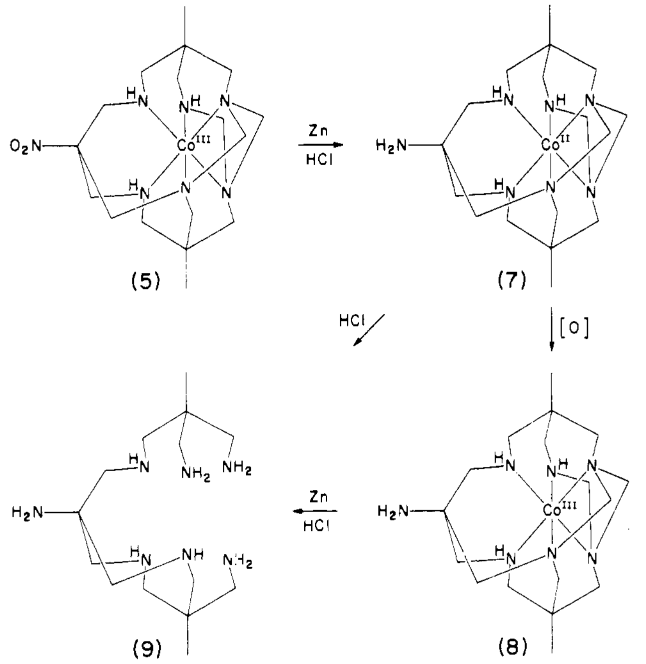
Scheme II



and −0.38 V (vs. the standard hydrogen electrode) for the nitro-capped complex **5** and the amino derivative **8**, respectively, and both reductions were quasi-reversible. The potentials are higher than that found for the macrotricyclic ion **6** (E = −0.51 V[9]), but it is clear from a comparison of the structures of **5** (Figure 1) and **6**[1] that the additional methylene bridge in **5** induces a further distortion of the nitrogen donor atoms over the cobalt sphere without significantly increasing the CoN_6 core size (Co–N distances are similar). This effectively opens up one side of **5** relative to the equivalent side of the macrotricyclic cage **6** and could be conceived to allow more favorable accommodation of the larger but more readily distorted Co^{2+} ion.

Registry No. **1**, 95674-09-2; **2**, 95674-10-5; **5**·Cl_3·$3H_2O$, 95674-08-1; **7**, 95674-11-6; **8**, 95674-12-7; **9**, 95674-13-8; tame, 15995-42-3; [Co(tame)$_2$]Cl_3, 60909-16-2; CH_2O, 50-00-0; NO_2CH_3, 75-52-5.

Supplementary Material Available: Listings of atomic coordinates, cobalt atom environments, ligand geometries, and anisotropic thermal parameters for the two independent molecules in the asymmetric unit (11 pages). Ordering information is given on any current masthead page.

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Metalloporphyrin Coordination Chemistry of Highly Oxidizing Oxyanions: The Chromate Complex of Iron(III) Tetraphenylporphyrin

Sir:

Iron (III) porphyrin coordination of a variety of unusual oxyanion ligands is possible as a consequence of the oxophilic character of iron(III) and the seemingly universal requirement for at least one axial ligand on the macrocyclic complex. Five-coordinate iron porphyrin complexes have been reported for the following: ClO_4^-,[1] NO_3^-,[2] SO_4^{2-},[2,3] OH^-,[4] O_2^{2-},[5] O^{2-},[6] μ-oxo,[7] μ-peroxo,[8] and various organic sulfonate,[2,9] carboxylate,[9,10] phenoxide,[10b,11] and alkoxide[10b,12] ligands. The general strategy for inducing coordination of weak-field oxyanions involves using a noncoordinating solvent and making only the ligand of interest available to the iron porphyrin. Thus, a wide variety of additional oxyanionic complexes conceivably are possible, and this preliminary report describes a group of newly prepared adducts with potentially strongly oxidizing oxyanions. Synthesis and spectroscopic properties of the novel μ-chromato dimeric complex are discussed in the greatest detail. Previous use of CrO_4^{2-} as a ligand has been largely restricted to generation of monomeric cobalt(III) ammine chromate complexes.[13]

Oxyanionic complexes were prepared by metathesis of the chloroiron(III) porphyrin with the respective silver salt or by hydrolysis of the μ-oxo dimeric iron(III) porphyrin with the oxyacid. Preparation of the chromate complex was carried out by stirring a 10% excess of solid Ag_2CrO_4 (Alfa) with chloroiron(III) tetraphenylporphyrin ((TPP)FeCl) in dry THF for 24 h. The mixture was protected from light by a foil wrap, and manipulations were conducted in a nitrogen-filled glovebox to preclude water contamination and subsequent μ-oxo dimer formation. Completion of reaction was judged by monitoring loss of the band at 380 nm characteristic of the (TPP)FeCl species. Removal of solid AgCl by filtration, evaporation of the THF to half the original volume, and addition of two volumes of heptane resulted in a microcrystalline product (the yield ranged to 75% if the heptane–THF solution was allowed to stand 24 h).

