rates being only 10–100 times smaller. Whether these differences reflect the lower flexibility of the macrocycle or are due to steric effects cannot be stated at the moment. It is, however, clear that more rigid rings must be studied to answer this question.

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REFERENCES

[1] *T.J. Lotz & Th.A. Kaden*, Helv. *61*, 1376 (1978).
[2] *A. Leugger, L. Hertli & Th.A. Kaden*, Helv. *61*, 2296 (1978).
[3] *R. Buxtorf & Th.A. Kaden*, Helv. *57*, 1035 (1974).
[4] *W. Steinmann & Th.A. Kaden*, Helv. *58*, 1358 (1975).
[5] *C.T. Lin, D.B. Rorabacher, G.R. Cayley & D.W. Margerum*, Inorg. Chemistry *14*, 919 (1975).
[6] *Th.A. Kaden*, Helv. *53*, 617 (1970).
[7] *J.L. Karn & D.H. Busch*, Inorg. Chemistry *8*, 1149 (1969); *R. Dewar & E. Fleischer*, Nature *222*, 372 (1969).
[8] *L. Rusnak & R.B. Jordan*, Inorg. Chemistry *10*, 2199 (1971).
[9] *Th.A. Kaden & A.D. Zuberbühler*, Talanta *18*, 61 (1971).
[10] *D.W. Marquardt*, J. Soc. ind. appl. Math. *11*, 431 (1963).
[11] *A.D. Zuberbühler & Th.A. Kaden*, unpublished.
[12] *P.R. Bevington*, 'Data reduction and error analysis for the physical sciences', McGraw-Hill, New York 1969, page 196.
[13] *D. Margerum, D. Rorabacher & J. Clarke*, Inorg. Chemistry *2*, 667 (1963).
[14] *M. Eigen*, Pure appl. Chemistry *6*, 105 (1963).

219. Metal Complexes with Macrocyclic Ligands. XI[1]). Ring Size Effect on the Complexation Rates with Transition Metal Ions

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(3.VII.78)

Summary

The 12–16 membered tetraazamacrocycles **1–6** were synthesized, their protonation constants and complexation kinetics measured at 25° and I = 0.5. The results of *Table 1* show that pK_3^H is strongly influenced by the ring size whereas pK_2^H and pK_1^H are relatively insensitive to it. This can be understood in terms of electrostatic interactions of the positive charges when located on adjacent amino groups.

The kinetics of complex formation between the macrocyclic ligands and several transition metal ions have been studied by pH-stat and stopped-flow techniques

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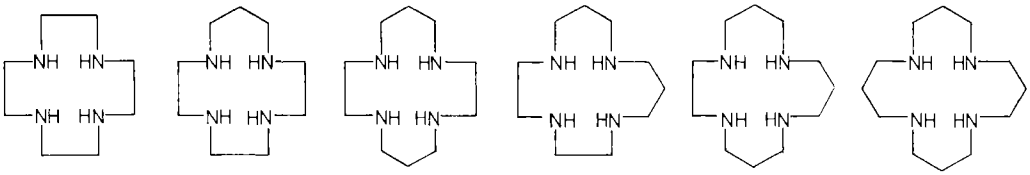
and the results have been analyzed as bimolecular reactions between the metal ion and the different protonated species of the ligands. The rate constants, given in *Table 2*, show that the macrocycles react less rapidly than analogous open chain amines. However, for a given protonated species of the ligand the rate of complexation follows the order $Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$ which parallels the sequence of their water exchange rates. For the diprotonated tetraamines LH_2^{2+} reacting with Cu^{2+} the slower rates seem to be mainly a consequence of electrostatic interactions, since a correlation between $\log k_{LH_2}^{Cu}$ and pK_3^H exists. For LH^+, however, the complexation rates of a metal ion with the different macrocycles are all in one order of magnitude and do not depend in a regular way on the ring size or the basicity of the ligand. It is therefore suggested that in this case other factors such as unfavourable preequilibria must be considered as important.

Since the observation that macrocyclic ligands in their protonated form react at a slower rate than the corresponding open chain polyamines [2] several factors which could affect the rate of complexation with transition metal ions have been studied.

N-alkylation in the series of mono-, di- and tetramethyl derivatives of 1,4,8,11-tetraazacyclotetradecane has relatively little effect on the bimolecular rate constants [3], in contrast to the fact that for open chain ligands the rate of complexation strongly decreases on going from secondary to tertiary amines [4]. Introduction of substituents in the α- and β-position to the amino nitrogen atoms was also investigated for the 13-membered ring ligands [5]. Whereas β-substituents do not significantly influence the reactivity, α-substituents slow down the complexation rate. Another factor determining the behaviour of polyazamacrocycles in their reaction with metal ions is the overall charge. Protonated macrocyles react about 10^3–10^4 times less rapidly than analogous open chain ligands [2] [3] [5], whereas the unprotonated form of both cyclic and open chain polyamines have similar rate constants provided that steric effects are equal [6].

