

Modeling the Peroxide/Superoxide Continuum in 1:1 Side-on Adducts of O₂ with Cu

Benjamin F. Gherman and Christopher J. Cramer*

Department of Chemistry and Supercomputer Institute, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455

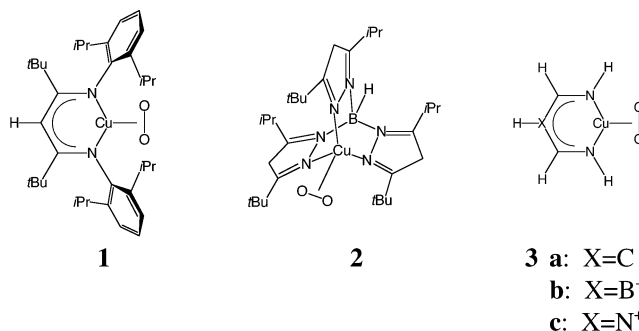
Received January 8, 2004

The character of singlet (C₃N₂H₅)CuO₂ ranges smoothly between copper(III) peroxide and copper(II) superoxide with variation of the electronic character of the supporting β -diketiminate ligand. Over the range of the variation, multireference second-order perturbation theory predicts the ¹A₁ singlet state always to be lower in energy than the lowest triplet state (³B₁). The multideterminantal character of the biradical-like superoxide mesomer causes density functional theory sometimes to fail badly in predicting the relative energies of these same states, although its predictions of other properties, such as geometry, are of good quality.

On the basis of an analysis of a number of different monomeric adducts of O₂ with various supported metals, one of us (C.J.C.) recently suggested, with others, that the O₂ fragment could vary smoothly in character from being more peroxide-like (characterized by an O–O bond length on the order of 1.4 Å and an O–O bond stretching frequency on the order of 950 cm⁻¹) to being more superoxide-like (characterized by an O–O bond length on the order of 1.3 Å and an O–O bond stretching frequency on the order of 1100 cm⁻¹) depending on the nature of the metal and its supporting ligand(s).¹ In the case of copper as the coordinating metal, the β -diketiminate complexes (**1**) of Tolman and co-workers^{1–3} have been assessed to be more peroxide-like in character, whereas the tris(pyrazolyl)hydroborate complex (**2**) of Kitajima and co-workers⁴ has been interpreted to be more superoxide-like;^{1,5} both molecules are ground-state singlets (Chart 1).

Pantazis and McGrady⁶ have questioned this analysis, asserting that peroxide and superoxide character derive from “fundamentally distinct states” and that any change in the

Chart 1. Structures of 1–3



metal–O₂ interaction that would tend to favor singlet superoxide character will still further stabilize an alternative triplet state to the extent that this state will become the ground state. They applied density functional theory (DFT) to a simplified model for **1** in which the aryl and *t*-butyl groups were replaced with hydrogen atoms (**3a**) and reported that, when they pulled the O₂ fragment away from the metal, the triplet state became the ground state prior to their observing any spin density appearing on either Cu or oxygen in the singlet state. Operating under the assumption that the O₂ dissociation coordinate was an adequate model for how ligand changes might be expected to influence Cu–O₂ binding (or generic metal O₂ binding), they concluded that “any significant deviation from dominant Cu^{III}-peroxide character in the ¹A₁ state will induce a switch to a fundamentally distinct triplet ground state with dominant Cu^{II}-superoxide character.”⁶

In this work, we show that the analysis of Pantazis and McGrady suffers from several fundamental flaws. We further show that, owing to the multideterminantal character of the superoxide singlet, DFT can fail badly in predicting the singlet–triplet state energy splitting.

First, we note that modifying the bonding between Cu and oxygen by dissociating the O₂ fragment is a rather artificial means to assess ligand effects, given that (i) the modification being made to the interfragment bonding is associated with overlap and not simply resonance and (ii) the dissociation coordinate in the gas phase clearly must produce triplet oxygen as the asymptote, so curve crossing is assured independent of ligands. We choose an alternative approach to explore ligand effects, namely, we alter the central atom of the β -

* To whom correspondence should be addressed. E-mail: cramer@chem.umn.edu.

