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PREVIEW

STUDIES OF FORMATION CONSTANTS OF
SOME DIAZAPOLYOXA MACROCYCLIC
LIGANDS

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To two El Paso families who will always mean more
to me than they will ever know:

Carol, Jim, Jimmy and Laurie Lopez;

Nyria Melchor and Rosa Chavez.

PREVIEW

STUDIES OF FORMATION CONSTANTS OF
SOME DIAZAPOLYOXA MACROCYCLIC
LIGANDS

by

VEN O. LOCHAYA, B.S.

THESIS

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I. INTRODUCTION

The problems of the stability of metal complexes and the selectivity of complex formation are of central importance in coordination chemistry, particularly in the chemistry of complexes and extractants. By virtue of their flexibility and multidentate nature, cyclic macrocycles have been found to form complexes with cations of different sizes. In recent years, considerable attention has been paid to the synthesis of highly selective reagents capable of selective chelation of specific cations. Of particular interest are the diazapolyoxya macrocycles, especially if the metal ions concerned are lanthanide (Ln), transition, or post-transition metal ions. The alkali and alkaline earth metal ions are already known to be better bound by the unsubstituted crown ethers.¹

The synthesis of such reagents has resulted in numerous applications, particularly in the nuclear industry and hydrometallurgy (for the extraction and separation of rare metals and radioactive isotopes), in medicine and pharmacology (for the elimination from the organism of harmful metals, especially radioactive ones, and the introduction into the organism of the essential metals (e.g., iron in iron-deficiency anaemia), and in chemical industry and catalysis (for the formation of complexes with a specified steric structure and with a specified stability in a particular medium).²

The preferred complexation of a substrate S by a ligand L implies a recognition of S by L and its selection among the collection of possible

substrates. Selectivity may be controlled by monitoring ligand structure, each specific feature representing an information bit.

Information may be stored in

- 1) topology of the ligand,
- 2) its binding sites, and
- 3) its other properties, to be reviewed later.

The medium and the counterion are also expected to affect the stability and possibly the selectivity of the complex as well.

PREVIEW

II. BACKGROUND

Variations in selectivity and stability by macrocyclic ligands have been deduced from various research studies to be due to a number of factors. For instance, the selectivity of the rigid complexones is actually determined solely by the size of the cavity within the macro-ring.³ The relative stabilities of the complexes of a series of porphyrins with different substituents are determined by electronic factors, since the substituents exert a strong influence on the conjugation in the ring.² Based on studies of this nature, it has become possible to create unique and specified ligands for virtually any type of heavy metal ions. The following are some of the factors affecting the selectivity and stability of such ion-macrocycle complexes.

A. Relative Ionic and Cavity Sizes

Pedersen's cyclic crown ethers were demonstrated to exhibit sharp selectivities toward the alkali and alkaline-earth ions as a function of ring size.¹ Since then, several other investigations have arrived at the same conclusion with different other macrocycles. For instance, Busch and co-workers⁴ have also demonstrated that there is an ideal ring size for any metal ion having a given metal-donor atom distance. The ligands used for the demonstration of this relationship are a series of unsubstituted, fully saturated, cyclic, tetraazahydrocarbons such as those given in structure I-V in Fig. 1. For ring sizes slightly smaller ($0.1-0.2 \text{ \AA}$ in terms of the M-N distance), the best fit ring showed

