85. Polyamines XV. Thermodynamics of Metal Complex Formation of Linear Tetraamines Containing Two Ethylenediamine Residues

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Summary

The complex formation of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Hg^{2+} with three tetraamines of type $H_2N-(CH_2)_2-NH-(CH_2)_n-NH-(CH_2)_2-NH_2$ ($=2,n,2$-tet) for $n = 2$. 3 and 4, and with N-methylethylenediamine ($=$ nmen) have been investigated at $25°$ and $I = 1(KNO_3)$. The stability constants and the heat evolved by formation of the (1:1)-complexes ML have been determined. It is shown that the more stable complexes are normally formed by 2,3,2-tet-ligands. These results are discussed relating the thermodynamic data obtained to the stereochemistry of the complexes and using the visible spectra of the complexes in solution. The change in enthalpy is found to be the dominant factor and the measure of the steric strain whereas the entropy of complex formation decreases slowly.

1. Introduction. – Linear tetraamines $2,n,2$-tet of type **I**, which contain two ethylenediamine molecules linked together by an alkylene chain ($n = 2$ and 3) through a N-atom of each molecule, have found a wide interest [1–6]. The investigations are extended here to the ligand with $n = 4$, *i.e.* 2,4,2-tet, for which the synthesis and the protonation equilibria have already been reported by us [7].

$$H_2N-CH_2CH_2-NH-(CH_2)_n-NH-CH_2CH_2-NH_2$$

I

This paper reports the stability constants and the thermodynamic data obtained under the same experimental conditions ($I = 1(KNO_3)$ and $25°$) for the formation of the (1:1)-complexes with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+}, for the ligands of type **I** (for $n = 2$, 3 and 4) as well as those for N-methylethylene-diamine ($=$ nmen). In the case of the tetraamines, the measurements are focussed in the investigation of the (1:1)-complexes, by choice of the appropriate molar ratio of the components. The species such as $[ML_2]$ [8] and $[M_2L_3]$ [9] have already been reported in the literature.

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[1])   Some results in this paper are taken from the thesis of *P. B.*, ETH Zürich, 1977.

2. Experimental. – The pure ligands [7] and metal nitrates *(p.a. Merck)* were used. All solutions were checked by quantitative standard procedures.

Alkalimetric titrations were employed for the investigation of the equilibria, and the hydrogen ion concentrations [H] were measured potentiometrically: $pH = -\log[H]$ for the chosen standard state: $I = 1(KNO_3)$ mol dm^{-3} and 25°. Only in the case of Hg(II) additional measurements of the Hg-ion concentration were necessary; these were carried out using a Hg-electrode [10] [11]. The results of titrations for different total concentrations of the metal ion ($[M]_{tot} = 1 \cdot 10^{-3} - 1 \cdot 10^{-2}$ M) and of the tetraprotonated ligands ($[H_4L]_{tot} = 1 \cdot 10^{-3} - 1 \cdot 10^{-2}$ M) were used for the calculation of the stability constants $K_1 = [ML]/([M][L])$, $K_{1,1,1} = [MHL]/([M][H][L])$, $K_{1,2,1} = [MH_2L]/([M][H]^2[L])$ as well as for nmen $K_2 = [ML_2]/([ML][L])$ and $K_3 = [ML_3]/([ML_2][L])$. The number of experimental points for each system was between 50 and 100. The constants were calculated using our programs [12] [13] and a *CDC 6400-6600* computer. Calorimetric measurements were carried out with a *LKB* reaction calorimeter *8700/2* by mixing the solutions of the tetraamine with those of the metal ion. Corrections are necessary for the protonation equilibria of the ligand and dilution of the solutions. The enthalpies were calculated from the measured evolved heats using the *CDC* computer [14].

Visible spectra of Cu(II)- and Ni(II)-complexes in solution were recorded at 25° using a *Techtron 635* spectrophotometer.

3. Results. – 3.1. *The stability constants.* – 3.1.1. *Metal complexes of nmen (Table 1).* Our values for Ni^{2+} and Cu^{2+} are in excellent agreement with those obtained by *Basolo & Murmann* [15] and by *Barbucci et al.* [16]. The values for Cd^{2+} and Hg^{2+} are new. As expected from the coordination numbers of these cations (1:1)-, (1:2)- and (1:3)-complexes are found. In the case of Hg(II), only the constant for the formation of the (1:2)-complex is observed, although also the protonated complex seems to be present ($[Hg(HL)_2]/([Hg][HL]^2) \approx 10^{12.8}$). This species was also found by *Bjerrum & Larsen* [20][2]) in the case of ethylenediamine, but the exact evaluation of its formation constant is normally complicated by the limited pH-range of the investigation, as this species is present together with other products.

