

essentially reversible on cooling, but the rate of reformation of the complex diminishes markedly with increasing pH.

Although detailed data on the structural organization of the poly G complex are lacking, several observations suggest that it arises from interactions between *more than two* polynucleotide strands helically wound around the same axis: the exceptional thermal stability of the poly G helix; the very slow rate of reactivity with poly C to form poly (G + C) and poly (G + C + G)⁶ at neutral pH; the difficulty in making perfect helices that melt sharply; and the tendency of poly G to aggregate and precipitate at neutral pH even at low polymer concentration. A three or four stranded model, not unlike those proposed for poly I,⁷ but containing additional hydrogen bonds linking the 2-amino substituent of each base to the N-7 of the adjacent one at each base-plane level, would not be inconsistent with the properties of the poly G helix reported here.^{8,9}

(6) These are helical complexes containing one strand of polycytidylic acid (poly C) and either one or two strands of poly G. J. R. Fresco, J. Massoulié and R. D. Blake, in preparation.

(7) A. Rich, *Biochim. Biophys. Acta*, **29**, 502 (1958).

(8) After completing this work, we learned that a 4-stranded model involving such a hydrogen bonding scheme has been proposed for helices formed in concentrated solutions of 5-GMP: M. Gellert, M. N. Lipsett and D. R. Davies, *Proc. Natl. Acad. Sci.*, **48**, 2013 (1962).

(9) We are indebted to Mr. Richard Blake for assistance in this investigation.

(10) Established Investigator of the American Heart Association.

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THE STRUCTURE OF COPPER TETRAPHENYLPORPHINE¹ Sir:

We wish to substantiate the report of the non-planarity of the porphyrin ring system in metalloporphyrin compounds.² The structure of copper tetraphenylporphine (Fig. 1) was determined by X-ray analysis.

Copper tetraphenylporphine crystals are tetragonal, space group I4₂d (No. 122 International Tables), with the following cell edges: $a = 15.03 \pm 0.01$ Å.; $c = 13.99 \pm 0.01$ Å. There are four molecules of the porphyrin per unit cell. A set of 465 independent structure factors was determined using CuK α radiation; each independent structure factor is the average of two equivalent reflections.

The space group requires that the copper atom be at $x = 0, y = 0, z = 0$ on a fourfold inversion axis. The structure was solved by utilizing the copper atom to determine the phases of the structure factors. The structure was refined by least-squares analysis employing a weighting scheme of unit weights for all reflections and anisotropic temperature factors in the final refinement procedure. Hydrogen atoms were included in the refinement.

The final R -factor including all reflections was 6.6%, and the standard deviations of the atomic coordinates, not including the hydrogen atoms, ranged from 0.007 to 0.015 Å. Table I lists the bond distances of the molecule; Table II lists the fractional atomic coordinates. The seven hydrogen-carbon bond lengths averaged 1.1 ± 0.1 Å.

The geometry of the porphyrin molecule has the following interesting features. The phenyl group is both tilted down from the porphyrin ring and is twisted out of the "plane" of the porphyrin ring. The C₅-C₆

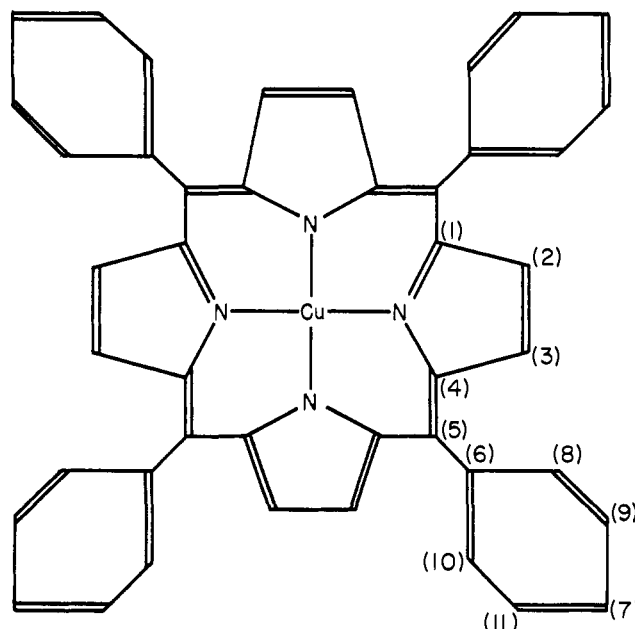


Fig. 1.—Copper tetraphenylporphine.

bond makes an angle of 13° with its projection on the 001 plane. The line through the atoms C₈ and C₁₀ makes an angle of 72° with its projection on the 001 plane. Thus, the phenyl group is almost perpendicular to the porphyrin ring. The C₅-C₆ bond distance is 1.51 Å. This is strong evidence that the phenyl group is electronically isolated from the porphyrin ring.

