11. Metal Complexes with Macrocyclic Ligands

Part XXVI[1])

Synthesis and Spectral Properties of Cu^{2+} Complexes with Mono-*N*-functionalized 1,4,8-Trimethyl-1,4,8,11-tetraazacyclotetradecanes

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A series of mono-*N*-functionalized 1,4,8-trimethyl-1,4,8,11-tetraazacyclotetradecanes **3**–**14** were synthesized by alkylating the secondary N-atom of the macrocycle **1**. The spectral properties of the Cu^{2+} complexes, studied under different pH conditions, are discussed in relation to the possibility of coordination of the donor group of the side chain to the axial position of the metal ion and to the effect of the length of the side chain.

Introduction. – Functionalized tetraazamacrocycles are a new class of ligands with interesting properties [2]. Beside the tetra-*N*-substituted derivatives, which show a relatively complicated coordination chemistry due to their many potential donor groups [3], *mono-N*-substituted tetraazamacrocycles, being more simple in their complexation reactions, have been studied from several points of view. The equilibria involving the coordination of the pendant side chain at one of the apical positions of the central ion [2] [4] [5], structural aspects of the coordination geometry of the metal ion [5] [6], the problems associated with the synthesis of these ligands [6] [7], and one example of metal-ion-induced reactivity [8] have been discussed in detail.

In this field, two classes of monosubstituted compounds have mainly been developed. The first one is derived from a tritosylated pseudo-cyclam, which selectively allows the introduction of one pendant group at the unprotected N-atom [7]. After cleavage of the Ts groups, the obtained free ligand can be complexed with a series of metal ions. The second group of compounds is based on 1,4,8-trimethyl-1,4,8,11-tetraazacyclotetradecane, first described by *Wagner* and *Barefield* [9], which also can be alkylated at the non-methylated N-atom and lead to macrocycles with only one pendant arm [5] [10]. So, metal complexes with an amino group in the side chain have been prepared, and the effect of steric hindrance has been studied [5]. In another example, the kinetics of the CN hydrolysis in the Cu^{2+} complex of **15** have been investigated and it has been shown that the reaction takes place by an intramolecular attack of a coordinated OH^- onto the CN group [8]. Finally, *Barefield et al.* [10] give an excellent survey of the synthetic possibilities and of the properties of several Ni^{2+} and Cu^{2+} complexes of this type.

Supplementing the results published by *Barefield et al.*, we describe in this paper a series of similar compounds, **3**–**14**, in which side chains can lead to five- or six-membered chelates through binding of the the donor group at the end of the chain to the metal ion.

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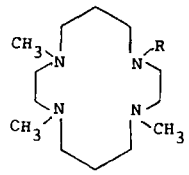

1 R = H
2 R = CH_3
3 R = CH_2COOCH_3
4 R = $CH_2COOC_2H_5$
5 R = $CH_2CH_2COOC_2H_5$
6 R = $CH_2CON(CH_3)_2$
7 R = $CH_2CH_2PO(OC_2H_5)_2$
8 R = CH_2CH_2CN
9 R = $CH_2CH_2CH_2NH_2$
10 R = $CH_2CH_2CONH_2$
11 R = CH_2CH_2SH
12 R = CH_2COOH
13 R = CH_2CH_2COOH
14 R = $CH_2CH_2PO(OC_2H_5)(OH)$
15 R = CH_2CN
16 R = CH_2CONH_2
17 R = $CH_2CH_2NH_2$
18 R = $CH_2CH_2N(CH_3)_2$

Experimental. – *1,4,8-Trimethyl-1,4,8,11-tetraazacyclotetradecane* (**1**) was prepared by the BuLi method described in [10] and was purified by distillation at 120–122°/0.15 Torr.