3.1.2. *Metal complexes of 2,2,2-tet.* The values obtained by *Schwarzenbach* [1] for the ionic strength of 0.1, corrected for the temperature of 25° [2], are also given in *Table 2*. These are lower than our values, for $I = 1(KNO_3)$, the difference in $\log K_1$ varying between 0.74 (for Cu^{2+}) and 0.12 (for Zn^{2+}). This could be due to changes in activity coefficients with different ionic strengths. As the two ions in equilibrium (M^{2+} and [ML]$^{2+}$) have the same charge, and the activity coefficient

Table 1. *The logarithm of the stability constants of the metal complexes of* N-*methylethylenediamine at 25° and I = 1(KNO₃)* (The numbers in parentheses indicate the standard deviation in the last figures)

	$\log K_1$	$\log K_2$	$\log \beta_2$	$\log K_3$	$\log \beta_3$
Co^{2+}	5.50 (3)	4.26 (3)	9.76	1.77 (5)	11.53
Ni^{2+a})	7.31 (3)	5.81 (3)	13.12	2.27 (5)	15.39
Cu^{2+b})	10.50 (3)	8.81 (3)	19.31		
Zn^{2+}	5.66 (3)	4.52 (3)	10.18		
Cd^{2+}	5.41 (3)	4.29 (3)	9.70	1.5 (3)	11.2
Hg^{2+}			22.45 (7)		

[a]) In 0.5 M KNO₃ and 25°: $\log K_1 = 7.36$ and $\log K_2 = 5.74$ [15].
[b]) In 0.5 M KNO₃ and 25°: $\log K_1 = 10.55$ and $\log K_2 = 8.56$ [15]; $\log K_1 = 10.40$ and $\log K_2 = 8.69$ [16].

[2]) In the calculations reported in this paper a correction is necessary for the presence of supersaturated solution of Hg(OH)₂ [21].

Table 2. *Logarithm of the stability constants of the metal complexes with 2,2,2-tet at 25° and $I = 1(KNO_3)$* (Literature values of the third column are valid at 25° and $I = 0.1$(KCl) (The numbers in the parentheses indicate the standard deviations in the last figures)

	$\log K_1$		$\log \beta_{1,1,1}$	pK of $[MHL]^{3+}$
	This work	[2]		
Co^{2+}	11.31 (3)	10.90	16.68 (30)	5.37
Ni^{2+}	14.45 (5)	13.83	18.95 (20)	4.50
Cu^{2+}	20.90 (7)	20.16	24.12 (10)	3.22
Zn^{2+}	12.14 (3)	12.02	17.15 (30)	5.01
Cd^{2+a})	11.12 (5)	10.65	16.67 (30)	5.55
Pb^{2+b})	10.36 (3)		16.28 (30)	5.92
Hg^{2+c})	24.15 (7)		26.35 (10)	2.20

a) $\log K_1 = 10.4$ at $I = 0.2$ [24]. b) $\log K_1 = 10.3$ (2) at $I = 0.2$ [25]. c) $\log K_1 = 24.5$ at $I = 0.2$ [26].

depends on the charge and the radius of the species, the change in K_1 should reflect the difference of ionic sizes. Calculation of this dependence, using the values of the activity coefficients of $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$ [22] for M^{2+} and $[ML]^{2+}$, respectively, shows that a change of $I = 0.1$ to 1 causes an increase of about 0.2 in $\log K_1$. An estimate for the salting coefficient of the neutral amine [23] would also justify a further small increase of about 0.05 in $\log K_1$. Thus, the trend of the experimental values of K_1 are in conformity with the expectations. Other literature values for Cd^{2+} [24], Pb^{2+} [25] and Hg^{2+} [26], given in the footnotes to *Table 2*, are also in agreement with our values. In general not only the (1:1)-complex $[ML]^{2+}$ is formed, but also the protonated species $[MHL]^{3+}$. This is the first indication for steric hindrance in $[ML]^{2+}$. This hindrance can be reduced in acidic solutions by protonation of an apical (primary) amino group of the ligand and consequent decrease from 4 to 3 in the number of the coordinated N-atoms.

