chemical shifts. However, the effect we see is too large to have such an origin.[5]

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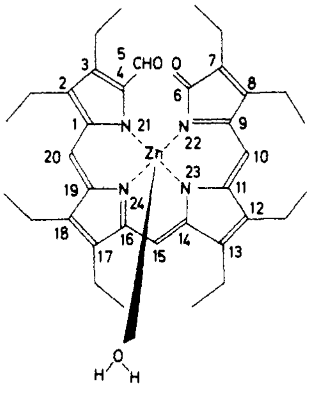
Structures of Zinc Octaethyl Formylbiliverdinate Hydrate and Its Dehydrated Bis-Helical Dimer

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.



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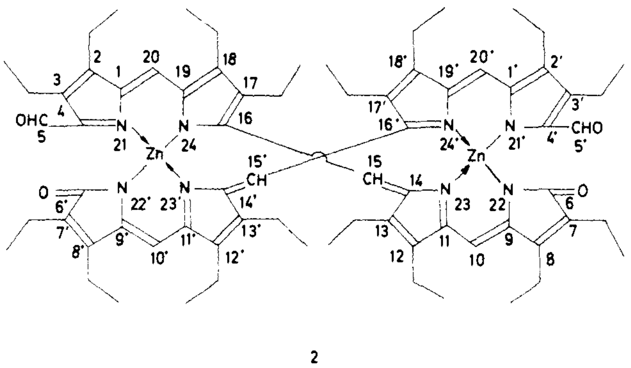

2

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.

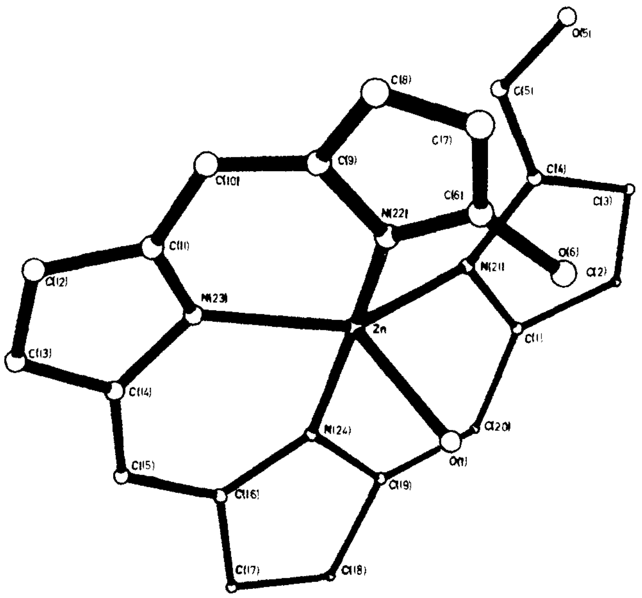

Figure 1. A perspective drawing of **1**. The ethyl groups have been omitted for clarity.

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)°) 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)°). Data were collected on a four circle diffractometer using Mo Kα radiation (λ 0.71069 Å). For **1**, 1042 independent reflections with $I \geqslant 3\sigma(I)$ were obtained up to $2\theta = 35°$ (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 ($R = \Sigma \| F_c| - |F_o\| / \Sigma |F_c|$) 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.

