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Tungsten(V) Tetraphenylporphine*

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Porphyrins, being macrocyclic chelating ligands, offer a convenient tool for studying the chemistry of unusual oxidation states of transition metals. Since chromium and molybdenum porphyrins have been synthesized recently [1], we were interested in synthesizing a tungsten porphyrin [2]. The following is a summary of our results.

The tungsten complex was synthesized by refluxing slight stoichiometric excess of tungsten hexacarbonyl and a gram of tetraphenylporphine (TPP) in 100 ml of dimethylformamide overnight. The reaction mixture was cooled, poured into a beaker containing 100 ml of cold water. The solid which separated was filtered, washed with distilled water and dried. The crude complex was purified by chromatography on a column of dried alumina using benzene as eluent until no further free base porphyrin was detected in the effluent. Methanolic chloroform (20%) was used to elute the compound from the column [3].

The visible spectrum of the complex in methanolic solution was recorded using a Beckman Acta III spectrophotometer. The spectrum of the complex contained two bands with maxima at 625 nm ($\epsilon = 7.53 \times 10^3$ cm^{-1} M^{-1}) and at 580 nm ($\epsilon = 9.78 \times 10^3$ cm^{-1} M^{-1}) in addition to the Soret at 446 nm ($\epsilon = 2.15 \times 10^5$ cm^{-1} M^{-1}) in alkaline methanol. In acidic methanol, an additional broad shoulder centered at 662 nm ($\epsilon = 5.88 \times 10^3$ cm^{-1} M^{-1}) is observed. Prolonged storage (a month or two) of acidic solution results in demetallation. The ir spectrum recorded both as KBr pellet and as nujol mull indicated a strong absorption at 935 cm^{-1} in addition to the normal metalloporphyrin stretches. This indicates the presence of tungstenyl (WO^{+3}) group in the complex [4]. The absence of any absorption around 2000 cm^{-1} rules out any carbonyl group in the complex [5]. Magnetic susceptibility measurements were made by the Faraday method from room temperature down to 90 °K. The susceptibility obeys the Curie–Weiss law with a Weiss constant of 3.0 °K. The effective moment of 1.52 B.M. found for this complex compares well with the 1.5 B.M. recently reported for the tungsten octaethylporphyrin complex [2]. The epr spectrum of the complex in benzene solution was determined both at 77 °K and at room temperature. The room temperature spectrum contains a set of broad lines. At 77 °K, the resolution was very good and $g_{\parallel}$ and $g_{\perp}$ values determined were 1.904 and 1.868 respectively. The hyperfine splitting parameter, A, due to ^{183}W (I = 1/2, 14.3% abundant) was calculated to be 95×10^{-4} cm^{-1}. This unusual reversal in $g_{\parallel}$ and $g_{\perp}$ has been noted earlier for oxochlorotungstates [6]. This reversal has been ascribed to spin–orbit interaction of the ligand by Manoharan and Rogers [7]. Thus we propose the newly synthesized complex to be W=O(OH)(TPP) [8].

References

1 See the review: D. Ostfeld and M. Tsutsui, *Accounts Chem. Res., 7,* 52 (1974).

2 While this work was in progress, a tungsten octaethylporphyrin was reported: J. W. Buchler and K. Rohbock, *Inorg. Nucl. Chem. Lett., 8,* 1073 (1972).

3 Elemental analysis was performed by Messrs. Chemalytics, Tempe, Arizona. Calcd. for $C_{44}H_{29}N_4WO_2 \cdot CH_3OH$: C = 62.72%, H = 3.83%, N = 6.50%. Found C = 62.68%, H = 3.89%, and N = 6.44%.

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7 P. T. Manoharan and M. T. Rogers, *J. Chem. Phys., 49,* 5510 (1968).

8 The X-ray diffraction precession photographs of a single crystal grown in chloroform–benzene mixture indicated the unit cell to be tetragonal with $a = b = 13.495$ Å and $c = 9.756$ Å.

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