

If ferrocene is codeposited with $\text{Co}_2(\text{CO})_8$ in NaX and a 3W plasma treatment is applied a broad SENMR signal at 228 MHz indicative of hcp cobalt is observed. Thermal treatment of similar samples yields fcc cobalt particles. These data suggest that not only does the microwave plasma route affect the type of particles produced but that coadsorption procedures also influence the structure of the metal particle that is formed.

Further evidence of the usefulness of coadsorption methods come from studies of coadsorbed $\text{Co}_2(\text{CO})_8$ and $\text{Fe}_2(\text{CO})_9$. The SENMR spectrum of these two metal carbonyls in zeolite NaX after microwave discharge decomposition of the carbonyls is shown in Figure 1. The signal at 228 MHz is due to hcp Co, and the signal at 250 MHz is assigned to a Co (5 atom% Fe) alloy. The relaxation time of this alloy is markedly different than all other samples we have studied. These data suggest that new alloys can be prepared by coadsorption of metal carbonyls into zeolites followed by microwave discharge decomposition.

The superparamagnetic cobalt, thermally produced fcc cobalt, and coadsorbed hcp cobalt particles show significant differences in their ability to crack, isomerize, and hydrogenate cyclopropane and such will be the focus of another report.¹³ Most importantly, we have shown here that the SENMR method is a very sensitive probe of relative metal particle size and of structural parameters which are difficult to determine for cobalt by other methods such as STEM, X-ray diffraction, Mössbauer spectroscopy, and ferromagnetic resonance. In addition, we have realized that synthetic modifications of plasma techniques for catalyst preparation can yield unique metal particles. Alloys and anchored¹⁴ bimetallic complexes are now under investigation in our laboratory¹⁵ as is the use of SENMR in heterogeneous catalysis.

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Ene Diimidazoles: Ligands for Biomimetic Chemistry

Teddy G. Traylor,* Kenneth W. Hill, and Zong-Qiang Tian

Department of Chemistry D-006
University of California, San Diego
La Jolla, California 92093

Arnold L. Rheingold*

Department of Chemistry, University of Delaware
Newark, Delaware 19716

Jack Peisach* and John McCracken

Departments of Molecular Pharmacology
Physiology and Biophysics
Albert Einstein College of Medicine
Bronx, New York 10461

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The preparation of model compounds related to nonheme metalloproteins has attracted much recent attention.¹⁻⁸ In an

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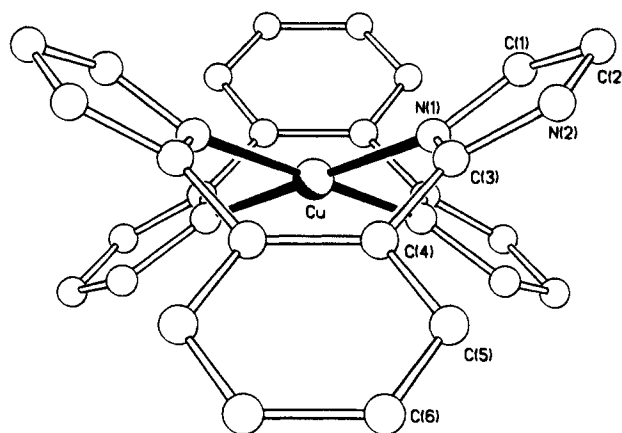
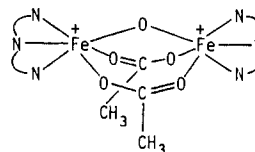
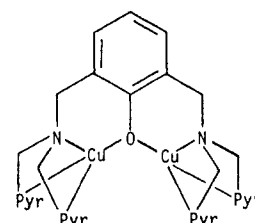


Figure 1. Cation structure for **2**: Cu-N(1), 1.996 (4); N(1)-C(1), 1.368 (6); C(1)-C(2), 1.349 (7); C(2)-N(2), 1.372 (7); C(3)-C(4), 1.469 (7) Å; N(1)-Cu-N(1a), 180; N(1)-Cu-N(1b), 90.6 (2); N(1)-Cu-N(1c), 89.4 (2)°. Two of four molecules of H_2O (not shown) form long axial bonds to Cu (Cu-O(4) = 2.624 (3) Å). A different view of the cation drawn with 40% thermal ellipsoids is available as Supplementary Material.

effort to duplicate the juxtapositions of ligands for iron and copper in biomolecules, several types of multidentate ligands have been prepared. The tridentate ligands such as tris(imidazolyl)phosphine,² tris(imidazolyl)methane,¹ and tris(pyrazolyl)borate⁹ have been used in elegant model compounds for carbonic anhydrase^{1,2} and hemerythrin,^{3,4,10a} the latter illustrated below. Further re-



duction in the number of degrees of freedom in these complex ligands has been provided by connecting the two tripod ligands through covalent chain to produce excellent model compounds⁵⁻⁷ for hemocyanin.^{10b,11}



