

A Calorimetric Titration Study of Uni- and Bivalent Metal Ion Interaction with Several Thia Derivatives of 9-Crown-3, 12-Crown-4, 15-Crown-5, 18-Crown-6, 24-Crown-8, and with Several Oxathiapentadecanes in Water or Water-Methanol Solvents at 25 °C**

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The interaction of several sulfur derivatives of crown-3, crown-4, crown-5, crown-6, crown-8, and three oxathiapentadecanes with Ag⁺, Hg²⁺, Tl⁺, and Pb²⁺ in water or water-methanol solvents has been studied by a calorimetric titration procedure. The partial substitution of sulfur for oxygen in the crown-5 and crown-6 ligands results in little change in the affinity of the ligand for Tl⁺ and Pb²⁺, but greatly increased affinity for Ag⁺ and Hg²⁺. Values of log K, ΔH, and TΔS are reported where their determination was possible. Cation-ligand stoichiometries of 1:2 were found for Ag⁺ and Hg²⁺ complexes of many of the cyclic thia ethers. Only 1:1 complexes were found for Tl⁺ and Pb²⁺.

Introduction

The cation selective properties of cyclic polyethers have been well delineated but few studies involving their sulfur derivatives have been reported [1]. Cation selectivity of the cyclic ethers appears to be determined primarily by the ratio of cation to ligand diameters and is not appreciably affected by the electronic structure of the cation, *i.e.*, noble gas, pseudo-noble gas [2, 3]. In contrast to this behavior, log K for the interaction of Ag⁺ and K⁺ with 18-crown-6 and its 1,10-dithia derivative [4] show that ligand affinity for K⁺ decreases while that for Ag⁺ increases in going from the hexaether to the dithia

tetraether. Unfortunately, the data were not obtained in the same solvent (K⁺:methanol; Ag⁺:water) thus making valid comparisons difficult.

Most studies of the metal complexes of polyether type compounds have been limited to ligand ring sizes adequate to accommodate the reacting cation, resulting in reactions with 1:1 stoichiometry. Previously, 1:2 cation to ligand stoichiometry has been found to be favored by a ligand cavity diameter too small to accommodate the cation [5, 6].

The Ba(SCN)₂-dicyclohexano-18-crown-6 (*cis-syn-cis* isomer) complex has been shown [7] by X-ray crystallography to have 1:1 stoichiometry with the Ba²⁺ ion located in the center of the ring cavity. In this configuration, the ring is approximately circular (5.4 × 5.6 Å) and the oxygen atoms lie in a plane. The uncomplexed ligand, however, is elliptical (4 × 7 Å) with two oxygen atoms directed away from the cavity [8]. Kinetic data [9] indicate a fast conformational rearrangement of 18-crown-6 immediately prior to its slower complexation with K⁺. X-ray crystallographic studies of uncomplexed 1,4-dithia-15-crown-5 [10], 1,4-dithia-18-crown-6 [11], and 1,10-dithia 18-crown-6 [10] show in each case that both sulfur atoms are directed out from the ring and that the rings are elliptical. If a 1:1 dithia-crown ether complex formed having a structure similar to that of the Ba(SCN)₂-dicyclohexano-18-crown-6 complex, a conformational change in the ring would have to take place during which the sulfur lone pairs of electrons would be oriented toward the center of the cavity.

In the present study, the following ligand and cation parameters are examined to learn the manner in which they affect the metal binding characteristics and stoichiometry of metal complexes of polyether type ligands: 1) replacement of oxygen by sulfur, 2)

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the number of sulfur atoms in the molecule, 3) the presence or absence of a ring structure, 4) the position of the sulfur atoms in the molecule, 5) ring cavity size, and 6) cation type and stereochemical preference. Specifically, the interactions of several thia derivatives of crown-3, crown-4, crown-5, crown-6, crown-8, and three oxathiapentadecanes with several uni- and bivalent cations have been investigated. Log K , ΔH , and $T\Delta S$ values for the 1:1 and 1:2 (where applicable) metal-ligand reactions are reported where their determination was possible.

Experimental

Materials

The metal salts were obtained in the best available purity from the sources indicated and used without further purification: NaCl, KCl, HgO (J. T. Baker, reagent); AgNO₃ (Baker and Adamson, reagent); SrCl₂·6H₂O, BaCl₂·6H₂O (Baker and Adamson, ACS reagent); Pb(ClO₄)·3H₂O (G. Frederick Smith, reagent); Ti₂CO₃ (Alpha Inorganics, Ultrapure). Reagent grade methanol (Baker and Adamson, Special Reagent Code 1217) and HCl (J. T. Baker) were used.

