

The Ru(II) $\rightarrow \pi^*$ SQ transition is broader in (RuQ,SQRu) than in (RuSQ,CAT), an observation inconsistent with model 1a, but consistent with 1b, especially if the twist angle of the excited-state differs significantly from that of the ground state. Thus (RuQ,SQRu) is a class II²¹ delocalized complex in which the (bpy)₂Ru^{II}Q^{••} and (bpy)₂Ru^{II}SQ^{••} chromophores can separately be identified spectroscopically but are significantly coupled.

The second reduced species (RuSQ,SQRu) shows a further red shift in the Ru(II) $\rightarrow \pi^*(1)$ bpy and Ru(II) $\rightarrow \pi^*(2)$ bpy transitions relative to (RuQ,SQRu). The Ru(II) $\rightarrow \pi^*$ SQ transition does not shift significantly, relative to (RuQ,SQRu), but it does become weaker and broader; its oscillator strength is probably little changed (Figure 3). A near-IR band is still observed, shifted to the blue, narrower and more intense than that observed in the spectrum of (RuQ,SQRu).

The decrease in molar intensity for the Ru(II) $\rightarrow \pi^*$ SQ MLCT transition is especially informative. If the halves of the molecule were independent and uncoupled, the oscillator strength of this transition might double relative to the (RuQ,SQRu) species, since the transition probability doubles.

Consider however that the two π^* orbitals on each SQ terminus couple to yield a lower energy orbital of odd parity that is filled and an upper empty orbital of even parity. The Ru(II) $\rightarrow \pi^*$ MLCT transitions terminate on this upper orbital. Coupling of the pairs of ruthenium *xz*, *xy*, and *yz* orbitals yields three pairs of orbitals of even and of odd parities. Transitions from the odd-parity combinations to the empty ligand orbital generate three possible transitions, one strongly allowed, one weakly allowed, and one forbidden. There is therefore one strongly allowed transition per (strongly coupled, delocalized) dinuclear molecule, rather than the two expected in a localized dinuclear molecule; thus the transition probability may not increase relative to (RuQ,SQRu), as observed.

The near-infrared absorption has a quite different shape in (RuSQ,SQRu), being narrower (half-bandwidth ca. 1500 cm⁻¹), indicative of a smaller difference between the equilibrium ground- and excited-state potential surfaces than for (RuQ,SQRu). This is also consistent with a delocalized species, with this transition being internal to the (RuSQ,SQRu) framework with little charge-transfer character. It is possibly a transition between the pair of SQ terminus molecular orbitals defined in the previous paragraph. Solvent dependence data are not yet available.

Further studies on this system are planned to probe the twist angles in both the ground and excited states and the variation in coupling between the two termini of the ligand as a function of oxidation state.

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Alkane Functionalization by Non-Porphyrin Iron Complexes: Mechanistic Insights

Biological catalysts capable of functionalizing alkanes include cytochrome P-450¹ (which contains a heme active site), methane

monooxygenase² (which has a diiron active site), and prolyl hydroxylase³ (which requires mononuclear iron and α -ketoglutarate). While an oxo(porphyrin cation radical)iron(IV) complex is strongly implicated as the active species in the cytochrome P-450 mechanism,⁴ less is known of corresponding species in the non-heme iron systems. We have thus initiated an effort to uncover alkane functionalization chemistry by non-porphyrin complexes of iron. Previous work toward this goal has included Fe(ClO₄)₂·3H₂O₂/CH₃CN,⁵ Fe₃O(OAc)₇/HOAc/pyridine/O₂,⁶ and Fe₂O(OAc)₂(bpy)₂Cl₂/t-BuOOH/CH₃CN⁷ systems. But mechanistic insights from these systems into the nature of the oxidizing species have not been forthcoming. On the basis of our work on modeling the reactivity of the catechol dioxygenases,⁸ we have initiated an investigation of the reactivity of iron complexes with tripodal ligands in the presence of oxygen atom donors to gain insight into how non-heme iron centers may affect such chemistry. Tripodal ligands were selected for this study since they offer the important advantage of control over the ligand environment at a labile iron center.

