4\text{-}T_218C6)_2^{2+}$. The molecular structures of Pd(II) complexes with both crown thioethers have been determined by single-crystal X-ray analysis. The complex $Pd(1,10\text{-}T_218C6)(NO_3)_2$ crystallizes in the orthorhombic *Pna*2_1 space group with $a = 10.508$ (4) Å, $b = 13.871$ (7) Å, $c = 13.772$ (7) Å, $Z = 4$, and $R = 0.064$. The complex $Pd(1,4\text{-}T_218C6)_2(NO_3)_2$ crystallizes in the orthorhombic *Pbca* space group with $a = 8.474$ (2) Å, $b = 18.349$ (5) Å, $c = 148.969$ (25) Å, $Z = 8$, and $R = 0.083$. A cis-square-planar configuration is found for the $Pd(1,10\text{-}T_218C6)^{2+}$ complex.

Introduction

Crown thioether ligands are noted for their significant affinity for Cu(I), Cu(II), Pd(II), Ag(I), Pt(II), Pt(IV), Au(I), Au(III), Hg(I), and Hg(II) in aqueous solution.[1-5] Hence, these crown thioethers represent potentially useful reagents for these specific metal ions in analytical determinations, recovery and separation processes, and homogeneous catalysis. Complexes of Pd and Pt have been shown to act as active homogeneous catalysts in reactions of industrial importance.[6,7] The coordination chemistry of Pd and Pt complexes with open-chain and crown thioethers has been elucidated by using X-ray diffraction results.[8,9] However, few thermodynamic quantities for crown thioether–Pt group metal interactions have been reported,[10] probably because of the difficulty in the determination of these quantities, particularly in aqueous media.[11]

In the present study, this difficulty is circumvented by using a competitive procedure combining calorimetric[11] and polarographic data. Since log *K* values for the formation of Pd(II)–thioether complexes are expected to be very large, determination of these constants is not possible by using direct methods.[12,13] For instance, potentiometric and spectrophotometric methods become invalid because Pd(II) forms very stable complexes with thioethers. Also, the polarographic method cannot be used because of the irreversibility of the reduction of the Pd(II) complex at the dropping-mercury electrode in aqueous solution. However, the polarographic determination of *K* values for Hg(II)–thioether interaction is not difficult. As will be seen in the Results and Discussion sections, the differences between log *K* (Δ log *K*) values for Hg(II) and Pd(II) interactions with these thioethers are of the correct magnitude to allow them to be determined by a competitive calorimetric technique. The combination of these Δ log *K* values with those for Hg(II) interaction with thioethers should lead to corresponding Pd(II) values. This method should be useful for the determination of the log *K* values for other Pd(II)–ligand interactions. Since Hg(II) is one of the few metal ions that can bind strongly to thioethers in aqueous media, these systems may provide the possibility of selective removal of Hg(II) from the environment. In the present paper, attention is directed to the investigation of *K*, ΔH, and ΔS values for the interaction of sulfur-substituted macrocyclic ligands with Pd(II) and Hg(II) and to the correlation of these quantities with structural data for the Pd(II) complexes.

Experimental Section

Materials. The crown thioethers and metal salts were obtained in the best purity available from the sources indicated and used without further purification: 1,10-dithia-18-crown-6 (1,10-$T_2$18C6) and 1,4-dithia-18-crown-6 (1,4-$T_2$18C6) (Parish Chemical Co.) (molecular structures shown in Figure 1); $Pd(NO_3)_2$ and $Hg(NO_3)_2$ (Morton Thiokol); HNO_3 (Mallinckrodt).

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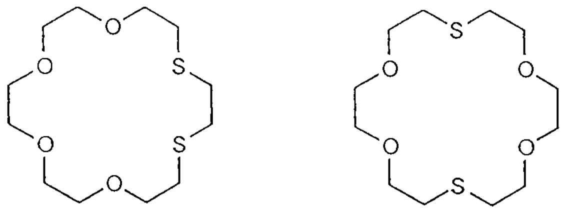
Table I. Details of the Crystallographic Analysis of $Pd(1,10\text{-}T_218C6)(NO_3)_2$ and $Pd(1,4\text{-}T_218C6)_2(NO_3)_2$ Complexes

