Calix[6]arene-Based N_3-Donors − A Versatile Supramolecular System with Tunable Electronic and Steric Properties − Study on the Formation of Tetrahedral Dicationic Zinc Complexes in a Biomimetic Environment

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Novel tridentate *N*-ligands containing tertiary amines, pyrazoles, or benzimidazole groups were synthesized from *t*Bu-calix[6]arene. Together with the previously described pyridine and imidazole-based ligands, they form a large family of biomimetic ligands ($X_6Me_3N_3$) with different electronic and steric properties. Their capacity at stabilizing a tetrahedral Zn dicationic center in acetonitrile was investigated. Tertiary amines were too basic and sterically hindered, leading to precipitation of $Zn(OH)_2$. The resulting protonated ligand was, in one case, structurally characterized by X-ray analysis. Ligands with pyrazole, benzimidazole and imidazole donors, all formed a stable Zn complex under stoichiometric conditions in acetonitrile. An ^1H NMR spectroscopic study together with X-ray crystallography showed that the metal ion is coordinated to the three nitrogen arms with MeCN as a fourth ligand included in the calixarene conic pocket. These complexes provide new but rare examples of stable dicationic tetrahedral Zn species. The calixarene functionalized by three pyridine groups, on the other hand, did not appear to be a good ligand, which stands in contrast with its remarkable ability at stabilizing copper(I). Finally, these *funnel complexes* are chiral due to their helical shape. In solution, both enantiomers are in equilibrium. However, sterically hindered *N*-donors increased the enantiomerization barrier above 16 kcal/mol.

Introduction

Zinc enzymes constitute an important class of metalloproteins. These are ubiquitous and play a fundamental role in living systems. They are mainly involved in hydrolytic processes but also catalyze hydride transfer reactions. Zn^{2+} is usually maintained in the active site through its coordination to three amino acid residues, either His, Cys, Asp, or Glu. In mononuclear zinc enzymes that have been structurally characterized, the most recurrent binding site is tris-histidine. Indeed this N_3 core has been found in snake venom proteases, matrix metalloproteases, collagenases, deaminases, β-lactamase, carbonic anhydrase, and a carboxypeptidase.[1] Model chemistry is a fundamental tool for understanding these important biological systems. To mimic the role of a tris(imidazole) core, the most widely used N_3-ligands[2,3] are macrocyclic triamines,[4] anionic tris(pyrazolyl)borates,[5−7] or neutral tris(imidazolyl)methane and -phosphane.[8] Although the steric hindrance at each synthetic core can be tuned through the introduction of appropriate substituents, their electronic properties can hardly be modulated (particularly through the change of the *N*-donor).

In the present paper, we report on a calix[6]arene-based system that not only preorganizes a binding site for the metal center but also provides a cavity next to it. This system is highly versatile since it allows the tuning of both the steric hindrance and the electronic properties due to the *N*-donor set. Here, we first describe the synthesis of a series of novel calix[6]arene-based N_3-ligands. They offer a wide variety of potential binding sites, either tertiary or aromatic amines, with various steric encumbrance. We then report on their relative ability at stabilizing a metal ion in a biomimetic environment. We previously described the first members of this family with pyridine-based Cu^I [9,10] and imidazole-based Zn^{II} complexes.[11] These so-called *funnel complexes* present a hydrophobic cavity that wraps around the free coordination site of the metal ion, thereby acting like a selective molecular funnel for small exogenous ligands and mimicking the enzyme pocket. Here, we focus on the binding part of these supramolecular systems and compare the ability of the various *N*-donors at stabilizing a tetrahedral Zn^{2+} ion.

Results and Discussion

Synthesis of Ligands

The calix[6]arene-based N_3-ligands $X_6Me_3N_3$ were synthesized in two steps starting from *t*Bu-calix[6]arene

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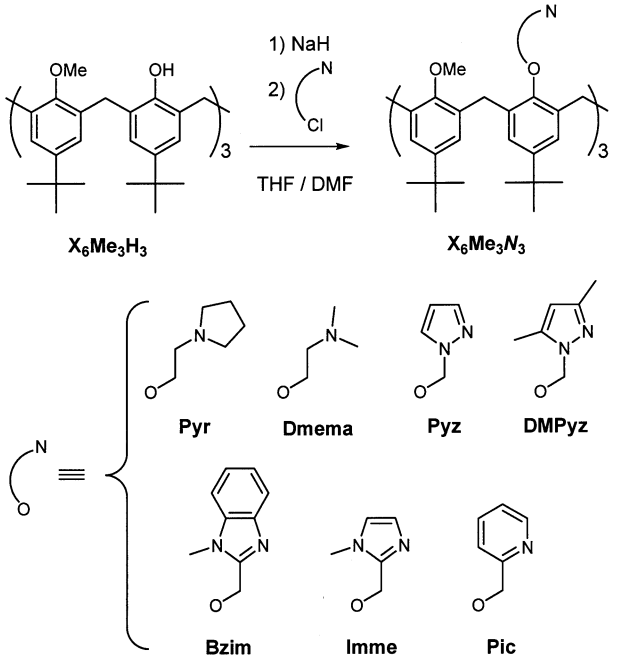
(X_6H_6).[12] The latter was first converted into its 1,3,5-trimethyl ether derivative ($X_6Me_3H_3$),[13] then treated with various alkyl chlorides in a THF/DMF mixture in the presence of excess NaH. The products $X_6Me_3N_3$ were obtained in good yields from $X_6Me_3H_3$ (ca. 80%). They constitute a very large family of tridentate ligands, presenting various *N*-donors: pyrrolidine (Pyr), dimethylamine (Dmema), pyrazole Pyz, 3,5-dimethylpyrazole (DMPyz), benzimidazole (Bzim), imidazole (Imme), and pyridine (Pic). All of them show good solubility in chlorinated solvents and are almost insoluble in acetonitrile (Scheme 1).



Scheme 1. Synthesis of the calix[6]arene-based N_3-ligands $X_6Me_3N_3$

Crystal Structures of $X_6Me_3Pyz_3$ and $[X_6Me_3Pyr_3.H_3](ClO_4)_3$

Two of these molecules were characterized by X-ray diffraction analysis. The molecular structures of ligand **$X_6Me_3Pyz_3$** and of the perchlorate salt of the ligand **$X_6Me_3Pyr_3$** are displayed in Figure 1 and 2, respectively. Both calix[6]arene structures stand in a flattened C_3-symmetrical cone conformation. The smallest *O*-substituents, the methoxy groups, point toward the inside of the cavity, close to the C_3 axis with the related *t*Bu groups lying in the *out*-position. The nitrogenous arms, which are the largest *O*-substituents, are projected outwards whereas the corresponding *t*Bu groups lie in the *in*-position. Figure 2 shows the regular head to head stacking of the protonated ligands forming a sandwich around a layer of perchlorates anions.

NMR Study of the Ligands

The $X_6Me_3N_3$ ligands underwent NMR spectroscopic analysis. In agreement with the X-ray structure of $X_6Me_3Pyz_3$, all of them displayed, at 298 K in $CDCl_3$, ^1H NMR spectroscopic profiles typical of a major cone conformer.

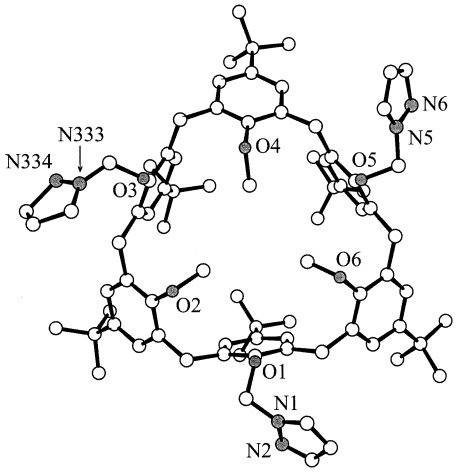


Figure 1. X-ray structure of $X_6Me_3Pyz_3$. Hydrogen atoms and solvent of crystallization were omitted for clarity. Only one out of the two isomers is shown (see Exp. Sect.)

