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**The Synthesis and Characterization of New Iron Coordination Complexes
Utilizing an Asymmetric Coordinating Chelate Ligand**

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P6 The Synthesis and Characterization of New Iron Coordination Complexes Utilizing an Asymmetric Coordinating Chelate Ligand

CONTRACT INFORMATION

Contract Number	FEW0003
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Period of Performance	Open

OBJECTIVES

We are investigating the structure/activity relationships of the bacterial enzyme methane monooxygenase, which catalyzes the specific oxidation of methane to methanol. We then utilize this information to design and synthesize inorganic coordination complexes that mimic the function of the native enzyme but are more robust and have higher catalytic site density. We envision these catalysts to be useful in process catalytic reactors in the conversion of methane in natural gas to liquid methanol.

BACKGROUND INFORMATION

The catalytic oxidation of light hydrocarbons, especially methane derived from natural gas, is an important research area attracting considerable attention. The potential for methane processing will depend on the development of catalyzed routes directly converting methane to higher valued products (heavier

hydrocarbons, olefins, and alcohols). However, methane is chemically quite inert and has not proved easy to convert to liquid hydrocarbons. Modeling studies suggest that a theoretical ceiling in overall yield exists as the rate constant of a catalyst is increased¹. The rate constant of the catalyst must be sufficient to overwhelm the non-specific gas phase reactions but low enough to prevent over oxidation. In theory this limits the yield to about 35%. As a result, no technologies are currently available to process methane economically.

It is well-known that a select group of aerobic soil/water bacteria called methanotrophs can efficiently and selectively utilize methane as the sole source of their energy and carbon for cellular growth.² The first reaction in this metabolic pathway is catalyzed by the enzyme methane monooxygenase (MMO) forming methanol. Methanol is a technologically important product from this partial oxidation of methane since it can be easily converted to liquid hydrocarbon transportation fuels, used directly as a liquid fuel itself, or serve as a feedstock for fine chemicals production.

Microorganisms can produce MMO in two distinct forms: a membrane-bound particulate form or a discrete soluble form. The soluble form contains an oxygenase subunit, whose active site includes a binuclear iron center.^{3,4,5} The X-ray crystal structure of the oxidized form has recently been determined,⁶ and reveals a carboxylato and hydroxo bridging system between the two iron atoms. There is also a semi-bridging carboxylate which leads to coordination number asymmetry for the two metals (Figure 1). The remaining ligands are derived from adjacent amino acid residues and the Fe-Fe distance is 3.4 Å. Recent Mössbauer and EPR studies on the reduced form of soluble MMO⁷ have demonstrated that coordination number asymmetry occurs about the two metal centers similar to that found in the related binuclear iron oxygen transport enzyme, hemerythrin. X-ray crystallography has clearly shown a 5,6 coordination sphere about the iron atoms in hemerythrin and reaction studies reveal that oxygen binding occurs at the five coordinate iron.⁸

