

6. Metal Complexes with Macrocyclic Ligands

Part XXII¹⁾

Synthesis of Two Bis-tetraaza-macrocycles and Study of the Structures, Electrochemistry, VIS and EPR Spectra of their Binuclear Cu²⁺ and Ni²⁺ Complexes

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The two bis-macrocycles **4** and **5**, in which the tetraaza units are separated by a chain of different length, have been synthesized using 1,4,7-tritosyl-1,4,7,11-tetraazacyclotetradecane as starting compound and bifunctional alkylating agents. The bis-macrocycles give binuclear complexes with Ni²⁺ and Cu²⁺, the properties of which have been studied to obtain information about the interaction of the two subunits as a function of the distance. The VIS spectra of the Ni²⁺ and Cu²⁺ complexes indicate that both metal ions are in a square-planar geometry as expected from the results of the analogous complexes with 1,4,7,11-tetraazacyclotetradecane **7**. Cyclic voltammetry and differential pulse polarography of the binuclear Ni²⁺ complexes in CH₃CN show a single two-electron step for ligand **5**, whereas two distinct one-electron redox processes can be observed for ligand **4**, indicating that the two metal ions interact with each other when the chain length is shorter. Similarly, the EPR studies of frozen solutions of the binuclear Cu²⁺ complexes clearly show that a magnetic dipolar interaction between the two paramagnetic centers exists, and that the strength of it depends upon the length of the bridge. Finally, from the X-ray structures of the binuclear Ni²⁺ complexes with **4** and **5**, it is seen that the two rings are kept apart as far as possible, the distances between the two metal ions determined in the solid correlate well with the observations in solution.

Introduction. – The use of binucleating ligands to bind two metal ions and keep them at a fixed distance has been described in [2–5]. Although several strategies have been employed, the use of appropriate monocyclic and bicyclic ligands has proven to be one of the best, since both the high kinetic and thermodynamic stabilities permit the study of such systems in solution with nearly no side reactions.

In many of the macrocycles reported, the two metal ions are either co-ordinated in a large single-ring [3] or in two smaller subunits [4] [5]. Both systems have their own special properties and have been proposed as models for binuclear metalloproteins, to study metal-metal interactions, the binding of bridging ligands and multi-electron redox processes [2].

In the last years, several tetraazamacrocycles have been used as subunits to build binucleating ligands. However, in most cases the distance between the two metal ions was not systematically varied, and the properties of the metal complexes were not studied as a function of the distance. Here, we present a synthesis which allows to prepare bis-macrocycles and to select the length of the connecting linkage between the two subunits in which the metal ions are accommodated.

¹⁾ Part XXI: [1].

Experimental. – *11,11'-Ethylenebis(1,4,7-tritosyl-1,4,7,11-tetraazacyclotetradecane)* (**2**). To 6.63 g (10 mmol) of **1** [6] and 2.76 g of K_2CO_3 in abs. CH_3CN (75 ml) 1,2-dibromoethane (0.43 ml, 5 mmol) in abs. CH_3CN (25 ml) was added, and the mixture was refluxed for 2 d. Thereafter, the soln. was evaporated to dryness, the residue taken up with $CHCl_3$ (250 ml), and extracted with 2M NaOH (100 ml). The org. phase was dried and evaporated. The product was chromatographed on Alox 90 (500 g; Merck) with $CH_2Cl_2/AcOEt$ 4:1. The fractions containing the product were collected, evaporated, and the residue dissolved in acetone (200 ml), to which so much H_2O was added that crystallization took place. Yield 2.03 g (30.0%). M.p. 212–214°. ^1H-NMR ($CDCl_3$): 1.7 (m, 8 H, C– CH_2 –C); 2.4 (m, 30 H, CH_2N , CH_3); 3.2 (m, 24 H, $TsNCH_2$); 7.5 (m, 24 arom. H). Anal. calc. for $C_{64}H_{86}N_8O_{12}S_6$ (1351.80): C 56.87, H 6.41, N 8.29; found: C 56.83, H 6.61, N 8.36.

