quite similar but with a slightly longer Mo–Mo distance of 2.746 (9) Å compared to the present value of 2.7171 (3) Å.

When all four of the structures whose average principal dimensions are listed in Table VIII are compared, it is clear that they have for the most part very similar dimensions. The only prominent exception to this generalization is the Mo–Mo distance in the anion of **1a**, which is 2.763 (2) Å while the other three are in the range 2.694 (3)–2.7171 (3) Å. While this may appear a little surprising, it is not really inconsistent with the structure of **1** nor with what we know of face-sharing bioctahedral compounds of molybdenum(III) generally. Structural studies of the $[Mo_2Cl_9]^{3-}$ ion in at least 10 compounds with different counterions[10-13] have revealed Mo–Mo distances ranging from 2.52 to 2.82 Å. Clearly the Mo^{III}–Mo^{III} bond in this structural context is not a rigid one, and the different environments of the independent anions in **1** compress them to different extents. The difference is modest compared to the range observed for the $[Mo_2Cl_9]^{3-}$ ion.

General trends to be seen in all four structures (i.e., in the gauche as well as the syn isomer) are the following. (1) Deviations of angles from those expected for the fusion of two ideal octahedra are small and thus suggest that the Mo–Mo attraction is only moderate. For the background of this interpretation, see ref 14. The average internal Cl_b–Mo–Cl_b angles are 92 ± 1°, the external Cl_t–Mo–P and Cl_t–Mo–Cl_t angles are about 88 and 92°, respectively, and the Mo–Cl_b–Mo angles are 66.3–68.1°, which are all indicative of only slight compression along the Mo–Mo axis. This, of course, supports the presence of some significant Mo–Mo bonding interaction, else there would be an expansion owing to the underlying Mo···Mo repulsive forces. (2) There is a small but consistent trans influence by the phosphine ligand compared to that of the Cl atom, since the Mo–$Cl_{b,P}$ distances are all 0.03–0.05 Å longer than the Mo–$Cl_{b,Cl}$ distances. (3) All Mo–$Cl_{b,Cl}$ distances are consistently about 0.05 Å longer than Mo–Cl_t distances, as is normal.

Concluding Remarks. This is the first time, to our knowledge, that both the syn and gauche isomers of a $LX_2M(\mu\text{-}X)_3MX_2L$ species have been isolated and structurally characterized. The great similarity in bond distances and angles for the isomers would suggest that bond energies and repulsive forces are about equal in the two, and that in turn is in accord with the fact that the equilibrium constant for a solution of the two isomers has the purely statistical value within experimental error. The interconversion presumably requires the loss of a tertiary phosphine ligand from one metal atom, whereupon the then five-coordinate half of the dimer can rearrange so that the reattachment of the tertiary phosphine may occur so as to form the isomeric product.

Finally, we should mention two unsolved problems raised in this work. (1) Why have we failed to obtain the product $Mo_2Cl_6(PMe_3)_4$, which was the original goal of the work? (2) What is the source of the hydrogen ion required to form the $PHMe_3^+$ cation, and why does the formation of this ion occur so easily?

Acknowledgment. We thank the National Science Foundation for financial support.

Supplementary Material Available: Full tables of bond distances and angles and anisotropic displacement parameters for complexes **1–3**, stereoviews of the crystal packing and unit cells of **1–3**, and figures showing the change in the intensity of the PMe_3 resonances in the ^1H NMR spectra of complexes **1** and **3**, a plot of ln (X/X_0) vs time, and a plot of the PMe_3 ^1H NMR chemical shifts vs. T^{-1} for complexes **1** and **3** (23 pages); listings of observed and calculated structure factors for **1–3** (60 pages). Ordering information is given on any current masthead page.

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Ligand Design for Complexation in Aqueous Solution. 1. Neutral Oxygen Donor Bearing Groups as a Means of Controlling Size-Based Selectivity for Metal Ions

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The synthesis of several novel macrocyclic ligands containing both oxygen and nitrogen donors and containing in some cases also pendent donor groups bearing one or more neutral oxygen donors is described. The protonation constants and formation constants with Ca(II), Sr(II), Ba(II), Pb(II), Zn(II), Cd(II), Cu(II), and Ni(II) are reported. The crystal structures of two complexes of the above ligands are reported, $[K(BHEE\text{-}18\text{-}aneN_2O_4)]I$ (I) and $[K(BHE\text{-}18\text{-}aneN_2O_4)]Cl$ (II). (The ligands $BHEE\text{-}18\text{-}aneN_2O_4$ and $BHE\text{-}18\text{-}aneN_2O_4$ are N-substituted derivatives of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, where the nitrogen substituents are respectively $CH_2CH_2OCH_2CH_2OH$ and CH_2CH_2OH.) Compound I crystallizes in space group $P2_1/c$, with cell constants $a = 8.805$ (4) Å, $b = 14.221$ (2) Å, $c = 21.957$ (3) Å, $\beta = 100.27$ (2)°, $Z = 4$, $V = 2705.16$ Å^3, $d_m = 1.46$ g cm^{-3}, and $d_c = 1.48$ g cm^{-3}. The final conventional R factor was 0.054. The complex appears to be sterically crowded, with the pendent donor groups occupying the unusual trans orientation and with at least two of the oxygen donors on the pendent groups being left uncoordinated. Compound II crystallizes in space group $C2/c$, with cell constants $a = 13.331$ (3) Å, $b = 15.716$ (2) Å, $c = 11.577$ (4) Å, $\beta = 117.69$ (3)°, $Z = 4$, $V = 2147.53$ Å^3, $d_m = 1.32$ g cm^{-3}, and $d_c = 1.32$ g cm^{-3}. The final conventional R factor was 0.029. In contrast to compound I, II appears not to be sterically crowded and adopts the more usual cis arrangement of the pendent donor groups. Analysis of the formation constants shows how the neutral oxygen donor atom can be used to achieve metal ion size-based selectivity. The results reinforce the ligand design principle observed previously, that addition of groups bearing neutral oxygen donors increases the selectivity of a ligand for large relative to small metal ions. The control of selectivity for the large Pb(II) ion relative to the small Zn(II) ion is examined, and it is shown that the extra pair of oxygen donors in $BHEE\text{-}18\text{-}aneN_2O_4$, for example, leads to greatly enhanced selectivity for the large Pb(II) ion over the small Zn(II) ion, as compared with the ligand $BHE\text{-}18\text{-}aneN_2O_4$. The point is emphasized that oxygen donors do not have to be part of a macrocyclic ring in order to generate selectivity for large metal ions.

Introduction

The neutral oxygen donor has for some time been of considerable interest because of its occurrence in crown ethers[1] and more recently because of its occurrence as alcoholic and ethereal oxygens in side arms on ligands such as the "lariat ethers".[2,3] An important

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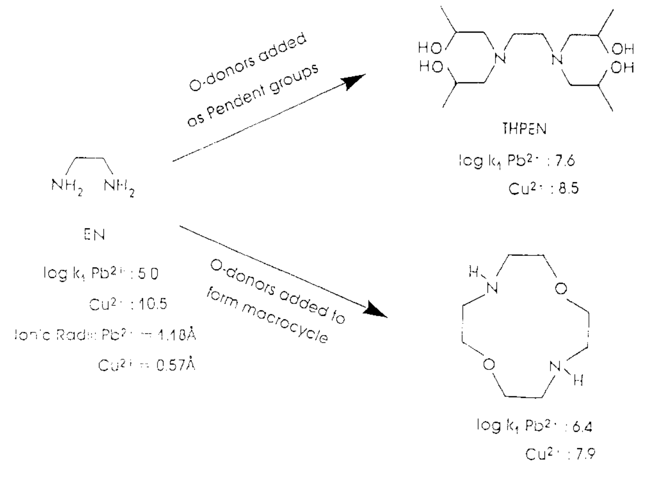
Scheme I



