ORIGINAL RESEARCH



Gas-phase structure and conformations of copper(II) 2,9,16,23tetra-*tert*-butyl phthalocyanine

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Abstract The molecular structure of copper(II) 2,9,16,-23-tetra-*tert*-butyl phthalocyanine (Cu(pc^{*t*})) was investigated by gas-phase electron diffraction with mass spectrometric control of vapor composition. Two conformers of C_{4h} symmetry and three conformers of C_s symmetry are predicted by quantum chemical calculations using the hybrid DFT method UB3LYP with 6-31G* and cc-pVTZ basis sets. According to the relative energies at the temperature of GED experiments (436 °C), the two C_{4h} symmetric conformers occur in 1.1 and 2.3 % abundance in the gas phase. The highest mole fraction (66.6 %) and lowest

Dedicated to Prof. Magdolna Hargittai on the Occasion of her 70th birthday.

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R-factor (4.25 %) correspond to one of the $C_{\rm s}$ symmetric conformers; however, the two $C_{\rm 4h}$ symmetric models cannot be disproved by the Hamilton *R*-factor ratio test. The GED structural data of the three models mentioned reliably confirm approximate local $D_{\rm 4h}$ symmetry of the phthalocyanine ligand core.

Keywords Copper(II) \cdot 2,9,16,23-tetra-*tert*-butyl phthalocyanine \cdot Molecular structure \cdot Gas-phase electron diffraction \cdot Mass spectrum

Introduction

The metal phthalocyanines (M(pc)) are unique coordination compounds. Numerous publications are dedicated to the understanding of the important properties of M(pc) such as high thermal stability [1, 2], nonlinear optical activity [3, 4], catalytic [5] and semiconductor capability [6]. A particular focus has been placed on water-soluble phthalocyanine derivatives. They are known to be capable of accumulating selectively in tumors and are therefore used in medicine for photo-diagnostics and phototherapy of cancerous diseases [7].

Insertion of peripheral and non-peripheral substituent groups (e.g., methyl, ethyl and *tert*-butyl) at the 16 reactive sites in the benzene rings of the pc macrocycle [8, 9] can have a pronounced influence on the properties, e.g., resulting in an increase in solubility and volatility by using substituents that constrict intermolecular attraction. This conclusion has been clearly supported from work [10], that contains results of mass spectrometric (MS) investigations of the vapor composition of tetra-*tert*-butyl substituted phthalocyanines $M(pc^t)$ with M = Cu(II), VO are presented. Investigations of the dependence of vapor pressure on temperature have revealed that tetra-*tert*-butyl substituted phthalocyanines have higher volatilities than the unsubstituted ones. The authors have explained this fact with the presence of bulky *tert*-butyl groups preventing coplanar π - π interaction between phthalocyanine molecules in the solid state and thus leading to weaker intermolecular interactions.

The influence of peripheral substitutions on the electronic structure of Cu(II) phthalocyanine (Cu(pc)), copper(II) 2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine (Cu(pc^t)) and copper(II) 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25hexadecafluoro-29H,31H-phthalocyanine (Cu(pc)^F) in various matrices has been investigated using combined continuous wave and pulse electron paramagnetic resonance (EPR) of solutions of these complexes in toluene and sulfuric acid as well as density functional theory (DFT) [9]. According to the EPR data, the in-plane metal-ligand σ -bonding and the out-ofplane π -bonding are more covalent for Cu(pc^t) in toluene than in sulfuric acid solution. Note that the covalent nature of this bonding is increased upon substitution with tert-butyl groups. This means that the introduction of peripheral groups can lead to changes in the covalent/ionic ratio of the metal-ligand bond in phthalocyanines [9]. The change in electron density distribution in chemical bond involves variations in bond lengths, and consequently the introduction of peripheral groups has an influence on the geometry of the coordination cavity. This conclusion seems reasonable for solutions, but to the best of our knowledge there is so far no experimental evidence of structural changes in phthalocyanine coordination cavities affected by peripheral substitutions for the gaseous phase.

On the other hand, the effects of alkyl substitutions (methyl) on the structure of metal porphyrins Mp (M = Cu, Sn; $p = C_{20}H_{12}N_4$) based on DFT investigations are presented in the works [11, 12]. The authors have performed calculations of unsubstituted (Cup and Snp) and methylsubstituted porphyrin molecules (Cu(omp) and Sn(omp); $omp = C_{28}H_{28}N_4$) for comparison of structural parameters. The substitution of the pyrrole hydrogen atoms by donortype methyl groups has a weak influence on the coordination cavity geometry of the porphyrins. The most significant changes are taking place in the carbon-carbon bonds of the pyrrole ligand fragment. Furthermore, a comparison of the experimental porphyrin structures Cu(omp) and Sn(omp) (gas-phase electron diffraction data; GED) with molecular structures of octaethylporphyrins Cu(oep) and Sn(oep) in their crystals has been reported [11, 12]. It should be noted that despite systematic differences between X-ray and electron diffraction geometries caused by different principles of scattering and the presence of eight ethyl substituents in crystalline Sn(oep) and Cu(oep), the geometry of the coordination cavity in Sn(oep) and Cu(oep) remains practically the same as in the free Cu(omp) and Sn(omp) molecules.

