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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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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 $[\text{Mo}_2\text{Cl}_9]^{3-}$ ion in at least 10 compounds with different counterions¹⁰⁻¹³ have revealed Mo-Mo distances ranging from 2.52 to 2.82 Å. Clearly the $\text{Mo}^{\text{III}}\text{-Mo}^{\text{III}}$ 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 $[\text{Mo}_2\text{Cl}_9]^{3-}$ 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 $\text{Cl}_b\text{-Mo-Cl}_b$ angles are $92 \pm 1^\circ$, the external $\text{Cl}_t\text{-Mo-P}$ and $\text{Cl}_t\text{-Mo-Cl}_t$ angles are about 88 and 92° , respectively, and the $\text{Mo-Cl}_b\text{-Mo}$ angles are $66.3\text{--}68.1^\circ$, 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 $\text{Mo-Cl}_b\text{P}$ distances are all $0.03\text{--}0.05$ Å longer than the $\text{Mo-Cl}_b\text{Cl}$ distances. (3) All $\text{Mo-Cl}_b\text{Cl}$ 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 $\text{LX}_2\text{M}(\mu\text{-X})_3\text{MX}_2\text{L}$ 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 $\text{Mo}_2\text{Cl}_6(\text{PMe}_3)_4$, 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, $[\text{K}(\text{BHEE-18-aneN}_2\text{O}_4)]\text{I}$ (I) and $[\text{K}(\text{BHE-18-aneN}_2\text{O}_4)]\text{Cl}$ (II). (The ligands $\text{BHEE-18-aneN}_2\text{O}_4$ and $\text{BHE-18-aneN}_2\text{O}_4$ are N-substituted derivatives of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, where the nitrogen substituents are respectively $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ and $\text{CH}_2\text{CH}_2\text{OH}$.) 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)°, $Z = 4$, $V = 2705.16$ Å³, $d_m = 1.46$ 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)°, $Z = 4$, $V = 2147.53$ Å³, $d_m = 1.32$ 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 $\text{BHEE-18-aneN}_2\text{O}_4$, for example, leads to greatly enhanced selectivity for the large Pb(II) ion over the small Zn(II) ion, as compared with the ligand $\text{BHE-18-aneN}_2\text{O}_4$. 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 ethers¹ and more

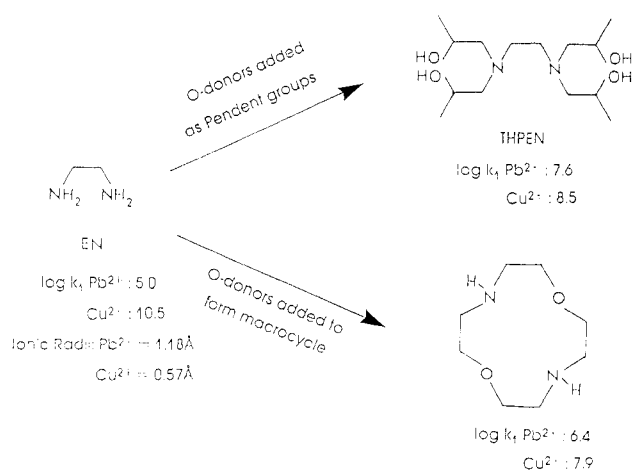
recently because of its occurrence as alcoholic and ethereal oxygens in side arms on ligands such as the "lariat ethers".^{2,3} An important

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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 part⁴ and that much of the observed behavior of these oxygen donor ligands is related to the presence of neutral oxygen donor ligands 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 ions¹ 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 design⁴ 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 medicine⁵ or for the treatment of metal intoxication in cases of metal poisoning⁶ and even in the design of complexing agents for use in detergents.⁷ Our own interest has been in the development⁸ of reagents for treating lead intoxication. Here the problem involves⁶ 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 review⁹ 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 calculations¹⁰ have supported the idea of a balance between steric and electronic effects, and work on crown ether complex stability with alkali-metal ions has shown¹¹ 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

