# Macrocyclic Polyfunctional Lewis Bases.
## VII. Size and Structure Controlled Stabilities of Polyaza-crown Ether Complexes with $Co^{2+}$–$Zn^{2+}$ Ions

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*Stability constants have been determined at 25 °C in aqueous 0.1 M $Et_4NClO_4$ medium by potentiometric method of the following ligands: 1,7-dioxa-4,10-diazacyclododecane 5, 1,4,10-trioxa-7,13-diazacyclopentadecane 6, 1,4,7,13-tetraoxa-10,16-diazacyclooctadecane 7, 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane 8, 1,4,7-trioxa-10,13-diazacyclopentadecane 9 and 1,10-dioxa-4,7,13,16-tetraazacyclooctadecane 10 with $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$ and $Zn^{2+}$ ions. The values of the stability constants are discussed in terms of the relative size of the metal ion and macrocyclic cavities, the spatial arrangement of the donor nitrogen atoms and the macrocyclic effect.*

## Introduction

The most characteristic property of macrocyclic complexones of type *1* (called crowns) is the fact that the stability constants are largest when there is a best fit between the metal ion and the cavity of the complexone. This is especially characteristic of first group and ammonium ions [1]. No analogous complexing selectivity towards individual transition metal ions occurs with macrocyclic polyamines *2* or macrocyclic polythioethers *3* [2–4]. Furthermore, crowns *1* usually do not form sufficiently stable complexes with the above ions, a fact that is accounted for by weak interactions according to the concept of hard and soft acids and bases. The interactions between a transition metal ion and *1* can be increased by substituting nitrogen atoms for some of the donor oxygen atoms in the ligand.

Such compounds had been investigated earlier [5, 6], but there exists neither any systematic data on their interactions with transition metal ions nor on the stability of the complexes in terms of the relation between the size of metal ion and ligand cavity. Type *4* compounds for which the stability constants with $NiCl_2$ have been determined are an exception [7, *cf.* also 2].
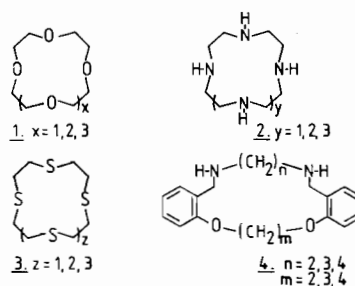


The complexing abilities of diazacyclopolyethers *5–9* and tetraazacyclopolyether *10* with transition metal ions were investigated. These ligands differ from each other by the arrangement of nitrogen atoms and by their ring size ranging from 12 through 15 to 18 atoms (cavity radii from 0.8 to 1.4 Å).

Compounds *5*, *6* and *8* have been investigated earlier, but there is no complete information on stability constants of their complexes and investigations have been carried out in a different ionic medium. Compounds *7*, *9* and *10* were obtained in our laboratory.



11  $H_2NCH_2CH_2NH_2$
12  $H_2NCH_2CH_2OCH_2CH_2NH_2$
13  $H_2NCH_2CH_2OCH_2CH_2OCH_2CH_2NH_2$
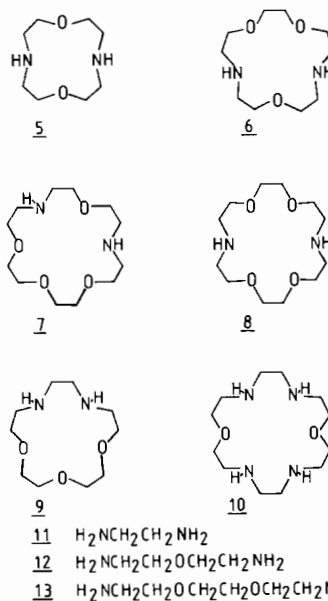
## Experimental

### Chemicals

Tetraethylammonium perchlorate and metal per-
chlorates or nitrates were prepared in the usual
way and crystallized from water. The stock solutions
were standardized by using complexometric, poten-
tiometric or conductimetric titration techniques.
Ligands 5, 6 and 8 were prepared as described [8].
Synthesis of compounds 7, 9 and 10 will be described
elsewhere [9]. Tetraethylammonium hydroxide was
prepared from the bromide using Amberlite IRA-410
exchange resin.

