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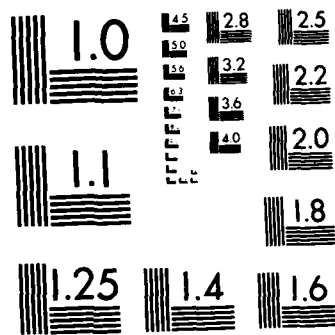
SYNTHESIS AND CHARACTERIZATION OF NEW LOW-DIMENSIONAL
METAL COMPLEX CONDUCTORS(U) NORTH CAROLINA UNIV AT
CHAPEL HILL DEPT OF CHEMISTRY W E HATFIELD 01 OCT 86
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FIELD	GROUP	SUB-GROUP	transition metal complexes electrical conductivities		
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<p>This research program was devoted to the synthesis and characterization of new transition metal compounds which had the potential of high electrical conductivities. Since band formation and electrical conductivity is enhanced by strong intermolecular interactions fully and partially oxidized metallomacrocyclic complexes were synthesized and characterized. Electrochemical methods were developed for crystal growth to overcome solubility problems which led to mixed phase products in earlier studies.</p> <p>These principles were extended to lanthanide complexes of phthalocyanine (HPcLaPc; Pc = phthalocyanine, La = lanthanide). These sandwich compounds contain an acidic proton which is thought to serve as a bridge between successive PcLaPc units. In some cases the phthalocyanine ring has an unpaired electron in its pi system. In this manner, strong interactions within a stack are formed. Doped materials were grown electrochemically, and the techniques led to the preparation of many new compounds.</p>					
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18. Subject Terms continued.

organometallic compounds
charge transfer compounds
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metallomacrocyclic compounds

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contd.

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19. Abstract continued.

A series of cationic copper complex-TCNQ charge transfer complexes, some of which exhibit high electrical conductivities, has been prepared and characterized. Other members of the series are currently under study. Hemiporphyrine and other chain compounds with high electrical conductivities were studied, along with a series of organometallic charge transfer compounds with TCNQ.

OFFICE OF NAVAL RESEARCH

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Task No. NR 053-617

Synthesis and Characterization of New Low-Dimensional Metal Complex Conductors

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Synthesis and Characterization of New Low-Dimensional Metal Complex Conductors

This research program was devoted to the synthesis and characterization of new transition metal compounds which had the potential of high electrical conductivities. The novel and highly anisotropic electrical and magnetic properties of low-dimensional systems are well known, and these studies were devoted to synthesis (Technical Rpts 2-7, 9-14) and characterization (Technical Rpts 1, 8, 15, 18-20) of such low-dimensional systems. Since band formation and electrical conductivity is enhanced by strong intermolecular interactions fully and partially oxidized metallomacrocylic complexes were synthesized and characterized (Technical Rpts 21-23). Electrochemical methods were developed for crystal growth (Technical Rpt. 23) to overcome solubility problems which led to mixed phase products in earlier studies (Technical Rpts 10, 12).

These principles were extended to lanthanide complexes of phthalocyanine (HPcLaPc). These sandwich compounds contain an acidic proton which is thought to serve as a bridge between successive PcLaPc units (Technical Rpt 22). In some cases the phthalocyanine ring has an unpaired electron in its pi system. In this manner, strong interactions within a stack are formed. Doped materials were grown electrochemically.

A series of cationic copper complex-TCNQ charge transfer complexes, some of which exhibit high electrical conductivities, was prepared and thoroughly characterized. A novel exocyclic-sigma bonded TCNQ dimer was found. The sigma bond is very weak and it was possible to study the excited triplet state by EPR (Technical Rpt 20). Other members of the series are currently under study. An oxo-bridged iron(IV) hemiporphyrzine chain with crystallographic equivalent iron ions which are different on the Mössbauer time scale as a result of disorder in the bridging oxygen atoms was discovered (Technical Rpt 21). Other chain compounds with high electrical conductivities (Technical Rpt 24) were studied, along with a series of organometallic charge transfer compounds with TCNQ (Technical Rpts 16, 17).

Attached is a list of technical reports issued during the period of the contract, a list of publications resulting from the research, and a list of personnel involved in the research.



Dist	Special
A-1	

Technical Report No. 1. "The Coupled Representation Matrix of the Pair Hamiltonian", Raymond P. Scaringe, Derek J. Hodgson, and William E. Hatfield.

Technical Report No. 2. "A Study of the Electrical Properties of the Charge-Transfer Derivatives of Diaminoanthraquinones", C. Webster Andrews, III, John R. Wasson and William E. Hatfield.

Technical Report No. 3. "Magnetic and Structural Characterization of Dibromo- and Dichlorobis(thiazole)copper(II)", William E. Estes, Diane P. Gavel, William E. Hatfield and Derek J. Hodgson.

Technical Report No. 4. "Unusual Magnetic Properties in Two Copper(II) Chelates of Schiff Bases Derived from α -Amino Acids: A Dimeric Interaction in a Structural Linear Chain", William E. Estes and William E. Hatfield.

Technical Report No. 5. "The Structural and Magnetic and Electrical Conductivity Properties of the Charge Transfer Compound 1,1'-Dimethylferrocenium Bis(Tetracyanoquinodimethane), $[(CH_3C_5H_4)_2Fe][TCNQ]_2$ ", Scott R. Wilson, Peter J. Corvan, Reginald P. Seiders,² Derek J. Hodgson, Maurice S. Brookhart, William E. Hatfield, Joel S. Miller, Arthur H. Reis, Jr., P. K. Rogan, Elizabeth Gebert and Arthur J. Epstein.