[1-(Methoxycarbonylmethyl)-4,8,11-trimethyl-1,4,8,11-tetracyclotetradecane]copper Diperchlorate ([Cu(**3**)$(ClO_4)_2$]). The macrocycle **1** (0.5 g, 2.1 mmol) and methyl bromoacetate (0.23 ml, 2.5 mmol) were reacted for 4 h in 20 ml of CH_2Cl_2. Thereafter, the solvent and the excess of alkylating agent were evaporated and the oily residue taken up with CH_2Cl_2 and aq. $NaHCO_3$ soln. The org. phase was dried (Na_2SO_4) and evaporated. The residue dissolved in abs. MeOH was reacted with 1 equiv. of $Cu(ClO_4)_2$ also dissolved in abs. MeOH. The Cu^{2+} complex precipitated and was recrystallized from H_2O/MeOH. Yield 550 mg (29.4%); blue crystals. IR (KBr): 1710 ($COOCH_3$). Anal. calc. for $C_{16}H_{34}Cl_2CuN_4O_{10}$ (576.92): C 33.31, H 5.94, N 9.71; found: C 33.5, H 5.9, N 9.8.

[1-(Ethoxycarbonylmethyl)-4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane]copper Diperchlorate ([Cu(**4**)$(ClO_4)_2$]) was prepared as **3** using ethyl bromoacetate and was recrystallized from EtOH/H_2O. Yield: 19.7%: blue crystals. IR (KBr): 1685 ($COOC_2H_5$). Anal. calc. for $C_{17}H_{36}Cl_2CuN_4O_{10}$ (590.95): C 34.55, H 6.14, N 9.48; found: C 34.33, H 5.98, N 9.37.

{1-[2-(Ethoxycarbonyl)ethyl]-4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane} copper Diperchlorate ([Cu(**5**)$(ClO_4)_2$]). Compound **1** (0.6 g, 2.5 mmol) was refluxed for 4 h in 15 ml of ethyl acrylate. The excess of ester was then evaporated and the residue taken up with CH_2Cl_2. After washing with H_2O, the org. phase was diluted with an equal amount of acetone and reacted with 1 equiv. of $Cu(ClO_4)_2$ (0.92 g, 2.5 mmol) dissolved in acetone. The complex precipitated and was recrystallized from H_2O/EtOH. Yield: 45.6%. IR (KBr): 1675 ($COOC_2H_5$). Anal. calc. for $C_{18}H_{38}Cl_2CuN_4O_{10}$ (604.97): C 35.74, H 6.33, Cl 11.72, N 9.26; found: C 35.76, H 6.32, Cl 11.60, N 9.32.

[1-(N,N-Dimethylcarbamoylmethyl)-4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane]copper Diperchlorate ([Cu(**6**)$(ClO_4)_2$]). Compound **1** (0.5 g, 2.1 mmol) in 30 ml of abs. MeOH was reacted with *N,N*-demethylchloroacetamide [11] (0.28 g, 2.3 mmol) and Cs_2CO_3 (0.74 g, 2.3 mmol) overnight. Since TLC (*Alox E 60*, H_2O/EtOH 1:1) still showed an appreciable amount of unreacted **1**, the soln. was reacted with a second portion of *N,N*-dimethylchloroacetamide (0.28 g, 2.3 mmol) for another 6 h. The mixture was then evaporated and extracted with CH_2Cl_2, which was washed once with H_2O. The org. phase was dried (Na_2SO_4) and evaporated. To a soln. of the residue in 20 ml of i-PrOH, a soln. of $Cu(ClO_4)_2$ (0.72 g, 2.1 mmol) in 20 ml of i-PrOH was added. After 1 h stirring, the sticky complex was separated from the solvent by decantation. The product is a mixture of the desired complex with **6** and that with the unreacted macrocycle **1**. For purification, the mixture dissolved in a little H_2O was filtrated and run over a *Sephadex G10* column. The first fraction containing the Cu^{2+} complex with **6** was evaporated and the solid recrystallized from H_2O/MeOH. Yield: 430 mg (35.3%); blue crystals. IR (KBr): 1635 ($CON(CH_3)_2$). Anal. calc. for $C_{17}H_{37}Cl_2CuN_5O_9 \cdot 0.5\ H_2O$ (604.97): C 34.09, H 6.23, Cl 11.84, Cu 10.61, N 11.69, H_2O 1.50; found: C 33.96, H 6.38, Cl 11.85, Cu 10.70, N 11.67, H_2O 1.33.