Variable amounts of solvent were retained in the presumably dimeric (μ-chromato)iron(III) tetraphenylporphyrin complex. Elemental analysis[14] revealed a chromium/iron ratio of 0.49 ±

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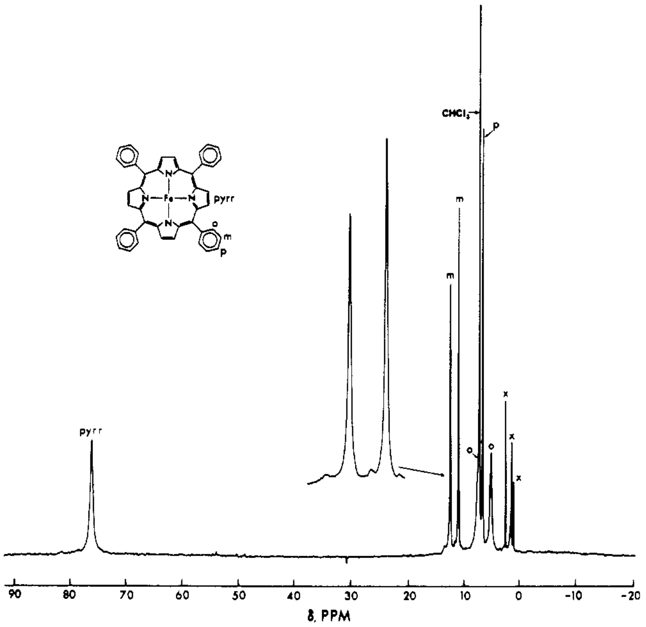

Figure 1. Proton NMR spectrum at 360 MHz of the μ-chromato dimer complex ($CDCl_3$ solvent, 25 °C, referenced to $(CH_3)_4Si$).

0.02. Chromate ion was quantitatively extracted into aqueous sodium hydroxide solution from a CH_2Cl_2 solution of the iron porphyrin complex, and the ion was identified by the UV spectrum. A molecular weight determination (vapor pressure osmometry, toluene solvent; Galbraith Laboratories) revealed a value of 1445 for $(C_{44}H_{28}N_4Fe)_2CrO_4{\cdot}0.71C_7H_{16}$) as compared with the expected value for the unsolvated dimer of 1453. The optical spectrum (CH_2Cl_2 solvent) revealed bands at 380 (shoulder), 415 (Soret), 512, 575, 655, and 687 nm much as is the case for other high-spin iron(III) porphyrin complexes. Infrared spectra (KBr pellet) revealed bands at 473 and 754 cm^{-1} that are distinctive for $[(TPP)Fe]_2CrO_4$ as compared with the μ-oxo dimeric and chloride complexes of the iron(III) porphyrin (proton NMR of the porphyrin complex, which was extracted from the KBr pellet with $CDCl_3$, verified that it was still the μ-chromato dimeric complex). Room-temperature magnetic moments on a per iron basis of 5.9 ± 0.1 and 6.0 ± 0.1 μ_B were measured respectively in the solid state and in $CDCl_3$ solution. Electron spin resonance signals for the dimer were not detected at −180 °C, analogous to the case for $[(TPP)Fe]_2SO_4$.[2,3]

