72. Metal Complexes with Macrocyclic Ligands

Part XLV[1])

Axial Coordination Tendency in Reinforced Tetraazamacrocyclic Complexes

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The Cu^{2+} and Ni^{2+} complexes of three reinforced tetraazamacrocycles, containing a piperazine subunit and one or two alkyl substituents at the other two N-atoms have been prepared and their structural properties studied. In solution, the Ni^{2+} complexes are square-planar and show no tendency to axially coordinate a solvent molecule or an N_3^- ion. In contrast, the Cu^{2+} complexes change their geometry depending upon the donor properties of the solvent, being square-planar in $MeNO_2$ and pentacoordinate in DMF. They also easily react in aqueous solution with N_3^- to give ternary species with pentacoordinate geometry, the stabilities of which have been determined. In the solid state, the X-ray crystal structures of three Cu^{2+} complexes also show both geometrical arrangements, two having a square-planar, the other one a distorted square pyramidal geometry. The difference behavior of Ni^{2+} and Cu^{2+} stems from the fact that the structural change from square-planar to square-pyramidal can easily be accomplished for Cu^{2+}, whereas, for Ni^{2+}, it is accompanied by an electronic rearrangement from the low-spin to the high-spin configuration. The relatively rigid ligands cannot adapt to the somewhat larger high-spin Ni^{2+} ion.

Introduction. – Structural aspects of macrocyclic metal complexes have been studied in detail, and the factors governing the stereochemistry and coordination geometry have extensively been discussed. One of the main factors is the ring size. If the cavity of the macrocycle is to small to encompass the metal ion, the macrocycle has to fold in order that all four donors can coordinate the metal ion. Several examples of such structures have been described in the literature for metal complexes of 1,4,7,10-tetraazacyclododecanes, which have either *cis*-octahedral [2] or pentacoordinate geometries [3]. On the other side, if the macrocycle is large enough to accommodate the metal ion in its centre, square-planar or *trans*-octahedral complexes are formed. Examples have been observed in many metal complexes of 1,4,8,11-tetraazacyclotetradecane (= cyclam) [4]. Enlarging the ring size even more allows to form tetrahedral species, especially when the metal ion has electronic properties which prefer this type of geometry. For example, in the series of N_2S_2 macrocycles with different ring size a tetrahedral Cu^+ complex is formed by the 16-membered ring [5]. In addition, it has been shown by *Hancock* that the selectivity patterns of tetraazamacrocycles is controlled more by chelate ring size than by macrocyclic ring size [6].

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A further factor, which seems to determine the structure of the metal complexes, is the degree of substitution at the N-atoms of the macrocycle. So, in the series of mono-, di-, tri-, and tetramethyl derivates of cyclam the spectra of the Cu^{2+} and Ni^{2+} complexes in aqueous solution show square-planar coordination up to three Me groups, whereas for the tetramethyl derivative (TMC) a mixture of two species with square-planar and pentacoordinate geometry is present for Ni^{2+}, and a pentacoordinate form is found for Cu^{2+} [7]. However, if the substituents at the N-atoms become sterically more demanding, the pentacoordinate form with an axially coordinated solvent cannot be formed any more, and tetrahedrally distorted square-planar complexes are observed [8].

Another factor, which is clearly involved in determing the structure of cyclic ligands is the presence of an additional bridge between two N-atoms, as in the so-called reinforced macrocycles. This type of ligands has been discussed in many contributions from the structural point of view using X-ray diffraction data and HMO calculations [9] [10].

We present here some new results on the structure and coordination geometry of the Ni^{2+} and Cu^{2+} complexes with ligands 1–3, in which beside the piperazine subunit the degree of substitution and the bulkiness of the substituents at the N-atoms have been changed.

1	R = Me, R' = H
2	R = R' = Me
3	R = R' = Et
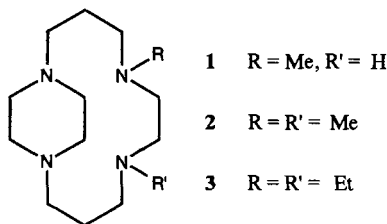
Experimental. – The Compounds *5-methyl-1,5,8,12-tetraazabicyclo[10.2.2]hexadecane* (= 5-methylpiperazinocyclam; **1**), *5,8-dimethyl-1,5,8,12-tetraazabicyclo[10.2.2]hexadecane* (= 5,8-dimethylpiperazinocyclam; **2**) [11], and *1,5,8,12-tetraazabicyclo[10.2.2]hexadecane-13,14-dione* (**4**) [12] were prepared according to the literature. UV/VIS Spectra were measured on a *Perkin-Elmer Lambda 2* spectrophotometer in 1-cm cells using *UVASOL* solvents. Typical concentrations of the complexes were $2–4 \cdot 10^{-3}$ M. IR Spectra were run as KBr pellets or as thin films on NaCl plates on a *Perkin-Elmer 1600* series *FTIR*. NMR Spectra were recorded on a *Varian Gemini 300* (δ rel. to SiMe$_4$ as internal standard). GC/MS Separations were performed on a *HP 5890* gas chromatograph (column: Me$_2$Si (25 m)). MS were recorded on a *Finnigan Mat 312*. Elemental analyses were performed in the analytical laboratory of *Ciba AG*, Basel.

