147. Metal Complexes with Macrocyclic Ligands, VI [1]). The Role of Substituents on the Complexation Rate of Transition Metal Ions with Several 1,4,7,10-Tetraazacyclotridecanes

by **Willi Steinmann** and **Thomas A. Kaden** [2])
Institut für Anorganische Chemie, Spitalstr. 51, CH–4056 Basel

(3. 11. 75)

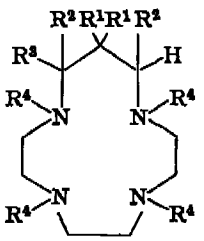
Summary. 12,12-Dimethyl-1,4,7,10-tetraazacyclotridecane (**I**), 11,13-dimethyl-1,4,7,10-tetraazacyclotridecane (**II**), 11,11,13-trimethyl-1,4,7,10-tetraazacyclotridecane (**III**) and 1,4,7,-10,12,12-hexamethyl-1,4,7,10-tetraazacyclotridecane (**IV**) have been synthesized and their properties are described.

While the Ni^{2+} and Cu^{2+} complexes of **I–III** have square planar geometries, those of **IV** are pentacoordinate according to their absorption spectra. Similarly, while the Co^{2+} complex of **I** is octahedral and readily oxygenated, the analogous complex with **IV** is pentacoordinate and not sensitive to oxygen.

The rate of complexation of these ligands with Cu^{2+} and Ni^{2+} decreases in the order **I** > **II** > **III** ≫ **IV**, indicating that the number as well as the position of the methyl groups are important. Finally for Cu^{2+} the formation of the thermodynamic stable end product is slown down by methyl substitution in α-position to the coordinating nitrogen atoms (ligand **II** and **III**) so that an intermediate can be observed, whereas with **I** Cu^{2+} directly forms the end product.

One of the factors which is responsible for the slowness of the complexation of tetraazacyclotetradecanes with transition metal ions was thought to be the high energy barrier for internal rotation [2]. This part of the activation energy can be influenced by introducing substituents into the cyclic ligands, which sterically interact with each other and thus inhibit conformational changes. In a previous paper we have reported that methyl substitution at the coordinating nitrogen atoms has only a little effect on the rate of complexation [3]. This might be expected since N-substitution mostly slows down first bond formation [4], which probably is not the rate determining step for these macrocycles. On the other side substitution at the carbon atoms of the ring does not directly influence first bond formation, but is known to increase the energy barrier for closing the chelate ring [5]. In fact we have observed that the formation of the square planar mauve complex of Cu^{2+} with 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (**tet a**) is a two step process, in which a slow reacting intermediate was found [6].

We have now systematically studied the role of substituents on the complexation rate with the following ligands (**I–IV**)



I: $R^1 = CH_3$; $R^2 = R^3 = R^4 = H$
II: $R^2 = CH_3$, $R^1 = R^3 = R^4 = H$
III: $R^2 = R^3 = CH_3$, $R^1 = R^4 = H$
IV: $R^1 = R^4 = CH_3$, $R^2 = R^3 = H$

1) Part V see [1].
2) Author to whom correspondence should be adressed.

Experimental Part. – $Ni_2(Trien)_2Cl_4 \cdot 2H_2O$ [7], 12,12-dimethyl-1,4,7,10-tetraazacyclotrideca-10-en-nickel-tetrachlorozincate (**V**) [8], 11,11,13-trimethyl-1,4,7,10-tetraazacyclotrideca-13-en-nickel-tetrachlorozincate (**VI**) [8] and 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-dienato-nickel-iodide (**VII**) [9] were synthesized according to the literature.

12,12-Dimethyl-1,4,7,10-tetraazacyclotridecane-nickel-diperchlorate (**VIII**). To 7.0 g of **V** in 200 ml water (*ca.* 3 g) $NaHCO_3$ was added until the solution was slightly alkaline and the precipitated $ZnCO_3$ was then filtered off. The clear solution was either treated with 0,85 g $NaBH_4$, which was added in small portions at 60°, or reacted with hydrogen (50 atm) at room temp. in the presence of 50 mg PtO_2 during three days. After adjusting the pH to 7 with acetic acid the reduced solution was evaporated to a small volume and a saturated $NaClO_4$ solution was added. From the $NaBH_4$ reduction 6 g (86%) of **VIII** were obtained, whereas 6.3 g (90%) were recovered from the catalytic reduction. The C=N band at 1660 cm^{-1} of the starting material is absent.

