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molecular weight than Jones and Wilson,⁸ and this might explain why they incorrectly observed an apparent total area loss while Jones and Wilson did not. The erroneous area observation led Hogan and Jardetsky⁹ to incorrectly propose that the internal motion of the DNA double helix backbone is essentially stopped when ethidium intercalates. The results reported here and earlier⁸ for the DNA ³¹P resonance in the DNA–ethidium complex are consistent with significant motion of the phosphate in the complex and with intermediate or fast exchange (depending on interpretation of the line widths) of ethidium among sites.

The ³¹P NMR linewidth in DNA samples such as those used in these studies depends on correlation time through both dipole–dipole and chemical shift anisotropy relaxation.^{6b,6d,7a} There is probably also a contribution from chemical shift heterogeneity^{3c,6d,7a} which could increase with added ethidium. Addition of ethidium could cause lifetime broadening of DNA ³¹P NMR signals which, along with changes in correlation time, might account for the large observed changes in line width with temperature. Detailed studies to evaluate the importance of all of these factors with a broad range of DNA–ligand complexes are in progress. We have illustrated, however, that ³¹P spectra can be obtained, even at high molecular weights, for DNA and its intercalation complexes in solution. This technique should prove to be a valuable tool in studying DNA–ligand interactions.

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A Hexanuclear Iron–Sulfide–Thiolate Cluster: Assembly and Properties of $[\text{Fe}_6\text{S}_9(\text{S}-t\text{-C}_4\text{H}_9)_2]^{4-}$ Containing Three Types of Bridging Sulfur Atoms

G. Christou† and R. H. Holm*

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

M. Sabat and James A. Ibers*

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

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The synthetic and biological chemistry of iron–sulfide–thiolate clusters, until lately, has been confined to bi- and tetranuclear species having planar $[2\text{Fe}-2\text{S}]^{2+,+}$ and cubane-type $[4\text{Fe}-4\text{S}]^{3+,2+,+}$ core units, respectively, capable of existence in multiple oxidation levels.^{1–4} Variations on these structural themes, viz., core S/Se atom exchange⁵ and terminal thiolate ligand substitution with nonsulfur ligands,⁶ have been accomplished with the synthetic clusters $[\text{Fe}_n\text{S}_n(\text{SR})_4]^{2-}$ ($n = 2, 4$). However, only upon the very recent spectroscopic detection of protein 3-Fe sites,⁷ and crystallographic demonstration of the cyclic $[3\text{Fe}-3\text{S}]$ core structure

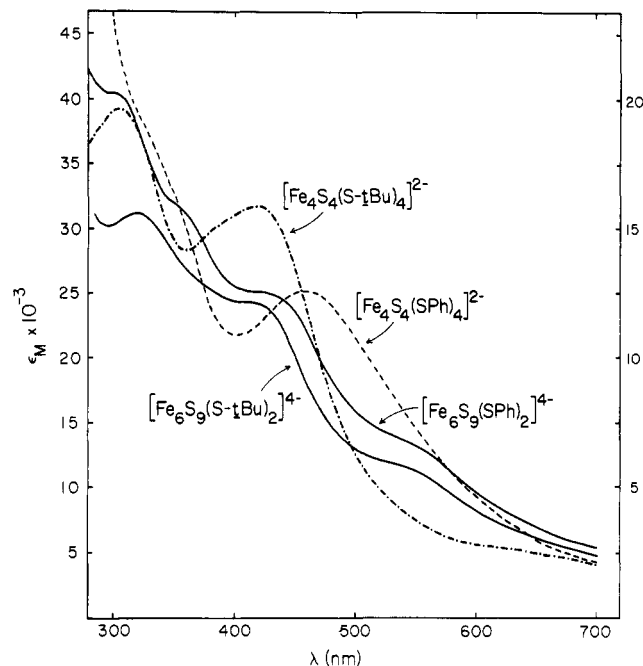
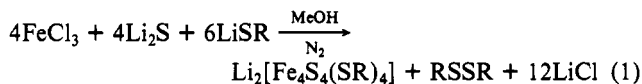


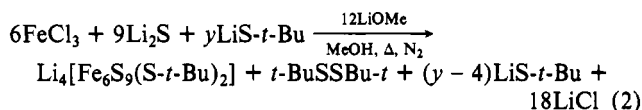
Figure 1. Absorption spectra in Me_2SO solutions: (a) authentic $[\text{Fe}_4\text{S}_4(\text{S}-t\text{-Bu})_4]^{2-}$, right-hand ϵ_M scale; (b) the product of reaction 2, $[\text{Fe}_6\text{S}_9(\text{S}-t\text{-Bu})_2]^{4-}$, after isolation as its $\text{Me}_3\text{NCH}_2\text{Ph}^+$ salt; (c) solution b + 2.0 equiv of PhSH , $[\text{Fe}_6\text{S}_9(\text{SPh})_2]^{4-}$; (d) solution b + 27.5 equiv of PhSH , $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$. Spectra b–d refer to left-hand ϵ_M scale, with $1.5 \times \epsilon_M$ plotted for spectrum d.

