THE NUCLEUS

April 1994 *Of the Northeastern Section of the American Chemical Society* *Vol. LXXII, No. 8*

Monthly Meeting

Gustavus John Esselen Award to Kary B. Mullis

Esselen Forum

Kary B. Mullis and other experts discuss applications of the Polymerase Chain Reaction

Summer Scholar

Photophysical Properties of Chiral Lanthanide Complexes

Historical Notes

Obituaries of recently deceased members

Call for Papers

208th National ACS Meeting
Washington, DC.
August 20-26, 1994

The ACS invites undergraduate students, including graduating seniors, to submit abstracts for presentation at the Undergraduate Research Poster Session, which will be part of the extensive programming for undergraduates at this national meeting. Send abstracts on standard ACS forms to:

John W. Higuchi
Student Affiliates Program
American Chemical Society
1155 Sixteenth St., NW
Washington, DC 20036

Deadline for receipt of abstracts is April 15, 1994

The Northeastern Section of the American Chemical Society, Inc.
Office: Marilou Cashman, 23 Cottage St., Natick, MA 01760. 1-800-872-2054 (Voice or FAX) or (508) 653-6329.
Any Section business may be conducted via the business office above.
Washington, D.C. ACS Hotline: 1-800-227-5558

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Cover: *Dr. Kary B. Mullis (photo by Alexandra, La Jolla, CA)*

THE NUCLEUS

Dedicated to the Memory of James Flack Norris
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Institute for Chemical Education

Summer 1994 Workshops for Teachers

The Institute has announced its 1994 Summer Workshops for Teachers, to be held on the campus of the University of Wisconsin, Madison, WI, sponsored by the National Science Foundation.

The following workshops will be available:

Super Science Connections (two weeks), for Kindergarten through Grade 3 curricula. Hands-on science activities are tied into works of children's literature, art projects and writing skills.

Chemistry Activities (two weeks) for hands-on science activities, teachers of elementary and middle schools.

Chemistry Fundamentals (four weeks) for teachers of physical science, Grades 6–9.

Chemistry Instrumentation (two or three weeks) for experienced high school science teachers to work with and study the theory of operation of modern chemical instruments. How to use them in cutting-edge research and how to build low-cost models for school use.

ICS workshops will be offered for college credit toward degrees at a number of colleges and universities.

ICE will pay fees, expenses and stipends for workshop participants.

For copies of the full announcement and a list of ICE publications available, call the NESACS office: Marilou Cashman, 800-872-2054.

For additional information on the workshops and application forms, write to: Institute of Chemical Education, Department of Chemistry, University of Wisconsin, 1101 University Ave., Madison, WI 53706–1396. ◇

Esselen Forum

Wednesday, April 13, 1994
Harvard University
Science Center
Lecture Hall B
1 Oxford St., Cambridge, MA

8:00 pm: Panel Discussion

We Can See Your Genes

Moderator:
Robert C. Cowen, *Christian Science Monitor, Natural Science Editor*

Panelists:
Kary B. Mullis, *La Jolla, CA.*
Leonard Lerman, *M.I.T.*
Dagmar Ringe, *Brandeis Univ.*
John W. Hicks, *Head, FBI Laboratory, Washington, D.C.*

NERM-24

Undergraduates invited to attend the 24th Northeast Regional ACS Meeting, Burlington, VT, June 19–22, 1994

A special program for undergraduates includes:

Undergraduate Research Poster Session
Workshops:
- Mentoring undergraduate students
- Looking toward the future (career, graduate school info, ACS employment services, resume review

Student Affiliates-Faculty Advisors Interactive Session
Mixers, lunches, excursions, socials with undergraduates of the Northeast (New England, Upstate New York)

Registration fee: $ 20. Dormitory or local housing available at reasonable rates.

For information and housing
See C&EN for April 25 or contact
Dr. Willem R. Leenstra,
Dept. of Chemistry, U. of Vermont,
Burlington, VT 05405.

