Introduction

Nature has taken advantage of cooperation phenomena between metal centers in the design of several metalloproteins where the close proximity of two metal centers mediates reactions that range from small molecule activation (N$_2$, O$_2$) to hydrolysis.$^3$ Proteins containing dinuclear copper centers are involved in a number of biologically important processes that extend from electron transfer to O$_2$ transport or activation.$^6$ For example, hemocyanin, the O$_2$ carrier protein in arthropods and mollusks, contains a dinuclear copper center in its active site. In the oxy and deoxy forms, each of the copper atoms is bound to three histidine residues.$^{11}$ Tyrosinase has a very similar active site, but its biological role is the ortho hydroxylation of phenols to catechols and catechols to quinones.$^{12}$ Catechol oxidases also contain nitrogen rich dinuclear copper centers in their active site and mediate the oxidation of catechols to quinones.

The synthesis and structural and spectroscopic characterization of a family of copper(I) complexes, containing a dinucelating hexaaza macrocyclic ligand, of general formula [Cu$_2$(L)(X)$_2$]$^{2+}$ (L = Me$_2$p, Me$_2$m, Me$_3$p, or Me$_3$m; X = MeCN, n-PrCN, CO, t BuNC, or PPh$_3$) is described. This family of complexes contains ligands that differ from one another in the number of methylenic units linking the tertiary amines and in the meta or para substitution of their aromatic rings. The structural characterization in the solid-state includes a single-crystal X-ray diffraction analysis of [Cu$_2$(Me$_2$p)(CO)$_2$]$^{2+}$ and of [Cu$_2$(Me$_2$m)(t BuNC)$_2$]$^{2+}$. In solution, those complexes are structurally characterized through NMR spectroscopy that also allows us to put forward and establish their fluxional behavior. Theoretical calculations at the DFT level have also been performed in order to further analyze the relative energy of the different potential isomers as well as to gain insight into their chemical properties. Finally, the influence of the hexaaza ligands over different structural aspects as well as on its potential chemical reactivity is discussed.

References

In this work, we are presenting the synthesis and spectroscopic and structural characterization of a series of dinuclear copper(I) complexes containing hexaaza macrocyclic ligands that solely contain tertiary amines. These macrocyclic ligands have been designed to allow the control of electronic, geometric, and spatial properties including the local and the relative Cu metal geometries.

**Experimental Section**

**Caution!** Perchlorate salts are all potentially explosive and should be handled with care.

**Materials and Synthesis.** Solvents were purchased from SDS as reagent grade. Acetonitrile was distilled over P2O5 and stored over molecular sieves. Diethyl ether and THF were distilled over Na/benzophenone under nitrogen. CH2Cl2 was distilled over CaH2 and stored over molecular sieves. Methanol was distilled over Mg and stored in the dark over molecular sieves. Acetone was dried over CaCl2 and stored over molecular sieves. Butyronitrile was used as received. Unless noted otherwise, all reagents were purchased from commercial sources and used as received. Preparation and handling of air-sensitive materials were carried out under argon or N2 atmosphere using standard Schlenk techniques.

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for 30 min, and ether (10 mL) was added to precipitate a white solid. The solvent was removed with a syringe and the residue dried under vacuum to obtain a white solid (60 mg, 0.063 mmol, 62%). FT-IR (KBr): ν = 2249, 1467, 1100, and 625 cm⁻¹. Anal. (%) Calcd for C₅₀H₆₈N₈Cu₂Cl₂O₈: C 47.80, N 11.15, H 7.02. Found: C 47.55, N 11.06, H 6.86. ¹H NMR (CD₃CN, 77 K): δ = 7.37 (s, 8H, arom.), 3.93 (s, 8H, ArCH₃), 3.46 (m, 10H, CH₂OTf), 2.83 (m broad, 16H, NCH₂), 2.60 (s, 6H, NCH₃), 2.36 (s, 12H, NCH₃), 2.30 (s, 2H, H₂O), 1.19 (m, 9H, CH₃TFH). ¹³C NMR (CD₃CN, 298 K): δ = 135.7, 132.8, 130.2, 128.6 (arom), 67.3 (CH₂OTf), 64.7 (ArCH₂), 57.3, 53.9 (NCH₃), 45.8, 43.0 (NCH₂), 25.3 (CH₃TFH). 1H NMR (CD₃CN, 338 K): δ = 2.1 (m broad, 16H, NCH₂), 1.9 (m, 8H, ArCH₂), 2.29 (s, 12H, NCH₃), 1.81 (m broad, 8H, CH₂CH₂CH₂).


1H NMR (CEM, 298 K): δ = 4.00 (s, 8H, Ar), 4.50 (s, 8H, ArCH₂), 2.83 (m broad, 16H, NCH₂), 2.60 (s, 6H, NCH₃), 2.36 (s, 12H, NCH₃), 2.30 (s, 2H, H₂O), 1.19 (m, 9H, CH₃TFH). ¹³C NMR (CD₃CN, 298 K): δ = 135.7, 132.8, 130.2, 128.6 (arom), 67.3 (CH₂OTf), 64.7 (ArCH₂), 57.3, 53.9 (NCH₃), 45.8, 43.0 (NCH₂), 25.3 (CH₃TFH).
Dinuclear Copper(I) Complexes

18 H, CH₃ isocyanide), ¹³C NMR (CD₂CN, 298 K): δ = 130.0, 128.5 (arom), 65.1, 64.7 (ArCH₃), 57.2, 54.3 (NCH₃), 46.9, 42.6 (NCH₃), 29.3 (CH₃ isocyanide).