5,8-Diethyl-1,5,8,12-tetraazabicyclo[10.2.2]hexadecane (= *5,8-Diethylpiperazinocyclam*; **3**). To a cooled soln. (0°) of AcCl (4.16 ml, 58.29 mmol) in dry CH$_2$Cl$_2$ (338 ml), a soln. of **4** (2.98 g, 11.72 mmol) and Et$_3$N (8.15 ml, 58.79 mmol) in dry CH$_2$Cl$_2$ (60 ml) was added over 30 min. The mixture was stirred for 24 h at r.t. The soln. was extracted once with aq. Na$_2$CO$_3$ soln. (140 ml, 1M), which was washed with CH$_2$Cl$_2$ (8 × 300 ml). The combined org. phases were dried (Na$_2$SO$_4$), filtered, and evaporated to dryness. The raw product was purified by FC (silica gel (*Merck*), 0.040–0.063 mm, MeOH/NH$_3$ (25%) 22:1, R_f 0.35). The combined fractions were evaporated to dryness under vacuum to give **5** (2.96 g, 75%). IR (KBr): 2985, 2922(CH); 1686, 1671, 1642 (CONH). MS: 339([$M + 1$]$^+$).

A soln. of **5** (2.94 g, 8.69 mmol) in dry THF (180 ml) was heated under N$_2$ to reflux (absolutely dry equipment). The condenser was connected to a flash containing a NaOCl soln. (13–14%) to destroy the Me$_2$S liberated during the reaction. BH$_3 \cdot$ SMe$_2$ (36 ml, 360 mmol) in dry THF (36 ml) was added over 20 min. To dilute the soln., two additional portions of dry THF were added during the reaction (60 ml after 4.5 h and 20 ml after 28 h). After 45 h, the mixture was cooled with ice, and the excess of BH$_3$ was destroyed by cautious addition of MeOH (200 ml). The mixture was stirred for 2 h under N$_2$, the solvent evaporated, and the BH$_3$ adduct dried *in*

high vacuum. To the solid BH_3 adduct, 18% HCl soln. (400 ml) was added during 20 min. The condenser was connected again with a flask containing a NaOCl soln. (13–14%) to destroy the remaining Me_2S. The mixture was heated during 80 min to reflux (large amounts of foam!). After 2 h, the soln. was ice-cooled and the black insoluble impurities were filtered off. To the ice-cooled soln., NaOH (400 ml, 10M) was added to adjust the pH value to 13.5. The soln. was extracted with $CHCl_3$ (10×300 ml). The org. extracts were dried (Na_2SO_4), filtered, and the solvent was evaporated. The resulting orange oil was dried under high vacuum and purified by FC (silica gel (*Merck*), 0.040–0.063 mm, $MeOH/NH_3$ (25%) 5:1, R_f 0.41). The fractions containing the product were dissolved in a little CH_2Cl_2 and filtered to remove the silica gel. Drying of the slightly yellow oil under high vacuum gave **3** (518 mg, 21%). IR (NaCl): 2926, 2789 (CH). ^{1}H-NMR ($CDCl_3$): 0.98 (t, $2 NCH_2Me$); 1.70 (*quint.*, $2 CH_2CH_2CH_2$); 2.50–2.57 (m, $6 CH_2N$); 2.59–2.68 (m, 4 H, $N(CH_2CH_2)_2N$); 2.88 (t, $2 NCH_2CH_2CH_2N$); 3.11–3.17 (m, 4 H, $N(CH_2CH_2)_2N$). ^{13}C-NMR ($CDCl_3$): 10.61 (Me); 24.02 ($CH_2CH_2CH_2$); 46.41, 47.27, 51.64, 51.92, 52.24 (NCH_2). GC/MS: 282 (M^+).

General Complexation Procedure. To a soln. of the ligand **1**, **2**, or **3** (1–2 mmol) in EtOH (2–4 ml) heated to reflux, a soln. of the metal perchlorate (1–2 mmol) in EtOH (2–4 ml) was added dropwise. The mixtures were generally refluxed for several h, then placed into the refrigerator overnight. The crystals were filtered and washed with ice-cooled dry EtOH and ice-cooled Et_2O.

(5-Methylpiperazinocyclam)copper(II) Diperchlorate ([Cu(**1**)] $(ClO_4)_2$; **6**). The violet crystals were recrystallized from $EtOH/H_2O$ and dried under high vacuum (333 mg, 67%). IR (KBr): 3222 (NH); 2945, 2875 (CH); 1090 (ClO_4^-). Ms: 402 ([$M - ClO_4^-$]). Anal. calc. for $C_{13}H_{28}Cl_2CuN_4O_8$ (502.84): C 31.05, H 5.61, N 11.14, Cl 14.10; found: C 31.23, H 5.70, N 11.09, Cl 13.68.