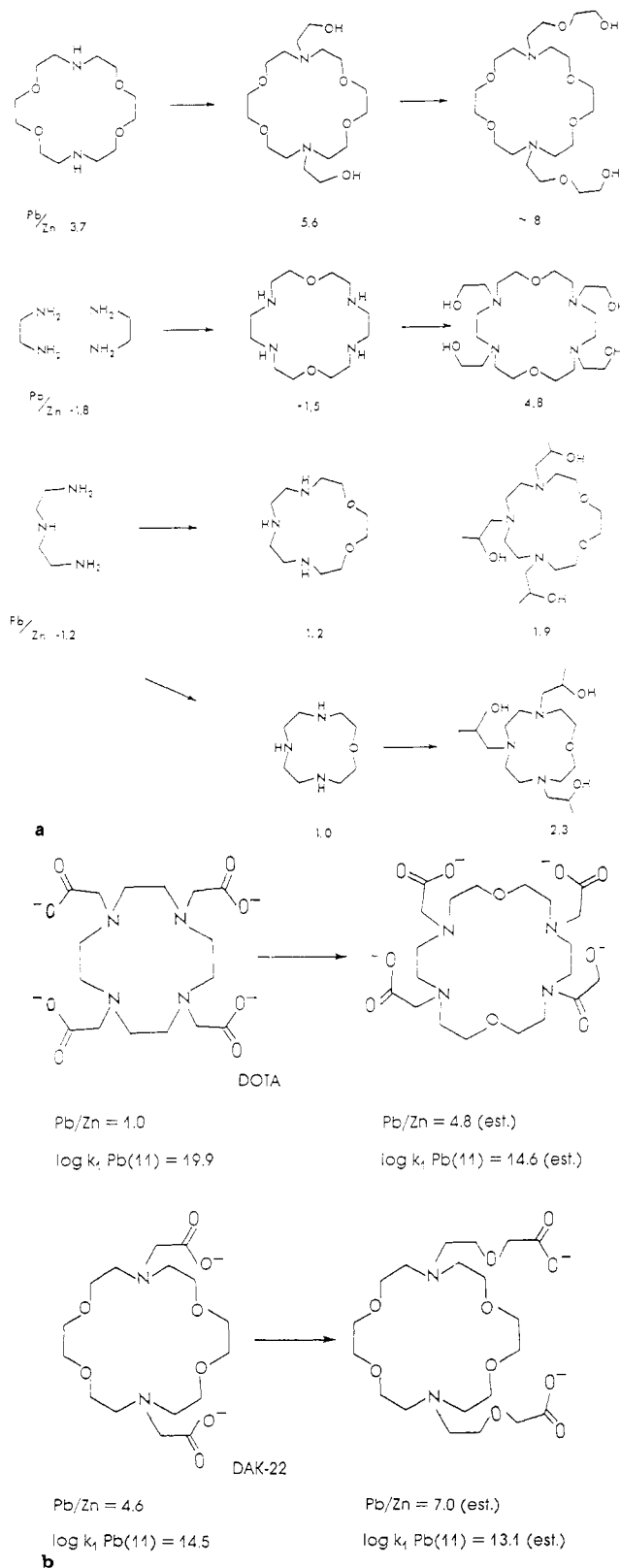


Figure 1. (a) Series of ligands discussed in this work, where the number of oxygen donors attached to an initial amine ligand increases along the series. The selectivities for the large Pb(II) ion over the small Zn(II) ion, Pb/Zn , are shown for each ligand and are the difference between the formation 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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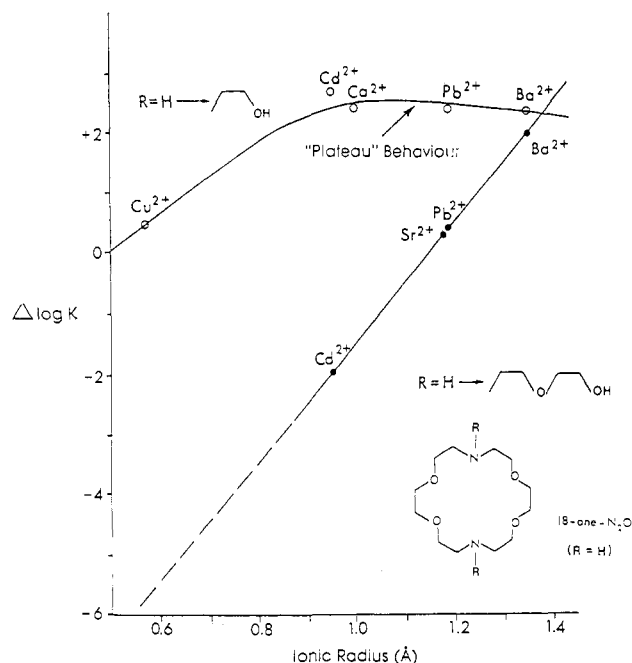


