

Issue 22 (August 15, 2015)

Organic • Inorganic • Physical
Biological • Materials

WILEY

Coming Soon

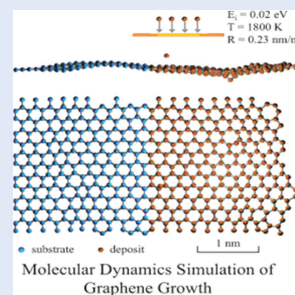
Look for these important papers
in upcoming issues

An analytical bond-order potential for carbon

X. W. Zhou, D. K. Ward, and
M. E. Foster

A new parameterization of Pettifor's bond order potential has been performed for carbon. The method captures the property trends of important carbon phases and passes stringent molecular dynamics simulation tests, not only allowing for the crystalline growth of graphene, graphite, and carbon nanotubes, but also the transformation of graphite to diamond at high pressure.

DOI: 10.1002/jcc.24000

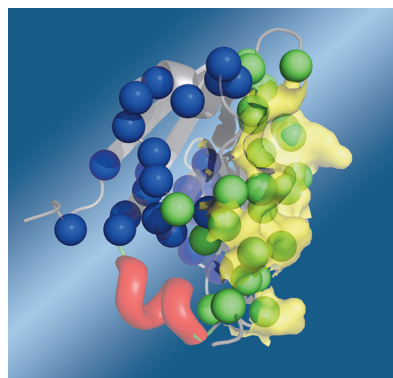
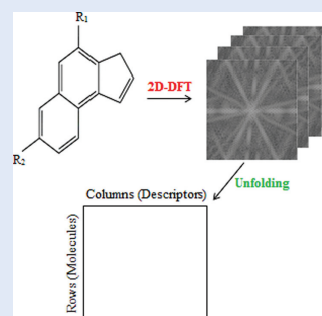


Is Molecular Alignment an Indispensable Requirement in the MIA-QSAR Method?

Stephen J. Barigye and
Matheus P. Freitas

The 2D-Discrete Fourier Transform (2D-DFT) is introduced as a strategy for creating a common base to construct multivariate images for chemical structures using their magnitude spectra. Thus, for the first time, the modeling of structurally diverse non-congruent chemical images in the MIA-QSAR context is possible.

DOI: 10.1002/jcc.23992

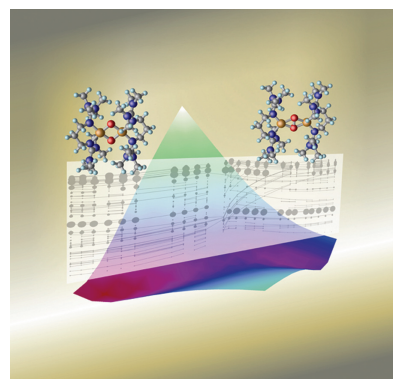


Residue-Residue Interactions

The third PDZ domain of a neuronal protein PSD-95 is a typical example that exhibits dynamic allostery. The figure shows the predicted dynamic subdomain architecture: two distinct subdomains, represented by blue and green spheres, are connected by the $\alpha 3$ helix (red tube) whose removal significantly reduces the ligand binding affinity. The yellow surface represents the binding pocket. The computational method by Takakazu Ishikawa, Yuki Iwata, Tatsuro Hatano, and Takahisa Yamato on page 1709 provides a useful tool for demonstrating the pattern of residue-residue interactions in a thermally fluctuating protein molecule with a graphical map of energy exchange network.

Density Functional Theory

The cover shows the singlet excitation energy surfaces along the minimum energy path from oxo to peroxy configuration of a biomimetic dinuclear copper complex on top of a 3D ground-state potential energy surface. The dot size reflects the oscillator strength from the ground state to the corresponding state. Below, Kohn-Sham orbitals relevant for the oxo-peroxy transitions are depicted. Density functional theory calculations of the equilibrium geometry, vibrational modes, ionisation energies, electron affinities and optical response of $[\text{Cu}_2(\text{btmgp})_2(\mu\text{-O}_2)]^{2+}$ (oxo) and $[\text{Cu}_2(\text{btmgp})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)]^{2+}$ (peroxy) are presented by Martin Rohrmüller, Alexander Hoffmann, Christian Thierfelder, Sonja Herres-Pawlis, and Wolf Gero Schmidt on page 1672.



The Cu₂O₂ Torture Track for a Real-Life System: [Cu₂(btmcp)₂O₂]²⁺ Oxo and Peroxo Species in Density Functional Calculations[†]

Martin Rohrmüller,^[a] Alexander Hoffmann,^[b] Christian Thierfelder,^[a] Sonja Herres-Pawlis,^{*,[b]} and Wolf Gero Schmidt^[a]

Density functional theory (DFT) calculations of the equilibrium geometry, vibrational modes, ionization energies, electron affinities, and optical response of [Cu₂(btmcp)₂(μ-O)₂]²⁺ (oxo) and [Cu₂(btmcp)₂(μ-η²:η²-O₂)]²⁺ (peroxo) are presented. Comprehensive benchmarking shows that the description of the oxo–peroxo energetics is still a torture track for DFT, but finds the molecular geometry to be comparatively robust with respect to changes in the exchange–correlation functionals and basis sets. Pure functionals favor the oxo core found experimentally, whereas hybrid functionals shift the bias toward the peroxo core. Further stabilization of peroxo core results from relaxing the spin degrees of freedom using the broken-symmetry (BS) approach. Dispersion effects, conversely, tend to favor the oxo configuration. Triple-zeta basis sets are

found to represent a sensible compromise between numerical accuracy and computational effort. Particular attention is paid to the modification of the electronic structure, optical transitions, and excited-state energies along the transition path between the oxo and peroxo species. The excited-state potential energy surface calculations indicate that two triplet states are involved in the transition that stabilize the BS solution. Charge decomposition and natural transition orbital analyses are used for obtaining microscopic insight into the molecular orbital interactions. Here, the crucial role of guanidine π-interactions is highlighted for the stabilization of the Cu₂O₂ core. © 2015 Wiley Periodicals, Inc.

DOI: 10.1002/jcc.23983

Introduction

Activation of dioxygen is mediated by several binuclear copper proteins, the so-called type 3 copper proteins.^[1] The subsequent oxygen transfer to phenolic substrates represents the more complicated task which is performed by tyrosinase and occurs during pigment formation as well as in the browning of fruits, hair, and feathers. In these type 3 proteins, oxygen is bound as side-on peroxide in a μ-η²:η²-peroxo dicopper(II) complex. Early biomimetic inorganic model studies by Kitajima and Moro-oka predicted this motif for type 3 proteins already in 1988.^[2] Only in 2006, this motif was found in tyrosinase. Each Cu(II) center in oxygenated tyrosinase (oxyTyr) is ligated by three imidazole nitrogen ligands, albeit one of the ligands is only weakly associated.^[3–5] Hence, extensive model studies used tridentate and bidentate nitrogen donor ligands to mimic type 3 centers, and led to the discovery of a multitude of Cu_nO_m species with various stoichiometries. The peroxo core (**P**, Fig. 1) itself often exists in a delicate equilibrium with its isomeric form, the bis(μ-oxo) dicopper(III) core (**O**, Fig. 1).^[6,7] This equilibrium was found to be shifted by ligand substituents, temperature, choice of counteranions, and solvents^[8,9] and is heavily discussed for its relevance for the final oxygen transfer.^[10–12] Besides these two species, the trans-μ-1,2-peroxo isomer has also been observed for hydroxylation reactivity in lab, but it can be ruled out for the natural system due to biological ligand restrictions.^[13] The computational modeling and thorough understanding of the subtle **O–P** equilib-

rium is expected to assist elucidating the tyrosinase-mediated hydroxylation mechanism.

Unfortunately, as stated earlier, the equilibrium between **P** and **O** cores is a “torture track” for computation as the amount of exact exchange (EX) strongly influences their relative energies and thus the **O–P** equilibrium.^[14] Several studies with multireference calculations based on wave-function theory methods such as CASPT2,^[15] MRCI+Q,^[16] DMRG,^[17] and RASPT2^[18] have been performed with ammonia ligands as a substitution for histidine residues.

However, the small model does not reproduce experimental Cu...Cu and O–O distances of more legitimate peroxo model complexes. Due to the ligand truncation in simplified models chelate effects can often not be taken into account. This leads to strong deviations with respect to the more realistic complex models.^[19] Further density functional theory (DFT) studies

[a] M. Rohrmüller, C. Thierfelder, W. G. Schmidt
Universität Paderborn, Department Physik, Lehrstuhl für Theoretische Physik, Pohlweg 55, 33095 Paderborn, Germany

[b] A. Hoffmann, S. Herres-Pawlis
RWTH Aachen University, Fachgruppe Chemie, Lehrstuhl für Bioanorganische Chemie, Landoltweg 1, 52074 Aachen, Germany
E-mail: sonja.herres-pawlis@ac.rwth-aachen.de

[†]Dedicated to Prof. Manfred Scheer on the occasion of his 60th birthday.

Contract grant sponsor: Deutsche Forschungsgemeinschaft (FOR 1405); Contract grant sponsor: European Commission's Seventh Framework Programme (FP7/2007–2013); Contract grant number: 312579 (ER-flow)

© 2015 Wiley Periodicals, Inc.

	trans μ -1,2-peroxo	μ - η^2 : η^2 -peroxo (P)	bis μ -oxo (O)
Cu-Cu avg	4.36	3.51	2.80
O-O avg	1.43	1.42	2.32
Cu-O avg	1.85	1.92	1.82

Figure 1. Binding motifs for Cu_2O_2 cores with typical bond lengths in Å. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

focused on larger real-life systems,^[11,12,20,21] but still cutting of the ligands or substrates resulted in sizeable structural deviations. In a recent study, Liu and Blomberg et al.^[12] reproduced excellently the experimental geometry reported by Stack and coworkers which opens up the discussion on the hydroxylation activity of the **O** core again.

Many calculations in this context^[10,14,22–24] use DFT with either the local generalized gradient approximation (GGA) functionals such as PW91, PBE, and BLYP or hybrid functionals such as B3LYP^[11,12,19,20,25–34] to describe the electron exchange and correlation (XC) energy. Although DFT is generally believed to result in reliable structures and energies in bioinorganic chemistry, a word of caution is in order if it is applied to antiferromagnetically coupled systems. In such instances, often large energy differences result from the use of different functionals.^[14,35] In any event, a multitude of charge-transfer (CT) transitions is present which is an additional challenge of copper chemistry.^[36] Moreover, the energy differences between closed-shell singlet, broken-symmetry (BS; open-shell) singlet and triplet are rather small, additionally complicating the analysis.^[14,24,37–41] We mention that strong electron correlation effects render the modelling of the electronic structure even of seemingly simple bulk CuO systems a complicated task.^[37] As far as we know, the transition between the two isomers **O** and **P** with realistic ligands has by now only been modelled using tridentate bis(pyrazolyl)pyridinylmethanes, as they stabilize a catalytically active model.^[42,43] Bidentate N donor ligands also stabilize **P** and **O** cores, but their theoretical treatment is even more complicated and the spectroscopic predictability limited.^[44] Here, guanidines have proven to be very useful for the stabilization of Cu_2O_2 species.^[45–47] Their CN_3 backbone is highly suited for the coordination to high-valent copper(III) and their CT properties are an intensively investigated field.^[48–52]

In this work, we focus on a bidentate ligand system comprising the strong tetramethylguanidine donor: benchmarking density functional calculations for a real-life chemical system, namely $[\text{Cu}_2(\text{btmcp})_2(\mu\text{-O})_2]^{2+}$ (Fig. 2) are presented. This system is known to strongly stabilize the bis(μ -oxo) core.^[20,45] Apart from using a range of local and hybrid XC functionals, we also address the accuracy due to the basis set. Localized functions, for example, Gaussians, frequently used as basis set for the expansion of the molecular electron wave functions, render the efficient and reliable control of the numerical convergence difficult. These problems do not exist if, instead, plane waves

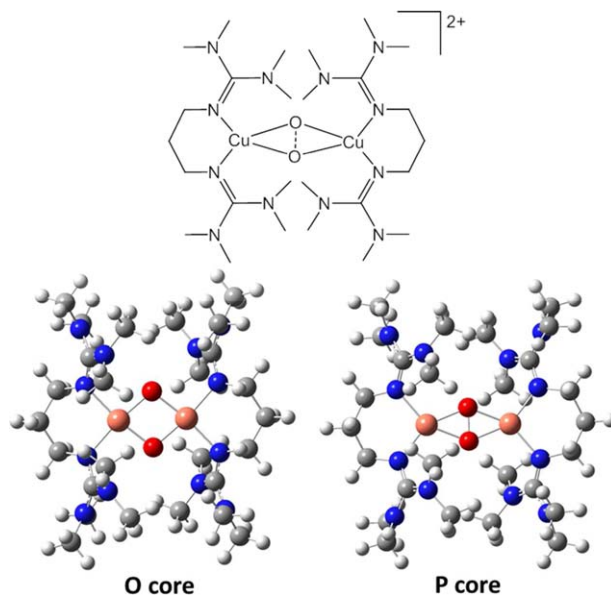


Figure 2. Chemical scheme and three-dimensional representations of $[\text{Cu}_2(\text{btmcp})_2(\mu\text{-O})_2]^{2+}$ (**O**) and $[\text{Cu}_2(\text{btmcp})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)]^{2+}$ (**P**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are used for the expansion of the electron orbitals. Plane waves furthermore do not suffer from the basis set superposition error that occurs for bases formed from a finite number of localized atom-centered functions. In this study, therefore, in addition to localized basis functions, plane waves are used for expanding the Kohn–Sham (KS) orbitals. Moreover, we investigate the potential energy surface (PES) for the transition between the **O** and **P** core complex, and calculate excitation energies as well as spectroscopic signatures along the transition path.

Methodology

The calculations are performed using DFT. On the one hand, we use the plane-wave-based Vienna *Ab initio* Simulation Package (VASP) implementation,^[53,54] where the electron-ion interaction is described by the projector-augmented wave scheme.^[55] Extensive convergence tests were performed using a $24 \times 24 \times 24 \text{ Å}^3$ supercell. The total energy as well as geometrical parameters are found to be converged within 10^{-3} eV and 10^{-3} Å , respectively, when the KS orbitals are expanded into plane waves up to a cutoff energy of 380 eV. The convergency is demonstrated for key structural parameters of the **O** core in Figure 3. A force relaxation criterion of 5 meV/Å is used throughout the calculations.

