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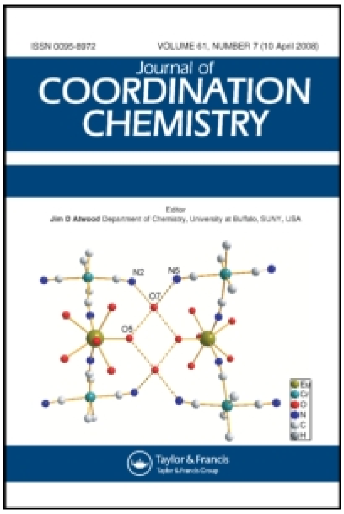

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Fabrizio Marsicano[a]; Robert D. Hancock[a]; Alison McGowan[a]
[a] Centre for Molecular Design, Department of Chemistry, University of the Wilwatersrand, South Africa

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THERMODYNAMIC ORIGIN OF THE CRYPTATE EFFECT IN COMPLEXES INVOLVING CRYPTAND-2,2,2

FABRIZIO MARSICANO,[†] ROBERT D. HANCOCK and ALISON McGOWAN

Centre for Molecular Design, Department of Chemistry, University of the Witwatersrand, P.O. WITS, 2050 South Africa

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This paper describes a titration calorimetric study of the heats of complex formation of the ligand bis(2-hydroxyethyl)-1,10-diaza-4,7,13,16-tetraoxocyclooctadecane (BHE-18-aneN_2O_4) with the metal ions Ag^+, Pb^{2+}, Sr^{2+}, and Ba^{2+}, and the ligand 1,10-diaza-4,7,13,16-tetraoxocyclooctadecane (18-aneN_2O_4) with the metal ions Ag^+ and Pb^{2+}. Thermodynamic quantities for complex formation of the ligand BHE-18-aneN_2O_4, which is a macrocycle with two pendant 2-hydroxyethyl groups, are compared with corresponding quantities for the ligand 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (cryptand-2,2,2), which is a cryptand consisting of the same basic macrocycle with a diether bridge. When the 'cryptate effect' is defined as the increase in complex stability that occurs when a cryptand ligand is produced by simple ring closure from a parent macrocycle with appropriate pendant chelating substituents, then it is demonstrated that, in the system studied, the cryptate effect is predominantly an enthalpy effect, attributable to preference of the metal ions for ethereal over alcoholic O-donors, and with a small but significant destabilizing entropy contribution. It is also demonstrated that the increase in complex stability that accompanies addition of pendant hydroxyethyl groups to a parent macrocycle is largely an entropy effect, related to desolvation of the terminal hydroxy groups.

Keywords: Cryptates, complexes, cryptate effect, calorimetry, thermodynamics

INTRODUCTION

The qualitative observation that complexes formed by cryptand ligands, *i.e.*, ligands possessing more than one macrocyclic ring, are in general much more stable than complexes formed by analogous macrocyclic ligands has been loosely termed the 'cryptate effect'. Thus, complexes formed by the cryptand ligand 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane (cryptand-2,2,2) are much more stable in terms of formation constants (or Gibbs functions of complex formation) than are complexes formed by the macrocycle 1,10-diaza-4,7,13,16-tetraoxocyclooctadecane (18-aneN_2O_4) (see Fig. 1).

A direct comparison of the stabilities of cryptand-2,2,2 and 18-aneN_2O_4 ignores the fact that the former ligand possesses eight donor atoms while the latter possesses six donors only. All or part of the increase in stability associated with the additional ring in cryptand-2,2,2 may be due to energy liberated on formation of two additional metal–O-donor bonds in cryptand-2,2,2. A more informative comparison could be made by comparing the stabilities of complexes of cryptand-2,2,2 with those of the

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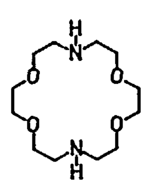
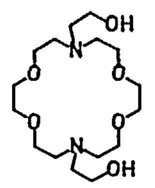
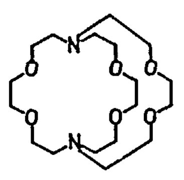
[†] Author for correspondence.



