a.

c.

b.

Figure 3. (a) Esr spectrum of $Cp_2Nb(CH_3)_2$ from Cp_2NbCl_2 and methyllithium, (b) central multiplet ($m_1 = \pm\frac{1}{2}$) at higher resolution, (c) computer simulation of (b).

solved. In contrast to these observations, the addition of an ethyl or *tert*-butyllithium or Grignard reagent to a solution of $(\pi\text{-}C_5H_5)_2NbCl_2$ readily collapsed the esr signal of IV without the appearance of a new spectrum corresponding to that of a dialkylniobium(IV) species. We conclude that the expected dialkyl species are quite unstable as shown previously for similar alkyl derivatives of dicyclopentadienylti-tanium(III) susceptible to β-elimination.[9,15]

The tantalum analogs to the niobium species described above showed similar behavior, but were generally less reactive. Thus, photolysis of a solution of $(\pi\text{-}C_5H_5)_2TaH_3$ and DTBP at $-50°$ afforded a spectrum consisting of eight lines ($a_{Ta} = 66$ G), but the line widths of 30 G precluded the observation of smaller hyperfine splittings. By analogy with the niobium compounds it is reasonable to assign the spectrum to that of a paramagnetic tantalum(IV) dihydride. Similarly the esr spectrum of $(\pi\text{-}CH_3C_5H_4)_2Ta(CH_3)_2$, a dark red solid, afforded a spectrum showing only tantalum hyperfine coupling. Unfortunately the line width of 17 G obscured any further splittings.

Finally, treatment of $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2\text{-}TaH_5$[3] with photochemically generated *tert*-butoxy radicals afforded an esr spectrum showing hyperfine coupling to one tantalum nucleus and a quintet due to coupling with four equivalent nuclei with $I = \frac{1}{2}$. The magnitude of the splitting suggests that the quintet arises from the phosphorus coupling.

The esr parameters for the niobium(IV) and tantalum(IV) compounds are summarized in Table I along with those of the analogous titanium(III) compounds. It can be seen that an increase in the metal hyperfine splitting in going from the dihydride to the dimethyl species is common for the three metals. A description of the bonding in these interesting species in the light of the Fenske-Hall model for MO calculations[16] will be deferred.[17]

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(12) The deuteron splitting is expected to be about one-sixth that of the proton splitting and unresolved in view of the linewidth (7.6 G).
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I. H. Elson, J. K. Kochi*

Department of Chemistry, Indiana University
Bloomington, Indiana 47401

U. Klabunde, L. E. Manzer
**G. W. Parshall,* F. N. Tebbe**

Central Research Department
Experimental Station, E. I. du Pont de Nemours and Co.
Wilmington, Delaware 19898

Received July 12, 1974

Structure Control in Organic Metals. Synthesis of Tetraselenofulvalene and Its Charge Transfer Salt with Tetracyano-*p*-quinodimethane[1]
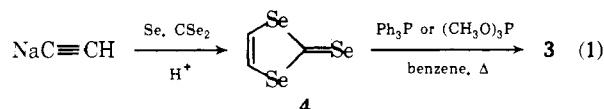
Sir:

