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This research is directed towards the synthesis and characterization of polymeric arrays of transition metal phthalocyanines and porphyrin complexes. Partially oxidized polymers of this type should exhibit unusual electron transport, optical, and magnetic properites. The synthesis and characterization of ruthenium and osmium porphyrin polymers bridged via bidentate ligands such as pyrazine were completed and their optical and electron transport properties were explored. The synthesis of liquid crystalline phthalocyanine or porphyrin complexes of ruthenium are still incomplete. A model EXAFS study of partially oxidized ruthenium porphyrin dimers has been completed.

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Final Project Report
"Liquid Crystalline 3d Porphyrin Complexes
NOOO14-84-K-0403 to James P. Collman
August 24, 1988

Introduction

The following is a final report summarizing the project goals and the work which was accomplished under the Navy Contract "Liquid Crystalline 3d Porphyrin Complexes," Contract number N00014-84-K-0403. The original contract was to be terminated 06/30/87, but was twice extended for six-month periods without additional funds so that the overall contract period encompassed by this report is 7/84–6/30/88. Throughout the period of this contract only a single experimental coworker was employed—at first a postdoctoral, Dr. Laughlin McCullough, who took employment with the Eastman Kodak Company in December, 1987, and thence a graduate student, Matthew Zisk (who is still at Stanford).

Project Goals

These are to prepare novel materials composed of transition metal porphyrin or phthalocyanine derivatives linked in a polymeric form. The linkage is either through bidentate bridging ligands such as oxide or cyanide or by direct metal-metal bonding. Partially-oxidized derivatives of these materials are expected to manifest unusual solid-state properties such as electrical conductivity, optical absorption in the infrared, and (in specific cases) collective magnetic properties. Our initial studies explored mesodiscotic liquid crystalline phtahlocyanine complexes, but as these proved difficult to characterize structurally, we then turned our attention to simple porphyrin derivatives of the 4d and 5d metals, especially ruthenium and osmium. We have developed a synthetic scheme to prepare liquid crystalline porphyrins which should prove more amenable to study and purification than the liquid crystalline phthalocyanines.

Accomplishments

We prepared a series of second and third row octaethylporphyrin complexes having cyanide and pyrazine as axial ligands. These substances are polymeric and, when oxidized, show evidence for electron transport down the polymer chain. This work was brought to fruition with three publications (see below).

We then turned our principal attention to the synthesis of liquid crystalline phthalocyanine complexes. We experienced difficulties in making large quantities of these interesting ligands, but eventually we were able to obtain adequate amounts of the free-base ligands. We made many attempts to introduce ruthenium into these liquid crystalline substances, but the results of these experiments were sporadic. The ruthenium-substituted phthalocyanines proved very difficult to purify and characterize. These compounds are especially interesting, since the presence of multiple bonds between the ruthenium centers should stabilize *the mesodiscotic state. In this state partially* oxidized units should exhibit facile electron transfer along the phthalocyanine core. The resulting materials are expected to exhibit ferromagnetism through the agency of electron exchange between pairs of antibonding doubly-degenerate π-orbitals associated with the ruthenium-ruthenium double bonds. We have previously shown that corresponding ruthenium porphyrin monomers spontaneously form discrete metal-metal bonded dimers which can be selectively oxidized to mono and dications (work supported by NSF). Those substances exhibit formal bond orders 2, 2.5, and 3. These diverse redox couples exchange electrons in solution by rapid outer-sphere electron transfer. We thus expect that a mesodiscotic liquid crystalline analogue would exhibit the same phenomenon in the solid-state and, according to McConnell's 1964 hypothesis, ferromagnetism might be observed below a "Curie temperature." However, our studies in this regard were frustrated by two factors—firstly, we were unable to obtain pure ruthenium derivatives of the poorly tractable liquid crystalline phthalocyanines. Secondly, we were frustrated by structural techniques for analyzing the resulting system. Three techniques would seem appropriate to examine these structures. These are: EXAFS (which should show the ruthenium-ruthenium bond distances), low-angle X-ray scattering (which should reveal the presence of the mesodiscotic state), and solid-state NMR (which might directly distinguish between the mesodiscotic state and the "herringbone" state). To that end we have explored EXAFS structural analysis of the neutral, monocationic, and dicationic ruthenium octaethylporphyrin dimers. Using as a standard an earlier X-ray crystallographic study of the neutral dimer, we were able to employ EXAFS to identify the metal-metal bond distances in these three redox couples. This work has been written up and is being submitted to *Chemical Communications.* The work was done in collaboration with Professor Keith Hodgson (Stanford Chemistry); EXAFS studies were performed at the Stanford Synchrotron Facility. We have not yet addressed the issue of low-angle X-ray scattering nor solid-state NMR spectroscopy of the liquid crystalline compounds. In future studies (supported by NSF) we intend to pursue these approaches.