In a typical reaction, a 0.77 M solution of cyclohexane was reacted with 0.10 M TBHP⁹ in acetonitrile in the presence of 0.70 mM [Fe^{III}(TPA)Cl₂](ClO₄)¹⁰ (**1**) at 25 °C under 1 atm of oxygen-free argon. A turnover number of 56 is observed after 2 h for the TBHP oxidation of cyclohexane catalyzed by **1**, resulting in the formation of cyclohexanol, cyclohexanone, chlorocyclohexane, and (*tert*-butylperoxy)cyclohexane (Table I). Similar products were obtained by using [Fe^{III}(TPA)Br₂](ClO₄) (**2**), except that bromocyclohexane formed in lieu of chlorocyclohexane. Replacement of TBHP with MCPBA in the **1**-catalyzed reaction afforded the same products, but no ROOR'. All of the oxidation products of cyclohexane were accounted for in these reactions, as mass balance of substrate was observed in each case. The cyclohexanone formed may at least partially result from the oxidation of cyclohexanol produced in this system, since the **1**-catalyzed TBHP oxidation of cyclohexanol (in the absence of cyclohexane) resulted in the formation of 33 catalyst turnovers of cyclohexanone. The fate of **1** was followed by ¹H NMR spectroscopy during the TBHP/cyclohexane oxidation, and the appearance of the (μ -oxo)diiron(III) species [Fe₂(TPA)₂O(Cl)₂]²⁺ was observed. In an independent reaction this species was found to be catalytically inactive under the conditions of the experiment.

The nature of the C-H bond cleavage step was probed for these reactions. Significant kinetic isotope effects observed in a competitive oxidation of cyclohexane and cyclohexane-*d*₁₂ indicate that C-H bond breaking is at least partially rate determining.¹¹ When

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- (9) Abbreviations used: BPG = *N,N*-bis(2-pyridylmethyl)glycine; NTB = tris(2-benzimidazolylmethyl)amine; TPA = tris(2-pyridylmethyl)amine; OAc = acetate; TBHP = *tert*-butyl hydroperoxide; MCPAc = *m*-chloroperbenzoic acid; salen = *N,N'*-ethylenebis(salicylideneamine).
- (10) The synthesis of [Fe^{III}(TPA)Cl₂](ClO₄) (**1**) proceeded as follows: a 135-mg sample of Fe^{III}Cl₃·6H₂O was added to a warm methanolic solution of TPA·3HClO₄ (295 mg in 75 mL of MeOH), which upon 2-3 days of standing yielded yellow crystals of [Fe^{III}(TPA)Cl₂](ClO₄) (35% yield). A similar scheme, but with Fe(ClO₄)₃/NaBr replacing FeCl₃, was utilized for the preparation of **2**. **Caution!** In the solid state, perchlorate salts of metal complexes with organic ligands are potentially explosive; care should be exercised in handling these complexes. See: (a) Wolsey, W. C. *J. Chem. Educ.* **1973**, *50*, A335-A337. (b) Raymond, K. *Chem. Eng. News* **1983**, *61*, (Dec 5), 4.

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Table I. Product Distributions for the Iron-Catalyzed TBHP or MCPBA Oxidation of Cyclohexane in Acetonitrile under 1 atm of Argon at 25 °C

catalyst ^a	reacn time, h	products ^b				product ratio ^c	% total yield ^d
		CyOH	CyO	CyOC- <i>t</i> -Bu	other		
TBHP Oxidation							
1	2	15	12	8	1 (CyCl)	4	37
1 (+CH ₂ Br ₂) ^e	2	11	11	7	1 (CyCl) 7 (CyBr)	4	37
2	1	9	13	9	1 (CyBr)	3	36
2 (+Me ₂ S) ^f	1	0	0	8	0.1 (CyBr) 8 (Me ₂ SO)		17
3	36	4	4	1	1 (CyCl)	9	33
4	36	10	13	4	1 (CyBr)	6	37
5	36	0.5	0.8	0.2	0.6 (CyBr)	10	28
MCPBA Oxidation							
1	1	20	9		1 (CyCl)		26

