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Trans-dioxo Manganese(V) Porphyrins

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Abstract: The relatively stable oxoMn(V) porphyrins generated by oxidation of Mn(III) porphyrins in alkaline solutions using peroxides are unambiguously identified as *trans*-dioxo species. Raman spectra revealed symmetric O=Mn^V=O stretching frequencies between 741 and 744 cm⁻¹ for five porphyrin complexes while the IR of dioxo-Mn^V-tetrapentafluoroporphyrin [Mn^V(O₂)(TPFPP)]⁻ displayed an antisymmetric stretch at 805 cm⁻¹. Both half-labeled and fully labeled ¹⁸O-Mn^V porphyrin complexes were prepared, and the Raman and IR shifts correspond well with a linear, three-body O=Mn=O oscillator model. Terminal, monooxo formulations such as HO-Mn^V=O or five-coordinate Mn^V=O are excluded by the data. The ¹H NMR spectrum of [Mn^V(O₂)(TMP)]⁻, which shows a single, sharp resonance for the two *o*-methyl groups, is also consistent with octahedral coordination of D_{4h} symmetry. The force constant F for the Mn=O double bond was calculated to be 454 N/m with a stretch-stretch force constant k = 67.2 N/m. Comparison with other Mn-O force constants revealed a very good agreement with Badger's rule spanning five Mn oxidation states. These dioxo-Mn^V porphyrins were shown to not exchange the oxo oxygens with bulk water solvent. Dioxo Mn^V porphyrins, which are anionic species [Por-Mn^V(O₂)]⁻, are unreactive toward olefins in the presence of excess base but efficiently epoxidize cyclooctene upon protonation at -70 °C. These compounds are the only *trans*-dioxomanganese complexes of any type to be characterized as such, thus extending the known -bonding arrangements for first-row transition metals.

