Synthesis of New Binucleating Cylindrical Macrotricyclic Ligands Where Two Cyclam Rings Are in a Face-to-Face Conformation. Characterization of Their Dicopper(II) and Dinickel(II) Complexes

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Synthesis of new symmetrical cylindrical macrotricyclic ligands **1a,b**, where two cyclam subunits are linked through nitrogen atoms by two aromatic chains of various lengths (*meta*-xylylenyl, *para*-xylylenyl) has been achieved. These compounds have been prepared according a five step procedure. The readily available trisheteroprotected cyclam **4** has been reacted with the appropriate bis(bromomethyl)benzene to give the bimacrocycle intermediates **5a,b**. The selective deprotection of the *tert*-butyloxycarbonyl group leads to the diamine bimacrocycles **6a,b**. Condensation of these diamines with the appropriate diacid dichloride under high-dilution conditions yields the diamide macrotricycles **7a,b** in a significant yield. After reduction of the amide moieties and deprotection of the tosyl groups, new cylindrical macrotricycles **1a,b** were obtained. Macrotricyclic ligands **1a,b** coordinate Cu^{2+} and Ni^{2+} to form binuclear species. The crystal structure of the $[Ni_2(\mathbf{1a})](ClO_4)_4 \cdot 2CH_3CN$ complex has been determined by single-crystal X-ray analysis. $C_{18}H_{30}N_4Ni(ClO_4)_2 \cdot CH_3CN$ crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions of $a = 10.716$ (3) Å, $b = 12.805(4)$ Å, $c = 9.292(3)$ Å, $\alpha = 95.82(2)°$, $\beta = 103.06(2)°$, $\gamma = 94.94(2)°$, and $V = 1227.8$ Å^3, $Z = 2$, 2396 observations, and $R(F) = 0.036$. The cationic part of the complex is a dimer lying on a crystallographic inversion center. Each metal ion is coordinated to four nitrogen atoms of a cyclam unit giving an approximatively square planar coordination geometry, with an intermetallic distance of 6.830(1) Å. The ESR spectra of the binuclear Cu^{2+} complexes clearly show metal−metal cooperative interactions.

Introduction

In the last two decades the synthesis of artificial receptors able to coordinate metal cations has undergone a spectacular growth.[1,2] Most of the attention has been focused on macrocyclic receptors capable to bind more than one transition metal ion.[3−9] Depending on the nature of subunits used for their construction, a variety of macropolycyclic structures have been synthesized: (1) compartmental receptors which contain a large macrocycle able to bind two metal centers into some predeterminate arrangements;[3,6,10−14] (ii) macrobicyclic receptors formed by the coaxial arrangement of two tripod subunits;[15−18] (III) bimacrocyclic receptors in which two macrocyclic subunits are linked together by one bridge;[19−38] (iv) macrotricyclic receptors

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which are formed by bridging two macrocycles.[39−48]

More recently, particular attention has been devoted to the preparation of complexes possessing two transition metal ions separated by a distance of 3.5−7 Å, preferably without bridging ligands.[14,49,50] No direct metal−metal interaction occurs, but a substrate can interact simultaneously with both ions. The presence of two metal ions at a suitable distance defines a cavity where the coordination of small molecules (O_2, N_2, CO, etc.) and/or organic substrates can favor oxidation or other reactions. Many such binuclear complexes have been synthesized in order to mimic the reactivity of molecular oxygen and carbon monoxide with hemocyanin,[51−54] which possesses a binuclear unit.[55] In addition, these binuclear complexes are good models

to study metal−metal interaction and investigate multielectron processes.[21,27,56]

Consequently, these systems have reached a very high level of sophistication in order to enhance their ability to form binuclear complexes. These various frames may affect deeply electronic and magnetic properties and also mutually influence the redox activity of each metal center. The intermetallic separation distance determines to a great extent the metal−metal interaction which in its turn plays an important role in the cooperative interaction of the complexes with the substrate.

We focused our attention on the preparation of cylindrical macrotricyclic ligands which are capable of maintaining two metal ions at a fixed distance and in a face-to-face conformation. They are prepared by linking two macrocycles together through two bridges defining three cavities: two lateral inside the macrocycles and a central one. Since the first cylindrical macrotricyclic ligands which have been reported by Lehn and co-workers,[57] many cylindrical macrotricyclic ligands have been synthesized. Most of these ligands contain both nitrogen and oxygen donor atoms and have a great affinity for alkali-metal and alkaline-earth-metal cations. To enhance the coordinating properties of these macrocycles, different modifications have been made such as the ring size, the nature of substituents, and the type of donor atoms.[58]

Although syntheses of cylindrical macrotricyclic ligands have been reported particularly with oxa−azamacrocyclic[39,42,44,47,48] or thia−azamacrocyclic[59,60] subunits, to our knowledge, the macrotricyclic containing only azamacrocycles were unknown. We therefore planned to develop the synthesis of such new macrotricyclic system that would contain only polyaza subunits, which are potentially soft binding sites.

In a recent communication[61] we have briefly reported the synthesis of new cylindrical macrotricyclic ligands in which two cyclam units are connected to each other in a face-to-face conformation. We describe in detail here the synthesis as well as the structural and spectral properties of the macrotricycles **1a,b** and those of their precursors. Further, we report the preparation of dicopper(II) and dinickel(II) complexes of ligands **1a,b**. The X-ray analysis of the dinickel complex **1a** is also reported.

Results and Discussion

Synthesis of Macrotricyclic Ligands 1a,b. 1,4,8,11-Tetraazacyclotetradecane (commonly named cyclam) was chosen to design the aimed macrotricyclic systems for the following reasons: (i) It is a strong ligand for complexing transition metal cations displaying a rich coordination chemistry.[1,62] (ii) Its cavity can incorporate transition metal ions in a very relaxed configuration, giving a particularly strong metal−nitrogen interaction.[63,64] (iii) Among polyazamacroles, cyclam presents

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the greatest thermodynamic[65] and kinetic[66] stabilities for divalent 3d metal ions. Particularly, the Ni(II) complex, showing surprising thermodynamic and kinetic stability,[67,68] has been used in a number of catalytic reactions under severe conditions. (iv) Cyclam being a 14-membered ring, the metal can be easily located within the macrocycle.[69,70] (v) The Cu(II) or Ni(II) ion coordinated to the cyclam unit can be reversibly oxidized, at a moderately positive electrode potential, to form an authentic trivalent copper or nickel species, respectively.[71−73]

It is therefore of major interest to incorporate two cyclam rings into a cylindrical macrotricyclic structure.

Synthetic Strategies. Various synthetic strategies are possible to build up a cylindrical macrotricyclic molecule.[58,74]
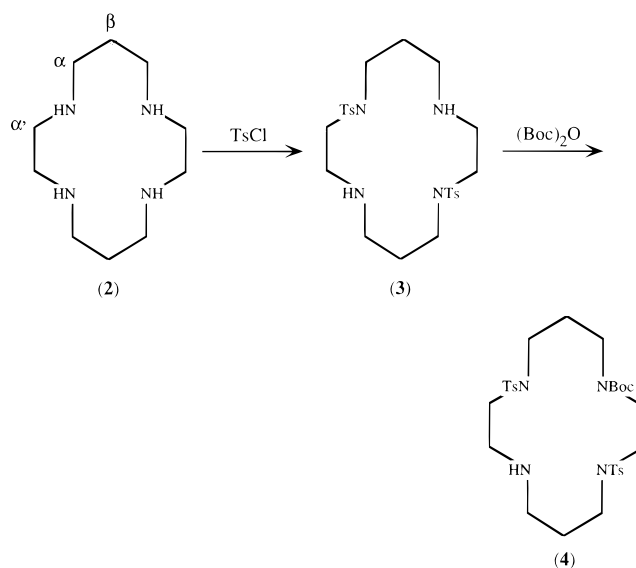
For the synthesis of macrotricycles **1a,b** a convenient reaction pathway proceeds from the 1,8-bis(*p*-tolylsulfonyl)-1,4,8,11-tetraazacyclotetradecane (**3**). The different steps of the reaction scheme can be summarized as follows: (a) One of the nitrogen atoms of the 1,8-ditosylcyclam (**3**) was first protected to give a trisheteroprotected cyclam (**4**). This product is a key intermediate to create the first bridge by a selective substitution of the free NH site of each macrocycle. (b) To ensure that the two macrocyclic subunits are located at a suitable distance, the spacer group is a disubstituted aromatic derivative. Thus condensation of the key intermediate **4** with appropriate difunctional aromatic reagents leads to the bimacrocycles **5a,b**. (c) After selective removal of the *tert*-butyloxycarbonyl groups (Boc), diamide macrotricycles **7a,b** are formed by condensation with the precursor of the second spacer group. (d) Finally, the new cylindrical macrotricyclic ligands **1a,b** are obtained as free amines by reduction of the amide groups and removal of the tosyl protecting groups.

Macrotricycles **1a,b** were also synthesized by direct acylation of ditosylcyclam (**3**) with an appropriate diacid dichloride using high-dilution conditions. The product is separated from the reaction mixture containing side products in very low yield (5−10%).[61,75] Indeed the macrotricycle, bimacrocycle, and macrobicycle are present at same time in the reaction mixture.

