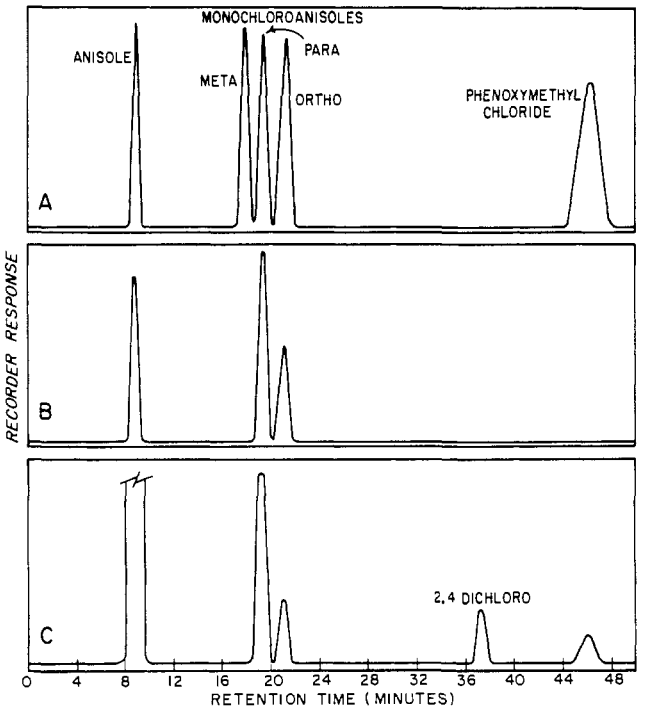


Figure 1. Gas chromatographic separation of anisole and its monochlorinated derivatives. (A) Anisole and its four monochloro isomers were separated from each other on an Aerograph Model A-350 B gas chromatograph equipped with a thermal conductivity detector using a 20 ft by 0.25 in. column with 30% FFAP (free fatty acid packing obtained from Wilkens Instrument and Research, Inc., Walnut Creek, Calif.) on acid-washed Chromosorb W 60–80 mesh. Chromatograph conditions: column, 213°; detector, 300°; injector, 280°; detector current, 225 ma; flow rate, 75 cc of helium/min. (B) Elution pattern of the products of the enzyme reaction. The reaction mixture contained 825 μmoles of anisole, 450 μmoles of hydrogen peroxide, 7.5 mmoles of sodium chloride, 75 μg of crystalline chloroperoxidase, and 10.5 mmoles of potassium phosphate buffer, pH 2.8, in a total volume of 105 ml. Chloroperoxidase was added to the incubation mixture at 5-min intervals in 16-μg aliquots. After 30-min incubation, the reaction mixture was extracted three times with 100-ml portions of ether. The ether extracts were combined, dried over magnesium sulfate, filtered, and evaporated to dryness under a stream of nitrogen. The residue was analyzed directly by gas chromatography as in A. (C) Elution pattern of the products of the free-radical halogenation reaction. The reaction mixture contained 2 ml of anisole in 100 ml of 0.1 *M* potassium phosphate buffer, pH 2.8, in a 500-ml, three-necked, round-bottom flask fitted with two dropping funnels and a reflux condenser. Five milliliters of sulfuryl chloride and 250 mg of benzoyl peroxide were added simultaneously from the two dropping funnels. The flask was illuminated by two 350-w photoflood lamps located 15 cm from either side of the flask. The flask was stirred constantly and heated to boiling while the additions were made and for 30 additional min after the completion of the additions. The products were then extracted with ether and analyzed as described in B and A.

with the halogenation of anisole using sulfuryl chloride, benzoyl peroxide, and light to generate chlorine free radicals. All of the halogenation reactions were carried out in aqueous medium at the same pH under essentially identical conditions. Figure 1A shows the gas chromatographic separation of anisole from its four monochlorinated derivatives, *o*-chloroanisole, *m*-chloroanisole, *p*-chloroanisole, and phenoxymethyl chloride. Figure 1B shows the same gas chromatographic separation of the products of the enzymatic reaction. The chloroperoxidase reaction produces only the *para* and *ortho* isomers at a *para*:*ortho* ratio of 1.9 (calculated from the area under each peak). The reaction of hypochlorous acid with anisole (0.5 HOCl:1 anisole)[5] under conditions identical with those employed in the enzymatic reaction yielded essentially the same results as found in the enzyme reaction. The reaction of hypochlorous acid with anisole yielded only the *ortho*- and *para*-monochlorinated anisole derivatives at a *para*:*ortho* ratio of 1.8. In contrast to these results, the reaction of chlorine free radicals with anisole under the conditions of the enzymatic reaction forms 2,4-dichloroanisole and *phenoxymethyl chloride* in addition to the *o*- and *p*-chloroanisoles (Figure 1C). The ratio of *para*:*ortho* chloroanisole formation in the free-radical reaction is 4.1. Thus, both the isomer distribution and the products, especially the formation of phenoxymethyl chloride, differ substantially between the enzyme and the free-radical reaction while the enzymatic chlorination and chlorination with hypochlorous acid are completely analogous.

