New side-bridged bismacrocycles and cross-bridged macrotricycles. Syntheses and Cu(II) complexation study†

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Eight new cyclen based constrained macropolycycles (**4a**–**4d**, **5a**–**5d**) have been obtained by reductive ring cleavage of polyaminal derivatives of bis-macrocycles or macrotricyclic polyammonium salts by sodium borohydride. The mononuclear and dinuclear Cu(II) complexes of these macropolycyclic ligands were isolated as solids and investigated by UV-Vis and EPR spectroscopies. The possibility to obtain the specific formation of mononuclear complexes constitutes an original feature of these new macropolycycles.

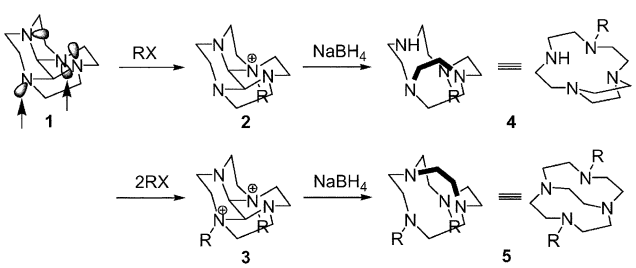
Introduction

The synthesis of bridged polyazacycloalkanes is of current interest because they exhibit unusual basicity (they are proton sponges),[1–6] redox behaviour[7,8] and coordination chemistry.[8–13] Structural modifications of the macrocycles based on the ethylene or propylene bridging of the adjacent[14–19] (side-bridged) or opposite[20–23] (cross-bridged) nitrogen atoms have been reported according to various procedures. These two kinds of reinforced (or constrained) macrocycles exhibit interesting and different behaviours in coordination chemistry. The bridging of adjacent nitrogen atoms in the macrocycle provides a convenient method for reducing the propensity of the macrocycle for binding to transition metal ions in a *cis*-(folded)-conformation rather than the *trans*-(planar)-conformation.[14–15] Crossbridging of non adjacent nitrogen atoms leads to bicyclic tetraamines which may adopt conformations having all four nitrogen lone pairs pointing inside of the cavity for complexation of metal ions.[20] Moreover, the short bridging chain induces a relative rigidity of the host ligand and the situation of the nitrogen lone pairs in a *cis*-folded geometry promotes distorted coordinations modes as tetrahedral, pseudo-octahedral, distorted-trigonal-bipyramidal or also distorted square pyramidal.[22] The combination of a large ligand field strength and a strained macrocyclic linkage favours an other unusual behaviour: authors generally observed that complexes exhibit exceptional stabilities even in strongly acidic conditions, useful for biomimetic applications.[6–8] As a consequence of these particular geometrical factors, these two classes of ligands act also as proton sponges: this behaviour has already been pointed out on several occasions.[1–6]

Wainwright and collaborators reported more than twenty years ago the first case of bridging by a simple *cis*-alkylation of the macrocycle.[14] Crossbridging of polyazacycloalkanes using an approach based on the bisaminal chemistry was reported for the first time by Weisman, Wong and coworkers.[20] This method was later derived and adopted by Kolinski to synthesize adjacent-bridged cyclam.[19] The common route (Scheme 1) involves the condensation of glyoxal and cyclic tetraamines to give tetracyclic *cis*-fused bisaminals **1** (example with cyclen) which are selectively mono- or cross-di-alkylated to obtain the resulting mono- or bis-quaternary ammonium salts (respectively, **2** and **3**). Reductive cleavage finally gives the two kinds of bridged tetraazacycloalkanes **4**–**5**, respectively named piperazino-tetraazacycloalkanes[19] and cross-bridged tetraamines[20] or adamanzanes[6] in the literature.

The properties described for these families of ligands are expected to persist in their dimeric derivatives which, however, are seldom reported in the literature: the only known example of macrotricyclic constrained dimers was described five years ago by Springborg and collaborators for bis-adamanzanes using a six-step procedure starting from cyclen[24] and some bismacrocyclic compounds in oral or poster communications presented by Weisman, Wong and coworkers.[25]

Bismacrocycles and macrotricyclic ligands, formed by linking two cycles with, respectively one or two spacers, are of great interest because of their ability to behave as multi-site receptors in the trapping of various substrates or coordinated metals. The consequence of such construction is that the metals coordinated by two "side by side" or "face to face" macrocyclic subunits are constrained to stay at a close



Scheme 1 Syntheses of cross- and side-bridged tetraazacycloalkanes.[19,20].