The free ligand **6** was obtained by refluxing the Cu^{2+} complex (100 mg, 0.17 mmol) with an excess of NaCN (66.5 mg, 1.35 mmol) in 5 ml of H_2O, until the blue colour disappeared. The aq. soln. was extracted with CH_2Cl_2 (3 × 5 ml). The org. phase dried (Na_2SO_4) was evaporated, whereupon an oil was obtained. ^{1}H-NMR ($CDCl_3$): 1.6 (*m*, 2 CH_2); 2.34, 2.48, 2.59 (3 *s*, 3 CH_3N); 2.99, 3.12 (2 *s*, $(CH_3)_2N$); 3.39 (*s*, NCH_2CO); 2.8 (*m*, 8 CH_2N).

[11-(2-Diethylphosphonoethyl)-1,4,8-trimethyl-1,4,8,11-tetraazacyclotetradecane] copper Diperchlorate ([Cu(**7**)$(ClO_4)_2$]). Macrocycle **1** (0.5 g, 2.1 mmol), (2-bromoethyl)diethylphosphonate (0.6 g, 2.4 mmol) and Cs_2CO_3 (0.4 g, 2.1 mmol) in 30 ml of abs. EtOH were refluxed overnight. Since TLC still showed that **1** was present, a second portion of (2-bromoethyl)diethylphosphonate (0.6 g, 2.4 mmol) was added and the mixture refluxed for another 3 h. Then, the solvent was evaporated and the residue worked up as described for **6**. The Cu^{2+} complex was recrystallized from H_2O, which was slowly evaporated in an exsiccator containing $CaCl_2$. Yield: 450 mg (32.0%); blue crystals. IR (KBr): 1210 (P=O). Anal. calc. for $C_{19}H_{43}Cl_2CuN_4O_{11}P \cdot 0.5\ H_2O$ (678.90): C 33.61, H 6.53, Cl 10.44, Cu 9.36, N 8.25, P 4.56, H_2O 1.33; found: C 33.72, H 6.57, Cl 10.39, Cu 9.57, N 8.29, P 4.58, H_2O 1.68.

The free ligand **7** can be prepared by decomposing the Cu^{2+}complex with NaCN as described for **6**. ^{1}H-NMR ($CDCl_3$): 1.20 (*t*, 2 CH_3C); 1.53 (*quint.*, 2 CH_2); 2.11 (*s*, 3 CH_3N); 4.46 (*quint.*, 2 CH_2O); 2.5 (*m*, 9 CH_2N, CH_2P).

3-(4,8,11-Trimethyl-1,4,8,11-tetraazacyclotetradec-1-yl)propionitrile (**8**). A soln. of **1** (4 g, 16.5 mmol) in 50 ml of acrylonitrile, to which 3 drops of glacial AcOH were added, was refluxed for 3 h. The excess acrylonitrile was then removed by evaporation and the residue taken up in 50 ml of CH_2Cl_2. The org. phase was first washed with H_2O and then extracted with 1M HCl (3 × 20 ml). After evaporating the aq. phase, one obtains a yellow solid, which recrystallized from H_2O/EtOH, gave white crystals of **8**·4 HCl. Yield: 4.27 g (58.6%). M.p. 236° (dec.). IR (KBr): 2260*w* (CN), 2500 (br., NH^+). ^{1}H-NMR (D_2O): 2.1 (*m*, 2 CH_2); 2.89 (*t*, CH_2CN); 2.99 (*s*, 3 CH_3N); 3.5 (*m*, 9 CH_2N). Anal. calc. for $C_{16}H_{37}Cl_4N_5$ (441.32): C 43.55, H 8.45, N 15.87; found: C 43.34, H 8.39, N 15.75.

[1-(3-Aminopropyl)-4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane]copper Diperchlorate ([Cu(**9**)$(ClO_4)_2$]). A soln. of **8** (320 mg, 1.1 mmol), obtained by extraction of an alkaline soln. of **8**·4 HCl with CH_2Cl_2, in 10 ml of EtOH and 10 ml of liq. NH_3 was hydrogenated with *Ra*-Ni at 80 atm for 60 h. After evaporation of the solvent, the oil was treated with HCl/EtOH, whereupon **9**·4 HCl crystallized (yield: 77%). Since TLC (*Alox*, EtOH/H_2O/NH_3 10:5:1) showed that the product was not pure and that recrystallization of the hydrochloride did not help, the Cu^{2+} complex was prepared. The free base **9** dissolved in 2 ml of i-PrOH was reacted with $Cu(ClO_4)_2$ to give the Cu^{2+} complex (yield: 70%). The solid was recrystallized from alkaline (NaOH) aq. soln. to give pure [Cu(**9**)$(ClO_4)_2$] (yield: 42%). Anal. calc. for $C_{16}H_{37}Cl_2CuN_5O_8$ (561.95): C 34.20, H 6.64, Cu 11.31, N 12.46; found: C 34.22, H 6.73, Cu 11.3, N 12.54.

