Dicopper(II) Metallacyclophanes with Electroswitchable Polymethyl-Substituted *para*-Phenylene Spacers

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Abstract: Double-stranded anionic dinuclear copper(II) metallacyclic complexes of the paracyclophane type $[Cu_2L_2]^{4-}$ have been prepared by the Cu^{II}-mediated self-assembly of different para-phenylenebis(oxamato) bridging ligands with either zero-, one-, or four-electron-donating methyl substituents (L = N, N'-para-phenylenebis-(oxamate) (ppba; 1), 2-methyl- N,N'para-phenylenebis(oxamate) (Meppba; 2), and 2,3,5,6-tetramethyl- N,N'-paraphenylenebis(oxamate) (Me₄ppba; **3**)). These complexes have been isolated as their tetra-n-butylammonium (1a-3a), lithium(I) (1b-3b), and tetraphenylphosphonium salts (1c-3c). The X-ray crystal structures of 1a and 3c show a parallel-displaced π -stacked conformation with a smaller deviation from perpendicularity between the two benzene rings and the basal planes of the square planar Cu^{II} ions when increasing the number of methyl substituents (average dihedral angles (ϕ) of 58.72(7) and $73.67(5)^{\circ}$ for **1a** and **3c**, respectively). Variable-temperature (2.0-300 K) magnetic-susceptibility measurements show an overall increase of the intramolecular antiferromagnetic coupling with the number of methyl substituents onto the *para*-phenylene spacers (-J=75-95,100–124, and 128–144 cm⁻¹ for **1a–c**, **2a–c**, and **3a–c**, respectively; H = $-JS_1 \times S_2$). Cyclic voltammetry (CV) measurements show a reversible oneelectron oxidation of the double polymethyl-substituted para-phenylenediamidate bridging skeleton at a relatively low formal potential that decreases with the number of methyl substituents $(E_1 = +0.33, +0.24, \text{ and } +0.15 \text{ V} \text{ vs.}$ SCE for 1-3, respectively). The monooxidized dicopper(II) π -radical cation species 3' prepared by the chemical oxidation of 3 with bromine exhibits intense metal-to-ligand charge-transfer (MLCT) transitions in the visible and

Keywords: copper • density functional calculations • magnetic properties • metallacycles • organic electronics • redox properties near-IR (λ_{max} = 595 and 875 nm, respectively) regions together with a rhombic EPR signal with a seven-line splitting pattern due to hyperfine coupling with the nuclear spin of the two Cu^{II} ions. Density functional (DF) calculations for 3' evidence a characteristic iminoquinonoid-type short-long-short alternating sequence of C-N and C-C bonds for both tetramethyl-para-phenylenediamidate bridges and a large amount of spin density of negative sign mainly delocalized along each of the four benzene C atoms directly attached to the amidate N atoms, which is in agreement with a fully delocalized π stacked monoradical ligand description. Hence, the spins of the two Cu^{II} ions $(S_{Cu}=1/2)$ that are antiparallel aligned in 3 (OFF state) become parallel in 3'(ON state). Further developments may be then envisaged for this new permethylated dicopper(II) paracyclophane with a redox noninnocent ligand as a prototype for molecular magnetic electroswitch.

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Introduction

The control of the electronic (redox, conducting, and/or magnetic) properties of polymetallic complexes by ligand design continues to attract attention in organometallic and coordination chemistry.^[1,2] Besides their interest as models for the fundamental research on electron-exchange (EE) and electron-transfer (ET) phenomena between distant metal centers through extended π -conjugated organic ligands, homo- and heterovalent dimetallic complexes could be also of great importance due to their potential application in electronic and magnetic devices.^[3]

The design and synthesis of redox-active ("noninnocent") aromatic bridging ligands that are able to connect two paramagnetic transition-metal ions to form exchange-coupled, metal-radical or mixed-valent dinuclear complexes, depending on the locus of oxidation/reduction, are a major goal in this field.^[2c,f-j,l-n,s-u] A well-known example is the noninnocent para-phenylenediamine ligand, which has been earlier demonstrated to act as an efficient bridge for the transmission of EE interactions between two Cu^{II} ions.^[4] In fact, N, N, N', N'-tetramethyl-para-phenylenediamine (TMPD) is easily oxidized to the corresponding π -radical iminium cation TMPD'+, referred to as Wurster blue, which is one of the oldest known stable π -radical organic cations.^[5] This work has been recently extended to related π -stacked radical (I) and diradical iminium cations (II) that result from the stepwise two-electron oxidation of doubly polymethylene-bridged bis(para-phenylenediamine)s, which belong to the class of N,N',N'',N'''-tetraalkyl-substituted tetraza-[n.n] para-cyclophane (n=5 and 7; R=Me, Et, and *i*Pr), socalled Wurster blue cyclophanes.^[6]



Metallacyclic complexes containing multiple redox-active, either metal- or ligand-based, paramagnetic centers are a current challenge in the multidisciplinary field of metallosupramolecular chemistry, which lies at the interface of several disciplines, including supramolecular electrochemistry and magnetochemistry.^[7] Moreover, these complexes are of large interest as potential candidates for molecular magnetic electroswitches.^[8,9] Our strategy in this field consists of the use of noninnocent, polymethyl-substituted *para*-phenylenebis(oxamato) bridging ligands that self-assemble with squareplanar Cu^{II} ions to give the corresponding double-stranded dinuclear copper(II) paracyclophanes (**1**–**3**; Scheme 1).^[10] Complex **3** shows intriguing electroswitching magnetic be-



Scheme 1. Illustration of the redox-triggered magnetic switching in dicopper(II) paracyclophanes featuring polymethyl-substituted *para*phenylenebis(oxamate) π -radical cations as bridging ligands.

havior upon a reversible one-electron oxidation of one of the two facing permethylated *para*-phenylene spacers to give the putative metallo π -radical cation species **3'**, as reported recently.^[10b] Indeed, the redox pair **3/3'** presents very different molecular and electronic structures, as supported by preliminary spectroscopic (UV/Vis–NIR and EPR) measurements and DFT calculations.

Herein, we report the complete synthesis, structural and spectroscopic characterization, and magnetic and redox properties of this series of dinuclear copper(II) paracyclophanes (1-3) with the parent N,N'-para-phenylenebis-(oxamate) ligand (ppba) and its 2-methyl- (Meppba) and 2,3,5,6-tetramethyl-substituted (Me₄ppba) derivatives (Scheme 1). The influence of the number of electron-donating methyl substituents in the benzene ring on their unique structural and electronic (magnetic and redox) properties is analyzed and discussed with the aid of calculations based on the density functional (DF) theory. Hence, DF calculations were carried out on 1-3 to elucidate the mechanism of the EE interaction and to examine the influence of steric and/or electronic effects on magnetic coupling along this series. Moreover, DF calculations were performed on the oxidized product of the permethylated derivative 3' to give further support to the putative ligand-based oxidation chemistry, which is ultimately responsible for the electroswitching magnetic behavior (Scheme 1).

Results and Discussion

Syntheses of the ligands and complexes: The ligands were isolated as the diethyl ester acid derivatives with the general formula Et_2H_2L (L=ppba, Meppba, and Me_4ppba; see the Experimental Section). The Et_2H_2ppba and $Et_2H_2Me_4ppba$ proligands were prepared from the straightforward condensation of the corresponding *para*-phenylenediamine and 2,3,5,6-tetramethyl-*para*-phenylenediamine precursors with

ethyl oxalyl chloride ester (1:2 molar ratio) in THF (Scheme 2a). The $Et_2H_2Meppba$ proligand was instead synthesized from the reaction of commercially available 2-methyl*para*-phenylenediamine dihydrogen sulfate with ethyl oxalyl chloride ester (1:2 molar ratio) in the presence of triethylamine as the base in THF (Scheme 2b).



Scheme 2. Synthetic procedure for the Et_2H_2L proligands (L=ppba, Meppba, and Me₄ppba): a) C₂O₂Cl(OEt), THF; b) C₂O₂Cl(OEt), Et₃N, THF.

Complexes 1–3 were isolated as their tetra-*n*-butylammonium, lithium(I), and tetraphenylphosphonium salts (see the Experimental Section). The tetra-*n*-butylammonium salts with the general formula $(nBu_4N)_4[Cu_2L_2]\cdot xH_2O\cdot yCH_3OH$ (L=ppba; x=0, y=2; 1a), Meppba (x=3, y=0; 2a), and Me₄ppba (x=5, y=0; 3a)) were prepared by the one-step

reaction of the corresponding Et₂H₂L proligands with copper(II) perchlorate (2:2 molar ratio) by using tetra-n-butylammonium hydroxide as the base in methanol (Scheme 3a). Alternatively, the lithium(I) salts with the general formula $Li_4[Cu_2L_2] \cdot x H_2O$ (L = ppba)(x=10; 1b), Meppba (x=7;**2b**), and Me₄ppba $(x=9; \mathbf{3b})$) were obtained from the reaction of the corresponding Et₂H₂L proligands with copper(II) nitrate (2:2 molar ratio) by using lithium(I) hydroxide as the base in water (Scheme 3b). The tetraphenylphosphonium salts with the general formula $(Ph_4P)_4$ - $[Cu_2L_2]$ ·xH₂O (L=ppba (x=8; 1c), Meppba (x=8; 2c), and Me₄ppba (x = 15; 3c)) were then synthesized by using two successive steps from the metathesis of the lithium(I) salts with tetraphenylphosphonium chloride in water/acetonitrile through the intermediacy of the silver(I) salts (Scheme 3c,d). The inorganic lithium(I) salts of 1-3 were only soluble in water, whereas the organic tetra-*n*-butylammonium and tetraphenylphosphonium salts were also soluble in organic solvents, such as acetonitrile or dichloromethane. X-ray-quality single crystals of 1 and 3 as their tetra-*n*-butylammonium (1a) and tetraphenylphosphonium (3c) salts were obtained by layering diethyl ether into a solution of 1a in methanol or by slow evaporation of a solution of 3c in water/acetronitrile.

