0.1 M with KNO_3. Solutions of picolinanilides (6×10^{-4} M) were prepared in absolute ethanol and were used fresh. The 1:1 Cu(II)–bpy complex was prepared by dissolving equimolar quantities of $Cu(NO_3)_2$ and bipyridine and 2.5 equiv H_2O in absolute ethanol, followed by evaporation to give a blue solid, and aqueous solutions of this solid (2×10^{-4} to 1×10^{-3} M) were employed in the metal ion catalyzed hydrolyses. The apparent pH values of the reaction mixtures were obtained at 40.0 °C by using a Fisher Accumet Model 810 meter and were corrected to the operational pH values by subtracting 0.06, the appropriate value of δ for 28% (by weight) aqueous ethanol at 298 °C (the required additional correction for 313 °C vs 298 °C would be in the third decimal, beyond the accuracy of our pH measurements).[20]

Hydrolysis reactions were carried out in 1-cm quartz cells kept at constant temperature (40.0 °C) by using a Perkin-Elmer Lambda 3B UV-vis spectrophotometer (with PECSS software) equipped with a temperature-controlled six-cell changer. The progress of reaction was monitored by following the increase in absorbance of the product anilines at their characteristic band maxima: 400 nm for (4-nitrophenyl)- and (2,4-dinitrophenyl)-*N*-methylaniline and 430 nm for (5-chloro-2-nitrophenyl)-*N*-methylaniline. In a typical reaction, 1 mL of the appropriate picolinanilide ethanolic solution was added to 2 mL of the buffer solution (with or without metal ion) maintained at 40 °C. The products and extent of hydrolysis were confirmed by TLC. For the faster reactions, first-order linearity was confirmed to at least 4 half-lives. The final spectrum in these cases exactly matched that of an equimolar mixture of picolinic acid and the appropriate substituted *N*-methylaniline (with the proper amount of Cu(II) catalyst added). For the very slow reactions, k_{obsd} was determined from the initial rate (in some cases only 1–2% reaction) by using the equation $\ln (A_\infty - A_0)/(A_\infty - A_t) = kt$. Calculation of k_{OH} values from the pH–rate data was performed by using $\log K_w = -14.04$, estimated by interpolation of $\log K_w$ values for various ethanol–water mixtures reported by Gutbezahl and Grunwald at 25.0 °C,[21] with correction, as done by these workers, to 40.0 °C using the same temperature coefficient measured in water.[22]

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Registry No. bpy, 366-18-7; $Cu(NO_3)_2$, 3251-23-8; picolinyl chloride, 29745-44-6; 4-nitro-*N*-methylaniline, 100-15-2; 5-chloro-2-nitro-*N*-methylaniline, 35966-84-8; 2,4-dinitro-*N*-methylaniline, 2044-88-4; *N*-methyl-*N*-(4-nitrophenyl)picolinamide, 134847-69-1; *N*-(2,4-dinitrophenyl)-*N*-methylpicolinamide, 134847-70-4; *N*-(5-chloro-2-nitrophenyl)-*N*-methylpicolinamide, 134847-71-5.

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Effect of Cyclohexylene Bridges on the Metal Ion Size Based Selectivity of Ligands in Aqueous Solution

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The effect on thermodynamic complex stability of use of the cyclohexylene bridge in place of ethylene bridges in various types of ligands is investigated. The synthesis of THEDACH [*N,N,N',N'*-tetrakis(2-hydroxyethyl)-*trans*-1,2-diaminocyclohexane] is reported, along with that of 7,16-bis(*trans*-2-hydroxycyclohexyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (Cy_2-K22). The formation constants of these ligands, as well as of BHEAC [*trans*-1-(bis(2-hydroxyethyl)amino)-2-hydroxycyclohexane], for complex formation with some or all of the metal ions Cu(II), Zn(II), Cd(II), Pb(II), Ca(II), Sr(II), Ba(II), La(III), Th(IV), and Ag(I) are reported, determined by glass electrode potentiometry in 0.1 M $NaNO_3$ at 25 °C. The results indicate that the presence of a cyclohexylene bridge leads to complex stabilization relative to the analogues with ethylene bridges, which appears to be dependent on the size of the metal ion. The complexes of small metal ions are stabilized by the cyclohexylene bridge, whereas those of larger metal ions tend to be destabilized.

