**11. Title (Include Security Classification):** UNCLASSIFIED: "Synthesis and Characterization of New Low-Dimensional Metal Complex Conductors"

**12. Personal Author(s):**
William E. Hatfield

**14. Date of Report (Year, Month, Day):** October 1, 1989

**19. Abstract:** (Continue on reverse if necessary and identify by block number)

Final report which contains a recapitulation of accomplishments and conclusions. A listing of all technical reports and journal articles emanating from the contract is included along with the names of all personnel who participated in the research.
No. 13. Subject terms continued

- electrical conductivity,
  inorganic solids,
  oxides,
  sulfides,
  halides,
  organic solids
  superconductivity,
  methal dithiolates,
OFFICE OF NAVAL RESEARCH

FINAL REPORT

for

Contract #N00014-86-K-0608
R & T Code 413A001---01

"Synthesis and Characterization of New Low-Dimensional Metal Complex Conductors"

William E. Hatfield
University of North Carolina
Department of Chemistry
Chapel Hill, North Carolina 27599-3290

Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

* This document has been approved for public release and sale: its distribution is unlimited.
This research program was devoted to the synthesis and characterization of new transition metal complex electrical conductors. The primary objective of the program is to develop guidelines which will lead to the rational synthesis of electrical conductors with desired properties, with a secondary mandate being to solve important scientific problems that are encountered in the research.

Mixed-valence compounds provide very good candidates for electrically conducting materials. Studies on the compounds KCu$_4$S, K$_3$Cu$_8$S$_6$, and KCu$_3$S$_2$ show that K$_3$Cu$_8$S$_6$ is a kinetic phase and displays behavior typical of systems with charge density waves. Magnetic, electrical, and X-ray studies on these compounds are discussed in detail in Technical Report No. 25 (Jan. 7, 1987). Magnetic, spectral, and electrical conductivity studies on the mixed-valence compounds with cationic copper complexes and donors such as TCNQ$^-$ have permitted an evaluation of the transport mechanism in this series of compounds. For example, as discussed in Technical Reports Nos. 26 (May 15, 1987) and 27 (July 10, 1987), one-third of an electron (per formula unit) is transferred from TCNQ$^-$ to [Cu(phen)$_2$]$^{2+}$, $E$ and $t$ are of comparable magnitudes, the bandwidth is appreciable, and high electrical conductivities and low activation energies are expected and observed. Current ideas concerning significant problems in low-dimensional crystalline inorganic and organic solids have been identified (Technical Report No. 31).
The new high-temperature copper ceramic superconductors fit naturally in our program because these are good examples of mixed-valence systems. Magnetic and electrical studies on the 1-2-3 compounds revealed frustration and spin-glass behavior (Technical Report No. 30) and variable-range hoping in oxygen-depleated samples (Technical Report No. 29). Studies on the Bi-Ca-Sr-Cu-O superconducting ceramics revealed effects of composition and firing conditions on the properties of these materials (Technical Report No. 32). Current studies are devoted to Sn doped samples of the new bismuth superconductors. Here Mossbauer spectroscopy is being used to probe electronic structures.

As a part of our continuing effort to produce two-dimensional mixed-valence copper complexes, we studied a number of suitable candidates including a series of copper carboxylates. As discussed in Technical Report No. 34, the two-dimensional complex copper(II) maleate monohydrate undergoes a transition to a ferromagnetically ordered state at 4 K. The ferromagnetic interaction occurs as a result of the relative orientation of the magnetic orbitals and the orbitals of the bridging carboxylate group which transmits the superexchange mechanism. Unusual materials have been generated in this phase of our work, and characterization of them is still underway.

Much attention was paid to the bis(phthalocyanato)-lanthanides which have sandwich-like structures and are capable of existing in two oxidation states. The compounds may also be doped with iodine, and single crystals may be grown by using
elecrochemical techniques. As discussed in Technical Report No. 34, the electrical conductivities of the iodine doped substances are several orders of magnitude higher than those of the undoped materials. The conductivity behavior may be explained in terms of the variable hopping mechanism for heavily doped semiconductors. Calculations using the angular overlap model were carried out the aim of reproducing magnetic properties, and as discussed in Technical Report No. 35, the results show that the pyrollic nitrogen donor atoms are weak sigma donors and moderate pi donors. Some very exciting new magnetic results have been obtained for the oxidized Ln(Pc)$_2$ compounds with Tb, Dy, Ho, Er, Tm, and Lu. These results form the basis for technical reports to be issued in the near future.
List of Publications:


Hatfield, W. E., Miller, J. H., Jr., Eds; Marcel Dekker, Inc.: New York 1988; 243-249.


List of Technical Reports:


Schwartz, M.; Hatfield, W. E. "Correlation of Spectroscopic and Magnetic Data of Two Charge Transfer Compounds of TCNQ with Cationic Copper Chelates", Technical Report No. 27.


Earth Oxide Superconductors GdBa$_2$Cu$_3$O$_{7-x}$ and YbBa$_2$Cu$_3$O$_{7-x}$": Technical Report No. 30.


List of names of graduate students and post-doctorals who participated in the project:

Martin Kirk - Graduate Student
Juan Padilla - Graduate Student
Lingqian Qian - Graduate Student
Y.-I. Kim - Post-doctoral Research Associate
Hye-Kyeong Ro - Graduate Student
J. L. Parkinson - Graduate Student
K. L. Trojan - Graduate Student