39. Metal Complexes with Macrocyclic Ligands

Part XXXVIII[1])

Steric Effects in the Copper(II) and Nickel(II) Complexes with Tetra-*N*-alkylated 1,4,8,11-Tetraazacyclotetradecanes

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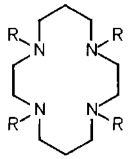
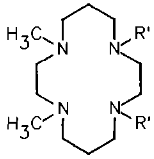
(16.I.95)

A series of tetra-*N*-alkylated 1,4,8,11-tetraazacyclotetradecanes have been synthesized and their complexation potential towards Ni^{2+} and Cu^{2+} studied. In the case of sterically demanding alkyl substituents, such as i-Pr, $PhCH_2$, or $2\text{-}MeC_6H_4CH_2$, no metal complexes are formed, whereas for substituents such as Me, Et, and Pr, the metal ion is incorporated into the macrocycle. The spectroscopic properties of the Ni^{2+} and Cu^{2+} complexes in aqueous solution indicate that, depending on the sterical hindrance of the *N*-substituents, the complexes are either square planar or pentacoordinated. All these Ni^{2+} and Cu^{2+} complexes react with N_3^- to give ternary species, the stability of which have been determined by spectrophotometric titrations. The tendency to bind N_3^- decreases with increasing steric hindrance of the alkyl substituents. The X-ray studies of the Ni^{2+} complex with the macrocycle **11**, substituted by two Me and two Pr groups, and that of the Cu^{2+} complex with the tetraethyl derivative **8** show that in the solid state, the metal ions exhibit square planar coordination with a small distortion towards tetrahedral geometry.

Introduction. – The stereochemistry of the metal complexes with 1,4,8,11-tetraazacyclotetradecanes has been studied in detail and reviewed in the literature [2]. Whereas the unsubstituted macrocycle **1** (cyclam) usually gives metal complexes with the *trans*-III



1 R = H
2 R = Me
3 R = Pr
4 R = $C_{12}H_{25}$
5 R = $PhCH_2$
6 R = *o*-$MeC_6H_4CH_2$
7 R = i-Pr
8 R = Et



9 R′ = H
10 R′ = Et
11 R′ = Pr

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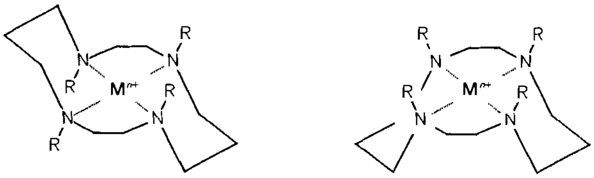
configuration [3], which seems to be the thermodynamically most stable arrangement, tetra-*N*-alkylated compounds such as **2**–**5** [4–6] tend to give complexes with the *trans*-I configuration in which all alkyl groups are directed to one side of the N_4-plane (*Fig. 1*).



trans-III *trans*-I

Fig. 1. *The* trans-*III and* trans-*I configuration in 1,4,8,11-tetraazacyclotetradecane complexes as proposed by* Bosnich et al. [3]

In the case of **2**, however, two forms of the Ni^{2+} complex with *trans*-I and *trans*-III configuration can be isolated [4] and their interconversion has been studied [7]. The geometry of the Ni^{2+} and Cu^{2+} complexes in the *trans*-I configuration generally is penta- or hexacoordinated, although there are indications that the Ni^{2+} complex of **2** can also be square planar in solution [8]. Because of the flexibility of such coordination geometries, it was interesting to systematically study the influence of sterical effects on the complexation properties and coordination geometries of the metal complexes with tetra-*N*-substituted 1,4,8,11-tetraazacyclotetradecanes. For this purpose, we have prepared the ligands **5**–**11**, in which the nature of the alkyl groups has been varied.

Experimental. – Compounds 1,4,8,11-tetraazacyclotetradecane (cyclam; **1**) and 1,4-dimethyl-1,4,8,11-tetraazacyclotetradecane (**9**) were prepared according to [9].

1,4,8,11-Tetrabenzyl-1,4,8,11-tetraazacyclotetradecane (**5**). To a mixture of **1** (4.00 g, 0.02 mol) and K_2CO_3 (13.8 g, 0.1 mol) in MeCN (300 ml) at 70°, a soln. of benzyl bromide (28.80 g, 1.67 mol, 20 ml) in MeCN (80 ml) was added over 1 h. The mixture was refluxed for 12 h, cooled to r.t., and filtered. The product was then extracted from the residue with $H_2O/CHCl_3$. The org. phase was dried (Na_2SO_4) and evaporated and the raw product purified by chromatography (alox, CH_2Cl_2/NH_3 19:0.15). Recrystallization from $MeCN/CH_2Cl_2$ yielded **5** (4.07 g, 36%). M.p. (dec.): 134–158° ([6]: 154–155°). ^{1}H-NMR ($CDCl_3$): 1.74 (*quint.*, 4H, $NCH_2CH_2CH_2N$); 2.51 (*t*, 8H, $NCH_2CH_2CH_2N$); 1.60 (*s*, 8H, NCH_2CH_2N); 3.43 (*s*, 4 $PhCH_2$); 7.22 (*m*, 20 arom. H). ^{13}C-NMR ($CDCl_3$): 23.86 ($NCH_2CH_2CH_2N$); 50.49, 51.43, 59.43 (CH_2N); 126.60, 127.98, 128.86, 139.98 (arom. C). Anal. calc. for $C_{38}H_{48}N_4$ (560.79): C 81.38, H 8.63, N 9.99; found: C 81.39, H 8.70, N 10.08.

