Inorg. Chem. **2003**, *42*, 7734–7736

Inorganic Chemistry
Communication

On the Nature of the Bonding in 1:1 Adducts of O_2

Dimitrios A. Pantazis and John E. McGrady*

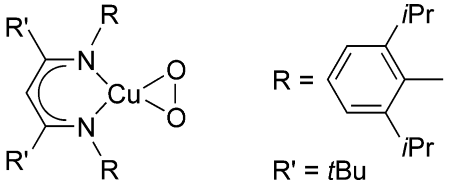
Department of Chemistry, University of York, Heslington, York YO10 5DD, U.K.

Received July 23, 2003

A survey of the potential energy surface for a 1:1 copper dioxygen complex, $(C_3N_2H_5)CuO_2$, reveals two distinct states in the valence region, a singlet ($^1A_1$) and a triplet ($^3B_1$). The former spans a continuum from $Cu^{III}–O_2^{2-}$ to $Cu^I–O_2(^1\Delta_g)$, while the latter spans $Cu^{II}–O_2^{1-}$ to $Cu^I–O_2(^3\Sigma_g^-)$. The point at which the potential energy curves for the two states cross marks an abrupt discontinuity in electron distribution, where the system shifts from dominant $Cu^{III}–O_2^{2-}$ character to $Cu^{II}–O_2^{1-}$. On this basis, we argue that there is no continuum between Cu^{III}–peroxide and Cu^{II}–superoxide: the two are represented by distinct states that differ both in symmetry and multiplicity.

The nature of the interaction beween transition metal centers and O_2 remains a topic of enduring interest. The O_2 unit in such complexes is redox “noninnocent” and can, in principle, be described as a coordinated dioxygen, superoxide, or peroxide ligand, depending on the extent of charge transfer between metal and ligand.[1,2] The 1:1 adducts are typically classified on the basis of the hapticity of the O_2 unit, η^1- or η^2-, and these structural descriptors have traditionally been viewed as being synonymous with the superoxide and peroxide oxidation states, respectively.[1] The recent characterization of a number of complexes containing η^2-O_2, but with structural and spectroscopic properties typical of the superoxide ligand, has, however, shown that there is no direct link between connectivity and electronic structure.[3,4c] In a series of papers, Tolman and co-workers have discussed these ideas in the context of a copper species, **1**, (Scheme 1) which was initially formulated as a Cu^{II}−superoxide complex.[4] This conclusion was, however, later revised in light of new spectroscopic, structural, and theoretical data that suggested the presence of considerable Cu^{III}−peroxide character.[4b] On the basis of calculations performed on a wider range of 1:1 adducts, the authors went on to conclude that peroxide and superoxide formulations were two limits of a continuum defined by the degree of mixing between metal and ligand orbitals, and that, in principle, transition metal complexes could sample all O−O bond orders along this continuum.[4c]

Scheme 1. Structure of Complex **1**



This interpretation of the electronic structure of η^2-coordinated dioxygen complexes differs markedly from that proposed in our recent discussion of the bonding in $[Cr(bipy)_2(O_2)]^{2+}$,[5] where we argued that the peroxide and superoxide are fundamentally distinct states, differing both in their symmetry and their multiplicity. This divergence of opinion encouraged us to reinvestigate the electronic structure of the copper system.[6] As a starting point to this investigation, we considered a highly simplified model of complex **1**, where $R = R' = H$. Potential energy curves, calculated using the BLYP functional[7] and the 6-311G(d,p) basis set, are plotted for the two most stable electronic states, $^1A_1$ and $^3B_1$, in Figure 1. In all cases, the separation between the copper

---

* To whom correspondence should be addressed. E-mail: jem15@york.ac.uk.

(1) Momenteau, M.; Reed, C. A. *Chem. Rev.* **1994**, *94*, 659−698.

(2) Que, L., Jr.; Tolman, W. B. *Angew. Chem., Int. Ed.* **2003**, *41*, 1114−1137.

(3) Qin, K.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 2333−2335.

(4) (a) Aboelella, N. W.; Lewis, E. A.; Reynolds, A. M.; Brennessel, W. M.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 10660−10661. (b) Spencer, D. J. E.; Aboellela, N. W.; Reynolds, A. M.; Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 2108−2109. (c) Cramer, C. J.; Tolman, W. B.; Theopold, K. H.; Rheingold, A. L. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 3635−3640.

(5) Howe, P. R.; McGrady, J. E.; McKenzie, C. J. *Inorg. Chem.* **2002**, *41*, 2026−2031.