For information about the undergraduate program, contact
Dr. Morton Z. Hoffman (617/353-2494)
or
Dr. Patricia L. Samuel (617/353-2124),
Dept. of Chemistry, Boston University,
Boston, MA 02215 ◇

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Zymark Corporation

B.U. Chemia Awarded Grant

For Undergraduate Programming

Chemia, the undergraduate chemistry club and Student Affiliate Chapter of the ACS at Boston University has been awarded a grant of $5,000 by the parent society for planning and implementing undergraduate programming at the June 19-22, 1994 ACS Northeast Regional Meeting at Burlington, VT.

The special program for undergraduates will include an undergraduate research poster session, workshops and social events. Students will be able to attend symposia and talks of the general meeting and attend the exposition of chemical equipment, instruments and books. As part of the grant, Mamta Parikh and Gail Prado, juniors at BU, have traveled to the spring ACS meeting in San Diego, CA to attend a training workshop with co-advisors of Chemia, Profs. Morton Z. Hoffman and Patricia L. Samuel.

This grant is part of the ACS commitment to undergraduate programming at regional and national meetings through its Student Affiliates Program and the Society Committee on Education. ◇

Monthly Meeting

The 761st Meeting of the Northeastern Section of the American Chemical Society

The Gustavus John Esselen Award for Chemistry in the Public Interest

Thursday, April 14, 1994

Harvard University, Cambridge, MA

5:30 Social Hour, Faculty Club, 20 Quincy St.

6:15 Dinner (black tie optional)

8:00 **Award Meeting, Dr. James Kaufman, presiding**
Hall B, Science Center, 1 Oxford St.
The Esselen Award — Dr. William O. Foye, Esselen Committee chairman
Kary B. Mullis — Leonard Lerman, M.I.T.
Presentation of the Award to Kary B. Mullis — Gustavus J. Esselen, III
Esselen Award Address — *The Polymerase Chain Reaction*

A reception with refreshments will follow the program.

Dinner reservations should be made no later than April 8. Please call Marilou Cashman at (800) 872-2054. Reservations not cancelled at least 24 hours in advance must be paid. Members, $21.00; Non-members, $23.00; Retirees, $12.50; Students, $8.00. THE PUBLIC IS INVITED. Anyone who needs special services or transportation, please call Marilou Cashman a few days in advance so that suitable arrangements can be made.

Parking: Free parking is available in the Felton St. Garage (3rd level or higher). Enter via Cambridge St. and Felton St. There will be no shuttle bus service. If you need transportation, call Marilou Cashman for arrangements.

Next meeting: Thursday, May 12, 1994. ***Education Night.*** *Social Hour 5:30, followed by dinner, Evening meeting 7:30. Brandeis University. Dr. Jerry Bell, AAAS, will address the Section.*

Biography

Kary B. Mullis obtained the B.S. in Chemistry from the Georgia Institute of Technology, followed by graduate work in Biochemistry at the U. of California, Berkeley where, in 1972, he obtained the Ph.D. under the guidance of John B. Neilands. He spent postdoctoral years as a Fellow at the U. of Kansas Medical School and at the U. of California, San Francisco (Pharmaceutical Chemistry). Between 1979 and 1988 he worked first for the Cetus Corporation, then for Xytronyx, Inc. in San Diego, CA, on DNA technology, photochemistry and photobiology. Since 1987 he has been a private consultant in nucleic acid chemistry. In 1992-3 he was Vice President for Research at Atom Tags, Inc. of La Jolla, CA and since 1992 he has been chairman of Stargene, Inc. of San Rafael, CA.

He is on the editorial board of *Biotechniques* and *PCR Methods and Applications*. He jointly holds 11 patents with several co-workers.

