*Syntheses of Two Kinds of Metal-free Tetra-azaporphines by the Urea-melt Method**

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In previous papers, it was shown that various metallo-derivatives (metal chelates) of ammonium phthalocyaninetetra-(4)-sulfonate[1] and of tetra-2, 3-pyridinoporphyrazine[1] were synthesized by the so-called urea-melt method in good yields and that the metal-free macrocycles of these metallo-derivatives, namely the parent substances, were prepared from the derivative of magnesium[2], of manganese[1], or of zinc[1]. In the present paper, it is reported that the metal-free macrocycles were obtained directly by the urea process.

No blue product was obtained from the mixtures of triammonium 4-sulfophthalate (10 g.) and urea (50~75 g.), or of quinolinic acid (10 g.) and urea (50~75 g.) by heating to 230°C. However, boric acid (0.5~1.5 g.) and ammonium molybdate (1.0~2.5 g.) were added to them as catalysts and heated together at 170~250°C for 0.5~1.5 hr., ammonium phthalocyaninetetra-(4)-sulfonate or tetra-2, 3-pyridinoporphyrazine was synthesized in fairly well yields (8~18%). It was further found that the metal-free macrocycles were prepared in high yields (26~42%), when a powdered metal (1.0~2.5 g.), such as chromium, molybdenum, or manganese, was used with boric acid and ammonium molybdate and that while in the absence of both boric acid and ammonium molybdate only very small amounts of the macrocycles were formed. When molybdenum was used, no metal chelate of the macrocycle was mixed, but when chromium or manganese was used, a small amount of the metal chelate was mingled. In the case of ammonium phthalocyaninetetra-(4)-sulfonate, a mixture of the metal-free macrocycle and the chromium chelate (about 9 : 1) was obtained. The chromium chelate was removed by extracting with a mixture of water, methanol and acetone (4 : 5 : 1). In the case of tetra-2, 3-pyridinoporphyrazine, a mixture of the free base and the

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[1] N. Fukada, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 378, 380, 586, 1141 (1954); **76**, 1378 (1955); **77**, 1421 (1956); **78**, 1378 (1957); **79**, 396, 980 (1958).

[2] R. P. Linstead et al., *J. Chem. Soc.*, 1937, 911.

chromium chelate (about 2 : 1), or of the free base and the manganese chelate (about 4 : 1) was obtained. The manganese chelate was converted into the free base by the action of 98% sulfuric acid. On the contrary, the chromium chelate, as its coordinated chromium could not be eliminated by dissolving in strong mineral acids, was separated from the free base by treating with aqueous solution (50∼75%) of benzenesulfonic acid because of the greater solubility of the free base.

The purification of crude ammonium phthalocyaninetetra-(4)-sulfonate was carried out as follows. The reaction mixture was powdered and extracted with water. The extract was evaporated to dryness. The residue was again extracted with water and the extract evaporated to dryness. This treatment was repeated about 10 times. The residue was thoroughly washed with 70% ethanol and added into an ammoniac saturated solution of ammonium carbonate and the solution was warmed. The macrocycle was salted out to give ammonium sulfonate. The crude ammonium salt was thoroughly washed with 70% ethanol and then boiled in 95% ethanol. Its chemical formula was $(C_8H_3N_2\cdot SO_3NH_4)_4H_2$ (Found: S, 14.0; N, 18.3; NH_3, 7.2%).

The tetraammonium sulfonate was converted into the corresponding tetrasulfonic acid by treating with 6 N or more concentrated hydrochloric acid. The blue crystalline product formed was collected by filtration, washed with 6 N hydrochloric acid and dissolved in a small amount of ethanol. The ethanol solution was evaporated to dryness. The sulfonic acid was recrystallized from 8 N hydrochloric acid to give long thready crystals. The chemical formula of the acid was $(C_8H_3N_2SO_3H)_4H_2$ (Found: S, 15.1; N, 13.0%). The tetrasulfonic acid in solid form had an intense purple reflex and was hygroscopic. The tetrasulfonic acid was found to be identical with the one reported previously¹⁾.

The purification of crude tetra-2, 3-pyridinoporphyrazine was carried out as follows. The reaction mixture was powdered, mixed with a large amount of 1 N hydrochloric acid, allowed to stand overnight at room temperature and filtered off. The residue was boiled with water, heated several times with 0.2 N hydrochloric acid at 80∼90°C for 0.5 hr. and heated further several times with 0.1 N sodium hydroxide solution at 80∼90°C for 0.5 hr., each time filtered off, and washed with dilute hydrochloric acid and with water. The bluish-black residue was dried at 100°C. The dried solid was dissolved in a small quantity of 98% sulfuric acid and the solution after being filtered was poured into a large excess of water. The blue crystalline product thereby deposited was collected, washed with hot dilute aqueous sodium hydroxide and with hot water, and dried at 100°C. The dried solid was powdered, heated under reflux (Soxhlet) with 95% ethanol, acetone and ether, successively, and filtered off. The purified product was dried at 185°C for 1 hr. Its chemical formula was $(C_7H_3N_3)_4H_2$ (Found: N, 31.5%). The metal-free macrocyclic pigment was found to be identical with the one reported previously by Linstead et al.²⁾ from its coincidence in physical and chemical properties as well as in elementary composition.

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