Correlation of Molecular Conformation and Thermodynamic Stability of Metal-Cation Complexes of 1,4,7,10,13-Pentaoxa-16-thiacyclooctadecane

By M. L. Campbell, N. K. Dalley,* R. M. Izatt and J. D. Lamb

*Department of Chemistry, Thermochemical Institute,† Brigham Young University, Provo, Utah 84602, USA*

Abstract

The results of crystal-structure analyses of 1,4,7,10,13-pentaoxa-16-thiacyclooctadecane (I) and its complexes with NaSCN, KSCN, RbSCN and AgNO$_3$ are discussed. In all four complexes the cation coordinates to the five O atoms of the polyether sulfide (I). The sulfur–cation interaction for the complexes depends on the cation. The sulfur–cation interaction is strong and partially covalent with the Ag$^+$ complex, but weak with the K$^+$ and Rb$^+$ complexes. In these three structures the S atom is directed into the cavity of the ligand. There is no interaction between the S and the cation in the Na$^+$ complex. In both the Na$^+$-complexed and uncomplexed ligand, the S atom is directed away from the cavity of the ligand. The cation–oxygen ion–dipole electrostatic interaction is the main factor in the thermodynamic stability of the alkali-metal complexes, while the Ag$^+$ complex is stabilized by both the cation–oxygen and cation–sulfur interactions. Correlations are made between the thermodynamic stabilities of cation complexes of 1,4,7,10,13,16-hexaoxacyclooctadecane, 1,4,7,10,13-pentaoxacyclopentadecane, 1,4,7,10,13,16-hexaoxacyclooctadecane-2,6-dione and (I), and molecular conformation determined by X-ray diffraction. These correlations provide a basis for determining the effect various ligand parameters have on the thermodynamic stability of polyether complexes.

Introduction

The synthesis and unique cation-complexing characteristics of a number of cyclic polyethers were first reported by Pedersen (1967). These polyethers are of considerable interest because of their ability to form unusually strong complexes with alkali and alkaline-earth cations, and because they enhance the transport of such metal ions through cellular membranes (Christensen, Eatough & Izatt, 1974; Simon, Morf &

Meier, 1973; Morf, Ammann, Bissig, Pretsch & Simon, 1979). The ability of the polyethers to form complexes with these cations is attributed to the ion–dipole electrostatic interaction between the positive cation and the negative dipoles of the O atoms of the polyether ring.

Several compounds which resemble the macrocyclic polyethers synthesized by Pedersen have been prepared in which one or more O atoms have been replaced by S atoms (Dann, Chiesa & Gates, 1961; Pedersen, 1971; Bradshaw, Hui, Chan, Haymore, Izatt & Christensen, 1974; Bradshaw & Hui, 1974). Like the cyclic ethers, the cyclic polyether sulfides form complexes with metal ions, but the thermodynamic stabilities of the complexes differ considerably from those of the all-oxygen compounds. For example, when S replaces O as a donor atom in 18- and 15-membered ligands the stabilities of Ag$^+$ and Hg$^+$ complexes increase while those of the alkali complexes decrease (Frensdorff, 1971; Izatt *et al.*, 1978). The decrease in stability of alkali-metal complexes of polyether sulfides is probably due to the lower electronegativity, the larger size, and the different bond lengths and angles associated with the S atom compared to those of O. These factors tend to weaken the electrostatic attraction for these cations. The molecule 1,4,7,10,13-pentaoxa-16-thiacyclooctadecane (I), the ligand which is the subject of the present study, is unusual in that it is one of the few S-containing ligands that form stable complexes with alkali-metal cations.
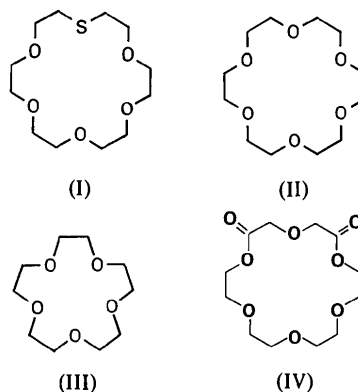
(I)   (II)