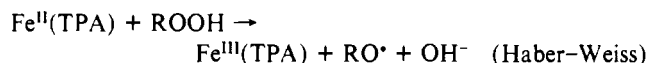
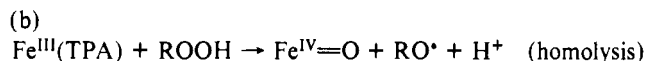
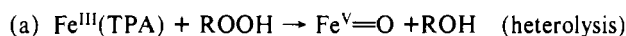
^a Catalysts: 1 = [Fe^{III}(TPA)Cl₂](ClO₄), 2 = [Fe^{III}(TPA)Br₂](ClO₄), 3 = [Fe^{III}(NTB)Cl₂](ClO₄), 4 = [Fe^{III}(NTB)Br₂](ClO₄), 5 = Fe^{III}(BPG)Br₂.

^b Moles of product per mole of catalyst. Abbreviations: CyOH = cyclohexanol, CyO = cyclohexanone, CyCl = chlorocyclohexane, CyBr = bromocyclohexane, CyOO-*t*-Bu = (*tert*-butylperoxy)cyclohexane, Me₂SO = dimethyl sulfoxide. ^c Product ratio = [CyOH + CyO + CyX (X = Cl, Br)]/CyOO-*t*-Bu. ^d Yield based on oxidant consumed. ^e Solvent = 90% acetonitrile/10% dibromomethane. ^f Substrate mixture = 7:1 mole ratio of cyclohexane to dimethyl sulfide.

the 1-catalyzed oxidation of cyclohexane was conducted in 90% CH₃CN/10% CH₂Br₂, significant amounts of bromocyclohexane were formed, demonstrating the involvement of radicals in this reaction.¹² These radicals appear to be trapped immediately since no bicyclohexyl is observed.¹³ Furthermore, a lack of nucleophilic trapping of the cyclohexyl moiety (by MeOH) discounts the intermediacy of free carbocations in this system.¹⁴

The alkyl radical may be generated by the reaction of alkane with a variety of species derived from the reaction of Fe(TPA) with TBHP, as illustrated by Scheme I. The dialkyl peroxide may arise from the coupling of R* and *t*-BuOO* in the termination step of a *t*-BuO*/*t*-BuOO* chain process. A similar mechanism was suggested by Kochi to explain the formation of 3-(*tert*-butylperoxy)cyclohexane in a cyclohexene/*t*-BuOOH/Mn^{III}(salen) reaction.¹⁵ Indeed, when adamantane was used as a substrate, the dialkyl peroxide formed showed a 3°/2° ratio¹⁶ identical with that displayed by *t*-BuO* abstraction.¹⁷ The *t*-BuO* radical may arise from mechanism b or c. But we consider the involvement of the Haber–Weiss reaction to be unlikely, since we have found that Fe^{II}(TPA)Cl₂ does not catalyze alkane functionalization by TBHP.

Scheme I



The alcohol/ketone products, on the other hand, appear to derive from mechanism a on the basis of the effect of the oxo-trapping agent, dimethyl sulfide. In the presence of a 7:1 mole ratio of cyclohexane and dimethyl sulfide, the 2-catalyzed TBHP oxidation of this substrate mixture resulted in production of the full complement of (*tert*-butylperoxy)cyclohexane, while no cyclohexanol or cyclohexanone was formed. In place of these