	$Pd(1,10\text{-}T_218C6)(NO_3)_2$	$Pd(1,4\text{-}T_218C6)_2(NO_3)_2$
formula	$[PdC_{12}H_{24}O_4S_2](NO_3)_2$	$[Pd(C_{12}H_{24}O_4S_2)_2](NO_3)_2\cdot 2H_2O$
fw	526.8	858.3
cryst size, mm	0.40 × 0.10 × 0.05	0.45 × 0.40 × 0.10
space group	$Pna2_1$	$Pbca$
a, Å	10.508 (4)	8.474 (2)
b, Å	13.871 (7)	18.394 (5)
c, Å	13.772 (7)	48.969 (25)
V, $Å^3$	2007.5 (1.7)	7613.8 (3.9)
no. of reflcns to determine cell consts	25 ($7.66 < 2\theta < 18.87$)	25 ($14.31 < 2\theta < 28.02$)
Z	4	8
D_x, g cm^{-3}	1.68	1.45
μ, cm^{-1}	11.49	7.49
$(\sin\theta)/\lambda$	0.59	0.54
no. of unique reflcns collcd	2137	4713
no. of reflcns used in refinement with $F \geq 3\sigma(F)$	1285	2808
final R	0.064	0.083
final R_w	0.056	0.085
goodness of fit	1.24	1.67
max and min peaks in Δ map, e $Å^{-3}$	0.79, −0.55	0.72, −0.71



1,4-Dithia-18-Crown-6

($1,4\text{-}T_218C6$)

1,10-Dithia-18-Crown-6

($1,10\text{-}T_218C6$)

Figure 1. Structural formulas of crown thioethers studied.

Solution Preparation. Solutions were prepared with 0.5 M HNO_3 as a solvent. A Pd(II) solution was prepared by dissolving an appropriate amount of $Pd(NO_3)_2$ in 0.5 M HNO_3 with rigorous stirring to prevent the irreversible formation of $Pd(OH)_2(s)$.[14] Metal ion concentrations were determined by atomic absorption spectrophotometry (Perkin-Elmer Model 603). The ligand solutions were standardized by calorimetric titration with a standard Hg(II) solution, which gave stoichiometric 1:1 and 1:2 end points in the cases of $1,10\text{-}T_218C6$ and $1,4\text{-}T_218C6$, respectively. The uncertainties associated with the endpoints were ±0.5%. UV/vis spectra were measured in a 1-cm cell by using a Perkin-Elmer Model 320 UV/vis spectrophotometer.

Calorimetric Procedures. Procedures used to determine log K, ΔH, and ΔS values by competitive and direct calorimetric titration have been described.[1,11,15] In the present study, direct calorimetric titrations were performed at 25 °C to obtain the ΔH values for the reactions of Hg(II) with crown thioethers, while competitive calorimetric titrations were used at 25 °C to obtain both log K and ΔH values for the reactions of Pd(II) with crown thioethers.

Polarograhic Procedures. The dc current–voltage curves of Hg(II) complexes were obtained with a Model 364 pen-recording polarography analyzer (EG&G Princeton Applied Research). Potential measurements were made vs a Ag/AgCl (3.5 M KCl) electrode. This reference electrode is kept in contact with the testing solution via a special porous plug (Vycor frit) supplied by EG&G Princeton Applied Research. The use of this special plug at the interface of the solutions assures very long periods of reliable operation without fear that the solution in the reference electrode will contaminate the test solution. The potential scanning rate was either 2 or 5 mV/s. The droppng time of the dropping-mercury electrode (DME) was regulated to be 2.0 s for both normal- and differential-pulse polarography by a Model 303 static DME (EG&G Princeton Applied Research). HNO_3 (0.5 M) was used as a supporting electrolyte. Values of the half-wave potentials of Hg anodic waves were read directly from the individual polarograms. This method introduces approximately ±3 mV uncertainty into the values. However, the uncertainties can be reduced by determining the half-wave potentials at various ligand concentrations. The temperature at which all experiments were performed was 25 °C.

Table II. Variation of Pulse Polarographic Data[a] with Varying Ligand Concentration in 0.5 M HNO_3 Media at 25 °C

system	$-\log [T_218C6]$	$E_{1/2}$, V vs Ag/AgCl (3.5 M KCl)
$1,4\text{-}T_218C6$	4.053	+0.110
	3.655	+0.098
	3.354	+0.087
	3.053	+0.078
	2.655	+0.067
	2.352	+0.059
$1,10\text{-}T_218C6$	4.352	+0.059
	3.653	+0.060
	3.352	+0.059
	2.352	+0.056

[a] 0.5 M HNO_3 was used as the supporting electrolyte.

