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Magnetic Resonance Spectral Characterization of Tetrathiotungstate Adducts with Iron(III) Porphyrins

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Various transition metal tetrathiometalate complexes have been synthesized in attempts to model the iron–molybdenum cofactor of the nitrogenase enzyme.[1] Examples of simple iron(II) complexes include $[Fe(MS_4)_2]^{2-}$,[2] and $[L_2Fe(MS_4)FeL_2]^{2-}$,[3] where M = Mo, W. Numerous tetrathiometalate adducts of organometallic compounds have also been reported that are of fundamental relevance to dehydrosulfurization chemistry.[4]

In spite of the fact that Mo and W are formally in the +6 oxidation state, the tetrathiometallate ion is effective for stabilization of low valent metal complexes. Reported derivatives generally have the central metal ion in the +2 or lower oxidation state. The present manuscript describes more diverse coordination chemistry for the WS_4^{2-} ion with binding in two different stoichiometric ratios to the higher valent iron(III) porphyrin. Not surprisingly, coordination is in competition with electron transfer to give the square planar iron(II) porphyrin.

The tetrabutylammonium salt, $(TBA)_2WS_4$, was prepared by reaction of (TBA)OH (Aldrich, 1 M in H_2O) and $(NH_4)_2WS_4$ (Alfa) in aqueous solution, followed by extraction with dichloromethane. A fine yellow solid was obtained by rapid solvent evaporation at reduced temperature. The solid was dried under vacuum and stored under an argon atmosphere. Absorption bands in the optical spectrum of $(TBA)_2WS_4$ at 393 nm and 277 nm in H_2O were in agreement with the reported values for tetraethylammonium tetrathiotungstate.[5]

The strategy for generation of a WS_4^{2-} complex was to utilize an iron(III) porphyrin complex with a weak-field, readily displaceable ligand, and to employ a noncoordinating solvent. Hence, reaction of the (triflato)iron(III) complex, $(TPP)FeSO_3CF_3$,[6] and $(TBA)_2WS_4$ was carried out under an inert atmosphere by addition of a cold (273 K) 4 mM toluene solution of $(TPP)FeSO_3CF_3$ into septum-capped NMR tubes at 273 K that contained solid $(TBA)_2WS_4$. The pyrrole-deuterated complex, $(d_8\text{-TPP})FeSO_3CF_3$, was utilized such that the reaction could be conveniently monitored by deuterium NMR spectroscopy. The reaction was also carried out in EPR tubes, in which case the reaction mixture was rapidly frozen in liquid nitrogen.

Tetrathiometalate reduction of the iron(III) porphyrin to the square planar iron(II) derivative is problematic, and MoS_4^{2-} gave only the iron(II) product. Little reduction was evident for WS_4^{2-} at temperatures below 260 K, but low solubilities (for toluene solvent) dictated a compromise temperature of 273 K. At 273 K the WS_4^{2-} adducts of iron(III) porphyrins described below were reduced with a half-life of a few hours. At ambient temperature the iron(II) product is predominant in the NMR spectrum after a period of two hours.

