AD-A249 263

(2)

ENTATION PAGE

Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION: UNCLASSIFIED

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

ELECTE APR 30 1992 S C D

3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for Public Release Distribution Unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION: Department of Chemistry, University of North Carolina

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION: Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code): Campus Box 3290, Chapel Hill, NC 27599-3290

7b. ADDRESS (City, State, and ZIP Code): Department of the Navy, Arlington, VA 22217

8a. NAME OF FUNDING/SPONSORING ORGANIZATION: Office of Naval Research

8b. OFFICE SYMBOL (If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: N0014-89-J-1734

8c. ADDRESS (City, State, and ZIP Code): 800 North Quincy Street, Arlington, VA 22217-5000

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification): UNCLASSIFIED:

12. PERSONAL AUTHOR(S)

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final Report	FROM 3/1/89 TO 11/30/91	92 April 22	9

16. SUPPLEMENTARY NOTATION

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number): yttrium barium electrical conductivity inorganic solids oxides sulfides halides organic solids superconductivity methal dithiolates

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.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT: ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION: UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL

22b. TELEPHONE (Include Area Code)

22c. OFFICE SYMBOL

DD Form 1473, JUN 86 — Previous editions are obsolete. — SECURITY CLASSIFICATION OF THIS PAGE: UNCLASSIFIED

OFFICE OF NAVAL RESEARCH

GRANT N00014-89-J-1734

R&T Code 4135007

FINAL REPORT

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

by

William E. Hatfield

University of North Carolina

Department of Chemistry

Chapel Hill, North Carolina 27599-3290

FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

UNC No.: 5-35754 #11 Final

1. Federal Agency and Organizational Element to Which Report is Submitted	2. Federal Grant or Other Identifying Number Assigned By Federal Agency	OMB Approval No.	Page	of
Office of Naval Research	N00014-89-J-1734	0348-0039	1	1 pages

3. Recipient Organization (Name and complete address, including ZIP code)

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4. Employer Identification Number	5. Recipient Account Number or Identifying Number	6. Final Report	7 Basis
56-600-1393	5-35754 FINAL	☒ Yes ☐ No	☒ Cash ☐ Accrual

8. Funding/Grant Period *(See Instructions)* From: (Month, Day, Year)	To: (Month, Day, Year)	9. Period Covered by this Report From: (Month, Day, Year)	To: (Month, Day, Year)
3/1/89	11/30/91	3/1/89	11/30/91

10. Transactions:	I Previously Reported	II This Period	III Cumulative
a. Total outlays	0.00	217,311.77	217,311.77
b. Recipient share of outlays	0.00	0.00	0.00
c. Federal share of outlays	0.00	217,311.77	217,311.77
d. Total unliquidated obligations			0.00
e. Recipient share of unliquidated obligations			0.00
f. Federal share of unliquidated obligations			0.00
g. Total Federal share *(Sum of lines c and f)*			217,311.77
h. Total Federal funds authorized for this funding period			220,000.00
i. Unobligated balance of Federal funds *(Line h minus line g)*			2,688.23

11. Indirect Expense	a. Type of Rate *(Place "X" in appropriate box)* ☐ Provisional ☒ Predetermined ☐ Final ☐ Fixed	b. Rate	c. Base	d. Total Amount	e. Federal Share
		44.5%	$150,388.77	$66,923.00	$66,923.00

12. *Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.*

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Prescribed by OMB Circulars A-102 and A-110

FINAL REPORT

1. Summary: This research program was devoted to the synthesis and characterization of new transition metal complex conductors. Essentially, compounds expected to have high and controllable electrical conductivities were designed based on principles evolved in our laboratory and other laboratories around the world. These new compounds were characterized by temperature-dependent electrical conductivity measurements, magnetic susceptibility measurements, electron paramagnetic resonance spectroscopy, structural determinations by X-ray studies on single crystal samples, elemental analyses, X-ray photoelectron spectroscopy, infrared, and ultra-violet spectroscopy. Results of the research have been described in several technical reports. Brief reviews of important results are presented in the following paragraphs:

Charge Transfer Compounds with Tetrathiafulvalene (TTF). Reactions of TTF with a variety of copper(II) complexes yielded highly conducting charge-transfer compounds of the general formula $(TTF)_nCuX_2$ ($X = Cl^-, Br^-$), where the stoichiometry depended on the copper(II) complex starting material. These new results clearly indicate that TTF-copper halide charge transfer complexes of controlled stoichiometry can be designed and prepared based on the redox potential of the copper complex. (See Technical Report No. 44.)

