whose Λ configuration was expected via its ^{1}H NMR spectrum.

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Registry No. H[Rh(*S*,*S*-EDDP)Cl$_2$], 89460-80-0; Δ-*cis*-α-H-[Rh(*S*,*S*-EDDP)Cl$_2$], 85504-79-6; Γ-*cis*-β-H[Rh(*S*,*S*-EDDP)Cl$_2$], 85107-97-7; Δ-*cis*-α-[Rh(*S*,*S*-EDDP)(H$_2$O)Cl], 89397-59-1.

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N,*N*′,*N*″,*N*‴-Tetrakis(2-hydroxyethyl)cyclam, an N-Donor Macrocycle with Rapid Metalation Reactions

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The nitrogen-donor macrocycles with their cavities of fairly fixed size[1] should display much greater selectivity for metal ions on the basis of the size of the metal ions than is found for open-chain polyamines. An immediate application might be the attachment of macrocycles such as cyclam (1,4,8,11-tetraazacyclotetradecane) to polystyrene beads so as to produce ion-exchange resins capable of selectively extracting metal ions, either in waste treatment or in hydrometallurgical applications. This has been done,[2] but it was found that the rate of metal ion extraction, even for the normally labile Cu(II) ion, was so slow that reasonable rates of extraction could only be obtained at 80 °C, at which temperature the lifetime of most polystyrene based ion-exchangers is very short. What is obviously required for the successful utilization of the greater size selectivity expected for macrocycles is an approach to speeding up their reaction rates, which are very slow[3,4] in comparison with those of noncyclic ligands.

It has been shown that the slowness of the metalation reactions of N-donor macrocycles relates to slow rates of reaction of the metal ion with protonated forms of the ligand.[3,4] This results from the fact that the incoming metal ion is formed in close proximity to any remaining protons on the macrocycle, and the reaction intermediate is thus destabilized by electrostatic repulsion. One approach to overcoming this problem is to attach a donor atom outside of the macrocyclic ring, which then forms a point of initial attachment for the metal ion where electrostatic repulsion with protons in the cavity of the macrocycle will not be as severe. This approach has been successful[5] in that attachment of acetate "arms" to porphyrins has lead to rapid metalation reactions.

At this stage several cyclam derivatives with groups substituted onto the nitrogens are known,[6-9] among which is a tetraacetate.[7] One might have expected this to produce the desired rapid metalation, but a detailed study[10] of the complexation reactions indicates that metal ions such as Co(II), Ni(II), and Cu(II) do not actually enter the cavity of the macrocycle but instead form complexes in which the metal ion is held outside of the ring, bonding to two acetates and only two of the nitrogens of the macrocyclic ring. This mode of bonding produces, instead of enhanced selectivity, an unusually closely bunched set of formation constants for the set of metal ions studied.[7] An interpretation of the unusual bonding found for cyclamtetraacetate might be that the complex formed held outside of the ring is actually more stable than that held in the ring and that the reluctance to move into the ring is not a simple kinetic effect, as will be discussed below.

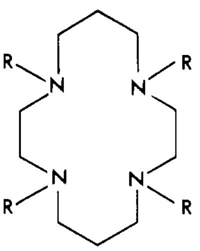

Figure 1. Structure of tetraaza macrocycles discussed in this paper. R = H is cyclam; R = CH$_3$ is TMC, tetramethylcyclam; R = CH$_2$COO$^-$ is CTA, cyclamtetraacetate; R = CH$_2$CH$_2$OH is THEC, tetrakis(2-hydroxyethyl)cyclam; R = CH$_2$CH$_2$CN is TCEC, tetrakis(2-cyanoethyl)cyclam.

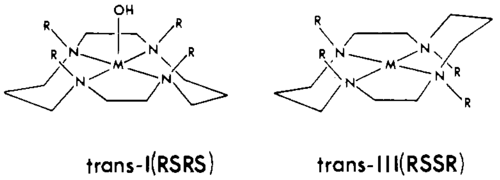

Figure 2. Structure of the *trans*-(*RSRS*)-I and *trans*-(*RSSR*)-III conformers of tetraaza macrocyclic complexes, showing the *trans*-(*RSRS*)-I form with a unidentate ligand coordinated in the axial position to give a square-pyramidal five-coordinate complex.

