Funnel Complexes with Co^{II} and Ni^{II}: New Probes into the Biomimetic Coordination Ability of the Calix[6]arene-Based Tris(imidazole) System

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The coordination properties of the calix[6]arene-based tris(imidazole) ligand $X_6Me_3Imme_3$ were further explored with Co^{II} and Ni^{II}. This imidazole system stabilizes tetrahedral mononuclear Co^{II} complexes with an exchangeable fourth exogenous ligand (water, alcohol, amide) located at the heart of the hydrophobic calixarene cavity. With a weak donor ligand such as a nitrile, both four-coordinate tetrahedral and five-coordinate trigonal bipyramidal complexes were obtained. The latter contains a second nitrile molecule *trans* to the included guest nitrile. These complexes were characterized in solution as well as in the solid state. The Ni^{II} complexes are square-based pyramidal five-coordinate edifices with a guest nitrile inside the cavity and a water molecule outside. A comparison with previously described Zn^{II} and Cu^{II} complexes emphasizes the flexibility of this ligand. A comparison with carbonic anhydrase, a mononuclear zinc enzyme with a tris(histidine) coordination core, shows that $X_6Me_3Imme_3$ displays many structural features of this enzyme except for the *cis* coordination of the exogenous ligands.
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Introduction

Coordination of metal ions by nitrogen donors is ubiquitous in metalloenzyme active sites. This has been a tremendously rich source of inspiration for coordination chemists, and over the last 25 years or so the syntheses of countless poly-aza ligands have been developed and their coordination chemistry explored. The tris(histidine) motif, frequently encountered in the case of zinc and copper enzymes,[1,2] has guided the architecture of the tri-aza ligands. Among the most famous artificial tripodal systems are the tris(pyrazolyl)borates,[3] also called scorpionate ligands, and triazacyclononanes.[4,5] However, the use of tris(imidazole) ligands, although closer to the tris(histidine) core, is somewhat rare in the modeling of active sites.[6−8]

In recent years we have described a novel supramolecular system based on a calix[6]arene bearing three nitrogen arms. Upon coordination to Cu^{I},[9,10] Cu^{II} [11,12] or Zn^{II} [13,14] the calixarene structure becomes constrained in a cone conformation accessible to a guest molecule. The most biomimetic ligand of the series, a tris(imidazole)-based system, provided the first structurally characterized model for the aqua dicationic tetrahedral Zn^{II} center found in hydrolytic enzymes.[15] The Cu^{I} complexes were able to bind CO reversibly, just as Cu^{I} enzymes do.[10]

A usual probe for the coordinating ability and flexibility of enzymatic active sites is the substitution of the native metal by other metals displaying different coordination requirements. As we were interested in further exploring the new perspectives offered by our supramolecular system and evaluating its flexibility as well as the geometrical constraints that it is able to provide on the metal ion coordination core, we decided to study its ability to bind to other first-row elements. In this paper, we describe the synthesis, characterization and host-guest behavior of Co^{II} and Ni^{II} complexes obtained with the tris(imidazole)-based system $X_6Me_3Imme_3$. A comparison with Zn^{II} and Cu^{II} complexes as well as with carbonic anhydrase, a zinc enzyme prototype,[16,17] highlights this ligand's biomimetic behavior.

Results

Synthesis and Characterization of a Tetrahedral Co^{II}-Aqua Complex

The calix[6]arene-based tris(imidazole) ligand $X_6Me_3Imme_3$ [13] was reacted with $[Co^{II}(H_2O)_6(ClO_4)_2]$ in THF.

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Upon addition of 1.1 equivalents of $X_6Me_3Imme_3$ to the pale pink cobalt solution, the color immediately changed to an intense purple. Precipitation with Et_2O led to a purple solid. Its IR spectrum attested to the presence of the perchlorate counterions, and its elemental analysis was in good agreement with a 1:1 ligand/Co ratio. The magnetic moment at 300 K was assessed by the Evans method in $CDCl_3$.[18,19] The measured value of 4.6(2) μ_B,[20] although exceeding the spin-only value of 3.87 μ_B for $S = 3/2$, falls in the typical range for high-spin cobalt(II) complexes.[21] The UV/Vis spectrum in CH_2Cl_2 exhibits three bands between 450 and 650 nm with extinction coefficients above 300 $\text{M}^{-1}\cdot\text{cm}^{-1}$ characteristic of the ${}^4A_2 \rightarrow {}^4T_1(P)$ d-d transitions of a tetrahedral (Td) high-spin cobalt(II) ion.[21,22]

In $CDCl_3$, the ${}^1H$ NMR spectrum of the complex (Figure 1A) displays well-defined isotropically shifted resonances in the $\delta = 0-90$ ppm spectral window, with the expected number of signals for a C_{3v} symmetrical species, thereby suggesting the coordination of all three imidazoles to Co^{II}. The assignment of the resonances was performed by integration of the peaks and comparison with similar complexes obtained with ligands bearing ethyl substituents instead of methyl on the phenyoxyl or imidazolyl rings.[10] Two sets of signals could be distinguished: the imidazole protons (OCH_2, NCH_3 and both ImH) are shifted downfield in the $\delta = 15-80$ ppm region, whereas the protons of the calixarene skeleton (ArH, *t*Bu, $ArCH_2Ar$, OMe) appear in the diamagnetic region with chemical shifts quite similar to those of the parent diamagnetic zinc(II) complex (Figure 1B).

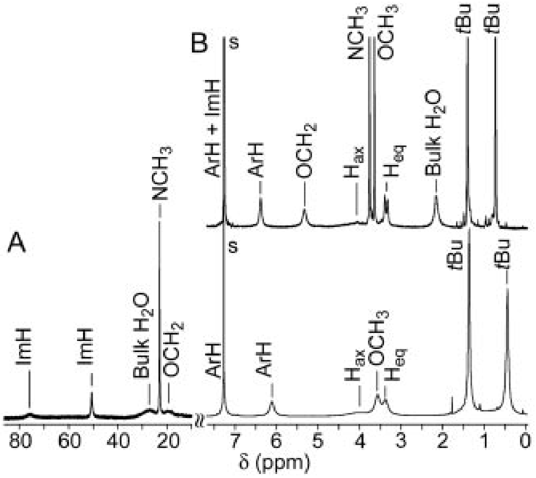
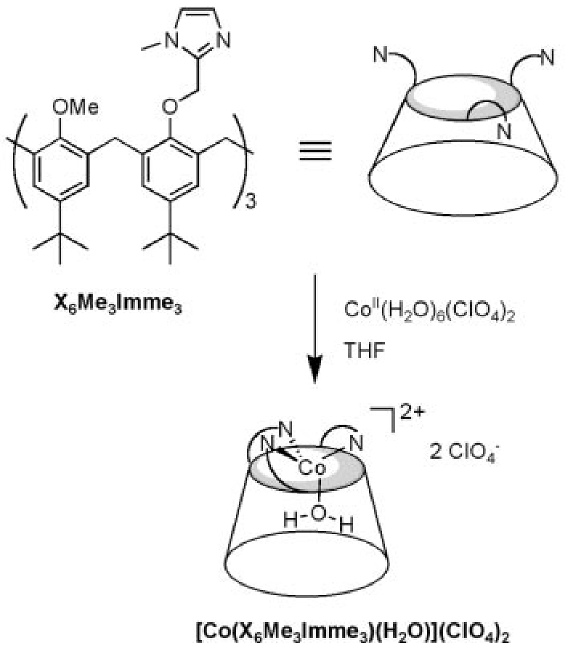