in *A. vinelandii* ferredoxin (Fd) I,⁸ has a fundamentally different Fe–S core structure emerged. These findings together with the possible occurrence of “unconventional” clusters $[\text{Fe}_n\text{S}_m(\text{S}-\text{Cys})_x]$ ($n, m \neq 2, 4$ and/or $x < n$) in other proteins (e.g., *D. africanus* Fd III⁹ and Mo–Fe–S protein,¹⁰ certain hydrogenases¹¹) have directed our attention toward the generation of heretofore unrecognized Fe/S/SR clusters.

While investigating the effect of reactant mole ratio variation on the standard cluster assembly system (eq 1),¹² it was observed



that in the presence of excess LiOMe an intensely colored filtrate persisted after precipitation of the sparingly soluble $n\text{-Bu}_4\text{N}^+$ salt of the $\text{R} = t\text{-Bu}$ cluster. From this filtrate a solid of composition $(\text{Me}_3\text{NCH}_2\text{Ph})_4[\text{Fe}_6\text{S}_9(\text{S}-t\text{-Bu})_2] \cdot \text{MeOH}$ (1), confirmed by crystallography, was isolated. Thereafter the reaction system (eq 2) was devised in order to improve yields by repressing tetramer formation. When conducted with the indicated stoichiometry



($y = 4\text{--}8$ equiv) a deep orange-brown solution is rapidly generated, which turns dark red brown upon stirring at $\sim 55^\circ\text{C}$ for 1–2 h. Precipitation of the product with $(\text{Me}_3\text{NCH}_2\text{Ph})\text{Br}$ followed by recrystallization from $\text{Me}_2\text{SO}/\text{MeOH}$ yields black prisms of 1 (55–70%), whose absorption spectrum (Figure 1) distinguishes

† U.K. Science Research Council/NATO Postdoctoral Fellow, 1980–1981.

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sites. However, judging from the fragmentation of $[\text{Fe}_6\text{S}_9(\text{S}-t\text{-Bu})_2]^{4-}$ by excess thiol it appears that any such site may not be securely identified by our usual applications of the core extrusion method.²³ Related behavior has been encountered in certain

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extrusions of protein $[\text{3Fe-3S}]$ core units, which did not remain intact under the experimental conditions employed.^{7a,24} Studies of Fe_6S_9 and other sulfur-rich clusters are continuing.

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Book Reviews*

Syntheses with Stable Isotopes of Carbon, Nitrogen, and Oxygen. By D. G. Ott (Los Alamos Scientific Laboratory). John Wiley & Sons, New York. 1981. viii + 224 pp. \$28.50.

Synthesis of organic compounds with isotopic labeling differs from conventional synthesis in that the cost of the isotope-enriched material makes it necessary to place the efficiency of its conversions above that of all other reactants. When this requirement is added to the necessity to work with rather small quantities, the result is often a preparative procedure substantially different from that used for ordinary compounds. This book is largely a collection of such procedures, gathered from the literature and presented with sufficient detail that they can be used directly in experimental work. It is a selective, rather than comprehensive, collection.

An introductory section of 15 pp gives general considerations, describes apparatus and techniques, and outlines the special features of designation and nomenclature applying to the subject. The six other chapters take up compounds by functional class. It is somewhat difficult to find what is included, because the table of contents gives no detail whatsoever, and there is no breakdown at the start of each chapter. One must either browse or use the index. The usefulness of this work goes beyond the specific preparations given, for they can serve as models for other preparations, but the indexing method makes it unnecessarily difficult to retrieve such information. There is, for example, no chapter devoted to hydrazine derivatives, and the index has no entry under "hydrazides", and one might easily overlook the fact that there is, indeed, a procedure given for an ^{15}N -labeled hydrazide (maleic hydrazide) in the book, in the chapter on heterocyclic compounds.

Reactive Intermediates. Volume I. Edited by R. A. Abramovitch. Plenum Press, New York and London. 1980. xiii + 522 pp. \$49.50.

This is the first volume in an open-ended series in which are presented reviews of "relatively new areas of the chemistry of reactive intermediates" at a detailed, specialized level. As the title implies, the topics may be drawn from all of chemistry, including biochemical, industrial, and atmospheric areas.