11,11'-p-Xylylenebis(1,4,7-tritosyl-1,4,7,11-tetraazacyclotetradecane) (**3**). To 6.63 g (10 mmol) of **1** and 2.76 g of K_2CO_3 in freshly distilled DMF (75 ml) at 95° a soln. of 1,4-bis(bromomethyl)-benzene (1.32 g, 5 mmol) in DMF (25 ml) was added. The mixture was kept at 95° for 2 h. After cooling to r.t., the soln. was decanted from the salts and evaporated to dryness. The residue was taken up in $CHCl_3$ (350 ml) and 2M NaOH (100 ml). After drying the org. phase was rotatory evaporated. The oily residue was treated with acetone (100 ml), in which it slowly dissolved and crystallized. Recrystallization from CH_2Cl_2 (210 ml) and MeOH (250 ml): 5.95 g (83.3%) of **3**. M.p. 229–231°. ^1H-NMR ($CDCl_3$): 1.7 (m, 8 H, C– CH_2 –C); 2.45 (m, 26 H, CH_3 , CH_2N); 3.3 (m, 28 H, $TsNCH_2$, $PhCH_2N$); 7.5 (m, 28 arom. H). Anal. calc. for $C_{70}H_{90}N_8O_{12}S_6$ (1427.90): C 58.88, H 6.35, N 7.85; found: C 58.57, H 6.30, N 7.72.

11,11'-Ethylenebis(1,4,7,11-tetraazacyclotetradecane) Octahydrochloride (**4**). A suspension of **2** (0.54 g, 0.4 mmol) in conc. H_2SO_4 (2 ml) was heated under N_2 to 100° for 3 d. After cooling, Et_2O (10 ml) was added, and the mixture was left in the ice-box. The precipitate was filtered off, dissolved in 6M NaOH (20 ml) and rotatory evaporated. The residue was extracted with hot CH_2Cl_2 (3×20 ml). After evaporation of the org. phase, the product was dissolved in 3M HCl (5 ml) and treated with EtOH (ca. 10 ml) so that precipitation of 4·8 HCl took place. Yield 0.24 g (74.2%). Anal. calc. for $C_{22}H_{58}Cl_8N_8 \cdot 5H_2O$ (808.46): C 32.68, H 8.48, N 13.86, Cl 35.08; found: C 32.77, H 8.48, N 13.83, Cl 34.99.

11,11'-p-Xylylenebis(1,4,7,11-tetraazacyclotetradecane) Octahydrochloride (**5**). A suspension of **3** (0.5 g, 0.35 mmol) in conc. H_2SO_4 (2 ml) was treated under N_2 for 3 d to 100°. After cooling, Et_2O (10 ml) was added. The precipitate formed over night in the ice-box was filtered off and dissolved in 6M NaOH (20 ml). This soln. was rotatory evaporated and the residue extracted with CH_2Cl_2 (3×20 ml). After evaporation of the org. solvent, the product was dissolved in 3M HCl (5 ml) to which hot EtOH (15 ml) was added to induce crystallization. Yield 0.25 g (89.3%). Anal. calc. for $C_{28}H_{62}Cl_8N_8 \cdot H_2O$ (812.50): C 41.39, H 7.94, N 13.79; found: C 41.83, H 7.86, N 13.89.

11,11'-Succinylbis(1,4,7-tritosyl-1,4,7,11-tetraazacyclotetradecane) (**6**). To **1** (3.32 g, 5 mmol) and Et_3N (2.2 ml) in $CHCl_3$ (80 ml; distilled over P_2O_{10}), a soln. of freshly distilled succinyl dichloride (0.7 ml, 6.2 mmol) in $CHCl_3$ (220 ml) (distilled over P_2O_{10}) was added during 4 h, so that the temp. remained constant at 21–23°. The mixture was filtered, the filtrate was diluted with $CHCl_3$ to 800 ml and treated with 100 g silica gel 40 (Merck, 0.063–0.2 mm). After stirring, the suspension for 4 h, it was filtered and the silica gel was put on top of a column (43.5 mm \varnothing), which was already loaded with 100 g of fresh silica gel 40. Elution with $CHCl_3/AcOEt$ 1:0, 1:1, and 0:1 gave the pure product, which was recrystallized from DMF/ Et_2O . Yield 3.15 g (88.4%). M.p. 275–276°. Anal. calc. for $C_{66}H_{88}N_8O_{15}S_6$ (1425.85): C 55.60, H 6.22, N 7.86, O 16.83, S 13.49; found: C 55.60, H 6.02, N 7.93, O 16.66, S 13.27.

