Figure 1. ORD curves for enzymatically produced (solid line) and chemically synthesized (dashed line) 7,8-epoxy-1-octene. The spectra were obtained using neat samples in a 1-mm path length cell.

tain a terminal methyl group, is converted exclusively to 7,8-epoxy-1-octene, and this product is in turn further oxidized to 1,2;7,8-diepoxyoctane. We wish to report that the epoxidation of octadiene catalyzed by this enzyme system proceeds with a high degree of stereoselectivity, and thus this reaction provides a clear example of enzymatic asymmetric synthesis.

The enzymatic epoxidation of octadiene on a preparative scale was carried out as follows. Three 3-1. Fernbach flasks, each containing 1000 ml of P_1 medium,[13] 10 ml of octane, 10 ml of fractionally distilled octadiene (bp 115°), and a 10 ml inoculum of a resting cell suspension of *P. oleovorans* strain TF4-1L[13,14] (approximately 10^9 cells/ml), were incubated for 20 hr at 30° on a gyrotory shaker at 200 rpm. The broths were then combined, extracted four times with 400-ml portions of hexane, and concentrated to 14 ml on a rotary evaporator. Gas chromatographic assay[2] showed that the recovered hexane contained a total of 2.5 g of 7,8-epoxy-1-octene. The product was purified by preparative gc using a 20 ft × 0.25 in. column of 10% Carbowax 20M on 80/100 Chromosorb W, maintained isothermally at 180°. Chemically synthesized 7,8-epoxy-1-octene was prepared from octadiene and *m*-chloroperbenzoic acid as described previously[2] and was purified using the same preparative gc procedure.

Mass spectral analysis gave parent peaks at *m/e* 126 and similar fragmentation patterns for both the enzymatic and chemical products, and both products gave identical peak area ratios when assayed by quantitative gc with 2-octanol as an internal standard.[2] The nmr spectra of the two products were identical and showed the typical terminal epoxide pattern: (δ, CCl_4) 2.70 (m, 1), 2.53 (d of d, 1), 2.26 (d of d, 1). *Anal.* Calcd for $C_6H_{14}O$: C, 76.14; H, 11.18. Found for enzymatic product: C, 76.01; H, 10.80. Found for chemical product: C, 75.61; H, 10.86.

Figure 1 shows the ORD curves obtained with neat samples of the enzymatic and chemical products. It is apparent that chemically synthesized 7,8-epoxy-1-octene is racemic, whereas the enzymatic product has a positive rotation, with $[\alpha]^{25}D$ +12.2°. By comparison, Coke and Shue[15] have recently reported an $[\alpha]^{16}D$ value of +12.4° for chemically synthesized (R)-(+)-1,2-epoxy-butane. Thus, the enzymatic epoxidation of octadiene proceeds with a high degree of stereoselectivity to give preferentially (R)-(+)-7,8-epoxy-1-octene. The optical purity of the enzymatic product was determined by nmr

(13) R. D. Schwartz, *Appl. Microbiol.*, **25**, 574 (1973).

(14) R. D. Schwartz and C. J. McCoy, *Appl. Microbiol.*, **26**, 217 (1973).

(15) J. L. Coke and R. S. Shue, *J. Org. Chem.*, **38**, 2210 (1973).

using the chiral shift reagent tris[3-(trifluoromethyl-hydroxymethylene)-*d*-camphorato]europium(III) and was found to be greater than 80%.[16]

If the enzyme-catalyzed epoxidation reaction involves the concerted addition of molecular oxygen to the π-electron system of the double bond, then formation of (R)-(+)-7,8-epoxy-1-octene must involve attack at the *si-si* face of the prochiral octadiene molecule. By comparison, it has been pointed out that the formation of (−)-(2R,3R)-*trans*-epoxysuccinate from fumarate by some strains of *Aspergillus fumigatus* must involve attack at the *re-re* face of fumarate.[17] The factors which are important in determining the mode of substrate binding to the epoxidation system of *P. oleovorans*, and an understanding of the role such factors play in imparting an unusual substrate specificity[4] and stereoselectivity to the epoxidation reaction, remain to be delineated.[18]

(16) The experimental conditions for this determination were as follows. At a concentration ratio of 0.137 mol of shift reagent per mole of chemically synthesized epoxide, two multiplets of equal intensity appear at δ 4.18 and 4.05. Under the same conditions with the enzymatic product, the ratio of the integrated intensity of the δ 4.18 multiplet to that of the δ 4.05 multiplet is greater than nine (M. T. Melchior, unpublished results).