Additionally, all electron calculations were performed using extensive, uncontracted Gaussian-type basis sets as well as Slater-type orbitals using the Gaussian09^[56] and the Amsterdam density functional (ADF) implementation^[57] of DFT, respectively. Thereby a range of exchange–correlation functionals is probed for modelling the electron–electron interaction. Specifically, we use the local GGA with the PBE,^[58] the PW91,^[59] and the BLYP,^[60–62] the meta-GGA M06-L^[63]

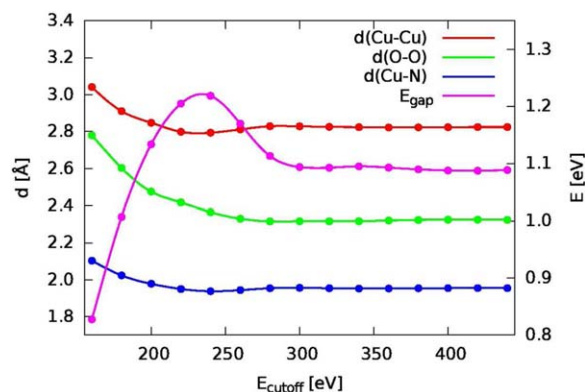


Figure 3. Calculated $[\text{Cu}_2(\text{btmgp})_2(\mu\text{-O})_2]^{2+}$ equilibrium bond lengths and KS gap in dependence on the plane wave cutoff energy used in the VASP implementation of DFT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

functional as well as the meta-hybrid functional TPSSh^[64] with 10% EX and the three-parameter B3LYP hybrid functional^[62,65,66] with 20% EX. Additionally, CAM-B3LYP is used.^[67] It is based on B3LYP but contains a long-range correction, which makes it more appropriate for the description of CT excitations. The influence of van der Waals forces is explored using the semiempirical D3 dispersion correction^[68–70] with Becke–Johnson (BJ) damping. Within Gaussian throughout the tight option for convergence of relaxations and the ultrafine integration grid are used. We searched for energetically low lying unrestricted KS wavefunctions with spatially conserved but broken spin symmetry (“broken-symmetry” wavefunctions) by starting from various trial wavefunctions obtained via fragmentation and forced opposite spin polarization for the copper atoms. For the Gaussian calculations, we used the “guess=mix” keyword. The programme AOMix^[71,72] was used as a postprocessing tool for charge decomposition and analysis.

Results and Discussion

Structure and energetics

The calculated bond lengths for **O** and **P** using various XC functionals and basis sets are depicted in Figure 4, an elaborate compilation is available in the Supporting Information (Tables S1 and S2). Overall, it is observed that the key structural parameters agree for the most of the tested double- or triple-zeta basis sets within ± 1 –2%. All calculations reproduced a planar copper–oxygen core. As most prominent discrepancy, all calculations for **P** that use the 6-31g(d) basis have a systematic offset, indicating the insufficiency of this small basis for the present system. A further remarkable exception from the otherwise astonishingly closely agreeing geometry results concerns the O–O bond that within CAM-B3LYP/cc-pVDZ is surprisingly short. Here, the closed-shell **P** state is conspicuous off and also adding dispersion forces does not lead to substantial changes. In contrast, the BS **P** state within CAM-B3LYP is very close to the results obtained within the common B3LYP functional. The relative changes of the calculated bond

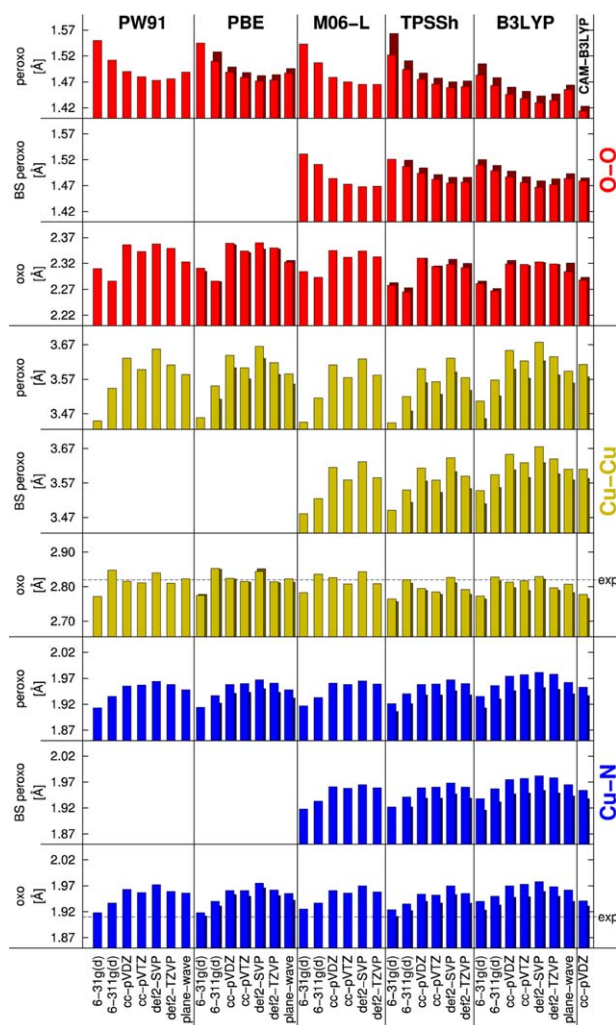


Figure 4. Calculated distances of **O** (oxo) and **P** (peroxo) in either its restricted or BS form. Results including D3 dispersion of Grimme with GD3BJ are plotted as shadow bars in the background. Experimental values^[20] are indicated by dashed lines.

lengths with respect to the basis set used are surprisingly robust with respect to the functional.

A closer look at the dependency of the geometry on the XC functional shows that the different bonding situation in the **O** and **P** cores leads partially to opposite trends with respect to the influence of the XC functional on specific bond lengths, which complicates the discussion. It is seen in the case of **P** that the GGA functionals PW91 and PBE give nearly same bond lengths, whereas M06–L results in about 0.03 Å shorter Cu···Cu distances. The meta-GGA M06–L geometries are closer to the ones obtained within TPSSh than to the results from the other GGA functionals.

Inclusion of dispersion interaction leads in general to slightly shorter Cu···Cu distances, this effect is most pronounced for the closed-shell **P**, slightly weaker for the open shell **P** and only marginal for **O**. Accordingly, the corresponding O–O bonds are in most cases prolonged.

The influence of the basis set and the XC functional on the calculated Cu–N bond lengths does generally not depend on whether the core is in the **O** or **P** configuration, either in its

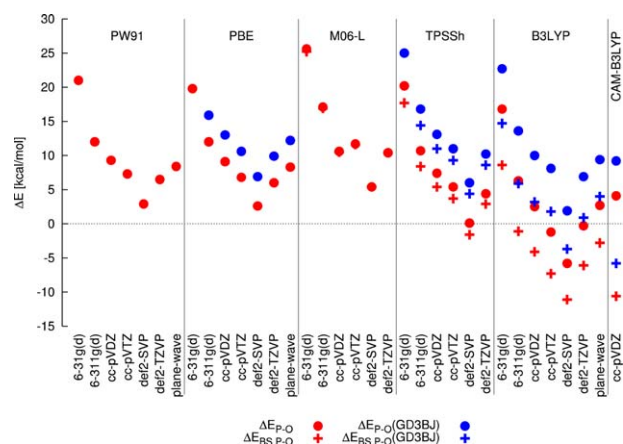


Figure 5. Calculated energy differences between oxo (E_O) and peroxy (E_P) isomer in kcal/mol. Energies resulting from peroxy BS open-shell calculation are denoted E_{BS} . Energies taking into account the Becke–Johnson dispersion (GD3BJ) are depicted in blue.

closed-shell or the BS configuration. The calculated Cu–N bond length is somewhat larger than the measured value for the **O** species,^[20] irrespective of the XC functional. In contrast, the Cu···Cu distance is reproduced nicely. The results scatter with small deviations around the experimental value. Especially, the GGA/plane wave and B3LYP/def2-SVP with dispersion calculations meet the experimental value perfectly. These results indicate that DFT provides an overall reliable description of the molecular structure.

Considering the structural differences between the BS **P** structure and the closed-shell singlet **P** geometry one finds that these depend on the XC functional used in the calculations, but show exactly the same trends with respect to the basis sets. A larger amount of EX leads to a slightly larger O–O bond length. The largest increase is found for CAM-B3LYP, where a difference of 0.06 Å is observed. This can also be nicely correlated with the S^2 expectation value (compare Supporting Information Table S2), which is increasing together with the deformation. The influence of including dispersion is negligible (max. 0.002 Å) for the difference between the BS-**P** and the **P** state. In general, the Cu···Cu distances of the two **P** states are close to each other, so the structures are comparable.

In Figure 5, the **O–P** stabilization energies calculated for various functionals and basis sets are compared. Positive values indicate the preference for the **O** core which is observed in the experiment.^[20] The explicit values are compiled in the Supporting Information Table 2. Many observations made for the molecular geometries discussed above hold as well for the relative energy of the **O** and **P** core. In particular, the general influence of the basis sets is again transferable between the different XC functionals. The range of calculated values within the same functional using different basis sets is as large as 20 kcal/mol (0.9 eV). The largest local basis sets used here, cc-pVTZ and def2-TZVP, result in energy differences close to plane-wave energies. In contrast to the geometries, where different triple zeta basis sets lead only to minor differences, the stabilization energies are more affected. The difference between cc-pVDZ and cc-pVTZ is about 2–3 kcal/mol (0.09–

0.13 eV) and between the cc-pVTZ and def2-TZVP about 1 kcal/mol (0.043 eV). Investigating the influence of the XC functional, the two extensively tested GGA functionals give nearly identical results for the stabilization energy, with differences below 1 kcal/mol (0.043 eV). The meta-hybrid functional TPSSH lowers the huge stabilization of **O**. As already described in literature by Cramer^[14] the amount of EX shifts the energy balance toward the preference of **P**. In our study, TPSSH/def2-TZVP with 10% EX favors the **P** state by 1.6 kcal/mol (0.069 eV) and B3LYP/def2-TZVP with 20% EX by 6.3 kcal/mol (0.27 eV) compared with PBE. Due to the energy lowering of the BS-**P** state, also the stabilization energy shifts necessarily toward the **P** species compared with stabilization energies, involving the closed-shell **P** state. For TPSSH/def2-TZVP this preference of **P** is 1.5 kcal/mol (0.065 eV) and for B3LYP/def2-TZVP 5.8 kcal/mol (0.25 eV), which is close to the B3LYP/plane wave result of 5.5 kcal/mol (0.24 eV). For other basis sets within B3LYP this stabilization due to BS is in the range from 5.3 kcal/mol for def2-SVP (0.23 eV) up to 8.2 kcal/mol for 6-31g(d) (0.36 eV). This shows that the small basis leads also here to the extreme values. Remarkable is the huge stabilization of the BS-**P** state for CAM-B3LYP, which is as large as 15 kcal/mol (0.65 eV). Dispersion has the effect of favoring **O** between 3.8 kcal/mol (0.16 eV) for PBE/cc-pVTZ and 9.3 kcal/mol (0.40 eV) within B3LYP/cc-pVTZ. The influence of dispersion effects on the **O–P** equilibrium had already been observed by Siegbahn et al.^[73] Generally, we find that dispersion effects in the stabilization energy increase from PBE via TPSSH to B3LYP.

Altogether, there is a remarkably strong basis set dependency and a large influence of the used XC-functional on the stabilization energy, also D3 dispersion of Grimme with Becke–Johnson damping (GD3BJ) and BS play a key role if one is interested in accurate energies. In almost all calculations, the **O** structure is favored over **P**. This agrees with the experimental finding, that **O** should be more stable than **P** by at least 9 kcal/mol (0.4 eV).^[20] The stabilization energies calculated here range from –11 kcal/mol (–0.5 eV) to 25 kcal/mol (1.1 eV). Thereby, we observe the trend that local XC functionals tend to favor **O** more than **P**, while larger basis sets shift the balance in the opposite direction. The usage of the hybrid functional again shifts in direction of **P**. Results for B3LYP are in a subtle balance of the **O** and **P** energies with a small preference for the former. In general, B3LYP is regarded to treat first row transition metal systems efficiently.^[24] Here, the weakness of this all-rounder functional becomes obvious.

O–P transition PES

For a more detailed understanding of the **O–P** energetics, we calculated a PES in dependence on the Cu···Cu distance and the O–O bond length, cf. Figure 6. As the combination of the local PW91 functional in conjunction with a plane wave basis has been found to result in meaningful structures and energies, this combination is used for the relaxation of structural degrees of freedom for a dense mesh of fixed Cu···Cu and O···O distances. Moreover, as

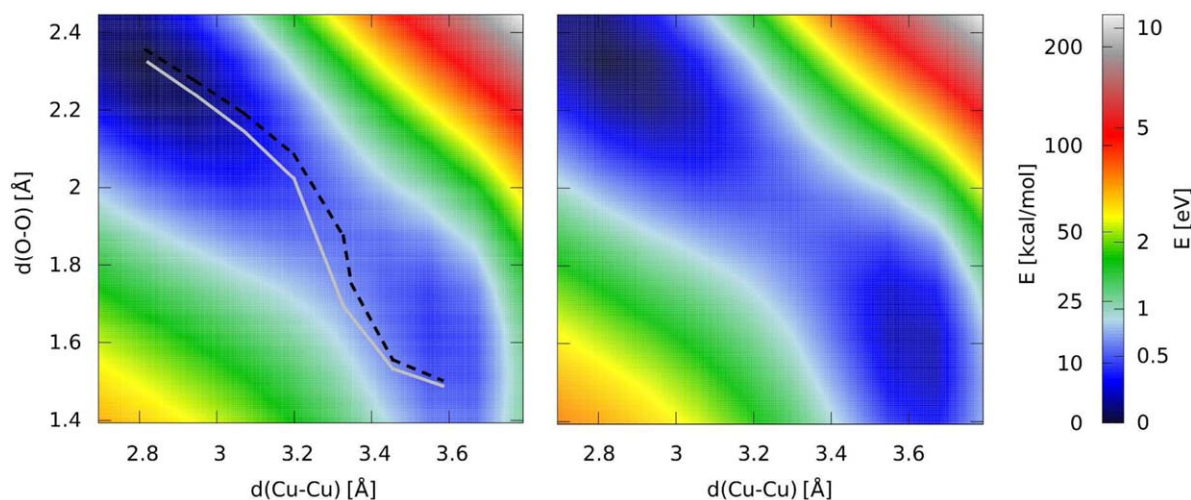


Figure 6. Closed-shell PES and MEP calculations. Energies are given with respect to the **O** ground state structure. Left: PW91/plane wave calculation with MEP from **O** (upper left minima) to **P** calculated with PW91/cc-pVDZ (dashed black) and PW91/plane wave (solid gray). Right: B3LYP energies calculated for the respective geometries obtained within PW91. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

representative of hybrid functionals we have studied the **O**–**P** relation using B3LYP. The left-hand side of Figure 6 shows the calculated energies for the respective geometries calculated within PW91, while the corresponding B3LYP energies for the same PW91 structures are plotted on the right-hand side of this figure. In both cases, two distinct minima and a saddle point are observable, which can be identified with the **O**, **P** and in between a transition state (TS). Additionally, the fully relaxed minimum energy paths (MEP) calculated within PW91 using both plane waves and a cc-pVDZ basis are shown in Figure 6. A closer look reveals, however, that the amount of EX clearly changes the relative energies of the two local minima found here for **O** and **P**, while it has little influence on the corresponding geometries, underlining the discussion above.