idea in crown ether chemistry has been that of size-match selectivity,[1] i.e. the idea that metal ions are most strongly complexed where the match between the size of the metal ion and of the cavity in the macrocycle is closest. More recent work has indicated that additional factors may play a part[4] and that much of the observed behavior of these oxygen donor ligands is related to the presence of neutral oxygen donors rather than of a macrocyclic structure. Thus, as will be discussed later, there does appear to be a contribution from cavity size, but a large part of the size selectivity of macrocyclic ligands is determined by the size-selective coordination observed in the presence of neutral oxygen donor groups. Thus, crown ethers complex well only with large metal ions[1] such as the alkali-metal ions, alkali-earth-metal ions, Pb(II), and Ag(I). Paralleling this, it is found that large metal ions show increased complex stability when groups containing neutral oxygen donors are added to an existing ligand, whereas small metal ions tend to show decreases in complex stability, as shown by the examples in Scheme I. Such observations have led to a guide for ligand design[4] to the effect that "addition of neutral oxygen donor containing groups to ligands will increase the selectivity of the ligand for large metal ions relative to small". The ability to control metal ion selectivity is clearly of interest in many areas, among which are the design of complexes to act as imaging agents in medicine[5] or for the treatment of metal intoxication in cases of metal poisoning[6] and even in the design of complexing agents for use in detergents.[7] Our own interest has been in the development[8] of reagents for treating lead intoxication. Here the problem involves[6] removing the large Pb(II) ion while leaving the essential small Zn(II) ion, and so presents a classical exercise in utilizing size-selective ligands.

The aim of this work is to investigate further the size-selective properties of the neutral oxygen donor evident in several examples in the literature. A recent review[9] has discussed the origin of the size-selective coordinating properties in terms of the balance between steric and inductive effects when a neutral oxygen donor group coordinates to a metal ion. Molecular mechanics calculations[10] have supported the idea of a balance between steric and electronic effects, and work on crown ether complex stability with alkali-metal ions has shown[11] that the idea of size-match selectivity is possibly an oversimplification. In order to investigate the origin of the size-selective coordination observed in the presence of differing numbers of neutral oxygen donor groups, we thus report

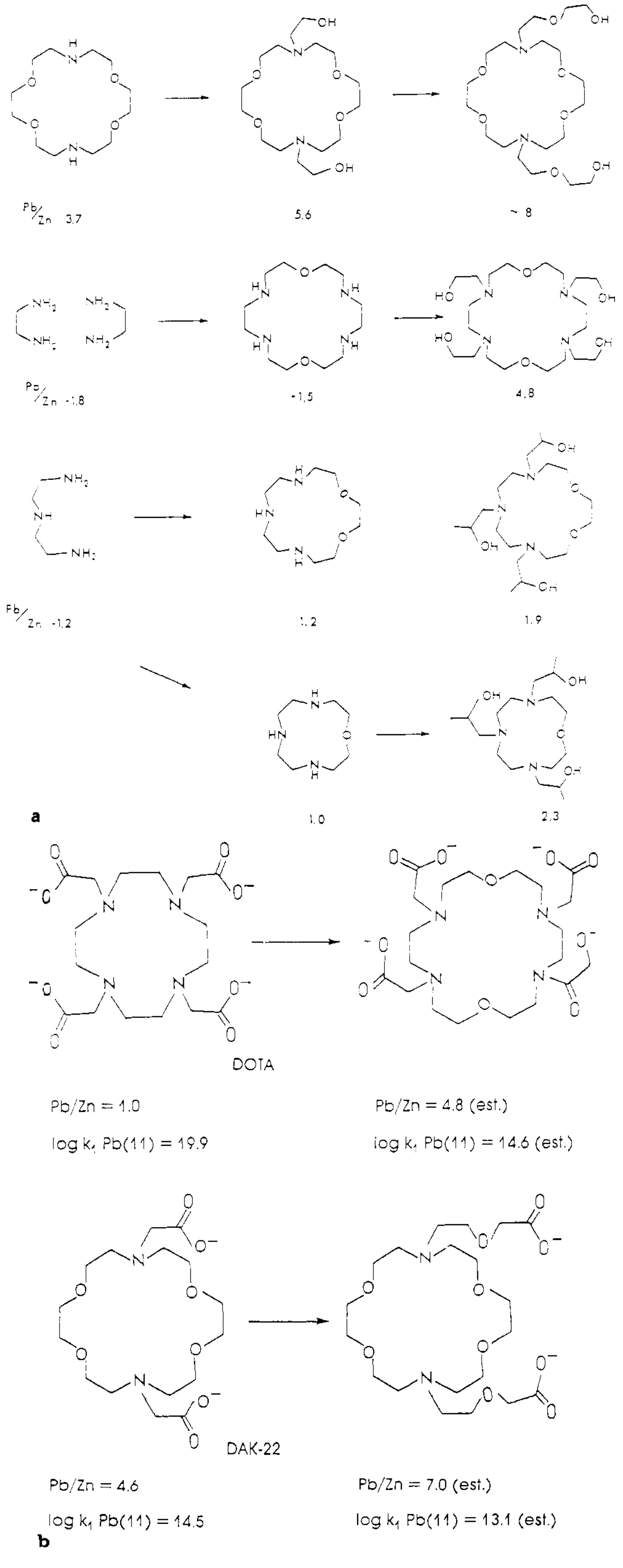


Figure 1. (a) Series of ligands discussed in this work, where the number of oxygen donors attached to an initial amine ligand increases along the series. The selectivities for the large Pb(II) ion over the small Zn(II) ion, Pb/Zn, are shown for each ligand and are the difference between the formation constants, log K_1, for the Pb(II) complex and for the Zn(II) complex of each ligand. (b) Possible ways of achieving high selectivity for Pb(II) over Zn(II) by adding oxygen donor bearing groups to existing ligands. The Pb/Zn selectivity is calculated as log K_1 for the complex of each ligand minus log K_1 for the complex with Zn(II). The absolute values of log K_1 for these *N*-acetate ligands were estimated by comparison with similar changes in stability and selectivity that occur when the substituents are hydroxyethyl groups.

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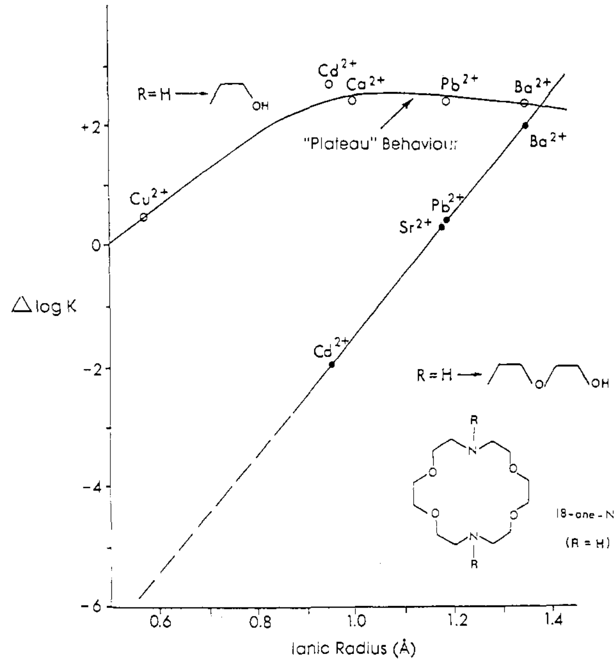

Figure 2. Relationship between the change in formation constant, log K_1, which occurs on adding pendent donor groups to 18-aneN_2O_4 (R = H), and the ionic radius[12] of the metal ion. The points in the upper relationship (○) are for the change in log K_1 that occurs when the N substituent on 18-aneN_2O_4 is changed from H to CH_2CH_2OH to give the ligand BHE-18-aneN_2O_4, while in the bottom relationship (●), R is changed to $CH_2CH_2OCH_2CH_2OH$ to give the ligand BHEE-18-aneN_2O_4. Formation constants were taken from this work and ref 21.

here the formation constants of three series of ligands with a variety of metal ions, where the addition of an increasing number of oxygen donors in a progressively more sterically demanding fashion is aimed at greatly increasing selectivity for large metal ions such as Pb(II) over small metal ions such as Zn(II). These three series are seen in Figure 1. Since the final members of these series require an ability to coordinate a large number of donor atoms, it was thus also of interest to compare the structure of [K(BHEE-18-aneN_2O_4)]I, reported in this work, with that of the less sterically crowded [K(BHE-18-aneN_2O_4)]Cl. While the structure determination of these two complexes was in progress, the structure of [K(BHE-18-aneN_2O_4)]I was reported. The structure of [K(BHE-18-aneN_2O_4)]Cl is thus reported here for comparison with that of [K(BHEE-18-aneN_2O_4)]I, although the structure of [K(BHE-18-aneN_2O_4)]Cl is very similar to that reported[13] for the iodide salt.