Replacement of the ethylene bridge connecting the two nitrogen donors of EDTA (Figure 1) with a cyclohexylene bridge leads to substantial increases in complex stability,[1] as measured by the formation constants, $\log K_1$, of the complexes formed for *trans*-CDTA (Figure 1; see also Chart I). This is an example[2] of "preorganisation",[3] in which it is thought[2] that the rigid cyclohexane ring of *trans*-CDTA holds its two nitrogens in the trans arrangement required for coordination to metal ions. In EDTA, by contrast, the low-energy form of the free ligand is thought to be the skew, and considerable energy must be expanded in transforming it to the trans form required for complex formation. It seemed that introduction of cyclohexylene groups as bridging groups in other chelating ligands would produce ligands of greatly increased complexing ability, and it was surprising that more ligands using the cyclohexylene bridge had not been synthesized.

The ligand THEEN (Figure 1) has an enhanced affinity for large metal ions relative to what is observed for EN, brought about by the presence of the 2-hydroxyethyl groups.[4] It was thought that by analogy with the case of CDTA, using *trans*-1,2-diaminocyclohexane rather than EN as the diamine to which 2-hydroxyethyl groups would be added would give THEDACH, a much more powerfully coordinating ligand than THEEN. As a further exploration of this idea, the ligand Cy_2-K22 was studied (Figure 1). This ligand has cyclohexylene groups bridging the nitrogen donors of the macrocyclic ring and the pendant alcoholic oxygen donors. This might give interesting effects on complex stability as compared with the case of BHE-K22, which has simple ethylene bridges linking the donor atoms of the pendant "arms" to the nitrogens of the macrocyclic ring.

It is found[1] that a cis conformation of the amines on the cyclohexylene group, as in *cis*-CDTA, leads to incorrect orientation of the nitrogen donor atoms for coordination to metal ions, and *cis*-CDTA shows little increase in complex stability as compared with EDTA. It is thus important that the hydroxyl group be trans to the nitrogen donors in Cy_2-K22. The method of synthesis employed here was the same as for many other nitrogen donor macrocycles with hydroxyalkyl pendant donor groups, namely

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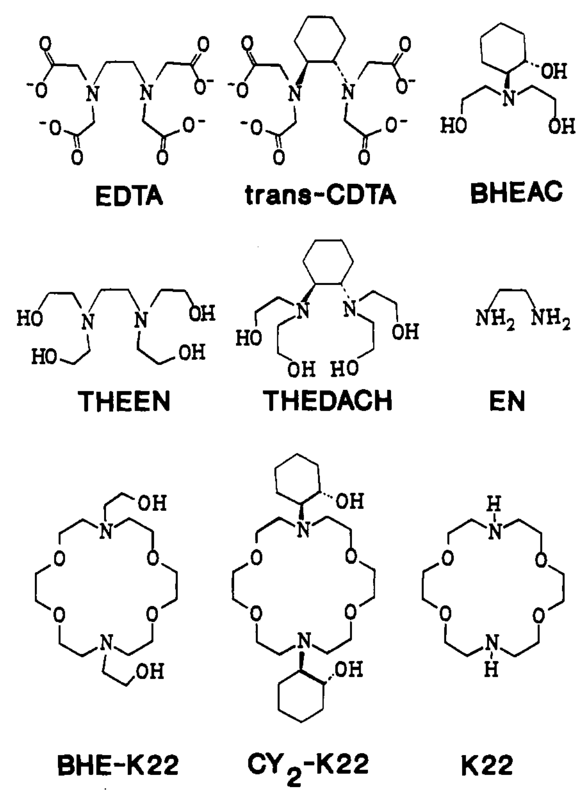
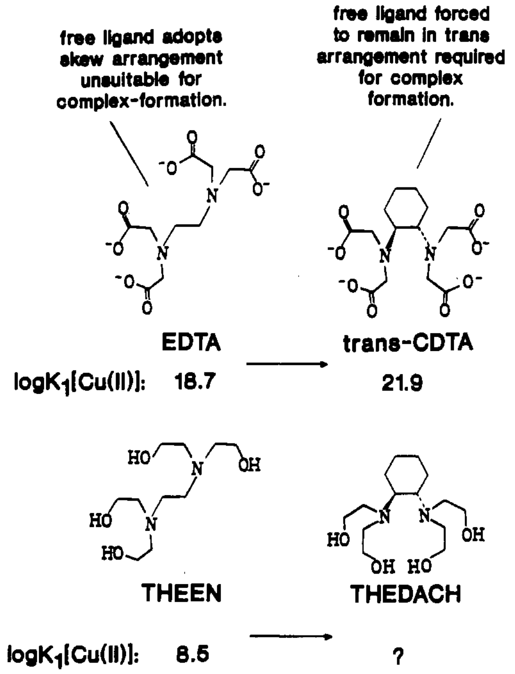


Figure 1. Ligands discussed in this work.