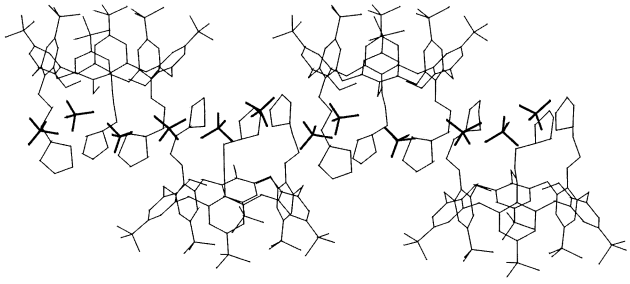


Figure 2. X-ray structure of $[X_6Me_3Pyr_3.H_3](ClO_4)_3$. Hydrogen atoms and solvent of crystallization were omitted for clarity

The high-field shift of the methoxy protons (δ_{OMe} = 2.14−2.33) attested to their partial inclusion in the calixarene π-basic cavity. It is well-known that calix[6]arenes are highly mobile molecules since interconversion processes between multiple conformers can occur via rotation through the annulus of both the *O*-alkyl and the *t*Bu groups.[14] Indeed, compounds $X_6Me_3Pyz_3$ and $X_6Me_3Dmema_3$ showed broad resonances with two large singlets for their bridging methylene protons, which is indicative of the beginning of a coalescence process at room temperature (Figure 2). In contrast, spectra of all others were sharp and well defined, with two doublets for the $ArCH_2Ar$ methylene protons. This indicated that the cone−cone interconversion was slower than the NMR timescale. In the specific case of compounds with the more sterically encumbered nitrogen arms (*N* = Pyr, DMPyz, and Bzim) a minor conformer was clearly detected at room temperature as six extra well-defined doublets for the bridging methylene groups were observed. This minor isomer probably corresponds to the 1,2,3-alternate conformer that was identified in the case of the closely related calix[6]arenes.[15] Hence, the comparative $ArCH_2Ar$ areas of the ^1H NMR spectra (displayed in Figure 3) are a good probe for the evaluation of calix[6]arene mobility.[16] A qualitative classification according to a decreasing mobility of the molecules can be made: $X_6Me_3Pyz_3$ and $X_6Me_3Dmema_3$ > $X_6Me_3Imme_3$ and $X_6Me_3Pic_3$ > $X_6Me_3Pyr_3$,

$X_6Me_3DMPyz_3$, and $X_6Me_3Bzim_3$. This indeed corresponds to an increasing steric encumbrance of the nitrogenous arms, that slows down their rotation through the annulus of the calix[6]arene.

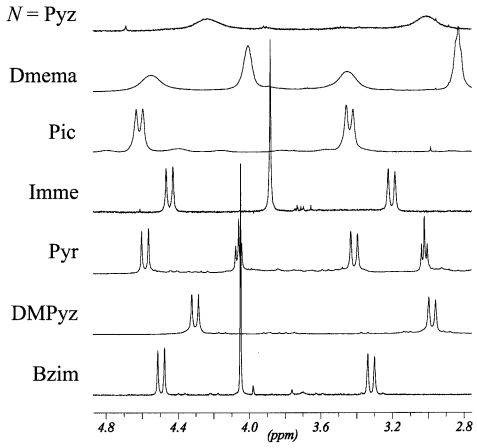


Figure 3. $ArCH_2Ar$ regions of the ^1H NMR spectra (400 MHz) of ligands $X_6Me_3N_3$ at 298 K in $CDCl_3$

Reaction with Zinc(II)

Compounds $X_6Me_3N_3$ were treated in acetonitrile with a stoichiometric quantity of $Zn(H_2O)_6(ClO_4)_2$ and the products were submitted for NMR spectroscopic analyses in CD_3CN.[17] In the case of ligands containing tertiary amine moieties ($X_6Me_3Dmema_3$ and $X_6Me_3Pyr_3$), the ^1H NMR spectra of the isolated compounds together with elemental analyses indicated the presence of three chlorine atoms per ligand which was due to the perchlorate salt of the tris-protonated ligands $[X_6Me_3N_3{\cdot}H_3](ClO_4)_3$ (N = Pyr and Dmema). Confirmation of these assignments was obtained by comparison with the authentic samples prepared with $HClO_4$. From these first results, it appears that the strong basicity of the tertiary amines-based ligands $X_6Me_3Pyr_3$ and $X_6Me_3Dmema_3$ together with the high steric hindrance at the nitrogen atoms, disfavors the formation of stable complexes and rather lead to their protonation with concomitant precipitation of $Zn(OH)_2$.

In contrast to these tertiary amine-based systems, calixarenes that have been functionalized with either pyrazole (Pyz and DMPyz), imidazole (Imme) or benzimidazole (Bzim) groups led to products with a 1:1 ligand/Zn ratio. One of them, $[Zn(X_6Me_3Imme_3)(CH_3CN)](ClO_4)_2$, was structurally characterized by X-ray analysis.

Crystal Structure of $[Zn(X_6Me_3Imme_3)(CH_3CN)](ClO_4)_2$

Single crystals were obtained by slow diffusion of Et_2O into a $CHCl_3/CH_3CN$ solution of $[Zn(X_6Me_3Imme_3)(CH_3CN)](ClO_4)_2$. The structure, displayed in Figure 4, shows a tetrahedral zinc center coordinated to all three imidazole arms and to an acetonitrile molecule. The latter is situated inside the calixarene cavity, along the C_3 axis. The calixarene is constrained in a flattened cone conformation with all OMe groups projected away from the cavity. The anisole *t*Bu groups are now in the *in*-position and the others are *out*. The average $Zn-N_{Im}$ bond length (1.973 Å) and the zinc−nitrile distance (2.008 Å) are particularly short, in accordance with the highly acidic nature of a tetrahedral zinc dication.[18] Finally, as previously observed for all other X-ray characterized *funnel complexes*, the coordinating arms (here the imidazole groups) form a chiral helix around the metal center and both enantiomers are present in the lattice.

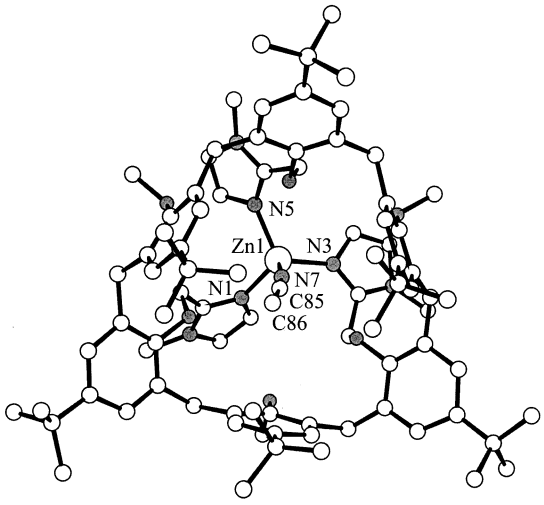


Figure 4. Crystal structure of complex $[Zn(X_6Me_3Imme_3)(CH_3CN)](ClO_4)_2$. Hydrogen atoms, counterions and solvent of crystallization were omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1−N1 1.956(9), Zn1−N3 1.993(10), Zn1−N5 1.972(9), Zn1−N7 2.008(11), N7−C85 1.132(15), N1−Zn1−N3 111.8(4), N1−Zn1−N5 110.5(4), N3−Zn1−N5 115.9(4), N1−Zn1−N7 106.3(4), N3−Zn1−N7 107.0(4), N5−Zn1−N7 104.4(4), Zn1−N7−C85 173.4(9), N7−C85−C86 174.2(2)

NMR Study of Zinc Complexes $[Zn(X_6Me_3N_3)(MeCN)](ClO_4)_2$

The Zn complexes obtained with ligands $X_6Me_3N_3$ (N = Pyz, DMPyz, Imme, Bzim) were analyzed by ^1H NMR spectroscopy in acetonitrile. Upon dissolution in CD_3CN, one equivalent of free CH_3CN was released, indicating that the isolated products possessed an acetonitrile molecule coordinated to the zinc ion.[19] In the case of $X_6Me_3Bzim_3$, the exchange process was slow enough to allow the observation of a vanishing resonance at $\delta = -0.80$.[20] This indeed corresponded to the coordinated protio-acetonitrile and its high-field shift attested to its location inside the calixarene π-basic cavity.