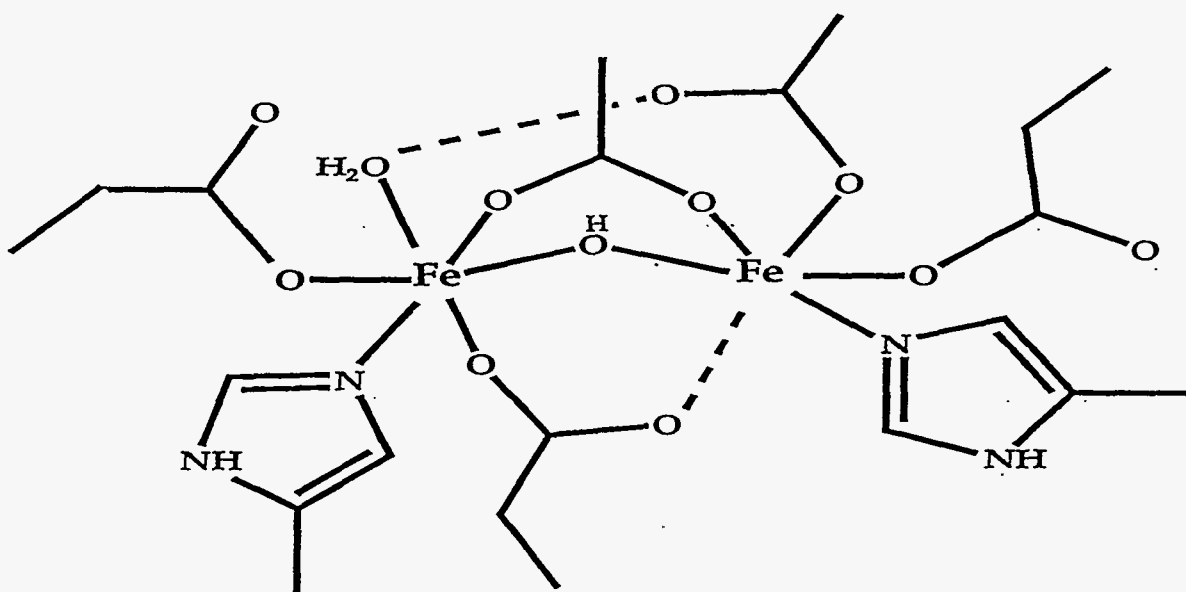


Figure 1. Schematic representation of MMO active site.

It is speculated that the active site of particulate form of the enzyme is similar to the soluble form, except that the coordinated metal is copper. We have previously reported on the synthesis of asymmetrically coordinated copper complexes and their ability to catalyze the oxidation of cyclohexane to a mixture of cyclohexanol and cyclohexanone^{9,10}.

PROJECT DESCRIPTION

Our work centers on the synthesis and characterization of inorganic/organic chemical models of the active site of MMO. We have focused on the synthesis of an asymmetrical, binuclear chelating ligand possessing an alkoxo group that can serve as a bridging ligand. The advantage of such a ligand system is twofold: (a) metal complexes of an asymmetric binucleating ligand will provide coordinative unsaturation at only one metal resulting in focused substrate reactivity at that site and (b) a single ligand with binuclear coordination provides a more robust environment for metal oxidation state changes and accompanying chemical reactivity.

We report here the synthesis of new prototype asymmetric iron complexes, and characterization of oxidized chelate compounds. This work provides the first proof-of-concept for the formation of binuclear iron complexes with different coordination

at each metal ion. Such complexes are relevant to the development of model systems for the active site of MMO.

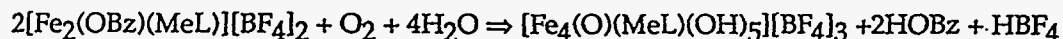
RESULTS

Synthesis of the chelating ligand HMeL obtained by a five step procedure has been described previously.¹⁰ When HMeL was allowed to react with iron(II)tetrafluoroborate and sodium benzoate in methanol under anaerobic conditions, yellow crystals of $[\text{Fe}_2(\text{OBz})(\text{MeL})][\text{BF}_4]_2$ (1) were deposited in 65% yield. In the crystal structure (Figure 2) one iron is five coordinate (distorted trigonal bipyramidal) utilizing three nitrogen donor atoms and an alkoxy oxygen atom from the chelate and an oxygen atom from a bridging benzoate group. The other iron atom is six coordinate (distorted octahedral) with nitrogen and oxygen donation from chelate and benzoate moieties and an additional donation from two methanol solvent molecules making a 5,6 coordinate pair. The ease of solvent removal (confirmed by elemental analysis) indicates that the molecule may be more appropriately considered 5,4 coordinate system. Attempts to demonstrate chemical reactivity at the coordinatively unsaturated iron center have led to crystalline adducts with thiocyanate and phosphate. These materials have been characterized by X-ray crystallography, and verify that exogenous ligand attachment occurs at the lower coordinated iron center.

