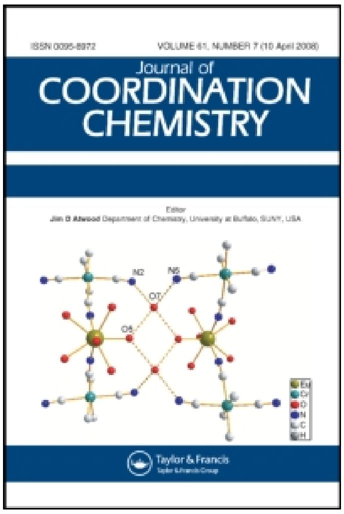

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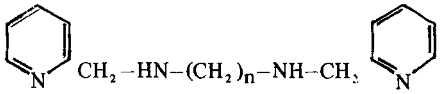
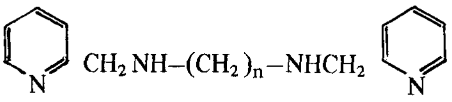
The complex formation of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Ag^+ with three amines of the type with n values from 2 to 4, has been investigated. The stability constants and the heats evolved by formation of the 1:1 complexes have been determined. The thermodynamic data are discussed in relation of the preferred stereochemistry of the cation and of the steric requirements of the ligands using also visible spectra of solutions, i.r. and reflection spectra of solid complex salts.



INTRODUCTION

In connection with our investigations of complex formation of ligands containing pyridyl residues,[1] we report the results with three homologues tetra-amine ligands of the type of N,N′-bis-(2-pyridyl-methyl)-α,ω-diaminoalkane(I) for n = 2, 3 and 4.



n = 2:DPEN; n = 3:DPTN; n = 4:DPTE (I)

These compounds form 1:1 complexes ML by coordination of the four nitrogen donors, which involve a system of three condensed chelate rings. By increase of n the size of the middle ring is varied from a five- to a seven-membered ring. These ligands show a similar tendency for complex formation as the analogous aliphatic tetra-amines(II) (Table I).

$$H_2NCH_2CH_2NH\text{–}(CH_2)_n\text{–}NHCH_2CH_2NH_2 \quad (II)$$

n = 2:2,2,2-tet; n = 3:2,3,3-tet

As demonstrated by Paoletti and coworkers[2] the increase in stability constants of these complexes by increase of the number n of methylene groups from 2 to 3 can be explained for Cu^{2+} and Ni^{2+} with the diminution of the accumulated steric strain by alternation of ring size. The ring sequence is 5,5,5 for the complexes of 2,2,2-tet and 5,6,5 for those of 2,3,2-tet. Indeed the complex formation becomes more exothermic, whereas the reaction entropy remains almost constant. No similar general trend is observed for the aromatic ligands. Because of the lower affinities of the latter ligands towards hydrogen ions the aromatic compounds bind metal ions more strongly near the neutral and the acid ranges.

The complexes with Hg^{2+}, Ni^{2+} and Cu^{2+} are too stable to be investigated with the usual pH method.[5] For Hg^{2+} the concentration of the free metal ion in the equilibrium solution has been obtained by use of a mercury electrode.[6] For the last two cations competition equilibria (1) and (2) are then used, in which a second metal ion

$$M(EDTA)^{2-} + Ca^{2+} + H_2L^{2+} \rightleftharpoons Ca(EDTA)^{2-} + ML^{2+} + 2H^+ \quad (1)$$

$$M^{2+} + HgL^{2+} \rightleftharpoons ML^{2+} + Hg(OH)_2 + 2H^+ \quad (2)$$

TABLE I

Logarithm of the stability constants of the 1:1 complexes of ligands of type (I) and (II) at 25° C and ionic strength 0.1 (KNO_3).

Ligand	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}	Ag^+
DPEN	5.60	11.96	14.48[a,b]	17.03[a]	11.13	9.66	19.1	6.15
DPTN	4.45	11.18	14.2	18.35	10.33	8.58	18.8	6.12
DPTE	2.57	7.95	11.13	15.54	7.68	7.04	17.52	5.82
2,2,2-[c] tet	4.9	10.92	13.78	20.09	12.0			
2,3,2-[d] tet		12.2	16.0	23.2	12.6	11.1		

[a] determined using equilibrium (1)
[b] determined using equilibrium (2)
[c] Reference 3
[d] Reference 4.

TABLE II

Stability constants[a] in relation with the competition equilibria (1) and (2) (I = 0.1 (KNO_3) and t = 25°C).