Taking into account the circumstances described above, we attempted to carry out experimental (GED/MS) and theoretical (DFT) structural investigation of copper(II) 2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine (Cu(pc^t)) in order to compare the results with those for the unsubstituted copper phthalocyanine (Cu(pc)).

Experimental part

Synthesis

Thoroughly triturated mix 0.920 g (5.0 mmol) of 4-tertbutyl phthalonitrile (Aldrich 42322-1G) and 0.300 g (1.5 mmol) of copper acetate monohydrate is kept for 4 h at 175–180 °C. Resulting copper(II) 2,9,16,23-tetra-*tert*butyl phthalocyanine was extracted with chloroform and twice chromatographed on aluminum oxide. The solvent was removed under vacuum, and the resulting compound was dried under vacuum at 80° C. Yield: 0.480 g (48 %); Found, %: C 71.85; N 14.04; H 6.33. C₄₈H₄₈CuN₈. Calculated, %: C 72.02; N 14.00; H 6.04. ES: λ_{max} (lg ε), (nm) in heptane: 671 (4.44); 640 (4.88); 606 (4.83).

GED/MS experiment

In work [10], it was shown that the sample $Cu(pc^{t})$ sublimes in the form of monomers and without thermal decomposition up to 600 °C. The mass spectrum consists of the molecular ion $Cu(pc^{t})^{+}$ ([M]⁺: m/z = 800) and doubly charged $Cu(pc^{t})^{2+}$.

However, a carried out pilot mass spectrometry experiment indicates slow change in the mass spectrum during a sample heating. The time dependence of the mass spectra monitoring the vapor composition over the heated sample is presented in Fig. 1. The most significant change with proceeding time observes for the ratio between the two peaks at 799 and 742 Da, corresponding to the molecular ion $[M]^+$ and the one with stoichiometry $[M-C_4H_9]^+$. Because for the first 15 min the molecular ion $[M]^+$ is dominant in the vapor over solid sample heated to 442 °C (see Fig. 1), and it is enough to perform GED experiments.

The electron diffraction patterns and the mass spectra were recorded simultaneously using a combined GED/MS unit based on EMR-100 and APDM-1 devices [13–15]. A sample was evaporated from a molybdenum effusion cell at 436 ± 8 °C, as measured with a W/Re-5/20 thermocouple. The electron wavelength was determined from the diffraction patterns of ZnO recorded before and after the GED/MS experiments. The conditions of the GED/MS experiment are given in Table 1. The diffraction patterns were recorded from two nozzle-to-plate distances ($L_1 = 598$ mm and $L_2 = 338$ mm) on Kodak Electron Image films SO-163. The

Fig. 1 Time dependence of the mass spectrum monitoring the vapor composition over the heated copper tetra-*tert*-butyl phthalocyanine (Cu(pc[']))



 Table 1 Conditions of the synchronous gas-phase electron diffraction experiment and mass spectrometric experiment

338	598
1.74	1.69
50(1)	50(1)
444(5)	428(5)
0.04381(4)	0.04443(2)
100	40
5.4×10^{-6}	6.8×10^{-6}
3.2-27.0/0.1	1.2-15.2/0.1
3	5
	$\begin{array}{c} 338 \\ 1.74 \\ 50(1) \\ 444(5) \\ 0.04381(4) \\ 100 \\ 5.4 \times 10^{-6} \\ 3.2 - 27.0 / 0.1 \\ 3 \end{array}$

rectangular area of 10 mm \times 130 mm was scanned at a diagonal direction (1299 point in line, 33 equidistant lines with a step of 0.1 mm along each line) by a modified [16] Carl Zeiss Jena MD-100 microdensitometer.

Simultaneously with performance of the electron diffraction experiments, the mass spectra of the vapor over solid sample were recorded. The relative intensities of ion currents are listed in Table 2, and visualization of these data is presented in Fig. 2.