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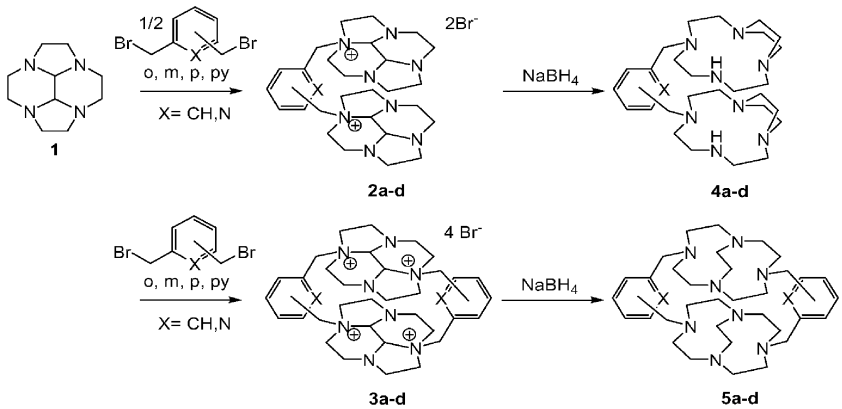


Scheme 2 Syntheses of side- and cross-bridged macropolycycles.

distance, which may induce possible metal–metal interactions, and then particular electronic properties.[26–28]

Results and discussion

Synthesis

Our three-step procedure (Scheme 2, Table 1) involves (a) the condensation of glyoxal and cyclen to give the tetracyclic *cis*-bisaminal,[21,29–31] (b) the dimerization and highly regioselective mono- or di-alkylation to give the bis- or tetra-quaternary ammonium bromides,[21,29,30,32] and (c) the reductive cleavage with $NaBH_4$ in ethanolic solution to give the side-bridged bismacrocycles or cross-bridged macrotricycles.[19,20] Authors generally used $NaBH_4$ in EtOH for reductive cleavage to prepare bridged polyamines; we found that this methodology consists indeed in an efficient route to dimeric bridged systems. Although the reductions of **2a**–**2d**, **3a**–**3d** are slow under these conditions, they are especially clean.

Evidence of the structure of **4a**–**4d** and **5a**–**5d** and their intermediates is obtained from ^{13}C and ^{1}H NMR spectra, microanalyses and mass spectrometry. As noted recently,[29–30] depending on the relative positions of the glyoxal bridges of the two macrocyclic subunits, two different configurations of the tetraammonium salts isomers may be found (observed in NMR for the **3b** and **3c** derivatives); however, after reaction with sodium borohydride, one unique structure is obtained.

After anionic exchange work up for **4a**–**4d** and **5a**–**5d** the microanalysis indicates that the ligand remains hydrated and a broad band is systematically observed in ^{1}H NMR at approximately 12 ppm. This signal which concerns a single proton is certainly due to an ammonium or a strongly H-bonded water complex[6] and gives evidence of the proton sponge behaviour of our ligands. One can also note that this NH^+ proton resonance (around 12 ppm) is more downfield than the values previously found for NH^+ hydrogen atoms situated in analogous monomeric mono-crossbridged azamacrocycles[6] (9–10 ppm), in favour of an inside coordinated proton shared among several nitrogen atoms. However the overall spectrum is symmetrical which indicates that the proton is rapidly exchanged between the two macrocyclic subunits. NMR investigations point out some similar spectra for the four members of each family (**4a**–**4d** and **5a**–**5d**). For **4a**–**d**, all methylenic protons are isochronous except those of the piperazine ring which are diastereotopic in pairs. For **5a**–**d**, all protons are diastereotopic except those of the ethylene bridge and benzyl linker which are isochronous. Because of the time-averaged symmetry of the dimeric structure (**4b** and **5c** are, respectively in C_{2v} and D_{2h} symmetry), spectra are relatively simple, particularly in the case of macrotricycles.

The 2D ^{1}H–^{1}H homonuclear and ^{1}H–^{13}C heteronuclear correlations and homonuclear decoupling experiments, allow us to fully assign the ^{1}H and ^{13}C signals; **4b** and **5c** have been chosen as examples in Fig. 1 (spectra are reported in experimental section).

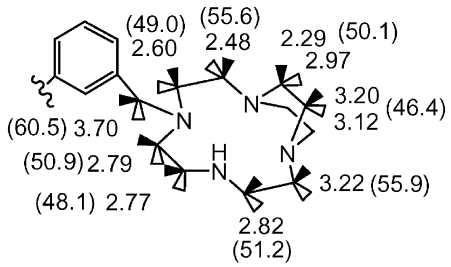
Complexation

The cage-like structures of the constrained macropolycycles are expected to affect the properties of their metal coordination compounds compared to the corresponding unbridged bismacrocycles or macrotricycles.[27,28,33–37] The configurations of **4a**–**d** and **5a**–**d** (having all eight lone pairs pointing inside the macrocyclic cavity) have still sizes and geometries appropriated for coordination of one metal in each of the two tetraamine units. However, the constrained geometry induces specific complexation mode: in the complex structure the metal adopts an external situation, out of the mean plane of

