

First Insights into the Electronic Properties of a Cu(II) Center Embedded in the PN₃ Cap of a Calix[6]arene-Based Ligand

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The first metal complex based on the calix[6]PN₃ cryptand is described. The solid-state and solution studies show a 5-coordinate Cu(II) center due to its coordination to the PN₃ cap and to an exchangeable guest molecule. Spectroscopic and electrochemical studies evidence surprising properties of the metal ion, which are tentatively assigned to the unusual P–Cu(II) bond enforced by the cryptand.

In our course of designing supramolecular models of mononuclear enzyme active sites, we have recently developed a general strategy for capping a calix[6]arene small rim by a tripodal polyaza core. Hence, calix[6]aza cryptands presenting either a tris(aminoethyl)amine (tren),¹ a tris(pyridyl-2-methyl)amine (tmpa),² or a tris(benzylamino)-phosphine (PN₃)³ cap have been synthesized. In the latter, a P atom plays the role of the tripodal linker that assembles the three amino arms instead of a N atom in the former cases. Whereas the tren and tmpa units have been widely used to model the first coordination sphere encountered in metallo-enzymes,⁴ the PN₃ core appears as almost unexplored,^{5,6} obviously because P donors are not present in natural

systems. Nevertheless, the study of its coordination properties is interesting in order to evaluate the impact of the replacement of a N donor by a soft donor on the intrinsic properties of the metal ion. Knowing that, in copper monooxygenases, a soft S atom is bound to the Cu ion that performs the catalysis,⁷ we decided to synthesize the corresponding copper(II) phosphine complex and explore its binding properties toward exogenous ligands in comparison with the tren system.

Calix[6]PN₃ reacted with 1 equiv of copper perchlorate in tetrahydrofuran to produce a blue-green complex. Elemental analyses showed a 1:1:2 ligand/Cu/CuO₄ ratio, thereby indicating the formation of a dicationic complex (Figure 1). Single crystals of [Cu(calix[6]PN₃)(DMF)]²⁺ were obtained by slow diffusion of pentane into a CH₂Cl₂ solution of the complex containing small amounts of methanol and dimethylformamide (DMF).

The X-ray diffraction (XRD) analysis of this complex reveals an approximate C₃ symmetry with a Cu(II) ion bound to the three amino arms and to the P atom of the PN₃ cap. A DMF ligand included in the calixarene cavity completes the slightly distorted ($\tau = 0.86$)⁸ trigonal bipyramid at the metal center. As has been observed for other calix[6]–Cu(II) complexes, the ^tBu groups of the phenylmethoxy moieties point to the inside of the cavity, while the other three ^tBu groups are in an *out* position, hence flattening the entire cone conformation. The invited guest molecule DMF is stabilized in this conformation by three CH/π interactions⁹ between the methyl groups of the DMF, buried in the cavity, and the phenyl rings of the anisole units. One DMF methyl group is facing a phenyl group at a distance of 3.47 Å, while the

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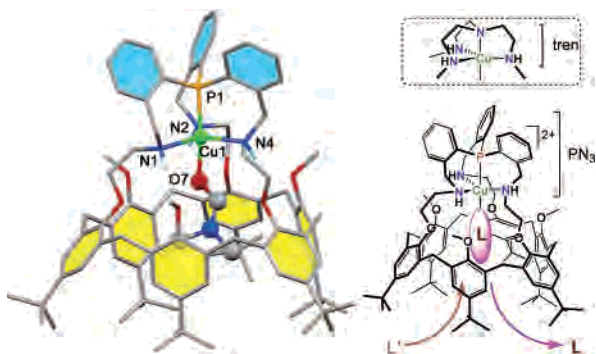


Figure 1. Right: schematic representation of the $[\text{Cu}(\text{calix}[6]\text{PN}_3)(\text{L})]^{2+}$ complexes and (top) the tren cap. Left: XRD structure of complex $[\text{Cu}(\text{calix}[6]\text{PN}_3)(\text{DMF})](\text{ClO}_4)_2$. H atoms, counterions, and the solvent of crystallization have been omitted for clarity. Selected bonds length [Å] and angles [deg]: Cu1–O7 2.018(3), Cu1–N1 2.102(3), Cu1–N2 2.116(3), Cu1–N4 2.079(3), Cu1–P1 2.263(1); O7–Cu1–N1 81.88(12), O7–Cu1–N2 88.39(12), O7–Cu1–N4 91.03(12), O7–Cu1–P1 175.47(9), N1–Cu1–N2 119.70(13), N1–Cu1–N4 123.94(13), N1–Cu1–P1 93.73(9), N2–Cu1–N4 115.55(12), N2–Cu1–P1 92.85(9), N4–Cu1–P1 92.37(9).

