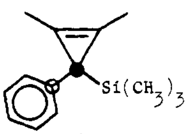

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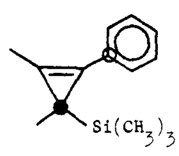
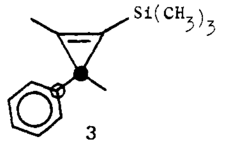


2

	1	2
● C_a (ppm)	23.3	14.5
○ C_b (ppm)	150.0	130.6
^{29}Si (ppm)	1.18	1.84



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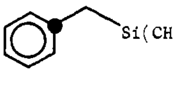
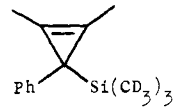


● (ppm)	140.16	144.1
$\underline{C}H_2$ (ppm)	26.94	29.2

The intramolecular nature of the reaction was demonstrated by a classical "crossover" experiment. Copyrolysis of 94.3% deuterated **4** and cyclopropene **5** for 10 half-lives, followed by gas chromatographic separation of the $C_{14}H_{20}Si$ and $C_{18}H_{28}Si$ components, showed no loss of deuterium in **4** or its isomer, $C_{14}D_9H_{11}Si$. There was no deuterium incorporation observed in **5** or its isomerization product.



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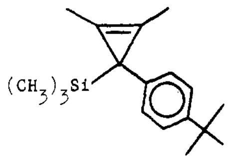

5

Furthermore, changing the solvent for pyrolysis of **1** from benzene-d_6 to benzene-d_6-nitrobenzene-d_5 (2:1) did not change the rate significantly. We conclude, therefore, that the process is intramolecular and proceeds without ionic intermediates.

It remains to determine the sterochemistry of the migration as well as the effect of other metals on the rate and to probe the application of this reaction to more complicated systems.

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Reactions of Superoxide in Aprotic Solvents. A Superoxo Complex of Copper(II) *rac*-5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane

Sir:

Understanding the nature of the interaction between copper and dioxygen (or species derived from it such as superoxide or peroxide) has been a continuing and often frustrating challenge to chemists[1] and biochemists[2] for many years. The few stable characterized copper dioxygen complexes are binuclear μ-peroxo species of the type $[Cu^{II}\text{-}O_2^{2-}\text{-}Cu^{II}]$ which are formed by reaction of Cu(I) with O_2.[3-5] Although 1:1 copper-dioxygen complexes have been proposed as intermediates in Cu(I) autoxidation reactions[1] and in reactions of Cu(II) with superoxide in aqueous media,[6] no 1:1 complexes have ever been directly detected by spectroscopic or other techniques. Presumably the 1:1 complex $[CuO_2]^+$ reacts rapidly with either Cu(I) or protons and therefore is not observed when these species are present.[1] We have taken a different experimental approach to the problem of synthesizing 1:1 complexes of dioxygen and copper. We react complexes of Cu(II) with superoxide in aprotic media to generate such species in the absence of Cu(I) or available protons. We have found that the choice of Cu(II) complex is critical because most previously studied Cu(II) complexes are reduced by superoxide to produce Cu(I) and dioxygen.[7-9] The complex we chose to study, therefore, was the perchlorate salt of the N_4 macrocyclic complex Cu(tet b)$^{2+}$ [10] which has a relatively low reduction potential[11,12] and an affinity for an additional anionic ligand.[13-15] Such factors are in part responsible for the recent successful synthesis of a stable Cu(tet b)$^{2+}$-thiolate complex.[15] We report here the characterization of a solution species best formulated as an ESR-silent pentacoordinate superoxide complex of Cu^{II} tet b synthesized by reaction of superoxide with Cu(tet b)$^{2+}$ in Me_2SO.

Addition of 18-crown-6 solubilized KO_2 (0.1 M)[7,8] to solutions of Cu(tet b)$(ClO_4)_2$[16] (1-5 mM) in Me_2SO caused the purple solutions to turn immediately to a dark forest green. The resulting solution was stable for several days in the absence of excess superoxide. The long-wavelength absorption band at 672 nm[17] (see Table I) that appeared upon reaction of Cu(tet b)$^{2+}$ with O_2^- is characteristic of $Cu^{II}N_4X^+$ chromophores where N_4 = tet b or 4,11-diene[10] and X^- = RS^-,[15] Cl^-,[14] or CN^- [13] (see Table I) and has been assigned as a ligand field transition of these low symmetry five-coordinate Cu(II) complexes. Similar spectra were obtained from reaction of Cu(tet b)$^{2+}$ with solutions of $(NEt_4)F$ or $(NBu_4)OH$ in Me_2SO or CH_3CN (see Table I) and are presumed to result from the corresponding X^- = F^- and OH^- species. The similarity of the visible spectra of the products formed by reaction with O_2^-, F^-, and OH^- implies that they are all structurally similar five-coordinate complexes. When an excess of O_2^- (>2 equiv), OH^- (>1.5 equiv), or F^- (>5 equiv) was added to the Cu(tet b)$^{2+}$ solution, the green color slowly turned to brown, the visible spectra had no distinct maxima, and, in the case of OH^-, the ESR signal due to Cu(II) disappeared. The strong basicity of O_2^-, F^-, and OH^- in Me_2SO solutions[8,18] suggests