$C_{11}H_{26}Cl_2N_4NiO_8$	Calc.	C 27.99	H 5.55	N 11.87%
(471.97)	Found	,, 27.87	,, 5.46	,, 11.78%

12,12-Dimethyl-1,4,7,10-tetraazacyclotridecane-trihydrochloride (**I**). 6.0 g of **VIII** in 150 ml water were reacted with 5 g KCN in 50 ml water. The pink colour which appears upon mixing rapidly changes to yellow $[Ni(CN)_4^{2-}]$. 150 ml $CHCl_3$ were then added and the mixture was shaken for 1–2 h. After separation of the organic phase the aqueous solution was extracted five more times with 50 ml $CHCl_3$. The combined extracts were dried over K_2CO_3 and evaporated to dryness whereupon 2.4 g of the free base crystallized. The hydrochloride of **I** was obtained by addition of alcoholic HCl-solution (yield 61%) and recrystallized from $EtOH/H_2O$. Dec. 257°

$C_{11}H_{29}Cl_3N_4$	Calc.	C 40.81	H 9.03	Cl 32.85%	N 17.31
(323.74)	Found	,, 40.81	,, 9.01	,, 32.96%	,, 17.47

11,11,13-Trimethyl-1,4,7,10-tetraazacyclotridecane-nickel-diperchlorate (**IX**). To 6.0 g of **VI** in 200 ml water solid $NaHCO_3$ was added until the pH of the solution was slightly alkaline. After filtration from the precipitated $ZnCO_3$ the solution was heated to 60° and reacted with 1.6 g NaOH and 2.4 g Ni-Al-alloy (50% Ni). Thereafter high-flow was added, the pH of the solution adjusted to 8–9 with conc. HCl-solution and the precipitated $Al(OH)_3$ filtered off. The filtrate was acidified to pH 4 with $HClO_4$ and concentrated. Upon addition of a saturated $NaClO_4$-solution to this concentrate yellow crystals of **IX** were obtained, which were recrystallized from water (5.4 g, 93%). The C=N band at 1665 cm^{-1} present in the starting material is absent.

$C_{12}H_{28}Cl_2N_4NiO_8$	Calc.	C 29.66	H 5.81	N 11.53%
(485.99)	Found	,, 29.51	,, 5.64	,, 11.27%

11,11,13-Trimethyl-1,4,7,10-tetraazacyclotridecane-tetrahydrochloride (**II**). The ligand was obtained from **IX** by a similar procedure and with similar yields (63%) as for **I**. Dec. **II**. 4 HCl > 250°.

$C_{12}H_{32}Cl_4N_4$	Calc.	C 38.51	H 8.62	Cl 37.89%	N 14.97
(374.23)	Found	,, 38.62	,, 8.61	,, 37.74%	,, 15.02

11,13-Dimethyl-1,4,7,10-tetraazacyclotridecane-nickel-diperchlorate (**X**). 8.0 g of **VII** were dissolved into 200 ml water and the pH was adjusted with HCl to 4. The hydrogenation was carried out at 40° and 180 atm. in the presence of 500 mg PtO_2 during 5 days. The catalyst was then filtered off, the solution was concentrated and to this a saturated $NaClO_4$ solution was added, whereupon yellow crystals of **X** were obtained. Crystallisation from MeOH gave 8.3 g (87%) of the pure product. The C=C and C=N bands at 1560 and 1525 cm^{-1} of the starting material are absent. ^{1}H-NMR. (100 MHz, D_2O): 1.06 (d, CH_3).

