

PROJECT ADMINISTRATION DATA SHEET

Revised to correct Accounting BOR number only

ORIGINAL



REVISION NO. _____

Project No. G-33-617 (R6041-OA1)

GTRC/GIT

DATE 10 / 9 / 85Project Director: L. A. BottomleySchool/~~XXX~~ChemistrySponsor: DHHS/PHS/NIH/NHLBIType Agreement: Grant No. 1 R01-HL33734-01Award Period: From 9/15/85 To 9/14/86 (Performance) 12/14/86 (Reports)

Sponsor Amount:

This ChangeTotal to DateEstimated: \$ _____ \$ 76,238Funded: \$ _____ \$ 76,238Cost Sharing Amount: \$ _____ Cost Sharing No: G-33-396Title: Electrochemical Studies of Capped Metalloporphyrins

ADMINISTRATIVE DATA

OCA Contact

John B. Schonkx-4820

1) Sponsor Technical Contact:

2) Sponsor Admin/Contractual Matters:

George NemoJon CarowNational Institute of HealthNational Institute of HealthNHLBINHLBIFederal Building, Room 540Grants ManagementBethesda, MD 20205Bethesda, MD 20205(301) 496-1537(301) 496-7255Defense Priority Rating: N/AMilitary Security Classification: N/A(or) Company/Industrial Proprietary: N/A

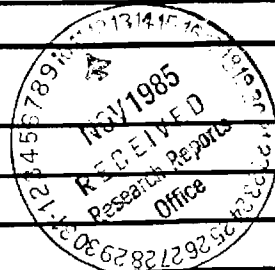
RESTRICTIONS

See Attached NIH Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval — Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of \$500 or 125% of approved proposal budget category.

Equipment: Title vests with GIT

COMMENTS:

No funds may be expended after 9/14/86

COPIES TO:

SPONSOR'S I. D. NO. 02.108.001.86.003Project Director
Research Administrative Network
Research Property Management
AccountingProcurement/GTRI Supply Services
Research Security Services
Reports Coordinator (OCA)
Research Communications (2)GTRC
Library
Project File

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEETDate 7/15/88Project No. G-33-617-R6041-1A0School/Lab Chem.Includes Subproject No.(s) N/AProject Director(s) L. A. BottomleyGTRC/GIT
XXXSponsor DHHS/PHS/NIH/NHLBITitle Electrochemical Studies of Capped MetalloporphyrinsEffective Completion Date: 9/14/86 (Performance) 12/14/86 (Reports)

Grant/Contract Closeout Actions Remaining:

☐

None

☒

Final Invoice or Copy of Last Invoice Serving as Final

☐

Release and Assignment

☐

Final Report of Inventions and/or Subcontract:

Patent and Subcontract Questionnaire
sent to Project Director ☐☐

Govt. Property Inventory & Related Certificate

☐

Classified Material Certificate

☐

Other _____

Continues Project No. _____ Continued by Project No. G-33-695

COPIES TO:

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Library

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Other _____

G-33-617

SECTION I (continued)
SUMMARY OF PROPOSED WORK

GRANT NUMBER
HL 33734-02

KEY PROFESSIONAL PERSONNEL ENGAGED ON PROJECT

NAME	POSITION TITLE	DEPARTMENT AND ORGANIZATION
Lawrence A. Bottomley	Associate Professor	School of Chemistry Georgia Institute of Technology
Jean-Noel Gorce	Research Assistant	
James S. Quick	Research Assistant	
Frank L. Neely	Research Assistant	
Grant N. Holder	Research Assistant	

Give a brief summary of plans for the next year of support, including the objectives and specific aims as well as the methodology to be used to achieve these aims. **DO NOT EXCEED THE SPACE PROVIDED.**

The global objective of the research program is the complete characterization of synthetic compounds which are models for the oxygen carrying hemoproteins. The specific class of synthetic compounds under investigation ("capped" porphyrins) possess a very high degree of steric encumbrance built onto only one side of the porphyrin. The specific objectives during second year of the grant are: 1) to investigate the redox reactivities of iron, ruthenium and osmium derivatives of the "capped" porphyrin. These compounds were prepared during the first year of the grant; 2) to react each of these compounds with nitrogen containing bases (similar to those found at the active site of *in vivo* hemoproteins) forming pentacoordinate complexes and 3) to react each of the pentacoordinate complexes with dioxygen, CO, CS and CSe to form six-coordinate metalloporphyrins in which the diatomic ligand resides under the cap inside its hydrophobic cavity. These reactions will be carried out in organic media and monitored both spectrally and electrochemically.

VERTEBRATE ANIMALS INVOLVED ☒ NO ☐ YES If "YES," identify by common names and underline primates.