There are some restrictions which must be noted, as follows:

Two protection steps are required before the first linkage. One of the two protecting groups must be selectively removed in the presence of the second one. The ease of removal of the *tert*-butyloxycarbonyl group (Boc) under very mild acid conditions immediately promotes its use. Many reasons can explain that *p*-toluenesulfonyl (Ts) has been selected as the second protecting group: tosyl groups are stable under drastic conditions used for removal of other protecting groups. The presence of tosyl groups in these molecules makes them easy to purify. Moreover, the tosyl groups can be removed in the last step of

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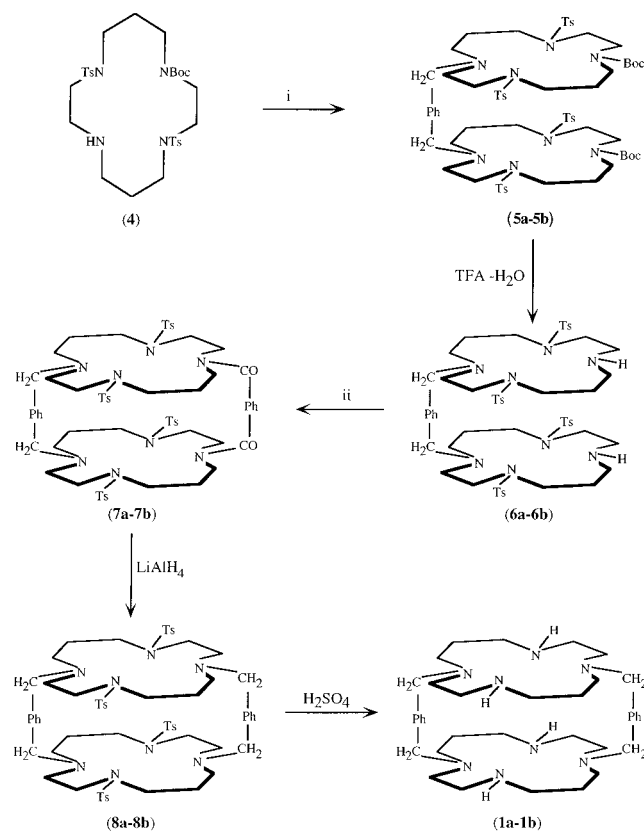(73) Zeigerson, E.; Ginzburg, G.; Meyerstein, D.; Kirschenbaum, L. J. *J. Chem. Soc., Dalton Trans.* **1980**, 1243−1247.
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Scheme 1

the reaction by various methods without cleavage of the tertiaryamine groups.

Polymer is formed when the high-dilution technique is not used. Thus, it is more easy to create the second bridge when the acylation reaction is done under high-dilution conditions by reaction of an α,α'-diacid dichloride with an α,α'-diamine using synchronized motor-driven syringes to deliver the reagents simultaneously. Failure to use this technique results in considerably reduced yields of the aimed macrotricycles.

Synthesis. Cyclam **2** is synthesized according to a well-known procedure.[76] Starting reactant **3**, 1,8-ditosylcyclam, is prepared by reacting cyclam **2** with 1.7 equiv of *p*-toluenesulfonyl chloride (TsCl) following the method described by Parker et al.[77](see Scheme 1, first step). Compound **3** is obtained after flash chromatography as a crystalline derivative within 30% yield. Monoacylation of the 1,8-ditosylcyclam (**3**) with di-*tert*-butyl dicarbonate affords the trisheteroprotected 1,8-(*p*-tolylsulfonyl)-11-(*tert*-butyloxycarbonyl)-1,4,8,11-tetraaza-cyclotetradecane (**4**) in 90% yield, but excess of starting material **3** and the tetraprotected derivative are also obtained.

The new macrotricycles **1a,b** are synthesized according to the reaction sequence shown in the Scheme 2. Condensation of the key intermediate **4** with *m*-dibromoxylene or *p*-dibromoxylene in refluxing acetonitrile and in the presence of potassium carbonate allows the linking of two rings leading respectively to the bimacrocycles **5a,b** in good yield (75−80%).

By treatment with trifluoroacetic acid (TFA), the *tert*-butyloxycarbonyl group is removed in the presence of tosyl groups. Hydrogen chloride (6 N) has also been employed for the selective removal of the Boc groups. Thus, acidic cleavage followed by an aqueous base treatment leads to the diamine bimacrocycles **6a,b** in 90% yield. Bimacrocycles **6a,b** each contain one free secondary amine site which could be linked to the second spacer group. The other amine functions are protected by the tosyl groups until the final step of the synthesis.

The high-dilution condensation of **6a** with isophthaloyl dichloride or **6b** with terephthaloyl dichloride in the presence of NEt$_3$ in dry tetrahydrofuran (THF) affords diamide macrotricyclic ligands **7a,b** after chromatography on silica gel in 53%

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Scheme 2[a]

[a] Key: (i) (a) *m*-BrCH₂PhCH₂Br, (b) *p*-BrCH₂PhCH₂Br; (ii) (a) *m*-ClCOPhCOCl, (b) *p*-ClCOPhCOCl.

Figure 1. ^{13}C NMR spectrum of macrotricycle **1a** in CDCl₃.

and 55% yield, respectively. Despite high-dilution conditions, it has to be noted that polymerization occurs.

Macrotricyclic diamides **7a,b** may be converted into cylindrical macrotricyclic octaamines **1a,b** either in two steps[17] via **8a,b** (reduction of the amide functions followed by cleavage of the tosyl groups) or by direct reduction with LiAlH₄ in tetrahydrofuran at reflux.[78] Attempts to reduce amide groups and simultaneously cleave off the tosyl groups using LiAlH₄ does not lead to a pure product. A two-step synthesis has been adopted. Reduction of **7a,b** with B₂H₆ in THF using a 10–15-fold excess of reagent and hydrolysis of the intermediate borane–amine with 6 N HCl at reflux deliver the macrotricycles **8a,b** in low yield (27–30%). A convenient yield of 90% for **8a** and 88% for **8b** has been obtained by reduction of **7a,b** with LiAlH₄ in tetrahydrofuran at room temperature.

The cleavage of the tosyl groups of **8a,b** is obtained by treatment with sulfuric acid. The octaamine salt is then treated with concentrated NaOH and extracted with chloroform to give the new cylindrical macrotricyclic molecules **1a,b** within 70% and 75% yield, respectively.

The use of dibromoxylene as the first linker and diacid chloride as the second one led to higher yields. The experimental details of the various steps of synthesis and the physical characteristics of the obtained compounds are reported in the Experimental Section.

Characteristics of the Ligands. Macrotricycles **1a,b** which are solids at room temperature are soluble in polar organic solvents (CH₂Cl₂, CHCl₃, CH₃CN, EtOH). All the compounds described herein are stable in solution as well as in the solid
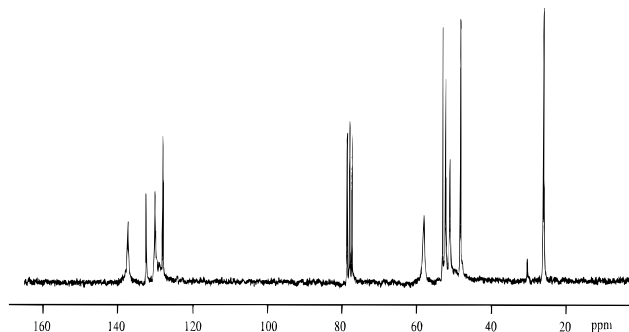
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state. The purity of the obtained compounds after chromatography on silica gel was checked by TLC, IR and/or NMR spectroscopy. These new ligands exhibit the expected spectral properties (^{1}H and ^{13}C NMR, IR, FAB-MS) as well as the elemental analyses corresponding to the proposed formulas (see Experimental Section). The ^{1}H and ^{13}C NMR spectra have been recorded for all the compounds.

The infrared spectra of ligands **4** and **5a,b**) display a strong band at 1693 cm^{-1} assignable to the ν(CO) of the *tert*-butyloxycarbonyl groups. Bimacrocycles **6a,b** are characterized by the lack of this stretching band in their IR spectra. Macrotricyclic diamide ligands **7a,b** show the normal IR absorption frequency of the amide carbonyl groups (strong band at 1634 cm^{-1}). Bands at about 1340 and 1158 cm^{-1} of **4**, **5a,b**, **6a,b**, **7a,b**, and **8a,b** are characteristic of a sulfonamide group (SO₂N). No absorptions around 1340 and at 1158 cm^{-1} were observed for the macrotricycles **1a,b** proving the absence of any tosyl groups.

Each macrotricycle **7a,b** shows a peak on the mass spectrum corresponding to the expected molecular ion at $m/z = 1248$. The FAB-MS spectrum of ligands **8a,b** shows the [M + H]$^+$ peak at $m/z = 1221$. FAB$^+$ mass spectrometry of macrotricycles **1a,b** in CH₂Cl₂ reveals the presence of the characteristic peak [M + H]$^+$ at $m/z = 605$.