The chemical identity of the ligands and complexes was determined by means of elemental analysis and ¹H NMR and FTIR spectroscopic analysis (see the Experimental Section).

Description of the structures: Single-crystal X-ray diffraction studies of **1a** and **3c** confirmed the expected metallacyclic dicopper(II)tetraaza[3.3]paracyclophane structure, which had been earlier observed for the related complex $Na_4[Cu_2(ppba)_2]$ ·11H₂O (see Figures 1 and 2 and Figures S1 and S2 in the Supporting Information).^[10a] A summary of the crystallographic data is given in Table 1, whereas selected bond lengths and interbond angles are listed in Tables 2 and 3.

The double-stranded dinuclear $[Cu_2^{II}L_2]^{4-}$ anions of **1a** (L=ppba) and **3c** (L=Me₄ppba) are centrosymmetric (see Figures 1a and 2a). The two centrosymmetrically related Cu(1) and Cu(1)^I atoms of **1a** and **3c** have an essentially square-planar coordination environment, CuN₂O₂, which is



Scheme 3. Synthetic procedure for the the tetra-*n*-butylammonium, lithium(I), and tetraphenylphosphonium salts of the $[Cu^{II}_{2}L_{2}]^{4-}$ complexes (L=ppba, Meppba, and Me₄ppba): a) *n*Bu₄NOH; Cu(ClO₄)₂, CH₃OH; b) LiOH · H₂O, Cu(NO₃)₂·3H₂O, H₂O; c) AgNO₃, H₂O; d) Ph₄PCl, H₂O/CH₃CN.

12126 -

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Chem. Eur. J. 2013, 19, 12124-12137

Table 1. Summary of crystallographic data.

	1 a	3 c
formula	C86H160Cu2N8O14	C ₁₂₄ H ₁₃₄ Cu ₂ N ₄ O ₂₇ P ₄
$M [\text{gmol}^{-1}]$	1657.30	2363.31
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a [Å]	10.6798(15)	13.5320(10)
<i>b</i> [Å]	13.9059(18)	15.7080(10)
<i>c</i> [Å]	18.099(2)	15.8360(10)
α [°]	69.861(5)	71.2170(10)
β [°]	74.331(6)	70.9200(10)
γ [°]	75.581(6)	68.9650(10)
$V[Å^3]$	2393.4(5)	2888.2(3)
Z	1	1
$\rho_{\rm calcd} [\rm g cm^{-3}]$	1.150	1.359
$\mu [{\rm mm}^{-1}]$	0.504	0.501
<i>T</i> [K]	296(2)	100(2)
indep. reflect.	8422	9167
obs. reflect. $[I > 2\sigma(I)]$	7479	9045
$R^{[a]}[I > 2\sigma(I)]$	0.0513	0.0412
$wR^{[b]}[I > 2\sigma(I)]$	0.1482	0.1104
<u>S^[c]</u>	1.084	1.036

[a] $R = \Sigma(|F_{\rm o}| - |F_{\rm c}|)/\Sigma |F_{\rm o}|$. [b] $wR = [\Sigma w(|F_{\rm o}| - |F_{\rm c}|)^2 / \Sigma w |F_{\rm o}|^2]^{1/2}$. [c] $S = [\Sigma w(|F_{\rm o}| - |F_{\rm c}|)^2 / (N_{\rm o} - N_{\rm p})]^{1/2}$.

Table 2. Selected bond lengths [Å] and interbond angles $[\circ]$ for 1a.^[a,b]

	1	a	
Cu(1)–N(1)	1.9832(18)	$Cu(1)-N(2)^{I}$	1.9775(18)
Cu(1)–O(1)	1.9693(17)	$Cu(1) - O(4)^{I}$	1.9611(16)
$N(1)-Cu(1)-N(2)^{I}$	108.79(7)	N(1)-Cu(1)-O(1)	83.43(7)
$N(1)-Cu(1)-O(4)^{I}$	164.81(7)	$N(2)^{I}-Cu(1)-O(1)$	164.10(7)
$N(2)^{I}-Cu(1)-O(4)^{I}$	83.45(7)	$O(1)-Cu(1)-O(4)^{I}$	86.34(7)

[a] The estimated standard deviations are given in parentheses. [b] Symmetry code: (I) = -x+2, -y+1, -z+1.

Table 3. Selected bond lengths [Å] and interbond angles [°] for **3c**.^[a,b]

3c			
Cu(1)–N(1)	1.9639(19)	$Cu(1)-N(2)^{I}$	1.9624(19)
Cu(1)–O(1)	1.9793(16)	$Cu(1) - O(4)^{I}$	1.9413(16)
$N(1)-Cu(1)-N(2)^{I}$	106.91(8)	N(1)-Cu(1)-O(1)	82.40(7)
$N(1)-Cu(1)-O(4)^{I}$	170.08(7)	$N(2)^{I}-Cu(1)-O(1)$	169.36(7)
$N(2)^{I}-Cu(1)-O(4)^{I}$	82.86(7)	$O(1)-Cu(1)-O(4)^{I}$	87.71(7)

[a] The estimated standard deviations are given in parentheses. [b] Symmetry code: (I) = -x+2, -y+1, -z.



Figure 1. a) Perspective view of the centrosymmetric anionic dicopper unit of **1a** with the atom-numbering scheme (symmetry code: (I) = -x + 2, -y + 1, -z + 1). b) Top and c) side projection views of the metallacyclic core of **1a**.



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Figure 2. a) Perspective view of the centrosymmetric anionic dicopper unit of **3c** with the atom-numbering scheme (symmetry code: (I) = -x + 2, -y + 1, -z). b) Top and c) side projection views of the metallacyclic core of **3c**.

formed by two amidate nitrogen atoms (Cu–N=1.9775(18)– 1.9832(18) and 1.9624(19)–1.9639(19) Å for **1a** and **3c**, respectively) and two carboxylate oxygen atoms (Cu–O= 1.9611(16)–1.9693(17) and 1.9413(16)–1.9793(16) Å for **1a** and **3c**, respectively) from two oxamato donor groups (mean plane deviations from the metal basal plane of $\pm 0.199(1)$ and ± 0.029 Å for N(1) and N(2)^I and of $\pm 0.166(1)$ and ± 0.034 Å for O(1) and O(4)^I in **1a** and **3c**, respectively). The values of the tetrahedral twist angle τ between the mean planes of Cu(1)N(1)O(1) and Cu(1)N(2)^IO(4)^I are 16.1(1) and 5.0(1)° for **1a** and **3c**, respectively, indicating thus a stronger tetrahedral distortion for the metal coordination site in the unsubstituted ancestor **1a**.

Within the dicopper(II) paracyclophane cores, Cu₂(p- $N_2C_6Me_n)_2$ (n=0 and 4 for **1a** and **3c**, respectively), the polymethyl-substituted para-phenylene spacers that are connected by the two N-Cu-N linkages have a parallel-displaced π -stacked conformation (Figures 1b and 2b). The values of the centroid-centroid interring distance h between the two benzene rings are 3.435(2) and 3.349(2) Å for 1a and 3c, respectively, whereas the values of the angle between the centroid-centroid vector and their normal θ are 23.27(4) and 17.56(5)° for **1a** and **3c**, respectively (Figures 1c and 2c). Hence, the entire metallacyclophane molecule of 1a and 3c has an approximate C_{2h} symmetry, in which the copper basal planes are not exactly oriented perpendicular to the benzene planes (Figures 1 c and 2 c). The values of the dihedral angle ϕ between the benzene and copper basal planes are 58.72(7) and 73.67(5)° for 1a and 3c, respectively. This difference reflects a significantly larger deviation from the ideal D_{2h} symmetry that corresponds to the alternative eclipsed π -stacked, orthogonal conformation ($\phi = 90^{\circ}$) in the unsubstituted ancestor 1a (Figures 1b and 2b). This situation is likely explained by the electron-donating nature of the methyl substituents, which favors the interring π - π stacking interactions between the two facing benzene rings in spite of the steric hindrance among their methyl substituents.

