

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 $(\pi$ -C₅H₅)₂NbCl₂ 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 dicyclopentadienyltitanium(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 $(\pi - C_5H_5)_2TaH_3$ and DTBP at -50° , afforded a spectrum consisting of eight lines $(a_{Ta} = 66 \text{ G})$, 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) dihydspectrum the of $(\pi$ ride. Similarly esr CH₃C₅H₄)₂Ta(CH₃)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 $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$ -TaH₅³ 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 calculations¹⁶ will be deferred.¹⁷

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References and Notes

- (1) H. K. Kaesz and R. B. Saillant, Chem. Rev., 72, 231 (1972); J. Chatt, Advan. Organometal. Chem., 12, 1 (1974). E. L. Muetterties, "Transition Metal Hydrides," Marcel Dekker, New
- (2)York, N.Y., 1971.
- (3) F. N. Tebbe and G. W. Parshall, J. Amer. Chem. Soc., 93, 3793 (1971); F. N. Tebbe, *ibid.*, **95**, 5823 (1973). E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, (4)
- 92, 5234 (1970); U. Klabunde and G. W. Parshall ibid., 94, 9081 (1972) See J. K. Kochi and P. J. Krusic, Chem. Soc., Spec. Publ., No. 24, 147 (5)
- (1970). Cf. K. S. Chen, F. Bertini, and J. K. Kochi, J. Amer. Chem. Soc., 95, (6)
- 1340 (1973). (7)When a similar solution of I and DTBP is continuously monitored in the
- light, the spectrum changes slowly as the reaction progresses. We can identify a variety of paramagnetic species including those showing the following niobium splittings: 103, 76, 127, and 110 G. (8) In the analogous dicyclopentadienyltitanium dihydride anion,⁹ these pro-
- ton splittings are 0.2-0.4 G. Titanium has no quadrupole moment. (9)
- H. Brintzinger, J. Amer. Chem. Soc., 89, 6871 (1967); J. Bercaw and H. Brintzinger, ibid., 91, 7301 (1969).
- (10) The relative importance of one- and two-electron processes are not indicated by the esr experiments. Product studies in progress will hopefulshed additional light on this point.
- (11) Subsequent studies suggest that III is a different derivative of dicyclopentadienyiniobium(IV). Unpublished results (I. H. Elson).
- (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).
- (13) Satisfactory analytical and mass spectral data for the paramagnetic dimethyl compounds of niobium(IV) and tantalum(IV) have been obtained.
- (14) W. Siegert and H. J. De Liefde Meijer, J. Organometal. Chem., 23, 177 (1970)
- (15) Moreover, our inability to observe the spectrum of species like II or III suggests that its steady-state concentration is too low when it is formed under these conditions. Alternatively, it may react further, possibly with the Grignard reagent, to form diamagnetic Nb species.
- (16) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, **11**, 768 (1972); J. L. Petersen and L. F. Dahl, *J. Amer. Chem. Soc.*, **96**, 2249 (1974); 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 2, 1974, Abstract INORG 47 and 50
- (17) Contribution No. 2502 (Indiana) and 2173 (DuPont).

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Structure Control in Organic Metals. Synthesis of Tetraselenofulvalene and Its Charge Transfer Salt with Tetracyano-p-quinodimethane¹

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 ($\sigma_{\max,58^{\circ}K}$ ca. 10^{4} (Ω cm)⁻¹) and metalliclike 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-TCNO crystal structure.

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

NaC = CH
$$\xrightarrow{\text{Se, CSe}_2}_{\text{H}^+}$$
 $\xrightarrow{\text{Se}}_{\text{Se}}$ $\xrightarrow{\text{Se}}_{\text{benzene, }\Delta}$ $\xrightarrow{\text{Ph}_3\text{P or }(CH_3\text{O})_3\text{P}}_{\text{benzene, }\Delta}$ 3 (1)

cedure of Mayer and Gebhardt⁹ for the preparation of 1,3dithiole-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



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-



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, $\lambda_{max}(\log \epsilon)$) 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 salt¹⁶ of TSeF with TCNQ were grown in acetonitrile by diffusion in a Utube¹⁷ (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-TCNO, 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 $10^4 (\Omega \text{ cm})^{-1}$. Detailed studies of the physical properties of TSeF-TCNQ are currently in progress and will be reported forthwith.