SECTION II (continued)
NEXT BUDGET PERIOD

GRANT NUMBER
HL 33734-02

B. Supplemental information regarding ITEMS in the proposed budget for the next period which require explanation or justification. (See instructions)

The summer salary of the principal investigator has increased over previously budgeted amount due to promotion and pay raises. This value will be prorated in the event of other grants. Research Assistant stipends have increased \$1,500 each. The value listed is the minimum amount approved by the School of Chemistry. As a result of these increases in personnel costs, the travel budget and other expenses categories have been reduced by over 50%. The supplies category has also been diminished by over 30%.

SECTION III CURRENT BUDGET PERIOD	FROM 09/15/85	THROUGH 09/14/86	GRANT NUMBER HL 33734-02
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The following pertains to your CURRENT PHS budget. Do not include cost sharing funds. This information in conjunction with that provided on Page 2 will be used in determining the amount of support for the NEXT budget period.

A. BUDGET	CURRENT BUDGET <i>(as approved by awarding unit)</i>	ACTUAL EXPENDITURES THRU (insert date): 6/30/86	ESTIMATED ADDITIONAL EXPENDITURES AND OBLIGATIONS FOR REMAINDER OF CURRENT BUDGET PERIOD	TOTAL ESTIMATED EXPENDITURES AND OBLIGATIONS <i>(Col. 2 plus Col. 3)</i>	ESTIMATED UNOBLIGATED BALANCE <i>(Subtract Col. 4 from Col. 1)</i>
	(1)	(2)	(3)	(4)	(5)
TOTAL DIRECT COSTS	49,737	22,786	26,957	49,737	-0-
DIRECT COSTS (as provided)	26,503	7,446	19,057	26,503	-0-
TOTALS →	76,240	30,232	46,008	76,240	-0-

Item B. THROUGH F.

Instructions and provide the information required in items B. through F. Use this page and continuation pages as necessary.

Item B. Professional Personnel

Name	Title	Category	Less than 25%
Lawrence A. Bottomley	Associate Professor	1	*
James S. Quick	Research Assistant	3	*
Sean-Noel Gorce	Research Assistant	3	*
Grant N. Holder	Research Assistant	3	*
Frank L. Neely	Research Assistant	3	*
John Helfrick	Research Assistant	3	*

Item C. Equipment

A PARC Model 273 Potentiostat/Galvanostat was purchased during the first quarter of the grant year.

Item D. Travel

Two trips were funded from the grant during the first year. The first trip was in January. The P.I. attended the Gordon Conference on Electrochemistry in Santa Barbara, CA. The second trip will be the week of Sept. 7-14th. The P.I. will present the group research findings at the National American Chemical Society meeting in Anaheim, CA.

Item F. Other Support

None

SECTION IV PROGRESS REPORT SUMMARY		GRANT NUMBER HL 33734-02	
PRINCIPAL INVESTIGATOR OR PROGRAM DIRECTOR Bottomley, Lawrence A.		PERIOD COVERED BY THIS REPORT	
NAME OF ORGANIZATION Georgia Institute of Technology		FROM 09/15/85	THROUGH 09/14/86
TITLE (Repeat title shown in item 1 on first page) Electrochemical Studies of Capped Metalloporphyrins			
(SEE INSTRUCTIONS)			

PUBLICATIONS

a) Published during the first year of the grant:

"Oxidative Electrochemistry of Iron-Selenocarbonyl Porphyrins" by J.-N. Gorce and L. A. Bottomley *Inorg. Chem.* 1985, 24, 1431.

"Spectroelectrochemistry of a u-Nitrido-Bridged Iron Phthalocyanine Dimer" by L. A. Bottomley, J.-N. Gorce, V. L. Goedken and C. Ercolani, *Inorg. Chem.* 1985, 24, 3733.

"The Electroreduction of Several Metallo-Octakis(methylthio)-tetraazaporphyrins" by L. A. Bottomley and W. J. H. Chiou, *J. Electroanal. Chem.* 1986, 198, 331.

"Spectroelectrochemistry of (u-Oxo)bis[(phthalocyaninato)iron-(III)]" by L. A. Bottomley, C. Ercolani, J.-N. Gorce, G. Pennesi and G. Rossi, *Inorg. Chem.* 1986, 25, 2338.

- * "Spectroelectrochemistry of Cobalt 'Capped' Porphyrins" by L. A. Bottomley, J.-N. Gorce and W. M. Davis, *J. Electroanal. Chem.* 1986, 202, 111.

b) Accepted for publication during the first year of the grant:

- * "Spectroelectrochemistry of a Urea-Linked Oxo-Bridged Iron Porphyrin Dimer" by L. A. Bottomley, J.-N. Gorce and J. T. Landrum, *Inorg. Chim. Acta*, 1986, 187, 0000.

c) Submitted for publication during the first year of the grant:

- * "Mononuclear and Binuclear Thiocarbonyl Iron Porphyrins" by J.-N. Gorce and L. A. Bottomley, submitted for publication in *J. Am. Chem. Soc.*
- * "The Electrochemistry of Thiocarbonyl and Selenocarbonyl Iron Octaethylporphyrins" by L. A. Bottomley and J.-N. Gorce, submitted for publication in *Inorg. Chem.*

* denotes work supported by this grant.