In the crystal lattice, the $[Cu^{II}_{2}L_{2}]^{4-}$ anions of **1a** and **3c** establish weak hydrogen bonds with the crystallization sol-

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- 12127

vent molecules of methanol and water for **1a** and **3c**, respectively, through the carbonyl and/or carboxylate oxygen atoms from the oxamato groups ($O \cdots O = 2.772(5)$ and 2.812(2)–2.919(2) Å for **1a** and **3c**, respectively). This situation gives rise to either discrete (**1a**) or extended layers of hydrogen-bonded anionic dicopper(II) units (**3c**), which are well separated from each other by the bulky tetra-*n*-butyl-ammonium or tetraphenylphosphonium cations in **1a** and **3c**, respectively (see Figures S1 and S2 in the Supporting Information). The values of the intramolecular Cu…Cu distance *r* across the double polymethyl-substituted *para*-phenylenediamidate bridges are 8.002(2) and 7.944(2) Å for **1a** and **3c**, respectively, whereas the shortest intermolecular Cu…Cu distances are 10.680(1) and 10.650(2) Å for **1a** and **3c**, respectively.

Magnetic properties: The magnetic properties of the tetra-*n*-butylammonium, lithium(I), and tetraphenylphosphonium salts of **1–3** in the form of χ_M versus *T* plots (χ_M is the molar magnetic susceptibility per dinuclear unit) are typical of antiferromagnetically coupled Cu^{II}₂ pairs (see Figure 3 and Fig-



Figure 3. Temperature dependence of χ_M for 1c (\bigcirc), 2c (\square), and 3c (\triangle). The solid lines are the best-fit curves (see Table 4).

ures S3 and S4 in the Supporting Information). In fact, the presence of $\chi_{\rm M}$ maxima in the ranges 65–85, 90–110, and 115–130 K for **1–3**, respectively, indicates a ground singlet (S=0) spin state that results from the antiferromagnetic coupling between the unpaired electron of each Cu^{II} ion ($S_{\rm Cu}=1/2$). The qualitatively similar magnetic behavior with variation in the countercation for **1–3** demonstrates that the magnetic coupling is intramolecular in origin; the intermolecular interactions through the Li^I ions, if any, are negligible.

The magnetic susceptibility data of the tetra-*n*-butylammonium, lithium(I), and tetraphenylphosphonium salts of **1**– **3** were analyzed according to the spin Hamiltonian for a dinuclear model [Eq. (1) with $S_1=S_2=S_{\rm Cu}=1/2$], where J is the magnetic coupling parameter and g is the Landé factor of the Cu^{II} ions. The least-squares fit of the experimental data obtained by using the Bleaney–Bowers expression [Eq. (2) where N is the Avogadro number, β is the Bohr magneton, and $k_{\rm B}$ is the Boltzmann constant] gave -J values in the ranges 75–95, 100–124, and 128–144 cm⁻¹ for **1–3**, respectively (Table 4). The moderately strong intramolecular antiferromagnetic coupling for **1–3**, despite the relatively

Table 4. Least-squares fitting magnetic data.

Complex	$-J [m cm^{-1}]^{[a]}$	g ^[b]	$R \times 10^{5[c]}$
1a	75	2.05	3.0
1b	95	2.05	1.1
1c	94	2.06	0.7
2a	112	2.05	1.0
2 b	100	2.04	0.4
2c	124	2.08	0.4
3a	128	2.04	1.5
3b	130	2.06	0.5
3c	144	2.10	2.7

[a] Magnetic coupling parameter. [b] Landé factor. [c] Agreement factor defined as $R = \Sigma[(\chi_M T)_{exp} - (\chi_M T)_{calcd}]^2 / \Sigma[(\chi_M T)_{exp}]^2$.

large intramolecular Cu···Cu separation ($r \approx 8.0$ Å), evidences that the EE interaction between the two Cu^{II} ions is mainly transmitted through the π -bond system of the polymethyl-substituted *para*-phenylenediamidate bridges.^[10a] The overall strengthening of the antiferromagnetic coupling with the number of methyl substituents along this series is remarkable and, more importantly, it agrees with the theoretical calculations (see discussion below).

$$\boldsymbol{H} = -J\boldsymbol{S}_1 \times \boldsymbol{S}_2 + g(\boldsymbol{S}_1 + \boldsymbol{S}_2)\boldsymbol{\beta}\boldsymbol{H}$$
(1)

$$\chi_{\rm M} = (2N\beta^2 g^2/k_{\rm B}T)/[3 + \exp(-J/k_{\rm B}T)]$$
(2)

Redox properties: The cyclic voltammograms (CVs) of the tetra-*n*-butylammonium and tetraphenylphosphonium salts of **1–3** in acetonitrile (25 °C 0.1 M *n*Bu₄NPF₆) show identical results independent of the nature of the countercation. They exhibit two well-separated one-electron oxidation waves at $E_1 = +0.33$, +0.24, and +0.15 V versus SCE and $E_2 = +$ 0.79, +0.80, and +0.86 V versus SCE for **1–3**, respectively (Table 5), with only the first oxidation wave being reversible (Figure 4). Indeed, the values of the anodic-peak to cathodic-peak separation of the first redox wave for **1–3** are comparable to that of the ferricinium/ferrocene couple (ΔE (Fc⁺/

Table 5. Selected electrochemical data.^[a]

Complex	$E_1 [V]^{[b]}$	$E_2 [V]^{[b]}$	$K_{\rm c}^{[{ m c}]}$
L	+0.33 (80)	+0.79 (i)	0.6×10^{8}
2	+0.24(80)	+0.80 (i)	0.3×10^{10}
3	+0.15(70)	+0.86 (i)	1.1×10^{12}

[a] In acetonitrile (25 °C 0.1 M *n*Bu₄NPF₆) with a scan rate of 100 mV s⁻¹. [b] All formal potential *E* values were taken as the half-wave potentials versus SCE, except for the irreversible (i) waves, for which the anodic peak potentials were given. The values of the peak-to-peak separation (ΔE /mV) between the anodic- and cathodic-peak potentials are given in parentheses. [c] The values of the comproportionation constant K_c were calculated from the difference in the formal potential values between the two one-electron oxidation waves ($\Delta E_{12} = E_2 - E_1$) through the expression log $K_c = \Delta E_{12}/0.059$.



Figure 4. CVs of **1** (dotted line), **2** (dashed line), and **3** (solid line) in acetonitrile at $25 \,^{\circ}$ C (0.1 M *n*Bu₄NPF₆) with a scan rate of 100 mV s⁻¹.

Fc)=70 mV). A perfect linear plot of the peak current against the square root of the scan rate is obtained for the first redox wave of **3**, which is then stated to be completely reversible on the voltammetric timescale.

These two redox processes for 1-3 would correspond to the stepwise ligand-centered oxidation of each of the two facing polymethyl-substituted para-phenylenediamidate bridges. Hence, the resulting dicopper(II)/ π radical and diradical species are the metallacyclic analogues of forms I and **II** from the N,N',N''-tetramethyltetraza[7.7]paracyclophane, which shows similar values of the formal potentials to those of **3** ($E_1 = +0.08$ and $E_2 = +0.69$ V vs. SCE).^[6a] The observed linear decrease of the E_1 values according to 1>2>3 indicates that the oxidation of the polymethylsubstituted para-phenylenediamidate bridge is favored as the number of electron-donating methyl substituents increases (Figure 5). On the contrary, the linear increase of the E_2 values along this series reflects the higher thermodynamic stability of the one-electron oxidized dicopper(II) π -radical species according to 1' < 2' < 3' (Figure 5). Hence, the estimated values of the comproportionation constant $(K_c = 0.6 \times 10^8, 0.3 \times 10^{10}, \text{ and } 1.1 \times 10^{12} \text{ for } 1'-3', \text{ respectively};$ Table 5) follow an almost perfect exponential increase with the number of methyl substituents n onto the paraphenylenediamidate bridges (inset of Figure 5).

Spectroscopic properties: Complex **3'** was prepared by chemical oxidation of the tetraphenylphosphonium salt of **3** with bromine in acetonitrile ($E(Br_2/Br^-) = +0.47$ V vs. SCE) (see the Experimental Section). The deep-blue dicopper(II) π -radical species prepared in situ is fairly stable in acetonitrile at 5 °C (see Figure S5 in the Supporting Information), but progressively decomposes when going up to room temperature. The decomposition reaction for **3'** follows second-order kinetics (more probably, a disproportionation reaction) with calculated half-life values of $t_{1/2}$ =9.4, 7.3, and 3.1 hours at 5,



FULL PAPER

Figure 5. Plot of the E_1 (\bigcirc) and E_2 (\square) values with the number of methyl substituents *n* for **1–3**. The inset show the exponential dependence of the calculated K_c values (data from Table 5). The solid lines correspond to the best-fit curves (see text).

Table 6. Selected kinetic data for the decomposition of 3'.[a]

<i>T</i> [°C]	$c_0 \times 10^4 [\text{m}]^{[b]}$	$k \; [\mathrm{M}^{-1} \mathrm{s}^{-1}]^{[\mathrm{b}]}$	$t_{1/2} [h]^{[c]}$
5	1.00(1)	0.295(3)	9.4
15	0.64(2)	0.598(6)	7.3
25	0.48(4)	1.86(2)	3.1

[a] In acetonitrile. [b] The initial concentration c_0 and second-order rate constant k values were calculated from the reciprocal of the absorbance at $\lambda_{\text{max}} = 875 \text{ nm} (1/A_{875})$ versus time plots through the expression $(1/c) = (1/c_0) + kt$ with $c = A_{875}/(l \times \varepsilon_{875})$, where l is the path length (l=1 cm) and ε_{875} is the molar extinction cofficient at $\lambda_{\text{max}} = 875 \text{ nm} (\varepsilon_{875} = 5660 \text{ m}^{-1} \text{ cm}^{-1})$. [c] The half-life $t_{1/2}$ is the time required for the concentration to fall from c_0 to $c_0/2 [t_{1/2} = (1/c_0)(1/k)]$.