1,4,8,11-Tetrakis(2-methylbenzyl)-1,4,8,11-tetraazacyclotetradecane (**6**). To a mixture of **1** (4.00 g, 0.02 mol) and K_2CO_3 (13.8 g, 0.1 mol) in MeCN (130 ml) at 75°, a soln. of 2-methylbenzyl chloride (28.1 g, 0.2 mol, 25.8 ml) in MeCN (50 ml) was added over 40 min. This was kept at reflux for 46 h, then filtered. The precipitate was taken up with CH_2Cl_2/H_2O and recrystallized from $MeCN/CH_2Cl_2$: 9.69 g (79%). M.p. (dec.): 167–169°. IR (KBr): 3030–3080 (arom. C–H), 2600–3000 (=CH_2, CH_3), 1650–2000 (comb.), 1575–1625 (arom. C–C). ^{1}H-NMR ($CDCl_3$): 1.72 (*quint.*, 4H, $NCH_2CH_2CH_2N$); 2.28 (*s*, 4 Me); 2.47 (*t*, 8H, $NCH_2CH_2CH_2N$); 2.59 (*s*, 8H, NCH_2CH_2N); 3.37 (*s*, 4 $MeC_6H_4CH_2$); 6.63 (*m*, 16 arom. H). ^{13}C-NMR ($CDCl_3$): 19.48 (Me), 23.77 ($NCH_2CH_2CH_2N$); 50.76, 51.76, 58.04 (CH_2N); 125.56, 126,79, 129,82, 130,22, 137,29, 137,97 (arom. C). Anal. calc. for $C_{42}H_{56}N_4$ (616.93): C 81.77, H 9.15, N 9.08; found: C 81.74, H 9.13, N 9.10.

1,4,8,11-Tetraisopropyl-1,4,8,11-tetraazacyclotetradecane Tetrakis(hydrobromide) Monohydrate (**7** · 4 HBr · H_2O). To a soln. of **1** (0.40 g, 2.0 mmol), NaI (0.06 g, 0.4 mmol), and K_2CO_3 (1.38 g, 0.01 mol) in MeCN (34 ml), 2-bromopropane (7.6 ml, 0.081 mol) was added. The mixture was refluxed for 25 h, filtered at 40°, and evaporated. The raw product was purified by flash chromatography (FC; silica gel (*Merck*) 0.040–0.063 mm, $MeOH/CH_2Cl_2/NH_3$ 2:6:0.3). From the pure product fractions, the free base was obtained as a colorless oil. After dissolving it in H_2O (20 ml) and 47% HBr soln. (3 ml), the precipitation of **7** · 4 HBr · H_2O was initiated by addition of EtOH (230 ml). After filtration, the product was dried for 24 h at 75° under high vacuum: 1.0 g (80%). ^{1}H-NMR ($CDCl_3$, free base): 0.99 (*d*, 4Me_2CH); 1.64 (*quint.*, 4H, $NCH_2C\mathit{H}_2CH_2N$); 2.46 (*t*, 8H, $NC\mathit{H}_2CH_2C\mathit{H}_2N$); 2.50 (*s*, 8H, $NC\mathit{H}_2C\mathit{H}_2N$); 2.85 (*sept.*, 4$Me_2C\mathit{H}$). ^{13}C-NMR ($CDCl_3$, free base): 19.02 ($\mathit{Me}_2CH$); 27.35 ($NCH_2\mathit{C}H_2CH_2N$); 49.30, 50.53, 52.70 (CHN, CH_2N). Anal. calc. for $C_{22}H_{48}N_4 \cdot 4HBr \cdot H_2O$ (710.30): C 37.54, H 7.47, Br 44.83, N 7.94; found: C 37.20, H 7.66, Br 45.00, N 7.89.

1,4,8,11-Tetraethyl-1,4,8,11-tetraazacyclotetradecane Tetrakis(hydrobromide) (**8**·4HBr). To a soln. of **1** (4.00 g, 0.02 mol), NaI (0.06 g, 4 mmol), and $(i\text{-}Pr)_2NH$ (70 ml, 0.4 mol) in THF (50 ml), ethyl bromide (30 ml, 0.40 mol) was added. The mixture was stirred first at r.t. for 3.5 h, then heated to 60° for 5 h. After cooling to r.t., it was filtered and evaporated. The raw product was purified by FC (silica gel (*Merck*) 0.040–0.063 mm, $MeOH/CH_2Cl_2/NH_3$ 2:4:0.2) and then the free base dissolved in H_2O (30 ml) and 47% HBr soln. (10 ml). After the addition of EtOH (200 ml), **8**·4HBr was obtained as a white powder (2.68 g, 21%). IR (KBr): 3441 (NH), 2600–3000 ($=CH_2$, $-CH_3$), 1631 (NH). ^{1}H-NMR (D_2O): 1.40 (*t*, 4$\mathit{Me}CH_2$); 2.19 (*quint.*, 4H, $NCH_2C\mathit{H}_2CH_2N$); 3.42 (*q*, 4$MeC\mathit{H}_2$); 3.57 (*t*, 8H, $NC\mathit{H}_2CH_2C\mathit{H}_2N$); 3.82 (*s*, 8H, $NC\mathit{H}_2C\mathit{H}_2N$). ^{13}C-NMR ($D_2O$): 12.19 (Me); 19.43 ($NCH_2\mathit{C}H_2CH_2N$); 45.21, 49.06, 54.17 ($CH_2N$). Anal. calc. for $C_{18}H_{44}Br_4N_4$ (636.18): C 33.98, H 6.97, N 8.81; found: C 33.94, H 6.92, N 8.84.