The ligands whose metal complexing properties were investigated are shown in Table I. Their synthesis, purification, and characterization have been described [12–16]. Compounds VIII and XII were studied previously [2] and are included in Table I for completeness. The crown nomenclature used to describe the cyclic compounds is an extension of that introduced by Pedersen [17], and has been used previously together with systematic names for the thia-crown compounds [16].

Solution Preparation

All solutions were prepared using methanol or oxygen free, doubly distilled water. The cation solutions (0.2–1 *M*) were prepared by dissolving a known amount of the metal salt in the appropriate solvent – water, acid, or 70 wt.% methanol–water – and standardized by conventional volumetric procedures. The ligand solutions were prepared by dissolving an accurately weighed amount of the ligand in the appropriate solvent to give 0.01–0.004 *M* solutions. The ligand concentrations were checked by calorimetric titration with either Ag⁺ (in the case of VI), Pb²⁺ (in the case of XII), or Hg²⁺ (in all other cases) which gave stoichiometric 1:1 endpoints to within ±1.8% except in the cases of IX which was 5% low and VI which was 3 to 6% higher than expected.

The sulfur to oxygen ratio coupled with the size of the ring appear to be largely responsible for the solubility characteristics of cyclic thiaether compounds. Crown-3 and crown-4 derivatives were insoluble in water necessitating the use of 70 wt.%

methanol–water as the solvent. The remaining ligands were all sufficiently soluble in water to give at least a 0.004 *M* solution, with the exception of XIV where it was necessary to heat the solution before each titration. The resulting solution was rapidly cooled to 25 °C and used immediately. Detectable precipitation from the cooled solution required approximately 25 minutes which was longer than the time required to perform the calorimetric titrations.

Procedure

The calorimetric determinations were carried out at 25 °C using isoperibol titration calorimeters. The equipment and operating procedures have been described [18–23]. Two sets of determinations were made depending on the availability of ligand using reaction vessels of different volumes, *viz.*, 50 ml and 3 ml. The straight chain thiapentadecanes, together with the crown-3, crown-4, and crown-5 thia derivatives, were studied by titrating 6 ml of titrant into 50 ml of titrate. In the cases of the crown-6 and crown-8 thia derivatives, 0.2 ml of titrant was added to 2.69 ml of titrate [21]. In all cases, the cation salt was the titrant and the ligand was the titrate. The approximate final ionic strength in the calorimeter was 0.03 to 0.09, depending upon the titrant used.

Calculations

The limitations of the calorimetric procedure for determining equilibrium constants have been discussed [21, 24, 25]. In the present study there were several systems where the heat of reaction was either very small or zero. In these cases, no attempt was made to calculate log K or ΔH values. In some cases, the reaction to produce either 1:1 or 1:2 complexes was quantitative making possible the calculation of ΔH , but not log K values. For the remaining reactions, log K , ΔH , and $T\Delta S$ values were calculated from the calorimetric titration data by methods similar to those described previously [18, 20, 23].

Supplementary Material Available

Calorimetric heat change and corresponding volume data sets not available elsewhere* can be obtained from the Thermochemical Institute, Brigham Young University, Provo, Utah 84602, U.S.A.

Results

Log K , ΔH , and $T\Delta S$ values for those systems wherein such a determination was possible are

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TABLE I. Log K, ΔH (kcal/mol) and T ΔS (kcal/mol) Values for the Reactions $M^{n+} + L = ML^{n+}$ (1), $ML^{n+} + L = ML_2^{n+}$ (2), and $M^{n+} + 2L = ML_2^{n+}$ (3) at 25 °C^a.