There are processes of dissociative ionization with progressive segregation of CH₃ groups under electron impact presented in the vapor. Additionally, the presence of the doubly charged molecular ion $[M]^{2+}$ and the ion corresponding to the quarter of macrocyclic ligand $\frac{1}{4}$ TTBPc (without *tert*-butyl fragment) in the vapor can be observed, the latter being typical for metal phthalocyanines [1, 17–19]. There is no significant change in the ratio between the peaks in the mass spectra during the GED/MS experiment, as long as the general time of exposure does not exceed 11 min. These circumstances allow assuming

 Table 2
 Relative abundances of ions in mass spectrum of vapor over solid sample

Ion	m/z	<i>I</i> _{rel.} (%)		
		$(U_{\text{ioniz}} = 50 \text{ eV})$ T = 444 °C L = 338 mm	$(U_{\text{ioniz}} = 50 \text{ eV})$ T = 428 °C L = 598 mm	
$[C_4H_9]^+$	57	14	15	
[1/4TTBPc-(CH ₃) ₂ C] ⁺	143	7	3	
[M-CH ₃] ²⁺	384	13	12	
$[M]^{2+}$	399	13	12	
$[M-10CH_3]^+$	649	11	4	
[M-9CH ₃] ⁺	664	15	5	
[M-8CH ₃] ⁺	679	22	8	
$[M-7CH_3]^+$	694	26	12	
$[M-6CH_3]^+$	709	30	16	
$[M-5CH_3]^+$	724	38	21	
$[M-C_4H_9]^+$	742	54	31	
$[M-3CH_3]^+$	754	45	30	
$[M-2CH_3]^+$	769	42	31	
$[M-CH_3]^+$	784	60	44	
$[M]^+$	799	100.0	100.0	

the presence of only $Cu(pc^t)$ in the vapor during the GED/ MS experiment.

Quantum chemical calculations

Computational methods

DFT geometry optimizations of $Cu(pc^{t})$ were carried out using the Becke's three-parameter hybrid functional



Fig. 2 Average relative abundances of the vapor over solid sample (GED/MS experiment)

B3LYP [20–22] and the one-parameter hybrid functional of Perdew, Burke and Ernzerhof PBE [23], using both unrestricted (UB3LYP) and restricted open-shell (ROB3LYP) treatment of odd number of electrons. Both DFT functionals were combined with 6-31G* [24-26] and cc-pVTZ (N,C,H) [27] basis sets. For the latter, the core electrons of the copper atom $(1s^22s^22p^6)$ were described by a relativistic effective core potential (ECP) of the Stuttgart group [28]. For the description of the copper valence shells (8s7p6d2f1g/6s5p3d2f1g), the basis sets described in the literature [28, 29] have been used. We will refer to this combination of ECP and basis set as ECP10MWB. All calculations were performed using the Gaussian 03 W program package [30]. Analysis of the natural bonding orbitals (NBO) for $Cu(pc^{t})$ and Cu(pc) was done on B3LYP/ECP10MWB (unrestricted and restricted openshell approaches) level of theory using the NBO 3.1 program [31] implemented in the GAUSSIAN 03 W program package. The visualization of molecular models and electronic orbitals is performed by CHEMCRAFT [32] program. Electronic structure analysis in terms of Bader's quantum theory atoms in molecules (QTAIM) [33] was performed using the AIMALL program [34].

The theoretical models for the Cu(pc^t) molecule

According to above-mentioned work [9], the EPR results for Cu(pc) and Cu(pc^{*t*}) indicate D_{4h} core symmetry in the molecules in their doublet ${}^{2}B_{1g}$ electronic ground states. The molecular structure of Cu(pc^{*t*}) was optimized under C_{4h} symmetry for the ${}^{2}B_{g}$ electronic state. According to preliminary UB3LYP/6-31G* calculations, there are two Cu(pc^{*t*}) conformers of C_{4h} symmetry shown in Fig. 3. The numbering of atoms is presented in Fig. 5 as well.



Fig. 3 Models of copper tetra-*tert*-butyl phthalocyanine: conformer 1 and 2 (C_{4h} symmetry)

According to frequency analysis, both conformers correspond to minimum on potential energy surface (PES). The theoretical structural parameters of the two conformers of Cu(pc') (see Fig. 3) are presented in Table S1. According to DFT calculations, the energy gap between both conformers is more than 1 kcal mol⁻¹, and conformer **2** is energetically preferred.

For investigating the conformational properties of $Cu(pc^{t})$, the energy barrier to internal rotation of one *tert*butyl group around the bond C4–C10 is determined by performing a relaxed energy surface scan with a step size of



Fig. 4 Potential function (UB3LYP/6-31G*) of internal rotation of *tert*-butyl group around bond C4–C10 with a step along the torsion angle 10°. Conformer **1** corresponds to a torsion angle of 60° , whereas conformer **2** exhibits a torsion angle of 0°

10° along the torsion angle τ (C12–C10–C4–C5) (UB3LYP/ 6-31G*, Fig. 4). The barrier of internal rotation for one *tert*butyl group could be determined as V = 0.79 kcal/mol. Since the thermal energy for the temperature of the experiment (T = 709 K) is kT = 1.48 kcal mol⁻¹, the internal rotation of *tert*-butyl groups is not negligible in Cu(pc^t).