The respective influence of basis set and XC functional can be seen more clearly in Figure 7, where we have plotted the ground-state energies for singlet configurations along the MEP as calculated within PW91 and B3LYP using both plane waves

as well as a localized cc-pVDZ basis set. Obviously, the functional is far more important for the relative stability of the respective species than the basis set. The latter, however, slightly modifies the calculated ground-state structures: The Cu···Cu distance in **P** is slightly shorter than in the case when a plane wave basis is used. Going along the MEP from the energetically favored **O** toward the **P** state, a TS has to be passed. The necessary activation energy accounts about 12.5/13.1 kcal/mol (0.54/0.57 eV) for PW91 and 11.4/9.9 kcal/mol (0.49/0.43 eV) using B3LYP (with plane wave/cc-pVDZ basis). Looking at the results calculated with the cc-pVDZ basis set, the PW91 functional predicts the singlet **O** to be 9.2 kcal/mol (0.40 eV) favored over **P**. This energy difference is reduced to 2.5 kcal/mol (0.11 eV) when B3LYP is used as XC functional. The trend that local XC functionals favor **O** over **P** more than hybrid functionals do, holds again.^[14]

Now, we focus more on the relaxation of the spin degrees of freedom. All the previous singlet calculations were checked for stability of the wave function. In Figure 8, the singlet, triplet, and BS energies calculated within B3LYP/cc-pVDZ along the MEP

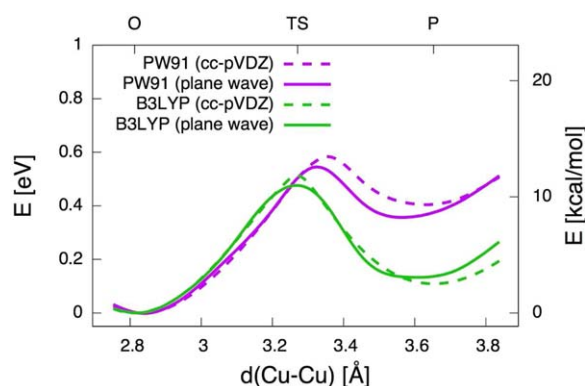


Figure 7. Comparison of singlet ground-state energies calculated with PW91 or B3LYP functional and localized cc-pVDZ or plane wave basis. B3LYP/plane wave calculations use the PW91 geometries. All coordinates apart from the fixed Cu–Cu distances are relaxed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

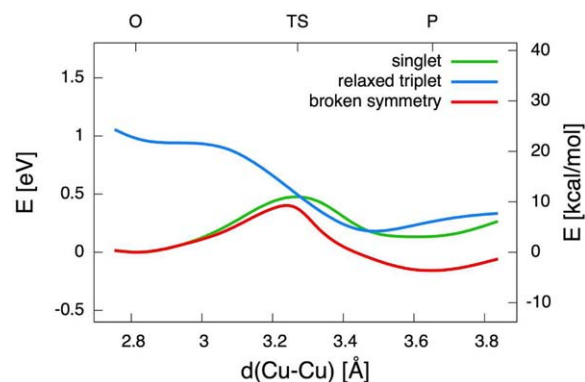


Figure 8. Comparison of closed-shell singlet with pure triplet and BS singlet calculated with B3LYP functional and local cc-pVDZ basis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

from **O** to **P** are shown. While the relaxation of the spin degrees of freedom does not lower the **O** energy, it is found that **P** profits energetically from the BS description. In fact, it does now correspond to the global energy minimum of the isomers. This does not hold, however, if a local XC functional is used in the calculation: The corresponding PW91 calculations favor the singlet solution along the whole path from **O** to **P**.

The B3LYP/cc-pVDZ finding that **P** is more favored than **O** provided the spin structure is relaxed, is not only in contrast with the PW91 results, but also contradicts the experimental observations.^[20] The BS description of **P** within B3LYP lowers its energy with respect to the pure singlet spin restricted calculation by 6.7 kcal/mol (0.29 eV). It results in a configuration that is 4.1 kcal/mol (0.18 eV) lower in energy than **O**. These energy differences refer to frozen singlet geometries. Additional relaxation of the structural degrees of freedom for the BS-**P** state leads to a small additional energy gain of 0.6 kcal/mol (0.03 eV). This corroborates the finding discussed above that the **O** and **P** geometries are far less sensitive to the theoretical modelling than their energies and electronic structures. The S^2 expectation value—which is zero for a pure singlet and 2.0 for a triplet—evolves within B3LYP from 0.0 for **O** via 0.56 at the TS to 0.67 for **P** along the **O**-TS-**P** transition path. The latter value is increased to 0.80 within CAM-B3LYP. A further increase by 0.01 occurs if dispersion is included using the D3-BJ scheme within either B3LYP or CAM-B3LYP.

Not for all basis sets the energy lowering of **P** due to relaxing the Cu spin degree of freedom within the BS approach is sufficient to lower its energy below **O**: B3LYP/DZ Slater orbital calculations lower the **P** energy by 6.1 kcal/mol (0.26 eV) on spin relaxation. Still, even the spin-relaxed **P** state is 1.1 kcal/mol (0.05 eV) higher in energy than **O**. We mention that the energy balance changes if spin projection is used to eliminate the spin contamination. B3LYP/TZP Slater orbital calculations favor **P** over **O** by 0.2 kcal/mol (0.01 eV) even without spin relaxation, in contrast to the experimental finding. The relative BS energy for **P** is lowered by another 5.6 kcal/mol (0.24 eV) compared with the singlet calculation. So, TZP Slater orbitals are absolutely comparable to the other used local TZ basis sets (cf. Supporting Information Table S2). Finally, we observe that allowing for spin contamination lowers the TS energy slightly, that is, decreases the energy barrier between **O** and **P**. This is also summarized in Figure 5.

In Figure 9, the magnetization density of the BS-**P** cation is plotted. As one might expect the copper d_{xy} orbitals interact via the oxygen π_g^* -orbitals and lead to locally separated spin accumulations of the two spin orientations. The local XC functionals probed here do not give rise to an energy lowering on spin relaxation. The triplet and singlet energies calculated with PW91 along the **O**-**P** transition are shown in Supporting Information Figure S1. Obviously they are well separated for all Cu...Cu distances, with the singlet description corresponding to the ground state in any case. Nevertheless, we observe that the electron configuration has a large influence on the molecular geometry. In particular, the energy of the **P** species is considerably lowered when the atoms are allowed to relax from their singlet equilibrium positions.

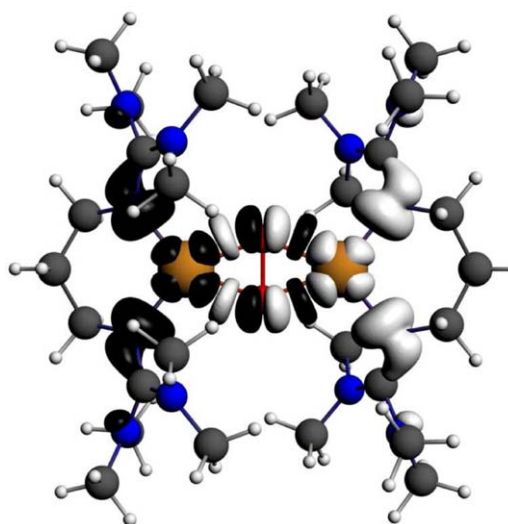


Figure 9. Isosurfaces of the magnetization density ($m(\vec{r}) = \rho^{\uparrow}(\vec{r}) - \rho^{\downarrow}(\vec{r})$) with positive and negative sign (black and white) of the BS-**P** cation (B3LYP/Slater DZ). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The structural relaxation is in particular important for geometries close to the transition structure between **O** and **P**. This is highlighted by the B3LYP calculations shown in Figure 10. There it can be seen that in a limited range of geometries close to the TS the triplet description leads to a lower energy than the singlet, provided that the structural degrees of freedom are allowed to relax. In contrast, spin flip for frozen geometries does not lower the total energy. This behavior is found for plane-wave as well as for localized basis set calculations.

The coupling constant of our system can be determined via spin projection^[74] from the high-spin (HS) and the low-spin (LS) state, which in the present case corresponds to the broken-symmetry (BS) state:

$$J_{Cu_1, Cu_2} = \frac{E_{BS} - E_{HS}}{\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS}} \quad (1)$$

For a fully relaxed BS **P** and the relaxed corresponding triplet state the coupling constant equals $-2838/-2708 \text{ cm}^{-1}$

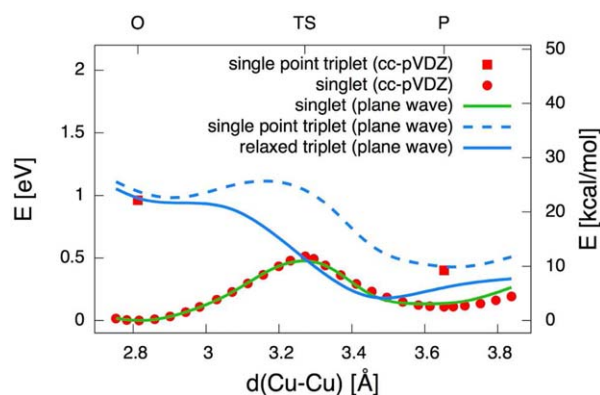


Figure 10. Comparison of singlet and triplet ground-state energies calculated with B3LYP functional (plane wave or localized cc-pVDZ). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

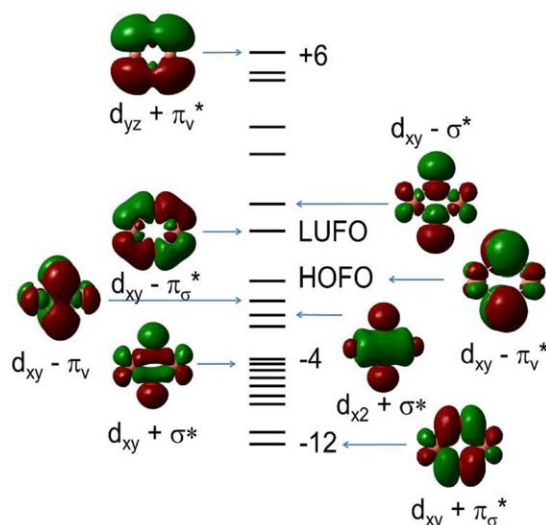


Figure 11. Fragment orbitals of the Cu_2O_2 fragment of relevance for the whole $\mathbf{O}$ core cation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for B3LYP/CAM-B3LYP. This is in accordance with experimental data of other peroxo complexes.^[45,75–77] Spin projection also allows for correcting the calculated total energy by accounting for the spin contamination. According to^[78] the corrected energy is given by:

$$E_{\text{Sing}} = \frac{\langle S^2 \rangle_{\text{HS}} E_{\text{BS}} - \langle S^2 \rangle_{\text{BS}} E_{\text{HS}}}{\langle S^2 \rangle_{\text{HS}} - \langle S^2 \rangle_{\text{BS}}} \quad (2)$$

This procedure leads here to an energy lowering by 5.4 kcal/mol (0.23 eV) compared with the BS solution in case of B3LYP/cc-pVDZ calculations. If, instead, the CAM-B3LYP functional is used the corresponding energy is lowered by 6.4 kcal/mol (0.27 eV). In contrast, GD3-BJ dispersion has nearly no influence on the energetics (<0.1 kcal/mol) in both cases.

Orbital analysis and charge decomposition analysis

As guanidines are not pure σ -donors but also π -donors, we have performed a thorough orbital analysis in combination with a charge decomposition analysis (CDA).^[79] Due to the Y-aromaticity,^[80] guanidines can stabilize high copper oxidation states.^[20,45,46] but the role of their π -system was not yet fully understood.

Therefore, we divided the $\mathbf{O}$ core into two fragments: the Cu_2O_2 moiety and the two btmgp ligands. The overall CT of the btmgp ligands to the Cu_2O_2 moiety amounts to 1.41 electron units, whereas the back-donation of Cu_2O_2 to the ligands is calculated to 0.03 electron units. These values are in line with the formally highly positively charged Cu(III) cations.

Figure 11 shows the fragment orbitals (FOs, see also Table S3 in Supporting Information) of the Cu_2O_2 moiety which are in accordance with previous theoretical studies.^[81] Supporting Information Figure S2 summarizes the FOs of the two btmgp ligands. As the whole $\mathbf{O}$ core cation has been simulated using C_{2h} point group symmetry, the symmetry assignments have been used in

Table 1. Fragment orbital descriptions of the two-ligand-fragment.

FO	Energy [eV]	FO composition
HOFO	−4.54	Sigma guanidine with a_u symmetry
HOFO-1	−4.54	Sigma guanidine with b_g symmetry
HOFO-2	−4.72	Sigma guanidine with b_g symmetry
HOFO-3	−4.76	Sigma guanidine with a_u symmetry
HOFO-4	−4.78	Pi guanidine with b_u symmetry
HOFO-5	−4.83	Pi guanidine with a_g symmetry
HOFO-6	−5.50	Sigma guanidine with a_g symmetry
HOFO-7	−5.52	Sigma guanidine with b_u symmetry
HOFO-8	−5.81	Pi guanidine with a_u symmetry
HOFO-9	−5.85	Pi guanidine with b_g symmetry
HOFO-10	−5.97	Sigma and Pi guanidine with a_g symmetry
HOFO-11	−5.99	Sigma and Pi guanidine with b_u symmetry
HOFO-12	−7.68	Pi guanidine with b_g symmetry
HOFO-13	−7.69	Pi guanidine with a_u symmetry
HOFO-14	−7.88	Pi guanidine with b_u symmetry
HOFO-15	−7.89	Pi guanidine with a_g symmetry
HOFO-16	−8.66	Pi guanidine with b_u symmetry
HOFO-17	−8.67	Pi guanidine with a_g symmetry
HOFO-18	−8.75	Pi guanidine with b_g symmetry
HOFO-19	−8.75	Pi guanidine with a_u symmetry

Table 1. It is noteworthy that only the occupied FOs of the two ligands contribute to the molecular orbitals of the whole $\mathbf{O}$ core.

The detailed analysis of the bonding orbitals of the guanidine donors allows for a better understanding of the complicated situation in these excellent donors: The guanidine units cannot only donate electron density via the classical σ -donation of the lone pair of the imine N atom of each guanidine unit (such as in the HOFO to HOFO-3) but also via the whole π -system of the guanidine. In principle, the CN_3 unit of a guanidine possesses a special type of Y-aromaticity (compare Fig. 12, HOFO-12-15)^[80] and in

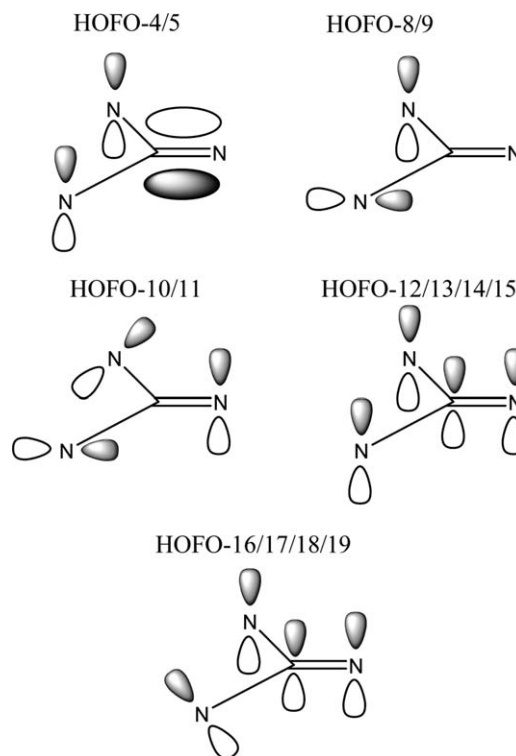


Figure 12. Guanidine π -contributions to the FOs of the ligand fragment.

