Crystal data for **2** ($C_{171}H_{206}Cl_{10}Mn_{10}N_{20}O_{57}$): $M_r = 4357.46$, dark brown crystal ($0.35 \times 0.40 \times 0.55$ mm), triclinic, space group $P\bar{1}$, $a = 14.5331(2)$, $b = 18.1704(1)$, $c = 21.3923(2)$ Å, $\alpha = 76.545(1)$, $\beta = 74.220(1)$, $\gamma = 86.025(1)$, $V = 5287.03(9)$ Å^3, $Z = 1$, $T = 293(2)$ K, $\rho_{calcd} = 1.369$ g cm^{-3}, $F(000) = 2248$, $\mu = 0.782$ mm^{-1}. Of the 28654 reflections ($(2\theta)_{max} = 50.14°$), 18480 unique reflections were collected. From these, 9215 reflections with $I > 2\sigma(I)$ were used to solve the structure and were refined on F^2 by full-matrix least-squares techniques (SHELXL-97). At convergence, $R_1 = 0.0834$ and the goodness-of-fit on F^2 is 1.121. The maximum and minimum residual peaks on the final difference Fourier map were 0.934 and -0.879 e Å^{-3}, respectively.

Crystal data for **3** ($C_{165.5}H_{196}Cl_6Fe_{10}N_{20}O_{57.5}$): $M_r = 4156.62$, black-brown crystal ($0.34 \times 0.35 \times 0.72$ mm), triclinic, space group $P\bar{1}$, $a = 14.7040(4)$, $b = 18.9081(5)$, $c = 21.0783(5)$ Å, $\alpha = 71.201(1)$, $\beta = 77.076(1)$, $\gamma = 84.757(1)$, $V = 5406.0(2)$ Å^3, $Z = 1$, $T = 293(2)$ K, $\rho_{calcd} = 1.277$ g cm^{-3}, $F(000) = 2151$, $\mu = 0.800$ mm^{-1}. Of the 23991 reflections ($(2\theta)_{max} = 47.10°$), 14784 unique reflections were collected. From these, 7372 reflections with $I > 2\sigma(I)$ were used to solve the structure and were refined on F^2 by full-matrix least-squares techniques (SHELXL-97). At convergence, $R_1 = 0.0945$ and the goodness-of-fit on F^2 is 1.017. The maximum and minimum residual peaks on the final difference Fourier map were 0.893 and -0.455 e Å^{-3}, respectively.

The magnetic susceptibility data were obtained by using a Quantum Design PPMS 6000 magnetometer in the temperature range from 4 to 275 K at an applied magnetic field of 10 KG; whereby the diamagnetic contributions were estimated from Pascal's constants.

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[14] $[Mn_6(C_8H_6N_3O_2S)_6(CH_3OH)_6] \cdot 11.5\,CH_3OH$ and $[Fe_6(C_8H_6N_3O_2S)_6 \cdot (CH_3OH)_6] \cdot 12\,CH_3OH \cdot 2\,H_2O$ were obtained by us, and their crystal structures are different from the structures of **2** and **3**. Details will be reported elsewhere.

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Coordination Chemistry in the Solid: Study of the Incorporation of Cu^{II} into Cyclam-Containing Hybrid Materials

Geraud Dubois, Catherine Reyé, Robert J. P. Corriu,[*]
Stéphane Brandès, Franck Denat, and Roger Guilard[*]

Nanostructured organic–inorganic hybrid materials have known a considerable expansion in the past decade,[1–5] because they may provide unique combinations of properties which cannot be obtained by other ways. Among the possibilities offered by this class of solids, the preparation of materials able to strongly chelate metal cations which could remain chemically accessible seemed to us to be of great interest. Indeed, such materials could be interesting to study the coordination chemistry within the solid state as well as for their potential applications in catalysis,[6] separations,[7] optical devices,[8] or magnetic properties for example. Such applications require the incorporation within the materials of a good chelating ligand. Saturated polyazamacrocycles and especially 1,4,8,11-tetraazacyclotetradecane[9–11] (cyclam) having attracted much attention because of their remarkable binding ability towards transition and heavy metal cations, we set out to prepare hybrid materials incorporating cyclam moieties by using the sol–gel process.