Reactions of TTF with a variety of other transition metal halides yielded highly conducting materials with TTF molecules stacked to form chains, notably with the metal halide coordinated to TTF molecules in the stacks. The new compounds exhibit unusual stoichiometries and magnetic properties. It is likely that these new compounds could be designed to function as sensors or, say, as switches in devices.

Bis-Phthalocyaninato-Lanthanide Complexes. This work was initiated when it was observed that $HNd(Pc)_2$ exhibited unusually high electrical conductivity. A number of analogues were prepared and characterized experimentally and theoretically (see Technical Reports 34-36,42). These compounds were small-gap semiconductors, and some of them exhibited unusual temperature dependencies of electrical conductivities. During the course of the research, a series of compounds which may be formulated as $Ln^{3+}(Pc^{2-})(Pc^{\cdot})$ were generated and remarkable properties were observed. Contrary to accepted dogma, there is strong exchange coupling between the lanthanide unpaired electron and the ligand-radical electron. Furthermore, $Yb(Pc)_2$, a compound with no unpaired electrons, exhibited a magnetic moment of 3.5 μ_{BM}, an unprecedented magnetic moment which arises from orbital angular momentum only. There is much fundamental research to be done with these interesting compounds, especially with a triple-decker series in which mixed-metal, mixed valence metals and ligands may be prepared. (See Technical Reports 38

and 41).

Studies on Alkali-Metal Coinage-Metal Chalcogenides. A number of such compounds, e. g. $K_3Cu_8S_6$, have been prepared and studied since electronic instabilities presumably arising from charge-density waves were observed in our laboratory. (See Technical Report No. 37). These compounds were selected for study since they occur in the region of the generic phase diagram common to high temperature superconductors. Although many of these compounds are metallic and exhibit unusual electrical conductivities, none have exhibited superconductivity. However, this is a fruitful area for fundamental research, and if current theories hold, superconducting compounds will be found in some of the large number of compounds that may be prepared. Systematic work and patience will be the key to success. Collaborative work on other systems which are precursors to high T_c materials was also undertaken. (See Technical Report No. 40).

2. Technical Reports Resulting from the Grant:

No. 34. Magnetic and Electrical Properties of Sandwich-Like Lanthanide Phthalocyanines, May 8, 1989.

No. 35. Application of the Angular Overlap Model to Lanthanide Phthalocyanines, July 15, 1989.

No. 36. Sigma and Pi Interactions of the Pyrrolic Ligand Sandwich-Like Lanthanide Phthalocyanines Determined from Magnetic Susceptibility and Ligand-Field Theory, June 25, 1990.

No. 37. Electronic Instabilities of Two-Dimensional Metals $K_3Cu_8S_6$ and $Rb_3Cu_8S_6$, July 13, 1990.

No. 38. Bis(phthalocyaninato) Lanthanide Sandwich Compounds Exhibiting Mixed Valence Ligands, July 13, 1990.

No. 39. Identification of a Novel Tetragonally-Compressed Six-Coordinate Copper(II) Complex: Preparation and Characterization of a 3-Chloroanilinium Copper Chloride Complex $(3\text{-Chloroanilinium})_8[CuCl_6]Cl_4$, October 12, 1990.

No. 40. A Planar Oxocuprate(II) Array Via Heterometallic Alkoxide Chemistry, November 14, 1990.

No. 41. Strong Exchange Coupling in Lanthanide Bis(Phthalocyaninato) Sandwich Compounds, 29 March, 1991.

