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THERMODYNAMIC ASPECTS OF THE POLYAZACYCLOALKANE COMPLEXES WITH CATIONS AND ANIONS

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CONTENTS

A. INTRODUCTION

A large number of macrocyclic ligands have been synthesized and their metal complexes have been extensively studied. There have been many reviews [1–13] and books [14–19] published on macrocyclic ligands and their complexes.

The chemistry of synthetic macrocyclic ligands can be divided into two broad parts, in the first of which are the cyclic polyethers of the 'crown' type [20]. The second category of macrocyclic ligands incorporates ring systems containing nitrogen donor atoms. Although the synthesis of cyclam (**1**) has

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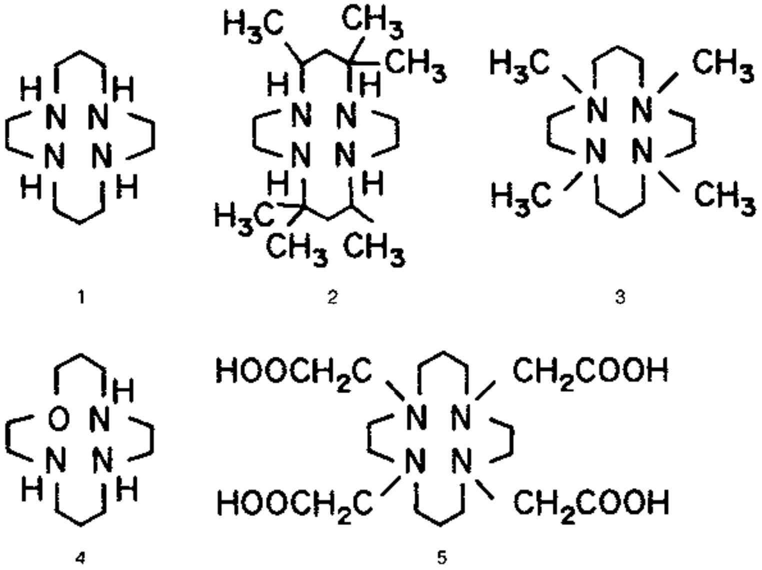
been known since 1936 [21], complexes with transition metal ions involving aza macrocycles were first reported by Curtis in the 1960s [22].

This review is dedicated to the thermodynamics of the equilibria, in aqueous solution, between saturated polyaza macrocycles and metal ions or anions. The macrocycles considered are those with nitrogen donor atoms and their derivatives, both carbon and nitrogen substituted. Following this rule, macrocycles (**1**)–(**3**) will be considered in this review while (**4**) and (**5**) will not.

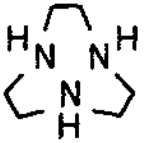


Scheme 1.

Ligands included in this review start from the smallest triazamacrocycle 1,4,7-triazacyclononane (**6**) up to the large polyazacycloalkane 1,4,7,10,13,16,19,22,25,28,31,34-dodecaazacyclohexatriacontane (**7**) containing 12 nitrogen donor atoms. Azapolycyclic compounds have also been considered provided they have been used in equilibrium studies.

These macrocyclic ligands are polyprotic bases in aqueous solution and the proton will always compete with the metal ion in complex formation. For this reason, equilibria between ligand and proton (protonation) will be considered first. Some special topics, such as 'synthetic methods', 'anion coordination' and 'blue to yellow equilibria' are treated in separate chapters.

Many aza macrocycles show an enhanced stability of their metal complexes compared with open-chain ligands, the so-called 'macrocyclic effect' [23]; although this effect is an experimental fact, a great deal of discussion has arisen over its thermodynamic origin. For this reason a chapter of this review has been dedicated to the Macrocyclic Effect.



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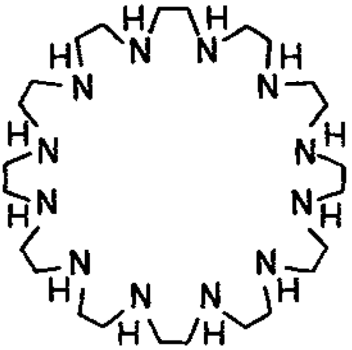

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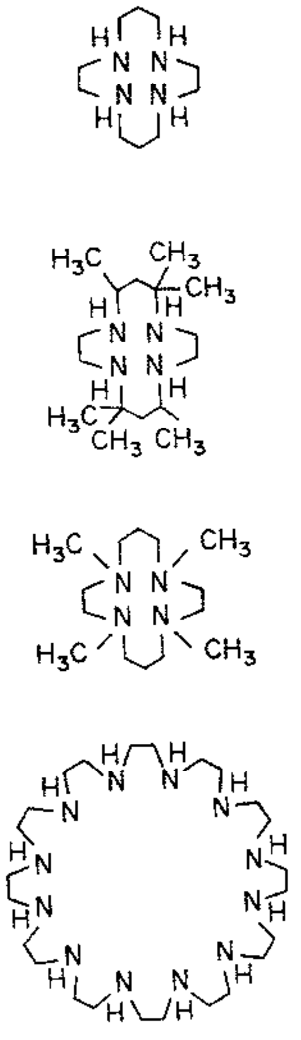
Obviously, when possible, the original paper has been used as a source of experimental data, including experimental conditions. However, a difficulty which is encountered in compiling a collection of thermodynamic equilibrium data is that the data are difficult to compare because they come from different sources and are obtained under different experimental conditions.

The nomenclature of macrocyclic ligands is difficult because in macrocycles, systematic names are cumbersome. Many different shorthand nomenclatures have been proposed for these ligands but even these can become ambiguous with substituted ligands. The first time that one ligand is encountered in the text we shall use the IUPAC designation and a numbered structural formula. Furthermore, for simple macrocycles, we will use also the system proposed by Busch and coworkers [24]. In order to keep our text as comprehensible as possible, we shall refer to each ligand by its number and in some cases by using a simplified notation. Figure 1 illustrates the nomenclature system and notation used in this review, which includes work published to 1989. If we have unintentionally omitted contributions from some laboratories, we offer apologies to the researchers concerned and to our readers.

B. SYNTHETIC METHODS

This section deals briefly with the most useful methods for the preparation of aza macrocycles. Reviews of their preparation have been published [25,26]. Two main types of procedures are used to prepare these compounds: (i) conventional organic synthesis, developed by Richman and Atkins [27] following the earlier work of Koyama and Yoshino [28]; (ii) metal ion-promoted (template) reactions, developed in the early 1960s [29–32].



1,4,8,11-tetraazacyclotetradecane
[14]aneN_4
cyclam

C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
tet *a*

1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
Me_4[14]aneN_4
tetramethylcyclam (TMC)

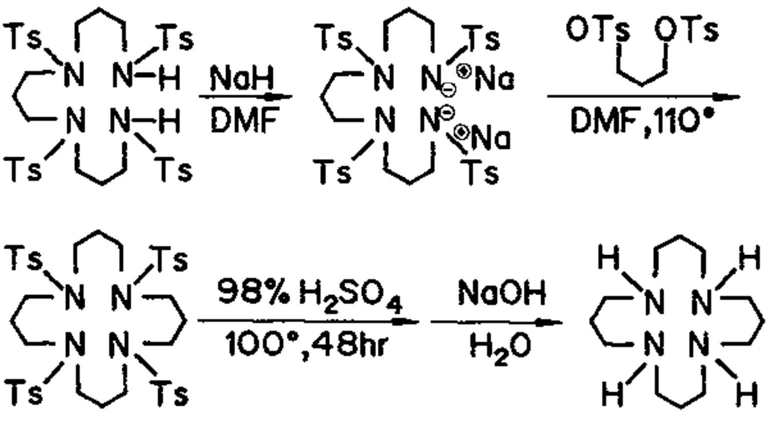
1,4,7,10,13,16,19,22,25,28,31,34-dodecaazacyclohexatriacontane
[36]aneN_{12}

Fig. 1. Examples of nomenclature system and notation used in the text. Numbered structural formula, IUPAC designation and simplified notation.

(i) Conventional organic synthesis

This general method involves the condensation of two segments of the target macrocycle in a polar aprotic solvent, usually dimethylformamide (DMF), following the synthetic path outlined in Scheme 2.

In the Richman and Atkins procedure [27], one precursor is a salt of a sulphonamide and the other precursor contains sulphonate esters as leaving groups. In this procedure no high dilution technique is required; concentrated solutions of the reagents give good yields. In this condition the cyclization



Scheme 2.

rate is increased and the hydrolysis of the sodium salts by trace moisture is less important. This method has been the one most often used to prepare saturated aza macrocycles containing 3–12, nitrogen atoms. Often, more than one synthetic pathway is possible to produce the same final product. The choice of one preparative method instead of another depends mainly on the availability and ease of preparation of the precursors. Different methods for the tosylation or mesylation of amine diols are used; some authors prefer methylene chloride as solvent and triethylamine as base, others prefer pyridine as both solvent and base. The preparation of salts of sulphonamides is carried out by adding either sodium, sodium hydride or sodium ethoxide to the solution of sulphonamides in dry solvent. The salts may be easily isolated, but because they are moisture-sensitive they are usually used immediately. Fairly drastic conditions are required to remove the protecting tosyl groups to yield the free macrocycle. The most used detosylation process is acid hydrolysis, which can be undertaken with concentrated (97%) sulphuric acid. This method works very well provided that great care is dedicated to the use of very pure, dry starting material and to the work-up of the resulting sulphuric acid solution. However, tosylate acid hydrolysis does not always give good yields [33]. Reductive cleavage of the tosyl group with HBr/acetic acid mixture is the other widely employed procedure to remove tosyl groups [28,34,35]. Other reducing agents, including sodium in liquid ammonia [36], and lithium aluminium hydride [37], have been employed in the reductive cleavage of the tosyl group. Isolation of the free cyclic amine or amine salts is usually straightforward. Standard methods, including chromatography, fractional crystallization and sublimation have been used to purify the amine or amine salts. A synthetic procedure involving the temporary chemical modification of the linear precursor has been reported [38]. Recently, much effort has been devoted to the development of synthetic pathways for the preparation of selectively protected macrocycles and the achievement of versatile intermediates [39–44]. Synthesis of bis-azamacrocycles [44,45] as well as azacages [46–49] have been described following the above strategy. Recently, Tomohiro et al. [50] have reported a convenient method for the synthesis of tetra-azamacrocycles with 28–44-membered rings.

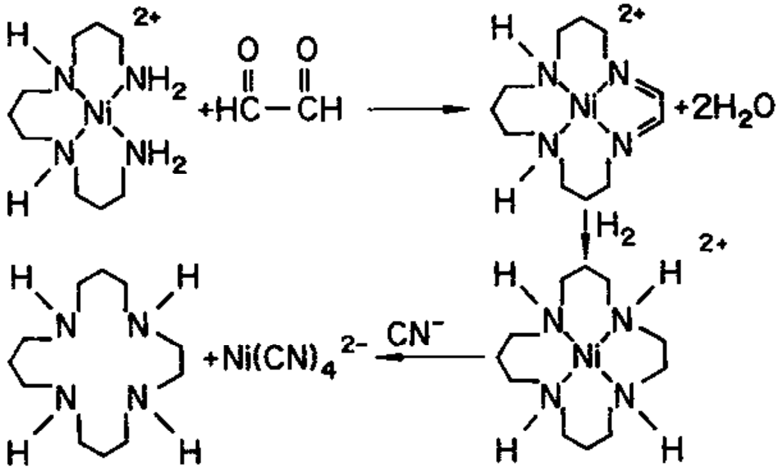
(ii) Metal ion-promoted reactions ('template reaction')

According to the kinetic template effect, the geometric arrangement of ligands within the coordination sphere of a metal ion provides constraints that control the kind of product obtained by reactions of coordinated ligands.

Many aza macrocycles in their complexed form have been obtained by condensation reactions in the presence of a metal ion, mainly Ni(II) and Cu(II). Different roles for the metal ion in a template reaction have been delineated and termed '*thermodynamic template effect*' and '*kinetic template effect*' [32]. In the first case, the metal ion complexes and sequesters the cyclic product from the reaction equilibrium mixture. In this way the formation of a macrocycle is promoted as its metal complex. In the second case, the metal ion influences the steric course of the condensation such that formation of the cyclic product is facilitated.

The $[Ni(en)_3]^{2+}$ complex reacts with acetone by rapid imine formation, followed by an aldol-type condensation, to give a β-amino ketone complex, which cyclizes by further imine formation [30]. Similar reaction could occur for 1,3-, and 1,4-diamine complexes giving macrocycles with atomicity greater than 14 [51].

The condensation of Ni(II) tetra-amine complexes with glyoxal yields tetraaza macrocycles with different overall atomicity (see Scheme 3). Reduc-



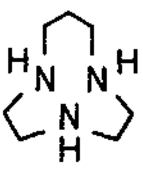
Scheme 3.

tion reactions, which convert unsaturated azamacrocycles to saturated azamacrocycles are usually carried out by using chemical reductants such as $NaBH_4$, H_2/Ni, etc. as well as by electrochemical means. The removal of the metal ion from the complex to yield the free macrocycle is usually carried out by treating with alkaline cyanide solution. The cyclic amine is then isolated by solvent extraction followed by solvent distillation and macrocycle purification. The synthesis of the metal-free ligand, in which a hydrogen-bonding network may act as a template, has been published [52].

C. TRIAZACYCLOALKANES

Basicity and metal complex formation constants of triazacycloalkanes have been reported (see Table 1). The protonation constants of triazacycloalkanes have been determined mainly by pH-metric methods [53–63], although some authors have reported [60,61,63] that the first protonation constants of 1,4,7-triazacyclononane (**6**), 1,4,7-triazacyclodecane (**8**), 1,5,9-triazacyclododecane (**9**) and C-2,2,4-trimethyl-1,5,9-triazacyclododecane (**10**) are too high to be determined potentiometrically. The values obtained by these authors following the ^{1}H NMR shift of the methylene groups as a function of pH are significantly higher than those obtained in the potentiometric studies. In the case of (**10**) a spectrophotometric method has been used to determine the first protonation constant [63]. Nevertheless, a recent determination of the protonation constants of (**6**) by ^{1}H NMR spectroscopy [64] is in agreement with the previous pH-metric results. In the same paper [64], the protonation constants for the *N*-methylated ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (**11**), obtained by a similar ^{1}H NMR method, were also reported.

The effect of ring closure on the basicity of triaza-amines is noted in the enhancement of the first protonation constant and in the lowering of the second shown by the cyclic amines with respect to the non-cyclic counterparts. This effect for proton binding in solution is probably due to an inside orientation of the lone pairs of the nitrogen atoms, imposed by the cyclic structure, in a similar fashion to that presented in the solid state by the



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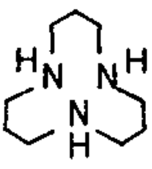

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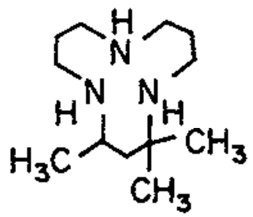

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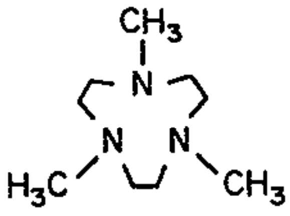

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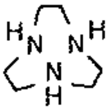
TABLE I

Log *K*, ΔH^0, and $T\Delta S^0$ values for cation–azamacrocycle equilibrium in aqueous solution

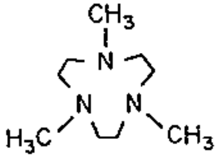
Only the left side (reactants) of the equilibrium reactions is indicated. Reactions including water molecules refer to: $mM + lL + nH_2O = M_mL_l(OH)_n + nH$. Charges have been omitted. Experimental methods for the determination of the equilibrium constants are abbreviated as follow: potentiometric (pot), spectrophotometric (spec), polarographic (pol), nuclear magnetic resonance (NMR), cyclic voltammetric (cv). Only direct calorimetric methods (cal) for the determination of $\Delta H°$ are indicated.



1,4,7-triazacyclononane
[9]aneN3

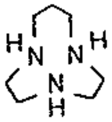
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10,68	pot			25	0.1 KNO_3	59
	L + H	10.42	pot	43.5 cal	16.2	25	0.1 KNO_3	56-58
	L + H	10.59	pot			25	0.2 $NaClO_4$	53,55
	L + H	10.80	pot			15	0.2 $NaClO_4$	53
	L + H	10.48	pot			35	0.2 $NaClO_4$	53
	L + H	12.6	NMR			25	0.5 KNO_3	60,61
	L + H	10.47	pot			25	0.1	62
	L + H	10.4	NMR			25		64
	LH + H	6,86	pot			25	0.1 KNO_3	59
	LH + H	6.82	pot	41.4 cal	-2.6	25	0.1 KNO_3	56-58
	LH + H	6.88	pot			25	0.2 $NaClO_4$	53,55
	LH + H	7.09	pot			15	0.2 $NaClO_4$	53
	LH + H	6.64	pot			35	0.2 $NaClO_4$	53
	LH + H	7,24	pot			25	0.5 KNO_3	60,61
	LH + H	6.80	pot			25	0.1	62
	LH + H	6.9	NMR			25		64
	LH_2 + H	2.1	pot			25	0.1 KNO_3	59
	LH_2 + H	<2.5	pot			25	0.1	62
	LH_2 + H	¯0.4	NMR			25		64
Mn(II)	L + Mn	5.8	pot			25	0.1	62
	L + MnL	3.6	pot			25	0.1	62
Co(II)	L + Co	11.2	pot			25	0.1 KNO_3	59
	L + Co	13.4	pot			25	0.1	62
	L + CoL	7,8	pot			25	0.1 KNO_3	59
	L + CoL	10.5	pot			25	0.1	62
Ni(II)	L + Ni	13.6	pot			25	0.1 KNO_3	59
	L + Ni	16.24	pot			25	0.1 KNO_3	56
	L + Ni	16.24	pot			25	0.1 KNO_3	58
	L + Ni	12.4	pot			25	0.1	62
	L + NiL	11.8	pot			25	0.1 KNO_3	59
	L + NiL	6.8	pot			25	0.1	62
Cu(II)	L + Cu	15.1	pot			25	0.1 KNO_3	59
	L + Cu	15.6				25	0.1 KNO_3	66
	L + Cu	15.7	spec			25	0.1 KCl	67
	L + Cu	15.5	pot			25	0.1 KNO_3	56
	L + Cu	16.2				25	0.2 $NaClO_4$	55
	L + Cu	15.52	pot	59.4 cal	29.2	25	0.1 KNO_3	57,58
	L + Cu	17.50	pot			25	0.5 KNO_3	60,61
	L + Cu	15.4	pot			25	0.1	62
	L + CuL	12.1	pot			25	0.1 KNO_3	59

	L + CuL	11.8	pot			25	0.1 KCl	67
	L + CuL	14.01	pot			25	0.5 KNO_3	60,61
	L + CuL	12.01	pot			25	0.1	62
	CuLOH + H	7.9	pot			25	0.1 KNO_3	59
	CuL + OH	8.25	pot			25	0.1 KNO_3	56
	L + Cu + OH	23.77	pot			25	0.1 KNO_3	58
	2CuL + 2OH	15.04	pot			25	0.5 KNO_3	60,61
Zn(II)	L + Zn	11.7	pot			25	0.1 KNO_3	59
	L + Zn	11.62	pot	49.8 cal	16.5	25	0.1 KNO_3	56-58,66
	L + Zn	11.3	pot	30.5	34.0	25	0.2 $NaClO_4$	53
	L + Zn	11.4	pot	29.3	35.7	25	0.2 $NaClO_4$	53
	L + Zn	11.3	pot			25	0.1	62
	L + ZnL	10.0	pot			25	0.1 KNO_3	59
	L + ZnL	9.2	pot			25	0.1	62
Cd(II)	L + Cd	9.5	pot			25	0.1 KNO_3	59
	L + Cd	9.2	pot	31.8	20.7	25	0.2 $NaClO_4$	53
	L + Cd	9.5	pot			25	0.1	62
	L + CdL	8.4	pot			25	0.1 KNO_3	59
	L + CdL	8.4	pot			25	0.1	62
Pb(II)	L + Pb	10.8	pot	34.3	27.3	25	0.2 $NaClO_4$	53
	L + Pb	10.3	pot			25	0.1	62
	L + PbL	5.1	pot			25	0.1	62
Hg(II)	L + Hg	12.5				25	0.1	62
	L + HgL	8.9				25	0.1	62



1,4,7-trimethyl-1,4,7-triazacyclononane
$Me_3[9]aneN_3$

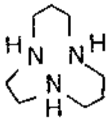
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	11.7	NMR			25		64
	LH + H	5.1	NMR			25		64
	LH_2 + H	-0.4	NMR			25		64



1,4,7-triazacyclodecane
$[10]aneN_3$

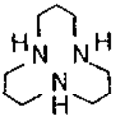
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	11.15	pot			15	0.2 $NaClO_4$	53
	L + H	10.85	pot			25	0.2 $NaClO_4$	53
	L + H	12.02	pot			25	0.1 KNO_3	58
	L + H	12.7	NMR			25	0.5 KNO_3	60
	L + H	10.55	pot			35	0.2 $NaClO_4$	53
	LH + H	6.95	pot			15	0.2 $NaClO_4$	53
	LH + H	6.76	pot			25	0.2 $NaClO_4$	53
	LH + H	6.59	pot			25	0.1 KNO_3	58
	LH + H	6.86	pot			25	0.5 KNO_3	60
	LH + H	6.57	pot			35	0.2 $NaClO_4$	53

Ni(II)	L + Ni	14.58	pot			25	0.1 KNO_3	58
Cu(II)	L + Cu	15.5	pot			25	0.1 KNO_3	66
	L + Cu	16.14	pot			25	0.5 KNO_3	60
	L + Cu	14.4	pot	62.3	19.9	25	0.2 $NaClO_4$	53
	L + Cu	15.48	pot			25	0.1 KNO_3	58
	L + CuL	10.26	pot			25	0.5 KNO_3	60,61
	2CuL + 2OH	14.52	pot			25	0.5 KNO_3	60,61
	L + Zn	11.2	pot			25	0.1 KNO_3	66
	L + Zn	11.28	pot			25	0.1 KNO_3	58
	L + Zn	10.3	pot	28.0	30.8	25	0.2 $NaClO_4$	53
	L + Cd	7.8	pot	30.5	14.0	25	0.2 $NaClO_4$	53
	L + Pb	8.8	pot	30.5	19.7	25	0.2 $NaClO_4$	53



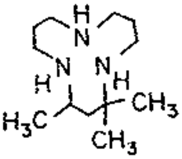
1,4,8-triazacycloundecane
[11]aneN_3

cation	reaction	logK	method	$-\Delta H^\circ$(kJ/mol)	$T\Delta S^\circ$(kJ/mol)	T °C	medium	ref
H	L + H	11.96	pot			25	0.1 KNO_3	58
	LH + H	7.61	pot			25	0.1 KNO_3	58
Ni(II)	L + Ni	12.88	pot			25	0.1 KNO_3	58
Cu(II)	L + Cu	14.4	pot			25	0.1 KNO_3	66
	L + Cu	14.44	pot			25	0.1 KNO_3	58
Zn (II)	L + Zn	10.41	pot			25	0.1 KNO_3	58
	L + Zn	10.4	pot			25	0.1 KNO_3	66
	L + Zn + OH	16.01	pot			25	0.1 KNO_3	58



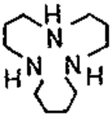
1,5,9-triazacyclododecane
[12]aneN_3

cation	reaction	logK	method	$-\Delta H$(kJ/mol)	$T\Delta S$(kJ/mol)	T °C	medium	ref
H	L + H	12.60	pot			25	0.1 KNO_3	58
	L + H	13.1	NMR			25	0.5 KNO_3	60
	LH + H	7.57	pot			25	0.1 KNO_3	58
	LH + H	7.97	pot			25	0.5 KNO_3	60
	LH_2 + H	2.41	pot			25	0.1 KNO_3	58
Ni(II)	L + Ni	10.93	pot			25	0.1 KNO_3	58
Cu(II)	L + Cu	12.6	pot			25	0.1 KNO_3	66
	L + Cu	13.16	pot			25	0.5 KNO_3	60,61
	L + Cu	12.63	pot			25	0.1 KNO_3	58
	L + CuL	7.68	pot			25	0.5 KNO_3	60,61
	L + Cu + OH	18.27	pot			25	0.1 KNO_3	58
	2CuL + 2OH	13.23	pot			25	0.5 KNO_3	60,61
Zn(II)	L + Zn	8.8	pot			25	0.1 KNO_3	66
	L + Zn	8.75	pot			25	0.1 KNO_3	58
	L + Zn + OH	15.04	pot			25	0.1 KNO_3	58



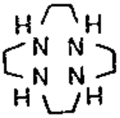
2,2',4-Trimethyl-1,5,9-triazacyclododecane
Me_3[12]aneN_3

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	12.3	spec			25	0.1 $NaNO_3$	63
	LH + H	7.34	pot			25	0.1 $NaNO_3$	63
	LH_2 + H	2.51	pot			25	0.1 $NaNO_3$	63
Ni(II)	NiLOH + H	9.8	pot			25	0.1 $NaNO_3$	63
	NiLOH + NiLOH	2.4	pot/spec			25	0.1 $NaNO_3$	63
Cu(II)	L + Cu	11.58	pot			25	0.1 $NaNO_3$	63
	CuLOH + H	8.48	pot			25	0.1 $NaNO_3$	63
	CuL$(OH)_2$ + H	11.9	pot			25	0.1 $NaNO_3$	63
	CuLOH + CuLOH	2.0	pot			25	0.1 $NaNO_3$	63
Zn(II)	L + Zn	7.68	pot			25	0.1 $NaNO_3$	63
	ZnLOH + H	9.6	pot			25	0.1 $NaNO_3$	63



1,5,9-triazacyclotridecane
[13]aneN_3

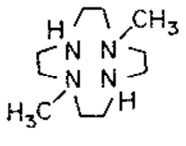
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	9.79	pot			25	0.2 $NaClO_4$	54
	LH + H	8.13	pot			25	0.2 $NaClO_4$	54
	LH_2 + H	4.18	pot			25	0.2 $NaClO_4$	54



1,4,7,10-tetraazacyclododecane
[12]aneN_4
cyclen

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.7	pot			25	0.2	73
	L + H	10.97	pot			25	0.5 KNO_3	75
	L + H	10.51	pot			35	0.2 $NaClO_4$	79
	LH + H	9.7	pot			25	0.2	73
	LH + H	9.87	pot			25	0.5 KNO_3	75
	LH + H	9.49	pot			35	0.2 $NaClO_4$	79
	LH_2 + H	1.5-2	pot			25	0.2	73
	LH_2 + H	< 2	pot			25	0.5 KNO_3	75
	LH_2 + H	1.6	pot			35	0.2 $NaClO_4$	79
	LH_3 + H	1.5-2	pot			25	0.2	73
	LH_3 + H	< 2	pot			25	0.2	75
	LH_3 + H	0.8	pot			35	0.2 $NaClO_4$	79

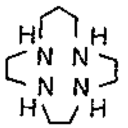
Co(II)	L + Co	13.8	pot			35	0.2 $NaClO_4$	79
Ni(II)	L + Ni	16.4	pot/spec			25	0.1 $NaNO_3$	80
	L + Ni			49.8 cal		25		82
Cu(II)	L + Cu	24.8	pol	76.6	64.1	25	0.2	73,83
	L + Cu			95.0 cal	45.2	25		84
	L + Cu	23.29	spec			25	0.5 $HNO_3/NaNO_3$	81
Zn(II)	L + Zn	16.2	pol	33.1	58.6	25	0.2	85
	L + Zn			60.7 cal		25		84
Cd(II)	L + Cd	14.3	pol	34.3	47.4	25	0.2	85
Hg(II)	L + Hg	25.5	pol	98.7	47.0	25	0.2 $NaClO_4$	86
Pb(II)	L + Pb	15.9	pol	27.7	63.6	25	0.2	85



1,7-dimethyl-1,4,7,10-tetraazacyclododecane

Me$_2$[12]aneN$_4$

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.76	pot			25	0.5 KNO_3	43
	LH + H	9.41	pot			25	0.5 KNO_3	43
Cu(II)	L + Cu	17.89	pot			25	0.5 KNO_3	43
	L + Cu + H	20.06	pot			25	0.5 KNO_3	43

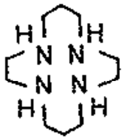


1,4,7,10-tetraazacyclotridecane

[13]aneN$_4$

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	11.1	pot			25	0.2 $NaClO_4$	74
	L + H	11.19	pot			25	0.5 KNO_3	75
	L + H	11.02	pot			25	0.1 $NaNO_3$	81
	L + H	10.90	pot			35	0.2 $NaClO_4$	79
	LH + H	10.1	pot			25	0.2 $NaClO_4$	74
	LH + H	10.12	pot			25	0.5 KNO_3	75
	LH + H	9.96	pot			25	0.1 $NaNO_3$	81
	LH + H	9.91	pot			35	0.2 $NaClO_4$	79
	LH_2 + H	1.7	pot			25	0.2 $NaClO_4$	74
	LH_2 + H	< 2	pot			25	0.5 KNO_3	75
	LH_2 + H	1.96	pot			25	0.1 $NaNO_3$	81
	LH_2 + H	1.6	pot			35	0.2 $NaClO_4$	79
	LH_3 + H	1	pot			25	0.2 $NaClO_4$	74
	LH_3 + H	< 2	pot			25	0.5 KNO_3	75
	LH_3 + H	0.9	pot			35	0.2 $NaClO_4$	79
Co(II)	L + Co	14.3	pot			35	0.2$NaClO_4$	79
Ni(II)	L + Ni	17.98	pot/spec			25	0.1 KNO_3	80
	L + Ni			56.5 cal		25		82
	L + Ni (h.s.)			83.7 cal		25		82
	L + Ni (l.s.)			52.3 cal		25		82

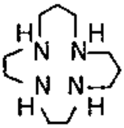
Cu(II)	L + Cu	29.1	pol	122.2	42.0	25	0.2 $NaClO_4$	74
	L + Cu	24.36	spec			25	0.5 $HNO_3/NaNO_3$	81
Zn(II)	L + Zn	15.6	pol	32.6		25	0.2 $NaClO_4$	85
	L + Zn	15.74	pot	64.0 cal		25	0.5 KNO_3	93
Cd(II)	L + Cd	12.71	pot			25	0.1 $NaNO_3$	81
Hg(II)	L + Hg	25.3	pol	103.3 pol	41.5	25	0.2 $NaClO_4$	86
Pb(II)	L + Pb	13.48	pot			25	0.1 $NaNO_3$	81



1,4,8,11-tetraazacyclotetradecane
[14]aneN$_4$
cyclam

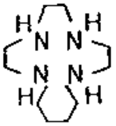
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.76	pot			20	0.1	97
	L + H	11.49	pot			25	0.1	98
	L + H	11.50	pot			25	0.2 $NaClO_4$	85
	L + H	11.83	pot			25	0.5 KNO_3	75
	L + H	11.58	pot	51.5 cal	14.6	25	0.5 KNO_3	76,77
	L + H	11.23	pot			35	0.2 $NaClO_4$	79, 85
	L + H	11.82	pot			15	0.2 $NaClO_4$	85
	L + H	11.3	pot			25	0.1 $NaNO_3$	81
	LH + H	10.18	pot			20	0.1	97
	LH + H	10.30	pot			25	0.2 $NaClO_4$	85
	LH + H	10.76	pot			25	0.5 KNO_3	75
	LH + H	10.62	pot	53.4 cal	7.2	25	0.5 KNO_3	76,77
	LH + H	10.30	pot			25	0.2 $NaClO_4$	85
	LH + H	10.50	pot			15	0.2 $NaClO_4$	85
	LH + H	10.23	pot			25	0.1 $NaNO_3$	81
	LH + H	10.30	pot			35	0.2 $NaClO_4$	79
	LH + H	10.15	pot			35	0.2 $NaClO_4$	85
	LH_2 + H	3.54	pot			20	0.1	97
	LH_2 + H	1.62	pot			25	0.2	85
	LH_2 + H	< 2	pot			25	0.5 KNO_3	75
	LH_2 + H	1.61	pot	11.7 cal	-2.5	25	0.5 KNO_3	76,77
	LH_2 + H	1.5	pot			35	0.2 $NaClO_4$	79
	LH_2 + H	1.43	pot			25	0.1 $NaNO_3$	81
	LH_3 + H	2.67	pot			20	0.1	97
	LH_3 + H	0.94	pot			25	0.2	85
	LH_3 + H	< 2	pot			25	0.5 KNO_3	75
	LH_3 + H	2.41	pot	32.2 cal	-18.7	25	0.5 KNO_3	76,77
	LH_3 + H	0.8	pot			35	0.2 $NaClO_4$	79
	LH_3 + H	2.27	pot			25	0.1 $NaNO_3$	81
Co(II)	L + Co	12.7	pot			35	0.2 $NaClO_4$	79
Ni(II)	L + Ni	22.2	spec	129.7	-3	25	0.1 NaOH	98
	L + Ni			84.9 cal	41.9	25		88
	L + Ni (h.s.)			100.8 cal	24.3	25		88
	L + Ni (l.s.)			78.2 cal	49.3	25		88
	L + Ni	20.1	pot/spec			25	0.5 NaCl	99
	L + Ni	23.5	spec			10	0.1 NaOH	98
	L + Ni	21.2	spec			40	0.1 NaOH	98
Cu(II)	L + Cu	27.2	pol	127.2		25	0.2	55
	L + Cu	26.5	spec			25	0.5 $HNO_3/NaNO_3$	81
	L + Cu			135.6 cal		25		84

