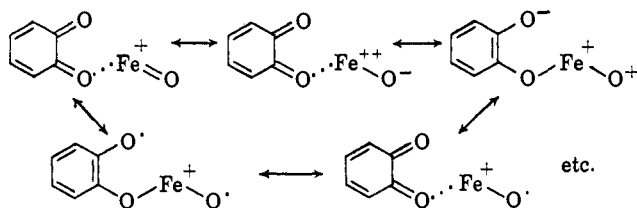droxylating species can be envisaged if II loses a molecule of water to give III. Several resonance structures of III can be written.

Electrophilic attack of intermediate III on anisole would give IV, which on migration of a proton and dissociation of the hydroxy anisole would give I, thus completing the cycle. According to this mechanism the catechol is oxidized in the conversion of II to III and reduced in the hydroxylation step, III to IV; hydroquinone would be expected to react similarly. With no anisole present, hydroxylation of catechol and reaction of III with water to give V could account for the uptake of 20 to 30% of the H_2O_2. Also, we observe that the less reactive chlorobenzene is not hydroxylated in this system; presumably III is removed (to give V) before it hydroxylates chlorobenzene.[7]

The function of the metal ion in the proposed scheme is to transfer electrons from the catechol to the hydrogen peroxide and then in the hydroxylation step back to the catechol. In effect, the metal ion extends the conjugation and allows an electronic link between two or more molecules. Presumably it can do this by the overlap of its d electron orbitals with the p orbitals of the ligands. The application of this type of mechanism to several other metal ion catalyzed reactions, including some enzymatic oxidation–reduction reactions, has been discussed[1] and will be the subject of future publications from this Laboratory.

(7) In Chart 1, the hydroxylation is depicted as an electrophilic substitution; however, III could presumably act as a free radical reagent as well. In the present case, the isomer distribution of products suggests an electrophilic attack rather than radical.

(8) Participant in the National Science Foundation undergraduate research program, summer, 1961.

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THE STRUCTURE OF THE CUPROUS CHLORIDE–CYCLOÖCTADIENE-1,5 COMPLEX[1]

Sir:

As part of a program concerned with metal–olefin pi-complexes, a structural investigation of these compounds has been initiated. We wish to report here our findings on the cuprous chloride–cycloöctadiene-1,5 complex (I). Previous studies of cuprous chloride complexes with unsaturates have provided either erroneous[2] or inconclusive[3] results. To the best of our knowledge this report represents the first successful elucidation of such a complex structure.

Samples of I were prepared according to the following procedures.

(Ia) Cuprous chloride (2 g.) was dissolved in 50 ml. of 0.18 N hydrochloric acid, and the solution was added to 5 g. of cycloöctadiene-1,5 (COD). The reaction mixture was shaken for 10 min., and the precipitate was separated by filtration. The complex was washed with water and pentane and was dried under vacuum over calcium chloride for 24 hr. (*Anal.* Calcd. for

(1) Presented in part at the American Crystallographic Association Meeting, Villanova, Pennsylvania, June, 1962.
(2) J. Österlöf, *Acta Chem. Scand.*, **4**, 374 (1950).
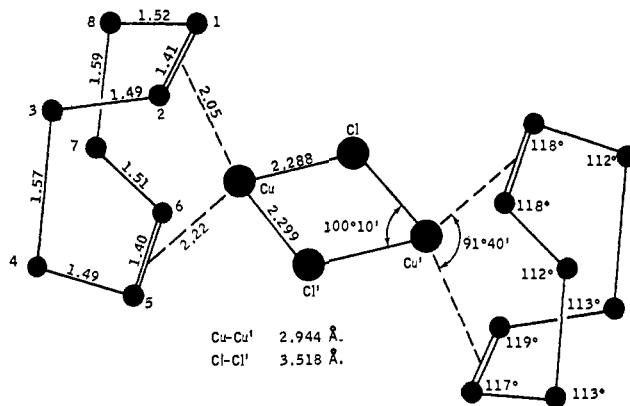(3) F. L. Carter and E. W. Hughes, *Acta Cryst.*, **10**, 801 (1957).

