

Figure 2. Illustration of the observed arrangements of $C^{18}O$ groups (represented as closed circles) in $M(CO)_5L^+$ derivatives.

species.²³ Therefore if oxygen-18 substitution did occur at the axial carbonyl ligand in these derivatives it would indeed be directly observable in the ir. For these highly enriched mono-substituted oxygen-18 derivatives, however, only bands due to the parent all $C^{16}O$ (a) species and the equatorial mono-substituted $C^{18}O$ species (b) were observed, indicating that oxygen exchange in these derivatives is as well occurring preferentially at an equatorial CO site or cis to the substituted ligand (L).

Therefore, these experimental findings demonstrate a cis oxygen labilization in $M(CO)_5L^+$ species with the manganese derivatives undergoing oxygen exchange more readily than their rhenium analogues.²⁴ It is important to note that since there is no carbonyl-metal bond cleavage occurring in these reactions it is not necessary to consider possible rearrangements in the intermediates as is necessary when unsaturated metal species are produced. The slow rates of these reactions as compared with other nucleophilic reactions which we have studied, e.g., reactions of $M(CO)_5L^+$ species with $RMgX$ and amines are instantaneous, are suggestive of hydroxyl attack at carbonyl since OH^- is present at such low concentration. These slow rates will allow us to carry out a detailed kinetic study of these reactions employing conventional techniques. The ability to stereospecifically label $M(CO)_5L^+$ derivatives is an essential step in assessing the fluxional (or lack of fluxional) behavior of the intermediates produced in reactions involving thermal dissociation of CO or L.^{25,26} The latter studies are in progress in our laboratories.

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- (19) Obtained from Monsanto Research Corporation, Mound Laboratory, Miamisburg, Ohio 45342.
- (20) In the case of the two equatorially substituted CO groups, approximately the same high frequency $\nu(CO)$ band is calculated (within 2 cm^{-1}) regardless of cis or trans geometry.
- (21) The force constants computed for the $Me_2PhPm(CO)_5^+$ derivatives were $k_1 = 17.43$, $k_2 = 17.44$, $k_c = 0.222$, $k_c' = 0.246$, and $k_t = 0.452$. Fourteen bands were calculated within $\pm 1.3\text{ cm}^{-1}$. Although there is still some discussion concerning the use of force constants obtained by the method of restricted $\nu(CO)$ force fields, there is widespread agreement that ^{13}CO or $C^{18}O$ frequencies calculated by these procedures are correct.²²
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- (23) This is a result of the fact that the low frequency A_1 vibration in these derivatives occurs at much lower frequency than the E mode in the $M(C^{18}O)_5L^+$ species. By contrast, in the phosphine substituted derivatives the low frequency A_1 and E modes are grossly overlapped.
- (24) We have made qualitative measurements of the rates of incorporation of oxygen-18 in $M(CO)_6^+$ vs. $M(CO)_5(\text{phosphine})^+$. The exchange was found to occur much more rapidly in the hexacarbonyl cations. This would be expected from force constant arguments.^{17,18} Therefore, cis labilization is not meant to imply that L is labilizing with respect to CO in the oxygen exchange process.¹²
- (25) We have observed some CO scrambling in the labeled mono- $C^{18}O$ equatorial $Mn(CO)_5(CH_3CN)^+$ species when it is allowed to stand in acetonitrile for long periods of time. This is presumably resulting from acetonitrile dissociation and scrambling occurring in the unsaturated $[Mn(CO)_5^+]$ species.
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- (27) Petroleum Research Fund Postdoctoral Fellow, 1973-1975.

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A Long Range Deuterium Isotope Effect on a Lanthanide Induced Chemical Shift

Sir:

Electrophilic ring opening of *cis*-1,2,3-trimethylcyclopropane (I) proceeds with a mixture of retention and inversion by the electrophile (D^+) and nearly complete inversion by the nucleophile.¹ When the solvent is methanol a mixture of two diastereomeric methyl ethers is formed (eq 1), erythro (IIE) and threo (IIT) which differ only in the relative positions of their hydrogen and deuterium atoms. We wish to report that a mixture of these two diastereomers gives rise to two different methoxyl signals when their NMR spectra are recorded in the presence of the lanthanide shift reagent $Eu(fod)_3$.

