X-Ray Crystal Structure of Dichlorophthalocyaninatotin(IV)

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Summary The phthalocyanine ring of the dichlorophthalo-cyaninatotin(IV) molecule is shown to be substantially 'crumpled'—a stepped deformation—apparently owing to an oversize tin atom.

THE structure of Sn^{II}phthalocyanine [or $Sn^{II}(pc)$ where $H_2(pc)$ = neutral phthalocyanine] shows that the covalent radius of Sn^{II} is so grossly oversize for the hole in the macrocycle that the tin atom lies 1·11 Å out of the plane of the quartet of ligand nitrogens, and the macrocycle is slightly deformed to a saucer shape.[1] [A similar deformation of the macrocycle has been reported in $U^{IV}(pc)_2^2$]. The average of the four Sn^{II}–N distances is 2·25 Å. Even with the smaller radius of Sn^{IV} (*ca.* 1·40 Å)[3] it seemed possible that the tin would be a tight fit in a phthalocyanine ring and that this might lead to the 'ruffling' found in analogous compounds.[4-6] We report that $Sn^{IV}Cl_2(pc)$ is a centrosymmetric molecule with nonplanar deformations about ten times those observed in $Sn^{II}(pc)$ and the ruffled ring analogues. It is interesting to compare the present results with those quoted by Cullen and Meyer[7] on $Sn^{IV}Cl_2$ octaethylporphyrin [$SnCl_2(Et_8pp)$], where the hole is slightly larger and the ring is essentially flat.

Crystals of $Sn^{IV}(Cl_2(pc)$, $C_{32}H_{16}Cl_2N_8Sn$, are dark blue monoclinic plates, $a = 21·104$, $b = 11·060$, $c = 11·392$ Å, $\beta = 96·04°$, space group either Aa or $A2/a$; $Z = 4$. Solution of the Patterson map and successful refinement have shown the space group to be $A2/a$ and the molecules to be centrosymmetric. 1959 significant reflections were measured on a Siemens single-crystal diffractometer using Cu-K_α

radiation, and the intensities were corrected for absorption. All the heavier atoms were refined anisotropically and the hydrogens isotropically, and allowance has been made for anomalous scattering by tin. R is now 0·0255.

The central co-ordination group approximates very closely to a regular square bipyramid, though the Sn–Cl axis is tilted 2·5° from the normal to the Sn–N(2)–N(4) plane. This geometry is in agreement with the interpretation of the spectra of this and related molecules.[8] Distances of the atoms from the Sn–N(2)–N(4) plane (Figure 1) reach ± 0·89 Å (while maximum displacements in ruffled analogues are *ca.* 0·07—0·10 Å). A model shows that the molecule is curled like two half saucers, centrosymmetrically related. The isoindole units are, however, fairly flat and both the A_1A_1' and A_2A_2' pairs can be represented as in Figure 2.
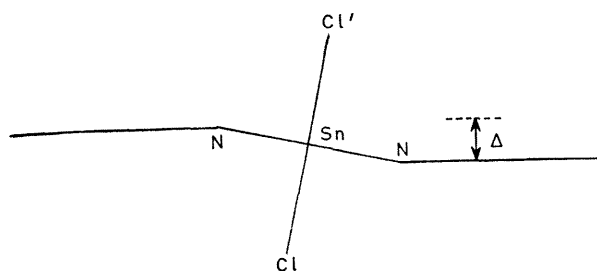

FIGURE 2

For A_1A_1' the offset, Δ, is 0·757 Å and the atoms in each unit are coplanar to ±0·037 Å. For A_2A_2', Δ is ±0·363 Å and atoms are coplanar to ±0·013 Å. No very meaningful best plane can be specified for the macrocycle, but it is clear that the Sn–N(2)–N(4)–Cl$_2$ octahedron is substantially tilted with respect to the general plane. This sort of crumpling might be expected to occur in a centrosymmetric molecule if the central atom is oversize if it is assumed that each isoindole group can hinge round the line BB' joining the two bridging atoms B, B' which link it to its neighbours. It is of interest, therefore, to compare the lengths of the Sn–N bonds and other dimensions in the girdle in this and several related molecules, including metal-free phthalocyanine [$H_2(pc)$][9] (see Table).