Chart I



reaction of the parent macrocycle with the epoxide.[5] In this case, the epoxide is cyclohexene oxide, and the mechanism of opening[6] of the epoxide ring on this molecule should certainly lead to a trans arrangement of the two substituents on the cyclohexyl group. In this paper are therefore described the synthesis of the ligand Cy_2-K22 and a potentiometric study of its constants of complex formation with Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, La^{3+}, and Ag^+. The results obtained were somewhat surprising in terms of the idea[7] that selectivity for large metal ions relative to small metal ions was increased when pendant groups containing neutral oxygen donor ligands were added to a ligand. In order to see whether the unusual pattern of selectivity for metal ions in relation to their size was dependent on the presence of the macrocyclic ring, the simple ligand BHEAC (Figure 1) was synthesized, which contains only a single 2-hydroxycyclohexyl group, a single nitrogen donor, and two pendant 2-hydroxyethyl groups, and the constants of complex formation of this ligand with the above selection of metal ions were determined.

Experimental Section

Ligand Syntheses. 7,16-Bis(*trans*-2-hydroxycyclohexyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (Cy_2-K22). The parent macrocycle K22 (Merck, 1.5 g, 5.76 mmol) was dissolved in ethanol (20 mL), and cyclohexene oxide (Aldrich, 3.5 mL, 35 mmol) was added. The mixture was refluxed at 110 °C for 2 weeks. The solvent was removed under vacuum, the resulting yellow solid was dissolved in a minimum of dry *n*-hexane, and the solution was allowed to stand for 2 days. Colorless crystals formed; mp 82–84 °C. Titration with acid indicated the material to be 99.5% pure Cy_2-K22. NMR ($CDCl_3$, ppm from TMS): 1.10–1.28 (m, 8 H), 1.68–1.86 (m, 6 H), 2.07–2.30 (m, 4 H), 2.61–2.90 (m, 8 H), 3.48–3.61 (m, 18 H), 4.21 (s, 2 H). Anal. Calcd for $C_{24}H_{46}N_2O_6$: C, 62.84; H, 10.13; N, 6.11. Found: C, 62.86, H, 10.51, N, 6.23.

***N,N,N',N'*-Tetrakis(2-hydroxyethyl)-*trans*-1,2-diaminocyclohexane (THEDACH).** A 2.8-g (0.025-mol) sample of *trans*-1,2-diaminocyclohexane (Aldrich 99%) was dissolved in 50 mL of absolute ethanol. This solution was stirred on an ice bath for 20 min. Ethylene oxide (4.6 g, 0.1 mol) was added dropwise. The flask was stoppered and stirring continued for 4 days. After removal of the solvent on a rotary evaporator, the ligand was dried under reduced pressure (1 mmHg), after which it solidified to a waxy solid. Anal. Calcd for $C_{14}H_{30}N_2O_4$: C, 57.90; H, 10.41; N, 9.65. Found: C, 57.87; H, 10.67; N, 9.81.

The ligand BHEAC was synthesized according to the method of Ponomarev and Sablina,[8] where diethanolamine is reacted with cyclohexene oxide. Standardization with acid showed the ligand to be better than 99% pure.

Potentiometry. Potentials were recorded on a Radiometer PHM 84 pH meter using a Radiometer G202B glass electrode and a jacketed cell thermostated to 25.0 ± 0.1 °C. The glass electrode was standardized from calculated acid concentrations in titrations covering the pH range from 2 to 12. Stock solutions of the ligands were prepared and standarized by titration with acid, and stock solutions of the metal ions were standarized by usual procedures. Three titrations were carried out for each metal ion, with ligand to metal ratios varying from 1:1 to 2.5:1, and the protonation constants of the ligands were also determined in triplicate. Metal ion concentrations were in the range 10^{-3}–10^{-2} M. Formation constants were calculated from the potentiometric data by using the programs MINIQUAD[9a] and ESTA.[9b]