18-aneN$_2$O$_4$



BHE-18-aneN$_2$O$_4$



cryptand-2,2,2

	log $K_1^{(1)}$	log $K_1^{(2)}$	log $K_1^{(1)}$	log K (cryptate effect)
Ag^+	7·8	7·25	9·6	2·35
Pb^{2+}	6·8	9·2	12·0	2·8
Sr^{2+}	2·65	4·0[†]	8·0	4·0
Ba^{2+}	3·0	(5·3)[*]	9·5	4·2

[†] This work
[*] Estimated in Ref· 3

FIGURE 1 Thermodynamic stabilities of complexes of the metal ions Ag^+, Pb^{2+}, Sr^{2+}, and Ba^{2+} with the structurally related ligands 18-aneN$_2$O$_4$, BHE-18-aneN$_2$O$_4$ and cryptand-2,2,2.

ligand bis-(2-hydroxyethyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (BHE-18-aneN$_2$O$_4$) (Fig. 1). This pair of ligands possesses the same numbers of O- and N-donors. It can be seen that for all of the metal ions Ag^+, Pb^{2+}, Sr^{2+}, and Ba^{2+}, a significant increase in stability occurs on linking the two hydroxyethyl arms through an ethylene bridge. It seems appropriate to reserve the use of the term 'cryptate effect' for the stabilization accompanying ring formation as takes place in the transition from BHE-18-aneN$_2$O$_4$ to cryptand-2,2,2, rather than for the stabilization accompanying a process involving *both* introduction of new donor atoms *and* ring closure, as takes place in the transition from 18-aneN$_2$O$_4$ to cryptand-2,2,2. It has been suggested by Hancock and Martell[3] that the increase in stability that takes place in the transition from 18-aneN$_2$O$_4$ to BHE-18-aneN$_2$O$_4$ may be due to the greater Lewis basicity of the alcoholic oxygens of BHE-18-aneN$_2$O$_4$ as compared with the oxygen donors of the solvent (water). It was therefore predicted that the stabilization of BHE-18-aneN$_2$O$_4$ relative to 18-aneN$_2$O$_4$ should be an enthalpy effect. It was also further suggested that a considerable proportion of the increase in stability that takes place in the transition BHE-18-aneN$_2$O$_4$ to cryptand-2,2,2 may be due to the greater Lewis basicity of secondary (ethereal) oxygens on the diether bridge of the cryptand as compared with the primary (alcoholic) oxygens on the hydroxyethyl substituents of BHE-18-aneN$_2$O$_4$. This increase in Lewis basicity could be attributed to the positive inductive effect of the bridging ethylene group, which in other circumstances (for example in polyamine chelating ligands) has been shown to affect significantly the complexing ability of ligand donor atoms.[5] If so, then one might expect the stabilization of cryptand-2,2,2 complexes relative to those of BHE-18-aneN$_2$O$_4$ to be also predominantly an enthalpy effect. Since the process of ring closure, which is central to the cryptate effect, could in principle be associated with both energetic and entropic effects, the present study was undertaken in order to ascertain whether and to what extent the cryptate effect in the present molecular system could be viewed as a predominantly energetic effect, as hypothesized by Hancock and Martell.[3]

To this end, the ligand BHE-18-aneN_2O_4 was synthesized and the enthalpies of complex formation with the metal ions Ag^+, Pb^{2+}, Sr^{2+} and Ba^{2+} determined by direct calorimetry.

EXPERIMENTAL

Enthalpy changes for complex formation were determined by titration calorimetry. All volumetric glassware used in this study was "A" grade.

Materials

BDH ANALAR KNO_3 was used as background electrolyte. Stock solutions of the background electrolyte were prepared by mass. Metal nitrate stock solutions were prepared from ANALAR grade lead nitrate, and MERCK p.a. grade silver nitrate, barium nitrate and strontium nitrate, and standardized against EDTA (MERCK p.a.) as described in Vogel.[6]

The ligand 18-aneN_2O_4 was purchased as 'Kryptofix 22' (purity > 99%) from MERCK-Schuchardt and used without further purification.