The relationship between the ring size of the macrocycle and its chemical reactivity has not been systematically studied. Comparison between the 13- and 14-membered tetraazacycloalkanes in their complexation with Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} indicates that the 13-membered ring complexes more rapidly that the 14-membered ligand [5]. A paper [7] on the reactivity of $Cu(CH_3COO)^+$ with the monoprotonated form of different macrocycles finds as a trend higher complexation rates with increasing ring size.

We present here a complete and systematic study of the complexation of tetraazamacrocycles **1**–**6** with several metal ions which shows how the ring size cor-



1 **2** **3** **4** **5** **6**

relates with the rate of complexation. A similar investigation with a series of 12- to 18-membered tetrathiacycloalkanes was recently reported by *Rorabacher et al.* [8].

Experimental Part. – Melting points are uncorrected. NMR. spectra were recorded on a *Varian* EM 360 instrument using tetramethylsilane as internal standard. Chemical shifts are given in δ-values, the multiplicity, the intensity and type of protons are indicated in parenthesis (s = singlet, t = triplet, qi = quintuplet, m = multiplet). *1,4,7,10-tetraazacyclododecane* (**1**) and *1,4,7,11-tetraazacyclotridecane* (**2**) were synthesized by the method of *Stetter & Mayer* [9] and isolated as tetrahydrochlorides. *1,4,8,11-tetraazacyclotetradecane* (**3**) was prepared according to the procedure of *Barefield et al.* [10]. *1,4,7,11-tetraazacyclotetradecane* (**4**), *1,4,8,12-tetraazacyclopentadecane* (**5**) and *1,5,9,13-tetraazacyclohexadecane* (**6**) were obtained by the procedure of *Richman & Atkins* [11]. The tosyl groups were cleaved off with 96% sulfuric acid.

1,4,7,11-Tetratosyl-1,4,7,11-tetraazacyclotetradecane. From *N,N',O*-tritosyldiethanolamine and 1,5,9-tritosyl-1,5,9-triazanonane. Yield 32%. Crystallized from formic acid, m.p. 232–233°. – NMR. ($CDCl_3$): 1.8 (m, 4 H, 2 C–CH_2–C); 2.45 (s, 12 H, 4 CH_3Ph); 3.25 (m, 16 H, 8 CH_2–N); 7.45 (m, 16 H, 4 PhH).

$C_{38}H_{48}N_4O_8S_4$	Calc.	C 55.86	H 5.92	N 6.86	S 15.70%
(817.06)	Found	„ 55.95	„ 5.93	„ 6.91	„ 15.97%

1,4,8,12-Tetratosyl-1,4,8,12-tetraazacyclopentadecane. From 1,5,8,12-tetratosyl-1,5,8,12-tetraazadodecane and ditosylpropyleneglykol. Yield 63%; crystallized from $CHCl_3$/EtOH, m.p. 219–220° (Phase change 116–126°). – NMR. ($CDCl_3$): 1.8 (m, 6 H, 3 C–CH_2–C); 2.45 (s, 12 H, 4 CH_3Ph); 3.2 (m, 16 H, 8 CH_2–N); 8.5 (m, 16 H, 4 PhH).

$C_{39}H_{50}N_4O_8S_4$	Calc.	C 56.36	H 6.06	N 6.74	S 15.43%
(831.11)	Found	„ 56.20	„ 5.96	„ 6.59	„ 15.22%

1,5,9,13-Tetratosyl-1,5,9,13-tetraazacyclohexadecane. From 1,5,9,13-tetratosyl-1,5,9,13-tetraazatridecane and ditosylpropyleneglykol. Yield 69%. Purified by extraction with MeOH, in which the product is insoluble, m.p. 277–278°.

$C_{40}H_{52}N_4O_8S_4$	Calc.	C 56.85	H 6.20	N 6.63	S 15.17%
(845.14)	Found	„ 57.05	„ 6.16	„ 6.87	„ 14.91%

1,4,7,11-Tetraazacyclotetradecane (**4**). Yield 72%. Crystallized from petroleum ether, m.p. 75–77°. – NMR. ($CDCl_3$): 1.7 (qi, 4 H, 2 C–CH_2–C); 2.2 (s, 4 H, 4 NH); 2.8 (m, 16 H, 8 CH_2–N).

4. *Tetrahydrobromide monohydrate.* Crystallized from H_2O/EtOH, Dec. 251°.

$C_{10}H_{30}Br_4N_4O$	Calc.	C 22.14	H 5.53	Br 58.97	N 10.35%
(541.90)	Found	„ 22.3	„ 5.5	„ 58.6	„ 10.5 %

1,4,8,12-Tetraazacyclopentadecane (**5**). Yield 58%. Crystallized from acetone, m.p. 101–102° (98–99° [12]). – NMR. ($CDCl_3$): 1.6 (qi, 6 H, 3 C–CH_2–C); 2.45 (s, 4 H, 4 NH); 2.85 (m, 16 H, 8 CH_2–N).

$C_{11}H_{26}N_4$	Calc.	C 61.64	H 12.23	N 26.14%
(214.36)	Found	„ 61.88	„ 12.48	„ 25.81%

5. *Tetrahydrobromide.* Crystallized from H_2O/EtOH, m.p. 228–231°.