[Cu₂(Me₂p)(PPh₃)₂](ClO₄)₂ (12). Me₂p (50 mg, 0.101 mmol) and [Cu(CH₃CN)₂]ClO₄ (66 mg, 0.202 mmol) were dissolved in acetonitrile (5 mL). Over this solution was added PPh₃ (0.202 mmol, 53 mg) dissolved in acetonitrile (3 mL). A white precipitate rapidly appears which is filtered, washed with acetone, and dried under vacuum (108 mg, 0.08 mmol, 79%). FT-IR (KBr): ν = 1467, 1495, 1100, and 625 cm⁻¹. Anal. (%): Calcd for Cu₂H₉N₃Cu₂P₃Cl₆O₅: C 58.16, N 6.37, H 6.01. Found: C 58.16, N 6.26, H 6.01. ¹H NMR (CD₃CN, 298 K): δ = 7.54–7.29 (m, 38H, arom.), 3.58 (s, 8H, ArCH₃), 2.97–2.63 (m, 16H, NCH₂), 2.25 (s, 12H, NCH₃), 2.13 (s, NCH₃). ¹³C NMR (DMSO-d₆, 298 K): δ = 7.54–7.10 (m, 38H), 3.52 (s, 8H), 2.7–2.5 (m, 16H), 2.34 (s, 6H), 2.27 (s, 9H), 2.1 (s, 4H). ¹³C NMR (DMSO-d₆, 298 K): δ = 134.0, 133.3, 131.3, 132.3, 131.6, 130.6, 129.8, 129.3, 129.1 (arom), 63.5, 54.5 (ArCH₂), 45.0, 43.6 (NCH₃), 30.7 (NCH₃). ³¹P NMR (DMSO-d₆, 298 K): δ = 1.1, Δδ = 10 ppm.

Physical Methods. IR spectra were taken in a Mattson-Galaxy FT-IR spectrophotometer as solid KBr pellets. Elemental analyses were conducted in a Carlo Erba Instrument, model CHNS 1108. NMR spectra were recorded on a Bruker DPX-200 operating at 200.13 MHz for ¹H, 50.32 MHz for ¹³C, and 80.01 MHz for ³¹P, at room temperature (298 K), or on a BRUKER ARX-400 spectrometer operating at 400.13 MHz for proton, equipped with a 5 mm triple-resonance inverse broadband probe head and a gradient coil. 2D COSY and HSQC experiments were recorded using standard pulse sequences, and 2D NOESY spectra using a mixing time of 500 ms were obtained at several temperatures to identify NOEs and chemical exchange cross-peaks. Spectra were referenced to the residual protio solvents peaks or TMS (tetramethylsilane) for ¹H and to external H₃PO₄ (85%) for ³¹P.

Crystallographic Studies. [Cu₂(Me₂p)(CO)₂](ClO₄)₂·2H₂O (8). A colorless cube with the dimensions 0.10 × 0.15 × 0.25 mm³ was coated with a viscous oil, stuck with glue on the end of a glass fiber, and mounted on the diffractometer equipped with an Oxford Cryostream low temperature device. Unit cell parameters were determined by carefully centering 25 independent, strong reflections with 14° ≤ θ ≤ 23°. Data collection has been carried out at 193 K using a Enraf-Nonius CAD4 diffractometer equipped with a Cu Ka fine focus sealed tube (λ = 1.5418 Å) and with a graphite monochromator. 6433 reflections with 2.42° ≤ 2θ ≤ 77.50° were measured. Three reflections monitored every 2 h showed an intensity loss of 6.12%. Absorption correction was carried out using DIFABS (minimum and maximum transmission: 0.60/1.00). The structure was solved by direct methods using the program SIR92. Anisotropic least-squares full-matrix refinement was carried out on all non-hydrogen atoms using the program CRYSTALS. All hydrogen atoms are in calculated positions. The protons of the water of crystallization could not be localized. The refinement of 487 parameters including 3350 reflections with I > 3σ(I) lead to a residual of 0.0588 (R_w = 0.0613). Chebychev polynomial weights have been used to complete the refinement. The density maximum in the last difference map was 0.94 e/Å³, and the last minimum was −0.76 e/Å³. Scattering factors have been taken from the International Tables, Vol. IV, Table 2.2B.

[Cu₂(Me₂m)(6-BuNC)₂](CF₃SO₃)₂ (11). A pale blue rod crystal was coated with a viscous oil, stuck with glue on the end of a glass fiber, and mounted on the diffractometer. The intensity data were collected at 223 K on a Stoe image plate diffraction system using Mo Kα graphite monochromated radiation: image plate distance 70 mm, φ oscillation scans 0°–200°, step Δφ = 1.0°, 2θ range 3.27°–52.11°, d_max−d_min = 12.45–0.81 Å. The structure was solved by direct methods using the program SHELXS-97. The refinement and all further calculations were carried out using SHELXL-97. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F². An empirical absorption correction was applied using the DIFABS routine in PLATON (transmission min/max = 0.452/0.820). One of the triflate anions undergoes considerable thermal motion.

CCDC 190908 and 190909 contain the supplementary crystallographic data for complexes [Cu₂(Me₂m)(6-BuNC)₂](CF₃SO₃)₂ (11), and [Cu₂(Me₂p)(CO)₂](ClO₄)₂·2H₂O, respectively, described in this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, U.K. Fax: (+44)1223-336-033. E-mail: deposit@ccdc.cam.ac.uk.).

Computational Details. The reported calculations were carried out by using the Amsterdam density functional (ADF) program system, developed by Baerends et al. The numerical integration scheme employed was that of te Velde and Baerends. An uncontracted triple-ζ basis set was used for describing the 3s, 3p, 3d, 4s, and 4p orbitals of carbon. For carbon (2s,2p), nitrogen (2s,2p), oxygen (1s), and hydrogen (1s), double-ζ basis sets were used.