The ligand BHE-18-aneN_2O_4 was synthesized using a method based on that described by Kulstad and Malmsten[4] involving the use of ethyleneoxide to produce 2-hydroxyethyl substitution of the secondary amine nitrogens on the starting material 18-aneN_2O_4. When a reaction mixture was stirred for 4 days it was found that polymerization of the side chains had occurred. Conditions were therefore modified to avoid multiple addition of ethylene oxide units to the side chains. Ethylene oxide (0.7 cm^3, 16 mmol) at 0°C was added to a solution of 18-aneN_2O_4 (1 g, 3.8 mmol) in ethanol (20 cm^3) on an ice bath. The mixture was left to stir (without refluxing) for 24 hours. The ethanol was evaporated *in vacuo* and the residue was dried under reduced pressure to yield the final product as an oil (1.74 g, 3.4 mmol), representing a yield of 89%. ^1H NMR (D_2O): δ 2.62; δ 2.75 (12 H adjacent to N); δ 3.65 (20 H adjacent to O). The chemical shifts and integrated peak intensities are in accord with the molecular structure of BHE-18-aneN_2O_4 ($C_{16}H_{34}N_4O_6$). The purity of the ligand was checked by calorimetric titration against standardized silver nitrate solution.

Calorimetric apparatus and procedure

Enthalpy changes were measured using a continuous titration calorimeter consisting of an LKB 8721-2 titration calorimeter assembly together with a home made electronic control and temperature monitoring unit. The construction and testing of this instrument has been described previously,[7] and the instrument has been changed only in minor respects.[8] A titrant solution, which in this instance was a solution containing the metal ion studied, was added at a known and constant rate to a titrate solution containing the ligand (all solutions being made up to the appropriate ionic strength using background electrolyte). The corresponding change in temperature was measured very precisely as a function of the volume of the titrant solution added. The way in which the data obtained was corrected for 'non-chemical' heat effects such as heat exchange with surroundings, heat generated by the stirrer, and by resistive heating of the thermistor used for detection and measurement of temperature change, the effect of initial temperature difference between the titrant and the titrate, as well as correction for heat of dilution effects, has been described,[8] and is based in part on a treatment given by Eatough *et al.*[9] A typical procedure for measurement of a heat of reaction would consist of a calorimetric titration involving addition of one reactant species to the other, as well as supporting measurements such as of the heat capacities of titrate and titrant, and a 'blank' experiment aimed at determining the heat of dilution of the titrant in the titrate. Owing to the scarcity of the ligand, the titrations were designed to consume as little of it as possible. A weighed amount of the ligand (normally approx. 0.2 g) was transferred quantitatively into the $100\,\mathrm{cm}^3$ calorimeter reaction vessel using measured amounts of background electrolyte solution as wash liquid.

All measurements were made at $I = 0.50\,\mathrm{mol\,dm^{-3}}$ and $T = 25°\mathrm{C}$.

Calibration of the calorimeter

Calibration of the calorimeter involves relating changes in the 'off-balance potential' of the Wheatstone Bridge containing the reaction vessel thermistor to the corresponding temperature changes in the reaction vessel, determination of the heat capacity of the hardware in contact with the solutions studied, testing of the accuracy of the titrant–delivery system and calibration of the electrical heater used for heat capacity determinations. The detailed procedure has been described elsewhere,[7,8] and will not be repeated here.

Calculations

Calorimetric data were corrected for non-chemical heat effects and enthalpy changes were calculated by use of the LETAGROP KALLE program.[10] The technique of titration calorimetry can be used to determine values of $\Delta H°$ for complex formation provided that the corresponding formation constants for the complexes are known. In favourable circumstances (such as when the value of log K for the reaction is below 4–5) the technique can be used to determine values of log K and $\Delta H°$ simultaneously,[9,11–13] since under those circumstances the shape of the enthalpogram obtained will depend on *both* of these quantities.