Based on the obtained potential function $\Delta E(\tau)$ and taking into account the independent rotation of the *tert*butyl substituent molecule Cu(pc^t), we found five different stable conformers given in Table 3. The denomination "conformer **2–1**" means that one *tert*-butyl group is rotated by 180° starting from conformer **2** and so on. The conformers are arranged in ascending order of relative electronic energy ΔE . For each conformer, frequencies and amplitudes of vibration at T = 709 K, as well as the Gibbs energy ΔG , mole fractions χ (according to Boltzmann's distribution), entropy S and molar heat capacity C_V , were calculated. It should be noted that the transition from conformer 2 to conformer 2–1 increases the total electronic energy ΔE in contrast to decreasing ΔG .

This fact can be explained by the entropy contribution being a lot higher for the asymmetrical conformers. Conformer **2–1** was predicted to occur in the highest mole fraction ($\chi = 66.6$ %) in the vapor composition, and therefore, this model of C_s symmetry should be taken into account in the experimental data refinement procedure. The conformer 2–1 of C_s symmetry and numbering of atoms is presented in Fig. 5.

The quadratic force fields of conformers **1** and **2** of Cu(pc^{*t*}) (UB3LYP/ECP10MWB) were used to calculate the set of vibrational corrections $\Delta r = r_{h1} - r_a$ and the root mean square amplitudes at the temperature of the electron diffraction experiment in second approximation using the program SHRINK [35–37]. For conformer **2–1**, a UB3LYP/6-31G* force field was used, but calculation of this was based on initial structural parameters from UB3LYP/ECP10MWB calculation of conformer **2**.

Structural analysis

Analysis of the electron diffraction data was performed, assuming that the vapor consists only of molecules having C_{4h} symmetry (1 and 2) or C_s symmetry (2–1). The molecular models included 15 independent parameters: (1) seven bond lengths, namely r(Cu-N1), r(N1-C1), r(C1-N2), r(C7-C8), r(C2-C7), r(C4-C10) and r(C3-H); (2) seven valence angles, videlicet $\angle(N1-Cu-X)$, $\angle(Cu-N1-C1)$, $\angle(N1-C8-C7)$, $\angle(C2-C7-C6)$, $\angle(C12-C10-C4)$, $\angle(C2-$ C3-H) and $\angle(C10-C12-H)$; and (3) single torsion angle $\tau_1(C12-C10-C4-C5)$ that determines the rotation of the *tert*butyl group relative to the plane of the phthalocyanine macrocycle; during the LS analysis, this parameter was fixed

Table 3 Relative full energies ΔE , relative Gibbs energies ΔG and mole fractions χ of Cu(pc¹) conformers obtained by DFT calculations (UB3LYP/6-31G*) according to GED experiment temperature T = 709 K

	Conformer 2	Conformer 2–1	Conformer 2–2	Conformer 2–3	Conformer 1
ΔE (kcal mol ⁻¹⁾	0.0	0.29	0.51	0.78	1.1
$\Delta G_{\rm T}$ (kcal mol ⁻¹)	2.8	0.0	1.6	2.9	3.8
χ (%)	2.3	66.6	21.7	8.3	1.1



Fig. 5 Models of copper tetra-*tert*-butyl phthalocyanine (C_s symmetry) and atomic numbering conformer 2–1

at 0°. The \angle (N1–Cu–X) angle was included in the set of independent parameters to describe the displacement of the Cu atom out-of-plane of the molecule (X is a dummy atom positioned at the center of the coordination cavity plane that was fixed at 90°).

The differences in similar C–C bond lengths and also in \angle (C–C–C), \angle (C–C–H) angles were fixed to those obtained from the quantum chemical calculations UB3LYP/ ECP10MWB. Starting values of independent parameters and also of the root mean square vibrational amplitudes were taken from the above-mentioned DFT calculations. The amplitudes were refined in groups corresponding to the peaks on the radial distribution curve. All amplitudes for distances greater than 15 Å were kept fixed to initial values.

Figures 6 and 7 display the plots of molecular intensity sM(s) and radial distribution f(r) experimental functions along with their model analogues and difference curves $\Delta sM(s)$ and $\Delta f(r)$ for all three conformers. The independent geometric parameters for all of the three above-mentioned molecular models are listed in Table 5. The independent geometric parameters, vibrational amplitudes and vibrational corrections Δr for the all three molecular models are presented in Tables S2, S3 and S4. Tables S5, S6 and S7 give the matrixes of parameter correlation. The Cartesian coordinates of the atoms for the least squares refinement r_{h1} structures of three conformers Cu(pc^{*t*}) are also available in Supplementary Material.