$C_{11}H_{30}Br_4N_4$	Calc.	C 24.56	H 5.62	N 10.41	Br 59.41%
(537.98)	Found	„ 24.82	„ 5.54	„ 10.28	„ 59.46%

1,5,9,13-Tetraazacyclohexadecane (**6**). Yield 75%. Crystallized from ether, m.p. 83–84°. – NMR. ($CDCl_3$): 1.65 (qi, 8 H, 4 C–CH_2–C); 1.7 (s, 4 H, 4 NH); 2.75 (t, 16 H, 8 CH_2–N).

$C_{12}H_{28}N_4$	Calc.	C 63.11	H 12.36	N 24.53%
(228.38)	Found	„ 62.93	„ 12.25	„ 24.29%

6. *Tetrahydrobromide.* Crystallized from H_2O/MeOH, Dec. 270°.

$C_{12}H_{32}Br_4N_4$	Calc.	C 26.11	H 5.84	Br 57.90	N 10.15%
(551.99)	Found	„ 25.92	„ 5.91	„ 57.82	„ 10.13%

Reagents of a analytical grade were used without further purification. $T = 25 \pm 0.05°$, $I = 0.5$ (KNO_3).

pK_H-determination. 10^{-2}M Ligand tetrahydrochloride or tetrahydrobromide were titrated under N_2 with 0.4M NaOH using a *Metrohm* compensator E388 with a combined glass electrode, which was calibrated against two buffer solutions of pH 4 and 7. Duplicate of each titration curve did not differ from each other by more than ± 0.01 pH units.

Kinetics measurements. The complex formation of the metal complexes with the different macrocycles was mostly followed under pseudo first-order conditions ($[M^{2+}] > 10 \cdot [\text{ligand}]$) with a pH-stat (Combititrator 3D, *Metrohm*) as described before [5]. 0.025M NaOH was used to keep the pH constant. Rate constants were calculated on a HP 9821 desk computer with appropriate programs for first or second order reactions. The more rapid reactions of Cu^{2+} were followed with a *Durrum* stopped-flow instrument on line with a *Datalab* 901 transient recorder and a HP 9821 computer [13] at 620 nm for **5** or 550 nm for **4**. Typical concentrations were $[\text{ligand}] = 1-2 \cdot 10^{-4}$M, $[Cu^{2+}] = 2-5 \cdot 10^{-3}$M in acetate buffers. By variation of the acetate concentration from 0.02 to 0.1M at different pH values the influence of acetate on the rate of complexation was determined. The acetate indipendent rate constants k_{obs} were obtained either by extrapolating c_{ACO} to 0 or by using (1), *i.e.* by correcting the observed rate constant k'_{obs} by the amount to which acetate increase the

$$k_{obs} = k'_{obs} - k_{ACO} \cdot c_{ACO} \quad (1)$$

rate. The error of k'_{obs} were smaller than 2%, when calculated from a single curve. Between duplicate the error was smaller than 5%.

Results. – The pK^H-values of the macrocycles calculated from their titration curves by the computer programm VARIAT [14] or a modified version based on *Marquard's* technique [15] for non linear regression are given in *Table 1.* Our values nicely correspond to those already published in the literature, with exception of those given by *Mayer* [16] and the pK_3^H and pK_4^H of **5** reported by the Japanese authors [17].

In the discussion of the pK^H-values of **3** a fully hydrogen bonded structure was first proposed by *Stetter & Mayer* [9]. Later *Bosnich et al.* suggested a structure with two transanular bonds [18], which leave the electron pairs of two nitrogen atoms easely accessible for two protons (pK_1^H and pK_2^H), whereas the other two are blocked and thus of low basicity (pK_3^H and pK_4^H). Two attempts to confirm the presence of strong hydrogen bonds in **3** were either unsuccessfull or equivocal[3]). The IR. study of **3** in CCl_4 solution, in which one would expect a high tendency for intramolecular hydrogen bond formation finds no such bonds [19]. Similary, the X-ray structure analysis of the diperchlorate of **3** only suggests the possibility of two weak hydrogen bonds [20]. The results of *Table 1*, in which the effect of the ring size on the different pK^H-values is given, show that the variation in pK_1^H and pK_2^H is minor compared to the change observed in pK_3^H and pK_4^H. The first observation is easily rationalized, then the second proton can always add to a nitrogen atom *trans* to the one to which the first proton is already bound. The distances are for all ring sizes such, that little or no interaction takes place, thus giving normal pK^H-values. The change in ring size but also the relative arrangement of ethylene and propylene bridges between the amino nitrogens strongly influences the values of the higher protonation constants. The third and fourth proton must bind between two positively charged ammonium groups whereby a strong electrostatic interaction results. Increasing the length of the bridges from two to three and having the propylene bridges close to each other, the protonation becomes easier and the pK^H-values increase. Thus it appears that the sequence

[3]) However, hydrogen bonds might exist in the crystalline state [18] [19].