We have shown that nanostructured materials are kinetically controlled.[3, 4, 12] The texture of the solids is highly dependent on all the parameters able to modify the kinetics of polycondensation (catalyst,[13] concentration of the reagent,[13] solvent,[13] temperature,[13a] and the organic spacer[13]). Furthermore, the importance of the organic moiety in the arrangement of solids obtained by the sol–gel process was displayed, giving rise to a possible short-range organization.[3, 4, 14, 15] In this context, it seemed interesting to investigate the incorporation of metal salts into cyclam-containing hybrid materials by two routes: the hydrolysis and polycondensation of metal salt/silylated cyclam derivatives complexes (Scheme 1, route A) or by hydrolysis and polycondensation of silylated cyclam derivatives followed by the direct incorporation of metal salts into the xerogels (Scheme 1, route B).

We have shown that the hydrolysis and polycondensation of silylated cyclam Cu^{II} and Co^{II} complexes (route A, Scheme 1) gives rise quantitatively to hybrid materials incorporating the Cu^{II} and Co^{II} salts,[16] thus the complexation of metal cations survives the sol–gel process. Herein we describe the direct incorporation of $CuCl_2$ into hybrid materials (route B). By using X-ray fluorescence and ESR spectroscopy, we show that the two routes of incorporation of the salts are not equivalent

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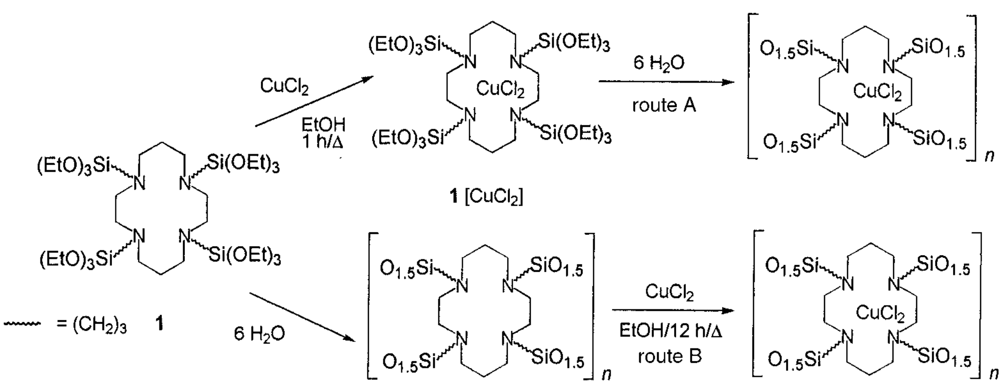
[*] Prof. R. J. P. Corriu, Dr. G. Dubois, Prof. C. Reyé
Université Montpellier II
34095 Montpellier Cedex 5 (France)
Fax: (+33) 467143852
E-mail: corriu@crit.univ-montp2.fr

Prof. R. Guilard, Dr. S. Brandès, Dr. F. Denat
UMR 5633 Université de Bourgogne
6 Boulevard Gabriel, 21100 Dijon (France)
Fax: (33) 380396117
E-mail: limsag@u-bourgogne.fr



Scheme 1.

and that the coordination chemistry within the solids and in solution are remarkably different.

The sol–gel polycondensation of **1**[16] gave rise to xerogels **X1**–**X3** the texture of which depends on the experimental conditions (Table 1). Hydrolysis and polycondensation of the complex **1**[CuCl$_2$] (route A) was also achieved leading to xerogels which were named as indicated in Table 1. The total amount of incorporated copper within the hybrid materials according to the route A was measured by X-ray fluorescence spectroscopy (Table 2). As the number of cyclam moieties per gram of solid was inferred from elemental analysis of the material (% of nitrogen), it was possible to calculate the percentage of sites metalated for each solid. Thus, as indicated in Table 2, the metal cations were quantitatively retained within the xerogels.