(5-Methylpiperazinocyclam)nickel(II) Diperchlorate ([Ni(**1**)] $(ClO_4)_2$; **7**). The orange powder was recrystallized from $EtOH/H_2O$, washed with ice-cooled dry EtOH and ice-cooled Et_2O, and dried under high vacuum (275 mg, 65%). IR (KBr): 3440 (NH); 3061, 2976, 2927, 2879 (CH); 1641, 1618 (NH); 1144, 1111, 1078 (ClO_4^-). MS: 397 ([$M - ClO_4^-$]). Anal. calc. for $C_{13}H_{28}Cl_2N_4NiO_8$ (497.99): C 31.35, H 5.67, N 11.25, Cl 14.42; found: C 31.65, H 5.74, N 11.31, Cl 14.37.

(5,8-Dimethylpiperazinocyclam)copper(II) Diperchlorate ([Cu(**2**)] $(ClO_4)_2$; **8**). The violet crystals were recrystallized from $EtOH/H_2O$, washed with ice-cooled dry EtOH and ice-cooled Et_2O and dried under high vacuum (672 mg, 68%). IR (KBr): 2872 (CH); 1090 (ClO_4^-). MS: 416 ([$M - ClO_4^-$]). Anal. calc. for $C_{14}H_{30}Cl_2$-$CuN_4O_8 \cdot 0.69 H_2O$ (529.30): C 31.77, H 5.98, N 10.59, Cl 13.40, H_2O 2.35; found: C 31.92, H 5.93, N 10.65, Cl 13.59, H_2O 2.34.

(5,8-Diethylpiperazinocyclam)copper(II) Diperchlorate ([Cu(**3**)] $(ClO_4)_2$; **9**). Decanting the mother liquor of the reaction and drying the violet compound under high vacuum gave **9** (83 mg 51%). IR (KBr): 2978, 2922, 2876 (CH); 1095 (ClO_4^-). MS: 444 ([$M - ClO_4^-$]).

(5,8-Dimethylpiperazinocyclam)nickel(II) Dihexafluorophosphate ([Ni(**2**)] $(PF_6)_2$; **10**). A soln. of **7** (950 mg, 1.19 mmol) in DMSO (15 ml; for UV spectroscopy, *Fluka*, dried over molecular sieves) was stirred and evacuated ($1.5 \cdot 10^{-2}$ mbar) for 1 h. Then, the flask was filled and purged for 20 min with N_2. A soln. of BuLi in hexane (1.30 ml, 1.6M, 2.08 mmol) was added during 20 min. The dark blue soln. was stirred for 30 min, and, during 5 min, MeI (0.32 ml, 5.12 mmol) was added. The orange soln. was stirred for another 40 min. Thereafter, MeI and hexane were evaporated. To the DMSO soln., a sat. soln. of NH_4PF_6 in 96% EtOH (160 ml) was added. An orange precipitate was formed, and the soln. was placed into the refrigerator for 2.5 h. The compound was filtered and was washed with ice-cooled dry EtOH. Recrystallization from MeOH/MeCN, filtration, and washing with ice-cooled dry EtOH gave the orange powder **10** (723 mg, 62%). IR (KBr): 2944, 2889 (CH); 839, 558 (PF_6^-). ^{1}H-NMR (CD_3CN): 1.65–1.86 (m, $2 NCH_2CH_2CH_2N$); 2.21–2.83 (m, $8 CH_2N$); 3.35–3.59 (m, CH_2N, 2 MeN); 4.56–4.68 (m, CH_2N). ^{13}C-NMR (CD_3CN): 23.34 ($CH_2CH_2CH_2$); 43.82 (Me); 51.82, 54.27, 58.85, 59.04, 59.31 (CH_2N). MS: 457 ([$M - PF_6^-$]). Anal. calc. for $C_{14}H_{30}F_{12}N_4NiP_2$ (603.04): C 27.88, H 5.01, N 9.29; found C 28.22, H 4.99, N 9.65.

Crystallography. To obtain crystals suitable for X-ray studies, **6** was dissolved in H_2O and **8** in a mixture of $EtOH/H_2O$, and the solvent was slowly evaporated. From the mother liquor of the complexation of **3** with $Cu(ClO_4)_2 \cdot 6 H_2O$ in EtOH (see above), suitable crystals of **9** were obtained by slow evaporation of the solvent. Crystals of $3 \cdot 2 HClO_4$ were obtained in the attempt to prepare the complex of **3** with $Ni(ClO_4)_2$ and were grown from H_2O.

X-Ray Diffraction Measurements. The crystal data and parameters of the data collection for the Cu^{2+} complexes with **1**, **2**, and **3**, and for $3 \cdot 2 HClO_4$ are given in the *Tables 1* and *2*.

