

Table I. 1:1 Metal Complexation Constants (log *K*)

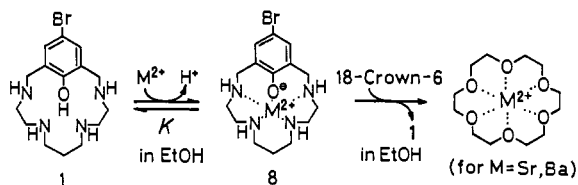
metal ion (ionic diamtr, Å)	1 ^{a,c}	2 ^{a,d}	15-crown-5 ^{b,e}	18-crown-6 ^{b,f}
Mg ²⁺ (1.30)	3.3	3.1	noncomplextn	unreported
Ca ²⁺ (1.98)	2.9	2.9	2.1	3.9
Sr ²⁺ (2.26)	2.3	2.6	2.6	>5.5
Ba ²⁺ (2.70)	1.6	2.4	unreported	7.0

^a*K* = [M²⁺-complex]/[M²⁺][H₁L] (M⁻¹) in EtOH at 25 °C. Standard deviation is ±0.1. ^b*K* = [M²⁺-L]/[M²⁺][L] (M⁻¹) in MeOH at 25 °C (Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* 1985, 85, 271-339). ^cCavity size (1.4-2.0 Å). ^dCavity size (1.8-2.2 Å). ^eCavity size (1.7-2.2 Å). ^fCavity size (2.6-3.2 Å).

trophotometrically), <2, and <1.¹⁴ The phenol p*K*_a value of 4.8 is much lower than 8.8 of *p*-bromophenol alone, presumably under the strong influence of +3 charge of the N₅ macrocycle. We could isolate crystalline triprotonated (on N₅) phenolate species **7** (as 2ClO₄⁻ salt) out of pH 7 aqueous solution containing excess NaClO₄. Its UV spectrum (in H₂O) of λ_{max} 309 nm (ε 3900) supports the phenolate form of **7**. On the other hand, the ratio of the phenolate species is minor (1:0.25) with tetraamine homologue **1** in EtOH. Its p*K*_a values in 0.1 M Et₄NClO₄ are 10.7, 10.5, 8.3 (phenol), 4.2, and 3.7. The phenol p*K*_a of 8.3 is not as low as 4.8 of **2**, under the lesser influence of +2 charge of the N₄ macrocycle. For the sake of comparison, p*K*_a values of the relevant phenol macrocycles are 11.8, 10.5, 8.9 (phenol), <2, and <2 for **5a**,¹⁰ 11.8, 10.4, 6.4 (phenol), <2, and <2 for **5b**,¹¹ 10.8 for **3a**, and 10.6 for **4a**.⁵ Apparently, self dissociation of the phenol protons should be negligible with **3** and **4** in EtOH⁵ and with **5a** in CHCl₃ and EtOH.¹¹ Thus, an enormous influence of the azacrowns on reactivity of the intraannular phenol protons is revealed.

The phenol ionization in EtOH is further promoted by addition of neutral alkaline earth metal salts MgCl₂, CaCl₂, SrCl₂, and Ba(SCN)₂, as illustrated by the increase in the phenolate form or accompanying decrease in the phenol form in the UV absorptions (see Figure 1b,c).¹⁵ In varying the [ligand]/[M²⁺] ratio ([ligand] + [M²⁺] = 1 mM), the total phenolate concentration reaches maximum at [ligand]/[M²⁺] = 1 with all the metals. The degree of 1:1 association uniformly varies with the size of metal ions, i.e., Mg > Ca > Sr > Ba, for **1** and **2**. Monovalent alkaline metal salts (LiCl, NaCl, KCl, CsCl), on the other hand, do not displace the phenolic protons of **1** and **2**. With crown homologues **3** and **4** basic conditions are needed to displace the phenol protons for M⁺ and M²⁺.⁵⁻⁹ The phenol-pendant N₄ homologues **5a** and **5b** do not interact with alkaline earth metal salts in EtOH solution.¹¹ Evidently, *synergism between the macrocyclic N donors and intraannular phenolate donor is essential for uptake of divalent metal ions in the nonbasic conditions*. The pH metric titration indicates the complexation of **2** with Mg²⁺ to occur above pH 9 in aqueous solution (at 25 °C, I = 0.1 M Et₄NClO₄).

The apparent constants for the 1:1 complexation between **1** (or **2**) and M²⁺ in EtOH are calculable in terms of *K* = [M²⁺-complex]/[M²⁺][H₁L] (M⁻¹) (where H₁L is a free ligand in phenolate anion form, and [M²⁺-complex] is the [total phenolate anion] - [H₁L]) with use of the UV spectral data. The results



(14) The standard deviation for p*K*_a values of **1** and **2** is ±0.05. The titration curves of **1** and **2** in 0.1 M Et₄NClO₄ completely overlap those in 0.1 M NaClO₄. These facts indicate that Na⁺ has no interaction with **1** and **2**.

