94. Fluorescence Quenching of 2,2′-Bithiazole-Containing Calix[4]arenes by Copper(I). Access to the Corresponding $[ML_2]$, [ML], and $[M_2L]$ Copper(I) Complexes

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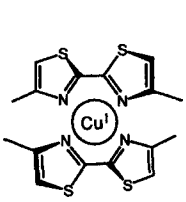
The complexing behaviour of 2,2′-bithiazole-containing calix[4]arenes towards Cu^I was investigated. The extinction of the intrinsic blue fluorescence of the free ligands upon addition of stoichiometric amounts of the metallic salt was used as complexation probe. This extinction was directly related to the chelation of the metal and allowed the controlled synthesis of new mono- and dimetallic complexes which were fully characterized.

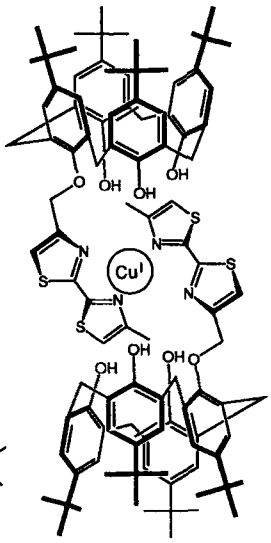
Introduction. – We have recently described the syntheses and the intrinsic blue-fluorescence properties of the new family of podands **1**–**5** incorporating the tetra-*p*-(*tert*-butyl)calix[4]arene platform and the blue-fluorescent 2,2′-bithiazole (btz) subunits [1]. Consistent with our previous work based on the chelation properties of bipyridyl-substituted calixarene podands [2], we pursued our investigations on the coordination properties of these new ligands.

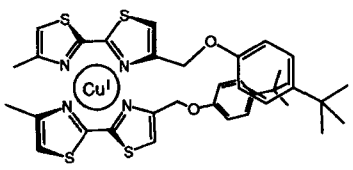
The 4,4′-dimethyl-2,2′-bithiazole (**6**) belongs to the family of N-donor ligands able to coordinate in a tetrahedral mode cations such as Cu^I. Among the very few reports related to the coordination chemistry of this unit [3], only one study has been devoted to the complexation of Cu^I [3c]. The ligand is thought to coordinate the metallic centre by means of one N and one S donor atom, with perchlorate as counter anion, a hypothesis based on analyses of IR data.

We attempted to isolate, in the manner of our previous report [2], the Cu^I complexes of the podands **1**–**5** without taking into account, except for **1**–**3**, specific hypotheses on the ligand-to-metal stoichiometries. The use of MeCN, typically employed in such complexation reactions, was rejected in this case, its own coordinating behaviour competing with the ligands in the chelation process of Cu^I. $CHCl_3$ and CH_2Cl_2 were thus chosen as reaction solvent, giving the expected red-orange solutions. Efficiency of column chromatography (alumina or silica gel), improved for the purification of the corresponding bipyridyl complexes [2], was in this case dramatically diminished, resulting in partial to full decomplexation, as shown by the loss of the orange colour on the stationary phase during elution and by the recovering of the characteristic blue fluorescence of the free ligands.



8[1]): [6-Cu-6]PF_6





9[1]): [7-Cu-7]PF_6

10[1]): [1-Cu-1]PF_6

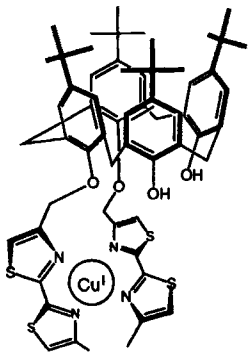
Checking the fluorescence activity of the crude complexes showed that Cu^I acted in fact as a quencher, no emission being recorded after excitation at their respective absorption wavelengths. We thought that the complexation properties of ligands **1**–**5** towards this cation could be analysed by this technique and that the good ligand-to-metal stoichiometry could be readily obtained, allowing direct access to the pure complexes.

Fluorescence-Quenching Studies. – All the measurements were performed in CH_2Cl_2. Upon addition of $[Cu^I(MeCN)_4]PF_6$, the ligand **6**, as well as the mono-substituted species 4-{[*p*-(*tert*-butyl)phenoxy]methyl}-4′-methyl-2,2′-bithiazole (**7**), showed a total extinction of fluorescence for an exact $[ML_2]$ stoichiometry, corresponding to the expected value in the case of a *td* coordination mode; the preparative syntheses of complexes **8**[1]) and **9**[1]) were monitored by this technique.

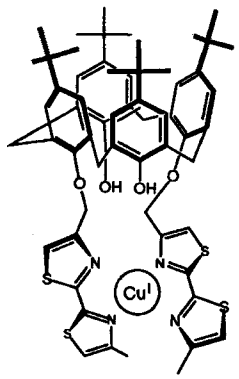
The same method was applied to the ligands **1**–**5**. Addition of the Cu^I salt to solutions of ligands did not produce any variation of emission wavelengths but resulted in a regular decrease in intensities, as featured for **4** and **5** in *Fig. 1*.

Reporting for each species the variation of the emission maxima *vs.* amount of added Cu^I salt gave the results of *Fig. 2*. As for **6** and **7**, fluorescence of **1** was quenched after addition of exactly 0.5 equiv. of Cu^I, corresponding to a $[ML_2]$ stoichiometry (see complex **10**[1])), as expected from previous results [2]. The disubstituted species **2** and **3** in which the btz units are adjacent and opposed, respectively, become non-emissive after addition of exactly 1 equiv. of Cu^I. The stoichiometry should be of the [ML] type (see complexes **11**[1]) and **12**[1])), considering that at the experimental concentration of $3.5 \cdot 10^{-6}$ M, a polymeric structure is improbable. Very surprisingly, a neat quenching of

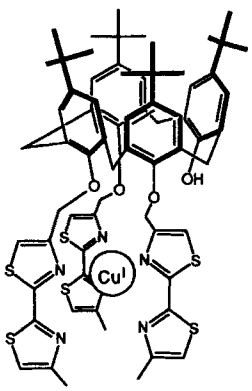
[1]) The key numbers **8**–**14** refer to the PF_6^- salts if not mentioned otherwise.



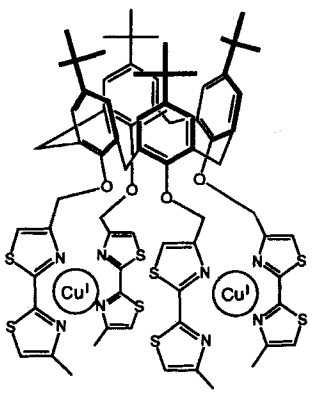
11^{1}): [2-Cu]PF$_6$



12^{1}) : [3-Cu]PF$_6$



13^{1}) : [4-Cu]PF$_6$



14^{1}) : [Cu-5-Cu](PF$_6$)$_2$

fluorescence was observed in the case of the trisubstituted species **4**, after addition of exactly 1 equiv. of Cu^{I} (see complex **13^{1}**)). This implied thus either the simultaneous participation of the three btz units in the complexation process ([$Cu^{I}(btz)_3$] system), or an extremely rapid exchange between two of them around the Cu^{I} centre, one staying free of metal, giving complex species similar to those obtained with ligands **2** and **3**. This could also imply a quenching property of the complexed Cu^{I} centre towards the residual proximal free btz unit. Finally, the total extinction of fluorescence was observed for the tetrasubstituted species **5** after addition of exactly 2 equiv. of Cu^{I}, corresponding to a M_2L stoichiometry (see complex **14^{1}**)).