Unit-cell parameters were determined by accurate centering of 16 to 25 independent strong reflections by the least-squares method. Three standard reflections monitored every 2 h during data collection showed no significant variation of the intensity, except for $3 \cdot 2 HClO_4$, which showed and even intensity decrease with no consequence

Table 1. *Crystal Data and Parameters of Data Collection for* $[Cu(1)](ClO_4)_2$ *and* $[Cu(2)](ClO_4)_2 \cdot 2H_2O$

	$[Cu(1)](ClO_4)_2$	$[Cu(2)](ClO_4)_2 \cdot 2H_2O$
Formula	$(C_{13}H_{28}CuN_4)(ClO_4)_2$	$(C_{14}H_{30}CuN_4)(ClO_4)_2$ $(2H_2O)$
Molecular weight [gmol^{-1}]	502.83	552.89
Crystal system	orthorhombic	orthorhombic
Space group	*Pbca*	$P2_1nb^a)$
a [Å]	15.503(1)	10.071(2)
b [Å]	19.760(3)	13.954(1)
c [Å]	26.404(5)	16.735(2)
α [°]	90.00	90.00
β [°]	90.00	90.00
γ [°]	90.00	90.00
V [Å^3]	8087.99	2351.8(5)
Z	16	4
$F(000)$	4176	1156
Density [gcm^{-3}]	1.65	1.56
μ [mm^{-1}]	4.43	3.93
Crystal size [mm]	$0.18 \times 0.32 \times 0.65$	$0.28 \times 0.35 \times 0.52$
Temp. [K]	293	293
Radiation	CuK_a ($\lambda = 1.54180$)	CuK_a ($\lambda = 1.54180$)
Scan type	$\omega/2\Theta$	$\omega/2\Theta$
Θ_{max} [°]	77.50	77.50
No. of measured refl.	7777	2459
No. of indep. refl.	7413	2354
No. of refl. in refinement	5717	2070
No. of variables	588	281
Final R	5.45	6.24
Final R_w	6.60	6.39
Weighting scheme	*Chebychev* polynomial [13]	*Chebychev* polynomial [13]
Last max./min. in diffr. map	0.63/−0.48	0.59/−0.48

[a]) Non-standard settings of $Pna2_1$

for the structure determination. The raw data set was corrected for polarization effects and X-ray diffraction absorption. The structure was solved by the direct method [14]. Anisotropic least-squares refinements were carried out on all non-H-atoms, using the program CRYSTALS [15]. Parts of the cations **2** and **3**, and some of the ClO_4^- ions, are disordered. They have been, except for **2**, refined using two split positions per atom keeping the sum of their occupancy equal to 1. H-Atoms are in calculated positions with C−H distances of 0.96 Å and fixed isotropic thermal parameters. Scattering factors are taken from the '*International Tables of Crystallography*' [16].

Spectrophotometric Titrations. The titrations of the Cu^{2+} complexes **6** and **8** with N_3^- were run at $25 \pm 0.1°$ and $I = 1.0$ (KNO_3) on the automatic computer-controlled titrator, consisting of an UV/VIS spectrometer (*Pye Unicam PU 8800, Philips*), a pH meter (*Metrohm 605*), and a dosimat (*Metrohm 665*) [17]. The computer (*IBM-AT-286*) ran the titration by adding small amounts of the titrant ([NaN$_3$] = 1M), waiting for equilibration and measuring the spectra from 400–700 nm for **6** and 450–750 nm for **8**. The pH was stabilized at 6.8–6.9 with 2,6 = dimethylpyridine ($pK_a = 6.64$) as buffer. The data were evaluated with the program SPECFIT [18]. The Ni^{2+} complexes **7** and **10** did not show any spectral changes by adding N_3^-.

Results and Discussion. – The syntheses of ligand **1** and **2** followed the literature procedure of *Kolinsky* [11]. Only the diethyl derivate **3** is new and has been prepared by acylation of **4** with AcCl and subsequent reduction of the amide groups with $BH_3 \cdot SMe_2$

Table 2. *Crystal Data and Parameters of Data Collection for* **3** · *2 HClO₄ and [Cu(3)](ClO₄)₂ · 2 H₂O*

	3 · 2 HClO₄	[Cu(3)](ClO₄)₂ · 2 H₂O
Formula	(C₁₆H₃₄N₄)(2 HClO₄)	(C₁₆H₃₄CuN₄)(ClO₄)₂ (2 H₂O)
Molecular weight [gmol⁻¹]	483.39	580.94
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	9.280(1)	7.9040(4)
b [Å]	18.085(2)	18.9443(10)
c [Å]	14.247(2)	16.9184(7)
α [°]	90	90
β [°]	103.1(9)	96.020(4)
γ [°]	90	90
V [Å³]	2328.7(6)	2519.3(2)
Z	4	4
$F(000)$	1032	1220
Density [gcm⁻³]	1.38	1.53
μ [mm⁻¹]	2.96	3.69
Crystal size [mm]	0.10 × 0.18 × 0.30	0.23 × 0.29 × 0.42
Temp. [K]	293	293
Radiation	CuK_α ($\lambda = 1.54180$)	CuK_α ($\lambda = 1.54180$)
Scan type	$\omega/2\Theta$	$\omega/2\Theta$
Θ_{max} [°]	77.50	77.50
No. of measured refl.	6933	5154
No. of indep. refl.	3949	4735
No. of refl. in refinement	2148	4092
No. of variables	279	442
Final R	4.94	4.38
Final R_w	6.14	5.64
Weighting scheme	*Chebychev* polynomial [13]	*Chebychev* polynomial [13]
Last max./min. in diffr. map	0.47/−0.24	0.46/−0.37

(*Scheme*). This method has previously proved to be superior than the direct alkylation in the synthesis of tetra-*N*-alkylated derivates of 1,4,8,11-tetraazacyclotetradecane [8] [19].

