A New Metal(II) Phthalocyanine Structure: X-Ray and Mössbauer Studies of the Triclinic Tin(II) Phthalocyanine

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Summary The metal atom in the triclinic tin(II) phthalocyanine is 1·11 Å out of the plane of the four co-ordinating nitrogen atoms; the phthalocyanine moiety is significantly non-planar.

METAL(II) derivatives of phthalocyanine of the general formula MPc (where H_2Pc represents neutral phthalocyanine) crystallize most commonly as the β-polymorph, and all those whose structures have been determined are planar.[1,2] Kroenke and Kenney[3] suggested that tin(II) phthalocyanine (abbreviated as SnPc) might have the same planar molecular structure as the simple MPc complexes but with a different crystal structure. However, the Mössbauer spectrum of SnPc suggested to us that the environment of the tin atom was asymmetric. An accurate structure determination using *X*-ray diffraction has confirmed this supposition for the triclinic crystals of SnPc, and has shown that the phthalocyanine ligand itself deviates significantly from planarity.

The tin atom in SnPc lies 1·11 Å above the plane formed by the four isoindole nitrogen atoms. The tin–nitrogen distances are 2·25, 2·24, 2·25, and 2·27 Å [estimated standard deviation (e.s.d.) 0·01 Å]; there are no other atoms bonded to the tin atom. The stereochemical environment of the tin atom is definitely not square-planar but closely resembles that found in the tetragonal form of SnO.[4] From the measured tin–nitrogen distance of 2·25 Å we estimate that the diameter of the tin atom is about 0·5 Å greater than the maximum value which would permit the tin atom to lie in the plane of the ligand.

About 3·4 Å above each SnPc molecule lie the phthalocyanine moieties of two neighbouring SnPc molecules. These are approximately coplanar and almost parallel to the reference SnPc molecule. They provide the four nearest non-bonded neighbours to the tin atom, comprising three symmetrically disposed hydrogen atoms at about 3·3 Å and one azamethine nitrogen atom at 3·79 Å. The resulting cavity above the tin atom is ideally suited to the accommodation of a lone pair of electrons if this were directed along the fourfold axis of the SnN_4-core. The observed bond lengths and angles are in accord with this square-pyramidal arrangement of four bonding electron pairs and one non-bonding electron pair above the central tin atom following the simple valence shell electron pair repulsion (V.S.E.P.R.) rules of Sidgwick and Powell[5] and Gillespie and Nyholm.[6]

The ^{119}Sn Mössbauer spectrum is consistent with the postulate of a stereochemically active lone pair of electrons. The ^{119}Sn Mössbauer spectrum of SnPc was recorded at 82°K using a tin–palladium source. The isomer shift relative to the source was $\delta = 1{\cdot}44 \pm 0{\cdot}01$ mm. sec.$^{-1}$ and the quadrupole splitting was $\Delta E_Q = 1{\cdot}43 \pm 0{\cdot}01$ mm. sec.$^{-1}$ which compare well with the values $\delta = 1{\cdot}41 \pm 0{\cdot}08$ mm. sec.$^{-1}$ and $\Delta E_Q = 1{\cdot}44 \pm 0{\cdot}08$ mm. sec.$^{-1}$ obtained at 80·5°K by Stöckler *et al.*[7] This large quadrupole splitting reflects an electric-field gradient (e.f.g.) at the tin nucleus produced by an imbalance in the $5p$-electron contribution to the bonding and non-bonding orbitals of the σ-framework. Since the p_z orbital (z-direction taken along the fourfold axis) produces an e.f.g. twice that produced by p_x and p_y orbitals (given equal amounts of p-type wave-functions), a lone pair of electrons asymmetrically oriented along the z-axis would provide a dominant contribution to the quadrupole splitting. The relatively large distances between the tin atom and its non-bonded neighbours preclude a significant contribution to the e.f.g. from the lattice.

The dimensions and angles shown in the Figure are averaged values for the four crystallographically independent isoindole moieties. The mean deviations (in parentheses) are somewhat less than approximate e.s.d.'s. The internal angles of the isoindole moieties as well as the comparable bond-lengths in SnPc agree well with those found for H_2Pc.[8] However, the four inner nitrogen atoms in SnPc very nearly form a square (sides: 2·76, 2·77, 2·77, and 2·81 Å; e.s.d. 0·01 Å) whereas in H_2Pc they form a rectangle (sides: 2·68 and 2·84 Å; e.s.d. 0·02 Å). The phenyl rings in SnPc are not perfectly hexagonal, an effect noted previously in $(MnPcPy)_2O$,[9] and evident also in CuPc[2] and H_2Pc.[8]

Although each isoindole moiety in SnPc is approximately planar, the phthalocyanine ligand as a whole is not. The average deviations of the two outermost carbon atoms of each phenyl ring from a reference mean plane through the C_8N_8 inner ring are 0·72, 0·54, 0·41, and 0·26 Å so that the phthalocyanine ligand may be described very crudely as saucer-shaped. Some puckering of the C_8N_8 inner ring is observed with a mean displacement of 0·05 Å (e.s.d. 0·01 Å) for the constituent atoms from the reference plane. These features have not been found for the phthalocyanine ligand in other bivalent metal phthalocyanines of the type MPc.

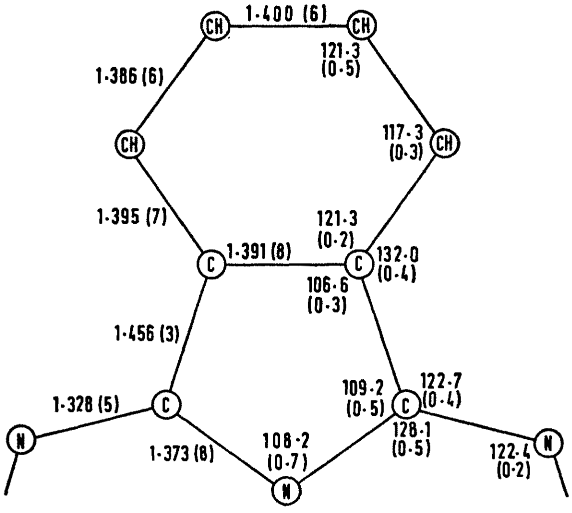

FIGURE. *Bond distances and angles in a quarter of the phthalocyanine ligand in tin*(II) *phthalocyanine. Mean deviations in parentheses.*

Crystal data: $C_{32}H_{16}N_8Sn$, $M = 631{\cdot}2$, triclinic, $a = 12{\cdot}060(1)$, $b = 12{\cdot}618(1)$, $c = 8{\cdot}675(1)$ Å, $\alpha = 95{\cdot}89(1)$, $\beta = 95{\cdot}08(1)$, $\gamma = 68{\cdot}17(1)°$, $U = 1217$ Å^3, $Z = 2$, $D_m =$ approx. 1·74 g. cm.$^{-3}$, $D_c = 1{\cdot}722$ g. cm.$^{-3}$, space group $P\bar{1}$ (C_i^1; No. 2), Cu-K_α radiation. A Siemens automatic diffractometer was used to measure about 4500 unique reflection intensities of which about 110 were rejected as unobserved. The structure was determined in the usual way, and after refining anisotropic thermal parameters by block-diagonal least-squares (using unit weights) and introducing the sixteen hydrogen atoms per molecule with isotropic temperature factors, R was 0·044.

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