Figure 1. ${}^1H$ NMR spectra (250 MHz, 300 K, $CDCl_3$) of (A) $[Co(X_6Me_3Imme_3)(H_2O)](ClO_4)_2$ and (B) $[Zn(X_6Me_3Imme_3)(H_2O)\cdot(H_2O)](ClO_4)_2$; the residual solvent peak is labeled "s"

The very small shifts observed for the calixarene protons are highly suggestive of a tetrahedral geometry, for which the magnetic susceptibility is isotropic and the Fermi-contact interaction, which propagates along covalent bonds, is the only contribution to the hyperfine shift (no dipolar contribution).[19] Indeed, in this system, the calixarene protons are separated from the cobalt ion by at least eight bonds.

Since no other ligand beside water is available in a non-coordinating solvent such as THF, diethyl ether or chloroform, in agreement with all the above described spectroscopic data, we conclude that the isolated species is a tetrahedral cobalt(II) complex in which a water molecule is the fourth ligand, as was found in the parent zinc complex (Scheme 1).[23]



Scheme 1. Formation of the tetrahedral Co^{II}-aqua complex

Host/Guest Chemistry: A Solid-State Study

X-ray quality crystals of the complex $[Co(X_6Me_3Imme_3)(CH_3COCH_3)](ClO_4)_2$ were obtained by slow diffusion of Et_2O into a solution of the aqua complex in acetone. Three other complexes $[Co(X_6Me_3Imme_3)(L)](ClO_4)_2$ (L = DMF, EtOH and EtCN) were crystallized using the same procedure, but with the addition of about 10 equivalents of L to the acetone solution.

All four complexes display a nearly tetrahedral cobalt(II) ion coordinated by the three imidazole rings of the calixarene ligand, which stands in a flattened-cone conformation (Figure 2, Table 1). The fourth ligand, L, sits inside the calixarene cavity. Two perchlorate ions attest to the dicationic nature of the complexes. The average $Co-N_{Im}$ distances are short and very similar in all complexes (2.003, 2.003, 2.004 and 2.000 Å for L = Me_2CO, DMF, EtOH and EtCN, respectively). The bond between the metal ion and the coordinating atom of the guest ligand is also quite short, thereby reflecting the high Lewis acidity of the metal center in such a tetrahedral dicationic environment. Supramolecular interactions are observed between the calixarene host cavity and the guest ligand L. The structure of the acetone complex displays several CH···π interactions: each methyl group of the guest selectively faces an anisole ring at a short perpen-

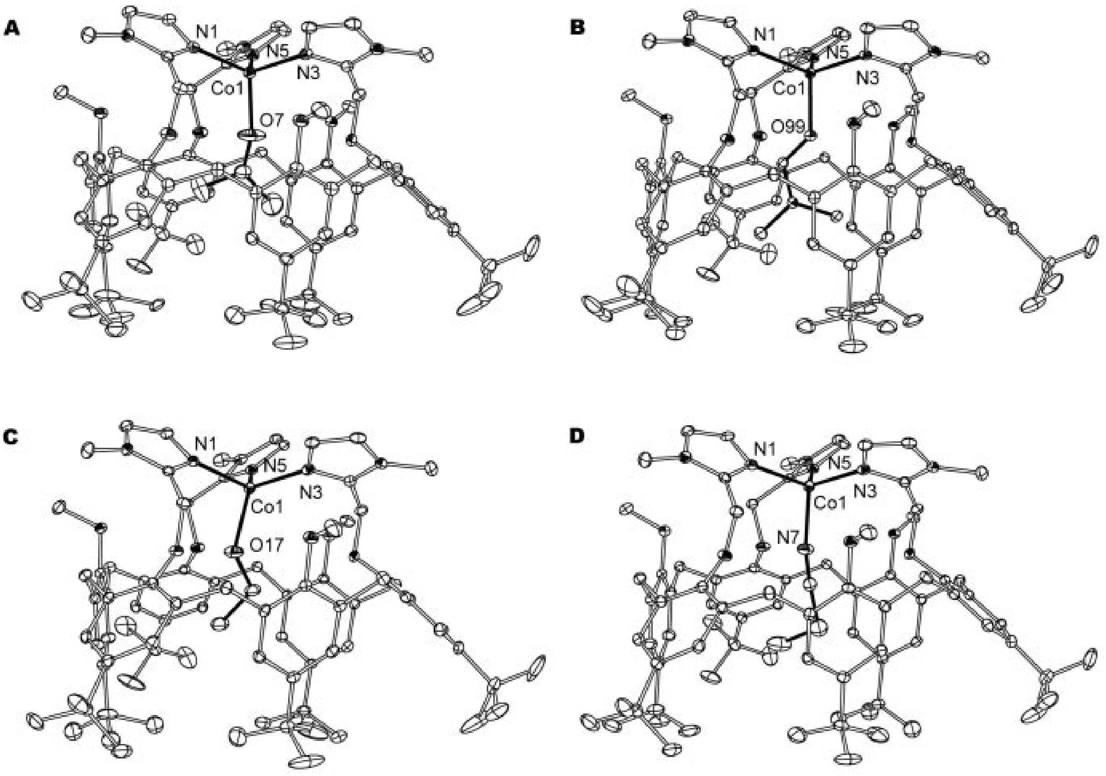


Figure 2. X-ray structures of tetrahedral complexes $[Co(X_6Me_3Imme_3)(L)](ClO_4)_2$ showing ellipsoids at 20% probability; L = (A) Me_2CO, (B) DMF, (C) EtOH, (D) EtCN; hydrogen atoms, perchlorate counterions and solvent of crystallization are omitted for clarity

Table 1. Selected bond lengths (Å) and angles (°) for complexes $[Co(X_6Me_3Imme_3)(L)](ClO_4)_2$

