12 February 2025

Ligand exchange in TREN-based Cobalt (II) funnel complexes in the solid state

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Abstract

The coordination of CoII with two calixarene-based TREN [tris(2-aminoethyl)amine] ligands is reported. The two ligands differ for the presence of three anisole groups (in Calix-TRENMe) or three phenol groups (in Calix-TRENH) in the macrocyclic structure surrounding the CoIITREN core. Dicationic complexes were synthesized and fully characterized both in solution and in the solid state. Surprisingly, a crystal-to-crystal transformation led to the substitution of the acetonitrile guest ligand by a pair of H-bonded water molecules. This gave rise to the first example of an X-ray characterized aqua-complex with a CoII center confined in a neutral, 5-coordinate N4(OH2) environment.

Keywords

Calixarenes, Cobalt, TREN, N-ligands, Funnel complex, Crystal to crystal transformation, Aqua-complex

https://doi.org/10.26434/chemrxiv-2025-mg4q6

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Abstract

The coordination of Co^{II} with two calixarene-based TREN [tris(2-aminoethyl)amine] ligands is reported. The two ligands differ for the presence of three anisole groups (in **Calix-TREN^{Me}**) or three phenol groups (in **Calix-TREN^{H}**) in the macrocyclic structure surrounding the Co^{II}TREN core. Dicationic complexes were synthesized and fully characterized both in solution and in the solid state. Surprisingly, a crystal-to-crystal transformation led to the substitution of the acetonitrile guest ligand by a pair of H-bonded water molecules. This gave rise to the first example of an X-ray characterized aqua-complex with a Co^{II} center confined in a neutral, 5-coordinate $N_4(OH_2)$ environment.

Keywords: Calixarenes – Cobalt – TREN – *N*-ligands – Funnel complex – Crystal to crystal transformation – Aqua-complex

Introduction

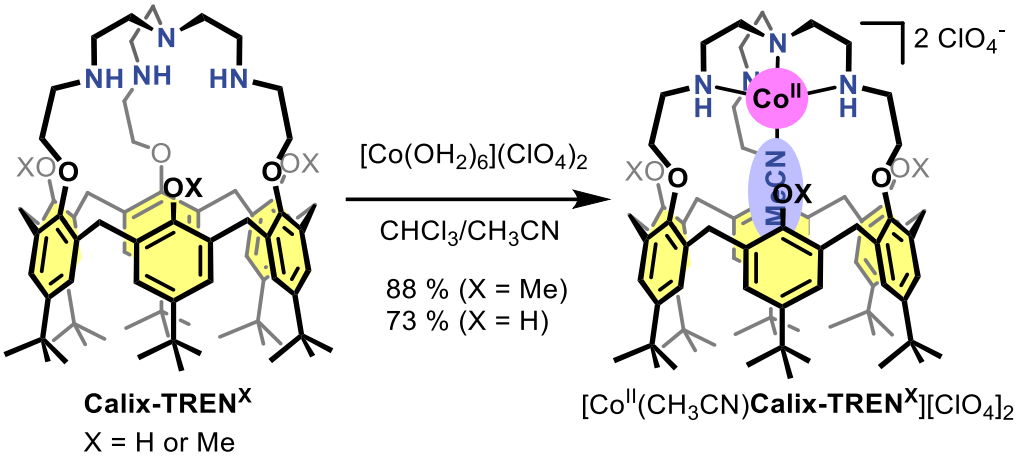
Tetradentate tripodal ligands can strongly bind to metal cations, leaving a fifth coordination site available for a solvent molecule. This site can be readily exchanged for a substrate, facilitating its activation at the metal centre and promoting catalytic activity. Among this class of ligands, tris(2-aminoethyl)amine) (TREN) represents a classical structure[1] that has also been incorporated into more sophisticated polymacrocyclic systems, such as cryptands.[2] Over the past decades, we have developed a family of cone-shaped ligands based on the calix[6]arene core, designed to serve as biomimetic models of metalloenzymes, wherein the metal centre is confined at the small rim of the calixarene conical cavity (funnel complexes).[3] In particular, Zn^{II} and $Cu^{II/I}$ complexes of a calix[6]arene-based ligand capped with a TREN unit, referred to as **Calix-TREN^{Me}** (Scheme 1), have been reported.[4] Guest-ligand exchange were explored in depth by NMR spectroscopy with the Zn^{II} complex, while $Cu^{II/I}$ complexes were studied for the detection of amines in water[5] and as redox centres for O_2 activation.[6] More recently, we demonstrated that the selective removal of the methyl groups from the three anisole moieties of the **Calix-TREN^{Me}** ligand, yielding the **Calix-TREN^{H}** ligand[7] (Scheme 1), significantly alters the coordination properties of Zn^{II} in the corresponding funnel complexes.[8] For instance, while the parent Zn^{II}**Calix-TREN^{Me}** complex appears reluctant to bind anionic guests, the Zn^{II}**Calix-TREN^{H}** complex, featuring phenol groups as a second coordination sphere, displays affinity for anions.