Fig. 6 Molecular intensity functions sM(s) of conformer 2–1 Cu(pc^{*t*}) (*dots* experimental; *solid line* model) and difference functions $\Delta sM(s)$ for molecular models: (*a*) conformer 2–1; (*b*) conformer 2; (*c*) conformer 1



Fig. 7 Radial distribution function f(r) of conformer 2–1 Cu(pc') (*dots* experimental; *solid line* model) and difference functions $\Delta f(r)$ for molecular models: (*a*) conformer 2–1; (*b*) conformer 2; (*c*) conformer 1

Discussion

Molecular structure by DFT calculations

The structural parameters of conformers **1** and **2** yielded by three theoretical approximations UB3LYP/6-31G*, UB3LYP/ECP10MWB and UPBE/ECP10MWB differ only for the benzene ring C2–C3, C3–C4 and C4–C5 distances (see Table S1). The largest differences in these distances amount to 0.005 Å, regardless of the theory level of calculation. The same is observed to the angle \angle (C5– C4–C10) corresponding to the position of the *tert*-butyl group in the plane of the macrocycle. By rotation of the *tert*-butyl groups from conformer **1** to **2**, this angle increases by 3° , regardless of the theoretical approach. All other structural parameters, in particular the Cu–N1 and Cu…N2 distances, remain almost unchanged for both conformers. Thus, having analyzed the structures of conformers **1** and **2** by DFT calculations, we conclude that internal rotation of the *tert*-butyl groups has no appreciable effect on the structure of the coordination complex cavity, but a small one on the geometry of the benzene rings of the phthalocyanine ligand.

The molecular structure determined by GED

During the LS optimization, the models of conformers 1, 2 and 2–1 resulted in almost the same agreement of the experimental and theoretical functions sM(s): $R_f = 4.46$ % for 1, $R_f = 4.34$ % for 2 and $R_f = 4.25$ % for 2–1. As shown in Table 5, the independent parameters for both C_{4h} and C_s symmetry models are consistent with each other within the error limits. Moreover, according to the statistical Hamilton criterion [38] at a significance level of 0.05, the ratio of *R*-factors of compared models, e.g., $R_f(1)/R_f(2-1) = 4.46/4.25 = 1.049$, is less than the critical value of 1.0718. Taking into account $R_f(2)/R_f(2-1) = 4.34/4.25 = 1.021$, we come to the conclusion that the all models of conformers 1, 2 and 2–1 can be presented as possible gas-phase structures (Table 4).

A comparison of structural parameters of the complexes $Cu(pc^{t})$ (conformer 2–1) and Cu(pc), obtained from DFT calculations and LS processing of GED data, is presented in Table 5. According to DFT calculations, the introduction of *tert*-butyl groups has a weak influence on the geometry of the coordination cavity. The maximal changes occur in the C3–C4 and C4–C5 distances of the benzene rings and amount to 0.01 and 0.005 Å, respectively.

Concerning the bond angles, the largest difference of 2.9° is observed for the \angle (C3–C4–C5) which is larger in Cu(pc) than in Cu(pc') angle. In contrast to the calculations, the experiments for Cu(pc) and Cu(pc') are in mutual agreement within experimental error for all bond lengths except for Cu–N1 and C1–C2. The Cu–N1 distance has a multiplicity of four, but does not appear as a distinct peak or shoulder in the radial distribution curve f(r). Therefore, its value cannot be determined as reliably as the corresponding one in Cu(pc) [17].

The difference between error limits of bond lengths C2–C7 as well as C4–C5 in Cu(pc^{*t*}) and Cu(pc) is the result of different set of structural parameters used for geometrical description of independent parameters in molecular model. The same relates to the bond angles \angle (C1–C2–C7) and \angle (C3–C4–C5).

Table 4 Independent structure parameters (r_{h1}/\angle_{h1}) of conformers **1**, **2** and **2–1** of Cu(pc^{*t*}) obtained by gas electron diffraction

Parameters ^{a,b}	1	2	2–1
	r _{h1}		
r(Cu–N1)	1.966(5)	1.964(5)	1.964(5)
r(N1–C1)	1.371(3)	1.376(3)	1.378(3)
r(C1–N2)	1.325(4)	1.317(4)	1.318(4)
r(C7–C8)	1.454(5)	1.452(4)	1.448(5)
r(C2–C7)	1.408(3)	1.405(3)	1.405(3)
r(C4–C10)	1.542(4)	1.540(4)	1.542(4)
r(C3–H)	1.086(5)	1.084(4)	1.084(4)
$\angle (Cu-N1-C1)^{c}$	125.5 ^c	125.6 ^c	125.6 ^c
∠(N1–C8–C7)	109.9(8)	109.7(11)	109.9(5)
∠(C2–C7–C6)	120.8(2)	120.7(2)	120.6(2)
∠(C2–C3–H)	123.1(62)	124.3(63)	122.9(60)
∠(C10–C12–H)	112.8(79)	111.1(100)	112.2(73)
∠(C12–C10–C4)	114.4(9)	112.6(16)	112.0(13)
$\tau_1(C12-C10-C4-C5)^c$	0.0	180.0	(1)0.0/(3)180.0
$R_{\rm f} (\%)^{\rm d}$	4.46	4.34	4.25

^a The values of bond lengths (Å) and angles (°)