Figure 2. Relationship between the change in formation constant, $\log K_1$, which occurs on adding pendent donor groups to 18-aneN₂O₄ (R = H), and the ionic radius¹² of the metal ion. The points in the upper relationship (O) are for the change in $\log K_1$ that occurs when the N substituent on 18-aneN₂O₄ is changed from H to CH₂CH₂OH to give the ligand BHE-18-aneN₂O₄, while in the bottom relationship (●), R is changed to CH₂CH₂OCH₂CH₂OH to give the ligand BHEE-18-aneN₂O₄. 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-aneN₂O₄)]I, reported in this work, with that of the less sterically crowded [K(BHE-18-aneN₂O₄)]Cl. While the structure determination of these two complexes was in progress, the structure of [K(BHE-18-aneN₂O₄)]I was reported. The structure of [K(BHE-18-aneN₂O₄)]Cl is thus reported here for comparison with that of [K(BHEE-18-aneN₂O₄)]I, although the structure of [K(BHE-18-aneN₂O₄)]Cl is very similar to that reported¹³ 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-Dioxo-7,10,13-triazacyclopentadecane (15-aneN₃O₂).** The cyclic tritosylate of 15-aneN₃O₂ 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 (D₂O): 3.46 (12 H, m, -CH₂-N), 3.76 ppm (8 H, m, -CH₂-O). Anal. Calcd for C₁₀H₂₆N₃O₂Br₃: 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-dioxo-7,10,13-triazacyclopentadecane. The free base of 15-aneN₃O₂ was obtained by extraction of the neutralized solution with chloroform. The 15-aneN₃O₂ (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 (CDCl₃): 1.1 (9 H, d, -CH₃); 2.15–2.9 (18 H, m, -CH₂-N), 3.6 (11 H, m, -O-CH₂ and -O-CH), 4.5 ppm (3 H, broad singlet, OH). Anal. Calcd for C₁₉H₄₄N₃O₅: C, 58.28; H, 10.55; N, 10.10. Found: C, 57.95; H, 10.10; N, 10.49.

1,4-Dioxo-7,10,13,16-tetraazacyclooctadecane (cis-18-aneN₄O₂). The cyclic tetraosylate was prepared by the condensation method of Richman and Atkins.¹⁴ Detosylation was carried out as described for 15-aneN₃O₂. Yield: 48%. Mp: 228–230 °C. NMR (D₂O): 3.56 (16 H, m, -CH₂-N), 3.7 ppm (8 H, m, -CH₂-O). Anal. Calcd for C₁₂H₃₂N₄O₂Br₄: C, 24.68; H, 5.52; N, 9.59. Found: C, 24.93; H, 5.61; N, 9.40.