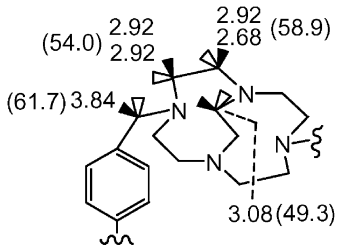
Table 1 Yields for **4a–d** and **5a–d** syntheses (*ortho*-, *meta*-, *para*-xylyl bridges: X = CH; 2,6-pyridinyl bridge: X = N)

Ligand	Bridge	Reduction yield (%)	Overall[a] yield (%)	Ligand	Bridge	Reduction yield (%)	Overall[a] yield (%)
4a	*ortho*	79	76	**5a**	*ortho*/*ortho*	93	56
4b	*meta*	87	78	**5b**	*meta*/*meta*	100	98
4c	*para*	69	67	**5c**	*para*/*para*	60	55
4d	2,6-pyr	54	54	**5d**	2,6-pyr/2,6-pyr	90	88

[a] Yields starting from **1**.



4b



5c

Fig. 1 NMR ^{1}H and ^{13}C atom assignments for **4b** and **5c**.

the ligand, which will certainly influence the intermetallic interactions.

Titration of each ligand of **4a–d** and **5a–d** series with Cu(II) perchlorate was monitored by UV-Vis spectrophotometry. The plot of absorbance *versus* Cu : ligand ratio shows an unambiguous 1 : 1 endpoint (Fig. 2), pointing out an unexpected stoichiometry for Cu binding in solution. No trace of dimetallic complexes was observed at room temperature for a long period (several days), meaning that the second metallation of constrained macropolyclic ligands is difficult under mild conditions. Subsequently, the formation of dimetallic complexes required heating or addition of a very large excess of metal in order to increase the rate of the second metallation. According to these results, mono- and di- nuclear complexes were synthesized (see in experimental part): on the one hand the dimetallic derivatives are obtained by refluxing a homogeneous solution of ligand and Cu(II) perchlorate and, on the other hand the monometallic complexes in ethanol at 0 °C. Generally when allowed to react with one eq. of metal ion, unbridged dimers give the statistical formation of the dimetallic complexes (see electronic supplementary information, ESI,† and ref. 27 and 28). The behaviour of our reinforced ligands is certainly in relation with their strong base properties. The complexation of the first non-protonated macrocyclic moiety is relatively easy, however the entry of the metal ion in the second protonated macrocyclic subunit implies electrostatic repulsions and consequently slower complexation rates.

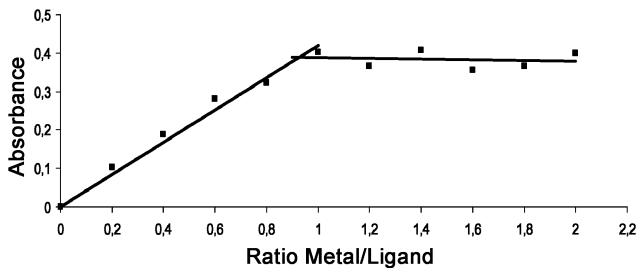


Fig. 2 Spectrophotometric titration curve for the addition of Cu(II) perchlorate hexahydrated to **5b** (5×10^{-3} mol L^{-1} in DMF).

Spectroscopic and electronic studies

Electronic spectra and EPR spectra (frozen solution 150 K) of DMF solutions (10^{-2} mol L^{-1}) have been recorded. Data are gathered in Table 2.

UV–Visible spectra for all compounds show evidence of a quite broad band located in the region 600–700 nm ascribable to the d–d transition which characterizes copper(II) complexes in a square pyramidal geometry.[38–39] These observations make obvious that, in DMF, the copper atom is displaced from the plane of the nitrogen donor atoms, the fifth position being occupied by the donor atom of the DMF molecule.[27,38] In the case of the reinforced macrotricyclic complexes [Cu**5a–d**] a red shift of the band suggests that this deplacement from the N_4 basal plane is more important. Besides, it is worthy to note that comparing the mononuclear complexes *vs.* the dinuclear complexes, one can notice a hypsochromic displacement of the absorption band for all derivatives except for the *ortho*-substituted macrocyclic [Cu_2**4a**] complex for which this displacement is bathochromic.