$C_{11}H_{26}Cl_2N_4NiO_8$ (471.97) Calc. C 27.99 H 5.55 N 11.87% Found C 27.95 H 5.39 N 11.67%

11,13-Dimethyl-1,4,7,10-tetraazacyclotridecane (**III**). The free ligand was obtained as described for **I** and recrystallized from ether, m.p. 88–88.5° (yield 81%).

$C_{11}H_{26}N_4$ (214.35) Calc. C 61.63 H 12.23 N 26.14% Found C 61.61 H 12.43 N 26.28%

1,4,7,10,12,12-Hexamethyl-1,4,7,10-tetraazacyclotridecane-trihydroperchlorate (**IV**). A solution of 1.8 g **I** in 10 ml 90% formic acid and 4 ml 35% formaldehyde was slowly heated until the CO_2 evolution stopped and then refluxed for 20 h. After addition of 5 ml 60% $HClO_4$-solution the

excess of formic acid and formaldehyde was removed at the rotatory evaporator. Addition of EtOH gave the product **IV**, which was recrystallized from MeOH/H_2O (1.7 g, 35%). Dec. > 240°

$C_{15}H_{37}Cl_3N_4O_{12}$ (571.84) Calc. C 31.51 H 6.52 N 9.80% Found C 31.80 H 6.49 N 9.86%

Measurements and equipement. – Reagents: analytical grade used without further purification. Measurements Temp. 25 ± 0.05°, $I = 0.5$ (KCl). Titration curves of the 10^{-2}M ligands were obtained on a potentiograph E 436 (*Metrohm*) equiped with a glass electrode UX (*Metrohm*) under nitrogen.

Absorption spectra were measured on a *Cary* 14 spectrophotometer in 1 or 2 cm cells with solutions containing equimolar amounts of metal ion and ligand, which were allowed to react at 60° until complexation was complete. The spectrum of the Co^{2+} complex with **I** was taken under anaerobic conditions in a *Tunberg* cuvette. The near IR. spectrum of the Ni^{2+} complex with **IV** was measured in D_2O. The pH dependence of the Co^{2+} spectrum of **IV** was studied by adjusting the pH of the stock solution with small amounts of NaOH or HCl. The rate of complexation of the macrocycles with Ni^{2+}, Cu^{2+}, Co^{2+} and Zn^{2+} was followed on a pH-stat and the rate constants calculated on an *Olivetti* Programma 101 as described previously [3]. The second step of the reaction of Cu^{2+} with **II** and **III** was followed spectrophotometrically at 50° in 0.1M *t*-butylamino-ethanol buffer ($I = 0.5$) at 520 nm. Stock solutions of the intermediates were prepared with the pH-stat at 25° and kept at 0°.

IR. spectra were measured on a *Beckman* IR-8 spectrophotometer in KBr pellets. NMR. spectra were obtained in D_2O solution on a *Varian* 100 MHz instrument.

Results and Discussion. – *Synthesis and pK^H values of the ligands.* All macrocycles were synthesized using template reactions described in the literature [8] [9] and the reduction of the imine groups was achieved either with $NaBH_4$, or PtO_2 and H_2 or Ni-Al-alloy in alkaline solution. Whereas the Ni^{2+} complex **V** can easely be reduced with $NaBH_4$ (see also [8]) or PtO_2/H_2, the complex **VI** does not react with these reagents [8]. However, Ni-Al-alloy in alkaline solution produces the product **IX**. The reduction of **VII** was the most difficult and had to be done with PtO_2 and H_2 under slightly acidic conditions. Below pH 6 protonation and localization of the double bonds occurs [10] making them more accessible to hydrogenation. This reaction can give two isomers. In the *meso* form the two methyl groups in position 11 and 13 are equivalent (probably equatorial) and will appear in the NMR. spectrum as one doublet. The methyl group of the racemic form are not equivalent (one being axial the other equatorial) and should give two doublets. The single doublet observed for our compound is therefore attributed to the absorption of the methyl protons of the *meso* form. In the IR. spectra of the ligands, obtained from their corresponding Ni^{2+} complexes by demetallation with cyanide, typical N–H bands at 3300 cm^{-1} and N–H deformation bands in the region 1580–1620 cm^{-1} are observed.