Table 1. Texture data of the xerogels prepared from **1** or **1**[CuCl$_2$] in EtOH and in the presence of tetrabutylammonium fluoride (TBAF) 1% as the catalyst.

Precursor	T [°C]	Xerogel	S_{BET} [m^2 g^{-1}][a]	Mean pore d [Å][b]
1	24[c]	**X1**	< 10	–
1	24	**X2**	370	< 30
1	110	**X3**	800	20–50
1[CuCl$_2$]	22	**X**[CuCl$_2$]**1A**[d]	< 10	–
1[CuCl$_2$]	22	**X**[CuCl$_2$]**1B**	< 10	–

[a] Measured according to the Brunauer-Emmett-Teller (BET) method. [b] Measured according to the Barret-Joyner-Halenda (BJH) method; d = diameter. [c] No catalyst. [d] THF as solvent.

Table 2. Amount of copper incorporated into the xerogels prepared by route A.

Xerogel	[Cu]$_{total}$ [mmol g^{-1}][a]	[Cyclam] [mmol g^{-1}][b]	Metalated sites [% (±3)]	[Cu^{II}]$_{ESR}$ [mmol g^{-1}]	$\frac{[Cu^{II}]_{ESR}}{[Cu]_{total}}$ [%]
X[CuCl$_2$]**1A**	0.95	0.97	98	0.79	83
X[CuCl$_2$]**1B**	0.97	0.97	100	0.80	82

[a] Measured by X-ray fluorescence spectroscopy. [b] Inferred from nitrogen elemental analysis.

An alternative method using ESR spectroscopy was devised to quantify the amount of Cu^{II} within the materials.[17] The calibration was done with Cu^{II}-cyclam complexes diluted to different concentrations (0.2–1 mmol g^{-1}) into silica. As indicated in Table 2, the amount of Cu^{II} ions measured by this method for materials prepared by route A is slightly lower than the total amount of copper found by X-ray fluorescence. That can be attributed to the standardization of the apparatus. Thus, it can be concluded that both the methods are in good agreement.

Let us now consider the direct incorporation of CuCl$_2$ into xerogels **X1**–**X3** prepared from **1** (route B, Scheme 1). After reaction, the xerogels were described as indicated in Table 3. The total amount of cation within the hybrid materials was first measured by X-ray fluorescence spectroscopy. From these results, it appears that the incorporation of CuCl$_2$ was quantitative (that is, 1 Cu^{II} per cyclam moiety) when the xerogels were treated with two equivalents of salts (Table 3 entries 1, 3, 5). When the xerogels were treated with one equivalent of salt (entries 2, 4, 6) or with less than one equivalent of salt (entry 7) the cation uptake was quite significant, in comparison to the amount of salt added. Thus, these results show that all the chelating sites of the materials are accessible under mild experimental conditions. Noteworthy is that the cation binding ability of the materials obtained by hydrolysis and polycondensation of dibenzo-[18]crown-6 ethers derivatives bearing four hydrolyzable Si(OR)$_3$ groups was quite different:[18] about 45% of crown ether sites are not accessible to K$^+$ or Na$^+$ ions. The better cation-binding ability of cyclam moieties is because of the high stability of copper–cyclam complexes[19] but also to the flexibility of tetraazamacrocycles even within the solid. Furthermore, a large surface area is not necessary for the complexation as, for example, the complexation was quantitative for both materials **X3** (entry 5, Table 3) with S_{BET} = 800 m^2 g^{-1}, and **X1** (entry 1, Table 3) with S_{BET} < 10 m^2 g^{-1}. This result is also explained by the flexibility of the cyclam moieties which allows an easy penetration and diffusion of the reagents into the materials.[20, 21]

Surprisingly, from all the materials prepared by route B, the amount of Cu^{II} measured by ESR spectroscopy (Table 3) appears notably lower than the total amount of Cu titrated by X-ray fluorescence. Furthermore, it is worth noting that the gap between the X-ray fluorescence and ESR measurements decreases as the amount of incorporated salt (compare in Table 3, entries 1 and 2; 3 and 4; 5 and 6) decreases.