(42) Stoe & Cie IPDS Software; Stoe & Cie GmbH: Germany, 2000.
bodied and augmented by an extra polarization function. Electrons in lower shells were treated within the frozen core approximation.46 A set of auxiliary s, p, d, f, and g functions,50 centered in all nuclei, was introduced in order to fit the molecular density and Coulomb potential accurately in each SCF cycle. Geometries were fully optimized within the local density approximation (LDA), which includes the Xα exchange (α = 2 /3),51 together with the electron gas correlation functional in the Vosko—Wilk—Nusair parametrization.52 The analytical gradients implemented by Versluis and Ziegler53 were employed to perform geometry optimizations. Energies were evaluated at the LDA molecular geometries using a generalized gradient approximation (GGA) that includes the nonlocal exchange correction of Becke54 and the nonlocal correlation correction of Perdew.55 This method is labeled throughout this work as BP86/DZP/VWN/DZP. Several authors have shown that this level of calculation provides excellent results for geometries and bond dissociation energies.56–61

Owing to computational limitations, both geometry optimizations and energy evaluations have been carried out with the QM/MM method available in the ADF program, which includes standard molecular mechanics force fields in such a way that the QM and MM parts are coupled self-consistently.62 In the QM/MM model considered in this work, the MM part involves the two aromatic rings in the ligand and the four CH2 units of the benzylic groups. As for the connection between the QM and MM parts, this occurs by means of the so-called “capping” dummy hydrogen atoms, which are placed in the real system by the corresponding “linking” carbon atoms.62,63 In the QM/MM optimizations, the ratio between the C−N bonds crossing the QM/MM border, and the corresponding optimized C−H distances, was fixed equal to 1.38. A more detailed description of the coupling scheme, as well as further comments on the methodology, can be found in previous papers.63–66 The AMBER95 force field66 was used for the MM potentials, except for Cu, which was treated with the UFF force field.59 To eliminate spurious stabilizations from the long-range attractive part of the Lennard-Jones potential,65,69–71 the QM/MM scheme in the ADF program has been successfully employed to investigate olefin polymerizations,64,72 epoxidation of olefins,73 and rhodium catalyzed carbonylation reactions.74 The 2000.02 release of the ADF package was used for all calculations.75

### Results

**Synthesis.** The four macrocyclic ligands used in this work are represented in Scheme 1 and are prepared according to literature procedures. This family of ligands is characterized by the number of methylenic units linking the tertiary amines, which can be two or three, and by the aromatic substitution that take place in the meta or para positions. Reaction of those ligands containing two methylenic units (Me2p and Me2m) with 2 equiv of [Cu(CH3CN)4][X] (X− = ClO4−, CP2SO+, or PF6−) in acetonitrile form the corresponding dinuclear complexes, in moderate to good yields, as shown in the following equation for the case of Me2p.

\[
\text{Me2p} + 2 \text{Cu(MeCN)4}^+ + \text{MeCN}^- \rightarrow [\text{Cu}_2(\text{Me2p})(\text{MeCN})_2]^{2+} + 6 \text{MeCN} \quad (1)
\]

The complexes thus obtained are white solids, which are air sensitive. The replacement of MeCN by n-PrCN in this

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**Scheme 1.** Macro cyclic Ligands Used in This Work

![Scheme 1](image)

- **Me2p**
- **Me2m**
- **Me3p**
- **Me3m**

**References**

reaction generates the corresponding complexes, [Cu$_2$(Me$_2$p)-(n-PrCN)$_2$](ClO$_4$)$_2$, 2, and [Cu$_2$(Me$_2$m)-(n-PrCN)$_2$](PF$_6$)$_2$, 3, which are less air sensitive and thus easier to manipulate.

For the analogous ligands with three methylenic units, Me$_3$p and Me$_3$m, the metal centers in [Cu$_2$(Me$_3$p)](ClO$_4$)$_2$, 4, [Cu$_2$(Me$_3$p)](CF$_3$SO$_3$)$_2$, 5, [Cu$_2$(Me$_3$m)](CF$_3$SO$_3$)$_2$, 6, and [Cu$_2$(Me$_3$m)](PF$_6$)$_2$, 7, are solely coordinated by the macrocyclic ligand, and therefore, a third coordination is obtained. This statement is supported analytically and spectroscopically by the absence of a nitrile band in the IR and the absence of the corresponding resonances in the NMR. Furthermore, the alkyltriamine moieties in the Me$_3$p and Me$_3$m ligands are almost identical to those in the recently crystallographically characterized [Cu$^+$][Me$_3$p(N$_3$)$_3$] (Me$_3$pN$_3$ = N,N,N”-pentamethyltriazenediimine) which also possesses a tricoordinate copper(I) center, even when isolated from acetonitrile as solvent.

For the dinuclear copper complexes containing the isomeric ligands with two methylenic units bonding tertiary amines, Me$_2$p and Me$_2$m, their monodentate ligand can easily be replaced by $\sigma$-donor/$\pi$-acceptor ligands L (CO, t-BuNC, PPh$_3$) as shown here for the particular case of Me$_2$p:

\[
[Cu_2(Me_2p)(MeCN)]^{2+} + 2 L \rightarrow [Cu_2(Me_2p)L_2]^{2+} + 2 MeCN
\]

These new complexes are generally obtained in good yields, precipitate as white solids, and are less air sensitive than their precursors. However, the stability of the complexes is somewhat dependent on the $\sigma$-donor/$\pi$-acceptor ligands L. Carbonyl complexes [Cu$_2$(Me$_2$p)(CO)$_2$](ClO$_4$)$_2$, 8, and [Cu$_2$(Me$_2$m)(CO)$_2$](CF$_3$SO$_3$)$_2$, 9, are rapidly oxidized in the solid-state and in solution upon exposure to O$_2$. PPh$_3$ complexes [Cu$_2$(Me$_2$p)(PPh$_3$)$_2$]ClO$_4$, 10, and [Cu$_2$(Me$_2$m)-(PPh$_3$)$_2$]ClO$_4$, 11, are relatively stable in the solid-state but become oxidized in O$_2$ exposed solutions, and acetonitrile solutions of t-BuNC complexes [Cu$_2$(Me$_2$p)(t-BuNC)$_2$]-

| formula | C$_2$H$_4$Cl$_2$Cu$_2$N$_2$O$_2$ | C$_2$H$_4$Cu$_3$F$_2$N$_2$O$_2$S$_2$
| crystal syst | monoclinic | orthorhombic
| space group | P2$_1$/a | Pnca
| a [Å] | 14.973(2) | 16.869(5)
| b [Å] | 14.744(4) | 22.3450(14)
| c [Å] | 18.374(2) | 27.3252(17)
| $\beta$ [deg] | 95.31(1) | 90.00(1)
| V [Å$^3$] | 4039(1) | 10300.2(11)
| Z | 4 | 8
| $\rho_{\text{calc}}$ [g/cm$^3$] | 1.401 | 1.001
| $\mu$ [mm$^{-1}$] | 3.07 | 0.979
| $T_{\text{max}}$ [e Å$^{-1}$] | 1.000.60 | 0.820.452
| crystal form | cubo | rod
| crystal size [mm$^3$] | 0.10 x 0.15 x 0.25 | 0.08 x 0.10 x 0.30
| $2\theta_{\text{max}}$ [deg] | 77.50 | 52.1
| no. refins | 6433 | 78116
| no. indep reflns | 6113 | 10036
| no. obsd reflns | 3350 | 3803
| restrains/params | 0/487 | (I > 3$\sigma$(I))
| final $R$ | 0.0588 | 0.0555
| final $R_{\text{free}}$ | 0.0613 | 0.1277
| max/min in diff map | 0.94/-0.76 | 0.988/-0.640