The ^{1}H and ^{13}C NMR spectra clearly prove the structural assignments. For example, the ^{1}H NMR spectra of ligands **4**, **5a,b** containing a *tert*-butyloxycarbonyl group show a singlet at 1.46 ppm due to the methyl groups. Bimacrocycles **6a,b** are characterized by the lack of this singlet on their ^{1}H NMR spectra. ^{1}H and ^{13}C NMR spectra of ligands **5a,b**, **6a,b** are in total accordance with a bimacrocycle arrangement. Macrotricyclic ligands **8a,b** show appropriate signals in their ^{1}H and ^{13}C NMR spectra. In the ^{1}H spectroscopy, the detection of only one singlet at 2.36 ppm for **8a** and at 2.35 ppm for **8b** due to the methyl of the tosyl groups reveals the high symmetry of these macrotricyclic ligands. The spectrum of **1b** exhibits one quintuplet at 1.77 ppm attributed to the β-hydrogens, a multiplet at 2.35, and a triplet at 3.24 ppm attributable to the α-hydrogens. The hydrogen atoms of the benzyl chains give rise to two doublets at 3.59 and 3.96 ppm, while the hydrogen resonances of aromatic rings appear as a singlet at 7.33 ppm. The ^{13}C NMR spectrum (Figure 1) of macrotricyclic ligand **1a** consists of 11 signals. The resonances at 25.9 and 30.2 ppm are assigned to the β-carbons, and the peaks at 48.1, 51.0, 52.1, and 52.9, to the α-carbon atoms. The carbon atoms of benzyl chains give rise to a signal at 57.8 ppm. The resonances at 128.0, 130.1, 132.5, and 137.3 ppm correspond to the carbon atoms of the aromatic spacer groups.

New cylindrical macrotricycles **1a,b** containing two cyclam units are potentially dinucleating ligands able to coordinate two transition metals and to maintain them at a suitable distance.
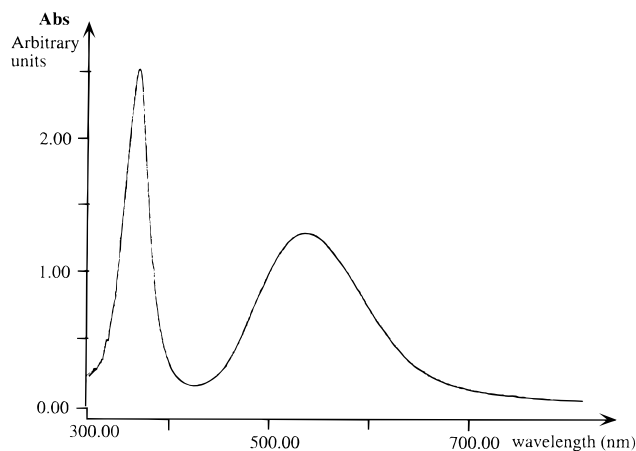
Figure 2. UV−visible spectrum of [Cu$_2$(**1a**)]$^{4+}$ in CH$_3$CN.

Table 1. Spectral Properties of the Cu^{2+} and Ni^{2+} Macrotricycle Complexes **1a,b** and of the Corresponding Monocycle Cyclam in CH$_3$CN

complex	λ, nm (ϵ, M^{-1} cm^{-1})	λ', nm (ϵ, M^{-1} cm^{-1})	ref
[Cu$_2$(**1a**)]$^{4+}$	351 (1097)	520 (569	this work
[Cu$_2$(**1b**)]$^{4+}$	345 (1644)	521 (807)	this work
[Cu(cyclam)]$^{2+}$		505 (74)	26, 73
[Ni$_2$(**1a**)]$^{4+}$	342 (293)	478 (259)	this work
[Ni$_2$(**1b**)]$^{4+}$	339 (315)	473 (273)	this work
[Ni(cyclam)]$^{2+}$		450 (45)	73, 76

Binuclear Copper(II) Complexes. To further characterize these new macrotricycles, their Cu(II) and Ni(II) complexes have been prepared and characterized by their visible and ESR spectra. Addition of 2 equiv of copper(II) perchlorate to ligands **1a,b** in refluxing ethanol results in immediate precipitation of the binuclear complexes as perchlorates. **Caution!** *Perchlorate salts of transition metal complexes are known to be explosive under conditions of mild shock and heat, and these compounds must be handled with great caution.* Elemental analysis indicates that the complexes contain only the ligand and Cu-(ClO$_4$)$_2$ in 1:2 stoichiometry.

The UV−visible spectral properties of the Cu^{2+} complexes of **1a,b** as well as that of the corresponding 1,4,8,11-tetraaza-cyclotetradecane[26,73] are given in Table 1. The visible absorption spectra of [Cu$_2$(**1a**)](ClO$_4$)$_4$ (see Figure 2) and [Cu$_2$(**1b**)]-(ClO$_4$)$_4$ (Table 1) are very similar to each other, both showing two prominent bands at 345−350 and 520 nm. The broad bands are due to the d−d* transition (ligand field transition) with a maximum absorption at 520 nm for [Cu$_2$(**1a**)](ClO$_4$)$_4$ and at 521 nm for [Cu$_2$(**1b**)](ClO$_4$)$_4$, which is expected for a CuN$_4$ chromophore.[79] Thus, the ligand field strength of **1a** is similar to that of **1b**.

The high intensity of the band in the region 345−350 nm rules out metal-centered d−d* transition. This transition involves some type of charge transfer between ligand and metal, i.e. $\sigma_s \rightarrow$ Cu^{2+} (LMCT).[60] The absorption maxima of these two macrotricycles can be compared to that of the copper(II) cyclam complex which absorbs at 505 nm. The small bathochromic shifts of ca. 15 nm observed for [Cu$_2$(**1a**)](ClO$_4$)$_4$ and 16 nm for [Cu$_2$(**1b**)](ClO$_4$)$_4$ are probably due to a somewhat weaker ligand field of the N-substituents.

The presence of noncoordinated perchlorate anion in [Cu$_2$-(**1a**)](ClO$_4$)$_4$ and [Cu$_2$(**1b**)](ClO$_4$)$_4$ is inferred by the presence of the broad band at 1090 cm^{-1} and the absence of an intense
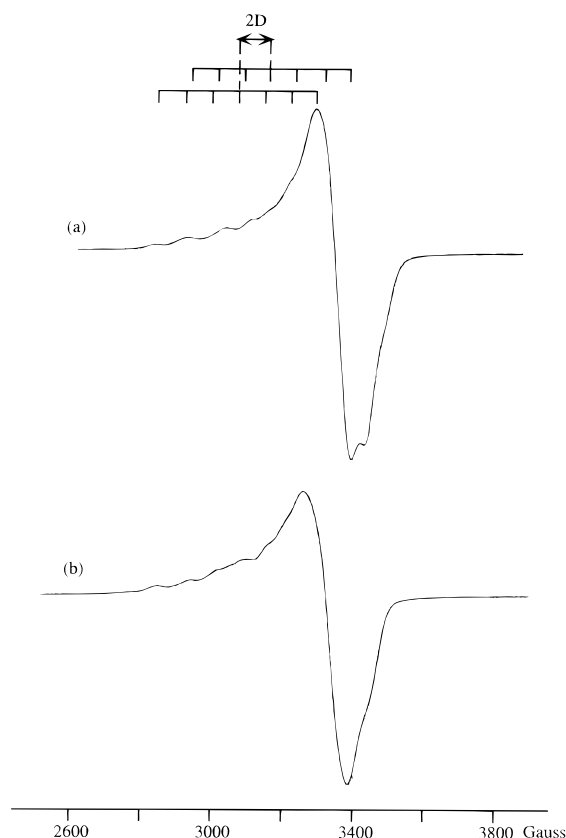
Figure 3. X-band ESR spectra of the allowed transitions for [Cu$_2$-(**1a**)]$^{4+}$ (a) and [Cu$_2$(**1b**)]$^{4+}$ (b) at 100 K in 3:1 EtOH/toluene solution.

Table 2. ESR Data for the Dicopper(II) Macrotricycles Complexes and Copper(II) Cyclam in Frozen Solution at 100 K in 3:1 EtOH/Toluene

compds	allowed transition			half-field transition		
	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (10^{-4} cm^{-1})	g	A (10^{-4} cm^{-1})	r_{Cu-Cu} (Å)
[Cu$_2$(**1a**)]$^{4+}$	2.218	2.060	101	4.376	187	6.5
[Cu$_2$(**1b**)]$^{4+}$	2.226	2.067	113	4.402	142	7.4
[Cu(cyclam)]$^{2+}$	2.185	2.047	206			

absorption band around 930 cm^{-1} typical of coordinated perchlorate.[80]

Visible and infrared spectral properties of these binuclear copper(II) complexes are characteristic of square planar coordination geometry.[81]

ESR Studies. Electron spin resonance of paramagnetic ions is a convenient technique to study metal−metal interactions. The ESR spectra of the Cu^{2+} complexes of **1a,b** and cyclam have been recorded. Measurements of spin−spin distances of dicopper(II) complexes from the half-field transition of ESR spectra are also reported (Table 2).

ESR spectra of copper(II) complexes possessing a square planar coordination geometry show typical pattern with four peaks corresponding to $g_{\parallel}$ and to $g_{\perp}$.[31] They are characterized by the sequence $g_{\parallel} > g_{\perp} > 2.00$ and $A_{\parallel}$ values in the range (150−210) × 10^{-4} cm^{-1}. Hence the $g_{\parallel}$ and $A_{\parallel}$ values are the pertinent parameters to provide structural assignments.