We conclude that these results indicate that the gross details of the chloroperoxidase reaction correspond to the chemical ionic electrophilic substitution model and add support to our hypothesis that halogen ions undergo an over-all two-electron oxidation in the formation of the active halogenating species in the chloroperoxidase reaction.

(5) The incubation conditions for the chlorination of anisole with hypochlorous acid were identical with those used in the enzyme reaction (Figure 1B) except for the replacement of enzyme, hydrogen peroxide, and chloride ion with 412 μmoles of sodium hypochlorite.

Frederick S. Brown, Lowell P. Hager
Biochemistry Division, Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois
Received December 7, 1966

The Structure of Two Seven-Coordinate Complexes of Iron(III)

Sir:

We report here preliminary results of three-dimensional X-ray analyses of two seven-coordinate iron(III) complexes of a pentadentate macrocyclic ligand, 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]-octadeca-1(18),2,12,14,16-pentaene (structure I).[1] Compound I, the dimer $[(H_2O)BFe{-}O{-}FeB(H_2O)](ClO_4)_4$, where B = macrocyclic ligand, was reported earlier[2] as $[FeB(OH)](ClO_4)_2$. This compound crystallizes as red-orange orthorhombic crystals with unit cell dimensions $a = 22.82$, $b = 21.35$, $c = 19.75 \pm 0.05$ A. From the extinctions observed on precession photographs, the space group was determined to be Pbca with eight molecules per unit cell. The intensity data were collected on the General Electric XRD-5 diffractometer, and 914 independent reflections were observed by the stationary–counterstationary crystal technique using Mo Kα radiation. The iron and chlorine positions were determined from a Patterson synthesis and the structure was solved from a Fourier map computed from the resulting phases. Owing to the large number of atoms per asymmetric unit (65

(1) J. D. Curry and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 592 (1964).
(2) S. M. Nelson, P. Bryan, and D. H. Busch, *Chem. Commun.*, 641 (1966).

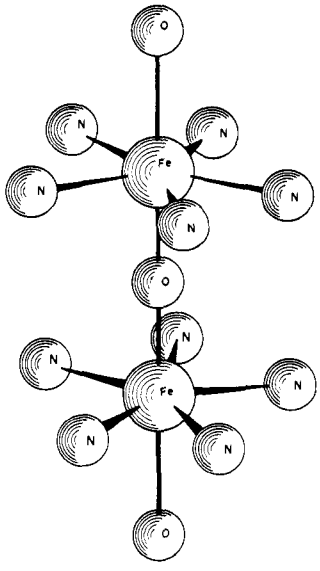
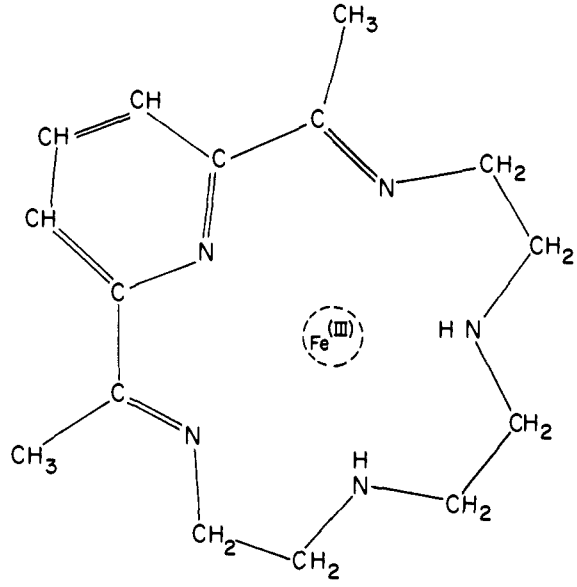


Figure 1. Illustration of the coordination about the iron atoms in $[(H_2O)BFe{-}O{-}FeB(H_2O)](ClO_4)_4$.

excluding hydrogens) and extreme disorder among the perchlorate oxygen atoms, only crude refinement was possible.[2a]



I

The arrangement of the ligands of compound I is illustrated in Figure 1. The configuration about the iron atom is approximately that of a pentagonal bipyramid with one shortened axial distance. A water molecule occupies the outer axial position, and the dimer is composed of two $FeB(H_2O)$ units linked together by a linear oxo bridge.[2] Approximate distances found are Fe–O, 1.8 A; Fe–(H_2O), 2.15 A, and Fe–N, 2.2 A.