Ligand	Method	Cation	Number exper. points	log K_1	log K_2	log K_3	log K_4
EDTA	pH	H^+	146	10.25(2)	6.16(2)	2.77(5)	2.2(1)
	pH	Ca^{2+} [c]	46	10.73(5)			
	comp.[b]	Cu^{2+}	22	19.00(5)			
	comp.	Ni^{2+}	25	18.52(5)			
tren	pH	H^+	93	10.11(2)	9.42(2)	8.39(2)	
	pH	Cu^{2+} [d]	70	18.86(5)			
	pH	Ni^{2+}	30	14.50(5)			

[a] In parentheses three times the standard deviation of the last digit
[b] comp: From measurements of the equilibrium: $M(EDTA)^{2-} + Ca^{2+} + H_3tren^{3+} \rightleftarrows Mtren^{2+} + Ca(EDTA)^{2-} + 3H^+$ [7]
[c] log([CaHL]/([Ca] [HL])) = 3.42(5)
[d] log([CuLOH] [H]/[CuL]) = 9.01(4)

(Ca^{2+}, Hg^{2+}) and a second ligand (EDTA, OH^-) are involved. This has also demanded the determination of some stability constants (Table II) of the species present in the mixtures in which reactions (1) and (2) take place.

For DPEN Lacoste and Martell[8] as well as Gruenwedel[9] have published the values of the stability constants of some 1:1 complexes. Cobalt(III), nickel(II), copper(II) and palladium(II) compounds of DPEN and DPTN have been described by Gibson and McKenzie.[10]

EXPERIMENTAL

a. Determination of Stability Constants

For the investigation of the equilibria in solution potentiometric measurements of pH and of pHg were done using an Orion digitalvoltmeter 801. Beckman (40498) or Philips (GA 110) glass electrode, 0.1 M calomel electrode and a salt bridge containing 0.1 M KNO_3 were used following the procedure previously described.[5,6] The protonation constants were derived from 108 experimental points for DPEN, 139 for DPTN and 75 for DPTE. For the metal ion equilibria, normally more than 40 experimental points are used (for Ag(I) 150 to 200 and for Hg(II) 100). The ratio between the total concentration of the metal ion (10^{-3}–10^{-2} M) and ligand (10^{-3} M) was 10:1, 1:1 and 1:2. The methods of calculations are described elsewhere.[6,7,11,12] In all cases appropriate programs[13] on a CDC (6500–6400) computer are used.

b. Calorimetric Measurements

The measurements were carried out with an LKB 8700/2 titration calorimeter. Solutions containing strong acid or the metal ion were titrated with a 0.05 M solution of the ligand. The heat changes corrected for the heat of dilution were calculated. The composition of the solution before and after the reaction is calculated by use of a program[14] and permits the calculation of the enthalpies involved.

c. Preparation of the Ligands

The ligands were prepared from pyridine-2-carbaldehyde and the diamine by the methods of Lacoste and Martell[8] and of Goodwin and Lions.[15] The best method of separation, giving the highest yield of the amine, is the treatment of the ethanolic solution of the amine with an ethanolic HCl solution. The tetrahydrochlorides can be purified by dissolving the product in the smallest volume of hot water and adding ethanol till the crystallisation begins. Also the tetrahydronitrates can be obtained after neutralization of the amine with nitric acid.

Analysis of the tetrahydronitrates:
DPEN$\cdot$4 HNO_3(494.4)
M.P. 175–177°
Calcd. for DPEN$\cdot$4 HNO_3: C,34.01; H,4.49; N, 22.67.
Found C,33.87; H,4.55; N,22.51.

DPTN$\cdot$4 HNO_3 (508.6)
M.P. 155–157°
Calcd. for DPTN$\cdot$4 HNO_3: C,35.43; H,4.76; N, 22.04.
Found C, 35.28; H, 4.72; N, 21.85.

DPTE$\cdot$4 HNO_3 (522.6)
M.P. 200–202°
Calcd. for DPTE 4$\cdot HNO_3$: C, 36.78, H, 5.02; N, 21.45.
Found C, 36.79; H, 5.04; N, 21.46.

d. Preparation of Complex Salts

Only substances not previously described in the literature are taken into consideration.

$Ni(DPEN)(ClO_4)_2$ and $Ni(DPTN)(ClO_4)_2$ 4 ml of a 0.25 M ligand solution were added to 2 ml of a 1 M $Ni(ClO_4)_2$ solution and the blue solution evaporated to 1.5 ml and saturated with $NaClO_4$. After two days at −10°C, the microcrystalline product is filtered, washed with ice cooled water and absolute ethanol. The product is dried over H_2SO_4. Yield 47%.

Anal. Cald. for $Ni(DPEN)(ClO_4)_2 \cdot 2\ H_2O$: C, 31.42; H, 4.12; N, 10.45; Ni, 10.95.
Found: C, 31.25; H, 4.04; N, 10.35; Ni, 10.71.
i.r. data†): 3450 s. H_2O, 3305 s. I, 2920, 1609 s. II, 1572 m. II, 1486 m., 1445 s., 1339 m., 1297 s., 1090 br. s., 1022 s., 930 s., 763 s., 720 m., 620 s. III.

