Support for this proposal is suggested by the reaction of $Rh_2(O_2CCF_3)_4$ with excess $P(OMe)_3$. This reaction was studied earlier, but difficulties in obtaining good NMR spectra were encountered. The reaction of $Rh_2(O_2CCF_3)_4$ with 10 equiv of $P(OMe)_3$ yields a pale yellow solid of empirical formula $Rh(O_2CCF_3)_2(P(OMe)_3)_3$. However, we suggested[5] that the complex was most likely $Rh(P(OMe)_3)_4{}^+Rh(O_2CCF_3)_4(P(OMe)_3)_2{}^-$, four-coordinate Rh(I) and six-coordinate Rh(III) species, respectively. The previously reported $^{31}P\{^1H\}$ and ^{19}F NMR spectra of this species were more complex than expected. This was probably due to interconversion between Rh complexes over time while in solution at room temperature. In this study, a $CDCl_3$ solution of the $P(OMe)_3$ complex was frozen at −70 °C and held at that temperature except when NMR spectra were obtained. The $^{31}P\{^1H\}$ NMR spectrum obtained in this manner showed two sharp doublets in a 2:1 area ratio over the temperature range −50 to +20 °C. No significant changes in either chemical shift or coupling constants were seen. The signals appeared at 135.0 ± 0.5 ppm (relative to 85% H_3PO_4), $J = 181.5 \pm 0.1$ Hz, and at 89.5 ± 0.5 ppm, $J = 132.5 \pm 0.5$ Hz. The ^{19}F spectrum showed a single sharp peak at −75.33 ppm at room temperature. $Rh(O_2CCF_3)_4(P(OMe)_3)_2{}^-$ is an AX_2 spin system as the trans isomer, showing a doublet in the X region, and would show a single ^{19}F signal for four equivalent monodentate $CF_3CO_2{}^-$ ligands (IR $\nu_{asy}(CO_2)$ at 1720 cm^{-1} in $CHCl_3$). $Rh(P(OMe)_3)_4{}^+$ is an AX_4 spin system and also shows a ^{31}P doublet. Over time, and probably as a result of O_2 and/or light, other Rh species could come about. The chemistry of transition-metal phosphite complexes is complicated, and a variety of species are known for cobalt[12] and other metals.[13] For rhodium, $Rh(P(OMe)_3)_5{}^+$ and $Rh(OP(OMe)_2)(P(OMe)_3)_4$ have been reported.[14,15] In the system reported here, the Rh–Rh bond in $Rh_2(O_2CCF_3)_4$ probably is cleaved asymmetrically by $P(OMe)_3$ to give a phosphite-coordinated Rh(I) species and a Rh(III) species containing all the $CF_3CO_2{}^-$ ligands. This type of reaction also occurs with phosphines, although oxidation to phosphine oxides complicates matters. Somehow asymmetric phosphorus donor coordination to the rhodium dimer polarizes the Rh–Rh bond and cleaves carboxylate bridges leading to formation of Rh(I) complexes that coordinate only the phosphorus donors and Rh(III) complexes that coordinate two phosphines and the $CF_3CO_2{}^-$ ions.

Experimental Section

$Rh_2(O_2CCF_3)_4$, $Rh_2(O_2CCF_3)_4(PPh_3)_2$, $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$, $Rh_2(O_2CCH_2CH_2CH_3)_4(PPh_3)_2$, and $Rh(O_2CCF_3)_2(P(OMe)_3)_3$ were synthesized as described previously.[5] $Rh_2(O_2CCF_3)_4(PCy_3)_2$ was prepared by dropwise addition of a toluene solution of PCy_3 (2 equiv, Aldrich) to a toluene solution of $Rh_2(O_2CCF_3)_4$. Removal of solvent by pumping and recrystallization from toluene gave brown $Rh_2(O_2CCF_3)_4(PCy_3)_2$. IR ($cm^{-1}$): $\nu_{asy}(CO_2)$ 1663 (Nujol), 1710 w, 1660 m ($CHCl_3$). ^{19}F NMR ($CDCl_3$, 27 C, ppm relative to $CFCl_3$): −72.73, −74.51, −75.42, −75.92 (1:1:2:1). Anal. Calcd for $Rh_2C_{44}H_{66}P_2F_{12}O_8$: C, 43.36; H, 5.46; P, 5.08. Found: C, 45.53; H, 5.49; P, 5.23. Following the above procedure but using excess PCy_3 (10 equiv) and $Rh_2(O_2CCF_3)_4$ in 1:1 toluene/acetonitrile led to a solution color change from brown to pale yellow after heating at 40 °C for 30 min. Removal of solvent by pumping and recrystallization from 1:1 CH_2Cl_2/hexane afforded a pale yellow solid. IR (cm^{-1}, Nujol): $\nu(CN)$ 2260 m; $\nu_{asy}(CO_2)$ 1735 s, 1680 s; $\nu(CF_3)$ 1180 s, 1140 s; $\delta(CO_2)$ 725 s. Anal. Calcd for $Rh(O_2CCF_3)(P(C_6H_{11})_3)(CH_3CN)$: C, 49.17; H, 6.75; N, 2.61; P, 5.76; C:H:N:P = 22:36:1:1. Found: C, 53.69; H, 7.40; N, 2.84: P, 6.50; C:H:N:P = 22.0:36.2:1.0:1.0. The product is contaminated with PCy_3 and complexes thereof, giving the high % C, % H, and % P.

NMR spectra were recorded on a Nicolet NT-300 instrument operating at a field of 7 T. $^{31}P\{^1H\}$ (121.5 MHz) sample were in $CDCl_3$ in 5-mm tubes coaxial in 12-mm tubes, the latter containing $P(OMe)_3$ in $CDCl_3$ as an external chemical shift reference (140.0 ppm relative to 85% H_3PO_4). ^{19}F (282.3 MHz) samples were in 5-mm tubes containing $CFCl_3$ as an internal reference.

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Registry No. $Rh_2(O_2CCH_2CH_2CH_3)_4(PPh_3)_2$, 90968-08-4; $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$, 77966-17-7; $Rh_2(O_2CCF_3)_4(PPh_3)_2$ (class I), 77966-16-6; $Rh_2(O_2CCF_3)_4(PPh_3)_2$ (class III), 102745-66-4; $Rh_2(O_2CCF_3)_4(PCy_3)_2$ (class I), 83398-63-4; $Rh_2(O_2CCF_3)_4(PCy_3)_2$ (class III), 102745-67-5; $[Rh(O_2CCF_3)_4[P(OMe)_3]_2]^-[Rh(P(OMe)_3)_4]^+$, 102745-69-7; $Rh(O_2CCF_3)(P(C_6H_{11})_3)(CH_3CN)$, 102745-70-0; $Rh_2(O_2CCF_3)_4$, 31126-95-1.

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Small Macrocyclic Ligands with Mixed Nitrogen- and Oxygen-Donor Atoms

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The stability of some of the complexes of the metal ions Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ca^{2+}, and Hg^{2+} with the ligands 9-aneN_2O (1-oxa-4,7-diazacyclononane), 12-aneN_3O (1-oxa-4,7,10-triazacyclododecane), 12-ane(1,4)N_2O_2 (1,4-dioxa-7,10-diazacyclododecane), 13-aneN_3O (1-oxa-4,7,11-triazacyclotridecane), 13-aneN_2O_2 (1,4-dioxa-7,11-diazacyclotridecane), HEEN (1-oxa-4,7-diazaheptane), ODEN (4-oxa-1,7-diazaheptane), DHEEN (1,10-dioxa-4,7-diazadecane), and 12-aneN_4 (1,4,7,10-tetraazacyclododecane) are reported. It is shown that addition of neutral oxygen donors to existing amine ligands leads to an increase in complex stability for large metal ions (e.g. Pb^{2+}, Ca^{2+}) and a decrease for small metal ions (e.g. Cu^{2+}, Zn^{2+}). This occurs whether the added oxygen donors are part of hydroxyalkyl groups, as in the addition of hydroxyethyl groups to en (ethylenediamine) to give DHEEN or the addition of ethereal oxygens that are part of a macrocyclic ring to en to give 12-ane(1,4)N_2O_2. It is found that the macrocyclic effect in mixed-donor ligands is much smaller than in the all-nitrogen-donor analogues. Thus, the increase in complex stability (the macrocyclic effect) in passing from DHEEN to 12-aneN_2O_2, for example, is much smaller than in passing from TRIEN (1,4,7,10-tetraazadecane) to 12-aneN_4. This is discussed in terms of ligand-related contributions to the macrocyclic effect, such as steric hindrance to the solvation of the free ligand. A feature of these ligand-related effects is that a metal ion such as Ca^{2+}, which ordinarily shows little affinity for ligands containing only nitrogen donors, will still form a complex of some stability with a ligand such as 12-aneN_4, with log K_1 at 25 °C in 0.1 M $NaNO_3$ of 3.1.

