

183. *Metal Chelates. Part I. A Micromethod for the Determination of the Valency of a Metal in a Phthalocyanine Complex.*

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0.01N-Dichromate disrupts the large ring of many metal phthalocyanines and substituted tetrazaporphins without causing dehydrogenation. Titration with this reagent thus permits the valency state of the metal to be determined.

DURING attempts to determine the hydrogenation level of hydrotetrazaporphins,¹ it was found that 0.01N-dichromate effects oxidative hydrolysis of the macrocyclic ring, quantitatively, without effecting dehydrogenation, in contrast to the behaviour of other

¹ Ficken, Linstead, Stephen, and Whalley, *J.*, 1958, 3879.

oxidants.^{2,3} It then appeared that if the reagent proved equally specific with tetrazaporphin metal derivatives, a ready method would be available for confirming the valency of the metal. Good results are obtained with metal phthalocyanines (see Table); metal tetrazaporphins give results consistently slightly high, but nevertheless useful.

The disruption of a phthalocyanine or tetrazaporphin ring requires 1 atom-equivalent of oxygen and gives 4 mols. of imide.² There is little interference under our conditions from substituents (in the cases examined). The observed oxygen uptake by a metal derivative will differ from 1 atom-equivalent only if the metal ion which is liberated subsequently undergoes valency change with the reagents. This will be known. Consequently the valency state of the metal in a tetrazaporphin complex can be deduced from the observed oxygen uptake.

The method gives results with substituted tetrazaporphins in agreement with previously assigned constitutions. The only exception is the parent tetrazaporphin and its metal complexes. These consume considerably more than 1 atom-equivalent of oxygen, evidently because the first-formed maleimide is unstable even to very dilute dichromate.⁴ The method confirmed that the iron in iron phthalocyanine⁵ and also in the octahedral dipyrindine-iron complex⁶ is in the bivalent state, but is trivalent in chloroiron phthalocyanine.⁶ Zinc phthalocyanine⁵ and its monopyridine solvate⁷ gave results similar to one another and to that from zinc chlorophthalocyanine,⁵ so that in the latter the metal is bivalent and the chlorine a peripheral substituent. The aluminium in chloroaluminium phthalocyanine⁵ is trivalent as expected, the chlorine being an anionic ligand, as must be the chlorine atoms in dichlorotin phthalocyanine⁵ which gave a result indicative of quadrivalent tin. Tin phthalocyanine⁵ and tin diphthalocyanine⁵ did not give quite such accurate results, but these nevertheless clearly indicate respectively bivalency and quadrivalency for the metal. The phthalocyanine complexes of bivalent cobalt,⁵ copper,⁸ lead,⁵ and nickel⁵ afforded expected results, although the last complex was perceptibly less easily oxidised and this necessitated a slight modification of the procedure. The only complex examined that failed to undergo oxidation smoothly by our procedure was platinum phthalocyanine. Its extreme resistance to oxidation has previously been mentioned.⁹

Most recently, the method has been used to confirm the valency states of the metal in the newly isolated phthalocyanine chromium(II) and chromium(III) hydroxide complexes.¹⁰ Further uses are likely to arise.

EXPERIMENTAL

Quantitative Oxidation.—The samples used were analytically pure. The tetrazaporphin pigment (4–6 mg.; powdered in an agate mortar) was weighed accurately into a 50 c.c. conical flask. A lead, from a supply of dry nitrogen, was hung over the side of the flask. As soon as the air had been displaced, concentrated sulphuric acid (3.0 c.c.) was pipetted in, and the pigment dissolved (by swirling). The flask was placed in crushed ice, and ice (from 3.0 c.c. of boiled-out distilled water) was added, followed *immediately* by 5.0 c.c. of 0.01N-potassium dichromate from a pipette, whilst the flask was gently swirled. By the time the pipette was empty, the pigment had been destroyed and the (hot) solution had regained room temperature. 0.01N-Ferrous sulphate (5.0 c.c.) was added, followed by internal indicator, *viz.*, 1.5 c.c. of acid (an aqueous solution containing 15 c.c. of sulphuric acid and 15 c.c. of syrupy phosphoric acid

² Dent, Linstead, and Lowe, *J.*, 1934, 1033.