Similarly the trans isomer III on ring opening gives rise to a mixture of four isomers (eq. 2). IIE and IIT come from deuterium attack on the carbon bearing the trans methyl group (33% of the ether product) and IVE and IVT (66%) arise from attack on the carbons bearing the cis methyls. In the presence of $Eu(fod)_3$ all four methyl ether peaks are clearly distinguished (Figure 1) and can be identified by

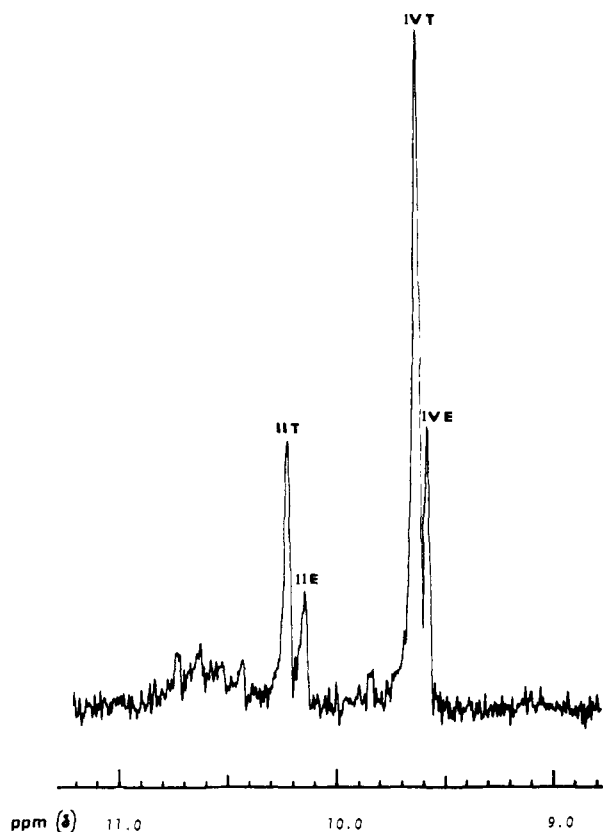
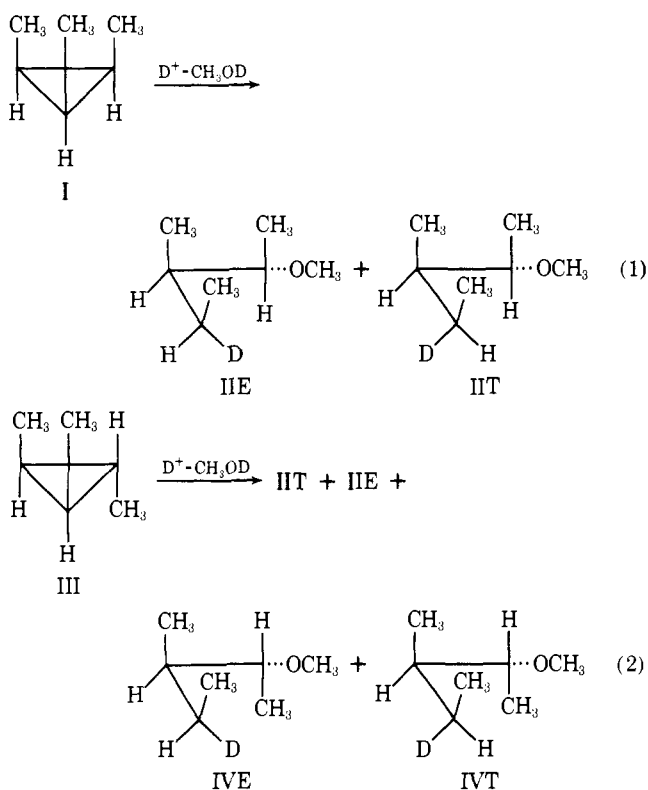


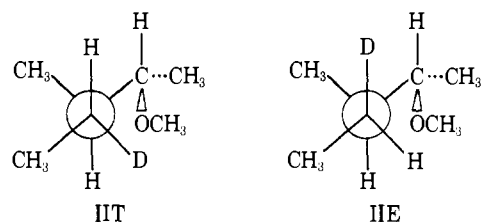
Figure 1.

comparison with authentic samples prepared from the corresponding alcohols!