- (1) Cramer, C. J.; Tolman, W. B.; Theopold, K. H.; Rheingold, A. L. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 3635.
- (2) Spencer, D. J. E.; Aboelella, N. W.; Reynolds, A. M.; Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 2108.
- (3) Aboelella, N. W.; Lewis, E. A.; Reynolds, A. M.; Brennessel, W. W.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 10660.
- (4) Fujisawa, K.; Tanaka, M.; Moro-oka, Y.; Kitajima, N. *J. Am. Chem. Soc.* **1994**, *116*, 12079.
- (5) Chen, P.; Root, D. E.; Campochiaro, C.; Fujisawa, K.; Solomon, E. I. *J. Am. Chem. Soc.* **2003**, *125*, 466.
- (6) Pantazis, D. A.; McGrady, J. E. *Inorg. Chem.* **2003**, *42*, 7734.

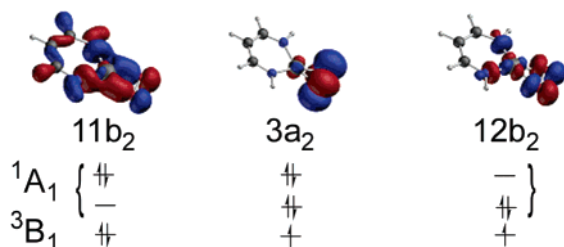


Figure 1. Key frontier orbitals showing partial occupation in 1A_1 and 3B_1 CASSCF wave functions.

diketimate backbone in **3** to allow for stronger or weaker π donation, and we also vary the nuclear charge on the β -diketimate N atoms in order to modify their donor/acceptor characteristics. Such variation in Z_N (ΔZ_N) is equivalent to modifying the electronegativity of the N atom and is an economical way to mimic substituent effects that would otherwise require the explicit incorporation of computationally taxing functional groups.

To discuss the nature of the electronic states, we first consider three key orbitals near the frontier orbital gap. Within a single-determinantal formalism, a closed-shell 1A_1 singlet state can be described as $|\dots 11b_2^2 3a_2^2\rangle$ and a 3B_1 triplet state as $|\dots 11b_2^2 3a_2 12b_2\rangle$, where the ellipses in the determinants represent all the other doubly occupied orbitals. The description of a so-called *open-shell* singlet is not formally possible within a single-determinant formalism (such as Kohn–Sham DFT) as it requires at least two determinants, e.g., $^1A_1 = c_1|\dots 11b_2^2 3a_2^2\rangle - c_2|\dots 3a_2^2 12b_2\rangle$, where $c_1 = c_2$ in the limit of a perfect singlet biradical (Figure 1).⁷ As singlet copper(II) superoxide is indeed formally a biradical with one electron localized on Cu and one on the O₂ fragment, any rigorous attempt to compare the energy of this state to that of the triplet should take account of its multideterminantal nature. To make such energy comparisons, we here employ multireference second-order perturbation theory (CASPT2).^{8,9}

The CASPT2 model has been shown in a wide variety of systems to be an excellent predictor of state-energy separations;¹⁰ to the extent that it displays any bias, it tends to favor higher-spin states over lower-spin states by a few kilocalories per mole in worst-case scenarios.¹¹ Optimization of molecular geometries, however, is tedious at this level of theory as ana-

(7) Note that, when the two orbitals involved in an open-shell singlet belong to the same irreducible representation, a difference of two closed-shell determinants such as that used here is algebraically identical to the more typically written sum of two determinants $[x(1)y(2) + x(2)y(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$, where (to within normalization) x would be $11b_2 + 12b_2$ and y would be $11b_2 - 12b_2$. See, for instance: Bally, T.; Borden, W. T. *Rev. Comput. Chem.* **1999**, *13*, 1.

(8) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(9) The complete active space (CAS) chosen for the reference wave functions included 12 electrons in 9 orbitals, where the orbitals included the three frontier orbitals in Figure 1 as well as three orbitals belonging to the a_1 irreducible representation (irrep), two orbitals belonging to the b_1 irrep, and one additional orbital belonging to the a_2 irrep. Initial calculations using the (18,12) space formed from all copper valence orbitals/electrons and all oxygen σ , σ^* , π , and π^* orbitals/electrons identified several orbitals that had occupation numbers either greater than 1.99 or less than 0.01 for every state/charge combination, and these orbitals were removed to generate the final (12,9) subspace. More complete details including basis set information are provided as Supporting Information.