3-(4,8,11-Trimethyl-1,4,8,11-tetraazacyclodec-1-yl)propionamide (**10**). A soln. of **8**·4 HCl (308 mg, 0.7 mmol) and $CuCl_2 \cdot 2\,H_2O$ (119 mg, 0.7 mmol) was kept first at pH 5 for 2 h, then at pH 12 for 15 min. The alkaline soln., treated with NaCN (206 mg, 4.2 mmol), whereby the colour quickly disappeared, was then extracted with $CHCl_3$ (4 × 5 ml). From the org. phase, 170 mg of an oil with a typical amide band at 1680 cm^{-1} (no nitrile band) was obtained. Treatment of the oil with MeOH/HCl gave 200 mg (yield: 57%) of **10**·4 HCl. M.p. 264–265°. ^{1}H-NMR (D_2O): 2.25 (*quint.*, 2 CCH_2C); 3.12 (*s*, 3 CH_3N); 2.8 (*m*, CH_2CONH_2); 3.5 (*m*, 9 CH_2N). Anal. calc. for $C_{16}H_{39}Cl_4N_5O \cdot 2.5\,H_2O$ (504.37): C 38.10, H 8.79, Cl 28.12, N 13.88; found: C 38.24, H 8.71, Cl 27.72, N 13.90.

2-(4,8,11-Trimethyl-1,4,8,11-tetraazacyclodec-1-yl)ethanethiol (**11**). A soln. of **1** (980 mg, 4 mmol) and thiirane (0.28 ml, 4.2 mmol) in 15 ml of toluene was heated to 100–110° for 3 h. The solvent was then evaporated. The oil was dissolved in 50 ml of EtOH and treated with 1.5 ml of conc. HCl, whereby a precipitate formed. The product was recrystallized from EtOH/H_2O/HCl to give 0.8 of **11**·4 HCl (yield: 45%). M.p. 273–274° (dec.). ^{1}H-NMR (D_2O): 2.20 (*m*, 2 CCH_2C); 3.10 (*s*+*m*, 3 CH_3N, CH_2/SH); 3.55 (*m*, 5 CH_2N); 3.83 (*s*, 4 CH_2N). Anal. calc. for $C_{15}H_{38}Cl_4N_4S \cdot 0.5\,H_2O$ (457.37) C 39.39, H 8.59, N 12.24, S 7.01; found: C 39.40, H 8.48, N 12.16, S 7.07.

Hydrolysis Experiments. The Cu^{2+} complexes with **12**, **13**, and **14** were obtained by heating the Cu^{2+} complexes of the corresponding ester derivatives **3**, **5**, and **7** with NaOH, and these solns. were used as obtained for the spectral measurements.

Spectrophotometric Measurements. The spectra of the Cu^{2+} complexes were measured on a *Cary 118C* spectrophotometer in 1-cm cells, after having adjusted the pH so that the protonated or non-protonated form of the side chain was present. For several of these complexes, dissociation takes place at low pH and thus prevents the exact determination of the molar absorptivity of the protonated form. The spectrophotometric titration of the Cu^{2+} complex with **9** was achieved using the fully automated set up described in [12], and the calculations were performed with the program SPECFIT [13].