Figure 3 shows ESR spectra of the Cu^{2+} complexes of **1a,b**. The spectra of binuclear complexes [Cu$_2$(**1a**)]$^{4+}$ and [Cu$_2$(**1b**)]$^{4+}$ are very similar and remarkably different from that of a

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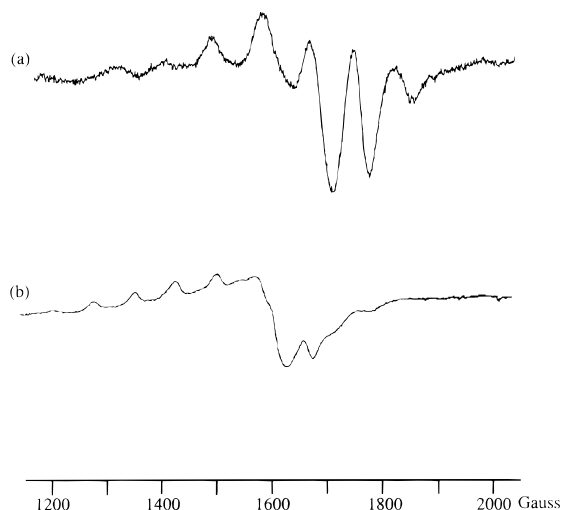(81) Buxtrof, R.; Kaden, T. A. *Helv. Chim. Acta* **1974**, *57*, 1035−1042.

Figure 4. X-band ESR spectra of the half-field transition for $[Cu_2\text{-}(\mathbf{1a})]^{4+}$ (a) and $[Cu_2(\mathbf{1b})]^{4+}$ (b) at 100 K in 3:1 EtOH/toluene solution.

mononuclear complex $[Cu(cyclam)]^{2+}$. The spectra of dinuclear derivatives (Figure 3) display a pattern indicating an axial symmetry for the coordination scheme of copper ions. Such a signal is typical for copper(II) dimers and can be interpreted as triplet state spectra originating from exchange-coupled pairs of copper(II) ions. Each of the spectra shows, in the $\Delta M_s = \pm 1$ region, a strong absorption at ≈ 3330 G with $g_{\parallel}$ values of 2.218 and 2.226 for $[Cu_2(\mathbf{1a})]^{4+}$ and for $[Cu_2(\mathbf{1b})]^{4+}$, respectively. In this region, due to the zero-field splitting 2D, two septets which are shifted with respect to each other are expected. Generally, it is difficult to observe all these lines. The coupling constant $A_{\parallel}$ for the binuclear complexes is about half of that of the mononuclear complex (Table 2), revealing that in both binuclear complexes metal−metal interactions are present.[82]

In the spectra (Figure 4) of $[Cu_2(\mathbf{1a})]^{4+}$ and $[Cu_2(\mathbf{1b})]^{4+}$, a half-field transition $\Delta M_s = \pm 2$, consistent with the presence of Cu(II) dimers,[83] is observed between 1200 and 1900 G. This signal presents a seven lines hyperfine pattern with an average hyperfine spacing of $(140-190) \times 10^{-4}$ cm^{-1}. This is also evidence for the spin coupling between the two copper ions.

The ESR study clearly shows the $Cu^{2+}-Cu^{2+}$ interaction by the existence of more than four hyperfine lines in the spectra of the dicopper(II) complexes and by the smaller values of $A_{\parallel}$, which are typical of dipole−dipole interactions in binuclear copper(II) complexes.[20−23,31,84]

The observed ESR as well as the electronic absorption and infrared spectra of the complexes are then consistent with a square planar geometry for each metal ion.

From the intensities of the half-field transition (I_1) and the high-field transition (I_2), the average distance (r) between the two paramagnetic cations can be calculated using the well-known empirical equation:[85,86]

$$I_1/I_2 = 20/r^6$$

Internuclear separation was estimated to be $r_{Cu-Cu} = 6.5$ and 7.4 Å for dicopper(II) complexes of $\mathbf{1a,b}$, respectively.

Binuclear Nickel(II) Complexes. Macrotricycles $\mathbf{1a,b}$ easily form homobinuclear complexes when treated with 2 equiv of nickel(II) perchlorate. The binuclear complexes $[Ni_2(\mathbf{1a})]$-$(ClO_4)_4$ and $[Ni_2(\mathbf{1b})](ClO_4)_4$ were synthesized in aqueous solution and crystallized as perchlorates from EtOH.

The absorption spectra of these complexes are collected in Table 1. In addition the spectrum of $[Ni(cyclam)](ClO_4)_2$ is included for comparison.[73,76] The spectra of these dinickel(II) complexes consist of a broad band at ≈ 480 nm in the visible region attributable to the d−d* transition with an extinction coefficient of ca. 259−270 M^{-1} cm^{-1}, which is typical of a yellow diamagnetic Ni(II) complex and can be related to the d−d* transition observed for other square planar nickel(II) complexes.[26,34] The bathochromic shift of this band is due to a weakening of the ligand field of the two tertiary amino groups, because the xylyl groups probably reduce the donor strength of the tertiary nitrogen atoms. The bands in the 330−350 nm region can be assigned to ligand−metal charge transfer (LMCT).

In the infrared spectra of binuclear Ni(II) complexes of $\mathbf{1a,b}$, the broad intense band at about 1090 cm^{-1} assigned to ClO_4^- showing no remarkable splitting indicates that practically no coordination of ClO_4^- occurs.[80] In both cases the coordination scheme of both nickel ions is square planar and typical of diamagnetic complexes (ESR silent). Similar absorption band ranges (440−480 nm) have already been reported for low-spin square planar Ni(II) complexes.[24,76,79]

Moreover it is well-known that Ni(II) complexes of polyazamacrocycles exist in aqueous solution in equilibrium between the diamagnetic square planar (low-spin) and paramagnetic pseudo octahedral (high-spin) species,[87,88] as shown in the following equation:

$$[Ni(L)]^{2+} + 2H_2O \leftrightarrows [Ni(L)(OH_2)_2]^{2+}$$
$$\text{yellow (low spin)} \qquad \text{blue (high spin)}$$
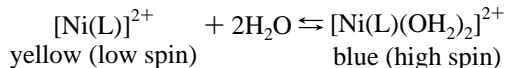
In acetonitrile, the square planar species should predominate because this solvent has a weaker coordinating ability than water. Indeed, the dinickel(II) complexes shows an absorption band around 400−500 nm indicating the presence of only square planar species.

Spectroscopic studies (visible, infrared, and ESR) are typical of square planar copper(II) and nickel(II) complexes with 14-membered tetradentate macrocycles. This suggests a similar structure of the chromophore for all the studied complexes. These data are corroborated by the crystal structure of $[Ni_2(\mathbf{1a})](ClO_4)_4$.

Crystal structure of $[Ni_2(\mathbf{1a})](ClO_4)_4$. To ascertain the macrotricyclic structure and the face-to-face arrangement of the two metal ions, the crystal structure of $[Ni_2(\mathbf{1a})](ClO_4)_4 \cdot 2CH_3\text{-}CN$ ($\mathbf{1a'}$) was determined. In Table 4 the coordinates of all non-hydrogen atoms are listed, and in Table 5 selected bond distances and angles are reported. Figure 5 shows a view of the cationic part of $\mathbf{1a'}$. In the crystal, the $[Ni_2(\mathbf{1a})]^{4+}$ dimers lie on crystallographic inversion centers. Each nickel atom is bound to four nitrogen atoms of one of the cyclams. The surroundings of the metal atoms are nearly square planar: the nickel atom is out of the mean plane of the 4 nitrogens by 0.026(1) Å, and the N1−Ni−N3 and N2−Ni−N4 bond angles are respectively equal to 177.26(7) and 174.76(7)°. The Ni−N bond distances range from 1.909(2) to 1.969(2) Å and are slightly shorter than 2.07 Å, the ideal value as calculated from

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Table 3. X-ray Experimental Data for [Ni$_2$(**1a**)](ClO$_4$)$_4$·2CH$_3$CN

formula	C$_{18}$H$_{30}$N$_4$Ni(ClO$_4$)$_2$·CH$_3$CN
MW	604.1
color	yellow
cryst system	triclinic
a (Å)	10.716(3)
b (Å)	12.805(4)
c (Å)	9.292(3)
α (deg)	95.82(2)
β (deg)	103.06(2)
γ (deg)	94.94(2)
V (Å^3)	1227.8
Z	2
D_{calc} (g cm^{-3})	1.634
wavelength (Å)	1.5418
μ (cm^{-1})	36.648
space group	P1
diffractometer	Philips PW1100/16
cryst dimens (mm)	0.20 × 0.15 × 0.15
temp (°C)	−100
radiation	Cu Kα graphite monochromated
mode	θ/2θ flying step-scan
scan speed (deg s^{-1})	0.020
step width (deg)	0.03
scan width (deg)	0.90 + 0.14 tan(θ)
octants	±h,±k,+l
θ min/max (deg)	3/52
no. of data collcd	2746
no. of data with $I > 3\sigma(I)$	2396
no. of variables	325
abs min/max	0.89/1.26
$R(F)$	0.036
$R_w(F)$	0.061
p	0.08
largest peak in final diff map (e Å^{-3})	0.06
GOF	1.482