He is the recipient of 15 awards, most notably, and announced after he was nominated for the 1994 Esselen Award, the Nobel Prize in Biochemistry. The Gustavus John Esselen Award is the first award he has received from any component of the American Chemical Society. ◇

Member News

Prof. Eric N. Jacobsen, of Harvard University received an 1993 Excellence in Chemistry Award from the Zeneca Pharmaceutical Group. The award carries with it an unrestricted research grant of $25,000. Dr. Jacobsen is active in catalysis, especially addressing questions of catalyst selectivity. *(from C&EN, 1/31/1994, p.70)*

Prof. Peter S. Kim , of Whitehead Institute and M.I.T. is the recipient of the Eli Lilly Award of the ACS Division of Biological Chemistry, to be presented at the 1994 fall ACS meeting in Washington, DC. He is being recognized for his work on protein folding. For an extensive description of his work, see *C&EN,* Feb. 21, 1994, p. 37–8. ◇

ACS News

"Science in American Life"

At the National Museum of American History, Washington, DC opens April 27

This permanent exhibit was four years in planning, the ACS is the major sponsor. From the opening of the first research laboratories in US universities in 1870 to a look into the future, the many aspects of science in America are covered in displays, artifacts, and 20 computer interactive exhibits.

A major goal of the exhibit is to highlight the roles played by minorities and women in science. There will be a "Hands-on Science Center" where visitors can engage in such activities as water-sample testing, exploring DNA fingerprinting and detecting radioactivity in common household objects. There is a case-study section featuring: A period setting which recreates a pioneering chemistry laboratory opened in 1876 at Johns Hopkins University (multimedia); posters, videos and equipment recalling the mobilization of science for World War II and the atomic bomb project; "Looking Ahead" which focuses on biotechnology and public attitudes to it, gene-based medical research, solid waste disposal alter-

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NESACS Trustees

Condensed Annual Report 1993

1. Status of the Trust Funds, December 31, 1993: The net worth (investments plus cash balances) of the assets of the seven Trust Funds in the charge of the Trustees was $1,348,311 on 12-31-93, a 7.2% increase over their value on 1-1-93. The Consolidated Trust (endowment) alone was valued at $932,633 on 12-31-93, compared to $872,682 on 12-31-92, an increase of 6.9%.

Changes in the Consolidated portfolio were purchases of 9 new stocks plus bonds, sales of 5 old stocks, and redemption (by recall) of 2 bonds. For these transactions, $25,213 of cash funds was added as new endowment to the Consolidated Trust Fund. No changes were made in the income accounts. The percentage of the Consolidated Trust allocated to the several funds was as follows: Richards Trust: 12.0%; Norris Trust: 58.3%; Publications Trust: 8.2%; Permanent Trust: 16.5%, Hill Trust: 5.0%. The Esselen Trust of $273,576 is not part of the Consolidated Trust.

2. Cash Flow in 1993 Changes in the endowment portfolio during 1993 returned 22% more income to the Consolidated and income accounts than had been projected from the investments owned at the start of the year—$65,297 actual *vs.* $53,560 projected. The income accounts received $32,000 by distribution from the Consolidated Trust, 58% of the earned income of this endowment fund. The Norris Trust spent essentially all of its new income for the year. Spending from the other Trusts ranged from a low of 35% (Publications) to a high of 303% (Hill) of their new income. Excesses were taken out of the surplus cash balances remaining from 1992, and deficiencies were kept to raise the surplus for 1993.

3. Projected Income and Expenses for 1994 The Trust Funds should have no trouble satisfying the expenses anticipated by the 1994 Section budget, if all Consolidated income is apportioned out, and surplus from 1993 is used to make up any shortfalls. However, it is suggested that no more than 75% of the expected Consolidated earned income need to be distributed to satisfy the projected budgets, with the remainder being kept available for contingencies, and possible enhancement of the endowment for reinvesting.

	est. income in 1994		*est. expense possible in 1994*			*Trust*
	new div+int	*cash bal. 1-1-94*	*committed 1-1-94*	*net un-committed*	*maximum if apportioned*	*Budgets 1994*
Consolidated	$51,038	$17,887	$ 144	$ 68,781	$ 1,781	$ 1,200
Richards	3,686	3,428	–0–	7,144	15,142	10,000
Norris	1,311	4,193	2,091	3,413	42,500	24,700
Publications	576	12,495	1,320	11,751	17,221	9,500
Permanent	1,644	8,452	508	9,588	20,657	12,750
Hill	–0–	1,540	8	1,532	4,878	1,500
	58,255	47,995	4,071	102,179	102,179	59,650
Esselen	11,000	2,509	123	13,386		11,000
TOTAL	69,255	50,504	4,194	115,565		70,650

2-7-94 Prepared by G. Richard Handrick ◇

ACS News

continued from page 5

natives, genetic engineering are presented from different viewpoints. Interactive video discs have been developed for use by middle school classrooms funded by a grant from Occidental Chemical Corp.

