The structural parameters, therefore, suggest to describe the molecule as containing a semiquinone and a quinone coordinated to the nickel ion, and charge compensation considerations require that the adduct is formulated as Ni(TCSQ)(TCQ). Whether these suggestions were shown to be false. In favor of the Ni(1) formulation are also the Ni-O distances of the chelate ring which are significantly practically independent of temperature in the range 300-20 K. The observed value of the effective magnetic moment of the complex is 2.97 μB, which is well with a system in which a nickel(1) is coupled with a radical.18 And nickel(II) complexes.21 The observed value of the effective magnetic moment is low for a nickel(II) complex, while it agrees well with a system in which a nickel(1) is coupled with a radical.18 By comparison the effective magnetic moment of the parent NiL(TCCat) corresponds to g = 2.27.

The two dioxygen moieties interact with each other as shown by the very short distances and the small angle between the planes.

planes19 which are stacked in a pseudoeclipsed configuration. A similar explanation was provided for justifying the stability of the HOMO of the semiquinone and the LUMO of the quinone. A MLCT character of this transition is also possible.

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planes19 which are stacked in a pseudoeclipsed configuration. A similar explanation was provided for justifying the stability of the HOMO of the semiquinone and the LUMO of the quinone. A MLCT character of this transition is also possible.

This compound sheds light on the mechanism of electron transfer in dioxolene molecules in the presence of metal ions. Indeed, although in the present case the two quinoid molecules have the ideal geometry for direct electron transfer, it is in fact the metal ion which acts as electron sink. We suggest that this is presumably due to the stabilization of the adduct determined by π back donation from the low valent metal to the quinone. Similar explanations were provided for justifying the stability of ruthenium(II) quinone complexes.21

It is tempting to speculate that the redox process in principle might proceed further with the transfer of the electron from nickel(I) to the quinone either via the t2g orbitals or via the semiquinone ligand.

Acknowledgment. The Italian Ministry of Public Education and the CNR are gratefully acknowledged for the financial support.

Supplementary Material Available: Tables of positional parameters and isotropic thermal factors, bond distances and angles, anisotropic thermal factors, and positional parameters of hydrogen atoms (8 pages); listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

Modeling the Dinuclear Sites of Iron Biomolecules: Synthesis and Properties of Fe₂O(OAc)₂Cl₂(bipy)₂ and Its Use as an Alkane Activation Catalyst

**John B. Vincent, John C. Huffman, and George Christou**

Department of Chemistry and the Molecular Structure Center, Indiana University

Bloomington, Indiana 47405

Qiaoying Li, Mark A. Nanny, and David N. Hendrickson

School of Chemical Sciences University of Illinois, Urbana, Illinois 61801

Raymond H. Fong and Richard H. Fish

Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

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The study of synthetic models containing the Fe₂O(O)₂(O₂CR)₃⁻⁺ core established in the oxygen carrier protein heme-ribyrin (Hr²) has received additional impetus and importance with the realization that such units may also be present in other dinuclear iron biomolecules. These include the purple acid phosphatases (PAP),² ribonucleotide reductases (RR),³ and methane monooxygenases (MMO).⁴ By using a variety of tridentate N-based ligands (L), a series of structures of the formula [Fe₂O(O₂CR)₃L₃] have been prepared,⁵ establishing the accessibility and stability of this unit outside a polypeptide environment. The tridentate ligands, however, block all terminal binding sites, precluding investigation of native substrate or substrate-analogue binding.⁶ Use of bidentate ligands to overcome this problem has led to dimerization of the [Fe₂O(O₂CR)₃]²⁺ unit to yield [Fe₂O(O₂CR)₃(bipy)₂]²⁺ containing products.⁷ However, we herein report a procedure employing 2,2'-bipyridine (bipy) that succeeds in overcoming the problem. The resulting complex possesses C1 ligands bound to the now available sixth coordination site.