1,4-Diethyl-8,11-dimethyl-1,4,8,11-tetraazacyclotetradecane (**10**). To a cooled soln. (0°) of acetyl chloride (3.6 ml, 0.05 mol) in dry CH_2Cl_2 (200 ml), a soln. of **9** (2.28 g, 0.01 mol) and Et_3N (6.8 ml, 0.049 mol) in dry CH_2Cl_2 (50 ml) was added over 30 min. The mixture was stirred for 23 h at r.t. After extraction with 1M NaOH, the org. phase was dried (Na_2SO_4) and evaporated giving the raw diamide. A soln. of the raw diamide in dry THF (70 ml) was heated under N_2 to reflux (important: absolutely dry equipment). The condenser, kept at 40° with thermostated H_2O, was connected to a flask containing NaOCl (14%) to destroy the SMe_2 liberated during the reaction. $BH_3 \cdot SMe_2$ (20 ml, 0.2 mol) in dry THF (20 ml) was added over 15 min. To dilute the soln., additional THF (20 ml) was added. After 6.5 h at reflux and cooling to r.t., the mixture was treated with MeOH (100 ml) to destroy the excess of BH_3. The solvent was then evaporated, and the BH_3 adduct, dried overnight under high vacuum, was hydrolized with refluxing 18% HCl soln. (200 ml) for 2.5 h. After cooling to *ca.* 10°, 6M NaOH was added to reach a pH value of 12–14. Extraction with $CHCl_3$ and destillation at 110–115°/10^{-3} Torr gave 2.18 g (77%) of yellowish oil. Purity (GC): 95% (5% BH_3 adduct). ^{1}H-NMR ($CDCl_3$): 1.01 (*t*, 2$\mathit{Me}CH_2$); 1.65 (*quint.*, 4H, $NCH_2C\mathit{H}_2CH_2N$); 2.23 (*s*, 2MeN); 2.45 (*t*, 4H, $NC\mathit{H}_2CH_2CH_2N$); 2.46 (*s*, 4H, $NC\mathit{H}_2C\mathit{H}_2N$); 2.50 (*q*, 2$MeC\mathit{H}_2$); 2.55 (*t*, 4H, $NC\mathit{H}_2CH_2CH_2N$); 2.55 (*s*, 4H, $NC\mathit{H}_2C\mathit{H}_2N$). ^{13}C-NMR ($CDCl_3$): 11.91 ($\mathit{Me}CH_2$); 24.08 ($NCH_2\mathit{C}H_2CH_2N$); 44.00 (MeN); 48.58, 50.15, 50.69, 53.95, 54.77 (CH_2N). MS (1% in EtOH): 284 (M^+).

1,4-Dimethyl-8,11-dipropyl-1,4,8,11-tetraazacyclotetradecane (**11**). After cooling a soln. of propionyl chloride (4.4 ml, 0.05 mol) in dry CH_2Cl_2 (200 ml) to 0°, **9** (2.28 g, 0.01 mol) and Et_3N (6.8 ml, 0.05 mol) in dry CH_2Cl_2 (50 ml) were added over 30 min. After extraction by 1M NaOH, the org. phase was dried (Na_2SO_4) and evaporated. The reduction of the raw diamide was done in analogy to **10**. Purification by destillation at 165–175°/4 · 10^{-2} Torr gave **11** (2.51 g, 80%). Colorless oil. Purity (GC): 92% (8% BH_3 adduct). ^{1}H-NMR ($CDCl_3$): 0.86 (*t*, 2$\mathit{Me}CH_2CH_2N$); 1.44 (*sext.*, 2$MeC\mathit{H}_2CH_2N$); 1.63 (*quint.*, 4H, $CH_2C\mathit{H}_2CH_2$); 2.23 (*s*, 2MeN); 2.34 (*t*, 4H, $NC\mathit{H}_2CH_2$); 2.45 (*t*, 4H, $NC\mathit{H}_2CH_2$); 2.45 (*s*, 4H, $NC\mathit{H}_2C\mathit{H}_2N$); 2.53 (*t*, 4H, $NC\mathit{H}_2CH_2$); 2.53 (*s*, 4H, $NC\mathit{H}_2C\mathit{H}_2N$). ^{13}C-NMR ($CDCl_3$): 12.50 ($\mathit{Me}CH_2CH_2$); 20.88 ($Me\mathit{C}H_2CH_2$); 24.75 ($CH_2\mathit{C}H_2CH_2$); 44.42 (MeN); 51.56, 51.86, 54.55, 55.27, 57.67 ($\mathit{C}H_2N$). MS (1% in EtOH): 312 (M^+).