Preparation of the Binuclear Metal Complexes. For the synthesis of the Cu^{2+} and Ni^{2+} complexes, the free base of the ligands was first prepared. The hydrochlorides of **4** and **5** (0.2 mmol of each), were dissolved in conc. NaOH, H_2O was evaporated and the solid was extracted with CH_2Cl_2 (3×20 ml). The org. phase was rotatory evaporated and the residue dissolved in hot abs. EtOH (4 ml). The soln. was mixed with $Cu(ClO_4)_2$ (2 equiv.) in EtOH, whereby the pure product precipitated once the solns. were cooled. In the case of the Ni^{2+} complexes, the residual free bases **4**, and **5**, were dissolved in H_2O (18 ml). $Ni(ClO_4)_2$ (2 equiv.) in H_2O (2 ml) was then added. After refluxing for ca. 1 h and cooling, only part of the product precipitated, so that the mother liquid was also worked up. Evaporation of H_2O and crystallization from $H_2O/i-PrOH$ gave an additional crop of the Ni^{2+} complexes.

Ni_2 (**4**) (ClO_4)₄. Purple crystals (yield 87.0%). Anal. calc. for $C_{22}H_{50}Cl_4N_8Ni_2O_{16}$ (941.92): C 28.05, H 5.35, N 11.90, Ni 12.47; found: C 28.19, H 5.30, N 11.97, Ni 12.2.

Cu_2 (**4**) (ClO_4)₄· H_2O . Violet crystals (yield 90.7%). Anal. calc. for $C_{22}H_{54}Cl_4Cu_2N_8O_{18}$ (987.61): C 26.76, H 5.51, N 11.35, Cu 12.87; found: C 26.93, H 5.11, N 11.37, Cu 13.1.

Ni_2 (**5**) (ClO_4)₄. Purple crystals (yield 75.0%). Anal. calc. for $C_{28}H_{54}Cl_4Ni_2O_{16}$ (1018.02): C 33.04, H 5.35, N 11.01, Ni 11.53; found: C 33.24, H 5.58, N 10.99, Ni 10.9.

Cu_2 (**5**) (ClO_4)₄· H_2O . Violet crystals (yield 96.2%). Anal. calc. for $C_{28}H_{58}Cl_4Cu_2N_8O_{18}$ (1063.71): C 31.62, H 5.50, N 10.53, Cu 11.95, Cl 13.33; found: C 31.77, H 5.14, N 10.45, Cu 11.3, Cl 13.29.

Measurements. The absorption spectra of the Ni^{2+} and Cu^{2+} complexes ($2 \cdot 10^{-3} \text{ M}$) were measured in a 1-cm cuvette using a *Perkin Elmer 550* spectrophotometer. The EPR spectra of the Cu^{2+} complexes were run on a *Varian E-9* spectrometer using $1 \cdot 10^{-3} \text{ M}$ soln. in $\text{H}_2\text{O}/\text{DMF}$ 2:1 at -120° . As external standard, α, γ -bis(diphenylene- β -phenyllallyl radical ($g = 2.00260$) was used.

