Crystal Structure of Dichloro-octaethylporphinatotin(IV)

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Summary The porphyrin molety in dichloro-octaethylporphinatotin(IV) is essentially planar with the metal atom lying in the plane of the ring complexes have recently been completed $^{1-3}$ These structures show marked differences, particularly between tin(II) phthalocyanine³ and dichlorotin(IV) phthalocyanine³ The metal ion in the former is significantly out of the plane of the macrocycle It is a commonly observed effect in

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The structure determinations of several tin phthalocyanine

phthalocyanine and porphyrin complexes that if the metal 10n-pyrrole nitrogen atom bond distance is larger than the ' hole ' in the macrocycle, the metal ion may be forced out of the plane and the ring may show significant ruffling 4,5 To provide a comparison with these results, the structure of dichloro-octaethylporphinatotin(IV) has been determined by three-dimensional X-ray crystallographic techniques

Dichloro-octaethylporphinatotin(IV) crystallizes as purple rod-shaped crystals From the density and structure determination there appear to be two nitromethane molecules per formula unit present as solvent of crystallization

Crystal data $C_{36}H_{44}N_4SnCl_2$, M = 7262, space group $P2_1/a$, $a = 16\ 571(5)$, $b = 15\ 173(5)$, $c = 8\ 231(4)$ Å, $\beta =$ $101 \ 12(4)^{\circ}$, Z = 2, $D_{\rm m} = 1.35$, $D_{\rm c}$ (assuming two nitromethane molecules per formula unit) = 1.38 g cm^{-3}

Three-dimensional intensity data were collected on a Datex-Syntex automated diffractometer using pyrolytic graphite monochromatized Mo- K_{α} radiation The data used in the structure determination were the 1095 independent reflections considered as observed out to 2θ ca 35° The structure was solved by Fourier techniques and refined by block-diagonal least-squares methods to the present discrepancy indexes of R = 0.054 (based on F) and weighted R = 0.078 Anisotropic thermal motion was assumed for all atoms except for hydrogen atoms and those in the disordered nitromethane solvent molecule, for which isotropic thermal motion was used

The metalloporphyrin is a centrosymmetric, tetragonally distorted octahedral complex The chloride ions are co-ordinated at the apical positions This supports the published interpretation of the spectra of various SnIV porphyrins⁶ Significant bond lengths are the Sn-Cl distance of 2.449(2) Å, and the Sn-N distances of 2 104(6) Å and 2 082(6) Å Other bond lengths at the current level of refinement are shown in the Figure They are normal except for the terminal bonds in the ethyl groups which are unusually short, possibly because of thermal shortening The esd's for individual C-C and C-N bonds are ca 001 Å The average bond distances and their rms deviations are C(methine)-C_{α} 1 40(2), C_{α}-C_{β} 1 43(1), C_{β}-C_{β} 1 37(1), C_{α}-N 1 38(1) Å Within the present limits of this determination there appear to be no significant differences between the C(methine)-C_{α} or C_{α}-N bond distances in this compound and in octaethylporphinatonickel(11) in which the N1-N distance is 1 929(3) Å⁷, the distance from the centre of the porphyrin ring to the methine carbon is significantly longer in this tin complex The bond angles around the tin(IV) ion vary only slightly from the ideal octahedral angles of 90°

There are two remarkable features about this metalloporphyrin The first is the fact the tin atom is in the plane of the four pyrrole nitrogen atoms Collins and Hoard⁸ have predicted that a strongly complexing ion like tin(IV) will lie in the plane of a porphyrin with a Sn-N bond length < 2.11 Å, which is the case in this structure In the

analogous phthalocyanine structures, in which the "hole' in the macrocycle is smaller, $PcSn^{IV}Cl_{2}$ (Pc = phthalocvanine) also has the metal atom in the plane, (Sn-N bond distance 2 05 Å),3 while in PcSnII, (Sn bond distances 2·25-2 27 Å) the tin atom lies 1·1 Å from the plane of the four co-ordinated nitrogen atoms ²



Bond lengths and angles in dichloro-octaethylporphin-FIGURE Atoms are labelled on only one half of the centrosym-cule $E \ s \ d's$ are $0\ 01\ \text{\AA}$ for C-C and C-N bonds, atotin(IV) metric molecule 0 006 Å for Sn-N bonds

The second interesting feature is the planarity of the macrocycle itself The maximum deviation from the plane of the porphyrin ring (excluding ethyl groups) is 0.02 Å [for C(4)] with most atoms deviating < 0.01 Å from the plane This is in contrast to PcSnIVCl₂³ and octaethylporphinatonickel(11)⁷ both of which have severe ruffling of the ring

The nitromethane molecules of solvation are apparently disordered The present model for this disorder has two molecules with half occupancy rotated 60° from each other around the central nitrogen atom Refinement of the structure is continuing using higher order data which should significantly improve the standard deviations

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