L	Bond length (Å)		Angles (°)			
Me_2CO	Co1−N1	2.000(4)	N1−Co1−N3	117.27(15)	O7−Co1−N1	114.0(3)
	Co1−N3	2.005(4)	N1−Co1−N5	105.95(16)	O7−Co1−N3	104.5(2)
	Co1−N5	2.004(4)	N3−Co1−N5	108.57(16)	O7−Co1−N5	106.0(2)
	Co1−O7	1.925(4)				
DMF	Co1−N1	1.994(3)	N1−Co1−N3	118.72(10)	O99−Co1−N1	108.38(10)
	Co1−N3	1.991(3)	N1−Co1−N5	106.81(10)	O99−Co1−N3	103.07(10)
	Co1−N5	2.025(2)	N3−Co1−N5	110.08(11)	O99−Co1−N5	109.54(10)
	Co1−O99	1.929(2)				
EtOH	Co1−N1	2.008(3)	N1−Co1−N3	116.41(13)	O17−Co1−N1	97.3(14)
	Co1−N3	2.005(3)	N1−Co1−N5	106.60(13)	O17−Co1−N3	113.96(16)
	Co1−N5	1.999(3)	N3−Co1−N5	107.37(14)	O17−Co1−N5	114.99(14)
	Co1−O17	1.986(3)				
EtCN	Co1−N1	1.996(3)	N1−Co1−N3	119.14(13)	N1−Co1−N7	105.97(16)
	Co1−N3	2.002(3)	N1−Co1−N5	106.37(13)	N3−Co1−N7	107.04(14)
	Co1−N5	2.003(3)	N3−Co1−N5	110.40(12)	N5−Co1−N7	107.32(15)
	Co1−N7	1.956(4)				

dicular distance, C···Ar, of 3.23 and 3.30 Å. With L = DMF, the guest methyl groups also appear selectively oriented towards an aromatic ring [d(C···Ar) = 3.37 and 3.45 Å] and an additional CH···π contact is observed between the O=C−H group and an anisole ring (3.90 Å). For L = EtOH and EtCN, CH···π interactions with both CH_2 and CH_3 groups are observed. In the case of the EtOH adduct, a hydrogen bond between the coordinated hydroxy group and one oxygen linked to an imidazole arm [*d*(O,O) = 2.78 Å] further stabilizes the edifice. Finally, it is noteworthy that the average distances between two *t*Bu groups in the "out" position (those of the aromatic rings bearing imidazole) are almost identical in all four complexes (12.89 Å, 12.67 Å, 12.70 Å and 12.81 Å for L = CH_3COCH_3, DMF, EtOH and EtCN, respectively) whereas those between two *t*Bu groups in the "in" position differ significantly (6.39 Å, 7.07 Å, 6.30 Å and 6.83 Å, respectively). This shows that coordination to Co^{II} ion freezes the positions of the *p*-*t*Bu-ArO-CH_2Im moieties, the equality of the *t*Bu−*t*Bu distances reflecting the equality of the $Co-N_{Im}$ bond lengths and geometry in the four complexes. In contrast, the positions of *p*-*t*Bu-ArOMe are adjusted by the supramolecular system in order to optimize the size of the cavity and the stabilizing interactions with the guests.

In addition to these four tetrahedral complexes, another complex was crystallized from pure MeCN by Et_2O vapor diffusion. The structure (Figure 3, Table 2) shows a cobalt ion surrounded by five ligands in a distorted trigonal bipyramidal geometry (TBP, $\tau = 0.69$).[24] The three imidazole moieties of $X_6Me_3Imme_3$ sit in the equatorial positions and the two axial positions are occupied by MeCN molecules, one of them being buried inside the calixarene cavity and the other lying outside. The average $Co-N_{Im}$ and Co−N7 (inner nitrile) bond lengths are longer (2.053 and 2.078 Å, respectively) in this complex than in the tetrahedral EtCN adduct. The Co−N8 distance (2.171 Å) reveals that the outer nitrile is bound more weakly to Co than the inner one.

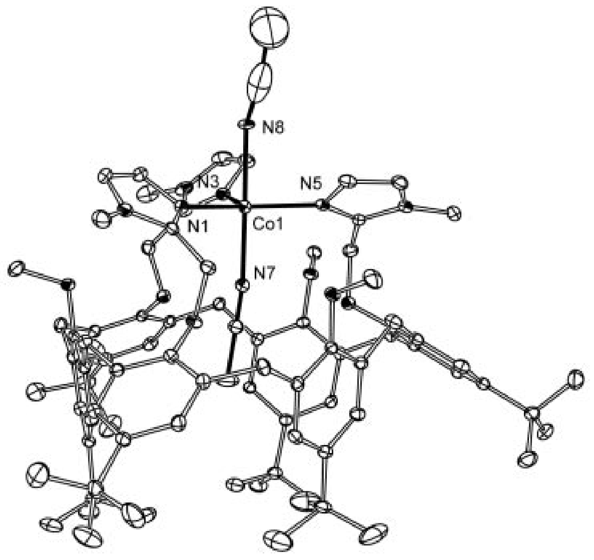


Figure 3. X-ray structure of $[Co(X_6Me_3Imme_3)(MeCN)_2](ClO_4)_2$ showing ellipsoids at 20% probability; hydrogen atoms, perchlorate counterions and solvent of crystallization are omitted for clarity

Table 2. Selected bond lengths (Å) and angles (°) for $[Co(X_6Me_3Imme_3)(MeCN)_2](ClO_4)_2$

Bond length (Å)			
Co1−N1	2.046(4)	Co1−N7	2.078(4)
Co1−N3	2.053(4)	Co1−N8	2.171(4)
Co1−N5	2.061(4)		
Angles (°)			
N1−Co1−N3	110.00(15)	N5−Co1−N7	93.76(14)
N1−Co1−N5	133.15(15)	N1−Co1−N8	84.95(15)
N3−Co1−N5	115.88(15)	N3−Co1−N8	89.93(16)
N1−Co1−N7	91.10(15)	N5−Co1−N8	86.13(15)
N3−Co1−N7	95.12(15)	N7−Co1−N8	174.43(17)

Thus, these structures confirm that the $X_6Me_3Imme_3$ system can stabilize dicationic tetrahedral cobalt(II) complexes with a guest in the cavity. The inner aqua ligand that is present in the complex isolated during the synthesis in a non-coordinating solvent is easily displaced by a coordinating molecule. In the specific case of MeCN, coordination of a second nitrile ligand was evidenced, yielding a five-coordinate species. This was further studied in solution.

Host/Guest Chemistry: UV/Vis and ^1H NMR Spectroscopic Studies in Solution

In solution the host/guest behavior of the calix[6]arene-Co^{II} system towards alcohols, nitriles and amides was monitored by UV/Vis and ^1H NMR spectroscopy by adding aliquots of these coordinating co-solvents, L, to a CH_2Cl_2 or $CDCl_3$ solution of $[Co(X_6Me_3Imme_3)(H_2O)](ClO_4)_2$. With L = EtOH, the extinction coefficients of the three $^4A_2 \rightarrow {}^4T_1(P)$ d-d transitions increased until a plateau was reached with ε values of 280, 400 and 450 $M^{-1}\cdot cm^{-1}$ at 524, 566 and 593 nm, respectively. An isosbestic point was observed at 615 nm, demonstrating the presence of only two species in solution. When increasing amounts of EtOH were introduced into an NMR tube containing a solution of $[Co(X_6Me_3Imme_3)(H_2O)](ClO_4)_2$ in $CDCl_3$ (approx. 10^{-2} M), resonances characteristic of a new complex progressively appeared while those of the aqua complex diminished. The profile of the new species resembled that of the tetrahedral aqua complex and remained unchanged whatever the EtOH concentration, with constant shifts for all signals. Here again, the signals of the calixarene structure were weakly hyperfine-shifted compared to the zinc analogue. Although the bound EtOH resonances were not located, these UV/Vis and NMR titrations are in agreement with the progressive exchange of the aqua ligand by EtOH until complete formation of the tetrahedral $[Co(X_6Me_3Imme_3)(EtOH)]^{2+}$ complex. A similar behavior was observed with other alcohols (*n*PrOH and *i*PrOH).