(1,4,8,11-Tetraethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) Diperchlorate ([Cu(**8**)] $(ClO_4)_2$; **12**). First **8**·4HBr (1.72 g, 2.7 mmol) was converted by ion-exchange (*Dowex 2 × 8* column) into the free base. To the latter in H_2O (20 ml), a soln. of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.0 g, 2.7 mmol) in H_2O (20 ml) was added. The mixture was heated to 60° for 10 h. Evaporation and recrystallization from $EtOH/H_2O$ gave violet needles of **12** (1.35 g, 87%). Anal. calc. for $C_{18}H_{40}Cl_2CuN_4O_8$ (574.98): C 37.60, H 7.01, Cl 12.33, Cu 11.05, N 9.74; found: C 37.73, H 7.19, Cl 12.34, Cu 10.90, N 9.94.

(1,4,8,11-Tetraethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) Diperchlorate ([Ni(**8**)] $(ClO_4)_2$; **13**). After conversion of **8**·4HBr (4.3 mmol) to the free base (see **12**), the latter was dissolved in H_2O (15 ml), and a soln. of $Ni(ClO_4)_2 \cdot 6H_2O$ (1.6 g, 4.34 mmol) in H_2O (15 ml) was added. Heating to 60° for 12 h gave a violet soln. Filtration, evaporation, and recrystallization produced violet crystals of **13** (0.52 g, 34%). Anal. calc. for $C_{18}H_{40}Cl_2N_4NiO_8$ (570.12): C 37.92, H 7.07, Cl 12.44, N 9.83, Ni 10.29; found: C 38.01, H 7.09, Cl 12.57, N 9.97, Ni 10.30.

(1,4-Diethyl-8,11-dimethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) Diperchlorate Hemihydrate ([Cu(**10**)] $(ClO_4)_2 \cdot 0.5H_2O$; **14**). A soln. of **10** (0.77 g, 2.71 mmol) in H_2O (20 ml) was mixed with a soln. of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.0 g, 2.7 mmol) in H_2O (20 ml; immediately violet soln.). The mixture was heated to 60° for 10 h, cooled to r.t., and evaporated. Recrystallization from $EtOH/H_2O$ gave violet crystals of **14** (0.35 g, 24%). Anal. calc. for $C_{16}H_{36}Cl_2CuN_4O_8 \cdot 0.5\,H_2O$ (555.94): C 34.56, H 6.71, Cl 12.75, Cu 11.43, N 10.07; found: C 34.57, H 6.66, Cl 12.61, Cu 11.35, N 10.07.

(1,4-Diethyl-8,11-dimethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) Diperchlorate ([Ni(**10**)](ClO_4)$_2$; **15**). To a soln. of **10** (0.71 g, 2.49 mmol) in H_2O (15 ml), a soln. of $Ni(ClO_4)_2 \cdot 6 H_2O$ (1.5 g, 4.1 mmol) in H_2O (15 ml) was added (immediately deep violet soln.). Heating to 65° for 10 h, followed by cooling to r.t. gave violet crystals of **15** (1.07 g, 79%). Anal. calc. for $C_{16}H_{36}Cl_2N_4NiO_8$ (542.08): C 35.45, H 6.69, Cl 13.08, N 10.34, Ni 10.83; found: C 35.58, H 6.82, Cl 12.81, N 10.36, Ni 10.70.

(1,4-Dimethyl-8,11-dipropyl-1,4,8,11-tetraazacyclotetradecane)copper(II) Diperchlorate ([Cu(**11**)](ClO_4)$_2$; **16**). To a soln. of **11** (0.85 g, 2.71 mmol) in H_2O (20 ml), a soln. of $Cu(ClO_4)_2 \cdot 6 H_2O$ (1.0 g, 2.7 mmol) in H_2O (20 ml) was added. The mixture was heated to 60° for 10 h. Cooling to r.t. caused precipitation. Recrystallization from EtOH/H_2O gave violet crystals of **16** (1.02 g, 66%). Anal. calc. for $C_{18}H_{40}Cl_2CuN_4O_8$ (574.99): C 37.60, H 7.01, Cl 12.33, Cu 11.05, N 9.74; found: C 37.68, H 6.96, Cl 12.32, Cu 11.00, N 9.61.

(1,4-Dimethyl-8,11-dipropyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) Diperchlorate ([Ni(**11**)](ClO_4)$_2$; **17**). A soln. of **11** (0.79 g, 2.54 mmol) in H_2O (20 ml) and a soln. of $Ni(ClO_4)_2 \cdot 6 H_2O$ (1.5 g, 4.1 mmol) in H_2O (20 ml) were mixed and kept for 41 h at 65°. Cooling to r.t. caused precipitation. Recrystallization from EtOH/H_2O gave mauve needles of **17** (0.64 g, 44%). Anal. calc. for $C_{18}H_{40}Cl_2N_4NiO_8$ (570.13): C 37.92, H 7.07, Cl 12.44, N 9.83, Ni 10.29; found: C 38.08, H 6.87, Cl 12.56, N 9.82, Ni 10.50.