Results and Discussion. – *Synthesis. 1,4,8-Trimethyl-1,4,8,11-tetraazacyclotetradecane* (**1**) is an ideal starting compound for the preparation of mono-*N*-substituted macrocycles. As previously shown [5] [8] [10], the secondary N-atom of this ligand can be alkylated either using halogen or acryl derivatives. In this work, we have employed these reactions to prepare the compounds **3**–**10**, whereas for the synthesis of **11** thiirane was used. In general, we have observed that even in presence of an excess of alkylating reagent it is relatively difficult to react all of **1**, so that the yields remain relatively low. Because of this and of possible side reactions, if the alkylating agent contains additional reactive functional groups such as the ester group, the purification of the product was often problematic. In general, it was easier to purify the products through their Cu^{2+} complexes. Thus, after alkylation and a preliminary workup, an equimolar amount of Cu^{2+} was added to isolate the Cu^{2+} complex. In some cases, the Cu^{2+} complex was recrystallized, in

Table 1. *Spectra of the Cu^{2+} Complexes with Mono-N-functionalyzed Macrocycles Capable of Forming a Five-Membered Chelate through Coordination of the Functional Group X in the Side Chain R*

Compound	R	X	λ_{max} (ε)
2	CH_3	None[a])	580
3	CH_2COOCH_3	–C=O	585 (280)
4	$CH_2COOC_2H_5$	–C=O	585 (256)
11	CH_2CH_2SH	–SH	622 (247)
12	CH_2COOH	–COOH	625[b])
6	$CH_2CON(CH_3)_2$	–C=O	635 (228)
2	CH_3	H_2O	640 (252)
16	CH_2CONH_2	–C=O	640 [8]
12	CH_2COO^-	$-COO^-$	640 (228)
18	$CH_2CH_2N(CH_3)_2$	H_2O	642 [5]
15	CH_2CN	H_2O	643 [8]
17	$CH_2CH_2NH_2$	$-NH_2$	684 [5]
16	CH_2CONH^-	$-CONH^-$	735 [8]
11	$CH_2CH_2S^-$ [c])	$-S^-$	826 (230), 645 (sh), 460 (178)

[a]) In CH_3NO_2.
[b]) ε cannot be determined because of dissociation of the complex at low pH.
[c]) Oxygen sensitive.

Table 2. *Spectra of the Cu^{2+} Complexes with Mono-N-functionalyzed Macrocycles Capable of Forming a Six-Membered Chelate through Coordination of the Functional Group X in the Side Chain R*

Compound	R	X	λ_{max} (ε)	
			This work	From [10]
2	CH_3	None[a])	580	
5	$CH_2CH_2COOC_2H_5$	–C=O	630 (253)	625 (264)[b])
2	CH_3	H_2O	640 (252)	640 (257)
8	CH_2CH_2CN	H_2O	646 (256)	
13	CH_2CH_2COOH	–COOH	648 (209)	
9	$CH_2CH_2CH_2NH_3^+$	H_2O	649 (264)	566 (255)
10	$CH_2CH_2CONH_2$	–C=O	669 (193)	667 (256)
7	$CH_2CH_2PO(OC_2H_5)_2$	–P=O	690 (230)	
13	$CH_2CH_2COO^-$	$-COO^-$	692 (217)	691 (228)
9	$CH_2CH_2CH_2NH_2$	$-NH_2$	735 (299)	671 (246)
14	$CH_2CH_2PO_2(OC_2H_5)^-$	$-PO^-$	745 (193)	
10	$CH_2CH_2CONH^-$	$-CONH^-$	781 (170), 690 (sh)	699 (238)

[a]) In CH_3NO_2.
[b]) Methyl ester.

other cases it was purified over a *Sephadex G10* column. The compounds **12**–**14**, bearing a carboxyl or ethylphosphono group in their side chain, were obtained by hydrolysis of the corresponding esters, and the products were used as obtained.

Spectral Properties of the Cu^{2+} Complexes. The spectra of the Cu^{2+} complexes with the functionalized macrocycles, which are able to form a five-membered chelate ring through their side chain, and those of the ligand which can give a six-membered chelate ring, are collected in *Table 1* and *2*, respectively. In addition, the spectrum of $[Cu(\mathbf{2})(ClO_4)_2]$ is included for comparison.