Results and Discussion

The formation constants for THEDACH, Cy_2K-22, and BHEAC are shown in Table I. In Table II are shown a selection of formation constants for THEDACH and those for THEEN and EN for comparsion.[10] Also shown in Table II are formation constants for the corresponding EDTA and *trans*-CDTA complexes. It is apparent that the increases in log K_1 are larger in going from EDTA to *trans*-CDTA than in going from THEEN to THEDACH. This suggests that part of the effect of the

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Table I. Constants for Complex Formation of the Ligands THEDACH, Cy_2-K22, and BHEAC with a Selection of Metal Ions[a]

metal ion	equilibrium[b]	log *K*
	L = THEDACH	
	$H + L \rightleftharpoons HL$	10.06 (1)
	$HL + H \rightleftharpoons H_2L$	1.55 (1)
Cu(II)	$M + L \rightleftharpoons ML$	9.52 (1)
	$ML + OH \rightleftharpoons MLOH$	7.43 (1)
	$MLOH + OH \rightleftharpoons MLOH_2$	5.10 (2)
Zn(II)	$M + L \rightleftharpoons ML$	5.95 (1)
	$ML + OH \rightleftharpoons MLOH$	5.40 (1)
	$MLOH + OH \rightleftharpoons MLOH_2$	5.11 (1)
	$MLOH_2 + OH \rightleftharpoons MLOH_3$	2.96 (3)
Cd(II)	$M + L \rightleftharpoons ML$	7.61 (1)
	$ML + L \rightleftharpoons ML_2$	2.68 (7)
	$ML + OH \rightleftharpoons MLOH$	3.25 (1)
	$3M + 2L \rightleftharpoons M_3L_2$	22.06 (2)
Pb(II)	$M + L \rightleftharpoons ML$	6.49 (1)
	$ML + OH \rightleftharpoons MLOH$	5.55 (1)
Th(IV)	$M + L + OH \rightleftharpoons MLOH$	19.36 (2)
	$MLOH + OH \rightleftharpoons MLOH_2$	9.46 (1)
	L = Cy_2-K22[c]	
	$H + L \rightleftharpoons HL$	8.88 (1)
	$H + HL \rightleftharpoons H_2L$	8.04 (1)
Cu(II)	$M + L \rightleftharpoons ML$	7.63 (2)
	$ML + OH \rightleftharpoons MLOH$	7.24 (2)
Zn(II)	$M + L \rightleftharpoons ML$	4.77 (2)
Cd(II)	$M + L \rightleftharpoons ML$	8.64 (2)
	$ML + OH \rightleftharpoons MLOH$	5.29 (7)
Ca(II)	$M + L \rightleftharpoons ML$	4.72 (1)
Sr(II)	$M + L \rightleftharpoons ML$	4.13 (2)
Ba(II)	$M + L \rightleftharpoons ML$	4.59 (1)
Pb(II)	$M + L \rightleftharpoons ML$	8.59 (1)
	$ML + OH \rightleftharpoons MLOH$	5.20 (3)
La(III)	$M + L \rightleftharpoons ML$	4.08 (8)
	$ML + OH \rightleftharpoons MLOH$	5.97 (2)
Ag(I)	$M + L \rightleftharpoons ML$	5.20 (1)
	L = BHEAC[c]	
	$L + H \rightleftharpoons LH$	8.48 (1)
Cu(II)	$M + L \rightleftharpoons ML$	4.99 (3)
	$ML + OH \rightleftharpoons MLOH$	8.23 (1)
Ni(II)	$M + L \rightleftharpoons ML$	3.60 (1)
	$ML + OH \rightleftharpoons MLOH$	5.06 (2)
Zn(II)	$M + L \rightleftharpoons ML$	2.78 (5)
Cd(II)	$M + L \rightleftharpoons ML$	3.23 (3)
Pb(II)	$M + L \rightleftharpoons ML$	3.72 (1)
	$M + 2L \rightleftharpoons ML_2$	6.87 (1)
Ag(I)	$M + L \rightleftharpoons ML$	2.09 (1)

[a] In 0.1 M $NaNO_3$ at 25 °C. [b] For simplicity, charges have been omitted. H is the proton, M is the metal ion indicated, OH is hydroxide ion, and L is the ligand indicated. [c] For key to ligand abbreviations, see Figure 1.