EPR data for compounds [Cu**4a–d**] and [Cu**5a–d**] clearly evidenced usual features, typical of mononuclear copper(II) derivatives supporting a square pyramidal geometry, which corroborate the electronic spectra comments. Indeed, for a copper(II) ion in an axial environment, the g factors are anisotropic ($g_z = g_{\parallel}$, g_x, $g_y = g_{\perp}$) such as $g_{\parallel} \gg g_{\perp} > 2.0$ for a $d_{x^2-y^2}$ elongated ground state with usual values $g_{\parallel}$ close to 2.05 and $g_{\perp}$ varying from 2.23–2.33. In present work, these values vary from 2.19 and 2.22 for $g_{\parallel}$ and 2.04 to 2.06 for $g_{\perp}$. Spectra show evidence of copper nuclear hyperfine splitting as the parallel signals appear as quartets owing to the hyperfine coupling with the copper ($I = 3/2$) nuclei, the coupling constant values ($A_{\parallel}$) being in the same order than those usually

Table 2 Spectroscopic (electronic and EPR) data for mono- and binuclear copper complexes[a]

	$g_{\parallel}$	$g_{\perp}$	$10^{-4}A_{\parallel}$/cm^{-1}	λ/nm	ε/L mol^{-1} cm^{-1}
[Cu**4a**]	2.19	2.05	161	627	223
[Cu**4b**]	2.19	2.05	180	631	376
[Cu**4c**]	2.19	2.05	175	678	288
[Cu**4d**]	2.19	2.05	176	687	302
[Cu_2**4a**]	2.25	2.06	112	648	521
[Cu_2**4b**]	2.25	2.08	114	590	626
[Cu_2**4c**]	2.25	2.08	113	617	527
[Cu_2**4d**]	2.26	2.08	116	629	431
[Cu**5a**]	2.21	2.06	159	681	123
[Cu**5b**]	2.21	2.04	156	706	126
[Cu**5c**]	2.19	2.05	168	689	245
[Cu**5d**]	2.22	2.05	170	723	162
[Cu_2**5a**]	2.26	2.08	115	650	258
[Cu_2**5b**]	2.26	2.08	119	686	285
[Cu_2**5c**]	2.27	2.07	113	674	156
[Cu_2**5d**]	2.26	2.08	115	679	289

[a] $A_{\parallel}$ data are experimental values.

observed for copper(II) in a similar environment *i.e.* 160–180 × 10^{-4} cm^{-1} (Table 2).

Within exchange-coupled metal systems, such as dinuclear copper(II) complexes, the metal–metal dipolar interaction is known to generate a zero field splitting parameter D, which can be determined by EPR spectrum measurements. Generally, this parameter D is less than 0.04 cm^{-1} and while, it does not significantly change the numerical value of the g and A factors, it does affect the appearance of the EPR spectrum. Additional forbidden transitions arise associated with the $\Delta M_s = 2$ values compared with the $\Delta M_s = 1$ values in mononuclear complexes. In general, it is possible to obtain evidence for zero field splitting from the nuclear hyperfine splitting patterns observed on the $\Delta M_s = 1$ transitions of copper(II) complex particularly the $g_{\|}$ or $g_{\perp}$ factors. The splitting observed range from the four lines normally associated with one copper(II) nucleus to a seven-line pattern and even range to a maximum of nine lines, the A values should be half of the one observed for the mononuclear species.[36,40,41]

Considering derivatives [Cu_2**4a**–**d**] and [Cu_2**5a**–**d**], they mostly display spectra different from those observed for the mononuclear complexes as shown in Fig. 3 for complexes of **4b** and **5b**. For all compounds, a significant lowering of the $A_{\|}$ values is noticed and the modification of the shape of the multi-lines signals as well. Normally, one should detect a similar seven lines signal at about $g = 4$. Upon experimental conditions, no signal susceptible to corroborate the existence of two Cu ions in interaction has been detected in the half-field region. However it is worthy to note that recently, Delgado and colleagues have described new dinuclear copper systems for which the signal was only detected at temperatures as low as 30 K.[26]

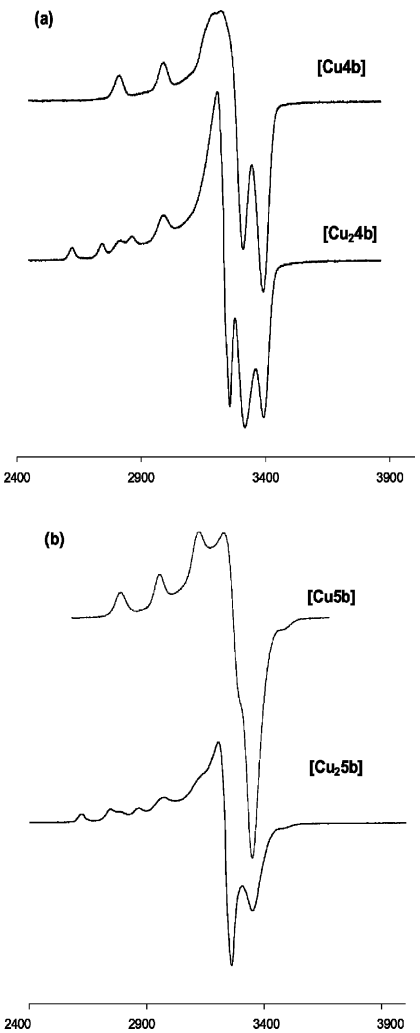


Fig. 3 EPR spectra of (a) complexes [Cu**4b**] and [Cu_2**4b**] and (b) [Cu**5b**] and [Cu_2**5b**] (in Gauss).