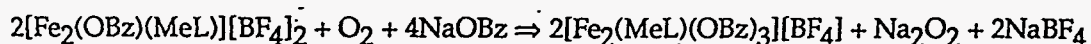
The study of the reaction of binuclear iron(II) complexes with molecular oxygen is essential in the development of model compounds. The oxidation of complex (1) with molecular oxygen in acetonitrile was found to conform to a 1:1 stoichiometry. When an acetonitrile solution of (1) is exposed to air and subsequently layered with ether a crystalline material $[\text{Fe}_4(\text{O})(\text{MeL})(\text{OH})_5][\text{BF}_4]_3$ (2) is formed (Figure 3). The structure reveals a tetrameric iron(III) unit supported by an alkoxy oxygen (intra-molecular) as well as oxo and hydroxo (inter-molecular) bridges, the bridging benzoate moiety has been eliminated. In addition there is a terminal hydroxy anion bound to two of the iron centers making all iron atoms six coordinate. It has not been determined at this point if the oxygen bridges are formed from molecular oxygen, however, in the oxidation of other binuclear iron(II) complexes the oxo bridges have been shown to be derived from molecular oxygen.¹¹ The lack of a benzoate bridge in this structure led to the investigation of the oxidation behavior in the presence of excess sodium benzoate. When an acetonitrile solution of (1) and five equivalents of sodium benzoate is exposed to air, single crystals of $[\text{Fe}_2(\text{OBz})_3(\text{MeL})][\text{BF}_4]$ (3) were formed in 55% yield (Figure 4). In this case the binuclear system remains intact supported by an endogenous alkoxy and two exogenous bidentate benzoate bridges. There is also a monodentate benzoate bound to one iron atom again making a 6,6

coordinate pair of metals. The crystal structure difference map shows only one tetrafluoroborate anion in the unit cell leading to Fe(II)/Fe(III) oxidation state assignment for charge balance. In both of the above oxidation structures the central core of the ligand remains intact and the metal:ligand ratio remains constant.

The importance of the formation of the oxidized binuclear complex (3) can be understood by considering the balanced reactions with and without excess benzoate. For the reaction of complex (1) without additional benzoate in acetonitrile we have:



In contrast, a balanced reaction in the presence of excess benzoate to yield complex (3) can be represented by:



In the first reaction; the atoms of molecular oxygen (as well as some from adventitious water) are incorporated into the tetranuclear complex (2). In the second reaction the reduced oxygen species does not become part of the oxidized molecule, being represented as Na_2O_2 for the purpose of chemical balance. Thus, by inhibiting the formation of higher nuclearity complexes, the reduced oxygen species is available to participate in other reaction chemistry. The identity of the reduced species and fate of molecular oxygen is currently under investigation.

CONCLUSIONS

A binuclear, unsymmetric coordinating ligand that is an effective metal chelator has been designed and synthesized. The new ligand has been shown to react readily with iron(II)/(III) forming a variety of coordination complexes. The binuclear complexes are of significant interest since they represent proof-of-principle for the development of coordinatively asymmetric, binuclear metal chelate compounds. Although this structural type of chelator now appears to be common in biological systems, it has not been previously described for inorganic coordination chemistry. The isolation of oxidation products will be helpful in establishing reaction mechanism(s) of these complexes with molecular oxygen. It is expected that this ligand and derivatives of it will play an important role in the development of bioinorganic complexes that aim to mimic enzyme active sites that function by substrate interaction at only one metal site of a multimetal active site.