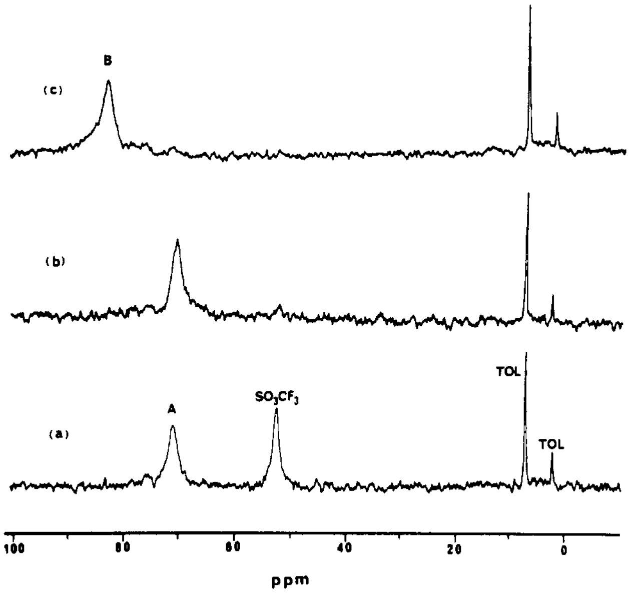

Figure 1. Deuterium NMR spectra (55 MHz) of $(d_8\text{-pyrrole-TPP})FeSO_3CF_3$ with various ratios of $(TBA)_2WS_4$, toluene solvent, N_2 atmosphere, 4.0 mM iron porphyrin, at 273 K. The reactant ratios, $(TBA)_2WS_4/(d_8\text{-TPP})FeSO_3CF_3$, are (a) 0.25, (b) 0.50, and (c) 1.0. Pyrrole deuteron signals are labeled "SO_3CF_3" for the starting material, and "A" and "B" for the resulting complexes. The natural abundance toluene solvent signals are labeled as "Tol".

Figure 1 shows the deuterium NMR spectra obtained from solutions perpared with $(TBA)_2WS_4/(TPP)FeSO_3CF_3$ ratios of 0.25, 0.50, and 1.0. The $(TPP)FeSO_3CF_3$ starting material has a pyrrole deuteron signal at 52.3 ppm at 273 K. Reaction of 0.25 equiv of WS_4^{2-} with a toluene solution of $(TPP)FeSO_3CF_3$ results in 50% conversion to a new iron(III) porphyrin complex with a pyrrole deuteron signal labeled "A" (Figure 1a). Formation of species A is complete with addition of 0.50 equiv. of $(TBA)_2WS_4$ (Figure 1b). The pyrrole deuteron chemical shift of 73.9 ppm at 273 K (65.3 ppm at 298 K) is consistent with the high spin iron(III) configuration.[7]

When more than half an equivalent of $(TBA)_2WS_4$ is added to the starting material, a second high spin iron(III) porphyrin derivative with pyrrole signal "B" is generated (pyrrole chemical shift; 85.8 ppm at 273 K, 75.8 ppm at 298 K). Complete conversion to species B is effected by addition of 1.0 equiv of $(TBA)_2WS_4$ (Figure 1c). Further addition of $(TBA)_2WS_4$ to species B causes no spectral change. Separate deuteron pyrrole signals are detected for mixtures of species A and B (not shown), indicating no rapid interconversion of the complexes on the 55 MHz NMR time scale at 273 K.

Generation of species A with 0.5 equivalent of WS_4^{2-} suggests a dinuclear iron(III) porphyrin complex with a bridging WS_4^{2-} unit. Variable temperature deuterium NMR measurements reveal a linear relationship between the pyrrole deuteron chemical shift and K^{-1} (Curie law behavior), thus suggesting that pyrrole signal A is that for a single species and not a dynamically averaged signal. The pyrrole signal for species A is less downfield than that of many high spin iron(III) porphyrin complexes (typically 80 ppm at 298 K), and this provides empirical evidence for the

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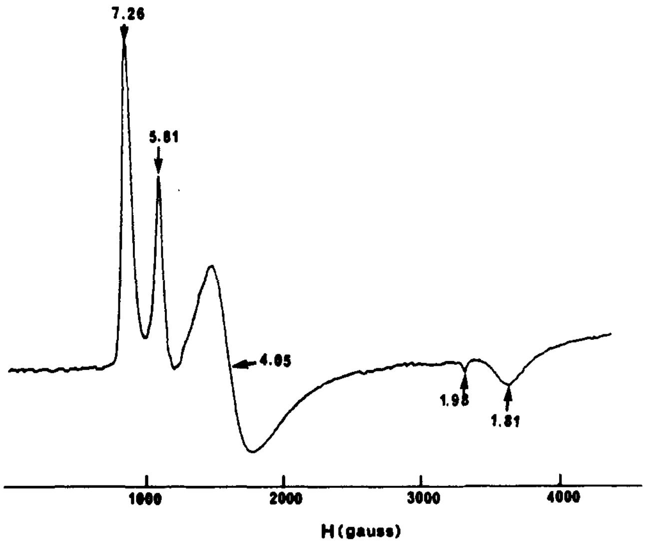
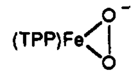


Figure 2. EPR spectrum of species B generated as described in Figure 1c, toluene solvent, at 5.2 K. A Varian E-104A X-band frequency EPR spectrometer with Air Products cryostat system was utilized.