Table 1. *pK^H values* [a]) *of the macrocyclic tetraamines with different ring sizes at 25°*

Compound	I	pK_1^H	pK_2^H	pK_3^H	pK_4^H	Ref.
1	0.5	10.97	9.87	< 2	< 2	
	0.2	10.7	9.7	1.73	0.94	[21] [25]
2	0.5	11.19	10.12	< 2	< 2	
	0.2	11.1	10.1	~ 1.7	~ 1	[7]
3	0.5	11.83	10.76	< 2	< 2	
	0.1[b])	10.76	10.18	3.54	2.67	[16]
	0.1	11.49				[22]
	0.2	11.50	10.30	1.62	0.94	[23] [25]
4	0.5	11.29	10.19	4.32	< 2	
5	0.5	11.23	10.28	5.32	3.79	
	0.2	11.2	10.1	~ 2	~ 2	[17]
6	0.5	10.85	9.80	7.21	5.69	

[a]) All values of this paper ± (0.02–0.05). [b]) At 20°.

of pK^H-values is mostly due to the electrostatic repulsions which in a macrocycle are much more relevant than in an open chain tetraamine. No intramolecular hydrogen bonds seem to be needed to explain the pK^H-values of **3** which nicely fits into the series of the other tetraazamacrocycles. For the largest ring **6** the pK^H-values closely resemble those observed in open chain tetraamines.

Kinetics. – The rates of complex formation between the macrocycles and the different metal ions are proportional to $[L]_{tot}$ and $[M^{2+}]_{tot}$. In addition they are a function of the pH. This comes from the fact that depending upon the pH region the ligands can react in their different protonated species. All pH dependencies *(Fig. 1–3)* were fitted assuming that the following reactions are possible:

$$\begin{array}{ccc} M^{2+}+L & \xrightarrow{k_L} & ML \\ K_1^H \uparrow\downarrow & & \uparrow\downarrow \text{ fast} \\ M^{2+}+LH & \xrightarrow{k_{LH}} & MLH \\ K_2^H \uparrow\downarrow & & \uparrow\downarrow \text{ fast} \\ M^{2+}+LH_2 & \xrightarrow{k_{LH_2}} & MLH_2 \\ K_3^H \uparrow\downarrow & & \uparrow\downarrow \text{ fast} \\ M^{2+}+LH_3 & \xrightarrow{k_{LH_3}} & MLH_3 \end{array}$$

The scheme gives for the observed rate constant k_{obs} equation (2).

$$k_{obs}=\frac{k_L K_1^H K_2^H K_3^H + k_{LH} K_1^H K_2^H [H^+] + k_{LH_2} K_1^H [H^+]^2 + k_{LH_3} [H^+]^3}{K_1^H K_2^H K_3^H + K_1^H K_2^H [H^+] + K_1^H [H^+]^2 + [H^+]^3} \qquad (2)$$