3.1.3. *Metal complexes of 2,3,2-tet.* The differences in $\log K_1$ between our values and those in the literature *(Table 3)* can be explained considering the different ionic media used. We note that *1)* as found by *Kodama & Kimura* [25] Pb(II) forms weak complexes, and *2)* the alkalimetric titration of the acidic ligand solution in presence of Hg(II) is accompanied by separation of an insoluble product which prevents the investigation of the possible formation of $[HgHL]^{3+}$.

3.1.4. *Metal complexes of 2,4,2-tet.* The complex formation with H_4L^{4+} occurs by independent coordination of the two ethylenediamine groups in two steps, with formation of $[MH_2L]^{4+}$ and $[ML]^{2+}$, respectively. Evidently in $[MH_2L]^{4+}$ only one ethylenediamine group is coordinated to the metal ion, whereas the two protons are bound to the other ethylenediamine group. The constant $K^{H_2L^{2+}}_{[MH_2L]^{4+}}$

Table 3. *Logarithm of the stability constants of the metal complexes with 2,3,2-tet at 25° and $I = 1(KNO_3)$* (The numbers in the parentheses indicate the standard deviation in the last figures)

	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}	Hg^{2+}
This work	12.20 (5)	16.00 (5)	23.20 (5)	12.60 (5)	11.05 (5)		23.28
Lit.		16.4 [8]	23.9 [8]	12.8 [8]		7.8 [25]	22.1 [26]

corresponds to *Reaction 1*, in which H_2L^{2+} is mainly monoprotonated at both and not at only one ethylenediamine group, as is the case of the protonated species

$$H_2L^{2+} + M^{2+} \rightarrow [MH_2L]^{4+} \tag{1}$$

$[MH_2L]^{4+}$. The expected values for the formation of $[MH_2L]^{4+}$ from the tautomeric form H_2L^{2+*}, in which only one ethylenediamine group is protonated, was then calculated using the values of the substituent effect of *Clark & Perrin* (*cf.* [7] [27]

$$\overset{H^+}{}\qquad \overset{H^+}{}$$
$$H_2N-(CH_2)_2NH-(CH_2)_4-NH(CH_2)_2NH_2(=H_2L^{2+*})$$
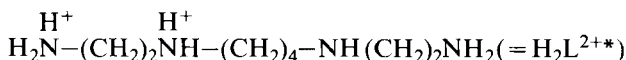
and literature cited therein) which gives: $K^{H_2L^{2+*}}_{[MH_2L]^{4+}} = K^{H_2L^{2+}}_{[MH_2L]^{4+}} \cdot 10^3$. Thus, the values of $\log K^{H_2L^{2+*}}_{[MH_2L]^{4+}}$, obtained by adding the factor 3 to $\log K^{H_2L^{2+}}_{[MH_2L]^{4+}}$ (*Table 4*) are very similar to $\log K_1$ for nmen. The difference $\log K_1$ (nmen)$-\log K^{H_2L^*}_{[MH_2L]^{4+}}$ is 0.13 for Cu^{2+}, 0.11 for Ni^{2+}, -0.11 for Zn^{2+}, -0.27 for Co^{2+} and -0.5 for Cd^{2+}, indicating that the influence of the charge $(2+)$ separated by 4 C-atoms on the stability of the complex $[MH_2L]^{4+}$ is small. The cation sequence obtained is similar to that found by *Schwarzenbach & Schneider* [27] for a substituted charged imino-diacetate, although the position of Cd^{2+} is different. The large error in $K^{H_2L}_{[MH_2L]^{4+}}$, mainly due to the low concentration of $[MH_2L]^{4+}$ which was always $<12\%$ of $[M]_{tot}$, does not allow a detailed discussion of this result.