1,10-Dioxo-4,7,13,16-tetraazacyclooctadecane (trans-18-aneN₄O₂). 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 K₂CO₃ (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 tetraosylate. The trans-18-aneN₄O₂ 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-dioxo-4,7,13,16-tetraazacyclooctadecane (THP-18-aneN₄O₂). The free base trans-18-aneN₄O₂ 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 (CDCl₃): 1.10 (12 H, CH₃-), 2.17–3.00 (24 H, m, CH₂-N), 3.33–3.90 (12 H, m, CH₂-O and -CHOH), 4.77 ppm (4 H, s, -OH). Anal. Calcd for C₂₄H₅₂N₄O₆: 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-dioxo-4,7,13,16-tetraazacyclooctadecane (THE-18-aneN₄O₂). 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 (CDCl₃): 2.43–2.87 (24 H, m, CH₂N), 3.40–3.73 (16 H, m, CH₂-O), 4.35 ppm (4 H, s, -OH). Mp: 69–70 °C. Anal. Calcd for C₂₀H₄₄N₄O₆: 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-aneN₂O₄). The method was as reported for other N-substituted 18-aneN₂O₄ 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 (CDCl₃): 3.66 (30 H, m, -CH₂-O and -OH), 2.6 ppm (12 H, m, -CH₂-N). Anal. Calcd for C₂₀H₄₂N₂O₈KI: 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 N₂ bubbled through the cell to exclude CO₂. 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 NaNO₃. 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 MINQUAD¹⁶ as well as EQUILIBRIA¹⁷ was used for data reduction to yield the formation constants. Species considered in fitting the data were the ML, MLH, MLH₂, MLOH, MLOH₂, and M₂L 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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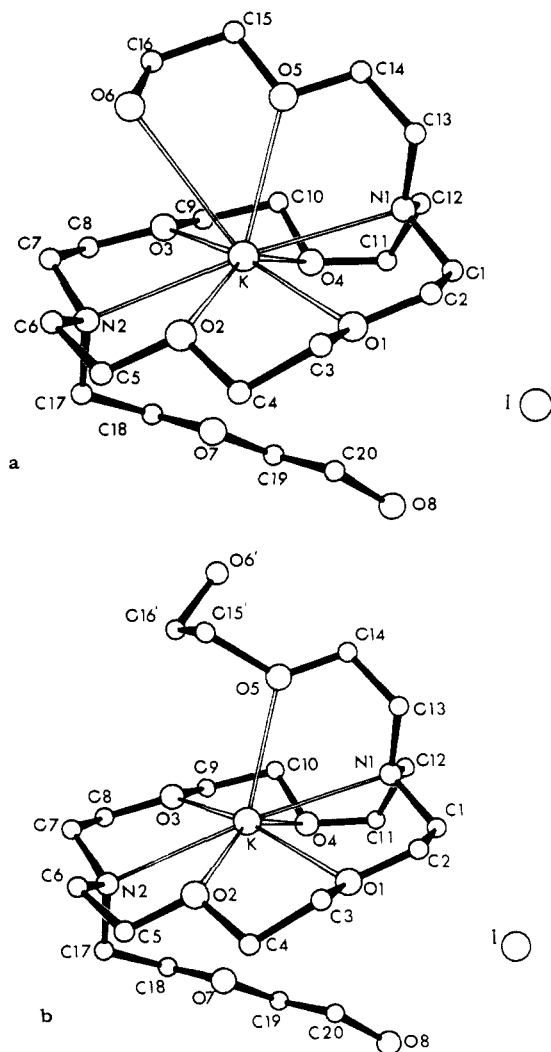


Figure 3. (a) ORTEP²⁷ drawing of the $[K(BHEE-18-aneN_2O_4)]^+$ cation, showing the atom-numbering scheme. The cation shown is present in the crystal with a site occupancy factor of 0.75. (b) ORTEP²⁷ drawing of the alternative structure for the $[K(BHEE-18-aneN_2O_4)]^+$ cation, which has a site occupancy 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. $[K(BHE-18-aneN_2O_4)]Cl$. A pale yellow solid obtained by evaporation of a 1:1 mixture of KCl and BHE-18-ane N_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.

$[K(BHEE-18-aneN_2O_4)]I$. 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 $K\alpha$ 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

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

	$C_{20}H_{42}N_2O_8KI$	$C_{16}H_{34}N_2O_6KCl$
fw	604.65	425.01
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
cell dims		
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 dims, mm	$0.14 \times 0.21 \times 0.30$	$0.25 \times 0.50 \times 0.50$
θ range, deg	$2 \leq \theta \leq 27$	$2 \leq \theta \leq 30$
range of h,k,l	$\pm 11, \pm 18, \pm 28$	$\pm 18, \pm 22, \pm 16$
scan speed, deg min ⁻¹	1.4–5.5	0.9–5.5
no. of measd reflns	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), 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 ($\times 10^4$; for I, $\times 10^5$) and Equivalent Isotropic Temperature Factors ($\text{\AA}^2 \times 10^3$; for I and K, $\text{\AA} \times 10^4$) 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 $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i a_j)$. ^b Isotropic temperature factor.