An interesting example of enhanced lability among nitrogen-donor macrocycles has been reported by Barefield et al.,[6] with the ligand TMC, tetramethylcyclam (Figure 1). Although the methyl groups on TMC are not potential donor groups, the ligand is fairly labile. This may relate in part to the lower pK_a values found for TMC,[11,12] which means that at any given pH the concentration of free TMC, and TMC species with few protons attached, is much higher than for cyclam, resulting in more rapid complex formation. Another important aspect here relates to the mode of entry of the metal ion into the cavity of a nitrogen-donor macrocycle. This involves initial reaction with the folded form of the macrocycle to produce the *trans*-(*RSRS*)-I type of structure, shown in Figure 2, followed by base-catalyzed conversion through inversion at the nitrogens to give the *trans*-(*RSSR*)-III type structure. As pointed out by Barefield et al.,[6] TMC complexes have tertiary nitrogens and so cannot be deprotonated to allow inversion at the nitrogens to give the final *trans*-(*RSSR*)-III structure. The unusual five-coordinate structure found[6] in the TMC complexes might lead to unusual selectivities in both TMC complexes and the complexes of other ligands where this

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Table I. pK_a Values of Some Tetraaza Macrocycles[a]

	THEC[b]	TMC[c]	TCEC[d]	cyclam[e]
pK_1	8.80	9.34	7.0	11.59
pK_2	8.24	8.99		10.62
pK_3	2.69	2.58		1.61
pK_4	~1.2	2.25		2.42

[a] For abbreviations and structure of ligands, see Figure 1. [b] This work; 25 °C in 0.1 M $NaNO_3$. [c] Reference 12; 25 °C in 0.1 M $NaNO_3$. [d] Wade, P.; Michael, J. P.; Hancock, R. D., unpublished work. [e] Reference 11; 0.5 M KNO_3, 25 °C.

unusual type of bonding is adopted.

In view of the undesirable nonentry of the metal into the cavity of the cyclamtetraacetate complexes, we have undertaken a study of nitrogen-donor macrocycles with other donor groups attached to the nitrogens to determine the effects these have on the lability and stability of the resulting complexes. We report here the synthesis and some metal-complexing properties of the ligand *N*,*N*′,*N*″,*N*‴-tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane, abbreviated THEC, shown in Figure 1.

Experimental Section

Synthesis of the Ligand. Cyclam was obtained as the free ligand from Strem Chemicals. A 1.998-g (10-mmol) amount of cyclam was dissolved in absolute ethanol (45 mL) and cooled in an ice bath. A 50% excess of the stoichiometrically required amount of cold liquefied ethylene oxide (3 mL, 60 mmol) was added to the ethanol solution. The mixture was allowed to stand overnight at room temperature, and the solvent was then evaporated off to give 3.8 g (100% yield) of a brownish crystalline solid, which was recrystallized from isopropyl alcohol to give the final product as colorless cubic crystals; mp 123 °C. Anal. Calcd for $C_{18}H_{40}N_4O_4$: C, 57.42; H, 10.71; N, 14.88. Found: C, 57.29; H, 10.84; N, 14.78. The ^1H NMR spectrum in $CHCl_3$ gave the following resonances: 1.5–2.0 ppm (m, 4 H, CH_2); 2.2–2.8 ppm (d, 24 H, CH_2-N); 3.4–3.8 ppm (m, 8 H, CH_2O); 5.0–5.4 ppm (s, 4 H, OH).

Formation Constant Studies. Recrystallized THEC was used to make up a stock solution of the ligand, which was standardized by titration with standard acid, which showed it to be in excess of 99% purity. Stock solutions of the metal nitrates were prepared from the AR salts (Merck) and standardized by EDTA titration. The electrodes, cell, and titration equipment used for carrying out the potentiometric titrations have been described previously.[13] In all cases equilibrium was rapid, so that no problems with long equilibration times during the potentiometric titration, as is usually found with nitrogen-donor macrocycles, were experienced. Analysis of the data was carried out with use of the program MINIQUAD of Sabatini et al.,[14] which showed that, apart from the metal–ligand complexes of 1:1 stoichiometry, deprotonated complexes of the composition ML(OH) were present but that no other species, including polymeric forms of the complexes, were present.

Instrumentation. UV–visible spectra were recorded on a Cary-17 spectrophotometer, while NMR spectra were recorded on a Varian EM 360A spectrometer.