Table II. Formation Constants for THEDACH, with Literature Values for THEEN, EN, EDTA, and *trans*-CDTA for Comparison[a]

Lewis acid	ionic radius[c]	log *K*[b]				
		THEDACH	THEEN	EN	EDTA	*trans*-CDTA
H^+		10.06	8.38	9.89	10.17	12.3[d]
		1.55	4.37	7.08	6.11	6.12
Zn(II)	0.74	5.95	4.74	5.7	16.44	19.35
Cu(II)	0.75	9.52	8.49	10.54	18.70	21.92
Cd(II)	0.95	7.61	7.04	5.45	16.36	19.84
Pb(II)	1.18	6.49	7.6[e]	5.04	17.88	20.24

[a] For ligand abbreviations, see Figure 1. Literature formation constants were taken from ref 10. [b] log *K* refers for metal ions to the equilibrium $M + L \rightleftharpoons ML$ and for the proton to $H + L \rightleftharpoons HL$ (first value) and $HL + H \rightleftharpoons HL_2$ (second value). [c] Ionic radii for octahedral coordination in angstroms were taken from ref 13. [d] This higher protonation constant is observed with K^+ or tetramethylammonium salts as background electrolyte but is only 9.9 with the complexing Na^+ ion. [e] For similar *N,N,N′,N′*-tetrakis(2-hydroxypropyl)ethylenediamine.

Table III. Formation Constants (log K_1) of K22 and Its Derivatives Having Pendant Oxygen Donor Groups with a Simple Ethylene Bridge (BHE-K22) and a *trans*-Cyclohexyl Group (Cy_2-K22)[a]

Lewis acid	ionic radius[b]	log K_1		
		K22	BHE-K22	Cy_2K22
H^+		9.08	8.70	8.88
		7.94	7.47	8.04
Zn(II)	0.74	3.1	(3.0)[c]	4.77
Cu(II)	0.75	6.1	6.60	7.63
Cd(II)	0.95	5.28	7.96	8.64
Ca(II)	1.00	1.74	4.08	4.72
La(III)	1.03		(3.24)[c]	4.08
Sr(II)	1.17	2.65	(4.05)[c]	4.13
Pb(II)	1.18	6.8	9.20	8.59
Ba(II)	1.36	2.97	5.3	4.59

[a] For key to ligand abbreviations, see Figure 1. [b] Octahedral ionic radii in angstroms were taken from ref 13. [c] For the very similar 2-hydroxypropyl analogue from ref 19.

cyclohexane ring is related to the presence of charged acetate groups on EDTA, which stabilize the skew relative to the trans conformer by electrostatic repulsion. This electrostatic contribution to stabilizing the skew conformer is overcome in *trans*-CDTA because the cyclohexylene bridge holds the ligand in the trans conformation. In THEEN and THEDACH the overall effect on complex stability of stabilizing the trans conformer in THEDACH is lessened because the 2-hydroxyethyl groups do not repel each other electrostatically.

The ligand THEDACH shows (Table II) an increase in protonation constant relative to THEEN, paralleling the increase observed for *trans*-CDTA relative to EDTA. This is presumably due to a mild "proton sponge" effect with the two nitrogens on THEDACH or *trans*-CDTA being held close to each other in a position suitable for cooperative hydrogen bonding. Subsequent protonation constants for cyclohexylene-bridged ligands are lower than for ethylene-bridged analogues, indicating that the cooperative hydrogen bonding must be broken for a second proton to be added to the nitrogen donors. The formation constants reported in Table I for THEDACH were measured in $NaNO_3$. To see whether the ligand was binding to the Na^+ present, the protonation constants were redetermined in 0.1 M tetramethylammonium nitrate but were found to be essentially unchanged from those obtained in 0.1 M $NaNO_3$, indicating little affinity of THEDACH for the Na^+ ion. In hindsight, this is to be expected from the large size of the Na^+ ion and the lower affinity of cyclohexylene-bridged ligands for larger metal ions discussed below. An interesting indication of the high level of preorganization of THEDACH is that its rate of complex formation with the Ni(II) ion is quite slow and required an out-of-cell technique for measuring the formation constant, which will be reported in a future paper. Slow rates of metalation and demetalation are found for *trans*-CDTA and other highly preorganized ligands and are characteristic of high levels of preorganization in ligands.[16]

In Table I is reported the formation constant of THEDACH with Th(IV). Only deprotonated $MLOH_n$ species were observed. This is typical behavior for the perhydroxyalkylated polyamines, which we are currently studying. These ligands are capable of stabilizing metal ions such as Fe(III) or Pu(IV) in solution up to pH values as high as 13, even forming stable ML complexes at low pH. This indicates interesting complexing properties for these ligands, with metal ions such as In(III), Ga(III), Th(IV), or Bi(III), which are not normally considered to have much affinity for neutral saturated nitrogen donor ligands. Present evidence indicates that these ligands complex virtually all metal ions of higher valence in the periodic table.