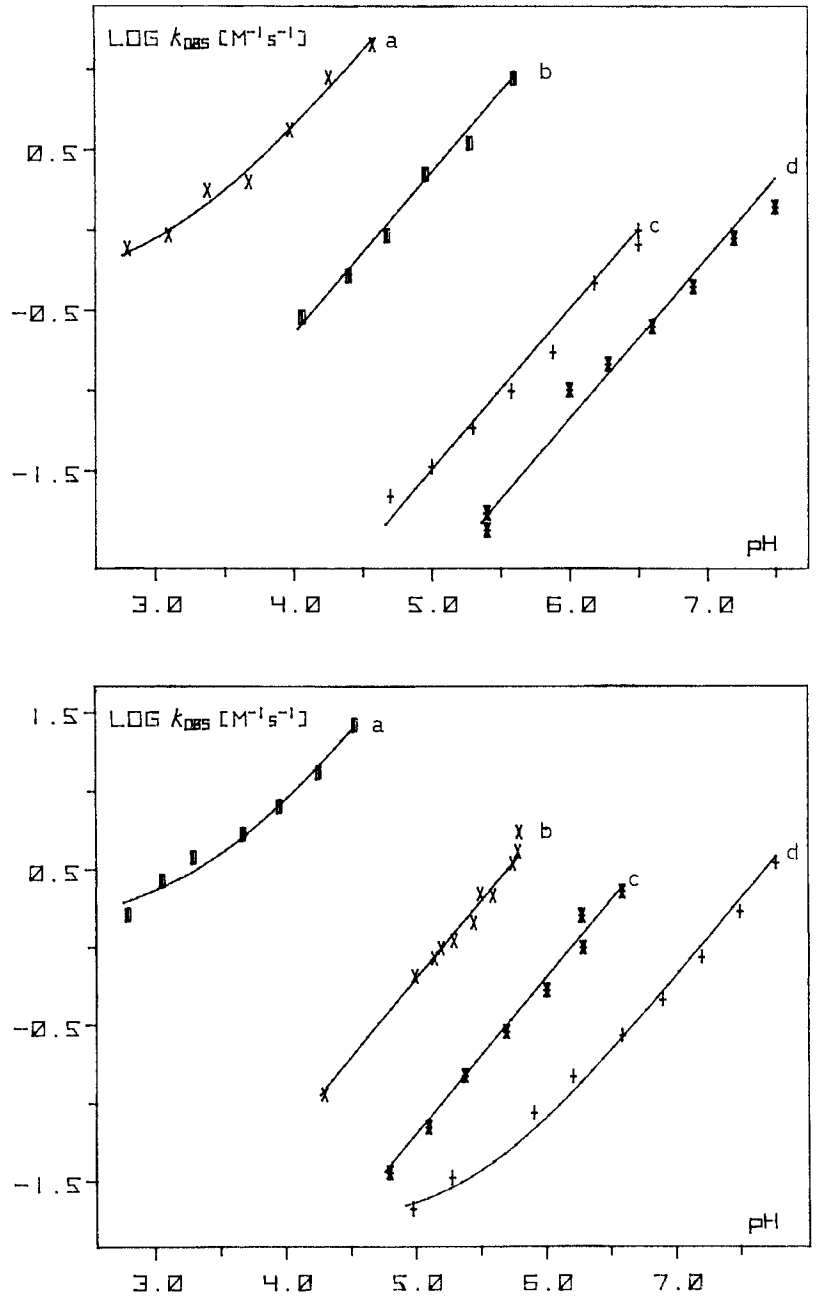


Fig. 1. *pH dependence of* k_{obs} *for the complexation of* **1** *(above) and* **2** *(below) with a)* Cu^{2+}, *b)* Zn^{2+}, *c)* Co^{2+} *and d)* Ni^{2+} *(for* **1** *with* Co^{2+}, Ni^{2+} *and* Zn^{2+} *and* **2** *with* Co^{2+} *and* Ni^{2+} $T = 40°$*).* The curves are calculated with the rate constants of *Table 2* and the size of the experimental points corresponds to $2\sigma_y$.

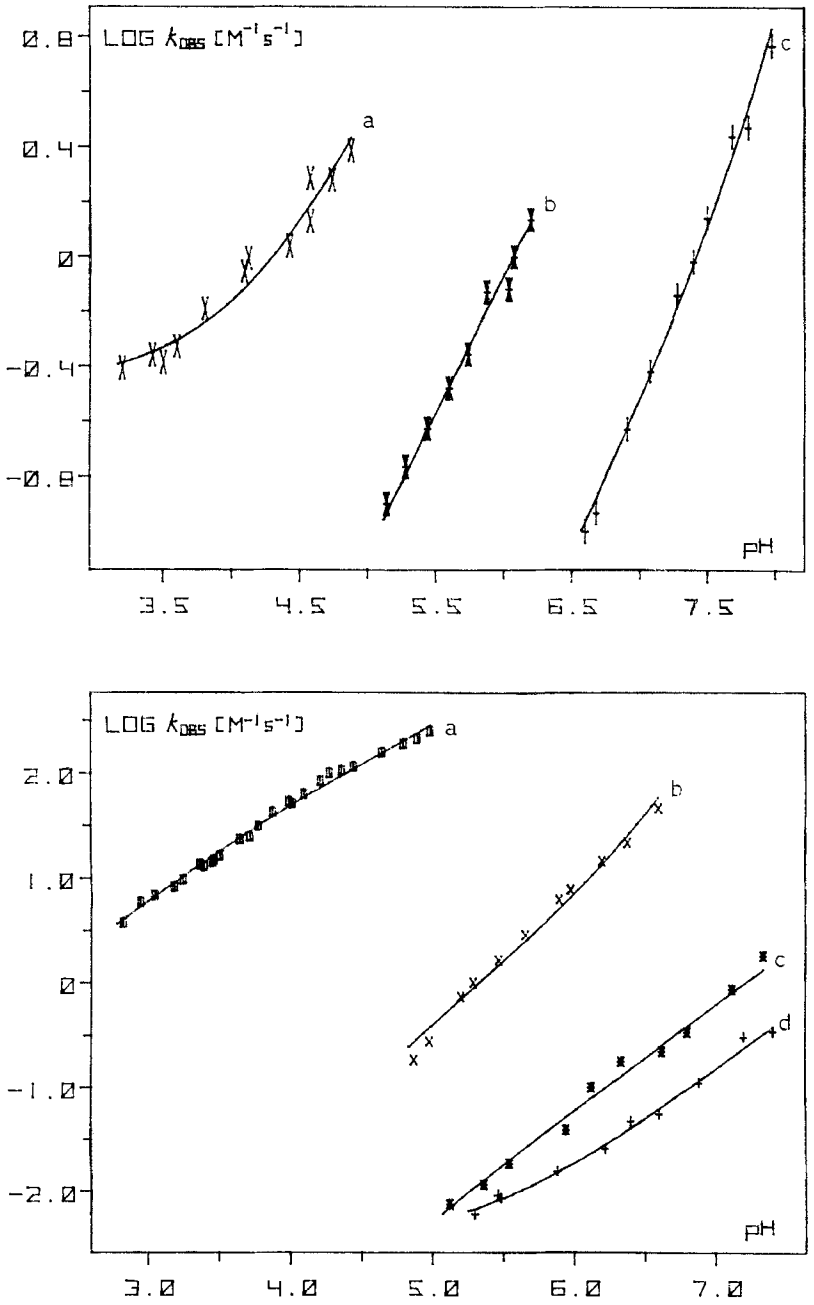


Fig. 2. *pH dependence of* k_{obs} *for the complexation of* **3** *(above) and* **4** *(below) with a)* Cu^{2+}, *b)* Zn^{2+}, *c)* Co^{2+} *and d)* Ni^{2+}. The curves are calculated with the rate constants of *Table 2* and the size of the experimental points corresponds to $2\sigma_y$.