Zn(II)	L + Zn	15.5	pot	31.8	57.4	25	0.2 $NaClO_4$	85
	L + Zn	15.34	pot	61.9 cal	25.6	25	0.5 KNO_3	84,93
Hg(II)	L + Hg	23.0	pot	137.7	-6.1	25	0.2 $NaClO_4$	86
Pb(II)	L + Pb	10.83	pot			25	0.1 $NaNO_3$	81
Cd(II)	L + Cd	11.23	pot			25	0.1 $NaNO_3$	81



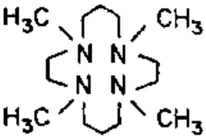
1,4,7,11-tetraazacyclotetradecane
iso-cyclam

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	11.29	pot			25	0.5 KNO_3	75
	L + H	11.05	pot			25	0.2 $NaClO_4$	79
	L + H	10.81	pot			35	0.2 $NaClO_4$	79
	LH + H	10.19	pot			25	0.5 KNO_3	75
	LH + H	9.98	pot			25	0.2 $NaClO_4$	79
	LH + H	9.74	pot			35	0.2 $NaClO_4$	79
	LH_2 + H	4.32	pot			25	0.5 KNO_3	75
	LH_2 + H	3.3	pot			25	0.2 $NaClO_4$	79
	LH_2 + H	3.03	pot			35	0.2 $NaClO_4$	79
	LH_3 + H	< 2	pot			25	0.5 KNO_3	75
	LH_3 + H	1.0	pot			25	0.2 $NaClO_4$	79
	LH_3 + H	0.9	pot			35	0.2 $NaClO_4$	79
Co(II)	L + Co	10.9	pot			35	0.2$NaClO_4$	79
Ni(II)	L + Ni			69.0 cal		25		100
	L + Ni (h. s.)			82.4 cal		25		100
	L + Ni (l. s.)			60.2		25		100
Cu(II)	L + Cu			116.3 cal		25		102



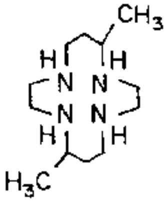
1,4,7,10-tetraazacyclotetradecane

cation	reaction	logK	method	-ΔH(kJ/mol)	TΔS(kJ/mol)	T °C	medium	ref
H	L + H	10.98	pot			25	0.5 KNO_3	101
	L + H	10.92	pot			25	0.1 $NaNO_3$	216
	LH + H	9.75	pot			25	0.5 KNO_3	101
	LH + H	9.40	pot			25	0.1 $NaNO_3$	216
	LH_2 + H	4.86	pot			25	0.5 KNO_3	101
	LH_2 + H	4.62	pot			25	0.1 $NaNO_3$	216
	LH_3 + H	2.00	pot			25	0.5 KNO_3	101
Ni(II)	L + Ni (h.s.)	14.81	pot	53.6 cal	31.0	25	0.5 KNO_3	101,87
	L + Ni (l.s.)	14.83	pot	36.4 cal	48	25	0.5 KNO_3	101,87
	L + Ni	15.47	pot			25	0.1 $NaNO_3$	216
	L + Ni + H	19.3	pot			25	0.5 KNO_3	87
Cu(II)	L + Cu	22.36	pot	87.5 cal		25	0.5 KNO_3	101
	L + Cu + H	25.44	pot			25	0.5 KNO_3	101
Zn(II)	L + Zn	12.90	pot			25	0.1 $NaNO_3$	216
Cd(II)	L + Cd	11.30	pot			25	0.1 $NaNO_3$	216
Pb(II)	L + Pb	11.59	pot			25	0.1 $NaNO_3$	216



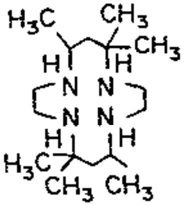
1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
Me$_4$[14]aneN$_4$
TMC

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	9.70	pot	21.3 cal	34.2	25	0.5 KNO$_3$	76,77
	L + H	9.34	pot			25	0.1 NaNO$_3$	106
	LH + H	9.31	pot	43.1 cal	10.1	25	0.5 KNO$_3$	76,77
	LH + H	8.99	pot			25	0.1 NaNO$_3$	106
	LH$_2$ + H	3.09	pot	15.1 cal	2.6	25	0.5 KNO$_3$	76,77
	LH$_2$ + H	2.58	pot			25	0.1 NaNO$_3$	106
	LH$_3$ + H	2.64	pot	28.9 cal	-13.7	25	0.5 KNO$_3$	76,77
	LH$_3$ + H	2.25	pot			25	0.1 NaNO$_3$	106
Co(II)	L + Co	7.58	pot			25	0.1 NaNO$_3$	106,107
	CoL + OH	5.76	pot			25	0.1 NaNO$_3$	106
	CoL + OH	5.28	spec	23.8 cal	6.2	25	0.5	196
Ni(II)	L + Ni	8.65	pot/spec			25	0.1 NaNO$_3$	107
	NiL + OH	3.72	spec			25	0.5 KNO$_3$	108
	NiL(h. s.) + OH	3.72	spec	17.5 cal	3.7	25	0.5	196
	NiL(l. s.) + OH	3.74	spec	29.7 cal	-8.3	25	0.5	196
Cu(II)	L + Cu	18.3	pot			25	0.1 NaNO$_3$	106,107
Zn(II)	L + Zn	10.35	pot			25	0.1 NaNO$_3$	106,107
	ZnL + OH	5.44	pot			25	0.1 NaNO$_3$	106,107
Cd(II)	L + Cd	9.0	pot			25	0.1 NaNO$_3$	106,107
	CdL + OH	5.60	pot			25	0.1 NaNO$_3$	106,107
Hg(II)	L + Hg	20.3	pot			25	0.1 NaNO$_3$	106,107



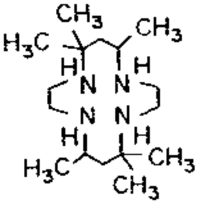
C-meso-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	11.69	pot			25		98
Ni(II)	L + Ni	23.1	spec			10	0.1	98
	L + Ni	21.9	spec	117.1	10	25	0.1	98
	L + Ni	21.0	spec			40	0.1	98



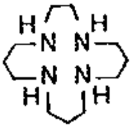
C-meso-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
tet a

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	>11	pot					109
	LH + H	10.5	pot					109
	LH_2 + H	2.2	pot					109
	LH_3 + H	<2	pot					109
Cu(II)	L + Cu (blue)	20	pot			25	0.1	23
	L + Cu (red)	28	pot			25	0.1	23
Ni(II)	L + Ni	~20	spec			25	0.1	98



C-rac-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
tet b

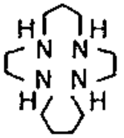
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	11.6	pot					109
	LH + H	10.7	pot					109
	LH_2 + H	2.7	pot					109
	LH_3 + H	2.3	pot					109
Ni(II)	L + Ni	18.2	spec			25	0.1	98



1,4,8,12-tetraazacyclopentadecane
$[15]aneN_4$

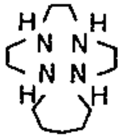
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	11.2	pot			25	0.2	115
	L + H	11.23	pot			25	0.5 KNO_3	75
	L + H	11.08	pot	45.2 cal	18	25	0.5 KNO_3	76,77
	LH + H	10.1	pot			25	0.2	115
	LH + H	10.28	pot			25	0.5 KNO_3	75
	LH + H	10.38	pot	51.5 cal	7.8	25	0.5 KNO_3	76,77
	LH_2 + H	2	pot			25	0.2	115
	LH_2 + H	5.32	pot			25	0.5 KNO_3	75
	LH_2 + H	5.28	pot	30.2 cal	-0.1	25	0.5 KNO_3	76,77

	LH_3 + H	2	pot			25	0.2	115
	LH_3 + H	3.79	pot			25	0.5 KNO_3	75
	LH_3 + H	3.60	pot	32.3 cal	-11.7	25	0.5 KNO_3	76,77
Ni(II)	L + Ni	18.38	pot	74.9 cal	30	25		82,87
	L + Ni + H	22.04	pot			25	0.5 KNO_3	87
Cu(II)	L + Cu	24.4	pol	110.9	28.3	25	0.2	115
	L + Cu	25.1	pol			15	0.2	115
	L + Cu	23.7	pol			35	0.2	115
	CuL + H	5.5	pol			25	0.2	115
	L + Cu			110.9 cal		25		84
Zn(II)	L + Zn	15.0	pol	34.3	51.1	25	0.2	85
	L + Zn	15.35	pot	69.0 cal	18.6	25		84,93
Hg(II)	L + Hg	23.7	pol	103.3	31.8	25	0.2 $NaClO_4$	86



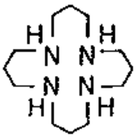
1,4,8,11-tetraazacyclopentadecane

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	11.04	pot	46.4 cal	16.7	25	0.5 KNO_3	78
	LH + H	10.47	pot	51.5 cal	8.4	25	0.5 KNO_3	78
	LH_2 + H	3.98	pot	27.2 cal	-4.6	25	0.5 KNO_3	78
	LH_3 + H	3.41	pot	30.5 cal	-10.9	25	0.5 KNO_3	78



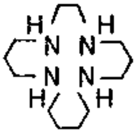
1,4,7,10-tetraazacyclopentadecane

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.33	pot			25	0.5 KNO_3	104
	L + H	9.83	pot			25	0.1 $NaNO_3$	216
	LH + H	9.48	pot			25	0.5 KNO_3	104
	LH + H	8.95	pot			25	0.1 $NaNO_3$	216
	LH_2 + H	5.71	pot			25	0.5 KNO_3	104
	LH_2 + H	5.40	pot			25	0.1 $NaNO_3$	216
	LH_3 + H	1.28	pot			25	0.5 KNO_3	104
	LH_3 + H	1.63	pot			25	0.1 $NaNO_3$	216
Ni(II)	L + Ni (h.s.)	11.75	pot	47.7 cal	19.2	25	0.5 KNO_3	104
	L + Ni (l.s.)	12.07	pot	32.2 cal	36.8	25	0.5 KNO_3	104
	L + Ni	11.74				25	0.1 $NaNO_3$	216
	L + Ni + H	18.0	pot			25	0.5 KNO_3	104
Cu(II)	L + Cu	20.40	pot	80.3 cal	36.0	25	0.5 KNO_3	104
	L + Cu	19.25	pot			25	0.1 $NaNO_3$	216
	L + Cu + H	22.35	pot			25	0.5 KNO_3	104
Zn(II)	L + Zn	10.70	pot			25	0.1 $NaNO_3$	216
Cd(II)	L + Cd	10.18	pot			25	0.1 $NaNO_3$	216
Pb(II)	L + Pb	9.50	pot			25	0.1 $NaNO_3$	216



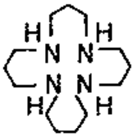
1,5,9,13-tetraazacyclohexadecane
[16]aneN4

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.85	pot	42.0 cal	20.1	25	0.5 KNO_3	75,116
	LH + H	9.80	pot	44.8 cal	11.3	25	0.5 KNO_3	75,116
	LH_2 + H	7.21	pot	43.0 cal	-1.7	25	0.5 KNO_3	75,116
	LH_3 + H	5.69	pot	44.2 cal	-11.7	25	0.5 KNO_3	75,116
Ni(II)	L + Ni	13.23	pot	40.6 cal	34.9	25	0.5 KNO_3	87
	L + Ni + H	18.80	pot			25	0.5 KNO_3	87
Cu(II)	L + Cu	20.92	pot	83.7 cal	35.6	25	0.5 KNO_3	116
	L + Cu + H	23.48	pot			25	0.5 KNO_3	116
Zn(II)	L + Zn	13.05	pot	29.7 cal	44.8	25	0.5 KNO_3	93



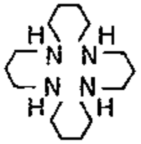
1,4,8,13-tetraazacyclohexadecane

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.73	pot	46.4 cal	14.6	25	0.5 KNO_3	78
	LH + H	9.85	pot	47.7 cal	8.4	25	0.5 KNO_3	78
	LH_2 + H	6.83	pot	42.7 cal	-3.8	25	0.5 KNO_3	78
	LH_3 + H	3.96	pot	33.5 cal	-10.9	25	0.5 KNO_3	78



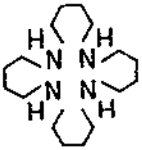
1,5,9,13-tetraazacycloheptadecane
[17]aneN4

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	11.20	pot	43.5 cal	20.5	25	0.5 KNO_3	78
	L + H	10.23	pot			25	0.2 $NaClO_4$	117
	LH + H	10.13	pot	46.4 cal	11.3	25	0.5 KNO_3	78
	LH + H	9.66	pot			25	0.2 $NaClO_4$	117
	LH_2 + H	7.96	pot	45.6 cal	0	25	0.5 KNO_3	78
	LH_2 + H	7.40	pot			25	0.2 $NaClO_4$	117
	LH_3 + H	6.30	pot	45.6 cal	-9.6	25	0.5 KNO_3	78
	LH_3 + H	5.31	pot			25	0.2 $NaClO_4$	117



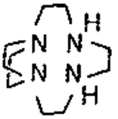
1,5,10,14-tetraazacyclooctadecane
[18]aneN_4

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	11.15	pot			25	0.5 KNO_3	182
	L + H	10.36	pot			25	0.2 $NaClO_4$	118
	L + H	11.44	pot			20	0.1 KNO_3	119
	LH + H	10.10	pot			25	0.5 KNO_3	182
	LH + H	9.97	pot			25	0.2 $NaClO_4$	118
	LH + H	10.51	pot			20	0.1 KNO_3	119
	LH_2 + H	8.88	pot			25	0.5 KNO_3	182
	LH_2 + H	7.00	pot			25	0.2 $NaClO_4$	118
	LH_2 + H	7.27	pot			20	0.1 KNO_3	119
	LH_3 + H	7.74	pot			25	0.5 KNO_3	182
	LH_3 + H	6.70	pot			25	0.2 $NaClO_4$	118
	LH_3 + H	6.90	pot			20	0.1 KNO_3	119
Ag(I)	2L + Ag	8.0	pot			20	0.1 KNO_3	119
	3L + 2Ag	16.6	pot			20	0.1 KNO_3	119



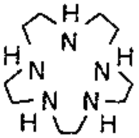
1,6,11,16-tetraazacycloicosane
[20]aneN_4

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	11.82	pot			20	0.1 KNO_3	119
	L + H	11.65	pot			20	0.1 KNO_3	202
	LH + H	11.38	pot			20	0.1 KNO_3	119
	LH + H	10.60	pot			20	0.1 KNO_3	202
	LH_2 + H	10.63	pot			20	0.1 KNO_3	119
	LH_2 + H	8.34	pot			20	0.1 KNO_3	202
	LH_3 + H	8.87	pot			20	0.1 KNO_3	119
	LH_3 + H	8.38	pot			20	0.1 KNO_3	202
Ag(I)	L + Ag	5.7	pot			20	0.1 KNO3	119
	2L + Ag	8.3	pot			20	0.1 KNO_3	119



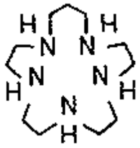
1,4,7,10-tetraazabicyclo[8.2.2]tetradecane

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.90	pot			20	0.1 $NaNO_3$	140
	LH + H	10.31	pot			20	0.1 $NaNO_3$	140
	LH_2 + H	6.50	pot			20	0.1 $NaNO_3$	140
	LH_3 + H	3.18	pot			20	0.1 $NaNO_3$	140
Ni(II)	L + Ni	14.3	pot			20	0.1 $NaNO_3$	91
Cu(II)	L + Cu	21.50	pot			20	0.1 $NaNO_3$	91
Zn(II)	L + Zn	10.95	pot			20	0.1 $NaNO_3$	91
Cd(II)	L + Cd	10.07	pot			20	0.1 $NaNO_3$	91
Pb(II)	L + Pb	11.71	pot			20	0.1 $NaNO_3$	91



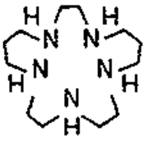
1,4,7,10,13-pentaazacyclopentadecane
[15]aneN_5

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	11.07	pot			15	0.2 $NaClO_4$	142
	L + H	10.85	pot			25	0.2 $NaClO_4$	142
	L + H	10.39	pot			25	0.2 KBr	143
	L + H	10.72	pot			35	0.2 $NaClO_4$	142
	LH + H	9.81	pot			15	0.2 $NaClO_4$	142
	LH + H	9.65	pot			25	0.2 $NaClO_4$	142
	LH + H	9.36	pot			25	0.2 KBr	143
	LH + H	9.45	pot			35	0.2 $NaClO_4$	142
	LH_2 + H	6.22	pot			15	0.2 $NaClO_4$	142
	LH_2 + H	6.00	pot			25	0.2 $NaClO_4$	142
	LH_2 + H	6.06	pot			25	0.2 KBr	143
	LH_2 + H	5.81	pot			35	0.2 $NaClO_4$	142
	LH_3 + H	1.74	pot			25	0.2 $NaClO_4$	142
	LH_4 + H	1.16	pot			25	0.2 $NaClO_4$	142
Mn(II)	L + Mn	10.65	pot			25	0.2 KBr	143
Co(II)	L + Co	16.76	pot			35	0.2 $NaClO_4$	145
Ni(II)	L + Ni	18.1				35	0.2 $NaClO_4$	151
	L + Ni			67.4 cal			0.5 KNO_3	150
Cu(II)	L + Cu	25.9				25	0.1 NaOH	146,147
	L + Cu	28.3	pot	137.7	27	25	0.2 $NaClO_4$	142
	L + Cu	28.0	pot			25	0.1 $NaNO_3$	91
Zn(II)	L + Zn	19.1	pot	57.3	51	25	0.2 $NaClO_4$	53
Cd(II)	L + Cd	19.2	pot	54.4	55	25	0.2 $NaClO_4$	53
	L + Cd	19.2	pot			25	0.1 $NaNO_3$	91
Pb(II)	L + Pb	17.3	pot	41.8	56	25	0.2 $NaClO_4$	53
Hg(II)	L + Hg	28.5	pot	136.8	25	25	0.2 $NaClO_4$	53



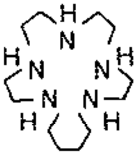
1,4,7,10,13-pentaazacyclohexadecane
[16]aneN$_5$

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.86	pot			15	0.2 NaClO$_4$	142
	L + H	10.64	pot			25	0.2 NaClO$_4$	142
	L + H	10.42	pot			35	0.2 NaClO$_4$	142
	LH + H	9.71	pot			15	0.2 NaClO$_4$	142
	LH + H	9.49	pot			25	0.2 NaClO$_4$	142
	LH + H	9.27	pot			35	0.2 NaClO$_4$	142
	LH$_2$ + H	7.50	pot			15	0.2 NaClO$_4$	142
	LH$_2$ + H	7.28	pot			25	0.2 NaClO$_4$	142
	LH$_2$ + H	7.06	pot			35	0.2 NaClO$_4$	142
	LH$_3$ + H	1.71	pot			25	0.2 NaClO$_4$	142
	LH$_4$ + H	1.45	pot			25	0.2 NaClO$_4$	142
Fe(II)	L + Fe	14.57	pot			35	0.2 NaClO$_4$	148
Co(II)	L + Co	15.95	pot			35	0.2 NaClO$_4$	145
	L + Co	15.85	pot			35	0.2 NaClO$_4$	149
Ni(II)	L + Ni	18.1						149
	L + Ni			96.2 cal			0.5 KNO$_3$	150
Cu(II)	L + Cu	27.1	pol	136.8	17	25	0.2 NaClO$_4$	142
Zn(II)	L + Zn	17.9	pot	56.5	46	25	0.2 NaClO$_4$	53
Cd(II)	L + Cd	18.1	pot	54.4	49	25	0.2 NaClO$_4$	53
Hg(II)	L + Hg	27.4	pol	143.9	12	25	0.2 NaClO$_4$	53
	L + Hg	27.38				25	0.2 NaClO$_4$	149
Pb(II)	L + Pb	14.3	pot	43.9	37	25	0.2 NaClO$_4$	53



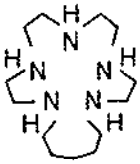
1,4,7,11,14-pentaazacycloheptadecane
[17]aneN$_5$

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.55	pot			15	0.2 NaClO$_4$	142
	L + H	10.32	pot			25	0.2 NaClO$_4$	142
	L + H	10.10	pot			35	0.2 NaClO$_4$	142
	LH + H	9.85	pot			15	0.2 NaClO$_4$	142
	LH + H	9.62	pot			25	0.2 NaClO$_4$	142
	LH + H	9.38	pot			35	0.2 NaClO$_4$	142
	LH$_2$ + H	7.58	pot			15	0.2 NaClO$_4$	142
	LH$_2$ + H	7.36	pot			25	0.2 NaClO$_4$	142
	LH$_2$ + H	7.13	pot			35	0.2 NaClO$_4$	142
	LH$_3$ + H	4.10	pot			25	0.2 NaClO$_4$	142
	LH$_4$ + H	2.38	pot			25	0.2 NaClO$_4$	142
Ni(II)	L + Ni			81.2 cal			0.5 KNO$_3$	150
Cu(II)	L + Cu	23.8	pol	113.8	22	25	0.2 NaClO$_4$	142
Zn(II)	L + Zn	15.8	pot	53.1	37	25	0.2 NaClO$_4$	53
Cd(II)	L + Cd	15.5	pot	52.7	36	25	0.2 NaClO$_4$	53
Hg(II)	L + Hg	26.5	pol	139.7	11	25	0.2 NaClO$_4$	53
Pb(II)	L + Pb	11.6	pot	41.4	37	25	0.2 NaClO$_4$	53



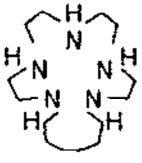
1,4,7,10,13-pentaazacycloheptadecane
[17]aneN_5

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.50	pot			35	0.2 $NaClO_4$	144
	LH + H	9.73	pot			35	0.2 $NaClO_4$	144
	LH_2 + H	7.97	pot			35	0.2 $NaClO_4$	144
	LH_3 + H	< 2	pot			35	0.2 $NaClO_4$	144
	LH_4 + H	< 2	pot			35	0.2 $NaClO_4$	144
Co(II)	L + Co	15.4	pot			35	0.2 $NaClO_4$	144



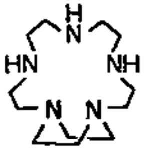
1,4,7,10,13-pentaazacyclootadecane
[18]aneN_5

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.15	pot			35	0.2 $NaClO_4$	144
	LH + H	9.52	pot			35	0.2 $NaClO_4$	144
	LH_2 + H	8.55	pot			35	0.2 $NaClO_4$	144
	LH_3 + H	< 2	pot			35	0.2 $NaClO_4$	144
	LH_4 + H	< 2	pot			35	0.2 $NaClO_4$	144
Co(II)	L + Co	11.5	pot			35	0.2 $NaClO_4$	144



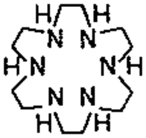
1,4,7,10,13-pentaazacyclononadecane
[19]aneN_5

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.11	pot			35	0.2 $NaClO_4$	144
	LH + H	9.52	pot			35	0.2 $NaClO_4$	144
	LH_2 + H	8.51	pot			35	0.2 $NaClO_4$	144
	LH_3 + H	2.5	pot			35	0.2 $NaClO_4$	144
	LH_4 + H	< 2	pot			35	0.2 $NaClO_4$	144
Co(II)	LH + Co	7.4	pot			35	0.2 $NaClO_4$	144



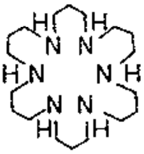
1,4,7,10,13-pentaazabicyclo[11.2.2]heptadecane

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Cu(II)	L + Cu	15.1	pot			25	0.1 $NaNO_3$	91
Cd(II)	L + Cd	14.7	pot			25	0.1 $NaNO_3$	91



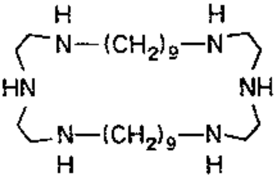
1,4,7,10,13,16,-hexaazacyclooctadecane
[18]aneN_6

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.19	pot			25	0.2	151
	L + H	10.46	pot			15	0.2	151
	L + H	9.92	pot			35	0.2	151
	LH + H	9.23	pot			25	0.2	151
	LH + H	9.51	pot			15	0.2	151
	LH + H	8.96	pot			35	0.2	151
	LH_2 + H	8.73	pot			25	0.2	151
	LH_2 + H	9.01	pot			15	0.2	151
	LH_2 + H	8.45	pot			35	0.2	151
	LH_3 + H	4.09	pot	59	12	25	0.2	151
	LH_3 + H	4.30	pot			15	0.2	151
	LH_3 + H	3.89	pot			35	0.2	151
	LH_4 + H	2	pot			25	0.2	151
	LH_4 + H	−2	pot			15	0.2	151
	LH_4 + H	~2	pot			35	0.2	151
	LH_5 + H	1	pot			25	0.2	151
	LH_5 + H	~1	pot			15	0.2	151
	LH_5 + H	~1	pot			35	0.2	151
K(I)	L + K	0.8	pot			25	0.2	151
La(III)	L + La	5.7	pot			25	0.2	151
Sr(II)	L + Sr	3.2	pot			25	0.2	151
Ca(II)	L + Ca	2.5	pot	29	-15	35	0.2	151
Pb(II)	L + Pb	14.1	pot	56	25	25	0.2	151
Hg(II)	L + Hg	29.1	pol	176	-5	25	0.2	151
Cd(II)	L + Cd	17.9	pot	59	42	25	0.2	151
	L + Cd	18.8	pot	64.0 cal	43.1	25	0.15 $NaClO_4$	155
Cu(II)	HL + Cu	21.6	pot	96	27	25	0.2	151
	H_2L + Cu	16.1	pot			25	0.2	151
Zn(II)	L + Zn	17.8	pot	52	50	25	0.2	151
	L + Zn	18.7	pot	58.6 cal		25	0.15 $NaClO_4$	154
	L + Zn + H	22.63	pot			25	0.15 $NaClO_4$	154
Ni(II)	L + Ni	19.6	pot			35	0.2	151
	HL + Ni	13.9	pot			35	0.2	151
Co(II)	L + Co	18.9	pot			35	0.2	151
	HL + Co	11.8	pot			35	0.2	151



1,5,9,13,17,21-hexaazacyclotetracosane
[24]aneN$_6$

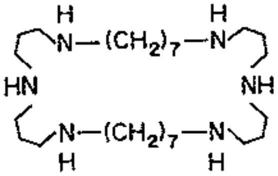
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.45	pot			25	0.1 Me$_4$NCl	152
	L + H	10.50	pot			25	0.1 NaTs	164
	L + H	10.50	pot			25	0.01 Me$_4$NCl	205
	LH + H	10.35	pot			25	0.1 Me$_4$NCl	152
	LH + H	10.20	pot			25	0.1 NaTs	164
	LH + H	10.20	pot			25	0.01 Me$_4$NCl	205
	LH$_2$ + H	9.05	pot			25	0.1 Me$_4$NCl	152
	LH$_2$ + H	9.25	pot			25	0.1 NaTs	164
	LH$_2$ + H	9.25	pot			25	0.01 Me$_4$NCl	205
	LH$_3$ + H	7.90	pot			25	0.1 Me$_4$NCl	152
	LH$_3$ + H	8.00	pot			25	0.1 NaTs	164
	LH$_3$ + H	8.00	pot			25	0.01 Me$_4$NCl	205
	LH$_4$ + H	7.15	pot			25	0.1 Me$_4$NCl	152
	LH$_4$ + H	7.05	pot			25	0.1 NaTs	164
	LH$_4$ + H	7.05	pot			25	0.01 Me$_4$NCl	205
	LH$_5$ + H	6.60	pot			25	0.1 Me$_4$NCl	152
	LH$_5$ + H	6.40	pot			25	0.1 NaTs	164
	LH$_5$ + H	6.40	pot			25	0.01 Me$_4$NCl	205



1,4,7,17,20,23-hexaazacyclodotriacontane

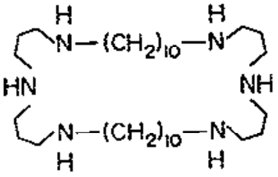
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	>9.70[a]	pot			25	0.1 Me$_4$NCl	205
	LH + H	>9.65[a]	pot			25	0.1 Me$_4$NCl	205
	LH$_2$ + H	9.60	pot			25	0.1 Me$_4$NCl	205
	LH$_3$ + H	9.25	pot			25	0.1 Me$_4$NCl	205
	LH$_4$ + H	4.15	pot			25	0.1 Me$_4$NCl	205
	LH$_5$ + H	3.55	pot			25	0.1 Me$_4$NCl	205

[a] Values not determined since the compound is not soluble in aqueous solution in their unprotonated form.



1,5,9,17,21,25-hexaazacyclodotriacontane
[32]aneN6

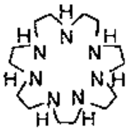
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.70	pot			25	0.1 Me_4NCl	153,205
	L + H	10.85	pot			25	0.01 Me_4NCl	153
	LH + H	~10.70	pot			25	0.1 Me_4NCl	153,205
	LH + H	10.60	pot			25	0.01 Me_4NCl	153
	LH_2 + H	9.85	pot			25	0.1 Me_4NCl	153,205
	LH_2 + H	9.80	pot			25	0.01 Me_4NCl	153
	LH_3 + H	9.60	pot			25	0.1 Me_4NCl	153,205
	LH_3 + H	9.05	pot			25	0.01 Me_4NCl	153
	LH_4 + H	7.90	pot			25	0.1 Me_4NCl	153,205
	LH_4 + H	7.40	pot			25	0.01 Me_4NCl	153
	LH_5 + H	7.30	pot			25	0.1 Me_4NCl	153,205
	LH_5 + H	6.65	pot			25	0.01 Me_4NCl	153



1,5,9,20,24,28-hexaazacyclooctatriacontane
[38]aneN6

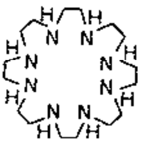
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	>10.25[a]	pot			25	0.1 Me_4NCl	205
	L + H	>10.3	pot			25	0.1 Me_4NCl	153
	L + H	>10.50[a]	pot			25	0.01 Me_4NCl	153
	LH + H	>10.25[a]	pot			25	0.1 Me_4NCl	205
	LH + H	~10.3	pot			25	0.1 Me_4NCl	153
	LH + H	~10.50[a]	pot			25	0.01 Me_4NCl	153
	LH_2 + H	10.10	pot			25	0.1 Me_4NCl	153,205
	LH_2 + H	10.15	pot			25	0.01 Me_4NCl	153
	LH_3 + H	9.60	pot			25	0.1 Me_4NCl	153,205
	LH_3 + H	9.45	pot			25	0.01 Me_4NCl	153
	LH_4 + H	7.95	pot			25	0.1 Me_4NCl	153,205
	LH_4 + H	7.65	pot			25	0.01 Me_4NCl	153
	LH_5 + H	7.30	pot			25	0.1 Me_4NCl	153,205
	LH_5 + H	6.95	pot			25	0.01 Me_4NCl	153

[a] Values not determined since the compound is not soluble in aqueous solution in their unprotonated form.