An interesting feature of macrocyclic chemistry is the fact that the oxygen-donor macrocycles complex strongly only with the alkali- and alkaline-earth-metal ions, plus a few large metal ions such as Pb^{2+} and Hg^{2+}. In contrast, the nitrogen-donor macrocycles appear to complex well only with the transition-metal and post-transition-metal ions, such as Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, or Cd^{2+}. A few metal ions such as Pb^{2+} and Hg^{2+} appear able to bond well to both classes of macrocycle. An obvious area for investigation

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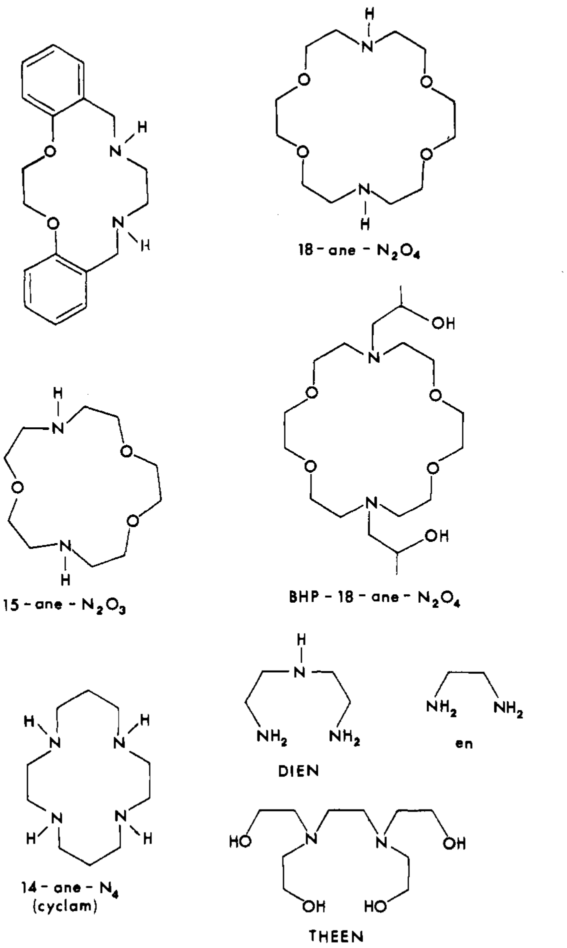

Figure 1. Structures of ligands discussed in this paper.

should be the mixed-donor macrocycles containing both nitrogen and oxygen donor atoms. In this regard Lindoy and co-workers[1] have studied the complexing properties of ligands such as I (Figure 1). Many interesting properties have been found for the complexes of these ligands, but they have no noncyclic analogues, and the presence of benzo groups makes comparison with macrocycles such as 14-aneN$_4$ (Figure 1) difficult. Larger macrocycles such as 18-crown-6 have had O-donors replaced with N-donors, and their complexing properties investigated,[2,3] as has also been done for 15-crown-5.[4] These ligands, 15-ane-N$_2$O$_3$ and 18-aneN$_2$O$_4$, showed low affinity for metal ions such as Cu(II), Ni(II), and Zn(II), lower than for any open-chain ligand of comparable structure. However, the cavities in such large macrocycles are too large for efficient coordination to such small metal ions. There are two short reports on the coordinating properties of 12-ane-(1,7)N$_2$O$_2$,[5] and we have previously reported in communication form those of the ligands 9-aneN$_2$O,[6] 13-aneN$_3$O,[7] and 13-aneN$_2$O$_2$.[8]

What is clearly needed is a study on ligands of this type, i.e. nitrogen–oxygen mixed-donor macrocycles of a size suitable for coordinating to the transition-metal ions, supplemented by studies on the open-chain analogues where necessary. At the same time the study should not be restricted to the metal ions that are traditionally included in studies of amine ligands, namely Cu(II), Ni(II), Cd(II), and Zn(II). We have included here Pb(II) as a representative of metal ions that complex well with oxygen-donor macrocycles, as well as some results on Ca(II) and Hg(II). The Ca(II) ion is of particular interest, since it has not been reported before as complexing to tetraaza macrocyclic ligands. We have expanded the number of ligands to include 12-aneN$_4$, 12-aneN$_3$O, and 12-ane(1,4)N$_2$O$_2$ and have performed as well some studies on the open-chain mixed-donor ligands HEEN, ODEN, and DHEEN.

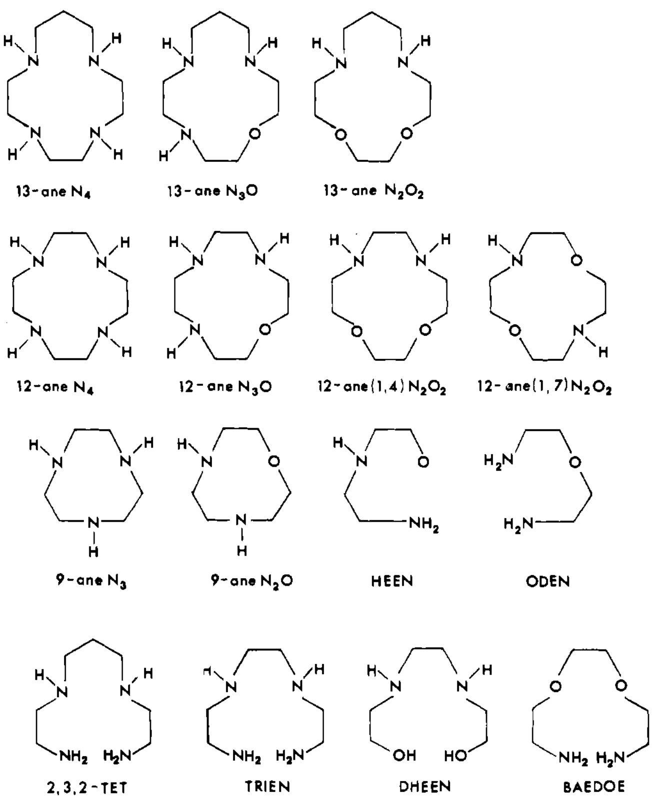

Figure 2. Structures of the oxygen–nitrogen mixed-donor macrocycles reported in this paper, together with those of their all-nitrogen-donor macrocyclic analogues and those of their open-chain analogues.

Experimental Section

Materials. The metal ion solutions used in the stability constant studies were prepared from AR nitrate salts. The ligand 12-aneN$_4$ was obtained from Parish Chemicals as the tetrahydrochloride salt. The ligands 12-aneN$_3$O and 12-ane(1,4)N$_2$O$_2$ were synthesized according to the method of Bühleier et al.[9] The tosylated cyclic precursors of 9-aneN$_2$O, 13-aneN$_3$O, and 13-aneN$_2$O$_2$ were prepared as described by Rasshofer, Wehner, and Vögtle.[10] These compounds were detosylated as described below.

1-Oxa-4,7-diazacyclononane. The cyclic ditosylate was first hydrolyzed in hot concentrated sulfuric acid,[9] but the ligand was obtained in low yield and in an impure state. A superior method is based on that of Koyama and Yoshino.[11] A solution containing 4.0 g (9 mmol) of *N*,*N'*-bis(*p*-tolylsulfonyl)-1-oxa-4,7-diazacyclononane in 200 mL of a 30% HBr/acetic acid mixture was heated under reflux with stirring for 48 h. The solution was filtered through glass wool while hot and concentrated under reduced pressure to 20 mL, and then 200 mL of a 1:1 ether/ethanol mixture was added. Finally, 2.41 g (92% yield) of the amine hydrobromide precipitated on standing, which was recrystallized from ethanol; mp 198–199 °C. Anal. Calcd for $C_6H_{16}N_2OBr_2$: C, 24.68; H, 5.52; N, 9.59. Found: C, 24.7; H, 5.4; N, 9.6. The ^{1}H NMR spectrum in D_2O gave the following resonances: 3.53 (4 H, m, CH_2O), 3.78 (4 H, s, NH-C*H*$_2$-C*H*$_2$-NH), 4.06 (4 H, m, NH-C*H*$_2$-CH$_2$-O) ppm.