Table 4. Atomic Coordinates and Their Esd's for [Ni$_2$(**1a**)](ClO$_4$)$_4$·2CH$_3$CN

atom	x	y	z	B^a (Å^2)
Ni	0.69899(5)	0.22370(4)	0.66355(5)	2.09(1)
N1	0.7216(2)	0.3263(2)	0.5267(3)	2.21(6)
C1	0.6413(3)	0.4160(2)	0.5365(4)	2.76(7)
C2	0.6230(3)	0.4411(3)	0.6927(4)	3.02(8)
C3	0.5265(3)	0.3620(3)	0.7327(4)	2.94(8)
N2	0.5261(3)	0.2549(2)	0.6516(3)	2.32(6)
C4	0.4530(3)	0.1709(3)	0.7070(4)	2.88(7)
C5	0.5431(3)	0.1356(3)	0.8352(4)	2.80(7)
N3	0.6682(2)	0.1178(2)	0.7948(3)	2.13(5)
C6	0.7690(3)	0.1242(3)	0.9367(4)	2.66(7)
C7	0.9060(3)	0.1226(3)	0.9198(4)	2.81(7)
C8	0.9495(3)	0.2136(3)	0.8466(4)	2.80(7)
N4	0.8796(2)	0.2042(2)	0.6872(3)	2.24(6)
C9	0.9406(3)	0.2784(3)	0.6027(4)	2.66(7)
C10	0.8610(3)	0.3691(2)	0.5813(4)	2.65(7)
C11	0.7006(3)	0.2795(3)	0.3650(4)	2.57(7)
C12	0.5657(3)	0.2316(2)	0.2893(3)	2.15(7)
C13	0.5174(3)	0.1337(2)	0.3179(3)	2.25(7)
C14	0.3941(3)	0.0868(2)	0.2485(3)	2.13(7)
C15	0.3173(3)	0.1392(2)	0.1415(3)	2.46(7)
C16	0.3655(3)	0.2345(3)	0.1085(4)	2.62(7)
C17	0.4883(3)	0.2816(2)	0.1820(3)	2.46(7)
C18	0.3420(3)	−0.0132(3)	0.2999(3)	2.31(7)
Cl1	0.84769(8)	0.00022(6)	0.31619(8)	2.72(2)
O1	0.7972(2)	0.0387(2)	0.4382(3)	3.66(6)
O2	0.7454(2)	−0.0302(2)	0.1884(3)	5.52(7)
O3	0.9106(3)	−0.0889(2)	0.3548(4)	6.71(8)
O4	0.9343(3)	0.0808(2)	0.2857(3)	5.78(7)
Cl2	0.78991(8)	0.49543(6)	1.11073(9)	2.93(2)
O5	0.6605(3)	0.5171(3)	1.0852(5)	8.4(1)
O6	0.8554(4)	0.5653(3)	1.0397(4)	8.08(9)
O7	0.8460(4)	0.5071(2)	1.2660(3)	6.21(8)
O8	0.7864(3)	0.3898(2)	1.0499(3)	5.52(8)
C19	0.0732(4)	0.3249(3)	0.2592(5)	4.7(1)
C20	0.1894(4)	0.3104(3)	0.3660(4)	3.48(8)
N5	0.2837(3)	0.2991(3)	0.4467(4)	5.04(9)

^{a} B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table 5. Selected Bond Distances (Å) and Angles (deg) for [Ni$_2$(**1a**)](ClO$_4$)$_4$·2CH$_3$CN

Ni−N1	1.956(2)	N2−C3	1.496(3)
Ni−N2	1.909(2)	N2−C4	1.479(3)
Ni−N3	1.969(2)	N3−C5	1.501(3)
Ni−N4	1.939(2)	N3−C6	1.493(3)
N1−C1	1.500(3)	N3−C18	1.508(3)
N1−C10	1.500(3)	N4−C8	1.489(3)
N1−C11	1.520(3)	N4−C9	1.491(3)
N1−Ni−N2	90.61(8)	N3−Ni−N4	94.03(8)
N1−Ni−N4	80.04(8)	N1−Ni−N3	177.26(7)
N2−Ni−N3	87.48(8)	N2−Ni−N4	174.76(7)

molecular mechanics by Thöm.[69] However, these values are in the range of those found for Ni^{2+} complexes with tetradentate ligands.[89,90] The Ni−N1 and Ni−N3 bond lengths are not significantly different, 1.965(2) and 1.969(2) Å (mean value 1.967(2) Å), but are longer than the Ni−N2 and Ni−N4 bonds, 1.909(2) and 1.939(2) Å (mean value 1.924(5) Å). This difference arises from the different nature of the amine groups: around N1 and N2, secondary amines, around N3 and N4, tertiary amines. It is noteworthy that Ni−N(tert) bond distances of Ni^{II}TMC complex are longer than Ni−N(sec) bond distances of the Ni^{II}cyclam complex.[91] The two cyclam moieties have the trans I configuration in Bosnich's definition with all nitrogen substituents on the same side of the four nitrogen mean plane.[92] This trans-I configuration is found for several complexes with tetra-N-alkylated-1,4,8,11-tetraazacyclotetradecane.[93,94] The trans-I conformer of 14-aneN$_4$ differs from those of 12- and 13-aneN$_4$ in that, except for a very long bond length, the metal ion lies very nearly in the mean plane of the four nitrogen donors.[69] The six-membered rings present in each cyclam unit assume chair conformations, while the carbon−carbon bonds in the five-membered rings adopt the usual skew conformation. The chelate angles subtended by the nitrogen donors at the nickel-(II) show small deviations from 90°: 87.48(8)° and 88.04(8)°

for the five-membered rings and 90.61(8) and 94.03(8)° for the six-membered rings. These angles are normal for planar tetraamine 14-membered macrocyclic ligand complexes of Ni-(II) with alternating five- and six-membered chelate rings.[90] The lengths of the N−C single bonds in [Ni$_2$(**1a**)](ClO$_4$)$_4$·2CH$_3$CN (**1a′**) show small variation from the normal range depending on the environments of the nitrogen atoms. The six bonds from tertiary nitrogen atoms N1 and N3 to the carbon atoms of the cyclam ring are longest with an average length of 1.504 Å. The N−C bonds involving secondary nitrogen donors N2 and N4 have an average value of 1.489 Å (Table 5). In a perchlorate group, the four Cl−O lengths are not very different from each other (see Table 6), and the average value of 1.413 Å is

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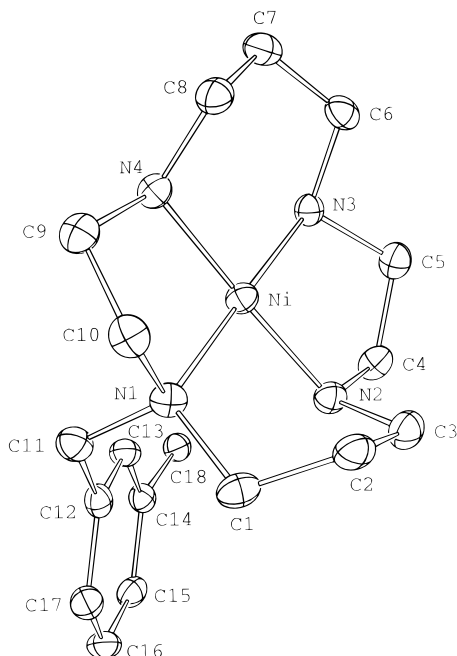
Figure 5. ORTEP plot of the cationic part of **1a′** showing the numbering scheme used. Ellipsoïds are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted.

Table 6. Intramolecular Bond Lengths (Å) and Angles (deg) Involving the Chlorine and Oxygen Atoms

Lengths			
Cl1−O1	1.426(2)	Cl2−O5	1.410(2)
Cl1−O2	1.417(2)	Cl2−O6	1.396(2)
Cl1−O3	1.411(2)	Cl2−O7	1.419(2)
Cl1−O4	1.421(2)	Cl2−O8	1.406(2)
Angles			
O1−Cl1−O2	109.6(1)	O5−Cl2−O6	108.0(2)
O1−Cl1−O3	107.9(1)	O5−Cl2−O7	110.0(2)
O1−Cl1−O4	109.7(1)	O5−Cl2−O8	106.0(2)
O2−Cl1−O3	109.3(2)	O6−Cl2−O7	111.0(2)
O2−Cl1−O4	109.2(1)	O6−Cl2−O8	111.9(2)
O3−Cl1−O4	111.2(2)	O7−Cl2−O8	109.7(1)

comparable with related compounds.[95] The O−Cl−O bond angles in [Ni$_2$(**1a**)](ClO$_4$)$_4$·2CH$_3$CN show only small deviations from the value expected for a regular ion with T_d symmetry (Table 6). In [Ni$_2$(**1a**)](ClO$_4$)$_4$·2CH$_3$CN, there appears to be no axial coordination for the complex ion as the closest contact of the Ni (II) ion with an oxygen atom of the perchlorate anions is 3.394 Å. Since this Ni(II)−O distance is dramatically longer than the normal axial Ni^{II} bonds, the Ni(II)−O interaction is not significant, and the Ni^{II} is four-coordinate. Thus the perchlorate groups are present in the lattice in an ionic form and are quite distinct from that associated with metal.[95] Complex [Ni$_2$(**1a**)](ClO$_4$)$_4$·2CH$_3$CN contain two molecules of acetonitrile that are not coordinated to the Ni(II) ion. The distance from the Ni(II) ion to the nitrogen atom of acetonitrile is 4.677 Å, and the shortest contact of this acetonitrile solvate is 2.988(4) Å with cyclam nitrogen N2. The distance between the two metal atoms in the same molecule is equal to 6.830(1) Å and no intermolecular Ni−Ni distance is less than 9 Å, precluding any metal−metal interaction. There are no unusual intramolecular contacts.