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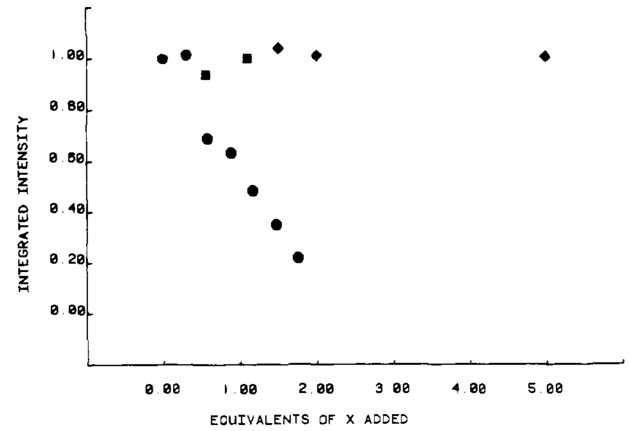

Figure 1. Integrated ESR signal intensity of frozen solutions (77 K) of Cu(tet b)$(ClO_4)_2$ in Me_2SO plus anions vs. equivalents of added O_2^- (●), OH^- (■), and F^- (◆). The concentration of Cu(tet b)$(ClO_4)_2$ was 5.03 mM for the O_2^- experiment and 2.50 mM for the OH^- and F^- experiments.

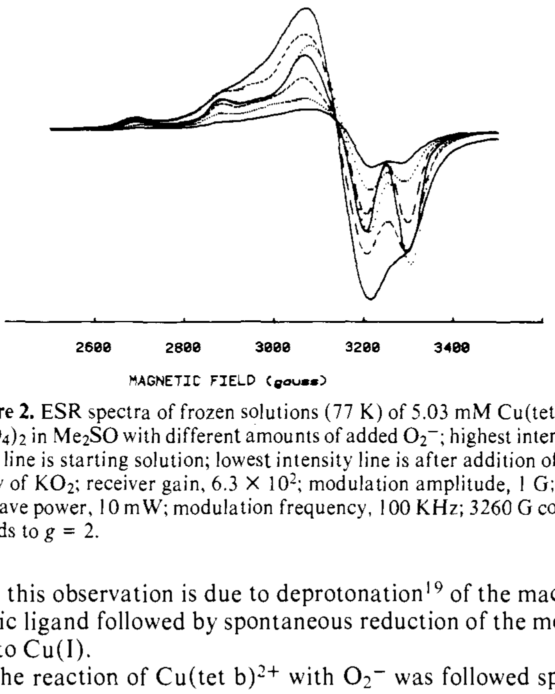

Figure 2. ESR spectra of frozen solutions (77 K) of 5.03 mM Cu(tet b)$(ClO_4)_2$ in Me_2SO with different amounts of added O_2^-; highest intensity solid line is starting solution; lowest intensity line is after addition of 1.8 equiv of KO_2; receiver gain, 6.3 × 10^2; modulation amplitude, 1 G; microwave power, 10 mW; modulation frequency, 100 KHz; 3260 G corresponds to $g = 2$.

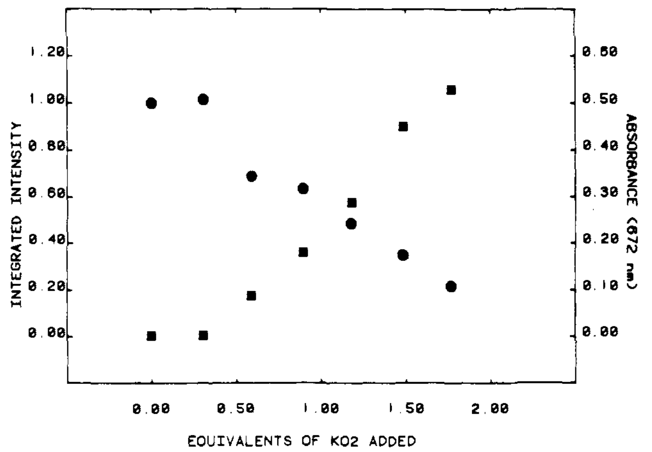

Figure 3. Integrated ESR signal intensity (●) as in Figure 1 and absorbance at 672 nm (■) of the solution described in Figure 2 vs. equivalents of KO_2 added. Note that the 672 nm band characteristic of the five-coordinate Cu(II) complex develops as the integrated intensity of the ESR signal disappears demonstrating that the product is ESR silent.

that this observation is due to deprotonation[19] of the macrocyclic ligand followed by spontaneous reduction of the metal ion to Cu(I).