All NMR profiles displayed in Figure 5 are sharp and characteristic of a calix[6]arene in a C_3-symmetrical cone conformation. The methoxy protons are downfield shifted compared to the free ligand ($\delta = 3.6$ instead of ca. $\delta = 2.3$[21]). This is indicative of the change in the calixarene conformation due to the Zn^{II} coordination. The small rim of the cone is now closed up by the three nitrogen arms, which are linked together by the metal ion, thereby projecting the OMe groups outwards. An acetonitrile molecule (here the solvent) completes the coordination sphere of the

tetrahedral metal ion and fills in the empty space offered by the cavity (Scheme 2).[22] HMQC and HMBC experiments showed that the *t*Bu groups connected to the anisole present the higher shift (ca. $\delta = 0.8$ compared to $\delta = 1.4$ for the other *t*Bu) and form a gate at the entrance of the hydrophobic pocket. Hence, the calixarene adopts the same conformation in CD_3CN solution as the one depicted by the X-ray structure shown in Figure 4. Interestingly, this conformation is the opposite of that observed[10] for the related copper(I) complex $[Cu(X_6Me_3Pic_3)(CH_3CH_2CN)]^+$. As it does not seem to be ligand dependent, this different behavior may be attributed to the nature of the coordinated metal ion, and more precisely to its charge. Indeed, in the zinc conformation, the cone is flatter than in the copper(I) conformation and the metal cation gets closer to the basic oxygen of the phenoxyl moieties (3.8 vs. 4.1 Å).

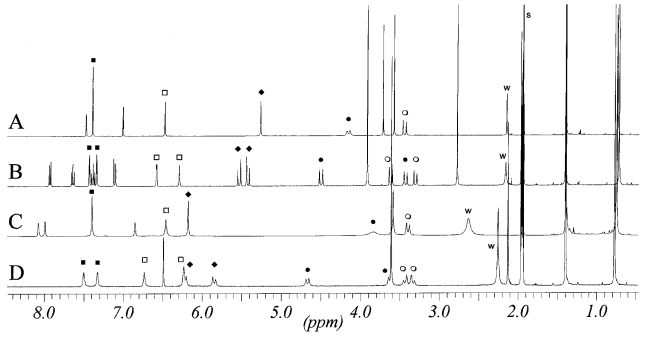
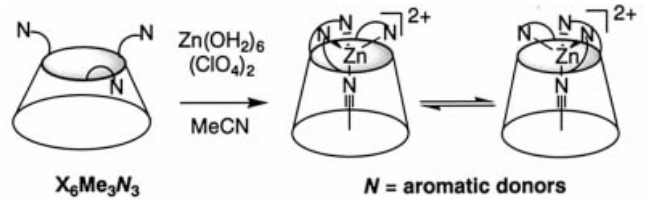


Figure 5. ^1H NMR spectra (400 MHz) of complexes $[Zn(X_6Me_3N_3)(CD_3CN)](ClO_4)_2$ at 298 K in CD_3CN. **A**: *N* = Imme, **B**: *N* = Bzim, **C**: *N* = Pyz, **D**: *N* = DMPyz. H_{Ar}: ■ and □; OCH_2: ◆; $ArCH_{ax}CH_{eq}Ar$: ●; $ArCH_{ax}CH_{eq}Ar$: ○. Solvent and water are labeled "s" and "w", respectively



Scheme 2. Formation of "Zn-funnel complexes"

Lastly, no compound of defined stoichiometry could be isolated through the reaction of one molar equivalent of zinc perchlorate with the pyridine-based ligand $X_6Me_3Pic_3$. The ^1H NMR spectrum of the crude product presented broad signals and was hardly interpretable. However, the addition of an excess of $Zn(H_2O)_6(ClO_4)_2$ directly into an NMR tube containing ligand $X_6Me_3Pic_3$ resulted in a sharp C_3 symmetrical spectrum, which was not that of $[X_6Me_3Pic_3{\cdot}H_3](ClO_4)_3$. The down-field shift of the OMe and pyridine resonances compared to the free ligand were indicative of the formation of the complex, $[Zn(X_6Me_3Pic_3)(CD_3CN)](ClO_4)_2$, with the same conformation as the other above described Zn complexes. However, the equilibrium constant for its formation in acetonitrile is probably weak, as an excess of zinc salt was needed for its NMR characterization. This stands in contrast with the very stable tetrahedral Cu^I complexes that were obtained with the same ligand $X_6Me_3Pic_3$.[9,10]

The Zn Complexes are Chiral

As observed in the crystal structure, each complex exists as a pair of enantiomers due to its helical structure. In solution, these enantiomers are in conformational equilibrium as depicted in Scheme 2. However, the diastereotopic protons could be differentiated by ^1H NMR spectroscopy at various temperatures, depending on the ligand. The calixarene aromatic protons appeared as two pairs of singlets of equal intensity. The OCH_2 and the bridging methylene ($Ar-CH_{eq}$ and $Ar-CH_{ax}$) groups were represented by one and two pairs of doublets, respectively. Interestingly, whereas with *N* = Pyz and Imme a low temperature study was required to observe the coalescence processes, for complexes based on $X_6Me_3DMPyz_3$ and $X_6Me_3Bzim_3$, the splitting of the resonances was observed above 298 K. This different behavior may be related to the steric hindrance next to the heart of the helix, i.e. the metal center. With *N* = DMPyz and Bzim there is an extra substituent in α-position of the coordinating nitrogen atoms: a methyl group on the pyrazole when *N* = DMPyz (to be compared with Pyz) and an aromatic CH from the benzimidazole for *N* = Bzim (to compare with the imidazole from Imme). Saturation transfer experiments, however, unambiguously demonstrated that the chemical exchange still occurs for these complexes. An estimation of the enantiomerization barriers, calculated from the variable temperature experiments,[23] is given in Table 1.

Table 1. Estimation of the enantiomerization barriers for the helical complexes $[Zn(X_6Me_3N_3)(MeCN)](ClO_4)_2$

N-donor	Imme	Bzim	Pyz	DMPyz
$\Delta G^{\neq}$ (kcal·mol^{-1})[a]	< 12[b]	> 17[c]	< 12[b]	16.0 (0.2)[d]

[a] $\Delta G^{\neq}$ was determined from the relationship[23] $k_c = \sqrt{(2.22)}\ (\delta\upsilon^2 + 6J^2_{AB})$. – [b] T_c for protons Ar-αCH$_{ax}$ were 278 and 258 K, respectively. However, the whole coalescence processes could not be observed. Therefore, only lower limits for the Δυ values were obtained. – [c] Only the beginning of the first coalescence process could be observed. Hence, T_c for OCH_2 was estimated to be just above 338 K. – [d] The diastereotopic protons Ar-αCHeq, ArH, and OCH_2 coalesced at T_c = 325, 328, and 338 K, respectively. Variation of the calculated $\Delta G^{\neq}$ values over this range of temperature was not significant.

Such a behavior was also observed for some copper(I) complexes, but only at low temperature.[9,24] These zinc complexes represent the first examples where the diastereotopic protons are differentiated above room temperature. Lastly, the more flattened helical structure of Zn^{II} complexes compared to the $(X_6Me_3Pic_3)$-based Cu^I complexes is reflected by a larger splitting of the diastereotopic proton resonances. All these observations are very promising for chiral recognition and we are currently working on this aspect.