^b In parentheses, the values of total errors: for bond lengths $\sigma = (\sigma_{scal.}^2 + (2.5\sigma_{LS})^2)^{1/2}$, where $\sigma_{scal.} = 0.002r$, and for the angles $\sigma = 3\sigma_{LS}$; the correlation coefficients higher than 0.6 are: conformer 1: r(C2-C7)/r(C7-C8) = -0.64; conformer 2: $\angle(C2C7C6)/\angle(N1C8C7) = 0.62, \angle(C12C10C4)/\angle(C10C12H) = 0.62$; conformer 2-1: r(C2-C7)/r(C7-C8) = -0.63

^c Fixed value at LS analysis

^d
$$R_f = \frac{\sum_{i}^{n} \omega_i(s_i) [s_i M_{\exp}(s_i) - k_M s_i M_{\text{theor}}(s_i)]^2}{\sum_{i}^{n} \omega_i(s_i) [s_i M_{\exp}(s_i)]^2}$$

NBO analysis results

An NBO analysis of $Cu(pc^{t})$, at the UB3LYP/ECP10MWB level of theory, provided bond orders and net atomic charges for conformers 1 and 2 as well as for the unsubstituted Cu(pc). Additionally, for Cu(pc) NBO analyses were performed in unrestricted and restricted open-shell approaches for comparison purposes. The above-mentioned NBO analyses show that the bond orders for all C-C and C-N bonds in the substituted and unsubstituted phthalocyanines are close to 1.5 (except for C1-C2 and C7-C8 in the isoindole fragments), which is consistent with the presence of π -conjugation in those fragments. The C–C bond orders in *tert*-butyl substituents are, as expected, very close to one. Atomic charge analyses for both conformers of Cu(pc^t) provide evidence for a significant role of covalent interaction in Cu-N bonding, and the same is true for the unsubstituted complex Cu(pc). Thus, the charge of the central copper ion for the studied complexes is substantially less than its formal magnitude of +2 (see Table 6).

Cu(pc)

Table 5 Comparison of the structural parameters of the molecules $Cu(pc^{t})$ (conformer 2–1 of C_s symmetry) and Cu(pc) obtained by GED and DFT

Table 6 Natural atomic charges (q) and Wiberg bond indexes (Q) in Cu(pc^{*t*}) of C_{4h} symmetry conformers and Cu(pc) as obtained by NBO analysis

 $Cu(pc^{t})$

Atom/bond

Parameters ^{a,b}	$\begin{array}{l} \text{Cu}(\text{pc}^t)\\ \text{GED, } r_{\text{h1}} \end{array}$	Cu(pc) [17]	$Cu(pc^t)$ DFT ^c , r_e	Cu(pc) [17]
r(Cu–N1)	1.964(5)	1.949(5)	1.965	1.964
<i>r</i> (N1–C1)	1.378(3)	1.381(5)	1.369	1.369
r(C1–N2)	1.318(4)	1.325(5)	1.320	1.320
<i>r</i> (Cu…N2)	3.369(7)	3.385(9)	3.363	3.362
r(C1–C2)	1.448(5)	1.459(5)	1.457	1.455
r(C2–C7)	1.405(3)	1.417(11)	1.400	1.402
r(C2–C3)	1.399(3)	1.399(4)	1.386	1.390
<i>r</i> (C3–C4)	1.401(3)	1.397(4)	1.398	1.388
r(C4–C5)	1.421(3)	1.429(18)	1.408	1.403
r(C10–C12)	1.543(3)	_	1.536	-
r(C10–C11)	1.550(3)	-	1.543	_
<i>r</i> (C3–H)	1.084(4)	1.091(9)	1.081	1.081
$\angle (N1-Cu-N4)^d$	90.0	90.0	90.0	90.0
∠(Cu–N1–C1)	125.6 ^d	125.9(2)	125.5	125.6
∠(N1–C1–N2)	127.5(4)	128.2(5)	127.7	127.6
∠(C8–N3–C9)	123.8(8)	121.9(7)	123.7	123.7
∠(C1–N1–C8)	108.8(10)	108.3(5)	108.9	108.9
∠(N1–C1–C2)	107.6(5)	109.5(5)	109.0	109.1
∠(C1–C2–C7)	108.6(8)	106.4(4)	106.4	106.5
∠(C2–C7–C6)	120.6(2)	121.3(2)	120.2	121.1
∠(C2–C3–C4)	117.5(7)	117.7(2)	119.4	117.7
∠(C3–C4–C5)	123.0(10)	121.1(4)	118.3	121.2
∠(C2–C3–H)	122.9(60)	123.2(44)	119.2	120.8

 $^a\,$ The values of bond lengths (Å) and angles (°)

^b In parentheses, the values of total errors for bond lengths are given as $\sigma = (\sigma_{\rm scal.}^2 + (2.5\sigma_{\rm LS})^2)^{1/2}$, where $\sigma_{\rm scal.} = 0.002r$, and for the angles $\sigma = 3\sigma_{\rm LS}$

^c UB3LYP/ECP10MWB

^d Fixed value at LS analysis

The supposed charge transfer interaction responsible for this effect could be proved by NBO analysis, which shows a donor-acceptor interaction between the donor " h_{sp2} " hybrid orbitals of the nitrogen atom and the acceptor " $3d_{x2-y2}$ " and "4s" orbitals of the copper atom. Interaction energies E(2) are listed in Table 7 for both Cu(pc^{*t*}) and Cu(pc).