15, and 25 °C respectively (see Table 6 and Figure S6 in the Supporting Information).

The electronic absorption spectrum of **3**' shows two intense bands in the Vis–NIR region at $\lambda_{max} = 595$ and 875 nm ($\varepsilon = 1460$ and $5660 \text{ m}^{-1} \text{ cm}^{-1}$, respectively) (Table 7 and Figure 6). In contrast, **3** exhibits two intense UV/Vis bands at $\lambda_{max} = 325$ and 420 nm ($\varepsilon = 6450$ and $3810 \text{ m}^{-1} \text{ cm}^{-1}$, respec-

Table 7. Selected UV/Vis–NIR^[a] and calculated EPR^[b] spectroscopic data.

Complex	λ_{\max} [nm] ^[c]	$ u$ $[\mathrm{cm}^{-1}]^{\mathrm{[d]}}$	$g_x^{[e]}$	$g_{y}^{[e]}$	$g_z^{[e]}$
3	325 (6450) 420 (3810)	30770 23810	2.005 (20)	2.085 (15)	2.239 (93)
3'	575 (180) 595 (1460) 875 (5660)	17 390 16 805 11 430	2.012 (30)	2.065 (20)	2.250 (108)

[a] In acetonitrile at 5°C. [b] In acetonitrile at 77 and 4 K for **3** and **3**', respectively. [c] The values of the molar extinction cofficient ε (m^{-1} cm⁻¹) are given in parentheses. [d] The wavenumber is defined as $\nu = 1/\lambda_{max}$. [e] The values of the Landé factors g_i and the hyperfine coupling constants A_i associated with the *x*, *y*, and *z* components of the allowed $M_s = 0 \rightarrow M_s = \pm 1$ transitions of the excited triplet (S=1) spin state for **3**, and the corresponding ones of the $M_s = -1/2 \rightarrow M_s = \pm 1/2$ transition of the ground doublet (S=1/2) spin state for **3**' were calculated by using the XSOPHE program. The values of the calculated hyperfine coupling constants (A_i/G) are given in parentheses.



A EUROPEAN JOURNAL

Figure 6. Electronic spectra of a) 3 and b) 3' in acetonitrile at 5 °C.

tively), together with a Vis band of lower intensity at λ_{max} = 575 nm (ε =180 M⁻¹ cm⁻¹), which corresponds to the typical d–d transitions of a square-planar Cu^{II} ion, as earlier found in related mononuclear oxamate copper(II) complexes.^[11] Because of their greater intensity, the unique Vis–NIR spectral features of **3'** would mainly correspond to either metal-to-ligand (MLCT) or ligand-to-metal charge-transfer (LMCT) transitions. Yet a partial contribution from interligand charge-transfer (ILCT) transitions cannot be discarded, by analogy with those found in fully delocalized, π -stacked radical cation species of Wurster blue cyclophanes (see the theoretical calculations below).^[6d]

The X-band EPR spectra of frozen solutions of 3 and 3' in acetonitrile at 77 and 4 K, respectively, show a rhombic signal with a complex multiline splitting pattern (Figure 7). These spectral features would be associated with either the excited triplet (S=1) spin state of the moderately strong antiferromagnetically coupled dicopper(II) pair (3) or the ground doublet (S=1/2) spin state of the very strong antiferromagnetically coupled dicopper(II) π -radical triad (3'), as confirmed by the temperature dependence of the X-band EPR spectra of 3 and 3' in frozen solutions of acetonitrile (see Figure S7 in the Supporting Information). So, the double integral of the intensity of the EPR signal for 3 exhibits a maximum at approximately 80 K, whereas it increases continuously as the temperature decreases for 3'(Figure 8), in agreement with the postulated magnetic switching behavior for the redox pair of permethylated derivatives 3/3' (see Scheme 1).

The least-squares fit of the double-integrated EPR signal intensity (*DI*) in arbitrary units of **3** through the Bleaney– Bowers expression gave J = -91 cm⁻¹ (solid line in Figure 8), as expected for a moderately strong antiferromagnetically coupled dicopper(II) species. This value is however somewhat smaller than that obtained from the fit of the magnetic susceptibility data of the structurally characterized tetraphenylphosphonium salt of **3** (J = -144 cm⁻¹), thus reflecting the small variations of the molecular geometry in solution with acetonitrile and in the solid state. On the other hand, the double-integrated EPR signal intensity of **3'** follows a Curie law behavior (solid line in Figure 8), as expected for a very strong antiferromagnetically coupled di-



Figure 7. X-band EPR spectra of a) **3** and b) **3**' in acetonitrile at 77 and 4 K, respectively. The bold lines are the simulated spectra (see Table 7).



Figure 8. Temperature dependence of the double-integrated EPR signal intensity for $\mathbf{3}$ (Δ) and $\mathbf{3}'$ (\blacktriangle). The solid lines are the best-fit curves (see text).

copper(II) π -radical species (see the theoretical calculations below).

The EPR spectra of **3** and **3'** were simulated by using the XSOPHE program^[12] that diagonalizes the full Hamiltonian matrix within the basis of the three S=1 spin functions $(M_s=0, \pm 1)$ for **3** or the two S=1/2 spin functions $(M_s=\pm 1/2)$ for **3'** (bold lines in Figure 7). The calculated values of

FULL PAPER

the Landé factors are $g_x = 2.005$ and 2.012, $g_y = 2.085$ and 2.065, and $g_z = 2.239$ and 2.250 for **3** and **3'**, respectively, whereas the hyperfine coupling constants are $A_x = 20$ and 30 G, $A_y = 15$ and 20 G, and $A_z = 93$ and 108 G for **3** and **3'**, respectively (Table 7).

The most remarkable feature of the X-band EPR spectra of **3** and **3**' is the well-resolved seven-line splitting of the g_z signal due to the hyperfine coupling with the nuclear spin of the two Cu^{II} ions $(2nI_{Cu}+1=7 \text{ with } n=2 \text{ and } I_{Cu}=3/2;$ Figure 7). This situation clearly contrasts with that expected for a metal-centered oxidation that would give a simple four-line splitting typical of a localized dicopper(II,III) species for **3**' $(2nI_{Cu}+1=4 \text{ with } n=1 \text{ and } I_{Cu}=3/2)$. Although an alternative delocalized dicopper(II,III) description cannot be definitely discarded for 3', this situation agrees more with that expected for an antiferromagnetically coupled dicopper(II) π -radical species that results from a ligand-centered oxidation. In fact, the calculated A_z value of 3' is almost four thirds that of 3 ($A_z = 93$ vs. 108 G for 3 and **3**', respectively), as expected from the different S=1 Cu^{II}₂ and S = 1/2 Cu^{II}₂ π -radical (3 and 3', respectively) formulations (A(S=1/2)=4/3A(S=1)) with $A(S=1)=1/2A_{Cu}$. In contrast, the calculated A_z value of a delocalized S = 1/2 Cu^{II,III}₂ mixed-valent formulation for 3' $(A(S=1/2)=1/2A_{Cu})$ would be identical to that of a S=1 Cu^{II}₂ formulation for **3** (A- $(S=1)=1/2A_{Cu}$), as both of them are half the value for a localized S = 1/2 Cu^{II,III}₂ mixed-valent formulation (A(S=1/2) = $A_{\rm Cu}$).

Theoretical calculations: DF calculations on the model complexes 1–3 with an imposed planar conformation of the copper basal planes ($\tau = 0^{\circ}$) and a perpendicular orientation of the copper basal planes with respect to the benzene rings ($\phi = 90^{\circ}$) are summarized in Table 8 (see the Computational Details in the Experimental Section). All four possible configurations of the methyl substituents from the two facing benzene rings were considered for 2 (Scheme 4). For all these orthogonal model complexes with polymethyl-substituted benzene spacers $-C_6H_{(4-n)}Me_n$ - (n=0, 1, and 4 for 1–3, respectively), the energy calculations show a ground broken-symmetry (BS) singlet (S=0) spin state that lies well below the excited triplet (S=1) spin state. The calculated value of the singlet/triplet energy gap ($\Delta E_{ST} = -J$) in-

Table 8. Selected calculated energy data for the orthogonal model complexes **1–3**.

	Molecular symmetry	$\Delta E_{ m ST} \ [m cm^{-1}]^{[a]}$	$\delta \ [ext{cm}^{-1}]^{[ext{b}]}$
1	D_{2h}	130 (106)	2992 (2702)
2 (pseudo-gem)	C_s	131	3057
2 (pseudo- <i>ortho</i>)	C_2	128	3008
2 (pseudo- <i>para</i>)	C_i	128	3017
2 (pseudo-meta)	C_2	129	3025
3	D.,	139(124)	3250 (2976)

[a] The calculated values of the singlet/triplet energy gap ($\Delta E_{ST} = -J$) of the optimized molecular geometries of **1** and **3** in acetonitrile are given in parentheses. [b] The calculated values of the energy gap between the two SOMOs for the triplet spin state of the optimized molecular geometries of **1** and **3** in acetonitrile are given in parentheses.