Conclusion

We have here described the synthesis of novel calix[6]arene-based N_3-ligands and studied the comparative ability of the whole series to stabilize a tetrahedral zinc dication in a biomimetic neutral environment. We previously described the first examples of such model compounds with the imidazole-based ligand. The present study shows that benzimidazole and pyrazole are also appropriate *N*-donors for the stabilization of such complexes. Indeed, stable tetrahedral Zn complexes of general formula $[Zn(X_6Me_3N_3)(MeCN)](ClO_4)_2$ were obtained in acetonitrile. The calixarene structure is constrained in a flattened cone conformation, thereby providing a hydrophobic cavity that envelops the exogeneous ligand, MeCN. The calixarene presenting three pyridine groups, however, did not give rise to a well-defined complex under stoichiometric conditions. Hence, pyridine appeared to be a *N*-donor not good enough for the stabilization of tetrahedral dicationic zinc complexes. This stands in contrast with its good capacity at stabilizing Cu^I and may be related to its relative softness. Calixarenes presenting tertiary amine groups did not behave as ligands, but rather acted as bases leading to the formation of zinc hydroxide.[25] Lastly, as revealed by X-ray and NMR analyses, complexes $[Zn(X_6Me_3N_3)(MeCN)](ClO_4)_2$ exist as a pair of helical enantiomers that are in conformational equilibrium in solution. Increasing the steric hindrance at the level of the coordinating atoms, however, considerably slowed the enantiomerization process. We are actively exploring the recognition and catalytic properties of these promising supramolecular biomimetic systems.

Experimental Section

Materials and Methods: All solvents and reagents were obtained commercially. DMF was stored over 4-Å molecular sieves under argon. THF and acetonitrile were distilled under argon over sodium/benzophenone and P_2O_5, respectively. − ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 400 and Bruker AC 200 spectrometers. ^1H and ^{13}C resonances corresponding to anisole moieties are noted as ^{1} (e.g. tBu^1, ArH^1, C^1_{Ar}) and the others are noted as ^{2}. They were assigned with HMBC and HMQC experiments. − IR spectra were recorded on a Perkin−Elmer 783 spectrometer. − Elemental analyses were performed at the Institut de Chimie des Substances Naturelles, France. − 1-Chloromethylpyrazole hydrochloride (PyzCl·HCl) and 1-chloromethyl-3,5-dimethylpyrazole hydrochloride (DMPyzCl·HCl) were obtained from the corresponding alcohols.[26] (2-Chloroethyl)dimethylamine hydrochloride (DmemaCl·HCl) and 1-(2-chloroethyl)pyrrolidine hydrochloride (PyrCl·HCl) were obtained commercially. 2-Chloromethyl-1-methylbenzymidazole (BzimCl) was synthesized through the reaction of *N*-methylphenylen-1,2-diamine with chloroacetic acid in 4 N HCl.[27]

Safety Note: ***Caution!*** Although we have not encountered any problems, it is noted that perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled only in small quantities with appropriate precautions.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,39,41-trimethoxy-38,40,42-tris[(1-pyrazolyl)methoxy]calix[6]arene ($X_6Me_3Pyz_3$): Under an argon atmosphere, a solution of 5,11,23,29,35-Hexa-*tert*-butyl-37,39,41-trimethoxycalix[6]aren-38,40,42-triol ($X_6Me_3H_3$) (1.0 g, 0.99 mmol) in dry THF (20 mL) was introduced into a flask containing NaH (60% in oil, washed with pentane; 1.18 g, 29.5 mmol), dry THF (20 mL), and DMF (10 mL). The mixture was stirred for 20 minutes and 1-chloromethylpyrazole hydrochloride (PyzCl·HCl) (1.50 g, 9.85 mmol) was added over a period of 10 minutes. After 3 hours on refluxing, the solvents were concentrated under reduced pressure to a quarter of the volume and water (150 mL) was poured into the solution. The resulting precipitate was collected by filtration and dried under vacuum. The crude product was washed with pentane and filtration led to $X_6Me_3Pyz_3$ as a white solid (800 mg). The filtrate was evaporated. The residue was recrystallized from MeOH/pentane to yield $X_6Me_3Pyz_3$ as a white solid (242 mg). For elemental analyses, a sample was filtered through silica gel (CH_2Cl_2/MeOH 95:5 as eluent) and dried overnight under vacuum (0.1 Torr, 50 °C). − Yield: 83%. − M.p. 265 °C (decomp.). − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.82 (s, 27 H, tBu^2), 1.33 (s, 27 H, tBu^1), 2.22 (s, 9 H, OCH_3), 3.01 (br. s, 6 H, Ar-αCH$_{eq}$), 4.23 (br. s, 6 H, Ar-αCH$_{ax}$), 5.83 (s, 6 H, Pz-αCH$_2$), 6.31 (s, 3 H, PzH), 6.64 (s, 6 H, ArH^2), 7.13 (s, 6 H, ArH^1), 7.56 (s, 6 H, PzH). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.8 (Ar-αCH$_2$), 30.2 [C(*C*H$_3$)$_3$], 30.7 [C(*C*H$_3$)$_3$], 33.1 [*C*(CH$_3$)$_3$], 33.3 [*C*(CH$_3$)$_3$], 59.0 (OCH_3), 80.8 (Pz-αCH$_2$), 106.4 ($C_{Pz}H$), 123.1 ($C_{Ar}H$), 126.8 ($C_{Ar}H$), 129.6 ($C_{Pz}H$), 132.1 (C_{Ar}-CH$_2$), 132.7 (C_{Ar}-CH$_2$), 139.8 ($C_{Pz}H$), 144.9 (C_{Ar}), 146.6 (C_{Ar}), 149.0 ($C_{Ar}O$), 153.4 ($C_{Ar}O$). − IR (KBr): $\tilde{\nu}$ = 3480 (H_2O), 1522 (C=N), 1440, 1417, 1395, 1365 cm^{-1}. − $C_{81}H_{102}N_6O_6\cdot H_2O$ (1273.75): calcd. C 76.38, H 8.23, N 6.60; found C 76.23, H 8.01, N 7.01.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,39,41-trimethoxy-38,40,42-tris[(3,5-dimethyl-1-pyrazolyl)methoxy]calix[6]arene ($X_6Me_3DMPyz_3$) was synthesized from $X_6Me_3H_3$ (1.0 g, 0.99 mmol) following the procedure described for $X_6Me_3Pyz_3$ with NaH (60% in oil, 1.18 g, 29.5 mmol) and 1-chloromethyl-3,5-dimethylpyrazole hydrochloride (DMPyzCl·HCl) (1.07 g, 5.91 mmol). The crude product was recrystallized from THF/H_2O and dried for four hours under vacuum (0.1 Torr, 60 °C) to afford pure $X_6Me_3DMPyz_3$ (1.11 g). − Yield: 84%. − M.p. 150 °C (decomp.). − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.76 (s, 27 H, tBu^2), 1.38 (s, 27 H, tBu^1), 2.15 (s, 9 H, OCH_3), 2.19 (s, 9 H, Pz-CH$_3$), 2.27 (s, 9 H, Pz-CH$_3$), 2.98 (d, J = 15.2 Hz, 6 H, Ar-αCH$_{eq}$), 4.30 (d, J = 15.2 Hz, 6 H, Ar-αCH$_{ax}$), 5.73 (s, 6 H, Pz-αCH$_2$), 5.86 (s, 3 H, PzH), 6.58 (s, 6 H, ArH^2), 7.17 (s, 6 H, ArH^1). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.6 (Pz-CH$_3$), 13.3 (Pz-CH$_3$), 29.1 (Ar-αCH$_2$), 30.9 [C(*C*H$_3$)$_3$], 31.4 [C(*C*H$_3$)$_3$], 34.0 [*C*(CH$_3$)$_3$], 34.9 [*C*(CH$_3$)$_3$], 59.8 (OCH_3), 78.9 (Pz-αCH$_2$), 106.8 (PzH), 123.3 ($C_{Ar}H$), 127.7 ($C_{Ar}H$), 132.9 (C_{Ar}-CH$_2$), 133.4 (C_{Ar}-CH$_2$), 140.2 ($C_{Pz}CH_3$), 145.5 (C_{Ar}), 146.1 ($C_{Ar}H$), 148.3 ($C_{Pz}CH_3$), 149.7 ($C_{Ar}O$), 154.2 ($C_{Ar}O$). − IR (KBr): $\tilde{\nu}$ = 3480 (H_2O), 1569 (C=N), 1486, 1468, 1440, 1422, 1397, 1365, 1290 cm^{-1}. − $C_{87}H_{114}N_6O_6\cdot 4H_2O$ (1411.95): calcd. C 74.00, H 8.64, N 5.94; found C 74.05, H 8.42, N 5.65.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,39,41-trimethoxy-38,40,42-tris[2-(*N*,*N*-dimethylamino)ethoxy]calix[6]arene ($X_6Me_3Dmema_3$) was synthesized from $X_6Me_3H_3$ (1.0 g, 0.99 mmol) following the procedure described for $X_6Me_3Pyz_3$ with NaH (60% in oil, 1.18 g, 29.5 mmol) and (2-chloroethyl)dimethylamine hydrochloride (DmemaCl·HCl) (1.42 g, 9.85 mmol). The crude product was recrystallized from THF/H_2O and dried for four hours under vacuum (0.1 Torr, 60 °C) to afford pure $X_6Me_3Dmema_3$ (1.04 g). − Yield: 86%. − M.p. 185 °C (decomp.). − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.82 (s, 27 H, tBu^2), 1.38 (s, 27 H, tBu^1), 2.20 (s, 9 H, OCH_3), 2.36 (s, 18 H, NCH_3), 2.83 (br. s, 6 H, NCH_2), 3.45 (br. s,