Anal. Cald. for $Ni(DPTN)(ClO_4)_2 \cdot 3\ H_2O$: C, 31.72; H, 4.61; N, 9.86; Ni, 10.33.
Found: C, 31.25; H, 4.10; N, 9.86; Ni, 9.82.
i.r. data: 3450 s. H_2O, 3300 s. I, 3265 s. I, 3075 m., 2940 s., 2880 s., 1612 s. II, 1576 s. II, 1480 s. II, 1447 s., 1352 m., 1294 s., 1100 br. s., 900 s., 768 s., 757 s., 718 m., 620 s.

Cu(II) complexes as perchlorates Warm solutions of copper(II)perchlorate (0.02 M; 5 ml) in water and ligand (1 mmole) in water (2 ml) were mixed. By cooling crystals are deposited. After recrystallisation from water, the product is filtered and dried at 110°C in vacuo. The anhydrous salts are obtained.

Anal. Calcd. for $Cu(DPEN)(ClO_4)_2$: C, 33.31; H, 3.49; N, 11.10; Cu, 12.62.
Found: C, 33.53; H, 3.69; N, 11.60; Cu, 13.33.
i.r. data: 3250 s. I, 3080 w., 2965 m, 2940 m., 2890 w., 1615 s. II, 1570 s. II, 1482 s, II, 1450 m., 1370 m., 1298 m., 1090 br. s., 992 s., 931 m., 762 s., 730 s., 620 s. III.

Anal. Calcd. for $Cu(DPTN)(ClO_4)_2$: C, 34.72; H, 3.89; N, 10.89; Cu, 12.27;
Found: C, 34.55; H, 3.87; N, 10.62; Cu, 11.68.
i.r. data: 3255 s. I, 3090 w., 2940 m., 2890 m., 1614 s. II, 1572 m. II, 1483 s. II, 1450 s., 1433 s., 1291 m., 1100 br. s., 930 m., 762 s., 730 m., 620 s., III.

Anal. Calcd. for $Cu(DPTE)(ClO_4)_2$: C, 36.06; H, 4.16; N, 10.52; Cu, 11.91.
Found: C, 36.08; H, 4.14; N, 10.54; Cu, 11.66.
i.r. data: 3235 s. I, 3095 w., 2925 s., 2875 s., 1618 s. II, 1576 m., 1490 m., 1477 m., 1454 s., 1299 m., 1100 br. s., 928 m., 788 m., 768 s., 728 m., 620 s. III.

$Hg(DPEN)(Cl_4)_2$ and $Hg(DPTE)(ClO_4)_2$ 10 ml 0.1 M ligand solution were heated and added to 1.5 ml 0.67 M $Hg(ClO_4)_2$ and 1 ml 0.1 M $HClO_4$. To avoid precipitation some concentrated perchloric acid was added if necessary. By cooling crystals (white needles) are obtained. After recrystallisation from 10 ml water the product was dried over H_2SO_4. For

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†s: strong
m: medium
w: weak
br: broad

DPTE firstly a yellow rubber-like substance was separated, which became a crystalline product over standing. Yield 80%.

Anal. Calcd. for Hg(DPEN)(ClO_4)$_2$: C, 26.63; H, 2.86; N, 8.92; Hg, 31.26.
Found: C, 28.00; H, 3.06; N, 9.44; Hg, 31.05.
i.r. data: 3257 s. I, 3090 w., 2925 m., 2875 m., 1600 s., II, 1572 m. II, 1480 m., 1455 s., 1438 s., 1385 m., 1300 m., 1260 m., 1155 s., 1090 br. s., 1010 s., 878 m., 769 s., 725 w., 632 m., 628 s.

Anal. Calcd. for Hg(DPTE)(ClO_4)$_2$: C, 28.72; H, 3.19; N, 8.38; Hg, 29.95.
Found: C, 28.41; H, 3.31; N, 8.44; Hg, 27.26.
i.r. data: 3240 s. I, 3080 w., 2928 s., 2860 s., 1603 s. II, 1573 m. II, 1482 m. II, 1440 s., 1367 m., 1294 m., 1090 br. s., 924 m., 761 s., 722 m., 630 w. sh., 620 s. III.

Anal. Calcd. for Ag(DPEN)(ClO_4)$_2$: C, 35.95; H, 4.31; N, 11.98.
Found: C, 35.78; H, 3.85; N, 12.05.
i.r. data: 3258 s. I, 3050 w., 2890 s., 2835 s., 1594 s. II, 1570 m. II, 1434 s., 1382 s., 1373 m., 1282 m., 1093 br s., 1008 m., 972 m., 877 m., 770 s., 730 w., 620 s. III.

e. Miscellanea

Electrical conductivity measurements were made at 25°C using a Metrohm conductometer E 382.