1,4,7,10,13,16,19-heptaazacycloheneicosane
[21]aneN_7

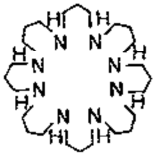
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	9.83	pot			25	0.5 $NaClO_4$	162
	L + H	9.76	pot			25	0.15 $NaClO_4$	154
	LH + H	9.53	pot			25	0.5 $NaClO_4$	162
	LH + H	9.28	pot			25	0.15 $NaClO_4$	154
	LH_2 + H	8.84	pot			25	0.5 $NaClO_4$	162
	LH_2 + H	8.63	pot			25	0.15 $NaClO_4$	154
	LH_3 + H	6.72	pot			25	0.5 $NaClO_4$	162
	LH_3 + H	6.42	pot			25	0.15 $NaClO_4$	154
	LH_4 + H	4.04	pot			25	0.5 $NaClO_4$	162
	LH_4 + H	3.73	pot			25	0.15 $NaClO_4$	154
	LH_5 + H	2.43	pot			25	0.5 $NaClO_4$	162
	LH_5 + H	2.13	pot			25	0.15 $NaClO_4$	154
	LH_6 + H	2.30	pot			25	0.5 $NaClO_4$	162
	LH_6 + H	2.0	pot			25	0.15 $NaClO_4$	154
Co(II)	L + Co	14.69	pot			25	0.15 $NaClO_4$	169
	L + Co + H	19.96	pot			25	0.15 $NaClO_4$	169
Ni(II)	L + Ni	16.56	pot			25	0.15 $NaClO_4$	170
	L + Ni + H	23.17	pot			25	0.15 $NaClO_4$	170
Cu(II)	L + Cu	24.4	pot			25	0.5 $NaClO_4$	162
	L + Cu + 2H	34.4	pot			25	0.5 $NaClO_4$	162
	L + 2Cu	30.7	pot			25	0.5 $NaClO_4$	162
	Cu_2L + OH	4.8	pot			25	0.5 $NaClO_4$	162
Zn(II)	L + Zn	13.33	pot			25	0.15 $NaClO_4$	154
	L + Zn + H	20.2	pot			25	0.15 $NaClO_4$	154
	L + Zn + 2H	25.15	pot			25	0.15 $NaClO_4$	154
	L + Zn + H_2O	1.5	pot			25	0.15 $NaClO_4$	154
Cd(II)	L + Cd	18.10	pot	67.4 cal	36.0	25	0.15 $NaClO_4$	155
	L + Cd + H	22.59	pot			25	0.15 $NaClO_4$	155
Mn(II)	L + Mn	9.79	pot	20.92 cal	34.3	25	0.15 $NaClO_4$	171



1,4,7,10,13,16,19,22-octaazacyclotetracosane
[24]aneN_8

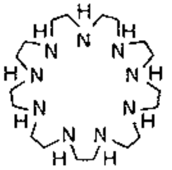
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.01	pot			25	0.5 $NaClO_4$	156
	L + H	9.65	pot			25	0.15 $NaClO_4$	154
	LH + H	9.50	pot			25	0.5 $NaClO_4$	156
	LH + H	9.33	pot			25	0.15 $NaClO_4$	154
	LH_2 + H	9.10	pot			25	0.5 $NaClO_4$	156
	LH_2 + H	8.76	pot			25	0.15 $NaClO_4$	154

	$LH_3 + H$	8.29	pot			25	0.5 $NaClO_4$	156
	$LH_3 + H$	7.87	pot			25	0.15 $NaClO_4$	154
	$LH_4 + H$	5.01	pot			25	0.5 $NaClO_4$	156
	$LH_4 + H$	4.55	pot			25	0.15 $NaClO_4$	154
	$LH_5 + H$	3.71	pot			25	0.5 $NaClO_4$	156
	$LH_5 + H$	3.42	pot			25	0.15 $NaClO_4$	154
	$LH_6 + H$	2.98	pot			25	0.5 $NaClO_4$	156
	$LH_6 + H$	2.71	pot			25	0.15 $NaClO_4$	154
	$LH_7 + H$	1.97	pot			25	0.5 $NaClO_4$	156
	$LH_7 + H$	1.95	pot			25	0.15 $NaClO_4$	154
Co(II)	L + Co	13.20	pot			25	0.15 $NaClO_4$	169
	L + Co + H	21.53	pot			25	0.15 $NaClO_4$	169
	L + Co + 2H	28.93	pot			25	0.15 $NaClO_4$	169
Ni(II)	L + Ni	13.94	pot			25	0.15 $NaClO_4$	170
	L + Ni + H	23.03	pot			25	0.15 $NaClO_4$	170
	L + Ni + 2H	30.26	pot			25	0.15 $NaClO_4$	170
	L + 2Ni	23.30	pot			25	0.15 $NaClO_4$	170
	L + 2Ni + H_2O	13.19	pot			25	0.15 $NaClO_4$	170
Cu(II)	L + 2Cu	36.63	pot	163.2 cal	46.0	25	0.5 $NaClO_4$	156
	L + 2Cu + 2H	42.02	pot			25	0.5 $NaClO_4$	156
	L + 2Cu + H_2O	26.12	pot			25	0.5 $NaClO_4$	156
Zn(II)	L + Zn	13.49	pot			25	0.15 $NaClO_4$	154
	L + Zn + H	22.07	pot			25	0.15 $NaClO_4$	154
	L + Zn + 2H	27.60	pot			25	0.15 $NaClO_4$	154
	L + Zn + H_2O	2.8	pot			25	0.15 $NaClO_4$	154
	L + 2Zn + H_2O	12.60	pot			25	0.15 $NaClO_4$	154
	L + 2Zn + $2H_2O$	3.0	pot			25	0.15 $NaClO_4$	154
Cd(II)	L + Cd	14.52	pot			25	0.15 $NaClO_4$	155
	L + Cd + H	21.67	pot			25	0.15 $NaClO_4$	155
	CdLH + H	5.86	pot			25	0.15 $NaClO_4$	155
	L + 2Cd	18.21	pot			25	0.15 $NaClO_4$	155



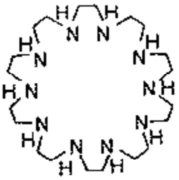
1,5,9,13,17,21,25,29-octaazacyclodotriacontane
[32]aneN_8

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.65	pot			25	0.1 NaTs	164
	L + H	10.70	pot			25	0.1 Me_4NCl	152
	LH + H	10.55	pot			25	0.1 NaTs	164
	LH + H	10.45	pot			25	0.1 Me_4NCl	152
	$LH_2 + H$	9.70	pot			25	0.1 NaTs	164
	$LH_2 + H$	9.65	pot			25	0.1 Me_4NCl	152
	$LH_3 + H$	9.20	pot			25	0.1 NaTs	164
	$LH_3 + H$	9.00	pot			25	0.1 Me_4NCl	152
	$LH_4 + H$	8.20	pot			25	0.1 NaTs	164
	$LH_4 + H$	8.05	pot			25	0.1 Me_4NCl	152
	$LH_5 + H$	7.55	pot			25	0.1 NaTs	164
	$LH_5 + H$	7.50	pot			25	0.1 Me_4NCl	152
	$LH_6 + H$	6.85	pot			25	0.1 NaTs	164
	$LH_6 + H$	6.95	pot			25	0.1 Me_4NCl	152
	$LH_7 + H$	6.50	pot			25	0.1 NaTs	164
	$LH_7 + H$	6.45	pot			25	0.1 Me_4NCl	152



1,4,7,10,13,16,19,22,25-nonaazacycloheptacosane
[27]aneN_9

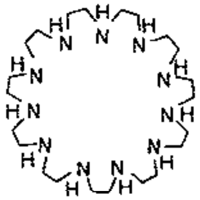
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	9.59	pot			25	0.15 $NaClO_4$	163
	LH + H	9.40	pot			25	0.15 $NaClO_4$	163
	LH_2 + H	8.77	pot			25	0.15 $NaClO_4$	163
	LH_3 + H	8.27	pot			25	0.15 $NaClO_4$	163
	LH_4 + H	6.37	pot			25	0.15 $NaClO_4$	163
	LH_5 + H	4.22	pot			25	0.15 $NaClO_4$	163
	LH_6 + H	3.24	pot			25	0.15 $NaClO_4$	163
	LH_7 + H	2.31	pot			25	0.15 $NaClO_4$	163
	LH_8 + H	1.8	pot			25	0.15 $NaClO_4$	163
Co(II)	L + Co	11.84	pot			25	0.15 $NaClO_4$	169
	L + Co + H	21.46	pot			25	0.15 $NaClO_4$	169
	L + Co + 2H	28.91	pot			25	0.15 $NaClO_4$	169
	L + 2Co	18.85	pot			25	0.15 $NaClO_4$	169
	L + 2Co + 2H	31.32	pot			25	0.15 $NaClO_4$	169
	L + 2Co + H_2O	9.88	pot			25	0.15 $NaClO_4$	169
Ni(II)	L + 2Ni	26.24	pot			25	0.15 $NaClO_4$	170
	L + 2Ni + H	31.46	pot			25	0.15 $NaClO_4$	170
	L + 2Ni + 2H	36.73	pot			25	0.15 $NaClO_4$	170
Cu(II)	L + 2Cu	36.03	pot	179.0 cal	26.0	25	0.15 $NaClO_4$	163
	L + 2Cu + H	40.66	pot			25	0.15 $NaClO_4$	163
	L + 2Cu + 2H	43.83	pot			25	0.15 $NaClO_4$	163
	L + 2Cu + 3H	47.10	pot			25	0.15 $NaClO_4$	163
	L + 2Cu + H_2O	26.24	pot			25	0.15 $NaClO_4$	163
Zn(II)	L + 2Zn	20.55	pot			25	0.15 $NaClO_4$	168
	L + 2Zn + H	26.98	pot			25	0.15 $NaClO_4$	168
	L + 2Zn + 2H	32.79	pot			25	0.15 $NaClO_4$	168
	L + 2Zn + H_2O	13.56	pot			25	0.15 $NaClO_4$	168
	L + 2Zn + $2H_2O$	4.71	pot			25	0.15 $NaClO_4$	168
Cd(II)	L + 2Cd	20.75	pot			25	0.15 $NaClO_4$	155
	L + 2Cd + H	26.38	pot			25	0.15 $NaClO_4$	155
	L + 2Cd + 2H	32.21	pot			25	0.15 $NaClO_4$	155



1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane
[30]aneN_{10}

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	9.85	pot			25	0.15 $NaClO_4$	159
	LH + H	9.44	pot			25	0.15 $NaClO_4$	159

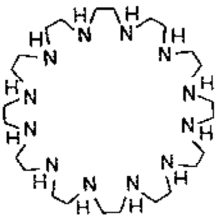
	LH_2 + H	8.95	pot			25	0.15 $NaClO_4$	159
	LH_3 + H	8.56	pot			25	0.15 $NaClO_4$	159
	LH_4 + H	7.79	pot			25	0.15 $NaClO_4$	159
	LH_5 + H	5.24	pot			25	0.15 $NaClO_4$	159
	LH_6 + H	3.84	pot			25	0.15 $NaClO_4$	159
	LH_7 + H	3.02	pot			25	0.15 $NaClO_4$	159
	LH_8 + H	1.97	pot			25	0.15 $NaClO_4$	159
	LH_9 + H	1.8	pot			25	0.15 $NaClO_4$	159
Co(II)	L + 2Co	21.85	pot			25	0.15 $NaClO_4$	169
	L + 2Co + 2H	34.67	pot			25	0.15 $NaClO_4$	169
	L + 2Co + 3H	39.79	pot			25	0.15 $NaClO_4$	169
	L + 2Co + H_2O	11.94	pot			25	0.15 $NaClO_4$	169
Ni(II)	L + 2Ni	30.02	pot			25	0.15 $NaClO_4$	170
	L + 2Ni + 2H	40.17	pot			25	0.15 $NaClO_4$	170
Cu(II)	L + 2Cu	37.77	pot	190.4 cal	25.1	25	0.15 $NaClO_4$	159
	L + 2Cu + H	43.36	pot			25	0.15 $NaClO_4$	159
	L + 2Cu + 2H	47.21	pot			25	0.15 $NaClO_4$	159
	L + 2Cu + 3H	50.52	pot			25	0.15 $NaClO_4$	159
	L + 2Cu + H_2O	26.43	pot			25	0.15 $NaClO_4$	159
Zn(II)	L + 2Zn	22.51	pot			25	0.15 $NaClO_4$	168
	L + 2Zn + 2H	35.22	pot			25	0.15 $NaClO_4$	168
	L + 2Zn + 3H	40.41	pot			25	0.15 $NaClO_4$	168
	L + 2Zn + H_2O	14.16	pot			25	0.15 $NaClO_4$	168
	L + 2Zn + $2H_2O$	3.19	pot			25	0.15 $NaClO_4$	168
Cd(II)	L + 2Cd	23.21	pot			25	0.15 $NaClO_4$	155
	L + 2Cd + 2H	35.07	pot			25	0.15 $NaClO_4$	155
	L + 2Cd + 3H	39.94	pot			25	0.15 $NaClO_4$	155



1,4,7,10,13,16,19,22,25,28,31-undecaazacyclotritriacontane
[33]aneN_{11}

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	9.79	pot			25	0.15 $NaClO_4$	160
	LH + H	9.48	pot			25	0.15 $NaClO_4$	160
	LH_2 + H	9.02	pot			25	0.15 $NaClO_4$	160
	LH_3 + H	8.64	pot			25	0.15 $NaClO_4$	160
	LH_4 + H	8.06	pot			25	0.15 $NaClO_4$	160
	LH_5 + H	6.44	pot			25	0.15 $NaClO_4$	160
	LH_6 + H	4.49	pot			25	0.15 $NaClO_4$	160
	LH_7 + H	3.58	pot			25	0.15 $NaClO_4$	160
	LH_8 + H	2.76	pot			25	0.15 $NaClO_4$	160
	LH_9 + H	2.26	pot			25	0.15 $NaClO_4$	160
	LH_{10} + H	1.7	pot			25	0.15 $NaClO_4$	160
Co(II)	L + 2Co	22.90	pot			25	0.15 $NaClO_4$	169
	L + 2Co + 2H	35.83	pot			25	0.15 $NaClO_4$	169
	L + 2Co + 3H	40.91	pot			25	0.15 $NaClO_4$	169
	L + 2Co + H_2O	12.72	pot			25	0.15 $NaClO_4$	169
Ni(II)	L + 2Ni	31.07	pot			25	0.15 $NaClO_4$	170
	L + 2Ni + H	36.98	pot			25	0.15 $NaClO_4$	170

	L + 2Ni + 2H	40.98	pot			25	0.15 NaClO$_4$	170
	L + 2Ni + 3H	46.44	pot			25	0.15 NaClO$_4$	170
Cu(II)	L + 2Cu	38.77	pot			25	0.15 NaClO$_4$	160
	L + 2Cu + H	45.28	pot			25	0.15 NaClO$_4$	160
	L + 2Cu + 2H	51.18	pot			25	0.15 NaClO$_4$	160
	L + 2Cu + 3H	53.86	pot			25	0.15 NaClO$_4$	160
	L + 2Cu + H$_2$O	27.29	pot			25	0.15 NaClO$_4$	160
	L + 3Cu	48.03	pot			25	0.15 NaClO$_4$	160
	L + 3Cu + H$_2$O	40.62	pot			25	0.15 NaClO$_4$	160
	L + 3Cu + 2H$_2$O	30.2	pot			25	0.15 NaClO$_4$	160
Zn(II)	L + 2Zn	23.91	pot			25	0.15 NaClO$_4$	168
	L + 2Zn + 2H	36.66	pot			25	0.15 NaClO$_4$	168
	L + 2Zn + 3H	42.17	pot			25	0.15 NaClO$_4$	168
	L + 2Zn + H$_2$O	15.40	pot			25	0.15 NaClO$_4$	168
	L + 2Zn + 2H$_2$O	4.87	pot			25	0.15 NaClO$_4$	168
Cd(II)	L + 2Cd	23.63	pot			25	0.15 NaClO$_4$	155
	L + 2Cd + 2H	36.06	pot			25	0.15 NaClO$_4$	155
	L + 2Cd + 3H	41.39	pot			25	0.15 NaClO$_4$	155

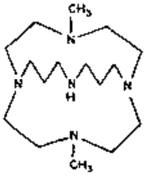


1,4,7,10,13,16,19,22,25,28,31,34-dodecaazacyclohexatriacontane

[36]aneN$_{12}$

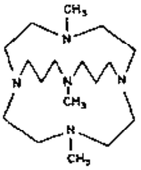
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	9.75	pot			25	0.15 NaClO$_4$	160
	LH + H	9.65	pot			25	0.15 NaClO$_4$	160
	LH$_2$ + H	8.88	pot			25	0.15 NaClO$_4$	160
	LH$_3$ + H	8.96	pot			25	0.15 NaClO$_4$	160
	LH$_4$ + H	8.12	pot			25	0.15 NaClO$_4$	160
	LH$_5$ + H	7.82	pot			25	0.15 NaClO$_4$	160
	LH$_6$ + H	5.66	pot			25	0.15 NaClO$_4$	160
	LH$_7$ + H	4.27	pot			25	0.15 NaClO$_4$	160
	LH$_8$ + H	3.58	pot			25	0.15 NaClO$_4$	160
	LH$_9$ + H	2.62	pot			25	0.15 NaClO$_4$	160
	LH$_{10}$ + H	2.3	pot			25	0.15 NaClO$_4$	160
	LH$_{11}$ + H	1.0	pot			25	0.15 NaClO$_4$	160
Co(II)	L + 2Co	24.55	pot			25	0.15 NaClO$_4$	169
	L + 2Co + H	31.29	pot			25	0.15 NaClO$_4$	169
	L + 2Co + 2H	37.62	pot			25	0.15 NaClO$_4$	169
	L + 2Co + 3H	43.45	pot			25	0.15 NaClO$_4$	169
	L + 2Co + 4H	48.76	pot			25	0.15 NaClO$_4$	169
	L + 2Co + H$_2$O	13.87	pot			25	0.15 NaClO$_4$	169
Ni(II)	L + 2Ni	32.09	pot			25	0.15 NaClO$_4$	170
	L + 2Ni + H	38.62	pot			25	0.15 NaClO$_4$	170
	L + 2Ni + 2H	44.46	pot			25	0.15 NaClO$_4$	170
	L + 2Ni + 3H	48.95	pot			25	0.15 NaClO$_4$	170
	L + 2Ni + 4H	53.42	pot			25	0.15 NaClO$_4$	170
Cu(II)	L + 2Cu	39.25	pot			25	0.15 NaClO$_4$	160
	L + 2Cu + H	47.09	pot			25	0.15 NaClO$_4$	160
	L + 2Cu + 2H	53.96	pot			25	0.15 NaClO$_4$	160

	L + 2Cu + 3H	58.07	pot			25	0.15 NaClO$_4$	160
	L + 2Cu + 4H	61.42	pot			25	0.15 NaClO$_4$	160
	L + 3Cu	51.43	pot			25	0.15 NaClO$_4$	160
	L + 3Cu + H	55.38	pot			25	0.15 NaClO$_4$	160
	L + 3Cu + H$_2$O	42.53	pot			25	0.15 NaClO$_4$	160
	L + 3Cu + 2H$_2$O	31.62	pot			25	0.15 NaClO$_4$	160
Zn(II)	L + 2Zn	26.27	pot			25	0.15 NaClO$_4$	154
	L + 2Zn + H	32.83	pot			25	0.15 NaClO$_4$	154
	L + 2Zn + 2H	39.16	pot			25	0.15 NaClO$_4$	154
	L + 2Zn + 3H	44.81	pot			25	0.15 NaClO$_4$	154
	L + 2Zn + 4H	49.99	pot			25	0.15 NaClO$_4$	154
	L + 2Zn + H$_2$O	16.09	pot			25	0.15 NaClO$_4$	154



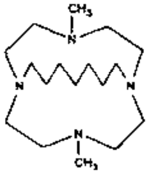
12,17-dimethyl-1,5,9,12,17-pentaazabicyclo[7.5.5]nonadecane

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	>14	pot			25	0.5 KNO$_3$	46
	LH + H	8.41	pot			25	0.5 KNO$_3$	46
	LH$_2$ + H	<2	pot			25	0.5 KNO$_3$	46



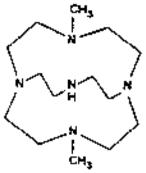
5,12,17-trimethyl-1,5,9,12,17-pentaazabicyclo[7.5.5]nonadecane

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	11.83	pot	54.4 cal	13.1	25	0.15 NaCl	47
	LH + H	9.53	pot	42.7 cal	11.7	25	0.15 NaCl	47
	LH$_2$ + H	3.43	pot	13.0 cal	6.6	25	0.15 NaCl	47
Li(I)	L + Li	3.2	pot	2.1 cal	16.2	25	0.15 NaCl	47



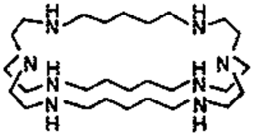
12,17-dimethyl-1,9,12,17-tetraazabicyclo[7.5.5]nonadecane

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	12.00	pot	54.0 cal	14.5	25	0.15 NaCl	174
	LH + H	7.86	pot	44.8 cal	~0	25	0.15 NaCl	174



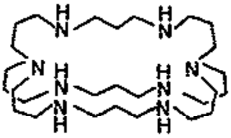
4,10-dimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	12.48	pot			25	0.15 NaCl	49
	LH + H	9.05	pot			25	0.15 NaCl	49
	LH_2 + H	<1	pot			25	0.15 NaCl	49
Li(I)	L + Li	4.8	pot			25	0.15 NaCl	49



1,4,10,13,16,22,27,33-octaazabicyclo[11.11.11]pentatriacontane

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H	L + H	10.35	pot			25	0.1 $NaClO_4$	177
	LH + H	9.88	pot			25	0.1 $NaClO_4$	177
	LH_2 + H	8.87	pot			25	0.1 $NaClO_4$	177
	LH_3 + H	8.38	pot			25	0.1 $NaClO_4$	177
	LH_4 + H	8.14	pot			25	0.1 $NaClO_4$	177
	LH_5 + H	7.72	pot			25	0.1 $NaClO_4$	177
Cu(II)	L + Cu	15.39	pot			25	0.1 $NaClO_4$	177
	CuL + H	10.08	pot			25	0.1 $NaClO_4$	177
	CuLH + H	8.70	pot			25	0.1 $NaClO_4$	177
	$CuLH_2$ + H	7.62	pot			25	0.1 $NaClO_4$	177
	L + 2Cu	28.76	pot			25	0.1 $NaClO_4$	177
	Cu_2L + H	5.40	pot			25	0.1 $NaClO_4$	177
	Cu_2L + H_2O	-7.59	pot			25	0.1 $NaClO_4$	177
	Cu_2LOH + H_2O	-10.81	pot			25	0.1 $NaClO_4$	177



1,5,9,13,17,21,28,32-octaazabicyclo[11.11.11]pentatriacontane

cation	reaction	logK	method	$-\Delta H°$(kJ/mol)	$T\Delta S°$(kJ/mol)	T °C	medium	ref
H	L + H	10.10	pot			25	0.1 NaTsO	192
	L + H	10.45	pot			25	0.1 Me_4NCl	192
	LH + H	10.45	pot			25	0.1 NaTsO	192
	LH + H	10.30	pot			25	0.1 Me_4NCl	192
	LH_2 + H	9.40	pot			25	0.1 NaTsO	192
	LH_2 + H	9.55	pot			25	0.1 Me_4NCl	192
	LH_3 + H	8.65	pot			25	0.1 NaTsO	192
	LH_3 + H	8.60	pot			25	0.1 Me_4NCl	192
	LH_4 + H	7.00	pot			25	0.1 NaTsO	192
	LH_4 + H	7.45	pot			25	0.1 Me_4NCl	192
	LH_5 + H	6.75	pot			25	0.1 NaTsO	192
	LH_5 + H	7.30	pot			25	0.1 Me_4NCl	192
	LH_6 + H	4.95	pot			25	0.1 NaTsO	192
	LH_6 + H	5.40	pot			25	0.1 Me_4NCl	192
	LH_7 + H	4.15	pot			25	0.1 NaTsO	192
	LH_7 + H	4.60	pot			25	0.1 Me_4NCl	192

crystal structure of $[H(\mathbf{11})](ClO_4)$ [65] (Fig. 2). In this compound, the proton is bound to one nitrogen atom of the tridentate ligand and interacts with the other two nitrogen atoms via in-ring hydrogen bonds. Therefore, the first protonation step of the cyclic triamines is favoured with respect to the linear triamines. On the other hand, the second protonation destroys this stable arrangement, producing a diprotonated form in which two positive charges are constrained to occupy neighbouring nitrogen atoms. The second proton is, therefore, more strongly bound by the non-cyclic triamines.

The enthalphy changes for the first and the second protonation steps of (**6**) have been obtained by calorimetric measurements [57]. The enthalpy changes for these protonation reactions are very similar in spite of the large decrease of the stepwise protonation constants (see Table 1). The great loss in entropy which takes place upon protonation of $[H(\mathbf{6})]^+$, could be ascribed to a strong solvation of the $[H_2(\mathbf{6})]^{2+}$ species.

The first report on the thermodynamics of formation of triaza macrocyclic complexes dealing with the smallest ligand $[9]aneN_3$ and the metal ions Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) was presented by Arishima et al. [59]. Stability constants for 1:1 and 1:2, metal-to-ligand molar ratio, complexes were reported for all these metal ions. When this paper appeared, the macrocyclic effect (see Sect. J) had already been observed for tetraazacycloalkanes [23]. By comparison between the stability constants of the 1:1 complexes of (**6**) and those obtained for the analogous species with the non-cyclic triamine 2,2′-diaminodiethylamine, it was observed that a similar effect is presented by the Co(II), Ni(II), Zn(II), and Cd(II) complexes of the tridentate cyclic ligand [59]. Only with Cu(II) does the ligand (**6**) form a 1:1 complex whose stability is lower than that observed for the linear triamine. These results, which were later reproduced by other authors [56,66], have been explained by considering that the small tridentate cyclic (**6**) is sterically constrained to occupy three facial sites on the coordination sphere of the metal ion (Fig. 3). On the other hand, the flexible 2,2′-diaminodiethylamine ligand may exert meridional coordination, which is, in the case of Cu(II), the preferred coordination mode. This different coordination feature can also explain the smaller enthalpy change, determined by direct calorimetric technique [57], for the

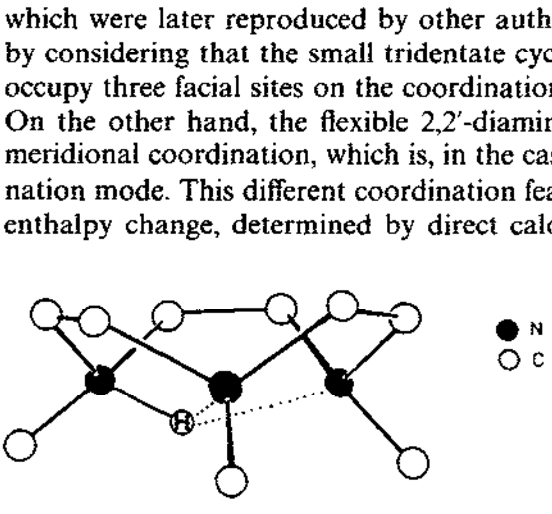


Fig. 2. View of the monoprotonated cation $[H(\mathbf{11})]^+$ showing the proton binding [65].

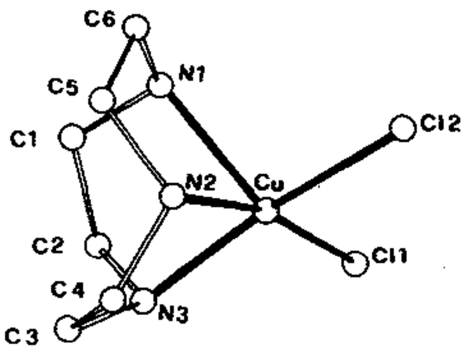


Fig. 3. View of the $[Cu(\mathbf{6})]Cl_2$ complex, showing the coordination polyhedron and the facial disposition of (**6**) [217].

reaction of formation of the complex $[Cu(\mathbf{6})]^{2+}$ ($\Delta G^0 = -88.6$ kJ mol^{-1}; $\Delta H^0 = -59.4$ kJ mol^{-1}; $T\Delta S^0 = 29.2$ kJ mol^{-1}) with respect to that obtained for [Cu(2,2′-diaminodiethylamine)]$^{2+}$ ($\Delta G^0 = -90.4$ kJ mol^{-1}; $\Delta H^0 = -75.3$ kJ mol^{-1}; $T\Delta S^0 = 15.1$ kJ mol^{-1}). On the other hand, complexation by the pre-oriented cyclic ligand is favoured by the entropic contribution. Otherwise, a macrocyclic effect is observed for the Cu(II) complex of (**6**) if the non-cyclic counterpart is also sterically constrained to facial coordination as in the case of 1,2,3-triaminopropane [56]. In most papers dealing with the Cu(II) complexes of (**6**), only 1:1 and 1:2 complexes have been considered [55,56,57,66,67]. However, other authors have reported that the hydroxo species $[Cu(\mathbf{6})OH]^+$ [58,59] and $[Cu_2(\mathbf{6})_2(OH)_2]^{2+}$ [60,61], respectively, had to be taken into account to fit the titration curves in their experiments.

Some wide discrepancies are present in values for the equilibrium constants reported for Cu(II) complexes. Although the implication of different experimental conditions and methods, as well as the use of different chemical models in the fitting of experimental data, may have affected the values of the stability constants, such discrepancies seem to be due mainly to different ligand protonation constants.

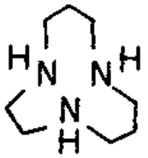
The visible and near infrared spectra of 1:1 copper triazacycloalkane complexes in solution contain two broad bands in the *d–d* region (15 000–9000 cm^{-1}) [66]. The spectral maxima shift toward higher energy as the dimension of the ring size increases from (**6**) to (**9**). Similar results for the Co(III) complexes of (**6**) and (**8**) were reported. It appears [66] that the decrease in ligand field strength is due to increasing distortion from the less strained tetragonal symmetry, likely presented by complexes of the large triazamacrocycles [68], to the pseudo-trigonal C_{3v} symmetry of the (**6**) complex. The formation constants for the complexes of (**6**) with several other metal ions such as Mn(II), Cd(II), Pb(II) and Hg(II) have been determined [53,59,62].

With the exception of the Hg(II) complex [62], greater stability has been observed for the complexes of (**6**) with respect to those of 2,2′-diaminodiethylamine.

The determination, by calorimetric measurements, of the enthalpy change relative to the reaction of Cu(II) and Zn(II) with (**6**) has shown that the stability of $[Cu(\mathbf{6})]^{2+}$ and $[Zn(\mathbf{6})]^{2+}$ is mainly enthalpic in nature [57]. For Zn(II), Cd(II) and Pb(II), the enthalpic contribution to the formation of their complexes with (**6**) has been estimated from the dependence of the stability constants upon the temperature [53]. In the case of Zn(II), the results strongly disagree with those previously obtained by direct calorimetric measurements [57].

A macrocyclic effect has been observed for complexes of all cyclic triamines, and the stability of their complexes follows the Irving–Williams order. The stability constants of these complexes decrease as the dimensions of the macrocyclic ligand increase. Microcalorimetric studies [57] and determination of the stability constants at different temperature [53] have been carried out to gain insight into the enthalpic or entropic origin of this trend. The interpretations on this point mostly agree with the enthalpic contribution [53,57,66] although wide discrepancies exist concerning the 1:1 complex of Zn(II) with (**6**) [53,57]. In terms of geometrical pre-orientation of the nitrogen donor atoms (multiple juxtapositional fixedness effect) a decrease of the ligand ring size produces better overlap of the metal orbitals with the orbitals of the donor atoms, determining increasing stability.