Table 1. Crystallographic Data of [Cu$_2$(Me$_2$p)(CO)$_2$](ClO$_4$)$_2$; 8, and [Cu$_2$(Me$_2$m)(t-BuNC)$_2$](CF$_3$SO$_3$)$_2$, 11

These new complexes are generally obtained in good yields, precipitate as white solids, and are less air sensitive than their precursors. However, the stability of the complexes is somewhat dependent on the $\sigma$-donor/$\pi$-acceptor ligands L. Carbonyl complexes [Cu$_2$(Me$_2$p)(CO)$_2$](ClO$_4$)$_2$, 8, and [Cu$_2$(Me$_2$m)(CO)$_2$](CF$_3$SO$_3$)$_2$, 9, are rapidly oxidized in the solid-state and in solution upon exposure to O$_2$. PPh$_3$ complexes [Cu$_2$(Me$_2$p)(PPh$_3$)$_2$]ClO$_4$, 10, and [Cu$_2$(Me$_2$m)-(PPh$_3$)$_2$]ClO$_4$, 11, are relatively stable in the solid-state but become oxidized in O$_2$ exposed solutions, and acetonitrile solutions of t-BuNC complexes [Cu$_2$(Me$_2$p)(t-BuNC)$_2$](ClO$_4$)$_2$, 10, and [Cu$_2$(Me$_2$m)(t-BuNC)$_2$](CF$_3$SO$_3$)$_2$, 11, could be manipulated in open atmosphere for short periods of time without apparent oxidation of the complexes.

The corresponding complexes containing the isomeric ligands Me$_3$p and Me$_3$m are also formed using acetone as the solvent, as evidenced by IR spectroscopy, but they cannot be isolated in the solid-state. In the workup process, the corresponding $\sigma$-donor/$\pi$-acceptor ligand is lost, thus generating the tricoordinated complexes. Furthermore, in the particular case of the complexes containing the carbonyl ligand, the established equilibrium process can be monitored by IR spectroscopy indicating the reversibility of the process in solution:

\[
[Cu_2(Me_3p)(MeCN)]^{2+} + 2 CO \rightarrow [Cu_2(Me_3p)(CO)]^{2+} + 2 MeCN
\]

The reaction is driven to the left by simply bubbling Ar or N$_2$ into the solution at room temperature.
in the monoclinic $P2_1/n$ and the orthorhombic $Pbca$ space groups with four and eight molecules per unit cell, respectively.

The cationic part of 8 consists of the macrocyclic ligand, binding two copper atoms and two CO molecules acting in a terminal mode. It has a pseudo-plane-of-symmetry that bisects the two aromatic rings and is also perpendicular to them, thus generating two very similar halves of the cationic molecule. The copper atoms have a significantly distorted tetrahedral coordination. Each one is bound to three N atoms of the macrocycle, and a CO molecule completes the tetrahedral coordination. Each one is bound to three N atoms associated with the copper center allowing us to grasp the type and degree of tetrahedral distortion suffered by the metal center. Two of the NCuN distances in 8 are significantly shorter than the other: 2.109(6) and 2.115-84 versus 2.176(5) Å, although all the values lie in the range of Cu−N distances reported in the literature.80 The NCuN angles are close to 90° (85.9(2)° and 87.0(2)°) whereas the third is slightly above the ideal 109.47° for a tetrahedral geometry (114.0(2)°). The Cu−CO distance is 1.813(8) Å, and the C−O is 1.113(9) Å, both indicative of a weak bonding interaction. In addition, the Cu−CO vector is bent toward N1 (C4−Cu1−N1, 112.8°) resulting in the opening of the C4−Cu1−N2 and C4−Cu1−N3 angles (122.9° and 125.3°, respectively). The aromatic rings are oriented almost perpendicular to each other (80.71°), and the benzylic CH₂ groups are slightly displaced from the plane defined by these aromatic rings. This is evidenced by the C20−C21−C16−C15 and C17−C18−C19−C22 torsion angles of 172.8° and 171.0°, respectively, which indicate the degree of constrain supported by the molecule. Cu−CO vectors point in the same direction (syn) relative to the cavity plane of the macrocyclic ligand with a torsion angle between CO ligands, C4−O5−O55−C54 of −5.3°.

The structure of 8 is completed with two water molecules and two perchlorate anions. One of the water molecules is bonded to one of the perchlorates via hydrogen bonding: O102−O12 is 2.906 Å.

The cationic part of [Cu₂(Me₂m)(t-BuNC)₂](CF₃SO₃)₂, 11, consists also of the macrocyclic ligand binding the two metal centers and two t-BuNC molecules acting in a terminal fashion (see Figure 1). The cationic moiety possesses a pseudo-C₂ axis perpendicular to the macrocyclic cavity. However, subtle differences between the structural parameters of the two copper centers are evident in 11. The local geometry around the metal center is relatively similar to that in the case of 8. Cu(1) has two long Cu−N distances (Cu1−N1 = 2.176(5) Å and Cu1−N3 = 2.181(4) Å) and a shorter one (Cu1−N2 = 2.100(5) Å) whereas Cu2 has three different Cu−N distances (Cu2−N5 = 2.169(5) Å, Cu2−N6 = 2.102(5) Å, and Cu2−N7 = 2.231(5) Å). The NCuN angles are similar to the previous case and thus reflect a relatively similar type of geometrical distortion for the local copper(I) center. Cu−C bonds in Cu−C≡N are short (Cu−C≡N₉ = 1.83 Å) and compare well with the shortest reported in the literature.80−84 In addition, the Cu−CN vectors point in the

[Image 127x503 to 485x744]
The calculated structure for syn-\([\text{Cu}_2(\text{Me}_2p)-(\text{CO})_2]^2+\), syn-8, is remarkably similar to that of the X-ray structure described in the previous section. The highest discrepancy between calculated and experimental metal–ligand bond distances is only 0.057 Å with a medium discrepancy of 0.026 Å (see Table 2). As expected, the main differences are found in the bonding angles; while most of the bonding angle discrepancies are roughly around only 3°, in this case the N2–Cu1–C4 discrepancy is of 10° which could even be ascribed to packing effects. Therefore, a very good agreement is found between the experimental and theoretical bond lengths and angles, thus providing confidence in the reliability of the QM/MM method to reproduce the geometries for this kind of complex.