Co^{II} complexes containing a TREN unit, whether embedded within a macrocyclic structure or not, have been widely reported over the last few decades, encompassing a variety of structures and interesting properties. These Co^{II}TREN-based complexes have been studied for applications such as CO_2 uptake[9] and reduction[10] CO_2 and O_2 transport,[11] and nitric oxide activation.[12] These remarkable properties of Co^{II}TREN-based complexes have strongly motivated our exploration of the coordination chemistry of Co^{II} confined within the macrocyclic structures offered by the **Calix-TREN^{X}** ligands. This article presents the synthesis, the comprehensive chemical and structural characterization of these Co^{II} funnel complexes as well as a single crystal to single crystal host-guest exchange.

Results and Discussion

Spectroscopic behavior of dicationic complexes. Complexes [Co^{II}(CH_3CN)**Calix-TREN^{X}**][ClO_4]$_2$ (X = Me or H) were synthesized in a 1:1 v/v mixture of $CHCl_3$ and CH_3CN by reacting **Calix-TREN^{X}** with cobalt (II) perchlorate hexahydrate at room temperature (Scheme 1). As with the previously reported Zn^{II} and Cu^{II} complexes obtained with the same

ligands,[4,8] the formation of the cobalt complex was instantaneous in both cases, with no competitive protonation of the ligand observed under these conditions.



Scheme 1. Synthesis of funnel complexes $[Co^{II}(CH_3CN)$**Calix-TREN**$^{X}][ClO_4]_2$.

Both complexes were characterized in solution by 1D and 2D NMR spectroscopy. They appeared to be quite stable in CH_3CN under dry, air-free conditions but started decomposing after a few days, particularly in the presence of moisture. They display similar ^{1}H NMR spectra in the -1 to +10 ppm region (Figure 1). Multiple singlets in the high-field region, integrating for a total of 54 H, can be confidently attributed to the *t*Bu protons in both cases. By combining integration data, HMQC, HSQC and COSY correlations, all aromatic protons were identified (Figures S1-S3 and S8). Consistently with the ligand structure, the ^{1}H spectrum of $[Co^{II}(CH_3CN)$**Calix-TREN**$^{Me}]^{2+}$ shows additional resonances assigned to the OCH_3 groups. Peaks assignable to methylene groups were also detected in the low-field region (+10 to +300 ppm) but not for $[Co^{II}(CH_3CN)$**Calix-TREN**$^{H}]$, likely due to broadening of the resonances (Figure S12). The multiple ^{1}H signals associated with the calixarene core indicate that both complexes are C_1 symmetrical, as previously observed for the diamagnetic Zn^{II} analogues.[4c] The lack of symmetry stems from the heterochirality of the nitrogen stereocenters coordinating the metal ion. All these observations made in solution align well with the solid-state structure of $[Co^{II}(CH_3CN)$**Calix-TREN**$^{Me}]$ (*vide infra*). The magnetic moment, measured using the Evans method,[13] yielded values of $\mu_{eff} = 3.94\ \mu_B$ for $[Co^{II}(CH_3CN)$**Calix-TREN**$^{Me}]^{2+}$ and 4.03 μ_B for $[Co^{II}(CH_3CN)$**Calix-TREN**$^{H}]^{2+}$, which is in agreement with the theoretical value of 3.87 for a high spin Co(II) complex with three unpaired electrons (S = 3/2, Table S1).