The museum is located at 14th St. and Constitution Ave., NW. Museum hours are 10 am to 5:30 pm daily (except Dec. 25). Admission is free. Several of the former Presidents of the ACS have been very active in getting this project started and keeping it going, despite some bumps in the road. ◇

Workforce Report on Chemical Technicians in the Workforce

From a report by Corinne A. Marasco, Office of Professional Services, American Chemical Society.

Recently stronger attention has been paid to the role of technicians in the chemical workforce. Due to global competition technicians are taking increased responsibilities. However, the traditional pool of technicians, those with 2-year degrees is low and, increasingly, 4-year degree people have filled these positions.

Technicians combine features of both white collar and blue collar workers. They are responsible for operating instruments, recording data and conducting experiments on which scientific knowledge is built.

Thus, technicians are required to use theories, diagnoses, and other critical thinking skills from the conceptual work they support.

Technician hiring patterns have changed dramatically over the past 20 years, as stated above. The number of technicians employed has remained quite steady at slightly above 80,000 between 1983 and 1991, the years included in the study, only dropping to 72,000 and 78,000 in 1984 and 1986, respectively.

From recent U.S. Department of Labor data it is seen that workers with associate degrees are represented most heavily in the health assessment and

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Consulting Chemists' Meeting

Sheraton Tara Lexington Hotel
Lexington, MA
April 21, 1994

Applications of Neural Networks for Optimization of Chemical Processes

Dr. Marc E. Parham, Manager of the Membrane and Biomedical Research Division, W.R. Grace & Co.

727 Marrett Rd., Exit 30B, Rte. 128, Rte. 2A west 1/4 mile to Hotel
5:30 optional dinner, 7:00 meeting

Call Debra Saez at (508) 521-1327 by April 19, 1994.
All interested persons are invited to attend

Dr. Parham will continue the series of discussions covering methods of design of experiments begun in the January meeting with this illuminating talk on the statistical method known as *Neural Networks.* Data obtained by the traditional design of experiment (DOE) approach are used by neural networks to predict accurately the outcome of a chemical process. This seminar will show how combinations of approaches may reduce time and effort required to optimize yields in laboratory processes. ◇

NEACT Summer Conference

August 15-18, 1994
At Framingham State College

The conference theme is *The Foods of Chemistry and the Chemistry of Foods.* Field trips and workshops are planned to help teachers to facilitate incorporating this topic into the curriculum.

Program Information: Dr. Brenda Braaten, Chairperson, Dept. of Chemistry and Food Science, Framingham State College, 100 State St., Framingham, MA 01701.

Registration Information: From the above, or Kenneth Brody, Chairperson of Arrangements, 20 Mountain St., Sharon, MA 02062. ◇

ACS Short Course

Synthetic Organic Chemistry: Modern Methods and Strategies
A Two-Day Short Course Sponsored by the Northeastern Section, ACS, Committee on Continuing Education

National ACS is making top-rated ACS Short Courses available to local sections at tuition fees greatly reduced from the normal $785. The NESACS Committee on Continuing Education is pleased to present this course, which has been offered successfully at each National ACS Meeting since 1981.

Dates and Time: Thursday, **May 12, 1994, 8:30 a.m. – 5:00 p.m.**
and Friday, **May 13, 1994, 8:30 a.m. – 5:00 p.m.**

Place: Frost Lounge, Ell Building, Northeastern University, 360 Huntington Ave., Boston, MA

Program Agenda:

Introduction to the strategy and planning of organic syntheses and other basic concepts such as synthetic equivalency and protecting groups.