(6) All calculations were performed using the Gaussian 98 program with the 6-311G(d, p) basis set (=Wachters−Hay + f for Cu). Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(7) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

10.1021/ic034867k CCC: $25.00

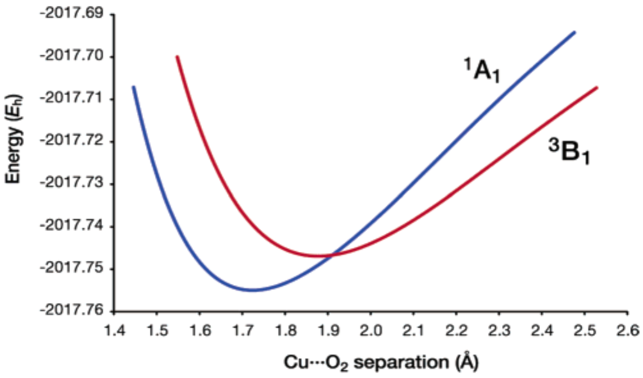
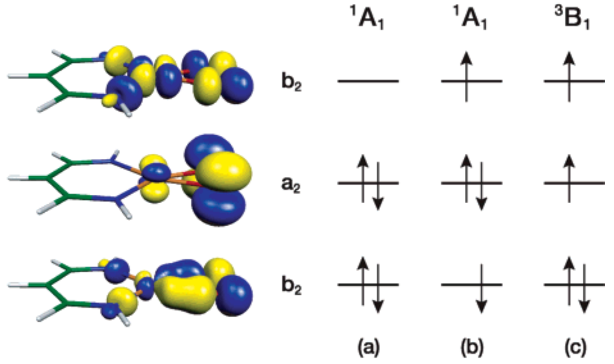


Figure 1. Potential energy curves for $^1A_1$ and $^3B_1$ states of $(C_3H_5N_2)Cu(O_2)$.

Scheme 2. Determinants that Contribute to the $^1A_1$ and $^3B_1$ States



nucleus and the center of the O−O bond is taken as the reaction coordinate.

Within an unrestricted single determinant approach, the $^1A_1$ state can be represented by two distinct types of determinant, one closed-shell [Scheme 2a] and one open-shell [Scheme 2b]. Depending on the character of the occupied b_2 orbital, the closed-shell determinant can vary from dominant $Cu^{III} + O_2^{2-}$ to dominant $Cu^I + O_2$ (singlet) character. The open-shell singlet, in contrast, corresponds unambiguously to $Cu^{II} + O_2^{1-}$, regardless of the distribution of metal and O_2 character between the b_2 orbitals.

The optimized geometry of the $^1A_1$ state (Table 1) is very similar to that reported by Tolman and co-workers, and the rather long O−O bond length (1.392 Å) and low ν(O−O) (997 cm^{-1}) are indeed characteristic of a peroxide ligand. As the Cu−O_2 distance is increased, the degree of mixing between Cu $d_{x^2-y^2}$ and in-plane π^* is reduced and $\langle S^2\rangle$ increases monotonically from 0.29 to a value of 0.93 at rO−O = 2.63 Å, indicating significant contamination from a higher lying triplet state. Tolman and co-workers have interpreted this nonzero value of $\langle S^2\rangle$ as being an indicator of increasing Cu^{II}−superoxide character.[4b,c] The increase in $\langle S^2\rangle$ along the $^1A_1$ curve is not, however, accompanied by the development of net spin density at either Cu or oxygen, as might be expected if the determinant took on significant open-shell character [Scheme 2b].[4c,5,8] In fact, the spatial distribution of spin α and β electrons remains identical as the Cu−O_2 distance is increased, but the occupied b_2 orbital takes on greater Cu $d_{x^2-y^2}$ character, leading to the Cu^I + singlet O_2 asymptote. In this case, the nonzero value of $\langle S^2\rangle$ is most likely associated with contamination of the singlet O_2 wave function by the $M_s = 0$ component of its triplet ground state, $^3\Sigma_g^-$, and does not indicate incipient Cu^{II}−superoxide character. It is clear, therefore, that the value of $\langle S^2\rangle$ should not be taken as an a priori indicator of Cu^{II}−superoxide character.