Mixing the ligands with the corresponding Cu²⁺ and Ni²⁺ salts gives the metal complexes, except for **2** and **3** which do not or only partially react with Ni²⁺. Interesting is that a Ni²⁺ complex with **2** can be prepared by alkylation of the performed complex with **1** following the procedure of *Barefield et al.* [20]. The UV/VIS spectra of the Cu²⁺ and Ni²⁺ complexes (*Table 3*) provide important structural informations. The Ni²⁺ complexes with **1** and **2** have one absorption band at 470–484 nm, which is typical for square-planar coordination geometry [21]. Changing the donor properties of the solvent has nearly no effect on the absorption maximum and indicates no participation of the solvent in the coordination sphere. This is in strong contrast with solvent effects observed for the Ni²⁺ complex with 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC), which changes from a square-planar geometry in poor-donor solvents to a pentacoordinate geometry in good-donor solvents [7]. In the case of the Cu²⁺ complexes, the absorption maximum depends on the donor properties of the solvent. Changing from MeNO₂ to DMF the value of λ_{max} shifts by 50–60 nm to longer wavelengths, which is typical when an axial ligand is added to a square-planar Cu²⁺ complex to give a

Scheme
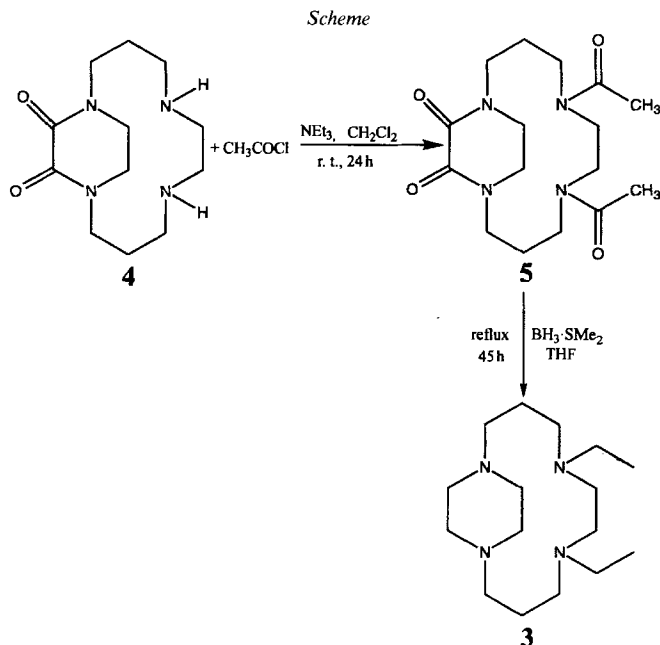

Table 3. *Spectral Properties of the Ni²⁺ and Cu²⁺ Complexes with 1 and 2, and of the Cu²⁺ Complex with 3 in Different Solvents [λ in nm (ε in M⁻¹cm⁻¹)]*

	H_2O	$MeNO_2$	DMF
[Cu(**1**)](ClO₄)₂	556 (328)	512 (447)	564 (340)
[Cu(**2**)](ClO₄)₂	ᵃ)	502 (613)	568 (334)
[Cu(**3**)](ClO₄)₂	510 (406)	502 (513)	539 (363)
[Ni(**1**)](ClO₄)₂	469 (244)	474 (263)	477 (248)
[Ni(**2**)](PF₆)₂	480 (429)	481 (453)	484 (437)

ᵃ) See *Fig. 1.*

pentacoordinate species [22]. So, in $MeNO_2$ the Cu^{2+} complexes are square-planar and in the more polar DMF pentacoordinate. Especially interesting is the observation that there is a temperature-dependent equilibrium (*Eqn. 1*) for L = **2** betweeen the square-planar species $[CuL]^{2+}$ and the pentacoordinate one $[CuL(H_2O)]^{2+}$.

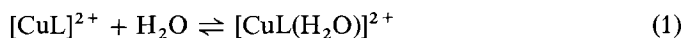$$[CuL]^{2+} + H_2O \rightleftharpoons [CuL(H_2O)]^{2+} \qquad (1)$$