atomic coordinates for the two structures are given in Tables II and III. During refinement of the structure of $[K(BHEE-18-aneN_2O_4)]^+$ 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

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Table III. Fractional Coordinates ($\times 10^4$; for Cl and K, $\times 10^5$) and Equivalent Isotropic Temperature Factors ($\text{\AA}^2 \times 10^4$) for $\text{C}_{16}\text{H}_{34}\text{N}_2\text{O}_6\text{KCl}$

	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)

$$^a U_{\text{eq}} = \frac{1}{3} \sum_i U_{ij} a_i^* a_j^* (a_i a_j).$$

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-ane N_3O_2 , THP-15-ane N_3O_2 , *trans*-18-ane N_4O_2 , *cis*-18-ane N_4O_2 , THP-18-ane N_4O_2 , THE-18-ane N_4O_2 , and BHEE-18-ane N_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-ane N_2O_4 to give BHE-18-ane N_2O_4 results in a 1.9 log unit increase in Pb/Zn selectivity. Addition of a further two oxygen donors to BHE-18-ane N_2O_4 to give BHEE-18-ane N_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 reported²⁰ 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 literature²¹ shows that even for a small ligand such as alanine, addition of two hydroxyethyl groups to give *N,N*-bis(2-hydroxy-

ethyl)alanine (BHE-alanine) results in a change in formation constants that is size selective toward larger metal ions:

metal ion	ionic radius, ¹² \AA	$\log K_1^{12}$		$\Delta \log K_1$
		alanine	BHE-alanine	
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)) results²² 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 shown²³ to be stronger in the order $\text{H}_2\text{O} < \text{CH}_3\text{OH} < (\text{CH}_3)_2\text{O}$. 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 \AA 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 ions⁹ very

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

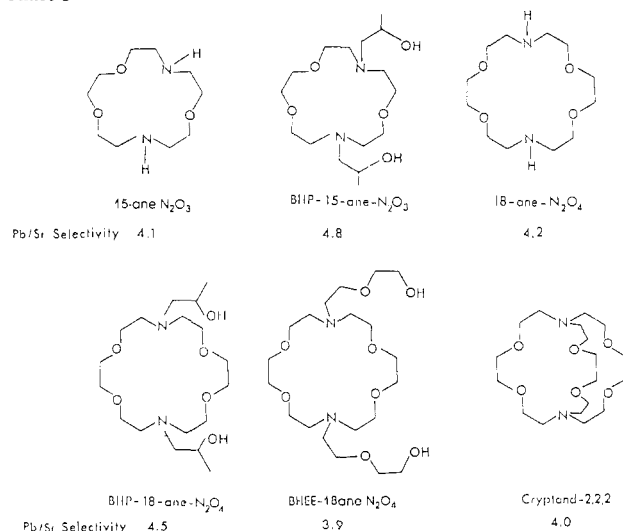
	15-aneN ₃ O ₂	THP- 15-aneN ₃ O ₂	trans- 18-aneN ₄ O ₂	THP- 18-aneN ₄ O ₂	THE- 18-aneN ₄ O ₂	BHEE- 18-aneN ₂ O ₄	cis- 18-aneN ₄ O ₂
pK ₁ ^b	9.29 (1)	8.87 (1)	9.36 (2)	8.79 (1)	8.54 (1)	8.03 (1)	9.19 (1)
pK ₂	8.50 (1)	6.70 (1)	8.40 (2)	8.02 (1)	7.73 (1)	6.92 (1)	8.51 (1)
pK ₃	2.12 (2)	1.93 (3)	6.27 (2)	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 ₂ L) ^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	
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