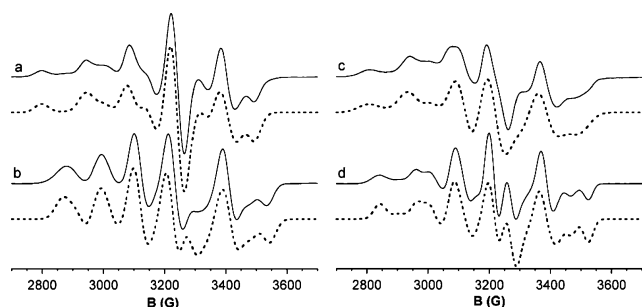


Figure 2. Experimental (solid lines) and simulated (dashed lines) EPR spectra (X band) of $[\text{Cu}(\text{calix}[6]\text{PN}_3)(\text{L})](\text{ClO}_4)_2$ in frozen CH_2Cl_2 (100 K) before (a; L = H_2O) and after the addition of guest L [10% (v/v)]: (b) L = MeCN; (c) L = EtOH; (d) L = DMF.

other one is at a close distance to the two additional aromatic rings at 3.51 and 3.60 Å. Cupric complexes presenting a Cu(II)–P bond have rarely been described in the literature. This XRD structure actually represents the fourth of its kind,¹⁰ and the Cu(II)–P distance (2.26 Å) is intermediate to those previously reported for a square-pyramidal (2.32 Å)⁵ and a tetrahedral complex (2.20 Å).⁶ The Cu–O and Cu–N bond distances are quite similar to those measured for the calix[6]tren-based Cu(II) complex.

In solution, the complex revealed itself to be very stable, and no phosphine oxidation has been observed, which allowed the study of its host–guest behavior. The electron paramagnetic resonance (EPR) spectrum of the isolated complex was first recorded after dissolution in pure CH_2Cl_2 and then in the presence of an exogenous ligand, namely, DMF, MeCN, or EtOH (Figure 2).

In each case, the EPR signature was attributed to one single mononuclear species. Although the spectra are particularly complicated, their simulation gave excellent results, considering in each case three different *g* values with a strong superhyperfine coupling with the P atom¹¹ in addition to the hyperfine coupling with Cu. This indicates that in solution as in the solid state the complex adopts a distorted trigonal-bipyramidal geometry and that the Cu–P bond is maintained. Yet, all parameters, although fairly close, vary with the nature of the exogenous ligand, thus attesting to the formation of

different species (Table 1). Indeed, in pure CH_2Cl_2 , a water molecule arising from the synthetic procedure is the guest ligand (L is H_2O) as for all previously reported M(II) complexes based on calix[6]arene ligands.^{1,12} Upon the addition of a coordinating molecule L (DMF, MeCN, and EtOH), the aqua complex $[\text{Cu}(\text{calix}[6]\text{PN}_3)(\text{H}_2\text{O})]^{2+}$ undergoes ligand exchange at its intracavity binding site to provide new dicationic 5-coordinate species $[\text{Cu}(\text{calix}[6]\text{PN}_3)(\text{L})]^{2+}$.

This was further confirmed by solution studies realized by electronic spectroscopy. The progressive addition of a coordinating guest L resulted invariably in the appearance of isobestic points, confirming the formation of a single new species due to the substitution of the water molecule in the cavity. In each case (L = DMF, MeCN, EtOH, and H_2O), the spectrum presents one intense band at about 400 nm ($\epsilon = 1400\text{--}2000 \text{ M}^{-1} \text{ cm}^{-1}$) and three d–d transitions between 550 and 850 nm (see Table 1). The latter d–d bands are characteristic of a more or less distorted trigonal-bipyramidal geometry. The origin of the intense absorption observed at ca. 400 nm is less clear. Indeed, its invariability toward the nature of the coordinated guest (same energy and intensity with π donors or π acceptors) suggests that this transition corresponds to a charge transfer between the PN_3 core and the Cu(II) center. Competition experiments gave the following order of relative affinities of Cu(II) for L: EtOH (1) < MeCN (8.6) \ll DMF (1400). Surprisingly, these values are quite different from those found for the analogous tren $[\text{MeCN} (1) < \text{EtOH} (3.7) < \text{DMF} (7.1)]^1$ and trisimidazole¹² $[\text{MeCN} (1) < \text{EtOH} (3) < \text{DMF} (10)]$ Cu(II) systems. With the PN_3 system, the affinity of MeCN is surprisingly higher than that of EtOH, and DMF displays an enormous affinity for the calix PN_3 complex in comparison to the other complexes. A careful comparison of the present XRD structure with those reported for related calix[6]-based complexes hosting DMF did not evidence any significant difference in the positioning of the DMF guest in the calix cone. Thus, the exceptional affinity of the metal center for DMF does not seem to be due to some steric effect but rather stems from the different electronic properties of the Cu(II) center due to its P ligand in the apical position. Indeed, a similar behavior has been observed with larger guests: adding a few molar equivalents of PrCN or PrCONH₂ into a 1:1 mixture of CH_2Cl_2 and BuOH containing the complex leads to the corresponding adducts $[\text{Cu}(\text{calix}[6]\text{PN}_3)(\text{L})]^{2+}$ with L = PrCN or PrCONH₂, which substantiates the hypothesis of an unusual affinity of Cu(II) for π acceptors.