X-ray Crystallographic Procedures. Suitable single crystals of Pd(II) complexes were obtained in a sraightforward manner by dissolving the ligand and $Pd(NO_3)_2$ in warm acetonitrile and cooling the solution. One of these crystals was mounted on a Nicolet P3 autodiffractometer. The radiation used for data collection was graphite-monochromated Mo Kα. Crystal data and experimental conditions are summarized in Table I. Structures of $Pd(1,10\text{-}T_218C6)(NO_3)_2$ and $Pd(1,4\text{-}T_218C6)_2(NO_3)_2$ were obtained by heavy-atom methods with the use of Patterson and Fourier maps.

Results

Polarographic Studies. Polarographic studies have been done for heavy-metal complexes of thiourea and various cyclams in aqueous solution.[16,17] In the present study, a well-defined single anodic wave of mercury was obtained in the presence of either $1,10\text{-}T_218C6$ or $1,4\text{-}T_218C6$ in 0.5 M HNO_3 solution. Plots of EMF_{DME} vs $\log [(i_d - i)/i]$ gave straight lines of Nernstian slope, 30 ± 3 mV, which confirms a two-electron reversible oxidation of mercury. Two series of polarograms were made by varying the concentrations of $1,4\text{-}T_218C6$ from 4.45×10^{-3} to 8.85×10^{-5} M and $1,10\text{-}T_218C6$ from 4.45×10^{-3} to 4.45×10^{-5} M in 0.5 M HNO_3 solution (Table II).

Because Hg is oxidized to Hg(II) in the presence of either thia macrocycle (denoted as T_218C6), the following equations are considered

$$Hg + xT_218C6 = Hg(T_218C6)_x{}^{2+} + 2e^- \qquad (1)$$

$$K = [Hg(T_218C6)_x{}^{2+}]/\{[Hg^{2+}][T_218C6]^x\} \qquad (2)$$

where x is the stoichiometry of the reaction. The half-wave potential of the DME is then expressed as

$$E_{1/2} = E°_{\text{cell}} - 0.0296\{\log K + \log [(T_218C6)/2]^{x-1} - \log [k_f/k_c]\} \qquad (3)$$

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Table III. log *K*, ΔH (kJ/mol), and ΔS (J/(K·mol)) Values for the Reactions in 0.5 M HNO_3 at 25 °C

		Hg(II)			Pd(II)		
ligand	reacn L:M ratio	log *K*	ΔH	ΔS	log *K*	ΔH	ΔS
1,4-$T_2$18C6	2:1	22.2 ± 0.1[a]	−116.5 ± 0.2[b]	34.9[b]	25.1 ± 0.4[c]	−184.1 ± 0.3[c]	−137[c]
1,10-$T_2$18C6	1:1	19.5 ± 0.1[a]	−74.0 ± 0.2[b]	125.0[b]	21.1 ± 0.2[c]	−82.4 ± 0.3[c]	127.6[c]
18C6	1:1	2.42[d]	−19.6[d]	−19.7			

[a] Polarography. [b] Direct calorimetry. [c] Competitive calorimetry. [d] Reference 1.

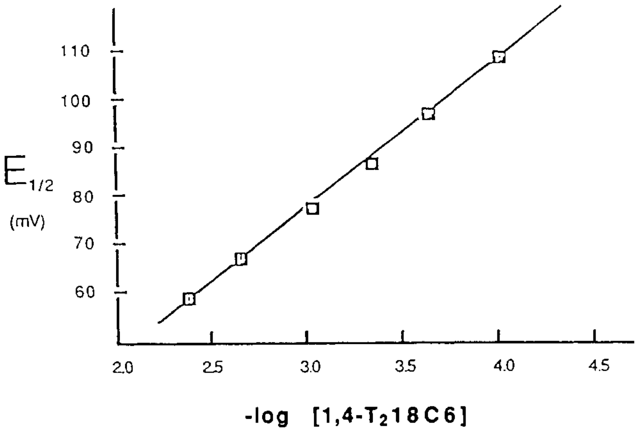

Figure 2. Variation of half-wave potential with logarithm of ligand concentration at DME.