We think that the discrepancy between the amount of Cu^{II} found from ESR measurements and the total amount of Cu titrated by X-ray fluorescence is because of the proximity of metal centers allowing the formation of antiferromagnetic Cu–Cu interactions[22–26] and thus leading to a lower intensity of the ESR signal at 3200 G.

As ESR spectroscopy is a convenient technique to study metal–metal interactions,[22–26] we recorded, at 100 K, the X-band ESR spectra of materials containing copper salts introduced by the two routes. The ESR spectrum of the

Table 3. Amount of copper incorporated into the xerogels prepared by route B.

Entry	Starting xerogel	[Cyclam] [mmol g^{-1}][a]	CuCl$_2$[b]	Xerogel after reaction	[Cu]$_{total}$ [mmol g^{-1}][c]	Metalated sites [% (±3)]	[Cu^{II}]$_{ESR}$ [mmol g^{-1}]	$\frac{[Cu^{II}]_{ESR}}{[Cu]_{total}}$ [%]
1	**X1**	1.27	2	**X1**[2 CuCl$_2$]	1.31	103	0.34	26
2	**X1**	1.27	1	**X1**[1 CuCl$_2$]	0.95	75	0.37	39
3	**X2**	1.28	2	**X2**[2 CuCl$_2$]	1.32	103	0.16	12
4	**X2**	1.28	1	**X2**[1 CuCl$_2$]	1.02	80	0.35	34
5	**X3**	1.33	2	**X3**[2 CuCl$_2$]	1.33	100	0.15	11
6	**X3**	1.33	1	**X3**[1 CuCl$_2$]	0.95	71	0.22	23
7	**X3**	1.33	0.5	**X3**[0.5 CuCl$_2$]	0.56	42	0.20	36

[a] Inferred from nitrogen elemental analysis. [b] Number of equivalents. [c] Measured by X-ray fluorescence spectroscopy.

material **X**[CuCl$_2$]**1A** (route A) exhibits a strong absorption at 3200 G ($g \cong 2.15$) characteristic for Cu^{II} centers and no signal at lower field (Figure 1 a and c). In contrast, the ESR spectrum of the material **X3**[1 CuCl$_2$] (route B) displays not only the signal at ≈3200 G but also a weak absorption at 1550 G ($g \cong 4.40$; Figure 1 b and d). The absorption at ≈3200 G was assigned to the allowed transition ($\Delta Ms = 1$) while the weaker one can be attributed to a forbidden transition[22–26] ($\Delta Ms = 2$) which is characteristic of dicopper interactions and attests to a dipolar exchange between two copper units. This phenomenon has been observed from the solution ESR spectra of dinuclear Cu^{II} complexes in which two cyclam rings are in a face-to-face conformation,[24] and was also observed from the solution ESR spectra of face-to-face dicopper bisporphyrin complexes[26] and of dinitroxyl radicals.[25] This observation suggests that during the sol–gel process of materials prepared by route B, the cyclam moieties arrange in such a way that two complexed copper ions are in an analogous situation to that in macrotricyclic ligands[24] designed for the study of metal–metal interactions. This conformation explains the difference between the total amount of copper determined from titration by X-ray fluorescence and the amount of Cu^{II} determined by ESR spectroscopy. It is worth noting that short-range organization in hybrid organic–inorganic materials has been observed.[3] In contrast, the arrangement of the solids prepared by route A does not give rise to such dinuclear species, as revealed by ESR spectra, and therefore there is a good agreement between the results of both the methods of titration of the copper in these materials.