To a stirred solution of [Fe₂O(OAc)₂(bipy)₂](ClO₄)₂ (0.60 g, 0.50 mmol) in MeCN was added bipy (0.69 g, 5.0 mmol) and NEt₄Cl.H₂O (1.48 g, 8.1 mmol). The dark green-brown solution was filtered and the filtrate was concentrated by rotary evaporation. The residue was washed with ether and collected to yield dark green crystals of [Fe₂O(OAc)₂Cl₂(bipy)₂](ClO₄)₂ (0.45 g, 56%).


(9) Vincent, J. B.; Huffman, J. C.; Christou, G., unpublished results. The structure of this complex is the same as its Mn analogue.
Communications to the Editor

probability level (hydrogen atoms are arbitrary size). Selected bond lengths (Å) and angles (deg) are as follows: Fe=Fe2, 3.151 (1); Fe1-013, 1.783 (4); Fe2-013, 1.787 (4); Fe2-C14, 2.156 (2); Fe1-05, 2.144 (4); Fe2-09, 2.009 (4); Fe2-011, 2.156 (4); Fe1-N14, 2.146 (5); Fe1-N25, 1.555 (5); Fe2-C14, 2.156 (2); Fel-05, 2.144 (4); Fe1-09, 2.009 (4); Fe2-07, 2.011 (4); Fe2-011, 2.156 (2); Fel-N14, 2.146 (5); Fel-N25, 2.204 (5); Fe2-N26, 2.155 (5); Fe2-N37, 2.212 (5); Fe1-03-Fe2, 123.9 (2); C13-Fel-Fe2-C14, 82.3 (2).

was left undisturbed for 18 h to produce dark green crystals of 1-MeCN in 66% yield.10 The procedure is summarized in eq 1.

\[
[Fe_2O_2(OAc)_2(bipy)]^2+ + 2bipy + 4Cl^- \rightarrow 2FeO(OAc)_2Cl_2(bipy) + 3AcO^-
\]

The formation of 1 can be considered as a cleavage of the \([Fe_2(O_2)]^+\) core into two \([Fe_2(O)]^-\) units, viz.

The structure1 of complex 1 is shown in Figure 1. Clearly evident is the \([Fe_2(O_2)]^+\) core present in methemerythrin (met-Hr) and the other model complexes, but terminal ligation -2JSl-S2) for two Fe** ions (S, K. The effective magnetic moment decreases gradually from 2.48 to 1.83 at 77 K. Values of 85.0, 78.5, and 68.0 G for the Fe1, Fe2, and Fe3 ions, respectively.17 Complex 1 displays only very broad, irreversible reduction peaks in the 0 to -0.5 V range (versus SCE) when studied by cyclic voltammetry in MeCN.18

Since the \([Fe_2(O_2)]^+\) unit may also be present in methane monoxygenase (MMO), biomimetic catalytic studies were conducted with complex 1 to investigate its ability to functionally the MMO enzyme in the hydroxylation of C2, C3, and cyclo-C6 hydrocarbons. Table I shows the results employing Bu'O0H as the monoxygen transfer reagent in MeCN at room temperature. Catalytic activity was observed in all cases, and, not surprisingly, the reactivity sequence follows the ease of C-H bond dissociation, i.e., C6 > C3 > C2. Since MMO utilizes molecular O2 as the monoxygen donor,3 we have also evaluated the activity of complex 1 in MeCN with O2 as the monoxygen transfer reagent in the presence of zinc powder and glacial acetic acid as electron and proton donors, respectively.19 Initial experiments with cyclohexane have yielded cyclohexanone, and no cyclohexanol, with a turnover number of 2.5.20 The activity of 1 is thus greater with Bu'O0H than with Zn/HOAc/O2, a result suggesting that formation of the active Fe-oxo species is more favorable in the former system or that the two systems generate different Fe-oxo intermediates.9

In summary, the synthetic analogue approach to Hr and other oxo-bridged Fe biomolecules has now been extended to the

Table I. Hydroxylation of C2, C3, and Cyclo-C6 Hydrocarbons with Complex 1 Using Bu'O0H as the Monoxygen Transfer Reagent