Fig. 2 shows that the titration curves are not linear and correspond to an excessive quenching which disappears close to the stoichiometry. Such behaviour is abnormal if we consider a direct and unequivocal relation between complexation and quenching involving the metal-to-ligand ratios obtained at the total extinction of fluorescence. We can consider that at room temperature, an additional quenching effect is present in each case. To understand this phenomenon, we suspected, with the help of the variable-temperature ^{1}H-NMR study of complex **11** (see below, *Fig. 4*), which suggests that some ligand-ex-

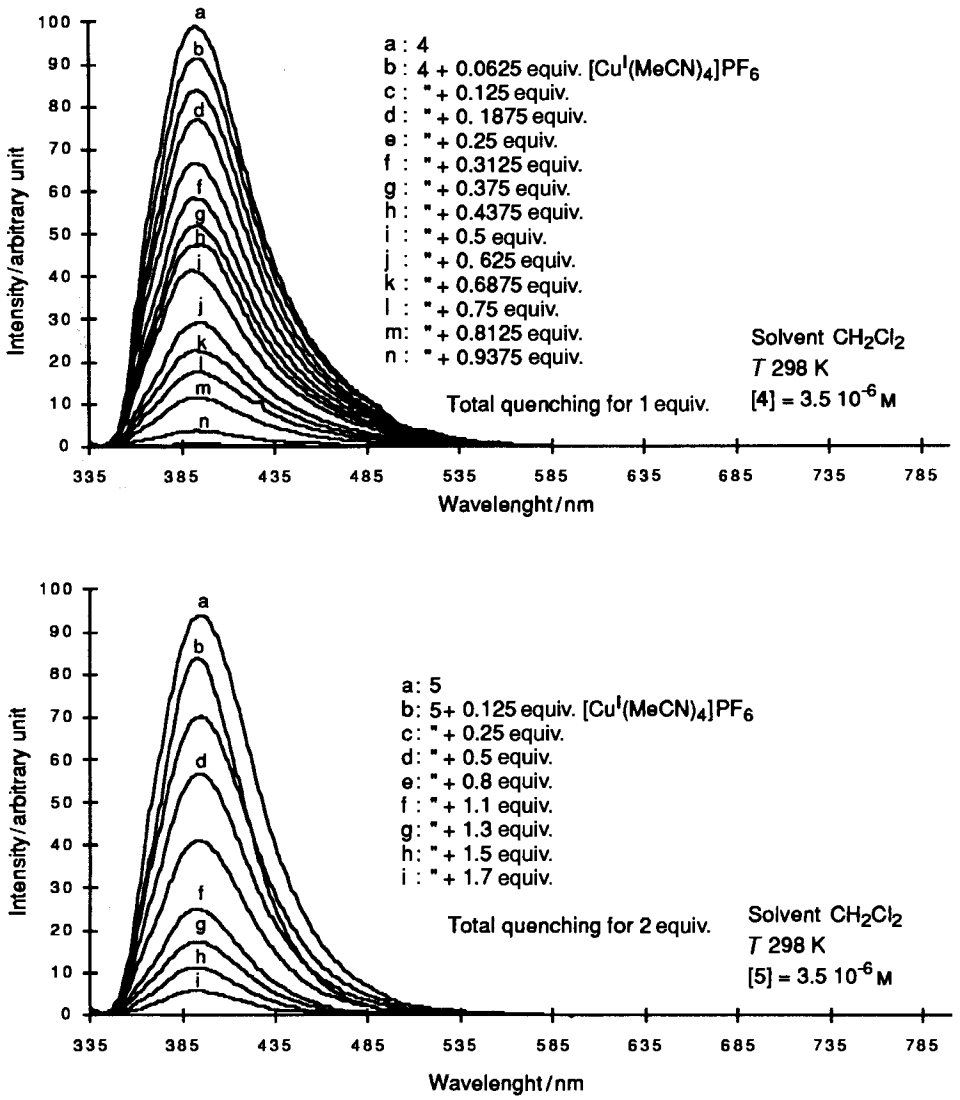


Fig. 1. *Fluorescence spectra of ligands* **4** *and* **5** *upon addition of* $[Cu(MeCN)_4]PF_6$ ($\lambda_{exc.}$ = 330 nm)

change process occurs around the metallic centre at room temperature, that some free metal could be present in solution, acting as a quencher by simple collisional effects. According to this study, we analysed this phenomenon at different temperatures and concentration of metallic cation. For this purpose, the fluorimeter was, for each temperature, calibrated with a $3.5 \cdot 10^{-6}$ M ligand solution before checking the ligand plus metal solutions. This gave, notably for the couples **2**/**11** and **4**/**13**, the results of *Fig. 3*. As expected, lowering the temperature to 193 K resulted in an almost linear decrease in fluorescence of **2** upon addition of the Cu^I salt, with a total extinction at exactly 1 equiv.

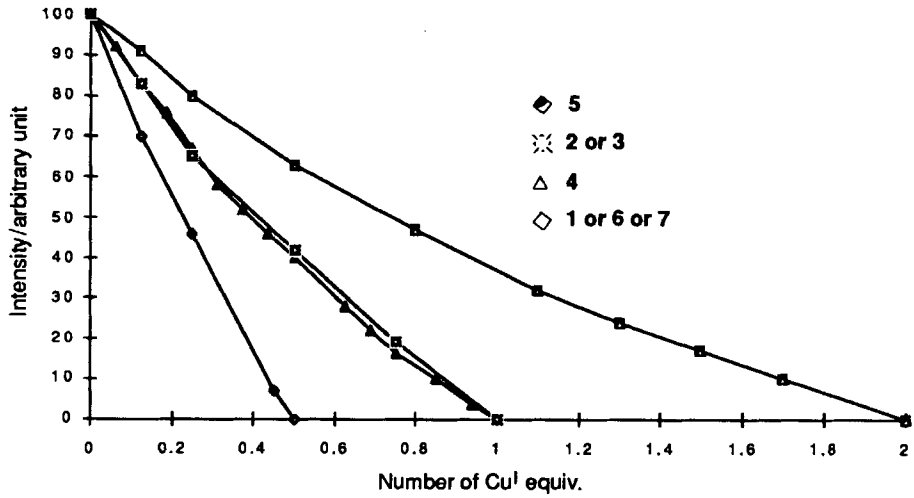


Fig. 2. *Determination of complex stoichiometries for ligands* **1**–**7** via *fluorescence quenching by addition of* $[Cu^{I}(MeCN)_4]PF_6$ ($\lambda_{exc.}$ = 330 nm; $\lambda_{em.}$ = 396 nm). Intensity scales are independant for each species [1].

Working at higher temperatures provided the same final result but involved a regular loss of linearity, confirming thus that the quench of fluorescence is directly related to the formation of the complex.

We thought that employing the same approach with the trisubstituted species **4** should allow us to recover, when cooling, the fluorescence of the normally non-coordinating bithiazolyl unit. This is in fact not the case: the linearity was recovered at 273 K and conserved at lower temperature, confirming, as for **2**, the influence of ligand exchange on the fluorescence quenching at room temperature; nevertheless, the latter was complete at exactly 1 equiv. of Cu^{I}. This confirmed that **4** is able to complex only one Cu^{I} cation and that, as above-mentioned, the resulting $[Cu^{I}(btz)_2]$ subunit acts as a quencher for the residual btz arm or that, even at 273 K, a rapid intramolecular exchange occurs around the metallic centre. Lowering the temperature to 263, 243, 223, and 198 K did not show any recovery of fluorescence. Suspecting that at this temperature these exchange processes are inhibited and considering that the final complex subunit is $[Cu^{I}(btz)_2]$, we conclude that the latter acts as a quencher for the third btz unit.

Each solution turned from uncoloured to pale orange upon addition of the salt, confirming the formation of the complexes. Preparative-scale syntheses of complexes **10**–**14** from ligands **1**–**5**, respectively, were achieved by a careful fluorescence quenching monitored addition of stoichiometric amounts of $[Cu^{I}(MeCN)_4]PF_6$ in CH_2Cl_2. Direct evaporation of the solvent gave the air-stable deep red solid complexes.