(17) R. Bentley, "Molecular Asymmetry in Biology," Vol. II, Academic Press, New York, N. Y., 1970, pp 150-151.

(18) The apparent inability of *Pseudomonas* to degrade the epoxide functionality (ref 2 and 5) renders stereoselective degradation of racemic epoxide an untenable explanation for our results.

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Synthesis and Molecular Structure of a Six-Coordinate Iron(IV) Complex with a New 1,1-Dithiolate Ligand

Sir:

Outstanding among the characteristics of the dithioacid and 1,1-dithiolate complexes[1] is the diversity of their redox properties. Numerous N,N'-substituted dithiocarbamate complexes which contain metal ions in unusually high formal oxidation states, such as Fe(IV),[2] Cu(III),[3] Ni(IV),[4] Mn(IV), Cr(IV),[5] Co(IV), Rh(IV), and Ru(IV),[6] have been described. Various reasons have been advanced for the apparently anomalous coexistence of a metal in a high oxidation state with the readily oxidizable sulfur ligands. Predominant among these are (a) delocalization of positive charge onto the ligand,[5,7] and (b) oxidative interligand interactions.[4] The importance of Fe-S bonding in numerous metalloproteins, such as the nonheme iron pro-

(1) D. Coucouvanis, *Progr. Inorg. Chem.*, **11**, 233 (1970).

(2) E. A. Pasek and D. K. Straub, *Inorg. Chem.*, **11**, 259 (1972).

(3) (a) P. T. Beurskens, J. A. Cras, and J. J. Steggerda, *Inorg. Chem.*, **7**, 810 (1968); (b) H. C. Brinkhoff, *Recl. Trav. Chim. Pays-Bas*, **90**, 377 (1971).

(4) (a) J. P. Fackler, A. Avdeef, and R. G. Fischer, *J. Amer. Chem. Soc.*, **95**, 774 (1973); (b) A. Avdeef, J. P. Fackler, and R. G. Fischer, *ibid.*, **92**, 6972 (1970).

(5) R. Chant, A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Aust. J. Chem.* 2533 **26**, (1973).

(6) L. R. Gahan and M. J. O'Connor, *J. Chem. Soc., Chem. Commun.*, 68 (1974).

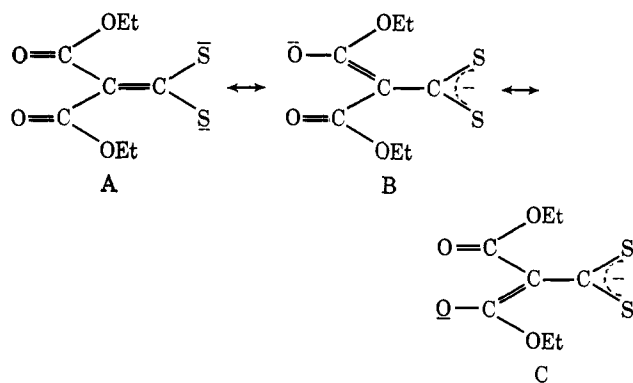(7) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suom. Kemistilehti B*, **29**, 75 (1956).

Figure 1. Resonance forms in the 1,1-dicarboethoxy-2,2-ethyl-enedithiolate (DED) ligand.

Figure 2. Molecular structure of $Fe[S_2CC(COOC_2H_5)_2]_3{}^{2-}$. Thermal vibrational ellipsoids are scaled to enclose 50% probability.

teins,[8] and the implication of Fe(IV) in the action of certain peroxidases[9,10] prompted us to investigate the nature of the Fe–S bond and the redox behavior of chelates of iron with new sulfur containing ligands.