Fig. 1 shows that, at high temperature, the equilibrium is on the $[CuL]^{2+}$ side with λ_{max} = 514 nm. When the temperature is lowered, the band at 514 nm decreases, and a new band at *ca.* 640 nm is formed. This equilibrium reminds the yellow-blue interconver-

sion observed in several macrocyclic Ni^{2+} complexes [23], in which, through solvent participation, the geometry changes from square-planar to octahedral. It also reminds the temperature dependency of the spectrum of $[Ni(TMC)]^{2+}$, which shows that both, a square-planar and a pentacoordinate, species are present in aqueous solution [7]. Worth pointing out are the relatively high molar absorptivities of the Cu^{2+} and Ni^{2+} complexes, which probably results through the tetrahedral distortion of the square-planar geometry as indicated by the X-ray results (see below).
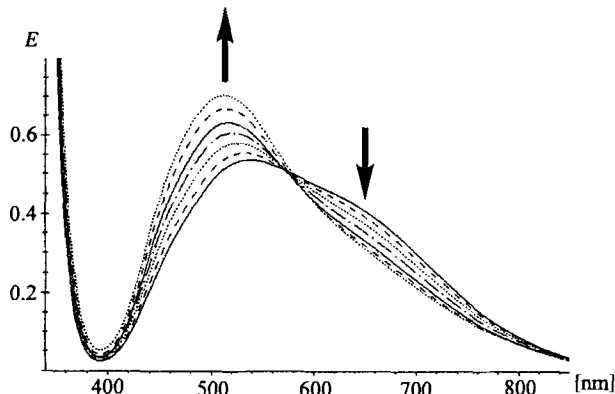

Fig. 1. *Absorption spectra of [Cu(2)]²⁺ in H₂O, recorded at different temperatures.* The arrows show the direction of spectral variations with increasing temperature: 11.4°, 20.5°, 29.4°, 39.3°, 49.5°, 60.0°, 69.5°. The limiting absorbance value at 496 nm evaluated in 7M $NaClO_4$ solution is 627 $M^{-1} cm^{-1}$ at 25.2°. This value did not change at 68.3°.

To further study the complexation properties in the axial position of these complexes, we measured the formation of the ternary species with N_3^- (*Eqn. 2*).

$$[ML]^{2+} + N_3^- \rightleftharpoons [Ml(N_3)]^+ ; K_{ter} \qquad (2)$$
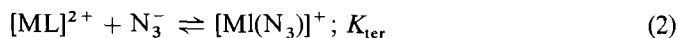
Spectrophotometric titrations of $[ML]^{2+}$ with N_3^- at fixed pH (*Fig. 2*) allow to determine with the help of the program SPECFIT [18] the stability constants K_{ter} as well as the spectra of the species $[ML]^{2+}$ and $[ML(N_3)]^+$ (*Table 4*). Whereas the Ni^{2+} complexes show no tendency at all to bind N_3^-, the Cu^{2+} complexes react according to *Eqn. 2* to give $[CuL(N_3)]^+$. This is very similar to the effect observed for the solvents (see above). The Ni^{2+} complexes have no tendency to change their geometry from square-planar to pentacoordinate, even in the presence of good donors. Whereas the structural change can easily be accomplished for Cu^{2+}, in the case of Ni^{2+} the geometry change is accompanied by a reorganization of the d-electrons from the low- to the high-spin arrangement. The relatively rigid ligands cannot expand the macrocyclic hole in order to bind the somewhat larger high-spin Ni^{2+} [10].

Structural aspects of the metal complexes were also studied using X-ray diffraction. Crystals of ligand **3** as diperchlorate were obtained, when we tried to synthesize the Ni^{2+} complex. The structure shows that the two acidic protons sit at two N-atoms *trans* two each other (N(2) and N(4)) in order minimize electrostatic repulsion (*Fig. 3*). The protons
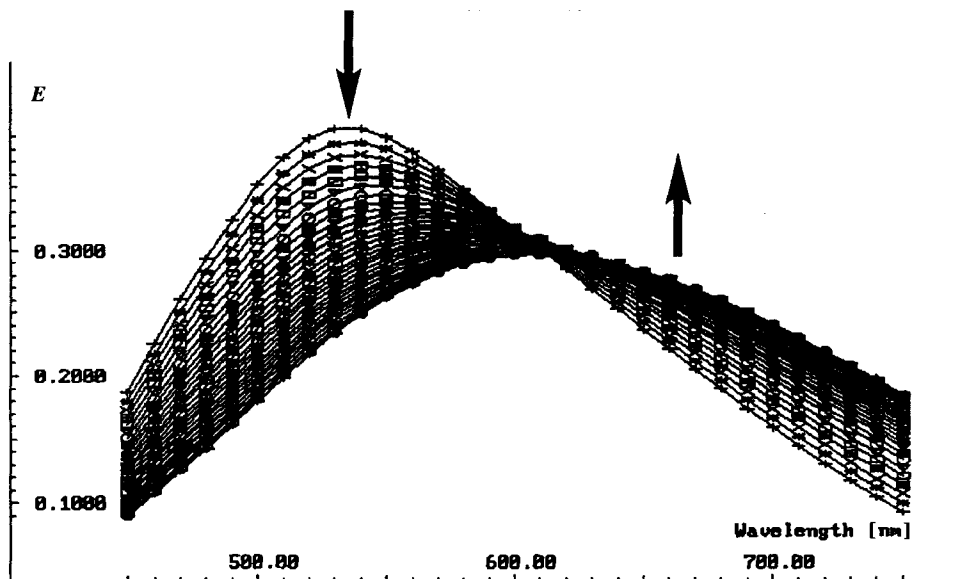
Fig. 2. *Spectra of the titration of* $[Cu(2)]^{2+}$ *with* N_3^- *at pH 6.8–6.9 and 25°*