Experimental Section

Materials. The metal ion nitrates were obtained as the AR salts, and stock solutions of these were standardized by conventional methods.

Synthesis of Ligands. 1,4-Dioxa-7,10,13-triazacyclopentadecane (15-aneN_3O_2). The cyclic tritosylate of 15-aneN_3O_2 was prepared by the method of Richman and Atkins.[14] It was hydrolyzed as follows: A solution of 18 g (0.0265 mol) of the tritosylate in 400 mL of glacial acetic acid and 590 mL of concentrated HBr was heated under reflux with stirring for 48 h. The solution was filtered while still hot and concentrated under reduced pressure to approximately 100 mL. Addition of an ethanol/ether mixture precipitated the trihydrobromide salt. Yield: 4.1 g (33.6%). Mp: 240 °C. NMR (D_2O): 3.46 (12 H, m, $-CH_2-N$), 3.76 ppm (8 H, m, $-CH_2-O$). Anal. Calcd for $C_{10}H_{26}N_3O_2Br_3$: C, 26.11; H, 5.70; N, 9.13; O, 6.96. Found: C, 26.44; H, 5.99; N, 9.09; O, 6.67.

7,10,13-Tris(2-hydroxypropyl)-1,4-dioxa-7,10,13-triazacyclopentadecane. The free base of 15-aneN_3O_2 was obtained by extraction of the neutralized solution with chloroform. The 15-aneN_3O_2 (1 g, 4.60 mmol) was dissolved in absolute ethanol (25 mL), and propylene oxide (3 mL, 42.8 mmol) was added. The solution was stirred for 5 days. The ethanol was evaporated to obtain a viscous liquid, which was distilled at 155–159 °C (0.5 mmHg). A pale yellow oil was obtained. Yield: 47.7%. NMR ($CDCl_3$): 1.1 (9 H, d, $-CH_3$); 2.15–2.9 (18 H, m, $-CH_2-N$), 3.6 (11 H, m, $-O-CH_2$ and $-O-CH$), 4.5 ppm (3 H, broad singlet, OH). Anal. Calcd for $C_{19}H_{44}N_3O_5$: C, 58.28; H, 10.55; N, 10.10. Found: C, 57.95; H, 10.10; N, 10.49.

1,4-Dioxa-7,10,13,16-tetraazacyclooctadecane (*cis*-18-aneN_4O_2). The cyclic tetratosylate was prepared by the condensation method of Richman and Atkins.[14] Detosylation was carried out as described for 15-aneN_3O_2. Yield: 48%. Mp: 228–230 °C. NMR (D_2O): 3.56 (16 H, m, $-CH_2-N$), 3.7 ppm (8 H, m, $-CH_2-O$). Anal. Calcd for $C_{12}H_{32}N_4O_2Br_4$: C, 24.68; H, 5.52; N, 9.59. Found: C, 24.93; H, 5.61; N, 9.40.

1,10-Dioxa-4,7,13,16-tetraazacyclooctadecane (*trans*-18-aneN_4O_2). This was prepared by a modification of the method of Biernat and Luboch.[15] A solution of ethylenediamine ditosylate (63.5 g, 172 mmol), bis(2-chloroethyl) ether (22.7 mL, 193 mmol), and K_2CO_3 (34.3 g) in DMF (350 mL) was refluxed at 170 °C for 5 h and cooled over 12 h. A large quantity of water was added to the reaction mixture while stirring slowly. A white solid precipitated, which was filtered, washed with water, and dried under reduced pressure. Yield: 75.5 g, 100%, calcd as the tetratosylate. The *trans*-18-aneN_4O_2 tosylate (150.9 g, 172 mmol) was slurried in acetic acid (1 L) and 48% HBr (1.5 L), and refluxed for 60 h. The reaction mixture was then evaporated to 10% of its volume. Half as much again of that volume of ethanol was added, the solution allowed to cool, and ether added until a separate ether layer became visible. The mixture was allowed to stand for 12 h, after which a crystalline precipitate separated out. Recrystallization from 48% HBr produced fine white crystals. Yield: 11.4 g, 11%.

4,7,13,16-Tetrakis(2-hydroxypropyl)-1,10-dioxa-4,7,13,16-tetraazacyclooctadecane (THP-18-aneN_4O_2). The free base *trans*-18aneN_4O_2 was obtained by passing the tetrahydrobromide through an Amberlite IRA 400 resin in the hydroxide form. The free base (0.99 g, 3.8 mmol) and propylene oxide (1.78 g, 30.4 mmol) were dissolved in absolute ethanol (25 mL) and stirred for 2 days. The solvent and excess propylene oxide were removed under reduced pressure to yield a pale solid (1.8 g, 3.8 mmol, 100% yield). NMR ($CDCl_3$): 1.10 (12 H, CH_3-), 2.17–3.00 (24 H, m, CH_2-N), 3.33–3.90 (12 H, m, CH_2-O and $-CHOH$), 4.77 ppm (4 H, s, $-OH$). Anal. Calcd for $C_{24}H_{52}N_4O_6$: C, 58.51; H, 10.64; N, 11.37. Found: C, 58.42; H, 10.48, N, 11.40. Mp: 64–68 °C.

4,7,13,16-Tetrakis(2-hydroxyethyl)-1,10-dioxa-4,7,13,16-tetraazacyclooctadecane (THE-18-aneN_4O_2). The method was as for the above ligand, except that ethylene oxide was used in the place of the propylene oxide. The product so obtained was shown by TLC to be slightly impure. The impure product was dissolved in 96% ethanol, and dry HCl was bubbled through the solution to precipitate the HCl salt. The HCl salt was recrystallized from the minimum of concentrated HCl. The pure salt was passed through Amberlite IRA 400 resin in the base form to remove the HCl and dried under reduced pressure to yield a white crystalline solid (80% yield). NMR ($CdCl_3$): 2.43–2.87 (24 H, m, CH_2N), 3.40–3.73 (16 H, m, CH_2-O), 4.35 ppm (4 H, s, $-OH$). Mp: 69–70 °C. Anal. Calcd for $C_{20}H_{44}N_4O_6$: C, 55.02; H, 10.16; N, 12.83. Found: C, 55.21; H, 10.22; N, 12.52.

7,16-Bis(((2-hydroxyethyl)oxy)ethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (BHEE-18-aneN_2O_4). The method was as reported for other N-substituted 18-aneN_2O_4 ligands,[3] involving the condensation of 1,10-diiodo-4,7-dioxadecane with (((hydroxyethyl)oxy)ethyl)amine. Recrystallization from THF gave the KI complex as white crystals. Yield: 7.2%. Mp: 97–100 °C. NMR ($CDCl_3$): 3.66 (30 H, m, $-CH_2-O$ and $-OH$), 2.6 ppm (12 H, m, $-CH_2-N$). Anal. Calcd for $C_{20}H_{42}N_2O_8KI$: C, 39.73; H, 7.00; N, 4.63; O, 21.17. Found: C, 39.94; H, 7.33; N, 4.36; O, 21.25.