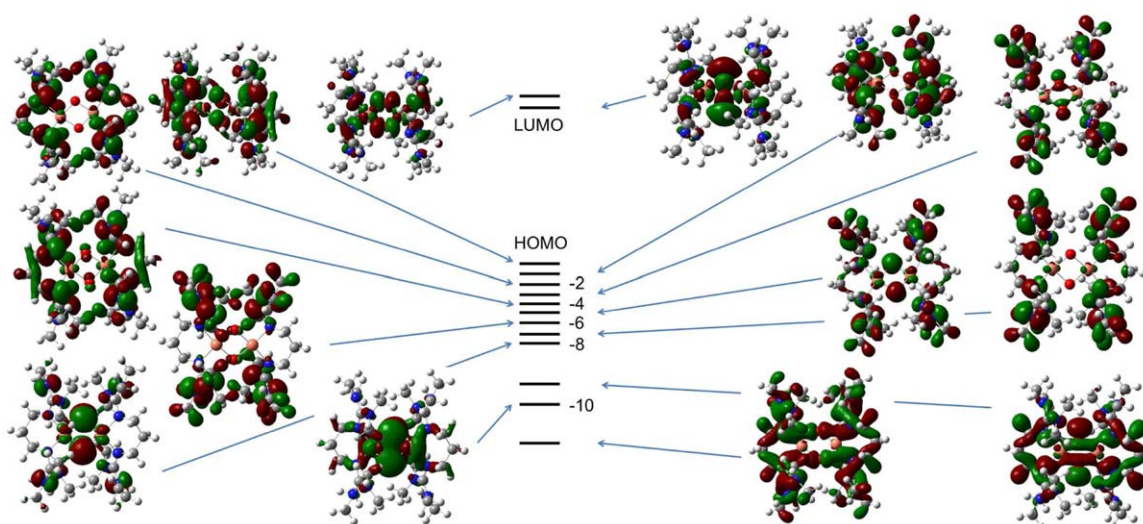


Figure 13. Molecular orbitals of $[\text{Cu}_2(\text{btmgp})_2(\mu\text{-O})_2]^{2+}$ (**O**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conjunction with a very positive charge more electrons can be activated for donation.^[45] Figure 12 depicts the π -donating FOs of the btmgp ligands. HOF0-4/5 represents the formal imine double bond which is indeed able to donate toward the Cu_2O_2 core. Especially, HOF0-4 is important as it contributes 80% to the final HOMO (compare Table 2 and Fig. 13) of the cation. Hence, we show that the guanidines act as σ - AND π -donor, which explains the strong **O** core stabilization against the isomerization to the **P** core.

Vibrational analysis

The relaxed geometries for the **O**, TS and **P** structure were used as starting points for the calculation of the vibrational modes in harmonic approximation. The calculated eigenmodes, eigenfrequencies, and relative infrared (IR) or Raman intensities are sum-

marized in Table 3. Thereby, we restrict ourselves to the modes that are clearly localized at the copper–oxygen core. Comparing **O** and **P** modes with similar displacement patterns, significant shifts in the frequencies are found for the modes 1 (–27%), 2 (–49%), 3 (50%), 4 (–50%), and 5 (–25%). This can be explained by the changed bonding situation. The shift in mode 8, for example, which is a copper–copper stretching mode, can be understood by a harmonic approximation to the **O** and **P** ground-state electronic potential at 2.8 and 3.6 Å, respectively, shown in Figure 8. One can see that the curvature of the potential corresponding to the **O** geometry at 2.8 Å is slightly larger than for **P**. Consequently, the corresponding frequency is blue-shifted. The sole negative (imaginary) frequency of mode 8 confirms the saddle-point character of the TS.

For mode 2 and 7, a large difference for the BS **P** and the closed-shell **P** is observed. The results are in agreement with experimental

Table 2. Composition of molecular orbitals of fragment orbitals.

MO	Cu_2O_2 fragment		btmgp fragment		
LUMO+1 (b_g)	70% LUFO		17% HOF0-2	10% HOF0-1	
LUMO (a_u)	77% LUFO+1	3% LUFO+6	9% HOF0	7% HOF0-3	
	3% HOF0-5				
HOMO (b_u)	11% HOF0-1	2% HOF0-11	81% HOF0-4		
HOMO-1 (b_g)	1% HOF0-1		45% HOF0-1	38% HOF0-2	11% HOF0-9
				2% HOF0-12	
HOMO-2 (a_u)	1% HOF0-7		38% HOF0	37% HOF0-3	21% HOF0-8
				1% HOF0-13	
HOMO-3 (a_u)	2% HOF0-5	2% LUFO+1	61% HOF0-8	31% HOF0-3	
HOMO-4 (a_g)	3% HOF0-2		62% HOF0-5	18% HOF0-10	13% HOF0-6
HOMO-5 (b_u)	23% HOF0		64% HOF0-9	9% HOF0-2	1% HOF0-1
HOMO-6 (b_u)			65% HOF0-11	33% HOF0-7	
HOMO-7 (a_g)			47% HOF0-10	26% HOF0-5	21% HOF0-6
				1% HOF0-15	
HOMO-8 (a_u)	75% HOF0		20% HOF0-9	2% HOF0-2	
HOMO-9 (a_u)	24% HOF0-5	16% LUFO+1	30% HOF0	17% HOF0-8	8% HOF0-3
	2% LUFO+13		1% HOF0-19		
HOMO-10 (b_u)	82% HOF0-1	2% HOF0-3	8% HOF0-4	2% HOF0-11	2% HOF0-7
				1% HOF0-21	
HOMO-11 (b_g)	13% LUFO	4% HOF0-12	29% HOF0-1	19% HOF0-12	15% HOF0-18
				14% HOF0-2	3% HOF0-9

Table 3. Calculated (B3LYP/cc-pVDZ) eigenmodes, eigenfrequencies in cm^{-1} and in parentheses, relative IR or Raman intensities. Arrows depict the direction of the oscillations. Here x/o indicate a motion into/out of the plane of projection. [Color table can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mode	1 (IR)	2 (Raman)	3 (Raman)	4 (IR)	5 (IR)
f_{oxo}	642 (109)	590 (56)	614 (189)	595/566 (44/5.8)	251 (5.3)
$f_{\text{BS TS}}$	588 (7.9)	557 (110)	494 (96)	423/383 (39/2.1)	198 (3.8)
$f_{\text{BS peroxo}}$	470 (22)	302 (21)	921/929 (39/47)	320/284 (0.1/45)	187 (3.1)
f_{peroxo}	446 (75)	395 (76)	887 (548)	322/301 (0.1/17)	198 (4.2)

mode	6 (Raman)	7 (Raman)	8 (Raman)	9 (Raman)
f_{oxo}	207 (3.5)	144 (0.8)	328 (45)	235/266/278 (0.6/1.4/5.6)
$f_{\text{BS TS}}$	186 (1.8)	171 (0.4)	-336 (674)	217/248/266 (0.7/1.2/1.6)
$f_{\text{BS peroxo}}$	181 (5.3)	102 (0.04)	301 (14)	206/242/264 (5.4/5.5/6.3)
f_{peroxo}	180 (1.9)	191 (5.8)	298 (18)	214/245/264 (0.9/1.3/3.8)

and theoretical reported values for comparable structures.^[11,19,22] Modes 1, 4, and 5 are IR active and accordingly modes 2, 3, 6, 7, 8, and 9 are Raman active. Other prominent intensive IR modes are 4 guanine in-plane vibrations around 1580 cm^{-1} .

Ionization energies and electron affinities

The calculation of ionization energies (IE) and electron affinities (EA) directly from the difference of the respective KS energies and the vacuum level suffers frequently from the inaccurate modelling of electronic excitations within ground-state DFT: Excitation energies calculated from the KS orbital energies of DFT are usually underestimated, due to the neglect of electronic self-energy effects. Quasi-particle (QP) calculations within the Many Body Perturbation Theory are a far more accurate, yet very expensive approach to single-electron excitations, see, for example, Refs. [37,85]. In the present case, fortunately, the localization of the electronic states allows for a numerically inexpensive treatment of the many-body effects by means of ΔSCF —also called constrained-DFT—calculations.^[44,84,85] Thereby, the total-energy differences between the ground states and the excited states of the molecules are calculated. The electrons are allowed to relax, while the occupation numbers are constrained to the excited configuration. Here, we determine the simplest single-electron excitation, the IE

$$\text{IE} = E(N-1) - E(N) \quad (3)$$

and the EA

$$\text{EA} = E(N) - E(N+1) \quad (4)$$

where $E(N)$ denotes the ground-state energy of the molecule with N electrons. The ionized molecules with one missing or

additional electron are characterized by the total energies $E(N-1)$ and $E(N+1)$, respectively. Using eqs. (3) and (4), the calculation of single-particle excitation energies reduces to the treatment of electronic ground states. Explicit calculations suffer from the limitations of the supercell approach. For that reason, we use monopole and dipole corrections in ΔSCF calculations for charged systems to compensate for the errors in the total-energy and forces induced by the spurious long-range interactions between neighboring supercells. The difference between IE and EA corresponds to the QP gap between occupied and unoccupied electron states. As the procedure used here takes self-energy effects into account, the QP gap $E_{\text{gap}}^{\text{qp}} = \text{IE} - \text{EA}$ is expected to be a far more realistic description of the highest occupied molecular orbital (HOMO)-lowest

Table 4. KS gap, IEs, EAs, and the QP gap (in eV) of O and P.

		$E_{\text{gap}}^{\text{KS}}$	IE	EA	$E_{\text{gap}}^{\text{QP}}$
O					
PW91	(plane wave)	1.09	11.61	6.97	4.64
PW91	(cc-pVDZ)	1.05			
B3LYP ^[a]	(plane wave)	2.90			
B3LYP	(plane wave)	2.92			
B3LYP	(cc-pVDZ)	2.87	12.30	6.91	5.39
Closed-shell P					
PW91	(plane wave)	1.53	11.38	6.39	3.99
PW91	(cc-pVDZ)	1.45			
B3LYP ^[a]	(plane wave)	2.64			
B3LYP	(plane wave)	2.66			
B3LYP	(cc-pVDZ)	2.57	11.74	6.73	5.01
BS-P					
B3LYP	(plane wave)	3.57			
B3LYP	(cc-pVDZ)	3.33	12.06	6.51	5.55

[a] Calculations based on PW91 plane wave geometries.

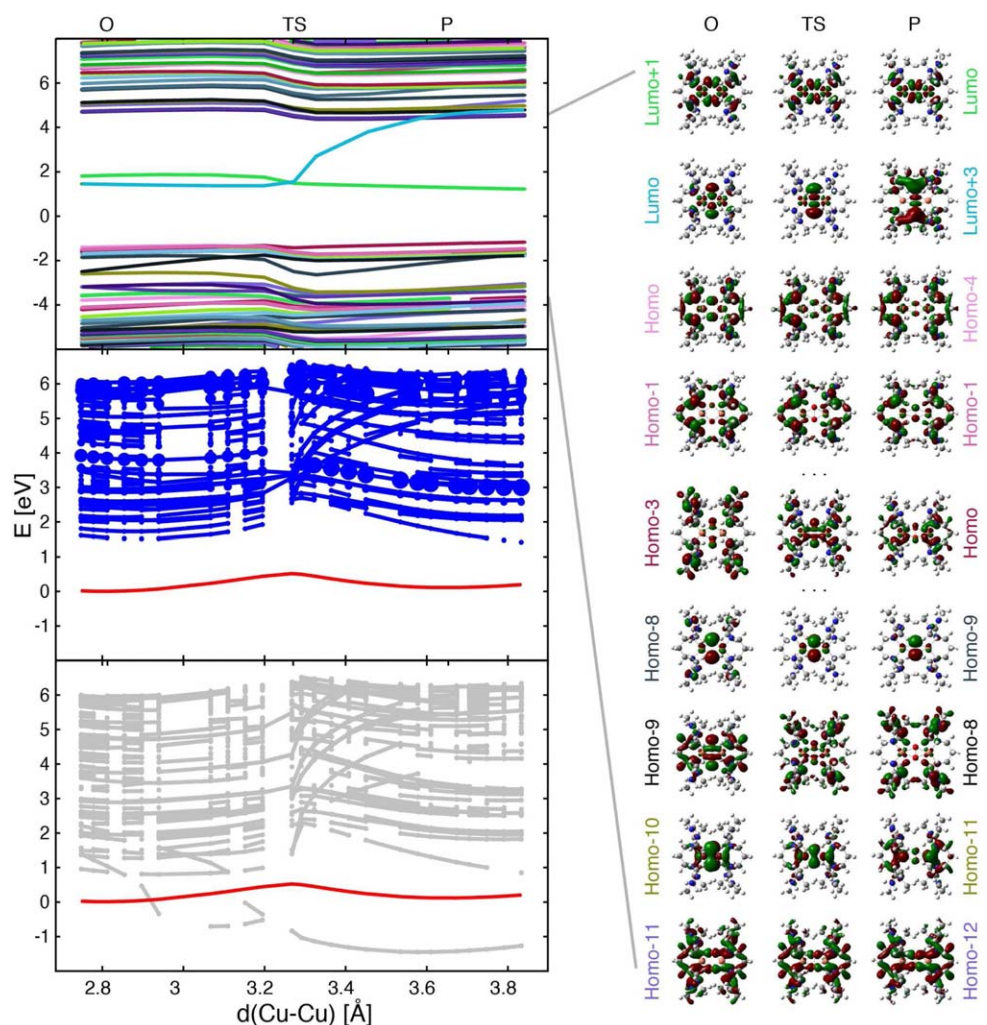


Figure 14. Top left: Single particle (KS) orbital energies from **O** to singlet **P** along the MEP (B3LYP/cc-pVDZ) and corresponding MOs (right). Middle and bottom left: DFT excited-state PES for singlet (blue) and triplet (gray) excitations. Dot size symbolizes the oscillator strength. Red lines show the energy of the singlet ground state. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

unoccupied molecular orbital (LUMO) transition energy than the difference of the corresponding KS eigenvalues, that suffers from the well-known DFT band-gap problem.^[84–86]

The adiabatic values of the IEs and EAs computed within the Δ SCF scheme are listed in Table 4. Focussing on the PW91 results: compared with **O**, the IE as well as the EA is lowered by 0.23 and 0.58 eV, respectively for the **P** species. The KS/QP gap, also reported in Table 4, is 1.09/4.64 and 1.53/3.99 eV for **O** and **P**, respectively. Interestingly, electronic self-energy effects change the trend observed for the HOMO–LUMO transition energy: while the KS gap increases when going from **O** to **P**, the opposite occurs for QP gap calculated here. This is surprising, given the experience that qualitative trends are typically reliably described within DFT and highlights the problem of GGA to account for electron correlation in strongly localized systems. Comparing this result with calculation using the hybrid B3LYP functional, which leads to KS/QP gaps of 2.87/5.39 and 2.57/5.01 eV for **O** and **P**, respectively, accordingly both gaps decrease from **O** to **P** by 0.30/0.38 eV. Calculations using plane wave basis sets result in marginally larger KS gaps, but show exactly the same behavior for using a hybrid func-

tional instead of GGA. The BS-**P** has a KS gap of 3.33 eV (B3LYP, cc-pVDZ), which is 0.76 eV larger than for the closed-shell **P** and even 0.46 eV larger than for **O**. Accordingly, the corresponding QP gap assumes the overall largest value of 5.55 eV, caused by an increase of the IE and decrease of EA compared to the closed-shell **P**.