In Table III is shown a selection of formation constants for Cy_2K-22, as well as literature[10-12] values for BHE-K22 and K22, for purposes of comparison. The metal ions are arranged in Tables II and III in order of increasing metal ion radius.[13] In their studies of the complexing properties of *trans*-CDTA, Schwarzenbach et al.[1] observed that the effect of the cyclohexylene bridge on stability of *trans*-CDTA relative to EDTA complexes appeared to be dependent on the size of the metal ion. It appears that the increase

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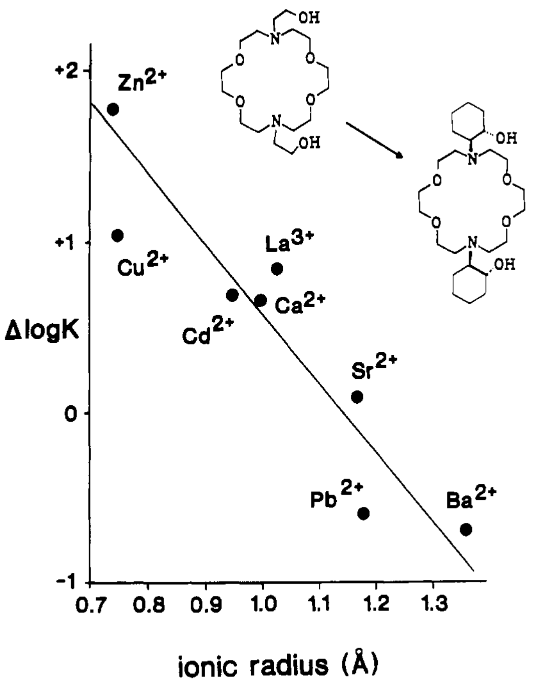

Figure 2. Effect on thermodynamic complex stability of changing the ethylene bridges of the pendant groups of BHE-K22 to cyclohexylene bridges in Cy_2-K22. (See Figure 1 for key to ligand abbreviations.) The change in log K_1, Δ log K, is log K_1 for Cy_2-K22 minus log K_1 for BHE-K22 for each metal ion, plotted as a function of its octahedral ionic radius.[13]

in formation constant in passing from THEEN to THEDACH, or BHE-K22 to Cy_2K-22, is related to size in a similar manner, with the smallest metal ions showing the strongest increase in log K_1 in changing the bridging ethylene groups to cyclohexylene bridges. This is a surprising result in terms of the view[14-16] that a five-membered chelate ring should promote complex stability for large metal ions relative to small metal ions. In this view, the geometry of the five-membered ring is such that in the minimum-strain arrangement the lone pairs on the donor atoms focus on a point some distance away, so that only large metal ions can coordinate with a minimum of steric strain. Increasing the rigidity of the five-membered chelate ring by fusing a cyclohexane group to the bridge of the chelate ring should thus serve only to sharpen this effect. In ethylenediamine complexes smaller metal ions are accomodated[17] by decrease of the N–C–C–N torsion angle from the minimum-strain value of 60°, which now becomes more difficult with fusion to the rigid cyclohexylene group in ligands such as THEDACH, *trans*-CDTA, or Cy_2-K22.

In Figure 2 is shown the relationship between Δ log K and the octahedral ionic radius[13] of the metal ions for Cy_2-K22 relative to BHE-K22. The Δ log K value is simply log K_1 for the Cy_2-K22 complex of each metal ion minus log K_1 for the corresponding BHE-K22 complex. Figure 2 shows a fairly strong inverse relationship between metal ion size and the effect on log K_1 of introducing a cyclohexylene bridge to the chelate ring. Figure 3 shows a similar relationship of Δ log K for *trans*-CDTA and EDTA. The points for Be^{2+} and Al^{3+} lie well off the relationship found. It is possible that for these very small metal ions, the geometric effects of the size of the five-membered rings overwhelms whatever factor is provided by the cyclohexylene bridge that favors smaller metal ions. In Figure 4 is seen the relationship of Δ log K with ionic radius for THEDACH and THEEN. All three relationships, as well as that for BHEAC and triethanolamine (not shown), show an inverse relationship between metal ion radius and the effect on complex stability of introducing a cyclohexylene bridge to a chelate ring. For the more complete relationship for *trans*-CDTA and EDTA, very small metal ions, with radii less than 0.6 Å, such as Be(II), deviate quite strongly from the relationship indicated. This may indicate that metal ion size, suggested by Schwarzenbach,[1] is not the only contributing factor. One possibility is that the effect is inductive in origin, as *N*-cyclohexyl groups do produce increases in log K_1 for simple unidentate ligands such as cyclohexylamine relative to methylamine for metal ions such as Ag(I).[18] This does not seem likely to be the major contribution, however, and we are currently carrying out molecular mechanics calculations aimed at deter-