Analyses of Complexes. – *Preliminary Remarks. Krause et al.* [3c] proposed for the perchlorate analogue **8** · ClO_4 that the coordination should occur by means of 1 N- and 1 S-atom of the btz units. They based their hypothesis on the analysis of IR data, which showed that the Me rocking-vibration band of **6** located at 978 cm^{-1} was split in the complex into two bands at 1251 and 909 cm^{-1}, thus suggesting the presence of two kinds of Me groups, and that the in-plane ring bending vibration band of the ligand, located

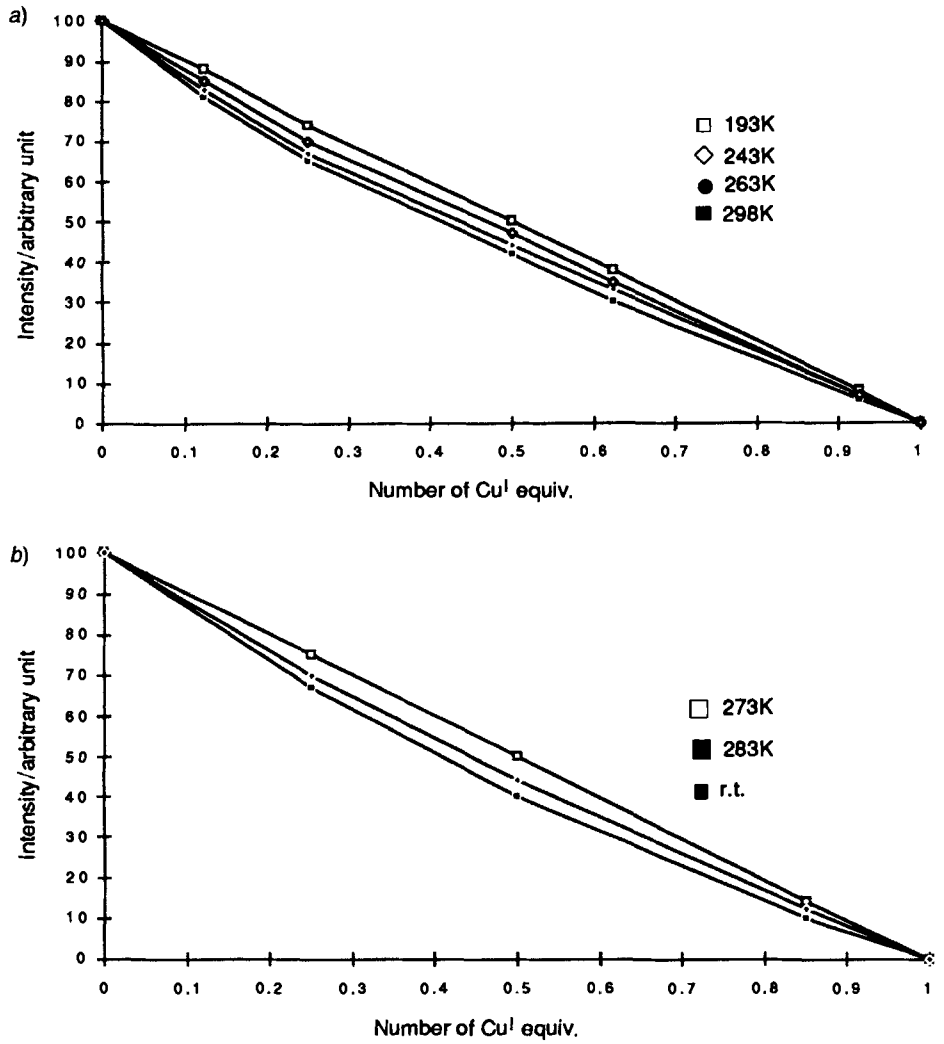


Fig. 3. *Fluorescence quenching of ligands* a) **2** *and* b) **4** *at low temperatures* ([L] = $3.5 \cdot 10^{-6}$ M; $\lambda_{exc.}$ = 330 nm; $\lambda_{em.}$ = 396 nm)

at 763 cm^{-1}, was transformed in the complex into four distinct bands between 786 and 734 cm^{-1}.

Infrared Spectroscopy. We found that in **8** the bands at 1251 and 909 cm^{-1} were absent, replaced by two bands of medium intensity at 1230 and 1050 cm^{-1}, and that only two distinct bands existed at 740 and 752 cm^{-1}. As only the counter anion changed between **8** and the complex of *Krause et al.*, we attributed a part of these differences to the presence of PF_6^-, instead of ClO_4^-, close to the metallic centre. Nevertheless, we found that such results were insufficient to ascertain the type of complexation, and we preferred to base our hypothesis on NMR results.

Two sharp IR bands of medium intensity appeared for all the complexes **9**–**14** at 1050 and 1100 cm^{-1}. The latter was not observed for **8**, indicating that it could be related to the OCH_2 links. Their intensities, compared with the CH stretching-vibration bands at 2700–2950 cm^{-1}, increased strongly between **10** and **14**, but slightly between **10** and **11** or **12** as well as **13**. This result was in correlation with the hypothesis of a $[M_2L]$ stoichiometry in **14**. Complex **9** exhibited a band at 1230 cm^{-1} which overlaps a band of medium intensity present in the free ligand **7**. The same phenomenon appeared in the couples **10**/**1** to **14**/**5**, with an increase in the intensity from **10** to **14**, leading to the same comment as before. Nevertheless, picking up interesting data from IR analyses of complexed podands was found to be rather difficult, the size of the PF_6^- band at 820–851 cm^{-1} and the vibration pattern of the calixarene platform overlapping in most of the cases the interesting bithiazole bands, thus lowering the analytical impact of this technique.

Ultraviolet-Visible Spectroscopy. UV Spectroscopy was performed in CH_2Cl_2. Complex **8** exhibited a metal-to-ligand charge transfer (MLCT) band at λ 436 nm with a molar absorptivity of 5300 $l \cdot mol^{-1} \cdot cm^{-1}$; this band shifted slightly to 442 nm for **9**, with a molar absorptivity of 4000 $l \cdot mol^{-1} \cdot cm^{-1}$. The phenoxy substitution resulted in the loss of absorptivity of 25% which was approximately recovered in **10**–**13**, thus indicating, if considering an association of two btz units around a Cu^I centre, that **10** is of the $[ML_2]$ type and **11**–**13** of the [ML] type. This ε value was doubled in the case of **14**, confirming the $[M_2L]$ stoichiometry suspected from the fluorescence-quenching experiment. Complex **13** was particularly interesting to study, in the sense that its MLCT band corresponded to a [ML] stoichiometry, confirming that only two btz units interact with Cu^I. This result eliminates the hypothesis of a $[Cu^I(btz)_3]$ system, deduced from fluorescence analysis.

The complexes also exhibited the specific calixarene bands at 280 and 290 nm with, for **10**, an ε value approximately the double of the one measured for **11**–**14**.

Btz-Related absorption bands were observed, as for **8** and **9**, at *ca.* 340 nm *plus* a shoulder at 330 nm, with ε values of *ca.* 25000 $l \cdot mol^{-1} \cdot cm^{-1}$ for **10**–**12**, confirming the presence of two btz units per complex. Band and shoulder collapsed at *ca.* 335 nm for **13** and **14** with ε values corresponding to the presence of three and four btz units per complex, respectively.

Mass Spectrometry. All the complexes were studied by the electrospray technique, positive mode, using a $CHCl_3$/i-PrOH/HCOOH medium. Involvement of two bithiazolyl units per complex was confirmed for **8** (457.1, 455.1 amu; [**6**-Cu-**6**]$^+$) and **9** (753.4, 751.4 amu; [**7**-Cu-**7**]$^+$), improving the hypothesis of a tetrahedral coordination mode. As expected, the monocharged species were found for **10** (1748.6 amu; [**1**-Cu-**1**]$^+$), **11** (1102.6–1099.7 amu; [**2**-Cu]$^+$), **12** (1102.6–1099.3 amu; [**3**-Cu]$^+$), and **13** (1297.6–1293.7 amu; [**4**-Cu]$^+$), but always accompanied by some charged [ligand-sodium] species.