Alkali metal salts of the 1,1-dicarboethoxyethylene-2,2-dithiolate anion (DED^{2-}) (Figure 1) are obtained readily by the action of CS_2 on malonic ester under basic conditions.[11] Reaction of $Fe(ClO_4)_3 \cdot H_2O$ with K_2DED in water and subsequent extraction by a solution of $BzPh_3PCl$ in CH_2Cl_2 afforded a dark brown CH_2Cl_2 solution of the complex. Addition of pentane resulted in a crude oil which was recrystallized from an acetone–ether mixture to give black crystals of the stoichiometry $(BzPh_3P)_2Fe(DED)_3$ (I). The magnetic moment, 2.92 ± 0.02 BM, and Mossbauer spectrum[12] of I are similar to those reported for the Fe(IV) dithiocarbamate complexes which have been described in terms of an octahedrally coordinated iron in a d^4 configuration and a $^3T_1$ ground state.[2] The infrared spectrum of I shows frequencies associated with the $C=CS_2$ vibration[13] at 1450 and 1465 cm^{-1} and $C=O$ vibrations at 1720 and 1660 cm^{-1}. The similarity of these frequencies to those found in $Ni(DED)_2{}^{2-}$ ($\nu_{C=CS_2}$ = 1445; $\nu_{C=O}$ = 1680, 1720 cm^{-1}) suggests that contributions of resonance forms B and C (Figure 1) to the structure of the ligand are very nearly the same in both complexes.

The oxidation potential for the reversible process

$$Fe(DED)_3{}^{3-} \rightleftharpoons Fe(DED)_3{}^{2-} + e^-$$

is −1.20 V in CH_2Cl_2 vs. Ag/AgI with Bu_4NClO_4 as the supporting electrolyte and accounts for the remarkable tendency of the Fe(III) complex to oxidize in the air.[14] An X-ray study was undertaken with the purpose of comparing the structural parameters of I to corresponding values in the Ni(II) and Cu(III) complexes.[16]

The crystals of I are monoclinic with cell dimensions

of a = 19.114 (6) Å, b = 15.424 (5) Å, c = 24.308 (8) Å, and β = 97.50 (2)°. The calculated density of 1.37 g/cm^3 (z = 4) compares favorably to 1.33 g/cm^3, found by pycnometry. The systematic extinctions were consistent with the space groups Cc or $C2/c$. The latter was confirmed by successful refinement. Intensity data on a crystal (0.19 × 0.24 × 0.35 mm) were obtained on a Picker FACS I automatic diffractometer using a θ–2θ scan technique employing graphite monochromatized Mo $K\alpha$ radiation (λ 0.7107 Å, $2\theta_m$ = 12.20°).

Of the 3335 unique reflections measured (sin θ/λ <0.481) 2350 had $F^2 > 3\sigma(F^2)$ and were used in refinement. The structure was solved by conventional Patterson and Fourier techniques. The least-squares refinement of 49 nonhydrogen atoms with the 37 hydrogen atoms included but not refined to a final R_1 value of 0.042. The structure of the Fe-$(DED)_3{}^{2-}$ anion is shown in Figure 2. The six sulfur atoms define an irregular octahedron. The metal ion and one of the ligands are located on a crystallographic twofold axis. Structural details are shown in Table I.

The coordination around the iron is distorted octahedral. The average[17] projected twist angle[18] of the two triangular faces of the FeS_6 polyhedron is 35.9°, intermediate between the 60 and 0° expected for the octahedral and trigonal prismatic geometry, respectively.

An examination of the structural parameters of the crystallographically unconstrained complexed DED ligand shows no significant differences when compared to corresponding values in the structure of the Ni-$(DED)_2{}^{2-}$ complex[15] in agreement with the infrared data. These results indicate that (a) inter or intraligand oxidation cannot adequately explain the formation of I and (b) the charge delocalization brought about in the ligand by the metal ion is insensitive to the formal oxidation state of the metal ion. The Fe–S bond lengths in

(8) J. C. M. Tsibris and R. W. Woody, Coord. Chem. Rev., 5, 417 (1970).

(9) R. H. Felton, G. S. Owen, D. Dolphin, and J. Fajer, J. Amer. Chem. Soc., 93, 6332 (1971).

(10) T. H. Moss, A. Ehrenberg, and A. J. Bearden, Biochemistry, 8, 4159 (1969).

(11) D. Coucouvanis, Ph.D. Thesis, Case Institute of Technology, 1967.

(12) A. Kostikas, Nuclear Research Center, "Demokritos," private communication.

(13) J. M. Burke, Ph.D. Thesis, Case Western Reserve University, 1971.

(14) It has been pointed out[15] that, in planar and dimeric dithiolenes, reduced species in couples less positive than 0.00 V are susceptible to air oxidation.

(15) A. Davison and R. H. Holm, Inorg. Syn., 10, 8 (1967).