With MeCN as a co-solvent, no isosbestic point was observed during the UV/Vis titration, suggesting that more than two species are present. Two steps were observed in the evolution of the electronic spectra. Upon addition of MeCN, the apparent extinction coefficients of three $^4A_2 \rightarrow {}^4T_1(P)$ bands first increased to over 500 $M^{-1}\cdot cm^{-1}$, then subsequently decreased, down to a plateau with lower ε values (170, 260 and 230 $M^{-1}\cdot cm^{-1}$ at 530, 566 and 595 nm, respectively). This can be interpreted as the successive formation of a four-coordinate complex, namely $[Co(X_6Me_3Imme_3)(MeCN)]^{2+}$, as shown by the increase of ε values, and then a five-coordinate one, $[Co(X_6Me_3Imme_3)(MeCN)_2]^{2+}$ becoming predominant at a high $MeCN/CH_2Cl_2$ ratio, in agreement with the decrease of ε, with final values lower than 300 $M^{-1}\cdot cm^{-1}$. ^1H NMR spectroscopy confirmed this observation (Figure 4). When aliquots of MeCN were added to a $CDCl_3$ solution of the aqua complex (approx. 10^{-2} M), additional sharp resonances developed, attesting to the coordination of MeCN to Co^{II}. At substoichiometric MeCN concentration, the CH_3 resonance of a bound MeCN was detected at $\delta \approx 40$ ppm; the new OCH_2, NCH_3 and ImH signals were close to those of the aqua complex. Upon further addition of MeCN, the

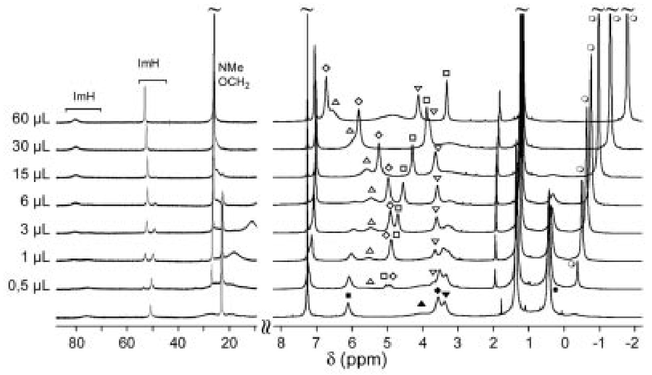
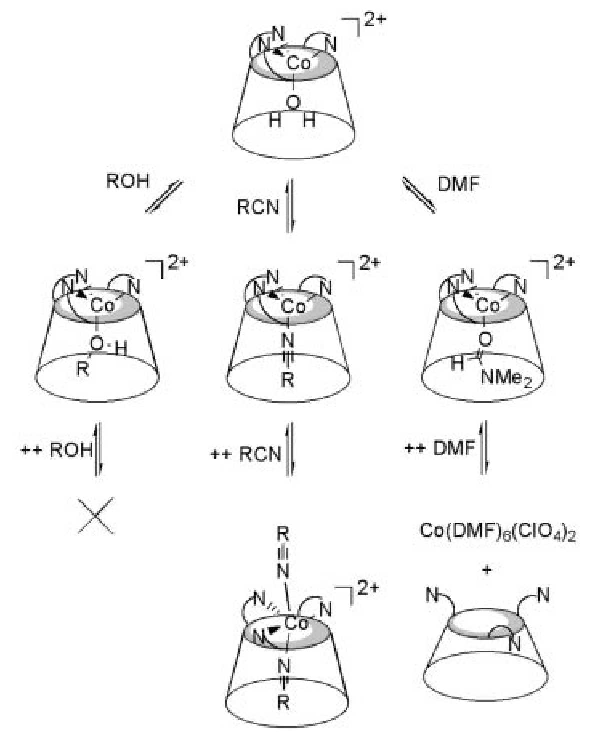


Figure 4. Evolution of ^{1}H NMR spectrum (250 MHz, 300 K) after successive additions of aliquots of acetonitrile (CH_3CN for the first spectrum, CD_3CN for the others) to a $CDCl_3$ solution of complex $[Co(X_6Me_3Imme_3)(H_2O)](ClO_4)_2$ (initial concentration: 12 mM); protons of the cobalt-aqua complex are indicated by filled symbols (ArH^1: ν, ArC*H*$_{ax}$H$_{eq}$Ar: ▲, ArCH$_{ax}$*H*$_{eq}$Ar: ▼, OCH$_3$: ◆, *t*Bu^1: ●) and those of the new species with open symbols (ArH^1: □, ArC*H*$_{ax}$H$_{eq}$Ar: Δ, ArCH$_{ax}$*H*$_{eq}$Ar: ▽, OCH$_3$: ★, *t*Bu^1: ○); ArH^1 and *t*Bu^1 belong to the anisole rings; the small shift of the aqua complex resonances during the titration is ascribed to a small change in the magnetic susceptibility of the solvent (spectra were calibrated with respect to residual $CHCl_3$) as they all shift the same way

guest resonance moved upfield, whereas some protons belonging to the calixarene structure shifted upfield (one *t*Bu and one ArH) and others shifted downfield (OMe and ArCH$_{ax}$H$_{eq}$Ar). In addition, the larger the MeCN concentration, the larger the shifts, which stands in strong contrast to the experiment with EtOH described above. In accordance with the UV/Vis titration, this attests to the formation of two different species that are in fast equilibrium on the NMR timescale. The up- and downfield shifts observed for the calix structure are indicative of a dipolar contribution to their hyperfine shifts, and, thus, of an anisotropy in the magnetic susceptibility consistent with a five-coordinate complex. All these observations account for an equilibrium between a four-coordinate tetrahedral nitrile complex, predominant at low MeCN concentration, and a five-coordinate bis(nitrile) complex, predominant at high MeCN concentration (Scheme 2).