Electronic spectra Solution spectra were recorded at room temperature using a Cary spectrophotometer. Reflectance spectra were obtained by use of a Cf 4 DR spectrophotometer (Optica, Milano). The i.r. spectra of Table IX were recorded with a Beckman IR 12 spectrophotometer by Dr. A. Wehrli and the others (mentioned in the experimental part) with a Perkin Elmer spectrophotometer model 257.

f. Vibrational Spectra

The vibrational spectra of solid salts of nickel(II), copper(II), mercury(II) and silver(I) have been used to detect eventual non coordination of the nitrogen donor atoms of the ligands.[16] The coordination with pyridyl groups is easily characterised because displacements of following bands occur:

a) the pyridyl ring vibration II (see Table III) at ca. 1590 cm^{-1} in the free ligand appears in the complex salts at 1610 cm^{-1};

b) the pyridine in plane IV and out plane V vibrations. We have found that for nickel(II) and copper(II) coordination of both pyridyl groups takes place. For mercury(II) the displacement of II is of only 9 cm^{-1}, but coordination of both pyridyl groups has been proved by comparison of spectra with those of [Hg(DPEN)Br] Br. This compound is a 1:1 electrolyte in nitromethane and shows a non coordinated pyridyl group with a band II at 1594 cm^{-1}. For silver(I) no coordination of the pyridyl groups takes place. Here the NH frequencies, which are complicated by hydrogen bonding, give no sure information of nitrogen coordination.[16] Table III contains exclusively the spectra of salts with DPEN as ligand. No significant changements take place by substituting DPEN with DPTN or DPTE.

TABLE III

Characteristic i.r. frequencies of DPEN complex compounds (cm^{-1})

	I	II	III	IV	V
DPEN	3290	1590 1569	–	610	403
Ni(DPEN)(ClO_4)$_2$	3259	1606 1569	624	631	427
Cu(DPEN)(ClO_4)$_2$	3257	1612 1571	624	631	424
Hg(DPEN)(ClO_4)$_2$	3257	1599 1572	628	632	413
[Hg(DPEN)Br] Br	3283 3250	1598 1594 1572	–	622 639	411
Ag(DPEN)ClO_4	3258	1594 1570	628	634	409

I: N–H st; II: pyridin ring deformation vibration;
III: $\nu_4(ClO_4)$; IV: pyridin ring in plane; V: pyridin ring out of plane.

RESULTS AND DISCUSSION

1. Thermodynamic Data of Protonation

The values of the enthalpy of protonation ΔH_1 (Table IV) lie between those for aliphatic nitrogen donors of approximately – 12 kcal/mol and those for pyridine nitrogen donors of about – 5 kcal/mol.

$$L + H^+ \rightleftharpoons HL^+ \quad \kappa_1 = [HL]/([H][L]);\ \Delta H_1 \tag{3}$$

$$L + 2H^+ \rightleftharpoons HL^{2+} \quad \kappa_2 = [H_2L]/([H]^2[L]);\ \Delta H_2 \tag{4}$$

Spectrophotometric data have evidenced for all three ligands, that protonation firstly occurs at the aliphatic nitrogen donors therefore ΔH_1 and ΔH_2 are

TABLE IV

Thermodynamic data of protonation of the ligands at 25°C and I = 0.1 (KNO_3). ΔH and ΔG in kcal/mol and ΔS in cal/(K . mol)

	DPEN		DPTN		DPTE	
	i = 1	i = 2	i = 1	i = 2	i = 1	i = 2
$\log \kappa_i$	8.16	13.49	8.33	15.73	9.06	16.62
ΔG_i	−11.1	−18.4	−12.1	−21.1	−12.4	−22.7
ΔH_i	−7.7	−14.4	−8.9	−17.7	−9.6	−19.2
ΔS_i	11.6	13.3	10.4	12.6	9.2	11.8

compared with those of aliphatic amines. The higher values of ΔH_1 and ΔS_1 with respect to those of ethylenediamine ($\Delta H_1 = -12.18$ kcal/mol and $\Delta S_1 = 4.8$ cal/(K • mol))[17] result from the presence of secondary aliphatic nitrogen donors[18] and of the pyridyl groups. The aromatic rings play the most important role in this context. The influence of the aminomethylpyridine group of one half of the molecule on the basicity of the other aliphatic nitrogen donor diminishes rapidly by increase of n. For DPTE, ΔG_1 and ΔH_1 are similar to those of 2-methylaminomethylpyridine ($\Delta G_1 = -12.15$, $\Delta H_1 = -9.85$ kcal/mol) and only the near aromatic group will influence the basicity of the aliphatic nitrogen atom in question. A similar value of ΔS_1 is also obtained by protonation of $(CH_3)_2NH$ and its value respect to those of other monoamines is correlated with the number of water molecules released by protonation.[18] The values of the protonation constants κ_1 and κ_2 of the three amines can be predicted with good agreement from the value for secondary amines and the base weakening effect $-\Delta pK$ of the substituent.[19] For the 2-pyridylmethyl substituent $-\Delta pK = 2$. Further protonation of H_2L^{2+} occurs in acidic solutions for all three ligands ($\log K_3 = 2$, $\log K_4 = 1.7$).