Results and Discussion

The pK_a values for THEC are listed in Table I and the formation constants in Table II for a variety of metal ions complexed to THEC. Also shown are formation constants and pK_a values for other N-substituted cyclams, where the substituents are methyl,[12] cyanoethyl,[15] or acetate,[7] as well as the constants for cyclam itself. Table II shows the low stability of the complexes of THEC, which are even lower than those formed by TMC. The TMC complexes have been shown[6] crystallographically to adopt the *trans*-(*RSRS*)-I type of structure, with a single unidentate ligand (water, azide, chloride[6]) occupying the axial coordination site to give the square-pyramidal type of structure shown in Figure 2. We have attempted without success to grow crystals of the THEC complexes. The electronic spectra of the THEC and TMC complexes of Ni(II), at both high and low pH, are shown in Figure 3. The resemblance of the high-pH form of the THEC complex of Ni(II) to the spectra of both the high- and low-pH forms of the TMC complexes is very strong, suggesting that the THEC complex has a similar five-coordinated square-pyramidal structure. The very much greater acidity of the THEC complexes suggests that the take-up of hydroxide is actually deprotonation of a coordinated hydroxyethyl arm. The nature of the blue low-pH THEC complexes is more problematic. The electronic spectrum of the Ni(II) complex is rather different from that of its green high-pH form. The lower band intensities suggest that we have here an octahedral species, with either water or oxygens from the hydroxyethyl groups occupying the remaining sites. We have added large excesses of other unidentate ligands such as ammonia, chloride, azide, and thiocyanate to the low-pH blue form of the Ni(II) complex of THEC and found that, apart from ammonia, there is no change in the electronic spectrum. Ammonia produces a spectrum identical with that obtained with hydroxide, so that we may assume that what we are seeing here is deprotonation of the complex rather than addition of ammonia. That no additional unidentate ligand can coordinate to the metal ion, as opposed to the case for the TMC complexes, where ligands such as azide are strongly coordinated,[16] suggests that the remaining coordination sites are occupied by oxygens from the hydroxyethyl groups rather than water. These are evidently tightly bound, since ligands such as azide are not able to displace them. What is important is that, if the nickel were held out of the ring, as with CTA complexes, we would expect additional unidentate ligands to be able to coordinate to it in its relatively more exposed position.

Table II. Formation Constants of Complexes of Some Tetraaza Macrocycles[a]

	THEC[b]		TMC[c]		CTA[d]	cyclam[e]
M	*K*(ML)[f]	*K*(MLOH)	*K*(ML)	*K*(MLOH)	*K*(ML)	*K*(ML)
Cu(II)	15.69	v small	18.3	v small	18.6	27.2
Ni(II)	7.31	5.01	8.6	3.7	15.3	22.2
Co(II)	6.10	6.85	7.6	5.2	15.0	
Zn(II)	6.43	7.32	10.4	5.4	15.8	15.5
Cd(II)	9.38	4.28	9.0	4.4	15.5	
Hg(II)	17.94		20.3			23.0
Pb(II)	6.28	~5.1[g]			14.7	
Mg(II)	1.86				3.0	

[a] For key to abbreviations, and structures of ligands, see Figure 1; all formation constants are log *K* values. [b] This work; 25 °C in 0.1 M $NaNO_3$. [c] Reference 12; 25 °C, 0.1 M $NaNO_3$. [d] Reference 7. [e] In order from top to bottom, ref 19–22. [f] *K*(ML) is the logarithm of the formation constant for the reaction $M + L \rightleftharpoons ML$. The standard deviation indicated for these constants by the program MINIQUAD was about 0.02 log unit. *K*(MLOH) is log K for the process $ML + OH^- \rightleftharpoons MLOH$. [g] Approximate value, as titration at this pH results in demetalation and formation of lead hydroxide.

Table II shows that the selectivity of the TMC and THEC complexes for Cu(II) over Ni(II) is greater than for any other ligand system in the literature.[17] This is interesting if we are looking to increase selectivity and suggests that, over and above their potential selectivity based on metal ion size, macrocycles should be able to produce enhanced selectivity by their ability to force unusual coordination geometries, such as the five-coordinate geometry forced by TMC.[6]

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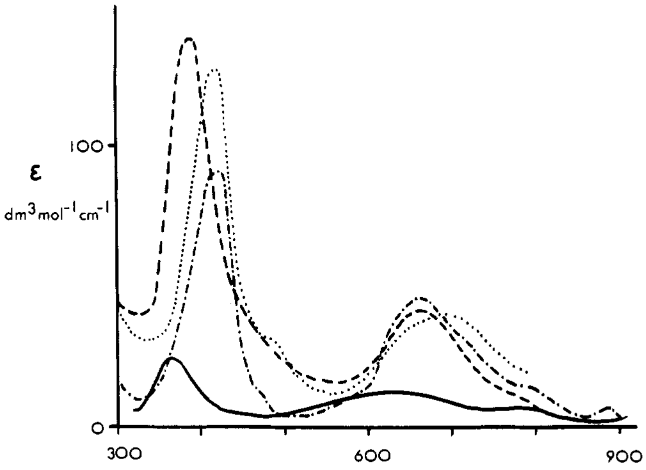

Figure 3. Electronic spectra of complexes of Ni(II) in aqueous solution: spectra of the Ni(II) complex with THEC at (—) pH 7.48, where the complex is blue, and (–•–•) pH 9.99, where it is an intense green. The other two spectra are those generated for the pure high-spin form of TMC at low pH (•••) with use of the reported equilibrium constant for the high-spin/low-spin equilibrium (Herron, N.; Moore, P. *Inorg. Chim. Acta* **1979**, *36*, 89) and that for the Ni(II) complex with TMC at high pH (- - -), where it is present as the monohydroxy complex. It should be noted that the THEC complex of Ni(II) does not produce a spin-paired form at high ionic strength.