Technical Report No. 6. "The Interaction of Hydrazine with Copper(II) Chloride in Acidic Solutions. The Formation, Spectral and Magnetic Properties, and Structures of Copper(II), Copper(I), and Mixed Valence Species", David B. Brown, Jeffrey A. Donner, James W. Hall, Scott Wilson, Roxy B. Wilson, Derek J. Hodgson and William E. Hatfield.

Technical Report No. 7. "Molecular Metals: New Organometallic Systems", L. Alcacer, R. J. H. Clark, W. E. Hatfield, K. Klabunde, J. S. Miller, G. D. Stucky, G. A. Toombs, F. Wudl, and Yoshimura, in "Molecular Metals", edited by William E. Hatfield, Plenum Press, pp. 517ff, New York, 1979.

Technical Report No. 8. "Magnetism of Mixed Valence Compounds", William E. Hatfield.

Technical Report No. 9. "Solid State Structure and Electronic Properties of A Mixed-Valence Two-Dimensional Metal, KCu_4S_3 ", David B. Brown, Jon A. Zubieta, P. A. Vella, James T. Wróblewski, Timothy Watt, William E. Hatfield and Peter Day.

Technical Report No. 10. "Synthesis and Characterization of Metallo-organic Conducting Materials with Tetraazaannulenes", William E. Hatfield.

Technical Reports - 2

Technical Report No. 11. "Exchange Coupling in the Sulfur Bridged Quasi Linear Chain Compound Bis(dimethyldithiocarbamate) copper(II). Observations on Exchange in Sulfur Bridged Copper(II) Compounds", William E. Hatfield, Robert R. Weller and James W. Hall.

Technical Report No. 12. "Synthesis and Characterization of Metallo-organic Conducting Materials with Tetraazaannulenes", William E. Hatfield, Symposium Series: Conductive Polymers, edited by R. B. Seymour, Plenum Press, 1980.

Technical Report No. 13. "Exchange Coupling in the Alternating Chain Compounds Catena-Di- μ -Chlorobis(4-Methylpyridine) Copper(II), Catena-Di- μ -Bromobis-(N-Methylimidazole)Copper(II), Catena-Hexanedionebis(Thiosemicarbazato)Copper(II), and Catena-Octanedionebis(Thiosemicarbazato)Copper(II)". J. W. Hall, W. E. Marsh, R. R. Weller and William E. Hatfield.

Technical Report No. 14. "Isolation of a Stable Binuclear Copper Complex Containing a Copper-Copper Bonded Unit. The X-Ray Structure Determination {(7,8,15,16,17,18,25,26,33,34,35,36-Dodecahydrotetrabenzo[e,m,s,a']-[1,4,8,11,15,18,22,25]Octa-Azacyclo-Octaicosine)Dicopper} Triperchlorate", K. P. Dancey, P. A. Tasker, R. Price, William E. Hatfield and D. C. Brower.

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Technical Report No. 16. "The Synthesis of 1,1'-Bicobaltocene Salts of Tetracyano-p-quinodimethanide and the Structure of 1,1'-Bicobaltocene [Co(III)Co(III)][TCNQ]₃", Chak-po Lau, Phirtu Singh, Susan J. Cline, Reginald Seiders, Maurice Brookhart, Wayne E. Marsh, Derek J. Hodgson and William E. Hatfield.

Technical Report No. 17. "Syntheses of 1,1'-Bicobaltocene Salts of Tetracyano-p-quinodimethane, tetrabromoquinone, and tetrabromodiphenoquinone; and the Structure of 1,1'-Bicobaltocene[Co(III)Co(III)][TCNQ]₃", Chak-po Lau, Phirtu Singh, Susan J. Cline, Reginald Seiders, Maurice Brookhart, Wayne E. Marsh, Derek J. Hodgson and William E. Hatfield.

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Technical Report No. 20. "Crystal Structure and Excited Triplet State Electron Paramagnetic Resonance of the Sigma Bonded TCNQ

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Dimer in Bis-2,9-Dimethyl-1,10-Phenanthrolinecopper(I) Tetracyanoquinodimethane $[\text{Cu}(\text{DMP})_2]_2[\text{TCNQ}]_2$ ", Stanislaw K. Hoffmann, Peter J. Corvan, Phirtu Singh, C. N. Sethulekshmi, Robert M. Metzger and William E. Hatfield.

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Technical Report No. 22. "Effects of Iodination on the Electrical Conductivity of Hydrogen Bis(Phthalocyaninato) Neodymium(III)", Leonard ter Haar, William E. Hatfield and M. Tsutsui.

Technical Report No. 23. "Preparation and Properties of Single Crystals of Hydrogen Bis(Phthalocyaninato) Neodymium(III)", Brian W. Sullivan, Raymond N. Dominey, Jeffrey H. Helms, Michael Schwartz, Leonard W. ter Haar, and William E. Hatfield.

Technical Report No. 24. "Magnetic Exchange Interactions in the Linear Chain Chromium(III) Compounds Catena-fluorophthalocyaninatochromium(III) and Catena-cyanophthalocyaninatochromium(III)", Michael Schwartz, William E. Hatfield, Melvin D. Joesten, Michael Hanack and Armin Datz.

"The Coupled Representation Matrix of the Pair Hamiltonian", Raymond P. Scaringe, Derek J. Hodgson, and William E. Hatfield, Mol Phys., 1978, 35, no. 3, 701-713.

"Magnetic and Structural Characterization of Dibromo- and Dichlorobis(thiazole)copper(II)", William E. Estes, Diane P. Gavel, William E. Hatfield and Derek J. Hodgson, Inorg. Chem., 1978, 17, 1415-1421.

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