6 H, Ar-αCH$_{eq}$), 4.00 (br. s, 6 H, OCH$_2$), 4.55 (br. s, 6 H, Ar-αCH$_{ax}$), 6.67 (s, 6 H, ArH^2), 7.27 (s, 6 H, ArH^1). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 29.2 (Ar-αCH$_2$), 30.3 [C(*C*H$_3$)$_3$], 30.8 [C(*C*H$_3$)$_3$], 33.1 [*C*(CH$_3$)$_3$], 33.4 [*C*(CH$_3$)$_3$], 45.3 (NCH$_3$), 58.2 (NCH$_2$), 59.2 (OCH$_3$), 70.0 (OCH$_2$), 122.8 (C$_{Ar}$H), 127.0 (C$_{Ar}$H), 132.3 (*C*$_{Ar}$-CH$_2$), 132.7 (*C*$_{Ar}$-CH$_2$), 144.7 (C$_{Ar}$), 144.8 (C$_{Ar}$), 151.2 (C$_{Ar}$O), 153.6 (C$_{Ar}$O). − IR (KBr): ṽ = 3560, 3480 (H$_2$O), 1485, 1470, 1460, 1440, 1417, 1395, 1365 cm^{-1}. − $C_{81}H_{117}N_3O_6{\cdot}H_2O$ (1246.85): calcd. C 78.03, H 9.62, N 3.37; found C 77.77, H 9.58, N 3.06.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,39,41-trimethoxy-38,40,42-tris[2-(pyrrolidinyl)ethoxy]calix[6]arene ($X_6Me_3Pyr_3$) was synthesized from $X_6Me_3H_3$ (1.0 g, 0.99 mmol) following the procedure described for $X_6Me_3Pyz_3$ with NaH (60% in oil, 1.18 g, 29.5 mmol) and 1-(2-chloroethyl)pyrrolidine hydrochloride (PyrCl·HCl) (1.68 g, 9.85 mmol). The crude product was recrystallized from CHCl$_3$/CH$_3$CN and dried overnight under vacuum (0.1 Torr, 60 °C) to afford pure $X_6Me_3Pyr_3$ (1.03 g). − Yield: 80%. − M.p. >230 °C (decomp.). − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.77 (s, 27 H, *t*Bu^2), 1.39 (s, 27 H, *t*Bu^1), 1.80 (br. s, 12 H, NCH$_2$C*H*$_2$), 2.19 (s, 9 H, OCH$_3$), 2.66 (br. s, 12 H, NC*H*$_2$CH$_2$), 3.02 (t, *J* = 6.4 Hz, 6 H, OCH$_2$C*H*$_2$N), 3.41 (d, *J* = 15.1 Hz, 6 H, Ar-αCH$_{eq}$), 4.06 (t, *J* = 6.4 Hz, 6 H, OC*H*$_2$CH$_2$N), 4.58 (d, *J* = 15.1 Hz, 6 H, Ar-αCH$_{ax}$), 6.64 (s, 6 H, ArH^2), 7.28 (s, 6 H, ArH^1). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 23.6 (NCH$_2$*C*H$_2$), 29.7 (Ar-αCH$_2$), 31.1 [C(*C*H$_3$)$_3$], 31.4 [C(*C*H$_3$)$_3$], 33.9 [*C*(CH$_3$)$_3$], 34.2 [*C*(CH$_3$)$_3$], 54.7 (N*C*H$_2$CH$_2$), 55.9 (OCH$_2$*C*H$_2$N), 60.1 (OCH$_3$), 71.7 (O*C*H$_2$CH$_2$N), 123.4 (C$_{Ar}$H), 128.0 (C$_{Ar}$H), 133.2 (*C*$_{Ar}$-CH$_2$), 133.6 (*C*$_{Ar}$-CH$_2$), 145.5 (C$_{ar}$), 145.8 (C$_{Ar}$), 151.8 (C$_{Ar}$O), 154.4 (C$_{Ar}$O). − IR (KBr): ṽ = 3490 (H$_2$O), 1482, 1460, 1438, 1418, 1395, 1363.1290, 1245 cm^{-1}. − $C_{87}H_{123}N_3O_6{\cdot}5H_2O$ (1397.02): calcd. C 74.79, H 9.52, N 3.00; found C 74.76, H 9.29, N 2.68.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,39,41-trimethoxy-38,40,42-tris[(1-methyl-2-benzimidazolyl)methoxy]calix[6]arene ($X_6Me_3Bzim_3$) was synthesized from $X_6Me_3H_3$ (0.80 g, 0.79 mmol) following the procedure described for $X_6Me_3Pyz_3$ with NaH (60% in oil, 0.94 g, 23.7 mmol) and 2-chloromethyl-1-methylbenzimidazole hydrochloride (BzimCl·HCl) (0.84 g, 4.72 mmol). The crude product was recrystallized from CH$_2$Cl$_2$/CH$_3$CN to afford $X_6Me_3Bzim_3$ (1.06 g). − Yield: 86%. − M.p. 276 °C (decomp.). − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.79 (s, 27 H, *t*Bu^2), 1.34 (s, 27 H, *t*Bu^1), 2.16 (s, 9 H, OCH$_3$), 3.31 (d, *J* = 15.0 Hz, 6 H, Ar-αCH$_{eq}$), 4.05 (s, 9 H, NCH$_3$), 4.49 (d, *J* = 15.0 Hz, 6 H, Ar-αCH$_{ax}$), 5.22 (s, 6 H, Bz-αCH$_2$), 6.65 (s, 6 H, ArH^2), 7.20 (s, 6 H, ArH^1), 7.26 (t, *J* = 7.7 Hz, 1 H, BzH), 7.31 (t, *J* = 7.7 Hz, 1 H, BzH), 7.38 (d, *J* = 7.7 Hz, 1 H, BzH), 7.74 (t, *J* = 7.7 Hz, 1 H, BzH). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 29.3 (Ar-αCH$_2$), 29.5 (NCH$_3$), 30.4 [C(*C*H$_3$)$_3$], 30.5 [C(*C*H$_3$)$_3$], 33.9 [*C*(CH$_3$)$_3$], 34.1 [*C*(CH$_3$)$_3$], 60.0 (OCH$_3$), 67.8 (Bz-αCH$_2$), 109.4 (C$_{Bz}$H), 120.0 (C$_{Bz}$H), 122.1 (C$_{Bz}$H), 123.0 (C$_{Bz}$H), 123.8 (C$_{Ar}$H), 127.9 (C$_{Ar}$H), 132.7 (C$_{Ar}$), 133.3 (C$_{Ar}$) 136.1 (C$_{Bz}$), 142.2 (C$_{Bz}$), 145.9 (C$_{Ar}$), 146.4 (C$_{Ar}$), 149.9 (C$_{Bz}$), 151.3 (C$_{Ar}$O), 154.1 (C$_{Ar}$O). − IR (KBr): ṽ = 1525 (sh, C=N), 1485, 1465, 1419, 1408, 1365, 1290, 1242 cm^{-1}. − $C_{96}H_{114}N_6O_6{\cdot}CH_2Cl_2{\cdot}0.5MeCN$ (1553.42): calcd. C 75.77, H 7.62, N 5.86; found C 75.85, H 7.53, N 5.76 (presence of solvent molecules was confirmed by ^{1}H NMR analysis).