Ligand ^b	Solvent	Reaction	Ag ⁺			Hg ²⁺			Tl ⁺			Pb ²⁺		
			Log K	ΔH	T ΔS	Log K	ΔH	T ΔS	Log K	ΔH	T ΔS	Log K	ΔH	T ΔS
-S-O-O-S- (I)	H ₂ O	1	4.46 (0.02)	-14.37 (0.12)	-8.28	5.3 (0.1)	-14.65 (0.05)	-7.4	d	d	d	d	d	d
		2	c			c								
-O-S-O-S-O- (II)	H ₂ O	1	e	-14.13 (0.08)		e	-14.02 (0.04)		d	d	d	d	d	d
		2	3.06 (0.01)	-3.68 (0.05)	0.49	3.22 (0.06)	-7.09 (0.03)	-2.70						
-O-S-S-S-O- (III)	H ₂ O	1	e	-17.56 (0.05)		e	-17.14 (0.06)		d	d	d	d	d	d
		2	3.75 (0.02)	-6.93 (0.10)	-1.81	4.69 (0.13)	-9.35 (0.13)	-2.95						
O-S-O (IV)	70% CH ₃ OH	1		0 ^f					d	d	d	d	d	d
		2												
		3												
O-S-S (V)	70% CH ₃ OH	1		d		e	-12.43 (0.07)		d	d	d	d	d	d
		2				e	-14.95 (0.16)							
S-O-O-O (VI)	H ₂ O	1	2.71 (0.06)	-10.23 (0.21)	-6.53	d			d	d	d	0.94 (0.01)	-5.86 (0.10)	-4.58
		2	c									c		
O-S-O-S (VII)	70% CH ₃ OH	1	e	-10.39 (0.19)		e	-12.00 (0.10)		d	d	d	d	d	d
		2	3.68 (0.06)	-10.54 (0.18)	-5.52	e	-12.44 (0.10)							
O-S-O-S (VII)	70% CH ₃ OH	1	e	-16.78 (0.07)		e	-16.69 (0.12)		d	d	d	d	d	d
		2	4.26 (0.01)	-11.79 (0.10)	-5.98	e	-14.94 (0.12)							

TABLE I. (Continued)

	H ₂ O	1	e	-13.8 (0.3)	e	-13.5 (0.6)	0 ^f	0 ^f
O-O-S-O-O-S-O (XVI)		2	c		c			

^a Values are the averages of 3 to 6 experimental determinations. The numbers in parentheses in the log K and ΔH columns give the uncertainties as the standard deviation of the mean. ^b In the abbreviated formulas given $-\text{CH}_2\text{CH}_2-$ groups are situated between each pair of donor atoms and in the cases of I, II, and III each terminal oxygen or sulfur is attached to a $-\text{CH}_3$ group. For example, $-\text{S-O-O-S-}$ (I) would read $\text{CH}_3\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SCH}_3$ and O-S-S (V) would read $\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2$. ^c No evidence of 2:1 L to M complex. ^d No determination made. ^e Log K too large for measurement by this technique. ^f No heat change; log K very small or $\Delta H = 0$. ^g Reference 2.

reported in Table I. No heat of reaction was found for the interaction of Na^+ , K^+ , Sr^{2+} , or Ba^{2+} with XIII, XIV, XV, or XVI. The absence of an enthalpy change in these cases probably indicates that no reaction occurs, since it is unlikely that the ΔH values would be zero for all the reactions.

Discussion

The factors affecting the cation binding characteristics of cyclic polyether type ligands have been presented and discussed [26], and those that pertain to this study are given in the Introduction. The results are now discussed in terms of these factors.

Replacement of Oxygen by Sulfur in Crown-5 and Crown-6 Ligands

A characteristic feature of the reaction of uni- and bivalent cations with 18-crown-6 in water, methanol, and water-methanol solvents is the strong dependence of cation selectivity on the ionic radius of the cation [2, 5]. This selectivity is not found for univalent cation interaction with 15-crown-5 in aqueous solution where the log K values for Na^+ , K^+ , Rb^+ , and Cs^+ are nearly the same while those for Ag^+ and Tl^+ are somewhat greater [2]. Data are given in Table I in those cases where one or two oxygen atoms in 15-crown-5 and 18-crown-6 are replaced by sulfur atoms. One notices immediately that for neither ligand type is there a correlation between the magnitude of log K and the cation radius. In fact, based on their reactions with the 1,4-dithia-15-crown-5 and thia-18-crown-6 ligands, the cations studied can be placed in one of three groups.

(1) Ag^+ and Hg^{2+} . Log K increases markedly with the introduction of sulfur with the increase being primarily the result of a more exothermic heat of reaction. This result is consistent with the fact that these polarizable cations have high affinity for the polarizable ligand sulfur atoms resulting in strong covalent interactions.

(2) Tl^+ and Pb^{2+} . Replacement of oxygen by sulfur in the 15-crown-5 and 18-crown-6 ligands results in each case in a significant decrease in log K. As in the cases of Ag^+ and Hg^{2+} , there is a favorable ΔH change in each system, however in the cases of Tl^+ and Pb^{2+} the favorable ΔH changes are more than offset by unfavorable $T\Delta S$ changes leading to smaller log K values.