Fundamentals of carbocyclic ring formation and associated principles such as stereoelectronic effects.

Construction of six-membered carbocyclic rings: enolate-based methods, Diels-Alder reactions, carbonation cyclizations, and others.

Formation of five-membered carbocyclic rings: use of dicarbonyl compounds, cycloaddition approaches, other annulative methods, and rearrangements of other ring systems.

Synthesis and uses of small-ring compounds: cyclopropane and cyclobutane derivatives.

Preparation of larger ring systems: cycloheptane derivatives, medium-ring compounds, and macrocycles.

Stereoselective construction of acyclic compounds: stereocontrolled alkene synthesis, sigmatropic rearrangements, and modern aldol chemistry.

Advanced examples of total syntheses.

Instructor: Paul Helquist, Professor of Chemistry, University of Notre Dame. Prof. Helquist is one of the most highly praised instructors in the ACS continuing education program.

Registration Fees:
ACS Members if mailed before April 25..... $225.00; after April 25.... $275.00
Non-ACS Members if mailed before April 25 . $325.00; after April 25.... $375.00
There will be a limited number of scholarships for unemployed ACS Members on a space-available basis.
Parking Fee $3.00/day University cafeterias will be available for lunches.
For further information contact: Prof. Alfred Viola - (617) 373 2809

Registration form for Short Course:
Synthetic Organic Chemistry: Modern Methods and Strategies

Name: _____ Affiliation: _____

Mailing Address _____ Telephone: _____

_____

Mail with remittance to :
(Please make checks payable to NESACS)

Prof. Alfred Viola, Chair
NESACS Committee on Cont. Ed.
Department of Chemistry
Northeastern University
Boston, MA 02115

1993 Summer Scholar's Report

Photophysical Properties of Chiral Lanthanide Complexes

by Jonathan E. Whittum† and Jerry P. Jasinski
Chemistry Department
Keene State College, Keene, New Hampshire 03431

1. Introduction

Lanthanide ions have been noted for their increasing applications as probes of biomolecular structure[1-7]. In this work it was our goal to obtain a better understanding of the photophysical aspects surrounding the complexation chemistry associated with lanthanide ternary complexes of two optically active, chiral ligands, saccharic and gluconic acid, by establishing ternary complexes with various multidentate achiral stabilizing ligands of high binding strength, ethylenediamminetetraacetic acid [EDTA], (2-hydroxyethyl) - EDTA [HEDTA], and nitrilotriacetic acid [NTA]. We performed luminescence and lifetime measurements of pH dependent formation complexes between Tb(III), the chiral ligand (CL) and a stabilizing, multidentate achiral ligand (AL). Measurements of the pH dependence associated with the emission intensities and lifetimes of the Tb(AL)(CL) ternary complexes provided an indication of the specific pH regions in which significant Tb(AL)-substrate interactions take place. Luminescence spectra-structure comparisons of the two chiral lanthanide ternary complexes involving hydroxy carboxylates with available circularly polarized luminescence