The pK^H values of the cyclic tetraamines are obtained from the titration curves using the computer program *Variat* [11]. The first three are given in Table 1, the fourth being to low to be determined potentiometrically. In analogy to the fourteen

Table 1. *pK^H values of* **I**, **II**, **III** *and* **IV** *at 25° and* $I = 0.5$

	I	**II**	**III**	**IV**
pK_1^H	11.53	11.57	11.40	11.53
pK_2^H	10.10	9.91	9.61	8.10
pK_3^H	< 2.5	< 2.5	< 2.5	< 2.5

membered rings [3], the protonation of the tetraazacyclotridecanes also takes place in two two-proton steps.

Structure of the complexes. The spectra of the Ni^{2+} complexes with **I–III** exhibit one band at 427–429 nm with molar absorptivities of 112 to 167 M^{-1} cm^{-1} (Fig. 1) and

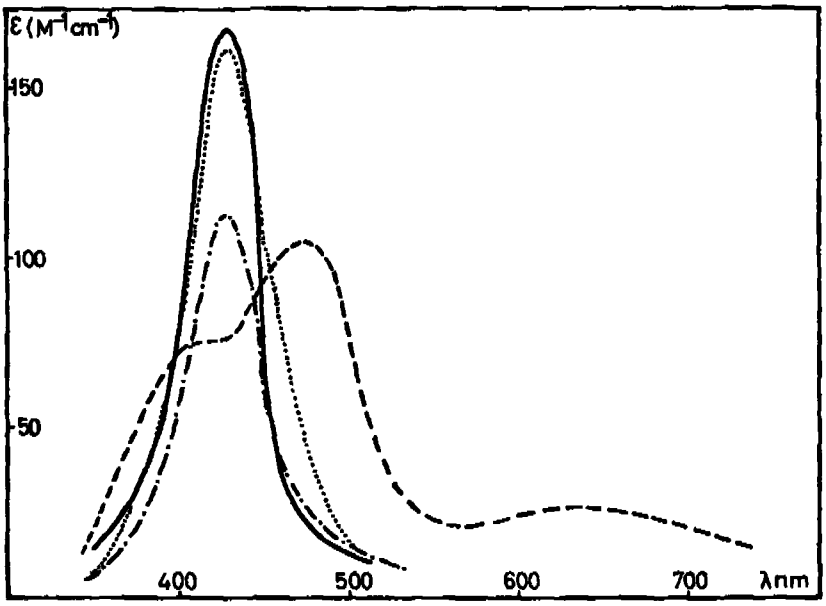


Fig. 1. *Absorption spectra of the Ni^{2+} complexes with* **I** (——), **II** (. . . .), **III** (—·—·—) *and* **IV** (– – – –)

clearly indicate a square planar geometry. In contrast the Ni^{2+} complex of **IV** shows three bands in the visible part of its spectrum at 410 (sh), 472 and 635 nm (Fig. 1) and an additional absorption in the near IR. at 1600 nm. A trigonal bipyramidal or square pyramidal arrangement is the most probable geometry for this complex, in analogy to the Ni^{2+} complex of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (4-Me-Cyclam-14) [3] [12] [13].

The end products of the complexation of Cu^{2+} with **I–III** absorb at 540–565 nm with molar absorptivities of 200–235 M^{-1} cm^{-1} (Fig. 2) and are typical for square planar chromophores with four nitrogens [14]. In contrast the spectrum of the Cu^{2+} complex with **IV** has a band at 630 nm with $\varepsilon \approx 375\,M^{-1}\,cm^{-1}$ and resembles that of the Cu^{2+} complex with 4-Me-Cyclam-14 for which pentacoordination has been proposed [12] [13] and that of the blue intermediate of the reaction of Cu^{2+} with **tet a** [6], which was shown to be trigonal bipyramidal [15].