### Procedure

The standard potentiometric method was used.
The pH measurements were performed using a N517
pH-meter (MERA ELWRO) equipped with a V628
digital voltmeter. A combined glass–silver/silver
chloride type SAgP-201W electrode was used to
measure the pH changes in a cell of the following
composition

Ag, AgCl (s) | tetraethylammonium per- | glass
             | chlorate 0.1 $M$        | electrode
             | $C_H$ (total concentration of
             | $H^+$)
             | $C_M$ (total concentration of
             | $M^{2+}$)
             | $C_L$ (total concentration of
             | ligand)

Solutions (25 cm$^3$) of the ligand perchlorates ($C_L$ =
$2 \times 10^{-3}$ mol dm$^{-3}$) were titrated with tetraethyl-
ammonium hydroxide ($C_{OH^-}$ = 0.05 mol dm$^{-3}$)
in the presence or absence of the Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$
and Zn$^{2+}$ metal ions ($C_M$ = $5 \times 10^{-4}$–$1 \times 10^{-2}$ mol
dm$^{-3}$). The reaction cell was thermostatted at 25.0$_5$
°C with water. The ionic medium was 0.1 $M$ Et$_4$-
NClO$_4$, because neither the tetraethylammonium
cation nor the perchlorate anion forms complexes
with the solution components [10, 11]. The working
system was checked using 1:1 phosphate (pH = 6.86),
phthalate (pH = 4.01) and borate (pH = 9.18) buffers
at 25 °C.

### Calculations

The protonation constants were calculated in the
usual way. When the successive protonation constants
differed by less than the order of 3, Schwarzenbach's
graphical method was applied [12]. When $C_M \leqslant C_L$,
stability constants were derived from the formation
curves. When $C_M > C_L$, Kodama and Kimura's [2]
method was used. All constants so obtained were
refined using the modified [13, 14] SCOGS [15]
programme correcting for hydrolysis of the transition
metal ions.

## Results and Discussion

The determined protonation constants of ligands
5–10 are summarized in Table I, together with values
reported by other authors. Protonation constants
of linear diamines 11–13 are also given for compari-
son [16]. The basicities of the macrocyclic diaza-
polyethers do not differ from each other appreciably.
The logK$_1$ values for the 15- and 18-membered
ligands, except 7, are similar and are thus indepen-
dent of ring size or nitrogen atoms distribution in
the molecule. The differences between logK$_2$ values
are insignificant; compound 9 is an exception, and
this may readily be explained by the field effect.
Comparison of protonation constants of macrocyclic
and linear diamines 11–13 shows that linear diamines
are more basic.

The determined protonation constants for com-
pound 8 are consistent with values reported earlier
[6]; the values obtained by us for compound 6 were
higher than those previously reported [5].

Table II shows the determined stability constants
for complexes of the ML type. A simulation with
the SCOGS programme has shown that no other
type of complexes (M$_2$L, ML$_2$, *etc.*) are present
in the system investigated, and that the existence
of the protonated MLH complexes may be neglected.

The formation constants of complexes with
ligand 6, and especially ligand 8, were determined
at $C_M/C_L \approx 10$, as suggested by Kodama and Kimura
[2]. Despite this, the titration curve sections used
for calculation were small, particularly for ligand
8 [*cf.* 6]. Thus, despite small standard deviations,
the constants for complexes of 8 should be treated
with caution.

Comparing the values of formation constants of
ligands 5, 6 and 7 (Table II) indicates that regardless
of the kind of cation, they are greatest for the
smallest diazacrown 5 and decrease with the increase
of the diazacrown ring. The constants for 7 and 8
do not differ appreciably showing that the arrange-
ment of nitrogen atoms in the molecule is of no
essential importance.

These observations contradict the results obtained
for complexes 4. NiCl$_2$, where the highest values for
stability constants in 95% methanol had been
obtained for the 16-membered ligand 4 where n =
m = 3 [7]. This difference may be due to the assump-
tion that the interaction of NiCl$_2$ moiety with the
macrocyclic ligand differs from the interactions
with Ni$^{2+}$ ion which occur in the system investigated
by us.