Under these conditions, the analysis of **14** resulted in the detection of the mono-copper(I) species, characterized by base-peaks at 1491.7–1487.9 amu ([**5**-Cu]$^+$). Considering that the alcoholic and acidic medium was responsible for this partial decomplexation, we replaced it by amylene (2-methylbut-2-ene) stabilized CH_2Cl_2. This gave the mass peak of the di-charged species **14** at 776.5–776.0 amu ([Cu-**5**-Cu]$^{2+}$/2), thus confirming the ability of ligand **5** to complex two metallic centres.

Elemental Analyses. Combustion analyses involving in most of the cases C, H, N, O, and S were consistent with the proposed ligand-to-metal stoichiometries.

NMR Study. ^{1}H-NMR study of **8** showed that the chelation should be focused on the two N-atoms of the btz units, both Me and aromatic protons being characterized, in $CDCl_3$, by a *s* at 2.24 and 7.37 ppm, respectively, *vs.* 2.49 ($\Delta = -0.25$) and 6.95 ($\Delta = +0.38$) ppm in the free ligand. The observed upfield shift of the Me group resonance signal, similar to the one observed in the bipyridyl analogue, and its multiplicity (*s*) indicated in fact that the coordination of the metallic centre involves both N-atoms.

Complex **9**, slightly soluble in $CDCl_3$, was studied in CD_2Cl_2. Considering that this solvent should not dramatically influence the resonance pattern of the complex, we compared it with **7** in $CDCl_3$. The expected ^{1}H-NMR upfield shift of 0.25 ppm was observed for the Me resonance signal which moved from 2.51 ppm in **7** to 2.26 ppm in **9**. The CH_2O groups also experienced the influence of the metallic cation, moving from 5.24 ppm in **7** to 4.77 ppm in the complex ($\Delta = -0.47$ ppm). An important modification of the aromatic pattern was observed, the two heterocyclic protons moving from 6.99 and 7.40 ppm in **7** to 7.27 and 7.64 ppm in **9**, similarly to the downfield shifts found for **8** *vs.* **6**. These results confirmed that the same symmetrical complexation occurs *via* the two N-atoms and that it could be expected in the podand complexes.

To confirm these results, natural abundance ^{1}H,^{15}N-HMBC experiments were performed. They were carried out at 295 K in CD_2Cl_2 using $MeNO_2$ as internal standard [4]. Thiazole was chosen as heterocyclic reference, giving by INEPT study a ^{15}N-resonance signal at −58 ppm, close to the reported value ([5]: −62 ppm, in $CDCl_3$). The results (see *Table*) showed that **6** is characterized by a single ^{15}N-resonance signal at −59.5 ppm which, upon complexation with Cu^I (complex **8**), is strongly upfield-shifted to −95.7 ppm. This shift of 36.2 ppm is similar to those obtained in the CP-MAS study of phenanthroline analogues developed by *Kitagawa et al.* [6]. As expected, the dissymmetric bithiazole **7** was characterized by two ^{15}N-resonance signals; the first one, located at −56.9 ppm, was correlated to the Me group, the second one, at −64.9 ppm, to the CH_2O group. As proposed by *von Philipsborn* and coworkers [5], the $+M$ effect of the CH_2O group is probably responsible for the observed shielding of the ^{15}N-resonance. This shielding diminished in the Cu^I complex **9**, characterized by two signals at −96.9 and −98.3 ppm. In accordance with the corresponding literature [6], our results confirmed that both N-atoms of bithiazole species **6** and **7** interact with the Cu^I centre in complexes **8** and **9**.

As for **7**, the podand **1** gave two resonance signals at −55.8 and −64.4 ppm. Unfortunately, the corresponding Cu^I complex **10** did not afford any results. In fact, its

Table. *^{15}N Chemical Shifts* [ppm] *of Some Thiazole-Containing Species*[a])

		**6**	**8**[1]) ([**6**-Cu-**6**] PF_6)	**7**	**9**[1]) ([**7**-Cu-**7**] PF_6)	**1**	**10**[1]) ([**1**-Cu-**1**] PF_6)
N (correlated to OCH_2)		–	–	−64.9	−98.25	−64.4	not observed
(correlated to Me)	−58[b])	−59.5	−95.7	−56.9	−96.88	−55.8	not observed

[a]) Solvent CD_2Cl_2, $MeNO_2$ as internal standard; 298 K; ^{1}H,^{15}N HMBC experiment.
[b]) INEPT; −62.0 ppm in $CDCl_3$ [5].

^{1}H-NMR spectrum exhibited resonance signals with $\Delta\nu_{1/2} > 10$ Hz, a value largely superior to the characteristic ^3J(H, N) coupling constant of 2.5 Hz measured in such heterocycles [5]; filtration over *Celite* to eliminate traces of paramagnetic species was ineffective; cooling resulted in the loss of resolution, while warming at T_{max} 308 K gave sharper peaks but was insufficient to detect correlations.

In $CDCl_3$ at room temperature, **10** displayed a well defined ^{1}H-NMR spectrum which was compared to **9**. The Me group of btz shifted from 2.51 ppm in **1** to 2.27 ppm in **10**, exactly as observed for **7** *vs.* **9**. The CH_2O *s* was also upfield shifted, moving from 5.36 ppm in **1** to 5.03 ppm in **10** ($\Delta = -0.33$ ppm), but less than observed for **7** *vs.* **9** ($\Delta = -0.47$ ppm). The heterocyclic protons experienced upon complexation a downfield shift from 6.98 and 7.92 ppm in **1** to 7.21 ($\Delta = +0.23$) and 8.34 ($\Delta = +0.42$) ppm in **10**, as expected from the results obtained, with some differences, for **7** *vs.* **9**. We attributed the resonance signal at 8.34 ppm of **10** to the heterocyclic protons of the thiazole ring bound to calixarene and the signal at 7.21 ppm to the terminal one. The stronger shift observed for the peak at 8.34 ppm in **10** *vs.* 7.64 ppm in **9** was related to a substituent effect. The ArCH_2Ar groups also supported a strong modification, the upfield 1/2 *AB* system integrating to 4 H at 3.42 ppm for **1** being split for **10** into two 1/2 *AB* patterns at 3.20 and 3.36 ppm, respectively, each integrating for 2 H. The two downfield 1/2 *AB* systems located at 4.24 and 4.43 ppm for **1** collapsed in one 1/2 *AB* system at 4.04 ppm. Finally, the OH groups were also upfield shifted from 9.30 (2 H) and 10.06 (1 H) ppm in **1** to 9.06 (2 H) and 9.71 (1 H) ppm in **10**.

Due to a better solubility in this medium, **11** was studied in CD_2Cl_2, giving at room temperature a relatively well resolved spectrum (*Fig. 4*) in which, notably, the ArCH_2Ar groups are featured as 1/2 *AB* systems. Four of them integrating to 1 H each, were located at 4.19, 3.62, 3.31, and 2.52 ppm, two overlapped at 3.47 ppm, and two of them were hidden. The large *s* at 2.22 ppm was attributed to the *Me*-btz groups which appear at 2.42 ppm in the free ligand **2**. The CH_2O groups, shaped as an *AB* system in **2** (5.01 and 5.35 ppm, $J = 12$ Hz; $CDCl_3$) became broad, indicating a strong fluxionality for this part of the molecule, with the expected upfield shift. Integration of this region denoted the presence of the two last ArCH_2Ar 1/2 *AB* systems.