The complexation of Cu^{2+} with **II** and **III** does not directly give the thermodynamically most stable square planar compound. Intermediates with bands at 590 nm ($\varepsilon \approx 235\,M^{-1}\,cm^{-1}$) for **II** and at 585 nm ($\varepsilon \approx 215\,M^{-1}\,cm^{-1}$) for **III** which slowly interconvert to the square planar end product are observed (Fig. 3). Although their structures are not yet known, it is clear that distortions from a regular geometry and that a weaker ligand field is present in these complexes.

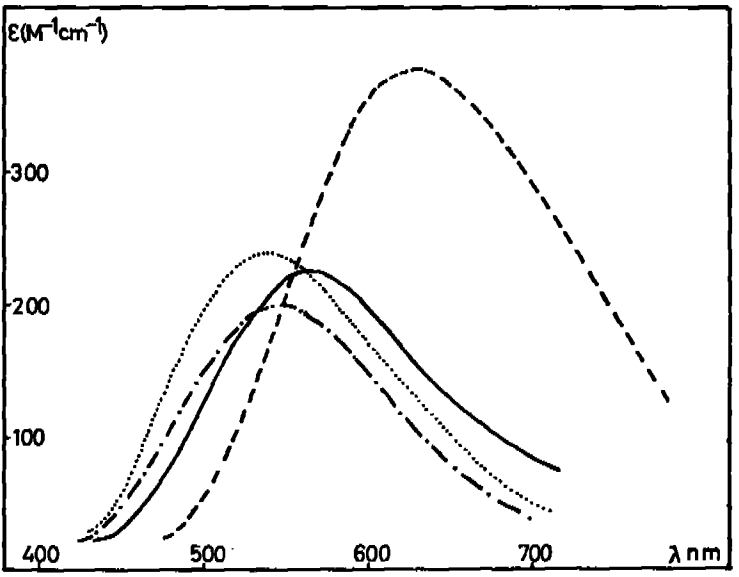


Fig. 2. *Absorption spectra of the Cu^{2+} complexes with* **I** (– —), **II** (. . . .), **III** (–·–) *and* **IV** (– – –)

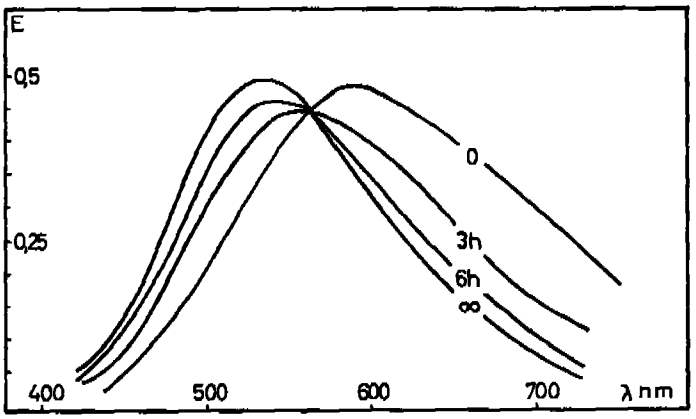


Fig. 3. *Base catalyzed interconversion of the blue to the mauve Cu^{2+} complex with* **II** *at pH 5.8 and 85°*

The Co^{2+} complexes of **I** and **IV** also exhibit stricking differencies. Whereas the complex with **I** absorbs at 450 nm ($\varepsilon = 35\,M^{-1}\,cm^{-1}$) and is extremely sensitive to oxygen, the Co^{2+} complex of **IV** has two structured bands in the visible spectrum (Fig. 4) and does not react with oxygen at all. In addition the spectrophotometric titration indicates as for Co(4-MeCyclam-14)$^{2+}$ [12] that the complex with **IV** reacts as a weak acid when titrated with NaOH ($pK^{H} = 7.98$). This together with the absorption spectrum allows to assume the presence of a water molecule coordinated in the fifth position.