The theoretical C–O triple bond in the CO free molecule (1.131 Å) is smaller than that of the coordinated CO at the complex (1.142 Å), as expected from the bonding mechanism that usually operates in M–CO bonds.\(^{85}\) Surprisingly, this is not reproduced by the experimental data since, experimentally, the C–O bond length in CO free molecule is 1.128 Å\(^{69a}\) and the X-ray data show that in the syn–\([\text{Cu}_2(\text{Me}_2p)-(\text{CO})_2]^2+\), syn-8, complex this bond length is shorter by 0.014 Å (1.114 Å). It is worth noting that we found previously a similar behavior for the experimental and theoretical triple bond lengths of the CO and CNCN ligands in the Cr(CO)\(_3\)CNCN system.\(^{86b}\) We have not been able to find an explanation for this discrepancy, although the expected lengthening and weakening of the CO bond in the complex fits in with the generally observed IR frequency lowering of the CO stretch vibration.

The energy difference between the syn- and anti-\([\text{Cu}_2(\text{Me}_2p)-(\text{CO})_2]^2+\), 8, complexes is listed in Table 3. In agreement with the experimental findings, we found that the syn-\([\text{Cu}_2(\text{Me}_2p)-(\text{CO})_2]^2+\), syn-8, complex is more stable than the anti complex by 7.6 kcal mol\(^{-1}\) at the QM(BP86/DZP//VWN/DZP/MM(AMBER95) level of theory.

In order to gain further insight into the different parameters that govern the relative stability of these complexes, their CO coordination energies were also calculated.

\[
[\text{Cu}_2\text{Mac}(\text{CO})]^2+ + \text{CO} \rightleftharpoons [\text{Cu}_2(\text{Mac})(\text{CO})_2]^{2+} \quad (4)
\]

The bond coordination energy of CO has been divided into deformation energy and interaction energy (\(\Delta E_{\text{CO}} = \Delta E_{\text{def}} + \Delta E_{\text{int}}\)). The deformation energy is the energy needed to modify the geometry of the free fragments to attain the geometry that they have in the complex, and it is split into the deformation of the CO molecule (\(\Delta E_{\text{def}}(\text{CO})\)) and the deformation of the rest of the complex (\(\Delta E_{\text{def}}(\text{rest})\)). The interaction energy is the energy released when the two free deformed fragments are brought to the position that they have in the complex.

In agreement with the higher stability of the syn-\([\text{Cu}_2(\text{Me}_2p)-(\text{CO})_2]^2+\), syn-8, complex with regard to the corre-

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**Table 3.** Energy of the Syn and Anti Cu–CO Complexes Taking the syn System as the Reference Species at Zero Energy, C–O Bond Length of the CO Molecule in the Complex, and Deformation, Interaction, and Bond Coordination Energies of a CO Molecule to the Complex. Bond Distances in Å and Energies in kcal mol\(^{-1}\)

<table>
<thead>
<tr>
<th></th>
<th>Me2p</th>
<th>Me2m</th>
<th>Me3p</th>
<th>Me3m</th>
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<td>anti</td>
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<td>anti</td>
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<td>0.0</td>
<td>5.4</td>
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<td>(\Delta E_{\text{def}}(\text{CO}))</td>
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<td>-20.3</td>
<td>-25.0</td>
<td>-21.0</td>
</tr>
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\(^{a}\) Calculated \(r(C–O)\) distance in free CO is 1.131 Å, the experimental X-ray value being 1.128 Å.\(^{69a}\) \(^{b}\) Deformation energy of the CO molecule in the \([\text{Cu}_2\text{L}(\text{CO})_2]^2+\) complex. \(^{c}\) Deformation energy of the \([\text{Cu}_2\text{L}(\text{CO})_2]^2+\) without a CO molecule fragment in the \([\text{Cu}_2\text{L}(\text{CO})_2]^2+\) complex. The energy of this fragment can be different for the syn and anti isomers. \(^{d}\) Total deformation energy, \(\Delta E_{\text{def}} = \Delta E_{\text{def}}(\text{CO}) + \Delta E_{\text{def}}(\text{rest})\).
sponding anti complex, we also find that the CO bond dissociation energy (the negative of the coordination energy in Table 3) for the latter is 8.0 kcal mol$^{-1}$ larger than for the former since it is favored by both terms, the deformation and the interaction energies.

The geometries of the syn- and anti-[Cu$_2$(Me2m)(CO)$_2$]$^{2+}$, 9, complexes were optimized starting from the already optimized syn-[Cu$_2$(Me2p)(CO)$_2$]$^{2+}$, syn-8, complex by merely moving the link of the two methylene groups to the aromatic rings from para to meta locations. For these species, we also find that the syn is more stable than the anti by 5.4 kcal mol$^{-1}$. The dissociation energy of the CO molecule is now 4.0 kcal mol$^{-1}$ larger for the syn isomer. As compared to the [Cu$_2$(Me2p)(CO)$_2$]$^{2+}$, 8, species (see Table 3), the bond dissociation energy of CO in the syn-[Cu$_2$(Me2m)(CO)$_2$]$^{2+}$, syn-9, complex is lower by 3.3 kcal mol$^{-1}$ due to a larger deformation energy (2.0 kcal mol$^{-1}$) and a slightly less favorable interaction (1.3 kcal mol$^{-1}$). Finally, the CO dissociation energies of the anti isomers in the [Cu$_2$(Me2p)-(CO)$_2$]$^{2+}$, 8, and [Cu$_2$(Me2m)(CO)$_2$]$^{2+}$, 9, complexes are quite similar, the latter being larger by only 0.7 kcal mol$^{-1}$.