TABLE I

BOND LENGTHS IN COPPER TETRAPHENYLPORPHINE

Bond	Length in Å. ^a	Bond	Length in Å. ^b
Cu-N	1.98	C ₈ -C ₈	1.38
N-C ₁	1.38	C ₈ -C ₉	1.40
N-C ₄	1.39	C ₉ -C ₇	1.39
C ₁ -C ₂	1.44	C ₇ -C ₁₁	1.36
C ₂ -C ₃	1.35	C ₁₀ -C ₁₁	1.42
C ₃ -C ₄	1.45	C ₁₀ -C ₆	1.40
C ₄ -C ₅	1.36		
C ₅ -C ₆	1.51		

^a Standard deviation of bond length ≤ 0.013 Å. ^b Standard deviation of bond length ≤ 0.021 Å.

TABLE II

FRACTIONAL COORDINATES FOR COPPER TETRAPHENYLPORPHINE

Atom	x	y	z
Cu	0.000	0.000	0.000
N	.114	.066	-.003
C ₁	.197	.032	.019
C ₂	.261	.103	.017
C ₃	.217	.178	-.007
C ₄	.124	.157	-.017
C ₅	.057	.217	-.030
C ₆	.081	.311	-.055
C ₇	.132	.484	-.102
C ₈	.104	.332	-.147
C ₉	.128	.419	-.172
C ₁₀	.087	.376	.017
C ₁₁	.111	.464	-.010

The porphyrin ring is non-planar. The extent of the non-planarity can be illustrated by the distance that atoms are from the plane parallel with the 001 plane and passing through the origin. These distances are given in Table III. It is evident from Table III that the molecule is highly distorted from a planar configuration.

(1) This research was supported by a Public Health Service Grant.

(2) E. B. Fleischer, *J. Am. Chem. Soc.*, **85**, 146 (1963).

TABLE III
DEVIATIONS OF ATOMS IN COPPER TETRAPHENYLPORPHINE FROM THE PLANE PARALLEL TO THE 001 PLANE AND PASSING THROUGH THE ORIGIN

Atom	Deviation in Å.
Cu	0.00
N	.04
C ₁	.26
C ₂	.24
C ₃	-.09
C ₄	-.24
C ₅	-.42
C ₆	-.76
C ₇	-1.42

The bond distances in the copper tetraphenylporphyrin and nickel etioporphyrin I² agree to within the experimental errors. Both molecules have a non-planar configuration of the porphyrin ring although the details of the non-planarity are different for the two molecules. The X-ray analysis of palladium tetraphenylporphyrin, which is isomorphous with copper tetraphenylporphyrin, is in progress, and both structures will be published in detail at a future time.

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VALENCE EXHIBITED BY ZINC AMALGAM ANODICALLY DISSOLVING IN NITRATE SOLUTIONS¹

Sir:

Sorenson, Davidson and Kleinberg² have proposed that zinc and cadmium dissolve anodically in certain oxidizing agents (chlorates and nitrates) with an initial mean valence between one and two. Other investigators³⁻⁶ have reported the anodic disintegration of such metals as Be, Mg, Al and Fe in salt solutions. In the case of Be and Mg "chunks" of metal have been obtained as a residue and shown to have originated from the electrode and not through nucleation.^{3,7} Therefore, any material dissolving in the electrolyte and not a part of the electrical circuit would not contribute to the faradaic current, and could account for apparent valencies of less than two. The presence of atomic aggregates of colloidal and sub-colloidal size also could account for the reducing properties of the anolyte.

In July, 1962, Dr. T. P. Hoar (Cambridge, England) suggested that the mechanism of anodic dissolution of zinc be studied by the use of a zinc amalgam electrode. The amalgamation would prevent the disintegration of the electrode and the formation of films such as are observed on pure zinc (99.99%) electrodes in nitrate solutions. As the diffusion of zinc ions of any valence would not be prevented by the amalgamation, one would expect the behavior of zinc amalgam to correspond to that of zinc in the same electrolyte as regards the initial mean valence.