1-Oxa-4,7,11-triazacyclotridecane. The tritosylated precursor was detosylated as for 9-aneN$_2$O above. The trihydrobromide salt obtained

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Table I. Values of the Protonation Constants of Nitrogen–Oxygen Mixed-Donor Macrocycles[a]

ligand[b]	log K_1	log K_2	log K_3
9-aneN_2O	9.60 (1)	5.34 (2)	
13-aneN_3O	10.35 (1)	8.64 (1)	2.78 (2)
13-aneN_2O_2	10.36 (1)	6.62 (1)	
12-aneN_3O	10.18 (1)	8.56 (2)	1.43 (5)
12-ane(1,4)N_2O_2	8.43 (3)	5.77 (3)	
12-ane(1,7)N_2O_2	9.53[c]	7.65[c]	

[a] This work, 25 °C in 0.1 M $NaNO_3$. Estimated errors (in brackets) are three times the standard deviation. The protonation constants of the ligand L, namely log K_1, log K_2, and log K_3, refer to the equilibria $L + H^+ \rightarrow LH^+$, $LH^+ + H^+ \rightarrow LH_2^{2+}$, and $LH_2^{2+} + H^+ \rightarrow LH_3^{3+}$, respectively. [b] For structures of ligands, see Figure 2. [c] Reference 5.

was recrystallized from methanol (70% yield); mp 265–275 °C dec. Anal. Calcd for $C_9H_{24}N_3OBr_3$: C, 25.1; H, 5.6; N, 9.8. Found: C, 25.4; H, 5.8; N, 9.5. The ^1H NMR spectrum in D_2O gave the following resonances: 2.26 (2 H, m, CH_2-CH_2-CH_2), 3.48 (12 H, m, CH_2NH), 3.95 (4 H, m, CH_2–O) ppm.

1,4-Dioxa-7,11-diazacyclotridecane. Attempts to detosylate the ditosylated cyclic precursor using the standard methods of sulfuric acid,[9] hydrobromic/acetic acid mixture,[11] and lithium aluminum hydride in tetrahydrofuran[9] all proved unsuccessful. An alternative method due to Klamann and Bertsch[12] was found to be satisfactory.

About 2 g (4 mmol) of *N,N'*-bis(*p*-tolylsulphonyl)-1,4-dioxa-7,11-diazacyclotridecane was added to a refluxing solution of 14 g of sodium in 200 mL of isoamyl alcohol. The solution was heated for a further 2 h and then cooled to 70 °C. Then 200 mL of water was added, and the mixture was allowed to cool to room temperature. The organic phase was washed with water, and the alcohol was removed under reduced pressure. The residue was distilled under vacuum to given an oil, which solidified on standing at 0 °C. The ligand was purified by forming the dihydrochloride salt by precipitation with HCl gas from ether. The dihydrochloride salt was recrystallized from a water/ethanol mixture (45% recrystallized yield); mp 266 °C. Anal. Calcd for $C_9H_{22}N_2O_2Cl_2$: C, 41.38; H, 8.49; N, 10.73. Found: C, 41.8; H, 8.3; N, 10.8. The ^1H NMR spectrum in D_2O gave the following resonances: 2.19 (2 H, m, CH_2-CH_2-CH_2), 3.35 (8 H, m, CH_2-NH) 3.80 (8 H, m, CH_2O) ppm.

The ligands DHEEN and the dihydrochloride salt of ODEN were purchased from Aldrich, while HEEN was obtained from BDH.

Instrumentation. Electronic spectra were recorded on a Varian Cary 2300 spectrophotometer with cells thermostated to 25 °C. NMR spectra were recorded on a Bruker WP80. Melting points were determined on a Reichert hot-stage microscope and are uncorrected.

Determination of Stability Constants. These were determined as described previously[13] at 25 °C in 0.1 M $NaNO_3$, by using glass electrode potentiometry. Formation constants were calculated from the potentiometric data by using the program EQUILIBRIA[14] and MINIQUAD.[15]

Results and Discussion

The formation constants determined in this study, together with literature values required for discussion, are seen in Table I. Some important effects are discernible in these results, as discussed below.

1. Effect of Added Oxygen Donor Groups That Are Not Part of a Macrocyclic Ring. In Figure 3a is shown the effect on complex stability of successive addition of *N*-hydroxyethyl groups to en to give the ligands HEEN, DHEEN, and THEEN. In Figure 3b is shown the effect on complex stability of adding increasing numbers of ether donors in the bridging group between the two carboxylates in the series of ligands oxalate through TTDA (TTDA is triethylenetetraoxydiacetate, with $n = 4$ in Figure 3b. It is seen that there is a strong tendency for large metal ions such as Ba^{2+}, Pb^{2+}, and Cd^{2+} to show increasing complex stability as more and more neutral oxygen donors are added, whereas smaller metal ions such as Cu^{2+}, Zn^{2+}, and Mg^{2+} show decreases in complex stability. It should be noted that the correlation appears to be mainly with metal ion size. For example, the behavior of

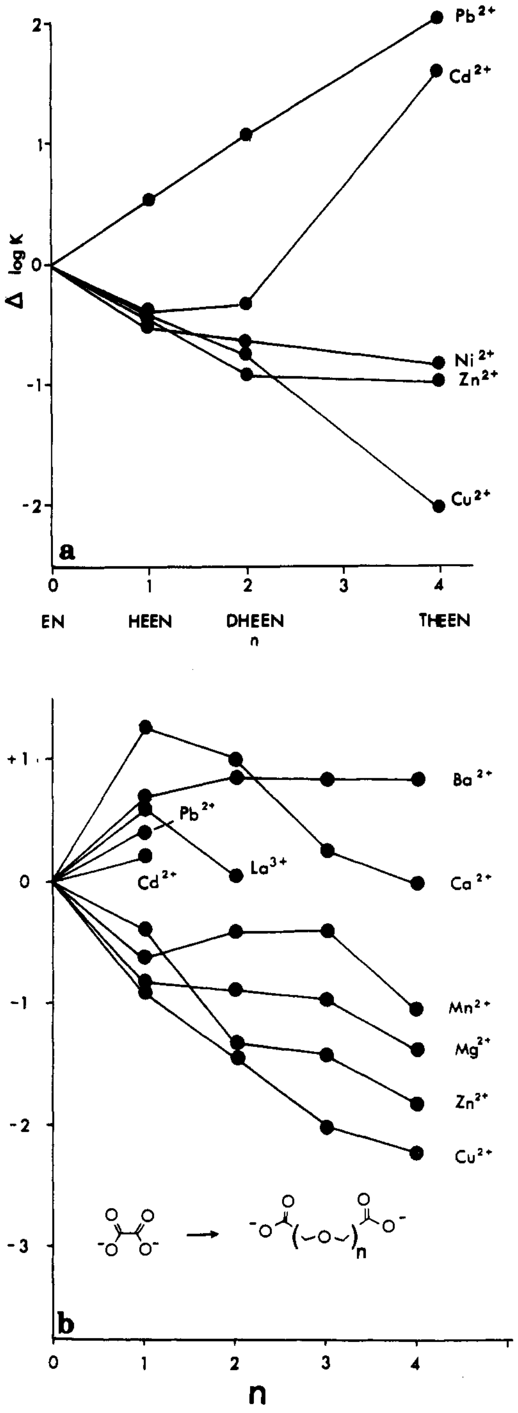

Figure 3. (a) Effect on complex stability of added hydroxyethyl groups. The vertical axis is the value of Δ(log K), i.e. the change in the value of log K_1 relative to that for the en complex, as hydroxyethyl groups are added to en to give, successively, HEEN, DHEEN, and THEEN. The horizontal axis shows the number of hydroxyethyl groups (n) added to en ($n = 0$) to give HEEN ($n = 1$), DHEEN ($n = 2$), and THEEN ($n = 4$). The point for Pb^{2+} with THEEN is actually estimated from that for the closely similar *N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine.[17] For meanings of abbreviations, see Figures 1 and 2. (b) Effect on complex stability of ethereal groups inserted between the carboxylates of oxalate. The vertical axis shows Δ(log *K*), the change in log K_1 for the formation of the polyether dicarboxylic acid relative to log K_1 for the oxalate complex of the metal ion shown. The horizontal axis shows the value of n, which is the number of ethereal oxygens in the bridging group between the two carboxylates of the ligand. The structures of oxalate and its polyether derivatives are shown on the diagram, where n indicates the number of ether donor atoms on the ligand. Formation constant data are from ref 40. Ionic radii[34] for the metal ions shown are as follows: Cu^{2+}, 0.62; Zn^{2+}, 0.74; Mg^{2+}, 0.72; Mn^{2+}, 0.83; Cd^{2+}, 0.95; Ca^{2+}, 1.00; La^{3+}, 1.03; Pb^{2+}, 1.18; Ba^{2+}, 1.36 Å.