³ Ficken and Linstead, *J.*, 1952, 4846; Linstead and Weiss, *J.*, 1950, 2981.

⁴ Cf. Linstead and Whalley, *J.*, 1952, 4839.

⁵ Barrett, Dent, and Linstead, *J.*, 1936, 1719.

⁶ Barrett, Frye, and Linstead, *J.*, 1938, 1157.

⁷ Whalley, preceding paper.

⁸ Dent and Linstead, *J.*, 1934, 1027.

⁹ Ref. 5, p. 1734.

¹⁰ Elvidge and Lever, *J.*, 1961, in the press.

in 100 c.c.) and 2 drops of 0.2% barium diphenylaminesulphonate, and the solution was titrated with the dichromate until a violet colour appeared.

Nickel phthalocyanine was oxidised smoothly if the sulphuric acid solution of the pigment was not cooled before addition of ice and oxidant.

The results are tabulated.

Pigment	M	Weight (mg.)	Titre (c.c.; 0.01N)	Atoms of O consumed:		Valency of metal
				Obs.	Calc.	
<i>Tetraazaporphins</i>						
(ref. 1, except as indicated)						
Me ₈	426	4.35	1.86	0.91	1.0	
		3.60	1.63	0.97		
H ₄ Me ₈	430	4.70	1.13	1.03	„	
		4.80	1.18	1.06		
Co Me ₈ (ref. 11)	483	3.86	2.07	1.30	„	2
		3.34	1.79	1.30		
Ni Me ₈ (ref. 11)	483	3.16	1.64	1.25	„	„
Ni Me ₄ (ref. 12)	427	4.67	2.70	1.24	„	„
Tetracyclohexeno	530	4.12	1.54	0.99	„	
H ₄ tetracyclohexeno	534	4.23	1.61	1.01	„	
<i>Phthalocyanines</i>						
(ref. 7, except as indicated)						
Fe	568	4.02	1.99	1.41	1.5	2
		4.29	2.23	1.47		
		4.62	2.38	1.46		
Fe, 2py	726	4.47	1.77	1.44	„	„
		4.65	1.97	1.54		
FeCl (ref. 6)	603.5	4.03	1.28	0.96	1.0	3
		4.68	1.54	0.99		
Zn (ref. 5)	577.5	4.27	1.53	1.03	„	2
Zn.py	656.5	4.23	1.40	1.08	„	„
Zn chlorophthalocyanine (ref. 5)	612	5.29	1.74	1.01	„	„
		5.42	1.62	0.91		
AlCl (ref. 5)	574.5	5.41	2.10	1.11	„	3
		5.29	1.94	1.05		
		5.36	1.96	1.05		
SnCl ₂ (ref. 5)	702	5.81	1.82	1.10	„	4
		4.81	1.62	1.18		
		5.30	1.76	1.16		
Sn (ref. 5)	603	5.19	2.87	1.74	2.0	2
		5.64	3.31	1.85		
Sn diphthalocyanine	1143	5.22	1.73	1.89	„	4
		4.82	1.60	1.90		
Co	571	5.19	2.19	1.15	1.0	2
		5.18	1.93	1.06		
Cu	575	4.62	1.80	1.12	„	„
		4.18	1.58	1.08		
Ph	719	4.34	1.20	0.99	„	„
		5.17	1.34	0.91		
Ni	571	4.96	1.87	1.07	„	„

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¹¹ Baguley, France, Linstead, and Whalley, *J.*, 1955, 3521

¹² Brown, Spiers, and Whalley, *J.*, 1957, 2882.