Table 1. Singlet Cu–O and O–O Bond Lengths and 1A_1 – 3B_1 Energy Splittings

compd	ΔZ_N (au)	bond lengths (Å) ^a		$E(^1A_1-^3B_1)$ (kcal mol ⁻¹)		
		Cu–O	O–O	CASPT2 ^a	BLYP ^a	BS–BLYP ^b
3a	−0.4	1.902	1.435	−9.0	−8.5	−8.5
	−0.3	1.898	1.427	−7.6	−6.0	−6.0
	−0.2	1.895	1.416	−6.6	−3.6	−3.7
	−0.1	1.893	1.411	−5.8	−0.8	−1.6
	0.0	1.891	1.402	−7.1	2.1	0.3
	0.1	1.890	1.394	−6.6	4.8	2.0
	0.2	1.890	1.386	−6.1	7.5	3.4
	0.3	1.891	1.378	−5.9	10.4	4.6
	0.4	1.897	1.368	−5.7	13.1	5.6
	3b	0.0	1.923	1.457	−9.6	−3.0
3c	0.0	1.897	1.370	−5.0	12.6	5.5

^a BLYP geometries. ^b BS–BLYP geometries. ^c Not computed.

lytic gradients are not available. We thus explored geometries from four different levels of theory: CAS(12,9), BLYP with a restricted formalism for the singlets, and BLYP and *mpPW91* both with broken symmetry (BS) allowed for the singlets.¹² (Symmetry-breaking in the singlet Kohn–Sham wave function is associated with instability in the single-determinantal representation.¹³) At the CASPT2 level, the geometries from the BLYP model with a restricted formalism for the singlets were always computed to be lowest in energy when any significant differences existed between levels (full details are available in the Supporting Information), so we restrict our discussion here primarily to results for those geometries. The superior quality of DFT geometries to CAS geometries even for instances where DFT energies fail to be reliable has been noted previously for singlet biradicals.¹⁴

Table 1 provides selected data for **3a** with a range of nitrogen atom charges as well as for **3b** and **3c**. In particular, the Cu–O and O–O distances are listed, as well as the CASPT2, BLYP, and BS–BLYP 1A_1 – 3B_1 energy separations. We note that, with increased positive charge in the β -diketimate ligand, whether introduced by modification of the nuclear charges or by a change of the central backbone atom from carbon to nitrogen, there is a smooth tendency for the O–O bond length to shorten and the opposite behavior is observed with increased negative charge. The full range of O–O bond-length variation from **3b** to **3c** is 0.087 Å; by varying ΔZ_N in **3a** from −0.4 to +0.4, a similar change of 0.067 Å is observed. This trend is consistent with what one would expect: as the ligand becomes more electron donating, the Cu^{III} oxidation state becomes better stabilized, and the O₂ fragment becomes more peroxide-like and vice versa. We note that there is no tendency for the Cu and O₂ fragments to dissociate with these modifications, so the exploration of this coordinate by Pantazis and McGrady in their prior analysis does not seem particularly relevant to modeling changes in ligand activity.

(10) Cramer, C. J., *Essentials of Computational Chemistry: Theories and Models*, 2nd ed.; Wiley: Chichester, U.K., 2004 and references therein. See also extensive discussion in Supporting Information.

(11) Andersson, K.; Roos, B. O. *Int. J. Quantum Chem.* **1993**, *45*, 591.

(12) BLYP: (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. *mpPW91*: (c) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664. More complete details are provided as Supporting Information.

(13) Polo, V.; Kraka, E.; Cremer, D. *Theor. Chem. Acc.* **2002**, *107*, 291.

(14) Cramer, C. J.; Squires, R. R. *Org. Lett.* **1999**, *1*, 215 and references therein.

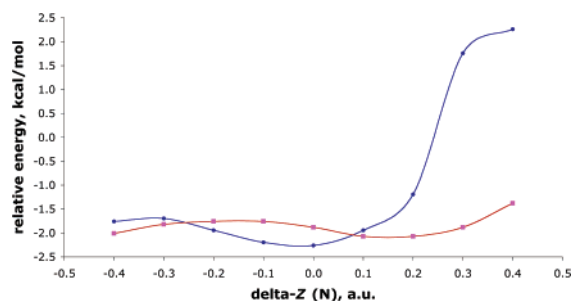


Figure 2. Energies of restricted (squares) and broken-symmetry (circles) BLYP singlet geometries relative to CAS(12,9) geometries as a function of ΔZ_N .

Although the O–O bond length correlates with superoxide character, we can carry out other analyses of this property as well. For example, oxygen partial atomic charges decrease by 0.2 a.u. as ΔZ_N goes from -0.4 to $+0.4$: the total charge transfer is 0.4 electrons from the O_2 fragment to the Cu.¹⁵ A similar charge transfer of about 0.5 electrons is associated with the difference between **3b** and **3c**.