It should be noted that the introduction of a *tert*-butyl substituent has no remarkable effect on either interaction energy or the distribution of electron density in the coordination cavity, but evokes a perturbation in the charges on atoms C3, C4 and C5. According to Table 6, the changes in the atomic charges on C3, C4 and C5 in the transition $Cu(pc) \rightarrow Cu(pc^{t})$ (which is accompanied by a decrease in Wiberg bond indexes from 1.47 to 1.42 for C3–C4 bond and from 1.40 to 1.37 for C4–C5 bond) are corresponding

^a The atomic charges are presented in the portions of elementary charge e

to an increase in the lengths of these bonds, which leads a decrease in repulsion between electron densities on orbitals σ (C3–C4) and σ (C5–C4) and finally to decrease in \angle (C3–C4–C5) angle in Cu(pc^{*t*}) as compared with those in Cu(pc) (see Table 5).

AIM analysis results

Another set of atomic charges and bond ellipticities as a measure for bond orders could be obtained from QTAIM analysis of the molecular wave functions for both conformers of $Cu(pc^t)$ and the unsubstituted Cu(pc) at UB3LYP/ECP10MWB approach (see Table 8). The tendencies for most of the atomic charges calculated in this approach are as expected. Though the central copper atom

	-		-	
	Conformer 1 UB3LYP	Conformer 2	ROB3L	YP
q(Cu) ^a	+1.32	+1.32	+1.32	+1.32
<i>q</i> (N1)	-0.66	-0.66	-0.66	-0.66
<i>q</i> (N2)	-0.47	-0.47	-0.47	-0.47
<i>q</i> (C1)	+0.41	+0.41	+0.41	+0.40
<i>q</i> (C2)	-0.06	-0.06	-0.07	-0.07
<i>q</i> (C3)	-0.18	-0.19	-0.17	-0.17
<i>q</i> (C4)	+0.004	+0.004	-0.19	-0.19
<i>q</i> (C5)	-0.21	-0.20	-0.19	-0.19
<i>q</i> (C6)	-0.16	-0.156	-0.17	-0.17
<i>q</i> (C7)	-0.08	-0.08	-0.07	-0.07
<i>q</i> (C10)	-0.003	-0.004	-	_
<i>q</i> (C11)	-0.58	-0.58	-	_
<i>q</i> (C12)	-0.59	-0.59	-	_
Q(Cu-N1)	0.20	0.20	0.20	0.20
Q(N1–C1)	1.23	1.23	1.23	1.23
Q(C1-N2)	1.38	1.38	1.38	1.38
Q(C1–C2)	1.09	1.09	1.09	1.09
<i>Q</i> (C2–C7)	1.29	1.30	1.30	1.30
Q(C2–C3)	1.38	1.35	1.36	1.36
<i>Q</i> (C7–C6)	1.37	1.35	1.36	1.36
<i>Q</i> (C3–C4)	1.42	1.45	1.47	1.47
<i>Q</i> (C6–C5)	1.46	1.49	1.47	1.47
<i>Q</i> (C4–C5)	1.37	1.35	1.40	1.40
Q(C4–C10)	0.98	0.98	-	_
Q(C10–C12)	1.00	1.00	-	_
<i>Q</i> (C10–C11)	0.99	0.99	-	-
9	1		· · · ·	

Table 7 Second-order perturbation energies $E^{(2)}$ (kcal mol⁻¹) of orbital interactions in the metal phthalocyanines: Cu(pc) and Cu(pc') (conformer 1)

 $E^{(2)}$ $\sum E^{(2)}(\mathbf{M} \leftarrow \mathbf{N})$ $M \leftarrow N$ direct donation **UB3LYP** $Cu(pc^{t})$ $hsp^{2.08}(N) \rightarrow 4s(Cu)$ α Spin 23.7 $hsp^{2.03}(N) \rightarrow 4s(Cu)$ β Spin 28.5 $hsp^{2.03}(N) \rightarrow 3d_{(x2-y2)}(Cu)$ 16.7 68.9 Cu(pc) $hsp^{2.05}(N) \rightarrow 4s(Cu)$ α Spin 23.4 $hsp^{1.99}(N) \rightarrow 4s(Cu)$ 28.1 β Spin $hsp^{1.99}(N) \rightarrow 3d_{(x2-y2)}(Cu)$ 16.4 67.9