The interaction of the carbon methylated (**10**) with Ni(II), Cu(II) and Zn(II) has been studied [63]. The stability constants for the complexes $[Cu(\mathbf{10})]^{2+}$ and $[Zn(\mathbf{10})]^{2+}$ are somewhat smaller than those reported for the analogous complexes of (**9**). On the other hand, the formation reaction at 25°C of $[Ni(\mathbf{10})]^{2+}$ is too slow to allow the equilibrium constant to be determined [63]. The ability of triazamacrocycles to form 1:2 (metal/ligand) complexes is markedly lower for the larger ligands so that, while (**6**) forms 1:2 complexes with all the metal ions studied [53,60,61,62], only $[Cu(L)_2]^{2+}$ complexes are reported for (**8**) and 1,5,8-triazacycloundecane (**12**) [60,61]. Hydrolysis of the Cu(II) and Zn(II) complexes with larger triazacyclic ligands has been observed and the stability constants of the species $[Cu(\mathbf{9})OH]^+$, $[Zn(\mathbf{9})OH]^+$ [58],



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$[Cu_2(\mathbf{9})_2(OH)_2]^{2+}$ [60,61], $[Cu(\mathbf{10})OH]^{+}$, $[Zn(\mathbf{10})(OH)]^{+}$, $[Cu(\mathbf{10})(OH)_2]$, $[Cu_2(\mathbf{10})_2(OH)_2]^{2+}$, $[Ni_2(\mathbf{10})_2(OH)_2]^{2+}$ [63], $[Zn(\mathbf{12})OH]^{+}$ [58] and $[Cu_2(\mathbf{8})_2(OH)_2]^{2+}$ [60,61], have been determined.

It was noted [69] that complexes of triaza macrocycles in which the ligand is present in a protonated form were not found in solution, and this was attributed to the favourable conformation of these amines as tridentate chelating ligands. However, with metal ions such as Pd(II) and Pt(II) (d^8, low spin) which require square geometry, preventing facial coordination of triaza macrocyclic amines, bidentate coordination of these ligands has been observed in the solid state [70–72]. By controlling the pH of the solution in which these complexes are formed, solid compounds containing monoprotonated and diprotonated forms of the triazacycloalkane coordinated ligands have been isolated [70–72]. It seems likely that similar species are also present in solution.

D. TETRAAZACYCLOALKANES

Tetraazacycloalkanes are by far the most studied aza macrocycles. The tetraaza macrocycle 1,4,8,11-tetraazacyclotetradecane (**1**) (cyclam), the most famous and studied aza macrocycle, was first synthesized by Van Alphen [21] by the reaction between 1,3-dibromopropane and 1,3-bis(2′-aminoethylamino)-propane in the presence of alkali. More recently, Stetter and Mayer [37] synthesized cyclam by a more efficient route.

Basicity and metal complex formation constants for tetraaza macrocycles are reported in Table 1. In most cases, pH-metric methods have been employed to determine the equilibrium constants [73–78], although other techniques, including ^{1}H NMR, spectrophotometry and polarography have occasionally been employed. The basicity behaviour of tetraaza macrocycles is greatly influenced by the length of the hydrocarbon chains connecting two adjacent nitrogen atoms. In general the main effect of cyclization on the basicity behaviour is an increase of base strength in the first two protonation steps with respect to the open chain polyamines and decrease of basicity in the last two protonation steps. This trend, which is more conspicuous for the smallest tetraaza macrocycle 1,4,7,10-tetraazacyclododecane (**13**), has been

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ascribed to the proximity of the NH_2^+ groups [76,77], resulting in strong electrostatic repulsions. For (**13**) only pK_1 and pK_2 have been accurately measured, pK_3 and pK_4 being very small and only estimated [73].

The thermodynamics of formation in aqueous solution of many complexes of (**13**) with different metal ions, including Co(II) [79], Ni(II) [80–82], Cu(II) [73,83,84], Zn(II) [85,86], Cd(II) [85], Hg(II) [86], and Pb(II) [85] has been reported. Only very stable 1:1 complexes were found. The equilibrium constant for the Co(II)/(**13**) system has been reported by Kodama and Kimura [79] who also studied the interaction of molecular oxygen with $[Co(\mathbf{13})]^{2+}$. In the case of the Ni(II) complex, a batchwise potentiometric technique, [87] was used on account of the long time required for chemical equilibrium to be reached.

The formation enthalpy of both octahedral, blue and yellow square-planar complexes $[Ni(\mathbf{13})]^{2+}$ [81] were determined by destruction of the preformed complex with excess of cyanide in strong alkaline solution as described in ref. 88. The polarographically determined equilibrium constant of the $[Cu(\mathbf{13})]^{2+}$ complex was reported by Kodama and Kimura [73,83]. The same authors determined the enthalpy of complex formation (-76.6 kJ mol^{-1}, see Table 1) by measuring the equilibrium constant at different temperatures (10–35°C). Later, a more reliable, calorimetrically determined value (-95.0 kJ mol^{-1}) was reported by Anichini et al. [84]. The enthalpy of reaction was correlated with the calculated ideal size of the aperture in the macrocyclic ligand in a minimum-strain conformation.

Macrocycle (**13**) is too small (ideal $M-N = 1.83$ Å) [89] to accommodate the metal ion in square coordination. The crystal structure of $[Cu(\mathbf{13})]^{2+}$, reported by Clay et al. [90] indicates that the complex contains five-coordinate Cu(II) in a square-pyramidal environment, the copper atom being 0.5 Å above the plane containing the four nitrogen atoms of the macrocycle (Fig. 4). The stabilities of $[Zn(\mathbf{13})]^{2+}$, $[Cd(\mathbf{13})]^{2+}$, $[Hg(\mathbf{13})]^{2+}$, and $[Pb(\mathbf{13})]^{2+}$ [85,86] were several orders of magnitude larger than those for corresponding linear homologues.

Recently, Hancock et al. [91] reported the formation constants of various metal ions including Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) with the structurally reinforced 12-membered macrocyclic ligand 1,4,7,10-tetraazabicyclo[8.2.2]tetradecane (**14**) [92]. The results indicated that this more rigid macrocycle shows an enhanced selectivity for metal ions in terms of matching in size between the metal ion and the macrocyclic cavity.

The partially methylated 12-membered macrocycle 1,7-dimethyl-1,4,7,10-tetraazacyclododecane (**15**) shows similar basicity behaviour [43] to the unmethylated derivative; pD-^{13}C NMR studies [43] indicated that only the two secondary nitrogens are involved in the first two protonation processes. The equilibrium constants for the two complexes $[Cu(\mathbf{15})]^{2+}$ and

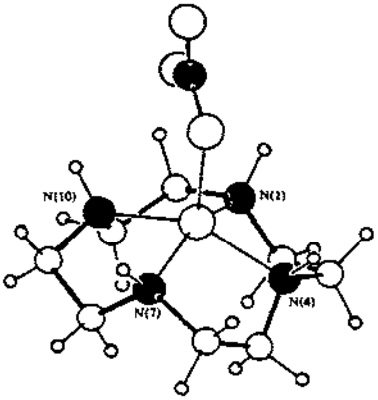
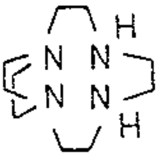


Fig. 4. Crystal structure of the $[Cu(\mathbf{13})NO_3]^+$ cation.



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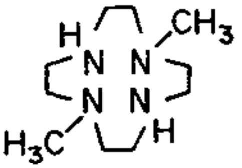

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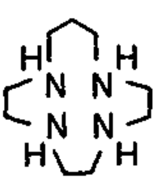
$[Cu(\mathbf{15})H]^{3+}$ were reported [43]. The stability of the $[Cu(\mathbf{15})]^{2+}$ complex ($\log K = 17.89$) was significantly lower than that found for the unmethylated derivative $[Cu(\mathbf{13})]^{2+}$ ($\log K = 24.8$) [73].

As expected, increasing the overall macrocyclic atomicity results in a parallel increase in the basicity: the values of $pK_1 = 11.1$ and $pK_2 = 10.1$ for 1,4,7,10-tetraazacyclotridecane (**16**) (see Table 1) found by Kodama and Kimura [74] are significantly higher than those found by the same authors for (**13**) [73]. Leugger et al. [75] reported pK values for (**16**), determined at a different ionic strength from those reported in ref. 74. Also, in the case of [13]aneN_4 pK_3 and pK_4 were very low and not accurately measured [74,75].



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The formation of the complex $[\mathrm{Co}(\mathbf{16})]^{2+}$ was studied by potentiometry [79] and $\log K = 14.3$ was among the highest found for tetraaza macrocycles.

The $[\mathrm{Ni}(\mathbf{16})]^{2+}$ complex, as other Ni(II) complexes with macrocyclic ligands, was found to exist in aqueous solution as a mixture of the high-spin (13%) and low-spin (87%) forms [82]. The enthalpies of formation of each species were reported [82] and compared with those of other tetraaza macrocyclic ligands. More recently, Thöm et al. reported the stability constant of the $[\mathrm{Ni}(\mathbf{16})]^{2+}$ complex determined by a batchwise procedure [80,81]. The thermodynamics of formation of the $[\mathrm{Cu}(\mathbf{16})]^{2+}$ complex was first reported by Kodama and Kimura [74] ($\log K = 29.1$) using polarography. Later, a more reliable value ($\log K = 24.36$) was reported by Thöm et al. [81]. For the $[\mathrm{Zn}(\mathbf{16})]^{2+}$ complex, while there is good agreement between the stability constants reported by different authors ($\log K = 15.6$ from ref. 85, $\log K = 15.74$ from ref. 93), there is disagreement for the enthalpy of formation. A value of $-32.6\ \mathrm{kJ\ mol^{-1}}$ was reported in ref. 85, determined by measuring the stability constants at three different temperatures between 10 and 35°C, and a value of $-64.0\ \mathrm{kJ\ mol^{-1}}$ was reported in ref. 93 by calorimetry.

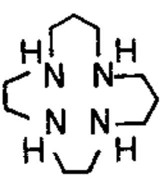
Equilibrium studies on Cd(II) [80,81], Hg(II) [86], and Pb(II) [80,81] have been reported.

The interpretation of the stepwise protonation constants of 1,4,8,11-tetraazacyclotetradecane $[14]\mathrm{aneN}_4$ (**1**) has frequently been discussed. A fully hydrogen-bonded structure was first proposed by Stetter and Mayer [37]. Later, Bosnich et al. [94] suggested a structure of (**1**) with two intramolecular hydrogen bonds, which leaves the electron pairs of two nitrogen atoms easily accessible for two hydrogen ions, whereas the other two are engaged and thus scarcely accessible (low basicity). Attempts to confirm the presence of strong hydrogen bonds in (**1**) were unsuccessful [75,95]. Indeed, X-ray structure analysis of the diperchlorate of (**1**) suggests only the possibility of two weak hydrogen bonds [96]. Many authors [75,85,97,98] have reported sets of values of the stepwise protonation constants of (**1**): while the agreement is good for the first two p*K*s, it is very poor for the last two steps ($\mathrm{p}K_3$ and $\mathrm{p}K_4$). More recently, a careful study has been reported [76,77], including both the measurement of the stepwise basicity constants and the relative heats of reaction. The first two protonation steps of (**1**) were found to be very exothermic, whereas the last two were much less exothermic with the fourth step, unexpectedly, more exothermic than the third. This inversion was also found in the basicity constants [76,77].

In general, it was stated [77] that, in order to rationalize the thermodynamic functions ΔH^0 and ΔS^0 of protonation of tetraaza macrocycles, two factors, which are not considered in the open-chain polyamines, have to be taken into account: (i) the presence of internal hydrogen bonds of the type $\mathrm{N{-}H\cdots N}$ and (ii) conformational rearrangements of the macrocyclic ring due to the nitrogen inversion: the lone pairs could be directed either towards the inside or the outside of the ring [77].

The formation of the $[\mathrm{Co}(\mathbf{1})]^{2+}$ complex, both in oxygenated and non-oxygenated aqueous solution, has been investigated by Kodama and Kimura [79]. The thermodynamics of formation of the $[\mathrm{Ni}(\mathbf{1})]^{2+}$ complex was first reported by Hinz and Margerum [98] in 1974 since when the formation equilibria of many metal complexes of (**1**) have been studied and their thermodynamic parameters reported. Much of this interest has arisen from the need to elucidate the nature of the so called 'macrocyclic effect' [23]. Fabbrizzi et al. [88] determined by calorimetry the enthalpy of formation of both octahedral (blue, high spin) and square-planar (yellow, low spin) forms of the $[\mathrm{Ni}(\mathbf{1})]^{2+}$ complex. Because the formation of macrocyclic Ni(II) complexes is too slow to be determined calorimetrically, a procedure involving the destruction of the macrocyclic complexes with cyanide in strongly alkaline solutions was developed [88]. Recently, Evers and Hancock [99] reported the formation constant for the $[\mathrm{Ni}(\mathbf{1})]^{2+}$ complex measured by an out-of-cell technique. The value found ($\log K = 20.1$) is somewhat lower than the value of $\log K = 22.2$ reported by Hinz and Margerum [98]. The formation of $[\mathrm{Cu}(\mathbf{1})]^{2+}$ was first studied by Kodama and Kimura [55]; later Anichini et al. [84] reported the enthalpy of formation of the same complex. The same authors compared the enthalpy of formation of the Cu(II) complex with those of other tetraaza macrocyclic ligands of different ring size. The results, which were correlated with the calculated ideal size of the aperture in the macrocycle required to maintain the ligand in a minimum-strain conformation, showed that the most exothermic enthalpy of reaction was associated with the $[\mathrm{Cu}(\mathbf{1})]^{2+}$ formation [84]. Analogous comparisons were made with Ni(II) complexes [82] and Zn(II) complexes [84,93]. More recently, Thöm et al. have reported the stability constants for the complexes $[\mathrm{Cu}(\mathbf{1})]^{2+}$, $[\mathrm{Pb}(\mathbf{1})]^{2+}$ and $[\mathrm{Cd}(\mathbf{1})]^{2+}$ [81].

Reports on Zn(II) complexes of (**1**) have been published by different authors [84,85,93,100]. Kodama and Kimura reported the thermodynamics of formation of the $[\mathrm{Hg}(\mathbf{1})]^{2+}$ complex [86]. Among 14-membered tetraaza macrocycles we have, beside (**1**), two other macrocycles 1,4,7,11-tetrazacyclotetradecane (**17**) and 1,4,7,10-tetraazacyclotetradecane (**18**) with the same overall atomicity but with a different sequence of hydrocarbon chains between



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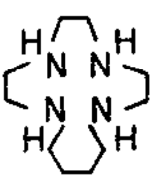

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the nitrogen atoms. The basicity constants of these two macrocycles have been reported in ref. 75 and 101, respectively.

It was reported [78] that, for macrocycles having the same atomicity, the overall basicity is influenced by the relative sequence of hydrocarbon chains between the nitrogen atoms in such a way that a less symmetric arrangement lowers the overall basicity.

As far as metal complexes of the two asymmetric 14-membered macrocycles (**17**) and (**18**) are concerned, various reports have been published in recent years [100,102,103]. The formation reactions of $[\mathrm{Co}(\mathbf{17})]^{2+}$, $[\mathrm{Ni}(\mathbf{17})]^{2+}$ and $[\mathrm{Cu}(\mathbf{17})]^{2+}$ were reported in refs. 79, 100, and 102 and 103, respectively. For the last two complexes, where a (5,5,6,6) chelate ring sequence is achieved, calorimetric results showed that the macrocycle (**17**) incorporated metal ions (Cu(II), Ni(II)) less exothermically than its more symmetric isomer cyclam (**1**) ((5,6,5,6) chelate ring sequence). The proposed explanation was the formation of weaker in-plane M—N interactions.

The introduction of a hindered seven-membered chelate ring, achieved with (**18**), was found to completely overrule the enthalpic advantage of the 14-membered cavity [101]. Indeed, the complexes $[\mathrm{Ni}(\mathbf{18})]^{2+}$ and $[\mathrm{Cu}(\mathbf{18})]^{2+}$, which contain a (5,5,5,7) chelate ring sequence, were found to be remarkably less exothermic than that of cyclam and (**17**) which form (5,6,5,6) and (5,5,6,6) chelate ring sequences, respectively. However, in spite of the low exothermicity of the $[\mathrm{Ni}(\mathbf{18})]^{2+}$ complex [101], it was more stable than the corresponding open-chain analogous 1,4,7,10-tetraazadecane (trien) [87].

The crystal structure of $[\mathrm{Cu}(\mathbf{18})](\mathrm{ClO_4})_2$ [104] (Fig. 5) shows the copper atom in a tetragonally distorted octahedral environment where the four nitrogen atoms are in a planar arrangement and two oxygen atoms of two perchlorate ions in the apical positions.

Among *N*-alkyl derivatives of cyclam, the tetramethyl-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (**3**) is most important. The thermodynamic protonation functions ΔG^0, ΔH^0 and ΔS^0 of (**3**) were determined [76,77]. Except for $\mathrm{p}K_3$, all stepwise protonation constants of (**3**) were lower than for the corresponding values of (**1**), in agreement with the fact that, in aqueous solution, tertiary amino groups are less basic than secondary amino groups.

Complexes of (**3**), first reported by Barefield and Wagner [105], are interesting because the metal ions are held in a square-pyramidal fashion (Fig. 6) rather than the octahedral conformation found for other saturated tetraaza macrocycles. Formation equilibria with many metal ions, including Cu(II), Co(II), Zn(II), Cd(II), and Hg(II), were studied by Nakani et al. [106] employing a potentiometric technique. The Ni(II) complex of (**3**) was studied by an out-of-cell potentiometric titration [107]. The low value found ($\log K = 8.65$) was discussed in terms of the unusual square-pyramidal coordination geometry forced on the metal ion by the ligand [108].

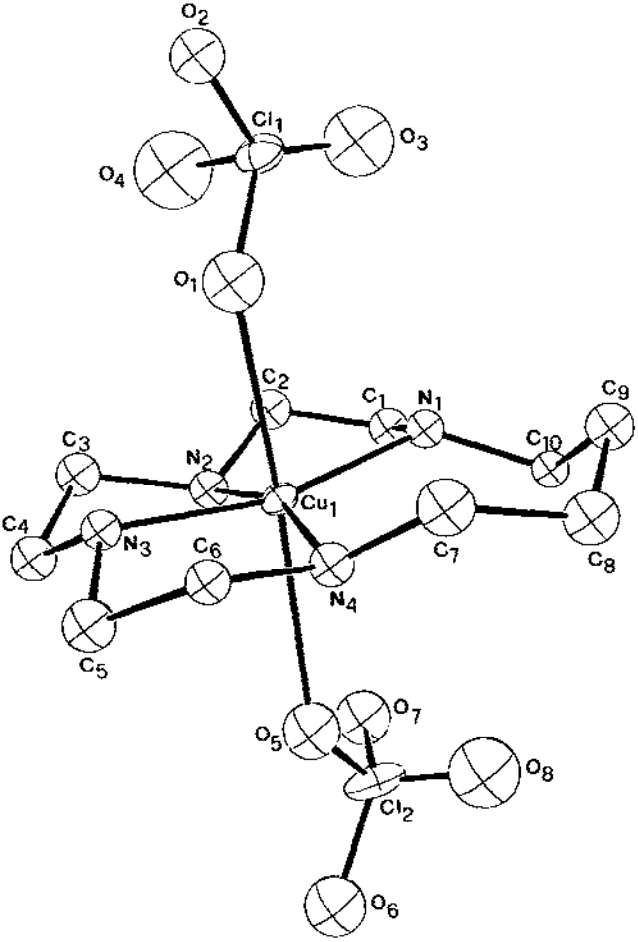


Fig. 5. ORTEP view of the $[Cu(18)](ClO_4)_2$ complex.

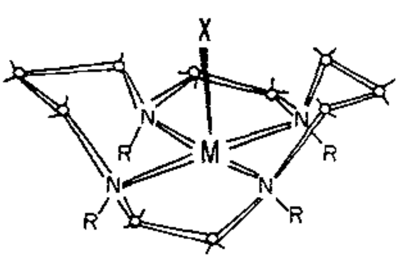
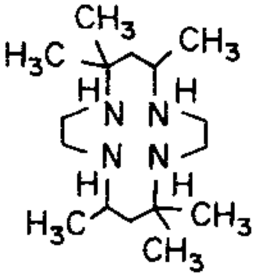


Fig. 6. Example of a square-pyramidal complex of (3) ($R = CH_3$).

Among the C-derivatives of 14-membered tetraaza macrocycles, the C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane **(2)** (tet *a*) and C-*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane **(19)** (tet *b*) merit special consideration because of the large amount of work which has been reported with these ligands [23,90,98,109–114].



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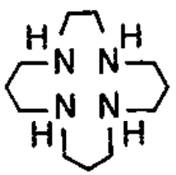
The basicity constants of these two macrocyclic isomers were first determined by Curtis [109] by pH titrations. The values found: $pK_1 = 11$, $pK_2 = 10.5$, $pK_3 = 2.2$, $pK_4 < 2$ for (tet *b*) and $pK_1 = 11.6$, $pK_2 = 10.7$, $pK_3 = 2.7$, $pK_4 = 2.3$ for (tet *a*) differ considerably from those found for the non-cyclic tetra-ammine and the difference was attributed to intramolecular hydrogen bonding in the cyclic amine [109].

In the original 'macrocyclic effect' paper, Cabbiness and Margerum [23] reported the stability constant for the Cu(II)/(tet *a*) system. The same authors also noted that Cu(II) forms two complexes with (tet *a*), a blue form ($\log K = 20$) and a thermodynamically more stable red form ($\log K = 28$) into which the blue form can be converted at high pH. Clay et al. [90] reported the crystal structures of both complexes and the calorimetrically determined enthalpy difference between the two complexes (14.9 kJ mol^{-1}). This value, combined with the free energy difference of 45.7 kJ mol^{-1} found by Cabbiness and Margerum [23], implied a $T\Delta S^0$ value of 30.7 kJ mol^{-1} for the blue→red conversion. As stated by Clay et al. [90], this entropy value is difficult to reconcile with the slight difference between the two complexes in the solid state, casting doubts on the accuracy of the equilibrium constants.

The stability constant of Ni(II) with (tet *a*) and (tet *b*), using cyanide ion competition, has been reported by Hinz and Margerum [98]. Because of the limited solubility of (tet *a*), the value ($\log K = 20$) for the $[Ni(\text{tet } a)]^{2+}$ complex is probably not very accurate.

Increasing the overall atomicity also increases the number of macrocyclic compounds that, having the same atomicity, differ by the relative sequence of hydrocarbon chains between nitrogen atoms. For 15-membered tetraaza macrocycles, protonation behaviour has been studied for 1,4,8,12-tetraazacyclopentadecane (**20**) [75–77,115], 1,4,8,11-tetraazacyclopentadecane (**21**) [78], and 1,4,7,10-tetraazacyclopentadecane (**22**) [104]. As expected, the overall basicity ($\log\beta_4$) increases with increasing molecular size. Among 15-membered tetraaza macrocycles, the most symmetric (**20**) shows the highest $\log\beta_4$ value [78].



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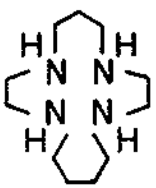

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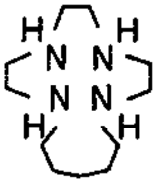

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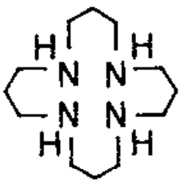
The enlargement of the cavity size also influenced the metal complex stability. In general, complexes with 15-membered macrocycles are less stable than the corresponding complexes with 14-membered azamacrocycles. This decrease of stability is due mainly to a less favourable enthalpic term [82,101].

The Ni(II)/(**20**) system was characterized by the absence of the low-spin species. Another significant effect of the macrocyclic ring expansion is a facile protonation of the complexed ligand, with formation of the monoprotonated species $[\mathrm{Ni}(\mathbf{20})\mathrm{H}]^{3+}$ [82,87].

The Cu(II)/(**20**) equilibrium system was characterized by two species $[\mathrm{Cu}(\mathbf{20})]^{2+}$ and $[\mathrm{Cu}(\mathbf{20})\mathrm{H}]^{3+}$ [115]. The enthalpy of formation of $[\mathrm{Cu}(\mathbf{20})]^{2+}$ was reported in ref. 84; in the same paper the formation enthalpies of a series of Cu(II) complexes with tetraaza macrocycles of different ring size were reported and discussed. The $[\mathrm{Zn}(\mathbf{20})]^{2+}$ complex was fully characterized from a thermodynamic point of view by Kodama and Kimura [85] and Micheloni and Paoletti [93]. The $[\mathrm{Hg}(\mathbf{20})]^{2+}$ complex was reported in ref. 86. The thermodynamics of Ni(II) and Cu(II) complexes with 1,4,7,10-tetraazacyclopentadecane (**22**) were reported in ref. 104. Among 15-membered tetraaza macrocycles (**22**) formed the weakest metal complexes.

For the 16-membered tetraaza macrocycle 1,5,9,13-tetraazacyclohexadecane (**23**), in which all propylenic chains are present, the stepwise protonation constants closely resemble those observed in open chain tetraamines [75,116]. The stepwise enthalpies of protonation were all very similar in contrast with those for smaller tetraaza macrocycles. The stepwise entropic contributions $T\Delta S^0$ decreased regularly as expected when the degree of protonation increased [116]. The less symmetric 16-membered derivative



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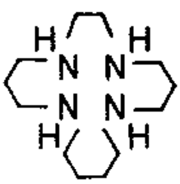

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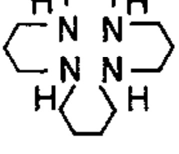
1,4,8,13-tetraazacyclohexadecane (**24**) showed a smaller logβ_4 than (**23**) [116,117].

The thermodynamics of formation of $[Ni(\mathbf{23})]^{2+}$ complexes were reported in refs. 87 and 116. The enthalpy of formation of the 1:1 species was discussed in terms of the unfavourable free-ligand conformation and the presence of a hindered chelate ring [116]. The monoprotonated species $[Ni(\mathbf{23})H]^{3+}$ was found at equilibrium and its stability constant determined [87]. Two mononuclear species: $[Cu(\mathbf{23})]^{2+}$ and $[Cu(\mathbf{23})H]^{3+}$ were found to describe the Cu(II)/(**23**) system [116]. For the Zn(II)/(**23**) system only the 1:1 species $[Zn(\mathbf{23})]^{2+}$ was observed and the thermodynamic parameters ΔG^0, ΔH^0 and $T\Delta S^0$ (see Table 1) determined [93]. Tetrahedral coordination of the zinc ion was suggested to explain the high formation entropy found for the $[Zn(\mathbf{23})]^{2+}$ complex [93]. In spite of the large macrocyclic cavity, the metal complexes are more stable than corresponding complexes with non-cyclic analogues.

For 1,5,9,13-tetraazacycloheptadecane (**25**) stepwise basicity constants were first reported by Kimura and Yatsunami [117]. More recently, Bartolini et al. [78] determined the thermodynamic parameters ΔG^0, ΔH^0, and ΔS^0 for the protonation of (**25**). The stepwise protonation enthalpies are very exothermic and are all very similar [78], indicating that, for large macrocycles, the nitrogen atoms can act independently of each other toward protons. The stepwise protonation entropies decrease regularly, as expected, when the degree of protonation increases [78].

For the 18-membered macrocycle 1,5,10,14-tetraazacyclooctadecane (**26**) three different sets of pK values were published (Table 1). The discrepancy in



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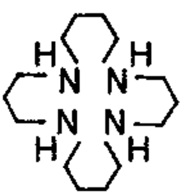

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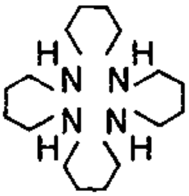

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the first two pK values in two sets [118,119] is huge and cannot be explained in terms of the different experimental conditions which were employed.

The Ag(I) complexes of (**26**) were reported in ref. 119. Suet et al. [119] have reported the basicity constants for the cyclic tetraamine 1,6,11,16-tetraazacycloicosane (**27**) and the equilibrium constants for the Ag(I) complexes: $[\mathrm{Ag}(\mathbf{27})]^+$ and $[\mathrm{Ag}(\mathbf{27})_2]^+$. These macrocycles (**26**) and (**27**) were studied mainly for anion coordination.

E. BLUE-TO-YELLOW EQUILIBRIA

The equilibrium between low-spin square planar and high-spin pseudo-octahedral Ni(II) complexes has been the subject of numerous investigations [120–126]. Initially, the ligands studied were linear polyamines, such as 1,4,7,10-tetraazedecane (trien) or 1,4,8,11-tetraazaundecane (2,3,2-tet), but more recently, attention has been focused on macrocycles and in particular on several tetraazacycloalkanes.

It was ascertained that the reaction (L-tetraazacycloalkane)

$$\underset{\substack{\text{blue, high spin}\\ \text{pseudo-octahedral}}}{[\mathrm{NiL(H_2O)_2}]^{2+}} \rightleftharpoons \underset{\substack{\text{yellow, low spin}\\ \text{square-planar}}}{[\mathrm{NiL}]^{2+}} + 2\,\mathrm{H_2O} \qquad (1)$$

is endothermic and the equilibrium is displaced to the right either by an increase in temperature or by an increase of the concentration of an inert salt [122]. The high-spin species is favoured at high pressure even if the measured $\Delta V = -RT\mathrm{d}\ln K/\mathrm{d}p$ has a small absolute value [121].

In Table 2 we report some selected thermodynamic parameters relevant to reaction (1).

In the blue-to-yellow conversion there is a contraction [123] and a consequent strengthening of the in-plane Ni—N bonds. This is an exothermic effect, which is more than compensated for by the endothermic breaking of the axial Ni—OH$_2$ bonds. The first effect is related to the capability of the ligand to dispose its donor atoms at the corners of the coordination square, having the lone pairs oriented towards the centre.

TABLE 2

Thermodynamic parameters at 25 °C and 0.1 $NaClO_4$ for reaction (1)

L	K_{eq}	ΔH^0 (kJ mol^{-1})	$T\Delta S^0$ (kJ mol^{-1})	ΔV[a]/cm^{3}mol^{-1}
(1)	2.45[b]	23[b]	25[b]	1.2
(18)	1.56[c]	20[c,e]	21[c,e]	5.0
(22)	3.00[c]	23[c]	26[c]	3.0
	2.14[d]	15[d]	18[d]	
(28)	0.79[c]	26[c]	25[c]	3.4

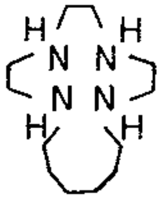
[a] Ref. 121.

[b] Ref. 122.

[c] Ref. 124.

[d] Ref. 104 25 °C, 0.5 KNO_3. **(28)** = 1,4,7,10-tetraazacycloexadecane.

[e] $\Delta H^0 = 17.2$ kJ mol^{-1}, $T\Delta S^0 = 17$ kJ mol^{-1} [87,101].



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Reaction (1) is entropy controlled and the greatest contribution to $T\Delta S^0$ is due to the increase in the number of free particles. The removal of water molecules is favoured by the addition of inert salt. For example, $[Ni(\mathbf{13})]^{2+}$ is less than 1% in the yellow form in pure water, 9% in 3 mol dm^{-3} $NaClO_4$ and 19% in 6 mol dm^{-3} $NaClO_4$ [127]. The ΔV value is also due to a partial compensation of two terms: that due to the contraction of Ni–N bonds and an expansion because the molar volume of a coordinated molecule of water is smaller than the molar volume of bulk water [121].