where $E°_{cell}$ is the formal potential of the Hg/Hg(II) half-cell vs the Ag/AgCl electrode (3.5 M KCl) and k_f and k_c are the diffusion coefficients of free ligand and complexed ion, respectively. The value of the formal potential was calculated by using 0.8535 V for the standard potential of the Hg/Hg(II) half-cell[18] and 0.2046 V for the Ag/AgCl (3.5 M KCl) half-cell.[19,20] The activity coefficients were calculated for 0.5 M ionic strength by using the revised Debye–Hückel equation.[21]

A plot of $E_{1/2}$ vs log [1,4-$T_2$18C6] (data from Table II) gave essentially a straight line of slope 30 mV, indicating that the predominant species present is $Hg(1,4\text{-}T_218C6)_2^{2+}$ ($x = 2$) within the range of experimental concentrations of 1,4-$T_2$18C6, as shown in Figure 2. The polargraphic data in Table II show that the $E_{1/2}$ value of the Hg anodic wave was independent of 1,10-$T_2$18C6 concentration, indicating that the predominant species present is $Hg(1,10\text{-}T_218C6)^{2+}$. The reaction stoichiometries were further confirmed by the end points of the thermograms of direct calorimetric titrations of both 1,4-$T_2$18C6 and 1,10-$T_2$18C6 with Hg^{2+}. The thermodynamic quantities obtained by direct and competitive calorimetric determinations together with those obtained polarographically are given in Table III.

Calorimetric Studies. The *K* and ΔH values for the formation of the Pd(II) complexes were determined simultaneously by competitive calorimetric titrations of $Hg(1,10\text{-}T_218C6)^{2+}$ and $Hg(1,4\text{-}T_218C6)_2^{2+}$ with Pd(II). The log *K* and ΔH values for the formation of Hg^{2+} complexes were determined polarographically and calorimetrically, respectively. Stoichiometries of reactions of M^{2+} (Pd^{2+}, Hg^{2+}) with 1,10-$T_2$18C6 and 1,4-$T_2$18C6 were confirmed calorimetrically as 1:1 and 1:2, respectively, by either the mole ratio method or nonlinear least-squares procedure. In order to perform the competitive calorimetric titration of Hg(II) complexes with Pd(II), 0.5 M HNO_3 was used as the solvent to prevent the formation[14] of either soluble or insoluble hydroxide species of Pd(II) during the course of the titration. Direct calorimetric titration of either Pd(II) with the ligands or the ligands with Pd(II) is not possible because neither of these titrant solutions can be prepared in concentrations greater than 0.02 M in 0.5 M HNO_3 media.

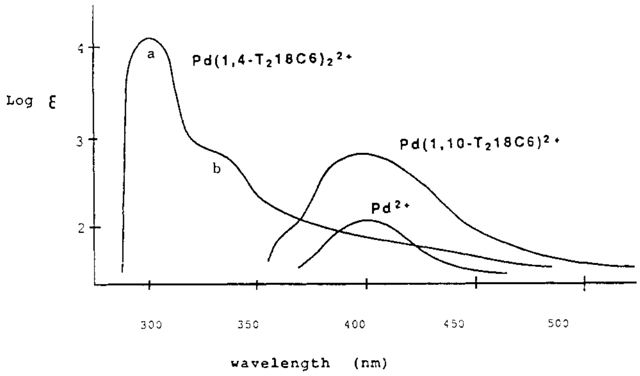

Figure 3. Spectra of Pd(II) and its crown thioether complexes in 0.5 M HNO_3.

Table IV. Wavelength (λ) and Extinction Coefficient (ϵ) Data for Pd^{2+}, $Pd(1,10\text{-}T_218C6)^{2+}$, and $Pd(1,4\text{-}T_218C6)_2^{2+}$ in HNO_3 Media at 25 °C

system	media	λ_{max}, nm	ϵ
$Pd(1,4\text{-}DT18C6)_2^{2+}$	0.5 M HNO_3	302	1.1 × 10^4
$Pd(1,10\text{-}DT18C6)^{2+}$	0.5 M HNO_3	398	1.1 × 10^3
Pd^{2+}	0.5 M HNO_3	400	105
Pd^{2+}[a]	1.1 M HNO_3	395	116

[a] Values from ref 14.