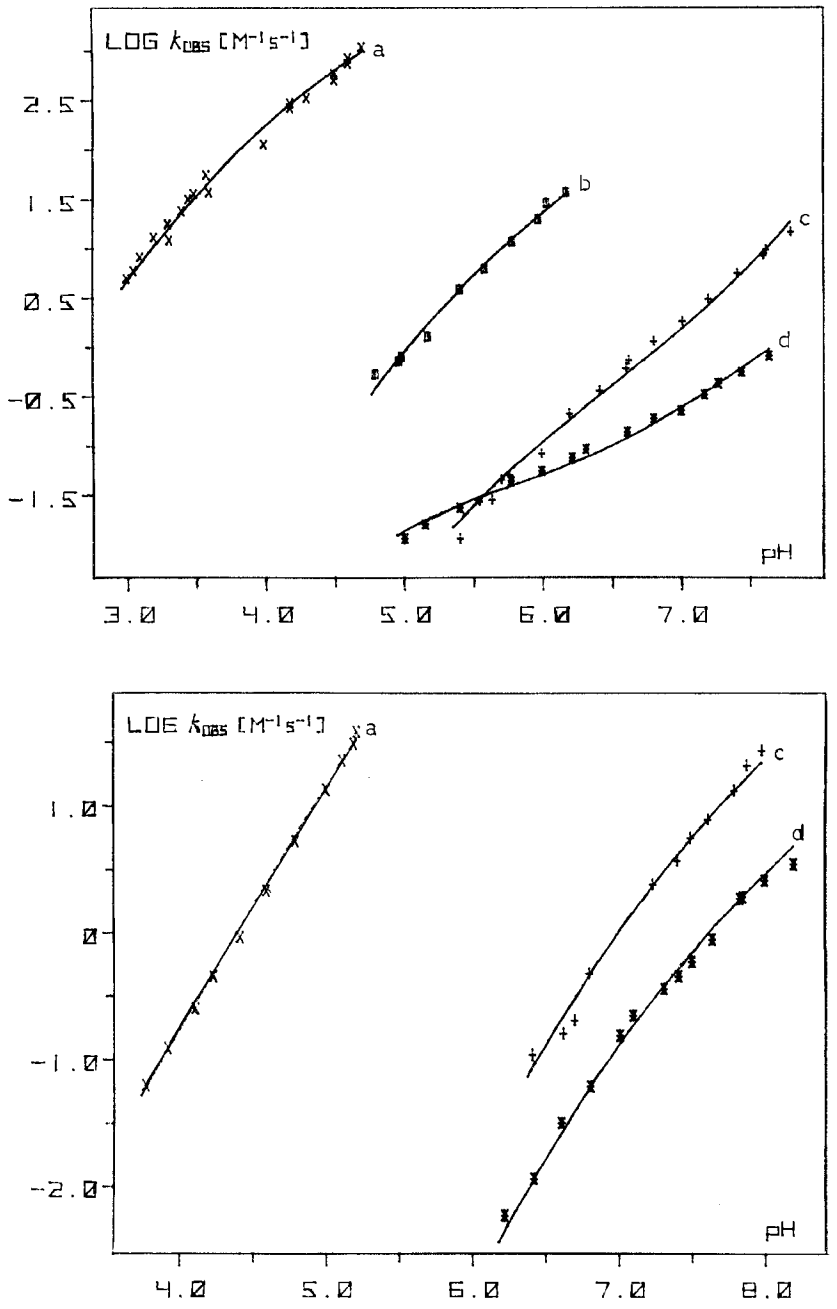


Fig. 3. *pH dependence of* k_{obs} *for the complexation of* **5** *(above) and* **6** *(below) with a)* Cu^{2+}, *b)* Zn^{2+}, *c)* Co^{2+} *and d)* Ni^{2+}. The curves are calculated with the rate constants of *Table 2* and the size of the experimental points corresponds to $2\sigma_y$.

Table 2. *Rate constants* $k(M^{-1}s^{-1})$ *for the complexation of the macrocyclic tetraamines* **1**–**6** *with* Co^{2+}, Ni^{2+}, Cu^{2+} *and* Zn^{2+}