Stability Constant Determination. The stability constants were determined by titration in cells thermostated to 25 °C with N_2 bubbled through the cell to exclude CO_2. The potentials were recorded on a RADIOMETER PHM 84 pH meter using RADIOMETER G202B glass electrodes with Ag/AgCl reference electrodes and a salt bridge to eliminate junction potentials. All measurements were made in 0.1 M $NaNO_3$. The glass electrodes were calibrated by recording the potentials as a function of calculated pH in the pH range 2–11. All the ligands appeared to equilibrate rapidly with the metal ions during the potentiometric titrations. The program MINIQUAD[16] as well as EQUILIBRIA[17] was used for data reduction to yield the formation constants. Species considered in fitting the data were the ML, MLH, MLH_2, MLOH, $MLOH_2$, and M_2L complexes. At least three separate titrations were carried out for each metal ion with each ligand, with a range of ligand

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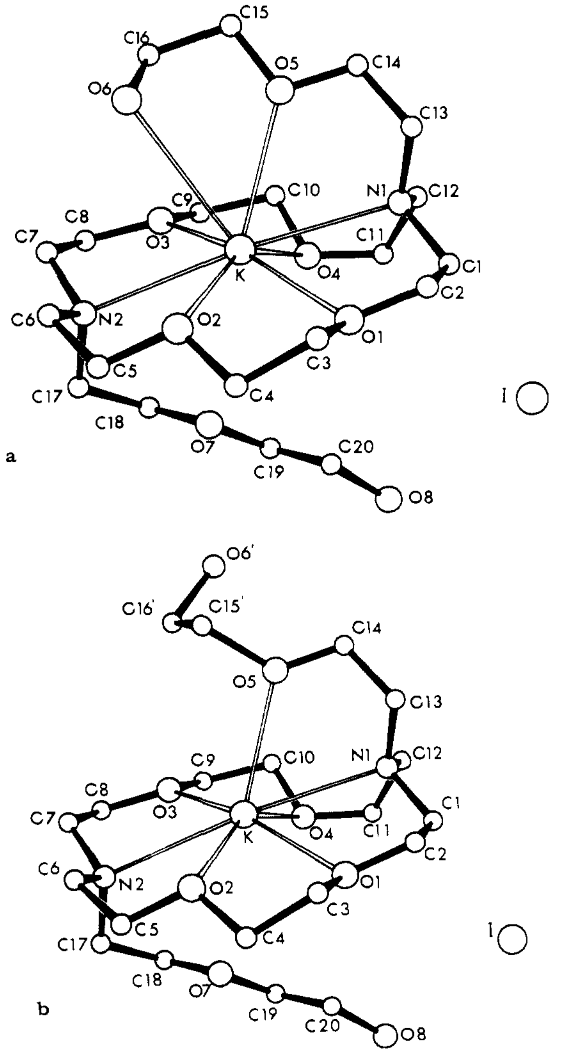

Figure 3. (a) ORTEP[27] drawing of the $[K(BHEE\text{-}18\text{-}aneN_2O_4)]^+$ cation, showing the atom-numbering scheme. The cation shown is present in the crystal with a site occupancy factor of 0.75. (b) ORTEP[27] drawing of the alternative structure for the $[K(BHEE\text{-}18\text{-}aneN_2O_4)]^+$ cation, which has a site occupancy factor of 0.25.

to metal concentration ratios so as to highlight the presence of complexes other than the ML complex. For those ligands that were obtained as salts with halide counterions, the halide ions were removed from the stock solution by addition of the calculated amount of $AgNO_3$, followed by filtration and restandardization.

Preparation of Crystals for Crystallography. $[K(BHE\text{-}18\text{-}aneN_2O_4)]Cl$. A pale yellow solid obtained by evaporation of a 1:1 mixture of KCl and BHE-18-aneN_2O_4 in water was recrystallized from a minimum quantity of ethanol. Anal. Calcd for $C_{12}H_{26}O_6N_2KCl$: C, 45.22; H, 8.06; N, 6.59. Found: C, 45.25; H, 8.24; N, 6.23. Mp: 172–173 °C.

$[K(BHEE\text{-}18\text{-}aneN_2O_4)]I$. The synthesis of the ligand gives the KI complex. However, these crystals were found to be twinned as obtained by recrystallization from THF. Recrystallization from benzene gave nontwinned crystals, which were used for the crystallographic study.

X-ray Crystallographic Studies. The data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The cell dimensions were obtained from least-squares refinement of 25 high-θ reflections. An ω–2θ scan mode was used with a scan width of $0.6 + 0.35 \tan \theta$ and a variable scan speed. Three standard reflections were monitored and showed no significant variation over the data collection. *Lp* and absorption corrections were applied to the data according to the method of North et al.[18] Crystal data and data collection parameters for the two structures are given in Table I. The structures were determined by using Patterson and Fourier techniques with the SHELX program.[19] Fractional atomic coordinates for the two structures are given in Tables II and III. During refinement of the structure of $[K(BHEE\text{-}18\text{-}aneN_2O_4)]^+$ it became apparent that there was disorder in the terminal portion of one of the side arms, represented by the atoms C(15)–C(16)–O(6). Refinement

Table I. Details of the Crystallographic Analysis of $[K(BHEE\text{-}18\text{-}aneN_2O_4)]I$ and $[K(BHE\text{-}18\text{-}aneN_2O_4)]Cl$

	$C_{20}H_{42}N_2O_8KI$	$C_{16}H_{34}N_2O_6KCl$
fw	604.65	425.01
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
cell dimens		
a, Å	8.805 (4)	13.331 (3)
b, Å	14.221 (2)	15.716 (2)
c, Å	21.957 (3)	11.577 (4)
β, deg	100.27 (2)	117.69 (3)
V, Å^3	2705.16	2147.53
Z	4	4
d_{obsd}, g cm^{-3}	1.46 (1)	1.32 (1)
d_{calcd}, g cm^{-3}	1.48	1.32
$F(000)$	1248	908
cryst color	colorless	pale yellow
crystal dimens, mm	0.14 × 0.21 × 0.30	0.25 × 0.50 × 0.50
θ range, deg	$2 \leq \theta \leq 27$	$2 \leq \theta \leq 30$
range of h,k,l	±11,+18,+28	±18,+22,+16
scan speed, deg min^{-1}	1.4–5.5	0.9–5.5
no. of measd reflcns	6289	3383
no. of unique data	4701	2877
R_{int}	0.0171	0.0106
no. of data used	2828	2325
cut-off criteria	$[F > 3\sigma(F_o)]$	$[F > 4\sigma(F_o)]$
abs coeff (μ_λ), cm^{-1}	12.70	3.55
range of transmissn factors, %	94.3–100.0	93.8–100.0
final R	0.054	0.029
no. of params	297	171
residual density, e Å^{-3}	0.89	0.22

Table II. Fractional Coordinates (×10^4; for I, ×10^5) and Equivalent Isotropic Temperature Factors (Å^2 × 10^3; for I and K, Å × 10^4) for $C_{20}H_{44}N_2O_8KI$

	x/a	y/b	z/c	U_{eq}[a]
I	21706 (9)	18354 (5)	12637 (3)	802 (2)
K	7534 (3)	2190 (1)	3869 (1)	615 (5)
N(1)	7633 (8)	2417 (5)	2552 (3)	52 (2)
N(2)	6857 (7)	2036 (4)	5117 (3)	50 (2)
O(1)	7548 (6)	576 (4)	3159 (2)	52 (1)
O(2)	8267 (6)	519 (4)	4470 (2)	54 (1)
O(3)	6528 (7)	3741 (4)	4402 (3)	62 (2)
O(4)	5289 (6)	3395 (4)	3171 (3)	64 (2)
O(5)	9846 (7)	3289 (5)	3479 (3)	81 (2)
O(6)	10620 (12)	2988 (8)	4692 (5)	102 (3)[b]
O(7)	4382 (7)	1246 (5)	4171 (3)	74 (2)
O(8)	12088 (7)	4381 (5)	7685 (3)	79 (2)
C(1)	7085 (11)	1522 (6)	2250 (4)	59 (2)
C(2)	7904 (11)	660 (6)	2558 (4)	62 (2)
C(3)	8409 (9)	−173 (5)	3497 (4)	54 (2)
C(4)	7834 (10)	−292 (6)	4101 (4)	60 (2)
C(5)	7870 (10)	418 (6)	5069 (4)	62 (2)
C(6)	8006 (11)	1339 (6)	5395 (4)	65 (2)
C(7)	7311 (11)	2978 (6)	5368 (4)	69 (2)
C(8)	6354 (12)	3762 (6)	5037 (4)	76 (3)
C(9)	5627 (11)	4421 (6)	4027 (5)	70 (3)
C(10)	5876 (11)	4301 (5)	3378 (4)	65 (2)
C(11)	5134 (11)	3251 (7)	2522 (4)	74 (3)
C(12)	6626 (11)	3195 (7)	2283 (4)	67 (2)
C(13)	9234 (11)	2596 (7)	2488 (4)	72 (3)
C(14)	9988 (12)	3393 (7)	2858 (5)	82 (3)
C(15)	10787 (19)	3988 (12)	3826 (8)	88 (4)[b]
C(16)	10529 (19)	3897 (12)	4477 (7)	82 (4)[b]
C(17)	5298 (9)	1785 (7)	5194 (4)	63 (2)
C(18)	4110 (9)	1912 (7)	4622 (4)	66 (2)
C(19)	3163 (12)	1330 (9)	3648 (5)	95 (3)
C(20)	3434 (13)	686 (9)	3203 (5)	108 (4)
O(6′)	10748 (36)	5144 (23)	3843 (14)	102 (3)[b]
C(15′)	11059 (55)	3574 (33)	4102 (24)	88 (4)[b]
C(16′)	10302 (54)	4433 (34)	4281 (21)	82 (4)[b]

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}\mathbf{a}_i^*\mathbf{a}_j^*(a_i \cdot a_j)$. [b] Isotropic temperature factor.