5,11,17,23,29,35-Hexa-*tert*-butyl-37,39,41-trimethoxy-38,40,42-tris[(1-methyl-2-imidazolyl)methoxy]calix[6]arene ($X_6Me_3Imme_3$) was previously described.[11] We report here the ^{13}C NMR spectroscopic data (50 MHz, CDCl$_3$): δ = 29.5 (Ar-αCH$_2$), 31.2 [C(*C*^{2}H$_3$)$_3$], 31.7 [C(*C*^{1}H$_3$)$_3$], 33.5 (NCH$_3$), 34.1 [*C*^{2}(CH$_3$)$_3$], 34.3 [*C*^{1}(CH$_3$)$_3$], 60.2 (OCH$_3$), 66.9 (Im-αCH$_2$), 122.4 (C$_{Im}$H), 123.8 (C$^2_{Ar}$H), 127.9 (C$_{Im}$H), 128.2 (C$^1_{Ar}$H), 133.0 (*C*$_{Ar}$-CH$_2$), 133.7 (*C*$_{Ar}$-CH$_2$), 144.4 (C$_{Im}$), 146.0 (C$^2_{Ar}$), 146.3 (C$^1_{Ar}$), 151.4 (C$^2_{Ar}$O), 154.4 (C$^1_{Ar}$O).

5,11,17,23,29,35-Hexa-*tert*-butyl-37,39,41-trimethoxy-38,40,42-tris[(2-pyridinyl)methoxy]calix[6]arene ($X_6Me_3Pic_3$) was previously described.[9] We report here the ^{13}C NMR spectroscopic data (50 MHz, CDCl$_3$): δ = 29.7 (Ar-αCH$_2$), 31.2 [C(*C*H$_3$)$_3$], 31.6 [C(*C*H$_3$)$_3$], 34.0 [*C*(CH$_3$)$_3$], 34.2 [*C*(CH$_3$)$_3$], 60.2 (OCH$_3$), 74.9 (Py-αCH$_2$), 121.5 (C$_{Py}$H), 122.4 (C$_{Py}$H), 123.7 (C$_{Ar}$H), 128.0 (C$_{Ar}$H), 133.0 (*C*$_{Ar}$-CH$_2$), 133.7 (*C*$_{Ar}$-CH$_2$), 136.9 (C$_{Py}$H), 145.8 (C$_{Ar}$), 146.1 (C$_{Ar}$), 148.8 (C$_{Py}$H), 151.4 (C$_{Ar}$O), 154.4 (C$_{Ar}$O), 158.0 (C$_{Py}$).

$[X_6Me_3Pic_3{\cdot}H_3]^{3+}(ClO_4^-)_3$: A mixture of 70% aq. HClO$_4$ (0.1 mL) and MeOH (0.3 mL) was added to a solution of $X_6Me_3Pic_3$ (10 mg, 0.008 mmol) in CHCl$_3$ (2 mL). Precipitation with Et$_2$O gave a white solid. − Yield: 100%. − ^{1}H NMR (200 MHz, CD$_3$CN): δ = 0.89 (s, 27 H, *t*Bu), 1.32 (s, 27 H, *t*Bu), 2.60 (s, 9 H, OCH$_3$), 3.60 (br. s, 6 H, Ar-αCH$_{eq}$), 4.25 (br. s, 6 H, Ar-αCH$_{ax}$), 5.41 (s, 6 H, Py-αCH$_2$), 6.83 (s, 6 H, ArH), 7.33 (s, 6 H, ArH), 8.02 (t, *J* = 6.8 Hz, 3 H, PyH), 8.11 (d, *J* = 8.0 Hz, 3 H, PyH), 8.61 (t, *J* = 8.0 Hz, 3 H, PyH), 8.83 (t, *J* = 6.8 Hz, 3 H, PyH), 13.7 (br. s, 3 H, NH). − $C_{87}H_{108}Cl_3N_3O_{18}{\cdot}3H_2O$ (1644.20): calcd. C 63.55, H 6.99, N 2.56; found C 63.47, H 6.95, N 2.56.

$[X_6Me_3Dmema_3{\cdot}H_3]^{3+}(ClO_4^-)_3$ can be prepared either by the procedure described above for $[X_6Me_3Pic_3{\cdot}H_3]^{3+}(ClO_4^-)_3$ or by reaction of $X_6Me_3Dmema_3$ with $Zn(H_2O)_6(ClO_4)_2$. Under an argon atmosphere, CH$_3$CN (3 mL) was added into a flask containing $Zn(H_2O)_6(ClO_4)_2$ (29.8 mg, 0.080 mmol) and $X_6Me_3Dmema_3$ (98.3 mg, 0.080 mmol). The mixture was stirred for 3 hours, filtered through celite and concentrated to a sixth of the volume, leading to a white precipitate, which was separated by centrifugation, washed with MeOH (0.5 mL). Recrystallization in CH$_3$CN/Et$_2$O gave a white solid (57.5 mg). − Yield: 47%. − ^{1}H NMR (200 MHz, CD$_3$CN): δ = 0.85 (s, 27 H, *t*Bu), 1.36 (s, 27 H, *t*Bu), 2.25 (s, 9 H, OCH$_3$), 2.96 (s, 18 H, NCH$_3$), 3.51 (br. s, 6 H, NCH$_2$), 3.60 (br. s, 6 H, Ar-αCH$_{eq}$), 4.09 (br. s, 6 H, OCH$_2$), 4.40 (br. s, 6 H, Ar-αCH$_{ax}$), 6.76 (s, 6 H, ArH), 7.36 (s, 6 H, ArH). − $C_{80}H_{120}Cl_3N_3O_{18}$ (1530.19): calcd. C 63.58, H 7.90, N 2.75, Cl 6.95; found C 62.95, H 7.82, N 2.56, Cl 7.22.

$[X_6Me_3Pyr_3{\cdot}H_3]^{3+}(ClO_4^-)_3$ can be prepared either by the procedure described above for $[X_6Me_3Pic_3{\cdot}H_3]^{3+}(ClO_4^-)_3$ or by reaction of $X_6Me_3Pyr_3$ with $Zn(H_2O)_6(ClO_4)_2$. Under an argon atmosphere, CH$_3$CN (3 mL) was added into a flask containing $Zn(H_2O)_6(ClO_4)_2$ (21.7 mg, 0.058 mmol) and $X_6Me_3Pyr_3$ (76.1 mg, 0.058 mmol). The mixture was stirred for 3 hours, filtered through celite and concentrated to the third of the volume. Addition of Et$_2$O gave a white precipitate, which was separated by centrifugation and washed with Et$_2$O (43.3 mg). − Yield: 46%. − ^{1}H NMR (200 MHz, CD$_3$CN): δ = 0.80 (s, 27 H, *t*Bu), 1.39 (s, 27 H, *t*Bu), 2.12 (br. s, 12 H, NCH$_2$C*H*$_2$), 2.20 (s, 9 H, OCH$_3$), 3.4−3.8 (m, 24 H, NC*H*$_2$CH$_2$ + OCH$_2$C*H*$_2$N + Ar-αCH$_{eq}$), 4.17 (br. t, 6 H, OC*H*$_2$CH$_2$N), 4.45 (br. d, 6 H, Ar-αCH$_{ax}$), 6.70 (s, 6 H, ArH), 7.39 (s, 6 H, ArH). − $C_{87}H_{126}Cl_3N_3O_{18}{\cdot}H_2O$ (1626.31): calcd. C 64.25, H 7.93, N 2.58, Cl 6.54; found C 63.27, H 7.81, N 2.59, Cl 7.21.