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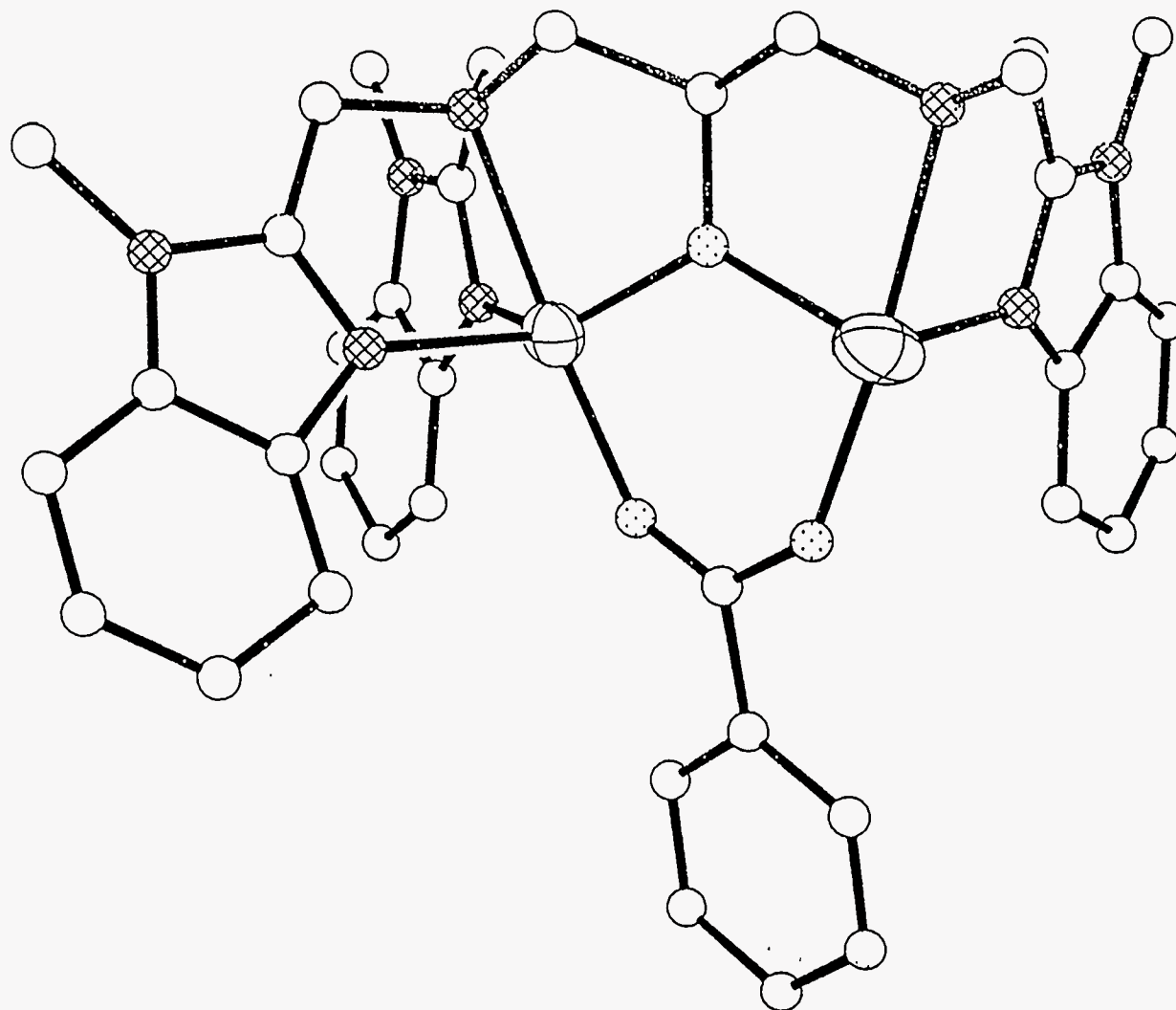


Figure 2. Cation of $[\text{Fe}_2(\text{OBz})(\text{MeL})][\text{BF}_4]_2$ (1). Bound solvent and hydrogen atoms omitted for clarity. Thermal ellipsoids-Iron; Open circles-Carbon; Dotted circles-Oxygen; Cross-hatched circles-Nitrogen.