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Table II. Values of Formation Constants of Nitrogen-Donor and Mixed-Donor Macrocycles and Open-Chain Ligands[a]

ligand		Cu(II)	Ni(II)	Zn(II)	Cd(II)	Hg(II)	Pb(II)	Ca(II)
9-aneN_3	log K_1	15.5[b]	16.2[b]	11.6[b]	9.4[b]		11.0[b]	
DIEN	log K_1	15.9[b]	10.5[b]	8.8[b]	8.3[b]		7.56[c]	
	log K_2	5.0[b]	8.1[b]	5.5[b]	5.8[b]			
9-aneN_2O	log K_1	10.86 (8)	8.49 (2)	6.36 (1)	4.48 (2)		5.17 (2)	
	log K_2	8.68 (2)	7.2 (1)	5.07 (1)	3.40 (2)			
HEEN	log K_1	10.09[b]	6.82[b]	5.28 (3)	5.02 (1)		5.58 (1)	
	log K_2	7.53 [b]	5.62[b]	4.79 (2)	4.17 (1)			
ODEN	log K_1	8.70[b]	5.62[b]	5.74[b]	5.27 (1)		6.10 (3)	
	log K_2	4.4[b]	3.39[b]	4.12[b]	4.06 (1)			
13-aneN_4	log K_1	24.41[d]	17.98[e]	15.6[b]	12.71[d]	25.3[b]	13.48[d]	
13-aneN_3O	log K_1	16.92 (1)	11.90 (2)	9.90 (2)	9.09 (1)	18.05 (2)	8.68 (1)	
13-aneN_2O_2	log K_1	8.39 (2)	5.83 (2)	4.89 (1)	5.40 (1)	13.30 (1)	5.70 (3)	
12-aneN_4	log K_1	23.29[d]	16.4[e]	16.2[b]	14.3[d]	25.5[b]	15.9[d]	3.1 (1)
12-aneN_3O	log K_1	15.85 (2)	12.15 (5)	10.53 (1)	10.78 (1)		11.54 (1)	2.3 (1)
12-ane(1,4)N_2O_2	log K_1	8.7 (1)[f]	5.0 (1)[f]				6.3 (1)[f]	
12-ane(1,7)N_2O_2	log K_1	7.92[g]	6.73[g]	6.51[g]	6.55[g]		6.37[g]	
2,3,2-tet	log K_1	23.2[b]	16.0[b]	12.6[b]	11.1[b]	22.1[b]	7.8[b]	
TRIEN	log K_1	20.1[b]	14.0[b]	12.0[b]	10.6[b]	24.8[b]	10.35[c]	
en	log K_1	10.50[b]	7.31[b]	5.7[b]	5.4[b]	14.3[b]	5.04[c]	
DHEEN	log K_1	9.77[b]	6.67[b]	4.79[b]	5.07[b]	12.10 (1)	6.12 (1)	
BAEDOE	log K_1	7.89[b]			5.68[b]	18.55[b]		
THEEN	log K_1	8.49[b]	6.5[b]	4.74[b]	7.04[b]		(7.2)[h]	

[a] Where no reference has been given, the values are from this work at 25 °C in 0.1 M $NaNO_3$. Estimated errors (in brackets) are three times the standard deviation given by the program. For the meaning of abbreviations and structures of ligands, see Figures 1 and 2. [b] Reference 40. [c] Reference 37. [d] Reference 41. [e] Reference 45. [f] Somewhat unreliable because of the low solubility of the ligand. [g] Reference 5b. [h] Estimated from the stability[17] of the rather similar *N,N,N′,N′*-tetrakis(2-hydroxypropyl)ethylenediamine.

the metal ions does not show any correlation with "hard and soft" acid character—the large ions Ba^{2+}, Pb^{2+}, and Cd^{2+}, are respectively hard, intermediate, and soft in character. A similar result has recently been found[17] where 2-hydroxypropyl groups were added to the nitrogens of 18-ane-N_2O_4 to give the ligand BHP-18-ane-N_2O_4 (Figure 1). Here large metal ions such as Pb^{2+}, La^{3+}, Ba^{2+} and Sr^{2+} showed a strong increase in log K_1 for BHP-18-ane-N_2O_4 relative to 18-ane-N_2O_4, whereas small metal ions such as Cu^{2+} or Zn^{2+} showed a decrease. These results are of interest in relation to the current interest in macrocyclic ligands bearing hydroxyalkyl groups,[18-21] such as the "lariat ethers" of Gokel et al.[18] Parts a and b of Figure 3 show some erratic behavior at low degrees of substitution with neutral oxygen donors. As pointed out by a referee, Cd^{2+} in Figure 3a shows an initial decrease in complex stability as hydroxyethyl groups are added, before registering a strong increase, while Ca^{2+} in Figure 3b initially shows a surprisingly strong increase in complex stability for its size. As will be discussed in a future paper, this behavior is not random, and it appears to reflect the balance between steric and inductive effects produced on adding the groups bearing neutral oxygen donors.

If we consider the origins of the chelate effect,[22,23] it is not clear why the addition of groups bearing neutral oxygen donors to existing ligands should lead to complex stabilization. From Adamson's proposals[22] regarding the asymmetry of the standard reference state, we should expect[23] a contribution of log 55.5 to the formation constant from each chelate ring formed on complexation. However, the neutral oxygen donor group is a special case. In the usual standard reference state the water, which is both solvent and ligand, is given an activity of unity, although its concentration is in fact 55.5 M. The concentration of any ligand other than water is in the usual standard state a 1 M solution in water, so that all else being equal, because there is 55.5 times as much water as any other ligand, we would expect the water to bind 55.5 times as strongly. In line with this, log K_1 for methanol with Cu^{2+} is −1.48, in reasonable agreement with log 1/55.5, which is −1.74. The log 55.5 contribution to the stability of a ligand bearing a hydroxyalkyl group, derived from the chelate effect,[22,23] should thus be nullified by the fact that the solvent water, which is formally the unidentate analogue of the hydroxyalkyl group, is present in a 55.5 times excess.

Table III. Change in Complex Stability of Polyamine Ligands Produced by Adding an Ethereal Oxygen Donor To Form a Macrocyclic Ring[a]

	log K_1			log K_1			
metal ion	DIEN	12-aneN_3O	Δ-(log *K*)[b]	en	12-aneN_2O_2	Δ-(log *K*)[c]	r^+[d]
Cu^{2+}	15.9	15.95	−0.05	10.50	8.66[e]	−1.84	0.62
Ni^{2+}	10.5	12.15	+1.65	7.31	5.91[e]	−1.40	0.70
Zn^{2+}	8.8	10.53	+1.73	5.7	6.22[e]	+0.52	0.74
Cd^{2+}	8.3	10.78	+2.48	5.4	6.55[e]	+1.15	0.95
Pb^{2+}	7.6	11.54	+3.94	5.04	6.34[e]	+1.30	1.18

[a] Data taken from Table II. [b] The stability difference, Δ(log *K*), is effectively log *K* for the reaction $M(DIEN)^{2+} + 12\text{-aneN}_3O \rightarrow M(12\text{-aneN}_3O)^{2+} + DIEN$. [c] Δ(log *K*) here is log *K* for the reaction $M(en)^{2+} + 12\text{-aneN}_2O_2 \rightarrow M(12\text{-aneN}_2O_2)^{2+} + en$. [d] Ionic radii are taken from ref 34 and are for octahedral coordination, except for Cu^{2+}, which is square-planar. Units are given in Å. [e] For the 1,7-dioxa isomer (ref 5b) except for Pb^{2+} and Cu^{2+}, for which data on the 1,4-isomer are available.

The important factor here is that water and alcohols are not inherently equally strong bases. Results in the gas phase[24-27] indicate a strongly increasing order of basicity $H_2O < ROH < R_2O$ (R = alkyl) both toward the proton and toward metal ions. From this we would expect all metal ions to show an increase in complex stability when hydroxyalkyl groups, or groups bearing ethereal oxygens, are added to an existing ligand. All our work to date shows that generally only large metal ions show such an increase in complex stability. The most reasonable explanation for this is that for small metal ions, the increase in steric strain,

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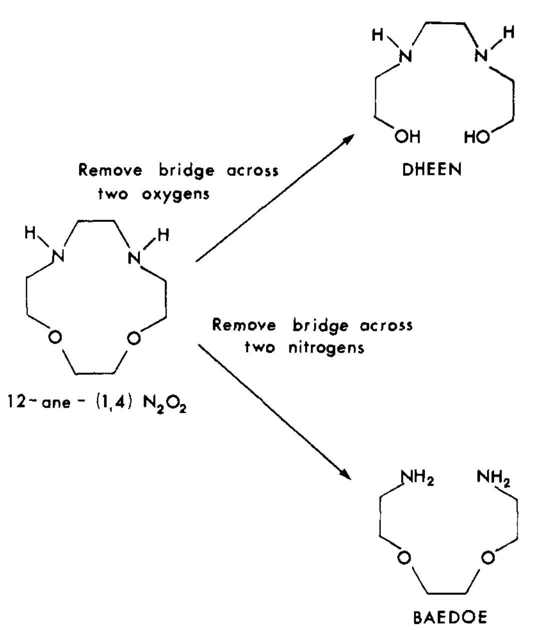

Figure 4. Two possible open-chain analogues for 12-ane(1,4)N_2O_2 created by removing an ethylene bridge across two oxygens (DHEEN) or two nitrogens (BAEDOE).

which normally accompanies complex formation,[28-30] outweighs any benefits from greater donor strength in passing from water to a hydroxyalkyl chelating group. This would relate to greater steric crowding around a small metal ion, as well as the higher strain resulting from distorting the coordination polyhedron of small metal ions, which generally have more covalent, and hence more directional, bonding than is the case for the larger, more ionically bound metal ions. The observations on the effect on complex stability of the addition of hydroxyalkyl groups should apply equally well to ethereal oxygen donors, which may be present in crown ethers[31,32] or cryptands.[33] In these cyclic types of ligands there appear also to be effects on the complex stability that derive from the presence of a macrocyclic ring, in addition to those deriving from the fact that the ethereal oxygen is a stronger donor than water.