†*Norris summer scholar*

Fig. 1

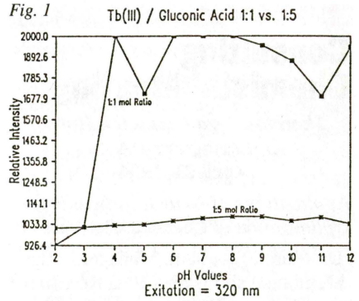


Fig. 2

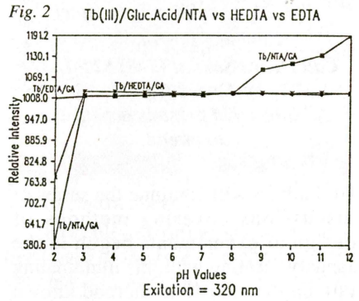


Fig. 3

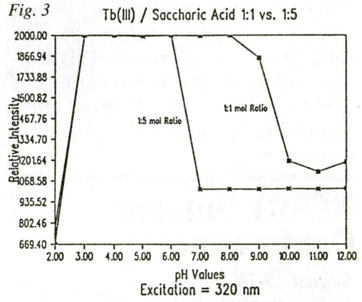


Fig. 4

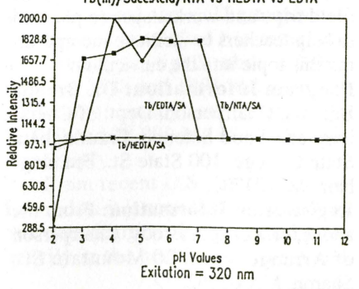


Fig. 5

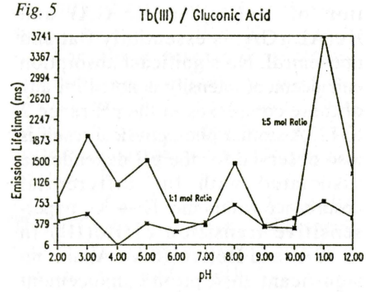


Fig. 6

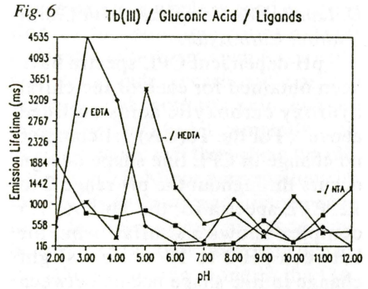


Fig. 7

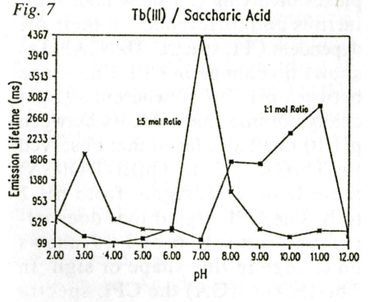
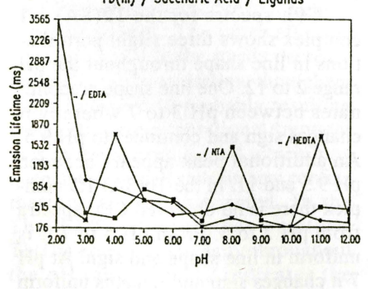
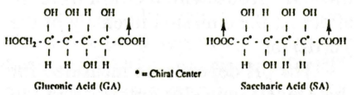


Fig. 8



(CPL) data has made it possible to include these techniques as appropriate to use for probing the structure of chiral molecules on a more quantitative level.

Chiral Ligands



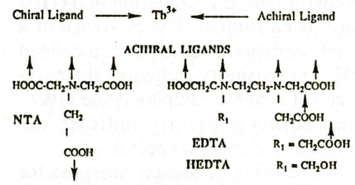
With this approach, a complex is first formed in which the lanthanide ion, Tb(III), is partially coordinated by a multidentate achiral ligand (AL): $Tb^{3+} + AL^{n-} \leftrightarrow Tb(AL)^{(3-n)+}$. The $Tb(AL)^{(3-n)+}$ complex is then allowed to bind the chiral ligand of interest:

$$Tb(AL)^{(3-n)+} + CL^{m-} \leftrightarrow Tb(AL)(CL)^{(3-n-m)+}$$

thus producing a ternary complex in the process. By using ternary complexes, systematic structure-spectra correlations useful for describing the nature of Tb(III) interactions with the chiral ligands may be obtained. The importance of applying CPL spectroscopy in ternary complexes of this type lies in its ability to differentiate between the situations where Tb(III) chirality was due to the presence of vicinal or vicinal/conformational effects. When a chiral ligand could bind Tb(III) merely in a monodentate fashion, only vicinal effects could yield Tb(III) optical activity. It has been shown that for 13 chiral ligands, the Tb(III) optical activity within the $^5D_4 \rightarrow {}^7F_5$ band system was weak and of one sign only[8]. The sign of this CPL correlated with the absolute configuration of the chiral ligand; substrates of the (S)-configuration led to the observation of positive CPL. On the other hand, simple alpha-hydroxycarboxylic acids were known to bind lanthanides in a bidentate fashion, and the chirality induced in the Tb(III) emission bands by these ligands would be dominated by conformational effects. Double-signed CPL spectra of much higher magnitude were observed in that case[9].