Fig. 1.—Relevant bond angles and distances for the Cu_2Cl_2-(cycloöctadiene-1,5)₂ complex.

$C_8H_{12}CuCl$: C, 46.38; H, 5.84; Cu, 30.67. Found: C, 44.08; H, 5.88; Cu, 31.48.)

(Ib) Cupric chloride dihydrate (2.5 g.) was dissolved in 15 ml. of 95% ethyl alcohol, and 3 g. of COD was added. Sulfur dioxide was passed into the reaction mixture for 10 min.[4] The precipitated complex was removed by filtration, washed three times with ethanol and vacuum dried over calcium chloride for 24 hr. (*Anal.* Found: C, 45.25; H, 5.88; Cu, 30.58.)

(Ic) A sample of freshly prepared complex Ia was recrystallized from 50 ml. of ethyl acetate. (*Anal.* Found: C, 46.35; H, 6.07; Cu, 30.70.)

Complexes Ib and Ic were obtained as well defined crystals; complex Ia separated as a fine powder. The heat of dissociation of the complex was determined as being 23.5 kcal./mole,[5] which is in accord with the observed high stability of the complex.

X-ray diffraction studies of single crystals of complex Ic showed it to be triclinic, space group P Ī, with the unit cell dimensions a = 9.028 (±0.003 Å.), b = 9.020 (±0.003 Å.), c = 6.387 (±0.005 Å.), α = 124.4°, β = 95.7°, γ = 104.9°. The observed density is between 1.60 and 1.65 g./cm.³ indicating the presence of two formula units ($C_8H_{12}CuCl$) per unit cell (calcd. density = 1.633 g./cm.³).

Reflection data were obtained using a single crystal orienter with an XRD-5 G.E. diffractometer. The integrated intensities were recorded for filtered Cu K-α radiation (λ = 1.5418 Å.) using the equatorial plane diffraction method with the specimen and counter rotating in a ratio of 1:2. Lorentz-polarization and absorption corrections were applied to the data. Patterson vector maps of three projections yielded the positions of the copper and chlorine atoms, and a calculation of a series of Fourier and difference-Fourier syntheses[6] determined the locations of the carbon atoms. Refinement of the three dimensional data[7] for approximately 600 reflections yielded a discrepancy factor of 0.13.

The complex is centro-symmetrical and consists of two formula units joined through chlorine–chlorine bridging with the copper and the chlorine atoms forming a rhombus. The copper atoms are quasi-tetrahedrally bonded to two chlorine atoms and the two double bonds of a COD molecule (Fig. 1). The COD molecule

(4) Private communication, H. Haight and J. R. Doyle, Chemistry Department, State University of Iowa, Iowa City, Iowa.
(5) Private communication from Dr. R. B. Long, Esso Research and Engineering Company, Linden, New Jersey.
(6) W. G. Sly, D. P. Shoemaker and J. H. van den Hende, Two- and Three-Dimensional Crystallographic Fourier Summation Program for the IBM 7090 Computer, IBM SHARE Library, No. 1344.
(7) J. H. van den Hende, Crystallographic Structure Factors and Least Squares Refinement Program for the IBM 7090 Computer, IBM SHARE Library, No. 1240.

is in the *boat* conformation[8] and is slightly staggered to relieve the transannular strain due to the intraannular interactions of the hydrogen atoms on carbons 4, 5, 7 and 8. The interatomic distances and the relevant bond angles are summarized in Fig. 1.