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Table III. Fractional Coordinates ($\times 10^4$; for Cl and K, $\times 10^5$) and Equivalent Isotropic Temperature Factors ($Å^2 \times 10^4$) for $C_{16}H_{34}N_2O_6KCl$

	x/a	y/b	z/c	$U_{eq}{}^a$
K(1)	0	29268 (3)	25000	350 (1)
Cl	50000	47844 (4)	25000	437 (1)
N(1)	448 (1)	2987 (1)	99 (1)	392 (3)
O(1)	2002 (1)	3695 (1)	2676 (1)	493 (3)
O(2)	1466 (1)	3854 (1)	4790 (1)	489 (3)
O(3)	421 (1)	1497 (1)	1478 (2)	586 (4)
C(1)	1615 (2)	3265 (1)	540 (2)	520 (5)
C(2)	1970 (2)	3987 (1)	1492 (2)	545 (5)
C(3)	2482 (2)	4314 (1)	3682 (2)	572 (5)
C(4)	2575 (2)	3953 (2)	4914 (2)	567 (5)
C(5)	1516 (2)	3547 (1)	5971 (2)	495 (4)
C(6)	347 (2)	3585 (1)	5854 (2)	496 (4)
C(7)	278 (2)	2129 (1)	−458 (2)	481 (4)
C(8)	810 (2)	1438 (1)	540 (2)	477 (4)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*(a_i \cdot a_j)$.

of the positions and site occupancy factors (SOF) for this disordered fragment indicated the two alternative orientations for C(15)–C(16)–O(6) [SOF = 0.75 (1)] and C(15′)–C(16′)–O(6′) [SOF = 0.25 (1)], seen in Figure 3.

Results and Discussion

The formation constants determined in this study for the ligands 15-aneN_3O_2, THP-15-aneN_3O_2, *trans*-18-aneN_4O_2, *cis*-18-aneN_4O_2, THP-18-aneN_4O_2, THE-18-aneN_4O_2, and BHEE-18-aneN_2O_4 are seen in Table IV. The aim of this investigation was to evaluate the effect of the neutral oxygen donor on size-selectivity patterns. In Figure 1 the selectivities of series of ligands for the large Pb(II) ion over the small Zn(II) ion are seen. It seems clear from Figure 1 that as the number of oxygen donor atoms is increased, so the Pb/Zn selectivity increases. (The Pb/Zn selectivity for any ligand is simply log K_1 for the Pb(II) complex minus log K_1 for the Zn(II) complex.) It is not necessarily addition of neutral oxygen donors so as to form a macrocyclic ring that produces the most dramatic increases in Pb/Zn selectivity. Rather, what appears to be important is that a sufficient number of oxygen donor atoms should be added so that a critical level of steric crowding around the metal ion is achieved. Thus addition of two hydroxymethyl arms to 18-aneN_2O_4 to give BHE-18-aneN_2O_4 results in a 1.9 log unit increase in Pb/Zn selectivity. Addition of a further two oxygen donors to BHE-18-aneN_2O_4 to give BHEE-18-aneN_2O_4 now results in a dramatic 4.4 log unit increase in Pb/Zn selectivity. The results in Figure 1, and those discussed elsewhere,[4] demonstrate fairly convincingly that addition of neutral oxygen donor groups is a useful tool in ligand design for the production of selectivity for large metal ions. This type of behavior is reminiscent of the behavior recently reported[20] by Lindoy et al. for the effect on metal ion selectivity of increase in the number of O donors in the macrocyclic ring of mixed oxygen–nitrogen donor macrocycles.

A point of interest here is the origin of the selectivity toward larger metal ions that accompanies addition of groups bearing neutral oxygen donors. One might feel here that this simply arises because larger metal ions have higher coordination numbers and so are able to accommodate the large number of donor atoms produced by adding a large number of extra donor groups. This interpretation, suggested by a reviewer, seems a likely contribution for ligand systems of high denticity, but one should emphasize that such size-selectivity effects can be strongly manifested in ligands of low denticity. Thus, for example, examination of the literature[21] shows that even for a small ligand such as alanine, addition of two hydroxyethyl groups to give *N*,*N*-bis(2-hydroxyethyl)alanine (BHE-alanine) results in a change in formation constants that is size selective toward larger metal ions:

metal ion	ionic radius,[12] Å	log K_1[12] alanine	log K_1[12] BHE-alanine	Δ log K_1
Cu(II)	0.57	8.13[a]	8.34[a]	+0.20
Ni(II)	0.69	5.40	5.98	+0.58
Zn(II)	0.74	4.58	5.16	+0.58
Cd(II)	0.95	3.80	4.97	+1.17
Ca(II)	1.00	0.80	2.26	+1.46
Pb(II)	1.18	4.15	6.20	+2.05

[a] Ionic strength = 0.1 M at 25 °C.

Such results appear unlikely to be explicable in terms of addition of a large number of neutral oxygen donors leading to a too high coordination number requirement in the metal ion, since the ligand BHE-alanine requires only that the metal ion be able to accommodate four donor atoms. Numerous other examples of the tendency to coordinate well only with large metal ions can be cited,[4] such as the fact that 12-crown-4 coordinates well only with large metal ions, even though it is only tetradentate and would at first sight appear to have a cavity better suited to complexing small metal ions. Even the addition of a single ethereal oxygen donor group to ethylenediamine to give ODEN (oxybis(2-aminoethane)) results[22] in a strong size-dependent change in complex stability. Here the increase in denticity in passing from EN to ODEN is only from two to three, which can hardly be exceeding the coordination number of any of the metal ions under consideration, and yet the change from EN to ODEN results in a change in Pb/Ni selectivity of +2.8 log units.[22]

The ability of the neutral oxygen donor group to generate selectivity for larger over smaller metal ions is thus not trivial. Were the effect simply a matter of exceeding the maximum coordination number of small metal ions, it would be of much less interest. The first point of importance here is the relative basicity of saturated neutral oxygen donors, which studies in the gas phase have shown[23] to be stronger in the order $H_2O < CH_3OH < (CH_3)_2O$. Since the alcoholic or ethereal oxygen donors of added groups must compete with water for coordination sites on the metal ion and alcohols and ethers are better bases than water, one would expect all metal ions to show increased complex stability when groups bearing neutral oxygen are added to existing ligands, provided the maximum coordination number of the metal ion is not exceeded. However, as will be discussed more fully in a future publication,[24] the five-membered chelate ring has a minimum strain energy with metal ions which have long metal to ligand bonds of about 2.5 Å and L–M–L bond angles of about 70°. Smaller metal ions with larger L–M–L bond angles cause large rises in strain energy. *The ability of larger metal ions to coordinate strongly with chelate rings containing neutral oxygen donor atoms thus derives from the fact that these larger metal ions coordinate with the production of less strain energy, i.e. are better suited geometrically to coordinating to the five-membered chelate ring.* One might ask why this effect is not readily apparent for all-nitrogen donor ligands such as EN or its larger homologues such as DIEN through PENTEN. In other words, if small metal ions are not well suited from a strain energy point of view for coordinating to five-membered rings, why does a small metal ion such as Cu(II) complex so well with a ligand such as EN that forms five-membered chelate rings? The strain energy effects in five-membered chelate rings whether they contain oxygen or nitrogen donors are similar, but the important difference is that alcoholic and ethereal donors are only slightly better bases than the water with which they compete for coordination sites on the metal ion, while nitrogen donors are for most metal ions[9] very