Table 4. *Stability Constants* K_{ter} *and Spectral Properties* [λ *in nm* (ε *in* $M^{-1}cm^{-1}$)] *at 25.0° and* $I = 1M$ (KNO_3) *of the Ternary Complexes with* N_3^-

	log K_{ter}	$\lambda(\varepsilon)$
$[Cu(1)](ClO_4)_2$	0.88 ± 0.04	618 (326)
$[Cu(2)](ClO_4)_2$	0.98 ± 0.03	656 (338)

form H-bonds with the non-protonated amine groups. So, $N(2)-H(1)\cdots N(3)$ is 147.4° with $H(1)\cdots N(3)$ 1.97 Å and $N(4)-H(2)\cdots N(1)$ is 152.5° with $H(2)\cdots N(1)$ 1.88 Å. With regard to the plane through the four N-atoms, the two Et groups are *trans*. The
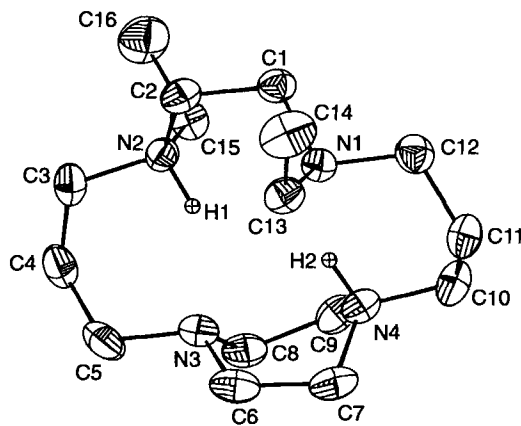

Fig. 3. *ORTEP Plot of* **3** · *2HClO₄*

piperazine ring is in the boat conformation with a $N(4) \cdots N(3)$ distance of 2.55 Å. All C–N and C–C bond lengths are in their normal range. Interesting is that, through complexation with Cu^{2+}, the two Et groups take up a *cis*-arrangement and point to the same side as the axial H_2O molecule (*Fig. 4*), which completes the pentacoordinate
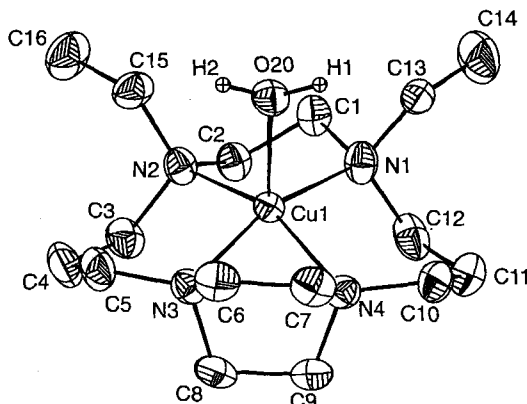

Fig. 4. *ORTEP Plot of [Cu(3)](ClO_4)_2*

geometry of the Cu^{2+}. The four N-atoms form a nearly perfect plane with small deriva-tions ($\pm$ 0.036 and $\pm$ 0.042 Å), whereas the Cu^{2+} is situated out of this plane by 0.34 Å towards the apical H_2O molecule. The Cu–N bonds are in the range 2.04–2.05 Å, and the axial Cu–O bond is 2.23 Å (*Table 5*). The N–Cu–N angles are all between 89° to 97° except the one involving the piperazine N-atoms which is only 73°, similar to the value observed in an analogous 15-membered reinforced macrocyclic Ni^{2+} complex [24]. This is clearly due to the small 'bite' of the piperazine, in which the N–N distance is reduced from 2.55 Å in the free ligand to 2.43 Å in the complex.

Table 5. *Selected Bond Lenghts [Å] and Angles [°] for [Cu(3)](ClO_4)_2*

Cu(1)–N(1)	2.047(2)	N(1)–Cu(1)–N(2)	88.73(9)
Cu(1)–N(2)	2.046(2)	N(1)–Cu(1)–N(3)	161.6(1)
Cu(1)–N(3)	2.034(2)	N(1)–Cu(1)–N(4)	96.6(1)
Cu(1)–N(4)	2.039(2)	N(2)–Cu(1)–N(3)	95.10(9)
		N(2)–Cu(1)–N(4)	156.9(1)
		N(3)–Cu(1)–N(4)	73.3(1)
Cu(1)–O(20)	2.226(2)	N(1)–Cu(1)–O(20)	95.78(9)
		N(2)–Cu(1)–O(20)	100.36(9)
		N(3)–Cu(1)–O(20)	101.18(9)
		N(4)–Cu(1)–O(20)	101.42(9)