Conclusion and Outlook

Ligands **1a,b** represent new types of cylindrical macrotricyclic molecule containing only N-donor atom in their framework. The

(95) Tasker, P. A.; Sklar, L. *J. Cryst. Mol. Struct.* **1975**, *5*, 329−344.

obvious advantage offered by these new ligands over other binucleating ligands is the well-defined constant coordination sphere imposed by the ligand. The metal−metal interaction can be deliberately altered by lengthening the spacer group. An especially interesting feature is that these macrotricycles are capable of maintaining two transition metal cations at a fixed distance. The macrotricycles **1a,1b** form binuclear complexes with copper(II) and nickel(II). From the ESR spectrum of the dicopper(II) complex of ligand **1a**, the internuclear separation was estimated to be 6.5 Å. In the solid state, the crystal structure of [Ni$_2$(**1a**)](ClO$_4$)$_4$·2CH$_3$CN reveals that Ni(II) cations are each located on one cyclam unit at a distance of 6.829 Å. Thus, the inclusion of substrate molecule in the cavity is sterically possible.

The cylindrical macrotricycles **1a,1b** are potentially versatile binuclear ligands since a wide range of compounds having different bridges, and hence different relationships between the two macrocyclic units, can be synthesized. Heteronuclear complexes may be formed when the two macrocycle units are different, and in the case of homonuclear complexes, the stabilization of different oxidations states may be also possible. Work aimed to design new asymmetrical receptors of this class of cylindrical macrotricycles and to study their complexation behavior toward different metal cations is currently under way.

Experimental Section

Reagents and Solvents. All reagents were of reagent-grade quality and were used without further purification. All reactions employing dry solvents were carried out under argon. Tetrahydrofuran (THF) was distilled from LiAlH$_4$ before use. CH$_3$CN was distilled from CaH$_2$ and stored on molecular sieves. Purification of compounds by column chromatography was performed with 60−200 mesh silica gel (for column chromatography) and with 40−60 mesh (for flash chromatography). Thin-layer chromatography (TLC) was carried out on silica gel plates (Merck 60 F$_{254}$).

Spectroscopic Methods. ^{1}H and ^{13}C NMR spectra have been measured in CDCl$_3$ solution on a Bruker AC200 spectrometer of the "Centre de Spectroscopie Moléculaire de l'Université de Bourgogne". The chemical shifts are given in ppm downfield from the ^{1}H and ^{13}C signals of tetramethylsilane (TMS). The following abreviations are used to describe NMR spectra: s, singlet; d, doublet; t, triplet; q, quintiplet; m, multiplet. Mass spectra were obtained on a Kratos Concept 321S spectrometer using DCI ionization and FAB modes. The microanalyses have been performed at the "Service Central d'Analyse du Centre National de la Recherche Scientifique", Vernaison, France. ESR spectra were recorded on a Bruker ESP 300 coupled to a Microware computer at microwave powers that did not cause saturation of the signal. To improve the signal-to-noise ratio of the spectra of the half-field transition, all spectra were recorded using modulation amplitudes of about 10 G. The intensity of the transitions were measured by double-integration. UV−visible spectra of the complexes were obtained on 10^{-3}−10^{-4} mol^{-1}·L^{-1} solutions in acetonitrile on a Varian Cary 1 apparatus using 1-cm silica cells. Infrared spectra were measured on a Bruker IFS 66v infrared spectrophotometer. Solid samples were prepared as a 1% dispersion in KBr.

Synthesis of the Compounds. 1,4,8,11-Tetraazacyclotetradecane (cyclam) (2) was synthesized according to well-known procedures.[76]

1,8-Bis(*p*-tolylsulfonyl)-1,4,8,11-tetraazacyclotetradecane (Ts$_2$ cyclam) (3) was synthesized as reported in ref 77.

Macrotricycles **1a,b** were obtained according to the synthetic procedure depicted in Scheme 2.

Chemistry. 1,8-Bis(*p*-tolylsulfonyl-11-(*tert*-butyloxycarbonyl-1,4,8,11-tetraazacyclotetradecane (4). A solution of di-*tert*-butyl dicarbonate (1.55 g; 7.08 mmol) in chloroform (200 mL) was added dropwise to a stirred solution of ditosylcyclam (**3**) (7.20 g; 14.17 mmol) in CHCl$_3$ (350 mL). The resulting mixture was stirred at room temperature for 3 h. The solvent was then evaporated, and the residue

was purified by chromatography on silica gel (98/2 CH_2Cl_2/MeOH) to give the trisheteroprotected cyclam **4** as a white powder (3.90 g; 90%).

^{1}H NMR (CDCl$_3$) [δ (ppm)]: 1.46 (s, 9H), 1.80 (q, 4H), 2.40 (s, 3H), 2.41 (s, 3H), 2.67 (t, 2H), 2.81 (t, 2H), 2.99 (t, 2H), 3.10 (t, 2H), 3.31 (m, 8H), 7.26−7.30 (d, 4H), 7.59−7.70 (dd, 4H). ^{13}C NMR (CDCl$_3$) [δ (ppm)]: 22.1, 28.9, 29.1, 30.3, 46.3, 48.5, 49.9, 51.9, 80.2, 127.8, 130.3, 130.4, 135.5, 143.9, 144.1, 1556.0. FAB MS (*m/z*) 609, (M + H)$^+$. IR (KBr, cm^{-1}): 1693 (CO (Boc)), 1339 and 1159 (SO$_2$N). Anal. Calcd for C$_{29}$H$_{44}$N$_4$O$_6$S$_2$ (608): C, 57.24; H, 7.24; N, 9.21; O, 15.79; S, 10.53. Found: C, 57.26; H, 7.27; N, 9.03; O, 15.35; S 10.17.

General Procedure P$_1$: Formation of Bimacrocycles. The appropriate α,α′-dibromoxylene (1 mol equiv) dissolved in dry acetonitrile was added to a solution of the trisheteroprotected cyclam **4** (2 mol equiv) in the same solvent containing anhydrous potassium carbonate (>5 mol equiv). The reaction mixture was refluxed under anhydrous atmosphere for 24 h. The reaction mixture was cooled and filtered. The residue washed with chloroform, and the combined filtrate and washings were evaporated. The crude product obtained was purified by column chromatography on silica gel giving the protected bimacrocycle.

11,11′-*m*-Xylylenebis[1,8-bis(*p*-tolylsulfonyl)-4-(*tert*-butyloxycarbonyl)-1,4,8,11-tetraazacyclotetradecane] (5a). The general procedure P$_1$ applied to 4.75 g (7.50 mmol.) of **4** and 1.00 g of α,α′-dibromo-*m*-xylene (3.76 mmol) gives, after purification by chromatography (99/1 CH_2Cl_2/MeOH), the title compound (3.80 g; 76%).

^{1}H NMR (CDCl$_3$) [δ (ppm)]: 1.46 (s, 18H), 1.69 (q, 4H), 1.88 (q, 4H), 2.38 (s, 12H), 2.47 (t, 4H), 2.72 (t, 4H), 3.03 (m, 16H), 3.31 (m, 8H), 3.57 (s, 4H), 7.18−7.28 (m, 12H), 7.55−7.63 (dd, 8H). ^{13}C NMR (CDCl$_3$) [δ (ppm)]: 22.1, 27.3, 28.2, 29.1, 46.2, 47.7, 48.4, 49.1, 52.2, 54.3, 60.3, 80.4, 127.9, 128.8, 128.8, 130.4, 131.2, 135.7, 136.7, 138.8, 144.0, 156.1. FAB MS (*m/z*): 1319, (M + H)$^+$; 1219, (M − Boc)$^+$; 1119, (M − 2Boc)$^+$. IR (KBr, cm^{-1}): 1693 (CO (Boc)), 1338 and 1159 (SO$_2$N). Anal. Calcd for C$_{66}$H$_{94}$N$_8$O$_{12}$S$_4$ (1318): C, 60.09; H, 7.13; N, 8.50; O, 14.57; S, 9.71. Found: C, 60.17; H, 7.21; N, 8.15; O, 14.17; S, 9.37.

11,11′-*p*-Xylylenebis[1,8-bis(*p*-tolylsulfonyl)-4-(*tert*-butyloxycarbonyl)-1,4,8,11-tetraazacyclotetradecane] (5b). The general procedure P$_1$ applied to 3.00 g (5.00 mmol) of **4** and 0.65 g of α,α′-dibromo-*p*-xylene (2.50 mmol) gives, after purification by chromatography (99/1 CH_2Cl_2/MeOH), the title compound (2.50 g; 77%).

^{1}H NMR (CDCl$_3$) [δ (ppm)]: 1.46 (s, 18H), 1.63 (q, 4H), 1.86 (q, 4H), 2.38 (s, 6H), 2.39 (s, 6H), 2.72 (t, 4H), 3.02 (m, 20H), 3.34 (t, 4H), 2.50 (t, 4H), 3.57 (s, 4H), 7.19−7.27 (m, 12H), 7.55−7.63 (dd, 8H). ^{13}C NMR (CDCl$_3$) [δ (ppm)]: 22.2, 27.4, 29.1, 34.0, 48.6, 49.00, 51.5, 54.3, 60.0, 80.6, 127.9, 129.6, 130.4, 135.6, 137.4, 139.4, 144.0, 156.1. FAB MS (*m/z*) 1342, (M + Na + H)$^+$; 1319, (M + H)$^+$; 1120, (M − 2Boc)$^+$. IR (KBr, cm^{-1}): 1693 (CO), 1341 and 1159 (SO$_2$N). Anal. Calcd for C$_{66}$H$_{94}$N$_8$O$_{12}$S$_4$ (1318): C, 60.09; H, 7.13; N, 8.50; O, 14.57; S, 9.71. Found: C, 60.13; H, 7.19; N, 8.21; O, 14.15; S, 9.29.