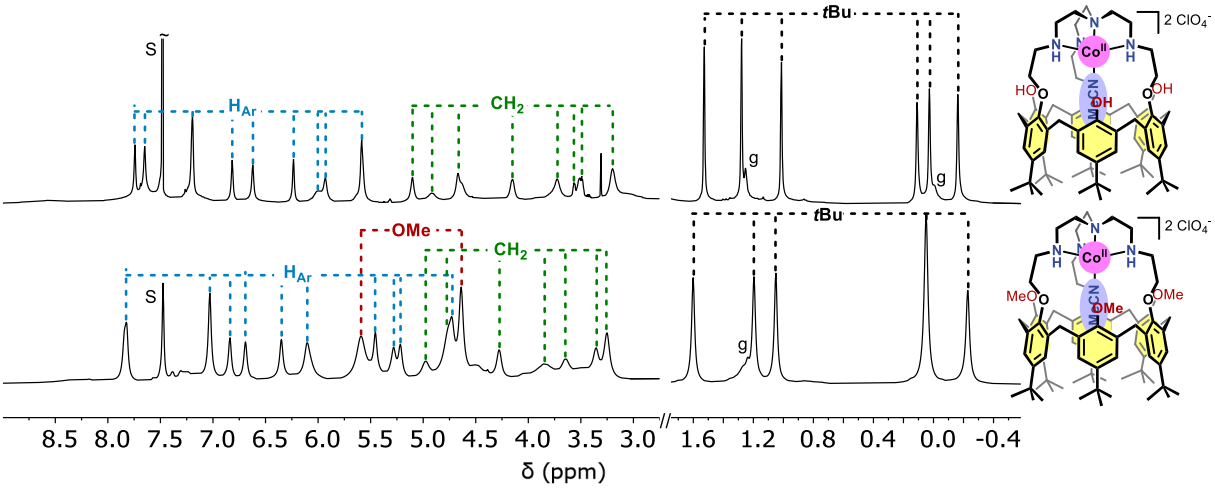


Figure 1. Regions (+2.5 to +9.5 ppm and -0.55 to +1.75 ppm) of the ^{1}H NMR spectra of [Co^{II}(CH$_3$CN)**Calix-TREN^{H}**][ClO$_4$]$_2$ (500 MHz, 298 K) (top) and [Co^{II}(CH$_3$CN)**Calix-TREN^{Me}**][ClO$_4$]$_2$ (600 MHz, 298 K) (bottom) in CD$_3$CN/CDCl$_3$ 1:1. The methylene protons detected here are part of the calixarene core, part of the TREN cap. Additional peaks are observable in the low-field region (+300 to +10 ppm) (see the SI), but some protons could not be detected. The *t*Bu region (-0.55 to 1.75 ppm) is unzoomed 8 times. "S" stands for CHCl$_3$ and "g" for grease.

The UV-Vis absorption spectra of the complexes showed two main absorption bands in the visible region at approximately 470 and 565/600 nm, with molar extinction coefficients (ε) in the range of 50 to 100 M^{-1}cm^{-1}, consistent with a 5-coordinate trigonal bipyramidal (TBP) environment (Figure 2).[14] Finally, their high-resolution mass (HRMS) (Figures S4 and S10) and FT-IR spectra further confirm the dicationic nature of the complexes associated with two perchlorate counterions (Figures S5 and S9, Table S2).[15]