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References and Notes

- (1) E. M. Engler, V. V. Patel, S. Etemad, T. Penny, Y. Tomkiewicz, F Mehran, J. Torrance, and B. A. Scott, presented in part at the 1974 March Meeting of the American Physical Society, Philadelphia, Pa.
- (2) Reviews: I. F. Shchegolev, Phys. Status Solidi A, 12, 9 (1972); A. F. Garito and A. J. Heeger, Accounts Chem. Res., 7, 232 (1974); Z. Soos, Annu. Rev. Phys. Chem., in press. J. Ferraris, D. O. Cowan, V. Walafka, Jr., and J. H. Perlstein, *J. Amer.*
- (a) Chem. Soc., 95, 948 (1973).
 (4) L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Gari-
- to, and A. J. Heeger, Solid State Commun., **12**, 1125 (1973); M. J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, Phys. Rev. B, **10**, 1298 (1974).
- (5) These results are the subject of considerable controversy. See for example: D. E. Schafer, F. Wudl, G. A. Thomas, J. P. Ferraris, and D. O. Cowan, Solid State Commun., 14, 347 (1974); R. P. Groff, A. Suna, and R. E. Merrifield, Phys. Rev. Lett., 33, 418 (1974).
- (6) (a) cis, trans-Dimethyltetrathiofulvalene, ref 4; (b) tetramethyltetrathiofulvalene, J. P. Ferraris, T. O. Poehler, A. N. Bloch, and D. O. Cowan, Tetrahedron Lett., 2553 (1973); (c) tetrathiomethoxytetrathiofulvalene, (d) dibenzotetrathiofulvalene, F. G. Yamagishi, D. J. Sandman, A. F. Garito, and A. J. Heeger, Abstracts, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., March 1973, No. ORGN 12
- (7) For example, X-ray diffraction powder patterns of the TCNQ salts of dimethyl- and tetramethyltetrathiofulvalene differ significantly from that for TTF-TCNQ. B. Scott and D. Green, unpublished work, IBM Thomas J. Watson Research Center, Yorktown Heights, N.Y. 10598.
- The selenium analog of tetramethyltetrathiofulvalene has been recently (8) prepared: K. Bechgaard, D. O. Cowan, and A. N. Bloch, J. Chem. Soc., Chem. Commun., submitted for publication.
- R. Mayer and B. Gebhardt, *Chem Ber.*, **97**, 1298 (1964); R. Mayer, B. Hunger, R. Prousa, and A. K. Müller, *J. Prakt. Chem.*, **35**, 294 (1967). (9)
- (10) For characterization of 4 and synthetic details see E. M. Engler and V. V. Patel, J. Org. Chem., submitted for publication.
- (11) E. Klingsberg, J. Amer. Chem. Soc., 86, 5290 (1964).
 (12) (a) F. Wudl, G. M. Smith, and E. J. Hufnagel, Chem. Commun., 1435 (1970); (b) D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Canfield, J. Amer. Chem. Soc., 93, 2258 (1971). D. L. Coffen, Tetrahedron Lett., 2633 (1970); (c) S. Hünig, G. Kiesslich, H. Quast, and D. Scheutzow, Justus Liebigs Ann. Chem., 310 (1973); cf, G. Kiesslich, Dissertation, Universität Wurzburg, 1968
- (13) Prepared by treating 4 with P2S5 in refluxing toluene. See ref 10 for the characterization of this material.

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- (14) The products of this reaction have not been characterized. In a related reaction, oxidation of 1,4-diselenane under similar conditions yields the corresponding 1,4-dioxide: E. S. Gould and W. Burlant, J. Amer. Chem.

- corresponding 1,4-dioxide: E. S. Gould and W. Burlant, J. Amer. Chem. Soc., **78**, 5825 (1956).
 (15) H. D. Hartzler, J. Amer. Chem. Soc., **95**, 4379 (1973); E. J. Corey, F. A. Carey, and R. A. E. Winter, *Ibld.*, **87**, 934 (1965).
 (16) Anal. Calcd for 1:1 TSeF-TCNQ (C₁₆H₈N₄Se₄): C, 36.25; H, 1.35; N, 9.40; Se, 53.00. Found: C, 36.26; H, 1.32; N, 9.32; Se, 52.90.
 (17) G. T. Pott and J. Kommandeur, *Mol. Phys.*, **13**, 373 (1967).
 (18) Preliminary indexing of the TSeF-TCNQ cell gave a = 12.51 Å, b = 3.88 Å, c = 18.51 Å, and β = 104.2°. The corresponding values for TTF-TCNQ are a = 12.30 Å, b = 3.82 Å, c = 18.47 Å, and β = 104.5° (T. E. Phillips, T. J. Kistenmacher, J. P. Ferraris, and D. O. Cowan, J. Chem. Soc., Chem. Commun., 471 (1973); T. J. Kistenmacher, T. F. Phillips, and D. O. Cowan, Acta Coverbloor. Sect. B 30, 763. er, T. E. Phillips, and D. O. Cowan, Acta Crystallogr., Sect. B, 30, 763 (1974).
- (19) For a more detailed analysis see S. Eternad, T. Penny, E. M. Engler, B. A. Scott, and P. E. Seiden, *Phys. Rev. Lett.*, submitted for publication.
- TTF-TCNO. (20) Comparative room temperature conductivities (Ω cm)⁻ JSO-500 (ref 3 and 4); dimethyl-TTF-TCNQ, ca. 50 (D. Cowan, unpub-lished microwave data); tetramethyl-TTF-TCNQ, ca. 10³ (microwave measurement, ref 6b); N-methylphenazinium-TCNQ, 170-380 (L. B. Coleman, J. A. Cohen, A. F. Garito, and A. J. Heeger, *Phys. Rev. B.*, 7, 2122 (1973)); quinolinium (TCNQ)₂,100 (V. Walatka, Jr., and J. H. Peristein, *Mol. Cryst. Liq. Cryst.*, **15**, 269 (1971)).

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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 lowspin 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 1¹⁸ in which two imidazole molecules dis-

$$Fe(deut)Cl + 2Im \implies Fe(deut)Im_2^*Cl^-$$
 (1)

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

place 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, β_{12} is found to be 7.75 × 10⁵ 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, $K_{\rm m}$ is found to be 2.7×10^2

 $Fe(deut)Im_2^*Cl^- + phen \implies Fe(deut)Im_2^*Cl^- phen$ (2)

$$K_{\rm m} = \frac{\left[{\rm Fe}({\rm deut}) {\rm Im}_2^{+} {\rm Cl}^{-} {\rm phen} \right]}{\left[{\rm Fe}({\rm deut}) {\rm Im}_2^{+} {\rm Cl}^{-} \right] \left[{\rm phen} \right]}$$

 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)Im₂+Cl⁻ and Fe(deut)Im₂+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)Im₂+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