Further deprotonation of $[MH_2L]^{4+}$ takes place in 'one step', *i.e.* without formation of the species $[MHL]^{3+}$. As soon as a third donor atom of the ligand is coordinated to M^{2+}, the last proton is split off immediately because of the improved stability by chelate ring formation and of the acidifying effect of the neighbouring positive charge of the ammonium group present in $[MHL]^{3+}$. In some cases also the complex $[M_2L]^{4+}$ has been detected $(\beta_{2,0,1} = [M_2L]/([M]^2[L]);\ \log\beta_{2,0,1} = 13.7$ (Ni^{2+}) and $11.15\ (Cd^{2+}))$. The formation of this species is an indication that, for this system, the $(1:1)$-complex shows no special preference to bind both ethylene-diamine groups with the same central ion, *i.e.* in presence of free metal ion *Reaction 2* takes place.

$$[ML]^{2+} + M^{2+} \rightarrow [M_2L]^{4+} \tag{2}$$

Table 4. *Logarithm of the stability constants of the metal complexes with 2,4,2-tet at 25° and $I=1(KNO_3)$* (The numbers in the parentheses indicate the standard deviations in the last figures)

	$\log K_1$	$\log K^{[ML]^{2+}}_{[M_2L]^{4+}}$	$\log\beta_{1,2,1}$	$\log K^{H_2L^{2+}}_{[MH_2L]^{4+}}$	pK of $[MH_2L]^{4+}$
Co^{2+}	9.01 (3)	–	22.9 (2)	2.77	6.65
Ni^{2+}	12.38 (3)	1.3	24.55 (20)	4.42	6.0
Cu^{2+}	19.34 (3)	–	27.50 (20)	7.37	4.1
Zn^{2+}	9.80 (3)	–	22.9 (2)	2.77	6.65
Cd^{2+}	8.95 (5)	2.2	23.05 (20)	2.92	7.05
Hg^{2+}	22.2 (1)	–	31.5 (3)	11.4	4.6

Table 5. *Spectral data for the Cu-complexes with 2, n, 2-tet*

n	λ_{max} (nm)	ε_{max}	$-\Delta H_{calc.}$	$-\Delta H_{exp}$
2	585	112.5	20.5	21.4
3	525	74.2	27.9	26.5
4	550	48.3	24.6	20.6

3.2. *The spectra.* For the three tetraamines, the solution with a (1:1)-molar ratio (metal/amine) contains only the complex $[ML]^{2+}$. The observed maxima in the wavelength λ_{max} [nm] and the molar absorption coefficient ε_{max} for the Cu(II) complexes are given in *Table 5*. While, the 2,3,2-tet-complex shows a maximum at lowest wavelength ($\lambda_{max} = 525$ nm), as recognized by the pink color of its solution. The solutions of the other two complexes show different colours, *i.e.*, violet to blue.

This absorption corresponds to three different spin-allowed transitions $^2B_{1g} \rightarrow ^2A_{1g}$, $^2B_{1g} \rightarrow ^2B_{2g}$ and $^2B_{1g} \rightarrow ^2E_g$ [4]. The values of λ_{max} of these amine complexes can be used for the calculation of the enthalpy of complex formation using an empirical relationship ($-\Delta H = -43.56 + 3.75 \cdot 10^4/\lambda_{max}$) obtained by *Paoletti et al.* [28], *Fabrizzi et al.* [29] and *Kennedy & Lever* [30]. The calculated ΔH-values are given in *Table 5*.

In the case of the Ni(II), the situation is complicated because two (1:1)-complexes for each ligand are formed, having a square planar $[NiL]^{2+}$ and an octahedral structure $[NiL(H_2O)_2]^{2+}$, respectively. An increase of the temperature or of the ionic strength favours the formation of the square planar complex ion according to *Reaction 3*, due to the parallel decrease of the activity of water. The spectral data obtained are summarized in *Table 6*. The square planar species show only one band

$$[NiL(H_2O)_2]^{2+} \rightleftharpoons [NiL]^{2+} + 2 H_2O \tag{3}$$
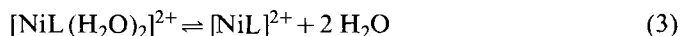
which corresponds to three spin-allowed transition: $^1A_{1g} \rightarrow ^1A_{2g}$, $^1A_{1g} \rightarrow ^1B_{1g}$, $^1A_{1g} \rightarrow ^1E_g$. In the case of octahedral complexes one expects three spin-allowed $^3A_{1g} \rightarrow ^3T_{2g}$ (expected λ_{max}: 800–1000 nm), $^2A_{2g} \rightarrow ^1E_g$ (700–800 nm), $^3A_{2g} \rightarrow ^3T_{1g}$(F) (500–600 nm) and eventually the spin-forbidden $^3A_{2g} \rightarrow ^3T_{1g}$(P) ($\approx 360$ nm) transi-