Replacement of the nitrogen bridging atoms by methines will allow a small expansion of the ring, so that the hole in a porphyrin ring will be marginally broader (*ca.* 0·04 Å) than in phthalocyanine, (see Table). However $Sn^{IV}Cl_2(pc)$ has, despite the crumpling, the shortest Sn^{IV}–N bonds yet recorded and the most distended phthalocyanine ring. The very close agreement between the Sn–Cl bond lengths (Table) is evidence of comparability. The minor difference in the size of the porphyrin and phthalocyanine rings is therefore critical in relation to the covalent radius of Sn^{IV}.

Parts of the macrocycle are only ∼ 3·35 Å from neighbouring rings, but these contacts appear mainly to be a consequence rather than a cause of the crumpling. There is also apparently a chain of intermolecular hydrogen bonds
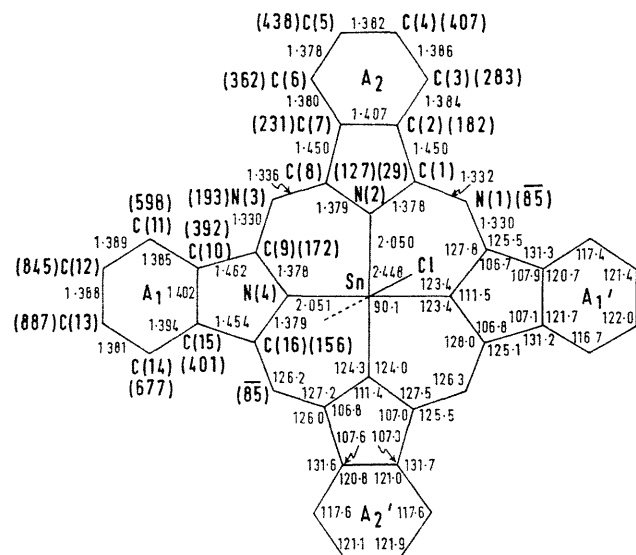

FIGURE 1. *Geometric details of the centrosymmetric molecule of* $SnCl_2(pc)$. *Bond lengths in Å; angles in degrees; displacements of the atoms from the plane of* Sn–N(2)–N(4) *are shown in parentheses in units of* 0·001 Å.
Calculated standard deviations: Sn–Cl 0·001; Sn–N 0·003; N–C, C–C 0·005 Å, *all angles* ∼ 0·2°.

Bond lengths (Å)

	$H_2(pc)$[a]	$Sn^{II}(pc)$[b]	$Sn^{IV}Cl_2(pc)$	$Sn^{IV}Cl_2(et_8pp)$[c]
M^d–N	1·95	2·24, 2·25, 2·25, 2·27	2·050, 2·051(3)	2·082, 2·104(6)
M^d–B[e]		3·58, 3·49, 3·61, 3·62	3·398, 3·402	3·43, 3·44
N–N	2·68, 2·84	2·76, 2·77, 2·77, 2·81	2·903, 2·896	2·94, 2·95
Sn–Cl			2·448(1)	2·449(2)

[a] Values from ref 9.   [b] Values from ref 1.   [c] Values from ref 7.   [d] M denotes Sn or the centre of the ring as appropriate. [e] B denotes the atom bridging the isoindole or pyrrole rings.

linking Cl with the hydrogen on C(13), the hydrogen being almost directly in the line joining Cl and C(13) [Cl–H = 2·70, Cl–C(13) = 3·70 Å]. A detailed study of the translational and librational motions of this molecule shows that the hydrogen bonds exert a detectable constraint, but do not cause the crumpling.

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