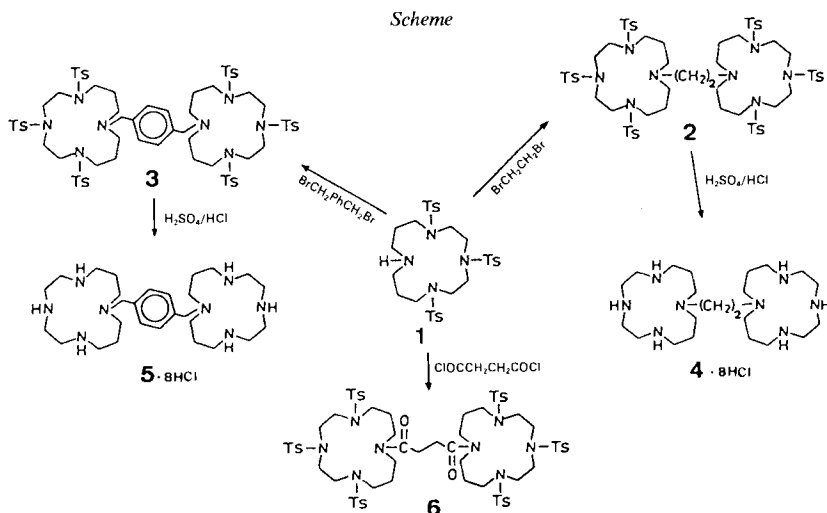
The cyclic voltammetry and differential pulse polarography were run with a *Metrohm VA-scanner E612* and a *VA-detector E611* using a Pt microsphere electrode as working electrode, surrounded by a Pt spiral as auxiliary electrode, and a AgCl/Ag reference electrode with a salt bridge. The experiments were carried out with $2 \cdot 10^{-4} \text{ M}$ $\text{Ni}_2(\mathbf{5})(\text{ClO}_4)_4$ and with a sat. soln. of $\text{Ni}_2(\mathbf{4})(\text{ClO}_4)_4$ in CH_3CN with LiClO_4 (0.1 M). To eliminate the effects of the diffusion potential, $E_{1/2}$ values are referred to the ferrocene-ferrocenium couple (+400 mV vs. NHE [7]) used as internal standard. Cyclic voltammograms were recorded at scan rates of 10–50 mV/s, whereas the differential pulse polarograms were run at 1 mV/s with a pulse amplitude of 10 mV.

Crystal Data. The atomic parameters of the two structures are available from the *Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW*. The list of the observed and calculated structure factors is available from the authors.

$\text{Ni}_2(\mathbf{4})(\text{ClO}_4)_4$: orthorhombic, $a = 7.880(3)$, $b = 24.170(4)$, $c = 9.482(1) \text{ \AA}$, space group $Pnm2$, $V = 1805.8(1.2) \text{ \AA}^3$, $D_{\text{calc.}} = 1.712 \text{ g cm}^{-3}$, $Z = 2$, $F(000) = 960$, $\mu = 13.36 \text{ cm}^{-1}$. Intensity data were collected with Mo- K_α radiation to $\theta = 24^\circ$ using the $\theta - 2\theta$ scan mode. Unit cell parameters were obtained from accurate centring of 25 strong reflections. Intensities of 1667 independent reflections were measured with an *Enraf-Nonius CAD4* diffractometer equipped with a graphite monochromator. No correction for absorbance was applied. The positional parameters of the Ni^{2+} cations were determined by a three-dimensional sharpened *Patterson* map. The remaining atoms were localized by weighted difference *Fourier* maps followed by least-squares refinements and further *Fourier* maps. In the final anisotropic refinement, 1003 reflections [$(F_o) > 1.5\sigma(F_o)$] were used with unit weights; the final R index was 0.081. Five atoms could not be refined anisotropically.

$\text{Ni}_2(\mathbf{5})(\text{ClO}_4)_4$: monoclinic, $a = 10.461(2)$, $b = 14.471(6)$, $c = 13.969(4) \text{ \AA}$, $\beta = 92.88(2)^\circ$, space group $P2_1/c$, $V = 2112.0(1.9) \text{ \AA}^3$, $D_{\text{calc.}} = 1.591 \text{ g cm}^{-3}$, $Z = 2$, $F(000) = 1040$, $\mu = 11.46 \text{ cm}^{-1}$. 3081 reflections were measured to $\theta = 23^\circ$. The phasing technique and the refinement were the same as stated above. In the final anisotropic refinement, 2181 reflections [$(F_o) > 2\sigma(F_o)$] were used; the R index was 0.101. In both structures the ClO_4^- anions are disordered so that the O-atoms exhibit large thermal parameters. Programs used were developed by *Sheldrick* [8], scattering factors were those of *Cromer et al.* [9].

Results and Discussion. – The synthetic approach for bridging two macrocyclic units makes use of the tritosylated tetraazamacrocyclic **1** described in [6]. Compound **1** allows to selectively acylate or alkylate one N-atom of the macrocycle. Thus, by using a difunctional agent, it is possible to connect two rings with each other (see the *Scheme*).