The redox behavior of the $[\text{Cu}(\text{calix}[6]\text{PN}_3)(\text{L})]^{2+}$ complexes, under anaerobic and strictly anhydrous conditions, has been studied in different solvents encompassing the

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- (10) A search in the Cambridge Crystallographic Centre database showed a total of eight complexes having a Cu(II)–P bond, among which only three display a mixed P,N environment. See refs 5 and 6.
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Table 1. Electrochemical, Visible–Near-IR, and EPR Data of $[\text{Cu}(\text{calix}[6]\text{PN}_3)(\text{L})]^{2+}$ in CH_2Cl_2 in the Presence of Various Guests L [$<2\%$ (v/v) for Visible–Near-IR and 10% (v/v) for EPR]

L	E°/V^a ($\Delta E_p/mV$)	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/M^{-1}\text{cm}^{-1}$)	EPR parameters (X band, 100 K, $A/10^{-4}\text{cm}^{-1}$)
H_2O	-0.17 (80)	408 (1584), 590 (162), 670 (182), 864 (137)	$g_1 = 2.019, g_2 = 2.076, g_3 = 2.162, A_1^{\text{Cu}} = 37.7, A_2^{\text{Cu}} = 64.3,$ $A_3^{\text{Cu}} = 138.0, A_1^{\text{P}} = 229.4, A_2^{\text{P}} = 164.8, A_3^{\text{P}} = 157.2$
MeCN	-0.24^b (80)	417 (1808), 560 (130), 736 (235), 850 (sh, 185)	$g_1 = 1.996, g_2 = 2.103, g_3 = 2.132, A_1^{\text{Cu}} = 45.3, A_2^{\text{Cu}} = 91.3,$ $A_3^{\text{Cu}} = 116.3, A_1^{\text{P}} = 228.2, A_2^{\text{P}} = 192.3, A_3^{\text{P}} = 165.8$
EtOH	-0.20^a (80)	416 (1534), 605 (147), 740 (187), 906 (sh, 138)	$g_1 = 2.014, g_2 = 2.085, g_3 = 2.159, A_1^{\text{Cu}} = 40.6, A_2^{\text{Cu}} = 57.9,$ $A_3^{\text{Cu}} = 130.5, A_1^{\text{P}} = 222.6, A_2^{\text{P}} = 170.7, A_3^{\text{P}} = 166.7$
DMF	-0.46^b (95)	402 (1987), 592 (144), 741 (249), 860 (sh, 202)	$g_1 = 2.002, g_2 = 2.109, g_3 = 2.146, A_1^{\text{Cu}} = 43.0, A_2^{\text{Cu}} = 84.3,$ $A_3^{\text{Cu}} = 120.0, A_1^{\text{P}} = 225.2, A_2^{\text{P}} = 175.3, A_3^{\text{P}} = 162.3$

^a Measured by cyclic voltammetry in $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$ at 0.1 V s^{-1} , V vs Fc^+/Fc ; 10% (v/v) for EtOH. ^b Measured in $\text{MeCN}/\text{NBu}_4\text{PF}_6$ or $\text{DMF}/\text{NBu}_4\text{PF}_6$.