2. *Thermodynamics of Complex Formation*

Table I shows that the difference between $\log K_1$ of Cu(II)L and of M(II)L for M = Mn, Co, Ni and Zn, is some units smaller for complexes of the aromatic ligands as for the aliphatic ones. This signifies a general destabilisation of the copper(II) complexes with the former ligands. For the 2,2,2-tet complexes it was found that the trans octahedral form CuN_4X_2 is destabilised by cumulative ring strain (C-strain[2,16]).

By increase of the middle ring size this strain decreases appreciably and a gain of −6.1 kcal/mol in ΔH of $Cu(2,3,2\text{-tet})^{2+}$ with respect to that of $Cu(2,2,2\text{-tet})^{2+}$ is observed.[2] With the aromatic

TABLE V

Thermodynamic data of complex formation at 25°C and I = 0.1 (KNO_3). (ΔH and ΔG in kcal/mol; ΔS in cal/(K . mol)

		Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}	Ag^+
DPEN	ΔG	−7.6	−16.3	−19.8	−23.2	−15.2	−13.2	−26.1[a]	[b]
	ΔH	−4.5	−14.2	−17.4	−18.2	−11.3	−9.7	−22.0	
	ΔS	10.4	7.0	8.0	16.8	13.1	11.7	13.7	
DPTN	ΔG	−6.1	−15.3	−19.4	−25.0	−14.1	−11.7	−25.6	−8.6
	ΔH	−3.2	−13.2	−16.3	−20.1	−9.7	−7.8	−22.6	−10.9
	ΔS	9.7	7.0	10.4	16.4	14.8	13.1	10.1	−7.7
DPTE	ΔG	−3.6	−10.9	−15.2	−21.2	−10.5	−9.6	−23.9	−7.9
	ΔH	−0.2	−8.4	−12.4	−16.8	−5.9	−6.7	−20.8	−11.5
	ΔS	11.4	8.4	9.4	14.8	15.4	9.7	10.3	−12.1

[a] $\log K_2 = 5.58$; ΔH = −5.5; ΔS = 7.2

[b] $\log([Ag_2L_2^{2+}]/([Ag^+]^2[L]^2)) = 15.9$; ΔH = −26.3; ΔS = −15.4

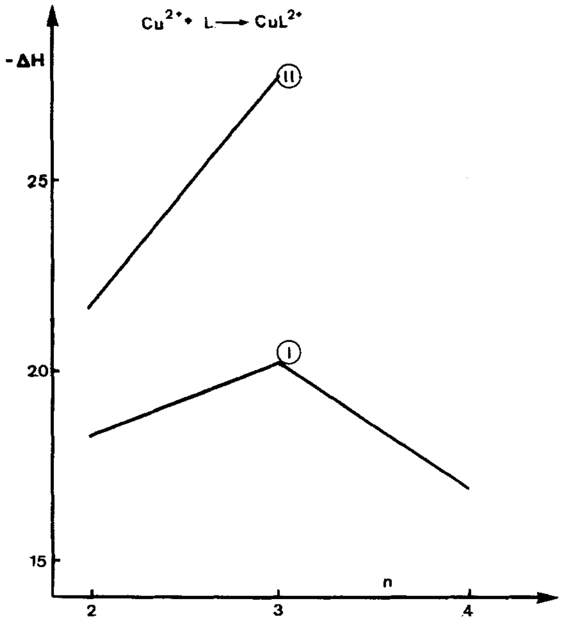


FIGURE 1 Enthalpies of formation of copper(II) complexes with ligands of type I and II for *n* = 2, 3 and 4.

amines this strain will be also important, but other effects appear for the presence of the two pyridyl groups, in which especially the 6–H atoms are mutually hindered.[10] A distortion of the planar CuN_4 structure is expected for the whole series of complexes, which justifies the small increase of –ΔH of 1.9 kcal/mol by change of the ring sequence size from 5,5,5 to 5,6,5 (Figure 1). The reduction of the formation enthalpy of $Cu(DPTE)^{2+}$ with respect to $Cu(DPTN)^{2+}$ of 3.3 kcal/mol can be explained by H–H repulsions in the alkylene chain (E-strain) as well as by C-strain.[20] The destabilisation of the copper(II) complexes seems due to the retention of the trans structure, whereas for the complexes with other 3d metal ions the cis octahedral structure is preferred, in which interactions between the two pyridyl residues are not possible. The perchlorates of the 1:1 copper(II) complex of the three ligands are purple and have spectra with a maximum absorption at near 17–18 kK (Table VI), i.e. at higher energy than for those in which anion bonding occurs.[10] The solution and reflection spectra (Table VI) fit well into the class of known copper(II)tetraamine compounds with four coplanar CuN_4 or tetragonal CuN_4X_2 structure. The increase in the molar extinction coefficient of the complex ion with respect to the 1:2 complex of

