$[CpRu(trop)](PF_6)_2$.[36] Unfortunately, bulk electrolyses of $[CpFe(CHT)]^+$ and $[CpRu(CHT)]^+$ at +1.9 V designed to oxidize the coordinated cycloheptatriene ligand to tropylium were unsuccessful due to passivation of the electrode surface. The partial abstraction of hydride by trityl cation from $[CpFe(CHT)]^+$ and the unsuccessful abstraction from $[CpRu(CHT)]^+$ with this reagent are consistent with the observed increase in the potential at which the oxidation occurs in the Ru case. The shift to more positive potentials first on CHT coordination to Fe and then the further positive shift observed for the Ru complex are indicative of either some degree of interaction between the C–H bond and the metal center or more likely an inductive effect that removes electron density from the C–H bonding orbital.

All the complexes studied exhibit electrochemically irreversible 1-electron-reductions processes at approximately −1.32 V for Ru and −1.10 V for Fe. The absence of a corresponding reduction in either free tropylium or CHT suggests a metal-centered assignment for these processes. These one-electron reductions are analogous to those observed for $[CpFe(arene)]^+$[37] (−1.50 V) and $[CpRu(C_6H_6)]^+$ (−1.85 V). The assignments for the CHT and $trop^+$ complexes are in harmony with the 0.35-V shift to more negative potentials observed for $[CpFe(C_6H_6)]^+$ to $[CpRu(C_6H_6)]^+$.

Conclusions

Unsuccessful attempts to synthesize pure $[CpFe(trop)]^{2+}$ via hydride abstraction from $[CpFe(CHT)]^+$ suggested that the corresponding Ru complexes might be favorably investigated. $[CpRu(CHT)](PF_6)$ was readily synthesized from $[CpRu(CH_3CN)_3](PF_6)$. $[CpRu(CHT)](PF_6)$ is similar in characteristics to the previously reported Fe analogue. While an attempt to abstract hydride from $[CpRu(CHT)](PF_6)$ with Ph_3CPF_6 in CH_2Cl_2 gave no reaction, the direct reaction of $[CpRu(CH_3CN)_3](PF_6)$ with $(trop)PF_6$ afforded $[CpRu(trop)](PF_6)_2$ in high yield as the first example of a η^7-tropylium complex formed via the direct reaction of $trop^+$ with a metal complex. Reduction of $[CpRu(trop)](PF_6)_2$ by Zn in $EtOH/CH_3CN$ forms $[CpRu(CHT)](PF_6)$ in high yield. Reaction of CH_3Li with $[CpRu(trop)](PF_6)_2$ in THF gave no isolable products. Photolysis of acetonitrile solutions of $[CpRu(trop)]^{2+}$ results in the quantitative displacement of the tropylium ring with formation of $[CpRu(CH_3CN)_3](PF_6)$.

Electrochemical studies indicate that ligand-centered oxidation of bound CHT to bound $trop^+$ occurs on the cyclic voltammetric time scale, but electrode passivation precludes quantitative conversion to products. A metal-centered reduction at potentials more negative than −1.0 V is also observed for the $[CpRu(trop)]^{2+}$, $[CpRu(CHT)]^+$, and $[CpFe(CHT)]^+$ complexes.

Acknowledgment. A.M.M. acknowledges a Louise T. Dosdall Fellowship in science. We thank the Engelhard Minerals and Chemicals Corp. for a generous loan of $RuCl_3 \cdot 3H_2O$. This work was supported by the U.S. Department of Energy, Grant DOE/DE-AC02-83ER13103.

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(36) The $[CpRu(trop)]^{2+}$ complex also exhibits a poorly defined two-electron oxidation near the solvent limit at +1.94 V that leads to rapid decomposition of the metal compound.

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Contribution from the Department of Chemistry,
Colorado State University, Fort Collins, Colorado 80523,
and Inorganic Chemistry Section, Radiation Oncology Branch,
National Cancer Institute, NIH, Bethesda, Maryland 20205

Iron Porphyrin and Hydroporphyrin Magnetic Anisotropies Derived from High-Field ^2H NMR Spectra

Steven H. Strauss,*[1a] Kim M. Long,[1a] Michael Magerstädt,[1b] and Otto A. Gansow[1b]