In Supporting Information Figure S3, the total density differences for the BS **P** are plotted. While the integral of these density differences results in the additional or missing electron, respectively, its spatial distribution shows the addition or removal of one electron does not only affect the LUMO and HOMO. Rather, it leads to an extended reorganization of the molecular charge density. This can be quantified by integrating the absolute value of the density difference that results in about two electrons, due to electronic relaxation and counting positively both donating and accepting regions. If the latter effect is accounted for, we find that the electron removal or addition leads to density redistribution of the remaining charge that amounts to 0.45 and 0.75 electrons, respectively. In case of the **P** configuration, it is found that the acceptance of an additional electron lifts, as expected,

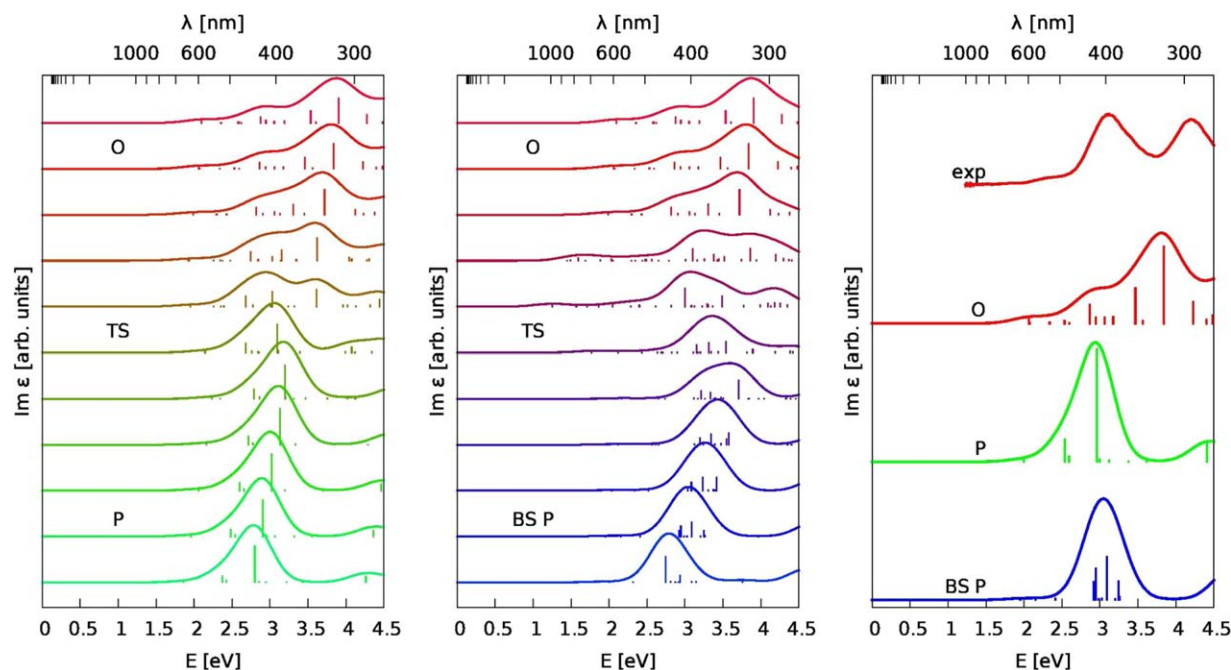


Figure 15. Calculated TD-DFT optical absorption spectra (B3LYP/cc-pVDZ) for geometries varying between **O** to closed-shell singlet **P** (left) and **O** to open-shell singlet (BS) **P** (middle) compared with experimental data^[20] (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the antiferromagnetic coupling of the Cu atoms due to the occupation of the respective *d* state.

Optical response and excited-state PESs

The calculation of the optical response and electron-hole pair excitation energies allows on the one hand for the identification of specific species using the comparison of measured and simulated spectroscopic fingerprints. On the other hand, it provides insight into possible activation scenarios based on optical excitation as well as presents the prerequisite for understanding dynamical processes taking place on excited-state PESs.

Optical spectra calculated within time-dependent DFT (TD-DFT) for **O** and **P** species on different levels of theory are compared in Supporting Information Figure S4. In contrast to the bond length and especially the **O-P** stabilization energies for the optical spectra, the deviation between cc-pVDZ and def2-TZVP is negligible, the maximum blueshift of the spectra is smaller than 0.01 eV for the three configurations under investigation. The influence of adding dispersion is observable but in contrast to the influence of the XC-functional only minor. In particular, the largest influence of dispersion is observed for the BS **P** calculated with B3LYP and is about 0.16 eV, but the shift of the absorption bands is not uniform as can be observed for the closed-shell **P**. The main absorption is shifted only slightly but two others around 2.3 eV are blueshifted by 0.13 eV. The different used XC-functional do not only shift the spectra but also have a large influence on oscillator strength, therefore, a direct comparison of single excitations is hard. In general, the main absorptions bands are blueshifted going from PW91 to B3LYP and CAM-B3LYP.

In the following, we will focus on excited energy PESs. This involves many excited state calculations. Therefore, the following results are due to computational feasibility based on B3LYP/cc-pVDZ TD-DFT calculations. Above, we have discussed the evolution of the ground-state energy along the MEP from **O** to **P**. The evolution of the KS eigenvalues as well as the singlet and triplet excitation energies calculated within linear-response TD-DFT in adiabatic approximation are shown in Figure 14. Thereby, the 80 lowest energy excitations are considered. By means of comparison with many-body perturbation theory calculations, we have shown earlier^[44,48,50] that TD-DFT can be expected to provide meaningful excitations energies for dicopper complexes such as studied here.

The upper and right panels of Figure 14 demonstrate the change of the orbital character of the DFT ground-state singlet calculation for the respective geometries along the MEP from **O** to **P**. It is seen that the two orbitals that correspond to LUMO and LUMO+3 interchange for the TS geometry. In fact, the **O**-LUMO is the antibonding combination of *d_{xy}* and σ^* which is the final orbital for the transition at ~400 nm.^[9] The corresponding bonding combination is **O**-HOMO-3 which shifts in energy to become the HOMO in the **P** configuration. The **O**-LUMO+1 is the antibonding combination of *d_{xy}* and π_{σ}^* and the final orbital of the ~300 nm transition. During the **O P** transition, it shifts to being the LUMO, which is the final orbital of the main CT at ~350 nm. This picture does not change substantially when the calculations are performed for the BS ground state. Only the orbitals incorporating large copper *d* and oxygen contributions around 2.5 eV below the HOMO are slightly affected.

Singlet and triplet excitation energies along the MEP are shown in the left middle and bottom panel in Figure 14. They

are obtained from B3LYP/cc-pVDZ calculations for the respective spin-restricted ground-state geometries. Several excitation energies show strong energy dispersion for geometries close to **P**. These excitations involve the **P** LUMO+3/**O** LUMO and can be expected to result in strong geometry changes that even lead to isomerization.

Obviously, the triplet states are unlikely to be optically excited from the singlet ground state, as spin conservation is only lifted by relativistic effects such as spin-orbit coupling that are of minor importance in the present case. Nevertheless, the excited triplet state PESs are of interest, as they correspond to possibly long-lived states.

Here, two triplet instabilities are observed. In case of the geometries close to the **P** geometry, the triplet instabilities arise from the fact that the ground state is characterized by antiferromagnetically coupled Cu atoms. The corresponding excitation involves mainly (90%) transitions between the **P** HOMO (d_{xy} states) to **P** LUMO/**O** LUMO+1 ($d_{xy}-\pi_{\sigma}^*$ states). Another instability is observed for geometries in between the **O** and TS structures. The corresponding excitation involves a variety of contributions from various states: **O** HOMO-8 (50%, $d_{yz}-\pi_{\nu}^*$), HOMO-3 (10%), and HOMO-2 (29%) ($d_x^2+N p_z$) to LUMO ($d_{xy}+-\sigma^*$).

The change of the excitation energies in dependence on the structural modifications does not only give rise to a highly structured energy landscape but also leads to strong modifications of the molecular optical response. This can be seen in Figure 15, where the calculated evolution of the optical absorption along the transition path from **O** to either **P** or the BS **P** is shown and compared with the experimental data available.

The evolution of the most intense peaks can be easily followed if the geometry is gradually changed from **O** toward the TS. They generally experience a feature-dependent redshift between 0.2 and 0.5 eV. A sudden change of the optical signatures occurs at the TS geometry. There two main absorption features arise that gradually change in energy as **P** is approached structurally. This results in a redshift of about 0.5 eV. During the evolution from **O** to the BS **P**, the first three spectra around the pure singlet **O** are the same as in the previous case. For geometries that resemble the TS structure, the spin splitting due to the antiferromagnetic coupling leads to larger rearrangements, but then again an overall shift to lower excitation energies is observed. One has to state that the spectral signatures of **P** and the BS **P** are very similar. Unambiguous identification by just comparing the optical spectra is impossible. For experimental **P** systems, a strong band at about 350 nm (3.5 eV) and a weak feature at about 500 nm (2.5 eV) are reported which are 0.4 eV higher in energy than the results reported here.^[2,11,43]

The deviation between calculated and experimental spectra of **O** cores is known^[20] and possibly related to the strong CT between copper(III) and donor ligands. It has been shown, however, that the use of range-separated functionals like HSE06 or the long-range corrected CAM-B3LYP does not substantially improve its theoretical modelling.^[44] Accounting for dispersion interaction in the calculation using the D3 scheme

with BJ damping leads to a shorter Cu...Cu distance (cf. Fig. 4), which results in blueshifts of the **O** and BS **P** optical absorption features by about 0.2 eV.

For the assignment of the transitions, natural transition orbitals (NTOs) are required because the transitions between canonical orbitals are heavily mixed.^[43,87,88] The NTOs for the **O** and the BS **P** species are summarized in Supporting Information Figure S5. Here, the accordance to the "classical" Cu_2O_2 theory becomes apparent: in the **P** species, all main CTs at around 3 eV are due to the $\pi_{\sigma}^* \rightarrow d_{xy}$ transition. This transition is directly related to the 3.84 eV transition of the **O** species (state 27). Additionally, in **O** species, a second intensive CT band is calculated at 2.86 eV (state 16), which is due to a $\sigma^* \rightarrow \pi_{\sigma}^*$ transition. State 25 has similar character. A very red-shifted transition appears at 2.06 eV (state 4) which is observed experimentally at around 2 eV as well. Here, a strong ligand contribution is found: the guanidine donors donate into the Cu_2O_2 core.

Conclusions

The structural, vibrational, electronic, and optical properties of $[\text{Cu}_2(\text{btmgp})_2(\mu\text{-O})_2]^{2+}$ and $[\text{Cu}_2(\text{btmgp})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)]^{2+}$ have been calculated within DFT using semilocal as well as hybrid density functionals in conjunction with both localized and plane wave basis sets. The geometrical data derived within the various theoretical approaches largely agree with each and are close to the experimental data available. This does also hold for the general shape of the energy landscape that describes the oxo-peroxo transition. Details, and in particular, the position of the global energy minimum of the PES, however, are strongly dependent on the XC functional and, in cases of small basis sets, depend additionally on the type of basis function. Notably, we find that hybrid-DFT calculations tend to favor the **P** species over **O**. If one additionally allows for spin relaxation—which leads to a favorable BS solution for **P**—this trend is enhanced. This behavior is not observed for local XC functionals, however. The inclusion of dispersion correction, conversely, leads to a small bias toward the **O** core.

The CDA analysis for the **O** state reveals the strong stabilization by the guanidine donors and highlights the role of the guanidine as σ - and π -donor.

The structural modification accompanying the **O-P** transition leads to pronounced changes of the excitation energies. In particular, the interchange of the **O** LUMO and **P** LUMO+3 at the TS geometry leads to strongly dispersive excited-state PESs that might be used for optically induced isomerization. The geometry changes along the **O-P** transition give rise to significant changes of the optical absorption features as well as modify the vibrational fingerprints of the Cu complex.

Acknowledgments

Generous grants of computer time at the Höchstleistungs-Rechenzentrum Stuttgart and the Paderborn Center for Parallel Computing PC² are gratefully acknowledged.

Keywords: copper · oxygen · density functional theory · time-dependent density functional theory · plane wave

How to cite this article: M. Rohrmüller, A. Hoffmann, C. Thierfelder, S. Herres-Pawlis, W. Gero Schmidt. *J. Comput. Chem.* **2015**, 36, 1672–1685. DOI: 10.1002/jcc.23983



Additional Supporting Information may be found in the online version of this article.