The optimization of the anti-[Cu$_2$(Me3p)(CO)$_2$]$^{2+}$ complex was started from the X-ray structure of the analogous anti-[Zn$_2$(Me3p)(NO$_3$)$_2$]$^{2+}$ complex.$^{87}$ The syn complex was optimized from the anti optimized form, by taking one of the two QM fragments and turning it upside down. In comparison with a strict tetrahedral coordination, the locations of the nitrogen atoms around the copper atom in the [Cu$_2$(Me3p)(CO)$_2$]$^{2+}$ complexes are less distorted than those of the anti-[Cu$_2$(Me2p)(CO)$_2$]$^{2+}$, anti-8, species (compare for instance the NCuN angles Table 2) due to the higher flexibility of the propylenic ligands.

For these species, we find low bond dissociation energies of CO and a similar stability of the syn and anti forms, the anti being somewhat more stable.

For the [Cu$_2$(Me3m)(CO)$_2$]$^{2+}$ complexes, we started the optimization from the geometry of the previously optimized anti-[Cu$_2$(Me3p)(CO)$_2$]$^{2+}$ complexes by just changing the link of two xylylic groups from para to meta locations. Similar energetic results as in the previous case are found here.

**NMR Spectroscopy and Fluxional Behavior.** The $^1$H NMR spectra at 320 K of the d$^{10}$ copper(1) complexes described in the present work are characterized by broad nonresolved signals due to the presence of fluxional behavior between different conformational isomers. A detailed analysis of this phenomenon was undertaken using complex [Cu$_2$(Me2p)(t-BuNC)$_2$](ClO$_4$)$_2$, 10. The $^1$H NMR spectra of complex 10 recorded in acetone-$d_6$ at different temperatures are presented in Figure 2. NOESY spectra at 250, 270, and 300 K for complex 10 are presented as Supporting Information. Similar spectra for compound [Cu$_2$(Me2m)(t-BuNC)$_2$]- (CF$_3$SO$_2$)$_2$, 11, are also collected as Supporting Information.

At 320 K, the aromatic region contains two broad singlets at 7.67 and 7.03 ppm. Upon lowering the temperature, the second signal broadens, and finally, at 220 K, it splits into two new signals centered at $\delta = 7.25$ and 6.62 ppm. Further lowering of the temperature to 190 K results in the decoalescence of the initial 7.67 ppm signal into two new singlets centered at 7.59 and 7.75 ppm. The evolution of the aliphatic region of the spectra in the same range of temperatures is rather complex, and a full understanding requires the use of bidimensional experiments. In general, though, lowering of the temperature changes the initially broad features into well-resolved signals. Analysis of the spectra reveals that the complex contains a plane of symmetry, crossing perpendicularly to the two aromatic rings, that divides the macrocycle in two parts magnetically and chemically equivalent. In addition, each of the CH$_3$ groups of the molecule is a geminal diastereotopic system. Finally, the presence of four different aromatic protons is evident. Further analysis was performed on the basis of NOESY spectra at different temperatures (Supporting Information). The proposed structure of the complex on the basis of these spectra is shown in Scheme 2.

Assignment is based on the observation in the spectra at 250 K of NOEs from H$_5$ with H$_3$ and H$_7$, H$_6$ with H$_4$ and H$_9$, H$_{11}$ with H$_{13}$ and H$_{15}$, and finally, H$_{12}$ with H$_{14}$ and H$_8$. NOEs between H$_2$/H$_3$ and H$_5$/H$_7$ and also between H$_{13}$/H$_{14}$ and H$_{15}$/H$_{16}$ allow for the assignment of the aromatic protons. The relative orientation of the methyl groups is also inferred from this experiment; Me$_{19}$ experiences NOEs with H$_7$ and H$_8$, Me$_{17}$ with H$_{14}$ and H$_{12}$, and finally, Me$_{18}$ with H$_6$, H$_{13}$, and H$_{11}$. Aromatic protons H$_1$ and H$_2$, equivalent at this temperature, can be assigned according to the observation of an NOE with H$_3$ and H$_4$. Similarly, H$_{15}$ and H$_{16}$, also equivalent at this temperature, can be assigned on the basis of NOEs with H$_{13}$ and H$_{14}$.

The X-ray structure of [Cu$_2$(Me2p)(CO)$_2$](ClO$_4$)$_2$, 8, indicates that the two aromatic rings are oriented almost perpendicularly relative to each other leading to four different aromatic protons, which are perfectly resolved in the $^1$H NMR spectra of [Cu$_2$(Me2p)(t-BuNC)$_2$](ClO$_4$)$_2$, 10, at 190 K. Two aromatic protons, H$_{16}$, are oriented toward the second aromatic ring, while H$_{15}$ protons are oriented in the opposite direction. H$_1$ and H$_2$ point perpendicularly to the plane defined by H$_{15}$ and H$_{16}$, upward and downward of the macrocyclic plane. Discrimination between H$_{15}$ and H$_{16}$ relies on the basis that the protons oriented toward the aromatic ring should be significantly upshifted. Variable temperature NOESY experiments also allow the study of the dynamic properties of the molecule. At 270 K, chemical interchange between H$_1$ and H$_{14}$, H$_2$ and H$_{13}$, H$_3$ and H$_{12}$, H$_6$ and H$_{11}$, Me$_{17}$ and Me$_{18}$, as well as among the aromatic protons, is observed. This suggests that the Cu–N bonds next to the benzylic CH$_2$ (Me$_{19}$ and Me$_{17}$) are weak, such that they can break allowing the exchange between the two aliphatic chains. H$_5$, H$_8$, H$_9$, and H$_{10}$ remain unaltered in this process. Schematic representation of the different isomeric forms involved in these equilibria is shown in Scheme 3.