L	Co^{2+}		Ni^{2+}		Cu^{2+}		Zn^{2+}	
	$10^{-3} \cdot k_{LH}$	$10^{-7} \cdot k_L$	$10^3 \cdot k_{LH_2}$	$10^{-2} k_{LH}$	k_{LH_2}	$10^{-6} k_{LH}$	$10^{-4} \cdot k_{LH}$	$10^{-9} k_L$
1	2.4 ±0.2[a])			5.0 ±0.6[a])	(6±1)10^{-1}	2.9±0.3	17 ±1[a])	
	0.31±0.03[g])			0.66±0.07[h])		5.5 [21]	3.3±0.3[i])	
2	8.4 ±0.7[a])		17 ±3[a])	8.5 ±0.8[a])	1.9 ±0.2	9.2±0.9	8.2±0.4	
	0.90±0.08[f])			1.7 ±0.2[e])	0.14 [7]	17 [7]		
3	1.5 ±0.1	1.9±0.3	3.3[b])	0.53[b])	(3.9±0.3)10^{-1}	1.8±0.2	5.0±0.2	
					7.6$10^{-2}$[24]	8 [24]		
4	1.0 ±0.07			3.5 ±0.4[c])	(1.3±0.04)10^2	36±3	7.4±0.8	8±2
			4.7±0.7	2.4 ±0.1[c])				
5	3.5 ±0.3[d])		42 ±3	4.7 ±0.3	(5.4±0.2)10^3		62 ±3	
	2.9 ±0.2[d])	0.8±0.2[d])						
6	1.9 ±0.1			2.4 ±0.1	(1.1±0.03)10^4			

[a])At 40°, all other values at 25°. [b])These values are different from the previously published ones [2], since for this table $pK_3^H = 10.76$ was used. [c])The square sum after curve fitting with k_{LH} was 0.254 (10 degrees of freedom (D.F.)) and 0.056 (9D.F.) with k_{LH_2} and k_{LH}. This gives $F = 4.08$ to compare with $F_{0.01} = 5.26$ and $F_{0.05} = 3.14$. [d])The square sum is 0.31 (15D.F.) with k_{LH} and 0.13 (14D.F.) with k_{LH_2} and k_{LH}. Thus $F = 2.22$ to compare with $F_{0.01} = 3.66$ and $F_{0.05} = 2.46$. [e])Calculated from the value at 40° with $\Delta E^* = 88$ kJmol^{-1}. [f])Calculated from the value at 40° with $\Delta E^* = 86$ kJmol^{-1}. [g])Calculated from the value at 40° with $\Delta E^* = 103$ kJmol^{-1}. [h])Calculated from the value at 40° with $\Delta E^* = 103$ kJmol^{-1}. [i])Calculated from the value at 40° with $\Delta E^* = 84$ kJmol^{-1}.

In order to determine which rate constants are relevant for the pH dependency of each system, the experimental points were fitted with equations of the type (2) using the known values of K_i^H *(Table 1)* and taking the rate constants as parameters. The 'best' sets of rate constants, found by a nonlinear least square method [15], are collected in *Table 2.*

In some cases sets of rate constants, which equally well satisfy the statistical F-test[4]), were found to fit the experimental points. These values are also given in *Table 2.*

The results of *Table 2* can be analyzed in different ways and the following points can be made:

1) The complexation of the cyclic ligands is slower than that of the corresponding open chain tetraamines, when protonated species of the same charge are compared;

2) For a given protonated species of a macrocycle the complexation rates follow the order $Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$ and parallel the sequence of solvent exchange rates;

3) For a given metal ion the complexation rate constants with LH^+ are all in one order of magnitude and do not vary in a regular way with the ring size;

[4]) For a full discussion of the use of the F-Test see [1].

4) In contrast the values of k_{LH_2} with Cu^{2+} strongly depend upon the nature of the macrocycle and increase with increasing ring size, except for **4**.

The first two observations, that the complexation rates with the protonated macrocycles are slower than those with open chain tetraamines, but follow the sequence found for their solvent exchange, indicate that an unfavourable step prior to the dissociation of a water molecule from the coordination sphere must exist. *Margerum et al.* [6] suggest that electrostatic interactions are mainly responsible for the slow reaction of the macrocycles, since the positive charge of the metal ion and that of the protonated ligand are closer to each other in cyclic than in open chain tetraamines. This was inferred from experiments in strongly alkaline solutions, which show that the macrocycles in their unprotonated from, *i.e.* as free bases, react as fast as the open chain polyamines.

Discussing the pK^H-values we have observed that the electrostatic repulsion is indeed important for the third proton addition, but not for the second one. Thus we would expect that the rate constants k_{LH_2}, describing the reactivity of the diprotonated species with M^{2+} would also be strongly affected by such electrostatic interactions. The correlation between $\log k^{Cu}_{LH_2}$ and pK^H_3 *(Fig. 4)* nicely illustrates that the same factors which determine the values of pK^H_3 also seem responsible for $k^{Cu}_{LH_2}$. It is interesting to note that the two isomeric 14-membered