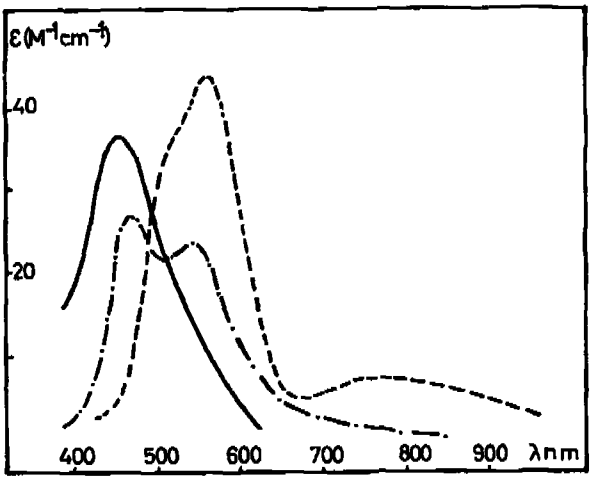


Fig. 4. *Absorption spectra of the Co^{2+} complexes with* **I** (——), *and* **IV** *at pH 6.9* (–.–.–) *and pH 11.0* (– – –)

Kinetics and mechanism of complexation. The kinetics of complexation of the macrocyclic ligands **I–IV** with Ni^{2+}, Cu^{2+}, Co^{2+} and Zn^{2+} follow in the pH region in which H_2L^{2+} is the predominant species of the ligand the rate equation (1) (Fig. 5).

$$v_f = (k_1/[H^+] + k_2/[H^+]^2)\,[M^{2+}]\,[H_2L^{2+}]. \quad (1)$$

In the case of Ni^{2+} and Cu^{2+} k_2 was to small to be measured. The corresponding rate constants, *Arrhenius* constants and activation energies are given in Table 2.

The pH dependence of the rate of formation can as usual be resolved into the bimolecular rate constants k_{HL} and k_L (Table 2) using the pK^H values given in Table 1. These results show that the 13-membered ring ligands react slower than open chain tetraamines but at rates similar to those observed for the tetraazacyclotetradecanes [1–3] [6]. This would indicate that also for these ligands first bond formation probably is not the rate determining step and that other factors discussed in [3] are responsible for the slow reaction. Secondly we find that the values of k_{HL} and k_L differ by factors of 10^3 to 10^6. The high values of k_L are probably due to a different and more reactive conformation of the free ligand and/or to a high conjugate base effect of the strongly basic nitrogen with a pK_1^H of about 11.5 [16]. A third interesting point is the correlation between the rate of complexation and the number and position of the substituents in the macrocyclic ring. In the case of Ni^{2+} and Cu^{2+} the introduction of two methyl groups in the β-position to the coordinating nitrogen atoms 1 and 10 (ligand **I**) has no influence on the rate of complexation, whereas a decrease of these rates is observed when two or three methyl groups are in the α-position (ligand **II** and **III**) or when six methyl groups are present (ligand **IV**). In addition **II** and **III** react with Cu^{2+} in a two step process. In a first reaction an intermediate is formed, which then slowly interconverts in a base catalyzed step to the end product (Fig. 3). The rate law for this second step (2)