Table V. Atom Coordinates (×10^4) and Equivalent Isotropic Temperature Factors (Å^2 × 10^3) for Atoms Involved in the Complex Formations of $Pd(1,10\text{-}T_218C6)(NO_3)_2$ and $Pd(1,4\text{-}T_218C6)_2(NO_3)_2$

atom	*x*	*y*	*z*	*U*[a]
	$Pd(1,10\text{-}T_218C6)(NO_3)_2$			
Pd	945 (1)	5393 (1)	0	51 (1)
S1	3045 (4)	5206 (3)	−353 (4)	61 (2)
S10	1304 (4)	6974 (3)	326 (4)	60 (2)
O1N1	562 (13)	4004 (6)	−397 (7)	79 (5)
O1N2	−911 (7)	5531 (9)	442 (6)	80 (5)
	$Pd(1,4\text{-}T_218C6)_2(NO_3)_2$			
Pd	5052 (1)	664 (1)	6252 (1)	51 (1)
S1	3926 (2)	1547 (4)	6395 (1)	56 (1)
S4	5342 (2)	−23 (4)	6695 (1)	56 (1)
S1′	4722 (2)	1206 (4)	5808 (1)	63 (1)
S4′	6210 (2)	−10 (4)	6112 (1)	71 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Spectroscopic Studies. The spectra of Pd^{2+}, $Pd(1,10\text{-}T_218C6)^{2+}$, and $Pd(1,4\text{-}T_218C6)_2^{2+}$ are given in Figure 3. The extinction coefficients and wavelength maxima values are given in Table IV. The spectrum of Pd^{2+} in HNO_3 media agrees well with that of Jorgensen and Parthasarathy.[14]

Crystallographic Studies. Structures of $Pd(1,10\text{-}T_218C6)(NO_3)_2$ and $Pd(1,4\text{-}T_218C6)_2(NO_3)_2$ were obtained by heavy-atom methods with the use of Patterson and Fourier maps. In complex $Pd(1,4\text{-}T_218C6)_2^{2+}$, one of the two ligands was ordered, while the other was highly disordered. In the disordered ligand, atoms C6′, C8′, C9′, O10′, C11′, C12′, O13′, C15′, C17′, and C18′ were found at two different positions, each with an occupancy factor of 0.5. In Figure 4, only one position was plotted. Also, one of the nitrate groups in $Pd(1,4\text{-}T_218C6)_2(NO_3)_2$ was highly disordered and could

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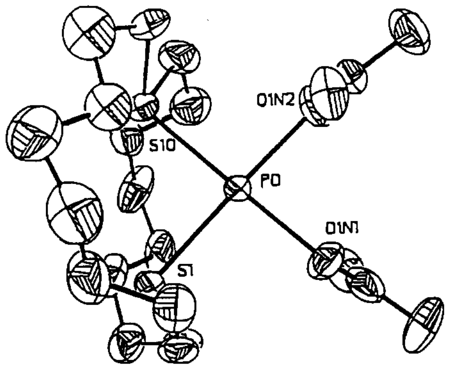
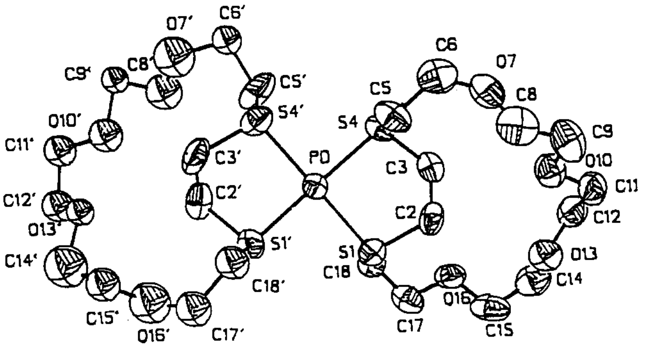


$Pd(1,10\text{-}T_218C6)(NO_3)_2$



$Pd(1,4\text{-}T_218C6)_2{}^{2+}$

Figure 4. Crystal structures of Pd(II) complexes with $1,10\text{-}T_218C6$ and $1,4\text{-}T_218C6$.