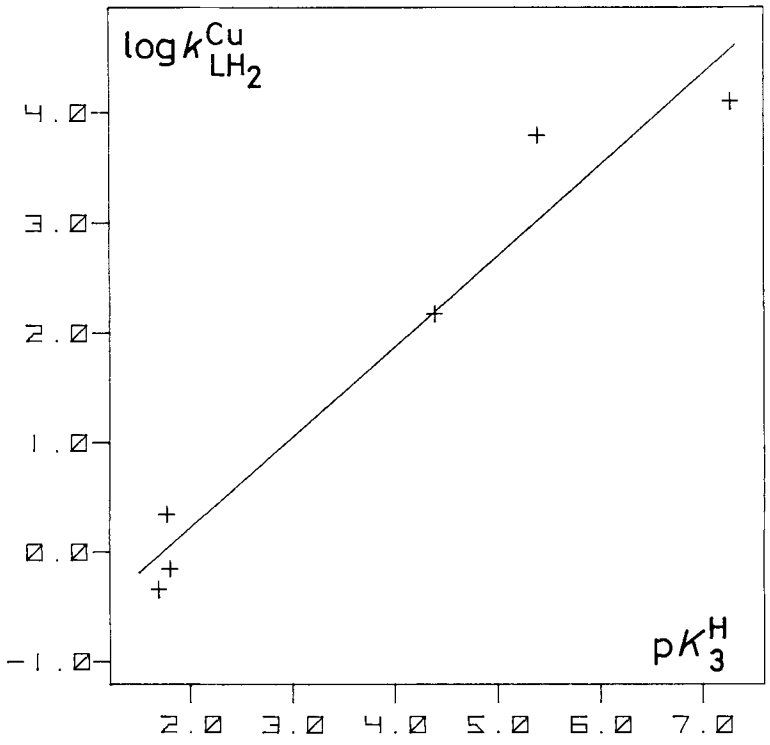


Fig. 4. *Correlation between* $\log k^{Cu}_{LH_2}$ *and* pK^H_3 *for the ligands* **1** *to* **6**

rings **3** and **4** have distinctly different rate constants $k_{LH_2}^{Cu}$ as well as different pK_3^H values. Thus not the ring size, but the relative arrangement of ethylene and propylene bridges is important.

The values of k_{LH} for the macrocycles reacting with a specific metal ion do not differ by more than an order of magnitude. In contrast to the behaviour of k_{LH_2} we do not find any correlation between k_{LH} and pK_2^H or the ring size. This opens the question whether the factors determining k_{LH_2} are also responsible for the slower complexation with LH^+. Since the pK_2^H values in the series of the 12–16 membered rings seem not to be determined by electrostatic interactions, we suggest that for k_{LH} some other effect is active. For example it is conceivable that an unfavourable conformation of the cyclic monoprotonated ligand could be the cause of the slower complexation rate as against to that of the open chain ligands.

In summary we think that one must carefully take attention of the different species of the ligand, when a comparison between the complexation of cyclic and open chain ligands is made. For LH_2^{2+} electrostatic factors determining the stability of the other-sphere complex are the main factor, for LH^+ conformational effects might play an important role, whereas for L no difference between the cyclic and open chain polyamine is found, except when steric hindrance is present.

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REFERENCES

[1] *P. Schultz-Grunow & Th.A. Kaden*, Helv. *61*, 2291 (1978).
[2] *Th.A. Kaden*, Helv. *53*, 617 (1970).
[3] *R. Buxtorf & Th.A. Kaden*, Helv. *57*, 1035 (1974).
[4] *T.S. Turan & D.B. Rorabacher*, Inorg. Chemistry *11*, 288 (1972).
[5] *W. Steinmann & Th.A. Kaden*, Helv. *58*, 1358 (1975).
[6] *C.T-Lin, D.B. Rorabacher, G.R. Cayley & D.W. Margerum*, Inorg. Chemistry *14*, 919 (1975).
[7] *M. Kodama & E. Kimura*, J. chem. Soc. Dalton 1976, 1720.
[8] *T.E. Jones, L.L. Zimmer, L.L. Diddario, D.B. Rorabacher & L.A. Ochrymowycz*, J. Amer. chem. Soc. *97*, 7163 (1975).
[9] *H. Stetter & K. Mayer*, Chem. Ber. *94*, 1410 (1961).
[10] *K. Barefield*, Inorg. Chemistry *11*, 2273 (1972).
[11] *J.E. Richman & T.J. Atkins*, J. Amer. chem. Soc. *96*, 2268 (1974).
[12] The Strem Chemiker *3*, 9 (1975).
[13] *A. Zuberbühler & Th.A. Kaden*, Chimia *31*, 442 (1977).
[14] *Th.A. Kaden & A.D. Zuberbühler*, Talanta *18*, 61 (1971).
[15] *D.W. Marquardt*, J. Soc. ind. appl. Math. *11*, 431 (1963).
[16] *K.H. Mayer*, Dissertation, München 1960.
[17] *M. Kodama & E. Kimura*, J. chem. Soc. Dalton 1976, 2341.
[18] *B. Bosnich, C.K. Poon & M.L. Tobe*, Inorg. Chemistry *12*, 2402 (1965).
[19] *H. Dodziuk, R.A. Kolinsky, B. Korybut-Daszkiewicz*, Spectrochim. Acta *29A*, 511 (1973).
[20] *C. Nave & M. Truter*, J. chem. Soc. Dalton 1974, 2351.
[21] *M. Kodama & E. Kimura*, J. chem. Soc. Dalton 1976, 116.
[22] *F.P. Hinz & D.W. Margerum*, Inorg. Chemistry *13*, 2941 (1974).
[23] *M. Kodama & E. Kimura*, J. chem. Soc. Dalton 1977, 2269.
[24] *M. Kodama & E. Kimura*, J. chem. Soc. Dalton 1977, 1473.
[25] *M. Kodama & E. Kimura*, Yuki Gosei Kagaku Kyokaishi *35*, 632 (1977).