(3) Na^+ , K^+ , Sr^{2+} , and Ba^{2+} . The absence of a heat of reaction between any of these cations and the sulfur derivatives of 15-crown-5 or 18-crown-6 is interpreted to mean that no reaction occurred. The absence of a reaction in these cases can be understood in terms of $T\Delta S$ and ΔH as follows. Large unfavorable $T\Delta S$ values are seen for the 1:1 reactions of Tl^+ and Pb^{2+} with the sulfur derivatives of 18-crown-6;

TABLE II. Log K, ΔH , and $T\Delta S$ Values for the 1:1 Reaction of K^+ with Several Crown Ethers at 25 °C.

Ligand	Log K	ΔH (kcal/mol)	$T\Delta S$ (kcal/mol)	Solvent
18-crown-6 ^a	2.03	-6.21	-3.42	H ₂ O
18-crown-6 ^b	6.05	-13.40	-5.20	CH ₃ OH
thia-18-crown-6 ^c	3.61	-9.01	-4.08	CH ₃ OH

^aReference 2. ^bR. M. Izatt, J. D. Lamb, G. E. Maas, R. E. Asay, J. S. Bradshaw, and J. J. Christensen, *J. Am. Chem. Soc.*, 99, 2365(1977). ^cR. M. Izatt, J. D. Lamb, and J. J. Christensen, unpublished results.

complexation only occurring as a result of favorable ΔH values. The $-\Delta H$ values for reaction of Na^+ , K^+ , Sr^{2+} , and Ba^{2+} would be expected to be much smaller than those for the reaction of Ag^+ , Hg^{2+} , Tl^+ , and Pb^{2+} with the sulfur ligands. Assuming that the magnitude of the $T\Delta S$ term would be similar for the two sets of metal ions, the $T\Delta S$ term would predominate and no complexation would occur with the alkali and alkaline earth cations. This assumption appears plausible from the data in Table II where the decreased stability of the K^+ complex of thia-18-crown-6 relative to that of the K^+ complex of 18-crown-6 in CH_3OH is seen to result from the ΔH term, $T\Delta S$ changing only slightly. The data for 18-crown-6 in water show that the stability decrease in going from CH_3OH to H_2O solvent is also essentially a ΔH effect.

The much larger $-T\Delta S$ terms for the 1:1 reaction of Tl^+ and Pb^{2+} with the dithia-18-crown-6 compounds XIII and XIV compared to those for the corresponding reactions with 18-crown-6 result from the replacement of oxygen by sulfur. It is probable that differences in ligand solvation significantly affect the magnitude of $T\Delta S$ in these cases, however data are not available to allow us to be more definite. This replacement could also affect $T\Delta S$ in the following way. X-ray crystallographic determinations show the cavity of the 18-crown-6 type ligands to be elliptical in the uncomplexed state, but nearly circular in metal complexes [27, 28]. A similar elliptical ligand conformation exists in the case of the 1,10-dithia-18-crown-6 [10] and a large decrease in $-T\Delta S$ should be associated with the significant conformational changes of the ring expected on complexation.

Number of Sulfur Atoms and Presence or Absence of a Ring Structure

The effect on complex stability of increasing the number of sulfur atoms is seen with two sets of compounds in Table I.

Oxathiapentadecanes

Increasing the number of sulfur atoms from two (I) to three (III) results in log K values for the 1:1 reactions in the cases of both Ag^+ and Hg^{2+} which are too large to be measured by calorimetric titration. The ΔH values in both cases become more favorable

by about 3 kcal/mol. Likewise, the log K values for the 2:1 (L to M^{n+}) reaction increase as the number of sulfur atoms increases from two (II) to three (III). These increases are accompanied by favorable ΔH and unfavorable $T\Delta S$ (somewhat less so in the case of Hg^{2+}) changes.

Crown-5 ligands

As was seen with the oxathiapentadecanes, increasing the number of sulfur atoms from zero (VIII) to one (IX) or two (X, XI) in the crown-5 ligands results in increased log K values for formation of Ag^+ and Hg^{2+} complexes. However, decreased log K values are found in this crown-5 series in the cases of Tl^+ and Pb^{2+} .