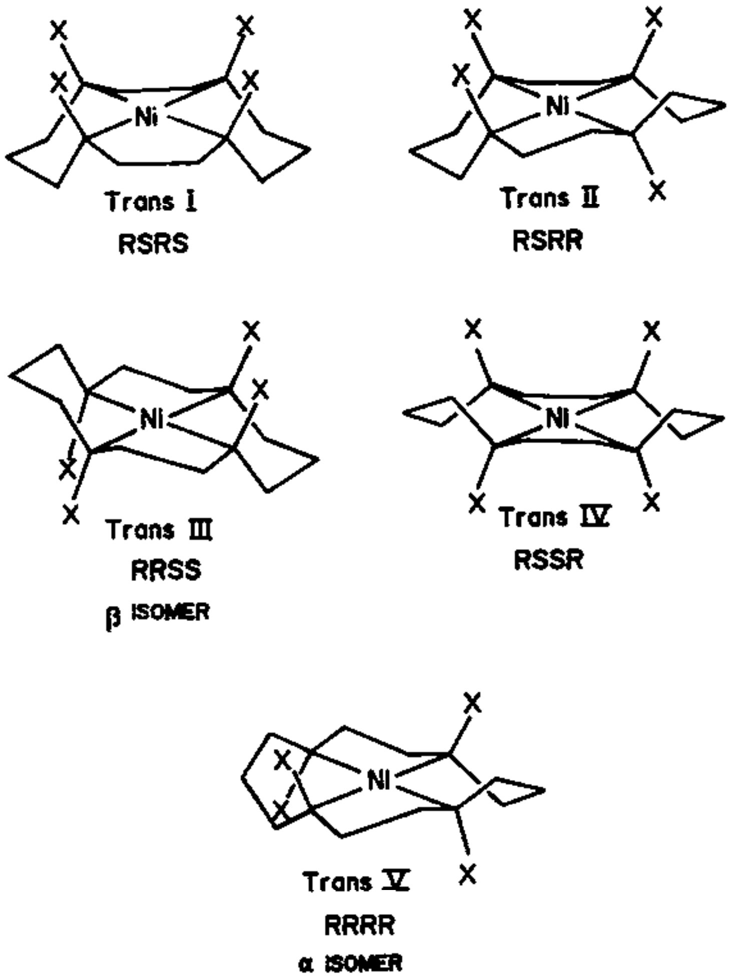
Table 3 reports the enthalpy changes for the blue to yellow conversion and percentages of each species at equilibrium for tetraazacycloalkanes of varying size. A spectroscopic investigation in 6 mol dm^{-3} $NaClO_4$ gave a ΔH^0 value of 7 kJ mol^{-1} and a $T\Delta S^0$ value of 7 kJ mol^{-1} for $[Ni(\mathbf{13})]^{2+}$ [130].

In Ni(II)/tetraazacycloalkane systems, the involvement of configurational isomers has been postulated. For Ni(II)/cyclam and its tetra *N*-derivatives the five isomers of the planar species are illustrated in Scheme 4 [131]. The most stable isomer is the *trans* **III**, but other isomers were isolated in the solid state.

TABLE 3

Enthalpy changes and percentages of the two species at equilibrium (25 °C) in aqueous solution (reaction (1))

	ΔH^0 (kJ mol^{-1})	High-spin	Low-spin	Ref.
[12]aneN_4 (**13**)		99		128
[13]aneN_4 (**16**)	31	13	87	129
[14]aneN_4 (**1**)	23	29	71	122
[15]aneN_4 (**20**)		99		128



Scheme 4.

Billo has shown, by using kinetic measurements that, in the Ni(II)/cyclam system at 25°C ($I = 0.1$), the blue form is 29% *trans*-diaquo and 2% *cis*-diaquo, the equilibrium constant of isomerization *trans*⇌*cis* being 0.055 [132]. The remaining 69% is in the yellow form. The structure of the cis RRRR diaquo complex was recently determined by X-ray diffraction [131(a)].

A value of ca. 1 for the equilibrium constant of the reaction

$$cis\text{-}[\mathrm{Ni}(\mathbf{16})(\mathrm{H_2O})_2]^{2+} \rightleftharpoons \alpha\text{-}[\mathrm{Ni}(\mathbf{16})]^{2+} + 2\,\mathrm{H_2O}$$

was reported [131(b)]. A kinetic study of the system

$$[\mathrm{Ni}(\mathbf{13})]^{2+} + 2\,\mathrm{H_2O} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Ni}(\mathbf{13})\mathrm{H_2O}]^{2+} + \mathrm{H_2O} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{Ni}(\mathbf{13})(\mathrm{H_2O})_2]^{2+}$$

has shown that the equilibrium k_1/k_{-1} is considered to be rate-determinining in establishing the overall equilibrium [133]. When the ligand contains *N*-substituted donors the reaction can stop, in aqueous solution, at the first step. A good example is represented by (**3**) (TMC). In moderately coordinating solvents such as water, the $[\mathrm{Ni}(\mathbf{3})]^{2+}$ complex exists as an equilibrium mixture involving four-coordinate R,S,R,S-$[\mathrm{Ni}(\mathbf{3})]^{2+}$, low-spin and five-coordinate R,S,R,S-$[\mathrm{Ni}(\mathbf{3})(\mathrm{solvent})]^{2+}$, high-spin species.

$$[\mathrm{Ni}(\mathbf{3})\mathrm{H_2O}]^{2+} \rightleftharpoons [\mathrm{Ni}(\mathbf{3})]^{2+} + \mathrm{H_2O}$$

The thermodynamic parameters for the above reaction are: $K = 0.55$, $\Delta H^0 = 17.3\ \mathrm{kJ\ mol^{-1}}$, $T\Delta S^0 = 15.8\ \mathrm{kJ\ mol^{-1}}$, and $\Delta V = 0.5\ \mathrm{cm^3 mol^{-1}}$ [134], or $K = 1.0$, $\Delta H^0 = 11.0\ \mathrm{kJ\ mol^{-1}}$, $T\Delta S^0 = 11.6\ \mathrm{kJ\ mol^{-1}}$ [135]. As expected, these values are lower than those relative to the equilibrium involving two water molecules for the Ni(II)/cyclam system.

The relative stabilities of three isomers of four-, five- and six-coordinate $[\mathrm{Ni}(\mathbf{3})]^{2+}$ solvent ions were determined by strain energy minimisation calculations [136].

The 14-membered hexaaza macrocycles 1,3,6,8,10,13-hexaazacyclotetradecane (**29**) ($\mathrm{R} = -\mathrm{CH_3}$, $-\mathrm{C_2H_5}$) display with Ni(II) a blue-yellow equilibrium similar to that for cyclam. The relevant thermodynamic parameters are reported in Table 4 [120].

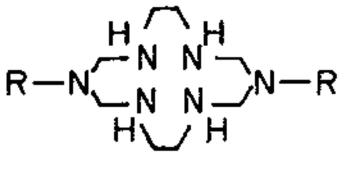


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TABLE 4

Thermodynamic parameters for the blue-to-yellow conversion of the [Ni(**29**)]$^{2+}$ complexes

L	K (25 °C)	ΔH^0 (kJ mol^{-1})	$T\Delta S^0$ (kJ mol^{-1})
$R=CH_3$	5.9[a]	36	40
	2.3[b]	17	19
$R=C_2H_5$	4.3[a]	19	22
	2.8[b]	10	13

[a] $I=0.1$ ($NaClO_4$).
[b] Pure water.

Steric effects influencing the blue to yellow equilibria were observed for Ni(II) complexes of the series of *N*-methyl derivatives of cyclam and iso-cyclam (**17**). The values reported in Table 5 were determined at 25°C in 0.1 M $NaClO_4$. While the enthalpic and entropic terms are similar for both cyclam and iso-cyclam, the *N*-methylation in both cases reduces the values of the two terms.

Axial ligations were studied for Ni(II) complexes of (5SR,7RS,12RS,14SR)-tetramethyl-1,4,8,11-tetraazacyclotetradecane (**33**), in solution and in the solid state. The metal complexes have the *trans* III arrangement of the chiral nitrogen centres, with the four methyl groups equatorial. The equilibrium at 25°C gives a ΔH^0 value of 22.1 kJ mol^{-1} and $T\Delta S^0 = 18.0$ kJ mol^{-1}. *C*-methylation does not alter the ΔH^0 value but reduces the ΔS^0 value as observed with *N*-methylation. For isomers with axial methyl groups, the addition is hindered [138].

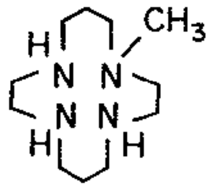
The effect of inert salts on the yellow-to-blue equilibrium for the Ni(II)/(**3**)

TABLE 5

Thermodynamic parameters for the blue-to-yellow conversion for some *N*-substituted tetraaza macrocycles

Ligand	% Yellow[a]	K[a]	ΔH^{0}[a] (kJ mol^{-1})	$T\Delta S^0$ (kJ mol^{-1})
(**1**)	71.0	2.5	23	25
(**30**)[b]	78.2	3.6	13	16
(**17**)[c]	61.2	1.6	22	23
(**31**)[b]	50.5	1.0	18	18
(**32**)[b]	65.5	1.9	15	17

[a] Ref. 126.
[b] Where (**30**) = 1-methyl-1,4,8,11-tetraazacyclotetradecane; (**31**) = 1-methyl-1,4,8,12-tetraazacyclotetradecane; (**32**) = 1-methyl-1,5,8,11-tetraazacyclotetradecane.
[c] Ref. 137.



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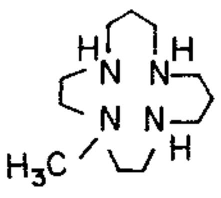

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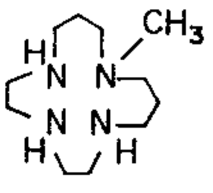

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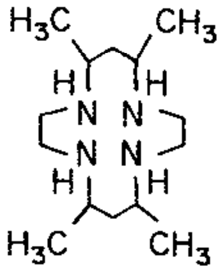

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system was investigated with different concentrations and different salts. The order of desolvation efficiency is $ClO_4^- \gg NO_3^- > SO_4^{2-}$ and with a less sensitive trend $Na^+ > K^+$ [139].

It was recently reported that the rigid 1,4,7,10-tetraazabicyclo[8.2.2]tetradecane (**14**) forms yellow low-spin Ni(II) complexes [140] in solution and in the solid state.

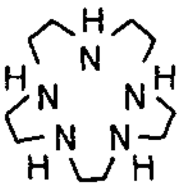
For Ni_2L (L = 6,6′-bis(1,4,8,11-tetraazacyclotetradecane)), the thermodynamic parameters are $\Delta H^0 = 33.5$ kJ mol^{-1} and $T\Delta S^0 = 37$ kJ mol^{-1} relative to the equilibrium

$$[Ni_2L(H_2O)_4]^{4+} \rightleftharpoons [Ni_2L]^{4+} + 4\,H_2O$$

These values are approximately twice the value for cyclam, indicating a weak interaction between the two metal ions [141].

F. PENTAAZACYCLOALKANES

The protonation constants of 1,4,7,10,13-pentaazacyclopentadecane (**34**), 1,4,7,10,13-pentaazacyclohexadecane (**35**) and 1,4,7,11,14-pentaazacycloheptadecane (**36**) were determined [142,143] at 15, 25 and 35°C, although all five constants are available only at 25°C. In the case of 1,4,7,10,13-pentaazacycloheptadecane (**37**), 1,4,7,10,13-pentaazacyclooctadecane (**38**) and 1,4,7,10,13-pentaazacyclononadecane (**39**), the determination of the protonation constants was carried out at 35°C [144]; the fourth and the fifth values for (**37**)



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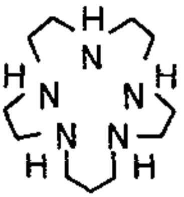

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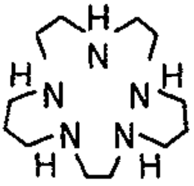

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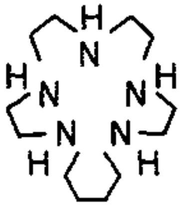

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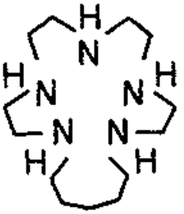

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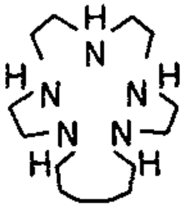

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and (**38**), and the fifth value for (**39**) were estimated to be lower than 100. For (**34**)–(**36**), the protonation constants decrease with increasing temperature, as expected for exothermic reactions. The first two protonation constants of (**34**) are grouped and largely separated from the last two, also grouped, while the third one presents an intermediate value between the two groups. This behaviour can be explained in terms of increasing electrostatic repulsion between the positive charges which accumulate on the macrocycles, as already observed in tetraazacycloalkanes.

The overall basicity of the three pentaaza macrocycles increases as the sizes of these pentaamines and the charge separation in the protonated forms increase. The effect of increasing ring size is especially observed on the third protonation constant of (**35**) with respect to (**34**) and on the fourth of (**36**) with respect to (**35**). The differences in the basicity behaviour of these six pentaamines seem to vanish for the largest terms.

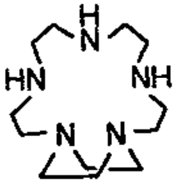
Complexes of pentaazacycloalkanes have not been extensively studied so far from a thermodynamic point of view, and few papers dealing with the determination of stability constants [53,142–149], and calorimetric measurements [150] have been published. Pentaazacycloalkanes with ring sizes varying from 15 to 19 terms have been studied; among these, two [17]aneN_5 isomers have been reported. In the case of (**37**)–(**39**), just the equilibria with Co(II) have been investigated [144], while the remaining three ligands have been rather more thoroughly considered. Most of thermodynamic data, stability constants [53,142,144,145,148,149] and enthalpy changes [150], have been published by the same authors.

A series of pentaaza macrocyclic ligands has been studied [144,145] only with Co(II). Along this series, two concomitant structural effects occur in determining the stability constant changes, the enlargement of the ligand ring from (**34**) to (**39**) and the fact that this enlargement is produced by an increasing length of only one aliphatic chain in the macrocyclic framework. As a result, a lowering of the stability constants is observed from (**34**), which disposes all five-membered chelate rings, to (**38**), in whose complex one eight-membered chelate ring is formed. A further increase in chelate ring dimension seems to reduce the pentadentating ability of pentaaza macrocycles since for (**39**) only the protonated complex $[\mathrm{CoH}(\mathbf{39})]^{3+}$, in which the ligand acts as tetradentate, has been observed [144]. With the possible exception of Ni(II), (**34**) forms the most stable complexes with all the metal ions considered [53,142,145,149,152] and the stability constants reported decrease progressively with increasing dimension of the macrocycles ($[15]\mathrm{aneN}_5 > [16]\mathrm{aneN}_5 > [17]\mathrm{aneN}_5$). The reaction enthalpies of (**34**)–(**36**) with Ni(II) have been measured directly [150] and a reduction in enthalpy change has been observed in the order $[16]\mathrm{aneN}_5 > [17]\mathrm{aneN}_5 > [15]\mathrm{aneN}_5$. The reason for this order is not clear, although an attempt to explain it in terms of the formation and disposition of six-membered chelate rings has been argued [150]. On the other hand, clarifying information on this point should be obtained from the stability constants of these complexes. In the case of (**34**) [151] and (**35**) [149] the stability constants for their Ni(II) complexes ($\log K = 18.1$ for both) have been reported, but no experimental details or errors were presented. Under these circumstances, no great confidence should be given to the results, especially if dealing with very slow equilibria.

An estimate of the enthalpies of reaction of Cu(II), Zn(II), Cd(II), Pb(II) and Hg(II) with the three smallest pentaazacycloalkanes has been obtained by determining the dependence of the stability constants upon the temperature [53,142]. The results seem to indicate that the stability decrease observed from (**34**) to (**35**) is due to the entropic term, while both enthalpic and entropic terms contribute to further reduce the stability for the complexes of $[17]\mathrm{aneN}_5$.

The equilibria between (**34**) and Mn(II) have also been studied [143]. The stability constant of the complex $[\mathrm{Mn}(\mathbf{34})]^{2+}$ is the smallest among those reported [53,142,144–149] for complexes of the same ligand. Data available [143] are consistent with Mn(II) bound to a distorted or folded ligand and able to accommodate one additional ligand.

Recently, the structurally reinforced ligand 1,4,7,10,13-pentaazabicyclo[11.2.2]heptadecane (**40**) has been studied for coordination to Cu^{2+} and Cd^{2+} [91]. The equilibrium constants for the formation of these complexes are lower than those for the analogous complexes of (**34**).



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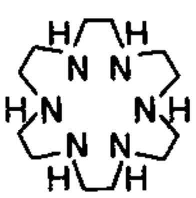
G. HEXAAZACYCLOALKANES

The hexaazacycloalkanes represent the intermediate terms between the 'small' and the 'large' polyazacycloalkanes. The protonation constants for the 1,4,7,10,13,16-hexaazacyclooctadecane (**41**), containing only ethylenic chains, are, as expected, divided into two groups, each containing three values [151]. In contrast, for 1,5,9,13,17,21-hexaazacyclotetracosane (**42**) [152] with propylenic chains, the stepwise protonation constants decrease smoothly from the first to the sixth. Similar behaviour is observed for 1,5,9,17,21,25-hexaazacycloditriacontane (**43**) [153]. Basicity constants were also determined [153] (see Table 1) for the largest hexaaza macrocycle, 1,5,9,20,24,28-hexaazacyclooctatriacontane [38]aneN_6 (**44**).

As shown in Table 1, (**41**) forms complexes in aqueous solution with transition metals and also with K^+, Sr^{2+}, Ca^{2+}, and Ln^{3+} [151]. In particular, Ca^{2+} has a higher affinity with (**41**) than with the analogous crown ether 1,4,7,10,13,16-hexaoxacyclooctadecane. The stability of the calcium compound is a balance between a favourable enthalpic contribution and an opposite entropic contribution. In contrast to Ca^{2+}, Mg^{2+} has no affinity with (**41**) [151].



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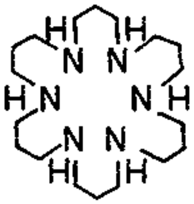

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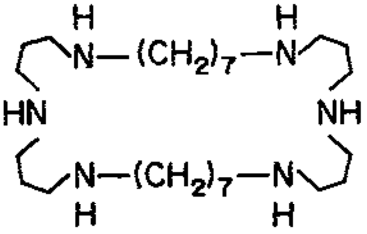

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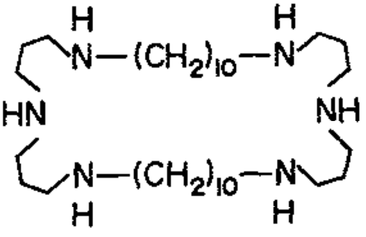

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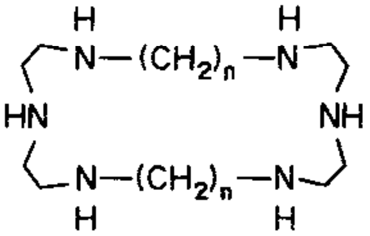
Equilibrium studies with the [Co(**41**)]$^{2+}$ complex were reported by Kodama et al. [151]. The high stability constant of [Co(**41**)]$^{2+}$, if compared with that of the pentaaza macrocyclic [Co(**35**)]$^{2+}$ complex, and the low protonation constant of [Co(**41**)]$^{2+}$ (log$K = 2.8$) [151] were indicative that the entire N_6 ligand donor set is involved in the formation of the [Co(**41**)]$^{2+}$ complex. In the [Ni(**41**)]$^{2+}$ complex, the macrocycle is fully engaged in forming an octahedral geometry. The addition of one proton to the complex to form the monoprotonated species [NiH(**41**)]$^{3+}$ was easier (log$K = 4.2$) [151] than the corresponding reaction for Co(II). In the case of the Cu(II)/(**41**) system, only protonated [CuH(**41**)]$^{3+}$ and [CuH$_2$(**41**)]$^{4+}$ complexes were found [151]. This behaviour has been ascribed to the strong Cu—N planar coordination. The thermodynamic parameters ΔG^0, ΔH^0 and ΔS^0 for the [Zn(**41**)]$^{2+}$ complex were determined [154], and are reported in Table 1. Comparison of these values with those of the corresponding complex [Zn(**35**)]$^{2+}$ permits one to conclude that only five of the six nitrogen atoms are involved in the formation of [Zn(**41**)]$^{2+}$. For the Cd(II) complex, the thermodynamic functions ΔG^0, ΔH^0 and ΔS^0 are consistent with the assumption that all six nitrogen atoms of (**41**) are involved in the formation of the [Cd(**41**)]$^{2+}$ complex [155].

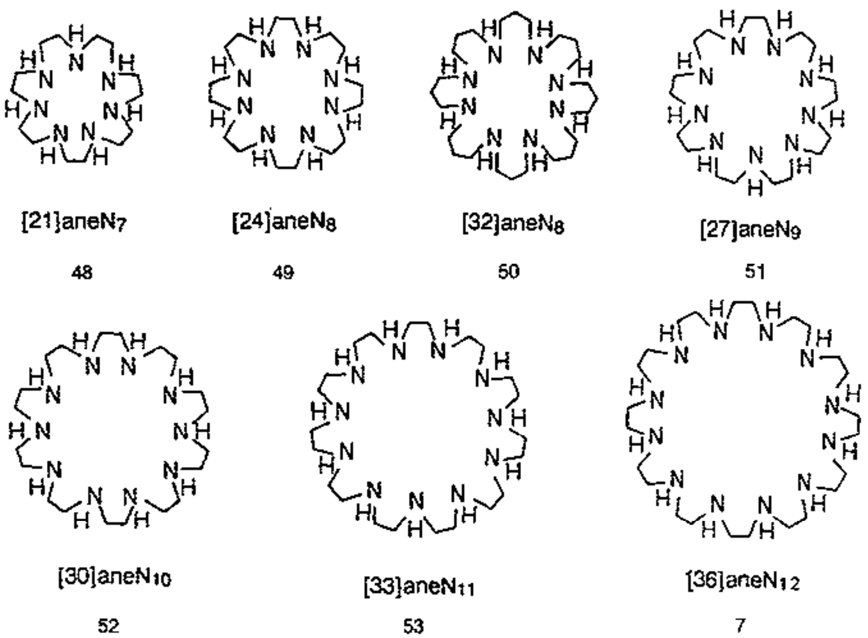
Other hexaazacycloalkanes, 1,4,7,12,15,18-hexaazacyclodiacosane (**45**), 1,4,7,13,16,19-hexaazacyclotetracosane (**46**) and 1,4,7,17,20,23-hexaazacyclo-ditriacontane (**47**), were synthesized and used for anion coordination studies.



n = 4 45
n = 5 46
n = 6 47

H. LARGE POLYAZACYCLOALKANES

The adjective 'large' has been used [156] to describe aza macrocycles having more than six nitrogen atoms. Figure 7 shows examples of large polyazacycloalkanes. The possibility of binding more than one metal ion within the molecular framework, as well as the employment of these com-



[21]aneN$_7$ 48

[24]aneN$_8$ 49

[32]aneN$_8$ 50

[27]aneN$_9$ 51

[30]aneN$_{10}$ 52

[33]aneN$_{11}$ 53

[36]aneN$_{12}$ 7

Fig. 7. Examples of large polyazacycloalkanes.

pounds in the development of the so-called 'anion coordination chemistry' [152,157,158] (see Sect. K), has prompted interest in these compounds in the last few years. The general synthetic route to synthesize these macrocycles has been modelled on that described by Richman and Atkins [27], cyclizing the appropriate polyamminic segments (see Scheme 2). Important steps in this procedure are the elongation of the linear polyammines and the cyclization reaction [159,160].

The basicity constants for large polyazacycloalkanes are reported in Table 1. When the hydrocarbon chains connecting two adjacent nitrogen atoms are two carbon atoms long, the following general statements can be made [161] concerning their basicity: (i) the overall basicity steadily increases by 5.9 log units (0.15 $NaClO_4$, 25°C) for each $-CH_2CH_2NH-$ unit added to the macrocyclic ring [161]; (ii) each macrocycle behaves as a relatively strong base in the first half of its protonation steps and as a weaker base in the second half. This grouping of the basicity constants is typical of aza macrocycles and has been ascribed to the electrostatic repulsion among the positively charged NH_2^+ groups arranged in the cyclic framework [156,159,160,162,163]. As already stated, the grouping of the stepwise basicity constants is much more evident for smaller aza macrocycles [75–77,116], where the charges that accumulate in the cyclic framework, as the degree of protonation increases, experience stronger repulsions than in the case of the larger macrocycles.

For the 1,5,9,13,17,21,25,29-octaazacycloditriacontane (**50**) macrocycle, where adjacent nitrogen atoms are connected by propylenic chains, the positive charges of the protonated forms are further away than in large macrocycles having ethylenic chains between the nitrogen atoms, and influence each other to a lesser degree. As a result, the grouping phenomenon for (**50**) is much less marked than in the other large macrocycles [164]. Thus the complete protonation of these macrocycles occurs within a narrower pH range with respect to the analogous ethylenic chain-containing macrocycles. For all large macrocycles, as the degree of protonation increases, factors such as molecular stiffening become important and must be taken into consideration in the interpretation of the last protonation steps.

The magnitudes of the protonation constants and the cyclic topology allow large polyaza macrocycles to form many highly protonated, charged, species in the neutral pH region [164–167].

Another interesting property of large polyazacycloalkanes is the significant tendency to form polynuclear metal complexes. The logarithms of the formation constants for Cu(II) complexes are reported in Table 1. The large macrocycles form dinuclear Cu(II) complexes with the exception of the macrocycle 1,4,7,10,13,16,19-heptaazacyclohenicosane (**48**), which forms a mononuclear complex. For the largest macrocycles, 1,4,7,10,13,16,19,22,25,28,31-undecaazacyclotritriacontane (**53**) and 1,4,7,10,13,16,19,22,25,28,31,34-dodecaazacyclohexatriacontane (**7**), the trinuclear $[Cu_3L]^{6+}$, $[Cu_3LOH]^{5+}$, and $[Cu_3L(OH)_2]^{4+}$ species are also formed (see Table 1). All the species are very stable. In a few cases, the strong interaction between the Cu(II) ion and the donor atoms has been confirmed through determining the enthalpy of complex formation. These are: -163.2 kJ mol^{-1} for $[Cu_2(\mathbf{49})]^{4+}$ [156], -179.1 kJ mol^{-1} for $[Cu_2(\mathbf{51})]^{4+}$ [163] and -190.4 kJ mol^{-1} for $[Cu_2(\mathbf{52})]^{4+}$ [159]. The exothermicity for dinuclear Cu(II) complex formation increases with the size of the macrocycle because the number of donor atoms involved in coordination to the Cu(II) ions, as well as the ligand flexibility, increases [159]. The abundance of donor atoms in the so-called 'large' macrocycles allows the formation of many protonated species at each equilibrium, as shown in Table 1. For macrocycle (**52**), the solid, monoprotonated, dinuclear complex $[Cu_2(\mathbf{52})HCl_2](ClO_4)_3\cdot 4H_2O$ has been isolated and characterized by X-ray analysis [159]. The ORTEP drawing of the $[Cu_2(\mathbf{52})H]^{5+}$ cation, taken from ref. 159, is reported in Fig. 8. Although Zn(II) rarely forms dinuclear complexes with synthetic ligands in aqueous media, the large macrocycles (**51**)–(**53**) and (**7**) were reported to form stable dinuclear Zn(II) complexes [159,160,163]. X-ray investigation has shown the presence of dinuclear Zn(II) cations in crystals of $[Zn_2(\mathbf{52})SCN](ClO_4)_3$ and

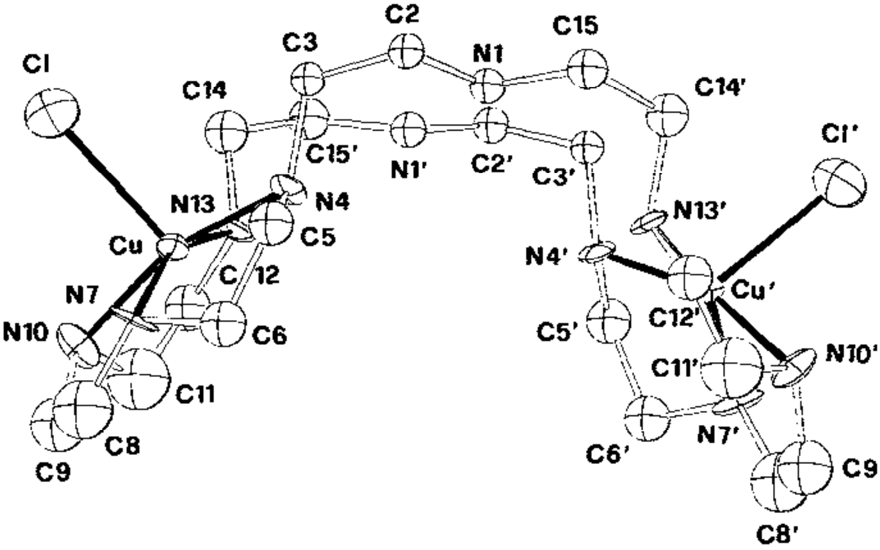


Fig. 8. ORTEP drawing of the binuclear $[Cu_2(\mathbf{52})H]^{5+}$ cation.

$[Zn_2(\mathbf{49})Cl_2]ClClO_4 \cdot H_2O$, [154,168]. In both cases, the zinc atoms are five-coordinate. Only the smaller macrocycles (**48**) and (**49**) form mononuclear Zn(II) complexes.

The formation of Cd(II) complexes with large polyazacycloalkanes has been studied [155] in 0.15 mol dm^{-3} $NaClO_4$. Both mononuclear and dinuclear complexes have been reported (see Table 1). Results for the $[3k]aneN_k$ ($k=3$–8) ligands indicate that the stability of the mononuclear complexes increases in going from the smallest macrocycle $[9]aneN_3$ to the pentadentate $[15]aneN_5$, then slightly decreases for $[18]aneN_6$ ($\log K = 18.8$) and $[21]aneN_7$ ($\log K = 18.10$), and finally sharply decreases for $[24]aneN_8$ ($\log K = 14.52$). Ligand strain and formation of large, unstable chelate rings have been invoked to explain this trend [155]. The formation enthalpies of $[Cd(\mathbf{41})]^{2+}$ ($\Delta H^0 = -64.0$ kJ mol^{-1}) and $[Cd(\mathbf{48})]^{2+}$ ($\Delta H^0 = -67.4$ kJ mol^{-1}) have been reported [155]. The larger macrocycles of the series (**49**) and (**51**)–(**53**) form stable dinuclear complexes. Many protonated species are formed but no hydroxo species were detected. In the case of the dinuclear complex $Na[Cd_2(\mathbf{52})Cl_2](ClO_4)_3$ a crystal structure was reported [155] (see Fig. 9), showing both Cd(II) ions six-coordinate although with different environments.

Co(II), in anaerobic conditions, is complexed by large polyazacycloalkanes [169] and both mononuclear and dinuclear complexes have been reported. The macrocycles (**48**), (**49**), and (**51**) only form mononuclear species (see Table 1), while larger macrocycles, (**52**), (**53**), and (**7**) form dinuclear species.

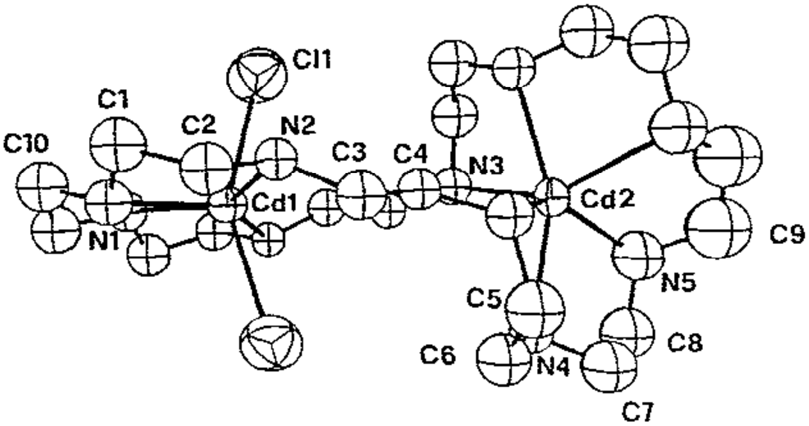


Fig. 9. ORTEP drawing of the binuclear $[Cd_2(52)Cl_2]^{2+}$ cation.