No. 42. Correlation Between Pi-Orbital Overlap and Conductivity in Bis-Phthalocyaninato Lanthanides, 10 June 1991.

No. 43. Properties of Tetrathiafulvalene Charge Transfer Compounds with Iron, Ruthenium, Rhodium, and Iridium Halides, 10 June 1991.

No. 44. Synthesis and Characterization of Tetrathiafulvalene Charge Transfer Compounds with Copper Halides, 19 August 1991.

3. Journal Articles Resulting from the Grant:

Padilla, J.; Hatfield, W. E. "Sigma and Pi Interactions of the Pyrrolic Ligand Sandwich-Like Lanthanide Phthalocyanines Determined From Magnetic Susceptibility and Ligand-Field Theory", Inorg. Chim. Acta **1990**, 172, 241.

Tucker, D. A.; White, P. S.; Trojan, K. L.; Kirk, M. L.; Hatfield, W. E. "Identification of a Novel Tetragonally-Compressed Six-Coordinate Copper(II) Complex: Preparation and Characterization of a 3-Chloroanilinium Copper Chloride Complex, (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$", Inorg. Chem. **1991**, 20, 823-826.

Samuels, J. A.; Vaartstra, B. A.; Huffman, J. C.; Trojan, K. L.; Hatfield, W. E.; Caulton, K. G. "A Planar Oxocuperate(II) Array Via Heterometallic Alkoxide Chemistry", J. Amer. Chem. Soc. **1990**, 112, 9623.

Trojan, K. L.; Hatfield, W. E.; Kepler, K. D.; Kirk, M. L. "Strong Exchange Coupling in Lanthanide bis-(phthalocyaninato) Sandwich Compounds", J. Appl. Phys., **1991**, 69, No. 8, 6007-6009.

Kim, Y. I.; Hatfield, W. E. "Electrical, Magnetic and Spectroscopic Properties of Tetrathiafulvalene Charge Transfer Compounds with Iron, Ruthenium, Rhodium and Iridium Halides", Inorg. Chim. Acta, **1991**, in press.

Padilla, J.; Hatfield, W. E. "Correlation Between π-Orbital Overlap and Conductivity in Bis-Phthalocyaninato Lanthanides", Inorg. Chim.Acta, **1991**, 185, 131.

Ro, H. K.; Hatfield, W. E. "Electronic Instabilities of Two-Dimensional Metals $K_3Cu_8S_6$ and $Rb_3Cu_{8S}6$", in Mixed Valency Systems: Applications in Chemistry, Physics, and Biology, K. Prassides, Ed.; 407-412, 1991.

Trojan, K. L.; Hatfield, W. E.; Kepler, K. D.; Kirk, M. L. "Bis(Phthalocyaninato) Lanthanide Sandwich Compounds Exhibiting Mixed Valence Ligands", in Mixed Valency Systems: Applications in Chemistry, Physics, and Biology, K. Prassides, Ed.; 407-412, 1991.

Kim, Y. I.; Hatfield, W. E. "Synthesis and Characterization of Tetrathiafulvalene Charge Transfer Compounds with Copper Halides", Inorg. Chim. Acta, **1991**, 189, 237.

Oki, A. R.; Zhang, H.; Maguire, J. A.; Hosmane, N. S.; Ro, H.; Hatfield, W. E. "Synthesis and Crystal Structure of the First Neutral Bis(η^5-C_2B_4-carborane)chromium(IV) Sandwich Complex", Organometallics, **1991**, 10, 2996.

Oki, A. R.; Zhang, H.; Hosmane, N. S.; Ro, H.; Hatfield, W. E. "Trinuclear, Mixed-Valence, Zwitterionic, and Sandwiched Manganacarborane: A Novel "Butterfly" Cluster", J. Am. Chem. Soc., **1991**, 113, 8531.

Trojan, K. L.; Kendall, J. L.; Kepler, K. D.; Hatfield Inorg. Chim. Acta, **1992**, 200, in press.

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Other co-authors listed above are collaborators or undergraduate students.

DL/1113/89/1

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