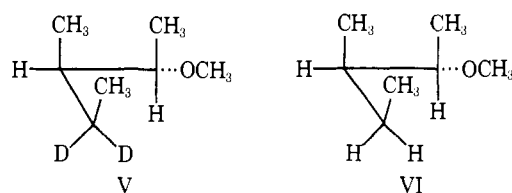
We suggest that the chemical shift differences are steric in origin, and reflect slightly different equilibrium constants for complexation by the shift reagent. From an examination of molecular models, the conformation shown below appears to be a favorable one, bringing the oxygen of the

methoxyl group close to the diastereomeric center. That isomer (IIT) with the oxygen closest to the deuterium in this conformation has the methoxyl protons shifted the farthest downfield.² Because of its smaller vibrational amplitude a

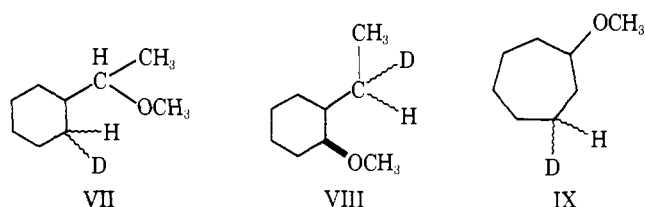


C-D bond may occupy slightly less space than a C-H bond³ and so allow a somewhat greater complexation by the shift reagent, leading to a downfield shift in IIT relative to IIE. The analogous conformations in IVT and IVE appear somewhat less favorable, and the methoxyl peaks are shifted less strongly and split to a lesser extent.

As a test of this hypothesis we have prepared both the di-deuterio and diprotio analogues of IIT and IIE, V and VI, respectively, and measured the absorption positions of their methoxyl protons in the presence of IIT and IIE. The meth-



oxyl protons of V absorb at the same positions as those of IIT, and the methoxyl protons of VI at the same position as those of IIE, showing that the effect is due solely to the presence of the one deuterium of IIT and is not cumulative. The threo and erythro isomers of 3-deuterio-2-butyl methyl ether do not show a splitting of their methoxyl signals under the same conditions, thus further ruling out an inductive origin for the effect.⁴ If a conformation is not possible in which the methoxyl is close to the deuterium, no splitting between diastereomers is observed. For example, both VII and VIII show splitting of their methoxyl protons in the two diastereomers while IX does not.



We have found the observed chemical shift differences extremely useful for determining deuterium stereochemistry in our continuing studies of electrophilic ring openings of cyclopropanes. We believe that they may be even more important in determining conformations of acyclic molecules in solution, and we are planning on extending the study to other shift reagents and to ¹³C NMR spectra.

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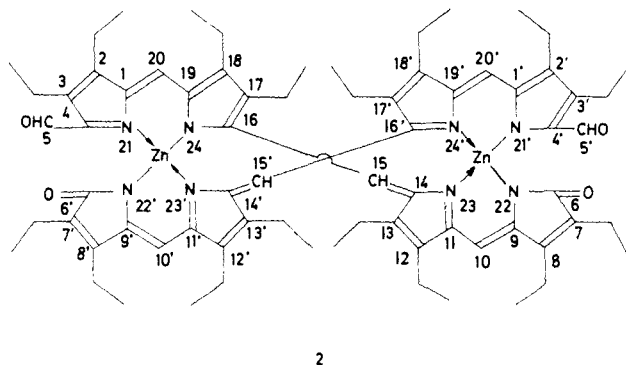
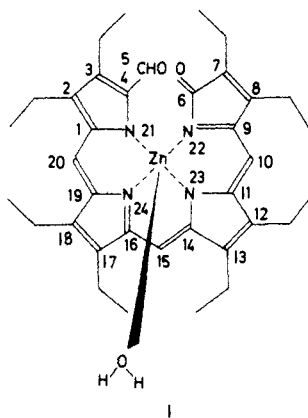
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Structures of Zinc Octaethyl Formylbiliverdinate Hydrate and Its Dehydrated Bis-Helical Dimer

Sir:

Synthetic zinc octaethyl formylbiliverdinate (**1**) in chloroform solution produces an absorption band in the near-infrared (λ_{\max} 830 nm, ϵ 12000) which shifts to shorter wavelengths (λ_{\max} 750 nm, ϵ 12000) when strong acids are added.¹ This spectral change is fully reversible with base. Similar shifts are observed with a variety of metal complexes of biliverdin dimethyl ester and mesobiliverdin dimethyl ester.² We wish to report here the structures of the zinc complex **1** and its "acid form" **2**. To our knowledge this is the first structural description of a biliverdin type chromophore.