Succinyl dichloride was used as a test agent and gave an excellent yield of the precursor of the bis-macrocyclic **6**. However, attempts to reduce the two amide groups and simultaneously cleave off the Ts groups using LiAlH_4 gave no pure product. Perhaps a two-step synthesis, in which first the amido groups are reduced, and then the Ts groups are cleaved off, as has been described by *Ciampolini et al.* [5] for the synthesis of bis-([12]aneN₄), would have been an alternative. Thus, instead of using acid dichlorides, we have alkylated the N-atom of **1** with 1,2-dibromoethane and 1,4-bis(dibromomethyl)-benzene (see the *Scheme*) to have a short and a relatively long and rigid bridge between the two macrocyclic units. Whereas the reaction with 1,4-bis(dibromomethyl)benzene gave good yields of **3** with short reaction time, the reaction with 1,2-dibromoethane was slower and gave a mixture of products. The bis-macrocyclic **2** was obtained in 30% yield after chromatography on silica gel. The desosylation of both **2** and **3** was achieved with conc. H_2SO_4 to give the octaamines which were isolated as octahydrochlorides.

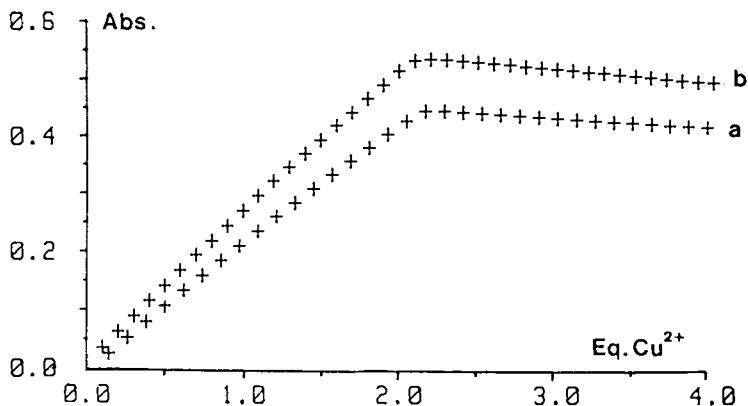


Fig. 1. Spectrophotometric titrations of **4** (a) and **5** (b) with Cu^{2+} at 550 nm and $\text{pH} = 5.5$

Both ligands **4** and **5** react with Cu^{2+} and Ni^{2+} to give binuclear complexes, as indicated by the analytical data of the solids. In solution, the spectrophotometric titration of **4** and **5** with Cu^{2+} at a fixed pH also clearly shows that binuclear complexes are formed (*Fig. 1*). The slopes of the titration curves remain constant from 0 to 2 equiv. indicating that the two Cu^{2+} have analogous spectral properties and similar binding constants. Only after the addition of 2 equiv. of Cu^{2+} , a sharp end point is observed. The spectral properties of the Cu^{2+} and Ni^{2+} complexes of **4** and **5** as well as those of the corresponding monocycle *1,4,7,11-tetraazacyclotetradecane* **7** are collected in *Table 1*. The absorption

Table 1. Spectral Data of the Cu^{2+} and Ni^{2+} Complexes with **4**, **5** and of the Corresponding Monocycle **7**

Complex	λ_{max} [nm]	ϵ_{max} [$\text{M}^{-1} \text{cm}^{-1}$]	Ref.
Cu_2 (4) ⁴⁺	554	335	
Cu_2 (5) ⁴⁺	553	360	
Cu (7) ²⁺	551	154	[6]
Ni_2 (4) ⁴⁺	480	73	
Ni_2 (5) ⁴⁺	475	93	
Ni (7) ²⁺	460	58	[6]
Ni (7) ²⁺	475	60	[12]

maxima and the values of the molar absorptivities are similar for the complexes of the bis-macrocycles and those of the monocycle, for which square-planar geometry of the metal ion was proposed [6].

The bis-macrocycles **4** and **5**, synthesized with different chain lengths to study the effect of distance on the properties of binuclear species, were investigated by electrochemical measurements for the Ni^{2+} complexes and EPR for the Cu^{2+} complexes.

The oxidation $\text{Ni}^{2+}/\text{Ni}^{3+}$ was studied in CH_3CN . Both systems are *quasi*-reversible, as indicated by the fact that in the cyclic voltammograms (CV) $i_a = i_c$ and that the peaks are nearly symmetric in the differential pulse polarograms (DPP). However, the two binuclear complexes give completely different results: Ni_2 (**4**) $(\text{ClO}_4)_4$ shows in DPP two distinct peaks of equal intensity separated by 98 mV, whereas Ni_2 (**5**) $(\text{ClO}_4)_4$ gives only one peak. Similarly the CV of Ni_2 (**4**) $(\text{ClO}_4)_4$ is more complex and shows two steps, whereas that of Ni_2 (**5**) $(\text{ClO}_4)_4$ gives only a single step (Fig. 2).