TABLE VI

Electronic spectra of perchlorates of the copper(II) complexes (λ in nm; $\tilde{\nu}$ in kK)

Complex ion	Solution spectra in water		Reflectance spectra	
	λ_{max}	ε	λ_{max}	ε
$Cu(DPEN)^{2+}$	603	153	560	17.9
$Cu(DPTN)^{2+}$	604	148	575	17.4
$Cu(DPTE)^{2+}$	603	132	567	17.6
$Cu(AMP)_2{}^{2+\,a}$	581	55	557	18.0

[a] AMP: Aminomethylpyridine

2-aminomethylpyridine AMP reveals also distortion of the square planar structure.

The nickel complexes of the aliphatic tetraamines(II) are of interest because of the possibility of formation not only of octahedral but also of planar diamagnetic complexes.[16] For Ni(2,2,2-tet) there are 2 percent diamagnetic species, and for $Ni(2,3,2\text{-tet})^{2+}$ 25%[2] at 25°C. The increase is probably due to the collapse of steric strain for the trans complexes. In the case of the investigated ligands, as discussed above for copper(II), this decrease does not take place, therefore trans complexes are always destabilised and cis structures are preferred. Indeed only under drastic conditions small amounts of the planar species can be found. The gain in –ΔH for the complex $Ni(2,3,2\text{-tet})^{2+}$ of 3.9 kcal/mole with respect to $Ni(2,2,2\text{-tet})^{2+}$ can be mainly ascribed to formation of of planar species and has no analogue for the aromatic amines (Figure 2). On the contrary a loss of –ΔH of 1 kcal/mol is observed from $Ni(DPEN)^{2+}$ to $Ni(DPTN)^{2+}$ and of 3.9 from $Ni(DPTN)^{2+}$ to $Ni(DPTE)^{2+}$. These effects are in great part due to steric strain (C and E) as a consequence of the enlargements of the alkylene chelate ring. For the formation of $Ni(DPEN)^{2+}$ and $Ni(DPTN)^{2+}$ almost the same entropy change ΔS is observed as indication, that no changement in the number of coordinated H_2O takes place.[2,21] Electronic spectra in water and reflectance spectra of the solid complex salts show also generally a cis-NiN_4X_2 rather than a trans configuration (Table VII). The Dq values for the complexes lie between 1042 and 1100 cm^{-1} and are very similar to the values obtained for $Ni(NH_3)_6{}^{2+}$(1080) or for $Nien_3{}^{2+}$ (1150 cm^{-1}). The preparation of salts of the 1:1 complexes of the aromatic ligands is in some cases complicated because of the separation of the more insoluble 2:3 complex salts $[Ni_2L_3]X_4$ with probable NiN_6 structure. Our

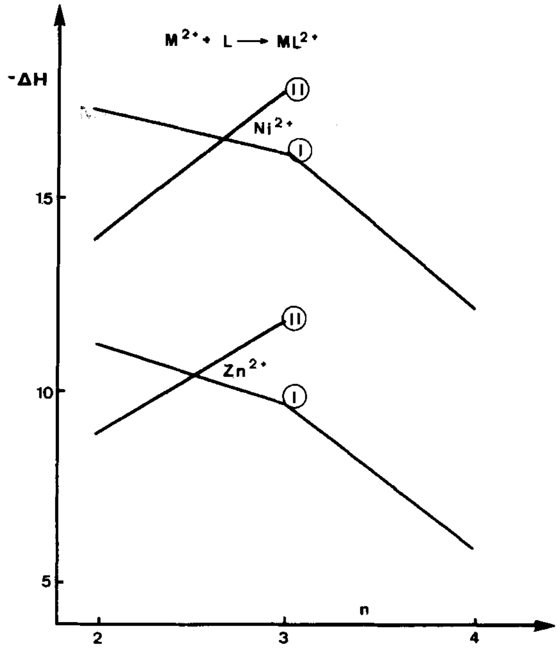


FIGURE 2 Enthalpies of formation of nickel(II) and zinc(II) complexes with ligands of type I and II for $n = 2$, 3 and 4.