The stability constants for the dinuclear species $[Co_2(L)]^{4+}$ were somewhat lower than those of the corresponding complexes of Zn(II), and the general trend of stability Co(II) < Ni(II) < Cu(II) > Zn(II) was observed for each large macrocycle [169]. Recently, a complete solution study of Ni(II) complexes with the polyazacycloalkanes of the series $[3k]aneN_k$ has been reported [170]. While $[21]aneN_7$ only forms mononuclear species, the macrocycle $[24]aneN_8$ forms both mono- and dinuclear complexes. For larger macrocycles, only the dinuclear species are formed.

With Cd(II) [155] and Ni(II) [170], the macrocyclic effect vanishes in mononuclear complexes as the number of donor atoms and the flexibility of the cyclic ligand increases. For larger macrocycles $[27-33]aneN_{(9-12)}$, only dinuclear species have been found at equilibrium [170].

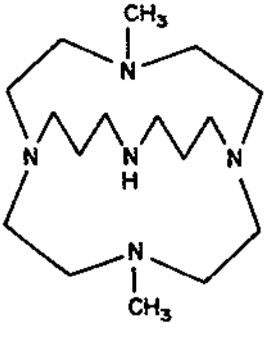
The electronic spectra of these Ni(II) complexes were consistent with high-spin octahedral species; only in the case of $[24]aneN_8$ was a dinuclear diamagnetic species found. For dinuclear species $[Ni_2L]^{4+}$, a steady increase in the overall stability was observed with the size of macrocycle. Equilibrium studies on the Mn(II)/(**48**) system have been carried out [171] and the mononuclear complex $[Mn(\mathbf{48})]^{2+}$ was characterized both from thermodynamic and structural points of view [171]. The complex is very stable ($\log K = 9.79$), mainly for entropic reasons ($\Delta H^0 = -20.92$ kJ mol^{-1}; $T\Delta S^0 =$ 34.3 kJ mol^{-1}). The crystal structure of the complex $[Mn(\mathbf{48})](ClO_4)_2$ indicated that the Mn(II) is heptacoordinated by (**48**), which disposes its nitrogen atoms at the vertices of an irregular polyhedron.

I. AZA CAGES

Aza-polycyclic compounds with cage-like molecular topology were synthesized in 1977 [172]. Most of these compounds have been synthesized by template reactions [172] and the metal complex obtained at the end of the synthetic procedure is so inert that its removal is impossible, even under drastic conditions. For this reason, equilibrium studies related to these compounds have been almost non-existent. More recently, aza cages were synthesized by non-template procedures and their protonation and complex formation reaction studied [46,173,174]. It appears that the proton binding characteristics of these compounds are influenced very much by the molecular topology.

The cage 12,17-dimethyl-1,5,9,12,17-pentaazabicyclo[7.5.5]nonadecane (**54**) was described [46], and its basicity in aqueous solution (0.5 mol dm^{-3} KNO_3) investigated by potentiometry and spectroscopic (^1H, ^{13}C NMR) techniques. The cage (**54**) can take up three protons under the experimental condition used. It behaves as a very weak base in the third protonation step ($\log K_3 < 2$) and as a moderate base in the second protonation step ($\log K_2 = 8.41$). In the first protonation step, (**54**) behaves as a 'fast proton sponge': the proton cannot be removed even in strong alkaline solution. ^1H NMR experiments indicate intermediate or fast proton exchange between the NH_2^+ protons and the 'external' active hydrogens. X-ray crystal structure analysis carried out with the $[H(\mathbf{54})]^+$ cation has further rationalized the basicity behaviour of (**54**) [175].

The methyl derivative of (**54**), 5,12,17-trimethyl-1,5,9,12,17-pentaazabicyclo[7.5.5]nonadecane (**55**) has been synthesized [47] and its protonation parameters measured by potentiometry and calorimetry in 0.15 mol dm^{-3} NaCl as ionic medium (see Table 1). High basicity is exhibited by (**55**) in the first protonation step ($\log K = 11.82$), a moderate basicity in the second ($\log K = 9.53$) and weak basicity in the last step ($\log K = 3.43$). The first two protonation steps are characterized by a very favourable enthalpic term, ($\Delta H_1^0 = -54.4$ kJ mol^{-1}, $\Delta H_2^0 = -42.7$ kJ mol^{-1}, $\Delta H_3^0 =$



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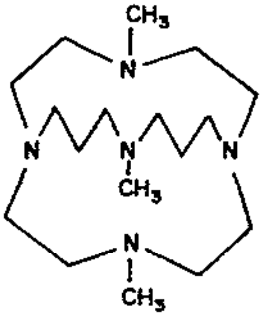

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-13.0 kJ mol^{-1}), indicating that the added hydrogen ions interact strongly with the nitrogen atoms to form the protonated species HL^+ and H_2L^{2+}. The entropy contribution is favourable in all steps and was explained by assuming that the main contribution to the overall stepwise entropy change is due to the release of water molecules from the hydrated proton which is bound to nitrogen atoms inside the cage cavity (translational entropy) [47]. In spite of the structural similarity of (**54**) and (**55**), the two cages behave very differently in the first protonation step, (**54**) being a 'fast proton sponge'. X-ray analysis of the two monoprotonated salts [H(**55**)](Cl) and [H(**54**)](Br) (Fig. 10) has demonstrated that the monoprotonated species $[H(\mathbf{55})]^+$ is thermodynamically less stable than the analogue $[H(\mathbf{54})]^+$ because a weaker hydrogen bond network stabilizes the former species.

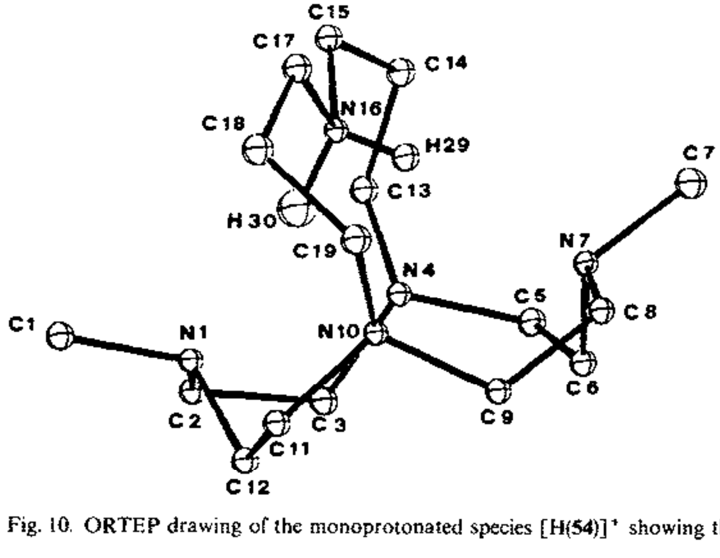
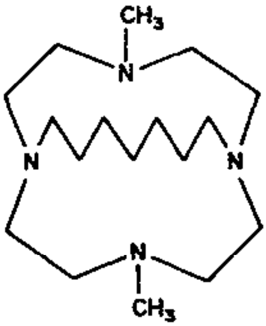


Fig. 10. ORTEP drawing of the monoprotonated species $[H(\mathbf{54})]^+$ showing the protonation site.



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The cage 12,17-dimethyl-1,9,12,17-tetraazabicyclo[7.5.5]nonadecane (**56**), where the 'apical group' is the non-donor —CH$_2$— group, has been synthesized [174]. It behaves as a fairly strong base (log$K$ = 12.00; $\Delta H^0 = -54$ kJ mol^{-1}; $T\Delta S^0 = 14.5$ kJ mol^{-1}) in the first protonation step and as a moderate base in the second (log = 7.86; $\Delta H^0 = -44.8$ kJ mol^{-1}; $T\Delta S^0 = 0$) [174]. The results were discussed and interpreted as a clear indication of the key role played by molecular topology in determining the proton-binding characteristics of (**56**) [174].

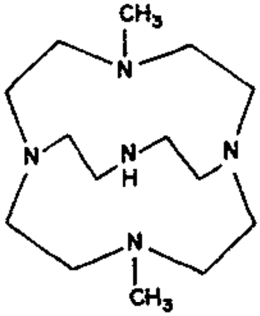
The cage (**55**) is able to encapsulate Li$^+$ in aqueous solution selectively.

$$\mathrm{Li}^+_{(aq)} + (\mathbf{55})_{(aq)} = [\mathrm{Li}(\mathbf{55})]^+_{(aq)} \qquad (2)$$

The thermodynamic parameters for the reaction in 0.15 mol dm^{-3} NaCl were determined by potentiometry and microcalorimetry (log$K$ = 3.2, $\Delta H^0 = -2.1$ kJ mol^{-1}, $\Delta S^0 = 16.2$ J mol^{-1} K^{-1}) [47].

Recently, the aza cage 4,10-dimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]-heptadecane (**57**), where all ethylenic chains are present, has been synthesized [49] and its basicity and lithium complex formation constants reported [49]. In this cage, where with respect to (**54**) a smaller cavity is present, the Li$^+$ is very tightly encapsulated, as demonstrated by the high [Li(57)]$^+$ complex formation constant (log$K$ = 4.8) in aqueous solution. The X-ray crystal structure of the [Li(55)][ClO$_4$] complex (Fig. 11) showed that the Li$^+$ ion is wholly enclosed in the cage cavity and adopts a five-coordinate geometry with a short Li–N mean distance of 2.06 Å [49]. Quite remarkably, the lithium encapsulation in these cages was not influenced by the presence of the Na$^+$ ion, even in high concentration, showing that both (**54**) and (**55**) were able to discriminate fully between lithium and sodium ions [47,49].

The large macrobicyclic cage (**58**), based on tripodal subunits, has been synthesized [176], and employed in Cu^{2+} coordination studies [177]. The



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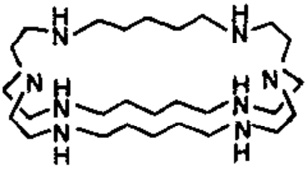

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stability constants for both mono- and binuclear Cu^{2+} complexes of (**58**) have been determined [177] (Table 1).

J. MACROCYCLIC EFFECT

This term was introduced in 1969 by Cabbiness and Margerum [23] to indicate the enhanced stability observed for the Cu(II) complex of the macro-

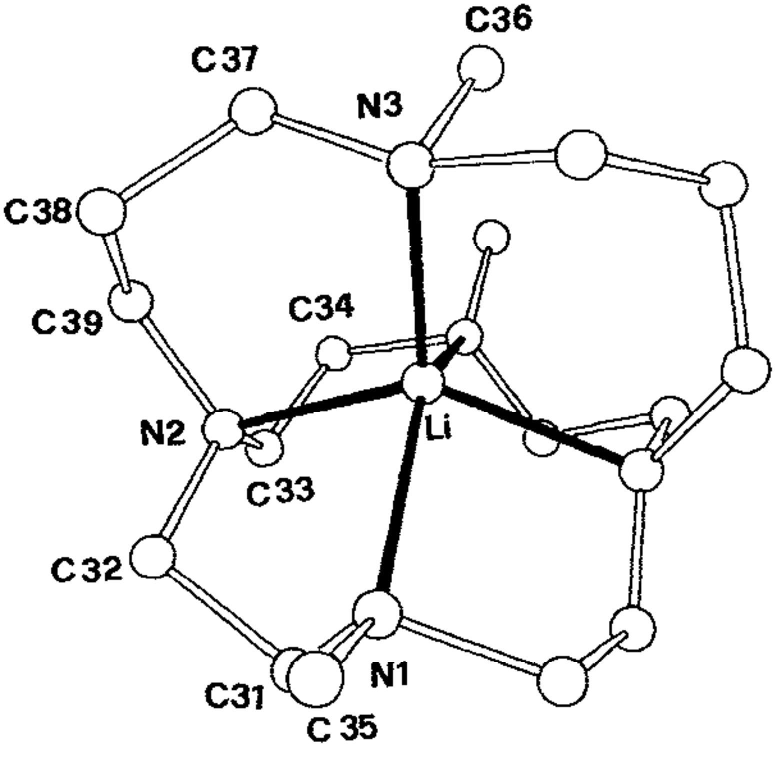

Fig. 11. Crystal structure of the $[Li(55)]^+$ cation.

cyclic tetramine tet *a* (**2**), with respect to the analogous complex of the acyclic tetramine 2,3,2-tet (1,4,8,11-tetraazaundecane). The stability constant of $[\mathrm{Cu(tet}\ a)]^{2+}$ ($\log K = 28$) was determined spectrophotometrically and employed the protonation constants of the free ligand, obtained by means of a solvent extraction method. This gave a result about 10^4 times higher than the corresponding stability constant ($\log K = 23.9$ [178]) for the complex $[\mathrm{Cu(2,3,2\text{-}tet)}]^{2+}$. The same authors pointed out [23] that the cyclic amine reacts with Cu(II) more slowly, by a factor of 10^3–10^4, than the acyclic amine.

Later, Paoletti et al. [179] estimated the enthalpy change for the reaction of tet *a* with Cu(II) ($\Delta H^0 = -125\ \mathrm{kJ\ mol^{-1}}$) by assuming a linear relationship between the absorption maximum in the electronic spectra and the enthalpy of formation of Cu(II)–polyamino complexes in aqueous solution [179]. The entropy change for the same reaction ($T\Delta S^0 = 34\ \mathrm{kJ\ mol^{-1}}$) was then calculated [179] by considering the value of the stability constant obtained by Cabbiness and Margerum [23]. The comparison of the thermodynamic parameters for the formation of $[\mathrm{Cu(tet}\ a)]^{2+}$ with those, previously obtained, for $[\mathrm{Cu(2,3,2\text{-}tet)}]^{2+}$ ($\Delta H^0 = -116\ \mathrm{kJ\ mol^{-1}}$, $T\Delta S^0 = 20.4\ \mathrm{kJ\ mol^{-1}}$) [180], led to the conclusion that both enthalpic and entropic terms contribute to the macrocyclic effect [179].

In 1974, Hinz and Margerum [181] determined, by means of a temperature dependence method, the thermodynamic parameters $\log K = 22.2$, $\Delta H^0 = -129.7\ \mathrm{kJ\ mol^{-1}}$ and $T\Delta S^0 = -3.7\ \mathrm{kJ\ mol^{-1}}$ for the formation of the $[\mathrm{Ni}(\mathbf{1})]^{2+}$ complex. Comparing these values with corresponding data for $[\mathrm{Ni(2,3,2\text{-}tet)}]^{2+}$, the authors concluded that the macrocyclic effect was due solely to a favourable enthalpic contribution, the entropy contribution being negligible. The strong enthalpic contribution was ascribed to lower solvation of the macrocyclic ligand with respect to the open-chain analogue [98].

A different conclusion about the origin of the macrocyclic effect was drawn by Kodama and Kimura [83] as a result of a polarographic investigation on the complex $[\mathrm{Cu}(\mathbf{13})]^{2+}$. The thermodynamic parameters obtained for the formation of this complex ($\log K = 24.8$, $\Delta H^0 = -76.6\ \mathrm{kJ\ mol^{-1}}$ and $T\Delta S^0 = 64.1\ \mathrm{kJ\ mol^{-1}}$) were compared with those for the formation of the analogous acyclic tetramine 1,4,7,10-tetraazadecane complex ($\log K = 20.1$, $\Delta H^0 = -90.2\ \mathrm{kJ\ mol^{-1}}$ and $T\Delta S^0 = 24.3\ \mathrm{kJ\ mol^{-1}}$ [183]). The higher value of the entropic term observed for the macrocyclic complex was attributed to a favourable orientation of the donor atoms already existing prior to complexation in the cyclic ligand.

These results disagree with a later determination of the enthalpy of formation ($\Delta H^0 = -95.0\ \mathrm{kJ\ mol^{-1}}$) of the $[\mathrm{Cu}(\mathbf{13})]^{2+}$ complex performed by the microcalorimetric technique [184]. The entropy change for the same reaction ($T\Delta S^0 = 45.2\ \mathrm{kJ\ mol^{-1}}$), calculated accordingly to the previous $\log K$ value reported by Kodama and Kimura, provided further evidence that both enthalpic and entropic terms can contribute favourably to the macrocyclic effect.

After the early work by Hinz and Margerum [181], the heat of formation of the Ni(II) complex of cyclam (**1**) was calorimetrically determined, following the demetallation reaction by cyanide ion [88]. As already reported (Sect. E), this complex is present in solution as an equilibrium mixture of low-spin square-planar species and high-spin diaquo octahedral species. The heat of formation referred to this mixture ($\Delta H^0 = -84.9$ kJ mol^{-1}) [88] was 45 kJ mol^{-1} lower than that obtained by Hinz and Margerum [181]. The thermodynamic parameters obtained for both species are $\Delta H^0 = -78.2$ kJ mol^{-1} and $T\Delta S^0 = 49.3$ kJ mol^{-1}, for the low-spin complex, and $\Delta H^0 = -100.8$ kJ mol^{-1} and $T\Delta S^0 = 24.3$ kJ mol^{-1}, for the high-spin complex [88]. Comparison with the corresponding values for the analogous species of $[\mathrm{Ni(2,3,2\text{-}tet)}]^{2+}$ ($\Delta H^0 = -66.1$ kJ mol^{-1} and $T\Delta S^0 = 21.7$ kJ mol^{-1}, for the low-spin form; $\Delta H^0 = -80.3$ kJ mol^{-1} and $T\Delta S^0 = 10.9$ kJ mol^{-1}, for the high-spin form) [88] showed that, in this case too, both enthalpic and entropic contributions contribute to the macrocyclic effect.

These new results did not invalidate the stimulating proposal of Hinz and Margerum [181] regarding the role played by ligand solvation. The effects due to solvation could be avoided by determining the thermodynamic parameters for complexation in the gaseous phase. The macrocyclic effect can be defined by the metathetic reactions:

$$\mathrm{ML}^{2+}_{2(\mathrm{aq})} + \mathrm{L}_{1(\mathrm{aq})} = \mathrm{ML}^{2+}_{1(\mathrm{aq})} + \mathrm{L}_{2(\mathrm{aq})} \tag{3}$$

in solution, and

$$\mathrm{ML}^{2+}_{2(\mathrm{gas})} + \mathrm{L}_{1(\mathrm{gas})} = \mathrm{ML}^{2+}_{1(\mathrm{gas})} + \mathrm{L}_{2(\mathrm{gas})} \tag{4}$$

in the gaseous phase, where L2 is the acyclic ligand and L_1 the cyclic ligand. The enthalpy change for the reaction in the gaseous phase, $\Delta H_{(\mathrm{gas})}$, can be calculated, if $\Delta H_{(\mathrm{aq})}$ is known, by means of the equation:

$$\Delta H_{(\mathrm{aq})} = \Delta H_{(\mathrm{gas})} + \{\Delta H_{\mathrm{h}(\mathrm{ML}_1^{2+})} - \Delta H_{\mathrm{h}(\mathrm{ML}_2^{2+})}\} + \{\Delta H_{\mathrm{h}(\mathrm{L}_2)} - \Delta H_{\mathrm{h}(\mathrm{L}_1)}\} \tag{5}$$

where h indicates hydration terms. In the case, for instance, of the Cu(II) and Ni(II) complexes of the cyclic ligand (**1**) and of its acyclic counterpart 2,3,2-tet, $\Delta H_{(\mathrm{aq})}$ values of -19.7 kJ mol^{-1}, for Cu(II), and -20.5 kJ mol^{-1}, for high-spin Ni(II) complexes, can be derived from the thermodynamic data reported above. The second term in parentheses (-19.2 kJ mol^{-1}) was obtained [185] by means of the calorimetric determination of the heats of combustion and the heats of solution of the free ligands (**1**) and 2,3,2-tet.

These results are in accord with the original hypothesis of Hinz and

Margerum [181] on the enthalpic nature of the macrocyclic effect, arising from the different solvation of the two ligands L_1 and L_2. However, the value of $\Delta H_{(gas)}$ requires evaluation of the first term in parentheses in eqn. (5) and, unfortunately, until now, no accurate method for its determination has been developed. A different approach involves calculating $\Delta H_{(gas)}$ using theoretical methods. The results obtained by Hancock and McDougall [186] and Reibnegger and Rode [187] seem to confirm the existence of a favourable enthalpic contribution.

The macrocyclic effect is an experimental observation, but its correct quantitative evaluation is an arduous task. Two main problems complicate this evaluation: (i) experimental difficulties, such as the kinetic inertness of some macrocyclic complexes, equilibria between different spin states of the coordinated metal ion, inadequate thermodynamic information in the gaseous phase; and (ii) the choice of the two ligands; they must give rise to similar coordination features, to the same spin state of the metal ion, they must present equally substituted donor atoms (for instance all secondary nitrogens) and form the same sequence of chelate rings.

As far as the sequence of chelate rings is concerned, the obvious counterparts of the macrocyclic ligands [12]aneN_4(**13**) and [16]aneN_4(**23**) are the tetraamines trien and 3,3,3-tet (1,5,9,13-tetraazatridecane) respectively. In the case of [15]aneN_4 (**20**) there is no evident reason for the choice of 3,3,3-tet or 3,2,3-tet (1,5,8,12-tetraazadodecane) or 2,3,3-tet (1,4,8,11-tetraazaundecane) as the 'best acyclic counterpart'.

Monomethylation of the two primary nitrogens of these acyclic ligands, which produces sets of donor atoms solely composed of secondary nitrogens, can lead to significant changes in the thermodynamic parameters which determine the macrocyclic effect. In the case of the Cu(II) complex of the two couples of the [12]aneN_4/Me_2-trien (Me_2-trien = 2,5,8,11-tetraazadodecane) and [16]aneN_4/Me_2-3,3,3-tet (Me_2-3,3,3-tet = 2,6,10,14-tetraazapentadecane) ligands, a more favourable enthalpic contribution to the macrocyclic effect was reported [188,189] than in the analogous systems containing the acyclic tetraamines trien and 3,3,3-tet. On the other hand, the entropic contribution decreases, still remaining favourable to the macrocyclic effect [188,189].

The macrocyclic effect was also observed for the triazacycloalkane complexes, although the thermodynamic results are sometimes in disagreement [70].

The macrocyclic effect is lost as the dimensions of the cyclic framework and the number of nitrogen donor atoms in the macrocyclic ligand increase [155,170]. Complexes of Cd(II) with the hexaazamacrocycle (**41**) [155] and of Ni(II) with the pentaaza macrocycle (**35**) [170] show stability constants very similar to those obtained for analogous complexes of the related acyclic ligands.

Actually, the main interest in polyazacycloalkanes has been in metal ion coordination; more recently, it was reported these ligands can also act efficiently as anion receptors. This arises through the formation, in aqueous solution, of highly charged polyprotonated species which can interact strongly with anions via electrostatic forces and hydrogen bonding. Thus, polyazacycloalkanes are very versatile ligands being able to turn their coordinating action from metal cations to their anionic partners (and vice versa), simply by changing the solution pH.

In view of the great number of anions, this overview of the thermodynamic aspects of anion coordination will be organised according to the following subdivision: (1) simple inorganic anions (ClO_4^-, IO_3^-, NO_3^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, etc.); (2) metal complexes ($Co(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$); (3) nucleotide phosphate anions (ATP^{4-}, ADP^{3-}, AMP^{2-}); (4) carboxylate and polycarboxylate anions.

Most reports on the thermodynamics of anion coordination presented here deal with stability constant determination [118, 152, 153, 157, 165, 167, 177, 190–195, 197–206]. A few [199–201] also present indirect estimations of the enthalpy contribution to the formation of anion complexes, while just one paper reports direct microcalorimetric data [191]. The logarithms of the stability constants, together with enthalpic and entropic data (when available), for anion binding are presented in Table 6. Great care must be exercised in drawing quantitative correlations between the reported values, since the data were obtained under rather different conditions and with different experimental methods. Furthermore, in some cases, the error in stability constant values and/or the experimental conditions under which they were determined were not reported. Nevertheless, some general features such as the non-covalent nature of the binding forces, the size effects and structural complementariness between anions and receptor ligands can be discussed to characterize the thermodynamics of this area of coordination chemistry.

(i) Simple inorganic anions

The interaction of F^- with polyazacycloalkanes has been studied with the tetraprotonated form of [16]aneN_4(**23**), [18]aneN_4(**26**), and [20]aneN_4(**27**) by Suet and Handel [190]. The stability constants of the relevant anion complexes increase with macrocycle ring size. This trend was attributed to the matching between the F^- ionic radius (1.36 Å) and the macrocyclic cavity dimensions (0.7 Å for $[H_4(\mathbf{23})]^{4+}$, 1.0 Å for $[H_4(\mathbf{26})]^{4+}$ and 1.4 Å for $[H_4(\mathbf{27})]^{4+}$ using CPK models [190]).

The stability constant of the anion complex $[H_6(\mathbf{58})F_2H]^{5+}$ has been reported by Motekaitis et al. [177], who proposed inclusive coordination of the F_2H^- anion into the cavity of the hexacharged macrobicyclic $[H_6(\mathbf{58})]^{6+}$ receptor.

Cullinane et al. reported that the tetraprotonated form of [18]aneN_6 (**41**) binds halogenide anions in aqueous solution [199]. The Cl^- complex is somewhat more stable than the Br^- complex, while the larger I^- interacts weakly. Since the charge density is higher for Cl^- (ionic radius 1.81 Å) than for Br^- (ionic radius 1.96 Å) and I^- (ionic radius 2.16 Å), the stability order observed for the $[H_4(\mathbf{41})]^{4+}$ complexes of these anions is that expected if electrostatic interactions predominate.

A reverse order of stability has been observed by Hosseini and Lehn [192] with the macrobicyclic ligand (**59**), for which, owing to the greater organization of the spherical molecule, size effects are of major importance. It is generally observed with this ligand that the most stable complexes are formed by the most highly charged forms of the ligand. Dealing with inclusion complexes of polyammonium ligands in solution, the equilibria between stereoisomeric species differing in the *in/out* configuration of the ammonium groups must be considered. Similar equilibria involve katapinand molecules in acidic solution (Fig. 12(a)) [207,208]. Inclusion complexes of halogenides with similar ligands can be stabilized by $N—H \cdots X^-$ hydrogen bonds if the ligands present ammonium groups in the *in* configuration (Fig. 12(b)) [209]. On the other hand, the chemical activation observed in Cl^- encapsulation into katapinands arises from prior ligand rearrangement from the *out–out* to the *in–in* conformations [209]. Of interest are the *N*-quaternarized 'cavity molecules' (**60**) and (**61**) which allow inclusion anion complexes to be studied independently of the configuration and protonation equilibria at the nitrogen atoms [204]. These ligands are unable to form hydrogen bonds and present an *out* N-configuration [203,204]. Anion/ligand mutual dimensions, ligand flexibility, electrostatic and hydrophobic interactions have been invoked to explain the two different stability sequences for halogenide complexes ($Cl^- < I^- < Br^-$) for (**60**) and ($Cl^- < Br^- < I^-$) for the larger (**61**) [203,204].

A number of simple inorganic anions (NO_3^-, ClO_4^-, IO_3^-, SO_4^{2-}) have been

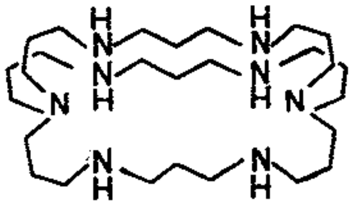

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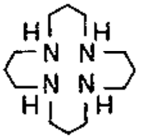
TABLE 6

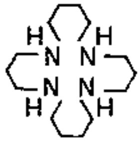
Log K, ΔH^0, and $T\Delta S^0$ values for anion–azamacrocycle equilibrium in solution

Only the left side (reactants) of the equilibrium reactions is indicated. Charges have been omitted. Experimental methods for the determination of the equilibrium constants are abbreviated as follow: potentiometric (pot), spectrophotometric (spec), polarographic (pol), nuclear magnetic resonance (NMR), cyclic voltammetric (cv). Only direct calorimetric methods (cal) for the determination of $\Delta H°$ are indicated.