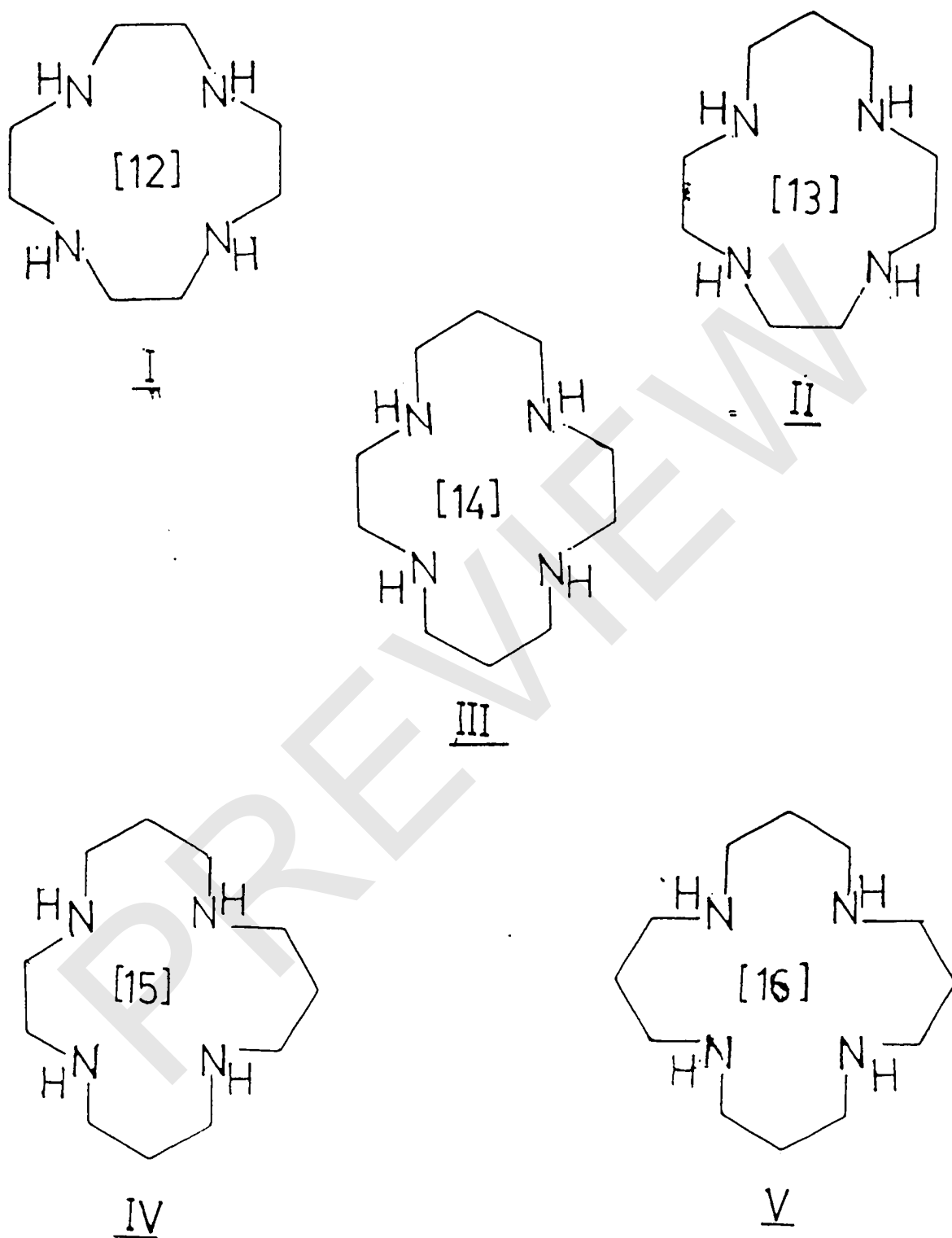


Fig. 1 Ligands for the demonstration of metal-donor distance and ring size relationship in macrocyclic complexes.

TABLE I^a Ligand field splitting parameter for trans-diacidotetraamine
Complexes of $[\text{Co}(\text{[13-16]ane N}_4)\text{Cl}_2]^+$ and $[\text{Ni}(\text{[13-16]ane N}_4)\text{Cl}_2]$

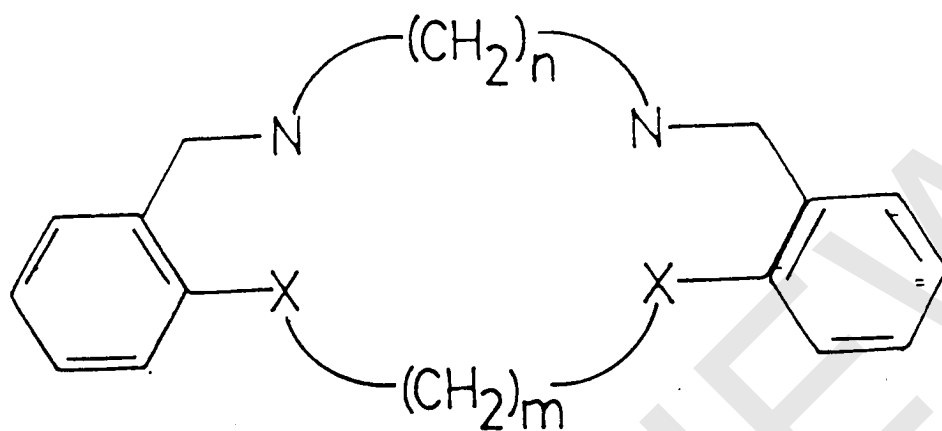
Ligand	Co^{2+}	$Dq, \text{ cm}^{-1}$	Ni^{2+}
[13] ane N_4	2750		a
[14] ane N_4	2480		1480
[15] ane N_4	2360		1250
[16] ane N_4	2250		1110
en	2530		-
Me_2en	-		1215

a Taken from Ref. 4.

b Ligand folds on metal to give cis complex.

abnormally strong metal donor bonds while rings that were slightly oversized showed substantially decreased metal-donor interactions. It was previously realized that in cases where the mismatch in size was more extreme, distortions from square planar coordination occurred. Examples of common distortions were ring folding to form cis-octahedral⁵ structures, ring folding to form trigonal bipyramidal structures,⁷ and extrusion of the metal ion from the donor atom plane to form a tetragonal pyramidal structure.⁷ Table I shows the values for the ligand field parameter Dq appropriate to the square planar coordinated macrocyclic ligands (along with the values for the unconstrained reference ligand ethylenediamine, en.) for the complexes of Co(III) and Ni(II).⁸ Dq values for these complexes deviate from the unconstrained values as ring size either exceeds or falls below the "best fit" value. This is a consequence of the effects of increased strain energy on the metal-ligand bonds.

More recently, several newer varieties of macrocyclic systems have been used by other research groups to study the effect of ionic and ring sizes on selectivity and bonding. Lindoy's work on the thermodynamic stabilities of six-coordinate Ni(II) complexes of structurally related 14- to 17- membered quadridentate macrocyclic ligands can serve as an example (Fig. 2). This was designed to show ring size vs. metal size relationship as well as to correlate the hole-size variations in macrocycles of the general type 1 with the previously documented transition metal ion chemistry of these systems.¹⁰⁻¹⁴ The procedure used for specifying ligand cavity sizes available to metal ions allowed the



1, X=O, NH, S

$n=2, 3;$

$m=2-4.$

Fig. 2 Ligands for illustrating the effect of hole-size variations on thermodynamic stability for Ni(II) complexes.