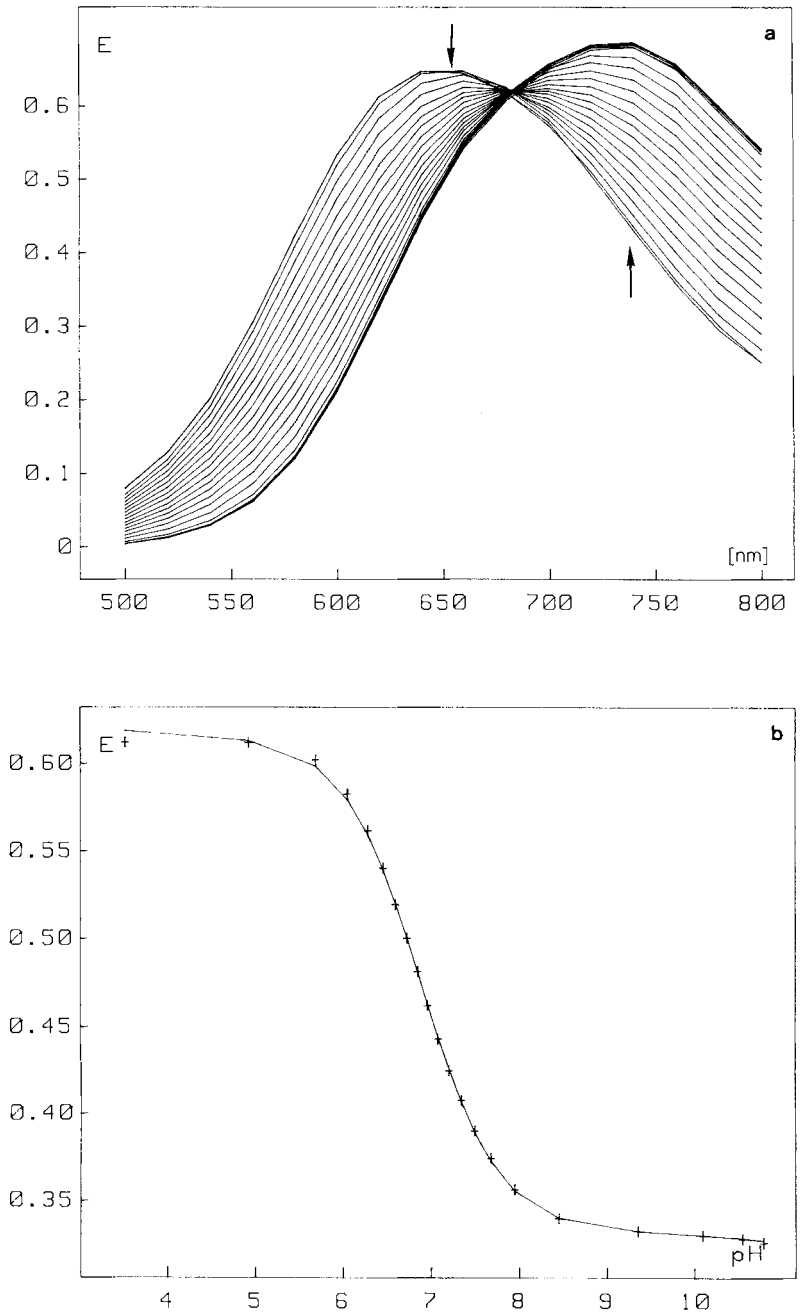

Figure. *Spectrophotometric titration of* 2.5×10^{-3} M *Cu*(**9**)$^{2+}$, 5×10^{-3} M *2,6-lutidine, and 0.5* M KNO_3 *with 0.1* M *NaOH. a*) Original data with increasing pH (arrow) starting from pH 3.56. *b*) Absorptivity at 620 nm as a function of pH. The curve was calculated with pK_H 6.93.

For several of the Cu^{2+} complexes, two values of λ_{max} are reported in the *Tables*. This is due to the fact that often a pH-dependent equilibrium between a protonated and deprotonated form of the functional group X in the side chain exists *(1)* [2]. In general, this equilibrium was not studied quantitatively, but care was taken

$$Cu(L{-}XH)^{2+} \leftrightarrows Cu(L{-}X)^{+} + H^{+} \quad (1)$$

to measure the spectra at appropriate pH values, at which the species were fully formed. However, a quantitative measurement of *(1)* was achieved by spectrophotometric pH-titration of $Cu(\mathbf{9})^{2+}$ *(Figure)* and the evaluation of this titration gave an apparent pK_H value of 6.93.