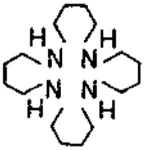
1,5,9,13-tetraazacyclohexadecane
[16]aneN$_4$

reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
$H_4L^{4+} + F^-$	1.9	pot			20	0.1 KNO_3	190



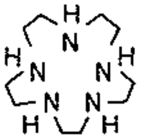
1,5,10,14-tetraazacyclooctadecane
[18]aneN$_4$

reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
$H_4L^{4+} + F^-$	2.0	pot			20	0.1 KNO_3	190
$H_4L^{4+} + AMP^{2-}$	3.84	pol			25	0.2 $NaClO_4$	118
$H_4L^{4+} + ADP^{3-}$	4.50	pol			25	0.2 $NaClO_4$	118
$H_4L^{4+} + ATP^{4-}$	6.65	pol			25	0.2 $NaClO_4$	118



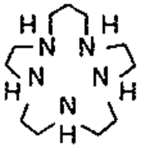
1,6,11,16-tetraazacycloeicosane
[20]aneN$_4$

reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
$H_4L^{4+} + F^-$	2.8	pot			20	0.1 KNO_3	190
$H_4L^{4+} + [Fe(CN)_6]^{4-}$	3.62	pot	4.6 cal	16.1	25	0.15 $NaClO_4$	191
$H_4L^{4+} + [Fe(CN)_6]^{3-}$	2.5	pot-cv			25	0.15 $NaClO_4$	191
$H_4L^{4+} + [Co(CN)_6]^{3-}$	2.38	pot	10.7 cal	2.9	25	0.15 $NaClO_4$	191
$H_4L^{4+} + ATP^{4-}$	3.81	pot			25	0.15 $NaClO_4$	202
$H_4L^{4+} + HATP^{3-}$	3.04	pot			25	0.15 $NaClO_4$	202



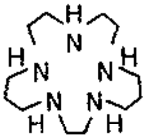
1,4,7,10,13-pentaazacyclopentadecane
[15]aneN$_5$

reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H_3L^{3+} + AMP^{2-}	3.19	pol			25	0.2 $NaClO_4$	118
H_3L^{3+} + ADP^{3-}	3.94	pol			25	0.2 $NaClO_4$	118
H_3L^{3+} + ATP^{4-}	4.01	pol			25	0.2 $NaClO_4$	118
H_3L^{3+} + $citrate^{3-}$	1.74	pol			20	0.1 KNO_3	157



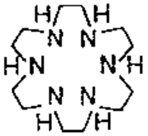
1,4,7,10,13-pentaazacyclohexadecane
[16]aneN$_5$

reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H_3L^{3+} + CO_3^{2-}	4.44	pol			25		197
H_3L^{3+} + HPO_4^{2-}	2.04	pol			25	0.2 $NaClO_4$	118
H_3L^{3+} + AMP^{4-}	3.11	pol			25	0.2 $NaClO_4$	118
H_3L^{3+} + ADP^{4-}	3.17	pol			25	0.2 $NaClO_4$	118
H_3L^{3+} + ATP^{4-}	3.63	pol			25	0.2 $NaClO_4$	118
H_3L^{3+} + $citrate^{3-}$	2.40	pol			25	0.2 $NaClO_4$	157
H_3L^{3+} + $succinate^{2-}$	2.08	pol			25	0.2 $NaClO_4$	157
H_3L^{3+} + $malonate^{2-}$	1.82	pol			25	0.2 $NaClO_4$	157
H_3L^{3+} + $malate^{2-}$	1.70	pol			25	0.2 $NaClO_4$	157
H_3L^{3+} + $maleate^{2-}$	1.88	pol			25	0.2 $NaClO_4$	157



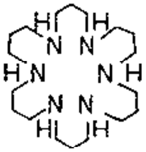
1,4,7,11,14-pentaazacycloeptadecane
[17]aneN$_5$

reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H_3L^{3+} + CO_3^{2-}	4.28	pol			25		197
H_3L^{3+} + AMP^{4-}	2.84	pol			25	0.2 $NaClO_4$	118
H_3L^{3+} + ADP^{4-}	3.00	pol			25	0.2 $NaClO_4$	118
H_3L^{3+} + ATP^{4-}	3.71	pol			25	0.2 $NaClO_4$	118
H_3L^{3+} + $citrate^{3-}$	3.00	pol			25	0.2 $NaClO_4$	157
H_3L^{3+} + $succinate^{2-}$	1.96	pol			25	0.2 $NaClO_4$	157
H_3L^{3+} + $malonate^{2-}$	1.40	pol			25	0.2 $NaClO_4$	157
H_3L^{3+} + $malate^{2-}$	1.41	pol			25	0.2 $NaClO_4$	157



1,4,7,10,13,16-hexaazacyclooctadecane
[18]aneN$_6$
hexacyclen

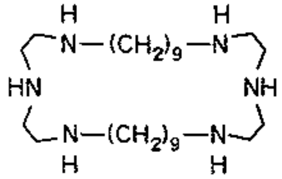
reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H_4L^{4+} + Cl^-	1.84	pot	-20	30	25	0.22	199
H_4L^{4+} + Br^-	1.46	pot			25	0.22	199
H_4L^{4+} + NO_3^-	2.32	pot	2	15	25	0.22	199
H_4L^{4+} + ClO_4^-	1.04	pot	10	-5	25	0.22	199,200
H_4L^{4+} + IO_3^-	2.78	pot	-5.4	21	25	0.22	200
H_4L^{4+} + $2IO_3^-$	3.86	pot	4	18	25	0.22	200
H_4L^{4+} + SO_4^{2-}	4.12	pot	-23	47	25	0.22	201
H_4L^{4+} + $2SO_4^{2-}$	6.02	pot	-32	66	25	0.22	201
H_4L^{4+} + benzenesulfonate$^-$	0.50	pot	-28	31	25	0.22	200
H_4L^{4+} + $CF_3CO_2^{2-}$	0.91	pot	-27	32	25	0.22	200
H_3L^{3+} + SO_4^{2-}	1.64	pot	-12	21	25	0.22	201
H_3L^{3+} + CO_3^{2-}	2.76	pol			25		197
H_3L^{3+} + HPO_4^{3-}	1.14	pol			25	0.2 $NaClO_4$	118
H_3L^{3+} + AMP^{4-}	3.25	pol			25	0.2 $NaClO_4$	118
H_3L^{3+} + ADP^{4-}	5.65	pol			25	0.2 $NaClO_4$	118
H_3L^{3+} + ATP^{4-}	6.40	pol			25	0.2 $NaClO_4$	118
H_3L^{3+} + citrate^{3-}	2.38	pol			25	0.2 $NaClO_4$	157
H_3L^{3+} + succinate^{2-}	1.25	pol			25	0.2 $NaClO_4$	157
H_3L^{3+} + malonate^{2-}	1.52	pol			25	0.2 $NaClO_4$	157
H_3L^{3+} + malate^{2-}	1.18	pol			25	0.2 $NaClO_4$	157
H_3L^{3+} + maleate^{2-}	1.46	pol			25	0.2 $NaClO_4$	157
H_3L^{3+} + vanillinate$^-$	2.69	pol			25	0.2 $NaClO_4$	198
H_3L^{3+} + veratrate$^-$	2.62	pol			25	0.2 $NaClO_4$	198
H_3L^{3+} + tropolonate$^-$	2.36	pol			25	0.2 $NaClO_4$	198
H_3L^{3+} + salicylate$^-$	2.67	pol			25	0.2 $NaClO_4$	198
H_3L^{3+} + p-aminosalicylate$^-$	2.65	pol			25	0.2 $NaClO_4$	198
H_3L^{3+} + a-picolinate$^-$	2.92	pol			25	0.2 $NaClO_4$	198



1,5,9,13,17,21-hexaazacyclotetracosane
[24]aneN$_6$

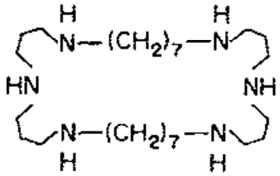
reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H_6L^{6+} + SO_4^{2-}	4.0	pot			25	0.1 Me_4NCl	152,192
H_5L^{5+} + SO_4^{2-}	3.0	pot			25	0.1 Me_4NCl	192
H_4L^{4+} + SO_4^{2-}	2.5	pot			25	0.1 Me_4NCl	192
H_6L^{6+} + $[Fe(CN)_6]^{4-}$	6.9	pot			25	0.1 Me_4NCl	152
H_6L^{6+} + $[Fe(CN)_6]^{4-}$	6.4	pot			25	0.1 KCl	193
H_6L^{6+} + $[Fe(CN)_6]^{3-}$	4.2	pot-cv			25	0.1 KCl	193

H_6L^{6+} + $[Fe(CN)_6]^{3-}$	4.3	pot-cv			25	0.1 Me_4NCl	194
H_6L^{6+} + $[Co(CN)_6]^{3-}$	3.9	pot			25	0.1 Me_4NCl	152
H_4L^{4+} + AMP^{4-}	1.7	pot			25	0.1 Me_4NCl	195
H_5L^{5+} + AMP^{4-}	2.7	pot			25	0.1 Me_4NCl	195
H_6L^{6+} + AMP^{4-}	3.4	pot			25	0.1 Me_4NCl	152,195
H_4L^{4+} + ADP^{4-}	4.0	pot			25	0.1 Me_4NCl	195
H_5L^{5+} + ADP^{4-}	4.5	pot			25	0.1 Me_4NCl	195
H_6L^{6+} + ADP^{4-}	6.5	pot			25	0.1 Me_4NCl	152,195
H_4L^{4+} + ATP^{4-}	5.0	pot			25	0.1 Me_4NCl	195
H_5L^{5+} + ATP^{4-}	6.8	pot			25	0.1 Me_4NCl	195
H_6L^{6+} + ATP^{4-}	8.9	pot			25	0.1 Me_4NCl	152,195
H_6L^{6+} + citrate^{3-}	4.7	pot			25	0.1 Me_4NCl	152
H_6L^{6+} + $C_2O_4^{2-}$	3.8	pot			25	0.1 Me_4NCl	152,205
H_5L^{5+} + $C_2O_4^{2-}$	3.2	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + $C_2O_4^{2-}$	2.6	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + malonate^{2-}	3.3	pot			25	0.1 Me_4NCl	152,205
H_5L^{5+} + malonate^{2-}	2.6	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + malonate^{2-}	2.4	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + succinate^{2-}	2.4	pot			25	0.1 Me_4NCl	152,205
H_5L^{5+} + succinate^{2-}	2.0	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + succinate^{2-}	1.8	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + glutarate^{2-}	2.3	pot			25	0.1 Me_4NCl	153,205
H_5L^{5+} + glutarate^{2-}	2.3	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + glutarate^{2-}	2.2	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + adipate^{2-}	2.3	pot			25	0.1 Me_4NCl	153,205
H_5L^{5+} + adipate^{2-}	2.3	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + adipate^{2-}	2.2	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + pimelate^{2-}	2.0	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + maleate^{2-}	3.7	pot			25	0.1 Me_4NCl	152,205
H_5L^{5+} + maleate^{2-}	2.9	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + maleate^{2-}	2.7	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + fumarate^{2-}	2.2	pot			25	0.1 Me_4NCl	152,205
H_5L^{5+} + fumarate^{2-}	1.9	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + fumarate^{2-}	1.7	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + tartrate^{2-}	2.5	pot			25	0.1 Me_4NCl	152
H_6L^{6+} + squarate^{2-}	3.2	pot			25	0.1 Me_4NCl	152
H_6L^{6+} + 1,3,5-benzen-tricarboxylate^{3-}	3.5	pot			25	0.1 Me_4NCl	152



1,4,7,17,20,23-hexaazacyclodotriacontane

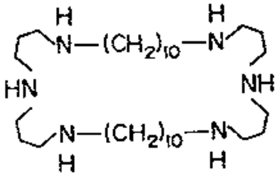
reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H_5L^{5+} + succinate^{2-}	3.6	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + succinate^{2-}	1.2	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + glutarate^{2-}	6.1	pot			25	0.1 Me_4NCl	205
H_5L^{5+} + glutarate^{2-}	5.5	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + glutarate^{2-}	2.9	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + adipate^{2-}	4.5	pot			25	0.1 Me_4NCl	205
H_5L^{5+} + adipate^{2-}	3.8	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + adipate^{2-}	1.5	pot			25	0.1 Me_4NCl	205
H_5L^{5+} + pimelate^{2-}	3.1	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + pimelate^{2-}	1.1	pot			25	0.1 Me_4NCl	205



1,5,9,17,21,25-hexaazacyclodotriacontane

reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
$H_6L^{6+} + C_2O_4^{2-}$	3.2	pot			25	0.1 Me_4NCl	153,205
$H_5L^{5+} + C_2O_4^{2-}$	2.5	pot			25	0.1 Me_4NCl	205
$H_4L^{4+} + C_2O_4^{2-}$	1.9	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + malonate^{2-}	3.8	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + malonate^{2-}	2.9	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + malonate^{2-}	1.5	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + malonate^{2-}	2.7	pot			25	0.1 Me_4NCl	153,205
H_5L^{5+} + malonate^{2-}	2.0	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + malonate^{2-}	1.3	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + succinate^{2-}	4.3	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + succinate^{2-}	3.3	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + succinate^{2-}	2.5	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + succinate^{2-}	3.4	pot			25	0.1 Me_4NCl	153,205
H_5L^{5+} + succinate^{2-}	2.8	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + succinate^{2-}	2.4	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + glutarate^{2-}	4.4	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + glutarate^{2-}	3.4	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + glutarate^{2-}	2.8	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + glutarate^{2-}	3.4	pot			25	0.1 Me_4NCl	153,205
H_5L^{5+} + glutarate^{2-}	2.9	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + glutarate^{2-}	2.5	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + adipate^{2-}	3.2	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + adipate^{2-}	2.6	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + adipate^{2-}	1.7	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + adipate^{2-}	2.3	pot			25	0.1 Me_4NCl	153,205
H_5L^{5+} + adipate^{2-}	1.9	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + adipate^{2-}	1.6	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + pimelate^{2-}	3.1	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + pimelate^{2-}	2.4	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + pimelate^{2-}	1.6	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + pimelate^{2-}	2.2	pot			25	0.1 Me_4NCl	153,205
H_5L^{5+} + pimelate^{2-}	1.8	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + pimelate^{2-}	1.8	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + maleate^{2-}	4.3	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + maleate^{2-}	3.3	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + maleate^{2-}	2.3	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + fumarate^{2-}	4.1	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + fumarate^{2-}	3.2	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + fumarate^{2-}	2.5	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + N-acetyl-(L)-aspartate^{2-}	4.1	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + N-acetyl-(L)-aspartate^{2-}	3.1	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + N-acetyl-(L)-							

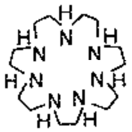
aspartate^{2-}	2.3	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + N-acetyl-(L)-glutamate^{2-}	4.1	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + N-acetyl-(L)-glutamate^{2-}	3.1	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + N-acetyl-(L)-glutamate^{2-}	2.3	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + N-acetyl-(L)-glutamyl-glycinate^{2-}	3.1	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + N-acetyl-(L)-glutamyl-glycinate^{2-}	2.4	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + N-acetyl-(L)-glutamyl-glycinate^{2-}	<2	pot			25	0.01 Me_4NCl	205



1,5,9,20,24,28-hexaazacyclooctatriacontane

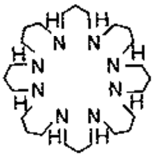
reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H_6L^{6+} + $C_2O_4^{2-}$	6.3	pot			25	0.1 Me_4NCl	153,205
H_5L^{5+} + $C_2O_4^{2-}$	4.7	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + $C_2O_4^{2-}$	2.8	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + malonate^{2-}	4.0	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + malonate^{2-}	3.0	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + malonate^{2-}	1.9	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + malonate^{2-}	3.2	pot			25	0.1 Me_4NCl	153
H_6L^{6+} + malonate^{2-}	3.8	pot			25	0.1 Me_4NCl	205
H_5L^{5+} + malonate^{2-}	2.6	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + malonate^{2-}	2.2	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + succinate^{2-}	3.1	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + succinate^{2-}	2.4	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + succinate^{2-}	<1.2	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + succinate^{2-}	3.0	pot			25	0.1 Me_4NCl	153,205
H_5L^{5+} + succinate^{2-}	2.3	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + succinate^{2-}	2.2	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + glutarate^{2-}	3.3	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + glutarate^{2-}	2.5	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + glutarate^{2-}	1.5	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + glutarate^{2-}	2.9	pot			25	0.1 Me_4NCl	153,205
H_5L^{5+} + glutarate^{2-}	2.4	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + glutarate^{2-}	2.4	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + adipate^{2-}	3.2	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + adipate^{2-}	2.5	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + adipate^{2-}	1.4	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + adipate^{2-}	2.9	pot			25	0.1 Me_4NCl	153,205
H_5L^{5+} + adipate^{2-}	2.5	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + adipate^{2-}	2.4	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + pimelate^{2-}	4.4	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + pimelate^{2-}	3.5	pot			25	0.01 Me_4NCl	205

H_4L^{4+} + pimelate^{2-}	2.7	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + pimelate^{2-}	3.4	pot			25	0.1 Me_4NCl	153,205
H_5L^{5+} + pimelate^{2-}	2.8	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + pimelate^{2-}	2.7	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + suberate^{2-}	4.2	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + suberate^{2-}	3.4	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + suberate^{2-}	2.6	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + suberate^{2-}	3.4	pot			25	0.1 Me_4NCl	153,205
H_5L^{5+} + suberate^{2-}	3.0	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + suberate^{2-}	2.6	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + azelate^{2-}	3.6	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + azelate^{2-}	3.1	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + azelate^{2-}	2.5	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + azelate^{2-}	3.2	pot			25	0.1 Me_4NCl	153,205
H_5L^{5+} + azelate^{2-}	2.8	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + azelate^{2-}	2.5	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + sebacate^{2-}	3.5	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + sebacate^{2-}	3.1	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + sebacate^{2-}	2.4	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + sebacate^{2-}	3.0	pot			25	0.1 Me_4NCl	153,205
H_5L^{5+} + sebacate^{2-}	2.9	pot			25	0.1 Me_4NCl	205
H_4L^{4+} + sebacate^{2-}	2.6	pot			25	0.1 Me_4NCl	205
H_6L^{6+} + butyrate^{2-}	<2.0	pot			25	0.01 Me_4NCl	153
H_6L^{6+} + N-acetyl-(L)-aspartate^{2-}	3.3	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + N-acetyl-(L)-aspartate^{2-}	2.6	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + N-acetyl-(L)-aspartate^{2-}	<2	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + N-acetyl-(L)-glutamate^{2-}	3.2	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + N-acetyl-(L)-glutamate^{2-}	2.6	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + N-acetyl-(L)-glutamate^{2-}	<2	pot			25	0.01 Me_4NCl	205
H_6L^{6+} + N-acetyl-(L)-glutamyl-glycinate^{2-}	4.3	pot			25	0.01 Me_4NCl	153,205
H_5L^{5+} + N-acetyl-(L)-glutamyl-glycinate^{2-}	3.5	pot			25	0.01 Me_4NCl	205
H_4L^{4+} + N-acetyl-(L)-glutamyl-glycinate^{2-}	2.4	pot			25	0.01 Me_4NCl	205



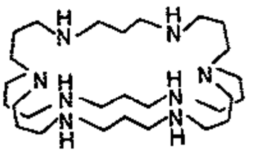
1,4,7,10,13,16,19-heptaazacycloheneicosane
[21]aneN7

reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H_4L^{4+} + $[Fe(CN)_6]^{4-}$	4.27	pot			25	0.1 KCl	165
H_5L^{5+} + $[Fe(CN)_6]^{4-}$	5.42	pot			25	0.1 KCl	165



1,5,9,13,17,21,25,29-octaazacyclodotriacontane
[32]aneN$_8$

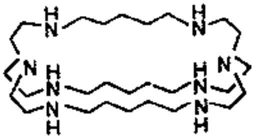
reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H_8L^{8+} + SO_4^{2-}	4.0	pot			25	0.1 Me_4NCl	152
H_8L^{8+} + $C_2O_4^{2-}$	3.7	pot			25	0.1 Me_4NCl	152
H_8L^{8+} + $[Fe(CN)_6]^{4-}$	8.9	pot			25	0.1 Me_4NCl	152
H_8L^{8+} + $[Fe(CN)_6]^{4-}$	7.8	pot			25	0.1 KCl	193
H_8L^{8+} + $[Fe(CN)_6]^{3-}$	5.0	pot-cv			25	0.1 KCl	193
H_8L^{8+} + $[Fe(CN)_6]^{3-}$	5.8	pot-cv			25	0.1 Me_4NCl	194
H_8L^{8+} + $[Co(CN)_6]^{3-}$	6.0	pot			25	0.1 Me_4NCl	152
H_8L^{8+} + AMP^{2-}	4.1	pot			25	0.1 Me_4NCl	152
H_5L^{5+} + $2AMP^{2-}$	5.0	pot			25	0.1 Me_4NCl	195
H_6L^{6+} + $2AMP^{2-}$	5.5	pot			25	0.1 Me_4NCl	195
H_7L^{7+} + $2AMP^{2-}$	5.9	pot			25	0.1 Me_4NCl	195
H_8L^{8+} + $2AMP^{2-}$	7.2	pot			25	0.1 Me_4NCl	152,195
H_8L^{8+} + ADP^{3-}	7.5	pot			25	0.1 Me_4NCl	152
H_5L^{5+} + $2ADP^{3-}$	7.0	pot			25	0.1 Me_4NCl	195
H_6L^{6+} + $2ADP^{3-}$	8.1	pot			25	0.1 Me_4NCl	195
H_7L^{7+} + $2ADP^{3-}$	9.1	pot			25	0.1 Me_4NCl	195
H_8L^{8+} + $2ADP^{3-}$	10.2	pot			25	0.1 Me_4NCl	152,195
H_8L^{8+} + ATP^{4-}	8.5	pot			25	0.1 Me_4NCl	152
H_5L^{5+} + $2ATP^{4-}$	8.0	pot			25	0.1 Me_4NCl	195
H_6L^{6+} + $2ATP^{4-}$	9.9	pot			25	0.1 Me_4NCl	195
H_7L^{7+} + $2ATP^{4-}$	11.5	pot			25	0.1 Me_4NCl	195
H_8L^{8+} + $2ATP^{4-}$	12.8	pot			25	0.1 Me_4NCl	152,195
H_8L^{8+} + citrate^{3-}	7.6	pot			25	0.1 Me_4NCl	152
H_8L^{8+} + succinate^{2-}	3.6	pot			25	0.1 Me_4NCl	152
H_8L^{8+} + malonate^{2-}	3.9	pot			25	0.1 Me_4NCl	152
H_8L^{8+} + maleate^{2-}	4.1	pot			25	0.1 Me_4NCl	152
H_8L^{8+} + fumarate^{2-}	2.9	pot			25	0.1 Me_4NCl	152
H_8L^{8+} + squarate^{2-}	3.6	pot			25	0.1 Me_4NCl	152
H_8L^{8+} + 1,3,5-benzentricarboxylate^{3-}	6.1	pot			25	0.1 Me_4NCl	152



1,5,9,13,17,21,28,32-octaazabicyclo[11.11.11]-pentatriacontane

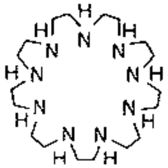
reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H_8L^{8+} + Cl^-	2.4	pot			25	0.1 NaTsO	192
H_7L^{7+} + Cl^-	2.1	pot			25	0.1 NaTsO	192
H_6L^{6+} + Cl^-	1.7	pot			25	0.1 NaTsO	192
H_5L^{5+} + Cl^-	1.5	pot			25	0.1 NaTsO	192

H_8L^{8+} + Br^-	2.9	pot			25	0.1 NaTsO	192
H_7L^{7+} + Br^-	2.6	pot			25	0.1 NaTsO	192
H_6L^{6+} + Br^-	2.2	pot			25	0.1 NaTsO	192
H_5L^{5+} + Br^-	1.7	pot			25	0.1 NaTsO	192
H_8L^{8+} + I^-	3.4	pot			25	0.1 NaTsO	192
H_7L^{7+} + I^-	3.0	pot			25	0.1 NaTsO	192
H_6L^{6+} + I^-	2.4	pot			25	0.1 NaTsO	192
H_5L^{5+} + I^-	1.9	pot			25	0.1 NaTsO	192
H_8L^{8+} + $SO_4{}^{2-}$	7.4	pot			25	0.1 Me_4NCl	192
H_7L^{7+} + $SO_4{}^{2-}$	5.6	pot			25	0.1 Me_4NCl	192
H_6L^{6+} + $SO_4{}^{2-}$	4.2	pot			25	0.1 Me_4NCl	192
H_5L^{5+} + $SO_4{}^{2-}$	3.2	pot			25	0.1 Me_4NCl	192
H_4L^{4+} + $SO_4{}^{2-}$	2.7	pot			25	0.1 Me_4NCl	192
H_8L^{8+} + $C_2O_4{}^{2-}$	6.5	pot			25	0.1 Me_4NCl	192
H_7L^{7+} + $C_2O_4{}^{2-}$	5.2	pot			25	0.1 Me_4NCl	192
H_6L^{6+} + $C_2O_4{}^{2-}$	4.5	pot			25	0.1 Me_4NCl	192
H_5L^{5+} + $C_2O_4{}^{2-}$	3.2	pot			25	0.1 Me_4NCl	192
H_8L^{8+} + malonate^{2-}	4.0	pot			25	0.1 Me_4NCl	192
H_7L^{7+} + malonate^{2-}	3.1	pot			25	0.1 Me_4NCl	192
H_6L^{6+} + malonate^{2-}	2.8	pot			25	0.1 Me_4NCl	192
H_5L^{5+} + malonate^{2-}	2.2	pot			25	0.1 Me_4NCl	192



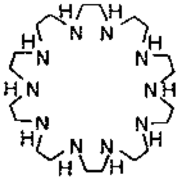
1,4,10,13,16,22,27,33-octaazabicyclo[11.11.11]-pentatriacontane

reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H_6L^{6+} + F_2H^-	5.2	pot			25	0.09 $NaClO_4$/ 0.01 NaF	177



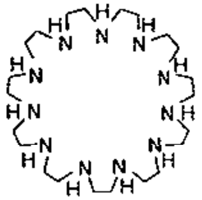
1,4,7,10,13,16,19,22,25-nonaazacycloheptacosane
[27]aneN$_9$

reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H_4L^{4+} + $[Fe(CN)_6]^{4-}$	4.06	pot			25	0.15 $NaClO_4$	167
H_5L^{5+} + $[Fe(CN)_6]^{4-}$	5.63	pot			25	0.15 $NaClO_4$	167
H_6L^{6+} + $[Fe(CN)_6]^{4-}$	7.60	pot			25	0.15 $NaClO_4$	167
H_7L^{7+} + $[Fe(CN)_6]^{4-}$	9.33	pot			25	0.15 $NaClO_4$	167
H_4L^{4+} + $[Co(CN)_6]^{3-}$	2.61	pot			25	0.15 $NaClO_4$	167
H_5L^{5+} + $[Co(CN)_6]^{3-}$	3.00	pot			25	0.15 $NaClO_4$	167
H_6L^{6+} + $[Co(CN)_6]^{3-}$	3.36	pot			25	0.15 $NaClO_4$	167
H_7L^{7+} + $[Co(CN)_6]^{3-}$	3.78	pot			25	0.15 $NaClO_4$	167
H_8L^{8+} + $[Co(CN)_6]^{3-}$	4.09	pot			25	0.15 $NaClO_4$	167



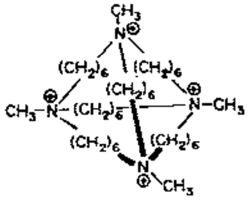
1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane
[30]aneN_{10}

reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H_4L^{4+} + $[Fe(CN)_6]^{4-}$	3.69	pot			25	0.15 $NaClO_4$	167
H_5L^{5+} + $[Fe(CN)_6]^{4-}$	4.78	pot			25	0.15 $NaClO_4$	167
H_6L^{6+} + $[Fe(CN)_6]^{4-}$	6.23	pot			25	0.15 $NaClO_4$	167
H_7L^{7+} + $[Fe(CN)_6]^{4-}$	7.92	pot			25	0.15 $NaClO_4$	167
H_8L^{8+} + $[Fe(CN)_6]^{4-}$	9.03	pot			25	0.15 $NaClO_4$	167
H_4L^{4+} + $[Co(CN)_6]^{3-}$	2.03	pot			25	0.15 $NaClO_4$	167
H_5L^{5+} + $[Co(CN)_6]^{3-}$	2.10	pot			25	0.15 $NaClO_4$	167
H_6L^{6+} + $[Co(CN)_6]^{3-}$	2.37	pot			25	0.15 $NaClO_4$	167
H_7L^{7+} + $[Co(CN)_6]^{3-}$	3.23	pot			25	0.15 $NaClO_4$	167
H_8L^{8+} + $[Co(CN)_6]^{3-}$	3.66	pot			25	0.15 $NaClO_4$	167
H_9L^{9+} + $[Co(CN)_6]^{3-}$	4.43	pot			25	0.15 $NaClO_4$	167



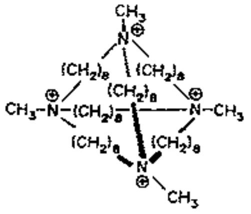
1,4,7,10,13,16,19,22,25,28,31-undecaazacyclotritriacontane
[33]aneN_{11}

reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
H_4L^{4+} + $[Fe(CN)_6]^{4-}$	3.61	pot			25	0.15 $NaClO_4$	167
H_5L^{5+} + $[Fe(CN)_6]^{4-}$	4.66	pot			25	0.15 $NaClO_4$	167
H_6L^{6+} + $[Fe(CN)_6]^{4-}$	5.72	pot			25	0.15 $NaClO_4$	167
H_7L^{7+} + $[Fe(CN)_6]^{4-}$	6.93	pot			25	0.15 $NaClO_4$	167
H_8L^{8+} + $[Fe(CN)_6]^{4-}$	8.07	pot			25	0.15 $NaClO_4$	167
H_4L^{4+} + $[Co(CN)_6]^{3-}$	2.63	pot			25	0.15 $NaClO_4$	167
H_5L^{5+} + $[Co(CN)_6]^{3-}$	3.05	pot			25	0.15 $NaClO_4$	167
H_6L^{6+} + $[Co(CN)_6]^{3-}$	3.52	pot			25	0.15 $NaClO_4$	167
H_7L^{7+} + $[Co(CN)_6]^{3-}$	4.05	pot			25	0.15 $NaClO_4$	167
H_8L^{8+} + $[Co(CN)_6]^{3-}$	4.55	pot			25	0.15 $NaClO_4$	167
H_9L^{9+} + $[Co(CN)_6]^{3-}$	4.87	pot			25	0.15 $NaClO_4$	167
$H_{10}L^{10+}$ + $[Co(CN)_6]^{3-}$	5.32	pot			25	0.15 $NaClO_4$	167



1,8,15,22-tetramethyl-1,8,15,22-tetrazoniatricyclo[13.13.6.6^{8,22}]tetracontane

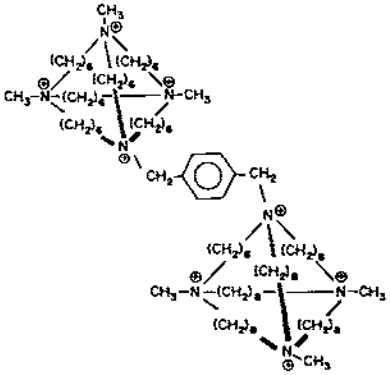
reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
L^{4+} + Cl^-	1.3					KNO_3	204
L^{4+} + Cl^-	1.7	pot			25	0.1 NaTsO	203
L^{4+} + Br^-	2.45					KNO_3	204
L^{4+} + Br^-	3.01	pot			25	0.1 NaTsO	203
L^{4+} + I^-	2.2					KF	204
L^{4+} + I^-	2.7	pot			25	0.1 NaTsO	203
L^{4+} + $HCOO^-$	1.34	pot			25	0.1 $N(C_2H_5)_4$TsO	203
L^{4+} + CH_3COO^-	1.86	pot			25	0.1 $N(C_2H_5)_4$TsO	203
$L^4{}_+$ + $CO_3{}^{2-}$	1.76	pot			25	0.1 $N(C_2H_5)_4$TsO	203
L^{4+} + $HCO_3{}^-$	2.36	pot			25	0.1 NaTsO	203
L^{4+} + $H_2PO_4{}^-$	2.1	pot			25	0.1 NaTsO	203
L^{4+} + $HPO_4{}^{2-}$	2.54	pot			25	0.1 NaTsO	203
L^{4+} + p-$O_2NC_6H_4OPO_3{}^{2-}$	2.11	pot			25	0.1 NaTsO	203
L^{4+} + glucose-1-phosphate^{2-}	2.24	pot			25	0.1 NaTsO	203
L^{4+} + glucose-6-phosphate^{2-}	2.2	pot			25	0.1 NaTsO	203
L^{4+} + AMP^{4-}	1.99	pot			25	0.1 NaTsO	203
L^{4+} + ATP^{4-}	2.46	pot			25	0.1 NaTsO	203
adenindinucleotide$^-$	2.08	pot			25	0.1 NaTsO	203
L^{4+} + p-$O_2NC_6H_4O^-$	<0.7	pot			25	0.22(Tris-TsO)	203
L^{4+} + 4-hydroxy-3-nitrobenzoate^{2-}	2.32	spec			27	0.25 NaF TAPS (0.25M pH 8.8)	206
L^{4+} + 4-hydroxy-3-nitrophenylacetate^{2-}	1.79	spec			25	0.1 NaF TAPS (0.25M pH 8.8)	206
L^{4+} + 3-(3-nitro-4-hydroxyphenyl)-tri-2-enoate^{2-}	2.74	spec			25	0.1 NaF TAPS (0.25M pH 8.8)	206
L^{4+} + 5-(3-nitro-4-hydroxyphenyl)-penta-2,4,-dienoate^{2-}	2.68	spec			25	0.1 NaF TAPS (0.25M pH 8.8)	206
L^{4+} + 5-(3-nitro-4-hydroxyphenyl)-hepta-2,4,6-trienoate^{2-}	3.02	spec			25	0.1 NaF TAPS (0.25M pH 8.8)	206



1,10,19,28-tetramethyl-1,10,19,28-tetrazoniatricyclo[17.17.8.8^{10,28}]dopentacontane

reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
L^{4+} + Cl^-	<0.5					KF	204
L^{4+} + Br^-	2.45					KF	204

L^{4+} + Br^-	2.0	spec			26	0.02 (Tris-F^-)	203
L^{4+} + Br^-	2.03	pot			26	0.55 NaGlucuronate	203
L^{4+} + I^-	2.4					KF	204
L^{4+} + I^-	2.46	spec			26	0.22 (Tris-F^-)	203
L^{4+} + N_3^-	1.90	spec			26	0.22 (Tris-F^-)	203
L^{4+} + SCN^-	2.91	spec			26	0.22 (Tris-F^-)	203
L^{4+} + HPO_4^{2-}	0.32	spec			26	0.22 (Tris-F^-)	203
L^{4+} + $HAsO_4^{2-}$	<0.15	spec			26	0.22 (Tris-F^-)	203
L^{4+} + $C_6H_5COO^-$	0.44	spec			26	0.22 (Tris-F^-)	203
L^{4+} + o-$C_6H_4(COO)_2^{2-}$	0.91	spec			26	0.22 (Tris-F^-)	203
L^{4+} + $I\text{-}CH_2\text{-}CO_2^-$	1.99	spec			26	0.22 (Tris-F^-)	203
L^{4+} + AMP^{4-}	1.04	spec			26	0.22 (Tris-F^-)	203
L^{4+} + ATP^{4-}	1.40	spec			26	0.22 (Tris-F^-)	203
L^{4+} + ATP^{4-}	1.92	spec			26	0.02 (Tris-F^-)	203
L^{4+} + p-nitrophenolate$^-$	2.25	spec			26	0.22 (Tris-F^-)	203
L^{4+} + 2,4-dinitrophenolate$^-$	2.36	spec			26	0.22 (Tris-F^-)	203
L^{4+} + 2,4-dinitrophenolate$^-$	2.68	spec			26	0.02 (Tris-F^-)	203
L^{4+} + 3,5-diiodotyrosine$^-$	1.14	spec			26	0.22 (Tris-F^-)	203
L^{4+} + N-acetyltryptophane$^-$	<0.7	spec			26	0.22 (Tris-F^-)	203



1-(4-(10,19,28-Trimethyl-1,10,19,28-tetrazoniatricyclo-[17.17.8.8^{10,28}]dopentacontylmethyl)-benzyl)-8,15,22-trimethyl-1,8,15,22-tetrazoniatricyclo[13.13.6.6^{8,22}]tetracontane

reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
L^{4+} + 4-hydroxy-3-nitrobenzoate^{2-}	2.85	spec			27	0.25 NaF TAPS (0.25M pH 8.8)	206
L^{4+} + 4-hydroxy-3-nitrophenylacetate^{2-}	2.51	spec			25	0.1 NaF TAPS (0.25M pH 8.8)	206
L^{4+} + 3-(3-nitro-4-hydroxyphenyl)-tri-2-enoate^{2-}	3.31	spec			25	0.1 NaF TAPS (0.25M pH 8.8)	206
L^{4+} + 5-(3-nitro-4-hydroxyphenyl)-penta-2,4,-dienoate^{2-}	3.72	spec			25	0.1 NaF TAPS (0.25M pH 8.8)	206
$^{4+}$ + 5-(3-nitro-4-hydroxyphenyl)-hepta-2,4,6-trienoate^{2-}	4.00	spec			25	0.1 NaF TAPS (0.25M pH 8.8)	206

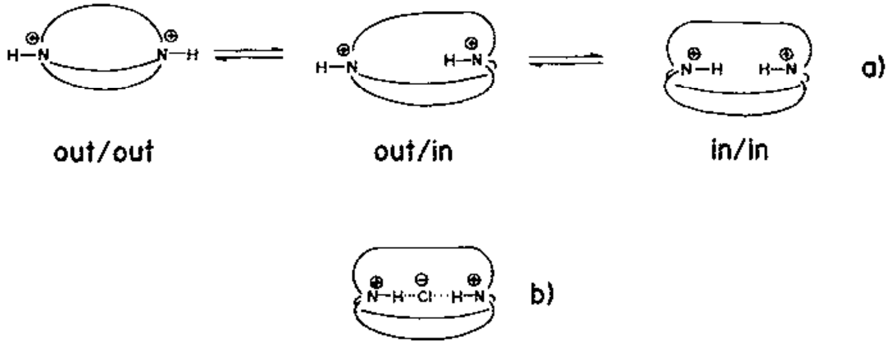
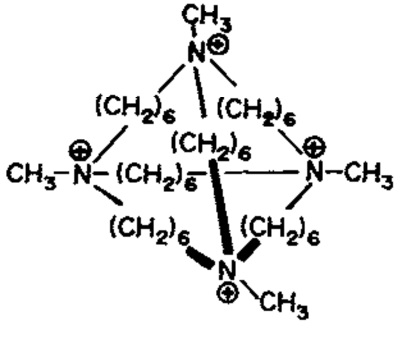


Fig. 12. (a) Equilibria between katapinand stereoisomeric species differing in the in–out configuration of the ammonium groups. (b) Inclusion complex of chloride, stabilized by hydrogen bonds.