Table 6. *Spectral data for the Ni-complexes with 2, n, 2-tet* (Absorbance (A) for 0.002M solutions with 10 cm path length at λ_{max})

2, n, 2-tet		n = 2	n = 3	n = 4	Conditions
$[NiL]^{2+}$	λ_{max}	440	450	455	
	A	0.09	0.35	0.13	I = 1, 25°
	A	0.12	0.49	0.15	I = 2.5, 40°
$[NiL(OH_2)_2]^{2+}$	λ_{max}	560	550	555	
$^3A_{2g} \rightarrow ^3T_{1g}$ (F)	A	0.15	0.18	0.15	I = 1, 25°
	A	0.14	0.13	0.10	I = 2.5, 40°
	λ_{max}	360	345	355	
$^3A_{2g} \rightarrow ^3T_{1g}$ (P)	A	0.18	0.23	0.2	I = 1, 25°

tions [4] [31]. In general only some of these transitions can be identified in unequiv-
ocal manner. Values for the shoulder at 550 nm and the band at 350 nm are given
in *Table 6* for *a*) I = 1(KNO$_3$) and 25°, and *b*) I = 2.5 (KNO$_3$) and 40°. Under the
latter conditions the planar complex [NiL]$^{2+}$ prevails: our data allow the rough
estimation of the concentrations of both Ni(II)-complexes at I = 1(KNO$_3$) and 25°.
The highest amount of the planar complex is found in the case of [Ni(2,3,2-tet)]$^{2+}$
30–50%; 25% [34] and 50% [35]). Its solution is yellow, whereas those of the other
two Ni(II)-complexes have a bluish tinge and contain only 20–40% [Ni(2,4,2-tet)]$^{2+}$
and 10–20% [Ni(2,2,2-tet)]$^{2+}$.

4. Discussion. – The thermodynamic data will be discussed by comparing the
values of log $K_n (\Delta G_n)$, ΔH_n and ΔS_n *(Table 7)* for the same metal ion, the same
reaction step and for similar ligands, *i.e.* *N*-methylethylenediamine and ethylene-
diamine or the three tetraamines. The differences in these quantities afford a
measure of the steric strain due, in the first case, to the bulky methyl group and,
in the second, to the introduction of one or two methylene groups, *i.e.* on going
from a five- to a six- and to a seven-membered chelate ring. A correction of
$K_n (\Delta H_n)$ will be made for the different basicities of the ligands, taking into con-
sideration the linear dependence of $K_n (\Delta H_n)$ on the basicity of ligands with the
same donor systems [13] [36]. This means, that without steric effects, the values
within the two groups of ligands should be practically identical in magnitude.

4.1. N-*Methylethylenediamine (= nmen)*. The correction for the difference in
basicity between en and nmen can be neglected because the overall protonation
constants κ_2 are very similar (10$^{17.66}$ for en [37] and 10$^{17.72}$ for nmen). The constants
for *N*-methylethylenediamine are, in general, lower than those for ethylenediamine
[17]. The decrease ranges from 0.2 to 0.4 for log K_1, 0.3 to 0.63 for log K_2 and 0.57
to 2.15 for log K_3. This could be mainly due to steric hindrance, because of the
presence of the bulky methyl group in nmen which, in the case of Zn^{2+}, prevents
the formation of the (1:3)-complex. Generally, the decrease in log K_n is larger for
smaller cations. A similar trend has been observed with other methyl-substituted
ligands [18] [19]. A comparison of the enthalpies of complex formations with nmen
shows that, in each step, ΔH_n is between 1.5 and 3 kcal mol^{-1} less negative, *i.e.*
the change in ΔH is much larger than that in ΔG ($-1.364 \cdot \log K$) but it is com-
pensated by a larger entropy of complex formation by about 5 to 10 cal mol^{-1} K^{-1}.
This can be interpreted in terms of a stronger endothermic dehydration of the
central ion by complex formation with nmen due to the bulky methyl group giving
a larger number of liberated water molecules than in the case with ethylenediamine.