(III)   (IV)

The thermodynamic stabilities of polyether–cation complexes in solution are influenced by a number of factors including cation size, type, and charge; ligand size, type, and spatial arrangement of donor atoms; and solvent type. Information obtained from structural studies of polyether ligands and their cation complexes is frequently useful in correlating these factors with the thermodynamic stability of the complex. Among the factors affecting complex stability, the spatial arrangement and type of ligating atoms in the ligand are expected to have a major influence. However, the spatial arrangement of donor atoms is unlikely to remain invariant with change in cation unless strong geometric constraints are present in the ligand (Dunitz, Dobler, Seiler & Phizackerley, 1974). That is, the conformation of a free ligand may change upon complexation in order to allow a more favorable interaction between the cation and the ligand donor atoms. The energy required for this change, as well as the probable decrease in ligand internal entropy, is expected to have a destabilizing effect on the resulting metal complex. In principle, the closer the equilibrium conformation of the free ligand is to its conformation in the complex, the smaller is the destabilization introduced by ligand deformation upon complexation. Therefore, comparisons of the conformation of the free ligand with that of the cation–ligand complex for a series of cations may help explain trends in complex stabilities determined from calorimetric measurements. It must be remembered, however, that the structures in the solid state may differ significantly from those in solution, although it is likely that there will be similarities between the conformations, particularly in the case of the cation-ordered complexes.

Discussion

We have carried out a series of X-ray analyses of the uncomplexed polyether sulfide (I) and its crystalline complexes with Na^+, K^+ and Rb^+ thiocyanates, and $AgNO_3$ to observe the effect of cation size and type on ligand conformation. Details of the individual analyses follow this paper (Huffman, Campbell, Dalley & Larson, 1981; Cambell, Larson & Dalley, 1981a,b; Campbell, Dalley & Simonsen, 1981; Campbell & Dalley, 1981), so that only a review of the results will be given here along with general conclusions. Unfortunately, of the five structures studied, the polyether
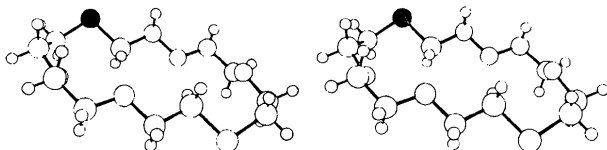
sulfide molecule is disordered in the Rb^+-complexed, Ag^+-complexed and uncomplexed ligand and, therefore, the bond lengths, bond angles and torsion angles in these three structures are somewhat uncertain. However, the gross features of the disordered ligands can be ascertained.

Structural features of the ligand

The ligand in all five structures (Figs. 1–5) shows the same general features as those found for other

Fig. 2. *ORTEP* stereoscopic view (Johnson, 1965) of the NaSCN complex of (I).
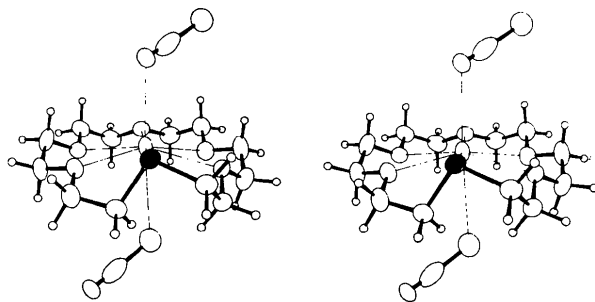

Fig. 3. *ORTEP* stereoscopic view (Johnson, 1965) of the KSCN complex of (I).