General Procedure P$_2$: Selective Removal of the Boc Groups. The bimacrocycles **5a,b** each containing two *tert*-butyloxycarbonyl groups were stirred at room temperature for 3 h with aqueous trifluoroacetic acid (90% TFA). After evaporation of the solution, the residue was dissolved in water, and sodium hydroxide pellets were added until the pH reached 12. The aqueous solution was extracted with chloroform. The combined chloroform extracts were dried over magnesium sulfate and evaporated to give the pure diamine bimacrocycles as white solids.

11,11′-*m*-Xylylenebis[1,8-bis(*p*-tolylsulfonyl)-1,4,8,11-tetraazacyclotetradecane] (6a). The general procedure P$_2$ applied to 3.50 g (2.65 mmol) of **5a** gives the title compound (2.83 g; 95%).

^{1}H NMR (CDCl$_3$) [δ (ppm)]: 1.69 (q, 4H), 1.84 (q, 4H), 2.38 (s, 12H), 2.63 (m, 12H), 2.81 (t, 4H), 3.07 (m, 8H), 3.22 (t, 4H), 3.36 (t, 4H), 3.55 (s, 4H), 7.17−7.27 (m, 12H), 7.51−7.63 (dd, 8H). ^{13}C NMR (CDCl$_3$) [δ (ppm)]: 22.1, 27.9, 29.6, 46.4, 46.8, 47.4, 48.8, 49.2, 51.0, 51.7, 52.0, 60.6, 127.7, 127.8, 130.0, 130.3, 136.1, 137.6, 139.6, 143.7, 143.8. FAB MS (*m/z*) 1119, (M + H)$^+$. IR (KBr, cm^{-1}): 1338 and 1159 (SO$_2$N). Anal. Calcd for C$_{58}$H$_{78}$N$_8$O$_8$S$_4$ (1118): C, 60.11; H, 6.98; N, 10.02; O, 11.45; S, 11.45. Found: C, 60.27; H, 7.03; N, 9.95; O, 11.15; S, 11.07.

11,11′-*p*-Xylylenebis[1,8-bis(*p*-tolylsulfonyl)-1,4,8,11-tetraazacyclotetradecane] (6b). Using the general procedure P$_2$, 2.10 g (1.59 mmol) of bimacrocycle **5b** gave 1.65 g of diamine bismacrocycle as a white solid (yield 93%).

^{1}H NMR (CDCl$_3$) [δ (ppm)]: 1.75 (q, 8H), 2.37 (s, 12H), 2.63 (m, 12H), 2.80 (t, 4H), 3.06 (m, 8H), 3.22 (t, 4H), 3.36 (t, 4H), 3.56 (s, 4H), 7.20−7.27 (d, 12H), 7.56−7.62 (dd, 8H). ^{13}C NMR (CDCl$_3$) [δ (ppm)]: 22.1, 27.8, 29.5, 46.3, 46.9, 47.5, 49.7, 49.8, 51.0, 51.6, 53.3, 60.4, 127.7, 127.9, 129.5, 130.3, 136.0, 137.5, 138.3, 143.7, 144.0. FAB MS (*m/z*) 1119, (M + H)$^+$. IR (KBr, cm^{-1}): 1341 and 1159 (SO$_2$N). Anal. Calcd for C$_{56}$H$_{78}$N$_8$O$_8$S$_4$ (1118): C, 60.11; H, 6.98; N, 10.02; O, 11.45; S, 11.45. Found: C, 60.22; H, 7.05; N, 9.93; O, 11.01; S, 11.12%.

General Procedure P$_3$: Synthesis of Cylindrical Macrotricyclic Diamides 7a,7b under High-Dilution Conditions. The obtained diamine bimacrocycles **6a,b** dissolved in dry tetrahydrofuran and the appropriate amount of phthaloyl dichloride in the same solvent were added at an equal rate and at the same time to a solution of tetrahydrofuran containing triethylamine over a period of 24 h at room temperature. After addition of the reagents, the resulting mixture was stirred for another 3 h, filtered, and then evaporated to dryness. The crude product was purified by silica column chromatography (97/3 CH_2Cl_2/MeOH).

11,24,30,35-Tetrakis(*p*-tolylsulfonyl)-3,5:16,18-dibenzo-1,7,11,14,-20,24,30,35-octaza-2,6-dioxotricyclo[18.6.6^{1,20}.6^{7,14}]octatriaconta-3,5,-16,18-tetraene (7a). According to the general procedure P$_3$, 2.50 g (2.24 mmol) of diamine bimacrocycle **6a** and 0.59 g of isophthaloyl dichloride (2.90 mmol) gave, after purification by chromatography, 1.50 g of diamide macrocycle **7a** in 53% yield.

^{1}H NMR (CDCl$_3$) [δ (ppm)]: 1.75 (q, 4H), 1.96 (q, 4H), 2.37 (s, 6H), 2.39 (s, 6H), 3.10−3.45 (m, 32H), 3.75 (s, 4H), 7.26−7.37 (m, 16H), 7.59−7.63 (m, 8H). ^{13}C NMR (CDCl$_3$) [δ (ppm)]: 22.2, 27.5, 29.3, 48.3, 50.3, 51.6, 54.3, 55.1, 60.7, 127.9, 128.2, 129.2, 130.4, 134.6, 135.5, 137.5, 144.1, 144.1, 171.3, 172.2. FAB MS (*m/z*) 1249, (M + H)$^+$. IR (KBr, cm^{-1}): 1637 (CO), 1338 and 1158 (SO$_2$N). Anal. Calcd for C$_{64}$H$_{80}$N$_8$O$_{10}$S$_4$·H$_2$O (1266): C, 60.66; H, 6.32; N, 8.85; O, 12.64; S, 10.11. Found: C, 60.55; H, 6.38; N, 8.77; O, 12.69; S, 10.22.

12,26,32,37-Tetrakis(*p*-tolylsulfonyl)-3,6:17,20-dibenzo-1,8,12,15,-22,26,32,37-octaaza-2,7-dioxotricyclo[20.6.6^{1,22}.6^{8,15}]tetraconta-3,5,-17,19-tetraene (7b). The general procedure P$_3$ applied to 1.65 g (1.48 mmol) of diamine bismacrocycle **6b** and 0.39 g of terephthaloyl dichloride (1.92 mmol) gave, after purification by chromatography, the title compound (1.02 g; 55%).

^{1}H NMR (CDCl$_3$) [δ (ppm)]: 1.64 (q, 8H), 2.35 (s, 6H), 2.41 (s, 6H), 2.90−3.45 (m, 32H), 3.59 (s, 4H), 7.33 (m, 16H), 7.63 (m, 8H). ^{13}C NMR (CDCl$_3$) [δ (ppm)]: 21.8, 21.9, 27.6, 28.4, 30.1, 30.3, 48.0, 48.7, 50.3, 52.2, 53.9, 59.8, 127.9, 128.0, 130.3, 130.5, 135.1, 135.9, 138.3, 142.1, 143.7, 171.9, 172.4. FAB MS (*m/z*) 1249, (M + H)$^+$. IR (KBr, cm^{-1}): 1636 (CO), 1339 and 1158 (SO$_2$N). Anal. Calcd for C$_{64}$H$_{80}$N$_8$O$_{10}$S$_4$,H$_2$O (1266): C, 60.66; H, 6.32; N, 8.85; O, 12.64; S, 10.11. Found: C, 60.53; H, 6.38; N, 8.72; O, 12.67; S, 10.12.

General Procedure P$_4$: Reduction of the Amide Groups. A solution of appropriate diamide **7a,b** in dry tetrahydrofuran was added to a suspension of lithium aluminum hydride (>10 mol equiv) in THF under an argon atmosphere. The reaction mixture was stirred at room temperature for at least 7 h. Excess hydride was destroyed by dropwise addition of water. The resulting white suspension was filtered, and the residual solid washed with chloroform. The organic solvents were evaporated giving the crude macrotricycle, which was purified by column chromatography (silica gel).

11,24,30,35-Tetrakis(*p*-tolylsulfonyl)-3,5:16,18-dibenzo-1,7,11,14,-20,24,30,35-octaazatricyclo[18.6.6^{1,20}.6^{7,14}]octatriaconta-3,5,16,18-tetraene (8a). The general procedure P$_4$ applied to 1.30 g (1.04 mmol) of diamide macrotricycle **7a** and 0.79 g of LiAlH$_4$ (20.80 mmol) yielded the title compound (1.15 g; 90%) after purification by chromatography (98/2 CH_2Cl_2/MeOH).

^{1}H NMR (CDCl$_3$) [δ (ppm)]: 1.75 (q, 8H), 2.36 (s, 12H), 2.48−3.40 (m, 32H), 3.52 (s, 8H), 7.02 (d, 4H), 7.15−7.24 (m, 12H), 7.51−7.62 (dd, 8H). ^{13}C NMR (CDCl$_3$) [δ (ppm)]: 22.2, 27.4, 27.7, 48.2, 49.0, 49.3, 51.7, 52.2, 52.5, 54.5, 55.1, 60.6, 60.8, 127.8, 128.3, 128.5, 130.3, 136.7, 136.9, 140.0, 140.1, 143.7, 143.8. FAB MS (*m/z*) 1222,

$(M + H + 1)^+$; 1220, $(M)^+$. IR (KBr, cm^{-1}): 1340 and 1158 (SO$_2$N). Anal. Calcd for C$_{64}$H$_{84}$N$_8$O$_8$S$_4$·H$_2$O (1238): C, 62.03; H, 6.94; N, 9.05; O, 10.34; S, 10.34. Found: C, 62.11; H, 7.01; N, 8.90; O, 10.03; S, 10.07.