Scheme 2. Reaction of complex $[Co(X_6Me_3Imme_3)(H_2O)]^{2+}$ with small coordinating organic molecules

In order to evaluate the geometry of the five-coordinate species, the experimental hyperfine chemical shifts measured in CD_3CN, δ^{HF}_{exp} (see Table 3), were compared to the theoretical value δ^{HF}_{calc} calculated from the X-ray structure of $[Co(X_6Me_3Imme_3)(MeCN)_2]^{2+}$. A TBP complex is known to display an axial anisotropy in the magnetic susceptibility ($\chi_z \neq \chi_{xy}$, z being the nitrile−Co−nitrile axis) with a dipolar shift given by $\delta^{dip} = A \times [3 \times \cos^2(\theta) - 1]/r^3_{Co-H}$ (r_{Co-H} is the distance between the cobalt ion and a proton and θ the angle between Co−H and the anisotropy

Table 3. Hyperfine chemical shifts δ^{HF}_{calc} calculated from the X-ray structure of complex $[Co(X_6Me_3Imme_3)(MeCN)_2](ClO_4)_2$ and experimental values δ^{HF}_{exp}

Protons	r_{Co-H} (Å)	θ (°)[a]	δ^{HF}_{calc} (ppm)[b]	δ_{Zn} (ppm)[c]	δ_{Co} (ppm)[d]	δ^{HF}_{exp} (ppm)[e]
*t*Bu^1 [f]	9.33	23.2	2.10	0.74	−1.55	2.29
*t*Bu^2 [f]	10.54	53.9	0.04	1.40	1.27	0.13
H$_{eq}$	6.78	60.4	−0.95	3.45	4.41	−0.96
OCH$_3$	6.32	76.8	−3.70	3.58	6.95	−3.37
H$_{ax}$	5.32	62.4	−2.63	4.16	6.95	−2.79
ArH^1	7.32	36.1	2.72	6.47	3.72	2.75
ArH^2	8.32	54.7	0.01	7.39	7.34	0.05

[a] Atoms N7, Co1 and N8 are not perfectly aligned in the X-ray structure; θ is taken as the mean value of angles Co−N7 and Co−N8 axis. [b] $\delta^{HF}_{calc} = \delta^{dip} = A \times (3 \times \cos^2(\theta) - 1]/r_{Co-H}{}^3$. $1/A = 9.05 \times 10^{-4}$ according to Figure 5. [c] δ_{Zn} is the chemical shift observed for the diamagnetic complex $[Zn(X_6Me_3Imme_3)(CD_3CN)](ClO_4)_2$ in CD_3CN.[14] [d] δ_{Co} is the chemical shift observed for the paramagnetic complex $[Co(X_6Me_3Imme_3)(CD_3CN)_2](ClO_4)_2$ in CD_3CN. [e] $\delta^{HF}_{exp} = \delta_{Zn} - \delta_{Co}$. [f] Resonances related to the anisole moieties are noted as ^{1} and the others as ^{2}.

axis). For *t*Bu, $ArCH_{ax}H_{eq}Ar$, OCH_3 and ArH, the Fermi-contact contribution is zero and thus $\delta^{HF}_{calc} = \delta^{dip}$. The plot of $(3 \times \cos^2(\theta) - 1]/r^3_{Co-H}$ versus δ^{HF}_{exp} displayed in Figure 5 shows a nice linear relationship; the δ^{HF}_{calc} and δ^{HF}_{exp} values are reported in Table 3.

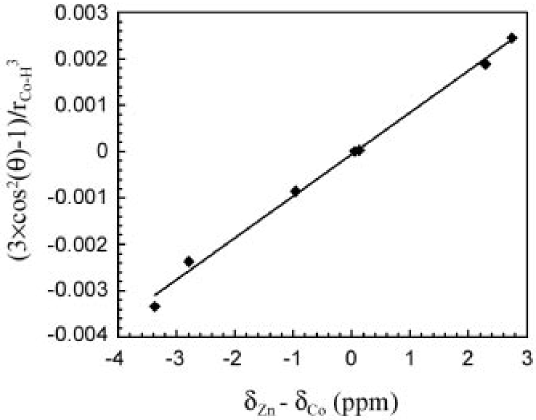


Figure 5. Plot of $(3 \times \cos^2(\theta)-1]/r^3_{Co-H}$ vs. δ^{HF}_{exp}; $y = x \times 9.05 \times 10^{-4}$; $R = 0.997$

The excellent agreement between the values calculated from the X-ray structure and those measured by NMR spectroscopy confirms the existence of a bipyramidal $[Co(X_6Me_3Imme_3)(MeCN)_2]^{2+}$ species in solution. A similar behavior was observed with EtCN, but no evidence for an interaction between PhCN and the aqua complex could be found.

Interaction with DMF was monitored by UV/Vis spectroscopy as for ROH and RCN. First, upon addition of DMF to the CH_2Cl_2 solution of the Co-aqua complex, the extinction coefficients of three $^4A_2 \rightarrow {}^4T_1(P)$ bands increased (up to a maximum over 500 $\text{M}^{-1}\cdot\text{cm}^{-1}$) attesting to the formation of tetrahedral $[Co(X_6Me_3Imme_3)(DMF)]^{2+}$. This was confirmed by ^1H NMR spectroscopy at low DMF concentration (coordinated DMF was identified at δ_{COH} = 135 ppm, δ_{CH_3} = 23.2 and 22.8 ppm). In the second part of the titration, the bands near 500 nm broadened and their intensities decreased. The final spectrum, in nearly pure DMF, displays a broad transition between 450 and 700 nm with ε_{max} = 25 $\text{M}^{-1}\cdot\text{cm}^{-1}$, characteristic of $[Co(DMF)_6(ClO_4)_2]$. All this accounts for the formation of a tetrahedral Co-DMF complex followed by demetallation at high DMF concentration (Scheme 2).

Electrochemistry

The electrochemical behavior of the tris(imidazole)-Co^{II} complex was examined under a nitrogen atmosphere in acetonitrile. Cyclic voltammetry showed a totally irreversible Co^{II}/Co^{I} reduction peak at E_p(red) = −1.8 V,[25] together with metal deposition at the electrode, as evidenced by an anodic redissolution peak on the reverse scan. A very broad irreversible oxidation wave was observed at $E_p(ox) \approx$ 1.3 V, ascribed to ligand oxidation. The same behavior was observed in dichloromethane. No interaction with O_2 could be evidenced. This indicates that the calix[6]arene-based tris(imidazole) system cannot stabilize any other oxidation state than Co^{II}. This was confirmed by the fact that all attempts to reduce the Co^{II} with a chemical reagent ($NaBH_4$ or $CoCp_2$) were unsuccessful, leading to decomplexation.

Synthesis and Characterization of a Five-Coordinate Ni^{II} Complex

Reaction of the tris(imidazole) ligand $X_6Me_3Imme_3$ with one equivalent of $[Ni(H_2O)_6(ClO_4)_2]$ in a THF/MeCN mixture,[26] followed by precipitation with Et_2O, yielded a green solid. IR spectroscopy and elemental analysis were consistent with the formula $[Ni(X_6Me_3Imme_3)(MeCN)(H_2O)](ClO_4)_2$. X-ray quality crystals were obtained by slow diffusion of Et_2O into an acetone/acetonitrile solution of the complex. The molecular structure (Figure 6) displays a five-coordinate nickel(II) ion in a distorted square-based pyramid geometry (SBP, τ = 0.45).[24] The base of the pyramid is formed by two imidazole arms of the calixarene ligand, one acetonitrile molecule, buried in the conic cavity of the calixarene, and a water molecule, *trans* to the acetonitrile guest. The axial ligand is the third imidazole arm. The Ni−O7 bond is slightly longer than the four Ni−N bonds (see Table 4). The coordinated water is part of a hydrogen bonding network implying a second water molecule and an Et_2O molecule [d(O7,O16) = 2.688 Å and d(O16,O17) = 2.833 Å].