Lowering the temperature resulted in strong modifications of each part of the ^{1}H-NMR spectrum (*Fig. 4*). The Me_3C groups evolved from a two-*s* pattern (18 H each) to three *s* (9:18:9) at *ca.* 213 K. The *s* at 2.22 ppm (*Me*-btz) split into two *s* at 2.09 and 2.25 ppm at 263 K with a coalescence temperature of 273 K. According to the following approximated *Eqn. 1* [7], this last observation corresponds to an activation energy of 56 kJ · mol^{-1} ($R = 8.31$ JK^{-1}, T_c = coalescence temperature = 273 K, $\delta\nu$ = NMR frequency difference between the two generated peaks = 48 Hz).

$$\Delta G^{\neq} = RT_c(22.96 + \ln(T_c/\delta\nu)) \quad (1)$$

The ArCH_2Ar and CH_2O region in the ^{1}H-NMR spectrum was strongly modified upon cooling. It appeared clearly that the broadened region contained the expected CH_2O and ArCH_2Ar 1/2 *AB* systems characterized by different coalescence temperatures. The aromatic region changed towards a well defined pattern from 273 to 193 K, involving notably the apparition at 273 K of four new *s* located at 6.76, 7.81, 8.10, and 8.61 ppm, and, at 243 K, the splitting of the *s* located at 7.41 ppm into two close *s*.

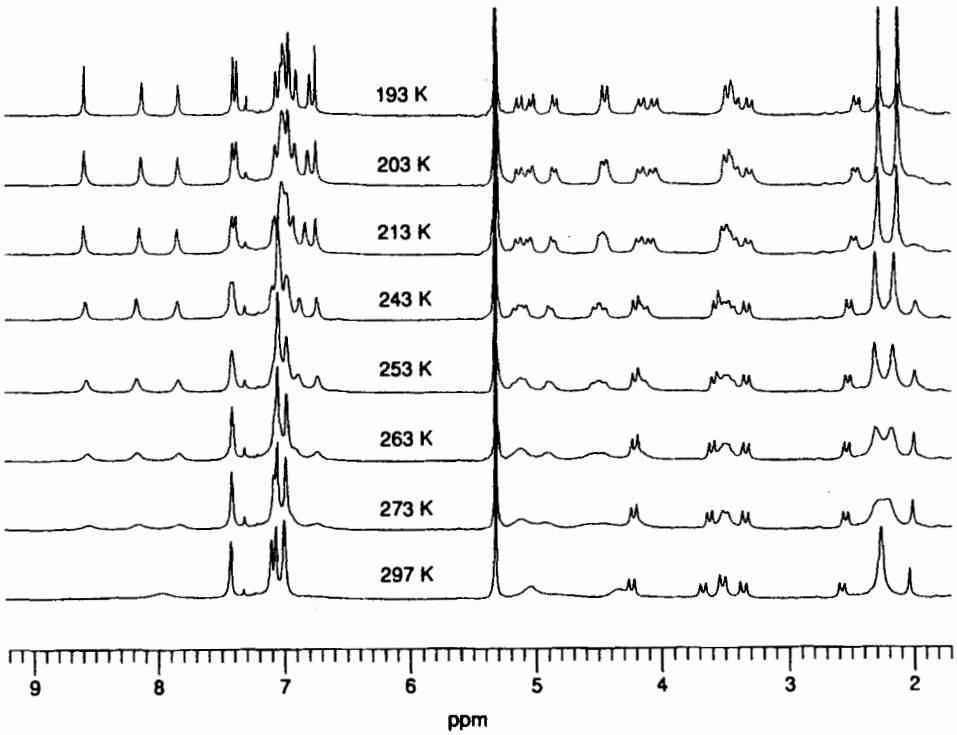


Fig. 4. *Variable temperature* ^{1}*H-NMR of complex* **11** (CD_2Cl_2). Me_3C resonance signals are suppressed.

A TOCSY experiment, performed at 193 K, confirmed that the two btz units of **11** were not equivalent. The two terminal thiazole rings were characterized by couples of Me and heterocyclic H-atom *s* at 2.09–7.37 and 2.25–7.40 ppm. *AB* Systems were built up at 2.43/3.46, 3.28/4.15, 3.40/4.04, 3.45/4.43, 4.44/5.13, and 4.85/5.03 ppm, but no correlation was found between these groups and the aromatic part of the spectrum.

As shown in the TOCSY pattern of the aromatic part of **11** (*Fig. 5*), the four aromatic proton couples were easily attributed. The two peaks at 8.10 and 7.81 ppm displayed correlations with the two aromatic couples located at 6.91/7.02 and 6.96/7.03 ppm and were thus attributed to the OH groups. They also displayed, as artefacts, little ROESY cross-peaks which confirmed that the corresponding phenols have the same orientation. The two extreme resonance signals at 6.76 and 8.61 ppm, correlated by an exchange cross-peak, were attributed to the anchored thiazole protons, this confirmed, in accordance with our previous work [8], that the complex should be a racemate. A conformational information was given by the ROESY interaction observed between the thiazole proton at 8.61 ppm and the OH group at 8.10 ppm, which denoted that one btz unit is pointing towards the calixarene lower rim (*Fig. 6*).

The heteronuclear HMBC technique allowed us to assigne the ^{13}C-NMR data of the heterocyclic system. It confirmed notably that the four thiazole rings of **11** were differentiated and that the molecule had no specific symmetry. Unfortunately, the very low

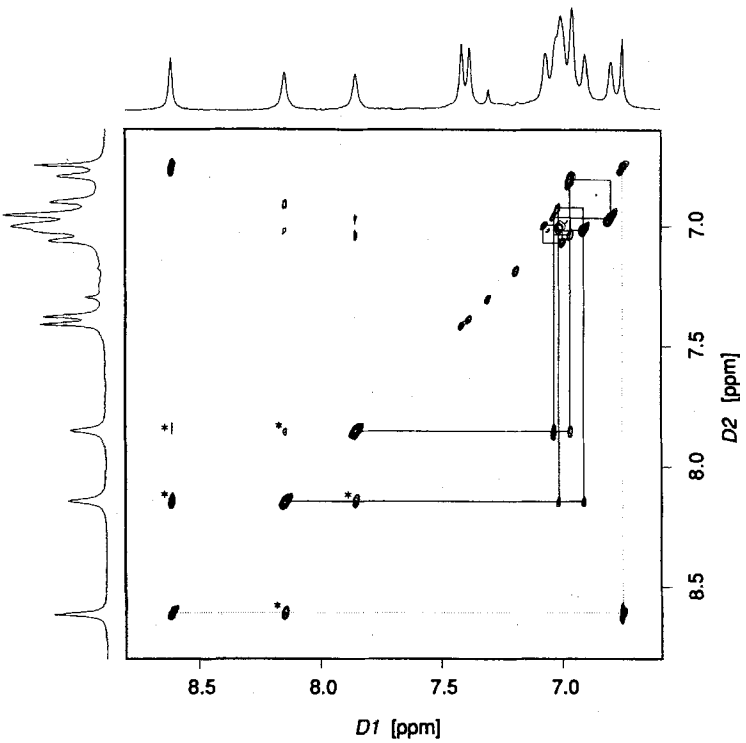


Fig. 5. *TOCSY Experiment in the aromatic region of complex* **11** (193 K, CD_2Cl_2; spin-lock time 170 ms). Full lines: TOCSY; dotted lines: exchange, *: ROESY.

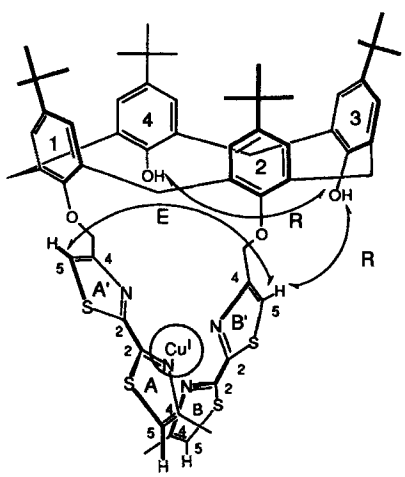


Fig. 6. *Schematic representation, cycle labeling, heterocyclic atoms numbering, and some significant dipolar interactions between protons in complex* **11** (E: exchange; R: ROESY)

response of the ArCH_2Ar groups alleviated the total attribution of the calixarene platform.