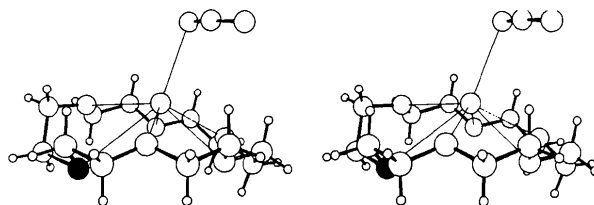Fig. 4. *ORTEP* stereoscopic view (Johnson, 1965) of the RbSCN complex of (I). Only the more populated SCN^- group site is shown (see Campbell, Dalley & Simonsen, 1981).
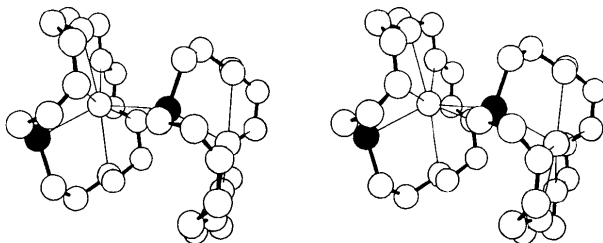

Fig. 5. *ORTEP* stereoscopic view (Johnson, 1965) of the $AgNO_3$ complex of (I). Only one conformation of the disordered ligand, molecule *A*, is shown (see Campbell & Dalley, 1981).

Fig. 1. *ORTEP* stereoscopic view (Johnson, 1965) of (I).

macrocyclic polyethers (Dalley, 1978). Specifically, torsion angles about the C—C bonds are close to 60°, the majority of those about the C—O bonds are close to 180°, while the C—S torsion angles are grouped into two classes, those close to 60° and those close to 180°. The C—C—O bond angles are roughly tetrahedral while the C—O—C and S—C—C angles are a few degrees wider. The C—S—C angles are close to 105°. As in other structures of macrocyclic polyethers, the C—C bonds found for (I) are short compared to the C—C bond distance of 1·523 Å for 1,4-dioxane (Davis & Hassel, 1963), while the C—O and C—S bond lengths appear to be normal (Dalley, 1978). The shortening of C—C bond lengths in cyclic polyethers has been discussed extensively (Mercer & Truter, 1973; Dunitz et al., 1974; Goldberg, 1975; Dalley, 1978).

The uncomplexed polyether sulfide (I), Fig. 1, has a centrosymmetric conformation and is isomorphous with the hexaether (II) (Dunitz & Seiler, 1974). The S atom position is disordered and has an occupancy of 0·5 S and 0·5 O. The S atom and one O atom are directed out of the cavity and give the molecule an elliptical shape.

In all four of the complexes the cation sits in the hole formed in the center of the ligand. The conformations of the complexed ligand differ drastically from that of the uncomplexed molecule in order to accommodate the different sizes and coordinating properties of the several cations. The ligand is large and flexible enough to accommodate an Na⁺, K⁺ or Ag⁺ cation inside its cavity. The Rb⁺ cation is slightly larger than the ligand cavity and is located about 1 Å above the mean plane of the donor atoms of the cavity. The S atom in the Na⁺ complex, Fig. 2, is directed away from the cavity of the ligand. The Na—S distance of 4·49 Å indicates no sulfur–cation interaction. In the K⁺, Rb⁺ and Ag⁺ complexes the S atom is directed into the cavity of the ligand. This is shown in Figs. 3, 4 and 5 respectively. S—O and S—ligand-centroid distances indicate the order Ag⁺ > Rb⁺ > K⁺ for the extent the S atom is directed into the cavity. The Ag⁺ complex is the only structure in which a sulfur–cation interaction strongly contributes to thermodynamic stability. Each Ag⁺ cation is bonded to two S atoms (see Fig. 5). Along with an intra-molecular Ag—S bond, there is an additional Ag—S intermolecular interaction from an adjacent ligand. The Ag—S distances (2·58–2·67 Å) are approximately 0·5 Å shorter than the sum of the van der Waals radii (see Table 1). The K—S (3·28 Å) and Rb—S (3·37 Å) contact distances are approximately equal to the sum

of the van der Waals radii, indicating at most a weak interaction. The cation–oxygen distances in the complexes are approximately equal to the sum of the van der Waals radii [Na⁺ complex, 2·48–2·58 Å, mean 2·53 (4) Å; K⁺ complex, 2·77–2·87 Å, mean 2·80 (4) Å; Rb⁺ complex, 2·86–3·04 Å, mean 2·98 (7) Å; Ag⁺ complex, 2·48–2·92 Å, mean 2·72 (15) Å]. The cation–oxygen ion–dipole electro-static interaction is undoubtedly the main factor in stabilizing the alkali-metal complexes, while the Ag⁺ complex is stabilized by both the cation–oxygen and cation–sulfur interactions.