Through studies on simple carboxylic acids, the CPL technique has been calibrated to the point where unknown coordination possibilities can be confirmed or discounted after comparison with the existing library of spectra-structure correlations. The ability to differentiate between monodentate and multidentate ligand bonding is extremely useful and is used as a complementary comparative technique to assist with the interpretations of the photophysical measurements.

The advantages associated with the use of these ternary complexes are: (1) the complexes are stable over much wider pH ranges, (2) no apparent upper limit on complex solubility exists, and (3) the Ln(III)/AL stoichiometry can be limited to the formation of 1:1 complexes eliminating the presence of polymeric Tb(III) compounds. The particular AL ligands chosen exhibit quite strong bonding constants for Tb(III), and consequently are not likely to be displaced by a chiral ligand. In addition, the number of Tb(III) coordinated positions each ligand will occupy varies in a systematic manner with the ligands: NTA is tetradentate, HEDTA is pentadentate, and EDTA is hexadentate. Hence, we have complete steric control over how accessible the Tb(III) ion will be for a chiral ligand.



2. Experimental

Saccharic acid and gluconic acid stock solutions were prepared by dissolution of appropriate quantities of material, and solutions were prepared by mixing stoichiometric amounts of the stock solutions. For the luminescence experiments, a final Tb(III) concentration of 10 mM was used. Saccharic acid, gluconic acid, NTA, EDTA and HEDTA were used as received from sigma Chemical Co. while $TbCl_3$ and $HoCl_3$ were used as received from Research Chemicals. Luminescence measurements were carried out on a Perkin Elmer LS-50 Fluorimeter interfaced to a SPECTRA-386-25 Mhz microcomputer. Lifetime mea-

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Scholar's Report

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surements were performed on a PTI PL2300 pulsed nitrogen laser system attached to a gated integrator and boxcar averager (Stanford Research Mdl. SR250) interfaced to a SPECTRA 386-25 Mhz microcomputer providing digitized data collection and subsequent manipulation. The luminescence decay times and rate constants were obtained by fitting the decay curve to a single exponential function. Hypersensitivity measurements were completed on a Cary 14 UV-VIS spectrophotometer with the OLIS upgrade and interfaced to a Gateway 2000 microcomputer. The reference cell in this series contained Ho(III) aquo-species at exactly the same concentration as the Ho/AL solution, thus yielding a differential absorbance value.

3. Results and Discussion

A. pH Dependence of Tb(III) Emission Intensity

Trends associated with the pH dependence of the $^5D_4 \rightarrow {}^7F_5$ transition related to the UV excitation of Tb(III) have been studied. The existence of a stable emission intensity over a defined pH range usually indicates the existence of a stable complex while inflection points generally indicate the formation of another species.

The pH dependence measured for the Tb(III) emission intensity in the Tb(GA) and Tb(AL) (GA) complexes is shown in Figures 1 and 2.

The pH dependence measured for the Tb(III) emission intensity in the Tb(SA) and Tb(AL) (SA) complexes is shown in Figures 3 and 4.

B. pH Dependence of Tb(Ill) Emission Lifetimes

Mechanisms which alter the luminescent lifetime of Tb(III) species are generally similar to those which affect emission intensity. Emission lifetime is quenched by deactivation of the $^5D_4$ Tb(III) state which is promoted by high energy vibrations (around 3500 cm^{-1}). The -OH stretching mode of coordinated water molecules is effective in this regard. Since most ligands do not contain the required group vibrational frequencies which quench the excited state, the binding of a ligand generally results in the expulsion of coordinated water molecules. However, in GA and SA both contain the -OH group which could have an affect on the emission intensity of the Tb(III) ion.