Hemocyanin Model Compound⁵

We present a method for further reducing the degrees of freedom and increasing rigidity of multidentate ligands by in-

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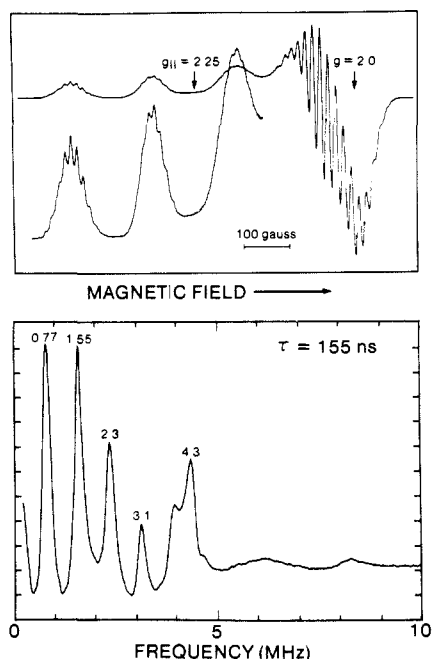
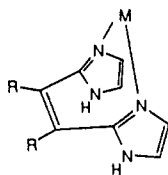
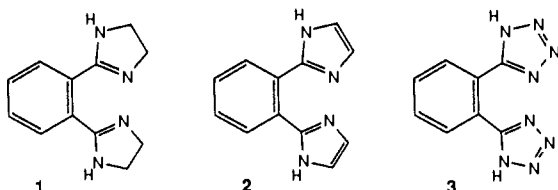


Figure 2. CW-EPR (upper) and stimulated ESEEM (lower) spectra of copper(II) bis(1,2-di-2-imidazole benzene) in a toluene/methanol glass. CW-EPR data were collected under the following conditions: microwave frequency, 9.097 GHz; microwave power, 5 mW; sample temperature, 77 K; field modulation, 5 G at 100 kHz. Pulsed EPR data were collected by using a stimulated echo (90- τ -90-T-90) sequence under the following conditions: microwave frequency, 8.8169 GHz; field strength, 3024 G; microwave pulse power, 50 W (20 μ s); sample temperature, 4.2 K, τ value, 155 ns.

incorporating the ligand groups such as imidazoles in bicyclic systems. This method requires a new type of ligand, here called ene diimidazole, which, through the formation of a strain-free seven-membered ring, holds the ligated metal about 2 Å away from the "ene" plane. This geometry is particularly advantageous for holding several imidazole ligands at fixed relative positions.



As the first examples of this approach we prepared compounds **1**, **2**, and **3**.^{12,13} All form crystalline complexes with metal salts such as Cu(ClO₄)₂, Ni(ClO₄)₂, Cr(ClO₄)₂, etc.



The structure of the bis complex of **2** with Cu(ClO₄)₂(H₂O)₄, has been determined by X-ray crystallography¹⁴ and is shown in

(12) (a) Compounds **1** and **3** were prepared by heating phthalonitrile with ethylene diamine^{12b} and NaN₃,^{12c} respectively. Oxidation of **1** with BaMnO₄^{12d} produced **2** in good yield: mp 250–252 °C; ¹H NMR (300 MHz, CD₃OD) δ 7.14 (s, 4 H), 7.52 (m, 2 H), 7.85 (m, 2 H). (b) Oxley, P.; Short, W. F. *J. Chem. Soc.* **1947**, 497. (c) Scheiner, P.; Stockel, D.; Cruset, D.; Noto, R. *J. Org. Chem.* **1972**, *37*, 4207. (d) Hughey, J. L., IV; Knapp, S.; Schugar, H. *Synthesis* **1980**, 489.