Table VI. Significant Bond Lengths (Å) and Bond Angles (deg)

	$Pd(1,10\text{-}T_218C6)(NO_3)_2$		
	Bond Lengths		
Pd-S1	2.274 (4)	Pd-O1N1	2.039 (10)
Pd-S10	2.270 (4)	Pd-O1N2	2.052 (8)
	Bond Angles		
Pd-S1-S10	89.6 (1)	Pd-S1-O1N1	91.5 (4)
Pd-O1N2-S10	90.5 (3)	Pd-O1N2-O1N1	88.8 (5)
	$Pd(1,4\text{-}T_218C6)_2(NO_3)_2$		
	Bond Lengths		
Pd-S1	2.307 (3)	Pd-S1′	2.304 (3)
Pd-S4	2.308 (3)	Pd-S4′	2.306 (3)
	Bond Angles		
Pd-S1-S4	90.2 (1)	Pd-S1′-S1	89.2 (1)
Pd-S4′-S4	90.3 (1)	Pd-S1′-S4′	90.6 (1)

not be located. Details of the crystallographic analysis are listed in Table I. Atomic coordinates for the atoms involved in coordination of the two Pd(II) complexes are listed in Table V. The most significant bond lengths and bond angles of these complexes are given in Table VI.

As observed previously,[9,22] $1,4\text{-}T_218C6$ forms an exodentate complex with Hg(II), while $1,10\text{-}T_218C6$ forms an endodentate complex. As indicated in Figure 4, oxygen donor atoms of the crown thioether ligand are not involved in the complexation of Pd(II) in the cases of $Pd(1,10\text{-}T_218C6)(NO_3)_2$ and $Pd(1,4\text{-}T_218C6)_2(NO_3)_2$. In $Pd(1,10\text{-}T_218C6)(NO_3)_2$, the palladium coordinates two sulfur atoms and two oxygen atoms from different nitrato groups. The coordination around Pd(II) is distorted square-planar, with small differences between donor–metal–donor angles, as seen in Table VI. In $Pd(1,4\text{-}T_218C6)_2{}^{2+}$, the platinum coordinates four sulfur atoms, which are chemically equivalent, and the resulting structure is a nearly undistorted square-planar conformation (Table VI). The planar configurations of both complexes are preserved on coordination. The atoms involved in the coordination of each cation are coplanar within ca. 0.1 Å.

Discussion

Ligand Field Stabilization Energy (LFSE) and Charge-Transfer Effects. As seen in Table III, ΔH values favor the complexation of M^{2+} with the crown thioethers in each case. A comparison of the ΔH values for the interactions of Hg(II) and Pd(II) with the crown thioethers indicates that the palladium–sulfur bond is stronger than the mercury–sulfur bond in these crown thioether complexes. The stability of Hg(II) complexes is a reflection of the presence of the polarizable sulfur atoms and the resulting stable Hg^{2+}–ligand covalent bonds. In addition to these factors, LFSE and, particularly, charge transfer might play important roles in the increased stability of $Pd(1,4\text{-}T_218C6)_2{}^{2+}$ over that of $Hg(1,4\text{-}T_218C6)_2{}^{2+}$. The difference between the ΔH values for the formation of $Pd(1,10\text{-}T_218C6)^{2+}$ and $Hg(1,10\text{-}T_218C6)^{2+}$ is much smaller than that for the formation of $Pd(1,4\text{-}T_218C6)_2{}^{2+}$ and $Hg(1,4\text{-}T_218C6)_2{}^{2+}$. Charge transfer from the ligand donor atoms to Pd(II) has been found in Pd(II)–tetraaza complexes.[23,24] In the case of $Pd(1,10\text{-}T_218C6)^{2+}$, the LFSE and, particularly, charge transfer are less evident. The contribution of LFSE and charge transfer to the stability of $Pd(1,4\text{-}T_218C6)_2{}^{2+}$ is evident by examining its spectrum. As shown in Figure 3, the spectrum of $Pd(1,4\text{-}T_218C6)_2{}^{2+}$ is composed of two bands, in which the strong charge-transfer band (a) merges with the second ligand field (b), which is a shoulder.

On the other hand, a comparison of the ΔH values for the interactions of $1,4\text{-}T_218C6$ and $1,10\text{-}T_218C6$ with the Hg(II) ion reveals that the metal–sulfur (M–S) bond strengths in both Hg(II) complexes are nearly the same and that oxygen atoms of the crown thioether might be involved in complexation. This is shown by subtracting[25] the contribution of the other four oxygen donor atoms of $1,10\text{-}T_218C6$. The average bond strengths in the two Pd(II) complexes are quite different (46 kJ compared to 41 kJ), even without subtracting the possible contribution of the other four oxygen atoms of $1,10\text{-}T_218C6$ in the case of the complex in solution. This difference between the two Pd(II) complexes indicates that a possible exodentation of $1,4\text{-}T_218C6$, which is similar to that of open-chain polythia ethers with the freedom of approaching to Pd(II), is more enthalpy favorable than the endodentation of $1,10\text{-}T_218C6$ adopted in the cis-Pd(II) complex (Figure 4). This difference also indicates that the oxygen atoms of the crown ligand may not coordinate to the Pd(II) ion and the structure of the $Pd^{II}(1,10\text{-}T_218C6)^{2+}$ complex in solution might be identical with that of the crystal.