Complex **12** was studied in $(D_6)Me_2CO$, exhibiting in the ^{1}H-NMR spectrum well defined zones containing large signals. Me_3C groups appeared as a broad *m* between 0.5 and 1.5 ppm, the ArCH_2Ar groups as a broad *AB* system at 3.37/4.10 ppm and the CH_2O units as a broad *s* at 5.58 ppm. The aromatic part exhibited broad *s* which were not precisely attributed. A *s* at 2.15 ppm was attributed to the *Me*-btz groups. Changing $(D_6)Me_2CO$ for CD_2Cl_2 did not give more information; lowering the temperature in this case resulted in the loss of resolution in each part of the spectrum, denoting a strong flexibility of this species, in comparison with **11**.

Complex **13** exhibited in $CDCl_3$ a broadened ^{1}H-NMR spectrum which was not in agreement with a species involving one free and two complexing btz units: two *s* attributed to the *Me*-btz groups were found at 2.14 and 2.49 ppm, integrating to 1 H and 2 H, respectively. Similar results were obtained in CD_2Cl_2 at 298 K. According to the results obtained with **10**–**12**, the spectrum of **13** corresponds to a species in which only one btz unit acts as a ligand. Taking into account a rapid exchange at room temperature, we can consider that only one btz unit, probably the central one, is in permanent contact with the Cu^I centre. Lowering the temperature down to 183 K resulted in the clean separation of three *s* for the *Me*-btz groups; one of them, located at 2.49 ppm, was attributed to a free btz unit, the other two at 2.19 and 2.09 ppm to two differentiated complexing units, as for **11**. This was accompanied by independent and overlapped 1/2 *AB* systems corresponding to the different kinds of CH_2 groups. Two of them were suspected, based on proton integration, to be hidden by the *Me*-btz resonance signals. The broadened aromatic part split into a complex group of *m*.

Complex **14** gave rather broad and complicated spectra in $CDCl_3$ and CD_2Cl_2 at 298 K. Lowering the temperature to 193 K resulted in the slight sharpening of peaks with a splitting in the region of the CH_2 groups. The aromatic part became sharper with apparition, as for **13** at 183 K and **11** at 193 K, of fine *s* at low fields. The *Me*-btz groups appeared as three *s* at 2.07, 2.17, and 2.57 ppm, integrating to 3 H, 6 H, and 3 H, respectively. This indicated, in disagreement with the proven $[M_2L]$ stoichiometry, that one btz unit should stay free (δ 2.57 ppm) while the three others are always, but differently, in contact with the metallic centre, or that, due to a strong steric hindrance generated by the proximity of the two sub-complex units, one of the terminal thiazole rings is complexing by its S-atom, taking away the corresponding Me group from the direct upfield-shifting influence of the Cu^I centre.

Low-temperature ^{1}H-NMR spectra of **12**–**14** were not sufficiently well resolved to allow, as for **11**, a full or even partial structure elucidation by a two-dimensional study.

Conclusion. – In the field of our investigations, we have developed a synthetic programme based on the ability of the calix[4]arene platform to act as a spatial organizer of chelating properties, taking copper ions as metallic model [2] [8].

In the present work, we have synthesized the Cu^I complexes of the full family of the previously described *O*-[([2,2′-bithiazole]-6-yl)methyl]-substituted tetra-*p*-(*tert*-butyl)-calix[4]arene-tetrols [1]. To eliminate destructive chromatographic purifications, we have monitored these syntheses by the extinction, upon complexation of Cu^I, of the intrinsic blue fluorescence of the free ligands. This directly afforded the pure complexes which

displayed, depending on the nature of the ligands, the known $[ML_2]$, [ML], and the new $[M_2L]$ stoichiometries. The latter were verified and measured in solution by means of relevant techniques involving notably UV/VIS and electrospray mass spectrometries, and confirmed in the solid state by elemental analysis. Structural and conformational information was available in some cases by high-resolution homo- or heteronuclear ^{1}H-, ^{13}C-, and ^{15}N-2D-NMR techniques.

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Experimental Part

General. See [2] [8]. UV Spectra: *Shimadzu-UV-2401-PC* apparatus; λ_{max} in nm, ε in $l \cdot mol^{-1} \cdot cm^{-1}$. Fluorescence measurements: at 25°; *Kontron-SFM-25* spectrofluorimeter; Xenon lamp, *PM R212*; all complexes were tested on spectrofluorimeter before analyses. Moreover: ^{1}H-, ^{13}C-, and ^{15}N-NMR Spectra: *Bruker AM 300* (300, 50.3, and 30.42 MHz, resp.); $SiMe_4$ (^{1}H and ^{13}C) and $MeNO_2$ (^{15}N) as internal standards, chemical shifts δ in ppm, J in Hz. TOCSY: at 193 K; SW = 3125 Hz; time domain 2048 points; $(\gamma/2\pi)B_1$ = 9.6 kHz, spin lock time 170 ms; NS = 8 and NE = 256 increments for the F_1 dimension. Data were processed with the Felix 2.1 package in the phase-sensitive mode with a square sine-bell window function in the two dimensions. ^{1}H,^{13}C Gradient HMBC: SW1H = 3125 Hz, SW13C = 12820 Hz, NE = 512, NS = 8; coupling evolution time 50 ms; T° 193K. ^{1}H,^{15}N Gradient HMBC: SW1H = 2564 Hz, SW15N = 12164 Hz, NE = 256, NS = 64; coupling evolution time 125 ms; T° 295 K.

Bis(4,4'-dimethyl-2,2'-bithiazole)copper(I) Hexafluorophosphate ([**6**-Cu-**6**]PF_6; **8**). A soln. of $[Cu(MeCN)_4]PF_6$ (0.145 g, 0.383 mmol) in CH_2Cl_2 (2 ml) was added under stirring to a soln. of **6** (0.150 g, 0.765 mmol) in CH_2Cl_2 (6 ml). The red soln. was stirred under N_2 for 5 min. After filtration through cotton and concentration, addition of Et_2O (10 ml) resulted in the separation of a red precipitate which was filtered off and dried *in vacuo*: **8** (0.225 g, 97%). M.p. 240–241°. UV (CH_2Cl_2): 436 (5300), 340 (24000), 324 (sh, 21800). IR (KBr): 851 (PF_6^-); 740, 752 (in-plane ring bending); 1050, 1230 (Me rocking). ^{1}H-NMR ($CDCl_3$): 2.24 (*s*, 2 *Me*-btz); 7.37 (*s*, 2 H, btz). ES-MS: 455.1 ([**6**-Cu-**6**]$^+$), 415 ([**6**-Na-**6**]$^+$), 219 ([**6** + Na]$^+$), 196.9 ([**6** + H]$^+$). Anal. calc. for $C_{16}H_{16}CuF_6N_4PS_4$ (601.0): C 31.97, H 2.68, N 9.32, S 21.34; found: C 32.08, H 2.79, N 9.05, S 21.14.

*Bis{4-{[4-(*tert*-butyl)phenoxy]methyl}-4'-methyl-2,2'-bithiazole}copper(I) Hexafluorophosphate* ([**7**-Cu-**7**]PF_6; **9**). As described for **8**, with $[Cu(MeCN)_4]PF_6$ (0.014 g, 0.0363 mmol) in CH_2Cl_2 (2 ml) and **7** (0.025, 0.0727 mmol) in CH_2Cl_2 (5 ml): **9** (0.031 g, 95%). M.p. 182–183°. UV (CH_2Cl_2): 442 (4000), 339 (25000), 321 (sh, 22000). IR (KBr): 851 (PF_6^-); 1050, 1100, 1230. ^{1}H-NMR (CD_2Cl_2): 1.25 (*s*, *t*-Bu); 2.26 (*s*, *Me*-btz); 4.77 (*s*, OCH_2-btz); 6.41 (*d*, J = 8.1, 2 H, Ar); 7.11 (*d*, J = 8.1, 2 H, Ar); 7.27 (*s*, 1 H, btz); 7.64 (*s*, 1 H, btz). ES-MS: 751.4 ([**7**-Cu-**7**]$^+$), 711.4 ([**7**-Na-**7**]$^+$), 367.2 ([**7** + Na]$^+$), 345.2 ([**7** + H]$^+$). Anal. calc. for $C_{36}H_{40}CuF_6N_4O_2PS_4$ (897.5): C 48.18, H 4.50, N 6.24, S 14.29, O 3.57; found: C 48.32, H 4.50, N 5.94, S 14.14, O 3.55.