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Scheme 1

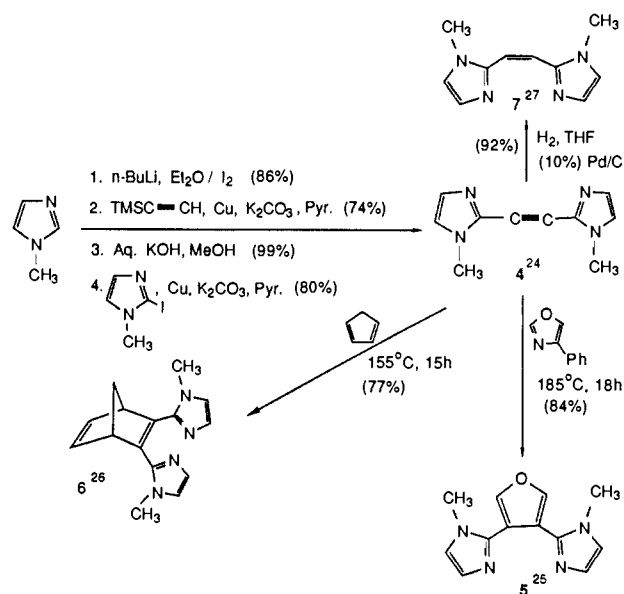


Figure 1. The geometry is in all respects very similar to those of tetraimidazole complexes of copper(II) salts.¹⁵

Continuous wave (CW) EPR and electron spin echo envelope modulation (ESEEM) spectra¹⁶ of frozen solution of the complex in toluene/methanol glass are shown in Figure 2. A detailed analysis of the ESEEM data using the density matrix formalism of Mims,¹⁷ together with the angle-selection scheme developed by Hurst et al.,¹⁸ yielded nuclear quadrupole interaction parameters for the remote, protonated nitrogen of the imidazole ligands that are identical with those determined by NQR studies on imidazole powders.¹⁹ In addition, the Fermi contact interaction and dipole-dipole distance between Cu(II) and the remote ¹⁴N nuclei were found to be identical with those determined previously for Cu^{II}(imid)₄.¹⁶ Finally, the appearance of strong "combination" lines at 2.3 and 3.1 MHz in the ESEEM spectra²⁰ (Figure 2) and the number of nitrogen shf lines found for the low field CW-EPR peak at $g_{||}$ are indicative of four equatorially bound imidazole ligands.²¹ These findings demonstrate that the proposed structure (Figure 1) is stable in frozen solution, that it has the magnetic properties of Cu^{II}(imid)₄, and that the binding of metal to ligands is not strained.

Other ene-diimidazole complexes have been prepared by well-known coupling²² and Diels-Alder reactions.²³ Compounds

(14) Crystal data for **2**: [C₂₄H₁₆Cu][ClO₄]₂·4H₂O, monoclinic, C2/m, $a = 11.520$ (2) Å, $b = 19.517$ (3) Å, $c = 7.131$ (1) Å, $\beta = 105.24$ (2)°, $V = 1546.9$ (5) Å³, $Z = 2$, D_{calc} = 1.372 g cm⁻³, μ (Mo K α) = 9.37 cm⁻¹. By using a purple crystal (0.28 × 0.42 × 0.42 mm), 1523 data were collected (Nicolet R3m/ μ , Mo K α , 23 °C, $4^\circ < 2\theta < 50^\circ$) and 1405 were independent ($R_{\text{int}} = 1.31\%$) and empirically corrected for absorption ($T_{\text{max}}/T_{\text{min}} = 1.19$ min). At the 5 σ (F_o) level, 1120 data were considered observed. The structure was solved intuitively by placing Cu at the origin. Four molecules of H₂O co-crystallize in the lattice for each Cu cation. With all non-hydrogen atoms anisotropic, and all hydrogen atoms (except those of the H₂O molecules) idealized, isotropic contributions are as follows: $R(F) = 4.62$, $R(wF) = 5.14$, $\text{GOF} = 1.414$, Δ/σ (max) = 0.03, $\Delta(\rho) = 0.59$ e Å⁻³, $N_o/N_v = 10.0$. SHELXTL (5.1) software was used for all calculations Sheldrick, G. W., distributed by Nicolet XRD, Madison, WI).

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5, 6, and 7 (see Scheme I) form stable complexes with $\text{Cu}(\text{ClO}_4)_2$, which have not yet been characterized.²⁸ The complexes formed and the successful implementation of Diels-Alder chemistry of the acetylene diimidazole demonstrate the viability of this approach. Further elaboration of these systems to structurally fixed multiple imidazole groups, e.g., through Diels-Alder reaction of 4 with 5, and to imidazole combinations with other ligands through Diels-Alder and carbene chemistry is underway.

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Supplementary Material Available: Listings of atomic coordinates and isotropic thermal parameters (Table I), bond lengths (Table II), bond angles (Table III), anisotropic thermal parameters (Table IV), H-atom coordinates and isotropic thermal parameters (Table V), and magnetic properties (Table VII) and an additional view of the crystal structure (4 pages); listing of observed and calculated structure factors (Table VI) (7 pages). Ordering information is given on any current masthead page.