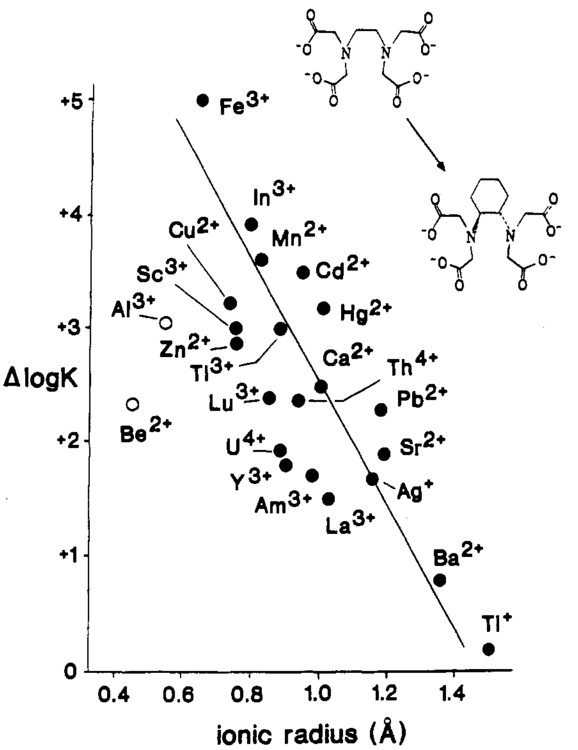

Figure 3. A similar relationship as in Figure 2, where Δ log K is log K_1 for *trans*-CDTA minus log K_1 for EDTA. Octahedral ionic radii were taken from ref 13.

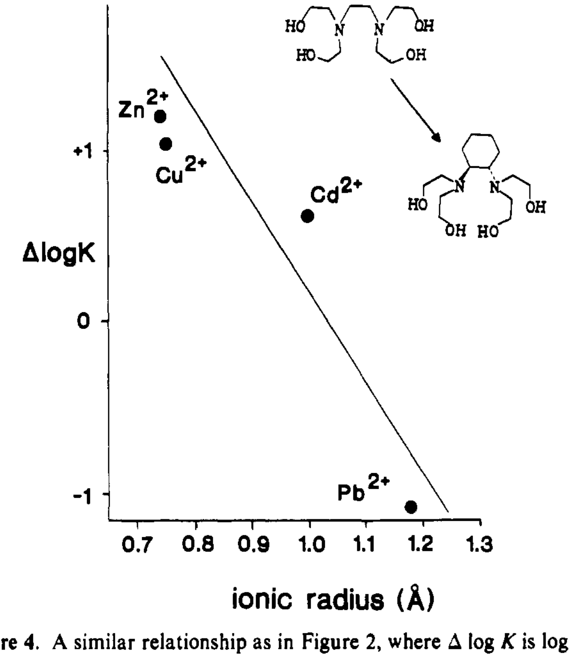

Figure 4. A similar relationship as in Figure 2, where Δ log K is log K_1 for THEDACH minus log K_1 for THEEN. Octahedral ionic radii were taken from ref 13.

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mining the origin of the effect of the cyclohexylene bridge on metal ion size based selectivity. It may be that the effect derives, not so much from the presence of the cyclohexylene bridge in a particular chelate ring, as from the effect of the increased rigidity of this chelate ring on the ability of the remaining donor groups of the ligand to be oriented for coordination to metal ions of differing sizes. This study has indicated that the cyclohexylene bridge could be a useful tool in altering the selectivities of ligands in favor of smaller metal ions and also in the synthesis of more powerfully complexing ligands.

