

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 tetraphenylporphine 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 tetraphenylporphine, which is isomorphous with copper tetraphenylporphine, 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).