The resulting splitting of the d orbitals in $Pd(1,10\text{-}T_218C6)^{2+}$ compared with that in nitrato-complexed Pd^{2+} is nearly negligible. This expectation is further confirmed by the comparison of the UV/vis absorption spectra of $Pd(NO_3)_x{}^{2-x}$, $Pd(1,4\text{-}T_218C6)_2{}^{2+}$, and $Pd(1,10\text{-}T_218C6)^{2+}$. As shown in Figure 3, the maximum absorption for the $Pd(1,4\text{-}T_218C6)_2{}^{2+}$ complex is found at a much shorter wavelength than that of either $Pd(NO_3)_x{}^{2-x}$ or $Pd(1,10\text{-}T_218C6)^{2+}$. The large shift in λ_{LFSE} from 400 nm for either $Pd(NO_3)_x{}^{2-x}$ or $Pd(1,10\text{-}T_218C6)^{2+}$ to around 330–340 nm (the shoulder band) of $Pd(1,4\text{-}T_218C6)_2{}^{2+}$ is attributed to the larger ligand field splitting by $1,4\text{-}T_218C6$. The large log ϵ value at λ_{max} (300 nm) in the case of $Pd(1,4\text{-}T_218C6)_2{}^{2+}$ results from the charge transfer superimposed on the double-band spectrum. The greater stability of $Pd(1,4\text{-}T_218C6)_2{}^{2+}$ is a combined result of the charge

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(25) Because Hg^{2+} bonds to all four sulfur atoms only in the $Hg(1,4\text{-}T_218C6)_2{}^{2+}$ complex, the enthalpy contribution of each Hg–S bond is −29.1 kJ/mol (−116.5 kJ/mol divided by 4). In the $Hg(1,10\text{-}T_218C6)^{2+}$ complex, the enthalpy contribution of each Hg–S bond is −30.4 kJ/mol, calculated by subtracting the enthalpy contribution of each Hg–O bond (−3.3 kJ/mol; e.g., −19.6 kJ/mol divided by six Hg–O bonds in $Hg(18C6)^{2+}$, as shown in Table III).

transfer and the LFSE. On the other hand, in spite of the 10-fold increase in the absorption of $Pd(1,10\text{-}T_218C6)^{2+}$ over that of $Pd(NO_3)_x^{2-x}$, λ_{max} remains nearly unchanged. The agreement of the difference in the ΔH values of the two Pd^{2+} complexes with their spectra confirms that stronger Pd–S bonds exist in $Pd(1,4\text{-}T_218C6)_2^{2+}$.

Macrocyclic and Entropic Effects. The relatively high stabilities per ligand bound of the $1,10\text{-}T_218C6$ complexes compared to those of the $1,4\text{-}T_218C6$ complexes may be a result of the macrocyclic effect of $1,10\text{-}T_218C6$ (see Table III). Also, the formation of $1,10\text{-}T_218C6$ with either Pd(II) or Hg(II) ion is very entropy favored as compared with the $1,4\text{-}T_218C6$ complexes. The ΔS values for the $M(II)/1,10\text{-}T_218C6$ systems are much more favorable than those for the $M(II)/1,4\text{-}T_218C6$ systems. These entropic differences probably result from the different abilities of the two ligands to effect dehydration of the metal ions and the different degrees of dehydration of the complexed ligands. The increased number of liberated solvent molecules from both metal ion and ligand ($1,10\text{-}T_218C6$) accounts for the more favorable ΔS values for these systems. Therefore, it seems reasonable to assign an entropic origin to the macrocyclic effect for these metal ions. The different entropies of formation of the $1,4\text{-}T_218C6$ complexes of Pd(II) (square planar) and Hg(II) (tetrahedron) may also be caused by the different degrees of dehydration of the two metal ions.