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Table IV. Formation Constants and Protonation Constants for Ligands Studied in This Paper[a]

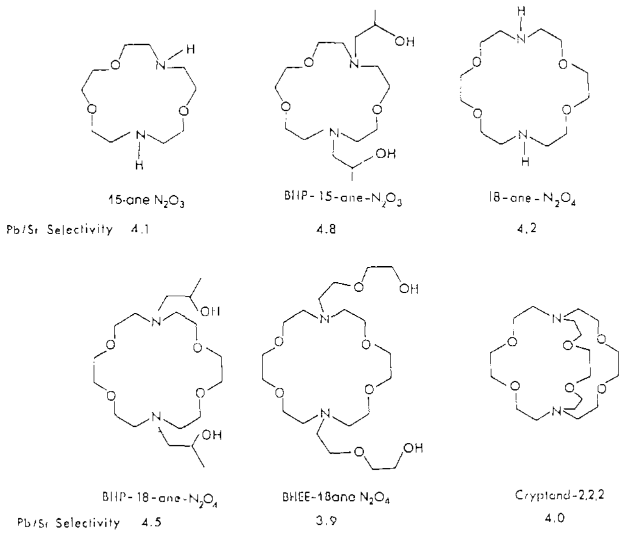
	15-aneN_3O_2	THP-15-aneN_3O_2	*trans*-18-aneN_4O_2	THP-18-aneN_4O_2	THE-18-aneN_4O_2	BHEE-18-aneN_2O_4	*cis*-18-aneN_4O_2
pK_1[b]	9.29 (1)	8.87 (1)	9.36 (2)	8.79 (1)	8.54 (1)	8.03 (1)	9.19 (1)
pK_2	8.50 (1)	6.70 (1)	8.40 (2)	8.02 (1)	7.73 (1)	6.92 (1)	8.51 (1)
pK_3	2.12 (2)	1.93 (3)	6.27 (2)	3.87 (1)	4.06 (1)		6.00 (1)
pK_4			5.23 (2)	3.11 (1)	3.09 (1)		2.56 (1)
log $K_1(Cu^{2+})$	15.27 (1)	12.68 (2)	16.27 (1)	11.8 (1)	11.7 (1)	NEC[c]	17.85 (7)[f]
log K(Cu_2L)[d]				3.5 (1)	3.3 (1)		
log K(Ni^{2+})	8.93 (1)	7.76 (1)	12.25 (1)	6.03 (9)	5.72 (5)	NEC	12.49 (2)[f]
log K(NiLH)[e]				7.3 (1)			4.65 (2)
log $K_1(Zn^{2+})$	8.85 (1)	7.21(1)	10.51 (1)	6.26 (5)	5.90 (1)	NEC	9.52 (3)[f]
log $K_1(Cd^{2+})$	10.05 (1)	9.15 (2)	10.90 (1)	8.39 (6)	8.84 (3)	3.30 (5)	10.00 (4)[f]
log $K_1(Ca^{2+})$						NEC	NEC
log $K_1(Sr^{2+})$			≤2.0	3.28 (2)	3.81 (2)	3.27 (1)	NEC
log $K_1(Ba^{2+})$			≤2.0	4.14 (1)	4.30 (3)	4.91 (1)	NEC
log $K_1(Pb^{2+})$	10.07 (1)	9.09 (2)	9.01 (1)	10.57 (7)	10.72 (3)	7.21 (2)	9.11 (7)[f]

[a] In 0.1 M $NaNO_3$ at 25 °C. [b] The equilibria are as follows: pK_1, $H^+ + L \rightleftharpoons HL^+$; p$K_2$, $H^+ + HL^+ \rightleftharpoons H_2L^{2+}$; etc. [c] NEC = no evidence for complex right up to the highest pH attained in titration, which for Cu(II), Ni(II), or Zn(II) corresponds to point at which solid metal hydroxide precipitated out. [d] Refers to the equilibrium $CuL^{2+} + Cu^{2+} \rightleftharpoons Cu_2L^{2+}$. [e] Refers to the equilibrium $NL^{2+} + H^+ \rightleftharpoons NiLH^{3+}$. [f] Additional constants found for these complexes were as follows. log $K(M^{2+} + L + H^+ \rightleftharpoons MLH^{3+})$: Cu^{2+}, 21.08 (4); Ni^{2+}, 17.14 (2); Zn^{2+}, 14.88 (6); Cd^{2+}, 16.02 (2); Pb^{2+}, 14.6 (2). log $K(M^{2+} + L + 2H^+ \rightleftharpoons MLH_2^{4+})$: Cu^{2+}, 23.2 (3); Zn^{2+}, 20.28 (8); Pb^{2+}, 20.65 (9).

much better donors than water. Thus, for the oxygen donor containing chelate ring, the steric effects are able to predominate over the bond strength effects (i.e. alcoholic and ethereal oxygens are better donors than the oxygen in water), whereas for nitrogen donors the very much larger free energy of M–N bond formation predominates over the steric effects.

It might seem a little simplistic to some readers to interpret changes in complex stability that accompany addition of neutral oxygen donor groups in terms only of metal ion size. One might feel that factors such as coordination geometry should also be considered, and it is reasonable to object to treating a metal ion such as Cu(II) with its more covalent M–L bonding along with, say, Ba(II) with its very ionic M–L bonding, in terms of size alone. The justification for the approach is that it works. An interesting prediction made by the idea of the size-related effect of the oxygen donor on complex stability is that the difference in complex stability for two metal ions of identical size should be a constant regardless of how many oxygen donors are added to an existing ligand or how the structure is modified with respect to presence or absence of macrocyclic rings. This prediction is borne out for the pair of metal ions Pb(II) and Sr(II), which have very similar ionic radii (in 6-coordination) of 1.18 and 1.17 Å respectively[12] (Chart I). All the ligands in Chart I have in common two saturated nitrogen donors, but otherwise there is considerable variation in the number and arrangement of the O-donors. It is seen that there is an approximately constant difference in log K_1 of about 4.2 log units in favor of the Pb(II) complexes as compared with the Sr(II) complexes. The higher stability of the Pb(II) complexes would be interpreted in terms of the higher affinity of Pb(II) for nitrogen donor groups. For ligands with greater numbers of nitrogen donors the difference between log K_1 for the Pb(II) and the Sr(II) complexes becomes even larger. A complication that results with even larger numbers of nitrogen donors is that[25] the inert pair of electrons on Pb(II) may become stereochemically active, leading to a decrease in the Pb(II) ionic radius and a dramatic change in complexing properties.