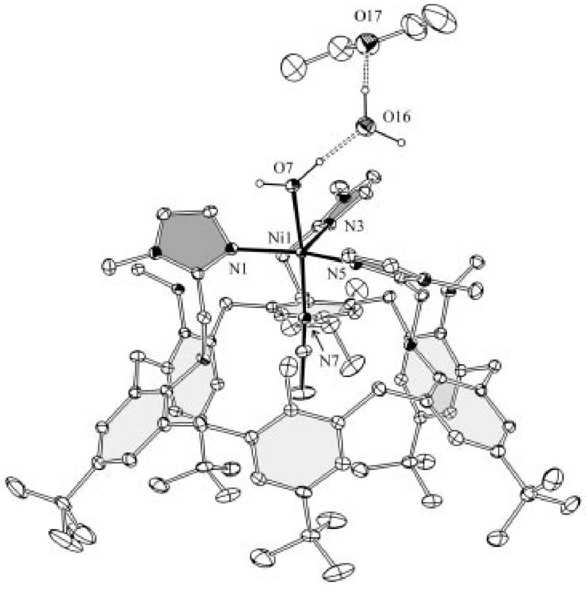


Figure 6. X-ray structure of $[Ni(X_6Me_3Imme_3)(MeCN)(H_2O)](ClO_4)_2\cdot H_2O\cdot Et_2O$ showing ellipsoids at 20% probability; some hydrogen atoms, perchlorate counterions and solvent of crystallization are omitted for clarity; all hydrogen atoms were located experimentally except those of the acetonitrile molecule

The magnetic moment of this Ni^{II} complex assessed by the Evans method in CD_3CN is 3.1(1) μ_B, which corresponds to a high-spin Ni^{2+} ion in a tetragonal environment.[27,28] Its UV/Vis spectrum in MeCN with five broad bands and weak extinction coefficients ε is suggestive of an SBP geometry. The ^1H NMR spectrum in CD_3CN presents

Table 4. Selected bond lengths (Å) and angles (°) for $[Ni(X_6Me_3Imme_3)(MeCN)(H_2O)](ClO_4)_2$

Bond lengths (Å)			
Ni1−N1	2.029(3)	Ni1−N7	2.024(3)
Ni1−N3	2.029(3)	Ni1−O7	2.077(2)
Ni1−N5	2.053(3)		
Angles (°)			
N1−Ni1−N3	104.36(11)	N5−Ni1−N7	93.53(10)
N1−Ni1−N5	146.40(11)	N1−Ni1−O7	84.69(10)
N3−Ni1−N5	108.34(11)	N3−Ni1−O7	91.70(10)
N1−Ni1−N7	91.46(10)	N5−Ni1−O7	86.79(10)
N3−Ni1−N7	94.44(11)	N7−Ni1−O7	173.41(11)

few resonances in the $\delta = -200$ to 200 ppm range. However, the diamagnetic region contains peaks attributable to $ArCH_2Ar$, ArH and *t*Bu, close to those of the tris(imidazole)Zn^{II} complex.[14] This shows that the dipolar contribution to the chemical shift is negligible and agrees with the non-degenerate $^3B_1$ ground state.[29] A putative attribution[30] of the UV/Vis data in MeCN is given in Table 5.

Table 5. UV/Vis data in MeCN of $[Ni(X_6Me_3Imme_3)(MeCN)(H_2O)](ClO_4)_2$

λ (nm)	ε ($M^{-1}\cdot cm^{-1}$)	Transition
325	65	$^3B_1 \rightarrow {}^3E(P)$
400	31	$^3B_1 \rightarrow {}^3A_2(P)$
617	11	$^3B_1 \rightarrow {}^3E$
545	4	$^3B_1 \rightarrow {}^3B_2$
965	5	$^3B_1 \rightarrow {}^3E$

The electrochemical behavior of the Ni^{II} complex was studied in acetonitrile under nitrogen. Cyclic voltammetry showed no oxidation wave up to 1.8 V. An irreversible reduction peak, corresponding to Ni^{II}/Ni^{I} was observed at $E_p(red) = -1.35V$ with Ni^0 deposition at the electrode, as shown by the redissolution peak on the reverse scan. In benzonitrile, the reduction wave was broader and shifted to −1.45 V indicating a slower reduction process. However, the Ni^I state was not stable enough to yield a reversible reduction, even at high scan-rates. Similar to cobalt, the calix[6]arene-based tris(imidazole) system does not appear to be capable of stabilizing nickel ions in any other oxidation state than +2.

Discussion and Conclusion

The calix[6]arene-based tris(imidazole) ligand $X_6Me_3Imme_3$ thus appears particularly well suited for the stabilization of Co^{II} and Ni^{II} complexes, but not for higher or lower oxidation states. All complexes display a host/guest behavior, with a preferential binding of the exogenous organic ligand inside the hydrophobic cavity of the calixarene.

As previously described with Cu^{II}, reaction of the N_3 ligand with Ni^{II} yields five-coordinate complexes with an SBP environment. Also, in both cases, the organic ligand (RCN) is selectively bound in the heart of the hydrophobic calixarene cavity whereas a water molecule, standing outside, caps the structure.

With Co^{II}, four-coordinate species that strongly resemble the parent Zn^{II} complexes were characterized. Indeed, the aqua complex resulting from the synthesis in a non-coordinating solvent was easily exchanged for various small molecules L (alcohol, nitrile or amide), yielding novel tetrahedral complexes with included L. In the specific case of L = RCN, the four-coordinate Co complex was found to be in equilibrium with a trigonal bipyramidal species containing a second nitrile ligand bound outside the cavity and *trans* to the first one. Interestingly, such a five-coordinate species could not be evidenced with L = H_2O or ROH. This can be explained by the lower σ-donor ability of RCN compared to water or alcohol and by its π-acceptor character. Indeed, its first binding weakens the Co^{II} electronic density, thereby enhancing its affinity for a fifth ligand.[31]

A comparison of the X-ray structural parameters of the five-coordinate acetonitrile complexes of each of these metal ions is given in Table 6. Zinc and cobalt are in a TBP geometry whereas copper and nickel are in an SBP geometry. This follows the tendency generally observed for these metal ions in a five-coordinate environment.[27,28] As expected because of its lack of a crystal field, zinc is closer to pure TBP. On the other hand, there is a strong axial

Table 6. Comparison between complexes $[M^{II}(X_6R_3ImR_3)(MeCN)(L)]^{2+}$ (R = Me or Et) with M = Zn, Cu, Ni (L = H_2O) and Co (L = MeCN)