Considerable interest has been shown recently in the study of highly conducting organic charge transfer salts.[2] The most attractive of these systems is the salt formed between tetrathiofulvalene (TTF, **1**) and tetracyano-*p*-quinodimethane (TCNQ, **2**), which displays exceptional electrical conductivity ($\sigma_{max,58°K}$ *ca.* 10^4 $(\Omega\ cm)^{-1}$) and metallic-like behavior over a wide temperature range.[3,4] Further, a few "anomalous" crystals of TTF-TCNQ have been reported to exhibit a giant conductivity maxima.[4,5] Attempts have been made to enhance the metallic properties of the tetrathiofulvalenium radical cation by substitution of electron releasing substituents.[6] However, such substitution distorts the original TTF-TCNQ crystal structure in an unpredictable way,[7] obscuring the electronic effect of the substituent on the solid state properties. In order to improve upon the metallic properties of fulvalenium systems in a more definable and controllable fashion, we have synthesized tetraselenofulvalene (TSeF, **3**) and its charge transfer salt with
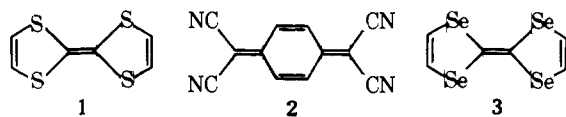
TCNQ.[8] The larger, more polarizable selenium is expected to reduce coulombic repulsions and increase electronic interactions, possibly by enhanced overlap between the cation radicals. Furthermore, this modification has essentially kept constant the steric requirements of the original TTF–TCNQ crystal structure.

Tetraselenofulvalene was prepared in two steps as outlined in eq 1. The first step involved an extention of the pro-

$$NaC\equiv CH \xrightarrow[H^+]{Se, CSe_2} \text{(structure)} \xrightarrow[benzene, \Delta]{Ph_3P \text{ or } (CH_3O)_3P} 3 \quad (1)$$

$$4$$

cedure of Mayer and Gebhardt[9] for the preparation of 1,3-dithiole-2-thione (5). Addition of selenium and carbon diselenide to sodium acetylide gave 1,3-diselenole-2-selone (4)[10] in 15–25% yield. In the synthesis of TTF, 5 was oxidized to a 1,3-dithiolium salt 6,[11] followed by coupling with base.[12] The analogous oxidation of 4 or 7[13] fails to give the

$$\text{(structure)} 5 \xrightarrow[0°, acetone]{CH_3CO_3H} \text{(structure)} 6 \text{ } HSO_4^-$$
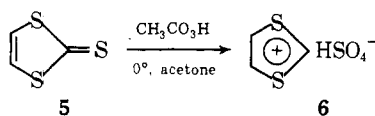
desired 1,3-diselenolium salt (8).[14] However, 4 can be readily coupled by treatment with either triphenylphosphine or trimethylphosphite in refluxing benzene for 5 hr.[8,12c,15] Re-

$$4 \text{ or } \text{(structure)} 7 \xrightarrow[0°, acetone]{CH_3CO_3H} \xmapsto{} \text{(structure)} 8$$
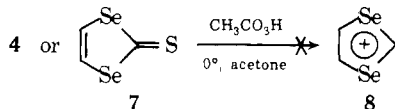
moval of benzene, followed by extraction with hot hexane, gave upon cooling purple-red needles of tetraselenofulvalene (3) in 70–80% yield. Further purification by eluting with hexane over a short silica gel column and gradient sublimation (90° and 0.1 Torr) gave 3 as a red solid: mp 132.5–133.0°; nmr (CDCl₃, δ relative to TMS) 7.25; u.v.-visible (hexane, λ$_{max}$(log ε)) 495(2.12), 365(3.15), 300(4.09), 287(4.08); m/e 396 (based on ⁸⁰Se).

Crystals of the 1:1 charge transfer salt[16] of TSeF with TCNQ were grown in acetonitrile by diffusion in a U-tube[17] (long black needles). Extinction of polarized light was noted along the long crystal axis. The powder X-ray diffraction pattern of TSeF–TCNQ indicated its crystal structure to have essentially the same unit cell dimensions as that found for TTF–TCNQ.[18] This represents the first time that the electronic properties of a highly conducting organic charge transfer salt has been altered in a significant way without changing the details of the original crystal structure, a factor important in the development of a systematic physical understanding of these materials.