$$v_{f,2} = k_3[CuL^{2+}(blue)]\,[OH^-] \quad (2)$$

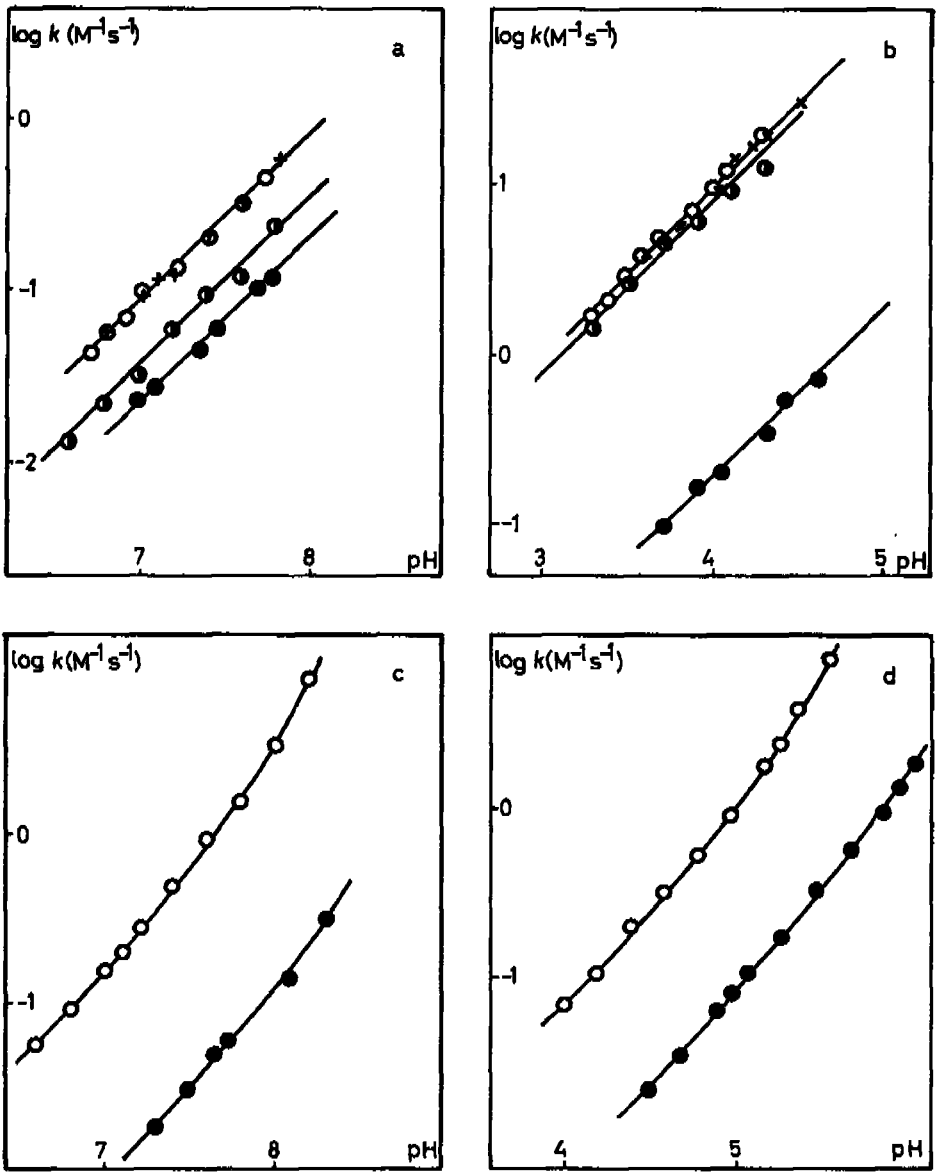


Fig. 5. *pH Dependence of the rate of complexation of* Ni^{2+} *(a),* Cu^{2+} *(b),* Co^{2+} *(c) and* Zn^{2+} *(d) with* **I** (○), **II** (+), **III** (◐) *and* **IV** (●) *at* 25° (40° for Ni^{2+} and **IV**) and $I = 0.5$

and the rate constants k_3 for **II** and **III** are similar to those observed for the reaction in which the blue Cu(**tet a**)$^{2+}$ complex gives the square planar end product [6]. Reaction (2) can be explained by assuming a rapid pre-equilibrium of CuL^{2+}(blue) with a species containing a deprotonated coordinated amino group ($H_{-1}L$ stands for the mono-deprotonated ligand L) (3) [17].

$$CuL^{2+}(\text{blue}) \underset{\text{fast}}{\overset{OH^-}{\rightleftharpoons}} CuH_{-1}L^+ \xrightarrow[\text{slow}]{} CuL^{2+}(\text{mauve}). \qquad (3)$$

Table 2. *Rate constants,* Arrhenius *constants and activation energies for the complexation of I–IV with* Ni^{2+}, Cu^{2+}, Co^{2+} *and* Zn^{2+} *at 25° and* $I = 0.5$