^aIn 0.1 M NaNO₃ at 25 °C. ^bThe equilibria are as follows: pK₁, H⁺ + L = HL⁺; pK₂, H⁺ + HL⁺ = H₂L²⁺; etc. ^cNEC = 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. ^dRefers to the equilibrium CuL²⁺ + Cu²⁺ = Cu₂L²⁺. ^eRefers to the equilibrium NL²⁺ + H⁺ = NiLH³⁺. ^fAdditional constants found for these complexes were as follows. log K(M²⁺ + L + H⁺ = MLH³⁺): Cu²⁺, 21.08 (4); Ni²⁺, 17.14 (2); Zn²⁺, 14.88 (6); Cd²⁺, 16.02 (2); Pb²⁺, 14.6 (2). log K(M²⁺ + L + 2H⁺ = MLH₂⁴⁺): Cu²⁺, 23.2 (3); Zn²⁺, 20.28 (8); Pb²⁺, 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 respectively¹² (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 K₁ 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 K₁ for the Pb(II) and the Sr(II) complexes becomes even larger. A complication that results with even larger numbers of nitrogen donors is that²⁵ 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.

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-(amino-

Chart I

methyl)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-aneN₂O₄ to give BHE-18-aneN₂O₄, 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 interpreted⁴ 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-aneN₂O₄, the very large Ba(II) ion is the only metal ion to show an increase in complex stability relative to BHE-18-aneN₂O₄. The smaller Pb(II) and Sr(II) ions show small drops in complex stability for their BHEE-18-aneN₂O₄ complexes relative to their BHE-18-aneN₂O₄ 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-aneN₂O₄ at all. Extrapolation of the relation of Δ log K versus ionic radius for the pair of ligands 18-aneN₂O₄ and BHEE-18-aneN₂O₄ in Figure 1 suggests that the Pb/Zn selectivity of BHEE-18-aneN₂O₄ 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-aneN₂O₄ a highly satisfactory reagent for the treatment of Pb(II) intoxication in terms of the required⁸ Pb/Zn selectivity, except that the

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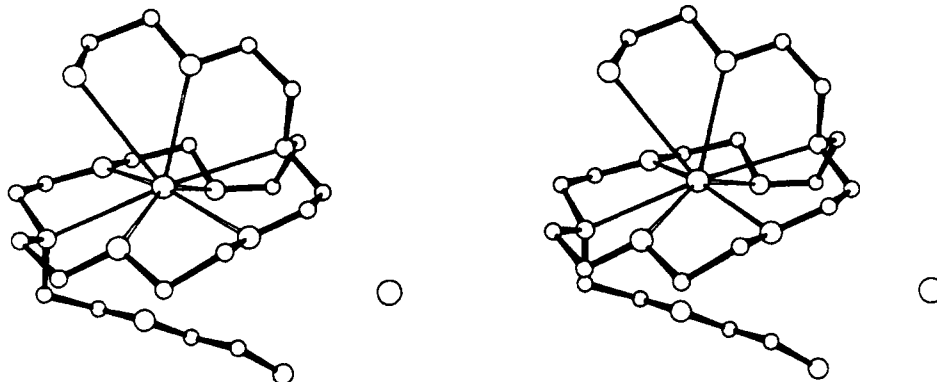


Figure 4. Stereoview of the predominant conformer of the $[K(BHEE-18-aneN_2O_4)]^+$ cation.

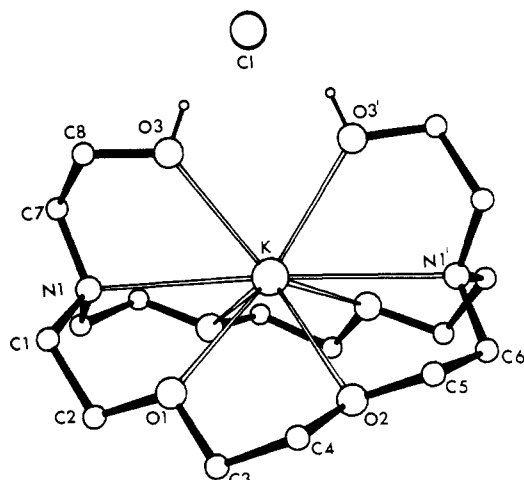


Figure 5. ORTEP²⁷ drawing of the $[K(BHE-18-aneN_2O_4)]^+$ cation plus a chloride counterion, showing the atom numbering scheme.