12,26,32,37-Tetrakis(*p*-tolylsulfonyl)-3,6:17,20-dibenzo-1,8,12,15,-22,26,32,37-octaazatricyclo [20.6.6^{1,22}.6^{8,15}]tetraconta-3,5,17,19-tetraene (8b). In a similar manner, using the general procedure P$_4$, 1.00 g (0.80 mmol) of diamide macrotricycle **7b** and 0.61 g (16.00 mmol) of LiAlH$_4$ gave macrotricycle **8b** (0.86 g; 88%) as a white solid after purification by column chromatography (98/2 CH$_2$Cl$_2$/MeOH).

^{1}H NMR (CDCl$_3$) [δ (ppm)]: 1.75 (q, 8H), 2.35 (s, 12H), 2.53–3.02 (m, 24H), 3.41 (m, 8H), 3.47 (s, 8H), 7.13–7.19 (dd, 8H), 7.25–7.38 (m, 8H), 7.53–7.63 (dd, 8H). ^{13}C NMR (CDCl$_3$) [δ (ppm)]: 22.2, 27.3, 27.7, 48.2, 49.0, 49.3, 51.7, 52.2, 52.4, 54.5, 55.1, 60.7, 127.8, 128.4, 128.5, 130.3, 136.7, 136.9, 140.0, 140.1, 143.7, 143.7. FAB MS (*m/z*) 1222, $(M + H + 1)^+$. IR (KBr, cm^{-1}): 1335 and 1155 (SO$_2$N). Anal. Calcd for C$_{64}$H$_{84}$N$_8$O$_8$S$_4$·H$_2$O (1238): C, 62.03; H, 6.94; N, 9.05; O, 10.34; S, 10.34. Found: C, 62.04; H, 6.78; N, 9.07; O, 10.04; S, 10.34.

General Procedure P$_5$: Sulfuric Acid Deprotection. The tetratosylated macrotricycles **8a,b** were dissolved in concentrated H$_2$SO$_4$ (4 mL for 1 g) and treated under argon for 48 h at 90 °C. The mixture was allowed to cool at room temperature. Ethanol and then ether were added slowly at 0 °C to the dark brown solution. The precipitate formed overnight in the ice-box was filtered off, washed with ether, and then dissolved in a solution of 8 M NaOH. The resulting aqueous solution was extracted with chloroform (5 × 100 mL), and the combined organic extracts were dried over MgSO$_4$ and evaporated to give pure macrotricycle as a free base.

3,5:16,18-Dibenzo-1,7,11,14,20,24,30,35-octaazatricyclo [18.6.6^{1,20}.6^{7,14}]octatriaconta-3,5,16,18-tetraene (1a). The general procedure P$_5$ applied to 1.10 g (0.90 mmol) of tetratosylated macrotricycle **8a** gave the title compound (0.38 g; 70%).

^{1}H NMR (CDCl$_3$) [δ (ppm)]: 2.09 (q, 8H), 2.40–2.95 (m, 32H), 3.62 (d, 4H), 3.93 (d, 4H), 4.23 (m, 4H), 6.97–7.01 (d, 4H), 7.17 (t, 2H), 7.53 (s, 2H). ^{13}C NMR (CDCl$_3$) [δ (ppm)]: 25.9, 30.2, 48.1, 51.0, 52.1, 52.9, 57.8, 128.0, 130.1, 132.5, 137.3. FAB MS (*m/z*) 605, $(M + H)^+$. Anal. Calcd for C$_{36}$H$_{60}$N$_8$·2H$_2$O (640): C, 67.50; H, 9.38; N, 17.50. Found: C, 67.70; H, 9.44; N, 16.95.

3,6:17,20-Dibenzo-1,8,12,15,22,26,32,37-octaazatricyclo-[20.6.6^{1,22}.6^{8,15}]tetraconta-3,5,17,19-tetraene (1b). Using the general procedure P$_5$, 0.80 g (0.65 mmol) of tetratosylated ligand **8b** and concentrated H$_2$SO$_4$ gave the title compound (0.30 g; 75%).

^{1}H NMR (CDCl$_3$) [δ (ppm)]: 1.77 (q, 8H), 2.35 (m, 28H), 3.24 (t, 4H), 3.59 (d, 4H), 3.96 (d, 4H), 7.33 (s, 8H). ^{13}C NMR (CDCl$_3$) [δ (ppm)]: 26.1, 30.3, 49.0, 49.5, 52.8, 53.0, 61.4, 130.0, 138.9. FAB MS (*m/z*) 605, $(M + H)^+$. Anal. Calcd for C$_{36}$H$_{60}$N$_8$·2H$_2$O (640): C, 67.50; H, 9.38; N, 17.50. Found: C, 67.08; H, 9.40; N, 16.73.

Preparation of the Binuclear Metal Complexes. Dicopper(II) Perchlorate Complexes. A solution of copper(II) perchlorate hexahydrate (0.30 mmol) in 5 mL of ethanol was added to an ethanolic solution (5 mL) of macrotricyclic ligands **1a,b** (0.15 mmol), and the mixture was heated at 60 °C for 30 min. A violet precipitate that formed immediately was filtered off, washed with ethanol and ether, and dried in a vacuum.

[Cu$_2$(1a)](ClO$_4$)$_4$. Violet crystals formed (yield 84%). Anal. Calcd for C$_{36}$H$_{60}$Cl$_4$Cu$_2$N$_8$O$_{16}$ (1128.9): C, 38.27; H, 5.32; N, 9.92; Cl, 12.56; Cu, 11.26. Found: C, 38.41; H, 5.39; N, 9.75; Cl, 12.34; Cu, 10.71.

[Cu$_2$(1b)](ClO$_4$)$_4$. Violet crystals formed (yield 76%). Anal. Calcd for C$_{36}$H$_{60}$Cl$_4$Cu$_2$N$_8$O$_{16}$ (1128.9): C, 38.27; H, 5.32; N, 9.92; Cl, 12.56; Cu, 11.26. Found: C, 38.36; H, 5.41; N, 9.83; Cl, 12.21; Cu, 10.71.

Dinickel(II) Perchlorate Complexes. Dinickel(II) macrotricyclic complexes were prepared by dissolving the ligands **1a,b** (0.15 mmol) in hot ethanol and adding to an ethanolic Ni(II)(ClO$_4$)$_2$·6H$_2$O solution.

The reaction mixture became yellow-orange upon adding the Ni^{II} solution and was heated at 60 °C for 30 min. The yellow crystalline precipitate was collected by filtration, washed with ethanol and then with ether, and dried under vacuum.

[Ni$_2$(1a)](ClO$_4$)$_4$. Yellow crystals formed (yield 88%). Anal. Calcd for C$_{36}$H$_{60}$Cl$_4$N$_8$Ni$_2$O$_{16}$ (1119.2): C, 38.60; H, 5.36; N, 10.01; Cl, 12.67; Ni, 10.49. Found: C, 38.79; H, 5.41; N, 9.91; Cl, 12.51; Ni, 10.11.

Crystals of the suitable complex for X-ray analysis were obtained by slow evaporation at room temperature of an acetonitrile solution.

[Ni$_2$(1b)](ClO$_4$)$_4$. Yellow crystals formed (yield 74%). Anal. Calcd for C$_{36}$H$_{60}$Cl$_4$N$_8$Ni$_2$O$_{16}$ (1119.2): C, 38.60; H, 5.36; N, 10.01; Cl, 12.67; Ni, 10.49. Found: C, 38.73; H, 5.45; N, 9.92; Cl, 12.73; Ni, 10.01.

Dicopper(II) Tetraacetate Complexes. To an ethanolic solution of macrotricyclic ligands **1a,b** (1 mol equiv) was added copper(II) acetate (2 mol equiv) in one portion. The solution turned dark blue almost immediately. The mixture was heated and stirred for 30 min and then triturated with ether to give a blue precipitate, which was collected by filtration and dried under vacuum giving [Cu$_2$(**1a**)](OAc)$_4$ or [Cu$_2$(**1b**)](OAc)$_4$. These dicopper tetraacetate derivatives were used for ESR studies.

X-ray Experimental Section

Suitable single crystals of [Ni$_2$(**1a**)](ClO$_4$)$_4$·2CH$_3$CN were obtained as described above. A systematic search in reciprocal space using a Philips PW1100/16 automatic diffractometer showed that crystals of **1a′** belong to the monoclinic system.

Quantitative data were obtained at −100 °C achieved using a local-built gas flow device. All experimental parameters used are given in Table 5. The resulting data-set was transferred to a DEC AXP3600S computer, and for all subsequent calculations the Nonius Molen package[96] was used with the exception of a local data reduction program.

Three standard reflections measured every 1 h during the entire data collection period showed no significant trend. The raw step-scan data were converted to intensities using the Lehmann–Larsen method[97] and then corrected for Lorentz and polarization factors.

The structure was solved using direct methods. After refinement of the heavy atoms, a difference Fourier map revealed maximas of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C–H = N–H = 0.95 Å) and isotropic temperature factors such as B(H) = 1.3 B_{eqv}(C or N) Å^2 but not refined. At this stage empirical absorption corrections were applied using the method of Walker and Stuart,[98] since face indexation was not possible under the cold gas stream. Full least-squares refinements, including anisotropic temperature factors for non-hydrogen atoms, were against |F|, with $w = 1/σ^2$ and $σ^2(F^2) = σ_{counts}^2 + (pI)^2$. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come respectively from ref 99a,b.

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