Thus far, we have focused only on the singlet state that was discussed by Tolman and Cramer.[4b,c] Figure 1, however, shows that an additional triplet state, $^3B_1$, is present in the valence region. The $^3B_1$ state [Scheme 2c] arises from the transfer of a single electron from the out-of-plane π^* orbital (a_2) into the antibonding combination of $d_{x^2-y^2}$ and in-plane π^*, the orthogonality of the resultant singly occupied orbitals ensuring ferromagnetic coupling of the two unpaired electrons.[8] The shorter O−O bond length and higher ν(O−O) suggest significant superoxide character in the $^3B_1$ state, a view that is confirmed by net spin densities of 0.57 and 1.29 on Cu and O_2, respectively. As the Cu−O_2 distance is increased, accumulation of Cu $d_{x^2-y^2}$ character in the doubly occupied b_2 orbital leads to the $Cu^I + O_2$ asymptote, but in this case with O_2 in its triplet ground state. The potential energy curves summarized in Figure 1 confirm that the global minimum is the $^1A_1$ state, an ordering that is consistent with the reported structure and vibrational spectrum of complex **1** and also with the conclusions put forward by Tolman and co-workers.[4b] However, the $^3B_1$ state is necessarily more stable than $^1A_1$ at the dissociation limit, and so the two curves must cross as the strength of the interaction between metal and O_2 is reduced. The minimum energy crossing point (MECP)[11] between the two curves has been located 5.2 kcal mol^{-1} above the $^1A_1$ minimum (BLYP), and the net spin densities at this point [Cu/O_2 = 0/0 ($^1A_1$) and 0.47/1.38 ($^3B_1$)] clearly indicate an abrupt discontinuity marking the transition from a Cu^{III}−peroxide complex to a Cu^{II}−superoxide. In terms of the determinants shown in Scheme 2, the development of open-shell character in the $^1A_1$ state [2b] will necessarily be accompanied by a relative stabilization of the $^3B_1$ state [2c]. Thus, any significant deviation from dominant Cu^{III}−peroxide character in the $^1A_1$ state will induce a switch to a fundamentally distinct triplet ground state with dominant Cu^{II}−superoxide character.

In Figure 1, the separation between the two minima is only 5.0 kcal mol^{-1}, and so, as pure density functionals such as BLYP are known to favor low-spin states,[8,9] the energies were reevaluated using a hybrid functional (B3LYP).[10] The result is a reversal in the stabilities of the two states (Table 1), and therefore, in this case, an incorrect prediction of the ground state. We have also probed the effect of incorporating the full ligand into the model, as Tolman and co-workers did in their original paper.[4b] The result is a 3.5 kcal mol^{-1}

---

(8) Chen, P.; Root, D. E.; Campochiaro, C.; Fujisawa, K.; Solomon, E. I. *J. Am. Chem. Soc*. **2003**, *125*, 466−474.

(9) (a) Reiher, M. *Inorg. Chem*. **2002**, *41*, 6928−6935. (b) Salomon, O.; Reiher, M.; Hess, B. A. *J. Chem. Phys*. **2002**, *117*, 4729−4737.

(10) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(11) Harvey, J. N.; Aschi, M.; Schwarz, H.; Koch, W. *Theor. Chem. Acc.* **1998**, *99*, 95−99.

Table 1. Optimized Structural Parameters and Relative Energies of the $^1A_1$ and $^3B_1$ States of $LCuO_2$

		$^1A_1$				$^3B_1$				$E^S - E^T$/ kcal mol^{-1}
		r(O−O)/Å	ν(O−O)/cm^{-1}	r(Cu−O)/Å	$\langle S^2 \rangle$	r(O−O)/Å	ν(O−O)/cm^{-1}	r(Cu−O)/Å	$\langle S^2 \rangle$	
R = R′ = H	BLYP	1.392	997	1.861	0.2921	1.339	1111	1.994	2.0042	−5.0
	B3LYP	1.358	1086	1.823	0.1404	1.310	1211	1.967	2.0082	2.5
R = $C_{12}H_{17}$	BLYP	1.417	944	1.867	0.1005	1.353	1068	2.020	2.0041	−8.5
R′ = ^{t}Bu	B3LYP	1.379	1042	1.827	0.0000	1.321	1180	1.993	2.0085	−0.9
	expt [ref 4b]	1.44(2)	961	1.852(8)						

stabilization of the $^1A_1$ state relative to $^3B_1$, which, for the B3LYP functional, is just sufficient to restore the original (correct) order of stability. It is not our aim here to establish the most appropriate choice of functional to describe spin-state transitions, an issue that has been debated extensively in the literature.[9] Our point is simply that there are two fundamentally distinct electronic states that lie close in energy, and subtle changes in the choice of functional, basis set, or model ligand can reverse their stability. A balanced discussion of dioxygen binding should therefore include a treatment of both.

To summarize, our survey of the potential energy surface for complex **1** has identified two distinct states, a singlet and a triplet. The former ($^1A_1$) spans the continuum between the $Cu^{III}-O_2^{2-}$ and $Cu^I-O_2(^1\Delta_g)$ asymptotes. The triplet potential energy curve, in contrast, spans a continuum from $Cu^{II}-O_2^{1-}$ to $Cu^I-O_2(^3\Sigma_g^-)$, and the point at which the two cross marks an abrupt discontinuity in electronic structure. Finally, we note that, while we have used the $Cu-O_2$ separation to control the strength of the metal−ligand interaction, the same effect is achieved in the laboratory by modifying the metal or ligand. The symmetries and multiplicities of the two states involved will then depend on the particular complex,[5] but the general conclusion remains valid: there is no continuum between peroxide and superoxide resonance forms. The two are represented by fundamentally distinct distributions of the valence electrons.

Acknowledgment. We are grateful to the EPSRC for financial support.

Supporting Information Available: Total energies and Cartesian coordinates for all reported minima and MECPs. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034867K