In the structures of all four complexes, the adjacent O—O distances of the ligand are approximately equal to the sum of the van der Waals radii of 2·8 Å [Na⁺ complex, 2·72–2·84 Å, mean 2·77 (5) Å; K⁺ complex, 2·79–2·88 Å, mean 2·83 (4) Å; Rb⁺ complex, 2·80–2·88 Å, mean 2·84 (4) Å; Ag⁺ complex, 2·70–2·87 Å, mean 2·80 (10) Å]. Thus, neighboring O atoms are in contact with one another. The S—O contact distances fall into two groups, those for the K⁺, Rb⁺, and Ag⁺ complexes in which the distances are significantly shorter than the sum of the van der Waals radii of 3·25 Å (K⁺ complex, 3·04 and 3·14 Å; Rb⁺ complex, 3·02 and 3·10 Å; Ag⁺ complex, 3·13 and 3·17 Å), and those for the uncomplexed ligand and the Na⁺ complex in which the distance is equal to or greater than the sum of the van der Waals radii (uncomplexed, 3·22 and 3·82 Å; Na⁺ complex, 3·24 and 3·31 Å). In the latter group of structures the S atom is not interacting with a cation. In the former group of structures the S is interacting with the cation. The cation–sulfur distances in these three complexes suggest that the electric field of the cation is polarizing the outer electrons of the S atom toward the cation. The electron distribution in the direction of the adjacent O atoms is therefore decreased allowing the S and O atoms to move closer together without incurring repulsive forces. The added electron distribution in the direction of the cation would also presumably stabilize the complex (ion-induced dipole stabilization).

Thermodynamics

Polyether–alkali-metal-cation complexes are formed in solution according to the equation: metal^{m+} (sol-vated) + polyether (solvated) = polyether–metal^{m+} (solvated) + x solvent. An expression relating the equilibrium constant for complexation to various free-energy changes is given by the equation: $-RT\ln K = \Delta G^{\circ}_{\text{bind}} - \Delta G^{\circ}_{\text{solv}}(M^+) - \Delta G^{\circ}_{\text{solv}}(L) + \Delta G^{\circ}_{\text{conf}}(L) + \Delta G^{\circ}_{\text{solv}}(ML^+)$, where the terms on the right of the equation refer to the free-energy changes involved in metal–ligand bonding, metal-ion solvation, ligand solvation, ligand conformational changes and solva-tion of the metal–ligand complex respectively (Srivanavit, Zink & Dechter, 1977). Thus, the stability

Table 1. *Van der Waals and ionic radii* (Å) (*Pauling, 1960*)

O	1·4	Na⁺	0·95
S	1·85	K⁺	1·33
Ag⁺	1·26	Rb⁺	1·48

of a cation complex results from a subtle balance among ΔG_{bind}, ΔG_{conf} and the three ΔG_{solv} terms. Furthermore, the free energy of complex formation results from a balance between the enthalpy and entropy of complexation. The enthalpy of complexation is due primarily to the stronger electrostatic interactions between the ligand and cation compared to those between the solvent and cation. Thus, the enthalpy of complexation is expected to be large and negative when the polyether is of the right size and conformation so that the cation can fit snugly in the cavity of the polyether where the charge density is highest. The enthalpy of complexation is expected to be small if the ligand cavity is either too small or too large so that the optimum contact distance between cation and donor atom cannot be obtained. The electronegativity and spatial arrangement of the donor atoms also influence the enthalpy. In addition, appreciable internal and solvation entropy changes result from complex formation. Internal entropy changes upon complexation are expected to be large and negative when the uncomplexed molecule is extremely flexible and/or the complex is inordinately constrained. Internal entropy changes are expected to be small when the complexed and uncomplexed ligand have similar conformations. It is curious that in the majority of the cases reported, the entropies of complexation are negative. This may be due to a marked decrease in ligand internal (and possibly ligand solvation) entropy, overcompensating the increase in translational entropy due to the release of solvent molecules from the solvation shell of the cation (Lehn, 1973). An excellent interpretation of the enthalpic and entropic contributions for complexation of cations by cryptates has been given by Kauffman, Lehn & Sauvage (1976).