In the past few months we changed the direction of our synthetic efforts and have been working towards the synthesis of analogous mesodiscotic liquid crystalline porphyrin compounds. Published syntheses of such compounds are based on lengthy, linear sequences and yield very small amounts of liquid crystalline material [Gregg, B.A.; Fox, M.A.; Bard, A.J. *J. Chem. Soc., Chem. Commun.* **1987**, 1134; and references therein.]. We have developed a promising approach to the synthesis of mesodiscotic liquid crystalline phthalocyanines, and have carried this about halfway (See Figure I). This work will be continued under support from NSF.

During the lifetime of this contract we have achieved only modest success; however, this work may eventually result in the synthesis and characterization of polymeric porphyrinic complexes which exhibit truly unusual optical, electrical, and especially magnetic properties. Our early studies on liquid crystalline compounds were frustrated by difficulties with the synthetic chemistry—both organic and inorganic aspects. These difficulties now seem to be resolved. We have also developed collaborations for future studies of these compounds. For example, we have arranged for magnetic measurements of our compounds at DuPont Central Research in collaboration with Dr. Joel Miller, who has recently discovered ferromagnetic interactions in organometallic solids. We have also established a strong collaboration with

Prof. Keith Hodgson in the context of EXAFS studies, and we are developing an association with Hodgson on low-angle X-ray scattering. A high-field NMR spectrometer has now been installed at Stanford in Geology, and we have developed an association with Prof. Jonathan Stebbins of that Department. We have also collaborated with Professor William A. Little (Stanford Physics) in electron-transport and optical measurements of our conducting porphyrin polymers.

DATA PAGE

(a) Publications Receiving Support under ONR Contract NOOO14-84-K-0403

1. Collman, J.P.; McDevitt, J.T.; Yee, G.T.; Leidner, C.R.; McCullough, L.G.; Little, W.A.; Torrance, J.B. "Conductive Polymers Derived from Iron, Ruthenium, and Osmium Metalloporphyrins: The Shish-Kebab Approach," *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 4581–4585.
2. Collman, J.P.; McDevitt, J.T.; Yee, G.T.; Zisk, M.B. "Optical and Conductive Properties of Pyrazine-Bridged Iron, Ruthenium, and Osmium Octaethylporphyrin Coordination Polymers," *Synth. Metals* **1986**, *15*, 129–140.
3. Collman, J.P.; McDevitt, J.T.; Leidner, C.R.; Yee, G.T.; Torrance, J.B.; Little, W.A. "Synthetic, Electrochemical, Optical, and Conductive Studies of Coordination Polymers of Iron, Ruthenium, and Osmium Octaethylporphyrin," *J. Am. Chem. Soc.* **1987**, *109*, 4606–4614. This paper received very minimal support from this ONR contract in the form of modest technical assistance from Dr. Laughlin McCullough, who was not a coauthor. For this reason ONR support was not acknowledged for this paper.
4. Asahina, H.; Zisk, M.B.; Hedman, B.; McDevitt, J.T.; Collman, J.P.; Hodgson, K.O. "X-Ray Absorption Spectroscopic Studies of Rutheniumoctaethylporphyrin Dimers," *J. Chem. Soc., Chem. Commun.* in submission. Preprint enclosed with this report.

b) Awards and Honors

Prof. James P. Collman: Guggenheim Fellow, 1985-86

Arthur C. Cope Scholar Award, 1986

Honorary Doctorate, University of Nebraska, 1988

First Allan V. Cox Medal for Excellence in Fostering Undergraduate Research, 1988