- [1] E. I. Solomon, D. E. Heppner, E. M. Johnston, J. W. Ginsbach, J. Cirera, M. Qayyum, M. T. Kieber-Emmons, C. H. Kjaergaard, R. G. Hadt, L. Tian, *Chem. Rev.* **2014**, 114, 3659.
- [2] N. Kitajima, Y. Moro-oka, *Chem. Rev.* **1994**, 94, 743.
- [3] S. G. Mauracher, C. Molitor, R. Al-Oweini, U. Kortz, A. Rompel, *Acta Cryst.* **2014**, D70, 2301.
- [4] Y. Matoba, T. Kumagai, A. Yamamoto, H. Yoshitsu, M. Sugiyama, *J. Biol. Chem.* **2006**, 281, 8981.
- [5] H. Decker, R. Dillinger, F. Tuzek, *Angew. Chem.* **2000**, 112, 1656.
- [6] J. A. Halfen, S. Mahapatra, E. C. Wilkinson, S. Kaderli, V. G. Young, Jr., L. Que, Jr., A. D. Zuberbühler, W. B. Tolman, *Science* **1996**, 271, 1397.
- [7] A. G. Blackman, W. B. Tolman, *Struct. Bond.* **2000**, 97, 179.
- [8] E. A. Lewis, W. B. Tolman, *Chem. Rev.* **2004**, 104, 1047.
- [9] L. M. Mirica, X. Ottenwaelde, T. D. P. Stack, *Chem. Rev.* **2004**, 104, 1013.
- [10] L. M. Mirica, M. Vance, D. J. Rudd, B. Hedman, K. O. Hodgson, E. I. Solomon, T. D. P. Stack, *Science* **2005**, 308, 1890.
- [11] B. T. Op't Holt, M. A. Vance, L. M. Mirica, D. E. Heppner, T. D. P. Stack, E. I. Solomon, *J. Am. Chem. Soc.* **2009**, 131, 6421.
- [12] Y. Fang Liu, J. Guo Yu, P. E. M. Siegbahn, M. R. A. Blomberg, *Chem. Eur. J.* **2013**, 19, 1942.
- [13] I. Garcia-Bosch, A. Company, J. R. Frisch, M. Torrent-Sucarrat, M. Cardellach, I. Gamba, M. Güell, L. Casella, L. Que, Jr., X. Ribas, J. M. Luis, M. Costas, *Angew. Chem.* **2010**, 122, 2456.
- [14] C. J. Cramer, M. Wloch, P. Piecuch, C. Puzzarini, L. Gagliardi, *J. Phys. Chem. A* **2006**, 110, 1991.
- [15] M. Flock, K. Pierloot, *J. Phys. Chem. A* **1999**, 103, 95.
- [16] M. F. Rode, H.-J. Werner, *Theor. Chem. Acc.* **2005**, 114, 309.
- [17] K. H. Marti, I. M. Ondík, G. Moritz, M. Reiher, *J. Chem. Phys.* **2008**, 128, 014104.
- [18] P. Å. Malmqvist, K. Pierloot, A. R. M. Shahi, C. J. Cramer, L. Gagliardi, *J. Chem. Phys.* **2008**, 128, 204109.
- [19] P. Kang, E. Bobyr, J. Dustman, K. O. Hodgson, B. Hedman, E. I. Solomon, T. D. P. Stack, *Inorg. Chem.* **2010**, 49, 11030.
- [20] S. Herres-Pawlis, P. Verma, R. Haase, P. Kang, C. T. Lyons, E. C. Wasinger, U. Flörke, G. Henkel, T. D. P. Stack, *J. Am. Chem. Soc.* **2009**, 131, 1154.
- [21] A. Company, S. Palavicini, I. Garcia-Bosch, R. Mas-Balleste, L. Que, E. V. Rybak-Akimova, L. Casella, X. Ribas, M. Costas, *Chem. Eur. J.* **2008**, 14, 3535.
- [22] M. J. Henson, P. Mukherjee, D. E. Root, T. D. P. Stack, E. I. Solomon, *J. Am. Chem. Soc.* **1999**, 121, 10332.
- [23] J. L. Lewin, D. E. Heppner, C. J. Cramer, *J. Biol. Inorg. Chem.* **2007**, 12, 1221.
- [24] B. F. Gherman, C. J. Cramer, *Coord. Chem. Rev.* **2009**, 253, 723.
- [25] P. E. M. Siegbahn, M. Wirstam, *J. Am. Chem. Soc.* **2001**, 123, 11819.
- [26] P. E. M. Siegbahn, *J. Biol. Inorg. Chem.* **2003**, 8, 577.
- [27] P. E. M. Siegbahn, *J. Biol. Inorg. Chem.* **2006**, 11, 695.
- [28] M. Güell, P. E. M. Siegbahn, *J. Biol. Inorg. Chem.* **2007**, 12, 1251.
- [29] P. E. M. Siegbahn, M. R. A. Blomberg, *J. Phys. Chem. A* **2008**, 112, 12772.
- [30] A. Poater, L. Cavallo, *Inorg. Chem.* **2009**, 48, 4062.
- [31] T. Saito, Y. Kataoka, Y. Nakanishi, T. Matsui, Y. Kitagawa, T. Kawakami, M. Okumura, K. Yamaguchi, *Int. J. Quantum Chem.* **2009**, 109, 3649.
- [32] Y. Takano, K. Koizumi, H. Nakamura, *Inorg. Chim. Acta* **2009**, 362, 4578.
- [33] M. Güell, J. M. Luis, M. Sola, P. E. M. Siegbahn, *J. Biol. Inorg. Chem.* **2009**, 14, 229.
- [34] T. Saito, Y. Kataoka, Y. Nakanishi, T. Matsui, Y. Kitagawa, T. Kawakami, M. Okumura, K. Yamaguchi, *Chem. Phys.* **2010**, 368, 1.
- [35] F. Neese, *J. Biol. Inorg. Chem.* **2006**, 11, 702.
- [36] (a) A. C. Tsipis, *Coord. Chem. Rev.* **2014**, 272, 1; (b) A. C. Tsipis, *RSC Adv.* **2014**, 4, 32504.
- [37] C. Rödl, F. Sottile, L. Reining, *Phys. Rev. B* **2015**, 91, 045102.
- [38] A. Poater, L. Cavallo, *Theor. Chem. Acc.* **2013**, 132, 1336.
- [39] S. Hong, S. M. Huber, L. Gagliardi, C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2007**, 129, 14190.
- [40] C. J. Cramer, A. Kinal, M. Wloch, P. Piecuch, L. Gagliardi, *J. Phys. Chem. A* **2006**, 110, 11557.
- [41] F. Bernardi, A. Bottoni, R. Casadio, P. Fariselli, A. Rigo, *Inorg. Chem.* **1996**, 35, 5207.
- [42] A. Hoffmann, S. Herres-Pawlis, *Chem. Commun.* **2014**, 50, 403.
- [43] (a) A. Hoffmann, C. Citek, S. Binder, A. Goos, M. Rübhausen, O. Troeppner, I. Ivanović-Burmazović, E. C. Wasinger, T. D. P. Stack, S. Herres-Pawlis, *Angew. Chem.* **2013**, 125, 5508; (b) A. Hoffmann, C. Citek, S. Binder, A. Goos, M. Rübhausen, O. Troeppner, I. Ivanović-Burmazović, E. C. Wasinger, T. D. P. Stack, S. Herres-Pawlis, *Angew. Chem. Int. Ed.* **2013**, 52, 5398.
- [44] M. Rohrmüller, S. Herres-Pawlis, M. Witte, W. G. Schmidt, *J. Comput. Chem.* **2013**, 34, 1035.
- [45] S. Herres-Pawlis, U. Flörke, G. Henkel, *Eur. J. Inorg. Chem.* **2005**, 3815.
- [46] R. Haase, T. Beschmitt, U. Flörke, S. Herres-Pawlis, *Inorg. Chim. Acta* **2011**, 374, 546.
- [47] D. Petrovic, L. M. R. Hill, P. G. Jones, W. B. Tolman, M. Tamm, *Dalton Trans.* **2008**, 887.
- [48] A. Jessor, M. Rohrmüller, W. G. Schmidt, S. Herres-Pawlis, *J. Comput. Chem.* **2014**, 35, 1.
- [49] A. Hoffmann, R. Grunzke, S. Herres-Pawlis, *J. Comput. Chem.* **2014**, 35, 1943.
- [50] A. Hoffmann, M. Rohrmüller, A. Jessor, I. dos Santos Vieira, W. G. Schmidt, S. Herres-Pawlis, *J. Comput. Chem.* **2014**, 35, 2146.
- [51] (a) A. Hoffmann, S. Binder, A. Jessor, R. Haase, U. Flörke, M. Gnida, M. Salomone Stagni, W. Meyer-Klaucke, B. Lebsanft, L. E. Grünig, S. Schneider, M. Hashemi, A. Goos, A. Wetzel, M. Rübhausen, S. Herres-Pawlis, *Angew. Chem.* **2014**, 126, 305; (b) A. Hoffmann, S. Binder, A. Jessor, R. Haase, U. Flörke, M. Gnida, M. Salomone Stagni, W. Meyer-Klaucke, B. Lebsanft, L. E. Grünig, S. Schneider, M. Hashemi, A. Goos, A. Wetzel, M. Rübhausen, S. Herres-Pawlis, *Angew. Chem. Int. Ed.* **2014**, 53, 299.
- [52] (a) P. Roquette, C. König, O. Hübner, A. Wagner, E. Kaifer, M. Enders, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2010**, 4770; (b) A. Peters, C. Trumm, M. Reinmuth, D. Emeljanenko, E. Kaifer, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2009**, 3791; (c) C. Trumm, O. Hübner, E. Kaifer, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2010**, 3102; (d) D. Emeljanenko, A. Peters, N. Wagner, J. Beck, E. Kaifer, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2010**, 1839.
- [53] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* **1996**, 6, 15.
- [54] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, 59, 1758.
- [55] P. E. Blöchl, *Phys. Rev. B* **1994**, 50, 17953.
- [56] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian: Wallingford CT, **2013**.
- [57] G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, 22, 931.
- [58] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, 77, 3865.
- [59] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B* **1992**, 46, 6671.
- [60] A. D. Becke, *Phys. Rev. A* **1988**, 38, 3098.

- [61] B. Miehl, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200.
- [62] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
- [63] Y. Zhao, D. G. Truhlar, *J. Chem. Phys.* **2006**, *125*, 194101-1.
- [64] J. M. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **2003**, *91*, 146401.
- [65] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
- [66] A. D. Becke, *J. Comput. Chem.* **1999**, *20*, 63.
- [67] T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.* **2004**, *393*, 51.
- [68] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
- [69] L. Goerigk, S. Grimme, *Phys. Chem. Chem. Phys.* **2011**, *13*, 6670.
- [70] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456.
- [71] S. I. Gorelsky, AOMix: Program for Molecular Orbital Analysis; version 6.80, University of Ottawa, **2013**, Available at: <http://www.sg-chem.net/>. accessed on April 2 2015.
- [72] S. I. Gorelsky, A. B. P. Lever, *J. Organomet. Chem.* **2001**, *635*, 187.
- [73] P. E. M. Siegbahn, M. R. A. Blomberg, S.-L. Chen, *J. Chem. Theory Comput.* **2010**, *6*, 2040.
- [74] S. Yamanaka, T. Kawakami, H. Nagao, K. Yamaguchi, *Chem. Phys. Lett.* **1994**, *231*, 25.
- [75] D. M. Dooley, R. A. Scott, J. Ellinghaus, E. I. Solomon, H. B. Gray, *Proc. Natl. Acad. Sci. USA* **1978**, *75*, 3019.
- [76] E. I. Solomon, D. M. Dooley, R.-H. Wang, H. B. Gray, *J. Am. Chem. Soc.* **1976**, *98*, 1029.
- [77] A. Walli, S. Dechert, M. Bauer, S. Demeshko, F. Meyer, *Eur. J. Inorg. Chem.* **2014**, 4660.
- [78] T. Ziegler, A. Rauk, E. J. Baerends, *Theor. Chim. Acta* **1977**, *43*, 261.
- [79] S. Dapprich, G. Frenking, *J. Phys. Chem.* **1995**, *99*, 9352.
- [80] A. Gobbi, G. Frenking, *J. Am. Chem. Soc.* **1993**, *115*, 2362.
- [81] P. K. Ross, E. I. Solomon, *J. Am. Chem. Soc.* **1991**, *113*, 3246.
- [82] S. Herres-Pawlis, A. Neuba, O. Seewald, T. Seshadri, H. Egold, U. Flörke, G. Henkel, *Eur. J. Org. Chem.* **2005**, 4879.
- [83] P. H. Hahn, W. G. Schmidt, F. Bechstedt, *Phys. Rev. B* **2005**, *72*, 245425.
- [84] A. Hermann, W. G. Schmidt, P. Schwerdtfeger, *Phys. Rev. Lett.* **2008**, *100*, 207403.
- [85] A. Rieger, E. Rauls, W. G. Schmidt, J. Eberhard, I. Stoll, J. Mattay, *Phys. Rev. B* **2012**, *85*, 165202.
- [86] T. Kowalczyk, S. R. Yost, T. Van Voorhis, *J. Chem. Phys.* **2011**, *134*, 054128.
- [87] R. L. Martin, *J. Chem. Phys.* **2003**, *118*, 4775.
- [88] C. Citek, C. T. Lyons, E. C. Wasinger, T. D. P. Stack, *Nat. Chem.* **2012**, *4*, 317.

Received: 15 April 2015
Revised: 26 May 2015
Accepted: 28 May 2015
Published online on 7 July 2015

Supporting Information for

The Cu₂O₂ torture track for a real-life system: [Cu₂(btmgp)₂O₂]²⁺ oxo and peroxo species in density-functional calculations

Martin Rohrmüller,¹ Alexander Hoffmann,² Christian Thierfelder,¹ Sonja Herres-Pawlis,^{*2} Wolf Gero Schmidt¹

¹ Universität Paderborn, Lehrstuhl für Theoretische Physik, Pohlweg 55, 33095 Paderborn, Germany.

² RWTH Aachen University, Lehrstuhl für Bioanorganische Chemie, Landoltweg 1, 52074 Aachen, Germany
Email: sonja.herres-pawlis@ac.rwth-aachen.de

Table S1. Calculated distances (in Å) and angles (deg) for [Cu₂(btmgp)₂(μ-O)₂]²⁺ (**O**) and [Cu₂(btmgp)₂(μ-O₂²⁻)]²⁺ (**P**). ¹no stable (local) minima.

	basis set	O-O	Cu...Cu	Cu-O	Cu-N	N-Cu-N
closed shell P						
BP86	(def2-TZVP)	1.473	3.669	1.977	1.971	102.2
PW91	(6-31g(d))	1.550	3.450	1.891	1.913	102.9
PW91	(6-311g(d))	1.512	3.544	1.927	1.935	102.4
PW91	(cc-pVDZ)	1.473	3.710	1.996	1.952	102.4
PW91	(cc-pVTZ)	1.480	3.598	1.945	1.957	101.6
PW91	(Slater TZP)	1.488	3.608	1.951	1.959	101.5
PW91	(def2-SVP)	1.473	3.657	1.971	1.964	102.3
PW91	(def2-TZVP)	1.476	3.612	1.951	1.958	101.7
PW91	(plane wave)	1.489	3.584	1.940	1.948	101.8
PBE	(6-31g(d))	1.545	3.459	1.894	1.914	102.9
PBE	(6-311g(d))	1.510	3.551	1.929	1.937	102.5
PBE	(cc-pVDZ)	1.489	3.639	1.966	1.958	101.8
PBE	(cc-pVTZ)	1.479	3.603	1.948	1.960	101.6
PBE	(def2-SVP)	1.472	3.665	1.975	1.967	102.3
PBE	(def2-TZVP)	1.474	3.618	1.953	1.961	101.7
PBE	(plane wave)	1.487	3.586	1.941	1.948	101.8
PBE GD3BJ	(6-31g(d))	¹	¹	¹	¹	¹
PBE GD3BJ	(6-311g(d))	1.528	3.512	1.915	1.922	102.5
PBE GD3BJ	(cc-pVDZ)	1.499	3.603	1.951	1.941	102.0
PBE GD3BJ	(cc-pVTZ)	1.488	3.571	1.934	1.943	101.8
PBE GD3BJ	(def2-SVP)	1.482	3.630	1.960	1.950	102.4
PBE GD3BJ	(def2-TZVP)	1.484	3.584	1.940	1.943	101.9
PBE GD3BJ	(plane wave)	1.496	3.556	1.929	1.932	102.1
BLYP	(6-31g(d))	1.580	3.476	1.909	1.939	102.2
BLYP	(cc-pVDZ)	1.508	3.673	1.985	1.987	101.4
M06-L	(6-31g(d))	1.543	3.446	1.888	1.917	101.6
M06-L	(6-311g(d))	1.507	3.516	1.913	1.933	101.4
M06-L	(cc-pVDZ)	1.479	3.612	1.952	1.961	100.6
M06-L	(cc-pVTZ)	1.470	3.575	1.932	1.958	100.7
M06-L	(def2-SVP)	1.465	3.629	1.957	1.965	100.9
M06-L	(def2-TZVP)	1.465	3.582	1.935	1.959	100.8