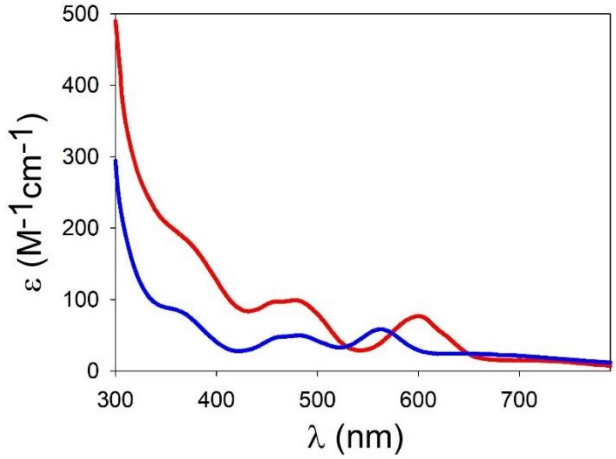


Figure 2. UV-Vis spectra (in CH$_3$CN/CH$_2$Cl$_2$ 1:1 v/v) of [Co^{II}(CH$_3$CN)**Calix-TREN^{Me}**][ClO$_4$]$_2$ (red) and [Co^{II}(CH$_3$CN)**Calix-TREN^{H}**][ClO$_4$]$_2$ (blue).

Molecular and crystal structures of [Co^{II}(G)Calix-$TREN^{Me}$][ClO_4]$_2$ complexes [G = CH_3CN or $(H_2O)_2$]. Pink crystals of [Co^{II}(CH_3CN)**Calix-$TREN^{Me}$**][ClO_4]$_2$ suitable for X-ray diffraction analysis were obtained by Et_2O diffusion into a CH_3CN solution of the complex. The structure, displayed in Figure 3, shows a 5-coordinate metal center with a CH_3CN guest ligand occupying the calixarene cavity. The Co^{II} cation reveals a slightly distorted TBP geometry with the τ parameter equaling 0.82 (1 for the ideal TBP and 0 for an ideal SQP) (Table S4).[16] The axis of the bipyramid is defined by the tertiary nitrogen from the TREN cap (N1), Co^{II} and the CH_3CN nitrogen (N5). The coordination mode of the NH groups is heterochiral, consistent with the ^{1}H NMR study in solution and as previously observed for analogous Cu^{II} and Zn^{II} complexes.[4] An intramolecular hydrogen bond connects an NH donor (N3) to one of the three methoxy oxygen atoms (O4) (Figure 3, Table S5). Two perchlorate ions per complex molecule balance the charge of the Co^{II} cation. One of them reveals a positional (static) disorder over two equally populated crystallographic positions, related by a twofold symmetry axis running through its oxygen O13 (Figure S13). The calixarene core adopts a flattened cone conformation, with the aromatic units alternatively oriented inward and outward relative to the cavity. The *t*Bu substituents of the anisole units are in *endo*-position, thus projecting the methoxy groups away from the guest coordination site. The same relative orientation, also observed with other metal ions (Zn^{II}, Cu^{II}), supports the idea that the nitrogen cap controls the conformation of the calixarene cavity. The complexes are interconnected via a *zig-zag* chain through two H-bonds involving the two remaining NH donors from the TREN cap (N2 and N4) and perchlorate oxygen atoms (O8, O9 and O14) (Figure S13, Table S5).