Scheme 4. Illustration of the metallacyclic core for the pseudo-*gem* (a), -*ortho* (b), -*para* (c), and -*meta* (d) isomers of **2**.

creases with the number of methyl substituents from 130 to 139 cm^{-1} for **1** and **3**, respectively, whereas they vary in the narrow range of $128-131 \text{ cm}^{-1}$ for the pseudo-*gem*, *-ortho*, *-para*, and *-meta* isomers of **2**, values which are closer to that of **1** than to that of **3**. However, the calculated -J values for these orthogonal model complexes **1**-**3** (ϕ =90° and τ =0°) significantly differ from the experimental ones (Figure 9). The larger deviations among the calculated and experimental values in **1** relative to **3** are likely due to the greater loss of orthogonality between the copper and benzene planes and/or the larger tetrahedral distortion of the copper center when decreasing the number of methyl substituents, as evidenced by the crystal structures of **1a** and **3c**.

DF energy calculations on the optimized molecular geometries of **1** and **3** in acetonitrile show a much better agreement with the experimental data (see the Computational Details). Hence, the calculated -J values (-J=106 and 124 cm^{-1} for **1** and **3**, respectively; Table 8) are close to the experimental values obtained from the fit of the magneticsusceptibility data in the solid state (-J=75-95 and 128-



Figure 9. Plot of the calculated values of the magnetic coupling parameter (-J) with the number of methyl substituents n for the orthogonal model complexes 1-3 (\blacktriangle) and for the optimized molecular geometries of 1 and 3 in acetonitrile (\bigtriangledown) (data from Table 8). The solid line corresponds to the second polynomial fit curve. The experimental (-J values for the tetra-n-butylammonium (\bigcirc), lithium(I) (\square), and tetraphenylphosphonium salts (\diamondsuit) of 1-3 are also shown for comparison (data from Table 4). The inset shows the linear dependence of the calculated -J values for the orthogonal model complexes 1-3 (\bigstar) with the square of the energy gap between the two SOMOs (data from Table 8). The solid line corresponds to the linear fit curve (see text).

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144 cm⁻¹ for **1a–c** and **3a–c**, respectively; Table 4). This situation reflects the structural similarities among the optimized molecular geometries ($\tau = 8.5$ and 1.9° ; $\phi = 63.9$ and 75.2° for 1 and 3, respectively, and the experimental values $(\tau = 16.1(1) \text{ and } 5.0(1)^\circ; \phi = 58.72(7) \text{ and } 73.67(5)^\circ \mathbf{1a} \text{ and}$ **3c**, respectively). As a matter of fact, the optimization geometry calculations of 1 and 3 in acetonitrile evidence a significantly lesser tetrahedral distortion of the metal environment and a smaller deviation from the ideal D_{2h} symmetry, which corresponds to the orthogonal conformation when going from the unsubstituted ancestor 1 to the tetramethylsubstituted derivative 3, as observed experimentally. More importantly, the calculated -J values for the optimized molecular geometries of 1 and 3 in acetonitrile increase with the increasing number of methyl substituents from n=0 to 4 for 1 and 3, respectively, in agreement with the observed experimental trend. Overall, this indicates that the magnetic coupling along this series is governed by both electronic and structural factors associated with the electron-donor properties and steric requirements of the methyl group (Figure 9).

DF molecular-orbital (MO) calculations on the optimized molecular geometries of 1 and 3 in acetonitrile reveal a parallel increase in the calculated energy separation between the two singly occupied molecular orbitals (SOMOs) ($\delta =$ 2702 and 2976 cm⁻¹ for **1** and **3**, respectively; Table 8). In fact, the calculated -J values vary almost linearly with the square of δ for the orthogonal models 1–3, in agreement with the simplest orbital models of the EE interaction (inset of Figure 9).^[13] This finding is explained by the electrondonor character of the methyl group, which increases the energy of the two π ligand orbitals involved in the EE mechanism, thus favoring the metal/ligand orbital mixing because of their smaller energy separation relative to the 3d metal orbitals (ΔE_{M-L} and ($\Delta E_{M-L} + \Delta E_L$); Scheme 5). This fact ultimately leads to an increased delocalization of the unpaired electrons of the Cu^{II} ions onto the π -conjugated electron system of the para-phenylene spacers with the increasing number of methyl substituents n for 1–3. This situation is clearly reflected on the two calculated SOMOs for the triplet spin state of 3, which show a high metal/ligand covalency and strongly ligand-delocalized character (Figure 10). These two SOMOs, noted b_{g}^{*} and b_{u}^{*} , are composed of the symmetric and antisymmetric combinations respectively, of the $d(x^2-y^2)$ orbitals of the square-planar Cu^{II} ions mixed with the corresponding combinations of appropriate symmetry of the two π -type orbitals of the tetramethyl-para-phenylenediamidate bridges, which are in turn made up of p(z) orbitals of the carbon and nitrogen atoms (Scheme 5).

DF calculations on the optimized molecular geometries of **3** and **3'** in acetonitrile show ground BS singlet (S=0) and doublet (S=1/2) spin states, respectively (see the Computational Details in the Experimental Section). Several electronic configurations were checked for **3'**, even by modifying the starting geometrical parameters to stabilize them, but in all cases the geometry optimization leads to a unique geometry that corresponds to a S=1/2 Cu^{II}₂ π -radical configura-



Scheme 5. Simplified energy-level diagram of the EE interaction in dicopper(II) paracyclophanes with polymethyl-substituted *para*phenylenebis(oxamate) bridging ligands.



Figure 10. Perspective views of the calculated SOMOs for the triplet spin state of **3**. The isoelectronic surface corresponds to a cutoff value of 0.003 ebohr^{-3} .

tion, which results from the one-electron oxidation of the double tetramethyl-*para*-phenylenediamidate bridge skeleton. This ground doublet (S=1/2) spin state of **3'**, labeled | $\uparrow \downarrow \uparrow >$, would result from the antiferromagnetic coupling between the central π -radical $(S_R=1/2)$ cation and the two peripheral Cu^{II} $(S_{Cu}=1/2)$ ions within the Cu^{II}₂ π -radical triad. In addition, there are two excited doublet (S=1/2) and quartet (S=3/2) spin states, labeled $(|\uparrow\uparrow\downarrow>)$ and $(|\uparrow\uparrow\uparrow>)$, respectively, which are located at 1897 and

12132 -

5550 cm⁻¹, respectively, well above the ground doublet (S =1/2) spin state. The metal/radical magnetic coupling parameter can then be calculated from the energy gap between the two low-lying doublet spin configurations ($\Delta E = E(|\uparrow\uparrow\downarrow\rangle)$) $- E(|\uparrow\downarrow\uparrow\rangle) = -J'$). The calculated -J' value of 1897 cm⁻¹ for 3' is very large, thus ensuring that only the ground doublet (S=1/2) spin state is thermally populated with essentially no population of the excited doublet (S=1/2) and quartet (S=3/2) spin states, as deduced from the EPR spectroscopic data of 3' in acetonitrile. This situation is that expected for a direct antiferromagnetic exchange interaction between the unpaired electrons that occupy the $d(x^2-y^2)$ orbitals of the square-planar Cu^{II} ions and that occupy the π type orbital of the tetramethyl-para-phenylene radical cation. By comparison, the ground BS singlet (S=0) spin state of 3 that results from the antiferromagnetic coupling between the two Cu^{II} ($S_{Cu} = 1/2$) ions within the Cu^{II}₂ pair lies at only 124 cm⁻¹ below the excited triplet (S=1) spin state. The magnetic coupling parameter can be calculated from the singlet/triplet energy gap between these two spin configurations, labeled $|\uparrow\downarrow\rangle$ and $|\uparrow\uparrow\rangle$, respectively ($\Delta E =$ $E(|\uparrow\uparrow\rangle) - E(|\uparrow\downarrow\rangle) = -J$). The calculated -J value of 124 cm^{-1} for **3** is close to the experimental value obtained from the fit of the EPR spectroscopic data in acetonitrile $(J = -91 \text{ cm}^{-1})$. This situation corresponds to an indirect (through-bond) antiferromagnetic exchange interaction between the unpaired electrons that occupy the $d(x^2-y^2)$ orbitals of the square-planar Cu^{II} ions through the diamagnetic tetramethyl-para-phenylene spacers.

The optimized molecular geometries for the ground BS singlet (3) and doublet (3') spin states in acetonitrile are consistent with the generation of a fully delocalized (mixed-valent), π -stacked monoradical ligand upon one-electron oxidation of the double tetramethyl-*para*-phenylenediamidate bridging skeleton (Table 9). The validity of this approach is confirmed by the structural similarities, in terms of both bond lengths and interbond angles, between the optimized structures of 3 in acetonitrile and the tetraphenylphosphonium salt 3c determined in the solid state by using single-crystal X-ray diffraction (Table 9).