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Product %</th>
<th>% Bu'O0H consumed</th>
<th>Turnover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene</td>
<td>95</td>
<td>1.2 d</td>
<td>2</td>
</tr>
<tr>
<td>Propane</td>
<td>82</td>
<td>13 d</td>
<td>2</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>90</td>
<td>72 d</td>
<td>2</td>
</tr>
</tbody>
</table>

*Reactions with ethane and propane were carried out in a Parr Kinetic Apparatus at pressures of 250 and 90 psi, respectively, at ambient temperature in MeCN with a catalyst concentration of 7 \(10^{-4}\) M. The Bu'O0H/catalyst ratio was 50:1. The cyclohexane reactions were run in Schlenk flasks at ambient temperature with a substrate Bu'O0H/catalyst ratio of 1100:150:1 and a catalyst concentration of 7 \(10^{-4}\) M. Yield is based on Bu'O0H consumed (iodometric titration). *Oxidizing equivalents/mmol catalyst. +3 days. +2 days.

for \([Fe_2(O_2)]^+\) complexes (J = -117 to -121 cm\(^{-1}\)).4,6,16 The 57Fe Mossbauer spectrum of 1 at 120 K shows one quadrupole-split doublet with parameters characteristic of high-spin Fe\(^{II}\), isomer shift \(\delta = 0.366 (1)\) mm/s versus Fe metal at room temperature and quadrupole splitting \(\Delta E_Q = 1.795 (2)\) mm/s. The corresponding values of \(\delta (\Delta E_Q)\) for met-Hr are 0.59 (2.12) and 0.50 (2.04) at 4.2 and 77 K, respectively.16 Complex 1 displays only very broad, irreversible reduction peaks in the 0 to -0.5 V range (versus SCE) when studied by cyclic voltammetry in MeCN.18

Since the \([Fe_2(O_2)]^+\) unit may also be present in methane monoxygenase (MMO), biomimetic catalytic studies were conducted with complex 1 to investigate its ability to functionally the MMO enzyme in the hydroxylation of C2, C3, and cyclo-C6 hydrocarbons. Table I shows the results employing Bu'O0H as the monoxygen transfer reagent in MeCN at room temperature. Catalytic activity was observed in all cases, and, not surprisingly, the reactivity sequence follows the ease of C-H bond dissociation, i.e., C6 > C3 > C2. Since MMO utilizes molecular O2 as the monoxygen donor,3 we have also evaluated the activity of complex 1 in MeCN with O2 as the monoxygen transfer reagent in the presence of zinc powder and glacial acetic acid as electron and proton donors, respectively.19 Initial experiments with cyclohexane have yielded cyclohexanone, and no cyclohexanol, with a turnover number of 2.5.20 The activity of 1 is thus greater with Bu'O0H than with Zn/HOAc/O2, a result suggesting that formation of the active Fe-oxo species is more favorable in the former system or that the two systems generate different Fe-oxo intermediates.9

In summary, the synthetic analogue approach to Hr and other oxo-bridged Fe biomolecules has now been extended to the...
preparation of a substrate-analogue-bound form and its properties described. Ligand exchange reactions with NaN₃ are being investigated to prepare the described. Ligand exchange reactions with NaN₃-Hr. While met-C₁-Hr and met-N₃-Hr possess C₁- and N₃-binding sites on both metals. For example, RR may contain a preparation of a substrate-analogue-bound form and its properties possesses Fe-OPh (tyrosine) linkages. Also under investigation is characterized the PhCOy/N₃-analogue of complex CHE-8507748 (G.C.), NIH Grant HL13652 (D.N.H.), and the Energy Contract No. DE-AC03-76SF00098 (R.H.F.). We thank (02CPh)₂(N₃)₂(bipy)₂, corresponding to met-N₃-Hr.22

Note Added in Proof. We have now prepared and structurally characterized the PhCO₂O₇/N₃-analogue of complex I, via Fe₂O₇(O₂CHPh)₂(N₃)₂(bipy)₂, corresponding to met-N₃-Hr.22

Acknowledgment. This work was supported by NSF Grant CHE-8507748 (G.C.), NIH Grant HL13652 (D.N.H.), and the Electric Power Research Institute under U.S. Department of Energy Contract No. DE-AC03-76SF00098 (R.H.F.). We thank the Bloomington Academic Computing Service for a gift of computer time.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles (8 pages). Ordering information is given on any current masthead page.