The five contributed chapters in the present volume show a marked bias toward organic chemistry. The growing field of atomic carbon is the subject of a short review by P. B. Shevlin, and is concerned with methods for generation of atomic carbon as well as its reactions. The adjacent chapter, Metal Atoms as Reactive Intermediates, by K. J. Klabunde, nicely complements the foregoing one. The subject has developed rapidly, and there are 238 references, starting with one to Michael Faraday in 1875, but mostly in the 1970's. The chapter on Aminium Radicals, by Y. L. Chow, deals with the derivatives of H_3N^+ , which are of importance in oxidation reactions and in photochemistry. Curt Wentrup is the author of a short chapter on a complex and intriguing subject, the formation and reactions of Arylmethylenes and Arylnitrenes in the gas phase. The last chapter, by D. S. Wulfman and B. Poling, again provides a complement, dealing with Metal-Salt-Catalyzed Carbenoids. One might be puzzled about how a substance, rather than a reaction, can be "catalyzed", but it soon becomes clear that the authors mean the formation and reactions of the enigmatic species conveniently called "carbenoids" that result from the interaction of diazoalkanes with many metal salts. It is a big and complex subject and the authors helpfully begin their review of it with a somewhat philosophical analysis of meaning of the terms "carbene" and "carbenoid" and their relation to the interpretation of experimental data. The size of the authors' task may be estimated from the fact they have digested the

material from 741 references and presented it critically.

The reviews cover the literature through 1977, and there is a subject index of moderate dimensions.

Versatility of Proteins. Edited by C. H. Li. Academic Press, New York. 1979. xiv + 465 pp. \$22.00.

This is a collection of the invited papers presented at the International Symposium on Proteins held in Taipei in 1978. There are 26 papers plus an introductory address by Hans Neurath. The papers are grouped under the headings Techniques of Protein Chemistry, Enzymes, Protein-Protein Interactions, and Regulatory Proteins. The papers are reproduced from typescripts of an interesting variety of fonts but are clear and well-illustrated. Usefulness of the book is enhanced by a subject index.

Kirk-Othmer Encyclopedia of Chemical Technology. Third Edition. Volume 14. Laminated Wood-based Composites to Mass Transfer. Edited by M. Grayson and D. Eckroth. John Wiley & Sons, New York. 1981. xxvi + 981 pp. \$145.00.

This would be an important volume if for no other reason than it includes the elements lead, lithium, magnesium, and manganese and their compounds. However, it also includes valuable reviews on lasers, lignin, lignite, liquid crystals, lubricants, maleic and malonic acids and their derivatives, etc. Readers of reviews of previous volumes will know that the content of the series maintains a high standard in both presentation and scientific approach. This volume is no exception, and chemists who are not engaged in applied chemistry will find themselves surprisingly well served with the balanced selection of material.

Correlation Analysis in Chemistry: Recent Advances. Edited by N. B. Chapman and J. Shorter (The University of Hull, England). Plenum Press, New York. 1978. xiii + 546 pp. \$49.50.

"Correlation analysis" is a discipline which has its origins in linear free energy relationships (LFER) but presently encompasses biochemical quantitative structure-activity relationships (QSAR) as well as pattern recognition. This book is a sequel to the earlier monograph "Advances in Linear Free Energy Relationships" by the authors.

The book consists of an authors' introduction followed by ten amply footnoted chapters which are cross-referenced and comprise a coherent presentation. They are: Chapter 1. Linear Free Energy Relationships as Tools for Investigating Chemical Similarity—Theory and Practice (S. Wold and M. Sjöström); Chapter 2. The Bronsted Equation—Its First Half-Century (R. P. Bell); Chapter 3. Theoretical Models for Interpreting Linear Correlations in Organic Chemistry (M. Godfrey); Chapter 4. Multiparameter Extensions of the Hammett Equation (J. Shorter); Chapter 5. Applications of Linear Free Energy Relationships to Polycyclic Arenes and to Heterocyclic Compounds (M. Charton); Chapter 6. Substituent Effects in Olefinic Systems (G. P. Ford, A. R. Katritzky, and R. D. Topsom); Chapter 7. The Correlation of Nucleophilicity (C. Duboc); Chapter 8. Correlation of NMR Chemical Shifts with Hammett Sigma Values and Analogous Parameters (D. F. Ewing); Chapter 9. Recent Advances in Biochemical QSAR (C. Hansch); Chapter 10. A Critical Compilation of Substituent Constants (O. Exner).

This book is highly recommended for the personal libraries of scientists including chemists, biologists, pharmacologists, and toxicologists. For those not immediately conversant in this area, a perusal of the appropriate section of an advanced organic chemistry textbook will allow entry into the present volume. This reviewer's one small gripe deals with the order of presentation of topics. The organization follows a logical one beginning with the theoretical justification of the approach, followed by theoretical chemistry, experimental organic chemistry, then biochemical

* Unsigned book reviews are by the Book Review Editor.