Proton NMR spectroscopy has been of utility for monitoring conversion from the chloro to the chromato complex, and for structural elucidation of the final product. The 360-MHz proton NMR spectrum of $[(TPP)Fe]_2CrO_4$ is shown in Figure 1. A pyrrole proton signal at 74.9 ppm is indicative of a high-spin iron(III) porphyrin configuration and compares closely with the value of 72.9 ppm ($CDCl_3$) for the analogous sulfato dimeric complex.[2,3] The chemical shift pattern shows no evidence for partial iron(III) porphyrin oxidation by the chromate ligand. The ortho and meta phenyl signals of $[(TPP)Fe]_2CrO_4$ are split as a consequence of an out-of-plane iron atom and orthogonality of phenyl groups with respect to the porphyrin plane. Significant line width differences are noted for meta phenyl signals, and the 1.48 ppm separation of the doublet is to be compared with a value of only 1.10 ppm observed for the (TPP)FeCl complex. The larger splitting and line width differences are fully consistent with a dimeric structure in which chemical shift and relaxation parameters of half the ortho and meta phenyl protons are partially modulated by the neighboring iron atom. Variable-temperature NMR spectra reveal deviations from the Curie law that are no larger than those for the monomeric (TPP)FeCl species. This observation and the measured spin-only magnetic moment (at ambient temperature) indicate that magnetic interactions between iron centers must be relatively small.

The carbon-13 NMR spectrum of $[(TPP)Fe]_2CrO_4$[15] is also revealing in terms of empirical correlations possible for other high-spin iron(III) porphyrin complexes.[16] A far-downfield methine carbon signal at 434 ppm is fully consistent with five-coordinate rather than six-coordinate geometry. Chemical shift values for this and other carbon atoms of $[(TPP)Fe]_2CrO_4$ indicate that the ligand field strength for bridging $CrO_4{}^{2-}$ is slightly greater than for $SO_4{}^{2-}$.

Additional new oxyanion iron(III) tetraphenylporphyrin complexes have been prepared by metathesis reactions or an acid cleavage route. Preliminary characterization of the species has relied largely on unique pyrrole proton chemical shift values. The following chemical shift values and synthetic routes are noted for the new, presumably monomeric, derivatives: iodate, 76.2 ppm (acid cleavage); perrhenate, 60.6 ppm (silver ion metathesis); vanadate, 73.0 ppm (silver ion metathesis). Two species with signals at 66.9 and 73.4 ppm are obtained from silver tungstate metathesis. One component is thought to be the dimeric complex, and the other may be the monomeric tungstate complex in which a single silver ion is retained. On the basis of chemical shift patterns, all these compounds appear to be in the iron(III) oxidation state with a predominant high-spin $S = {}^5/_2$ configuration. Minor admixture of the $S = {}^3/_2$ state is possible for the $ReO_4{}^-$ adduct in view of the upfield bias of the pyrrole proton signal.

Investigation of a variety of organic substrate oxidations by oxyanion metalloporphyrin complexes is in progress.

Acknowledgment. Support from National Science Foundation Grant CHE 83-17451 is gratefully acknowledged. The Bruker WM-360 NMR spectrometer was purchased in part with National Science Foundation Grant CHE 82-01836.

Registry No. (TPP)FeCl, 16456-81-8; $[(TPP)Fe]_2CrO_4$, 95978-30-6; $[(TPP)Fe]_2O$, 12582-61-5; $(TPP)Fe(IO_3)$, 95978-31-7; $(TPP)Fe(ReO_4)$, 95978-32-8; $(TPP)Fe(VO_4)$, 95978-33-9; $[(TPP)Fe]_2WO_4$, 95978-34-0; $[(TPP)Fe]WO_4Ag$, 95978-35-1.

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[14] Anal. Calcd for $(C_{44}H_{28}N_4Fe)_2CrO_4{\cdot}0.71C_7H_{16}$: C, 73.23; H, 4.45; N, 7.38; Fe, 7.33; Cr, 3.41. Found: C, 72.47; H, 4.23; N, 7.29; Fe, 7.16; Cr, 3.28.

[15] Carbon-13 NMR assignments (ppm, $CDCl_3$ solvent, 25 °C, Me_4Si reference): pyrroles, 1243; methine, 434; quaternary phenyl, −30.6; ortho phenyl, 361.5, 354.3; meta phenyl, 148.9, 145.8; para phenyl, 140.8.

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Specific Transport of Copper(II) Ions across a Liquid Membrane Mediated by a Lipophilic Tetraaza Macrocycle

Sir:

We report the specific and uphill transport of Cu(II) ions across a liquid CH_2Cl_2 membrane, mediated by a polyaza macrocycle and driven by a pH gradient, between two aqueous phases.

The experiment of transport of metal ions through liquid membranes mediated by appropriate ligands has recently attracted much attention for both biological (as a model for the transport across natural membranes)[1] and practical implications (waste water treatment, recovery of metals from effluents).[2]

Crown ethers and related ligands have been found to be very efficient and specific in the transport of alkaline and alkaline-earth

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