RESULTS

Results for the enthalpy changes for all metal–ligand systems studied experimentally are given in the following Table together with estimated confidence limits. Formation constant values (log K) for complex formation of 18-aneN_2O_4 with Ag^+(8.1) and Pb^{2+}(7.0) and of BHE-18-aneN_2O_4 with Pb^{2+}(9.2), and Ag^+(7.25), were obtained from the literature,[1,2] as was an estimate for Ba^{2+}(5.3).[3] Since these values of log K are all above 5, reactions with these metal ions proceed effectively to completion and the values of $\Delta H°$ quoted in Table I for these metal ions are fairly independent of uncertainties in the values of these formation constants. Since no value was available from the literature for Sr^{2+}, an attempt was made to determine log K and $\Delta H°$ simultaneously from titration calorimetric data. A value of log $K = 4.0 \pm 0.5$ was obtained for this metal ion. This value should however be treated with some caution since it is 'borderline' to the region in which formation constants and enthalpy changes can be successfully determined simultaneously by titration calorimetry.

TABLE I
Experimentally determined enthalpy changes for complex formation for metal ions with 18-aneN_2O_4 and BHE-18-aneN_2O_4.

Ligand	Metal ion	$\Delta H°(\pm\sigma)$/kJ mol^{-1}
18-aneN_2O_4	Ag^+	-39 ± 1
18-aneN_2O_4	Pb^{2+}	-28 ± 1
BHE-18-aneN_2O_4	Ag^+	-36 ± 1
BHE-18-aneN_2O_4	Pb^{2+}	-34 ± 2
BHE-18-aneN_2O_4	Sr^{2+}	-10 ± 1
BHE-18-aneN_2O_4	Ba^{2+}	-18 ± 2

Allowance was made for any (probably minor) hydrolysis effects involving the formation of soluble metal-hydroxy species (in the instances of Pb^{2+}, Ba^{2+}, and Sr^{2+}) and ligand protonation (for the ligands 18-aneN_2O_4 and BHE-18-aneN_2O_4) during the course of the calorimetric titrations by incorporation of the appropriate values of log K and ΔH for such side reactions in the calculation of the desired heats of reaction.

DISCUSSION

Formation constants (log K) and thermodynamic properties ($\Delta G°$, $\Delta H°$, and $-T\Delta S°$) for complex formation of the metal ions Ag^+, Pb^{2+}, Sr^{2+}, and Ba^{2+} with the ligands 18-aneN_2O_4 and BHE-18-aneN_2O_4 are presented in Table II. This Table also contains calculated values of the following quantities.

$$\Delta \log K = \log K(\text{BHE-18-ane}N_2O_4) - \log K(\text{18-ane}N_2O_4)$$

$$\Delta(\Delta G°) = \Delta G°(\text{BHE-18-ane}N_2O_4) - \Delta G°(\text{18-ane}N_2O_4)$$

$$\Delta(\Delta H°) = \Delta H°(\text{BHE-18-ane}N_2O_4) - \Delta H°(\text{18-ane}N_2O_4)$$

$$\Delta(-T\Delta S°) = [-T\Delta S°(\text{BHE-18-ane}N_2O_4)] - [-T\Delta S°(\text{18-ane}N_2O_4)]$$

The quantities Δ log K, $\Delta(\Delta G°)$, $\Delta(\Delta H°)$, and $\Delta(-T\Delta S°)$ represent thermodynamic properties relating to the ligand replacement reaction, (*1*),

$$[M(\text{18-ane}N_2O_4)]^{n+} + \text{BHE-18-ane}N_2O_4) = [M(\text{BHE-18-ane}N_2O_4)]^{n+} + \text{18-ane}N_2O_4 \quad (1)$$

for the various metal ions M.