Unfortunately, due to the difficulty of interpreting solvent effects, valid comparisons of thermodynamic data cannot be made for different cations. However, meaningful comparisons of data for the same cation complexed with different types of ligands are possible. The four ligands, (I), (II), (III) and (IV), are representative of the ways in which ligand parameters can affect thermodynamic properties for complex formation. X-ray structural studies of compounds (I), (II) (Dunitz & Seiler, 1974; Dobler, Dunitz & Seiler, 1974; Seiler, Dobler & Dunitz, 1974; Dobler & Phizackerley, 1974), and (IV) (Dalley & Larson, 1979; Larson & Dalley, 1981) have been reported. Structural studies of (III) have not been published; however, structures of the benzo derivative and its Na^+ and K^+ complexes have been reported (Hanson, 1978; Bush & Truter, 1972; Mallinson & Truter, 1972). We will assume that the structural features of (III) and its benzo derivative are similar in correlating thermodynamic stability and conformation. The thermodynamic data for the complexation of Na^+, K^+, Rb^+, and Ag^+ with these ligands are listed in Table 2. The instrumentation and

Table 2. Log K, ΔH and $T\Delta S$ for reaction of Na^+, K^+, Rb^+ and Ag^+ cations with (I), (II), (III) and (IV) in methanol at 298 K (Lamb, Izatt, Swain & Christensen, 1980; Lamb, Izatt, Swain, Bradshaw & Christensen, 1980); ΔH and $T\Delta S$ are in kJ mol^{-1}

		Na^+	K^+	Rb^+	Ag^+
(I)	Log K	2·57	3·61	2·99 ± 0·01[a]	>5·5
	ΔH	−20·9	−37·8	−35·99 ± 0·38[a]	−51
	$T\Delta S$	−6·20	−17·1	−18·9	b
(II)	Log K	4·36	6·06	5·3	4·58
	ΔH	−35	−56·2	−50·7	−39
	$T\Delta S$	−10	−21·4	−20·8	−12
(III)	Log K	3·48	3·8	c	3·62
	ΔH	−20·9	−32·3		−27·6
	$T\Delta S$	−1·0	−10·8		−6·9
(IV)	Log K	2·50	2·79	2·09	2·50
	ΔH	−9·6	−24·6	−29	−6·41
	$T\Delta S$	4·6	−8·63	−17	8·0

(a) Unpublished results.
(b) Equilibrium constant too large to calculate log K and $T\Delta S$ using calorimetric methods.
(c) Has not been reported.

data processing procedures used to obtain the data have been described (Christensen, Ruckman, Eatough & Izatt, 1972; Eatough, Christensen & Izatt, 1972; Eatough, Izatt & Christensen, 1972).

Sodium complexes

The stability constants for the sodium complexes of the four ligands decrease in the order (II) > (III) > (I) $\simeq$ (IV). There are a number of conclusions that can be drawn with respect to this stability trend from the thermodynamic and structural data. The enthalpy terms for (I) and (III) are equal, and this may be better understood by examining the structures of the two complexes. In both cases five O atoms are involved in complex formation (Bush & Truter, 1972). The larger enthalpy term of (II) is expected from the structure which shows that six O atoms coordinate to the Na^+ ion (Dobler, Dunitz & Seiler, 1974). The enthalpy term for (IV) is small compared to those of the other three ligands. This trend is seen for all of the cations in Table 2. The less negative enthalpy change is due to the electron-withdrawing character of the ester carbonyl groups. The electron density on the two ester O atoms in the ring is decreased, causing a corresponding decrease in the ion–dipole interaction (Izatt, Lamb, Maas, Asay, Bradshaw & Christensen, 1977). It appears that the carbonyl oxygens of the ligand do not take part directly in alkali-metal complexation (Larson & Dalley, 1981).