Conclusion

In summary, a facile and efficient three-step synthesis has yielded two new classes of constrained macrocyclic dimers which present attractive reactivity and coordination properties. Further, neither high dilution conditions nor fastidious protection steps were needed and good overall yields were obtained.

The complexation studies informed us on the univocal formation of monometallic complexes with these kind of dimers, certainly due to their strong base properties. This behaviour is rather unusual as aza-bismacrocycles generally lead to a mixture of mono- and di-metallic complexes. Electronic and EPR characterisations gave unambiguous results about the 1 : 1 or 2 : 1 stoichiometry of the respective mono- and di-metallic species. Monometallic cyclen dimers complexes are interesting as potential intermediates for the synthesis of heterodinuclear complexes. These compounds, rarely reported in the literature, will certainly exhibit remarkable magnetic properties.

Another interesting and accepted behaviour of bridged polyazacycloalkanes is their ability to act as proton sponges. Potentiometric measurements are also in progress to evaluate this possible nature of our bismacrocycles and macrotricycles and to connect this ligand basicity to the complexation behaviour.

Experimental

General

All reagents were of commercial quality and solvents were dried using standard procedures. Elemental analyses were performed at the Service de Microanalyse, CNRS, 91198 Gif sur Yvette, France. Mass spectrometry analyses were performed at the Centre Régional de Mesures Physiques de l'Ouest, Rennes, France. EPR spectra were run on a Brucker Elexys spectrometer (X-band).

Ligand synthesis

Cyclen–glyoxal **1** and the corresponding bismacrocycles or macrotricycles polyammonium salts **2a**–**d** and **3a**–**d** were synthesized according to our previous works.[27,28] Excess of $NaBH_4$ (24 equiv.) was added in small portions over 1 h to a stirred polyammonium salts ethanolic solution (1×10^{-3} mol) cooled at 0 °C. The mixture was allowed to stir at room temperature for one week. Excess of $NaBH_4$ was then

destroyed by slow addition (with cooling) of HCl 4 M and solvents were removed. The resulting white solid was dissolved in H_2O and the pH adjusted to basic conditions with KOH. For bismacrocycles, the aqueous phase was extracted with chloroform (3 × 40 mL) and dried with $MgSO_4$. After solvent evaporation **4a–d** were obtained as white or pale yellow solids/oils in good yields (Table 1). We observed that despite the basic conditions of the final extraction (pH > 12), the products were isolated as polyprotonated (bromide or chloride) salts. This indicates that **4a–d** were probably very strong bases. The compounds were then dissolved in water and eluted through an anion exchange resin (Dowex 1×2-200, OH^- form).

In some cases for macrotricycles **5a–d**, extraction of the aqueous solution with chloroform failed. Then aqueous phase was totally removed, absolute ethanol is added to the residue to dissolve the pale oil and the white solid was filtered. Ethanol was then evaporated to give the compound and an anionic exchange work up was performed as described for compounds **4a–d**.

4a was obtained as a pale yellow powder (79% yield); Found: C, 65.44; H, 10.34; N, 22.12. Calc. for $C_{28}H_{50}N_8 \cdot 1H_2O$: C, 65.08; H, 10.14; N, 21.68%; δ_H ($CDCl_3$, 400 MHz) 1.51 (1H, s), 2.19 (4H, m); 2.53 (2H, m); 2.65 (2H, m); 2.69 (2H, m); 2.71 (2H, m); 2.77 (2H, m); 3.02 (2H, m); 3.12 (2H, m); 3.16 (2H, m); 3.75 (2H, s); 7.18–7.32 (2H, m); δ_C ($CDCl_3$, 100 MHz) 46.5 (2C); 48.6; 49.3; 50.5 (2C); 51.3; 51.4; 56.3; 56.9; 57.8; 127.1; 129.6; 137.8. FAB-MS (MeOH): m/z 499.51, $[M + H]^+$.

4b was obtained as a pale yellow powder (87% yield); Found: C, 53.91; H, 10.51; N, 18.05%. Calc. for $C_{28}H_{50}N_8 \cdot 7H_2O$: C, 53.82; H, 10.32; N, 17.93%; δ_H ($CDCl_3$, 400 MHz): 2.18 (2H, m); 2.41 (2H, m); 2.61 (2H, m); 2.84 (2H, m); 2.86 (2H, m); 3.02 (2H, m); 3.12 (2H, m); 3.15 (2H, m); 3.17 (2H, m); 3.27 (2H, m); 3.78 (2H, s); 7.28 (2H, m); 11.14 (1H, 1s). δ_C ($CDCl_3$, 100 MHz): 45.5 (2C); 47.7; 48.7; 49.7 (2C); 50.8; 51.0; 54.2; 55.1; 59.9; 128.1; 128.4; 138.6. FAB-MS (MeOH): m/z 499.51, $[M + H]^+$.