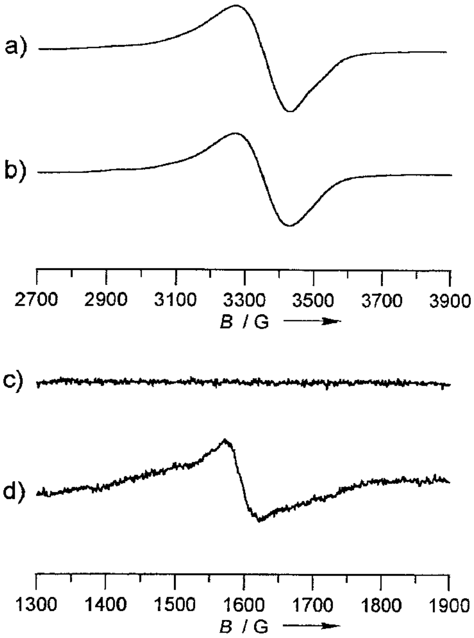


Figure 1. X-band ESR spectra recorded at 100 K of the allowed transitions for a) **X**[CuCl$_2$]**1A**, b) **X3**[1CuCl$_2$], and of the half-field transitions for c) **X**[CuCl$_2$]**1A**, d) **X3**[1 CuCl$_2$].

This study describes two routes for the incorporation of copper salts within cyclam-containing hybrid materials, however, the routes are not equivalent. The incorporation of Cu^{II} centers into materials by route B gives rise to Cu–Cu interactions which are not observed when the metal centers are introduced by route A. These differences are probably because of the nature of the precursor material which has not the same flexibility in both cases. The precursor material in route B is a flexible cyclam derivative while the precursor material of route A is a more rigid copper–cyclam complex (Scheme 1). Thus, the results suggest a coordination chemistry in the solid state which is not a copy of that in solution as it depends on the solid organization.

Experimental Section

The ESR spectra were recorded in the solid state on a Bruker ESP 300 spectrometer at X-band (9.6 GHz), from the Centre de Spectrométrie Moléculaire de l'Université de Bourgogne, equipped with a double cavity and a liquid nitrogen cooling accessory. The X-Ray fluorescence measurements were performed on a Oxford Lab-X 3000.

Incorporation of CuCl$_2$ by route B: The direct incorporation of CuCl$_2$ into the xerogels **X1**–**X3** was carried out as follows: xerogels **X1**–**X3** (500 mg) were stirred under reflux for 12 h in an ethanol (20 mL) solution of CuCl$_2$ (0.5, 1, or 2 equiv). The reaction mixture was then filtered and washed four times with ethanol. The resulting powder was dried at 120 °C under 20 mm Hg for 12 h and the xerogels were described as indicated in Table 3.

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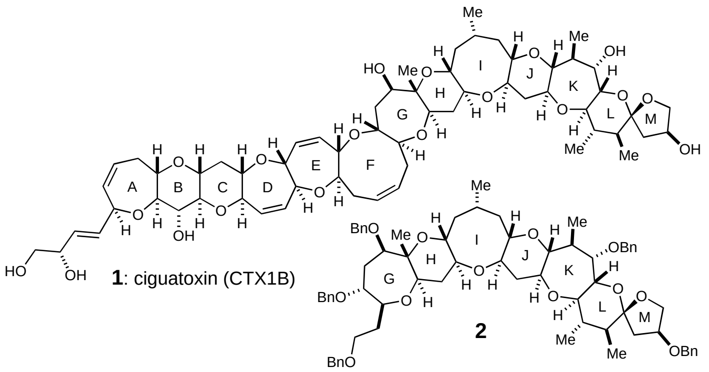
Synthetic Studies on Ciguatoxin: A Highly Convergent Synthesis of the GHIJKLM Ring System Based on *B*-Alkyl Suzuki Coupling