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Magnetic anisotropies have been studied by biological and porphyrin chemists to deduce the electronic structures and, hence, molecular structures of active sites of important classes of proteins and enzymes. Single-crystal susceptibility measurements,[2] analyses of dipolar contributions to isotropic shifts in NMR spectra,[3] or interpretations of g-value anisotropies in EPR spectra[4] have been used to calculate $\Delta\chi_\parallel$ $(\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy}))$ and $\Delta\chi_\perp$ $(\chi_{xx} - \chi_{yy})$. A recent technique has been developed by MacLean and coworkers for measurement of diamagnetic anisotropies in aromatic compounds: very large magnetic fields cause a sufficient dynamic alignment of anisotropic molecules so that measurable quadrupole splittings are observed in ^2H NMR spectra of solutions of these compounds.[5] The observed splittings, $\Delta\nu$, are directly related to $\Delta\chi_\parallel$ and $\Delta\chi_\perp$ (see below). The technique is applicable to paramagnetic metal complexes.[6] In this paper we report ^2H NMR spectra and derived magnetic anisotropies for deuteriated samples of the four-coordinate, square-planar $S = 1$ complexes Fe(OEP)[7] and Fe(OEC).[7] This is the first application of this new technique to the study of the magnetic properties of iron porphyrins and related hydroporphyrins,[8,9] an area in which several of us are particularly active.[10]

Experimental Section

Selective deuteriation of $H_2(OEP)$ and $H_2(OEC)$ was accomplished by the use of literature procedures.[11,12] Samples of Fe(OEP-*meso*-d_4)

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(7) Abbreviations: OEP, 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion; OEC, 7,8-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrinato dianion (octaethylchlorinato dianion); TPP, 5,10,15,20-tetraphenylporphyrinato dianion.

(8) While this work was in progress, we learned of a study of cobalt(II) *N*-alkylporphyrins in which $\Delta\chi$ values were calculated from ^2H NMR data: Goff, H. M., personal communication.

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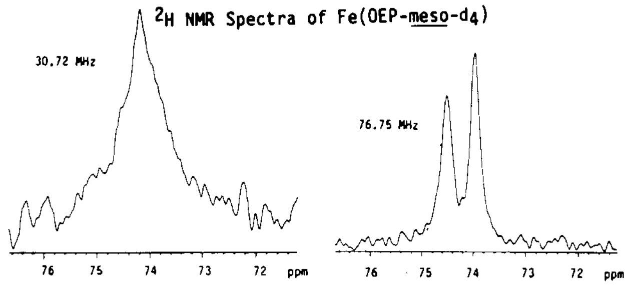

Figure 1. 30.72- and 76.75-MHz ^{2}H NMR spectra of Fe(OEP-*meso*-d_4) in toluene at 298 K.

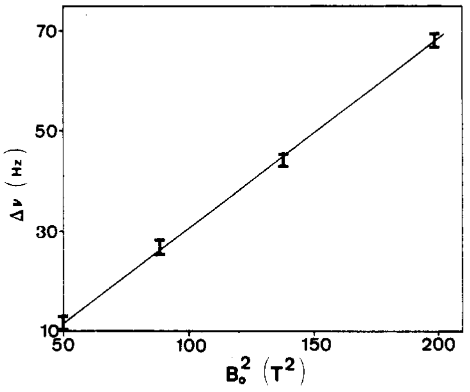

Figure 2. Quadrupole line splittings, $\Delta\nu$, for Fe(OEP-*meso*-d_4) vs. the square of the magnetic induction, B_0. The probe temperatures were 298 ± 2 K.

(I), Fe(OEC-*meso*-d_4) (II), and Fe(OEC-*7,8*-d_2) (III) dissolved in toluene were prepared as previously described.[10a,13] Room-temperature (298 K) ^{2}H NMR spectra were obtained for I–III at 30.72 MHz (Bruker SY-200) and at 76.75 MHz (Nicolet NTC500). In addition, spectra of I were obtained at 46.1, 61.4, and 92.1 MHz.

Results and Discussion

For all three compounds, the 30.72-MHz (4.7-T) resonances appear as broad singlets for each deuteriated position, at 75.0 ppm in samples of I, at 65.6 ppm and 70.3 ppm in samples of II, and at 24.5 ppm in samples of III, in correspondence with ^{1}H chemical shifts reported by us for Fe(OEP) and Fe(OEC).[10a] Evidence for partial orientation of these compounds is provided by a study of the field dependence at 298 K of the *meso* ^{2}H resonance of I, shown in Figures 1 and 2.[14] The doublets observed at magnetic fields from 7.05 T (46.1 MHz) to 14.1 T (92.1 MHz) are in accordance with that expected for quadrupole line splittings in that $\Delta\nu$ is dependent on B_0^2.[5] At 76.75 MHz doublets are also seen for II and III. The data at 76.75 MHz are as follows [compound, δ ($\Delta\nu$) (estimated error in peak separation)]: I, 74.2 (44 (1) Hz); II, 64.7, (35 (1) Hz) and 70.5 (32 (2) Hz); III, 22.3 (<100 Hz). Unfortunately, the resonance in samples of III is very broad (fwhh = 100 Hz), preventing a meaningful measurement of $\Delta\nu$ for this sample.