2. Effect of Addition of Oxygen Donors That Are Part of a Macrocyclic Ring. Just as we regard THEEN as being a derivative of en, so we can regard 12-ane-N_2O_2 as being derived from en, or 12-ane-N_3O from DIEN. If we examine the changes in complex stability produced in passing from DIEN to 12-ane-N_3O as ligand, we see a size-dependent stability change, $\Delta(\log K)$, in Table III. The difference in complex stability, $\Delta(\log K)$, between the DIEN and the 12-ane-N_3O complex increases with increasing size of metal ion, as does $\Delta(\log K)$ for the en and 12-aneN_2O_2 complexes. This type of size-dependent increase in $\Delta(\log K)$ appears to be general for polyamines on adding an ethereal group to form a macrocyclic ring. Good relationships between $\Delta(\log K)$ and r^+, the ionic radii[34] of the metal ions, are virtually always observed for such changes. An exception appears to be the Hg^{2+} ion, where the overriding factor in complex stability with polyamine ligands appears to be whether the Hg^{2+} ion can achieve the favored linear coordination geometry or not, so that a correspondence between $\Delta(\log K)$ and the size of the Hg^{2+} ion is usually not observed. The very large $\Delta(\log K)$ between the Hg^{2+} complexes of DHEEN and BAEDOE seen in Table II can be understood in this way. The ligand 9-aneN_2O is also unusual in that the greatest stabilization relative to the en complexes is observed for small metal ions. This might relate to the conformation of the 9-membered ring of 9-aneN_2O favoring coordination to an octahedral face of a small metal ion rather than a large metal ion. In support of this, molecular mechanics calculations show[35] that the best size metal ion for fitting into the analogous 9-aneN_3 complexes has a metal to nitrogen bond length of 2.1 Å, or an ionic radius of about 0.7 Å.

Table IV. Change in Complex Stability Produced on Changing from a Primary to a Secondary Nitrogen Donor for a Variety of Metal Ions[a]

params	metal ion				
	Cu^{2+}	Ni^{2+}	Cd^{2+}	Zn^{2+}	Pb^{2+}
$\log K_1$(HEEN)[b]	10.09	6.82	5.28	5.28	5.58
$\log K_1$(ODEN)[b]	8.70	5.62	5.27	5.74	6.10
$\Delta(\log K)$[c]	−1.39	−1.20	−0.01	+0.46	+0.52
$\log K_1(NH_3)$[d]	4.1	2.70	2.65	2.18	1.60
H_A[e]	2.68	3.37	3.31	4.26	6.69

[a] $\log K_1$ values were taken from Table II. [b] For the structure of ligands, see Figure 1. [c] $\Delta(\log K)$ is effectively $\log K$ for the equilibrium $M(HEEN)^{2+}$ + ODEN → $M(ODEN)^{2+}$ + HEEN. [d] From ref 40. [e] From ref 36.

3. Relative Donor Strength of Primary vs. Secondary Amines and of Alcohols vs. Ethers. With the mixed-donor macrocycles, to decide whether a macrocyclic effect exists, we have the problem of which ethylene bridge to remove in order to generate an open-chain analogue. As seen in Figure 4, we can either remove an ethylene bridge that links two oxygen donors from 12-ane-(1,4)N_2O_2, to give DHEEN as an open-chain analogue, or remove an ethylene bridge that links two nitrogens, to give BAEDOE as an open-chain analogue. (The third possibility, which is to remove a bridge linking one oxygen and one nitrogen from 12-ane-(1,4)N_2O_2, would complicate matters in that we would not be able to factor out the two effects, i.e. bridging across nitrogens or bridging across oxygens.) Which bridge to remove is not a trivial point, as we have shown[30] that whether a nitrogen donor is primary or secondary will strongly affect its ability to coordinate to metal ions. This is best illustrated with the pair of ligands HEEN and ODEN, in Table IV. The ligand HEEN has one primary and one secondary nitrogen where ODEN has two primary nitrogens. At the same time HEEN has an alcoholic oxygen where ODEN has an ethereal. The value of $\Delta(\log K)$ in passing from the HEEN to the ODEN complex should thus be a measure of the relative preference for bonding to a secondary nitrogen plus an alcoholic oxygen, as against a primary nitrogen plus an ethereal oxygen. It is thus a measure of whether the metal ion responds better to the increased inductive effect of the change in donor from RXH to R_2X where X is an NH or O donor. As one might expect, the value of $\Delta(\log K)$ reflects the covalence of the metal ion–ligand bonding, with more covalently bound metal ions such as Cu^{2+} showing a negative value of $\Delta(\log K)$, reflecting the better response to inductive effects on nitrogen than oxygen. The positive value of $\Delta(\log K)$ for Pb^{2+} indicates a better response to oxygen, in line with its more ionic bonding. Table IV shows a reasonably good correspondence between $\Delta(\log K)$ and the parameter H_A, which has been derived[36] as a measure of the ionic vs. covalent nature of the metal–ligand bond. One should of course consider that the neutral oxygens in HEEN and ODEN might not be coordinated to the metal ions under consideration, which would invalidate the above conclusions. However, the HEEN complexes, at least, are

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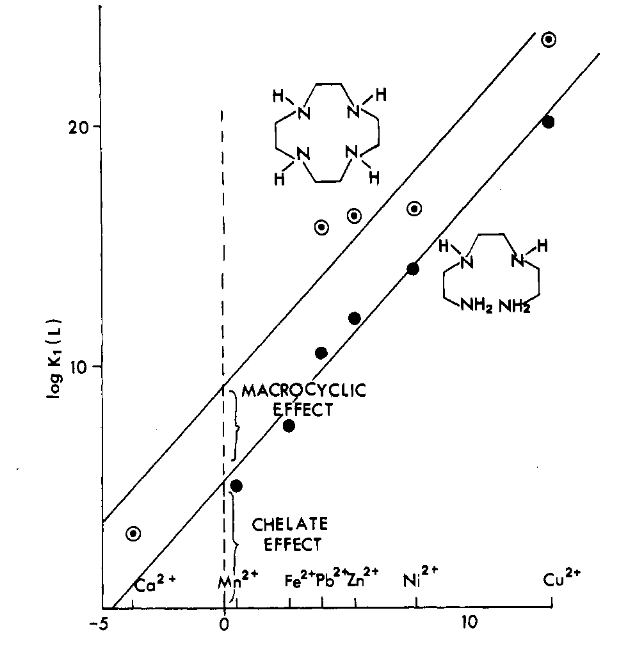

Figure 5. Relationship between log K_1, the formation constant for 12-aneN_4 (⊙) or trien (●) complexes, and log β_4 for the ammonia complexes. The values of log $\beta_4(NH_3)$ for each metal ion indicated on the x axis of the diagram was either taken from ref 40 or estimated as described in the text. The value of log $\beta_4(NH_3)$ is thus a measure of how strongly the metal ion binds four unidentate nitrogen donor ligands. The intercept at log $\beta_4(NH_3) = 0$ is thus for the TRIEN complexes a measure of the chelate effect, since it indicates how strongly a metal ion will bind to the tetradentate TRIEN ligand when the metal ion has a zero free energy change on complex formation with four similar nitrogen donors that are not held together in a single chelating ligand. In agreement with ideas[22,23] on the chelate effect, this intercept has a value very close to 3 log 55.5. The further increase in this same intercept for the ligand 12-aneN_4 is similarly a measure of the macrocylic effect.

of higher complex stability than those of *N*-ethylethylenediamine,[40] which suggests that the alcoholic oxygen is coordinated and the crystal structure of the $[Ni(HEEN)_2]^{2+}$ complex shows the oxygens to be coordinated.[14] If the ethereal oxygens of the ODEN complexes were not coordinated, this would be equivalent to a very large chelate ring, and experience here suggests that such eight-membered chelate rings would be unlikely to give complexes only slightly less stable than for analogous en complexes.