Hiroyuki Takakura, Katsuhiko Noguchi,
Makoto Sasaki,* and Kazuo Tachibana

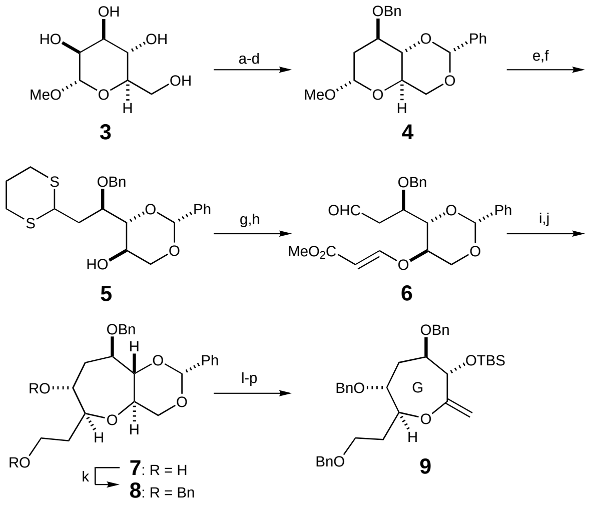
Ciguatoxin (CTX1B, **1**) and its congeners, naturally occurring polycyclic ethers originating from marine unicellular algae, are the principal toxins associated with ciguatera fish poisoning.[1, 2] These potent neurotoxins reportedly bind to the same site of voltage-sensitive sodium channels as brevetoxins, another class of structurally related marine toxins.[3] Their structural complexity and exceptionally potent neurotoxicity, as well as their limited availability from natural sources, have attracted the interest of synthetic chemists, and a number of synthetic studies by us[4] and others[5, 6] have been reported. Recently, we developed a powerful strategy for the convergent assembly of a polyether structure based on *B*-alkyl Suzuki coupling.[7–9] Here we describe the application of this strategy to a more highly functionalized system, which led to a convergent synthesis of the GHIJKLM ring fragment **2** of ciguatoxin.



1: ciguatoxin (CTX1B)

2

Synthesis of exo-olefin **9**, corresponding to the G ring, started with methyl α-D-mannopyranoside (**3**), which was converted into **4** by a four-step sequence including benzylidene acetal formation, regioselective tin-mediated benzylation of the equatorial alcohol,[10] and Barton deoxygenation of the remaining hydroxy group[11] (Scheme 1). Compound **4** was treated with 1,3-propanedithiol in the presence of concen-



Scheme 1. Synthesis of the G ring exo-olefin **9**. a) $PhCH(OMe)_2$, CSA, DMF, RT; b) nBu_2SnO, benzene, reflux, then CsF, BnBr, DMF, RT; c) NaH, CS_2, MeI, THF, RT; d) nBu_3SnH, AIBN, benzene, reflux, 24 % (4 steps); e) $HS(CH_2)_3SH$, conc. HCl, $CHCl_3$, RT; f) $PhCH(OMe)_2$, CSA, CH_2Cl_2, RT, 46 % (2 steps); g) methyl propiolate, NMM, CH_2Cl_2, RT, 97 %: h) MeI, $NaHCO_3$, $MeCN/H_2O$, RT, 98 %; i) SmI_2, MeOH, THF/HMPA, 0 °C; j) $LiAlH_4$, THF, RT, 72 % (2 steps): k) NaH, BnBr, DMF, RT, 84 %; l) CSA, MeOH, RT, 89 %; m) TBSOTf, 2,6-lutidine, CH_2Cl_2, RT; n) CSA, MeOH, 0 °C, 89 % (2 steps); o) I_2, PPh_3, imidazole, THF, RT, p) *t*BuOK, THF, RT, 85 % (2 steps). AIBN = 2,2′-azobisisobutyronitrile, Bn = benzyl, CSA = camphorsulfonic acid, DMF = *N*,*N*-dimethylformamide, HMPA = hexamethylphosphoric triamide, NMM = *N*-methylmorpholine, OTf = trifluoromethanesulfonate, TBS = *tert*-butyldimethylsilyl, THF = tetrahydrofuran.

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[*] Dr. M. Sasaki, Dr. H. Takakura, K. Noguchi, Prof. Dr. K. Tachibana
Department of Chemistry, Graduate School of Science
The University of Tokyo
and
CREST, Japan Science and Technology Corporation (JST)
Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan)
Fax: (+81) 3-5841-8380
E-mail: msasaki@chem.s.u-tokyo.ac.jp

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