X-Ray Diffraction. The crystal data and parameters of the data collection of the two complexes [Cu(**8**)](ClO_4)$_2$ and [Ni(**11**)](ClO_4)$_2$ are given in *Table 1.*

Table 1. *Crystal Data and Parameters of Data Collection for [Cu(**8**)](ClO_4)$_2$ and [Ni(**11**)](ClO_4)$_2$*

	[Cu(**8**)](ClO_4)$_2$	[Ni(**11**)](ClO_4)$_2$
Formula	$C_{18}H_{40}Cl_2CuN_4O_8$	$C_{18}H_{40}Cl_2N_4NiO_8$
Molecular weight [gmol^{-1}]	574.984	570.142
Temp. [K]	298	298
Crystal size [mm]	0.3 × 0.3 × 0.4	0.3 × 0.3 × 0.3
Absorption coeff. [cm^{-1}]	10.952	10.314
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$ (No. 14; [12])	$Pc2_1n$[a])
a [Å]	9.819 ± 0.002	9.407 ± 0.001
b [Å]	19.378 ± 0.002	11.966 ± 0.002
c [Å]	13.648 ± 0.003	22.427 ± 0.002
α [deg]	90	90
β [deg]	90.325 ± 0.018	90
γ [deg]	90	90
Z; V [Å^3]	4; 2597.18 ± 0.88	4; 2524.57 ± 0.57
Calc. density [gcm^{-3}]	1.470	1.500
Θ_{max} [deg]	28	30.44
Radiation	MoK_α, 0.71069 Å	MoK_α, 0.71069 Å
Scan type	$\omega/2\Theta$	$\omega/2\Theta$
F(000)	1212	1208
No. of indep. refl.	6236	3985
No. of refl. in refin.	4578	2905
No. of variables	298	298
Last max./min.	+1.01/−0.55	+0.49/−0.49
Final R	5.87	3.96
Final R_w	7.02	4.54
Weighting scheme	weight $\cdot [1-(\Delta(F)/6\sigma F)^2]^2$	weight $\cdot [1-(\Delta(F)/6\sigma F)^2]^2$

[a]) Non-standard setting of $Pna2_1$ (No. 33; [12]).

Unit cell parameters were determined by accurate centering of 25 independent strong reflections by the least-squares method. The raw data set was corrected for polarization effects and X-ray diffraction absorption. The structures were solved by the *Patterson* technique using the program SHELX-86 [10]. Anisotropic least-square refinements were carried out on all non-H-atoms using the program CRYSTALS [11]. H-Atoms are in calculated positions with C–H distance of 1.0 Å and fixed isotropic thermal parameters. Scattering factors are taken from International Tables for Crystallography, Vol. IV [12].

Spectrophotometric Titrations. The titrations of the complexes $[ML]^{2+}$ ($M = Cu^{2+}$ and Ni^{2+}; L = **8**, **10**, and **11**) with N_3^- were run at 25 ± 0.1° and $I = 1.0$ M (KNO_3), on the automatic computer-controlled titrator, consisting of an UV/VIS spectrophotometer (*Pye Unicam PU 8800, Philips*), a pH meter (*Metrohm 605*), a dosimat (*Metrohm 665*), and a thermostated water bath (*Haake D8*) [13]. The computer (*IBM-AT-286*) ran the titration by adding small amounts of the titrant ($[NaN_3] = 1$ M), waiting for equilibration, and measuring the spectra from 850 to 420 nm for $[CuL]^{2+}$, and from 800 to 330 nm for $[NiL]^{2+}$. To stabilize the pH at 7.0, 10^{-2} M 2,6-dimethylpyridine (pK_a 6.64) was used as a buffer. The complex concentration at the beginning of the titration was 10^{-3} M. The data were evaluated with the program SPECFIT [14].

Results and Discussion. – The tetra-*N*-alkylated macrocycles were prepared either by alkylation (**6**–**8**) or by acylation and subsequent reduction of the amide (**10**, **11**) starting from the cyclic amines. Alkylation worked especially well with benzyl halides, because of their high reactivity, and with alkyl halides with large steric hindrance at C(α), since the tendency to form quaternary ammonium salts is strongly reduced. For the synthesis of **10** and **11**, the two-step sequence proved, to be superior, as also observed by *Alcock et al.* [5].

When the new macrocycles were reacted with Ni^{2+} or Cu^{2+}, only **8**, **10**, and **11** gave metal complexes. The ligands **5**–**7** with four benzyl, four 2-methylbenzyl, or four isopropyl substituents, respectively, did not complex the two metal ions, even over a longer reaction time at 60° in different solvents (H_2O, EtOH, DMF, and DMSO). Although a strong steric hindrance for these compounds is expected, the result is somewhat surprising, since the tetra-*N*-benzyl and tetra-*N*-(2-methylbenzyl) derivatives of 1,4,7,10-tetraazacyclododecane easely complex Cu^{2+} [15]. The 12-membered ring is too small to encompass a transition-metal ion, so it has to fold in such a way that the metal ion is out of the plane of the four N-atoms, and thus the *N*-substituents are pushed away from each other. A similar folding for the 14-membered ring seems not possible.