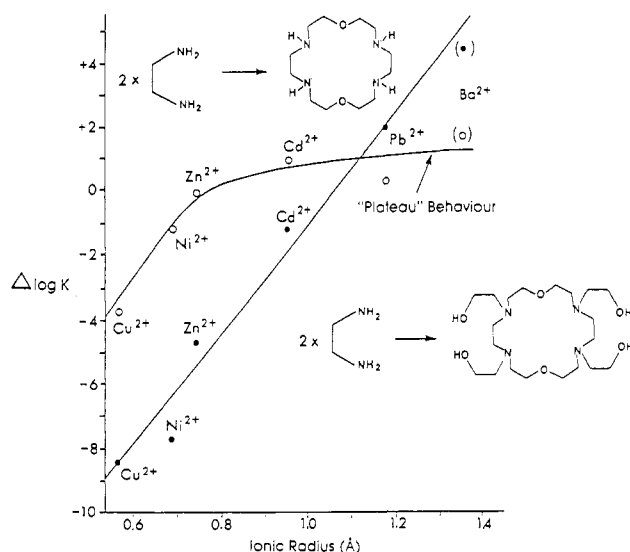


Figure 6. Changes in formation constant that occur on adding oxygen donor groups to two ethylenediamine ligands, as a function of metal ionic radius.¹² The upper relationship (O) shows the variation in $\log K$ as two etheral groups are used to connect the two ethylenediamine ligands to form the macrocycle 18-ane N_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-18-ane N_4O_2 .

$\log K_1$ value of BHEE-18-ane N_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

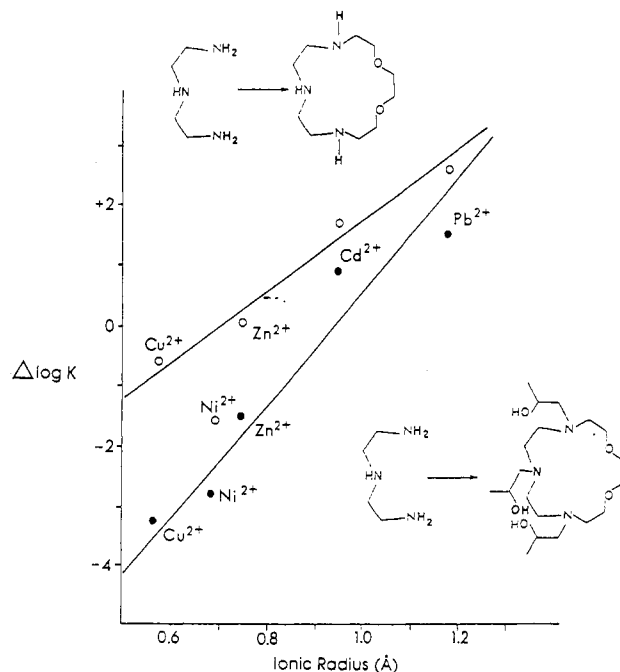


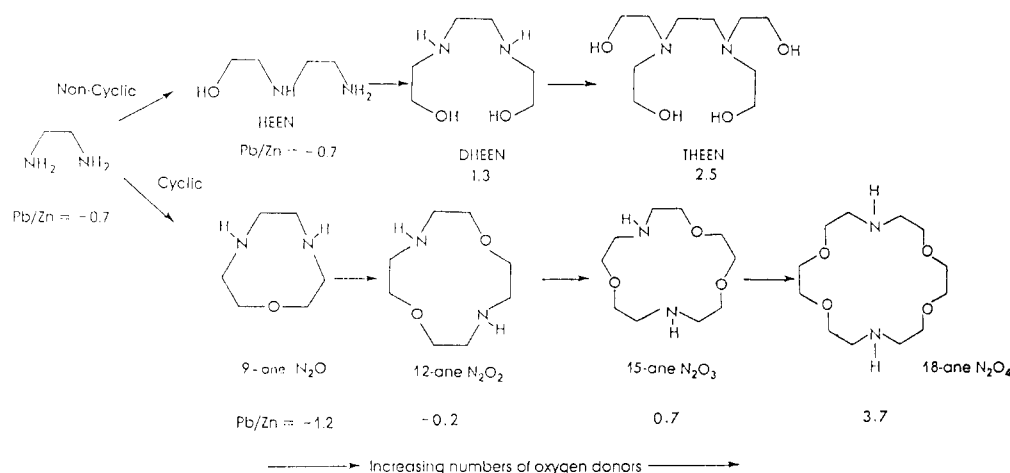
Figure 7. Changes in formation constant, $\log K$, as a function of metal ionic radius as two ether groups are added to DIEN to give 15-ane N_3O_2 (O), or where two ether and three alcoholic groups are added to DIEN to give THP-15-ane N_3O_2 (●).