The entropy contribution to complex stability is more difficult to interpret than the enthalpy contribution due to the many factors contributing to ΔS. Assuming solvent effects for complexes with the same cation are approximately equal, then the entropy terms will differ from ligand to ligand due primarily to

differences in the internal entropies of the free and of the complexed ligands. It is interesting that while the Na^+ complex of (II) is thermodynamically more stable than the Na^+ complexes of (I), (III), and (IV), the entropy terms actually favor (I), (III) and (IV) over (II). The unfavorable entropy term for (II) is probably a result of two effects. First, X-ray studies (Seiler *et al.*, 1974) indicate that the Na^+ complex of (II) is probably more constrained than those of the others. Second, (II) has more stable conformations in the uncomplexed form than do (I), (III), and (IV). In particular, low-energy conformations of uncomplexed (I) require that the S point away from the cavity of the ligand. No such restrictions hold for (II). That (II) has more low-energy conformations than (III) is a direct consequence of its larger ring size. For (IV), X-ray studies (Dalley & Larson, 1979) indicate that the ester groups make the ring rigid in the uncomplexed form.

The stability of the Na^+ complex of (III) is greater than that of (I) as a direct consequence of the difference in ΔS. Proton magnetic resonance spectra indicate that the S atom and its adjacent C atoms are constrained in the Na^+ complex of (I) but not in the free ligand (Campbell, 1979, unpublished observations). Therefore, the number of low-energy conformations is less in the complex than in the free ligand, *ergo* decreasing the internal entropy upon complexation. The slightly more favorable entropy term for the complex of (III) relative to (I) is probably due to similar conformations of the uncomplexed and complexed ligand (Hanson, 1978). Kinetic studies using ultrasonic absorption support this view (Rodriguez, Liesegang, White, Farrow, Purdie & Eyring, 1977). The phenomenon of a favorable entropy contribution (relative to other polyethers) upon complexation due to similar ligand conformations in the complexed and uncomplexed species is also seen in compound (IV). Upon complexation, the ligand has a comparable number of low-energy conformations as the free ligand, causing a favorable entropy contribution for complex formation. In fact, in the Na^+ complex of (IV), the solvent entropy dominates over the internal entropy of the ligand resulting in a positive $T\Delta S$ term for complex formation.

Potassium complexes

The stability constants of the complexes show the trend (II) > (III) > (I) > (IV). The large K for (II) is due to the enthalpy term, which results primarily from the close interaction of all six O atoms with the K^+ cation (Seiler *et al.*, 1974). The difference between the stabilities of the K^+ complexes of (I) and (III) is much less than in the Na^+ complexes. This is due to a balance of the entropy and enthalpy terms. The enthalpy term favors (I), while the entropy term favors (III). Again, structural studies help to explain this trend. X-ray studies show that there are probably two factors involved in the enthalpy terms. First, the cavity of (III) is smaller than the K^+ ion (Mallinson & Truter, 1972). The cation is displaced upward out of the cavity of the ligand decreasing the stability of the complex. By contrast the cavity of (I) is large enough to allow the cation to fit snugly in the cavity. Second, only the five O atoms of (III) take part in complexation. However, in the case of (I) the S atom coordinates to the cation along with the five O atoms. This added interaction is expected to increase the magnitude of the enthalpy contribution of (I) over that of (III).

The same trends in the entropy contribution occur in the K^+ complexes as in the Na^+ complexes. The same general arguments apply; however, it is interesting to note that in each case the K^+ complexes have more negative $T\Delta S$ terms than the Na^+ complexes. This is undoubtedly due to the different solvent effects on the two different cations.