The oxathiapentadecanes are analogs of the crown-5 compounds, allowing a comparison of complexation behavior between cyclic and straight chain sulfur compounds (I vs. X and II vs. XI). With Ag^+ and Hg^{2+} , both 1:1 and 1:2 complexes are formed by II, X, and XI, but not by I which formed only 1:1 complexes. Comparing I and X, the increased stability of the 1:1 cyclic complex over the non-cyclic complex is seen to result from a favorable $T\Delta S$ term for Ag^+ . $T\Delta S$ data are not available in the remaining cases although $T\Delta S$ for the Hg^{2+} -X system is sufficiently more favorable than for the Hg^{2+} -I system to overcome a 3 kcal/mol drop in ΔH and still have a quantitative reaction (log K approximately 6). The data for II and XI show no stability increase for the Ag^+ -XI and Hg^{2+} -XI systems over the corresponding non-cyclic systems although log K data are available only for the second consecutive reaction. The data available for Tl^+ and Pb^{2+} are not sufficient to determine whether there is a macrocyclic effect in these cases for either system.

Position of the Sulfur Atoms, Ring Cavity Size, and Cation Stereochemical Preference

The location of the sulfur atoms is a primary factor in determining the stoichiometries of the complexes. In the oxathiapentadecanes only 1:1 complexation is found when the two sulfur atoms are at the ends of the molecule (I) while 1:1 and 1:2 metal:ligand complexes are found when the two sulfur atoms are in the 5 and 11 positions (II) or three sulfur atoms are in the 5, 8, and 11 positions (III).

In the smaller rings (crown-3 and crown-4) the sulfur and oxygen atoms are in close proximity and there is not sufficient space for the Ag^+ and Hg^{2+} to lie inside the cavity. Actual structures of these cation complexes have not been determined. However, in both ring systems 1:1 and 1:2 cation: ligand stoichiometries are found with Hg^{2+} . The reaction of thia-crown-3 (IV) with Hg^{2+} is unusual in that no 1:1 complex is detectable from the calorimetric data, but a 1:2 metal-ligand complex is formed quantitatively.

Although 1:2 metal to ligand stoichiometry was not found for the reaction of Ag^+ and Hg^{2+} with 15-crown-5, it was observed for the reaction of these metal ions with the thia, 1,4-dithia-, and 1,7-dithia 15-crown-5 ligands. The structures of these complexes are not known. The large increases in $-\Delta H$ with the increasing number of sulfur atoms through the series VIII, IX, X (or XI) suggest the increasing involvement of sulfur in the bonding through this series. In compound X, the sulfur atoms are situated in adjacent donor atom sites, and in XI they are separated by an oxygen. The $-\Delta H$ values for formation of the 1:1 complexes (Ag^+ and Hg^{2+}) increase although the $-\Delta H$ values for the second consecutive reaction decrease in the above series suggesting different interligand steric interactions when two ligands are bound to one metal ion.

The larger ring systems, crown-6 and crown-8, show a different type of pattern, possibly because insertion of the cation into the ring can occur. Except for the Hg^{2+} -XIII system where 1:2 and Ag^+ -XV system where 1:1 and 1:2 metal to ligand stoichiometries are found, only 1:1 complexes are observed for ligands XIII-XVI. Typical thermograms for the systems Ag^+ -XIII and Ag^+ -XIV illustrating the effect of donor atom position on complexation stoichiometry have been presented and discussed [29]. Molecular models show that sulfur atoms located at adjacent donor atom sites encounter considerable steric hindrance when both are directed to the inside of the ligand cavity (crown-5 > crown-6 > crown-8). In the larger rings, the sulfur and oxygen atoms cannot come into the same plane. Presumably, the location of the sulfur atoms opposite each other in the crown-6 and crown-8 ligands allows sufficient entry of the cations into the ring so that 1:2 complexes do not result. Particularly in the larger ring systems, the specific stereochemical requirements of the cation may become important in determining complex stoichiometry, structure, and thermodynamic stability. A good example of this is the finding of Metz, *et al.* [30] that in the crystal, PdCl_2 -XIV, a *cis*-square planar configuration is found around the Pd(II) with the two sulfur atoms from XIV and the two Cl atoms involved in the bonding. The Pd atom does not lie within the cavity of XIV which is bent like a bow. Likewise, Dalley [11] has determined the structure of $2\text{HgCl}_2 \cdot \text{XIII}$ to be one in

which a Hg^{2+} is associated with two Cl atoms and both sulfur atoms of XIII while the second Hg^{2+} is bound to two Cl atoms and shares a third Cl atom with the first Hg^{2+} .

No complexation with the 24-crown-8 ligands is observed for Tl^+ and Pb^{2+} .

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