4c was obtained as a white powder (69% yield); Found: C, 62.53; H, 11.09; N, 20.56. Calc for $C_{28}H_{50}N_8 \cdot 4H_2O$: C, 62.87; H, 10.93; N, 20.95%; δ_H ($CDCl_3$, 400 MHz) 2.29 (2H, m) 2.48 (2H, m); 2.60 (2H, m); 2.77 (2H, m); 2.79 (2H, m); 2.82 (2H, m); 2.97 (2H, m); 3.12 (2H, m); 3.20 (2H, m); 3.22 (2H, m); 3.70 (2H, s); 7.28 (2H, m); 12.14 (1H, s); δ_C ($CDCl_3$, 100 MHz): 46.4 (2C); 48.1; 49.0; 50.1 (2C); 50.9; 51.2; 55.6; 55.9; 60.5; 128.5; 137.5. FAB-MS (MeOH): m/z 499.51, $[M + H]^+$.

4d was obtained as a brown powder (54% yield); Found: C, 60.28; H, 10.11; N, 23.15. Calc. for $C_{27}H_{49}N_9 \cdot 2H_2O$: C, 60.52; H, 9.97; N, 23.53%. δ_H ($CDCl_3$, 400 MHz): 2.11 (2H, m); 2.41 (2H, m); 2.67 (2H, m); 2.92 (2H, m); 2.94 (2H, m); 2.96 (2H, m); 2.99 (2H, m); 3.14 (2H, m); 3.16 (2H, m); 3.26 (2H, m); 3.76 (2H, s); 7.26 (2H, d); 7.74 (1H, t); 11.30 (1H, 1s). δ_C ($CDCl_3$, 100 MHz): 45.5 (2C); 47.2; 48.8; 49.6; 49.7; 49.9 (2C); 53.7; 55.3; 60.4; 122.1; 137.2; 157.7. FAB-MS (MeOH): m/z 500.8, $[M + H]^+$.

5a was obtained as a pale yellow powder (93% yield); Found: C, 60.62; H, 9.41; N, 15.53. Calc. for $C_{36}H_{56}N_8 \cdot 6H_2O$: C, 60.99; H, 9.66; N, 15.80%; δ_H (D_2O, 400 MHz): 2.72 (4H, m); 2.86 (4 + 4 + 4H, m); 3.14 (4H, s, CH_2 bridge); 3.90 (4H, s, CH_2Ph); 7.18–7.47 (4H, m); δ_C (D_2O, 100 MHz): 48.8; 55.0; 58.0; 59.6; 129.7; 132.2; 140.2. FAB-MS (MeOH): m/z 601.9, $[M + H]^+$.

5b was obtained as a pale yellow powder (100% yield). Found: C, 60.68; H, 9.22; N, 15.59. Calc. for $C_{36}H_{56}N_8 \cdot 6H_2O$: C, 60.99; H, 9.66; N, 15.80%; δ_H (D_2O, 400 MHz): 2.68 (4H, m); 2.92 (4 + 4 + 4H, m); 3.10 (4H, s, CH_2 bridge); 3.86 (4H, s, CH_2Ph); 7.35 (4H, m). δ_C (D_2O, 100 MHz): 49.3; 54.00; 58.9; 61.7; 131.0; 131,4; 132.7; 142.1. FAB-MS (MeOH): m/z 601.9, $[M + H]^+$.

5c was obtained as a pale yellow powder (60% yield); Found: C, 64.02; H, 9.22; N, 16.32. Calc. for $C_{36}H_{56}N_8 \cdot 4H_2O$: C, 64.25; H, 9.58; N, 16.65%; δ_H (D_2O, 400 MHz): 2.52 (4H, m); 2.78 (4 + 4 + 4H, m); 3.00 (4H, s, CH_2 bridge); 3.67 (4H, s, CH_2Ph); 7.20–7.37 (4H, m). δ_C (D_2O, 100 MHz): 49.8; 54.6; 59.1; 62.2; 132.3; 141.0. FAB-MS (MeOH): m/z 601.9, $[M + H]^+$.

5d was obtained as pale yellow powder (90% yield); Found: C, 57.09; H, 9.40; N, 19.39. Calc. for $C_{34}H_{54}N_{10} \cdot 6H_2O$: C, 57.44; H, 9.36; N, 19.70%; δ_H (D_2O, 400 MHz): 2.85 (4 + 4 + 4H, m); 2.94 (4H, m); 3.03 (4H, s, CH_2 bridge); 4.67 (4H, s, CH_2Ph); 7.48 (2H, d); 7.86 (1H, t). δ_C (D_2O, 100 MHz): 46.5; 50.7; 55.4; 58.8; 123.0; 136.1; 158.9. FAB-MS (MeOH): m/z 603.9, $[M + H]^+$.