The most interesting property of THEC is its ability to complex rapidly with metal ions. In a recent study of the formation constants of TMC complexes,[12] it was found necessary to allow several hours between each addition of acid in the potentiometric titrations with metal ions such as Co^{II} and up to 1 week for equilibration with the Ni^{II} complex.[18] Equilibration with the complexes of THEC appeared instantaneous on the time scale of the potentiometric titration, except for Ni(II), where equilibrium was established within 2 min after each addition of acid. This is in contrast to tetrakis(2-cyanoethyl)cyclam, which, in spite of having lower pK_a values than THEC (Table I), equilibrates only very slowly even with Cu^{II}. We must conclude, therefore, that a lowering of the pK_a values of the macrocycle is by itself insufficient to produce rapid metalation of macrocycles and that the hydroxyethyl groups of THEC are aiding the metalation reaction by providing points of attachment outside the macrocyclic ring for the incoming metal ion. What is important about these points of initial attachment is that they should not provide a structure of such stability that, as with CTA, the metal ion prefers to remain outside of the macrocyclic ring. The reason for nonentry of the metal ions into the macrocyclic ring of CTA becomes clear in examining Table II, where we see that the stability of the TMC and THEC complexes which appear to be bound in the macrocyclic ring is very much lower than that of the analogous CTA complexes.

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Reversible Binding of Dinitrogen and Dihydrogen by Mo(η^6-PhPMePh)(PMePh$_2$)$_3$: Use of [9-BBN]$_2$ as a Phosphine Sponge Reagent

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There are only a few complexes known that react with dinitrogen by dissociation of a tertiary phosphine ligand, PR$_3$ (eq 1). These include Ni(PEt$_3$)$_4$,[1] Mo(N$_2$)(PMe$_3$)$_5$,[2]

$$L_nM\text{–}PR_3 + N_2 \overset{K_1}{\rightleftharpoons} L_nM\text{—}N{\equiv}N + PR_3 \qquad (1)$$

RuH$_2$(PPh$_3$)$_4$,[3] FeH$_2$(PEt$_2$Ph)$_4$,[4] Mo(PMe$_3$)$_6$,[5] and Ta(C$_2$H$_4$)(PMe$_3$)$_4$Cl[6] written qualitatively in the order of increasing values of K_1. The sizes of these equilibrium constants are determined by the strength of the metal–nitrogen and metal–phosphorus interactions, the latter being weakened usually because of steric congestion around the binding site. These compounds are powerful reductants, and all[2–5] but two[1,6] have been reported to give dihydride complexes upon reaction with dihydrogen (eq 2).[7]

$$L_nM\text{—}PR_3 + H_2 \overset{K_2}{\rightleftharpoons} L_nM\begin{matrix}H\\H\end{matrix} + PR_3 \qquad (2)$$

Difficulties sometime arise in the separation of the product complexes from these equilibrium mixtures containing free phosphine ligand and starting material.[1,3,4] Ideally a "phosphine sponge" reagent[8] is needed to drive these equilibria to the right, but metal complexes[8a] or methyl iodide[8b] added to such mixtures in order to remove free phosphine is expected to oxidize or modify the desired complexes. In one case, the method of reverse osmosis was successfully applied to the purification of RuH$_2$(N$_2$)(PPh$_3$)$_3$.[3a]

We report here the discovery of such equilibria in the reactions of Mo(η^6-PhPMePh)(PMePh$_2$)$_3$ (**1**)[9] with dinitrogen and dihydrogen to give dinitrogen and dihydride derivatives (**2** and **4**, respectively) and the use of the dimeric borane 9,9′-bi-borabicyclo[3.3.1]nonane, [9-BBN]$_2$,[10] as a Lewis acid or "phosphine sponge" reagent to drive eq 1 to the right. We have described elsewhere some properties of other derivatives of **1** containing strongly coordinating ligands[9] including the crystal structure of Mo(η^6-PhPMePh)(CN-*t*-Bu)(PMePh$_2$)$_2$.[9c] Other complexes of the type Mo(η^6-arene)(PR$_3$)$_3$ are

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