4.2. *2,2,2-tet, 2,3,2-tet and 2,4,2-tet.* In the *Figure* are plotted the values of
$-\Delta G_1$, the increase in $-\Delta H_1$ and in TΔS_1 for the formation of [M(2,3,2-tet)]$^{2+}$
and [M(2,4,2-tet)]$^{2+}$ with respect to that of [M(2,2,2-tet)]$^{2+}$, taking the value of
$-\Delta G_1$ for [M(2,2,2-tet)]$^{2+}$ as origin. In this way the variation of $-\Delta G_1$ for the
formation of the complex with 2,n,2-tet (n = 3,4) with respect to that with 2,2,2-tet
is directly compared with the corresponding enthalpic and entropic changes. For
instance, the full straight line representing $-\Delta G_1$ shows that for Hg(II) this quantity
decreases on going from n = 2 to n = 3: this is due to the decrease in $-\Delta H_1$ (pointed
straight line) being larger than the increase in TΔS_1 (dotted straight line). The

Table 7. *Thermodynamic data of the complex formations at 25° and I = 1(KNO₃)* (ΔH and ΔS in kcal mol⁻¹, ΔS in cal mol⁻¹ K⁻¹)

		Co²⁺	Ni²⁺	Cu²⁺	Zn²⁺	Cd²⁺	Hg²⁺
nmen	ΔG_1		− 10.0	− 14.3	− 7.7	− 7.4	
	ΔH_1	a)	− 6.95	− 10.8	− 2.9	− 4.55	
	ΔS_1		10.2	11.8	16.2	9.5	
	ΔG_2		− 17.9	− 26.3	− 13.9	− 13.2	− 30.7
	ΔH_2	a)	− 15.15	− 22.6	− 6.55	− 10.6	− 26.4
	ΔS_2		9.2	12.4	24.6	8.8	14.0
2,2,2-tet	ΔG_1	− 15.4	− 19.7	− 28.5	− 16.6	− 15.2	− 32.9
	ΔH_1	− 10.6	− 13.6	− 21.4	− 8.7	− 9.8b)	− 29.6c)
	ΔS_1	16.1	20.6	24.0	26.4	18.1	11.3
2,3,2-tet a)	ΔG_1	− 16.6	− 21.8	− 31.6	− 17.2	− 15.1	− 31.8
	ΔH_1	− 13.5	− 16.9	− 26.5	− 11.6	− 11.1	− 26.2
	ΔS_1	10.3	16.5	17.3	18.6	13.5	18.6
2,4,2-tet	ΔG_1	− 12.3	− 16.9	− 26.4	− 13.4	− 12.2	− 30.3
	ΔH_1	− 9.7	− 13.2	− 20.6	− 7.4	− 7.4	− 23.6
	ΔS_1	8.8	12.5	19.3	19.2	16.0	22.4

a) Unexpected values are obtained, probably because of reaction of the complexes with oxygen.
b) $\Delta H_1 = -9.2$; $\Delta S = 19$ at I = 0.1 [24].
c) $\Delta H_1 = -30.2$ (5); $\Delta S_1 = 11$ (3) at I = 0.2 [26].
d) Values for I = 0.5 are given by *Fabbrizzi et al.* [3].