TABLE VII

Electronic spectra of perchlorates of the nickel(II) complexes (λ in nm, $\tilde{\upsilon}$ in cm^{-1})

(α) Solution spectra in water^a

Complex ion	λ_1	ϵ	λ_2	ϵ	λ_{sh}	ϵ
$Ni(DPEN)^{2+}$	913	9.5	561	5.8	764	4.1
$Ni(DPTN)^{2+}$	892	8.8	548	6.0	771	5.8
$Ni(DPTN)^{2+}$	938	7.5	567	7.2	780	2.5
$Ni(AMP)_2{}^{2+}$	900	9.7	558	4.5	780	4.7

(β) Reflection spectra

Complex ion	λ	$\tilde{\upsilon}$
$Ni(DPEN)^{2+}$	560	17.9
$Ni(DPTN)^{2+}$	553	18.0

^{a}Bands assignment: λ_1 :!$^3A_{2g} \rightarrow {}^3T_{2g}$; λ_2: $^3A_{2g} \rightarrow {}^3T_{1g}$; λ_{sh} : $^3A_{2g} \rightarrow {}^1T_{2g}$

TABLE VIII

Electronic spectra of perchlorates of the cobalt(II) complexes in water.
(λ_3 : $^4T_{1g} \rightarrow {}^4T_{1g}(P)$; λ in nm)

Complex ion	λ_3	ϵ
$Co(DPEN)^{2+}$	477	14
$Co(DPTN)^{2+}$	482	14
$Co(DPTE)^{2+}$	485	20

investigation of equilibria have proved, that in aqueous solution no significant amount of the complex $[Ni_2L_3]^{4+}$ is formed. For the other metal ions Mn^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} a cis octahedral structure can explain the parallelism in the changements of the thermodynamic functions with those of Ni^{2+}. Electronic spectra of the cobalt(II) complexes in solution are also in agreement with this structure (Table VIII). For Cd^{2+}, because of its greater ionic radius, the different groups of the ligand cannot come as near as to cause appreciable strain with a much smaller decrease in –ΔH. The results with mercury(II) and silver(I), which show a strong tendency to form two-coordinate linear species, are examined by considering the enthalpy of reaction (5). It gives the gain in enthalpy by coordination of two pyridine nitrogen

$$M(NH_3)_2{}^{2+} + DPEN \longrightarrow M(DPEN)^{2+} + 2\,NH_3 \tag{5}$$

donors to the diammine complex ion and normally is strongly negative (Figure 3). For Hg^{2+} and Ag^+ the reaction is endothermic because the two aliphatic nitrogen atoms cannot occupy the preferred position. A tetrahedral arrangement of the donors is then expected, with a less negative reaction enthalpy. The steric strain is smaller than for $Cu(DPEN)^{2+}$ as revealed by the difference in ΔH with ligands for $n = 2$ and 3, but enough to allow the formation of a 1:2 complex $Hg(DPEN)_2{}^{2+}$.

The gain in –ΔH by this process of 5.5 kcal/mol is possibly due to the formation of a species with coordination of two aliphatic nitrogen donors, each of a different ligand molecule, in the preferred linear arrangement. The participation of the other donor atoms can give rise to an octahedral structure. In the case of silver(I) the strain in $Ag(DPEN)^+$ is reduced by formation of dimer complexes $Ag_2(DPEN)_2{}^{2+}$, in which the aliphatic nitrogen donors assume the linear coordination as supposed for the dimer $Ag_2en_2{}^{2+}$.[22] The i.r. spectra of the solid complex salt have proved the coordination of the aliphatic

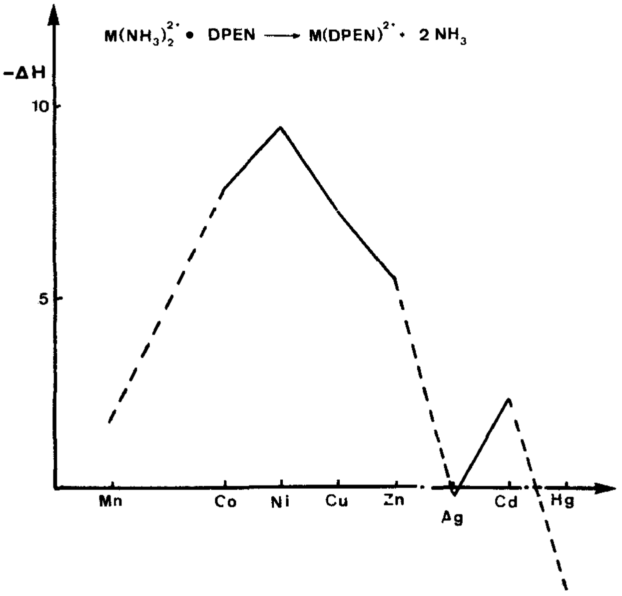
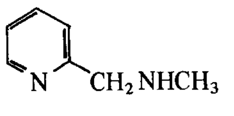


FIGURE 3 Enthalpies of reaction (5) with seven divalent metal ions and Ag^+.