The reaction of Cu(tet b)$^{2+}$ with O_2^- was followed spectrophotometrically at 672 nm. Complete conversion into product required >1 equiv of O_2^- indicating that the binding constant is only moderate. The same was true also for F^-. Nevertheless, using the method of continuous variations, the reaction stoichiometry was determined to be 1:1 Cu(tet b)$^{2+}$ to O_2^-.[20] The quantity of noncondensable gases evolved during the reaction of O_2^- and Cu(tet b)$(ClO_4)_2$ in Me_2SO was determined using vacuum line and Toeppler pump techniques. The results of these experiments showed that <0.15 equiv of O_2/equiv of Cu(tet b)$^{2+}$ was generated. This amount can be accounted for by normal decomposition of free O_2^- in Me_2SO during the course of the reaction. This observation rules out the possibility that we were observing a disproportionation of the type $2O_2^- + 2Cu^{II} \rightarrow O_2 + Cu^{II}\text{-}O_2^{2-}\text{-}Cu^{II}$.

Table I. Electronic Spectra

complex	solvent	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})	ref
Cu(tet b)$^{2+}$	Me_2SO	523 (110)	this work
Cu(tet b)$^{2+}$	CH_3CN	517 (138)	11
Cu(tet b)$^{2+}$ + O_2^- ^{a}	Me_2SO	672	this work
Cu(tet b)$^{2+}$ + F^-	Me_2SO	690	this work
Cu(tet b)$^{2+}$ + OH^-	Me_2SO	675	this work
Cu(tet b)(RS)$^+$ ^{b}	methanolic KOH	725 (550)	15
Cu_2(4,11-diene)$_2CN^{3+}$ ^{c}	KBr pellet	736	13
	Me_2SO	733	this work
Cu_2(tet b)$_2Cl^{3+}$ ^{c}	KBr pellet	667	13
	Me_2SO	690	this work

[a] See ref 17. [b] RS^- = *o*-mercaptobenzoate. [c] These are cyano- and chloro-bridged binuclear complexes of Cu(II).

The reactions of Cu(tet b)$^{2+}$ with O_2^-, OH^-, and F^- were also followed by changes in the ESR spectra. Addition of small amounts of OH^- or O_2^- (≪1 equiv) caused changes in the ESR spectrum which were presumably due to base-induced isomerization of Cu(tet b)$^{2+}$ to a more stable geometric isomer.[21,22] Addition of enough F^- or OH^- to cause complete conversion into the five-coordinate complex (as judged by the visible spectra) caused pronounced changes in the ESR spectra consistent with major changes in the coordination environment around Cu(II). The integrated signal intensities of the spectra, however, remained constant (Figure 1). By contrast, addition of O_2^- caused the ESR spectra to disappear (Figures 2 and 3) indicating that the product formed was ESR silent. Decomposition of superoxide by addition of a proton source[8,9] (in this case CF_3COOH) caused the intensity of the Cu(II) ESR signal to reappear.

Cyclic voltammetry of Cu(tet b)$(ClO_4)_2$ in Me_2SO between −1.5 and +0.5 V (using 0.1 M $(Me_4N)ClO_4$ as supporting electrolyte and a platinum button electrode) showed two reduction waves at −0.70 and −0.52 V but only one oxidation wave at −0.41 V (vs. Ag/AgCl 3 M NaCl reference electrode[23]). The two reduction waves can be attributed to Cu(tet b)$^{2+}$ with differing modes of solvation[24] or ion pairing or to different configurational isomers of Cu(tet b)$^{2+}$.[21,22] Upon reaction of Cu(tet b)$^{2+}$ with ~1 equiv of O_2^-, a new quasi-reversible wave centered at −0.17 V was observed. This wave is tentatively attributed to reduction of coordinated superoxide to peroxide followed by quasi-reversible oxidation. Similar electrochemical behavior was observed for the reaction product of Cu(tet b)$(ClO_4)_2$ plus superoxide in acetonitrile. In a separate experiment, Cu(tet b)$^{2+}$ in Me_2SO was saturated with O_2 and the potential scanned cathodically to −1.5 V to produce O_2^- near the electrode surface. Under these conditions, waves similar to those observed in the Cu(tet b)$^{2+}$ plus KO_2-crown ether system were seen. Upon flushing Ar through the solution, the original cyclic voltammagram due to Cu(tet b)$^{2+}$ was observed.