The structure of the Cu^{2+} complex with **2** (*Fig. 5*) is very similar to that just discus-sed, but somewhat more disordered. The Cu^{2+} is pentacoordinated by the four N-atoms of the macrocycle and a H_2O molecule. The N-atoms form a nearly perfect plane ($\pm$ 0.014 and $\pm$ 0.016 Å), whereas the Cu^{2+} is out of the plane by 0.330 Å. Bond length and angles are given in *Table 6*.
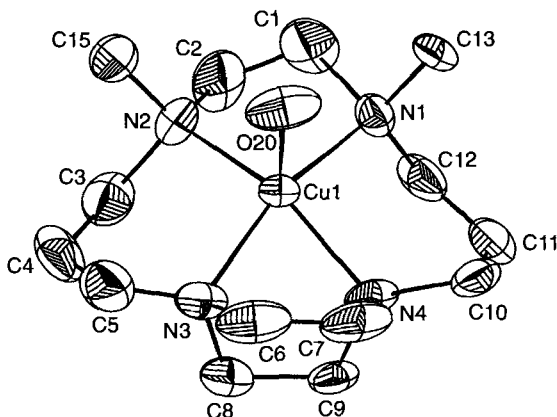
Fig. 5. *ORTEP Plot of* $[Cu(2)](ClO_4)_2$

Table 6. *Selected Bond Lenghts* [Å] *and Angles* [°] *for* $[Cu(2)](ClO_4)_2$

Cu(1)–N(1)	2.09(1)	N(1)–Cu(1)–N(2)	89.2(3)
Cu(1)–N(2)	1.94(1)	N(1)–Cu(1)–N(3)	159.9(4)
Cu(1)–N(3)	2.04(1)	N(1)–Cu(1)–N(4)	94.0(6)
Cu(1)–N(4)	2.04(1)	N(2)–Cu(1)–N(3)	97.3(6)
		N(2)–Cu(1)–N(4)	159.0(4)
		N(3)–Cu(1)–N(4)	73.4(3)
Cu(1)–O(20)	2.235(5)	N(1)–Cu(1)–O(20)	100.3(5)
		N(2)–Cu(1)–O(20)	96.0(5)
		N(3)–Cu(1)–O(20)	98.0(5)
		N(4)–Cu(1)–O(20)	103.8(4)

The structure of the Cu^{2+} complex with **1** shows that two very similar molecules are present in the unit cell. In both, the metal ion is coordinated by the four N-atoms of the macrocycle in a tetrahedrally distorted square-planar geometry (*Fig. 6*). The four N-atoms have large deviations (± 0.26 to ± 0.30 Å) from the best plane, whereas the
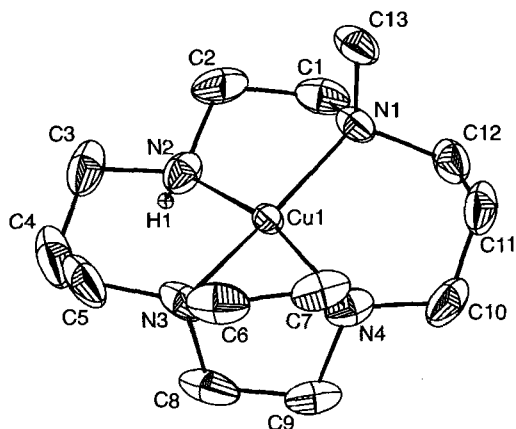
Fig. 6. *ORTEP Plot of* $[Cu(1)](ClO_4)_2$

Table 7. *Selected Bond Lenghts* [Å] *and Angles* [°] *for* [Cu(1)](ClO_4)_2 [a])

Cu(1)–N(1)	2.012(3)	Cu(21)–N(21)	2.007(3)
Cu(1)–N(2)	1.979(4)	Cu(21)–N(22)	1.980(3)
Cu(1)–N(3)	2.003(4)	Cu(21)–N(23)	2.010(3)
Cu(1)–N(4)	2.016(4)	Cu(21)–N(24)	2.008(3)
N(1)–Cu(1)–N(2)	88.0(2)	N(21)–Cu(21)–N(22)	88.11(1)
N(1)–Cu(1)–N(3)	167.3(2)	N(21)–Cu(21)–N(23)	163.4(1)
N(1)–Cu(1)–N(4)	102.3(2)	N(21)–Cu(21)–N(24)	101.6(1)
N(2)–Cu(1)–N(3)	98.9(2)	N(22)–Cu(21)–N(23)	99.6(1)
N(2)–Cu(1)–N(4)	158.3(2)	N(22)–Cu(21)–N(24)	161.6(1)
N(3)–Cu(1)–N(4)	75.0(2)	N(23)–Cu(21)–N(24)	75.3(1)

[a])   Two independent cations are found in the asymmetric unit. The left row refers to the first, the right row to the second cation.

Cu^{2+} sits in it with only 0.070 and 0.007 Å deviation for Cu(1) and Cu(21), respectively. The Me group and the H-atom at the N-atoms N(1) and N(2) are *trans* to each other, which is in contrast to the previous structure. The Cu–N bond lengths are distinctly shorter (1.98–2.02 Å) than in the structure of Cu^{2+} with **2** and **3**. Again the angle N–Cu–N involving the piperazine N-atoms is only *ca.* 75° (*Table 7*).

Our results clearly show that reinforced macrocycles tend to compress the metal ion and cannot adapt easily themselves to the geometrical requirements of the central ion. So low-spin Ni^{2+} is prefered over high-spin Ni^{2+}, which is somewhat larger.

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