products, dimethyl sulfoxide was found. These results indicate that the species responsible for the hydroxylation of cyclohexane (but not ROOR' formation) is effectively trapped by the sulfide.¹⁸ Since the sulfide-to-sulfoxide transformation is effected by metal–oxo complexes,¹⁹ alcohol formation must also involve such a species, presumably derived from peroxide heterolysis (mechanism a). The formation of a high-valent iron–oxo intermediate in this system agrees with the 1-catalyzed MCPBA oxidation of cyclohexane conducted in the presence of H₂¹⁸O, which resulted in 10% incorporation of ¹⁸O in the alcohol product,²⁰ reminiscent of ¹⁸O exchange observed for high-valent metal–oxo intermediates in metal-catalyzed oxygenations.^{21,22} This proposal is consistent with the heterolytic cleavage of MCPBA by Fe^{III}(EDTA) reported by Bruce and co-workers.²³ Thus the [FeTPAX₂]⁺ catalyst appears capable of both homolysis and heterolysis of peroxides.

The stoichiometry of haloalkane formation is mechanistically quite interesting: for the FeTPA catalysts only 1 equiv of haloalkane is produced/molecule of catalyst. This stoichiometry is maintained even in the presence of excess Me₄N⁺Br⁻ (10–750 equiv) and implicates the metal center directly in the formation of the haloalkane. We propose that hydrogen abstraction by the Fe^V=O species generates [LFe^{IV}(X)OH...R*] in the solvent cage. The transient radical would then have the choice of combining with OH or X in the cage collapse, forming alcohol or haloalkane, respectively. The trapping of halide in the non-heme system is analogous to some porphyrin N-alkylations observed in the inactivation of cytochrome P-450 during the oxidation of organic substrates.²⁴

Table I demonstrates clearly that the metal center plays a role in determining the mode of peroxide cleavage and the rate of the reaction. The TPA catalysts, 1 and 2, react the fastest and

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generate a substantial amount of ROOR'. On the other hand, $[\text{Fe}^{\text{III}}(\text{NTB})\text{Cl}_2](\text{ClO}_4)$ (3) and $[\text{Fe}^{\text{III}}(\text{NTB})\text{Br}_2](\text{ClO}_4)$ (4) are much slower catalysts but produce smaller proportions of ROOR' compared to the $\text{Fe}^{\text{III}}(\text{TPA})$ species. Finally, the catalyst $\text{Fe}^{\text{III}}(\text{BPG})\text{Br}_2$ (5) proved to be the slowest and forms the smallest proportion of ROOR'. The rate of catalysis slows as the tripod ligand used becomes more electron-donating; however the catalyst becomes more selective for peroxide heterolysis. The greater basicity of the latter ligands may help stabilize the putative $\text{Fe}^{\text{V}}=\text{O}$ intermediate and provide the opportunity for characterizing this intermediate. Such efforts as well as investigations of the effect of catalyst nuclearity on the course of alkane functionalization are in progress.

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A New Ambient-Pressure Organic Superconductor, $\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$, with the Highest Transition Temperature Yet Observed (Inductive Onset $T_c = 11.6$ K, Resistive Onset = 12.5 K)

In this communication, we report the discovery of a new ambient-pressure organic superconductor $\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$, with the highest inductive onset transition temperature, $T_c = 11.6$ K (resistive onset = 12.5 K), reported to date in such systems. Cation-radical salts derived from the electron-donor molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or "ET", $\text{C}_{10}\text{H}_8\text{S}_8$) are of great interest because of the subtle interplay between a rich variety of structural types and the varied solid-state properties, most notably superconductivity, that they exhibit. The only structure-property correlations for ET materials that have been developed are those for the $\beta\text{-(ET)}_2\text{X}$, X = monovalent linear anion, superconductors.¹ In these salts, both the S...S distances in the corrugated-sheet² networks and T_c increase concomitantly with linear anion length, i.e., T_c of I_3^- (0.5 kbar), 8 K > T_c of AuI_2^- , 4.98 K > T_c of IBr_2^- , 2.8 K.¹ These findings, combined with the negative pressure dependence of T_c (ca. -1 K/kbar) in these materials,^{3,4} led to the suggestion that $\beta\text{-(ET)}_2\text{X}$ superconductors with even higher T_c 's might be realized by further increasing the conducting S...S contact distances inside the donor molecule lattice if isostructural salts with anions longer than I_3^- could be prepared.^{1,5} Thus, candidate anions such as $(\text{NC-Ag-CN})^-$, $(\text{I-Ag-I})^-$, and $(\text{NCS-Au-SCN})^-$ were suggested,¹ which, coupled with the introduction of the in situ crown ether-anion preparatory route,⁶ led to the synthesis of the first polymeric