The infrared spectra of the complexes were measured in potassium bromide. In all cases the absorption bands characteristic of the cycloöctadiene double bonds at 1660 cm.$^{-1}$ (C=C) and 710 cm.$^{-1}$ (=CH) were absent. New bands appearing at 1612 cm.$^{-1}$ and 746 cm.$^{-1}$ were assigned to the complexed olefin. The spectrum of Ia exhibited a pair of bands at 1230 cm.$^{-1}$ and 1192 cm.$^{-1}$ of equal intensity, complexes Ib and Ic exhibited a similar pair of bands at 1238 cm.$^{-1}$ and 1188 cm.$^{-1}$, the intensity of the former being approximately twice that of the latter. A minor difference was also observed in a pair of bands that occurred at 971 cm.$^{-1}$ and 966 cm.$^{-1}$ in Ia and at 971 cm.$^{-1}$ and 957 cm.$^{-1}$ in Ib and Ic. X-Ray powder diffraction data also show that the structure of complex Ia is different from complexes Ib and Ic.

Hendra and Powell[9] have suggested that the cuprous chloride-COD-1,5-complex prepared from hydrochloric acid solution involves the *chair* conformer of the olefin rather than the *boat*. The infrared spectra of complexes Ia–c are virtually identical with that reported by these authors. Since the crystal structure determination of Ic has shown that the complexed olefin exists in the *boat* conformation, it would certainly appear that complexes Ia–c all involve the *boat* conformation of the olefin. If this were not the case, then the various complexes should exhibit major differences in the 1000–500 cm.$^{-1}$ region where most of the absorption bands are due to the skeletal vibrations of the eight-membered ring. We believe that the minor spectral differences observed between Ia and Ib and Ic may be attributed to two structurally different complexes. Complexes Ib and Ic possess the determined dimeric structure; complex Ia is polymeric and consists of COD molecules in the *boat* conformation joined by exocyclic cuprous chloride bridging. The spectral differences may then reside in the non-symmetrical nature of Ib and Ic as opposed to the more symmetrical structure of Ia.

A more complete structural analysis of this complex will be reported elsewhere.

(8) COD-1,5 has been found to exist in the *boat* configuration in its rhodium chloride complex; J. A. Ibers and R. G. Snyder, *Acta Cryst.*, **15**, 923 (1962).

(9) P. J. Hendra and D. B. Powell, *Spectrochim. Acta*, **17**, 913 (1961).

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EVIDENCE FOR THE EXISTENCE OF AN ORGANODITIN DIHYDRIDE[1]

Sir:

We wish to record what we believe to be the first preparation of an organoditin dihydride, specifically, 1,1,2,2-tetra-*n*-butyl-1,2-dihydroditin.
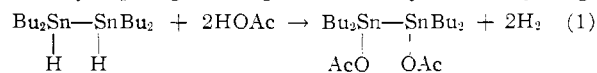
1,1,2,2-Tetra-*n*-butyl-1,2-dichloroditin,[2] prepared by treating 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin with hydrogen chloride in anhydrous ether, was reduced[3]

(1) We thank M and T Chemicals, Inc., for support of a portion of this work.

(2) A. J. Gibbons, A. K. Sawyer and A. Ross, *J. Org. Chem.*, **26**, 2304 (1961).

(3) This reduction was attempted by J. G. Noltes and G. J. M. van der Kerk, "Functionally Substituted Organotin Compounds," Tin Research Institute, Greenford, Middlesex, England, 1958. It was later shown by the following workers that the compound which they believed to be 1,1,2,2-tetra-*n*-butyl-1,2-dichloroditin was in reality bis-(di-*n*-butylchlorotin) oxide: (a) ref. 2; (b) D. L. Alleston and A. G. Davis, *Chem. Ind.* (London), 949 (1961); (c) O. H. Johnson, *J. Org. Chem.*, **26**, 2262 (1960).