exhibits a positive charge, its magnitude at +1.14e is less than the formal charge of +2e due to N \rightarrow Cu electron donation. Indeed, the positive charge hereby induced in atom N1 is, according to QTAIM analysis, further delocalized over the adjacent carbon atoms C1 and C8 and their neighboring N2 atom. This results in atomic charges of -1.17e for N1, +0.99e for C1 and C8 and -1.21e for N2. These results are in very good agreement with those for Cu(pc) with +1.15e (N1), +0.99e (C1/C8) and -1.21e (N2), respectively. The bond ellipticities for the Cu–N1 bonds in both $Cu(pc^{t})$ and Cu(pc) are at 0.03, very close to that of a single bond (0.00 [39]). These bonds exhibit a strongly ionic character, since the electron density at the bond critical point (BCP) is calculated to be 0.61 $e \text{ \AA}^{-3}$, whereas it amounts to 2.0-2.7 $e \text{ \AA}^{-3}$ for all the C-C and C-N bonds. This observation applies to both conformers of $Cu(pc^{t})$ as well as Cu(pc). Concerning the electron density distribution in the benzene moieties of the phthalocyanine ligand in both conformers, there is no significant difference observed for the carbon atoms separated from the substitution site by minimum one atom, namely C2, C6 and C7. For the transition of $Cu(pc) \rightarrow Cu(pc^{t})$, the atomic charges of the *ipso* and ortho carbon atoms C3, C4 and C5 undergo changes, as they are all smaller in magnitude by approximately 0.01. Altogether it should be noted that with QTAIM analyses no differences in the electron density distribution between the $Cu(pc^{T})$ conformers 1 and 2 can be observed.

Bader atomic charges are known to overestimate the charge separation between atoms of different effective nuclear charges or electronegativities, frequently summarized under the term *Perrin effect* [40]. Therefore, we refrain from comparing the atomic charges obtained from NBO and AIM analyses, respectively, but instead want to focus on the similarities which can mostly be seen in the

Table 8 Atomic charges and bond ellipticities of $Cu(pc') C_{4h}$ symmetry conformers and Cu(pc) as obtained by QTAIM analysis

Atom/bond	$Cu(pc^{t})$	Cu(pc)	
	Conformer 1	Conformer 1 Conformer 2	
Atomic charges	3		
Cu	+1.14	+1.14	+1.15
N1	-1.17	-1.17	-1.17
C1	+0.99	+0.99	+0.99
C8	+0.99	+0.99	+0.99
N2	-1.21	-1.21	-1.21
C7	-0.02	-0.02	-0.02
C2	-0.02	-0.02	-0.02
C6	+0.01	+0.01	+0.01
C3	+0.00	+0.00	+0.01
C5	-0.02	-0.02	-0.01
C4	-0.01	-0.01	-0.01
C10	+0.09	+0.09	_
C11	+0.05	+0.05	-
C12	+0.05	+0.05	-
C13	+0.05	+0.05	_
Bond ellipticitie	es		
Cu-N1	0.03	0.03	0.03
C5-C4	0.18	0.17	0.18
C3–C4	0.20	0.21	0.20
C6-C5	0.20	0.21	0.20
C2–C3	0.18	0.17	0.18
C7–C6	0.18	0.17	0.18
C7–C2	0.16	0.17	0.16

^a The atomic charges are presented in the portions of elementary charge e

tendencies of charge perturbation resulting from the tertbutyl substitution. Both NBO and QTAIM analyses show almost no remarkable difference in the bonding situation of the coordination cavity in Cu(pc) and the $Cu(pc^{t})$ conformers. According to QTAIM analysis, the benzene moiety or rather the atoms C3, C4 and C5 just become more electron rich while undergoing tert-butyl substitution, whereas NBO for those atoms reliably reproduce the firstsemester organic chemistry rule of a positively inductive substituent increasing the electron density in ortho-position and decreasing it in ipso- and meta-position. The same conclusions can be drawn from the results of the abovementioned calculations in ROB3LYP, UHF and ROHF approaches as well as from the calculations of the free ligand double anions pc^{2-} and $(pc^{t})^{2-}$ in B3LYP approach. The results of these calculations are summarized in Tables S8 and S9.

Conclusion

By combination of experimental and theoretical results, the coordination center in copper(II) 2,9,16,23-tetra-tert-butyl phthalocyanine, $CuC_{48}N_8H_{48}$, was determined to adopt D_{4h} symmetry in the gas phase. According to GED and DFT results, the internal rotation of *tert*-butyl groups has no significant influence on the phthalocyanine ligand structure. Comparison of the DFT results for the structures of Cu(pc) and $Cu(pc^{t})$ shows that the *tert*-butyl substituents in the ring have a minor effect on the geometry of the coordination center. According to NBO and AIM analyses of the electron density distribution in Cu(pc) and $Cu(pc^{t})$, both molecules are close to ideal ionic compound where the central copper cation Cu^{2+} surrounded by the anionic ligand pc^{2-} and $(pc^{t})^{2-}$. The deviation of the calculated atomic charges from this ideal model is evidence for the partly covalent nature of the Cu-N bonds.

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