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 $\Delta \log K$ versus ionic radius for the changes in complex stability accompanying addition of two etheral oxygens to two EN ligands to give *trans*-18-ane N_4O_2 or addition of two etheral plus four hydroxyethyl oxygens to two EN ligands to give THE-18-ane N_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-ane N_4O_2 a flattening off of $\Delta \log K$ 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 $\Delta \log K$ on ionic radius. It would seem reasonable that a major contributing factor in the stability of the complexes of the decadentate THE-18-ane N_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 capable¹² of achieving a coordination number of 10, and one would argue that the higher value of $\Delta \log K$ 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 etheral oxygens are added to dien to give 15-ane N_3O_2 , or hydroxyethyl groups are also added to give THP-15-ane N_3O_2 .

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

Scheme II

**Table V.** Comparison of Selected Structural and Binding Parameters for [K(BHEE-18-aneN₂O₄)]I and [K(BHE-18-aneN₂O₄)]Cl

interactn	[K(BHEE-18-aneN ₂ O ₄)]I	[K(BHE-18-aneN ₂ O ₄)]Cl
M-O, Å		
ring	2.775	2.850
	2.739	2.850
	2.718	2.857
side arm	2.849	2.857
	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-aneN₂O₄ 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-aneN₂O₄)]⁺ is *cis*, with the hydroxyethyl "arms" on the same side of the macrocyclic ring, as has been found for other 18-aneN₂O₄ derivatives with pendent donor groups.¹³ In contrast, the pendent groups on the [K-(BHEE-18-aneN₂O₄)]⁺ 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-aneN₂O₄ ring. It is of interest to note that the Ba²⁺ ion shows an increase in complex stability in passing from BHE-18-aneN₂O₄ to BHEE-18-aneN₂O₄, when in fact the crystal structure of the similarly sized¹² K⁺ complex of BHEE-18-aneN₂O₄ shows that the extra oxygen donors are not in fact coordinated. A crystal structure of [Ba(BHEE-18-aneN₂O₄)]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-aneN₂O₄.

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-aneN₂O 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-aneN₂O 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-aneN₂O₄ appears to be somewhat larger than for the noncyclic analogue THENN. 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-aneN₂O₄ and by a little over a log unit in favor of the small Zn(II) ion with the small-cavity 9-aneN₂O ligand. Because of the presence of cavities of intermediate size, the selectivities of the 12-aneN₂O₂ and 15-aneN₂O₃ 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 THENN shows sharper size-selectivity for Pb(II) than does the macrocycle 15-aneN₂O₃.

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Registry No. 15-aneN₃O₂, 60350-18-7; 15-aneN₃O₂ (tritosylate), 60147-29-7; 15-aneN₃O₂·3HBr, 118018-03-4; *cis*-18-aneN₄O₂, 40025-71-6; *cis*-18-aneN₄O₂ (tetraosylate), 60147-34-4; *cis*-18-aneN₄O₂·4HBr, 118018-04-5; *trans*-18-aneN₄O₂, 296-36-6; *trans*-18-aneN₄O₂ (tetraosylate), 93274-33-0; THP-18-aneN₄O₂, 118018-00-1; THP-18-aneN₄O₂·4HBr, 118041-57-9; THE-18-aneN₄O₂, 118018-01-2; BHEE-18-aneN₂O₄, 106113-01-3; [K(BHEE-18-aneN₂O₄)]I, 118018-05-6; [K-(BHE-18-aneN₂O₄)]Cl, 118101-05-6; 7,10,13-tris(2-hydroxypropyl)-1,4-dioxo-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)ethylamine, 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-aneN₂O₄)]Cl and [K(BHEE-18-aneN₂O₄)]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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