	Ni^{2+}					Cu^{2+}				
	k_1 (s^{-1})	log A	ΔE^* kcal/mol	k_{HL} ($M^{-1}\,s^{-1}$)		k_1 (s^{-1})	log A	ΔE^* kcal/mol	k_{HL} ($M^{-1}\,s^{-1}$)	k_3[g] ($M^{-1}\,s^{-1}$)
Cyclam 13[f]				145[a]					$1.1.10^{7}$[a]	
I	$8.7.10^{-9}$	12.1	18.0	110		$9.6.10^{-4}$	17.6	23.4	$1.2.10^{7}$	
II	$6.8.10^{-9}$	11.9	17.5	55		$8.0.10^{-4}$	13.5	17.2	$6.5.10^{6}$	$1.1.10^{3}$
III	$3.6.10^{-9}$	12.9	19.4	14		$8.3.10^{-4}$	16.6	21.7	$3.4.10^{6}$	$2.5.10^{3}$
IV	$3.6.10^{-10}$	11.0	18.0	$4.5.10^{-2}$		$1.8.10^{-5}$	15.4	22.2	$2.2.10^{3}$	

	Co^{2+}						Zn^{2+}					
	k_1 (s^{-1})	k_2 ($M\,s^{-1}$)	log A	ΔE^* kcal/mol	k_{HL} ($M^{-1}\,s^{-1}$)	k_L ($M^{-1}\,s^{-1}$)	k_1 (s^{-1})	k_2 ($M\,s^{-1}$)	log A	ΔE^* kcal/mol	k_{HL} ($M^{-1}\,s^{-1}$)	k_L ($M^{-1}\,s^{-1}$)
I	$1.4.10^{-8}$	$2.4.10^{-16}$	18.4[b]	26.4[b]	$1.8.10^{2}$	$1.0.10^{6}$	$6.4.10^{-6}$	$2.8.10^{-11}$	21.9[c]	30.8[c]	$8.0.10^{4}$	$1.2.10^{11}$
IV	$9.0.10^{-10}$	$2.7.10^{-18}$	15.3[d]	23.0[d]	$1.1.10^{-1}$	$1.1.10^{2}$	$7.2.10^{-7}$	$7.3.10^{-13}$	17.4[e]	25.4[e]	88	$3.0.10^{7}$

[a] *Th. A. Kaden,* unpublished results. [b] at pH 7.0. [c] at pH 7.5. [d] at pH 4.0. [e] at pH 4.5. [f] Cyclam-13 = 1,4,7,10-Tetraazacyclotridecane. [g] at 50°.

These results show that substituents in α-position not only slow down the first step of the reaction, but in the case of Cu^{2+} also strongly inhibit the interconversion to the square planar end product. α-Methyl groups are thought to interact sterically more strongly than similar groups in β-position.

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148. 2-Oxo-$9^{C(3)}$-hydroxy- und 2-Oxo-$9^{C(7)}$-hydroxy-bicyclo[3.3.1]nonan[1])

von **Rudolf Otto Duthaler** und **Camille Ganter**

Laboratorium für Organische Chemie der Eidg. Technischen Hochschule, CH–8006 Zürich

(5. V. 75)

Summary. A synthesis of the two C(9) epimers **14** and **15** of 2-oxo-9-hydroxy-bicyclo[3.3.1]-nonane is described starting from the two C(2) epimers **3** and **4** of 2-hydroxy-9-oxo-bicyclo[3.3.1]-nonane.

Im Zusammenhang mit UV.-Bestrahlungen von 2-Oxo-bicyclo[3.3.1]nonan (**1**) [1] war es erforderlich, eine gezielte Synthese der beiden bisher unbekannten C(9)-Epimeren 2-Oxo-$9^{C(3)}$-hydroxy- und 2-Oxo-$9^{C(7)}$-hydroxy-bicyclo[3.3.1]nonan (**14** und **15**) auszuarbeiten.

1) Mit den hochgestellten Indices C(3) werden diejenigen Substituenten an C(9) bezeichnet, die gegen C(3) hin und mit C(7) jene, welche gegen C(7) hin orientiert sind.