A small but non-negligible bond alternation is observed within the two equivalent benzene rings of 3', with average short and long intraring C(Me)-C(Me) and C-C(Me) distances of 1.406 and 1.430 Å, respectively. In contrast, 3 shows no appreciable bond alternation, with a mean value of the intraring C(Me)-C(Me) and C-C(Me) distances of 1.416 and 1.420 Å, respectively. Moreover, the amidate substituents of the benzene rings in 3' have a common value of the C-N distance of 1.411 Å, which is significantly shorter than that of 1.436 Å in 3, thus indicating the development of a partial double bond character typical of imines. Overall, these small but non-negligible bond-length changes evidence an iminoquinonoid character for both tetramethyl-para-phenylenediamidate bridges of 3', in rather good agreement with the recently reported X-ray crystal structure of the fully delocalized, π -stacked radical iminium cation I of the 2,2-dimethylpropylene-bridged N,N',N'',N'''- Table 9. Selected structural data for the optimized geometries in acetonitrile of the ground BS singlet and doublet spin states of **3** and **3**', respectively.

	3 ^[a]	3′
C–N [Å]	1.436 (1.427)	1.411
	1.436 (1.431)	1.411
C–C(Me) (intraring) [Å]	1.417 (1.398)	1.426
	1.417 (1.401)	1.426
	1.424 (1.401)	1.434
	1.424 (1.402)	1.434
C(Me)–C(Me) (intra-ring) [Å]	1.415 (1.394)	1.405
	1.417 (1.401)	1.407
C…C (inter-ring) [Å]	3.456 (3.290)	3.245
	3.456 (3.290)	3.245
C(Me)…C(Me) (inter-ring) [Å]	3.540 (3.359)	3.338
	3.540 (3.359)	3.338
	3.544 (3.399)	3.338
	3.544 (3.399)	3.338
$\phi \ [^{\mathbf{o}}]^{[\mathbf{b}]}$	75.23 (73.67)	80.91

[a] The experimental structural data of 3c are given in parentheses.[b] Dihedral angle between the copper basal and benzene planes.

tetramethyltetraza[5.5]paracyclophane (CH–CH=1.364(4)–1.376(4), C–CH=1.399(4)–1.420(4), and C–N=1.374(4)–1.386(4) Å).^[6d]

The most salient structural feature for 3' is, however, the inter-ring C…C and C(Me)…C(Me) distances of 3.245 and 3.338 Å, respectively, values which are significantly shorter than the Van der Waals contact (3.40 Å). By comparison, the average inter-ring C···C and C(Me)···C(Me) distances for 3 are 3.456 and 3.542 Å, respectively. The approach of the benzene rings is accompanied by slightly smaller deviations from the eclipsed π -stacked, orthogonal molecular conformation on going from 3 to 3' ($\phi = 75.23$ and 80.91°, respectively). These inter-ring close contacts reveal the occurrence of an incipient π - π long-bond formation between the two facing tetramethyl-para-phenylene spacers within the metallacyclophane core of 3', as expected from the ligand delocalized nature of this monooxidized metallacyclic radical species. This situation has also been found in the fully delocalized, π -stacked radical iminium cation I of the N, N', N'', N'''-tetramethyl-2,2-dimethylpropylene-bridged tetraza[5.5] paracyclophane, which have similar inter-ring π stacking bonding interactions (C···C=3.188(4)-3.448(4) and CH···CH=3.216(4)-3.492(4) Å).^[6d]

Spin densities obtained by natural-bond orbital (NBO) analysis on the ground BS singlet (3) and doublet (3') spin states in acetonitrile agree with a switch from antiparallel to parallel alignment of the local spin moments of the Cu^{II} ions by the presence of the delocalized π -radical cation generated upon one-electron oxidation of the double tetramethyl*para*-phenylenediamidate bridge skeleton (Table 10 and Figure 11). So, the spin-density distribution for the ground BS singlet spin state of 3 shows spin densities of opposite sign at the metal atoms ($\rho_{\rm M} = \pm 0.5553$ e) and small but nonnegligible spin densities of alternating sign at the adjacent carbon atoms of the benzene rings that result from spin-polarization effects by the amidate nitrogen atoms (Figure 11a). On the contrary, the spin-density distribution for the ground doublet spin state of 3' reflects spin densities of

Table 10. Selected calculated atomic spin-density data for the optimized geometries in acetonitrile of the ground BS singlet and doublet spin states of **3** and **3'**, respectively.^[a,b]

	3	3′
Cu(1)	± 0.5553	+0.4915
N(1)	-0.1027	+0.0390
N(2)	+0.1021	+0.0389
O(1)	-0.0947	+0.0815
O(2)	-0.0078	+0.0086
O(3)	-0.0068	-0.0017
O(4)	+0.0946	+0.0813
O(5)	+0.0077	+0.0086
O(6)	+0.0067	-0.0018
C(1)	+0.0401	-0.1121
C(2)	-0.0346	+0.0039
C(3)	+0.0345	+0.0037
C(4)	-0.0401	-0.1121
C(5)	+0.0344	-0.0027
C(6)	-0.0343	-0.0030
C(7)	+0.0026	-0.0045
C(8)	+0.0067	-0.0055
C(9)	-0.0025	-0.0045
C(10)	-0.0068	-0.0055
C(20)	+0.0026	+0.0006
C(30)	-0.0025	+0.0006
C(50)	-0.0025	+0.0017
C(60)	+0.0025	+0.0017

[a] The calculated values of the atomic spin density (ρ_x) are given in e units. [b] The atom-numbering scheme is given in Figure 2 a.



Figure 11. Perspective views of the calculated spin density distribution for the ground BS singlet and doublet spin configurations of a) **3** and b) **3'**, respectively. Deep- and light-gray contours represent positive and negative spin densities, respectively. The isodensity surface corresponds to a cutoff value of 0.003 ebohr^{-3} .

the same sign at the metal atoms ($\rho_{\rm M} = +0.4915$ e) and a large amount of spin density of opposite sign mainly delocalized along each of the four benzene carbon atoms directly attached to the amidate nitrogen atoms ($\rho_{\rm C} = -0.1122$ e; Figure 11b). This picture nicely corresponds to that expected for a metallacyclic analogue of the purely organic Wurster blue cyclophanes, which would be described by the four equivalent resonance forms I of a fully delocalized, π stacked radical iminium cation species.

Conclusion

We have presented a combined experimental and theoretical study on a novel family of electroactive, antiferromagneti-

cally coupled dicopper(II) paracyclophanes with polymethyl-substituted benzene spacers $-C_6H_{(4-n)}Me_n$ - (n=0, 1, and 4). The overall strengthening of the antiferromagnetic coupling along this series is due to an increased delocalization of the unpaired electrons of the Cu^{II} ions onto the π -conjugated electron system of the para-phenylene spacers with an increasing number of electron-donating methyl substituents. This phenomenon is ultimately responsible for the higher stability of the one-electron oxidized dicopper(II) π -radical species that results from the oxidation of the polymethylsubstituted para-phenylenediamidate bridge as the number of electron-donating methyl substituents increases. Interestingly, the permethylated dicopper(II) paracyclophane exhibits a unique magnetic electroswitching (ON/OFF) behavior, as shown both experimentally and theoretically. The magnetic bistability obeys to the change from antiparallel (OFF) to parallel (ON) spin alignment of the metal centers by the π -stacked delocalized monoradical ligand generated upon one-electron oxidation of the double tetramethyl-para-phenylenediamidate bridge skeleton. Permethylation in this metallacyclic system thus constitutes a unique example of ligand design for the supramolecular control of magnetic properties and electrochemical reactivity. Current efforts are devoted to obtaining additional examples of oxamato-based dicopper(II) metallacyclophanes with higher electrochemical stability, both thermodynamic and kinetic, as new prototypes of magnetic electroswitches in the emerging field of molecular spintronics.

Experimental Section

Materials: All chemicals were of reagent-grade quality, purchased from commercial sources, and used as received, except those for electrochemical measurements. The nBu_4NPF_6 salt was recrystallized twice from ethyl acetate/diethyl ether, dried at 80 °C under vacuum, and kept in an oven at 110 °C. Acetonitrile was purified by distillation from calcium hydride on activated 3 Å molecular sieves and stored under argon.

Physical techniques: Elemental analyses (C, H, N) were performed at the Servicio Central de Soporte a la Investigación (SCSIE) at the Universitat de València (Spain). ¹H NMR spectra were recorded at room temperature on a Bruker AC 200 (200.1 MHz) spectrometer. Chemical shifts are reported in δ (ppm) versus SiMe₄. C₂D₆SO was used as solvent and internal standard (δ =2.50 ppm). FTIR spectra were recorded on a Nicolet-5700 spectrophotometer as KBr pellets.

Preparation of the ligands

Et₂H₂ppba: Ethyl oxalyl chloride ester (14.0 mL, 120 mmol) was poured into a solution of 2,3,5,6-tetramethyl-*para*-phenylenediamine (6.5 g, 60 mmol) in THF (250 mL) with vigorous stirring at 0 °C on an icebath. The reaction mixture was heated to reflux for 1 h. After cooling, the solid was collected by filtration, washed with diethyl ether, and dried under vacuum (15.7 g, 85%). ¹H NMR (C₂D₆SO): δ = 1.32 (t, 6H; 2× CH₃), 4.30 (q, 4H; 2×CH₂O), 7.73 (s, 4H; C₆H₄), 10.82 ppm (s, 2H; 2× NH); IR (KBr): $\tilde{\nu}$ = 3252 (N-H), 1734, 1686 cm⁻¹ (C=O); elemental analysis (%) calcd for C₁₄H₁₆N₂O₆ (M_r =308): C 54.55, H 5.19, N 9.09; found: C 54.42, H 5.21, N 9.21.