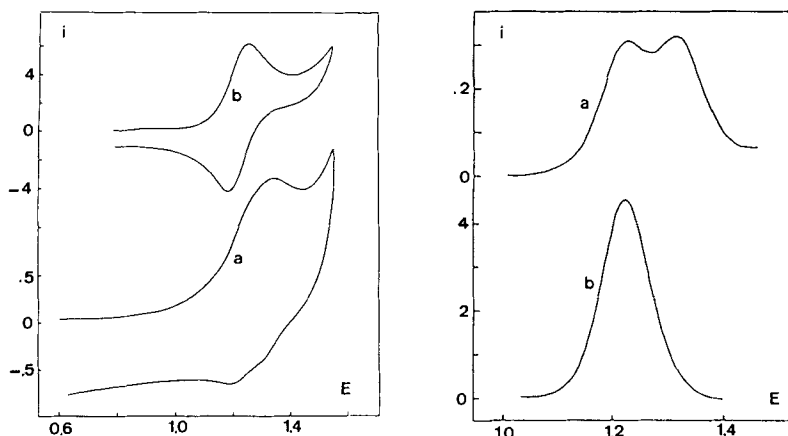


Fig. 2. Cyclic voltammetry (left) and differential pulse polarography (right) of the binuclear Ni^{2+} complexes with **4** (a) and **5** (b) in $\text{CH}_3\text{CN}/\text{LiClO}_4$. E in Volt against SHE, and i in μA .

Table 2. Half-Wave Potentials of the Ni^{2+} Complexes of **4**, **5**, and **7** (in $\text{CH}_3\text{CN}/0.1\text{M LiClO}_4$ at 25°)

	$E_{1/2}$ [V] (against SHE)	
	CV	DPP
Ni_2 (4) ^{4/6+}	1.226, 1.324	1.229, 1.327
Ni_2 (5) ^{4/6+}	1.214, 1.250 ^{a)}	1.210, 1.246 ^{a)}
Ni (7) ^{2/3+}	1.096	

^{a)} Calculated with the statistical separation of 36 mV.

On a statistical base, the consecutive oxidation of two equivalent and independent centres involves a potential separation of 36 mV ($= (RT/F) \ln 4$) [10], which is difficult to observe. A larger separation as found for the complex with **4** indicates an interaction between the two metal cations (Table 2). Thus, we conclude that in the binuclear Ni^{2+} complex with **4**, which has the shorter chain, the two oxidation steps are separated, since the repulsive interaction between the cations is large. On the contrary, in the binuclear complex with **5** the two oxidations occur at potentials which are only separated by the

statistically determined value, since the distance between the two metal ions is so large that electrostatic effects do not play a role any more and the two metal ions are equivalent.

A comparison with the value of the Ni^{2+} complex of the monocycle **7** shows that the potentials for the $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+}$ oxidation are larger in the bis-macrocycles, which means that it is more difficult to oxidize Ni^{2+} in the bis-macrocycles. This can be due either to a weakening of the ligand field, since one N-atom is tertiary, and/or to the bulky substituent which sterically interferes with the redox process.

Another way to study metal-metal interactions involves EPR measurements. So, we have measured the EPR spectra of the three Cu^{2+} complexes with **4**, **5**, and **7** (Fig. 3). The spectra are typical for axial symmetry, with g_{\parallel} split by the hyperfine coupling constant into a multiplet. The coupling constants A_{\parallel} for the binuclear complexes are about half of that of $\text{Cu}(\mathbf{7})^{2+}$ (Table 3), indicating that in both binuclear complexes metal-metal