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Complexation of Sodium(I) and Other Monovalent Ions by 4,7,13,16-Tetraoxa-1,10-diazabicyclo[8.8.2]eicosane in a Range of Solvents. A Potentiometric Titration and ^{23}Na Nuclear Magnetic Resonance Study

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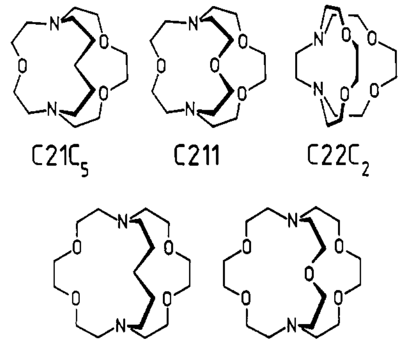
Complexation of Li^+, Na^+, K^+, Cs^+, Ag^+, and Tl^+ by the clamlike cryptand 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.2]eicosane ($C22C_2$) to form the cryptate $[M.C22C_2]^+$ has been studied in six solvents by potentiometric titration and ^{23}Na NMR spectroscopy. A considerable variation in the stability of $[M.C22C_2]^+$ occurs as M^+ is varied in the sequence Li^+ (3.5), Na^+ (6.1), K^+ (3.2), Cs^+ (2.7), Ag^+ (9.4), and Tl^+ (6.7), where the figures in parentheses are log (K/dm^3 mol^{-1}) and K is the apparent stability constant of $[M.C22C_2]^+$ in dimethylformamide at 298.2 K. Crystallographic data show that the dihedral angle between the jaws of $C22C_2$ in the free cryptand, $[Li.C22C_2]^+$, $[Na.C22C_2]^+$, and $[K.C22C_2]^+$ is 88.4, 70.9, 89.6, and 100°, respectively. These two data sets indicate that a dominant factor controlling the stability of the alkali-metal cryptates is the increase in strain energy associated with the deviation of the $C22C_2$ jaw angle in $[M.C22C_2]^+$ from that in free $C22C_2$, with the consequence that $[Na.C22C_2]^+$ is the most stable cryptate. The relative magnitudes of K are similar in other solvents, but the absolute magnitude exhibits substantial variation as the nature of the solvent changes. The exchange of Na^+ on $[Na.C22C_2]^+$ falls within the ^{23}Na NMR time scale in water, dimethylformamide, and dimethyl sulfoxide in which the monomolecular decomplexation process is characterized by k_d(298.2 K) = 255 ± 3, 12.3 ± 0.4, and 11.1 ± 0.5 s^{-1}, respectively; $\Delta H_d^{\ddagger} = 56.5 \pm 0.5$, 64.0 ± 0.5, and 65.8 ± 0.9 kJ mol^{-1}, respectively; and $\Delta S_d^{\ddagger} = -9.4 \pm 1.7$, −9.5 ± 1.5, and −4.1 ± 2.6 J K^{-1} mol^{-1}, respectively. In acetonitrile, methanol, and pyridine the exchange rate is in the very slow regime of the ^{23}Na NMR time scale. These data are discussed in terms of the effects of cryptand structure and metal ion and solvent characteristics on cryptate stability and lability.

Introduction

Chart I. Cryptand Structures



The cryptand 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.2]eicosane ($C22C_2$, Chart I) has a clamlike structure in which the two $-(CH_2)_2O(CH_2)_2O(CH_2)_2-$ jaws are hinged about the $>N(CH_2)_2N<$ moiety.[1-6] In alkali-metal $[M.C22C_2]^+$ cryptates a series of bond angle changes have the overall effect of varying the angle between the jaws to give optimal bonding distances appropriate to the nature of M^+ in the solid state.[1,3-5] (Using these crystallographic data, we calculate that the angle between the jaws of $C22C_2$, defined as the dihedral angle between the mean planes delineated by the two hinge nitrogens and the pairs of oxygens in each jaw, is 88.4, 70.9, 89.6, and 100° in the free $C22C_2$, $[Li.C22C_2]^+$, $[Na.C22C_2]^+$, and $[K.C22C_2]^+$, respectively.) This mode of potential metal ion selectivity differs from that exhibited by less flexible cryptands (e.g. $C21C_5$, C211, C221, and C222 shown in Chart I) where the selectivity is predominantly determined by the fit of the metal ion into the approximately spherical cryptand cavity whose size is predetermined by the bicyclic nature of the cryptand.[6-18] Accordingly, it is of considerable interest to investigate the effect of this uncommon characteristic of $C22C_2$ on its selectivity for metal ions in the formation of cryptates in solution. Thus, the stabilities of $[M.C22C_2]^+$, where $M^+ = Na^+$, K^+, Cs^+, and Tl^+, have been determined by potentiometric titration

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