MacLean et al. have shown that the quadrupolar line splitting, $\Delta\nu$, for each resonance in a ^{2}H NMR spectrum can be related to the magnetic anisotropies $\Delta\chi_\parallel$ and $\Delta\chi_\perp$ as follows:[5]

$$\Delta\nu = \left[\frac{(e^2qQ/h)B_0^2}{20kT}\right]\left[(3\cos^2\alpha - 1)(\Delta\chi_\parallel) + \left(\frac{3}{2}\sin^2\alpha\cos 2\beta\right)(\Delta\chi_\perp)\right]$$

where e^2qQ/h is the ^{2}H quadrupole coupling constant and α and β are the polar angles that define the orientation of the C–D bond with respect to the principal magnetic axes. The formula above requires that the C–D bond has axial symmetry, which is generally true to within a few percent.[15] We assume that e^2qQ/h is 186 kHz for the meso deuterons in I and II (the same as for other aromatic compounds[15]). The polar angles α and β were calculated by using our crystal structure coordinates with the Fe–N vectors chosen to coincide with the magnetic x and y axes.[10a] We assume that the solid-state values are reasonable ones for these compounds dissolved in toluene. For Fe(OEP) there are two chemically equivalent but crystallographically distinct pairs of *meso* positions.[10a] For the C5 C–D bond $\alpha = 86.7°$ and $\beta = 44.1°$; for the C10 C–D bond $\alpha = 90.0°$ and $\beta = 44.7°$. Either value of α can be used, leading to differences of only 1% in the calculation of $\Delta\chi_\parallel$ for this compound. Note that $\Delta\chi_\perp = 0$ for Fe(OEP) by symmetry. For Fe(OEC) there are two chemically distinct pairs of *meso* positions.[10a] For the C5 C–D bond ($\delta = 64.7$) $\alpha = 76.3°$ and $\beta = 44.4°$; for the C10 bond ($\delta = 70.5$) $\alpha = 72.3°$ and $\beta = 44.8°$. Since the splitting ($\Delta\nu$) is known more precisely for the 64.7 ppm resonances, these values of α and β were used in the calculation of $\Delta\chi_\parallel$ for this compound. Despite the nonzero value of $\Delta\chi_\perp$ for Fe(OEC),[10a] $\Delta\chi_\parallel$ can be calculated from the $\Delta\nu$ value for the C5 deuteron because $\cos 2\beta \sim 0$ for $\beta = 44.4°$.

Thus, we calculate for Fe(OEP) $\Delta\chi_\parallel = -8.7 \times 10^{-3}$ cm^3/mol while for Fe(OEC) $\Delta\chi_\parallel = -8.1 \times 10^{-3}$ cm^3/mol.[16] These values represent *total magnetic anisotropies*, the sum of the respective paramagnetic and diamagnetic anisotropies. Since $\Delta\chi_\parallel$(dia) < 0 for aromatic compounds (z perpendicular to the molecular plane), $\Delta\chi_\parallel$(para) for Fe(OEP) and Fe(OEC) are less negative than the values given above. Attempts to measure $\Delta\chi_\parallel$(dia) for H_2(OEP-*meso*-d_4) and H_2(OEC-*meso*-d_4) have failed thus far because the respective deuterium resonances are too broad (~15–20 Hz in a variety of solvents at 298 K) to observe the quadrupole splitting. We estimate that $\Delta\chi_\parallel$(dia) for the OEP macrocycle is the same as that measured for porphine, -0.75×10^{-3} cm^3/mol,[17] while $\Delta\chi_\parallel$(dia) for the OEC macrocycle is the same as that measured for methylpheophorbide, -0.48×10^{-3} cm^3/mol.[17] Thus, for Fe(OEP) $\Delta\chi_\parallel$(para) = -7.9 (8) $\times 10^{-3}$ cm^3/mol while for Fe(OEC) $\Delta\chi_\parallel$(para) = -7.6 (8) $\times 10^{-3}$ cm^3/mol.[18] These values can be compared with $\Delta\chi_\parallel$(para) for Fe(TPP)[7] at 298 K: -5.6 (9) $\times 10^{-3}$ cm^3/mol, estimated from variable temperature ^{1}H NMR spectra;[19] -8 (1) $\times 10^{-3}$ cm^3/mol, determined by single-crystal magnetic susceptibility measurements.[20]