anion ET conductors,^{6,7} viz., $(\text{ET})\text{Ag}_4(\text{CN})_3$, and $(\text{ET})_3\text{Ag}_{6.4}\text{I}_8$, respectively. These findings were necessary precursors to the discovery⁸ of ambient-pressure superconductivity in the first polymeric anion superconductor, $\kappa\text{-(ET)}_2\text{Cu}(\text{NCS})_2$, with the highest resistive T_c (10.4 K) in an organic superconductor at that time.⁸⁻¹⁰ However, this salt belongs to an entirely different structural class than the β -phase salts, viz., the so-called " κ -type" containing orthogonally arranged molecular dimers as opposed to a corrugated-sheet network.^{9,10a} Thus, complex polymeric anions offered a new route to the synthesis of ET superconductors.

The negative pressure derivative of T_c for $\kappa\text{-(ET)}_2\text{Cu}(\text{NCS})_2$ is even larger than that for $\beta\text{-(ET)}_2\text{X}$ salts, and, in fact, is the largest known (-3 to -3.6 K/kbar) for any superconductor.^{11,12} These results, and the recent analyses of structural features of other known κ -phase salts,^{13,14,25} again suggest that the expansion of the ET donor molecule network, perhaps attainable through the incorporation of even larger polymeric anions, is a viable approach to further raise T_c 's in κ -phase materials. Similar arguments based on the "effective volume" of ET have also been put forward by Saito et al.¹⁵

Our investigations based on these guidelines have now resulted in the discovery of a new superconducting cation-radical salt, $\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$, where $[\text{N}(\text{CN})_2]^-$ is the dicyanamide ion, which, although bent, is larger than the thiocyanate anion. The material is an ambient-pressure superconductor with $T_c = 11.6$ K (resistive onset = 12.5 K), which represents a new high for an organic superconductor. In this communication, we present its preparation, crystallographic and band electronic structure, ESR characteristics, and its superconducting transition.

Synthesis and ESR Study. Our interest in synthesizing cation-radical salts of ET with other bis(pseudohalo)cuprate(I) type of anions larger than $\text{Cu}(\text{NCS})_2^-$ prompted us to consider the dicyanamide ion, $(\text{NC-N-CN})^-$, as a possible pseudohalide. While there is no literature precedent for an anionic bis(dicyanamido)cuprate(I) species, we set out to synthesize it by analogy to the bis(thiocyanato)cuprate(I) salt.¹⁶ During the course of our initial synthetic studies, in addition to the desired bis(dicyanamido)cuprate(I) salt, we also prepared another complex $[\text{Cu}_2[\text{N}(\text{CN})_2]_3\text{Br}]^{2-}$, isolated as the tetraphenylphosphonium salt.¹⁷ Electrocrystallization of ET by use of this latter salt in 1,1,2-trichloroethane (TCE) under galvanostatic conditions (current

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- Reaction of CuBr with 2 equiv of $\text{Ph}_4\text{PN}(\text{CN})_2$ in refluxing acetonitrile resulted in a clear solution, which when cooled, yielded colorless crystals, mp 135-136 °C. Anal. Calcd for $(\text{Ph}_4\text{P})_2[\text{Cu}_2(\text{C}_2\text{N}_3)_2\text{Br}]\cdot\text{CH}_3\text{CN}$: C, 59.79; H, 3.83; N, 12.45; P, 5.52; Br, 7.12. Found: C, 59.85; H, 3.81; N, 12.55; P, 5.30; Br, 6.52.