Chart I



The effect of neutral oxygen donors on size selectivity, indicated in Figure 1, may be more closely analyzed by using plots of the change in complex stability, Δ log *K*, which occurs on making a particular structural change in the ligand, as a function of the ionic radius of the metal ion. In drawing up such plots, almost any reference ligand can be used to which the oxygen donor bearing groups are added. Thus, a good linear relationship for Δ log *K* may be obtained where the cryptand 2,2,2 is compared with EN as a starting ligand,[4] or a small change may be examined, as when two hydroxyethyl groups are added to 2-(aminomethyl)pyridine.[8] Generally, the greater the number of oxygen donors added, the steeper is the slope of a plot of Δ log *K* versus ionic radius. Thus, in Figure 2 it is seen that when two hydroxyethyl groups are added to 18-aneN_2O_4 to give BHE-18-aneN_2O_4, that above a metal ionic radius of about 0.9 Å, there is very little further increase in Δ log *K*. This type of "plateau" behavior is interpreted[4] in terms of the balance between steric and electronic effects being constant above a certain metal ion size and is typically found where small increases in the number of oxygen donors is made to a ligand that is already of high denticity. However, if the level of steric crowding is further increased by changing the hydroxyethyl groups into ((hydroxyethyl)oxy)ethyl groups, the changes in complex stability show a very strong dependence on metal ion size. Thus, with BHEE-18-aneN_2O_4, the very large Ba(*II*) ion is the only metal ion to show an increase in complex stability relative to BHE-18-aneN_2O_4. The smaller Pb(II) and Sr(II) ions show small drops in complex stability for their BHEE-18-aneN_2O_4 complexes relative to their BHE-18-aneN_2O_4 complexes, while the medium-sized Cd(II) shows a large drop in complex stability. Small metal ions such as Cu(II) and Zn(II) are not complexed by BHEE-18-aneN_2O_4 at all. Extrapolation of the relation of Δ log *K* versus ionic radius for the pair of ligands 18-aneN_2O_4 and BHEE-18-aneN_2O_4 in Figure 1 suggests that the Pb/Zn selectivity of BHEE-18-aneN_2O_4 may be in the vicinity of 10 log units, which is rivaled only by the Pb/Zn selectivity of cryptand-222. This would make BHEE-aneN_2O_4 a highly satisfactory reagent for the treatment of Pb(II) intoxication in terms of the required[8] Pb/Zn selectivity, except that the

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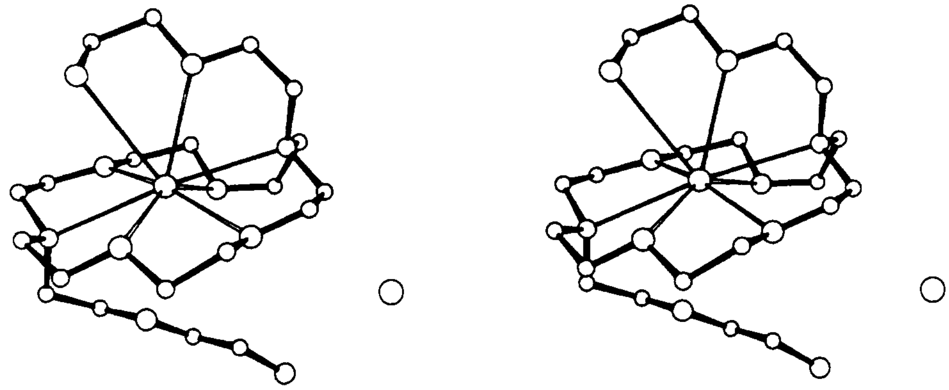

Figure 4. Stereoview of the predominant conformer of the $[K(BHEE\text{-}18\text{-}aneN_2O_4)]^+$ cation.

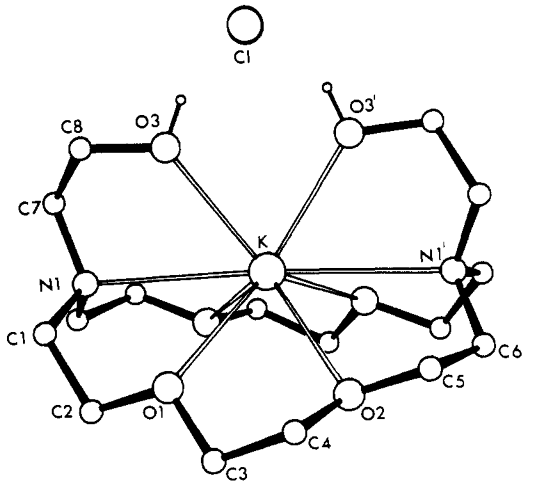

Figure 5. ORTEP[27] drawing of the $[K(BHE\text{-}18\text{-}aneN_2O_4)]^+$ cation plus a chloride counterion, showing the atom numbering scheme.

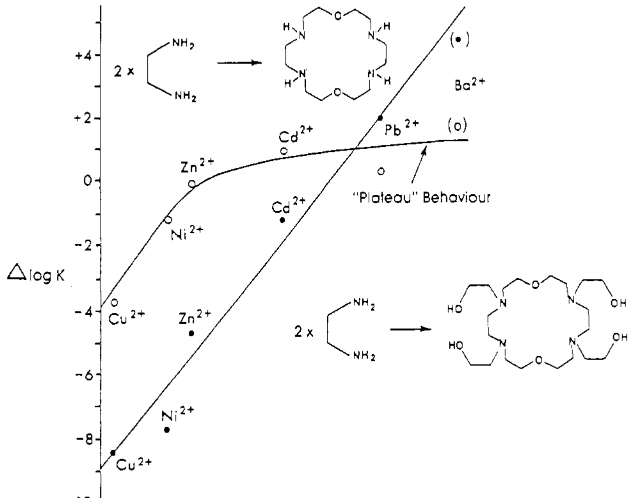

Figure 6. Changes in formation constant that occur on adding oxygen donor groups to two ethylenediamine ligands, as a function of metal ionic radius.[12] The upper relationship (O) shows the variation in log K as two ethereal groups are used to connect the two ethylenediamine ligands to form the macrocycle $18\text{-}aneN_4O_2$, while the lower relationship (●) shows the change in log K as two ethylenediamines are altered by addition of oxygen donor groups to give the ligand $THE\text{-}18\text{-}aneN_4O_2$.

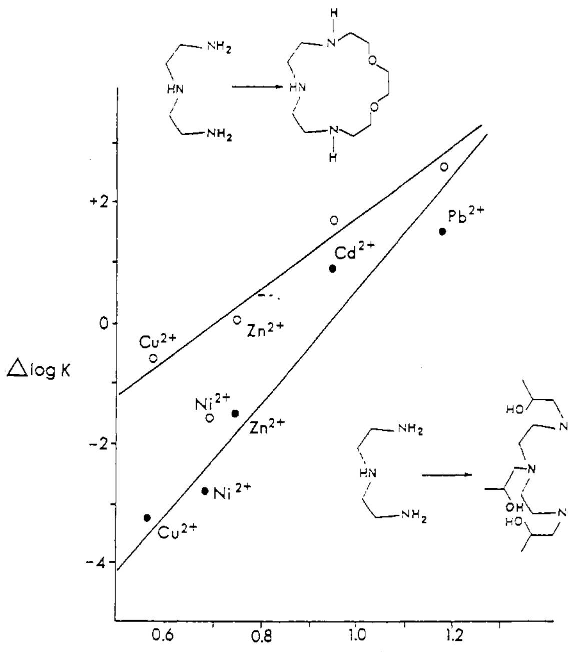

Figure 7. Changes in formation constant, log K, as a function of metal ionic radius as two ether groups are added to DIEN to give $15\text{-}aneN_3O_2$ (O), or where two ether and three alcoholic groups are added to DIEN to give $THP\text{-}15\text{-}aneN_3O_2$ (●).

log K_1 value of $BHEE\text{-}18\text{-}aneN_2O_4$ with Pb(II) is, at 7.81 log units, rather too low. However, it is clear that by addition of sufficient neutral oxygen donor groups, the Pb/Zn selectivity can be pushed up to very high levels indeed, and use of pendent donors with their much simpler synthesis than is true for macrocycles suggests that this may be an important means of synthesizing size-selective ligands for a variety of practical applications. Thus, simple modifications of existing ligands that already have a high affinity for Pb(II) may, as seen in Figure 1b, lead to satisfactory Pb(II) binding properties, as well as high Pb/Zn selectivity.

In Figure 6 is seen the relation of Δ log K versus ionic radius for the changes in complex stability accompanying addition of two ethereal oxygens to two EN ligands to give *trans*-$18\text{-}aneN_4O_2$ or addition of two ethereal plus four hydroxyethyl oxygens to two EN ligands to give $THE\text{-}18\text{-}aneN_4O_2$. It is seen that once again with the increase in structural complexity accompanying the change in ligand from two EN ligands to *trans*-$18\text{-}aneN_4O_2$ a flattening off of Δ log K at larger ionic radii occurs. However, with the much more drastic increases in steric crowding that occur when four hydroxyethyl groups are also added, there is a linear dependence of Δ log K on ionic radius. It would seem reasonable that a major contributing factor in the stability of the complexes of the decadentate $THE\text{-}18\text{-}aneN_4O_2$ would be the ability of the metal ion to achieve such a high coordination number. Even so, both Pb(II) and Ba(II) are capable[12] of achieving a coordination number of 10, and one would argue that the higher value of Δ log K for Ba(II) than for Pb(II) in Figures 2 and 6 reflects geometric factors involving differing sizes. Similar behavior is seen in Figure 7, where two ethereal oxygens are added to dien to give $15\text{-}aneN_3O_2$, or hydroxyethyl groups are also added to give $THP\text{-}15\text{-}aneN_3O_2$.