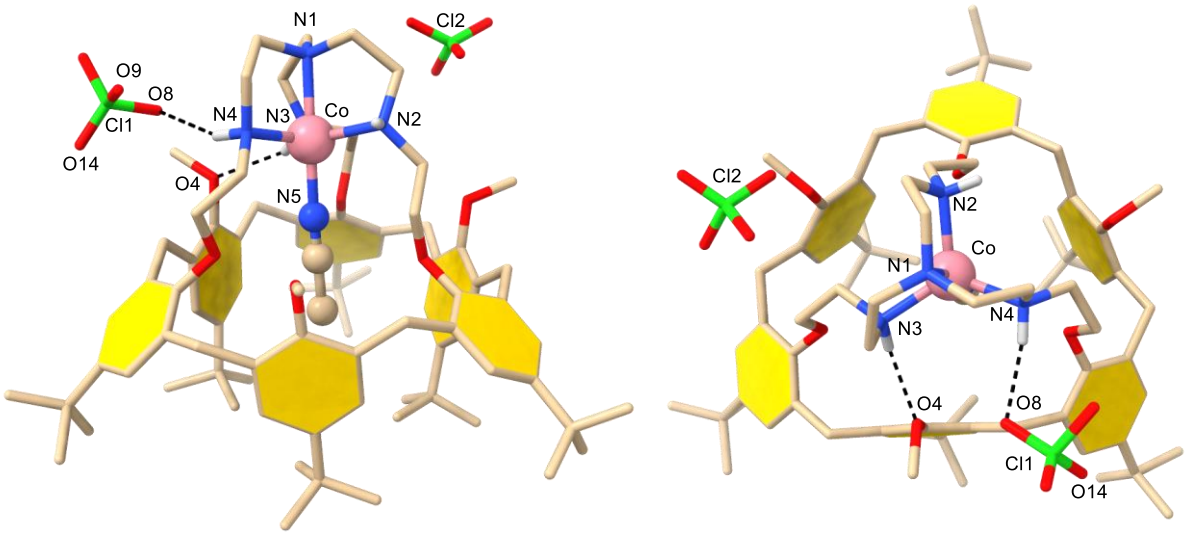


Figure 3. Side and top views of the crystal structure of [Co^{II}(CH_3CN)**Calix-$TREN^{Me}$**][ClO_4]$_2$. Hydrogen-bonds are indicated by dashed lines. H-atoms, except polar ones, are omitted for clarity.

Upon standing on the bench for six months, during which time the mother liquor had completely evaporated, the above described single crystals of [Co^{II}(CH_3CN)**Calix-TREN^{Me}**](ClO_4)$_2$ lost their intense pink color but their morphology was retained. A new dataset was thus collected at one of the pale pink specimens. The resulting XRD structure is shown in Figure 4.

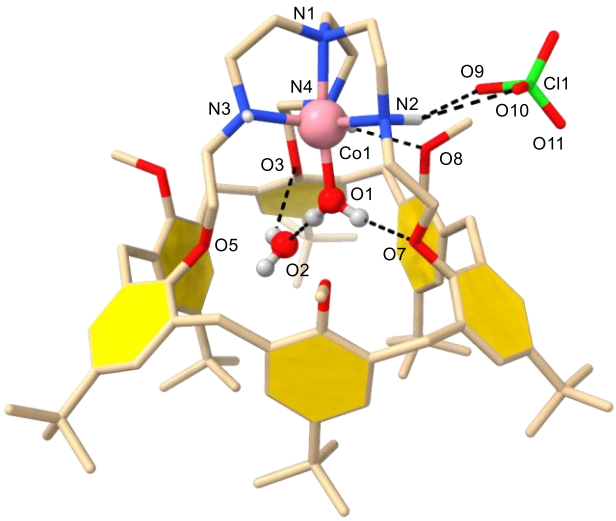


Figure 4. Crystal structure of [Co^{II}(OH_2···OH_2)**Calix-TREN^{Me}**][ClO_4]$_2$. Hydrogen bonds are indicated by black dashed lines. H-atoms, except polar ones, are omitted for clarity. Only one counterion is represented as the second one is highly disordered.

One out of the two perchlorate ions is involved in Hydrogen bonding, as in the case of [Co^{II}(H_2O)$_2$**Calix-TREN^{Me}**][ClO_4]$_2$, forming an infinite *zig-zag* chain of complex molecules connected *via* perchlorate anions (Cl1) (Figures 4 and S14, Table S5). The second perchlorate anion (positioned roughly at the emplacement equivalent to the disordered perchlorate of Cl2 in the parent structure of [Co^{II}(CH_3CN)**Calix-TREN^{Me}**][ClO_4]$_2$, see Figures S13 and S14), is hereby so heavily disordered, that modelling was not possible. However, high residual electrons density observed in this area (of 109 e^-) attests to the presence of the strongly positionally disordered perchlorate anion. In the final stages of refinement, this electron density was removed by the application of the solvent mask procedure.[17] This new structure mainly differs from the structure of the parent [Co^{II}(CH_3CN)**Calix-TREN^{Me}**][ClO_4]$_2$ by the absence in the calixarene cavity of the CH_3CN guest ligand and the presence of two water molecules, one being coordinated to the metal center. In this new complex, Co^{II} retains a slightly distorted trigonal bipyramidal coordination environment (τ = 0.78) with the parameters that are negligibly altered with respect to the analogue values observed in the parent structure (Table S4). The Co^{II}-O1(w) bond length is 2.007(5) Å, which is similar to that found in the parent