Preliminary dc electrical conductivity measurements (four probe method) on single crystals of TSeF–TCNQ indicate it to be more metallic than TTF–TCNQ.[19] A typical plot of the conductivities of TTF–TCNQ and TSeF–TCNQ, normalized to their room temperature values, is shown in Figure 1 as a function of temperature. The room temperature conductivity of ca. 800 (Ω cm)⁻¹ for TSeF–TCNQ is one of the highest reported to date for an organic charge transfer salt, nearly double the usual values found for TTF–TCNQ.[20] More importantly, the metal to semiconductor transition, characteristic of these one-dimension-
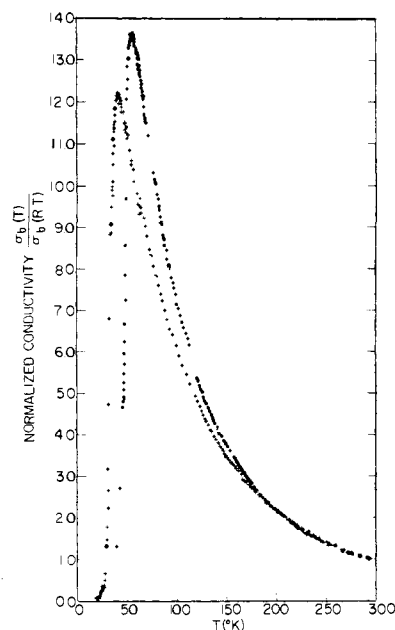

Figure 1. Plot of the normalized conductivities of TTF–TCNQ (●) and TSeF–TCNQ (+) vs. temperature.

al metals,[2–4] has been lowered to ca. 40°K, some 18°K below that of TTF–TCNQ (Figure 1). At 40°K, the conductivity of TSeF–TCNQ is greater than 10⁴ (Ω cm)⁻¹. Detailed studies of the physical properties of TSeF–TCNQ are currently in progress and will be reported forthwith.

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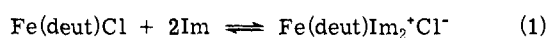
Edward M. Engler,* Vishnu V. Patel

IBM Thomas J. Watson Research Center
Yorktown Heights, New York 10598

Received July 3, 1974

Enhancement of Ligand Binding by Iron(III) Deuteroporphyrin (IX) Dimethyl Ester via Interaction with 1,10-Phenanthroline at a Site Remote from the Metal Ion

Sir:

It is well established that porphyrins, metalloporphyrins, and porphyrin-like molecules may form donor–acceptor complexes with either good electron donors or good electron acceptors.[1-11] It has also been observed in heme proteins that aromatic moieties of amino acids like phenylalanine, tyrosine, and histidine are often oriented so as to be parallel to the porphyrin ring and are sufficiently close to it that extensive overlap of their π orbitals with those of the porphyrin must occur.[12-16] As part of an effort to learn how such interactions might modify or "tailor" the reactivity of a metal ion held within the macrocycle, we have been investigating the influence of good aromatic electron donors on the ligand binding of metalloporphyrins. Herein we wish to report thermodynamic evidence indicating that the electron donor 1,10-phenanthroline interacts in a 1:1 stoichiometry with the low-spin complex bis(imidazole)deuteroporphyrin (IX) dimethyl ester iron(III) chlorde at a point remote from the metal ion. This results in stabilization of the low-spin complex and suggests a possible model for cooperative oxygen binding in hemoglobin.

The stepwise addition of imidazole to dichloromethane solutions of the high-spin five-coordinate complex deuteroporphyrin(IX) dimethyl ester iron(III) chloride results in changes of the visible absorption spectrum which show isosbestic points. As with tetraphenylporphine iron(III) chloride,[17] the equilibrium that exists may be satisfactorily accounted for by eq 1[18] in which two imidazole molecules displace the chloride ion to form the low-spin bisimidazole complex. No detectable concentration of the intermediate monoimidazole complex is observed. With the assumption that the bisimidazole complex is a tightly bound ion pair,

$$Fe(deut)Cl + 2Im \rightleftharpoons Fe(deut)Im_2^+Cl^- \qquad (1)$$

$$\beta_{12} = \frac{[Fe(deut)Im_2^+ \cdot Cl^-]}{[Fe(deut)Cl][Im]^2}$$

β_{12} is found to be $7.75 \times 10^5 \, M^{-2}$ at 30°, ΔH is -22 kcal/mol, and ΔS is -46 cal/(mol deg). These values are constant over a hundredfold range of concentrations.