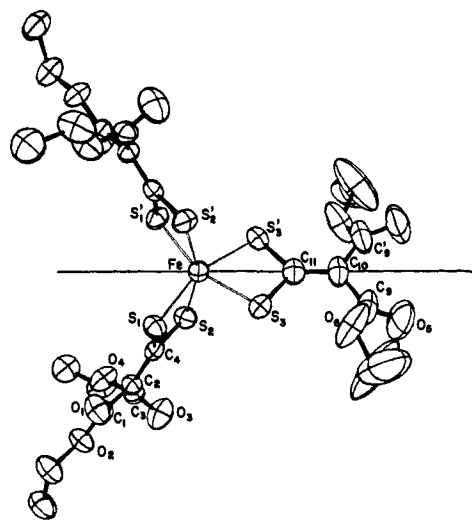(16) F. Hollander, M. L. Caffery, and D. Coucouvanis, J. Amer. Chem. Soc., in press.

(17) The projection was made perpendicular to a plane containing the crystallographic twofold axis and bisecting the dihedral angle (~6°) between the triangular faces defined by S_1, S_2', and S_3 and S_1', S_2, and S_3'.

(18) E. I. Stiefel and G. F. Brown, Inorg. Chem., 11, 434 (1972).
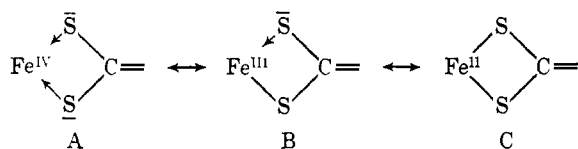
Figure 3.

Table I. Selected Structural Parameters (Å, deg) in the Fe(DED)$_3^{2-}$ Anion

	(A) Bond Distances		
M—S$_1$	2.289 (2)	M—S$_3$	2.301 (2)
M—S$_2$	2.305 (2)		
S$_1$—S$_2$ (bite)	2.786 (2)	S$_3$—S$_3'$	2.737 (3)
S$\cdots$S (range of	3.226 (2)–		
contacts	3.744 (3)		
C$_4$—S$_1$	1.735 (5)	C$_{11}$—S$_3$	1.739 (6)
C$_4$—S$_2$	1.735 (6)		
C$_4$—C$_2$	1.369 (7)	C$_{10}$—C$_{11}$	1.363 (12)
C$_2$—C$_1$	1.450 (8)		
C$_2$—C$_3$	1.487 (8)	C$_9$—C$_{10}$	1.485 (9)
C$_1$=O$_1$	1.215 (6)		
C$_3$=O$_3$	1.190 (7)	C$_9$=O$_5$	1.196 (8)
	(B) Bond Angles		
S$_1$—Fe—S$_2$	74.66 (6)	S$_3$—Fe—S$_3'$	72.97 (5)
Fe—S$_1$—C$_4$	89.5 (2)		
Fe—S$_2$—C$_4$	89.0 (2)	Fe—S$_3$—C$_{11}$	91.6 (2)
S$_1$—C$_4$—S$_2$	106.8 (2)	S$_3$—C$_{11}$—S$_3'$	103.8 (2)

the present structure are significantly shorter than those found in the high spin iron(III) tris-dithiocarbamate chelates such as the Fe(pyrrolidine-Dtc)$_3$[19] and Fe-(Et$_2$Dtc)$_3$,[20] at 297°K (2.41 (1) and 2.357 (5) Å, respectively). However, they are similar to those found in the structures of the low spin Fe(MePhDtc)$_3$[19] and Fe-(Et$_2$Dtc)$_3$[23] complexes, at 79°K (2.31 (1) and 2.306 (2) Å, respectively).

Recently a study of the metal ion and ligand dependency of the redox properties of some first-row transition metal dithiocarbamate complexes[5] was reported. The results of this study show a dependence of the oxidation potentials, for the process

$$[M(R_2Dtc)_n]^0 \rightleftharpoons [M(R_2Dtc)_n]^+ + e^-$$
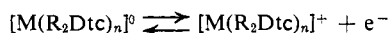
on (a) the R groups on the Dtc$^-$ ligands and (b) the d orbital populations of the metal ions.

The results of the present study and similar studies on the dithiocarbamate complexes indicate that the electrons removed from iron–sulfur chelates reside in molecular orbitals which involve primarily iron and sulfur functions. The relative importance of resonance forms such as those shown in Figure 3 is difficult to ascertain. However, covalency in the Fe–S bond (Figure 3b, 3c) cannot be ruled out and may well be important in the stabilization of the oxidized complexes.