structure for Co^{II}-N5(MeCN), [2.046(4) Å] and lies in the typical range for Co^{II} centers bound to a neutral ligand (as attested by an analysis of a current version of CSD). The coordinated water molecule (O1) lies at a very short distance from the second water molecule (O2) [2.601(8) Å], denoting a very strong hydrogen bond linking these two guests. The coordinated water ligand (O1) is also, by means of an H-bond, connected to the calixarene skeleton, more precisely to one of the oxygen atom (O7) linked to the aza cap [*d*(O1 – O7) = 2.730(6) Å] (Table S5). Distances between O1 and two remaining oxygen linkers O3 and O5 are considerably longer (4.281 and 3.492 Å, respectively). The non-coordinated water guest (O2) is itself playing a role of an H donor in two H-bonding interactions within the cavity: one H-bond to the O3 from the calixarene linker [*d*(O2 – O3) = 3.074(8) Å], and an O-H···π interaction with one phenyl ring constitutive of the calixarene cavity [d (O2) ··· Centroid = 3.34 Å].[18]

We have previously reported on a *tris*(imidazolyl)-calixarene Zn^{II} complex in which two water molecules were also hosted in the cavity: the first water molecule was coordinated to the metal center while the second one was maintained via multiple H-bonds.[19] Interestingly, even if the first coordination sphere is different (*tris*(*N*-ethylimidazol *vs*. TREN), a virtually identical arrangement of coordinated and second intra-cavity water molecules is observed in this previously reported structure and in $[Co^{II}(H_2O)_2$**Calix-TREN^{Me}**$][ClO_4]_2$ (Figure 5). In both structures, the metal-coordinated water (O1 in Co complex, O7 in Zn complex) is involved in two hydrogen bonds – one with the bridging oxygen atom belonging to the linkers between the coordination core and the calixarene macrocycle (O7 in the Co complex, O1 in the Zn complex), and the other with the second intracavity entrapped water molecule (O2 in Co complex, O16 in Zn complex). The latter is involved, as a donor, to one such H-bond towards an oxygen (denoted O3 in both complexes) from the linker, and in an OH···π interaction with one of the phenyl rings of the calixarene basket (denoted cen1 in Co complex and cen2 in Zn complex).