$[Zn(X_6Me_3Bzim_3)(CH_3CN)](ClO_4)_2$: Under an argon atmosphere, CH$_3$CN (3 mL) was added into a flask containing $Zn(H_2O)_6(ClO_4)_2$ (32.9 mg, 0.088 mmol) and $X_6Me_3Bzim_3$ (128 mg, 0.088 mmol). The mixture was stirred for 3 hours, filtered through celite, and concentrated to a sixth of the volume, leading to a white precipitate, which was separated by centrifugation, washed with CH$_3$CN (0.1 mL) and dried under vacuum to yield a white solid (114 mg). − Yield: 72%. − M.p. 282 °C (decomp.). − ^{1}H NMR (400 MHz, CD$_3$CN): δ = 0.71 (s, 27 H, *t*Bu^1), 1.39 (s, 27 H, *t*Bu^2),

1.96 (s, 3 H, free CH_3CN), 2.77 (s, 9 H, OCH_3), 3.31 (d, J = 15.6 Hz, 3 H, Ar-αCH$_{eq}$), 3.42 (d, J = 15.2 Hz, 3 H, Ar-αCH$_{ax}$), 3.61 (d, J = 15.6 Hz, 3 H, Ar-αCH$_{eq}$), 3.91 (s, 9 H, NCH_3), 4.49 (d, J = 15.2 Hz, 3 H, Ar-αCH$_{ax}$), 5.48 (AB, J = 14.5 Hz, Δυ = 42.2 Hz, 6 H, Bz-αCH_2), 6.29 (d, J = 2.4 Hz, 3 H, ArH^1), 6.58 (d, J = 2.4 Hz, 3 H, ArH^1), 7.11 (d, J = 8.2 Hz, 3 H, BzH), 7.33 (d, J = 2.3 Hz, 3 H, ArH^2), 7.38 (t, J = 8.2 Hz, 3 H, BzH), 7.43 (d, J = 2.3 Hz, 3 H, ArH^2), 7.64 (t, J = 8.2 Hz, 3 H, BzH), 7.93 (d, J = 8.2 Hz, 3 H, BzH). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.7 (Ar-αCH$_{eq}$), 31.3 (Ar-αCH$_{ax}$), 31.5 [C(C^1H_3)$_3$], 31.7 [C(C^2H_3)$_3$], 32.9 (NCH_3), 34.6 [C^1(CH_3)$_3$], 35.0 [C^2(CH_3)$_3$], 60.0 (OCH_3), 65.1 (Bz-αCH_2), 113.6 ($C_{Bz}H$), 118.8 ($C_{Bz}H$), 122.7 ($C^1_{Ar}H$), 124.0 ($C^1_{Ar}H$), 126.4 ($C_{Bz}H$), 126.6 ($C_{Bz}H$), 129.6 ($C^2_{Ar}H$), 130.0 ($C^2_{Ar}H$), 132.3 (C_{Ar}-CH_2), 133.2 (C_{Ar}-CH_2), 133.7 (C_{Ar}-CH_2), 134.0 (C_{Ar}-CH_2), 135.9 (C_{Bz}), 139.5 (C_{Bz}), 146.6 (C^1_{Ar}), 148.5 (C^2_{Ar}), 153.0 ($C^1_{Ar}O$), 154.2 (C_{Bz}) 154.5 ($C^2_{Ar}O$). − IR (KBr): $\tilde{\nu}$ = 3490 (H_2O), 3420 (sh, H_2O), 1515 (sh, C=N), 1488, 1467, 1419, 1365, 1299, 1265, 1242, 1102 (ClO_4^-), 624 (ClO_4^-) cm^{-1}. − $C_{98}H_{117}Cl_2N_7O_{14}Zn{\cdot}3H_2O$ (1807.36): calcd. C 65.13, H 6.86, N 5.42; found C 65.03, H 6.76, N 5.31.

[Zn($X_6Me_3DMPyz_3$)(CH_3CN)](ClO_4)$_2$: Under an argon atmosphere, CH_3CN (3 mL) was added into a flask containing Zn(H_2O-)$_6$(ClO_4)$_2$ (35.6 mg, 0.096 mmol) and $X_6Me_3DMPyz_3$ (128 mg, 0.096 mmol). The mixture was stirred overnight, filtered through celite. Addition of Et_2O (5 mL) led to a yellow precipitate, which was separated by centrifugation. Recrystallization in CH_3CN/Et_2O yielded a white solid (77 mg). − Yield: 47%. − M.p. 256 °C (decomp.). − ^{1}H NMR (400 MHz, CD_3CN): δ = 0.77 (s, 27 H, tBu^1), 1.40 (s, 27 H, tBu^2), 1.95 (s, 9 H, $PzCH_3$), 1.96 (s, 3 H, free CH_3CN), 2.12 (s, 9 H, $PzCH_3$), 3.38 (AB, J = 15.8 Hz, Δν = 36 Hz, 6 H, Ar-αCH$_{eq}$), 3.61 (s, 9 H, OCH_3), 3.63 (d, J = 15.2 Hz, 3 H, Ar-αCH$_{ax}$), 4.66 (d, J = 15.2 Hz, 3 H, Ar-αCH$_{ax}$), 6.03 (AB, J = 14.1 Hz, Δν = 147 Hz, 6 H, Pz-αCH_2), 6.23 (s, 3 H, ArH^1), 6.49 (s, 3 H, PzH), 6.73 (s, 3 H, ArH^1), 7.33 (s, 3 H, ArH^2), 7.50 (s, 3 H, ArH^2). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.6 (Pz-CH_3), 13.3 (Pz-CH_3), 29.8 (Ar-αCH$_{eq}$), 31.5 [C(C^1H_3)$_3$], 31.6 (Ar-αCH$_{ax}$), 31.7 [C(C^2H_3)$_3$], 34.0 [C^1(CH_3)$_3$], 34.9 [C^2(CH_3)$_3$], 61.1 (OCH_3), 79.3 (Pz-αCH_2), 111.3 (PzH), 123.0 ($C_{Ar}H^1$), 124.6 ($C_{Ar}H^1$), 129.8 ($C_{Ar}H^2$), 129.9 (br, C_{Ar}-CH_2), 133.3 (br, C_{Ar}-CH_2), 133.9 (br, C_{Ar}-CH_2), 146.9 (C_{Ar}), 148.9 ($C_{Pz}CH_3$), 149.4 ($C_{Ar}H$), 153.1 ($C^2_{Ar}O$), 153.5 ($C^1_{Ar}O$), 154.9 ($C_{Pz}CH_3$). − IR (KBr): $\tilde{\nu}$ = 3460 (H_2O), 1560 (C=N), 1486, 1468, 1440, 1420, 1392, 1365, 1300, 1110 (ClO_4^-), 623 (ClO_4^-) cm^{-1}. − $C_{89}H_{117}Cl_2N_7O_{14}Zn{\cdot}4H_2O$ (1717.28): calcd. C 62.25, H 7.34, N 5.71; found C 61.92, H 7.13, N 5.51.

[Zn($X_6Me_3Pyz_3$)(H_2O)](ClO_4)$_2$: Under an argon atmosphere, CH_3CN (3 mL) was added into a flask containing Zn(H_2O)$_6$-(ClO_4)$_2$ (45.5 mg, 0.122 mmol) and $X_6Me_3Pyz_3$ (154 mg, 0.122 mmol). The mixture was stirred overnight and then evaporated under vacuum to give a white solid. − Yield: 100%. − M.p. 258 °C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3500 (H_2O), 1526 (C=N), 1485, 1468, 1417, 1398, 1365, 1120 (ClO_4^-), 625 (ClO_4^-) cm^{-1}. − $C_{81}H_{104}Cl_2N_6O_{15}Zn{\cdot}4H_2O$ (1610.08): calcd. C 60.42, H 7.01, N 5.22; found C 60.37, H 6.52, N 4.97.