4. Stability of Complexes of Nitrogen-Donor Macrocycles. The Ca^{2+} ion has a low affinity for nitrogen-donor ligands,[37] as evidenced by its value of log K_1 with ammonia of −0.2 log units.[40] We might thus expect that the stability of the complex of 12-aneN_4 would also be low. However, a considerable portion of the macrocyclic effect is thought to arise from effects within the ligand, such as the proposal of Margerum et al.[38] concerning the role of desolvation of the dipoles on the nitrogens within the cavity of the macrocycle, or from the macrocycle being "preoriented",[39] or "prestrained".[28] These effects appear to contribute some four or five log units to the stabilization of the complexes of macrocycles as compared with open-chain ligands, which should also accrue to the complexes of metal ions such as Ca^{2+} with macrocycles. Thus, Ca^{2+} should complex quite strongly with a ligand such as 12-aneN_4, in spite of the generally poor complexing ability of Ca^{2+} with nitrogen-donor ligands. This result can be analyzed graphically, as can be seen in Figure 5. Here log K_1 for the 12-aneN_4 complexes, as well as for TRIEN complexes, has been plotted against log β_4 for the ammonia complexes. (For metal ions for which only log $K_1(NH_3)$ was available, log $\beta_4(NH_3)$ was calculated from 4 log $K_1(NH_3) - 6\lambda$, where λ is the stepwise decrease in log K_n with increasing n and has the value 0.5[23].) If there were no chelate effect, we would expect the relationship for log K_1(TRIEN) to pass through the origin of the diagram at log $\beta_4(NH_3) = 0$. The actual relationship for log K_1(TRIEN) vs. log $\beta_4(NH_3)$ has an intercept at log $\beta_4(NH_3)$ equals zero of about 5 log units on the vertical axis. This is shown as the "chelate effect" in Figure 5 and is close to the value expected for a tetradentate ligand[22,23] of 3 log 55.5, i.e. 5.22 log units. The relationship for 12-aneN_4 runs roughly parallel to that for TRIEN, but has an intercept some 3–4 log units higher than for TRIEN, which is an average value for the macrocyclic effect. This diagram then suggests that virtually all of the stability of the Ca^{2+} complex of 12-aneN_4, with log K_1 = 3.1, derives from the "macrocyclic effect" and supports the idea that the macrocyclic effect is derived from ligand-related effects[28,38,39] to a large extent.

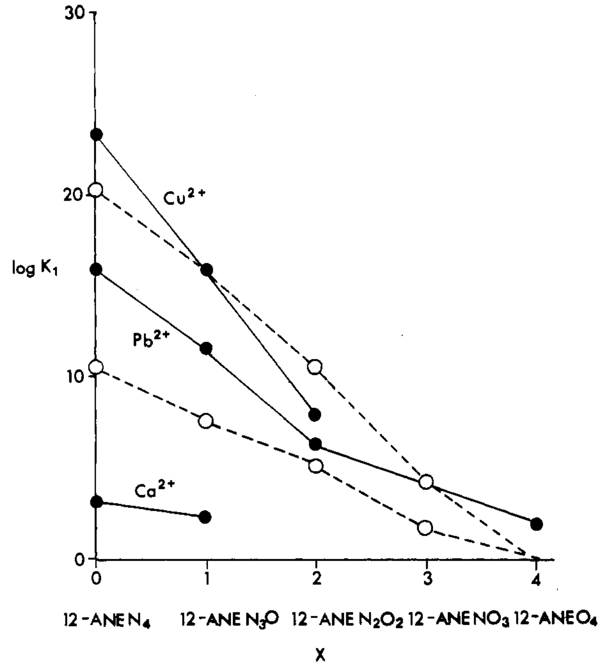

Figure 6. Effect on complex stability of substituting nitrogen donors with oxygen donors in 12-ane$N_{4-x}O_x$ macrocycles. The number of N donors replaced by oxygens is given by x on the horizontal axis, while log K_1 for the complexes is given on the vertical axis. The filled circles (●) are for the 12-aneN_4 to 12-aneO_4 series, while the open circles (○) are for the open-chain series from TRIEN to ammonia. The absence of points for the Ca^{2+} ion beyond 12-aneN_4 and 12-aneN_3O is due to the difficulty of determining the constants of such weak complexes when the ligands are of such low solubility in water.

5. Effect on Complex Stability of Replacing Nitrogen with Oxygen Donors in Macrocyclic Ligands. In Figure 6 is seen a plot of stability of complexes of 12-ane$N_{(4-x)}O_x$ macrocycles of Cu^{2+}, Pb^{2+}, and Ca^{2+} as a function of x, the number of N donors, which are replaced by O donors to give the series of ligands 12-aneN_4, 12-aneN_3O, 12-aneN_2O_2, 12-aneNO_3, and 12-aneO_4. Also shown is the variation in log K, as the number of nitrogen donors is reduced along the series TRIEN, DIEN, en, and ammonia. Including the metal ions not shown on Figure 6 for the sake of clarity, the rate of fall-off in stability along the series 12-aneN_4 through 12-aneN_2O_2 is roughly in line with what would be expected from the affinity of the metal ions for a ligand such as ammonia.

If we look at Pb^{2+} and Cu^{2+} in Figure 6, we see that the Pb^{2+} points for the macrocycles lie much higher above the points for the series of open-chain ligands TRIEN through ammonia than is the case for Cu^{2+}. This probably reflects the greater tolerance of Pb^{2+} to steric demands than is the case for Cu^{2+}. If we consider the macrocyclic effect for O donors as compared with N-donor macrocycles, it seems clear that a major requisite in both cases is tolerance of the steric requirements of the ligand. We thus find that a large ionically bound metal ion such as Pb(II) with largely

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Table V. Macrocyclic Effect in Comparable Nitrogen-Donor and Mixed-Donor Systems

All-Nitrogen System

	log K_1[a]		log K(MAC)[c]	log K_1[a]		log K(MAC)
	9-aneN_3[b]	DIEN		13-aneN_4	TRIEN	
Cu^{2+}	15.5	15.9	−0.4	24.41	20.1	+4.3
Ni^{2+}	16.2	10.5	+5.7	17.98	14.0	+3.98
Zn^{2+}	11.6	8.8	+2.8	15.60	12.0	+3.60
Cd^{2+}	9.4	8.3	+1.1	12.71	10.6	+2.11
Pb^{2+}	11.0 (?)	7.6	+3.4 (?)	13.48	10.4	+3.08

Mixed-Donor System

	log K_2		log K(MAC)	log K_2		log K(MAC)
	9-aneN_2O	ODEN		13-aneN_2O_2	BAEDOE	
Cu^{2+}	10.86	8.70	+2.1	8.39	7.89	+0.60
Ni^{2+}	8.49	5.62	+2.87	5.83	(6.67)[d]	(−0.84)
Zn^{2+}	6.36	5.74	+0.62	4.89	(4.79)[d]	(+0.10)
Cd^{2+}	4.48	5.27	−0.79	5.40	5.68	−0.28
Pb^{2+}	5.17	6.10	−0.93	5.70	(6.12)[d]	(−0.42)

[a] From ref 40. [b] For ligand abbreviations, see Figure 2. [c] The thermodynamic manifestation of the macrocyclic effect, log K(MAC), is the difference in log K_1 for the macrocyclic ligand and its open-chain analogue. [d] Figures in parentheses are actually for DHEEN.

nondirectional M–L bonds displays a larger macrocyclic effect with both N-donor and O-donor macrocycles than is found for Cu(II) with its more covalent and directional M–L bonds. Thus, in general, large metal ions such as Pb^{2+} or Ca^{2+} are well complexed by both nitrogen- and oxygen-donor ligands, whereas small metal ions such as Zn^{2+} or Cu^{2+} show decreased stability in the presence of oxygen-donor atoms, whether these are part of a macrocyclic ring or are alcoholic or ethereal oxygens not part of a macrocyclic ring.

Table V contains values of log K(MAC), the thermodynamic measure of the macrocyclic effect, for pairs of nitrogen-donor ligands, e.g. 13-aneN_4 and TRIEN (log K(MAC) = log K_1(13-aneN_4) − log K_1(TRIEN)), and analogous pairs of mixed-donor ligands, e.g. 13-aneN_2O_2 and BAEDOE. It is seen that log K(MAC) is generally about 3 log units for the all-nitrogen-donor ligands, whereas it is small or even negative for most metal ions with the mixed-donor ligand pairs. It should be noted here that a large metal ion such as Pb^{2+} does not display an enhanced macrocyclic effect with the mixed-donor macrocycle. For Pb^{2+} the increase in stability of the macrocyclic complex caused by the tolerance of the metal ion to steric strain is matched by the increase in stability of the complex of the open-chain analogue, which has an exactly parallel need for tolerance to the strain caused by its own O donors.