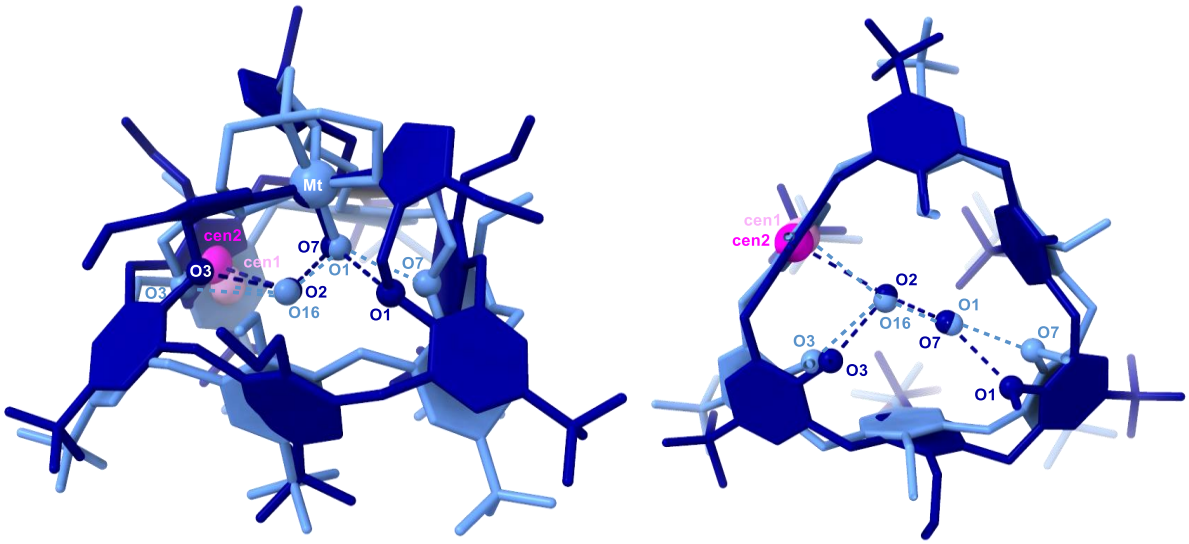


Figure 5. Side and top views of the overlap of the crystal structures of tris(N-ethylimidazol)calix[6]arene Zn-aqua complex (dark blue) and $[Co^{II}(H_2O)_2$**Calix-TREN**$^{Me}][ClO_4]_2$ (pale blue). In the case of the top view, the small rim substituents have been removed for clarity. Counter anions as well as H-atoms are omitted for clarity. Intracavity water molecules as well as atoms involved in the non-covalent interactions with them are presented in ball-and-stick style and labelled. The purple spheres represent the centroids (cen1 and cen2) of the aromatic units involved in OH···π interactions. Mt = Co^{2+} or Zn^{2+}.

Hence, the crystals underwent a single-crystal-to-single-crystal transformation by ligand exchange, a phenomenon previously studied and reported in a variety of cases.[20] This ligand exchange in which the acetonitrile guest molecule from the parent complex was replaced by a cluster containing two water molecules, was driven by the evaporation of acetonitrile. The coordination changes at the metal center did not at all impact the conformation of the calixarene macrocycle (Figure 6).

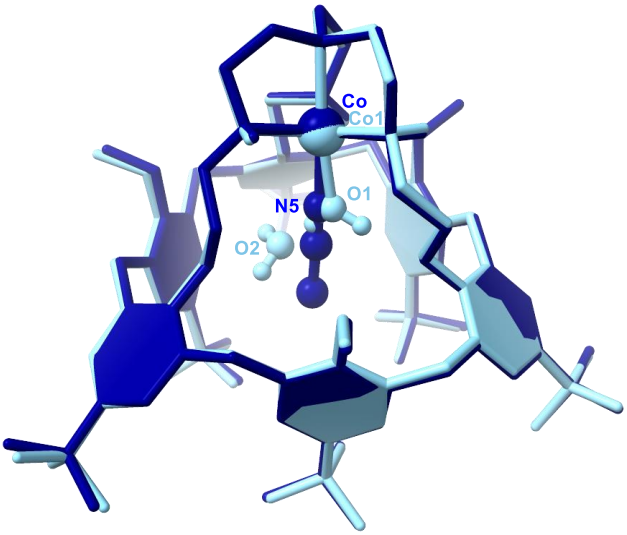


Figure 6. Overlap of the crystal structures of $[Co^{II}(H_2O)_2$**Calix-TREN^{Me}**$][ClO_4]_2$ (pale blue) and $[Co^{II}(CH_3CN)$**Calix-TREN^{Me}**$][ClO_4]_2$ (dark blue). H atoms, except polar ones, are omitted for clarity. Atoms of the intra-cavity guests are represented in ball-and-stick style.

Discussion and conclusion

This study reports on the synthesis and characterization in solution and in the solid state of Co^{II} complexes based on two ligands, **Calix-TREN^{Me}** and **Calix-TREN^{H}**. The two dicationic Co^{II} funnel complexes display a ^1H signature indicative of low C_1-symmetry, consistent with the crystal structures revealing heterochirality at the level of the three coordinating NH groups. All complexes have a high-spin state (S= 3/2) in solution. Two XRD structures were obtained, with the 5-coordinate TBP geometry at the metal center when bound to **Calix-TREN^{Me}**.