(24) ^1H NMR (300 MHz, CDCl_3) δ 3.78 (s, 6 H), 6.95 (s, 2 H), 7.08 (s, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 33.66, 81.82, 122.10, 129.94, 131.29; MS (70 eV), m/z (rel intensity) 186.0905 (M^+ , 74) (calcd for $\text{C}_{10}\text{H}_{10}\text{N}_4$ 186.0905).

(25) ^1H NMR (300 MHz, CDCl_3) δ 3.19 (s, 6 H), 6.87 (s, 2 H), 7.03 (s, 2 H), 7.78 (s, 2 H); ^{13}C NMR (75 MHz, CD_3OD) δ 33.97, 116.25, 124.14, 127.78, 140.47, 154.64; MS (70 eV), m/z (rel intensity) 228.101 (calcd for $\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}$ 228.0978).

(26) ^1H NMR (300 MHz, CDCl_3) δ 2.11 (d, $J = 6.5$ Hz, 1 H), 2.44 (d, $J = 6.5$ Hz, 1 H), 2.84 (s, 6 H), 4.06 (br s, 2 H), 6.77 (s, 2 H), 7.00 (m, 2 H), 7.07 (s, 2 H).

(27) ^1H NMR (300 MHz, CDCl_3) δ 3.34 (s, 6 H), 6.61 (s, 2 H), 6.80 (s, 2 H), 7.03 (s, 2 H).

(28) Preliminary crystal structure data indicates that 5 forms a complex with $\text{Cu}(\text{II})$ in which the two furan rings lie on the same side of Cu and parallel to each other, in contrast to the complex of 2.

The $[\text{MoFe}_6\text{S}_6(\text{CO})_{16}]^{2-}$ Ion: A New Model for the FeMo-Cofactor of Nitrogenase

Patricia A. Eldredge,¹ Robert F. Bryan, Ekkehard Sinn, and Bruce A. Averill*

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

Received February 18, 1988

The iron-molybdenum cofactor (FeMo-co) of nitrogenase² consists of a small dissociable cluster of approximate composition $\text{MoFe}_{6-7}\text{S}_{8-10}$ ^{2,3} that appears to constitute the site at which dinitrogen is reduced.⁴ Despite its importance and the application of a host of spectroscopic techniques,^{3d,5-9} the structure of FeMo-co

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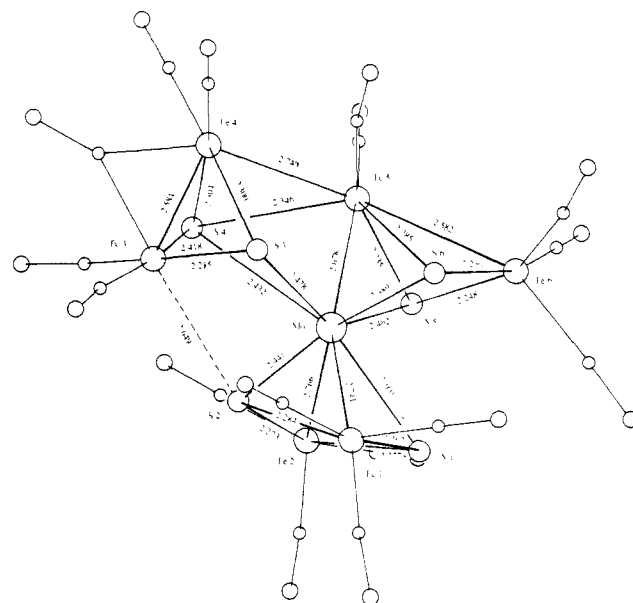


Figure 1. A ball and stick drawing of the structure of the $[\text{MoFe}_6\text{S}_6(\text{CO})_{16}]^{2-}$ ion, illustrating the heavy atom numbering scheme and showing selected distances.

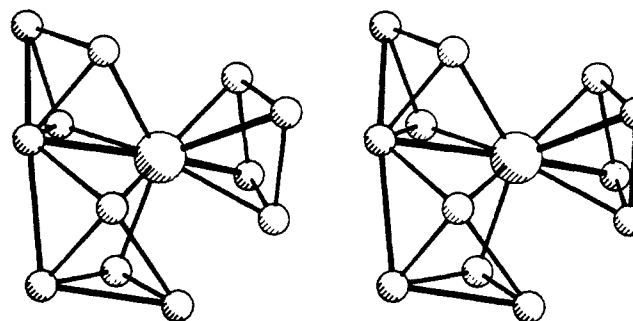


Figure 2. Stereoview of the MoFe_6S_6 core of the $[\text{MoFe}_6\text{S}_6(\text{CO})_{16}]^{2-}$ ion

remains one of the major unresolved problems in contemporary bioinorganic chemistry. None of the many attempts to produce synthetic analogues¹⁰ of FeMo-co has resulted in the preparatio

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