(1) This work supported by a research grant from ONR.

(2) D. T. Sorenson, A. W. Davidson and J. Kleinberg, *J. Inorg. Nucl. Chem.*, **13**, 64 (1960).

(3) M. E. Straumanis and D. C. Mathis, *J. Electrochem. Soc.*, **109**, 434 (1962); *J. Less-Common Metals*, **4**, 213 (1962).

(4) W. J. James, M. E. Straumanis, B. K. Bhatia and J. W. Johnson, *J. Electrochem. Soc.*, **109**, 199C (1962).

(5) B. Roald and M. A. Streicher, *ibid.*, **97**, 283 (1950).

(6) G. A. Marsh and E. Schaschl, *ibid.*, **107**, 960 (1960).

(7) M. E. Straumanis and B. K. Bhatia, *ibid.*, **110** (1963).

Accordingly, zinc electrodes were electrolyzed in 3% potassium chloride and in 3% potassium sulfate at 25° employing a current density of 60 ma. cm.⁻². The results confirm the studies of Sorenson, *et al.*, that anodic dissolution in non-oxidizing electrolytes involves only the formation of bivalent ions. Anodic dissolution of zinc in 3% potassium nitrate at 25 and 58° results in valences of less than two (1.82-1.87 at 25°) considerably outside of experimental errors. This is in harmony with results obtained by Sorenson, *et al.*, for zinc dissolving in sodium nitrate.

However, when zinc amalgam is electrolyzed at 60 ma. cm.⁻² in nitrate solution, there is no evidence of univalent ions; the agreement between the faradaic equivalent obtained from the current based on bivalent ions compares excellently with the amount of zinc dissolved as determined by titration with EDTA, and confirmed by weight measurements of the electrode (Table I).

TABLE I

Wt. zinc (calcd.), g.	Wt. zinc (exptl.), g.	Temp., °C.	Apparent valence
0.1262	0.1269	25 ± 0.2	1.99
.1939	.1951	25	1.99
.2851	.2817	25	2.02
.2864	.2734	58	2.09
.0892	.0903	58	1.98

No mercury was detected in solution. A loosely adhering black film was observed on the zinc anode during electrolysis in potassium nitrate but was not present on the amalgam or on zinc in other electrolytes (sulfate and chloride).

The value of 2.09 is higher than normal experimental error can account for and suggests the possibility of a competing electrolytic anode reaction which might conceivably compensate for a decrease in apparent valence arising from non-electrolytic oxidation of univalent zinc ion by the electrolyte. However, the only possible competing electrolytic oxidation would require oxygen evolution and no evolution was observed at the anode. Furthermore, no nitrite ion was detectable in the anolyte after prolonged electrolysis.

The results clearly show, inasmuch as the concept of uncommon valence states is inadequate to explain the anodic dissolution of zinc in oxidizing electrolytes, that mechanisms involving breakdown of the anode into atoms and/or atomic aggregates cannot be rejected.

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SOME CHARGE-TRANSFER SALTS OF 1,2,3,4,5-PENTACARBOMETHOXYCYCLOPENTADIENYL ANION

Sir:

In the course of studying the chemistry of 1,2,3,4,5-pentacarbomethoxycyclopentadiene¹ we found that its anion, I, will function as a planar donor in a series of organic charge-transfer salts, in which the isoelectronic planar cations tropylium, 2,4,6-trimethylpyrylium, pentaphenylpyrylium, N-methylpyridinium and N-methylquinolinium serve as acceptors. Good yields of these stable salts² are obtained by stirring a suspen-

(1) O. Diels, *Ber.*, **75**, 1452 (1942).

(2) Salt formation no doubt is a result of the low nucleophilicity of I. Less substituted cyclopentadienyl anions (thus, less delocalization of the negative charge) have been shown to form covalent compounds with tropylium,³ pyrylium⁴ and pyridium.⁵

(3) W. von E. Doering and H. Krauch, *Angew. Chem.*, **68**, 661 (1956); M. E. Vol'pin, I. S. Akhrem and D. N. Kursanov, *Zh. Obshch. Khim.*, **28**, 330 (1958); K. Hafner, *Angew. Chem.*, **75**, 43 (1963).