Acknowledgments. We are grateful to the National Science Foundation and the National Institute of Health for financial support of this research.

(19) P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1163 (1972).
(20) J. G. Leipoldt and P. Coppens, *Inorg. Chem.*, 12, 2269 (1973).
(21) Fellow of the Alfred P. Sloan Foundation and author to whom correspondence should be addressed.

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Antibiotic X-5108. VIII. Absolute Stereochemistry of Antibiotic X-5108 and Mocimycin[1]

Sir:

The structure of antibiotic X-5108 including the configuration of all double bonds,[2] the chiral centers C(2) and C(3) of the octadienal derived from goldinamine[1] and corresponding to C(1) and C(2) of **1**, the absolute configuration of the goldinonyl moiety,[3] and the relative configuration of the central tetrahydrofuran ring[4] has been established. Two possible configurations of antibiotic X-5108, differing only with respect to the enantiomorphism of their tetrasubstituted tetrahydrofuran rings, remain for consideration.

To establish the chirality of the substituted tetrahydrofuran ring, we attempted to fuse a ring system containing the two known chiral centers C(1) and C(2), originating from **1**, onto the tetrahydrofuran ring and to generate a structure of sufficient conformational stability as to enable application of the Karplus relationship to the dihedral angle H–C(5')–C(1)–H. Thus, N-acetyl-O-isopropylidenegoldinamine 4-bromobenzyl ether (**1**) was degraded (Scheme I) with a mixture of

Scheme I
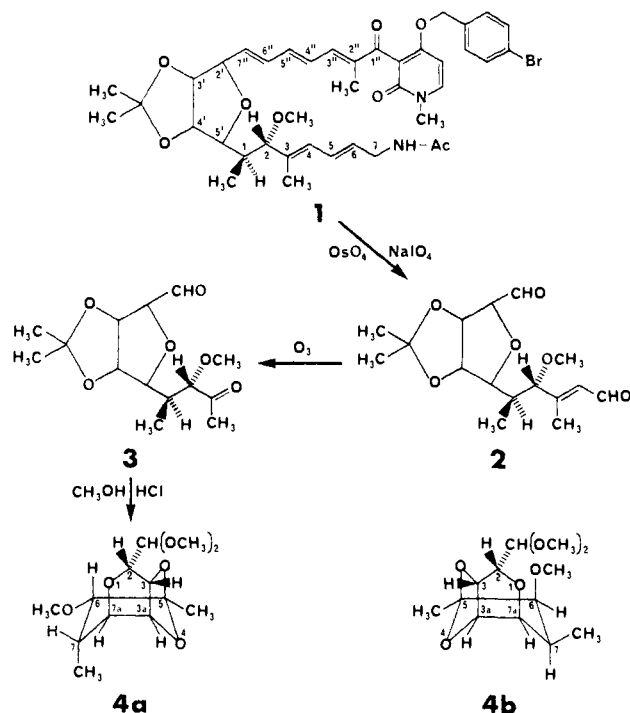
osmium tetroxide and sodium metaperiodate affording dialdehyde **2** which was further cleaved with ozone to give **3**, the desired starting material for the cyclization reaction. Treatment of **3** with methanolic hydrogen chloride yielded 3,5-epoxyhexahydro-2-dimethoxymethyl-6-methoxy-5,7-dimethyl-2H-furo[3,2-b]pyran the structure of which is either **4a** or **4b**; both structures contain identical chiral centers at positions 6 and 7 derived from positions 1 and 2, respectively, of the diene

(1) Paper VII in this series: H. Maehr, J. F. Blount, M. Leach, and A. Stempel, *Helv. Chim. Acta*, 57, 936 (1974).
(2) H. Maehr, M. Leach, L. Yarmchuk, and A. Stempel, *J. Amer. Chem. Soc.*, 95, 8449 (1973).
(3) H. Maehr, J. F. Blount, R. H. Evans, Jr., M. Leach, J. W. Westley, T. H. Williams, A. Stempel, and G. Büchi, *Helv. Chim. Acta*, 55, 3051 (1972).
(4) H. Maehr, T. H. Williams, M. Leach, and A. Stempel, *Helv. Chim. Acta*, 57, 212 (1974).