In the presence of 1,10-phenanthroline (phen), variation of imidazole concentration results in spectral changes identical with those in the absence of phen except that in the presence of phen the bisimidazole complex is observed to form at lower concentrations of imidazole. Addition of phen to an equilibrium solution increases the proportion of bisimidazole complex, but no spectral changes are observed when phen is added to solutions of Fe(deut)Cl or of the fully formed Fe(deut)Im$_2^+$Cl$^-$. This indicates that phen cannot bind to the metal ion directly under these conditions. Variation of phen concentration at constant total porphyrin and imidazole concentrations gives spectral changes with isosbestic points. These spectral changes are accurately rationalized by addition of eq 2 to eq 1 above. Varing concentration over a hundredfold range, K_m is found to be 2.7×10^2

$$Fe(deut)Im_2^+Cl^- + phen \rightleftharpoons Fe(deut)Im_2^+Cl^- \cdot phen \qquad (2)$$
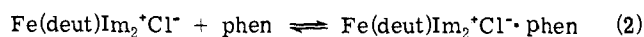
$$K_m = \frac{[Fe(deut)Im_2^+Cl^- phen]}{[Fe(deut)Im_2^+Cl^-][phen]}$$

M^{-1}. For reaction 2 ΔH is -7.7 kcal/mol and $\Delta S = -15$ cal/(mol deg). Since isosbestic points are observed in the presence of phen, Fe(deut)Im$_2^+$Cl$^-$ and Fe(deut)Im$_2^+$Cl$^-$ · phen are assumed to have identical extinction coefficients.

These equilibria data indicate that phen interacts with Fe(deut)Im$_2^+$Cl$^-$ to form a 1:1 complex. The lack of change in spectrum for the complex formed indicates that the point(s) of attachment are far removed from the metal ion. Fe(deut)Im$_2^+$Cl$^-$ is an ion pair and is probably more polar than Fe(deut)Cl. Since phen is highly polar, one might attribute enhanced formation of Fe(deut)Im$_2^+$Cl$^-$ to a general increase in solvent polarity. A number of arguments may be raised against this. First K_m is functionally a good 1:1 constant over a wide range of conditions. Second, we have studied other highly polar species which are not donors such as nitrobenzene and have found that they have virtually no effect over the same concentration range. Third, other less polar aromatic donors including phenanthrene and imidazole itself are currently being studied and are found to behave similarly to phen. It should also be pointed out that we observe similar effects in other solvents and with other porphines such as tetraphenylporphine.

Although these thermodynamic data reveal neither the structure of the interacting species nor the nature of the interactions, it is apparent that the donor molecule phen interacts with the low-spin bisimidazole complex much more strongly than with the high-spin Fe(deut)Cl. Evidently, the site of interaction is far removed from the metal ion, a point made all the more striking by the fact that the bisimidazole complex is stabilized over the reactant despite the greater steric requirement of the bisimidazole complex. Whatever the detailed interpretation of this interaction, it is important to consider the possible biological implications of the ability of such a donor molecule to stabilize the low-spin iron(III) state by interaction remote from the metal ion site. It is well known that the heme sites of hemoglobin bind oxygen cooperatively. This means that when each heme of a hemoglobin molecule binds an oxygen molecule the equilibrium constant for binding subsequent oxygen molecules increases for the other sites. One view of cooperativity is that the binding of oxygen at one site causes a structural change in the protein which enhances the equilibrium constant for binding of oxygen at another site.[19-21] If one considers the state of the iron when oxygen is bound to be low-spin iron(III), it may