The spectral properties of the Ni^{2+} and the Cu^{2+} complexes with the ligands **2**, **8**, **10**, and **11** and of their ternary complexes with N_3^- are given in *Table 2*. In the series of the Ni^{2+} complexes, the spectrum of $[Ni(\mathbf{2})]^{2+}$ is distinctly different from those of the other ones. From previous studies, it is known that $[Ni(\mathbf{2})]^{2+}$ in aqueous solution is present in a square planar form, which absorbs at 512 nm and in a square pyramidal form with an axial H_2O molecule exhibiting two absorptions at 394 and 650 nm [8]. The other complexes

Table 2. *Spectral Properties of the Ni^{2+} and Cu^{2+} Complexes with* **2**, **8**, **10**, *and* **11** *and of Their Ternary Species with N_3^- in Aqueous Solution*

	λ_{max} [nm]	ε [$M^{-1}cm^{-1}$]		λ_{max} [nm]	ε [$M^{-1}cm^{-1}$]
$[Ni(\mathbf{2})]^{2+\,a)}$	394, 512, 650	95, 82, 33	$[Ni(\mathbf{2})(N_3)]^{+\,a)}$	405, 668	133, 46
$[Ni(\mathbf{8})]^{2+}$	544	258	$[Ni(\mathbf{8})(N_3)]^{+}$	354, 417$^{b)}$, 689	1217, 123$^{b)}$, 49
$[Ni(\mathbf{10})]^{2+}$	530	186	$[Ni(\mathbf{10})(N_3)]^{+}$	354, 416$^{b)}$, 680	1314, 125$^{b)}$, 45
$[Ni(\mathbf{11})]^{2+}$	531	216	$[Ni(\mathbf{11})(N_3)]^{+}$	354, 415$^{b)}$, 681	1261, 129$^{b)}$, 52
$[Cu(\mathbf{2})]^{2+\,a)}$	640	257	$[Cu(\mathbf{2})(N_3)]^{+\,a)}$	690	264
$[Cu(\mathbf{8})]^{2+}$	524	427	$[Cu(\mathbf{8})(N_3)]^{+}$	711	251
$[Cu(\mathbf{10})]^{2+}$	644	226	$[Cu(\mathbf{10})(N_3)]^{+}$	706	268
$[Cu(\mathbf{11})]^{2+}$	628	214	$[Cu(\mathbf{11})(N_3)]^{+}$	689	263

$^{a)}$ Values from [8]. $^{b)}$ Only shoulder, no maximum.

exhibit only one absorption band at 530–544 nm, indicating that they are all square planar and that the steric hindrance of the N-substituents is so large that it prevents the axial coordination of a H_2O molecule. In the series of the Cu^{2+} complexes, the spectrum of $[Cu(\mathbf{8})]^{2+}$ with λ_{max} 524 nm and $\varepsilon = 427 \text{M}^{-1}\text{cm}^{-1}$ is unique, whereas the other complexes with λ_{max} between 628 and 644 nm have absorption characteristics typical for pentacoordinated Cu^{2+}, in which four N-atoms of the macrocycle and an axial H_2O molecule are bound [16]. The low value of 524 nm for $[Cu(\mathbf{8})]^{2+}$ indicates that no axial H_2O molecule is coordinated in this instance, and the high value of ε suggests distortion from the square planar geometry.

To further test the effects of steric hindrance of the alkyl side chains on the reactivity of the Ni^{2+} and Cu^{2+} complexes, we studied the formation of the ternary species with N_3^- (*Eqn. 1*). The spectrophotometric titrations (*Figs. 2* and *3*) allowed to determine, with

$$[ML]^{2+} + N_3^- \rightleftharpoons [ML(N_3)]^+; \quad K_{ter} \tag{1}$$

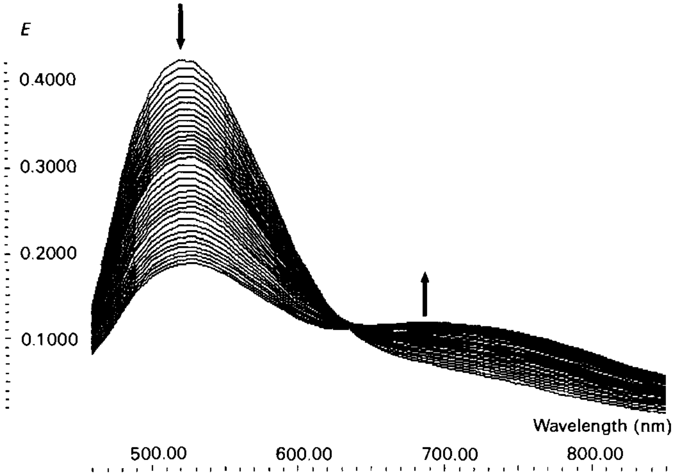


Fig. 2. *Original spectra of the titration of* $[Cu(\mathbf{8})](ClO_4)_2$ (10^{-3} M) *with azide at pH 7*