In conclusion, the relative magnitude of the enthalpy contribution is mainly dependent on the number of S-donor atoms coordinated to the central cations and their orientation with respect to these cations. The magnitude of the entropy contribution is mainly dependent on the dehydration of both the ligand and central cations. The size selectivity for these crown thioether ligands is not critical for the formation of stable complexes of transition-metal and post-transition-metal ions as was found in the complexation of alkali-metal and alkaline-earth-metal ions with crown ethers.

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Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic temperature factors, and atomic coordinates and related temperature factors for both Pd(II) complexes (16 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, Spectroscopy, and Reactivity of $M(Se_4)_2^{2-}$ Anions, M = Ni, Pd, Zn, Cd, Hg, and Mn

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The $M(Se_4)_2^{2-}$ ions, M = Ni, Pd, Zn, Cd, and Hg, have been synthesized by reaction of the metal xanthate with a polyselenide solution in CH_3CN-DMF. The corresponding $Mn(Se_4)_2^{2-}$ ion was synthesized by reaction of $MnCl_2$ with a polyselenide solution in DMF. The $Pt(Se_4)_2^{2-}$ ion was synthesized in situ by reaction of $Pt(Se_4)_3^{2-}$ with excess BH_4^-. The crystal structures of $[PEtPh_3]_2[Ni(Se_4)_2]$ and of $[PPh_4]_2[Zn(Se_4)_2]$ have been determined. The Ni center in the centrosymmetric $Ni(Se_4)_2^{2-}$ ion is essentially square planar with Ni–Se distances of 2.298 (1) and 2.315 (1) Å. The two independent $Zn(Se_4)_2^{2-}$ ions have approximately tetrahedral Zn centers, but they show significant metrical differences. Zn–Se distances range from 2.450 (5) to 2.493 (6) Å. The MSe_4 rings have the distorted envelope conformation. The ions (except $Mn(Se_4)_2^{2-}$) show two ^{77}Se NMR resonances. These occur for the following M (δ(metal-bound Se), ppm; δ(ring Se), ppm): Ni (820; 748); Pd (893; 758); Pt (727; 642); Zn (127; 598); Cd (62; 608); Hg (76; 594). Trends in these resonance positions are rationalized in terms of the d-electron configurations of the metal. Reaction of the corresponding $M(Se_4)_2^{2-}$ ion with dimethyl acetylenedicarboxylate affords the ions $M(Se_2C_2(COOCH_3)_2)_2^{2-}$ (M = Zn, Ni).

Introduction

The chemistry of soluble transition-metal chalcogenides began more than 100 years ago with the synthesis of the MS_4^{2-} (M = Mo, W) anions[1] and continues to be the subject of intense investigation. The chemistry is rich and presents a variety of structural types,[2] most of which do not have oxide analogues. Although the transition-metal sulfides have been studied extensively,[2] the corresponding selenium and tellurium chemistry is in an embryonic stage.[3] While many of the soluble selenide ions discovered in the last three years do not have sulfide analogues, the $M(Se_4)_2^{2-}$ ions do. These $M(Q_4)_2^{2-}$ ions (Q = S, Se) appear to be especially stable and accessible. Thus, $Ni(S_4)_2^{2-}$,[4,5] $Pd(S_4)_2^{2-}$,[4] $Zn(S_4)_2^{2-}$,[5] and $Hg(S_4)_2^{2-}$[6] are known. While the present work was in progress, new $M(Se_4)_2^{2-}$ ions were reported for M = Zn,[3,7,8] Cd,[7,8] Hg,[7,8] Ni,[8] Pb,[8] and Mn.[9] Here we report a general method of preparation of $M(Se_4)_2^{2-}$ anions, M = Ni, Pd, Zn, Cd, and Hg, a new route to $Mn(Se_4)_2^{2-}$, the in situ synthesis of $Pt(Se_4)_2^{2-}$, their ^{77}Se NMR spectroscopy (except for Mn), selected structural characterization, and the reactivity of $M(Se_4)_2^{2-}$ (M = Ni, Zn) toward dimethyl acetylenedicarboxylate (DMA).

Experimental Section

Syntheses. All the manipulations were carried out under N_2 with the use of standard Schlenk-line techniques. Solvents were distilled and dried. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. UV-vis and IR spectra were recorded on a Perkin-Elmer 330 spectrophotometer and a Perkin-Elmer 283 spectrometer, respectively. ^{77}Se NMR spectra were obtained on a Varian XLA-400 spectrometer with a 10-mm tunable probe and a deuterium lock. All chem-

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