From the above results it is apparent that stabilization of BHE-18-aneN_2O_4 relative to 18-aneN_2O_4 is not, in general, primarily an enthalpy effect, as predicted by Hancock and Martell.[3] For the metal ions Pb^{2+}, Sr^{2+}, and Ba^{2+} the ligand replacement reaction (*1*) is in fact predominantly entropy driven. It would appear that solvation effects are important here. The free ligand BHE-18-aneN_2O_4 contains two pendant hydroxyethyl groups per molecule and is probably more extensively solvated in aqueous solution than the free ligand 18-aneN_2O_4, which has no hydrogen bonding alcohol groups. Thus the ligand replacement reaction (*1*) would lead to a net release of water molecules of solvation, a feature which would contribute to a negative value of $\Delta(-T\Delta S^\circ)$ for the ligand replacement reaction. Release of water molecules of solvation would require an input of energy, leading to a less exothermic than expected ligand replacement reaction. A plot of values of $\Delta(\Delta H^\circ)$ *vs* $\Delta(\Delta G^\circ)$ (see Figure 2) indicates that the enthalpy changes for the ligand replacement reactions for the metal ions Pb^{2+}, Ba^{2+}, and Sr^{2+} vary more or less linearly with the corresponding Gibbs function changes, with a gradient of unity, as would be expected if the values of $\Delta(-T\Delta S^\circ)$ were independent of the metal ion. Indeed inspection of Table I shows that the value of $\Delta(-T\Delta S^\circ)$ is approximately constant for these three metal ions, having a value of about -4 kJ mol^{-1} per hydroxyethyl group. The fact that the Ag^+ ion deviates from the behaviour of the other metal ions studied, and lies almost exactly where expected on the basis of no entropy contribution, suggests that in the instance of Ag^+ the hydroxyethyl groups on the ligand BHE-18-aneN_2O_4 are *not coordinated.* This would be completely in accord with the well known tendency of Ag^+ to coordinate linearly to two donors. Indeed, comparison of the values logK(BHE-18-aneN_2O_4) = 7.25 and logK(18-aneN_2O_4) = 7.8 for the metal ion Ag^+ shows that addition of hydroxyethyl groups to the basic macrocycle leads to a decrease and not an increase in complex stability. The observed decrease in stability could be attributed to steric effects, *i.e.*, the hydroxyethyl groups are behaving like non-coordinating ethyl groups in this instance. The observation that the data for the metal ions Pb^{2+}, Ba^{2+} and Sr^{2+} fall on a line that is parallel to the one that would be expected on the basis of $\Delta(\Delta H^\circ) = \Delta(\Delta G^\circ)$ indicates that, but for a constant metal ion-independent contribution from desolvation, increases in stability of complexes of BHE-18-aneN_2O_4 relative to those of 18-aneN_2O_4 can be accounted for in terms of energetic effects.

TABLE II

Thermodynamic quantities for complex formation for various metal ions with BHE-18-aneN_2O_4 and 18-aneN_2O_4, together with corresponding values for the ligand replacement reaction (*1*). Values of ΔH°(BHE-18-aneN_2O_4) are from this work; other values were obtained from the literature.[1] Values of ΔG°, ΔH°, and $-T\Delta S^\circ$ in this table are given in units of kJ mol^{-1}.

Metal ion Ionic radius/Å	Ag^+ 1.15	Pb^{2+} 1.18	Sr^{2+} 1.17	Ba^{2+} 1.36
log K(BHE-18-aneN_2O_4)	7.25	9.2	4.0	5.3
log K(18-aneN_2O_4)	7.8	6.8	2.6	2.97
Δ log K	−0.55	2.4	1.4	2.3
ΔG°(BHE-18-aneN_2O_4)	−41.4	−52.5	−22.8	−30.3
ΔG°(18-aneN_2O_4)	−44.5	−38.8	−14.8	−17.0
$\Delta(\Delta G^\circ)$	+3.1	−13.7	−8.0	−13.1
ΔH°(BHE-18-aneN_2O_4)	−36.	−34.	−10.	−18.
ΔH°(18-aneN_2O_4)	−38.5	−28.	−10.9	−12.6
$\Delta(\Delta H^\circ)$	+3.	−6.	+1.	−5.
$-T\Delta S^\circ$(BHE-18-aneN_2O_4)	−5.	−18.	−12.	−13.
$-T\Delta S^\circ$(18-aneN_2O_4)	−6.0	−11.	−4.2	−4.5
$\Delta(-T\Delta S^\circ)$	+1.	−7.	−8.	−9.