1. Goals for the previous year:

The research goals for the first year of the grant were:

- a) to complete preliminary studies on the cobalt derivative of the "capped" porphyrin;
- b) to complete our investigation of sterically unencumbered chalcocarbonyl iron porphyrins in preparation for studies with the analogous "capped" porphyrin derivatives; and
- c) to synthesize Fe, Ru, and Os derivatives of the "capped" porphyrin;

2. Description of studies conducted during first year of the grant.

During the first quarter of this grant year, we focused our efforts on completing preliminary studies on the cobalt "capped" porphyrin (hereafter abbreviated CoCap). Through a combined voltammetric and spectroelectrochemical investigation, we learned several points of interest. Firstly, the potentials for electrooxidation of Co(II)Cap were not those predicted from consideration of the phenyl ring substituent effect alone. This suggested that the presence of the cap causes a significant change in solvation of the porphyrin as compared to other sterically unencumbered porphyrins. Secondly, the kinetics of the heterogeneous electron transfer of both the "capped" and unencumbered homologs were comparable in non-coordinating media. Thirdly, the cap prevented the formation of hexacoordinate Co(III) porphyrin complexes. Fourthly, the oxidation of the Co(II)Cap(nitrogenous base) complexes proceeded reversibly whereas the oxidation of the unencumbered porphyrins did not. In the latter complexes, electron transfer occurred concomitantly with changes in the number of ligands coordinated to the Co center. In the former complex, only outer sphere electron transfer reactions were observed. Although our understanding of the redox reactivity of CoCap is far from complete, we submitted the work for publication. A reprint is included in the appendix of this application.

For the next two quarters, our research efforts were devoted to completing our characterisation of iron porphyrins without steric encumbering groups attached to the porphyrin. Our objectives during this phase of the work were to understand the cis-trans effects operative for the chalcocarbonyl iron complexes and to investigate the possibility of forming novel binuclear iron porphyrin complexes. The porphyrins studied were the thiocarbonyl and selenocarbonyl adducts of 2,3,7,8,12,13,17,18-octaethyl- and 5,10,15,20-tetraphenyl-porphyrins, hereafter abbreviated (OEP)FeCS, (OEP)FeCSe, (TPP)FeCS and (TPP)FeCSe, respectively. The redox reactivity of these compounds was investigated at Pt electrodes in nonaqueous media. All underwent a series of charge transfer reactions with complete retention of the diatomic ligand.

As many as three electrooxidation and two electroreduction processes were observable within the potential limits of the halocarbon solvent/supporting electrolyte system. This reactivity is indeed unique. The isoelectronic (OEP)FeCO and (TPP)FeCO complexes both lose the diatomic concomitantly with charge transfer.

Reaction of (OEP)FeCZ and (TPP)FeCZ (where Z = CS or CSe) with a series of monodentate nitrogenous bases (L), produced exceptionally stable six-coordinate mononuclear complexes. These adducts could be oxidized and reduced without loss of the diatomic axial ligand. The reaction of (OEP)FeCZ and (TPP)FeCZ with a series of exo-bidentate nitrogenous bases (L') also produced exceptionally stable six-coordinate complexes. However, this reaction produced either mononuclear or binuclear complexes in dynamic equilibrium. The equilibrium was readily monitored as each species gave distinctive proton NMR resonances. The predominant species in solution could be controlled by varying both the temperature and the relative concentration of base to porphyrin.

The redox reactivity of (OEP)FeCZ(L') and (TPP)FeCZ(L') mirrored that observed when L' was replaced with L. The redox reactivity of the binuclear complexes was consistent only with two non-interacting metal centers. From this work we learned that the Fe-C bond in the chalcocarbonyl Fe porphyrins is exceptionally stable when compared to the bond strength found in carboxy or carbenoid Fe porphyrins. This bond is not broken in the presence of a large excess of secondary amines or by successive charge transfer reactions. Changes in the basicity of the porphyrin N core modifies the total electron density on the Fe atom, but does not alter the stability of the Fe-C bond. Two separate manuscripts describing our results during this phase of the research have been submitted for publication. Preprints are included in the appendix of this application.

Efforts during the final quarter of the budget year were directed towards preparing gram quantities of the "capped" porphyrin. This is a five step time consuming process with an overall yield of less than 5%. We were successful in preparing 2 grams of the porphyrin and have converted a portion to the Fe, Ru and Os derivatives.

3. Specific objectives for the upcoming year:

The research goals for the second year of the grant are:

- a) to investigate, in detail, the electrode reactions of Fe, Ru and Os "capped" porphyrins. Special emphasis will be placed on determining the identities of all species generated at the electrode.

- b) to react each of these with a series of nitrogenous bases to form pentacoordinate complexes.
- c) to synthesize hexacoordinate Fe, Ru and Os "capped" porphyrin complexes with selected nitrogenous bases as the first axial ligand and either dioxygen, O_2 , CS or CSe as the second axial ligand coordinated to the central metal ion.