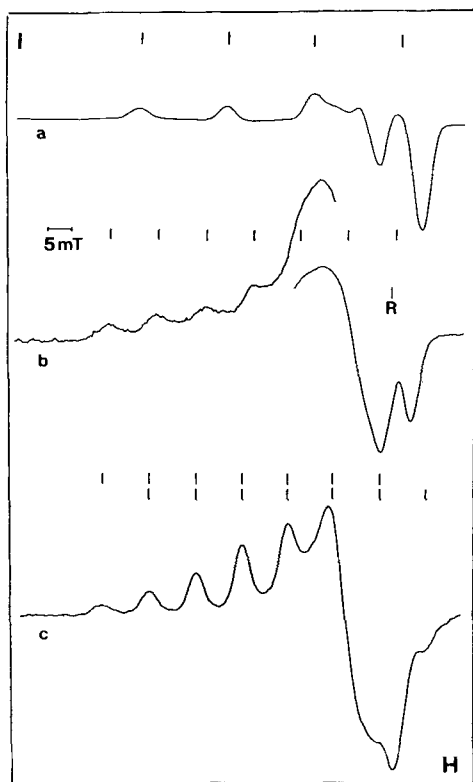


Fig. 3. EPR spectra of $\text{Cu}(\mathbf{7})(\text{ClO}_4)_2$ (a), $\text{Cu}_2(\mathbf{5})(\text{ClO}_4)_4$ (b), and $\text{Cu}_2(\mathbf{4})(\text{ClO}_4)_4$ (c) in $\text{DMF}/\text{H}_2\text{O}$ at -120° . R indicates the g value of the external reference ($= 2.00260$).

Table 3. EPR Data of the Cu^{2+} Complexes of **4**, **5**, and **7** (in 30% DMF glass at -120°)

	g_{\parallel}	A_{\parallel} [10^4 cm^{-1}]
$\text{Cu}_2(\mathbf{4})^{4+}$	2.18	94
$\text{Cu}_2(\mathbf{5})^{4+}$	2.20	97
$\text{Cu}(\mathbf{7})^{2+}$	2.19	176

interactions are present. Therefore, one expects two septets which are shifted, with respect to each other, by the zero-field splitting $2 D_{\parallel}$. In general, it is difficult to observe all the expected lines, and additional assumptions must be made in the interpretation of these spectra. In our case, we have assumed that in Cu_2 (**4**) $(\text{ClO}_4)_4$ the two septets are displaced by A_{\parallel} , whereas in Cu_2 (**5**) $(\text{ClO}_4)_4$ the displacement must be very small. With this assumption, the g_{\parallel} values for all systems are very consistent, as expected, since also the geometry of the complexes is very similar. The zero-field splitting parameter D_{\parallel} can be determined to 0.0047 cm^{-1} for Cu_2 (**4**) $(\text{ClO}_4)_4$ and guessed for Cu_2 (**5**) $(\text{ClO}_4)_4$ to $< 0.0028 \text{ cm}^{-1}$. From these values, one can calculate the mean distance between the two paramagnetic cations, provided that the zero-field splitting is due to a pure dipole-dipole interaction [11]. From Eqn. 1, one obtains $R_{\text{Cu-Cu}} = 8.7 \text{ \AA}$ for ligand **4** and $R_{\text{Cu-Cu}} \geq 13 \text{ \AA}$ for ligand **5**. This would indicate that in solution the binuclear complexes adopt a conformation in which the metal ions tend to be as far as possible from each other. The values published by Ciampolini *et al.* [5] for an analogous binuclear Cu^{2+} complex with an ethylene bridge are somewhat smaller than ours, although the distance between the two metal ions is comparable.