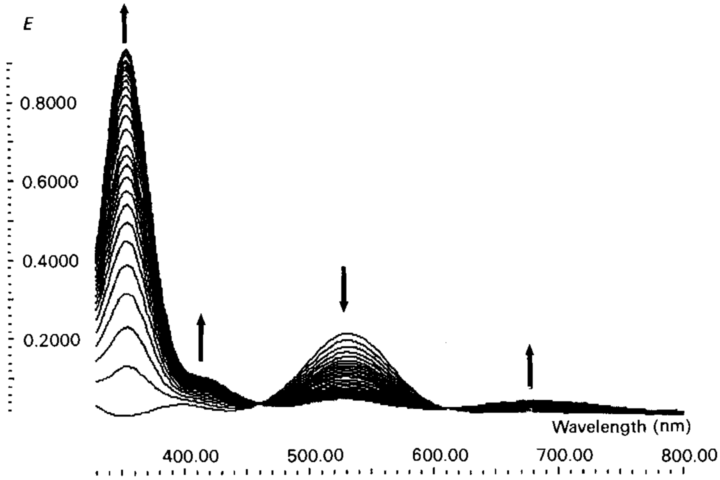


Fig. 3. *Original spectra of the titration of* $[Ni(\mathbf{11})](ClO_4)_2$ (10^{-3} M) *with azide at pH 7*

the help of the program SPECFIT [14], the stability constants K_{ter} as well as the spectra of the species $[ML]^{2+}$ and $[ML(N_3)]^+$. One example of the fitting is shown in *Fig. 4*. The spectra of the $[NiL(N_3)]^+$ complexes are very similar to each other, all showing d-d* transition bands at 405–417 nm and 668–689 nm which can be assigned to the transition in C_{4v} symmetry, as previously described for $[Ni(\mathbf{2})(N_3)]^+$ [8]. The bands at 354 nm are charge-transfer absorptions as indicated by their large ε values. The spectra of the $[CuL(N_3)]^+$ complexes can also be interpreted assuming pentacoordination of the metal ion. The shift to larger wavelengths, when N_3^- is coordinated, is a clear indication that a stronger axial ligand has been bound [16]. The stability constants K_{ter} are given in *Table 3* and show that the Ni^{2+} complexes are more stable than the analogous Cu^{2+} complexes. The effects of steric hindrance can be seen from the values of K_{ter} (*Table 3*), which decrease as the *N*-substituents become sterically more demanding. The most stable ternary species are formed by the tetramethyl derivative **2**, the less stable ones by the tetraethyl-substituted macrocycle **8**.

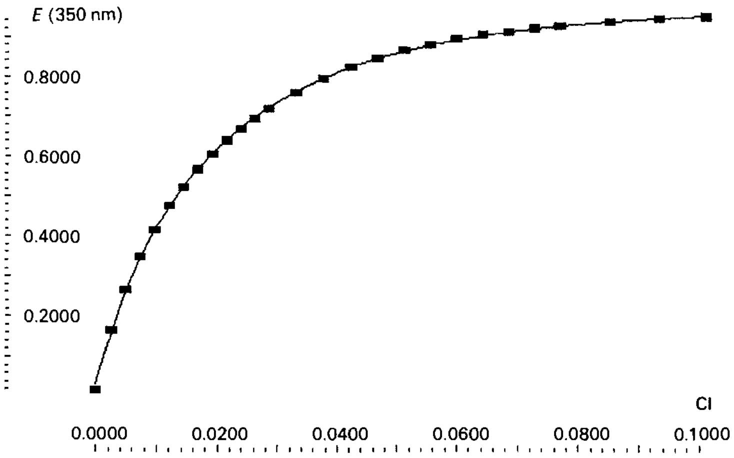


Fig. 4. *Quality of the fitting for the titration of* $[Ni(\mathbf{11})](ClO_4)_2$ *with azide*

Table 3. *Stability Constants* K_{ter} *of the Ternary Complexes* $[NiL(N_3)]^+$ *and* $[CuL(N_3)]^+$ *with* L = **2**, **8**, **10**, *and* **11** *at 25° and* I = *1* M (KNO_3)

	K_{ter}		K_{ter}
$[Ni(\mathbf{2})(N)_3]^{+}$ [a])	2.250 ± 0.050	$[Cu(\mathbf{2})(N_3)]^{+}$ [a])	1.290 ± 0.050
$[Ni(\mathbf{8})(N_3)]^+$	1.275 ± 0.009	$[Cu(\mathbf{8})(N_3)]^+$	0.601 ± 0.005
$[Ni(\mathbf{10})(N_3)]^+$	1.714 ± 0.008	$[Cu(\mathbf{10})(N_3)]^+$	1.098 ± 0.006
$[Ni(\mathbf{11})(N_3)]^+$	1.671 ± 0.007	$[Cu(\mathbf{11})(N_3)]^+$	1.098 ± 0.003

[a]) Values from [8].

The X-ray structures of $[Cu(\mathbf{8})](ClO_4)_2$ and $[Ni(\mathbf{11})](ClO_4)_2$ were determined. The molecular geometries of the two complexes, together with the atomic numbering scheme are given in *Figs. 5* and *6*. The relevant bond lengths and angles are collected in *Tables 4* and *5*.