$(-\Delta G_1)$-plots show that for the 3d-cations and Zn²⁺, 2,3,2-tet forms the most stable complexes. This effect was observed by *Fabbrizzi et al.* [3] for Cu²⁺, Ni²⁺ and Zn²⁺ and explained by a decrease of steric strain by alternation of the ring size, *i.e.* the difficulty in ring formation for 2,2,2-tet is strongly reduced in 2,3,2-tet because the ring-size sequence 5,5,5 in the former is modified to 5,6,5 in the latter ligand [4]. This explanation did not take into account the effect of the ligand basicity on the stability of the metal complexes. The overall protonation constant κ_4 of 2,n,2-tet greatly increases with increasing n ($\log \kappa_4 = 30.74$ (n = 2), 33.22 (n = 3) and 34.45 (n = 4)). Thus a proportional increase of $\log K_1$ could be expected. Using the data for substituted ethylenediamines [13], for the Cu(II)-complexes, an increase in $\log K_1$ of 2.0 on going from 2,2,2-tet to 2,3,2-tet and of 1.0 from 2,3,2- to 2,4,2-tet is estimated. This effect would explain the K_1-value of [Cu(2,3,2-tet)]²⁺. For [Cu(2,4,2-tet)]²⁺ the expected $\log K_1$ (23.9) is much higher than the experimental value (19.34) suggesting the presence of strong steric strain. The values of K_1 of the other cations can be explained in a similar way, although for them data are not sufficient to estimate the increase of K_1 caused by an increase of ligand basicity [13]. Furthermore the complexes of the same composition can often assume structures other than the square planar. Additionally, in the case of Ni(II) the equilibrium between octahedral and square planar complexes contributes to K_1. Probably partly for these reasons the change in K_1 is generally less drastic than in the case of the Cu(II)-complexes. In the extreme case of Cd and Hg the values of K_1 show a decrease on going from [M(2,2,2-tet)]²⁺
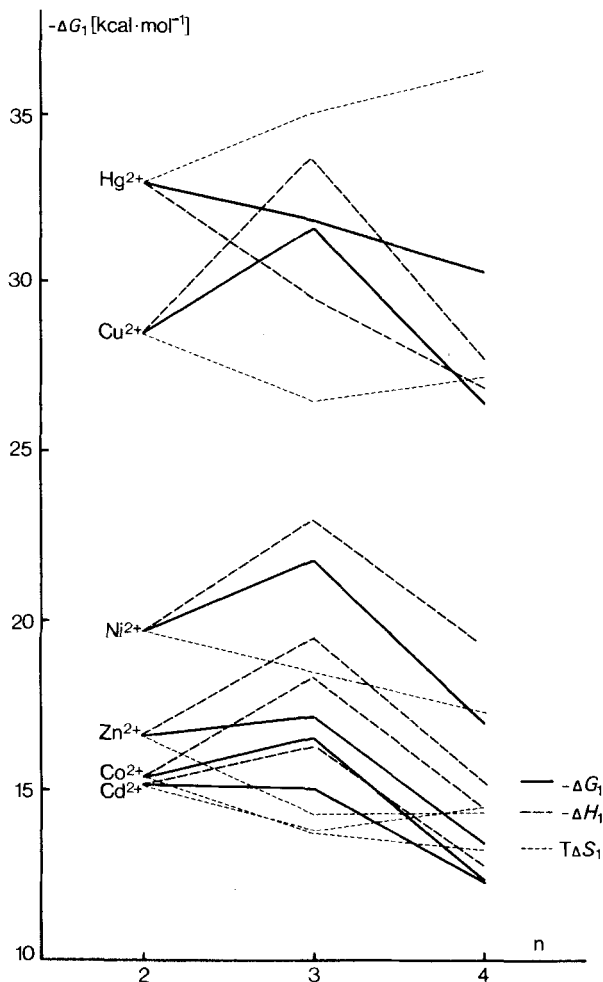
Figure. *Values of* $-\Delta G_1$, $-\Delta H_1$- *and* $T\Delta S_1$ *for the formation of the* (1:1)-complexes of 2,2,2-tet with metal ions vs. *the number of methylene groups n* (see also the text)

to $[M(2,4,2\text{-tet})]^{2+}$. Both cations are much larger than the divalent 3d-cations and can show different coordination geometries.

It is established that a decrease in ΔG_1 always corresponds to a decrease of ΔH_1, *i.e.* the change in K_1 originates primarily from differences in the enthalpy of complex formation. This justifies the interpretation mentioned above, *i.e.* that the observed trend is mainly caused by steric effects. For complexes with known crystal structure, it is possible, by use of empirical force-field calculations, to esti-mate the different strain contributions to verify the sign and the magnitude of the variation in ΔH_1. In the case of several Ni(II)-polyamine complexes crystal-structure data are known and therefore this method has been applied [38] [39].

The more important contributions are found to be, first, the deformation of the valence angle N–M–N, and then the non-bonded interactions, while minor contributions arise from torsional strain and bond elongation. As already claimed [7], the situation should be very similar in the case of the Cu(II)-complexes, with the further restriction due to the formation of almost planar complexes with tetraamines. As indicated by the structural data of the (2,2,2-tet)- and (2,3,2-tet)-complexes [5] [6] the Cu,N-bond distances are insensitive to steric strains. The larger negative ΔH_1-value of the complex formation with 2,3,2-tet should then reflect 1) a less distorted structure in which the angle between the trans-N,M,N-bonds is close to 180°, 2) the almost planar structure of the CuN_4-unit [6] and 3) the difference in ligand basicity.