The quantitative study of this system was necessary, since our values of λ_{max} were distinctly different from those already published [10]. The discrepancy could arise from several factors: *a*) no analytical identification of the complex used by *Barefield et al.*, or *b*) no effective control of the pH at which the spectra were measured. Similarly, the difference between our λ_{max} and the published one for $Cu(\mathbf{10})^{2+}$ in alkaline solution could also arise from the same reasons. In this case, a pH > 12 is necessary to obtain the final spectrum of the species with the deprotonated amide group.

Looking at the results of *Tables 1* and *2*, one can see that there are three groups of Cu^{2+} complexes: *a*) those with λ_{max} smaller than that of $Cu(\mathbf{2})^{2+}$ in H_2O, *b*) those with λ_{max} nearly equal to that of $Cu(\mathbf{2})^{2+}$, and *c*) those with λ_{max} larger than that of $Cu(\mathbf{2})^{2+}$. According to the studies of *Billo* [14] and *Kurganov and Davankov* [15], one expects a red shift of λ_{max}, when the apical position of a Cu^{2+} complex is occupied by an additional ligand, and the geometry changes from a square planar to a penta-coordinated one. So the question arises, whether $Cu(\mathbf{2})^{2+}$ in H_2O is the right compound for comparison, since in aqueous solution the apical position of the Cu^{2+} is probably occupied by a H_2O molecule. If we want a compound with no axial ligand as reference, we should use $Cu(\mathbf{2})^{2+}$ in CH_3NO_2, which does not coordinate at all. Taking this species with λ_{max} 580 nm as a fix point, then all other complexes have a red-shifted λ_{max} as expected.

If we compare the compounds of *Table 1*, which are able to form five-membered chelate rings, with those of *Table 2*, which are capable of giving six-membered chelate rings, we find the same sequence of axial ligand-field strenght for the different donor groups. However, we observe that all compounds of *Table 2* absorb at somewhat longer wavelengths than the analogous ones of *Table 1*. This could mean that the six-membered chelate ring, being less strained than the five-membered one, allows the coordinating group X at the end of the side chain to come into the ideal position to give a stronger coordinative bond, which induces as a consequence a larger red-shift. This, however, contrasts with the observation that it is easier to dissociate the NH_2 group of **9** than that of **17** in their corresponding Cu^{2+} complexes, when protons are added.

In our discussion, we have so far implicitly assumed that the four N-atoms of the macrocycle are not displaced, when the side-chain coordinates, *i.e.* the equatorial ligand field remains constant. Inspection of models, however, shows that this is not completely true. In the case of the five-membered chelate-ring, the side chain can take up a conformation, in which all atoms of the chain nearly lie in one plane, and thus, does not influence the conformation of the macrocycle. However, when the chain, which forms a six-membered chelate ring, coordinates apically, it must displace at least one of the N-atoms of the macrocycle in order to adopt the thermodynamically stable chair conformation. If this is

the case, a weaker equatorial field would result, and thus, as a consequence the absorption maxima should be at longer wavelengths than those of the analogous compounds with the shorter chain.

Not only groups with $\lambda_{max} > 640$ nm and a stronger ligand field than that of H_2O can axially bind to the Cu^{2+}, as previously demonstrated [5][8][10], but also donors which have a weaker ligand-field strength can effectively compete with H_2O, because, being attached at the end of the side chain, they are present at an extremely high local concentration. In line with this, we predict that the ester group with λ_{max} 585–630 nm (**3**, **4**, and **5**) and probably also the carboxyl group with λ_{max} 625–648 nm (**12** and **13**) coordinate in the axial position. Similarly, the amide group in **6**, **16**, and **8**, and the thiol group in **11** also bind to the Cu^{2+}. On the other hand, the complexes with a nitrile (**8** and **15**) or with a dimethylamino group (**18**) are typical examples of species with a non-coordinating donor function, either because of electronical or of sterical reasons. Finally, the complexes with a carboxylate (λ_{max} 640–692 nm), with an amino (λ_{max} 684–735 nm), with a deprotonated amide (λ_{max} 735–781 nm), with a diethyl-phosphonate (λ_{max} 690 nm), with a monoethyl-phosphonate group (λ_{max} 745 nm), or with a mercapto group (λ_{max} 826 nm) are typical examples of donors which bind to the axial position of the Cu^{2+}.

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