Rubidium complexes

The stability-constant trend for the Rb^+ complexes is (II) > (I) > (IV). The Rb^+ is too large to fit in the cavity of any of the ligands studied. Instead, it lies somewhat above the mean plane of the ligand donor atoms. This structural difference between the Rb^+ complexes and the corresponding K^+ complexes is reflected in the smaller log K values for the Rb^+ complexes in (I) and (II). The difference in ΔH values between the K^+ and Rb^+ complexes is greater in (II) than in (I). This difference could reflect the greater ability of (I) to adjust itself to the larger cation as shown by the shorter Rb^+–O distances in (I) as compared to those in (II) (Dobler & Phizackerley, 1974). Unfortunately, the thermodynamic data for the Rb^+ complex of (III) have not been reported and so its position in the stability sequence is not known. However, in view of the structural information available the enthalpy change for formation of the Rb^+–(III) complex would be expected to be less negative than those for the corresponding (I) and (II) complexes. The difference in the ΔH values between the complexes of (I) and (III) will probably not be as large in the case of the Rb^+ complexes as in the K^+ complexes because the Rb^+ lies above the ligand cavity in both complexes. Whether the entropy change still favors (III) and (I) and, if so, by what magnitude will determine the relative stabilities of the two complexes. Work is currently in progress to determine the thermodynamic stability of (III) with Rb^+ and will be reported elsewhere.

Silver complexes

The Ag^+ complexes show the trend (I) > (II) > (III) > (IV) for log K. This trend is explained by Pearson's theory of soft and hard acids and bases (Pearson, 1963). The soft Ag^+ cation has a strong

interaction with the soft S atom along with the electrostatic ion–dipole interactions of the five O atoms of (I). Ligands (II), (III), and (IV) interact with Ag^+ only by the ion–dipole interaction. Frensdorff (1971) was the first to conclude from thermodynamic data that Ag^+ complexes of S-containing macrocycles involve a covalent interaction between the S and Ag atoms. The Ag–S contact distances reported for (I) are considerably less than the sum of the van der Waals radii and indicate considerable covalent character in the Ag–S interaction. Short Ag–S contact distances in other macrocycles have been reported (Louis, Pélissard & Weiss, 1976; Louis, Agnus & Weiss, 1977).

References

BRADSHAW, J. S. & HUI, J. Y. (1974). *J. Heterocycl. Chem.* **11**, 649–673.

BRADSHAW, J. S., HUI, J. Y., CHAN, Y., HAYMORE, B. L., IZATT, R. M. & CHRISTENSEN, J. J. (1974). *J. Heterocycl. Chem.* **11**, 45–49.

BUSH, M. A. & TRUTER, M. R. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 341–344.

CAMPBELL, M. L. & DALLEY, N. K. (1981). *Acta Cryst.* **B37**, 1750–1753.

CAMPBELL, M. L., DALLEY, N. K. & SIMONSEN, S. H. (1981). *Acta Cryst.* **B37**, 1747–1750.

CAMPBELL, M. L., LARSON, S. B. & DALLEY, N. K. (1981a). *Acta Cryst.* **B37**, 1741–1744.

CAMPBELL, M. L., LARSON, S. B. & DALLEY, N. K. (1981b). *Acta Cryst.* **B37**, 1744–1747.

CHRISTENSEN, J. J., EATOUGH, D. J. & IZATT, R. M. (1974). *Chem. Rev.* **74**, 351–382.

CHRISTENSEN, J. J., RUCKMAN, J., EATOUGH, D. J. & IZATT, R. M. (1972). *Thermochim. Acta*, **3**, 203–218.

DALLEY, N. K. (1978). *Synthetic Multidentate Macrocyclic Compounds*, ch. 4, *Structural Studies*, edited by R. M. IZATT & J. J. CHRISTENSEN, pp. 207–243. New York: Academic Press.

DALLEY, N. K. & LARSON, S. B. (1979). *Acta Cryst.* **B35**, 1901–1903.

DANN, J. R., CHIESA, P. P. & GATES, J. W. JR (1961). *J. Org. Chem.* **26**, 1991–1995.

DAVIS, M. & HASSEL, O. (1963). *Acta Chem. Scand.* **17**, 1181.

DOBLER, M., DUNITZ, J. D. & SEILER, P. (1974). *Acta Cryst.* **B30**, 2741–2743.

DOBLER, M. & PHIZACKERLEY, R. P. (1974). *Acta Cryst.* **B30**, 2746–2748.

DUNITZ, J. D., DOBLER, M., SEILER, P. & PHIZACKERLEY, R. P. (1974). *Acta Cryst.* **B30**, 2733–2738.