Although the ΔH_1- and ΔG_1-variations are not so large, the change in ΔH_1 for the other 3d-cations as well as for Zn^{2+} and Cd^{2+} can be interpreted in a similar way. Figure shows a decrease for the entropic term $T\Delta S_1$, with exception of Hg(II). The ΔS_1-decrease depends on the cation and amounts from 2 to 8 cal mol^{-1} K^{-1}. This could be due to the increase of the standard ligand entropy after addition of one or two methylene groups but other reasons cannot be excluded such as variations in the denticity of the ligand, in the number of coordinated water molecules or in the rigidity of the coordinated ligand, depending upon changes of the coordination geometry of the complex. Only the exact determination of the structure of the complex ion would allow to make a distinction of the different contributions. The more unexpected ΔS_1 values are those of the complexes with Hg(II), in which the entropy of complex formation, in contrast to all other cases, increases with n. This can be explained by a parallel increase in the number of H_2O-molecules liberated by complex formation with the change of the coordination geometry from octahedral for $[Hg(2,2,2-tet)(H_2O)_2]^{2+}$ to tetrahedral for $[Hg(2,4,2-tet)]^{2+}$. This endothermic release of water molecules could contribute to the observed decrease of $-\Delta H_1$ by 6 kcal mol^{-1}.

Comparison of the stability constant K_1 of $[M(2,n,2-tet)]^{2+}$ with β_2 of $[M(nmen)_2]^{2+}$ shows that the chelate effect Chel[3] ($= \log K_1 - \log \beta_2$) is positive for all complexes of 2,2,2-tet and 2,3,2-tet, and negative for those of 2,4,2-tet. For the 3d-cations and Zn^{2+} it amounts to 1.7 ± 0.3 for the first, 3.2 ± 0.7 for the second and -0.5 ± 0.4 for the third ligand. The data for Ni^{2+} and Cu^{2+} of Table 7, show that for 2,2,2-tet Chel is only due to an entropy effect. In this context the data for Zn^{2+} cannot be used because the (1:2)-complex with nmen seems to have a tetrahedral structure as found for that with en [40] [41]. The entropy of the $[Zn(nmen)_2]^{2+}$ formation is indeed much higher with respect to that of the other cations (Table 7), indicating the liberation of a larger number of H_2O-molecules. This last process is endothermic and makes its enthalpy ΔH_2 more positive respect to ΔH_1 for the octahedral $[Zn(2,2,2-tet)(H_2O)_2]$-complex in contrast with the corresponding values of the Cu^{2+}- and Ni^{2+}-complexes. In the case of $[Zn(en)_2]^{2+}$, its tetrahedral structure was firstly postulated on the basis of thermodynamic results [40] and recently corroborated by X-ray diffraction in solution [42]. Also

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[3]   This definition of Chel [44] compares the stability constants of two ligands with different basicity. The consequences of this oversimplification will not be discussed here.

the data for the complex formation of nmen and 2,2,2-tet with $Hg(II)$ show the same trend as with $Zn(II)$. This leads us to propose a tetrahedral structure for $[Hg(nmen)_2]^{2+}$ similar to that found for $[Hg(en)_2]^{2+}$ in the solid perchlorate [44], while $[Hg(2,2,2-tet)(H_2O_2)]^{2+}$, as already discussed, seems to be octahedral.

The data of Ni^{2+} and Cu^{2+} show that, for (2,3,2-tet)-complexes, *Chel* contains not only an entropic contribution of 1.6 but also an enthalpic contribution ($\log K$) of 1.2 (Ni^{2+}) and 2.9 (Cu^{2+})[4]).

Finally, in the case of the complex formation with 2,4,2-tet *Chel* becomes equal to zero (Cu^{2+}) or is negative (Zn^{2+}) as a consequence of the strong drop of $-\Delta H_1$, making the enthalpic contribution negative (≈ -1.5) and not very different in magnitude from the entropic term ($\approx +1.2$). In conclusion, the variation of the stability of complexes with variable chelate ring size is mainly regulated by the variation of the enthalpic term which is already unfavourable for seven-membered chelate rings. Similar results have already been obtained with the series of homologous ligands of ethylenediaminetetraacetic acid [45] and of N,N'-bis(2-pyridyl-methyl)ethylenediamine [46].

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