Compound II, $[FeB(NCS)_2]ClO_4$,[2] crystallizes as orange, monoclinic crystals with dimensions a = 8.91 ± 0.01, b = 17.96 ± 0.06, c = 14.37 ± 0.05 A, γ = 92.80 ± 0.03°. The space group, determined from precession photographs, is $P2_1/b$ with four molecules per unit cell. The 1278 independent reflections were observed using PAILRED,[3] and the data were reduced to $|F|$'s in the usual manner. The structure was solved by symbolic addition methods[4] using the fully automated computer program MAGIC.[5]

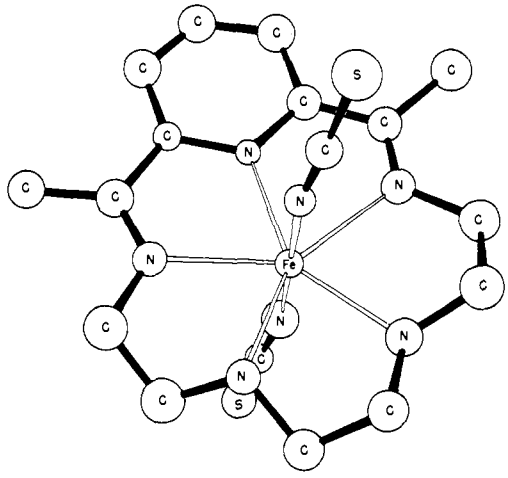


Figure 2. Perspective drawing of the $FeB(NCS)_2(ClO_4)$ molecule.

From the 700 highest E's (normalized structure factors), 666 signs were determined as symbolic combinations. The most consistent sign combination gave an E map which showed all atoms but the perchlorate oxygens. Preliminary refinement (R = 0.16) of the structure yielded the configuration shown in Figure 2. The perchlorate group is substantially disordered, and final refinement must await introduction of a suitable model for this disorder.

The configuration about the iron atom of compound II is also that of a pentagonal bipyramid (within the error of the refinement at this stage, ϵ = ±0.025 A for nitrogen atomic parameters). The thiocyanate ligands are N-bonded at the axial positions (Fe–N, 2.01 ± 0.02 A). The five nitrogen atoms of the B ligand form the equatorial apices (Fe–N, 2.23 ± 0.05 A) and are coplanar with the iron atom (out-of-plane deviations < ±0.09 A). At this point the azomethine linkages appear to force the associated nitrogens to be approximately 0.1 A farther from the iron atom than the other three nitrogen atoms. Thus the assignment of D_{5h} symmetry is only approximate.

Both compounds exhibit substantially different seven-coordination of iron(III) than that found in $Fe(EDTA)(H_2O)^-$ structures.[6]

Acknowledgments. We wish to thank A. L. Stone, D. C. Mendelson, and E. Klem for their preliminary work on compound I and J. D. Wright for his helpful work on compound II. We are especially grateful to D. H. Busch who supplied us with crystals of these novel compounds. This work was supported by grants from the National Institutes of Health and National Science Foundation.

(2a) NOTE ADDED IN PROOF. The number of data per parameter refined for this structure is 4; the small amount of data leads to the lower than usual precision of the refinement.

(3) Phillips Automatic Indexing Linear Reciprocal-Space Exploring Diffractometer.
(4) I. L. Karle and J. Karle, *Acta Cryst.*, **16**, 969 (1963).
(5) E. B. Fleischer, *Trans. Am. Crystallographic Assoc.*, **2**, 75 (1966).
(6) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, **3**, 34 (1964).
(7) Alfred P. Sloan Fellow.
(8) National Science Foundation Trainee.

E. Fleischer,[7] S. Hawkinson[8]
Department of Chemistry, University of Chicago
Chicago, Illinois 60637
Received November 21, 1966