The spectra are consistent with the presence of four different interconverting isomers, A, C, E, and G, each of

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$^{87}$ Anda, C.; Llobet, A. Unpublished results.
which contains a plane of symmetry. Isomeric forms A and G are predominant at this temperature. Inversion of Me\textsubscript{17} or Me\textsubscript{18} results in nonsymmetric forms B, D, H, and F, which undergo a second Me\textsubscript{17} or Me\textsubscript{18} inversion faster than the \textsuperscript{1}H NMR time scale.

At 300 K (Figure S3), interchange phenomena are extended to the four benzylic protons (H\textsubscript{3}, H\textsubscript{4}, H\textsubscript{13}, and H\textsubscript{14}) and also among H\textsubscript{5}, H\textsubscript{6}, H\textsubscript{11}, and H\textsubscript{12}. H\textsubscript{7}, H\textsubscript{8}, H\textsubscript{9}, and H\textsubscript{10} also interchange at this temperature, indicating that the third Cu–N bond (Cu–NMe\textsubscript{19}) is also breaking and forming continuously. From this temperature, thermal energy accelerates interchange processes, and at 323 K, H\textsubscript{1}–H\textsubscript{2} and H\textsubscript{15}–H\textsubscript{16} collapse into an aromatic singlet, H\textsubscript{3}, H\textsubscript{4}, H\textsubscript{13}, and H\textsubscript{14} collapse into a benzylic singlet, the corresponding signals to Me\textsubscript{17} and Me\textsubscript{18} also become a singlet, and H\textsubscript{5}–H\textsubscript{12} appear together as a broad singlet. Additional increase of the temperature results in the sharpening of the signals suggesting that the interchange processes become faster than the \textsuperscript{1}H NMR time scale. The study of the conditions of coalescence of H\textsubscript{15} and H\textsubscript{16} reveals that the activation energy for interconversion between both protons is 10.10 kcal/mol.\textsuperscript{88} Similarly, interconversion between H\textsubscript{1} and H\textsubscript{2} has an activation barrier of 9.34 kcal/mol. Finally, the barrier for the interconversion between the two aromatic rings is 14.92 kcal/mol.

Figure 2. VT \textsuperscript{1}H NMR spectra of [Cu\textsubscript{2}(Me2p)(t-BuNC)\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2}, \textbf{10}, in acetone-\textit{d}_6.

Scheme 2. Partial Structural Drawing of Complex [Cu\textsubscript{2}(Me2p)(t-BuNC)\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2}, \textbf{10}, in Solution at Low \textit{T} with the Corresponding \textsuperscript{1}H NMR Assignment (ppm)\textsuperscript{a}

\textsuperscript{a} The isocyanide \textit{t}-BuNC ligand is not shown for clarity reasons.
Discussion

Para versus Meta Substitution Effect in the Macrocyclic Ligands. The simple change in the aromatic substitution of the macrocyclic ligands from para to meta produces a shrinkage of cavity by two member ring units. While the local geometry of the copper complexes remains relatively unaffected by this modification, the relative geometry between the two copper centers changes dramatically, even though the Cu⋯Cu metal distance is not significantly different (6.810 Å for [Cu₂(Me₂p)(CO)₂]²⁺, 8; 6.860 Å for [Cu₂(Me₂m)(CO)₂]²⁺, 9; 6.776 Å for [Cu₂-(Me₂m)(t-BuNC)₂]²⁺, 11). A feature that illustrates this difference is the relative orientation of the terminal ligands bonded to the copper metal center. For the [Cu₂(Me₂p)(CO)₂]²⁺, 8, complex, the vectors defined by the terminal CO ligand face each other with a torsion angle of only 5.6°. In the case of [Cu₂(Me₂m)(L₂)²⁺, the vectors defined by the NC bond (L = t-BuNC, 11) of the isocyanide ligand and by the CO bond (L = CO, 9) are tilted by 76.5° and 80.0°, respectively. In order to further compare the relative geometrical rearrangement between the copper metals, it is interesting to point out here the distances between these terminal ligands. Thus, the O5⋯O5 distance for the [Cu₂-(Me₂p)(CO)₂]²⁺, 8, complex is only 3.122 Å while the equivalent distance for [Cu₂-(Me₂m)(CO)₂]²⁺, 9, is 4.063 Å, and for [Cu₂(Me₂m)(t-BuNC)₂]²⁺, 11, the equivalent N⋯N distance is 3.989 Å.

Syn versus Anti Preferences. X-ray diffraction analysis and low T NMR are consistent with the presence of the same single isomer in the solid-state and in solution. For complexes [Cu₂(Me₂p)(CO)₂]²⁺, 8, and [Cu₂(Me₂m)(CO)₂]²⁺, 9, this single isomer has a syn conformation with regard to the relative orientation of the terminal carbonyl ligands (see Figure 1A).

At first glance, one would expect the anti conformation for complex [Cu₂(Me₂p)(CO)₂]²⁺, 8, to be more energetically stable than the syn given the steric hindrance caused by the proximity of the carbonyl ligands facing each other. In order to understand the origin of this unexpected phenomenon, a theoretical study was undertaken using the ADF type of calculations for dicarbonyl dinuclear copper complexes containing the four ligands studied in the present work both in the syn and anti conformations. We have found that the larger bond dissociation energy of CO in the syn species is due in part to a smaller deformation energy of the [Cu₂-(Me₂p)(CO)]²⁺, 8, fragment (without a CO molecule) and also to a more favorable interaction energy in the syn form. This is also reflected in the larger C–O bond length in the syn complex as compared to the anti.

The key interactions between the incoming CO molecule and the [Cu₂-(Me₂p)(CO)]²⁺ fragment (without one CO ligand) involve, first, the donation from the HOMO Ï€-orbital of CO, which corresponds to the lone pair on the C atom, to the unoccupied 1b orbital (2a₁ in C₃ᵥ symmetry; see Scheme 4) of the [Cu₂-(Me₂p)(CO)]²⁺, 8, fragment, and second, the back-donation from the occupied 1a orbital (1e in C₃ᵥ symmetry) of the metal complex fragment to the LUMO Ï€*-orbital of CO. One can therefore understand the particular position of the two CO molecules one facing the other since back-donation is specially favored when the CO molecule is

(88) $\Delta G^\ddagger = RT[22.96 + \ln(T/\Delta H)]$, where $T_c$ is coalescence temperature and $\Delta H$ is the difference in the ¹H NMR shift of the two decoalesced signals at $T_c$. See for example: Ritzeler, O.; Parel, S.; Therrien, B.; Bensel, N.; Reymond, J.-L.; Schenk, K. Eur. J. Org. Chem. 2000, 1365–1372.

somewhat tilted. In such a position, the overlap between the LUMO $\pi^*$-orbital of CO and the 1a orbital is maximized.