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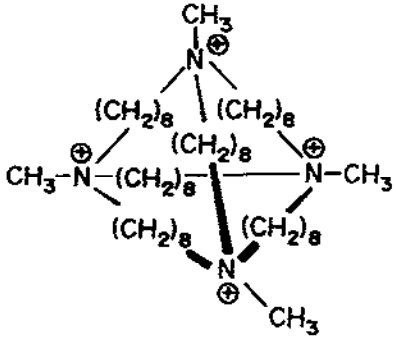

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studied at various temperatures for binding to the tetraprotonated and triprotonated forms of [18]aneN_6 (**41**) [199,200,201]. In the case of IO_3^- [200] and SO_4^{2-} [201], both 1:1 and 1:2 $[H_4(\mathbf{41})]^{4+}$ anion complexes are formed, while NO_3^- and ClO_4^- form only 1:1 species [199,200]. The association constants for these complexes were determined at each temperature and the relevant enthalpy changes estimated from van't Hoff analysis. The thermodynamic data agree with a general favourable entropic contribution towards the stability of these complexes, with the enthalpic term being mostly unfavourable or slightly favourable. These results were interpreted in terms of solvent ordering by the $[H_4(\mathbf{41})]^{4+}$ species and water loss from both the ligand and anion solvation sphere [199–201]. Although the NO_3^- complex is more stable than the chloride complex [199], it appears that, in the solid state, Cl^- forms stronger bonds to $[H_4(\mathbf{41})]^{4+}$. X-ray crystallographic analysis of NO_3^- and Cl^- salts of $[H_4(\mathbf{41})]^{4+}$ showed that at least one water molecule intercedes between $[H_4(\mathbf{41})]^{4+}$ and NO_3^-, while Cl^- interacts directly with the ammonium sites [199]. These crystallographic features are apparently connected with the thermodynamic properties of $[H_4(\mathbf{41})]^{4+}$ complexes of NO_3^- and Cl^- [201], since a lower solvation of the Cl^- anion leads the complexation reaction to be more endothermic and more entropy producing than in the case of the NO_3^- ion.

The protonated hexamine ligand [24]aneN_6 (**42**) forms weaker Cl^- complexes than the analogous [18]aneN_6(**41**) ligand [164]. Comparison of SO_4^{2-} complexes leads to similar conclusions. The presence of propylenic chains connecting the amino groups in [24]aneN_6 (**42**) allows the positive charges to disperse in a greater volume than in the case of the ethylenic chained [18]aneN_6 (**41**). The choice of propylenic-chained azamacrocycles, as noted above, facilitates protonation of the ligands [164] but, on the other hand, produces protonated species of reduced charge density which interact less with anions than the ethylenic-chained azamacrocycles. This is a generally observed feature in [4*k*]aneN_k and [3*k*]aneN_k ligands.

The stability constants for SO_4^{2-} complexes of the tetra- to octa-protonated species of the bicyclic ligand (**59**) have been reported [192]. The stability constants for the tetra-, penta- and hexa-protonated species are equal, within experimental error, to the values reported [152] for the analogous species formed with [24]aneN_6 (**42**). The stability of SO_4^{2-} complexes seems to be unaffected by further extension of the dimensions and charges, since equal stability constants for $[H_6(\mathbf{42})SO_4]^{4+}$ and $[H_8(\mathbf{53})SO_4]^{6+}$ have also been found [152]. On the other hand, exhaustive protonation of bicyclic (**58**) produce a SO_4^{2-} complex whose stability is much greater than that observed for the parent ligand $[H_8(\mathbf{53})]^{8+}$.

The equilibrium constants referring to the complexation of CO_3^{2-} anion and $[H_3(\mathbf{36})]^{3+}$, $[H_3(\mathbf{37})]^{3+}$, $[H_3(\mathbf{41})]^{3+}$ [197] and (**60**) [203] have been determined. The two pentaaza ligands show a high affinity for carbonate binding at neutral pH and have been proposed as possible models for carbonate physiological receptors [197]. 1:1 complexes with HPO_4^{2-} are formed by $[H_3(\mathbf{36})]^{3+}$, $[H_3(\mathbf{41})]^{3+}$ [118] and by the tetrammonium cage-like compounds (**60**) and (**61**) [203]. Phosphate complexes with these protonated macrocycles are stabilized by electrostatic interaction and hydrogen bond formation. On the other hand, the stability of the inclusion complexes of the tetracharged (**60**) and (**61**) with the hydrophilic HPO_4^{2-} can be ascribed to a different coordinating ability of the two tetrammonium cages, being mainly electrostatic in (**60**) and hydrophobic in (**61**).

The present results with simple inorganic anions show that the molecular architecture of the anion receptors produces selectivity criteria which could define 'macrocyclic and macropolycyclic effects for anion complexation'.

(ii) Metal complex anions

An earlier observation of ion association in solution between simple quaternary ammonium anions and $[Fe(CN)_6]^{3-}$ was evident from an NMR study [210]. More recently, the interaction of metal hexacyanide anions $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$, $[Ru(CN)_6]^{4-}$ with polyprotonated aza macrocycles has been studied from thermodynamic [191,152,193,194,165,167], electrochemical [191,193,194,165,167], photochemical [211–213] and structural [191,167,166] points of view. The interaction of these polyammonium receptors with the complex anion gives rise to second sphere coordinated species, namely complexes of complexes (supercomplexes), which deserve account in the field of supramolecular chemistry.

The stability constants for $[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$ binding with polyammonium ions of large polyazacycloalkanes of the series $[3k]aneN_k$ ($[21]aneN_7$(**48**) [165], $[27]aneN_9$(**51**), $[30]aneN_{10}$(**52**), $[33]aneN_{11}$ (**53**) [167]) and $[4k]aneN_k$ ($[24]aneN_6$ (**42**) and $[32]aneN_8$ (**50**) [152,193]), as well as for the tetraaza macrocycle $[20]aneN_4$ (**27**) [191] have been determined by pH-metric titration. In the series $[3k]aneN_k$ and for $[20]aneN_4$ (**27**), 1:1 complexes have been observed, in which the ligand is at least tetracharged while only the stability constants for the 1:1 complexes formed by the two fully protonated $[4k]aneN_k$ ligands have been reported. All the complexes are very stable.

For the same macrocycle, the stability of the supercomplexed species increases as the macrocycle becomes more highly protonated (charged) [165,167]. Furthermore, the supercomplexes formed with the tetra-anion $[Fe(CN)_6]^{4-}$ are always much more stable than the corresponding species involving the tri-anion $[Co(CN)_6]^{3-}$ [152,165,167,191,193]. These general considerations lead to the understanding that the interactions which produce these supercomplexed species are essentially electrostatic in nature. Indeed, complexes of $[Fe(CN)_6]^{4-}$ show a clear trend, indicating that the species with equal degrees of protonation are somewhat more stable with smaller macrocycles where the positive charges are more gathered.

However, in addition to electrostatic forces, size effects and topological effects, hydrogen bond formation may play an important role in determining the stability of the supercomplexed species. This is the case for the $[Co(CN)_6]^{3-}$ complexes of protonated $[33]aneN_{11}$ (**53**) for which a small increase in stability is observed with respect to $[30]aneN_{10}$ (**52**). This has been ascribed [213], on the basis of the photochemical quantum yield of CN^- release from these $[Co(CN)_6]^{3-}$ supercomplexes, to the inclusion of the anion into the macrocyclic cavity of the polyammonium receptor.

A simple scheme (Fig. 13) was proposed to describe both inclusive (Fig. 13(a)) and outer (Fig. 13(b)) coordination of the $Co(CN)_6^{3-}$ ion. CN^- ions which are involved in hydrogen bonds are prevented from photodissocia-

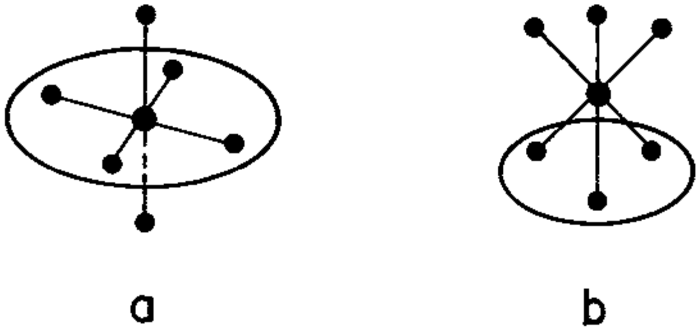


Fig. 13. Schematic representation of inclusive and outer coordination of $[Co(CN)_6]^{3-}$ to a large protonated polyazacycloalkane.

tion. Bianchi et al. [166,167] reported a crystal structure for $\{[H_8(\mathbf{52})][Co(CN)_6]\}^{5+}$ (Fig. 14) which showed that this supercomplex is of the outer type in accord with photochemical data [213]. In the complex, the $[H_8(\mathbf{52})]^{8+}$ receptor adopts an elliptical-shaped disposition.

The complexation of $[Fe(CN)_6]^{4-}$ by polyammonium ligands affects the electrochemical properties of this complex anion by stabilizing the more highly charged forms, i.e. the lower oxidation state of the central metal ion [165,167,191,193,194]. The value of the redox potential of the couple $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ can be modulated by increasing the charge of the polyammonium receptors [167,193–195] (Fig. 15). The stability constants for some $[Fe(CN)_6]^{3-}$ supercomplexes have been obtained from the value of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox potential and the stability constants determined for the reduced supercomplexes [191,193,194]. Smaller stability constants are observed for $[Fe(CN)_6]^{3-}$ with respect to $[Fe(CN)_6]^{4-}$ in accord with a smaller electrostatic interaction with the polyammonium receptors.

In the case of $[H_4(\mathbf{27})]^{4+}$ [191], the enthalpy of reaction with both $[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$ has been determined by direct microcalorimetry by Bianchi et al. [191]. Thermodynamic results show that both complexes have favourable enthalpic and entropic contributions. The stability of $\{[Fe(CN)_6][H_4(\mathbf{27})]\}$ is mainly entropic in nature while the enthalpic contribution predominates in the formation of $\{[Co(CN)_6][H_4(\mathbf{27})]\}^{+}$. An increasing number of released solvating water molecules from the reacting species (entropy producing effect) with charge neutralization and heats of desolvation (enthalpy consuming effect) has been proposed to explain the above behaviour [191].

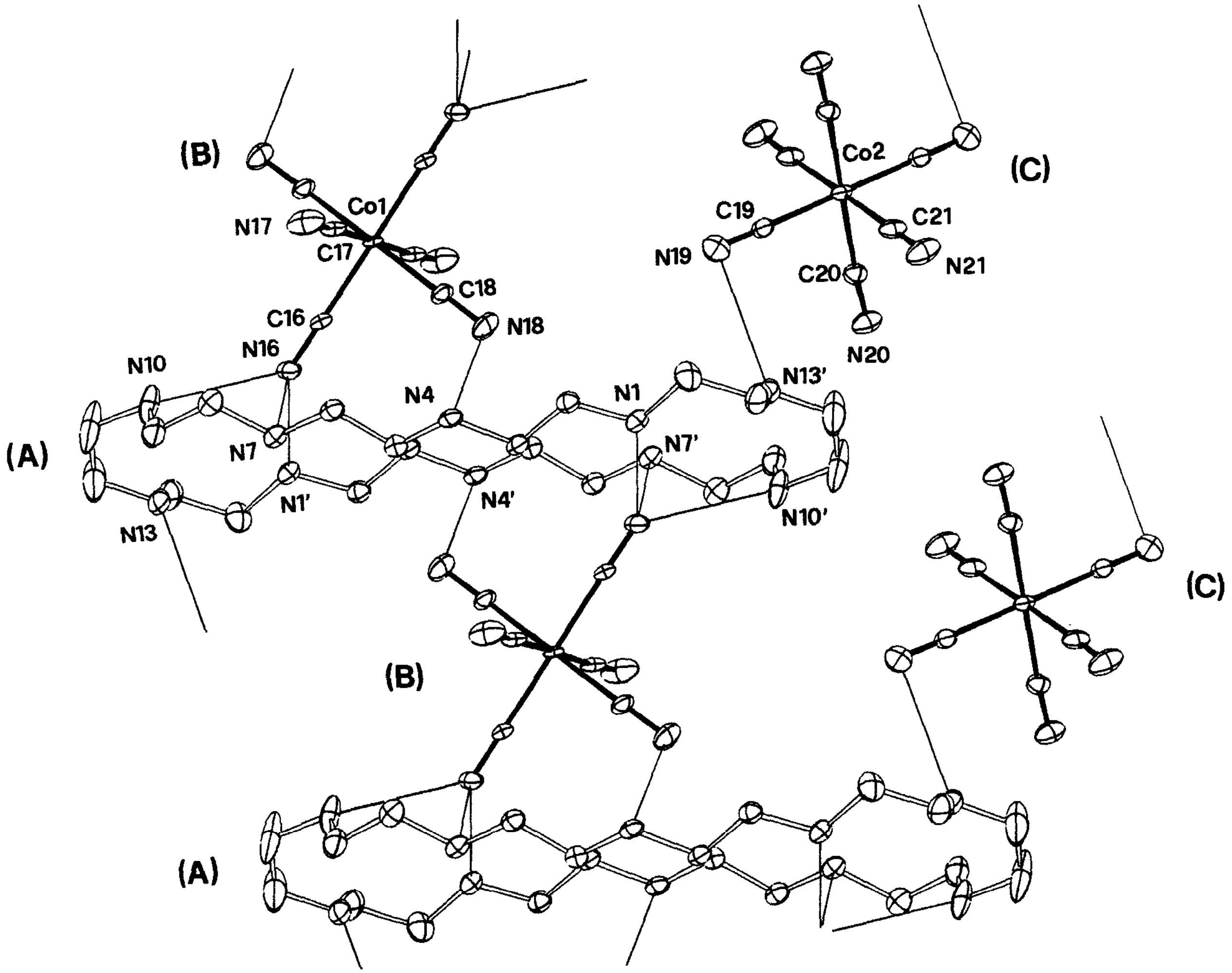


Fig. 14. Crystal structure of the 'supercomplex' $\{[H_8(\mathbf{52})][Co(CN)_6]\}^{5+}$.

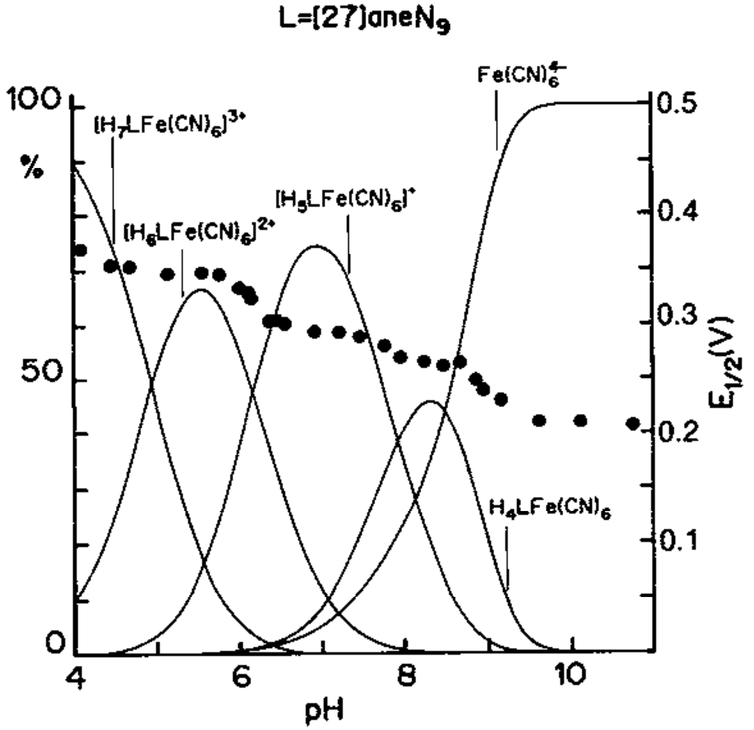


Fig. 15. Distribution diagram (—) for the system H^+/(51)/$[Fe(CN)_6]^{4-}$ and $E_{1/2}$ (mV) in cyclic voltammogram (●) for the couple $[H_n(51)][Fe(CN)_6]^{(n-4)+}/[H_n(51)][Fe(CN)_6]^{(n-3)+}$ vs. pH.

(iii) Nucleotidic phosphate anions

In a first report by Dietrich et al. [152], it was shown by pH-metric measurements that the fully protonated forms of the polyazacycloalkanes [24]aneN_6 (**42**) and [32]aneN_8 (**50**) form stable complexes with the nucleotide anions AMP^{2-}, ADP^{3-} and ATP^{4-}. 1:1 ligand-to-anion complexes were observed for both ligands, while 1:2 species are also formed by the larger octaaza macrocycle. Later, the stability constants were presented [195] for the formation of analogous complexes with less protonated species of these two ligands. In the meantime, Kodama and coworkers investigated [118] the interaction of these anions with a series of tetra-, penta- and hexaaza macrocycles by polarographic methods, and determined the stability constants for the relevant complexes. In all these cases, it was observed that the stability of the complex of a given ligand increases with the charge of the anion (AMP^{2-} ADP^{3-} ATP^{4-}) [118,152,195]. Moreover, for a given anion, the stability increases with the charge (degree of protonation) of the given ligand [195]. These trends agree with a predominant electrostatic contribution to the interaction between these anions and the polyammonium receptors. However, size effects can alter the above trends even for nucleotidic phosphate anion complexes, as in the case of triprotonated (**41**), which forms ADP^{3-} and ATP^{4-} complexes which are more stable than those of the equally protonated forms of the pentaaza macrocycles [15]aneN$_5$ (**34**), [16]aneN$_5$ (**35**) and [17]aneN$_5$ (**36**).

A model for the [H$_3$(**41**)]$^{3+}$ complex of ATP^{4-} in which the nucleotide adopts a bent conformation in order to allow both phosphate and adenine sites to interact with the tricharged receptor (Fig. 16) was proposed by Kimura et al. on the basis of ^{1}H NMR measurements [118]. In the case of [16]aneN$_5$ (**35**) and [18]aneN$_6$ (**41**), for which binding of both HPO$_4^{2-}$ and of the equally charged AMP^{2-} have been reported, more stable complexes are formed with the nucleotide anion, although its charge density is lowered by the presence of the adenosine group.

The binding of AMP^{2-} and ATP^{4-} by quaternarized cage-like ligands (**60**) and (**61**) was presented in an early paper by Schmidtchen [203]. The complexes are of reduced stability with respect to the analogous polyazacycloakanes. The disposition of ammonium binding sites, the low charge density of the receptor as well as the inhibition (by *N*-quaternarization) of hydrogen bondings can be invoked to explain this behaviour. The effect of hydrogen bond formation on nucleotide anion binding has recently been

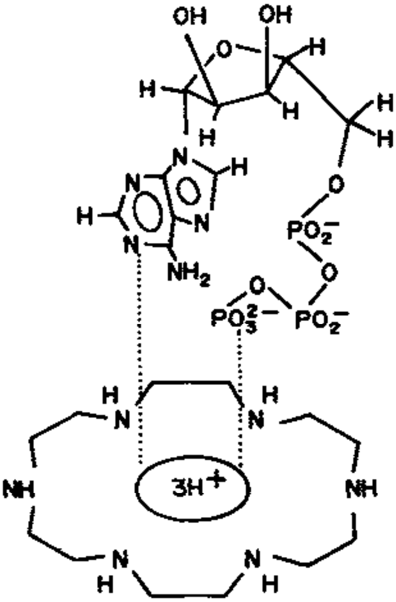
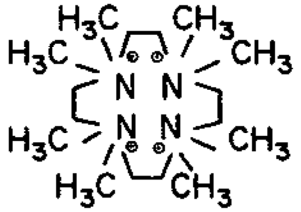


Fig. 16. Schematic representation proposed by Kimura et al. [118] for the interaction between ATP^{4-} and the tricharged receptor [H$_3$(**41**)]$^{3+}$.

analyzed [202] by comparing, through potentiometric measurements, the coordinating ability toward ATP^{4-} of the two tetracharged formula isomers $[H_4(\mathbf{27})]^{4+}$ and [1,1′,4,4′,7,7′,10,10′-octamethyl-1,4,7,10-tetraazacyclododecane]$^{4+}$ (**62**). (**62**) presents a closer assembly of positive charges than $[H_4(\mathbf{27})]^{4+}$, but it is unable to form hydrogen bonds. As a consequence, while $[H_4(\mathbf{27})]^{4+}$ forms a stable complex with ATP^{4-}, no detectable interaction arises with (**62**).



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An important consequence of ATP^{4-} binding by polyammonium macrocyclic receptors is the acceleration of ATP hydrolysis. This catalytic effect has been extensively studied by ^{31}P NMR and HPLC methods from a kinetic point of view. This subject is beyond the purpose of the present review and consequently it will not be presented here. Readers interested in this part of supramolecular catalysis will find exhaustive reports in the literature ([214,215] and references cited therein).

(iv) Carboxylate and polycarboxylate anions

The equilibrium constants for polycarboxylate anion binding by protonated species of the pentaazacycloalkanes [15]aneN_5 (**34**), [16]aneN_5 (**35**) and [17]aneN_5 (**36**) have been determined by the polarographic method [157]. The tricarboxylate anion, citrate^{3-}, is bound more strongly than any other dicarboxylate^{2-} studied, indicating the fundamental implication of electrostatic forces. Also, in the case of hexaaza [18]aneN_6 (**41**) [157] and [24]aneN_6 (**42**) [152,205] and of the octaaza [32]aneN_8 (**50**) [152], citrate^{3-} forms more stable complexes than dicarboxylate^{2-} anions. Further evidence for the major role played by electrostatic interactions comes from the increasing stability observed for complexes of a given polycarboxylate anion with the degree of protonation of the receptor [205]. However, the binding of monocharged carboxylate derivatives of catechol anions by protonated (**41**) gives rise to complexed species [198] whose stability compares well with that of the citrate^{3-} complex. Some tetraaza and pentaaza macrocycles were also tested for catechol binding [198] but only [18]aneN$_6$ (**41**) was a successful receptor, indicating stricter geometrical requirements for catechol recognition.

Selective features in dicarboxylate^{2-} anion binding are shown by ditopic polyammonium macrocycles, whose binding sites are located at opposite poles of the molecules (**42**)–(**44**) [153,205]. The most stable complexes are produced by the best fit between the length of the hydrocarbon chain connecting the two carboxylate groups (*m* in Fig. 17) and the separation of the binding sites in the polyammonium ligand (*n* in Fig. 17). The best fit is observed [153,205] between (**43**) ($n = 7$) and glutarate^{2-} ($m = 3$), and between (**44**) ($n = 10$) and pimelate^{2-} ($m = 5$), respectively (Fig. 18). The stability con-

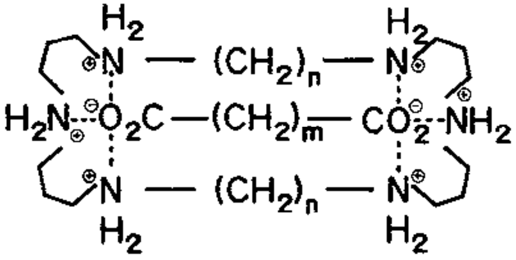


Fig. 17. Ditopic polyammonium macrocycles whose binding sites are located at opposite poles of the molecule. The best fit between the length of the chains connecting the two carboxylate groups (*m*) and the separation of the binding sites in the ligand produces the most stable complexes.

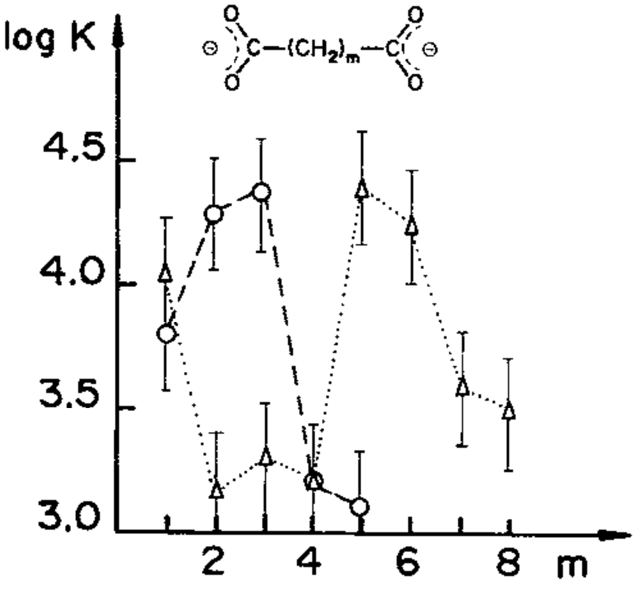
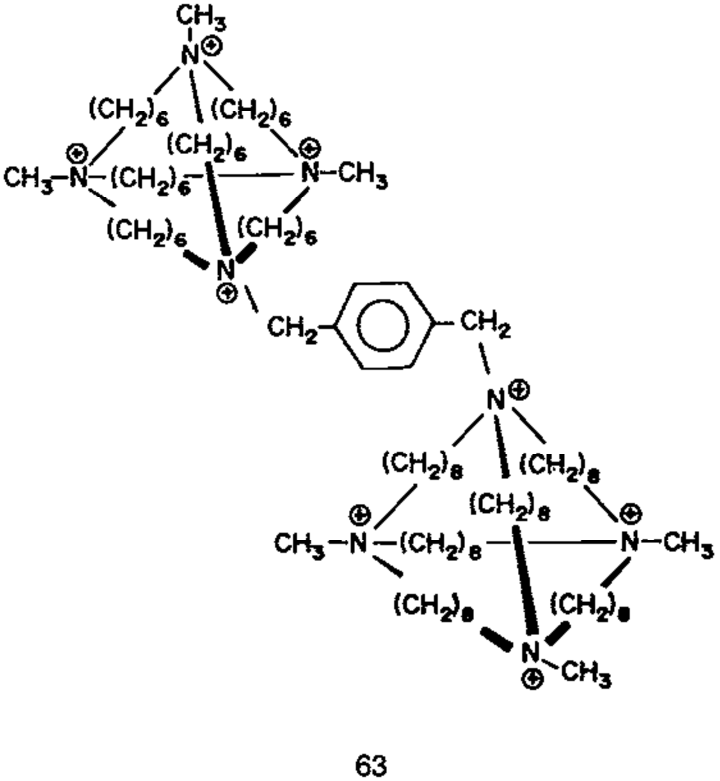


Fig. 18. Representation of the stabilities (logarithms) of the complexes between (**43**) and [glutarate]$^{2-}$ (○) and (**44**) with [pimelate]$^{2-}$ (Δ). Taken from ref. 153.

stants reported [153,205] for the binding of the oxalate^{2-} anion do not follow the above trend. Their higher values are probably affected by the presence of 2:1 oxalate^{2-} to receptor species [153]. Comparison with respect to [24]aneN_6 (**43**) [152,164] of the binding features of the ditopic ligands (**43**) and (**44**), toward dicarboxylate^{2-} anions clearly shows a gain in molecular recognition ability brought about by the separation of the binding subunits. Replacement of the dipropylenetriamine binding subunits (**43**) and (**44**) by diethylenetriamine (**42**) provides a general increase in the stability of the dicarboxylate^{2-} anion complexes [205].

Another ditopic receptor (**63**) was prepared by connecting (**60**) with (**61**) molecules by means of a *p*-xylene bridge [206] in an attempt to increase the host–guest selectivity of the single subunits. The coordinating ability of this new ligand has been tested toward a series of dicharged anions containing one carboxylate and one *o*-nitrophenolate moiety, chained at various separation lengths (Fig. 19), and compared with results obtained for (**61**) [206]. Larger stability constants were found for complexes of the ditopic receptor than for the analogous complexes of (**61**). The largest gain in stability is



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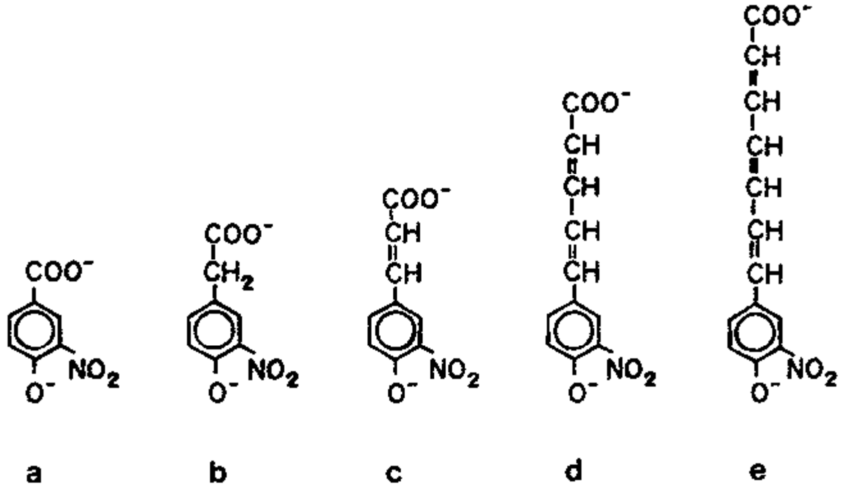

Fig. 19. *o*-Nitrophenolate moieties with anionic charges at various separation lengths.

observed for the dicharged anion (d in Fig. 19) which best matches the receptor hosting requirement [206].

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