

Preparation, Purification, and X-Ray Crystal Structure of a Dimeric Manganese(IV) Porphyrin Complex

By BRUCE C. SCHARDT, FREDERICK J. HOLLANDER, and CRAIG L. HILL*
(Department of Chemistry, University of California, Berkeley, CA 94720)

Summary The highly reactive dimeric complex μ -oxo-bis[azidotetraphenylporphyrinatomanganese(IV)] has been prepared, purified, characterized by X-ray crystallography and other physical methods, and some of its reactions examined.

MUCH recent research activity has been directed to the investigation of manganese(IV) porphyrin complexes owing to their ability thermally¹ and photochemically² to oxidize water and to oxidize a variety of other substrates.³ Despite the importance of these complexes and the rapidly expanding literature dealing with their preparation and characterization, little or nothing is known with certainty regarding their structure.⁴ The lack of structural characterization of manganese(IV) porphyrin complexes is a consequence of the

fact that all these species prepared thus far are highly reactive at 25 °C rendering their purification very difficult. We report here the first purification and X-ray crystal structure determination of a manganese(IV) porphyrin complex.

A solution of manganese(III) tetraphenylporphyrin (TPP) azide⁵ (7.1×10^{-4} mol) in 25 ml of rigorously purified chlorobenzene[†] was vigorously stirred under nitrogen with iodobenzene (3 equiv.) for 4 min, and then the mixture was filtered into 350 ml of deoxygenated hexane at -78 °C. The amorphous brown impure precipitated product was recrystallized to yield large lustrous black diffraction-quality crystals of a chlorobenzene solvate dimer [$\{N_3Mn^{IV}(TPP)_2O\} \cdot 3PhCl$], by layering a 21 mM chlorobenzene solution of the impure dimer with heptane at 25 °C. A crystal of the dimeric complex, a non-stoichiometric

[†] The optimal preparations and manipulations of the manganese(IV) porphyrins require the use of scrupulously purified solvents and anaerobic reaction conditions.

chlorobenzene solvate, was selected for structural analysis by X-ray crystallography.

Crystal data: $[\{N_3Mn^{IV}(TPP)\}_2O] \cdot nPhCl$, $n = ca. 1.5$, $M = 1604.2$, orthorhombic, space group $Pbcn$; $a = 21.208(5)$, $b = 16.826(4)$, $c = 22.620(3)$ Å, $U = 8072(4)$ Å³, $D_c = 1.320$, $D_m = 1.36(2)$ g/cm³. 3276 Unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were measured using Mo- K_α radiation on an Enraf-Nonius CAD-4 automatic diffractometer. The structure was solved by the heavy-atom method and refined by least-squares to a final R factor of 0.094.†

The crystal structure consists of well separated molecules of the $[\{N_3Mn^{IV}(TPP)\}_2O]$ dimer with chlorobenzene mole-

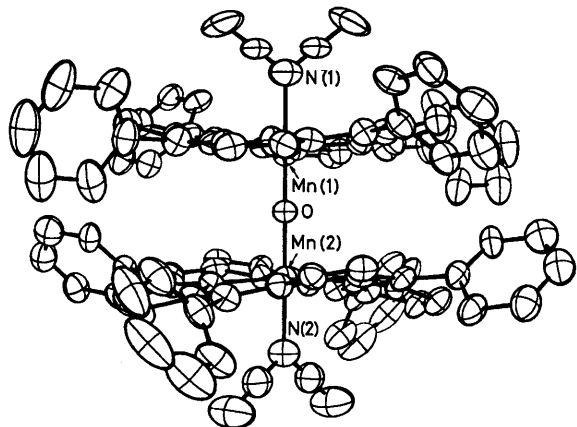


FIGURE. ORTEP⁶ plot of $\{N_3Mn^{IV}(TPP)\}_2O$ viewed from the side, perpendicular to the two-fold axis. Atoms are represented by 50% probability ellipsoids. The terminal azide ligands are two-fold disordered in the crystal.

cules partially occupying the holes resulting from the packing of the dimers. Each dimer possesses rigorous crystallographic C_2 symmetry, with both Mn atoms, the bridging oxygen atom, and the ligating nitrogen atoms of each N_3 ligand lying on the two-fold axis parallel to b (see Figure). The terminal azide ligands are two-fold disordered in the crystal as is apparent from the Figure, the two Mn atoms are displaced from the mean N_4 planes of the two TPP ligands toward the bridging oxygen by 0.10 and 0.08 Å, respectively, and the N_4 plane shows some S_4 ruffling. Important distances are as follows: Mn-N(TPP) (average of the four unique distances) 2.014(19) Å; Mn(1)-N(1) (azide) 1.998(8); Mn(2)-N(2) (azide) 1.993(7); Mn(1)-O 1.743(4); Mn(2)-O 1.794(4) Å.

The pure dimeric complex gives no e.s.r. spectrum from 4 to 300 K and has a magnetic moment at 25 °C determined by the Gouy method of 2.01 μ_B per dimer, implying an antiferromagnetic coupling interaction between the two manganese atoms. The complex reacts with triphenylphosphine to give triphenylphosphine oxide in 99% yield and with alkanes, alkenes, or chlorocarbons to give a variety of products in low yields. In all the reactions the manganese(IV) is reduced to manganese(III) with the monomeric $[Mn^{III}(TPP)]^+$ chromophore being produced in effectively quantitative yield.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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