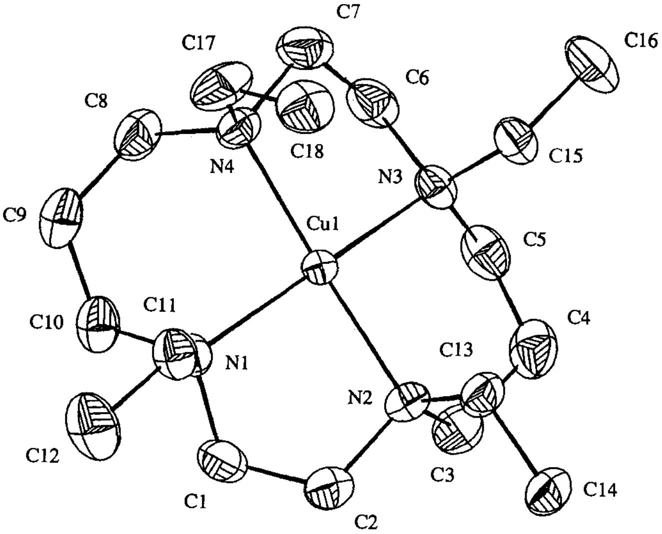


Fig. 5. *X-Ray structure of* [*Cu*(**8**)](*ClO*$_4$)$_2$

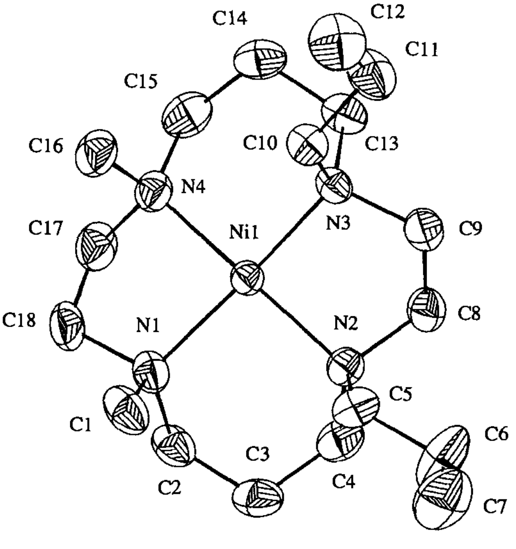


Fig. 6. *X-Ray structure of* [*Ni*(**11**)](*ClO*$_4$)$_2$

Table 4. *Selected Bond Lengths* [Å] *and Angles* [deg] *for* [*Cu*(**8**)](*ClO*$_4$)$_2$

Cu(1)–N(1)	2.044(3)	N(2)–Cu(1)–N(1)	86.0(1)	N(4)–Cu(1)–N(2)	169.4(1)
Cu(1)–N(2)	2.073(3)	N(3)–Cu(1)–N(1)	165.4(1)	N(4)–Cu(1)–N(3)	87.7(1)
Cu(1)–N(3)	2.060(3)	N(3)–Cu(1)–N(2)	95.2(1)		
Cu(1)–N(4)	2.075(3)	N(4)–Cu(1)–N(1)	93.8(1)		

Table 5. *Selected Bond Lengths* [Å] *and Angles* [deg] *for* [$Ni(\mathbf{11})$]$(ClO_4)_2$

Ni(1)–N(1)	2.017(4)	N(2)–Ni(1)–N(1)	94.0(2)	N(4)–Ni(1)–N(2)	166.6(2)
Ni(1)–N(2)	1.973(3)	N(3)–Ni(1)–N(1)	169.5(1)	N(4)–Ni(1)–N(3)	94.7(1)
Ni(1)–N(3)	1.972(3)	N(3)–Ni(1)–N(2)	88.0(1)		
Ni(1)–N(4)	1.997(4)	N(4)–Ni(1)–N(1)	85.7(2)		

In both cases, the metal ion is tetracoordinated in a roughly square planar geometry somewhat distorted towards a tetrahedral one. The dihedral angle between the two planes defined by N(1), N(2), M and N(3), N(4), M are 17.37 and 16.37° for the Cu^{2+} and the Ni^{2+} complex, respectively. The macrocycle is in the *trans*-I configuration, as found for several complexes with tetra-*N*-alkylated 1,4,8,11-tetraazacyclotetradecane [2]. The substituents tend to point away from the metal ion, except one of the Et groups in [Cu(**8**)]$(ClO_4)_2$. This is probably due to packing effects in the crystal. The best plane through the four N-atoms show that the N-atoms are alternatively up and down by ±0.20 and ±0.21 Å for the Cu^{2+} and Ni^{2+} complex, respectively. In contrast, the metal ion sits very closely in this plane, being displaced by only 0.056 and 0.025 Å for Cu^{2+} and Ni^{2+}, respectively, out of it in the direction of the substituents. The Cu–N bond lengths (2.04–2.07 Å) and the Ni–N bond lengths (1.97–2.02 Å) are in their normal range. For example in [Ni(**1**)]$^{2+}$, a low-spin square planar complex, the Ni–N distances are 1.93 Å, whereas in [Ni(**2**)]$^{2+}$, they are 1.99 Å. The lengthening has been attributed to the nonbonded repulsions between the H-atoms of the MeN group [17], and this is probably also true for ligand **11**.

This work was supported by the *Swiss National Science Foundation* (project No. 20-39270.93), and this is gratefully acknowledged.

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