Complex preparation

The perchlorate salt $Cu(ClO_4)_2 \cdot 6H_2O$ was purchased from Aldrich. **Caution:** Perchlorate salts combined with organic ligands are potentially explosive and should be handled in small quantity and with necessary precautions.

Dinuclear complexes: $[Cu_2(L)][ClO_4]_4$. A 1.4 mmol amount of $Cu(ClO_4)_2 \cdot 6H_2O$ in ethanol (10 mL) was slowly added to a refluxing solution of L (0.5 mmol) in ethanol (10 mL). After precipitation, distillated water or acetonitrile was added (20 mL) and the clear mixture was stirred during 24 h. After cooling, ethanol is added (50 mL) and the precipitated colored powder was filtered and dissolved again in boiling distillated water (5 mL). After mixture cooling, the appeared resulting microcrystalline aggregates were collected by filtration and dried to give the complexes $[Cu_2(L)][ClO_4]_4 \cdot nH_2O \cdot mEtOH$.

Mononuclear complexes: $[Cu_1(L)][ClO_4]_2$. A 0.45 mmol amount of $Cu(ClO_4)_2 \cdot 6H_2O$ in frozen ethanol (10 mL) was slowly added to a solution of L (0.5 mmol) in ethanol at 0 °C (10 mL). The colored powder which precipitated was filtered and dissolved again in boiling distillated water (5 mL). After mixture cooling, the resulting microcrystalline aggregates were collected by filtration and dried to give the complexes $[Cu_1(L)][ClO_4]_8 \cdot nH_2O \cdot mEtOH$.

Homodinuclear complexes of constrained bismacrocycles. $[Cu_2(\mathbf{4a})][ClO_4]_4 \cdot 1H_2O$: Found: C, 32.77; H, 5.21; N, 10.45. Calc. for $C_{28}H_{50}N_8O_{16}Cl_4Cu_2 \cdot 1H_2O$: C, 32.28; H, 5.03; N, 10.76%; λ_{max}(DMF)/nm 648 (ε dm^3 mol^{-1} cm^{-1} 521); ν_{max}(KBr)/cm^{-1} 3225 (NH).

$[Cu_2(\mathbf{4b})][ClO_4]_4 \cdot 3H_2O$: Found: C, 31.21; H, 5.01; N, 10.21. Calc. for $C_{28}H_{50}N_8O_{16}Cl_4Cu_2 \cdot 3H_2O$: C, 31.21; H, 5.24; N, 10.40%; λ_{max} (DMF)/nm 590 (626); ν_{max}(KBr)/cm^{-1} 3216 (NH).

$[Cu_2(\mathbf{4c})][ClO_4]_4 \cdot 3H_2O \cdot 3CH_3CN$: Found: C, 28.28; H, 4.44; N, 9.00. Calc. for $C_{28}H_{50}N_8O_{16}Cl_4Cu_2 \cdot 1H_2O \cdot 3CH_3CN$: C, 28.01; H, 4.70; N, 9.33%; λ_{max}(DMF)/nm 617 (527); ν_{max}(KBr)/cm^{-1} 3227 (NH).

$[Cu_2(\mathbf{4d})][ClO_4]_4 \cdot 1H_2O \cdot 2CH_3CN$: Found: C, 28.82; H, 4.61; N, 11.37. Calc. for $C_{27}H_{49}N_9O_{16}Cl_4Cu_2,H_2O,2CH_3CN$: C, 28.83; H, 4.57; N, 11.21%; λ_{max}(DMF)/nm 629 (431); ν_{max}(KBr)/cm^{-1} 3221 (NH).

Mononuclear complexes of constrained bismacrocycles. $[Cu_1(\mathbf{4a})][ClO_4]_2 \cdot 2EtOH$: Found: C, 39.42; H, 5.86; N, 13.27. Calc. for $C_{28}H_{50}N_8O_8Cl_2Cu_1 \cdot 2EtOH$: C, 39.41; H, 5.91; N, 13.13%; λ_{max} (DMF)/nm 627 (223); ν_{max}(KBr)/cm^{-1} 3230 (NH).

$[Cu_1(\mathbf{4b})][ClO_4]_2 \cdot 2EtOH$: Found: C, 39.99; H, 5.91; N, 13.37. Calc. for $C_{28}H_{50}N_8O_8Cl_2Cu_1 \cdot 2EtOH$: C, 39.63; H, 5.94; N, 13.20%; λ_{max} (DMF)/nm 631 (376); ν_{max}(KBr)/cm^{-1} 3225 (NH).