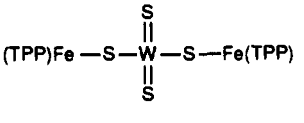
proposed [(TPP)Fe]$_2$WS$_4$ formulation. Hence, the ambient temperature pyrrole deuteron chemical shift of 65.3 ppm for species A is reminiscent of the 69.6 ppm value for the sulfate-bridged complex, [(TPP)Fe]$_2$SO$_4$.[8] The bridging WS$_4^{2-}$ ligand does not promote strong antiferromagnetic coupling for known iron(II) dinuclear complexes,[9] and this would appear to be the case for the proposed dinuclear iron(III) porphyrin complex, given the NMR Curie law behavior and detectable EPR signals described below.

The room temperature pyrrole chemical shift for species B at 75.8 ppm is also in accord with known five-coordinate monomeric iron(III) porphyrin complexes. Variable temperature measurements demonstrated Curie law behavior (linear plots and near zero intercepts). Phenyl proton signals for species B at 298 K are assigned as follows: ortho-phenyl, 7.9, 4.7 ppm; meta-phenyl, 13.2, 11.5 ppm; and para-phenyl, 6.0 ppm. Splitting of the ortho- and meta-phenyl proton signals is unusually large (compare a meta-phenyl proton signal splitting of 1.1 ppm for the chloroiron(III) complex), and must reflect the presence of an unprecedented ligand or unusual ligand geometry.

EPR signals at apparent values of $g = 5.81$ and $g = 2.05$ are observed for species A in a toluene glass at 5.2 K. These values are typical for a high-spin iron(III) configuration, and are not unlike those seen for the dimeric (dicyanoethylenedithiolato)-iron(III) porphyrin complex.[10] However, a novel set of rhombic EPR signals are observed for species B at $g = 7.26$, $g = 4.05$ and $g = 1.81$ as shown in Figure 2. As the ratios of intensities for $g = 7.26$ and $g = 5.81$ signals are variable (ratios of $g = 7.26$, 4.05, and 1.81 signals were constant), the $g = 5.81$ and $g = 1.98$ signals are assigned to species A or another high-spin iron(III) component. The rhombic spectrum is unusual for a symmetric iron(III) tetraarylporphyrin, but one other relevant example is found in the high-spin peroxoiron(III) porphyrin anionic complex with signals located at $g = 9.5$, $g = 4.2$, and $g = 1.3$ in the solid state.[11] Vibrational spectroscopy is consistent with edge-on, bidentate peroxide coordination,

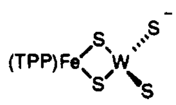


Given the axial EPR signal pattern and NMR chemical shift perturbations analogous to those of the sulfato-bridged complex, a reasonable proposal for the structure of species A is one that resembles the dinuclear sulfate complex:[12]



$$(\mathrm{TPP})\mathrm{Fe}-\mathrm{S}-\underset{\underset{\mathrm{S}}{\|}}{\overset{\overset{\mathrm{S}}{\|}}{\mathrm{W}}}-\mathrm{S}-\mathrm{Fe}(\mathrm{TPP})$$

The rhombic EPR spectrum for species B points to a coordination type that is rare for iron porphyrins, but is common for other WS$_4^{2-}$ metal complexes. Hence, the bidentate coordination geometry is favored:



The absence of a strong rhombic perturbation for other synthetic mondentate thiolate iron(III) porphyrin complexes[10] supports this conclusion.

The redox instability of both complexes complicates crystal growth and further structural characterization. Nonetheless, these in situ generated complexes are of relevance to modeling the active site coordination chemistry of sulfite reductase in that this enzyme presumably has a heme iron atom linked to a four-iron-sulfur ferredoxin unit by one or more sulfide ions.[13] Both the lability and redox activity of iron–sulfur clusters have complicated the preparation of suitable models of the heme-iron–sulfur active site.[14]

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