*Bis{5,11,17,23-tetra(*tert*-butyl)-28-[(4'-methyl[2,2'-bithiazol]-4-yl)methoxy]calix[4]arene-25,26,27-triol}copper(I) Hexafluorophosphate*[2]) ([**1**-Cu-**1**]PF_6; **10**). A soln. of $[Cu(MeCN)_4PF_6]$ (0.012 g, 0.03 mmol) in CH_2Cl_2 (2 ml) was added under stirring to a soln. of **1** (0.05 g, 0.06 mmol) in CH_2Cl_2 (5 ml). The orange soln. was stirred under N_2 for 5 min, then filtered through cotton, and evaporated: **10** (0.055 g, 97%). M.p. 188–189°. UV (CH_2Cl_2): 428 (4200), 340 (27000), 330 (sh, 25600), 290 (18000), 280 (18000). IR (KBr): 851 (PF_6^-); 1050, 1100, 1230. ^{1}H-NMR ($CDCl_3$): 1.14 (*s*, 2Me_3C); 1.21 (*s*, 6 Me_3C); 2.27 (*s*, 2*Me*-btz); 3.20–4.30 (*'q'*, *AB*, J_{AB} = 13, 4 ArCH_2Ar); 3.36–4.30 (*'q'*, *AB*, J_{AB} = 13, 4 ArCH_2Ar); 5.03 (*s*, 2 OCH_2-btz); 6.95 (*s*, 4 H, Ar); 7.00 (*s*, 8 H, Ar); 7.02 (*s*, 4 H, Ar); 7.21 (*s*, 2 H, btz); 8.34 (*s*, 2 H, btz); 9.06 (*s*, 4 OH); 9.71 (*s*, 2 OH). ES-MS: 1748.5 ([**1**-Cu-**1**]$^+$), 1708.6 ([**1**-Na-**1**]$^+$), 865.6 ([**1** + Na]$^+$), 843.6 ([**1** + H]$^+$). Anal. calc. for $C_{104}H_{124}CuF_6N_4O_8PS_4$ (1894.8): C 65.93, H 6.60, N 2.96, S 6.76, O 6.77; found: C 65.93, H 6.60, N 3.05, S 6.61, O 6.75.

*{5,11,17,23-Tetra(*tert*-butyl)-27,28-bis[(4'-methyl[2,2'-bithiazol]-4-yl)methoxy]calix[4]arene-25,26-diol}-copper(I) Hexafluorophosphate*[2]) ([**2**-Cu]PF_6; **11**). As described for **10**, with $[Cu(MeCN)_4]$ PF_6 (0.009 g, 0.024 mmol) in CH_2Cl_2 (1 ml) and **2** (0.025 g, 0.024 mmol) in CH_2Cl_2 (5 ml) under N_2 during 5 min: **11** (0.029 g,

[2]) Calix[4]arene = pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene.

97%). M.p. 224–225°. UV (CH_2Cl_2): 445 (4500), 340 (25000), 328 (sh, 23000), 287 (7500), 280 (7000). IR (KBr): 851 (PF_6^-); 1050, 1100, 1230. ^{1}H-NMR (CD_2Cl_2, 193 K; see *Fig. 6*): 1.01 (*s*, Me_3C); 1.07 (*s*, $2Me_3C$); 1.12 (*s*, Me_3C); 2.09 (*s*, *Me*-btz); 2.25 (*s*, *Me*-btz); 2.43, 3.455 (*'q'*, *AB*, J_{AB} = 11.7, $ArCH_2Ar$); 3.28, 4.15 (*'q'*, *AB*, J_{AB} = 13.0, $ArCH_2Ar$); 3.40, 4.04 (*'q'*, *AB*, J_{AB} = 13.2, $ArCH_2Ar$); 3.465, 4.43 (*'q'*, *AB*, J_{AB} = 12.3, $ArCH_2Ar$); 4.45, 5.13 (*'q'*, *AB*, J_{AB} = 12.0, OCH_2-btz); 4.85, 5.03 (*'q'*, *AB*, J_{AB} = 10.4, OCH_2-btz); 6.76 (*s*, H–(5), A′ or B′); 6.81, 6.97 (*AB*, 2 H, Ar(1) or Ar(2)); 6.91, 7.016 (*AB*, 2 H, Ar(3) or Ar(4)); 6.96, 7.03 (*AB*, 2 H, Ar(4) or Ar(3)); 7.00, 7.07 (*AB*, 2 H, Ar(2) or Ar(1)); 7.37 (*s*, H–(5), A or B); 7.40 (*s*, H–(5), B or A); 8.61 (*s*, H–(5), B′ or A′); 7.81 (*s*, OH); 8.10 (*s*, OH). ^{13}C-NMR (HMBC, CD_2Cl_2, 193 K; see *Fig. 6*): 17.00, 17.50 (*Me*-btz); 31.30, 31.45, 31.60 (Me_3C); *ca.* 32.00 ($ArCH_2Ar$); 34.20, 34.44, 34.61, 34.63 (Me_3C); 119.30, 119.35 (C(5), A; C(5), B); 125.31 (C(5), A′; C(5), B′); *ca.* 125.00, 128.00 (C_m of Ar); 127.43, 129.73 (C_o of Ar(3) and Ar(4)); 135.23 (C_o of Ar(1) and Ar(2)); 143.40, 144.60, 147.90, 148.18 (C_p of Ar(1), Ar(2), Ar(3), and Ar(4)); 147.29 (C_{ipso} of Ar(1) or Ar(2)); 147.52, 149.60 (C_{ipso} of Ar(3) and Ar(4)); 149.475 (C(4), A′ or B′); 150.48 (C_{ipso} of Ar(2) or Ar(1)); 150.56 (C(4), B′ or A′); 152.73 (C(4), A; C(4), B); 158.68, 159.93 (C(2), A; C(2), B); 160.07, 161.00 (C(2), A′, C(2), B′). ES-MS: 1101.6 ([**2**-Cu]$^+$), 1059.7 ([**2** + Na]$^+$), 1037.7 ([**2** + H]$^+$). Anal. calc. for $C_{60}H_{68}CuF_6N_4O_4PS_4 \cdot 0.5\ CH_2Cl_2$ (1288.40): C 56.40, H 5.39, N 4.35, S 9.95; found: C 56.48, H 5.54, N 4.13, S 9.65.

*{5,11,17,23-Tetra(*tert*-butyl)-26,28-bis[(4′-methyl[2,2′-bithiazol]-4-yl)methoxy]calix[4]arene-25,27-diol}-copper(I) Hexafluorophosphate*[2] ([**3**-Cu]PF_6; **12**). As described for **10**, with $[Cu(MeCN)_4]PF_6$ (0.04 g, 0.097 mmol) in CH_2Cl_2 (1 ml) and **3** (0.1 g, 0.097 mmol) in CH_2Cl_2 (6 ml): **12** (0.121 g, 99%). M.p. 228–229°. UV (CH_2Cl_2): 428 (4000), 337 (25500), 327 (sh, 23500), 294 (12000), 283 (sh, 11500). IR (KBr): 851 (PF_6^-); 1050, 1100, 1230. ^{1}H-NMR ($(D_6)Me_2CO$, r.t.): 0.5–1.5 (br. *m*, 4 Me_3C); 2.15 (*s*, 2 *Me*-btz); 3.37, 4.10 (br. *AB*, 4 $ArCH_2Ar$); 5.58 (br. *s*, 2 OCH_2-btz); 6.80–7.40 (br. *m*, 8 H of Ar and 1 H of btz or 1 OH); 7.74 (br. *s*, 1H of btz or 1 OH); 8.18 (br. *s*, 2 H, btz and/or OH); 8.57 (br. *s*, 1 H, btz or OH). ES-MS: 1099.3 ([**3**-Cu]$^+$), 1059.4 ([**3** + Na]$^+$), 1037.4 ([**3** + H]$^+$). Anal. calc. for $C_{60}H_{68}CuF_6N_4O_4PS_4 \cdot CH_2Cl_2 \cdot H_2O$ (1348.8): C 54.32, H 5.34, O 5.93, N 4.15; found: C 54.48, H 5.13, O 5.97, N 4.18.