$[Cu_1(\mathbf{4c})][ClO_4]_2 \cdot 2.2EtOH$: Found: C, 38.93; H, 5.79; N, 12.90. Calc. for $C_{28}H_{50}N_8O_8Cl_2Cu_1 \cdot 2.2EtOH$: C, 38.99; H, 5.84; N, 12.99%; λ_{max} (DMF)/nm 678 (288); ν_{max}(KBr)/cm^{-1} 3237 (NH).

$[Cu_1(\mathbf{4d})][ClO_4]_2 \cdot 1H_2O \cdot 3EtOH$: Found: C, 35.69; H, 5.53; N, 13.39. Calc. for $C_{27}H_{49}N_8O_8Cl_2Cu_1 \cdot 1H_2O \cdot 3EtOH$: C, 35.31; H, 5.60; N, 13.73%; λ_{max} (DMF)/nm 687 (302); ν_{max}(KBr)/cm^{-1} 3233 (NH).

Homodinuclear complexes of constrained macrotricycles. $[Cu_2(\mathbf{5a})][ClO_4]_4 \cdot 3H_2O$: Found: C, 40.61; H, 5.57; N, 10.36. Calc. for $C_{36}H_{56}N_8O_{16}Cl_4Cu_2 \cdot 3H_2O$: C, 40.93; H, 5.96; N, 10.61%; λ_{max} (DMF)/nm 650 (258); ν_{max}(KBr)/cm^{-1} 3356 (NH).

$[Cu_2(\mathbf{5b})][ClO_4]_4 \cdot 2H_2O$: Found: C, 37.40; H, 5.11; N, 9.80. Calc. for $C_{36}H_{56}N_8O_{16}Cl_4Cu_2 \cdot 2H_2O$: C, 37.22; H, 5.21; N, 9.64%; λ_{max} (DMF)/nm 686 (285); ν_{max}(KBr)/cm^{-1} 3269 (NH).

$[Cu_2(\mathbf{5c})][ClO_4]_3 \cdot 1H_2O$: Found: C, 41.64; H, 5.85; N, 10.53. Calc. for $C_{36}H_{56}N_8O_{12}Cl_3Cu_2 \cdot 1H_2O$: C, 41.40; H, 5.60; N, 10.73%; λ_{max} (DMF)/nm 674 (156); ν_{max}(KBr)/cm^{-1} 3278 (NH).

$[Cu_2(\mathbf{5d})][ClO_4]_3 \cdot 2H_2O \cdot 2EtOH$: Found: C, 32.37; H, 5.00; N, 10.86. Calc. for $C_{34}H_{54}N_{10}O_{16}Cl_4Cu_2 \cdot 2H_2O \cdot 2EtOH$: C, 32.52; H, 4.66; N, 11.15%; λ_{max} (DMF)/nm 679 (289); ν_{max}(KBr)/cm^{-1} 3276 (NH).

Mononuclear complexes of constrained macrotricycles. $[Cu_1(\mathbf{5a})][ClO_4]_2 \cdot 1H_2O \cdot 2EtOH$: Found: C, 42.29; H, 5.90; N, 11.36. Calc. for $C_{36}H_{56}N_8O_8Cl_2Cu_1,1H_2O,2EtOH$: C, 44.42; H, 6.01; N, 11.51%; λ_{max} (DMF)/nm 681 (123); ν_{max}(KBr)/cm^{-1} 3227 (NH).

$[Cu_1(\mathbf{5b})][ClO_4]_2 \cdot 2H_2O \cdot 1EtOH$: Found: C, 46.12; H, 6.16; N, 11.63. Calc. for $C_{36}H_{56}N_8O_8Cl_2Cu_1 \cdot 2H_2O \cdot 1EtOH$: C, 45.74; H, 6.40; N, 11.85%; λ_{max} (DMF)/nm 706 (126); ν_{max}(KBr)/cm^{-1} 3225 (NH).

$[Cu_1(\mathbf{5c})][ClO_4]_2 \cdot 1H_2O \cdot 3EtOH$: Found: C, 42.24; H, 5.91; N, 10.93. Calc. for $C_{36}H_{56}N_8O_8Cl_2Cu_1,1H_2O,3EtOH$: C, 42.41; H, 5.73; N, 10.99%; λ_{max} (DMF)/nm 689 (245); ν_{max}(KBr)/cm^{-1} 3237 (NH).

$[Cu_1(\mathbf{5d})][ClO_4]_2 \cdot 1H_2O \cdot 4EtOH$: Found: C, 38.08; H, 5.27; N, 12.81. Calc. for $C_{34}H_{54}N_{10}O_8Cl_2Cu_1 \cdot 1H_2O \cdot 4EtOH$: C, 38.25; H, 5.29; N, 13.12%;. λ_{max} (DMF)/nm 723 (162); ν_{max}(KBr)/cm^{-1} 3221 (NH).

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