(15) With **3** and **4**, M⁺ and M²⁺ ion size correlate linearly with wave numbers of the phenolate absorption maxima, suggesting some degree of ion pairing in nonaqueous solvents.⁵⁻⁹ On the other hand, the absorption maxima (300 nm) remain practically the same regardless of M²⁺ with **1** and **2**.

are summarized in Table I, in comparison with reported *K* values for crown ether complexes.¹⁶ Very interestingly, Mg²⁺ uptake is more favored with smaller macrocyclic **1** than with larger **2**, despite the fact that the self dissociation of the former phenol hydrogen is less feasible. As the M²⁺ size increases, complexation becomes more favorable with larger macro ligand **2**. These size effects suggest that the metal inclusion into the size-fitted polyamine hole is a determining factor for the selective uptake. It is to be emphasized that the macrocyclic polyamine ligands are most appropriate for the smallest Mg²⁺, while crown ethers favor larger M²⁺.

Furthermore, in EtOH the complexation of Mg²⁺ and Ca²⁺ with **1** or **2** is proved stronger than with 15-crown-5 or 18-crown-6,¹⁷ while that of Sr²⁺ and Ba²⁺ with **1** or **2** proved to be weaker than with 18-crown-6. This is revealed by the change of the phenolate UV absorptions upon addition of crown ethers (1 equiv) to a 1:1 mixture of **1** (or **2**) and MX₂ in EtOH.

Finally, the 1:1 complexation of **1** with Mg²⁺ was proven by isolation of its monoperchlorate salt, Mg²⁺-H₁L·ClO₄·H₂O (as light yellow powder), out of aqueous EtOH solution. The structure was characterized by elemental analysis (C, H, N), UV spectra (λ_{max} 301 nm, ε 3800 in EtOH at 25 °C), and analysis of Mg by atomic absorption technique.

The present results have thus revealed new potentials of macrocyclic polyamines for selective receptors of hard metal ions.

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(16) The 1:2 complexation is reported for M²⁺ and **3b**.^{8,9} However, the stoichiometry with **4**, and the complexation constants are unknown.

(17) Despite the fact that the reported log *K* value (3.9) for 18-crown-6 (in MeOH) is greater than 2.9 for **1** and **2** in EtOH, see Table I.

Enantioface Differentiation in Cis Dihydroxylation of C-C Double Bonds by Osmium Tetroxide with Use of a Chiral Diamine with D₂ Symmetry

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Molecules with a high symmetry have been shown to be effective auxiliary ligands in asymmetric reactions.^{1,2} Here we describe extremely efficient enantioface differentiation in the dihydroxylation of C-C double bonds by osmium tetroxide using a chiral diamine with D₂ symmetry.² Virtually complete asymmetric induction was observed in the reaction of *trans*-1-phenylpropene.

We used the D₂ symmetric chiral diamine **1**, which consists of two *trans*-3,4-diphenylpyrrolidine units with C₂ symmetry at the both ends of the ethylene chain.³ A typical experimental pro-

(1) C₂ symmetric ligands follow. Noyori, R.; Tomino, I.; Tanimoto, Y. *J. Am. Chem. Soc.* 1979, 101, 3129. Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* 1980, 102, 5974. Fujiwara, J.; Fukutani, Y.; Hasegawa, M.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* 1984, 106, 5004. Choi, V. M. F.; Elliot, J. D.; Johnson, W. S. *Tetrahedron Lett.* 1984, 25, 591. Ito, Y.; Katsuki, T.; Yamaguchi, M. *Tetrahedron Lett.* 1985, 26, 4643. Masamune, S.; Kim, B.-M.; Petersen, J. S.; Sato, T.; Veenstra, S. J.; Imai, T. *J. Am. Chem. Soc.* 1985, 107, 4549. Noyori, R.; Ohta, M.; Hsiao, Y.; Kimura, M.; Ohta, T.; Takaya, H. *J. Am. Chem. Soc.* 1986, 108, 7117. Kelly, T. R.; Whiting, A.; Chandrakumar, N. S. *J. Am. Chem. Soc.* 1986, 108, 3510. Narasaka, K.; Inoue, M.; Yamada, T. *Chem. Lett.* 1986, 1967.

(2) D₂ symmetric ligands follow. Cram, D. J.; Sogah, G. D. Y. *J. Chem. Soc., Chem. Commun.* 1981, 625. Mazaleyrat, J.-P.; Cram, D. J. *J. Am. Chem. Soc.* 1981, 103, 4585.

(3) Tomioka, K.; Nakajima, M.; Koga, K. *Chem. Lett.* 1987, 65. Tomioka, K.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* 1987, 28, 1291.