DUNITZ, J. D. & SEILER, P. (1974). *Acta Cryst.* **B30**, 2739–2741.

EATOUGH, D. J., CHRISTENSEN, J. J. & IZATT, R. M. (1972). *Thermochim. Acta*, **3**, 219–232.

EATOUGH, D. J., IZATT, R. M. & CHRISTENSEN, J. J. (1972). *Thermochim. Acta*, **3**, 233–246.

FRENSDORFF, H. K. (1971). *J. Am. Chem. Soc.* **93**, 600–606.

GOLDBERG, I. (1975). *Acta Cryst.* **B31**, 754–762.

HANSON, I. R. (1978). *Acta Cryst.* **B34**, 1026–1028.

HUFFMAN, J. C., CAMPBELL, M. L., DALLEY, N. K. & LARSON, S. B. (1981). *Acta Cryst.* **B37**, 1739–1741.

IZATT, R. M., LAMB, J. D., MAAS, G. E., ASAY, R. E., BRADSHAW, J. S. & CHRISTENSEN, J. J. (1977). *J. Am. Chem. Soc.* **99**, 2365–2366.

IZATT, R. M., TERRY, R. E., HANSEN, L. D., AVONDET, A. G., BRADSHAW, J. S., DALLEY, N. K., JENSEN, T. E., CHRISTENSEN, J. J. & HAYMORE, B. L. (1978). *Inorg. Chim. Acta*, **30**, 1–8.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KAUFFMAN, E., LEHN, J. M. & SAUVAGE, J. P. (1976). *Helv. Chim. Acta*, **59**, 1099–1111.

LAMB, J. D., IZATT, R. M., SWAIN, C. S., BRADSHAW, J. S. & CHRISTENSEN, J. J. (1980). *J. Am. Chem. Soc.* **102**, 479–482.

LAMB, J. D., IZATT, R. M., SWAIN, C. S. & CHRISTENSEN, J. J. (1980). *J. Am. Chem. Soc.* **102**, 475–479.

LARSON, S. B. & DALLEY, N. K. (1981). To be submitted.

LEHN, J. M. (1973). *Struct. Bonding (Berlin)*, **16**, 1–65.

LOUIS, P. R., AGNUS, Y. & WEISS, R. (1977). *Acta Cryst.* **B33**, 1418–1421.

LOUIS, P. R., PÉLISSARD, D. & WEISS, R. (1976). *Acta Cryst.* **B32**, 1480–1485.

MALLINSON, P. R. & TRUTER, M. R. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 1818–1823.

MERCER, M. & TRUTER, M. R. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2215–2220.

MORF, W. E., AMMANN, D., BISSIG, R., PRETSCH, E. & SIMON, W. (1979). *Cation Selectivity of Neutral Macrocyclic and Nonmacrocyclic Complexing Agents in Membrane* in *Progress in Macrocyclic Chemistry*, Vol. 1, edited by R. M. IZATT & J. J. CHRISTENSEN, pp. 1–61. New York: John Wiley.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., pp. 260, 514. Ithaca: Cornell Univ. Press.

PEARSON, R. G. (1963). *J. Am. Chem. Soc.* **85**, 3532–3539.

PEDERSEN, C. J. (1967). *J. Am. Chem. Soc.* **89**, 2495–2496.

PEDERSEN, C. J. (1971). *J. Org. Chem.* **36**, 254–257.

RODRIGUEZ, L. J., LIESEGANG, G. W., WHITE, R. D., FARROW, M. M., PURDIE, N. & EYRING, E. M. (1977). *J. Am. Chem. Soc.* **81**, 2118–2122.

SEILER, P., DOBLER, M. & DUNITZ, J. D. (1974). *Acta Cryst.* **B30**, 2744–2745.

SIMON, W., MORF, W. E. & MEIER, P. C. (1973). *Struct. Bonding (Berlin)*, **16**, 113–160.

SRIVANAVIT, C., ZINK, J. I. & DECHTER, J. J. (1977). *J. Am. Chem. Soc.* **99**, 5876–5881.