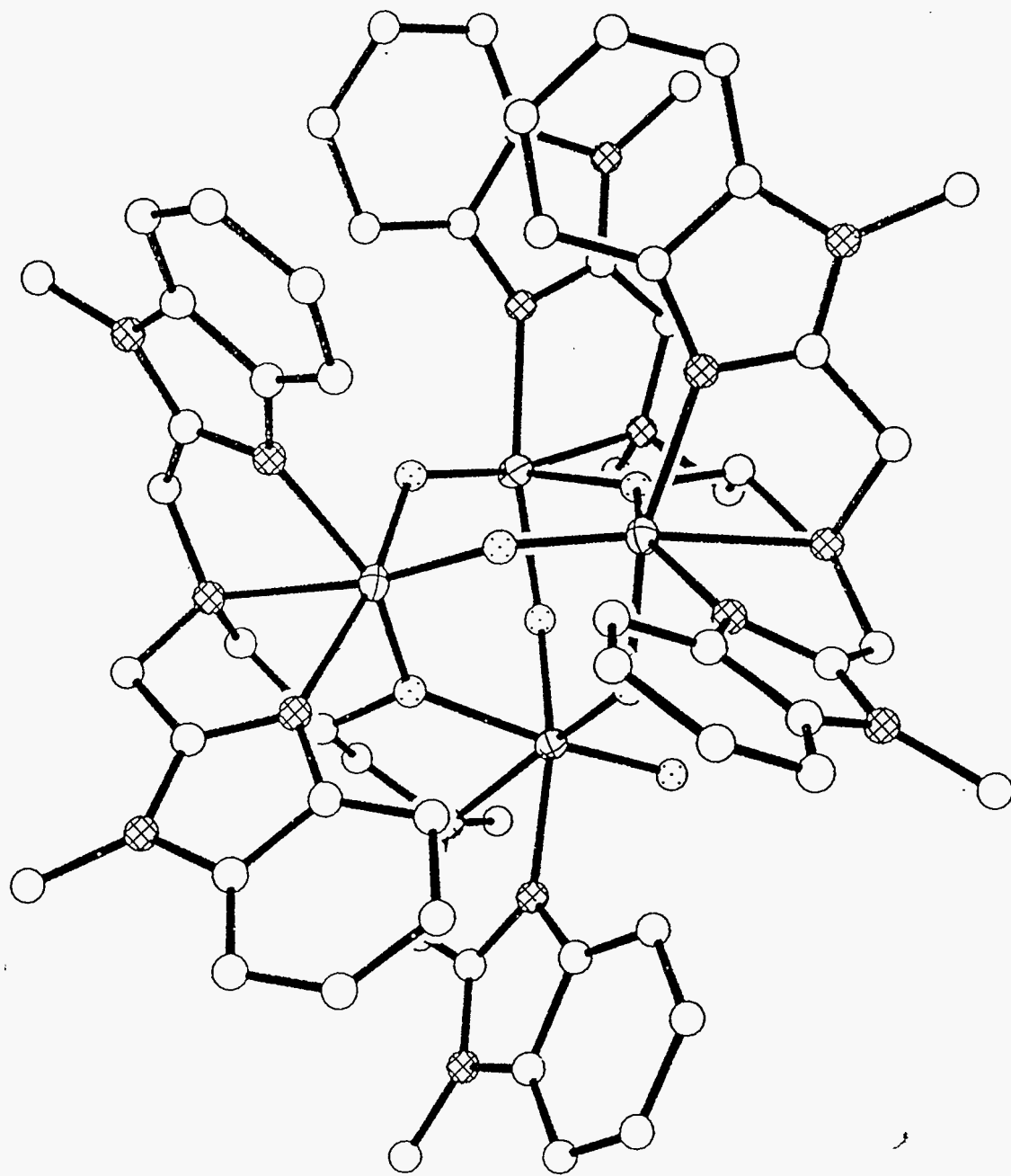


Figure 3. Cation of $[\text{Fe}_4(\text{O})(\text{MeL})(\text{OH})_5][\text{BF}_4]_3$ (2). Hydrogen atoms omitted for clarity.
Thermal ellipsoids-Iron; Open circles-Carbon; Dotted circles-Oxygen;
Cross-hatched circles-Nitrogen.