The structure and numbering scheme of the two disordered individuals of the $[K(BHEE\text{-}18\text{-}aneN_2O_4)]^+$ cation are seen in

Scheme II

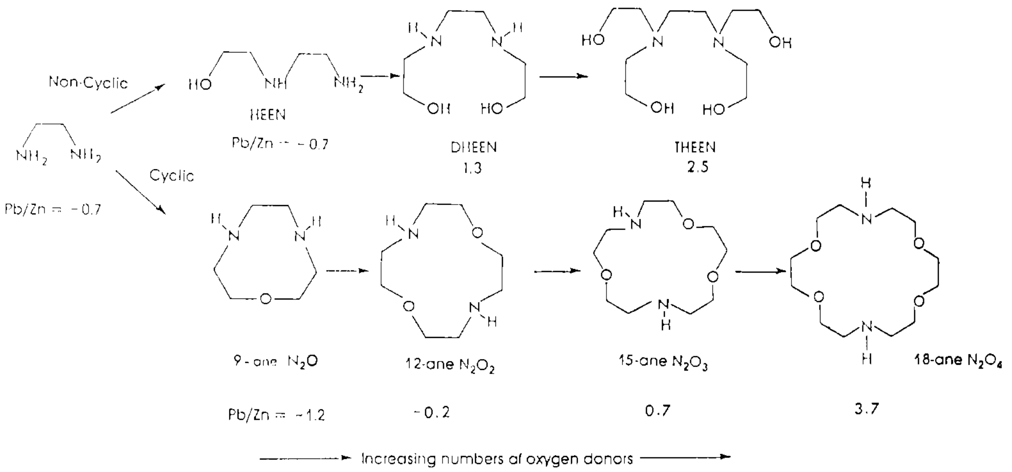

Table V. Comparison of Selected Structural and Binding Parameters for [K(BHEE-18-aneN_2O_4)]I and [K(BHE-18-aneN_2O_4)]Cl

interacn	[K(BHEE-18-aneN_2O_4)]I	[K(BHE-18-aneN_2O_4)]Cl
M-O, Å		
ring	2.775	2.850
	2.739	2.850
	2.718	2.857
	2.849	2.857
side arm	2.818	2.718
	3.192	2.718
	3.256	
M-N, Å	2.926	3.104
	2.915	3.104
N-M-N, deg	169.89	176.51
R, Å		1.46
major compt	1.44 (8-coord)	
	1.49 (9-coord)	
minor compt	1.39 (7-coord)	
	1.45 (8-coord)	
coord no.		
major compt	8 or 9	
minor compt	7 or 8	

Figure 3. In Figure 4 is seen a stereoview of the predominant conformer. The two disordered individuals differ only in that in the major form the terminal oxygen O(6) is coordinated to the metal ion, whereas in the minor form it is not. The hydrogen of O(6) is hydrogen bonded to an iodide in the same unit cell, whereas that on O(6′) is hydrogen bonded to an iodide in a neighboring unit cell. The level of steric crowding present in the BHEE-18-aneN_2O_4 complex of even so large a metal ion as K^+ is seen in the fact that two or three oxygens are left uncoordinated. By contrast, the structure of [K(BHE-18-aneN_2O_4)]$^+$ is cis, with the hydroxyethyl "arms" on the same side of the macrocyclic ring, as has been found for other 18-aneN_2O_4 derivatives with pendent donor groups.[13] In contrast, the pendent groups on the [K-(BHEE-18-aneN_2O_4)]$^+$ cation are arranged trans to each other, which appears from work being carried out by the present authors to be true when bulky N substituents are present on the 18-aneN_2O_4 ring. It is of interest to note that the Ba^{2+} ion shows an increase in complex stability in passing from BHE-18-aneN_2O_4 to BHEE-18-aneN_2O_4, when in fact the crystal structure of the similarly sized[12] K^+ complex of BHEE-18-aneN_2O_4 shows that the extra oxygen donors are not in fact coordinated. A crystal structure of [Ba(BHEE-18-aneN_2O_4)]$^{2+}$ currently being completed by the present authors shows that the Ba(II) ion is in fact 10-coordinate in this complex, accounting for the higher complex stability as compared with the 8-coordinate complex of Ba(II) with BHE-18-aneN_2O_4.

If it seems that adding neutral oxygen donors that are not part of a macrocyclic ring to existing ligands produces effects very similar to adding neutral oxygen donors so as to form a macrocyclic ring, as appears to be the case in this work, this leaves the question of what role there might be for macrocyclic rings in producing metal ion size selectivity. The results shown in Scheme II indicate that the presence of a macrocyclic structure may enhance size selectivity, but that this is not always readily discernible. The ligand 9-aneN_2O has a small cavity such that metal ions of the size of high-spin Ni(II) (ionic radius 0.69 Å) fit best,[26] so that Zn(II) (ionic radius 0.74 Å) will fit very much better than will Pb(II) (ionic radius 1.18 Å). For 9-aneN_2O the selectivity is turned very much in favor of the Zn(II) ion, which is not observed in the case of the noncyclic ligand HEEN. At the other end of the series, the Pb/Zn selectivity of the large cavity 18-aneN_2O_4 appears to be somewhat larger than for the noncyclic analogue THEEN. What one sees in the above series is that the macrocyclic hole size appears able to sharpen up the size-selectivity of the macrocycles, probably by a log unit in favor of the large Pb(II) ion with the large-cavity ligand 18-aneN_2O_4 and by a little over a log unit in favor of the small Zn(II) ion with the small-cavity 9-aneN_2O ligand. Because of the presence of cavities of intermediate size, the selectivities of the 12-aneN_2O_2 and 15-aneN_2O_3 for either the large Pb(II) or small Zn(II) are not very different from those of their noncyclic analogues such as DHEEN. Macrocyclic structures may sharpen size selectivity, but in synthetic terms, it may prove easier to add a large number of oxygens so as to produce a noncyclic structure. Thus, the noncyclic THEEN shows sharper size-selectivity for Pb(II) than does the macrocycle 15-aneN_2O_3.

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Registry No. 15-aneN_3O_2, 60350-18-7; 15-aneN_3O_2 (tritosylate), 60147-29-7; 15-aneN_3O_2·3HBr, 118018-03-4; *cis*-18-aneN_4O_2, 40025-71-6; *cis*-18-aneN_4O_2 (tetratosylate), 60147-34-4; *cis*-18-aneN_4O_2·4HBr, 118018-04-5; *trans*-18-aneN_4O_2, 296-36-6; *trans*-18-aneN_4O_2 (tetratosylate), 93274-33-0; THP-18-aneN_4O_2, 118018-00-1; THP-18-aneN_4O_2·4HBr, 118041-57-9; THE-18-aneN_4O_2, 118018-01-2; BHEE-18-aneN_2O_4, 106113-01-3; [K(BHEE-18-aneN_2O_4)]I, 118018-05-6; [K-(BHE-18-aneN_2O_4)]Cl, 118101-05-6; 7,10,13-tris(2-hydroxypropyl)-1,4-dioxa-7,10,13-triazacyclopentadecane, 118017-99-5; propylene oxide, 75-56-9; ethylenediamine ditosylate, 4403-78-5; bis(2-chloroethyl) ether, 111-44-4; ethylene oxide, 75-21-8; 1,10-diiodo-4,7-dioxadecane, 118018-02-3; (((hydroxyethyl)oxy)ethyl)amine, 929-06-6.

Supplementary Material Available: Tables of anisotropic temperature factors, fractional coordinates and isotropic temperature factors for hydrogen atoms, bond lengths, and bond angles for [K(BHE-18-aneN_2O_4)]Cl and [K(BHEE-18-aneN_2O_4)]I (8 pages); tables of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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