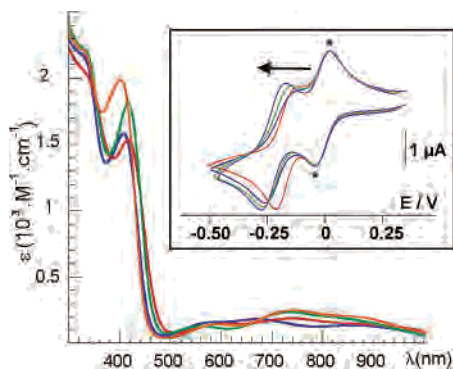


Figure 3. UV–vis spectra of $[\text{Cu}(\text{calix}[6]\text{PN}_3)(\text{L})](\text{ClO}_4)_2$ [L = H_2O (blue), EtOH (red), MeCN (green), DMF (orange)]. Inset: Cyclic voltammograms of $[\text{Cu}(\text{calix}[6]\text{PN}_3)(\text{L})]^{2+}$ in pure CH_2Cl_2 ($3 \times 10^{-3}\text{ M}$ red) and after the addition of MeCN [2%, 5%, and 10% (v/v)] (* = Fc^+/Fc system).

potential guests L, at the Cu(II) redox state. Cyclic voltammetry at different scan rates ($0.02\text{ V s}^{-1} < \nu < 10\text{ V s}^{-1}$) evidences Cu(II)/Cu(I) processes that are remarkably reversible in any of the solvents. As reported in Table 1, the E° value is a function of the solvent and is constant over the scan rates. The peak separation, ΔE_p , increases only at the highest scan rates. The i_p/i_{pa} values, close to unity, and the $i_p/\nu^{1/2}$ ratio remain constant with the scan rates. In PhCN, the Cu(II) reduction peak was exactly at the same potential as that for the MeCN complex, but departure from reversibility was observed with a broader return peak and anodically shifted. Addition of MeCN in the PhCN solution led to a perfectly reversible process, as observed in a pure MeCN solution. Electrolysis coulometry performed at a reduction potential for the Cu(II) complex, in CH_2Cl_2 , MeCN, and DMF, led, after exchange of 1 electron/mol, to a solution displaying exactly the same characteristics as those observed by cyclic voltammetry. By rotating-disk electrode voltammetry, the wave was converted from anodic to cathodic current; the $E_{1/2}$ value in each solvent remained the same by both techniques before and after the electrolysis. Addition of MeCN in a CH_2Cl_2 solution resulted in the replacement of the reversible L = H_2O process by the L = MeCN one with a more cathodic potential (Figure 3). Addition of DMF in the MeCN solution led to the disappearance of the L = MeCN reduction peak and to the appearance of the L = DMF peak. On the return scan, however, almost only the reoxidation peak with L = MeCN was detected because of a $\text{DMF} \rightarrow \text{MeCN}$ guest interconversion at the Cu(I) state.

Hence, the values of the redox potentials in the different solvents (E° : $\text{DMF} < \text{MeCN} < \text{EtOH} \approx \text{H}_2\text{O}$) as well as

the conversion of the processes when adding different guests clearly illustrate the same extraordinary order of affinities of the Cu(II) ion as shown by electronic spectroscopy. Moreover, the reversibility of the processes indicates that no change in the coordination sphere of the Cu(II) and Cu(I) complexes can be detected under these conditions. This is especially surprising in view of the poor affinity of classical Cu(I) centers toward O donor ligands such as H_2O , EtOH, and DMF. This was clearly observed in our previous study with the $[\text{Cu}(\text{calix}[6]\text{tren})(\text{L})]^{2+}$ complexes, where these guests are ejected from the cone after reduction to Cu(I).¹ Another remarkable feature of this study is the observation that the potential values for this new system are completely shifted to much higher values (up to ca. 0.45 V for DMF and MeCN and 1.1 V for H_2O), again compared to the tren system. All of these observations suggest that the Cu–P bond confers unusual electronic properties to both cupric and cuprous states.

Here, we have presented the first metal complex based on calix[6]PN₃. The Cu(II) complex, containing a Cu(II)–P bond, is remarkably stable thanks to the strong chelating effect of the cryptand. As a result, for the first time, it has been possible to study the electronic properties of this type of complex. As in the tren system, this new compound acts as a receptor for small neutral guest ligands, however, with a different selectivity. Again the flexibility of the calixarene system adapts to the nature of the invited guest, yet the unique P atom in the axial position seems to play an important role in stabilizing the guest ligands in the trans position. Spectroscopic studies suggest a reinforced affinity of Cu(II) for π acceptor ligands, which is substantiated by electrochemical data, which, in turn, have evidenced the special affinity of Cu(I) for O donor ligands. More work is needed to rationalize the redox behavior of this new compound. In particular, the characterization of the corresponding Cu(I) compound and the study of its reactivity are underway.

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Supporting Information Available: Synthetic procedure, characterization, and crystallographic data for the complex (in CIF and PDF formats). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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