As a whole, the preference of the CO ligand to coordinate in the syn form in both the Me2p and Me2m can be attributed to more favorable orbital interaction energy and reduced strain energy of the ligand in this isomer.

In sharp contrast for the Me3p and Me3m complexes, the energy strain of the ligands is reversed with the syn isomers in the 2080–2102 cm$^{-1}$ range commonly found for complexes containing neutral ligands.

From a structural viewpoint, the ligands bearing three methylenic units between tertiary amines have a better geometric arrangement than those with two to better fit the demands of a tetrahedral coordination, giving rise to six-member chelate rings with the metal center. Thus, now the lowest NCuN bond angle is 96.08° in contrast with the 85.07° of the previous structurally described complexes.

From an electronic viewpoint, the addition of two methylenic units per copper center produces a significant enhancement of electronic density over the tertiary amine and in turn to the metal center. This is supported experimentally by potentiometric titration studies of the free ligand and theoretically by the values of the Mulliken charge obtained on the ligand (+1.29 and +1.42 electrons for the syn-[Cu2-(Me2p)(CO)2]$^{2+}$, 8, and syn-[Cu2(Me3p)(CO)2]$^{2+}$ complexes, respectively).

Furthermore, as a consequence of this greater charge transfer, the energy of the 1b orbital in the [Cu2(Me3p)]$^{2+}$ fragment is raised by about 0.5 eV. In turn, the donation from the HOMO $\sigma$-orbital of CO to the unoccupied 1b orbital is reduced, thus in turn decreasing the back-donation from the 1a orbital to the LUMO $\pi^*$ orbital of CO. This effect is clearly seen in the bond dissociation energies of the CO molecule gathered in Table 3. As compared to the [Cu2-(Me2p)(CO)2]$^{2+}$, 8, counterparts, the [Cu2(Me3p)(CO)2]$^{2+}$ species have bond dissociation energies of CO that are about 10 kcal mol$^{-1}$ lower, in agreement with the fact that experimentally CO is easily removed from the anti-[Cu2-(Me3p)(CO)2]$^{2+}$ complex.

Overall, the electronic factor just described favors tricoordination over tetracoordination for copper(I) complexes with ligands containing three methylenic units, and thus shifts eq 4 to the left.

$$[\text{Cu}_2(\text{Me}_3\text{p})(\text{Me}_3\text{n})]^2+ = [\text{Cu}_2(\text{Me}_3\text{p})]^2+ + 2 \text{MeCN} \quad (5)$$

which had been previously proposed by Karlin in related complexes. The low CO stretching frequency displayed by [Cu2(L)(CO)2]$^{2+}$ ($L = \text{Me}_3\text{p}$ and Me3m) resembles those of copper-containing proteins possessing tris(imidazole) coordination cores for the copper center (hemocyanins, amine oxidases, peptidylglycine monooxygenase, and cytochrome C oxidase) which exhibit $\nu$(CO) in the range 2043–2063 cm$^{-1}$. Such a low frequency range in synthetic complexes had only been observed so far with nonchelating imidazole ligands or anionic tris(pyrrozyl)borate ligands.

On the other hand, [Cu2(L)(CO)2]$^{2+}$ ($L = \text{Me}_3\text{p}$, 8, and Me2m, 9) display a single $\nu$(CO) at 2087 cm$^{-1}$, which falls in the 2080–2102 cm$^{-1}$ range commonly found for complexes containing neutral ligands.

For the present carbonyl and isocyane complexes, IR spectroscopy unambiguously indicates a terminal coordination mode of the monodentate ligand. Furthermore, the presence of a single band in both cases also indicates that both copper centers are symmetrically related even though this symmetry does not strictly exist in the respective X-ray structures at low temperatures. IR spectroscopy is also very useful to put forward and monitor the existence of a substitution reversible process as shown in eq 3, which is also indicative of the lability of the Cu–C bond. The lability of the rest of the metal–ligand bonds (Cu–N bonds) is also evidenced by variable $T$ NMR spectroscopy.

$[\text{Cu}_2(\text{Me}_3\text{p})]^2+$ (4 and 5) and $[\text{Cu}_2(\text{Me}_3\text{m})]^2+$ (6 and 7) are isolated as tricoordinated complexes in the solid-state. IR spectroscopy is again a very useful tool that allows us to monitor the reaction of these complexes with carbon monoxide in acetone to form presumably the corresponding tetracoordinated complexes $[\text{Cu}_2(L)(\text{CO})_2]^{2+}$ ($L = \text{Me}_3\text{p}$ and Me3m) ($\nu = 2060$ cm$^{-1}$). It is interesting to note that this reaction does not take place using acetonitrile as the solvent in agreement with the existence of the following equilibrium:

(92) We thank one of the reviewers for making us aware of this similarity.
Conclusions and Future Perspectives. The four macrocyclic ligands described in the present paper allow us to gain a certain control of the chemical properties of their corresponding copper(I) dinuclear complexes. In particular, it turns out that the number of methylenic units, two or three, bonding each tertiary amine in the ligands, significantly influences (a) the copper(I) tendency to three or four coordination and (b) relative spatial arrangement between copper(I) metal centers (syn vs anti). Preliminary results related to the oxidative chemistry of these complexes reveal that these two parameters, carefully controlled, produce different reactivity patterns. We are at present dedicating our efforts toward the characterization and rationalization of the oxidative reactivity of these complexes both in an stoichiometric and a catalytic manner.

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Supporting Information Available: Bidimensional NMR spectral characterization data for 10 and 11, VT NMR spectral characterization data for 11. Cartesian atomic coordinates for all the calculated complexes. Crystallographic information files (CIFs) for 8 and 11. This material is available free of charge at http://pubs.acs.org.

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