nitrogen atoms only. The thermodynamic data of complex formation of the tetradentate ligands can be compared with those of the bidentate 2-methylaminomethylpyridine (MAMP) (Table IX), because



MAMP

in their 1:2 complexes ML_2 the same donors (and in the same number) are coordinated as for the tetraamines. Some information can be obtained about the gain in stability by chelation[23] on the basis of the equilibrium (6)

$$M(MAMP)_2{}^{2+} + DPEN \rightleftharpoons M(DPEN)^{2+} + 2\ MAMP \tag{6}$$

The data reveal the following trend:

1) $\Delta H = \pm 1$ kcal/mol. The only exception is copper(II), for which $\Delta H = 2$ kcal/mol, because of the difficulties encountered by the ligand forced to assume a tetragonal structure.

2) $\Delta S = 10 - 12$ cal/(K · mol) as a consequence of the increase of the number of species.

In Figure 4 the data of ΔS for reaction (6) with

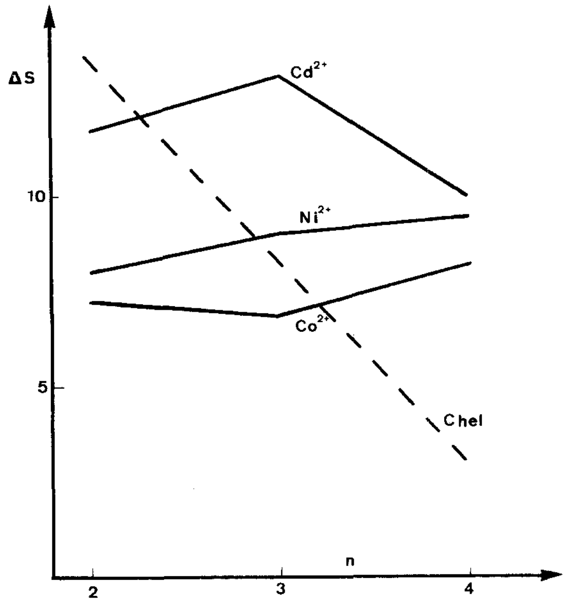


FIGURE 4 Entropies of reaction (6) of Cd^{2+}, Ni^{2+} and Co^{2+} with ligands of type I for $n = 2$, 3 and 4 in comparison with relative values after the model of Schwarzenbach (Chel).

TABLE IX

Thermodynamic data of association of MAMP at 25°C and I = 0.1 (KNO_3 (ΔH and ΔG in Kcal/mol; ΔS in cal/(K . mol)

	ΔH_1	ΔG_1	ΔS_1	ΔG_2	ΔH_2	ΔS_2	ΔG_3	ΔH_3	ΔS_3
H^+	−12.15	−9.86	7.7						
Co^{2+}	−6.95	−6.6	1.5	−12.05	−12.9	−2.8			
Ni^{2+}	−9.14	−9.0	0.5	−16.4	−17.2	−2.5	−20.0	−22.0	−6.7
Cu^{2+}	−12.43	−11.1	4.4	−21.4	−20.3	3.5			
Zn^{2+}	−6.58	−5.8	2.4	−11.46	−10.5	3.2			
Cd^{2+}	−6.14	−5.3	2.9	−11.0	−9.9	3.7			
Hg^{2+}				−25.6	−22.2	11.4			

$M^{2+} = Cd^{2+}$, Ni^{2+} and Co^{2+} are plotted versus n. They show the same trend as for the entropy of chelation for the EDTA homologous.[24] In spite of the different ligand charge, for each metal ion the values of ΔS remain almost constant, showing no dependence on ring size. Exceptions to this behaviour could be expected, if these complexes show a different number of coordinated water molecules[25] but they seem to be absent for those of the investigated amines. For the EDTA homologous and for the ligands of type I the decrease of the stability constants by enlargement of chelate ring size is almost due to a decrease of the heat of complex formation. A further increase of ring size, for $n > 4$, leads to systems in which also polynuclear species are present.

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20. The difficulties encountered by formation of the four-coplanar complex with DPTN has been corroborated by Gibson and McKenzie,[2] who have shown that $Pd(DPTN)Cl_2$ can form terdentate species $[PdLCl]^+$ in aqueous solution. We have obtained no evidence for the formation of the cation $[Pd(DPTN)H_2O]^+$ which should be present in solutions of $Pd(DPTN)(ClO_4)_2$. This cation should lose a proton in similar way as does the palladium(II) complex of the terdentate diethylenetriamine (pK = 7.8).[26]
21. For this reason the results for the corresponding aliphatic species[2] are unexpected, because an increase of the percentual amount of the planar species would also be reflected in an increase of Δ*S*. Indeed for the formation of the planar species two further H_2O molecules have to be lost!
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