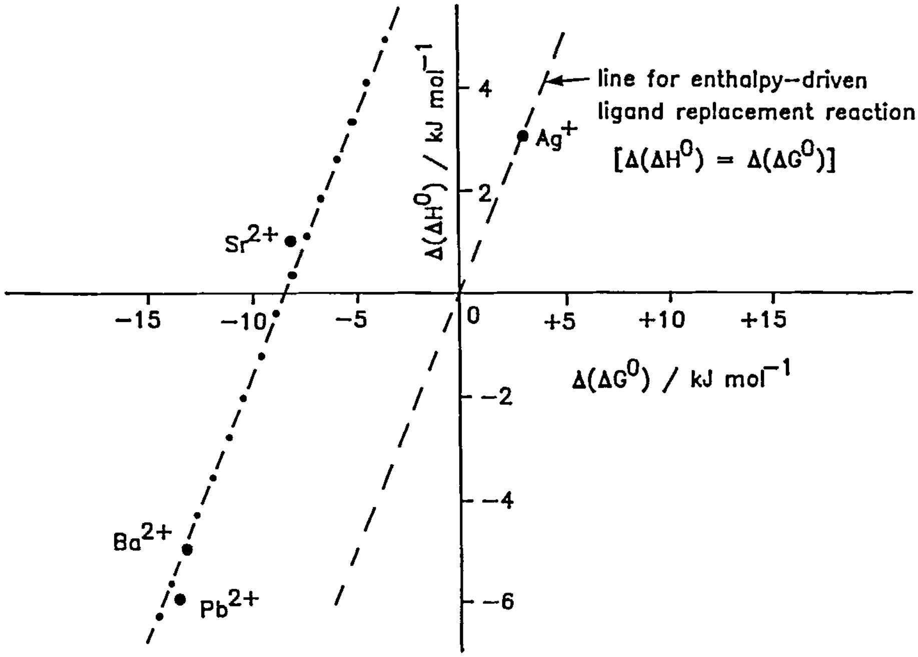


FIGURE 2 Plot of the enthalpy change (denoted $\Delta(\Delta H^\circ)$) for the ligand replacement reaction $[M(18\text{-aneN}_2O_4)]^{n+} + \text{BHE-18-aneN}_2O_4 = [M(\text{BHE-18-aneN}_2O_4)]^{n+} + 18\text{-aneN}_2O_4$ against the corresponding change in Gibbs function (denoted $\Delta(\Delta G^\circ)$).

TABLE III

Thermodynamic quantities for complex formation for various metal ions with BHE-18-aneN$_2$O$_4$ and cryptand-2,2,2, together with corresponding values for the ligand replacement reaction (*2*). Values of ΔH°(BHE-18-aneN$_2$O$_4$) are from this work; other values were obtained from the literature.[1] Values of ΔG°, ΔH°, and $-T\Delta S^\circ$ in this table are given in units of kJ mol^{-1}.

Metal ion Ionic radius/Å	Ag^+ 1.15	Pb^{2+} 1.18	Sr^{2+} 1.17	Ba^{2+} 1.36
log K(cryptand-2,2,2)	9.6	12.0	8.0	9.5
log K(BHE-18-aneN$_2$O$_4$)	7.25	9.2	4.0	5.3
log K(cryptate effect)	2.4	2.8	4.0	4.2
ΔG°(cryptand-2,2,2)	−54.8	−68.5	−45.7	−54.2
ΔG°(BHE-18-aneN$_2$O$_4$)	−41.4	−52.5	−22.8	−30.3
ΔG°(cryptate effect)	−13.4	−16.0	−22.9	−23.9
ΔH°(cryptand-2,2,2)	−53.6	−57.	−44.4	−59.5
ΔH°(BHE-18-aneN$_2$O$_4$)	−36.	−34.	−10.	−18.
ΔH°(cryptate effect)	−17.	−23.	−34.	−42.
$-T\Delta S^\circ$(cryptand-2,2,2)	1.2	−11.5	−1.3	5.2
$-T\Delta S^\circ$(BHE-18-aneN$_2$O$_4$)	−5.0	−18.	−12.	−13.
$-T\Delta S^\circ$(cryptate effect)	3.8	7.	11.	18.