Attempts to isolate Cu(tet b)$(O_2)^+$ have been frustrated by the base-induced decomposition that occurs when excess O_2^- is present and the lack of solvents for Cu(tet b)X_2 that are compatible with O_2^-. Having established that this approach is a suitable general strategy for synthesis of mononuclear copper dioxygen complexes, however, we are investigating the reactions of other copper macrocyclic complexes with superoxide with the expectation that complexes of this type can be synthesized which are more stable and more amenable to isolation and crystallization.

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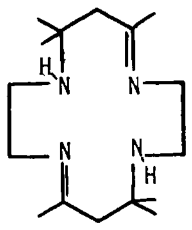
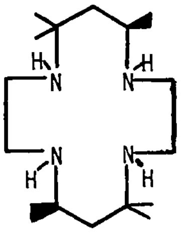


4,11-diene



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(16) Cu(tet b)$(ClO_4)_2 \cdot H_2O$ was synthesized by literature methods[15] and dried at 87 °C in vacuo for 24 h, at which point the broad IR band at ~3200 cm^{-1}, due to water, had disappeared.
(17) A relatively weak band appears in the visible spectrum at ~410 nm when Cu(tet b)$^{2+}$ is reacted with O_2^- in Me_2SO, with OH^- in Me_2SO or CH_3CN, and with F^- in Me_2SO but not in CH_3CN. At this point, we cannot be certain whether this band is due to the anion complex or is the result of a small amount of base-induced decomposition or deprotonation of the N_4 macrocycle.
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Chemical Generation of Excited-State Radicals: Succinimidoyl

Sir:

Skell and co-workers[1] have proposed that two electronic states of the succinimidoyl radical, the π ground state and a σ_N excited state,[2] may be chemically generated. We have used MNDO semiempirical molecular orbital theory[3,4] to investigate the mechanism of generation of these two radicals from *N*-chlorosuccinimide (NCS). Our results show that the electronic state of the product succinimidoyl radical is dependent on the nucleophilicity or electrophilicity of the generating radical.

N-Chlorosuccinimide is calculated to be slightly nonplanar at MNDO[5] with a heat of formation of −63.3 kcal mol^{-1}, which is reasonable in view of the experimental heat of formation of −85.6 kcal mol^{-1} for crystalline NCS.[6] There is some question as to the ordering of the molecular orbitals in NCS. Worley et al.[7] have interpreted the PE spectral band at 10.29 eV as being due to both the n_{CO}^- and the n_{CO}^+ orbitals. MNDO, on the other hand, predicts the HOMO to be the π^*_{NCl} orbital shown in Figure 1. This conclusion is supported by a single-point RHF/STO-3G calculation on the MNDO optimum geometry for NCS. The original PES assignment[7] is based on the vibrational structure observed for the band at 10.29 eV, compared with the relatively sharp band at 11.12 eV. The n_{CO}^- band in succinimide,[7] however, does not show the same type of vibrational structure as that found for the 10.29-eV band in NCS, suggesting that this is a new type of band. Furthermore, the n_{CO}^-/n_{CO}^+ splitting in 1,3 diketones has been shown to be independent of the twist angle between the carbonyls,[8] so that they are unlikely to be almost degenerate in NCS. The calculated (MNDO, Koopman's theorem) ionization potentials for NCS (10.92, 11.32, and 12.32 eV) are also in accord with the experimental values (10.29, 11.12, and 12.32 eV). The exact ordering of the occupied and unoccupied MO's in NCS is, however, for the purpose of this paper, unimportant. What is important is that the highest occupied and lowest unoccupied molecular orbitals *with significant contributions at N and Cl* are the orbitals shown in Figure 1,[9] which are calculated to be HOMO and LUMO at MNDO.[10] These orbitals are both N-Cl antibonding and, equally significantly, correspond to the SOMO's of the π and σ_N succinimidoyl radicals, respectively.

The π and σ_N succinimidoyl radicals have calculated heats of formation of −30.4 and −16.6 kcal mol^{-1}, respectively, so that any reaction which leads to the latter must be kinetically controlled. Skell[1] has speculated that alternative in- and out-of-plane modes of attack may lead to the two different radical electronic states. Interaction of the HOMO and the LUMO of NCS with the SOMO of an attacking radical shows how this is possible.

The SOMO of an electrophilic radical will interact most strongly with the NCS HOMO. The preferred interaction is shown in Scheme I (a), and leads to attack from above the NCS plane. Further reaction yields the new Cl-Cl bonding orbital and the SOMO of the π succinimidoyl radical.

If, on the other hand, the SOMO of the attacking radical is high lying (i.e., the radical is nucleophilic), it will interact strongly with the NCS LUMO, as shown in Scheme I (b). The

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