For both the open-chain ligands DIEN and ODEN, or both TRIEN and BAEDOE, bridging occurs across two primary nitrogens to create two extra secondary nitrogens in the macrocyclic analogue. The inductive effect contributions of secondary relative to primary nitrogens[35] can thus not be invoked to account for the falloff in the macrocyclic effect as nitrogens are replaced by oxygens. The most plausible explanation[6] for this would seem to be in terms of the steric hindrance to solvation proposal of Margerum.[38] If solvation of the nitrogen donors with their extra N–H hydrogen atom is stronger than is the case for ethereal oxygens, then the steric hindrance caused by cyclization is a less important contribution to the macrocyclic effect for macrocycles containing oxygen donors.

In addition to the tolerance of the metal ion to M–L bond deformation, pointed out above, principal contributions to the macrocyclic effect appear to be (1) the increased inductive effects of the secondary nitrogen donors formed by cyclization, which is not offset by a high-strain situation as is the case for open-chain N-donor ligands and (2) the high-energy state of the macrocyclic ligand, which is released on complex formation. The high-energy state may be caused by steric hindrance to solvation,[38] as well as electrostatic repulsion between the lone pairs on the nitrogen donors[6] forced into close proximity in the macrocyclic cavity. For oxygen-donor macrocycles the important contribution appears to be the ability of the metal ion to complex with only a small increase in steric strain. Steric hindrance to solvation effects appear to be unimportant for O donors, and inductive-effect contributions for O donors are smaller than those for N donors and are easily overwhelmed by adverse strain effects. The implication of the above arguments is that Pb^{2+} should always have a larger log K(MAC), because of the low steric strain present in its complexes. This appears to be true for the data that are available for the N-donor macrocycles, as seen in Table VI, and for oxygen-donor macrocycles it appears to be true in that only large metal ions forming low-strain complexes can coordinate well to the crown ethers. However, the magnitude of the macrocyclic effect will also depend on the fit of the metal ion into the cavity of the macrocycle, and we may find with ligands such as 9-ane-N_2O, which prefer small metal ions, that (Table V) large metal ions such as Pb^{2+} show the smallest macrocyclic effect.

Table VI. Macrocyclic Effect in Complexes of Nitrogen-donor Macrocycles[a]

ligand[b]	Cu^{2+}	Ni^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
log K_1(2,3,2-tet)[c]	23.2	16.4	12.6	11.1	7.80
log K_1(13-ane-N_4)[c]	24.4	18.0	15.6	12.7	13.48
log K(MAC)	1.2	1.6	3.0	1.6	5.68
log K_1(TRIEN)[c]	20.1	14.0	12.0	10.6	10.4
log K_1(12-ane-N_4)[c]	23.3	16.4	16.2	14.3	15.9
log K(MAC)	3.2	2.4	4.2	3.7	5.5

[a] The macrocyclic effect, log K(MAC), is log K_1 for the macrocyclic complex (e.g. 13-ane-N_4) minus log K_1 for the open-chain complex (e.g. 2,3,2,tet). [b] For structures of ligands, see Figure 2. [c] log K_1 values from ref 40, 41, and 45.

6. Effect of Cavity Size on the Stability of Complexes Formed by Oxygen–Nitrogen Mixed-Donor Macrocycles. Molecular mechanics calculations[35,42] indicate that the cavity sizes of the tetraaza macrocycles decrease 14-ane-N_4 > 13-aneN_4 > 12-aneN_4 when the metal ions are constrained to lie in the plane of the four nitrogen-donor atoms. However, the ligand may adopt different conformers that allow coordination out of the plane of the nitrogen donors,[43] with the interesting result that the ability of the ligands to accommodate large metal ions is 12-aneN_4 > 13-aneN_4 > 14-aneN_4.[41,43] We were interested to see whether the same result would be obtained for 12-aneN_3O vs. 13-aneN_3O. In Figure 7 is shown Δ(log K_1), which is the difference in log K values between that of the 12-aneN_3O complex and that of the 13-aneN_3O complex, plotted as a function of ionic radius[34] of the metal ion. It is seen that, as with the all-nitrogen-donor analogues, the larger

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(42) Martin, L. Y.; DeHayes, L. J.; Zompa, L. J.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 4047–4048.

(43) Thöm, V. J.; Fox, C. C.; Boeyens, J. C. A.; Hancock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 5947–5955.

Table VII. Electronic Absorption Maxima and Ligand Field Parameters, 10*Dq*, of Ni(II) Complexes

complex	band maxima, cm^{-1}				10*Dq*,[a] cm^{-1}
$[Ni(9\text{-}aneN_3)_2]^{2+}$					12 350[b]
$[Ni(9\text{-}aneN_2O)_2]^{2+}$	11 600	12 500	18 800	28 250	11 900
$[Ni(dien)_2]^{2+}$					11 700[b]
$[Ni(HEEN)_2]^{2+}$					11 250[b]
$[Ni(13\text{-}aneN_3O)(H_2O)_2]^{2+}$	10 800	13 140	17 150	27 320	10 810
$[Ni(13\text{-}aneN_2O_2)(H_2O)_2]^{2+}$	9 500	13 160	16 390	26 810	9 500
$[Ni(12\text{-}aneN_3O)(H_2O)_2]^{2+}$	10 850	13 140	17 240	27 170	10 850
$[Ni(DHEEN)(H_2O)_2]^{2+}$	10 160	13 480	16 450	27 170	10 160
$[Ni(ODEN)_2]^{2+}$					~10 200[c]

[a] Calculated by assuming regular octahedral coordination about the metal ion. [b] From ref 46, corrected for spin–orbit coupling. [c] Marsicano, F.; Hancock, R. D., unpublished work.

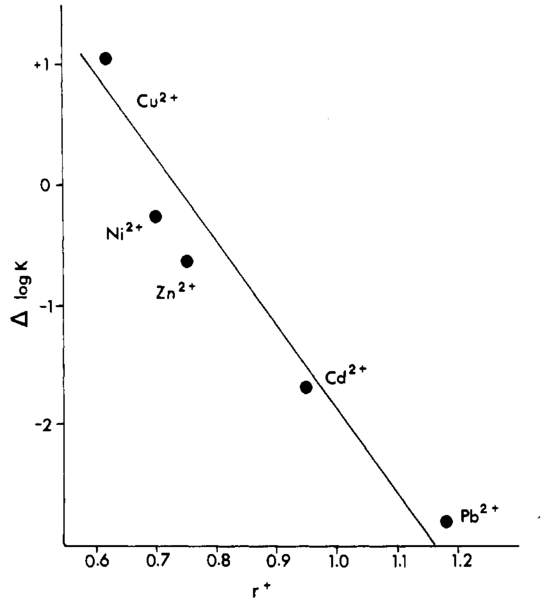

Figure 7. Effect of size of the macrocyclic ring and size of the metal ion on the stability of complexes with the mixed-donor macrocycles 12-aneN_3O and 13-aneN_3O. The vertical axis is $\Delta(\log K_1)$, the difference in log K_1 between the 12-aneN_3O and 13-aneN_3O complex, i.e. log K_1(13-aneN_3O) − log K_1(12-aneN_3O). The horizontal axis shows r^+, the ionic radius of the metal ion.[34] It is seen that as the size of the metal ion increases, so the preference for 12-aneN_3O over the larger 13-aneN_3O steadily increases.

the metal ion, the more strongly is it complexed by the smaller macrocycle, in this case 12-aneN_3O. (It was for this reason that the 12-aneN_4 and 12-aneN_3O complexes of the large metal ion Ca^{2+} were studied, rather than a possibly more obvious choice of cyclam.) This effect is not, however, to any marked extent, due to the presence of a macrocyclic ring, but is a function of the presence of five or six-membered chelate rings, and is just as strongly present in the complexes of open-chain ligands. Thus, the reader will find in inspecting Table II, that a relationship similar to that in Figure 7 is obtained in calculating Δ(log *K*) for TRIEN and 2,3,2-TET, the first of which forms a five-membered chelate ring where the second forms a six-membered chelate ring. The reason for this appears[41,43] to be the greater flexibility of the five-membered chelate ring, which allows it to increase its bite size more easily than the six-membered ring can.