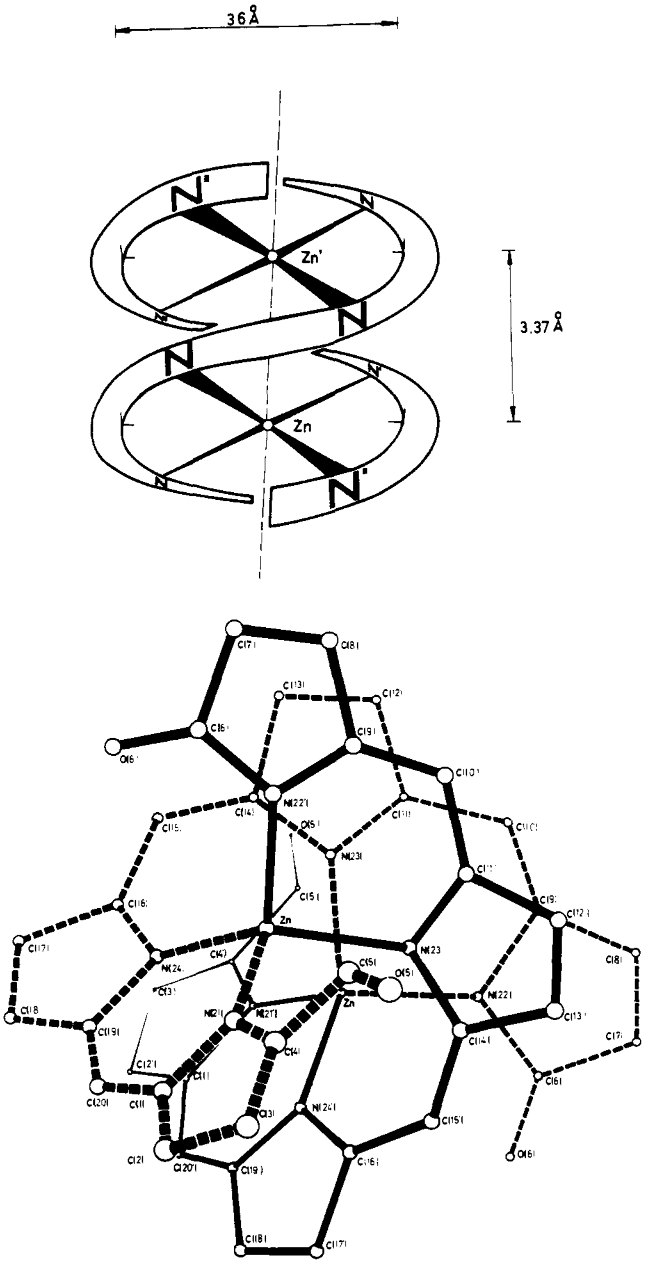

Figure 2. (Top) A schematic drawing of 2. (Bottom) A perspective drawing of 2. The ethyl groups have been omitted for clarity.

The height of the chromophore helix, as defined by the distance of N(21) and N(22) parallel to the Zn-Zn axis, is 5.2 Å. No anion is found in the dimer 2, which strongly suggests that the effect of acid addition in solution is not the expected protonation of the chromophore but simply the removal of the water molecule from the hydrate 1.

The importance of these findings on a correlation between electronic spectra and conformation of a bilatriene chromophore lies in its possible relation to the structural phytochrome problem. Phytochrome is presumably a biliprotein which controls many light responses of higher plants.[6] Its far-red form produces a broad peak at 710 nm, which is reversibly converted into a more intense peak at 660 nm (red form) by light.[6] It has been speculated that these spectral shifts may be related to cis-trans isomerizations of a bilatriene chromophore around the methine bridge atoms.[7] Calculated intensities[7] and energies[2] of bilatriene chromophores in different conformations support this hyothesis. The above results suggest that simple stretching of the molecule perpendicular to its molecular plane also produces such spectroscopic shifts without cis-trans isomerizations.

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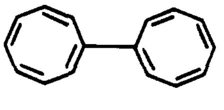
The Bicyclooctatetraenyl Tetraanion. A Quadruply Charged 20 π-Electron Biphenyl Analogue

Sir:

The ready generation of cyclooctatetraenyl dianions by alkali metal reduction of cyclooctatetraene precursors[1] constitutes convincing experimental support for the Hückel concept that a closed shell of $(4n + 2)$ π electrons (here $n = 2$) can result in a high degree of resonance stabilization. Such high affinity for 2ε uptake is especially remarkable when it is recognized that compressional strain energy of approximately 14 kcal/mol[2] and repulsive electron-electron interaction perhaps as high as 90 kcal/mol[3] need be overcome in arriving at such stable, planar species. These untoward energetic elements are revealed by the tendency of the apparently aromatic COT^{2-} to enter into concentration dependent disproportionation equilibria with neutral COT to generate $COT\cdot^{-}$.[4]

These properties intrinsic to COT^{2-} might be construed as a signal that attempts to generate more highly charged congeners of these dianions would meet with difficulty. Indeed, Stevenson and Concepción have found it possible to generate the dianion of 1 (K, THF, −110° to +60°) but were unable to obtain evidence for its further reduction.[5] We now report the successful synthesis of 2, believed to be



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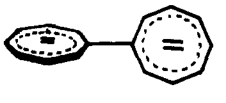

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