Et₂H₂Meppba: Ethyl oxalyl chloride ester (14.0 mL, 120 mmol) was poured into a solution of 2-methyl-*para*-phenylenediamine dihydrogen sulfate (13.2 g, 60 mmol) and triethylamine (16.8 mL, 120 mmol) in THF (250 mL) with vigorous stirring at 0°C on an icebath. The reaction mixture was heated to reflux for 1 h. After cooling, the solid was collected

FULL PAPER

by filtration, washed thoroughly with water to remove the precipitate of $(Et_3NH)_2SO_4$, washed with diethyl ether, and dried under vacuum (15.5 g, 80 %). ¹H NMR (C₂D₆SO): $\delta = 1.28$ (t, 6H; 2×CH₃), 2.18 (s, 3H; C₆H₃CH₃), 4.23 (q, 4H; 2×CH₂O), 7.29 (d, 1H; 5-H of C₆H₃CH₃), 7.58 (d, 1H; 4-H of C₆H₃CH₃), 7.63 (s, 1H; 3-H of C₆H₃CH₃), 10.32 (s, 1H; 1 NH), 10.80 ppm (s, 1H; 1 NH); IR (KBr): $\tilde{\nu} = 3399$ (N-H), 1732, 1704 cm⁻¹ (C=O); elemental analysis (%) calcd for C₁₅H₁₈N₂O₆ ($M_r = 322$): C 55.90, H 5.59, N 8.70; found: C 55.87, H 5.29, N 8.91.

Et₂H₂Me₄ppba: Ethyl oxalyl chloride ester (14.0 mL, 120 mmol) was poured into a solution of 2,3,5,6-tetramethyl-*para*-phenylenediamine (9.9 g, 60 mmol) in THF (250 mL) with vigorous stirring at 0°C on an icebath. The reaction mixture was heated to reflux for 1 h. After cooling, the solid was collected by filtration, washed with diethyl ether, and dried under vacuum (19.7 g, 90%). ¹H NMR (C₂D₆SO): δ =1.34 (t, 6H; 2× CH₃), 2.02 (s, 12 H; C₆(CH₃)₄), 4.32 (q, 4H; 2×CH₂O), 10.43 ppm (s, 2H; 2 NH); IR (KBr): $\tilde{\nu}$ =3245 (N-H), 1728, 1676 cm⁻¹ (C=O); elemental analysis (%) calcd for C₁₈H₂₄N₂O₆ (*M*_r=364): C 59.33, H 6.64, N 7.68; found: C 58.98, H 6.67, N 7.74.

Preparation of the complexes

(*n*Bu₄N)₄[Cu₂(ppba)₂]·2CH₃OH (1a): A solution of *n*Bu₄NOH (20 mL, 20.0 mmol, 1.0 M) in methanol was added in one portion to a suspension of H₂Et₂ppba (1.6 g, 5.0 mmol) in methanol (50 mL). A solution of Cu-(ClO₄)₂·6H₂O (1.85 g, 5.0 mmol) in methanol (10 mL) was added dropwise to the reaction mixture with stirring at room temperature. The deep-green solution was filtered to eliminate the small amount of solid particles produced and the solvent was removed under vacuum. The green solid was recuperated with acetone, collected by filtration, washed thoroughly with THF to remove the precipitate of *n*Bu₄NClO₄, and air dried. Recrystallization from a solution in methanol gave large green prisms of **1a** suitable for single-crystal X-ray diffraction studies upon layering of diethyl ether (3.3 g, 80%). IR (KBr): $\bar{\nu}$ =1638, 1612 cm⁻¹ (C= O); elemental analysis (%) calcd for C₈₆H₁₆₀Cu₂N₈O₁₄ (*M*_r=1657): C 62.32, H 9.73, N 6.76; found: C 61.98, H 9.51, N 6.74.

Li₄[Cu₂(ppba)₂]·10H₂O (1b): An aqueous solution (10 mL) of Cu-(NO₃)₂·3 H₂O (1.2 g, 5.0 mmol) was added dropwise to an aqueous solution (50 mL) of Et₂H₂ppba (1.5 g, 5.0 mmol) and LiOH·H₂O (0.8 g, 20.0 mmol) with stirring at room temperature. The resulting deep-green solution was filtered, and the solvent was reduced under vacuum until a solid appeared. The light-green solid was collected by filtration, washed with acetone and diethyl ether, and air dried (1.6 g, 75%). IR (KBr): $\tilde{\nu}$ = 1624, 1616 cm⁻¹ (C=O); elemental analysis (%) calcd for C₂₀H₂₈Cu₂Li₄N₄O₂₂ (M_r =831): C 28.88, H 3.37, N 6.74; found: C 28.75, H 3.28, N 6.67.

 $(\mathbf{Ph_4P})_4[\mathbf{Cu_2(ppba)_2}]$ -8H₂O (1c): An aqueous solution (10 mL) of AgNO₃ (1.4 g, 8.0 mmol) was added to an aqueous solution (20 mL) of 1b (1.7 g, 2.0 mmol) with stirring at room temperature. The dark-green solid that appeared was collected by filtration, suspended in water (10 mL), and charged with a solution of Ph₄PCl (3.0 g, 8.0 mmol) in acetonitrile (5 mL). The reaction mixture was further stirred for 30 min with gentle warming and then filtered to remove the precipitate of AgCl. Slow evaporation of the filtered deep-green solution gave dark-green crystals of 1c, which were not suitable for single-crystal X-ray diffraction after several days in the open air at room temperature (4.2 g, 95 %). IR (KBr): $\tilde{\nu}$ = 1644, 1603 cm⁻¹ (C=O); elemental analysis (%) calcd for C₁₁₆H₁₀₄Cu₂N₄O₂₀P₄ (M_r =2123): C 65.56, H 4.89, N 2.63; found: C 65.65, H 4.82, N 2.47.

(*n*Bu₄N)₄[Cu₂(Meppba)₂]·3H₂O (2a): A solution of *n*Bu₄NOH (20 mL, 20.0 mmol) in methanol (1.0 m) was added in one portion to a suspension of H₂Et₂Meppba (1.6 g, 5 mmol) in methanol (50 mL). A solution of Cu-(ClO₄)₂·6H₂O (1.85 g, 5.0 mmol) in methanol (10 mL) was then added dropwise with stirring at room temperature to the reaction mixture. The deep-brown solution was filtered to eliminate a small amount of solid particles and the solvent was removed under vacuum. The dark-brown solid was recuperated with acetone, collected by filtration, washed thoroughly with THF to remove the precipitate of *n*Bu₄NClO₄, and air dried (3.4 g, 80%). IR (KBr): $\tilde{\nu}$ =1638, 1615 cm⁻¹ (C=O); elemental analysis (%) calcd for C₈₈H₁₆₂Cu₂N₈O₁₅ (M_r =1700): C 61.65, H 9.75, N 6.69; found: C 61.53, H 9.61, N 6.51.

Li₄[Cu₂(Meppba)₂]·7H₂O (2b): An aqueous solution (10 mL) of Cu-(NO₃)₂·3H₂O (1.2 g, 5.0 mmol) was added dropwise to an aqueous solution (50 mL) of Et₂H₂Meppba (1.6 g, 5.0 mmol) and LiOH·H₂O (0.8 g, 20.0 mmol) with stirring at room temperature. The resulting deep-brown solution was filtered, and the solvent was reduced under vacuum until a solid appeared. The dark-brown solid was collected by filtration, washed with acetone and diethyl ether, and dried under vacuum. Recrystallization from an aqueous solution gave dark-brown prisms of **2b**, which gave crystals upon layering of methanol that were not suitable for single-crystal X-ray diffraction (1.7 g, 85%). IR (KBr): $\tilde{\nu}$ = 1645, 1618 cm⁻¹ (C=O); elemental analysis (%) caled for C₂₂H₂₆Cu₂Li₄N₄O₁₉ (M_r =804): C 32.81, H 3.25, N 6.96; found: C 31.34, H 3.20, N 6.89.

(**Ph₄P)₄[Cu₂(Meppba)₂]·8H₂O (2 c)**: An aqueous solution (10 mL) of AgNO₃ (1.4 g, 8.0 mmol) was added to an aqueous solution (20 mL) of **2b** (1.6 g, 2.0 mmol) with stirring at room temperature. The dark-brown solid that appeared was collected by filtration, suspended in water (10 mL), and charged with a solution of Ph₄PCl (3.0 g, 8.0 mmol)) in acetonitrile (5 mL). The reaction mixture was further stirred for 30 min with gentle warming and then filtered to remove the precipitate of AgCl. Slow evaporation of the filtered deep-brown solution gave dark-brown crystals of **2 c**, which were not suitable for single-crystal X-ray diffraction after several days in the open air at room temperature (3.9 g, 90%). IR (KBr): \bar{v} = 3425 (O-H), 1642, 1617 cm⁻¹ (C=O); elemental analysis (%) calcd for C₁₁₈H₁₀₈Cu₂N₄O₂₀P₄ (M_r =2151): C 65.82, H 5.06, N 2.60; found: C 65.45, H 4.99, N 2.77.