A chemical transformation within the single crystal of $[Co^{II}(CH_3CN)$**Calix-TREN^{Me}**$](ClO_4)_2$ is also reported. The long standing of the initial crystals in their mother liquor under air, favored the evaporation of CH_3CN to the benefit of water from the air. This triggered the substitution of the guest CH_3CN by two molecules of water. Apparently, the rigidification and protection provided by the macrocycle around the metal center made such a transformation possible within the crystal, providing further proof of the capacity of our systems to ensure an environment favoring the molecular exchange at the metal center even in the solid state. In order to further explore the influence of the calixarene cavity to the coordination behavior of Co^{II}, we have searched the current version of the CSD[21] for X-ray structures with determined 3D coordinates of mononuclear penta-coordinated aqua-Co^{II} complexes with a neutral N_4O coordination core, and we have found none at all. The structure of $[Co^{II}(H_2O)_2$**Calix-TREN^{Me}**$][ClO_4]_2$ is hence the first X-ray structure with such an coordination environment, which is apparently stabilized with the calixarene cavity. We have further searched the current version of CSD for structures

with the determined 3D coordinates for penta-coordinated mononuclear Co^{II} complexes of the TREN unit. In the set of resulting X-ray structures, the labile fifth position is occupied, in the vast majority of cases, by an anionic ligand (e.g. OH^-,[22] Cl^-,[23] N_3^-,[24] and NCS^-).[25] Very rare are the examples where the fifth donor is neutral: only two such structures are found containing CH_3CN[26] and only one with DMF[27] as a fifth ligand. Two of these structures feature some kind of a shield/cavity grafted to the TREN unit, in which this neutral ligand is entrapped: in one case, the CH_3CN guest is embedded in a resorcinarene unit capped by the TREN ligand, and in the second one, the DMF ligand sits in the aromatic environment provided by the *N*-benzyl substituents. Finally, it is interesting to relate the herein presented guest ligand substitution in the solid state to one of our previous reports concerning copper complexes obtained with a calix[6]arene capped by a TMPA [*tris*(2-methylpyridylamine] core. Indeed, we noticed that traces of acetonitrile vapor led to the substitution of the water guest ligand not only in solution[28] but also in the solid state when the complex was kept as a powder.[29] In the case of the Cu^I state, we also reported an oxygenation reaction occurring in the solid state. In this transformation, dioxygen from air is kept and activated by the Cu^I center confined in the TMPA cap linked to the calixarene funnel.[30]

Hence, these funnel complexes exhibit quite unique properties that are promising for catalysis, and we are currently exploring the redox behavior of their cobalt versions. We expect that the confinement of the guest at the labile site in a funnel-shape cavity may lead to unusual catalytic properties (in terms of selectivity and products obtained), *e.g.* in electroreduction of small molecules such as water or CO_2.

Acknowledgements.

This research was supported by the French Ministry for Higher Education and Research, the Agence Nationale pour la Recherche (MARCEL project, grant number ANR-21-CE50-0034-MARCEL) as well as by Croatian Science Foundation (grant: IP-2020-02-3786, PI: A. Višnjevac). The authors acknowledge the support of the Biomedical NMR platform, Université Paris Cité, Paris, France. We thank the Centre d'Instrumentation en REsonance Magnétique – CIREM (Université libre de Bruxelles – ULB, Belgium) for providing support and access to its infrastructure. The CIREM NMR spectrometers used in this work have been funded by the Fonds de la Recherche Scientifique (F.R.S.-FNRS – GEQ2011-2.5014.12 and F.R.S.-FNRS – FRFC-2.4.517.05) and the Fonds d'Encouragement à la Recherche (FER-ULB).

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Notes

The authors declare no competing financial interest.

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15 The number of perchlorate ions is calculated by relative integration of one peak characteristic of ClO4 and one peak characteristic of the calix[6]arene core. The obtained ratios are then compared to those calculated for many different calix[6]arene-based complexes that we reported previously, either mono- or di-cationic.

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