TPSSh	(6-31g(d))	1.522	3.444	1.883	1.921	102.4
TPSSh	(6-311g(d))	1.494	3.520	1.912	1.940	101.9
TPSSh	(cc-pVDZ)	1.475	3.601	1.946	1.958	101.5
TPSSh	(cc-pVTZ)	1.466	3.563	1.927	1.959	101.4
TPSSh	(def2-SVP)	1.459	3.631	1.956	1.967	102.0
TPSSh	(def2-TZVP)	1.461	3.575	1.931	1.960	101.4
TPSSh GD3BJ	(6-31g(d))	1.563	3.385	1.864	1.906	102.3
TPSSh GD3BJ	(6-311g(d))	1.511	3.478	1.896	1.921	102.0
TPSSh GD3BJ	(cc-pVDZ)	1.487	3.560	1.929	1.938	101.7
TPSSh GD3BJ	(cc-pVTZ)	1.477	3.526	1.911	1.938	101.6
TPSSh GD3BJ	(def2-SVP)	1.470	3.591	1.940	1.946	102.1
TPSSh GD3BJ	(def2-TZVP)	1.472	3.538	1.916	1.938	101.6
B3LYP	(6-31g(d))	1.483	3.507	1.904	1.935	102.9
B3LYP	(6-311g(d))	1.463	3.568	1.928	1.956	102.4
B3LYP	(cc-pVDZ)	1.446	3.653	1.964	1.974	101.8
B3LYP	(cc-pVTZ)	1.438	3.623	1.949	1.977	101.6
B3LYP	(Slater TZP)	1.451	3.629	1.954	1.977	101.2
B3LYP	(def2-SVP)	1.430	3.677	1.973	1.981	102.3
B3LYP	(def2-TZVP)	1.434	3.635	1.954	1.978	101.6
B3LYP	(plane wave)	1.455	3.594	1.939	1.962	101.9
B3LYP GD3BJ	(6-31g(d))	1.505	3.456	1.885	1.913	102.7
B3LYP GD3BJ	(6-311g(d))	1.478	3.522	1.910	1.930	102.6
B3LYP GD3BJ	(cc-pVDZ)	1.460	3.599	1.942	1.946	102.0
B3LYP GD3BJ	(cc-pVTZ)	1.452	3.573	1.928	1.949	101.9
B3LYP GD3BJ	(def2-SVP)	1.443	3.623	1.950	1.952	102.5
B3LYP GD3BJ	(def2-TZVP)	1.447	3.583	1.932	1.949	102.0
B3LYP GD3BJ	(plane wave)	1.464	3.559	1.924	1.940	102.1
CAM-B3LYP	(cc-pVDZ)	1.414	3.613	1.940	1.953	102.7
CAM-B3LYP GD3BJ	(cc-pVDZ)	1.423	3.577	1.925	1.937	102.9
open shell P						
M06-L	(6-31g(d))	1.531	3.481	1.901	1.918	101.5
M06-L	(6-311g(d))	1.511	3.525	1.918	1.933	101.2
M06-L	(cc-pVDZ)	1.484	3.615	1.954	1.961	100.4
M06-L	(cc-pVTZ)	1.473	3.579	1.935	1.958	100.6
M06-L	(def2-SVP)	1.468	3.631	1.958	1.965	100.8
M06-L	(def2-TZVP)	1.469	3.585	1.937	1.959	100.7
TPSSh	(6-31g(d))	1.521	3.491	1.904	1.922	102.0
TPSSh	(6-311g(d))	1.507	3.550	1.929	1.941	101.4
TPSSh	(cc-pVDZ)	1.494	3.613	1.955	1.959	100.9
TPSSh	(cc-pVTZ)	1.482	3.578	1.936	1.960	100.8
TPSSh	(def2-SVP)	1.475	3.643	1.965	1.968	101.3
TPSSh	(def2-TZVP)	1.477	3.590	1.941	1.960	101.0
TPSSh GD3BJ	(6-31g(d))	₋₁	₋₁	₋₁	₋₁	₋₁
TPSSh GD3BJ	(6-311g(d))	1.519	3.514	1.914	1.922	101.5
TPSSh GD3BJ	(cc-pVDZ)	1.504	3.576	1.940	1.939	101.1
TPSSh GD3BJ	(cc-pVTZ)	1.491	3.543	1.922	1.939	101.0
TPSSh GD3BJ	(def2-SVP)	1.486	3.603	1.949	1.947	101.5
TPSSh GD3BJ	(def2-TZVP)	1.486	3.554	1.926	1.939	101.1
B3LYP	(6-31g(d))	1.510	3.548	1.928	1.938	101.8
B3LYP	(6-311g(d))	1.499	3.594	1.948	1.957	101.2

B3LYP	(cc-pVDZ)	1.487	3.653	1.972	1.975	100.6
B3LYP	(cc-pVTZ)	1.476	3.629	1.959	1.977	100.5
B3LYP	(Slater TZP)	1.484	3.640	1.965	1.975	100.4
B3LYP	(def2-SVP)	1.467	3.675	1.978	1.982	101.1
B3LYP	(def2-TZVP)	1.472	3.640	1.963	1.978	100.6
B3LYP	(plane wave)	1.484	3.610	1.951	1.965	101.0
B3LYP GD3BJ	(6-31g(d))	1.520	3.510	1.912	1.916	101.8
B3LYP GD3BJ	(6-311g(d))	1.509	3.557	1.932	1.932	101.5
B3LYP GD3BJ	(cc-pVDZ)	1.498	3.608	1.954	1.947	100.9
B3LYP GD3BJ	(cc-pVTZ)	1.487	3.586	1.941	1.949	100.8
B3LYP GD3BJ	(def2-SVP)	1.479	3.629	1.959	1.954	101.3
B3LYP GD3BJ	(def2-TZVP)	1.483	3.596	1.945	1.949	100.9
B3LYP GD3BJ	(plane wave)	1.493	3.579	1.939	1.943	100.9
CAM-B3LYP	(cc-pVDZ)	1.479	3.610	1.951	1.954	100.7
CAM-B3LYP GD3BJ	(cc-pVDZ)	1.485	3.583	1.939	1.938	100.9
O						
BP86	(def2-TZVP)	2.363	2.841	1.851	1.974	95.7
PW91	(6-31g(d))	2.310	2.772	1.804	1.918	97.0
PW91	(6-311g(d))	2.286	2.848	1.826	1.937	96.4
PW91	(cc-pVDZ)	2.356	2.816	1.836	1.963	95.1
PW91	(cc-pVTZ)	2.343	2.811	1.830	1.957	95.4
PW91	(Slater TZP)	2.321	2.835	1.832	1.965	95.3
PW91	(def2-SVP)	2.358	2.840	1.846	1.972	95.7
PW91	(def2-TZVP)	2.349	2.810	1.831	1.959	95.5
PW91	(plane wave)	2.323	2.823	1.828	1.956	95.5
PBE	(6-31g(d))	2.311	2.775	1.810	1.918	96.7
PBE	(6-311g(d))	2.286	2.853	1.828	1.940	96.4
PBE	(cc-pVDZ)	2.359	2.824	1.840	1.961	95.3
PBE	(cc-pVTZ)	2.344	2.815	1.832	1.961	95.3
PBE	(def2-SVP)	2.360	2.844	1.848	1.975	95.7
PBE	(def2-TZVP)	2.350	2.814	1.833	1.962	95.4
PBE	(plane wave)	2.323	2.823	1.828	1.955	95.4
PBE GD3BJ	(6-31g(d))	2.305	2.778	1.805	1.912	96.8
PBE GD3BJ	(6-311g(d))	2.285	2.850	1.827	1.931	96.4
PBE GD3BJ	(cc-pVDZ)	2.356	2.822	1.836	1.953	95.4
PBE GD3BJ	(cc-pVTZ)	2.341	2.813	1.828	1.950	95.4
PBE GD3BJ	(def2-SVP)	2.348	2.852	1.847	1.966	95.6
PBE GD3BJ	(def2-TZVP)	2.348	2.811	1.831	1.951	95.5
PBE GD3BJ	(plane wave)	2.326	2.813	1.825	1.942	95.6
BLYP	(6-31g(d))	2.308	2.817	1.821	1.951	96.5
BLYP	(cc-pVDZ)	2.364	2.858	1.855	1.989	95.0
M06-L	(6-31g(d))	2.304	2.783	1.806	1.925	95.9
M06-L	(6-311g(d))	2.293	2.836	1.824	1.937	96.0
M06-L	(cc-pVDZ)	2.345	2.826	1.836	1.961	95.1
M06-L	(cc-pVTZ)	2.332	2.808	1.825	1.956	95.2
M06-L	(def2-SVP)	2.344	2.843	1.842	1.970	95.4
M06-L	(def2-TZVP)	2.333	2.809	1.826	1.958	95.4
TPSSh	(6-31g(d))	2.278	2.765	1.791	1.924	96.3
TPSSh	(6-311g(d))	2.265	2.820	1.809	1.935	96.1
TPSSh	(cc-pVDZ)	2.330	2.795	1.819	1.954	95.2

TPSSh	(cc-pVTZ)	2.314	2.785	1.808	1.952	95.3
TPSSh	(def2-SVP)	2.318	2.827	1.828	1.970	95.5
TPSSh	(def2-TZVP)	2.312	2.792	1.812	1.955	95.4
TPSSh GD3BJ	(6-31g(d))	2.283	2.757	1.790	1.911	96.1
TPSSh GD3BJ	(6-311g(d))	2.273	2.810	1.807	1.922	96.0
TPSSh GD3BJ	(cc-pVDZ)	2.330	2.789	1.817	1.940	95.3
TPSSh GD3BJ	(cc-pVTZ)	2.315	2.778	1.808	1.937	95.4
TPSSh GD3BJ	(def2-SVP)	2.328	2.811	1.825	1.953	95.6
TPSSh GD3BJ	(def2-TZVP)	2.320	2.778	1.810	1.937	95.5
B3LYP	(6-31g(d))	2.281	2.773	1.795	1.940	96.1
B3LYP	(6-311g(d))	2.267	2.828	1.812	1.950	96.1
B3LYP	(cc-pVDZ)	2.319	2.813	1.823	1.970	95.0
B3LYP	(cc-pVTZ)	2.318	2.817	1.826	1.973	94.6
B3LYP	(Slater TZP)	2.320	2.801	1.818	1.974	94.7
B3LYP	(def2-SVP)	2.323	2.829	1.830	1.978	95.5
B3LYP	(def2-TZVP)	2.319	2.797	1.817	1.968	95.2
B3LYP	(plane wave)	2.304	2.807	1.816	1.962	95.3
B3LYP GD3BJ	(6-31g(d))	2.286	2.764	1.793	1.923	96.0
B3LYP GD3BJ	(6-311g(d))	2.272	2.817	1.810	1.933	96.0
B3LYP GD3BJ	(cc-pVDZ)	2.326	2.797	1.819	1.948	95.2
B3LYP GD3BJ	(cc-pVTZ)	2.316	2.789	1.813	1.949	95.3
B3LYP GD3BJ	(def2-SVP)	2.322	2.822	1.827	1.959	95.5
B3LYP GD3BJ	(def2-TZVP)	2.318	2.790	1.814	1.950	95.4
B3LYP GD3BJ	(plane wave)	2.321	2.783	1.812	1.940	95.3
CAM-B3LYP	(cc-pVDZ)	2.288	2.778	1.798	1.941	95.9
CAM-B3LYP GD3BJ	(cc-pVDZ)	2.293	2.766	1.796	1.931	95.6
Exp. (Ref. [JACS])			2.82	1.80	1.91	

Table S2. Calculated energy differences between oxo (E_O) and peroxo (E_P) isomer in kcal/mol. Energies resulting from broken-symmetry calculation for the peroxo species are denoted $E_{BS P}$. ¹SCF energies based on the PW91/plane wave structures. ²SCF energies based on B3LYP/cc-pVDZ structure. ³ no open-shell solution. ⁴ no stable (local) peroxo minima. ⁵ not implemented.

	basis set	$\Delta E = E_P - E_O$	$\Delta E = E_{BS P} - E_O$	S^2
BP86	(def2-TZVP)	1.4	- ³	0
PW91	(6-31g(d))	21.0	- ³	0
PW91	(6-311g(d))	12.0	- ³	0
PW91	(cc-pVDZ)	9.2	- ³	0
PW91	(cc-pVTZ)	7.3	- ³	0
PW91 ²	(Slater DZ)	15.5	- ³	0
PW91 ²	(Slater TZP)	7.0	- ³	0
PW91	(Slater TZP)	6.7	- ³	0
PW91	(def2-SVP)	2.9	- ³	0
PW91	(def2-TZVP)	6.5	- ³	0
PW91	(plane wave)	8.4	- ³	- ⁵
PBE	(6-31g(d))	19.8	- ³	0
PBE	(6-311g(d))	12.0	- ³	0
PBE	(cc-pVDZ)	9.1	- ³	0
PBE	(cc-pVTZ)	6.8	- ³	0
PBE	(def2-SVP)	2.6	- ³	0

PBE	(def2-TZVP)	6.0	- ³	0
PBE	(plane wave)	8.3	- ³	- ⁵
PBE GD3BJ	(6-31g(d))	- ⁴	- ³	0
PBE GD3BJ	(6-311g(d))	15.9	- ³	0
PBE GD3BJ	(cc-pVDZ)	13.0	- ³	0
PBE GD3BJ	(cc-pVTZ)	10.6	- ³	0
PBE GD3BJ	(def2-SVP)	6.9	- ³	0
PBE GD3BJ	(def2-TZVP)	9.9	- ³	0
PBE GD3BJ	(plane wave)	12.2	- ³	- ⁵
BLYP	(6-31g(d))	19.6	- ³	0
BLYP	(cc-pVDZ)	8.0	- ³	0
M06-L	(6-31g(d))	25.6	25.2	0.25
M06-L	(6-311g(d))	17.1	16.9	0.19
M06-L	(cc-pVDZ)	10.6	10.5	0.14
M06-L	(cc-pVTZ)	11.7	11.6	0.13
M06-L	(def2-SVP)	5.4	5.4	0.1
M06-L	(def2-TZVP)	10.4	10.4	0.12
TPSSh	(6-31g(d))	20.2	17.7	0.50
TPSSh	(6-311g(d))	10.7	8.4	0.50
TPSSh	(cc-pVDZ)	7.4	5.4	0.46
TPSSh	(cc-pVTZ)	5.4	3.7	0.43
TPSSh	(def2-SVP)	0.1	-1.6	0.43
TPSSh	(def2-TZVP)	4.4	2.9	0.41
TPSSh GD3BJ	(6-31g(d))	25.0	- ³	- ³
TPSSh GD3BJ	(6-311g(d))	16.8	14.4	0.49
TPSSh GD3BJ	(cc-pVDZ)	13.1	11.0	0.46
TPSSh GD3BJ	(cc-pVTZ)	11.0	9.3	0.43
TPSSh GD3BJ	(def2-SVP)	6.0	4.4	0.43
TPSSh GD3BJ	(def2-TZVP)	10.2	8.6	0.41
B3LYP	(6-31g(d))	16.8	8.6	0.71
B3LYP	(6-311g(d))	6.3	-1.1	0.70
B3LYP	(cc-pVDZ)	2.5	-4.1	0.67
B3LYP	(cc-pVTZ)	-1.2	-7.3	0.65
B3LYP ²	(Slater DZ)	7.9	1.1	0.63
B3LYP ²	(Slater TZP)	-0.2	-5.8	0.62
B3LYP	(Slater TZP)	1.0	-5.0	0.65
B3LYP	(def2-SVP)	-5.8	-11.1	0.62
B3LYP	(def2-TZVP)	-0.3	-6.1	0.64
B3LYP ¹	(plane wave)	2.9	-2.7	- ⁵
B3LYP	(plane wave)	2.7	-2.8	- ⁵
B3LYP GD3BJ	(6-31g(d))	22.7	14.7	0.70
B3LYP GD3BJ	(6-311g(d))	13.6	5.9	0.70
B3LYP GD3BJ	(cc-pVDZ)	10.0	3.2	0.68
B3LYP GD3BJ	(cc-pVTZ)	8.1	1.8	0.66
B3LYP GD3BJ	(def2-SVP)	1.9	-3.7	0.64
B3LYP GD3BJ	(def2-TZVP)	6.9	0.9	0.65
B3LYP GD3BJ	(plane wave)	9.4	4.0	- ⁵
CAM-B3LYP	(cc-pVDZ)	4.1	-10.6	0.80
CAM-B3LYP GD3BJ	(cc-pVDZ)	9.2	-5.8	0.81
Exp. (Ref. [JACS])			> 9	