Compound	Geometry[a]	τ[b]	$d(M,L_{ax})$[c] (Å)	$d(M,L_{eq})$[c] (Å)
$[Zn^{II}(X_6Et_3Imet_3)(MeCN)(H_2O)]^{2+}$ [d]	TBP	0.86	2.13 $(MeCN)_i$ [e] 2.37 $(H_2O)_o$	2.03
$[Co^{II}(X_6Me_3Imme_3)(MeCN)(MeCN)]^{2+}$	TBP	0.69	2.08 $(MeCN)_i$ 2.17 $(MeCN)_o$	2.05
$[Cu^{II}(X_6Me_3Imme_3)(MeCN)(H_2O)]^{2+}$ [f]	SBP	0.49	2.19 (Imme)	2.01
$[Ni^{II}(X_6Me_3Imme_3)(MeCN)(H_2O)]^{2+}$	SBP	0.45	2.05 (Imme)	2.04

[a] TBP: trigonal bipyramid, SBP: square-based pyramid. [b] τ quantifies the distortion between ideal TBP (τ = 1) and SBP (τ = 0) geometries.[24] [c] $d(M,L_{ax})$ is the distance between metal and axial ligand and $d(M,L_{eq})$ is the mean distance between metal and equatorial ligands. [d] $X_6Et_3Imet_3$ is the OEt and NEt analogue of $X_6Me_3Imme_3$. See supporting information for the X-ray structure of the complex. [e] "*i*" refers to the ligand included in the calixarene cavity and "*o*" to the external one. [f] See ref.[11]

distortion in the case of copper due to the Jahn−Teller effect, which does not exist for nickel.

It thus appears that the calix[6]arene-based tris(imidazole) ligand is flexible enough to allow the metal ion to adopt the most favorable geometry, although it precludes a six-coordinate environment. The position of the acetonitrile guest in the cavity does not seem to be influenced by the nature of the metal ion, as variations of the $CH_3 \cdots Ar$, C···O and N···O distances remain minor (± 0.015 Å). This shows that the calixarene/guest interaction is relatively strong and that the nitrogen arms are flexible enough to accommodate the metal ion with a fixed calixarene conformation. This flexibility is reminiscent of what has been observed in carbonic anhydrase.[16,17] In its native form, this enzyme presents a mono-zinc active site, with a tetrahedral environment provided by three histidine residues and a water molecule. For the Co^{II}-substituted protein, both four- and five-coordinate metal centers have been characterized, whereas Cu^{II} is in a TBP environment and Ni^{II} octahedral. Hence, like the calixarene-based system, carbonic anhydrase favors a tetrahedral environment for Zn and can stabilize both four- and five-coordinate Co^{II} species. For copper, the two systems differ in the geometry of the metal ion. This shows that the calixarene system is more flexible than the enzyme active site as it does not constrain Cu^{II} in a TBP geometry. On the other hand, the enzyme active site can provide an octahedral environment for Ni, which seems to be precluded by the calixarene system. In conclusion, comparison with carbonic anhydrase confirms that the calixarene-based supramolecular system is a good model for Michaelis adducts, reproducing many structural aspects encountered in natural active sites but not the *cis* coordination of the exogenous ligands. We are currently working on controlling the fifth (outer) coordination site.

Experimental Section

Material and Methods: All solvents and reagents were obtained commercially. THF was distilled from over sodium/benzophenone under argon. CH_2Cl_2 and MeCN were distilled from over CaH_2 under argon. ^1H NMR spectra were recorded on a Bruker ARX 250 spectrometer. Electrochemical experiments were carried out under a dry dioxygen-free atmosphere (N_2) in a dry-box manufactured by Jacomex. The electrochemical cell was specifically designed to fit the rotating disk electrode (EDI Tacussel) for a minimum volume of solution in the main compartment. The auxiliary and reference (ferrocenium/ferrocene = Fc^+/Fc) electrodes were in separate compartments connected to the main compartment through ground joints terminated by frits (Vycor tips from PAR). For voltammetric measurements, a platinum disk (diameter = 2 mm) was employed, and the electrolyses were performed with the same electrode, but rotated, equipped with a 4 mm diameter disk. A model PAR 173 potentiostat equipped with a PAR 179 digital coulometric unit, was monitored by a PAR 175 programmer. The chart recorder was a T-2Y SEFRAM ENERTEC. IR spectra were recorded on a Perkin−Elmer 783 spectrometer. UV/Vis spectra were recorded on a SAFAS UVmc^2 spectrophotometer. Elemental analyses were performed at the Institut de Chimie des Substances Naturelles, France.

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

Table 7. Crystallographic data for the four-coordinate complexes $[Co(X_6Me_3Imme_3)(L)](ClO_4)_2$

L	Me_2CO	DMF	EtOH	EtCN
Formula	$C_{90}H_{120}Cl_2CoN_6O_{16}$	$C_{90}H_{121}Cl_2CoN_7O_{16}$	$C_{89}H_{120}Cl_2CoN_6O_{16}$	$C_{90}H_{119}Cl_2CoN_7O_{15}$
Temp. (K)	193	193	193	193
Crystal colour	Purple	Purple	Purple	Purple
Crystal size (mm^3)	0.4 × 0.4 × 0.3	0.3 × 0.3 × 0.2	0.4 × 0.4 × 0.3	0.4 × 0.3 × 0.2
Mol. mass	1671.81	1686.77	1658.73	1668.75
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.687(1)	13.8246(4)	13.6243(7)	13.6902(6)
b (Å)	16.140(1)	16.1590(4)	16.0153(7)	16.1470(7)
c (Å)	22.739(2)	22.3976(7)	22.803(1)	22.5562(7)
α (°)	88.444(4)	88.029(1)	88.782(2)	88.021(2)
β (°)	78.274(4)	78.934(1)	78.078(2)	78.648(2)
γ (°)	68.267(5)	68.358(1)	68.444(2)	68.713(2)
V (Å^3)	4562.4(6)	4560.6(2)	4519.6(4)	4551.4(3)
Z	2	2	2	2
ρ(calcd.) (g·cm^{-3})	1.22	1.23	1.21	1.21
μ(Mo-K_α) (cm^{-1})	3.12	3.13	3.11	3.11
θ range (°)	3−26	5−27	6−26	2−26
No. of unique data	15914	16643	16325	16803
No. parameters refined	1045	1166	1134	1031
No. refl. in refinement	15914	16643	16325	16803
R [$F^2 > 4\sigma F^2$]	0.104	0.086	0.080	0.087
wR[a]	0.213[b]	0.181[c]	0.173[d]	0.244[e]
Goodness of fit	1.081	0.992	0.976	1.07
Residual Fourier (e·Å^{-3})	0.71, −0.86	1.15, −1.31	0.83, −0.78	1.07, −1.41

[a] $P = (F_o^2 + 2F_c^2)/3$ for [b] $w = 1/[\sigma^2(F_o^2) + (0.0701P)^2 + 12.398P]$. [c] $w = 1/[\sigma^2(F_o^2) + (0.0924P)^2 + 9.1861P]$. [d] $w = 1/[\sigma^2(F_o^2) + (0.0619P)^2 + 15.9154P]$. [e] $w = 1/[\sigma^2(F_o^2) + (0.1696P)^2 + 6.8382P]$.