$$D_{\parallel} = 0.65 g_{\parallel}^2 / R^3 \quad (1)$$

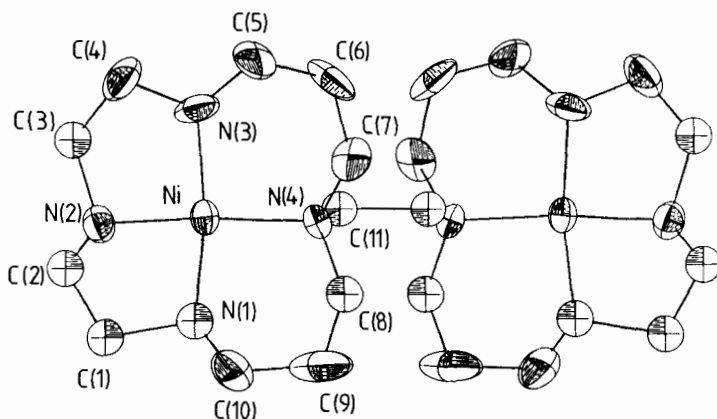


Fig. 4. Structure of the binuclear Ni^{2+} complex of **4**

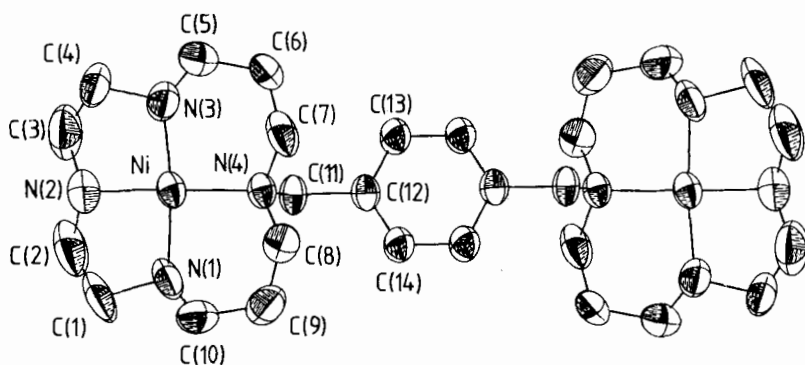


Fig. 5. Structure of the binuclear Ni^{2+} complex of **5**

Finally the structures of the two binuclear Ni^{2+} complexes with **4** and **5** were also determined (Fig. 4 and 5). In both complexes Ni_2 (**4**) (ClO_4)₄ and Ni_2 (**5**) (ClO_4)₄ the Ni^{2+} ion has square-planar geometry, with the four N-atoms of the macrocycle at the edges of the square. The Ni–N bond lengths (Table 4) in the range of 1.9 to 2.0 Å are normal. The longest bond in both complexes is Ni–N(4), N(4) being the tertiary N-atom, at which the bridge is connected. The arrangement of the chelate rings in the 1,4,7,11-tetraazacyclotetradecane unit might be the reason for the distortion of the N–Ni–N angles, which were determined to be $< 90^\circ$ in the five-membered chelate ring and $> 90^\circ$ in the six-membered ones. The structure of $\text{Ni}(\mathbf{7})^{2+}$ has not been reported, but the Ni^{2+} complex of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane [13] has the same features.

Table 4. Selected Bond Distances, Bond Angles, and their Standard Deviations for the Binuclear Ni^{2+} Complexes with **4** and **5**

Atoms	Ni_2 (4) ⁴⁺	Ni_2 (5) ⁴⁺
	Distances [Å]	
Ni–N(1)	1.865(36)	1.944(12)
Ni–N(2)	1.900(15)	1.922(12)
Ni–N(3)	1.958(28)	1.939(12)
Ni–N(4)	1.999(12)	1.989(9)
	Angles [°]	
N(1)–Ni–N(2)	82.4(1.6)	84.8(5)
N(1)–Ni–N(3)	162.2(1.6)	166.4(5)
N(1)–Ni–N(4)	93.0(1.3)	93.7(4)
N(2)–Ni–N(3)	87.2(1.7)	85.7(5)
N(2)–Ni–N(4)	174.7(1.5)	178.3(3)
N(3)–Ni–N(4)	97.9(1.5)	96.0(4)
Ni–N(4)–C(11)	106.0(0.9)	105.4(7)

Both bis-macrocyclic complexes are found to be in an *anti*-conformation: the Ni^{2+} ions are separated from each other with the greatest possible distance: 7.05 Å in the case of $\text{Ni}_2(\mathbf{4})^{4+}$, 11.56 Å for $\text{Ni}_2(\mathbf{5})^{4+}$. In $\text{Ni}_2(\mathbf{4})^{4+}$, a crystallographic symmetry axis perpendicular to the C(11)–C(11') bond and horizontal to the two macrocyclic planes makes the two halves of the bis-macrocycle equivalent. $\text{Ni}_2(\mathbf{5})^{4+}$ has C_i symmetry. The strongly disordered ClO_4^- ions (not shown) are not within bonding distance with any atom of the cation. The results obtained from the structure analysis compare well with those found in solution, so that one can assume that the species have the same conformation in the solid state as in solution.

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