*{5,11,17,23-Tetra(*tert*-butyl)-26,27,28-tris[(4′-methyl[2,2′-bithiazol]-4-yl)methoxy]calix[4]arene-25-ol}-copper(I) Hexafluorophosphate*[2] ([**4**-Cu]PF_6; **13**). As described for **10**, with $[Cu(MeCN)_4]PF_6$ (0.0077 g, 0.02 mmol) in CH_2Cl_2 (1 ml) and **4** (0.025 g, 0.02 mmol) in CH_2Cl_2 (5 ml): **13** (0.0285 g, 96%). M.p. 235–236°. UV (CH_2Cl_2): 432 (4000), 333 (36700), 292 (10500), 280 (sh, 10000). IR (KBr): 851 (PF_6^-); 1050, 1100, 1230. ^{1}H-NMR (CD_2Cl_2, 193 K): 0.5–1.6 (br. *m*, 4 Me_3C); 2.09 (*s*, *Me*-btz); 2.19 (*s*, *Me*-btz); 2.49 (*s*, *Me*-btz); 2.24, 2.45 (hidden 1/2 *AB*, 2 H of $ArCH_2Ar$); 2.92 (1/2 *AB*, 1 H of $ArCH_2Ar$); 3.33 (br. *m*, 3 H of $ArCH_2Ar$); 3.67 (br. 1/2 *AB*, 1 H of $ArCH_2Ar$); 3.97 (br. 1/2 *AB*, 1 H of $ArCH_2Ar$); 4.12 (br. 1/2 *AB*, 1 H of OCH_2-btz); 4.52 (br. 1/2 *AB*, 1 H of OCH_2-btz); 4.65–5.00 (br. *m*, 3 H of OCH_2-btz); 5.19 (br. 1/2 *AB*, 1 H of OCH_2-btz); 6.10 (*s*, OH); 6.40–7.80 (*m*, 8 H of Ar, 5 H of btz); 9.38 (1 H of btz). ES-MS: 1293.7 ([**4**-Cu]$^+$), 1231.8 ([**4** + H]$^+$), 1253.7 ([**4** + Na]$^+$). Anal. calc. for $C_{68}H_{74}CuF_6N_6O_4PS_6$ (1440.21): C 56.71, H 5.18, N 5.84, S 13.36, O 4.44; found: C 56.64, H 5.23, N 5.46, S 13.20, O 4.30.

*{4,4′,4″,4‴-{[5,11,17,23-Tetra(*tert*-butyl)calix[4]arene-25,26,27,28-tetrayl]tetrakis(oxymethylene)}tetrakis-[4′-methyl-2,2′-bithiazol]}dicopper(I) Bis(hexafluorophosphate)* ([Cu-**5**-Cu]$(PF_6)_2$; **14**). As described for **8**, with $[Cu(MeCN)_4]PF_6$ (0.0266 g, 0.07 mmol) in CH_2Cl_2 (2 ml) and **5** (0.05 g, 0.035 mmol) in CH_2Cl_2 (5 ml): **14** (0.064 g, 98%). M.p. 255–256°. UV (CH_2Cl_2): 436 (8000), 336 (47000). IR (KBr): 851 (PF_6^-); 1050, 1100, 1230. ^{1}H-NMR (CD_2Cl_2, 183 K): 0.60–1.50 (*m*, 4 Me_3C); 2.07 (*s*, *Me*-btz); 2.17 (*s*, 2 *Me*-btz); 2.57 (*s*, *Me*-btz); 2.10 (hidden 1/2 *AB*, 1 H of $ArCH_2Ar$); 2.50 (hidden 1/2 *AB*, 1 H of $ArCH_2Ar$); 2.76 (br. 1/2 *AB*, 1 H of $ArCH_2Ar$); 3.38 (br. *s*, 2 H of $ArCH_2Ar$); 3.61 (br. 1/2 *AB*, 1 H of $ArCH_2Ar$); 3.89 (br. 1/2 *AB*, 1 H of $ArCH_2Ar$); 3.96 (br. 1/2 *AB*, 1 H of $ArCH_2Ar$); 4.09 (br. 1/2 *AB*, 1 H of OCH_2-btz); 4.41 (br. *s*, 2 H of OCH_2-btz); 4.51 (br. 1/2 *AB*, 1 H of OCH_2-btz); 4.86 (br. *s*, 3 H of OCH_2-btz); 5.35 (hidden 1/2 *AB*, 1 H of OCH_2-btz); 6.41 (*s*, 1H of btz or Ar); 6.51 (*s*, 2H of btz or Ar); 6.84 (*s*, 4 H of btz or Ar); 7.00–7.45 (*m*, 6 H of Ar and/or btz); 7.59 (1 H of btz); 8.01 (1 H of btz); 8.96 (1 H of btz). ES-MS: 1490.5 ([**5**-Cu]$^+$), 776 ([Cu-**5**-Cu]$^{2+}$/2). Anal. calc. for $C_{76}H_{80}Cu_2F_{12}N_8O_4P_2S_8 \cdot Et_2O$ (1917.09): C 50.12, H 4.73, N 5.84, S 13.38, O 4.17; found: C 50.42, H 4.44, N 5.65, S 13.41, O 3.87.

REFERENCES

[1] S. Pellet-Rostaing, J.-B. Regnouf-de-Vains, R. Lamartine, *Tetrahedron Lett.* **1996**, *37*, 5889.

[2] J.-B. Regnouf-de-Vains, R. Lamartine, *Helv. Chim. Acta* **1994**, *77*, 1817.

[3] a) Iron: H. Erlenmeyer, H. Ueberwasser, *Helv. Chim. Acta* **1940**, *23*, 1268; b) nickel: H. Erlenmeyer, E. H. Schmid, *ibid.* **1941**, *24*, 869; c) K. Krause, R. A. Krause, S. Lamtruong, *J. Coord. Chem.* **1988**, *19*, 91; d) ruthenium: D. Rillema, G. Allen, T. J. Meyer, D. Conrad, *Inorg. Chem.* **1983**, *22*, 1617, G. Orellana,

M. L. Quiroga, A. M. Braun, *Helv. Chim. Acta* **1987**, *70*, 2073; G. Orellana, C. A. Ibarra, J. Santoro, *Inorg. Chem.* **1988**, *27*, 1025.

[4] W. von Philipsborn, R. Müller, *Angew. Chem. Int. Ed.* **1986**, *25*, 383.

[5] B. C. Chen, W. von Philipsborn, K. Nagarajan, *Helv. Chem. Acta* **1983**, *66*, 1537.

[6] S. Kitagawa, M. Munakata, K. Deguchi, T. Fujito, *Magn. Reson. Chem.* **1991**, *29*, 566.

[7] H. Günther, 'La Spectroscopie de RMN. Principes de Base, Concepts et Applications de la Spectroscopie de Resonance Magnétique Nucléaire du Proton et du Carbone 13 en Chimie', Masson, Paris, 1994, p. 333.

[8] J.-B. Regnouf-de-Vains, R. Lamartine, B. Fenet, C. Bavoux, A. Thozet, M. Perrin, *Helv. Chim. Acta* **1995**, *78*, 1607.