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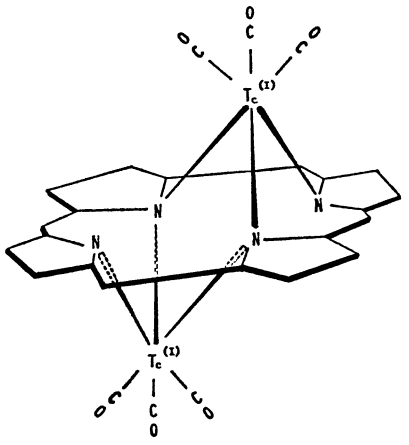
A TECHNETIUM PORPHYRIN: μ-[MESOPORPHYRIN IX DIMETHYL ESTERATO]BIS[TRICARBONYLTECHNETIUM(I)][1]

Minoru TSUTSUI* and C.P.HRUNG
Department of Chemistry, Texas A & M University,
College Station, Texas 77843

The preparation and the characterization of the first technetium porphyrin is reported. The structure of the complex is proposed to have an identical one to that of μ-[mesoporphyrin IX dimethyl esterato]bis-[tricarbonylrhenium(I)].

Rapid progress is being made in synthesis of novel metalloporphyrins[2], because of significance in coordination chemistry and biochemical implications. To our knowledge, however, no technetium porphyrin has been reported. We wish to report the first preparation of a technetium porphyrin: μ-[mesoporphyrin IX dimethyl esterato]bis[tricarbonyltechnetium(I)] (Fig. 1).

FIGURE I: Schematic picture of μ-[mesoporphyrin IX dimethyl esterato]bis[tricarbonyl-technetium(I)]; the alkyl substituents on the porphine ring are left out of the figure for clarity.



Mesoporphyrin IX dimethyl ester[3] and ditechnetium decacarbonyl[4] in 1 to 1.2 mole ratio were refluxed in decalin[5] under argon. Completion of the reaction was determined by visible spectroscopy. When the absorptions at 396 (soret) and 507 nm reached maxima, the reaction was stopped. The decalin solution was centrifuged, decanted, and evaporated in vacuo; the resulting solid was dissolved in benzene and chromatographed on a talcum column. A large chocolate colored band was eluted with a benzene/cyclohexane (50/50) solution. This solution was evaporated to dryness, dissolved in dichloromethane, centrifuged, and decanted. Finally it was evaporated to dryness and washed with n-pentane to give a dark red solid, mp 227-229°, which decomposed above 260°. Anal.[6] Calcd. for $Tc_2C_{42}H_{40}N_4O_{10}$: C, 52.60; H, 4.18; N, 5.84; Tc, 20.65; Mol. Wt., 958.0. Found: C, 52.44; H, 4.08; N, 5.92; Tc, 20.54; Mol. Wt., ∿1062 (measured by vapor pressure osmometry in acetone). The dark red solid (I) in dichloromethane gave a reddish brown solution with visible absorptions at 507 nm (ε, 8.47×10^3), 480 nm (shoulder) (3.94×10^3), 396 nm (2.69×10^4), and 370 nm (shoulder) (1.07×10^4). The infrared spectrum of $\underset{\sim}{I}$ in the solid phase (KBr) showed two strong metal-carbonyl stretches at 2036 and 1925 cm^{-1} and a sharp ester carbonyl peak at 1740 cm^{-1}. The mass spectrum of $\underset{\sim}{I}$ provided only $(M-5CO)^+$, $(M-6CO)^+$, and

several doubly charged peaks. A complete mass spectrum was not obtained due to the thermal instability of the complex.

Similar results have previously been found for μ-[mesoporphyrin IX dimethyl esterato]bis-[tricarbonylrhenium(I)][7,8,9]; mp 250-252°, sublimed at 240° under vacuum, visible absorptions in benzene at 519, 480 (shoulder), and 400 nm; infrared spectrum in solid phase (KBr) having strong absorptions at 1900 and 2015 cm^{-1}; mass spectrum giving parent peak at m/e 1130, and $(M-5CO)^+$, $(M-6CO)^+$, and several doubly charged peaks. Since such a close similarity was observed between the rhenium and technetium porphyrin complexes, a structure identical to the rhenium porphyrin[10] was proposed for I (Fig. 1).

Comparing with the stable rhenium porphyrins, the thermal instability of the technetium porphyrin might be due to its smaller metal ionic size.

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