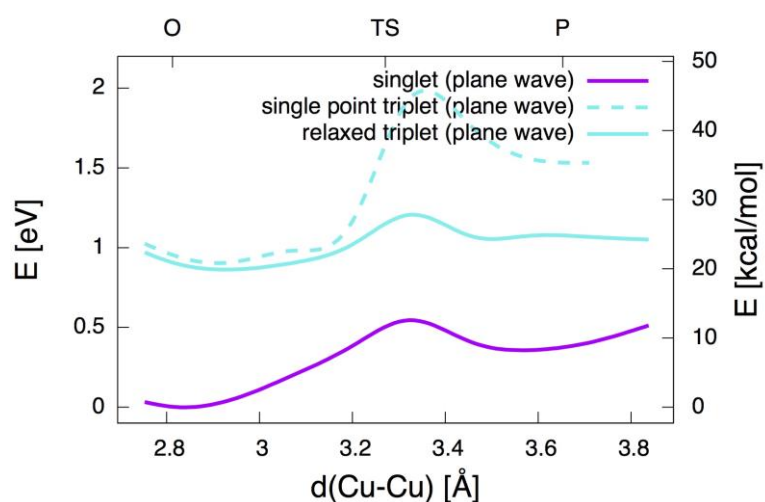


Figure S1. Comparison of singlet and triplet ground-state energies calculated with PW91 functional.

Table S3. Fragment orbitals of the Cu_2O_2 fragment of relevance for the whole **O** core cation

FO	Energy [eV]	FO composition
LUFO+1	-18.53	Cu $d_{xy} - \sigma^*$
LUFO	-19.41	Cu $d_{xy} - \pi_{\sigma}^*$
HOFO	-21.34	Cu $d_{xy} - \pi_{\nu}^*$
HOFO-1	-21.92	Cu $d_{xy} - \pi_{\nu}$
HOFO-2	-22.47	Cu $d_{x^2} + \sigma^*$
HOFO-3	-22.82	Cu $d_{xy} - \pi_{\sigma}$
HOFO-4	-24.01	Cu $d_{yz} + \sigma$
HOFO-5	-24.03	Cu $d_{xy} + \sigma^*$
HOFO-6	-24.18	Cu d_{xz}
HOFO-7	-24.21	Cu d_{yz}
HOFO-8	-24.63	Cu $d_{xy} + \pi_{\nu}^* (\delta)$
HOFO-9	-24.71	Cu $d_{z^2} + \pi_{\sigma}$
HOFO-10	-25.09	Cu $d_{xy} + \pi_{\nu}$
HOFO-11	-25.56	Cu $d_{xy} + \pi_{\sigma}$
HOFO-12	-25.98	Cu $d_{xy} + \pi_{\sigma}^*$

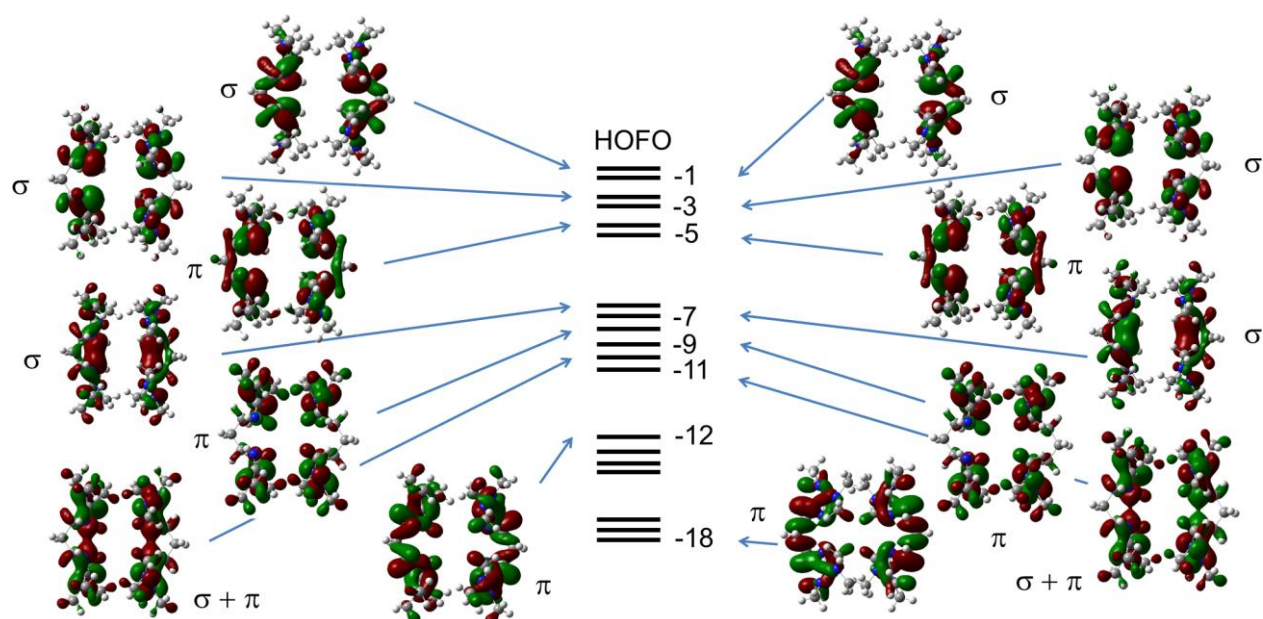


Figure S2. Fragment orbitals of the two-ligand-fragment of relevance for the whole **O** core cation.

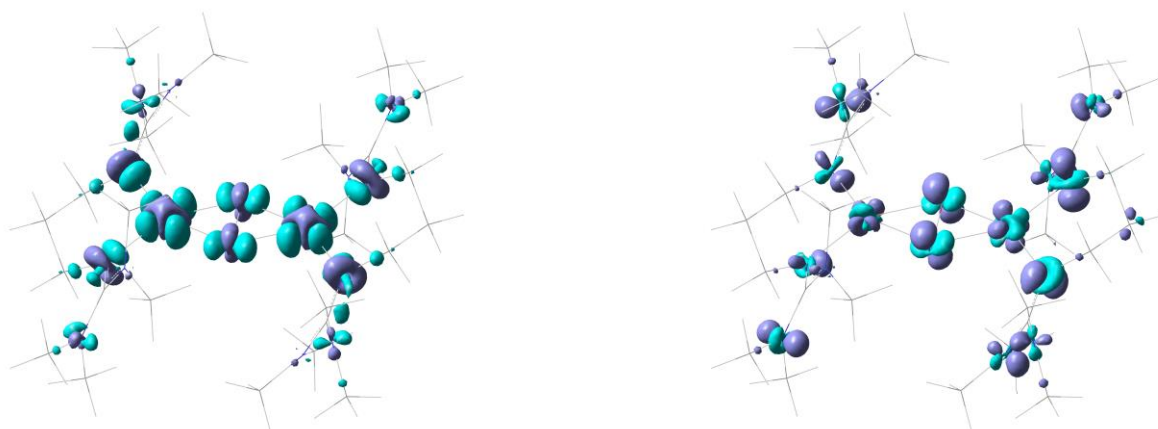


Figure S3. Density difference plots of $\rho(N) - \rho(N + 1)$ linked to the EA (left) and $\rho(N) - \rho(N - 1)$ linked to the IE (right). Blue values represent $\rho > 0$, turquoise $\rho < 0$.

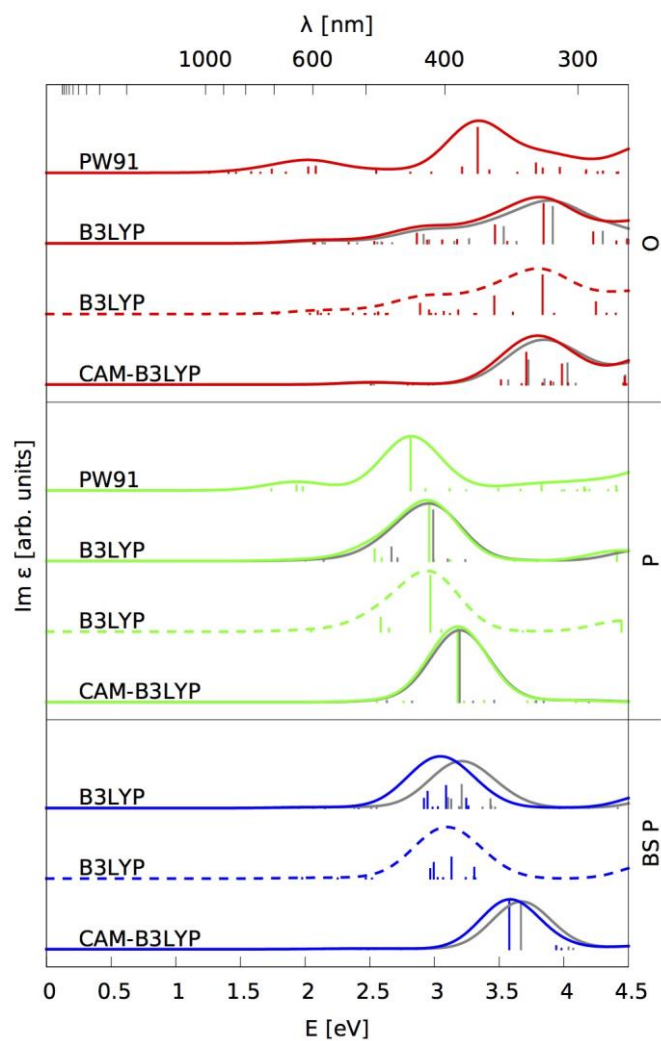


Figure S4. Comparison of optical spectra calculated within TD-DFT using different XC functionals for oxo (red), peroxo (green) and the broken-symmetry peroxo (blue) for the correspondingly relaxed geometries. Respective results obtained with Grimme D3 dispersion with Becke-Johnson damping are plotted in grey. B3LYP/def2-TZVP spectra are dashed, solid lines indicate calculations with cc-pVDZ basis.

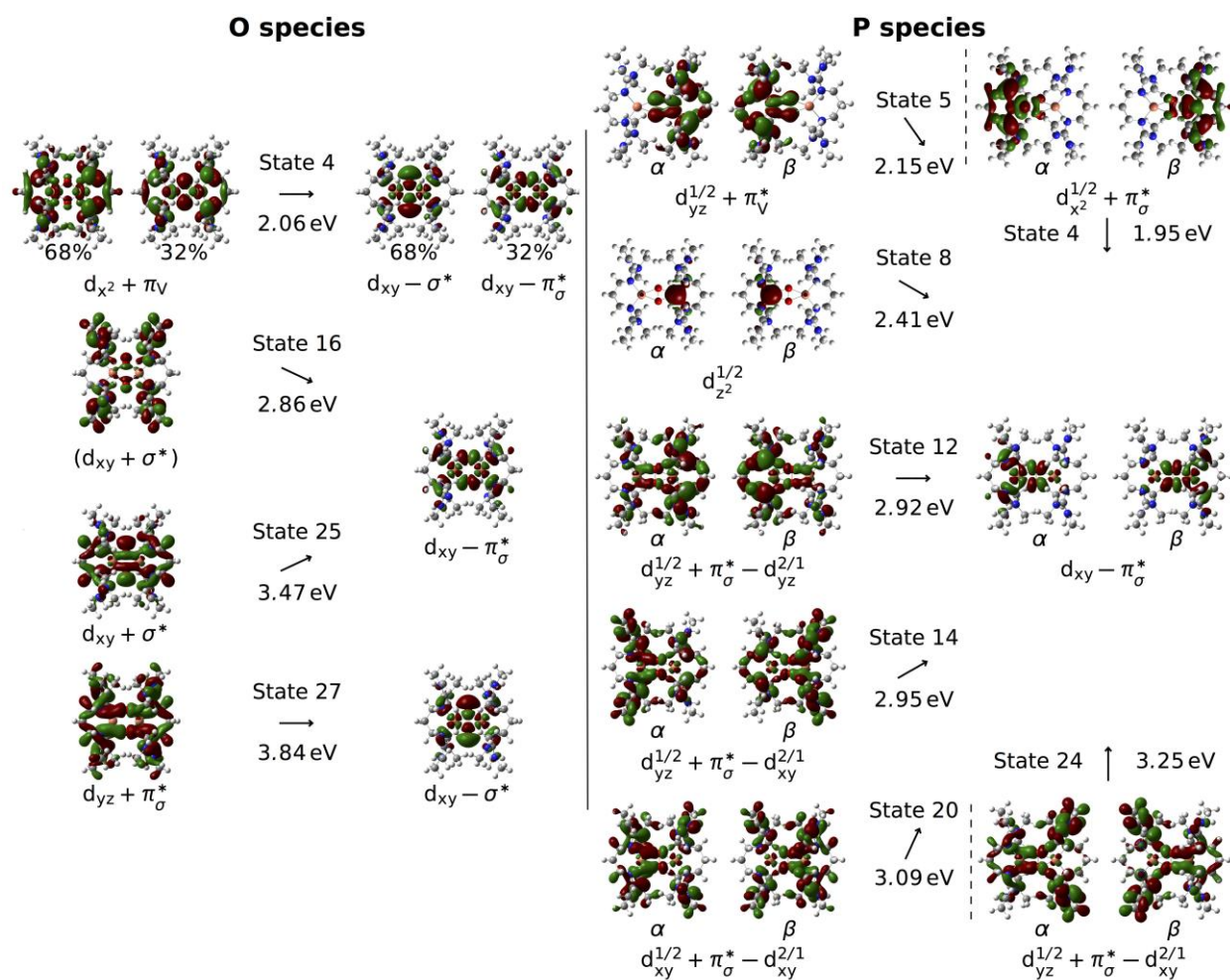


Figure S5. Calculated (B3LYP/cc-pVDZ) natural transition orbitals of **O** and open-shell **P**. The notation was chosen in accordance to the bare Cu_2O_2 core (neglecting large ligand contributions).