[Zn($X_6Me_3Pyz_3$)(CD_3CN)](ClO_4)$_2$ was obtained by dissolving [Zn($X_6Me_3Pyz_3$)(OH_2)](ClO_4)$_2$ in the NMR tube containing CD_3CN. − ^{1}H NMR (400 MHz, CD_3CN): δ = 0.75 (s, 27 H, tBu^1), 1.39 (s, 27 H, tBu^2), 3.40 (d, J = 15.4 Hz, 6 H, Ar-αCH$_{eq}$), 3.59 (s, 9 H, OCH_3), 3.84 (br. s, 6 H, Ar-αCH$_{ax}$), 6.18 (s, 6 H, Pz-αCH_2), 6.46 (s, 6 H, ArH^1), 6.85 (t, J = 2.3 Hz, 3 H, PzH), 7.40 (s, 6 H, ArH^2), 7.99 (d, J = 2.3 Hz, 3 H, PzH), 8.08 (d, J = 2.3 Hz, 3 H, PzH). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.5 (Ar-αCH_2), 31.5 [C(C^1H_3)$_3$], 31.7 [C(C^2H_3)$_3$], 34.6 [C^1(CH_3)$_3$], 35.1 [C^2(CH_3)$_3$], 60.8 (OCH_3), 82.9 (Pz-αCH_2), 109.9 ($C_{Pz}H$), 123.7 ($C^1_{Ar}H$), 129.6 ($C^2_{Ar}H$), 133.3 (C_{Ar}-CH_2), 133.5 (C_{Ar}-CH_2), 138.1 ($C_{Pz}H$), 146.2 ($C_{Pz}H$), 146.7 (C^1_{Ar}), 149.0 (C^2_{Ar}), 153.1 ($C^2_{Ar}O$), 153.5 ($C^1_{Ar}O$).

[Zn($X_6Me_3Imme_3$)(CD_3CN)](ClO_4)$_2$ was obtained by dissolving the previously described[11] [Zn($X_6Me_3Imme_3$)(OH_2)](ClO_4)$_2$ in the

Table 2. Crystallographic data

Compound	$X_6Me_3Pyz_3$	[$X_6Me_3Pyr_3{\cdot}H_3$](ClO_4)$_3$	[Zn($X_6Me_3Imme_3$)(CH_3CN)](ClO_4)$_2$
Empirical formula	$C_{185}H_{208}N_{13}O_{13}$	$C_{190}H_{292}Cl_6N_6O_{40}$	$C_{176}H_{232}Cl_{36}N_{12}O_{12}Zn_2$
M	2581.44	3513.00	4114.92
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	Cc
a [Å]	14.6920(5)	20.431(1)	16.6180(2)
b [Å]	16.5900(6)	39.929(1)	28.8930(7)
c [Å]	19.1340(7)	25.772(1)	48.0280(1)
α [°]	73.508(1)		
β [°]	73.222(1)	107.835(1)	98.060(1)
γ [°]	66.769(1)		
V [Å^3]	4025.8(8)	20014(1)	22832.6(8)
Z	1	4	8
D_c [g·cm^{-3}]	1.06	1.16	2.39
Crystal colour	colorless	colorless	colorless
Crystal size [mm^3]	0.4 × 0.3 × 0.05	0.4 × 0.3 × 0.1	0.4 × 0.3 × 0.1
μ(Mo-K_α) [cm^{-1}]	0.67	13.57	13.6
Number of unique data	14840	8490	11547
Number of parameters refined	1825	2291	2424
Number used in refinement	14840	8490	11547
$R[F^2 > 4\sigma F^2]$	0.087	0.101	0.088
wR	0.236[a]	0.263[b]	0.252[c]
Goodness of fit	1.012	1.189	1.365
Residual Fourier [e·Å^{-3}]	−0.295; 0.678	−0.325; 0.072	0.648; 0.848

[a] $w = 1/[\sigma^2(F_o^2) + (0.1764P)^2 + 2.5989P]$ where $P = (F_o^2 + 2F_c^2)/3$. − [b] $w = 1/[\sigma^2(F_o^2) + (0.123P)^2 + 155.5258P]$ where $P = (F_o^2 + 2F_c^2)/3$. − [c] $w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

NMR tube containing CD_3CN. – ^1H NMR (400 MHz, CD_3CN): δ = 0.74 (s, 27 H, tBu^1), 1.40 (s, 27 H, tBu^2), 3.45 (d, J = 15.0 Hz, 6 H, Ar-αCH_{eq}), 3.58 (s, 9 H, OCH_3), 3.72 (s, 9 H, NCH_3), 4.16 (d, J = 15.0 Hz, 6 H, Ar-αCH_{ax}), 5.27 (s, 6 H, Im-αCH_2), 6.47 (s, 6 H, ArH^1), 7.00 (d, J = 1.5 Hz, 3 H, ImH), 7.39 (s, 6 H, ArH^2), 7.49 (d, J = 1.5 Hz, 3 H, ImH). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.5 (Ar-αCH_2), 31.5 [$C(C^1H_3)_3$], 31.8 [$C(C^2H_3)_3$], 34.6 [$C^1(CH_3)_3$], 34.9 [$C^2(CH_3)_3$], 35.2 (NCH_3), 60.8 (OCH_3), 64.8 (Im-αCH_2), 123.5 ($C^1_{Ar}H$), 124.7 ($C_{Im}H$), 128.2 ($C_{Im}H$), 129.6 ($C^2_{Ar}H$), 133.0 (C_{Ar}-CH_2), 133.5 (C_{Ar}-CH_2), 146.3 (C^1_{Ar}), 148.0 (C^2_{Ar}), 148.4 (C_{Im}), 153.4 ($C^1_{Ar}O$), 155.2 ($C^2_{Ar}O$).

Crystal Structure Determinations:[28] Diffraction data were measured on a Nonius KappaCCD diffractometer. Structures were solved by direct methods and refined using the program SHELXL97.[29] In all cases, the crystals were very sensitive to desolvation. Data are listed in Table 2.

$X_6Me_3Pyz_3$: Crystals were obtained by slow evaporation of a solution of ligand in a $CHCl_3/CH_3OH/CH_3CN$ mixture. The two ligands of the asymmetric unit co-crystallized with a CH_3CN solvate and one molecule of methanol. Interestingly, a mixture of two conformations could be determined from these molecules: one conformer corresponds to a ligand in which one pyrazole moiety is in the same relative orientation as the other two, with a methanol solvate inserted between the two molecules of the asymmetric unit; the second conformer corresponds to a ligand in which the same pyrazole is in a reverse orientation relative to the others, without methanol co-crystallized. The multiplicity of the disordered pyrazole arm and of the MeOH molecule was found to be equal to 0.5.

$[X_6Me_3Pyr_3{\cdot}H_3](ClO_4)_3$: Single crystals were grown by slow diffusion of Et_2O into an acetonitrile solution of the perchlorate salt. Each ligand co-crystallized with two molecules of Et_2O, and three ClO_4^- counterions. A static disorder could be determined for one pyrrolidine moiety in each molecule of the asymmetric unit, and they were split into two sites of equal multiplicity of 0.5. Due to the low data to parameter ratio, the structure was refined as two anisotropic blocs of parameters of roughly equal size, including some overlapping between them.

$[Zn(X_6Me_3Imme_3)(CH_3CN)](ClO_4)_2$: Single crystals were obtained by slow diffusion of Et_2O into a $CHCl_3/CH_3CN$ solution of the complex. The complex co-crystallized with some amount of $CHCl_3$ solvate, most of these molecules being characterized without ambiguity. However, two fragments were not well identified and correspond probably to disordered solvate. Due to the low data to parameter ratio, the structure was refined as two anisotropic blocs of parameters of roughly equal size, including some overlapping between them.

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[18] This average $Zn-N_{Im}$ bond length is slightly shorter and the zinc-nitrile distance slightly longer than those reported for the parent propionitrile adduct (1.996 Å and 1.985 Å, respectively), see ref.[11] This is in accordance with the lower donor ability of MeCN compared to EtCN.
[19] Except for $[Zn(X_6Me_3Pyz_3)(MeCN)](ClO_4)_2$, which was too soluble to be crystallized out of an acetonitrile solution.
[20] Under millimolar conditions, the half-life time was ca. 5 minutes. Kinetic and mechanistic studies on the exchange process are under investigation.
[21] In the case of $[Zn(X_6Me_3Bzim_3)(MeCN)](ClO_4)_2$ an unusual up-field shift for the OMe resonance is observed. A Dreiding model in fact showed that these methoxy groups are situated in the anisotropic cone of the aromatic benzimidazole moieties.
[22] Similar NMR profiles were obtained when the complexes were dissolved in $CDCl_3$ in the presence of CH_3CN, with a broad resonance at δ = –0.7. This confirmed the presence of a coordinating acetonitrile molecule inside the aromatic cavity in solution; see ref. [11].
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