Zinc complexes with all macrocyclic ligands have
higher stability constants than those expected.
Similarly, Ni$^{2+}$ complexes with ligands 6–9 are char-
acterized by small stability constants as compared to
the corresponding Co$^{2+}$ complexes. Inversion of the

TABLE 1. Protonation Constants[a] of Azacrowns and Polyetheroamines.

| Ligand | $\log K_1$ | $\log K_2$ | $\log K_3$ | $\log K_4$ | References |
|---|---|---|---|---|---|
| 5 | 9.53 ± 0.05 | 7.65 ± 0.07 | | | |
| 6 | 9.26 ± 0.03 | 8.12 ± 0.03 | | | |
| | 8.76 ± 0.008 | 8.04 ± 0.006 | | | [5] |
| 7 | 9.59 ± 0.04 | 8.01 ± 0.05 | | | |
| 8 | 9.30 ± 0.04 | 8.15 ± 0.04 | | | |
| | 9.245 ± 0.007 | 8.225 ± 0.002 | | | [6] |
| 9 | 9.20 ± 0.06 | 6.30 ± 0.09 | | | |
| 10 | 9.67 ± 0.14 | 8.85 ± 0.13 | 6.61 ± 0.20 | 3.21 ± 0.20 | |
| 11 | 9.89 ± 0.07 | 7.08 ± 0.03 | | | [16] |
| 12 | 9.75 | 8.90 | | | [16] |
| 13 | 9.73 | 8.75 | | | [16] |

The limits of errors in our work correspond to two standard deviations.
[a]$K_n = [LH_n][LH_{n-1}]^{-1}\{H^+\}^{-1}$.

TABLE II. Stability Constants of Polyazacrown Complexes and Complexes of Some Diamines.

| Ligand | $\log K_1{}^{\ddagger}$ | | | | References |
|---|---|---|---|---|---|
| | $Co^{2+}$ 0.82[a] | $Ni^{2+}$ 0.78 | $Cu^{2+}$ 0.73 | $Zn^{2+}$ 0.83 | |
| 5 0.8[b] | 5.76 ± 0.10 | 5.91 ± 0.40 | 8.16 ± 0.11 | 6.22 ± 0.07 | |
| 6 1.0 | 5.22 ± 0.08 5.05 ± 0.02 | 4.05 ± 0.16 3.73 ± 0.03 | 8.15 ± 0.16 7.17 ± 0.006 | 5.34 ± 0.08 5.19 ± 0.014 | [5] |
| 7 1.4 | 3.26 ± 0.12 | 3.21 ± 0.16 | 7.40 ± 0.09 | 4.26 ± 0.14 | |
| 8 1.4 | 3.25 ± 0.20 ≤2.5 | 3.43 ± 0.32 ≤2.5 | 7.59 ± 0.02 6.18 ± 0.06 | 4.31 ± 0.18 3.19 ± 0.32 | [5] |
| 9 1.0 | 4.90 ± 0.16 | 5.05 ± 0.15 | 8.86 ± 0.07 | 5.04 ± 0.16 | |
| 10 1.4 | 9.68 ± 0.05 | 12.49 ± 0.15 | 15.50 ± 0.08 | 10.90 ± 0.06 | |
| 11 | 5.89[d] 10.72[c] | 7.66[d] 14.06[c] | 10.55[e] 19.60[c] | 5.71[e] 10.37[c] | [d][17] [e][18] |
| 12 | -- | 5.62 | 8.70 | -- | [16] |
| 13 | -- | -- | 7.89 | -- | [16] |

[a]Ionic radii in Å according to [20].　[b]Cavity radius in Å.　[c]$\log \beta_2$ values.　[‡]$K_1 = [ML][L]^{-1}[M]^{-1}$.

Irving—Williams series is most evident for $Ni^{2+}$ and $Co^{2+}$ complexes of diazacrown 6 [*cf.* 5].

Thermodynamic parameters of $Cu^{2+}$ complexation by ligand 9, calculated from stability constants data obtained from potentiometric titrations at 15, 25 and 35 °C ($\Delta H° = 48 \pm 4$ kJ mol$^{-1}$ and $\Delta S° = 16 \pm 14$ J K$^{-1}$ mol$^{-1}$), points to a small contribution of the entropy effect, a fact that can be accounted for by inconsiderable dehydration of the metal ion during complexation.

Comparison of formation constants for complexes with ligands 5-8 and the corresponding complexes of compounds 12 and 13 (as well as for compound 9 and ethylenediamine 11) shows that there is no macrocyclic effect [19] in the systems investigated. Similarly, a comparison of the $K_1$ values of the complexes of 10 with the $\beta_2$ values of the corresponding ethylenediamine complexes supports the above observation. The absence of the macrocyclic effect and small differences in formation constants

regardless of the structure of the investigated ligands may be taken as evidence of insignificant interaction between the oxygen atoms and the investigated transition metal ions.

## Acknowledgement

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