by lithium aluminum hydride in anhydrous ether to give the colorless liquid, 1,1,2,2-tetra-*n*-butyl-1,2-dihydroditin (76%) (found: Sn, 50.51; calcd. for $C_{16}H_{36}Sn_2H_2$: Sn, 50.75), $n^{25}D$ 1.5205. A large Sn–H absorption band was found at 1795 cm.$^{-1}$ with a faint shoulder at 1835 cm.$^{-1}$. The reaction of this hydride with a 100% excess of glacial acetic acid over that required by eq. 1 gave a quantitative yield of hydrogen

$$\underset{\substack{| \quad | \\ H \quad H}}{Bu_2Sn\!-\!SnBu_2} + 2HOAc \rightarrow \underset{\substack{| \quad | \\ AcO \quad OAc}}{Bu_2Sn\!-\!SnBu_2} + 2H_2 \quad (1)$$

and 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin. That the product of this reaction is a ditin was shown by its quantitative reaction with bromine forming di-*n* butylacetoxybromotin[4] isolated in 70% yield. In previous work it has been shown that di-*n*-butyltin dihydride reacts with two moles of acetic acid to produce di-*n*-butyltin diacetate.[4] It follows that di-*n*-butyltin dihydride is not present in appreciable amount in the reduction product, which, therefore, must be 1,1,2,2-tetra-*n*-butyl-1,2-dihydroditin.

This hydride is more reactive toward acid than is di-*n*-butyltin dihydride, and, on exposure to air, rapidly forms a white solid whose tin analysis corresponds to that for di-*n*-butyltin oxide.

Formation of this ditin dihydride, or a polytin dihydride,[5] is indicated in other reactions of di-*n*-butyltin dihydride.

(a) Di-*n*-butyltin dihydride reacts with acetone to form isopropyl alcohol and di-*n*-butyltin.[6] Infrared spectra of the reaction product mixture taken at intervals showed not only the disappearance of Sn–H absorption of di-*n*-butyltin dihydride at 1835 cm.$^{-1}$ but also the simultaneous appearance of new Sn–H absorption at about 1785 cm.$^{-1}$.

(b) Decomposition of di-*n*-butyltin dihydride at 100° constitutes a method for the preparation of di-*n*-butyltin. (Found: C, 41.34; H, 7.78; Sn, 51.10. Calcd.

$$Bu_2SnH_2 \longrightarrow Bu_2Sn + H_2 \quad (2)$$
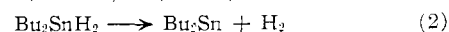
for $C_8H_{18}Sn$: C, 41.45; H, 7.79; Sn, 50.96.) Infrared spectra of the reaction product mixture taken during the decomposition showed a decrease in the intensity of the Sn–H absorption at 1835 cm.$^{-1}$ accompanied by the appearance and increase in intensity of a Sn–H band at 1780 cm.$^{-1}$; when the decomposition was somewhat more than 70% complete, only the latter band remained. Decrease in intensity of this band required prolonged heating.

(c) Treatment of di-*n*-butyltin with di-*n*-butyltin dihydride in a 1:1 molar ratio results in new Sn–H absorption at about 1780 cm.$^{-1}$.

It has been reported by Neumann and König[5] that, in the case of diphenyltin dihydride, substitution of one hydride hydrogen by tin results in a lowering of the frequency of Sn–H absorption to about 1790 cm.$^{-1}$.

(4) (a) A. K. Sawyer and H. G. Kuivila, *J. Am. Chem. Soc.*, **82**, 5958 (1960); (b) A. K. Sawyer and H. G. Kuivila, *J. Org. Chem.*, **27**, 610 (1962).

(5) W. P. Neumann and K. König, *Angew. Chem.*, **74**, 215 (1962).

(6) H. G. Kuivila and O. F. Beumel, *J. Am. Chem. Soc.*, **83**, 1246 (1961).

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THE ASSIGNMENT OF N.M.R. SPECTRA USING THE NUCLEAR OVERHAUSER EFFECT

Sir:

In the analysis of nuclear magnetic double resonance (n.m.d.r.) experiments, three main effects must be considered: the perturbation of individual spin systems by the second r.f. field which gives rise to transitions