The interpretation of these results rests on the assumption that the complexes studied do not dimerize to any appreciable extent. Migita and La Mar have shown[21] that four-coordinate iron(II) porphyrins *containing polar substituents* can exhibit observable dimerization at concentrations as low as 1 mM, the concentration used in our work. In their study, ~10% dimer was present in benzene at 25 °C if the monomer concentration was ~1 mM. We find no evidence for dimerization with our octaethyl complexes. For example, isotropic shifts in ^{1}H NMR spectra of Fe(OEC) in toluene-d_8 are the same to within experimental error for samples that are ~1 and ~10 mM.[22]

The significance of this work is twofold. We previously showed that Fe(OEP) and Fe(OEC) do not have congruent electronic

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(13) Strauss, S. H.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 863–868.

(14) (a) ^{2}H NMR chemical shifts are referenced to the 2.05 ppm triplet for $C_6H_5CH_2D$ in toluene. (b) Note that the two resonances in the 76.75-MHz spectrum of I (Figure 1) have different peak heights but have the same peak intensity within experimental error. The origin of this effect is not known, but it is probably related to the fast electronic relaxation of these $S = 1$ compounds.

(15) Loewenstein, A. *Adv. Nucl. Quadrupole Reson.* **1983**, *5*, 53–82 and references therein.

(16) We transfer the coordinate system of Fe(OEP) to Fe(OEC), treating the loss of 4-fold symmetry from the reduction of one pyrrole ring as a perturbation. Thus z is perpendicular to the plane of Fe(OEC) and y is coincident with the molecular C_2 axis.

(17) See ref 5a and references therein.

(18) We estimate the total uncertainty in our measurements and calculations to be ±10%.

(19) Goff, H.; La Mar, G. N.; Reed, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 3641–3646.

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structures.[10a] The porphyrin complex possesses axial magnetic anisotropy while Fe(OEC) is rhombic. The two complexes have *different effective magnetic moments and Mössbauer spectra.* Despite this, the present results demonstrate that $\Delta\chi_{\parallel}$(para) is the same for the two complexes, confirming a tentative conclusion made from an analysis of isotropic ^{1}H chemical shifts.[10a] Any theoretical model developed to explain the electronic *differences* between $S = 1$ iron(II) porphyrins and hydroporphyrins must also account for the *similarities* in $\Delta\chi_{\parallel}$(para) values. Another tentative conclusion from our earlier work, that $\Delta\chi_{\perp}(\text{para}) = -\Delta\chi_{\parallel}(\text{para})$ for Fe(OEC), cannot be confirmed with the present data. Our inability to measure $\Delta\nu$ for samples of III precludes a calculation of $\Delta\chi_{\perp}$(para) for Fe(OEC). It is not clear at the present time why the *7,8-d*$_2$ resonance in samples of III is so broad.

The more general significance is the demonstration that magnetic anisotropies can be measured for an important class of paramagnetic transition-metal complexes. High-field ^{2}H NMR spectroscopy can now be added to the list of physicochemical techniques used to study the electronic structures of iron porphyrins. The comparison of $\Delta\chi$(para) values and their temperature dependencies for iron porphyrins and hydroporphyrins is continuing in these laboratories.

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Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201,
and Molecular Structure Corporation,
College Station, Texas 77840

Crystal Structure of the New Ternary Chalcogenide $Ta_2Cu_{0.80}S_6$. Relationship to Known Copper and Tantalum Chalcogenides

Philip J. Squattrito,[1a] Paul N. Swepston,[1b] and James A. Ibers*[1a]

Received September 9, 1986

In an attempt to prepare ternary phases in the system Au–Ta–S, we have unexpectedly isolated a new ternary phase in the Cu–Ta–S system.[2-5] The structure of the new compound $Ta_2Cu_{0.80}S_6$ is related to the structures of the known chalcogenides $CuTaS_3$[3] and TaS_3.[6] We report here the crystal structure of $Ta_2Cu_{0.80}S_6$, the experimental conditions that inadvertently led to the synthesis of this material, and our so far unsuccessful efforts to prepare the compound in a rational manner. The structural interrelationships of the tantalum–copper chalcogenides are described, and on this basis the physical properties of the new compound are anticipated.