A Novel Type of Selectivity in Anionotropic Rearrangements

Vittorio Lucchini*
Dipartimento di Scienze Ambientali, Università di Venezia Dorsoduro 2137, 30123 Venezia, Italy

Giorgio Modena* and Lucia Pasquato
Centro Meccanismi di Reazioni Organiche CNR Dipartimento di Chimica Organica, Università di Padova Via Marzolo 1, 35131 Padova, Italy Received April 18, 1988

Anionotropic rearrangements (i.e., those where the migrating group moves with its electron pair) prefer that geometric situation which maximizes orbital overlap in the transition state. When the rearrangement occurs under SN1 type conditions, the maximum overlap is obtained in the two configurations with zero dihedral angle between the vacant p-orbital and the migrating bond. In SN2 type rearrangements the maximum overlap between the migrating bond and the bond associated with the leaving group occurs for anti-periplanar or syn-periplanar geometries. The difference in configurational stability dictates a preference for the anti-periplanar rearrangement. In this communication we wish to report about a novel restriction imposed to an SN2 type anionotropic rearrangement by the particular molecular asymmetry.

During our investigations on the mechanistic details of the addition of sulfenyldihalides to olefins and acetylenes, we have been concerned with the identification and isolation of thiranium and thireinium ions, with their structure-stability relationships, their reactivity toward nucleophiles, and the alternative reaction paths, which are possible in long living ions (when the reactions with nucleophiles are suppressed).

Our search for stable ions led us to reconsider a rather old report on the reaction of arnesulfonyl chloride on (Z)-diter-butylethylene (1) which gives a stable adduct and on the E isomer (2) with formation of an adduct which rearranges and eliminates HCl. In our hands the addition of methanesulfonyl chloride to 1 in CD₂Cl₂ gives instantaneously and quantitatively the stable adduct 3 (as monitored by NMR spectroscopy), while the adduct from 2 is formed in about 1 h at room temperature and converts within 24 h into a series of decomposition products, which were not further investigated.

At first sight, the different stability of adducts 3 and 4 may be attributed to their conformational preference, as dictated by the steric repulsion of the two tert-butyl groups. In conformer 4 the methylthio and chloride groups are anti-periplanar, thus favoring the formation of a thiranion ion which may be supposed to mediate the rearrangement process. As a matter of fact, in a solvent such as sulfur dioxide, with strong solvolytic power toward saturated and unsaturated @-chlorosulfides, the adduct 3 is indefinitely stable, while the adduct 4 converts instantaneously to thiranium chloride 7, which then undergoes the slow rearrangement described below. This is however only an incomplete rationale for this process.

The hexachloroantimonate salts of thiranion ions 6 and 7 can be easily prepared through the action of methyldithio(sulfonium)hexachloroantimoniate (5) on 1 and 2. As their behavior demonstrates that the intermediacy of thiranion ion is a necessary but not a sufficient condition for the occurrence of the rearrangement process. In fact at room temperature in CH₂Cl₂ thiranion ion 6 is indefinitely stable, while thiranion ion 7 converts quantitatively in about 5 days to thietanium ion 8. The hexachloroantimoniates of ions 6, 7, and 8 can be isolated and fully characterized. The addition of chloride ion (from N-methylpyridinium chloride) to a solution of salt 8 in CH₂Cl₂ yields quantitatively the rearranged product 9.

At this stage of the investigation the other necessary condition can be tentatively proposed: only that anti-periplanar methide group can migrate, which belongs to the tert-butyl moiety syn to the S-methyl group. This condition is substantiated by the analysis of the rearrangement kinetics of the thiranion ions 10 and 11.

(10) For other observations of thietanium ions: (a) Trost, B. M.; Schinski, W. L.; Manz, I. J. B. J. Am. Chem. Soc. 1971, 93, 676.
(11) The stereochemistry of hexachloroantimoniate salts of 6, 7, 8, 10, 11, and 13 was ascertained through NOE analysis in the differential mode.