7. Macrocyclic Effect on the d–d Transitions in the Electronic Spectra of Complexes of Mixed-Donor Macrocycles. A striking feature of the complexes of N-donor macrocycles with transition-metal ions is the way in which they show much higher ligand field (LF) strengths than is found for the complexes of their open-chain analogues. This has been attributed[35,44] to the greater inductive effect of secondary nitrogens as compared to primary nitrogens, without the high steric strain that normally negates the inductive effect. This is illustrated[35] by the LF splitting parameters, 10*Dq*, for the following series: $[Ni(NH_3)_6]^{2+}$, 10 750 cm^{-1}; $[Ni(en)_3]^{2+}$, 11 500 cm^{-1}; $[Ni(9\text{-}aneN_3)_2]^{2+}$, 12 350 cm^{-1}. In this series, we are steadily replacing hydrogens by alkyl groups. If this inductive effect interpretation is correct, we should see similar increases in 10*Dq* in passing from a complex such as $[Ni(ODEN)_2]^{2+}$ to $[Ni(9\text{-}ane\text{-}N_2O)_2]^{2+}$. As seen in Table VII, this expectation is borne out, showing that the presence of the oxygen donors does not affect the inductive effects produced by bridging across the two primary nitrogens of ODEN to give secondary nitrogens in 9-aneN_2O.

Folded coordination of macrocycles produces[43] higher steric strain in complexes of small metal ions, so that higher 10*Dq* values are not observed. The ligands 12-aneN_3O and 13-aneN_3O are too small to coordinate to Ni^{II} in a planar fashion, and the complexes of these ligands therefore do not display unusually large 10*Dq* values. The other feature of Table VII worthy of note is the steady drop in the value of 10*Dq* for Ni^{II}, as nitrogen donors are replaced by oxygen, which is expected from the lower position of oxygen than nitrogen donors in the spectrochemical series.

Conclusions

From the results reported in this paper one can draw the following conclusions.

(1) Addition of alcoholic or ethereal donors to amine ligands leads to changes in complex stability, which appear to be mainly controlled by the size of the metal ion. Other factors may play a role, but the predominant effect appears to be that large metal ions show a much more favorable change in complex stability than small metal ions when neutral oxygen donors are added. An important feature here is that this effect appears to be independent of whether the added oxygen donor is part of a macrocyclic ring or not.

(2) Exchange of the positions of donor atoms in a ligand so that a primary amine becomes a secondary amine, while an ethereal oxygen becomes an alcoholic oxygen, leads to increases in complex stability for covalently bound metal ions such as Cu^{2+}, but decreases for ionically bound metal ions such as Pb^{2+}. This is seen in that the relative preference for HEEN ($NH_2CH_2CH_2NHCH_2CH_2OH$) over ODEN ($NH_2CH_2CH_2OCH_2CH_2NH_2$) decreases in the order $Cu^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+} > Pb^{2+}$.

(3) Contributions to the stability of complexes of N-donor macrocycles that are ligand related, such as steric hindrance to solvation of the N donors in the macrocyclic cavity, mean that metal ions such as Ca^{II}, which ordinarily show no affinity for N-donor ligands, can form complexes of considerable stability with ligands such as 12-aneN_4.

(4) Replacing nitrogen by oxygen donors in macrocyclic ligands leads to a drop in complex stability. For large ionically bound metal ions such as Pb^{2+}, the rate of falloff in complex stability is lower, so that complexes of some stability are still observed when all the nitrogens have been replaced by oxygens; i.e., crown ethers

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(44) Hancock, R. D.; McDougall, G. J. *J. Am. Chem. Soc.* **1980**, *102*, 6551–6553.

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(46) Hart, S. M.; Boeyens, J. C. A.; Hancock, R. D. *Inorg. Chem.* **1983**, *22*, 982–986.

have been produced. For all the complexes of the mixed-donor macrocycles the macrocyclic effect is much smaller than is the case for the all-nitrogen-donor analogues.

(5) For the tetradentate macrocycles, an increase in the number of atoms forming the macrocyclic ring is usually considered to lead to an increase in the size of the macrocyclic cavity. However, for both the all-nitrogen- and the nitrogen-oxygen mixed-donor macrocycles studied here, the results suggest that the ligands with smaller macrocyclic rings, e.g. 12-aneN_4 or 12-aneN_3O, complex larger metal ions such as Pb^{2+} more strongly than do those with larger macrocyclic rings, e.g. 13-aneN_4 or 13-aneN_3O. In contrast, small metal ions such as Cu^{2+} show a strong preference for the macrocycles with larger macrocyclic rings. This effect does not appear to depend on the presence of a macrocyclic ring, but is rather related to the presence of five-membered vs. six-membered chelate rings in the complexes formed, since similar size-selectivity patterns are observed in the open-chain analogues.

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Registry No. 9-aneN_2O, 80289-59-4; 13-aneN_3O, 88915-58-6; 13-aneN_2O_2, 60350-15-4; 12-aneN_3O, 53835-21-5; 12-ane(1,4)N_2O_2, 60350-13-2.

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Structure and Dynamic Behavior in Solution of Binuclear Nickel(II) Face-to-Face Complexes with Bis(cyclidene) Ligands

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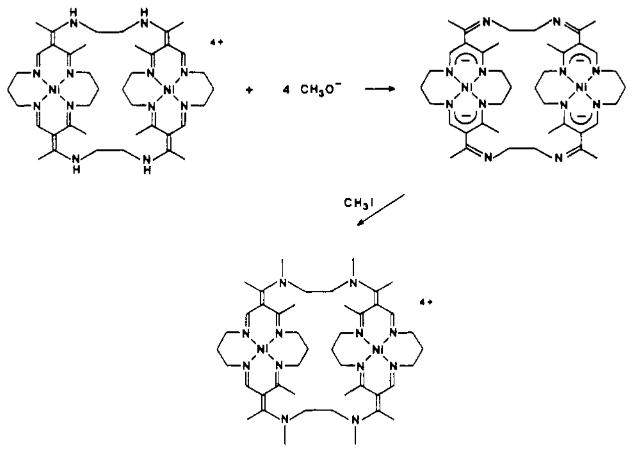
A series of dinickel(II) complexes having macrotricyclic bis(cyclidene) ligands has been prepared and characterized. NMR studies revealed a dynamic molecular motion in solution, and electrochemical investigations showed that the difference in redox couples ($\Delta E_{1/2}$) for the two Ni-cyclidene units correlates well with the sequence of intermetallic distances.

Introduction

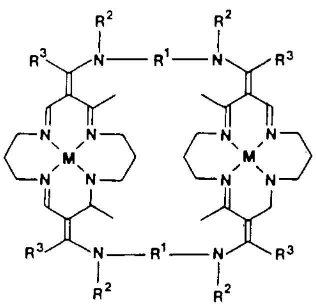
The number of synthetic model compounds for metalloproteins having more than one metal center has continuously increased and the structure types have been diversified substantially since the first report on a side-by-side example in 1970.[1] One advantage for such bioinorganic models is that the coordination geometry around the metal center and its surroundings can be easily controlled by ligand design; e.g., bridging two macrocyclic units into a stacked pair leads to the "face-to-face" structure.[2,3]

Face-to-face diporphyrins, whose electrochemical applications have been extensively investigated,[4,5] exemplify stacked macrocyclic systems. Efforts in this area have focused on the relationships between electrocatalytic activity in the reduction of O_2 to H_2O and structural parameters of the cobalt-containing catalyst.

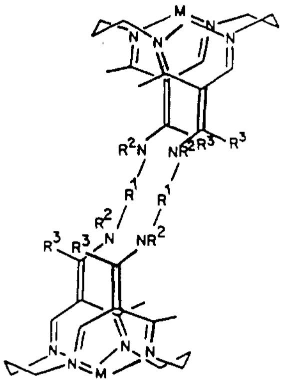
Scheme I



We have developed a distinct family of dinuclear transition-metal complexes in which two macrocyclic units, called *cyclidene* rings,[6] are joined together in a macrotricyclic ligand. The cyclidene groups have approximately face-to-face orientations, but they may be displaced with respect to a common axis or tilted with respect to that same axis. Because of the saddle shape of the cyclidene rings, many of these dinucleating ligands will maintain a constant separation between the two chelated metal ions. Structure Ia indicates the bonding in the complex while structure Ib shows the 3-dimensional array of atoms. These dinuclear complexes fall



Ia



Ib

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[1] Pilkington, N. H.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 2225-2236.

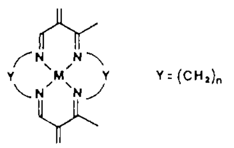
[2] See for example: Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 6027-6036.

[3] Eaton, S. S.; Eaton, G. R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 3177-3184 and references therein.

[4] For example: Durand, R. R., Jr.; Bencosme, C. S.; Collman, J. P.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 2710-2718.

[5] Liu, H. Y.; Abdalmuhdi, I.; Chang, C. K.; Anson, F. C. *J. Phys. Chem.* **1985**, *89*, 665-670.

[6] The cyclidene notation is based on the tetraimine macrocycle



n = 2, [14]cyclidene

n = 3, [16]cyclidene

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