Experimental Section

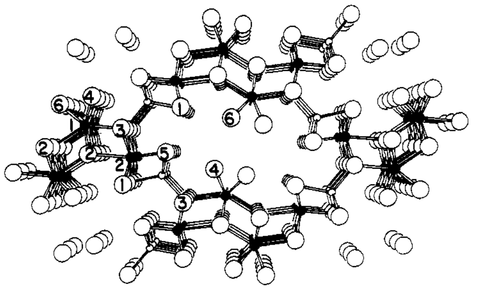

Figure 1. Perspective view of the $Ta_2Cu_{0.80}S_6$ structure along [010]. The numbering scheme is shown. Here and in Figure 2 Ta atoms are small filled circles, Cu atoms are small open circles, and S atoms are large open circles.

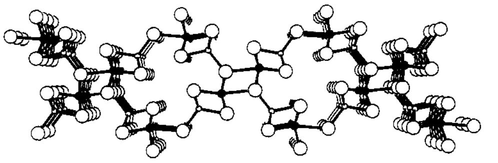

Figure 2. Perspective view of the $CuTaS_3$ structure along [010].

Synthesis. Several small (<0.3 mm in length), black, needle-shaped crystals of $Ta_2Cu_{0.80}S_6$ were isolated from a reaction of a 1:2:5 ratio of Au (AESAR, 99.95%), Ta (AESAR, 99.98%), and S (ATOMERGIC, 99.999%) powders. This charge was heated in a sealed, evacuated silica tube with ~3 μL of Br_2 for 5 days at 1000 K. The sample was then crushed, passed through a 60-mesh bronze screen, and resealed with Br_2 in a fresh silica tube that was heated for 7 days at 1125 K and then cooled. The principal product of this reaction was TaS_3, while no ternary Au–Ta–S compounds were formed. Microprobe analysis confirmed the presence of Ta, Cu, and S in the crystals and an approximate composition of 2:1:6 (Ta:Cu:S). We believe that the source of the Cu was the brass screen rather than a possible Cu impurity in the Au powder, especially since we have observed inadvertent introduction of Cu in systems where a brass screen but no Au powder was involved.[7] Direct combination reactions of Ta, Cu, and S in various ratios at temperatures between 950 and 1100 K have so far yielded $CuTaS_3$ as the only ternary product. These efforts to identify a synthetic route to $Ta_2Cu_{0.80}S_6$ have clearly been hindered by the structural similarity of the two phases (vide infra) and the apparent stability of $CuTaS_3$.

Crystallographic Study of $Ta_2Cu_{0.80}S_6$. Preliminary Weissenberg photographs (Cu Kα) established the orthorhombic symmetry and cell dimensions later confirmed by diffractometry. Intensity data were collected on a Rigaku AFC5-R four-circle diffractometer equipped with a 12-kW rotating-anode Cu X-ray source. Cell parameters were determined at 298 K from the setting angles of 10 accurately centered reflections in the range $10° < 2\theta(\text{Cu K}\alpha_1) < 33°$. No decay was observed in the intensities of three standard reflections monitored periodically during data collection. Cell data and crystallographic details are given in Table I.

Initial calculations were performed on a VAX 11/730 computer with the use of the TEXSAN[8] crystallographic computing package. The structure was solved by direct methods (MITHRIL[9]) in space group *Pnma*. An *E* map revealed the location of all independent atoms. All subsequent calculations were performed on a Harris 1000 computer, employing standard programs and methods.[10] Initial refinements of the data indicated that the Cu site is only partially occupied; subsequent refinements included a variable occupancy factor for the Cu atom. A full anisotropic refinement was attempted; anisotropic thermal parameters for several atoms became nonpositive definite. Probably this results from a somewhat inaccurate correction for absorption. We were unable to measure accurately the dimensions of the extremely small crystal, and as the absorption coefficient is very high, the absorption correction is significant. Accordingly, the final cycle of refinement of the 521 unique $F_o{}^2$ values included an isotropic parameter for each atom. From the refined occupancy of the Cu atom, the composition of the crystal used is $Ta_2Cu_{0.797(9)}S_6$. The height of the largest peak in the final difference electron density map is 3.5% that of a Ta atom. Final agreement indices are given in Table I. Final positional parameters are presented in Table II.

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(1) (a) Northwestern University. (b) Molecular Structure Corp.

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