Crystals of **1** and **2** were obtained simultaneously by slow evaporation of a methylene chloride-methanol solution of **1** at room temperature. The green and brown crystals were separated manually. Qualitative electronic spectra of the solids in KBr pellets showed that the green crystals were identical with the compounds which had been obtained by acid titration in chloroform solution whereas the spectrum of the brown crystals was that of the neutral solution. Redissolved crystals showed the corresponding spectra.

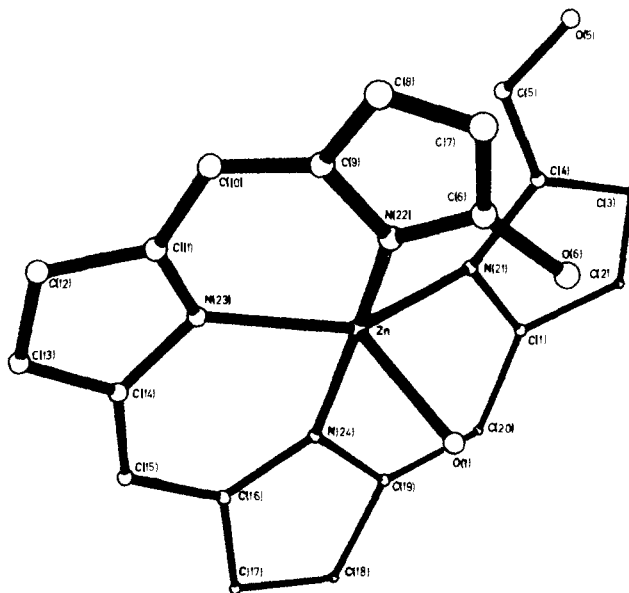


Figure 1. A perspective drawing of **1**. The ethyl groups have been omitted for clarity.

Compound **1** appears as brown ill-formed parallelepipeds (crystal data: monoclinic; space group $P2_1/c$; $Z = 4$; $a = 11.019$ (7), $b = 39.378$ (30), $c = 7.751$ (2) Å; $\beta = 95.39$ (6) $^\circ$) whereas the dimer **2** occurs as green prisms (crystal data: triclinic; $P\bar{1}$; $Z = 2$; $a = 20.317$ (3), $b = 15.101$ (2), $c = 13.665$ (2) Å; $\alpha = 125.11$, $\beta = 95.48$ (2), $\gamma = 96.63$ (2) $^\circ$). Data were collected on a four circle diffractometer using Mo $K\alpha$ radiation (λ 0.71069 Å). For **1**, 1042 independent reflections with $I \geq 3\sigma(I)$ were obtained up to $2\theta = 35^\circ$ (each intensity measured twice) and were used in the subsequent calculation.³ The corresponding number of reflections for **2** was 1459. Both structures were solved by the heavy-atom technique. Coordinates of the atoms, along with anisotropic temperature factors for the zinc atom and isotropic temperature factors for the other atoms (except hydrogen atoms which were not included in the calculations), were refined by full-matrix least squares.

The R index ($R = \sum \|F_o\| - |F_c| / \sum \|F_o\|$) at present is 0.091 for **1** and 0.102 for **2**. For some of the ethyl groups we observed positional disorders.

Figure 1 shows that the four nitrogen atoms of the formylbiliverdin ligand deviate to some extent from a square planar configuration around the zinc ion. This is presumably caused by steric interactions of atoms O(6), C(5), and O(5), which precludes the complete planarity of the chromophore. The average Zn-N distance in **1** (2.04 (2) Å) is identical with the one in zinc tetraphenylporphyrin (2.042 Å).⁴ This conformation is very similar to that of the corresponding copper complex, where a detailed analysis of the solution ESR spectrum has been published.⁵ A water molecule is bonded to the zinc ion as a fifth ligand (Zn-O distance 2.10 (2) Å).

The axial water molecule may be removed either in the course of crystallization or, in solution, by addition of acids. The coordination number of zinc changes from five to four. For four-coordinated zinc, a tetrahedral configuration of the ligands is normally energetically preferred. Such an arrangement of the nitrogen ligands around the zinc ion is obtained in the present case by the formation of a wide bilatriene helix (inner diameter, 3.6 Å) and formation of a bis-helical dimer (Figure 2). In this dimer each zinc ion is bound to the two nitrogen atoms of both chromophore molecules, and the coordination sphere is indeed a distorted tetrahedral one. The distance between both zinc ions is 3.37 Å.