Table 8. Crystallographic data for five-coordinate complexes $[Co(X_6Me_3Imme_3)(MeCN)_2](ClO_4)_2$ and $[Ni(X_6Me_3Imme_3)(MeCN)(H_2O)](ClO_4)_2$

Compound	$[Co(X_6Me_3Imme_3)(MeCN)_2](ClO_4)_2$	$[Ni(X_6Me_3Imme_3)(MeCN)(H_2O)](ClO_4)_2$
Formula	$C_{94}H_{127}Cl_2CoN_9O_{16}$	$C_{93}H_{131}Cl_2N_7NiO_{18}$
Temp. (K)	173	193
Crystal colour	Purple	Green
Crystal size (mm^3)	0.4 × 0.3 × 0.3	0.4 × 0.4 × 0.2
Mol. mass	1768.94	1764.66
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	22.4259(5)	22.583(1)
b (Å)	16.3266(4)	16.337(1)
c (Å)	26.6529(5)	26.626(1)
β (°)	93.580(1)	93.913(1)
V ($Å^3$)	9739.6(4)	9800.5(8)
Z	4	4
ρ(calcd.) ($g.cm^{-3}$)	1.206	1.196
μ(Mo-K_α) (cm^{-1})	3.0	3.18
θ range (°)	5−25	2−33
No. of unique data	16989	22948
No. parameters refined	1150	1090
No. refl. in refinement	16989	22948
R [$F^2 > 4\sigma F^2$]	0.098	0.087
wR[a]	0.214[b]	0.196[c]
Goodness of fit	1.144	1.062
Residual Fourier (e·$Å^{-3}$)	0.54, −0.59	0.71, −0.59

[a] $P = (F_o{}^2 + 2Fc^2)/3$ for [b] $w = 1/[\sigma^2(F_o{}^2) + (0.08P)^2 + 25.50P]$. [c] $w = 1/[\sigma^2(F_o{}^2) + (0.081P)^2 + 15.1143P]$.

$[Co(X_6Me_3Imme_3)(H_2O)](ClO_4)_2$: Under an argon atmosphere, dry THF (2 mL) was added to a mixture of $[Co(H_2O)_6(ClO_4)_2]$ (36.6 mg, 0.10 mmol) and $X_6Me_3Imme_3$ (143 mg, 0.11 mmol).[13] The purple solution was stirred for one hour at room temperature and the product precipitated with Et_2O (5 mL). The solid was separated from the supernatant by centrifugation and washed with Et_2O. It was further purified by dissolution in CH_2Cl_2 and precipitation with pentane (twice) then dried under vacuum to yield a purple solid (138 mg, 85%). M.p. > 250 °C (decomp). ^1H NMR (250 MHz, $CDCl_3$, 298 K): δ = 0.44 (s, 27 H, *t*Bu), 1.35 (s, 27 H, *t*Bu), 3.37 (s, 6 H, Ar-αCH_{eq}), 3.56 (s, 9 H, OCH_3), 3.5−4.5 (br. s, 6 H, Ar-αCH_{ax}), 6.10 (s, 6 H, ArH), 7.26 (s, 6 H, ArH), 18−22 (br., 6 H, Im-αCH_2), 22.9 (br., 9 H, NCH_3), 50.5 (br., 3 H, ImH), 70−80 (br., 3 H, ImH). μ_{eff} = 4.6(1) μ_B. UV/Vis (CH_2Cl_2): λ (ε) = 523 (230), 564 (336), 592 nm (339 M^{-1}·cm^{-1}). IR (KBr): $\tilde{\nu}$ = 3460 (H_2O), 1505, 1487, 1462, 1421, 1398, 1367, 1110 (ClO_4^-), 628 (ClO_4^-) cm^{-1}. $C_{84}H_{110}Cl_2CoN_6O_{15}\cdot 3H_2O$ (1627.7): calcd. C 61.98, H 7.18, N 5.16; found C 61.75, H 6.91, N 4.83.

$[Ni(X_6Me_3Imme_3)(MeCN)(H_2O)](ClO_4)_2$: Under an argon atmosphere, dry MeCN (0.25 mL) and THF (1 mL) were added to a mixture of $[Ni(H_2O)_6(ClO_4)_2]$ (30.7 mg, 0.084 mmol) and $X_6Me_3Imme_3$ (109 mg, 0.084 mmol).[13] The green solution was stirred for 30 minutes at room temperature and the product precipitated with Et_2O (6 mL). The solid was separated from the supernatant by centrifugation and washed with Et_2O. It was further purified by dissolution in MeCN and precipitation with Et_2O then dried under vacuum to yield a green solid (105 mg, 75%). M.p. > 270 °C (decomp). μ_{eff} = 3.1(1) μ_B. UV/Vis (CH_2CN): λ (ε) = 400 (sh, 31), 617 (11), 965 nm (5 M^{-1}·cm^{-1}). IR (KBr): $\tilde{\nu}$ = 3400 (H_2O), 1483, 1462, 1363, 1113 (ClO_4^-), 626 (ClO_4^-) cm^{-1}. $C_{86}H_{113}Cl_2N_7NiO_{15}\cdot 2H_2O$ (1410.5): calcd. C 62.58, H 7.15, N 5.94; found C 62.17, H 6.86, N 6.12.

X-ray Structure Determinations:[32] Crystallographic data for $[Co(X_6Me_3Imme_3)(L)](ClO_4)_2$ (L = Me_2CO, DMF, EtOH and EtCN), $[Co(X_6Me_3Imme_3)(MeCN)_2](ClO_4)_2$ and $[Ni(X_6Me_3Imme_3)(MeCN)(H_2O)](ClO_4)_2$ are listed in Table 7 and 8. Diffraction data were collected on a Bruker−Nonius−KappaCCD diffractometer.[33] Structures were solved by direct methods and refined using the program SHELXL-97.[34]

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[32] CCDC-193247 for $\mathrm{[Co(X_6Me_3ImMe_3)(CH_3COCH_3)](ClO_4)_2}$, -193249 for $\mathrm{[Co(X_6Me_3ImMe_3)(DMF)](ClO_4)_2}$, -193240 for $\mathrm{[Co(X_6Me_3ImMe_3)(EtOH)](ClO_4)_2}$, -193241 for $\mathrm{[Co(X_6Me_3ImMe_3)(EtCN)](ClO_4)_2}$, -193248 for $\mathrm{[Co(X_6Me_3ImMe_3)(MeCN)_2](ClO_4)_2}$, and -193246 for $\mathrm{[Ni(X_6Me_3ImMe_3)(MeCN)(H_2O)](ClO_4)_2}$ contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.ac.uk].

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