(*n*Bu₄N)₄[Cu₂(Me₄ppba)₂]. 5H₂O (3a): A solution of *n*Bu₄NOH (20 mL, 20.0 mmol) in methanol (1.0 m) was added in one portion to a suspension of H₂Et₂Me₄ppba (1.8 g, 5.0 mmol) in methanol (50 mL). A solution of Cu(ClO₄)₂·6H₂O (1.85 g, 5.0 mmol) in methanol (10 mL) was added dropwise with stirring at room temperature to the reaction mixture. The deep-brown solution was filtered to eliminate a small amount of solid particles, and the solvent was removed under vacuum. The dark-brown solid was recuperated with acetone, collected by filtration, washed thoroughly with THF to remove the precipitate of *n*Bu₄NClO₄, and air dried (3.9 g, 85%). IR (KBr): $\tilde{\nu}$ =1642, 1615 cm⁻¹ (C=O); elemental analysis (%) calcd for C₉₄H₁₇₈Cu₂N₈O₁₇ (*M*_r=1820): C 61.54, H 9.99, N 6.24; found: C 61.91, H 9.90, N 5.99

Li₄[Cu₂(Me₄ppba)₂]·9H₂O (3b): An aqueous solution (10 mL) of Cu₁(NO₃)₂·3 H₂O (1.2 g, 5.0 mmol) was added dropwise to an aqueous solution (50 mL) of Et₂H₂Me₄ppba (1.8 g, 5.0 mmol) and LiOH·H₂O (0.8 g, 20.0 mmol) with stirring at room temperature. The resulting deep-brown solution was then filtered, and the solvent was reduced under vacuum until a solid appeared. The dark-brown solid was collected by filtration, washed with acetone and diethyl ether, and air dried (2.0 g, 85%). IR (KBr): $\tilde{\nu}$ =3473 (O-H), 1634, 1605 cm⁻¹ (C=O); elemental analysis (%) calcd for C₂₈H₄₂Cu₂Li₄N₄O₂₁ (M_r =924): C 36.34, H 4.57, N 6.05; found: C 36.63, H 4.40, N 6.03

(**Ph₄P)₄**[**Cu₂(Me₄ppba)₂]-15 H₂O (3c)**: An aqueous solution (10 mL) of AgNO₃ (1.4 g, 8.0 mmol) was added to an aqueous solution (20 mL) of **3b** (1.9 g, 2.0 mmol) with stirring at room temperature. The dark-brown solid that appeared was collected by filtration, suspended in water (10 mL), and charged with a solution of Ph₄PCl (3.0 g, 8.0 mmol) in acetonitrile (5 mL). The reaction mixture was further stirred for 30 min with gentle warming and filtered to remove the precipitate of AgCl. Slow evaporation of the filtered solution gave small dark-brown prisms of **3c**, which were suitable for single-crystal X-ray diffraction after several days in the open air at room temperature (4.2 g, 90%). IR (KBr): $\tilde{\nu}$ =3413 (O–H), 1637, 1604 cm⁻¹ (C=O); elemental analysis (%) calcd for C₁₂₄H₁₃₄Cu₂N₄O₂₇P₄ (*M_r*=2363): C 63.02, H 5.71, N 2.37; found: C 63.99, H 5.59, N 2.46.

Chemical oxidation and spectroscopic measurements: Variable-temperature (5–25 °C) UV/Vis–NIR spectra of solutions in acetonitrile were recorded on an Agilent Technologies-8453 spectrophotometer equipped with a thermostated Chem Station. Varying amounts of a solution of bromine (0.01 m, 0–15 µL) were added stepwise to a solution of **3c** in acetonitrile (0.1 mm, 2.5 mL) at 5, 15, and 25 °C. In each case, the course of the decomposition reaction of the monooxidized species was followed by measuring the absorbance at λ_{max} =875 nm as a function of time.

Chem. Eur. J. 2013, 19, 12124-12137

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Variable-temperature (4.0–150 K) X-band EPR spectra (ν =9.47 GHz) of frozen-matrix solutions in acetonitrile were recorded under nonsaturating conditions on a Bruker ER 200 D spectrometer equipped with a helium cryostat. The monooxidized species was obtained by addition of an excess of Br₂ to a solution of **3c** in acetonitrile (0.1 m, 0.5 mL) at -40 °C.

Magnetic measurements: Variable-temperature (2.0–300 K) magnetic susceptibility measurements were carried out on powdered samples of **1a**-**3a**, **1b**-**3b**, and **1c**-**3c** with a SQUID magnetometer under an applied field of 10 kOe ($T \ge 50$ K) and 100 Oe (T < 50 K). The experimental data were corrected for the diamagnetic contributions of the constituent atoms and sample holder and for the temperature-independent paramagnetism (tip) of the Cu^{II} ion (60×10^{-6} cm³mol⁻¹).

Electrochemical measurements: The cyclic voltammetry measurements were performed by using a PAR 273 A scanning potentiostat operating at a scan rate of 10-1000 mV s⁻¹. Cyclic voltammograms were carried out in acetonitrile with 0.1 м nBu₄NPF₆ as a supporting electrolyte and 1.0 mм of either 1a-3a or 1c-3c. The working electrode was a glassy carbon disk (0.32 cm²) that was polished with diamond powder (1.0 µm), sonicated, washed with absolute ethanol and acetone, and air dried. The reference electrode was AgClO₄/Ag separated from the test solution by a salt bridge containing the solvent/supporting electrolyte, with platinum as an auxiliary electrode. All the experiments were performed in standard electrochemical cells at 25 °C under argon. The potential range investigated was between -2.00 and +1.80 V versus SCE. The formal potentials were measured at a scan rate of 100 mVs⁻¹ and were referred to the SCE, which was consistently measured as -0.26 V versus the AgClO₄/Ag electrode. Ferrocene (Fc) was added as an internal standard at the end of the measurements ($E(Fc^+/Fc) = +0.40$ V vs. SCE).

Collection and refinement of the crystal-structure data: The X-ray diffraction data of 1a were collected with graphite-monochromated Mo_{Ka} radiation ($\lambda = 0.7107$ Å) by means of a Bruker-Nonius X8APEXII CCD area detector diffractometer, whereas the data of 3c were collected by using synchrotron radiation ($\lambda = 0.7513$ Å) at the BM16-CRG beamline in the ESRF (Grenoble, France). The X-ray diffraction data of 3c were indexed, integrated, and scaled using the HKL2000 program.^[14] All the calculations for data reduction, structure solution, and refinement were done by using the SAINT and SADABS programs (1a) or the WINGX program (3c).^[15,16] The structures were solved by direct methods and refined with full-matrix least-squares technique on F^2 by using the SHELXTL software package (1a) or the SHELXS-97 and SHELXL-97 programs (3c).^[17,18] All the non-hydrogen atoms of 1a and 3c were refined anisotropically. Some thermal disorder was however observed for the *n*-butyl chains of the nBu_4N^+ cations in **1a**. The hydrogen atoms from the benzene ring of 1a and 3c were calculated and refined with isotropic thermal parameters, whereas those of the crystallization water molecules of 3c were neither found nor calculated. The final geometrical calculations and the graphical manipulations were carried out with PARST97 and CRYSTAL MAKER programs, respectively.^[19]

CCDC-911161 (1a) and CCDC-856597 (3c) contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details: DF calculations were carried out on the brokensymmetry (BS) singlet and triplet spin states of the orthogonal model complexes **1–3** by using the hybrid B3LYP method^[20] combined with the BS approach,^[21] as implemented in the Gaussian09 program.^[22] Tripleand double- ζ quality basis sets proposed by Ahlrichs and co-workers were used for the metal and nonmetal atoms, respectively.^[23] All four possible configurations of the methyl substituents from the two facing benzene rings were considered for **2**. The molecular geometries of the model complexes **1** and **3** with D_{2h} molecular symmetry and those of the pseudo-*gem*, *-ortho*, *-para*, and *-meta* isomers of **2** with C_s , C_2 , C_i , and C_2 molecular symmetries, respectively, were not optimized but their metal bond lengths and metal interbond angles were taken from the crystal structure of **3c** with an imposed planar conformation of the copper basal planes ($\tau = 0^\circ$) and a perpendicular orientation of the copper basal planes with respect to the benzene rings ($\phi = 90^\circ$). DF calculations were also performed on the optimized molecular geometries of **1**, **3**, and **3'** in acetonitrile. Different ground electronic configurations are available for **3'** depending on the oxidized center (metal- or ligand-based oxidation) and the overall spin state (doublet or quartet). The starting geometry was modified in each case to come closer to those experimentally observed in either copper(III) or copper(II) complexes with radical ligands. However, a unique result was found in all cases during the geometry optimization process. In fact, the $S = 1/2 \text{ Cu}_2^{II} \pi$ -radical configuration is the most stable one and moreover, there is no energy barrier with other possible electronic configurations. Solvation effects were introduced by using a polarizable continuum model (PCM), in which the cavity is created through a series of overlapping spheres.^[24] The calculated spin spin density data for **3** and **3'** were obtained from NBO analysis.^[25]

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12136 -

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FULL PAPER

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