c) Presentations

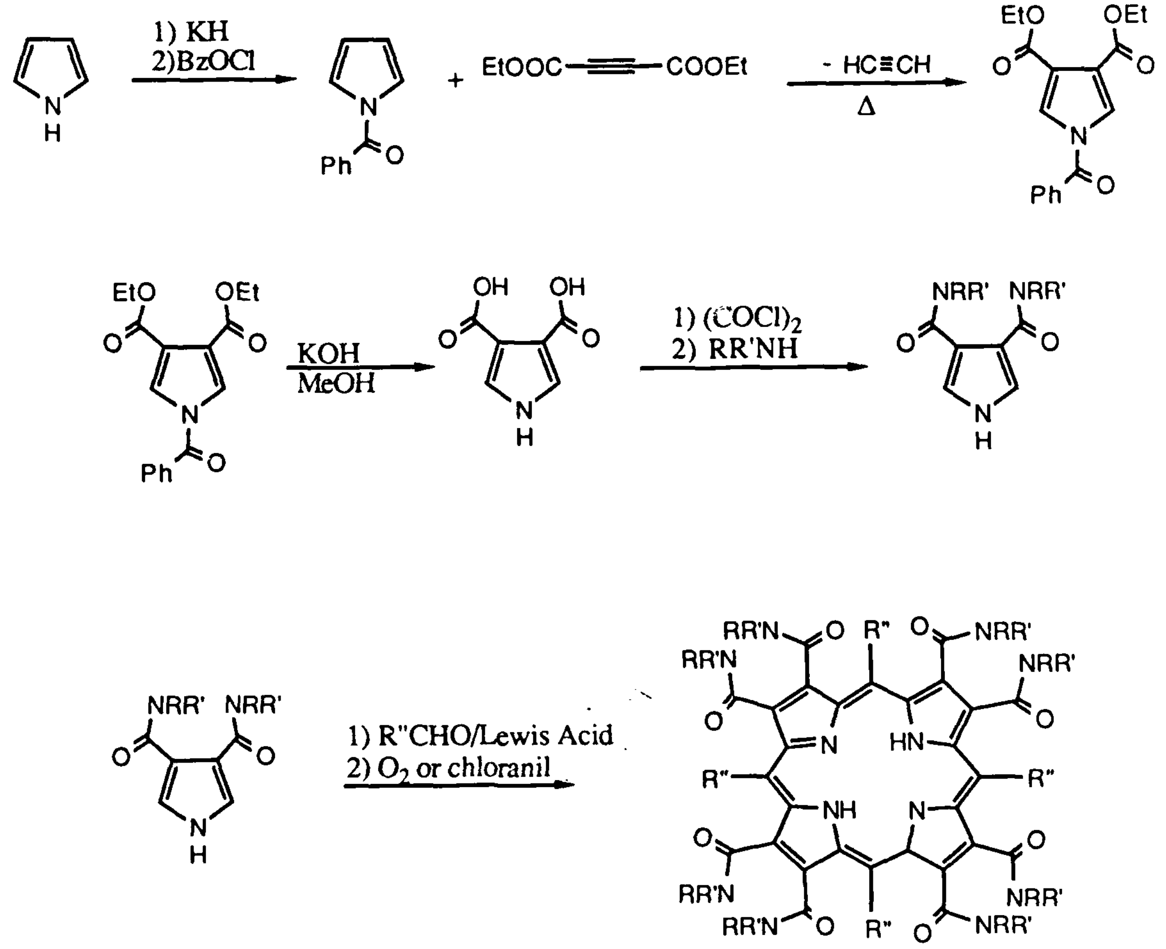
Case Western University, "Frontiers in Chemistry" lecture series, *Shish Kebab Polymeric Porphyrins*, March, 1987.

International Conference on Macrocyclic Chemistry, Hiroshima, Japan, *Shish-Kebab Porphyrin Polymers: A New Class of Molecular Conductors,* July, 1987.

c) Graduate students and Postdoctorals receiving support

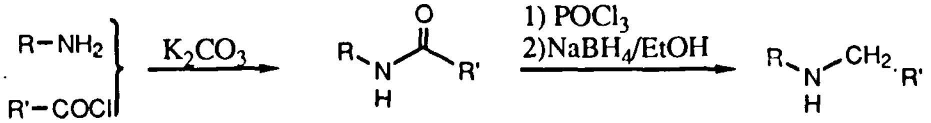
Matthew Zisk (graduate student, no minority status) received support from this contract 4/1/87–6/30/88. Dr. Laughlin McCullough (postdoctoral, no minority status) was supported on this contract 7/84–12/86.

Figure I Synthesis of Liquid-Crystalline Porphyrins



Reaction sequence carried out completely for R = R' = Et , R" = H.

Secondary Amine Synthesis



Reaction sequence carried out completely for R = Me, R' = *n*-$C_{11}H_{23}$ and R = *n*-$C_{10}H_{21}$, R' = Me