Formation constants (log K) and thermodynamic properties (ΔG°, ΔH°, and −TΔS°) for complex formation of the metal ions Ag^+, Pb^{2+}, Sr^{2+}, and Ba^{2+} with the ligands cryptand-2,2,2 and BHE-18-aneN_2O_4 are presented in Table III. This Table also contains calculated values for the following.

$$\log K(\text{cryptate effect}) = \log K(\text{cryptand-2,2,2}) - \log K(\text{BHE-18-aneN}_2\text{O}_4)$$
$$\Delta G^\circ(\text{cryptate effect}) = \Delta G^\circ(\text{cryptand-2,2,2}) - \Delta G^\circ(\text{BHE-18-aneN}_2\text{O}_4)$$
$$\Delta H^\circ(\text{cryptate effect}) = \Delta H^\circ(\text{cryptand-2,2,2}) - \Delta H^\circ(\text{BHE-18-aneN}_2\text{O}_4)$$
$$-T\Delta S^\circ(\text{cryptate effect}) = -T\Delta S^\circ(\text{cryptand-2,2,2}) - [-T\Delta S^\circ(\text{BHE-18-aneN}_2\text{O}_4)]$$

The quantities log K(cryptate effect), ΔG°(cryptate effect), ΔH°(cryptate effect), and −TΔS°(cryptate effect) represent thermodynamic properties relating to the ligand replacement reaction, (*2*),

$$[\text{M(BHE-18-aneN}_2\text{O}_4)]^{n+} + \text{cryptand-2,2,2} = [\text{M(cryptand-2,2,2)}]^{n+} + \text{BHE-18-aneN}_2\text{O}_4 \qquad (2)$$

for the various metal ions M, and can be thought of as thermodynamic properties characteristic of the 'cryptate effect' in the systems studied.

It is apparent from the results of Table III that, for all the metal ions studied, the ligand replacement reaction (*2*) is enthalpy driven, with the entropy term making a small but significantly unfavourable contribution. The effect of joining the two pendant hydroxyethyl oxygen donors with an ethylene bridge is to produce more stable complexes. This increase in stability is seen to be predominantly an energetic effect, with a smaller but nevertheless significant destabilizing contribution from entropic terms.

It seems likely that the positive inductive effect of the ethylene bridge would increase electron density on the ether oxygen atom, thereby making it a better donor atom than the oxygen of a terminal hydroxy group. This could account for additional energy liberated on complex formation by the cryptand. The difference amounts to some 11.5 kJ mol^{-1} per donor for Pb^{2+}, 17 kJ mol^{-1} per donor for Sr^{2+}, and 21 *kJ* mol^{-1} per oxygen donor for Ba^{2+}. The position relating to the Ag^+ ion is complicated by the probability that coordination about the Ag^+ ion in the complex [Ag(BHE-18-aneN_2O_4)]$^+$ is likely to differ materially from the coordination geometry in the complex [Ag(cryptand-2,2,2)]$^+$, with attendant energetic effects. With regard to the metal ions Pb^{2+}, Sr^{2+} and Ba^{2+}, it is entirely feasible that the internal steric strain energy of a [M(cryptand-2,2,2)]$^{n+}$ complex may be larger than the steric strain energy of a [M(BHE-18-aneN_2O_4)]$^{n+}$ complex for some or all of the metal ions M. Accordingly, the values given above for the energetic preferences of the metal ions studied for ethereal over alcoholic O-donors may significantly underestimate the preferences for ethereal over alcoholic O-donors *in the absence* of steric strain effects.

The unfavourable entropy contribution to the ligand replacement reactions (*2*) in these systems may, once again, be due to better solvation of the free ligand BHE-18-aneN_2O_4 with pendant hydroxyethyl groups than the free ligand cryptand-2,2,2 with a polyether bridge. This in turn would be expected to contribute to the release of energy during the ligand replacement reaction. Thus, solvation effects, particularly those involving the free ligands, may also contribute to the observed energy changes and make a contribution towards the apparent preference of the metal ions studied towards ethereal over alcoholic oxygen donors.

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