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X-Ray Crystal Structure of the Zinc Complex of 1,2,3,7,8,12,13,17,18,19-decamethylbiladiene-*a,c*

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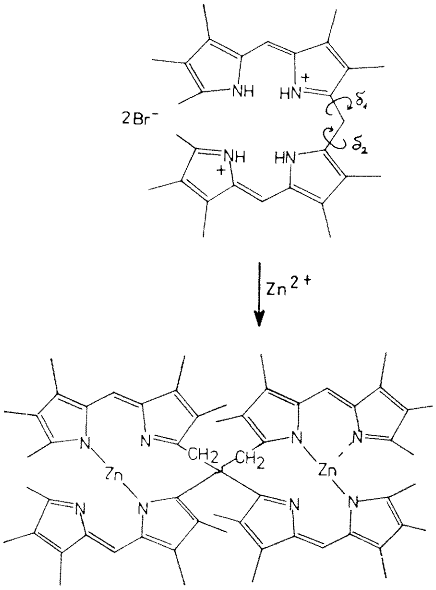
Summary The *X*-ray crystal structure of the zinc complex of 1,2,3,7,8,12,13,17,18,19-decamethylbiladiene-*a,c* (**1**) shows it to be dimeric with two distorted tetrahedral zinc atoms and two tetradentate biladiene-*a,c* ligands in a 'ridge-tile' conformation

Biladiene-*a,c* metal complexes (for nomenclature see ref 1) are important intermediates in the synthesis of corrinoid and porphyrinoid macrocycles[2] Their cyclisation behaviour is not, however, well understood[1] For instance, the Ni-,Co-, and Pd-complexes of 1,2,3,7,8,12,13,17,18,19-decamethylbiladiene-*a,c* yield tetradehydrocorrin metal complexes upon cyclisation under oxidative conditions[2] In contrast, the analogous Cu-complex yields a metalloporphyrin upon ring closure, and for the Zn-complex no cyclisation has previously been reported The initial stages in the cyclisation of biladienes-*a,c* to metal complexes of corroles and dehydrocorrins in the presence of nickel or cobalt salts have been discussed in terms of the formation of a cyclic monomeric metal–biladiene-*a,c* complex followed by the production of a conjugated chromophore by deprotonation at C-10[2] However, no molecular structure of a metal-biladiene-*a,c*-complex has been previously reported by *X*-ray analysis Such species are also of interest because of their potential structural similarity to metal complexes of the naturally occurring bile pigment, bilirubin As part of our studies on the conformations of linear polypyrroles we report the *X*-ray structure of (**1**)



(1)

Figure 1 Synthesis of (**1**)

Compound (**1**) was prepared by heating zinc acetate with 1,2,3,7,8,12,13,17,18,19-decamethylbiladiene-*a,c* dihydrobromide in a methanolic solution[3] Suitable crystals were obtained by slow evaporation of a methylene dichloride solution.

Crystal data: $C_{58}H_{68}N_8Zn_2$, $M = 1008·0$, tetragonal $P4_32_12$, $a = b = 13·837(1)$, $c = 26·498(2)$ Å, $Z = 4$, $D_c = 1·32$ g cm^{-3}, $F(000) = 2128$, $\mu(\text{Cu-}K_\alpha) = 16·4$ cm^{-1}. The structure was refined to $R = 0·052$, $R_w = 0·049$ for 2032 independent reflections [$F \geqslant 3·0\sigma(F)$, $3·5 \leqslant 2\theta \leqslant 135°$, Syntex $P2_1$ diffractometer].†

The compound is dimeric containing two distorted tetrahedral zinc atoms and two tetradentate biladiene-*a,c* ligands. A similar structure was proposed by Dolphin *et al.* on the basis of mass spectral data for an analogous biladiene-*a,c* cobalt complex.[4] A molecule of (**1**) shows twofold symmetry with the zinc atoms positioned on a crystallographic diad axis. The tetrapyrrole chromophore displays a 'ridge-tile' conformation similar to that observed for a biladiene-*a,c* dihydrobromide,[5] bilirubin,[6] mesobilirubin,[7] and di-isopropylammonium bilirubinate.[8] However, the interplanar angle between the two *syn-Z* configurated pyrromethene units is only 88·8° in (**1**), significantly smaller than those of 107, 98, 104, and 98°, respectively, in the above mentioned derivatives. This is the result of contrasting degrees of twist of the individual pyrromethene units in (**1**) with respect to the central methylene bridge. The dihedral angles, δ_1 and δ_2 (Figure 1), are 30·7 and 61·7° in (**1**) as compared to 63·9 and 57·3°, for example, in mesobilirubin. δ_1 is defined as the dihedral angle between the plane through C-9, C-10 and C-11 and the least squares plane of the pyrromethene system of rings A and B (excluding substituents), δ_2 is the dihedral angle between the former plane and the least squares plane of the pyrromethene system of rings C and D. In addition, the Zn–N distances of 1·991(4) and 1·992(4) to the first pyrromethene unit are significantly longer than those of 1·970(4) and 1·976(4) Å to the second.

The observation of a dimeric structure for (**1**) is not surprising as it is considerably less strained than would be a cyclic monomer. As both the analogous Ni- and Co-complexes are, on the basis of their mass spectral data,[3,4] also dimeric, it is reasonable to assume that their structures are similar to that of (**1**). If such dimeric complexes are also of significance in solution then they would provide support for the hypothesis of Fuhrhop[9] that any template effect of the central metal atom is relatively unimportant in the base-catalysed cyclisation behaviour of biladiene-*a,c* chelates. Of course, it is possible that in solution the dimeric complex dissociates into a monomeric 1 : 1 complex which subsequently cyclises. However, it appears that the ability of a metal cation to accept an electron pair is essential for a successful ring closure.[9] As the zinc cation is not capable of functioning as an 'electron sink' no cyclisation is observed in its case.

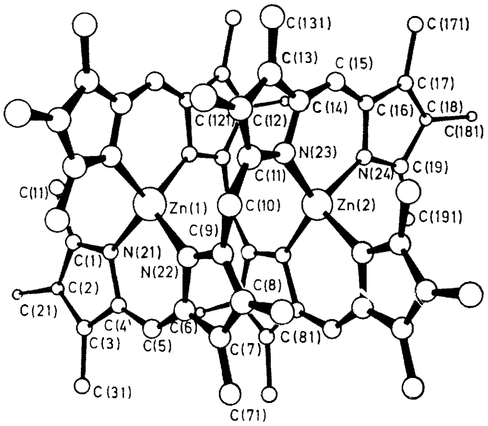


FIGURE 2 Molecular structure of (**1**) with the numbering scheme used.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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