Critically, we note that, over this same large range of O_2 character, the triplet state is *never* predicted to be lower than the singlet state at the CASPT2 level. By comparison, it is evident that the utility of the less rigorous BLYP level for the computation of the state-energy splitting is very low. In those cases that are most peroxide-like (i.e., with the smallest degree of biradical character), there is reasonable agreement between BLYP and CASPT2. However, for **3c**, the two levels disagree by more than 17 kcal mol^{-1} . An error of an equivalent magnitude is seen in the change in state-energy splitting predicted by the two models for **3a** as the nitrogen nuclear charge modification, ΔZ_N , is varied from -0.4 to $+0.4$ a.u.: BLYP predicts that change to favor the triplet state over the singlet by $21.5 \text{ kcal mol}^{-1}$, but CASPT2 predicts the change to be only $3.3 \text{ kcal mol}^{-1}$, preserving the singlet as the ground state. BS–BLYP results reduce the BLYP errors somewhat, but spin contamination becomes unacceptable in systems with more superoxide character, so this is partly an artifact (see below discussion and Figure 2 and Supporting Information).

We emphasize that whether the fictional molecules **3a–c** have singlet or triplet ground states is *not* a question of particular interest. Rather, the issue is that DFT is capable neither of predicting the *magnitude* nor of addressing the *variation* of this state-energy splitting as the singlet develops increased biradical character, whether through changes in ligands or metals.

We close by addressing some technical points associated with the modeling of these species. First, Pantazis and McGrady discounted the contribution of superoxide character to the 1A_1 state because they failed to compute “development of net spin density at either Cu or oxygen, as might be expected if the determinant took on significant open-shell character.”⁶ However, *a true singlet state has zero spin density everywhere*. Spin density can appear in Kohn–Sham

DFT wave functions with equal numbers of α and β electrons *if* the wave function breaks symmetry because of instability associated with the failure of the single-determinantal formalism to address nondynamical correlation. However, this is purely an artifact of attempting to describe a multideterminantal state within a single-determinantal formalism. Although one might empirically observe in particular systems that unpaired *spin* density matches one’s qualitative expectations of *charge localization*, there is no rigorous basis for such an interpretation, and any such analysis should be employed only with caution.¹⁶

This is not to say, however, that DFT is not useful for the study of singlet biradicals. Quite the contrary, DFT has proven remarkably successful in characterizing many properties of such systems—it is simply that modern DFT functionals designed to be employed with the single-determinantal Kohn–Sham formalism tend to predict the *energies* to be too high for singlets having substantial biradical character. This does not prevent *other* properties of the biradicals (e.g., geometries, electrical moments, bond strengths, etc.) from being well predicted, as a bad energy does not necessarily imply a bad density for computation of other observables.

The present copper system provides a sensitive example of limitations in Kohn–Sham DFT when applied to singlet biradicals. Figure 2 depicts the CASPT2 energies for restricted and broken-symmetry BLYP singlet geometries relative to CAS(12,9) geometries as a function of ΔZ_N . Note that there is negligible difference in the energies of the two DFT structures up to $\Delta Z_N = 0.1$. At this point, the broken-symmetry BLYP wave function has $\langle S^2 \rangle = 0.580$, this value having grown from nearly 0.000 for $\Delta Z_N = -0.4$. After this point, $\langle S^2 \rangle$ continues to increase, but this is clearly not associated with better accounting for nondynamical correlation; instead, spin contamination begins to poison the singlet wave function, and the relative energies of the broken-symmetry structures rise markedly.

In summary, side-on adducts of O_2 with Cu can indeed vary in a continuous fashion from peroxide-like to superoxide-like in character, and further studies of ligand effects should reveal other interesting aspects in these systems (such as illuminating further the differences between bi- and tridentate ligands such as those found in **1** and **2**). Single-determinantal DFT, however, will not be an appropriate choice for evaluating the ground-state spin multiplicity in superoxide-like cases.

Acknowledgment. We thank Max Holthausen for stimulating conversations. This work was supported by the National Science Foundation (CHE-0203346).

Supporting Information Available: Computational details including basis set information. Additional technical discussion of CASPT2 vs DFT. Geometries and energies for **3a–3c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC049958B

(15) The magnitude of this transfer is about the same from either BLYP or CASPT2 Mulliken analysis or from fitting of the partial atomic charges to the BLYP electrostatic potential.

(16) (a) Gräfenstein, J.; Kraka, E.; Cremer, D. *Chem. Phys. Lett.* **1998**, *288*, 593. (b) Cramer, C. J. *J. Am. Chem. Soc.* **1998**, *120*, 6261. (c) Davidson, E. *Int. J. Quantum Chem.* **1998**, *69*, 241. (d) Gräfenstein, J.; Cremer, D. *Mol. Phys.* **2001**, *99*, 981.