The pH dependence measured for the Tb(III) emission intensity in the Tb(GA) and Tb(AL)(GA) complexes is shown in Figures 5 and 6.

The pH dependence measured for the Tb(III) emission intensity in the Tb(SA) and Tb(AL)(SA) complexes is shown in Figures 7 and 8.

The presence of major and minor inflections in both the GA and SA complexes indicates that a significant amount of cooperativity and conformational adjustments occur when both the chiral and achiral ligands bind to the Tb(III) ion. Both vicinal and vicinal/conformational effects can be seen in these cases. The addition of the achiral multidentate ligands HEDTA and NTA follow binding patterns similar to those for the chiral ligands, GA and SA, while in EDTA, with only one major inflection point, different effects are implied.

C. pH Dependence of Ho(III) Hypersensitivity

While the intensity of most lanthanide absorption bands are independent of the nature of the coordination sphere, it is known that certain bands termed "hypersensitive transitions" exhibit absorptivities which are strongly dependent on the environment[10]. These transitions are characterized by a change in the J quantum number of two. The $^5I_9 \rightarrow {}^5G_6$ transition of Ho(III) (located around 450 nm) is such a transition, and has been used to obtain further characterizations of lanthanide complexes in aqueous solution. Since the observed molar absorptivities are so small, the data are best examined as the difference between the absorbance of the Ho(III) complex and the aquo-ion.

The pH dependence associated with the differential absorbance within the $^5I_9 \rightarrow {}^5G_6$ hypersensitive transition of Ho(III) in Ho(GA) and Ho(AL)(GA) is essentially flat and uneventful. No significant absorption enhancement intensity is noted for any of these complexes in the pH range 2 to 12. A similar photophysical result is also observed for the pH dependence associated with the differential absorbance within the $^5I_9 \rightarrow {}^5G_6$ hypersensitive transition of Ho(III) in Ho(SA) and Ho(AL)(SA). Again, no significant absorption enhancement intensity is noted for any of these complexes in the pH range 2 to 12.

D. Lanthanide Complexes With Chiral Hydroxy Carboxylates

pH dependent CPL spectra have been obtained for each of the chiral hydroxy carboxylic acids outlined above[11]. For the Tb(GA) 1:1 complex no change in CPL line shape or sign occurs throughout the pH range 2 to 12. CPL spectra for the Tb(GA) 1:5 complex shows a similar behavior between pH 2 to 10 while a slight change in line shape occurs between pH 10 to 12.

Each of the three ternary complexes involving GA show both similarities and differences in their pH dependent CPL spectra. Tb(NTA)(GA) shows no change in CPL line shape between pH 2 to 10 wherein a slight change in line shape occurs between pH 10 to 12 similar to that observed for Tb(GA) 1:5. In Tb(EDTA)(GA) there is no CPL signal from pH 2 to 6. The CPL signal that does occur between pH 6 and 12 shows no change in line shape or sign. In Tb(HEDTA)(GA) the CPL spectra does not change from pH 2 to 9 whereby it changes sign at pH 9 and continues that way to 12.

CPL spectra for the Tb(SA) 1:1 complex shows three slight perturbations in line shape throughout the pH range 2 to 12. One line shape predominates between pH 3 to 7 whereby it changes sign and continues to pH 9.5. An additional peak appears between pH 9.5 and 11. In the Tb(SA) 1:5 complex there is no observed CPL spectra from pH 2 to 5. From pH 5 to 7 it is uniform in line shape and sign. At pH 7 it changes sign and remains uniform until pH 10 where an additional peak appears between pH 10 to 11.

The three ternary complexes involving SA also have unique CPL spectra. Tb(NTA)(SA) shows no CPL signal until pH 7 whereupon it remains uniform in shape and sign to pH 12. Tb(HEDTA)(SA) shows a uniform signal from pH 2 to 12. With the Tb(EDTA)(SA) complex, CPL spectrum first appears at pH 6.5 and then continues uniformly to pH 12.

4. Conclusions

When comparing all the spectroscopic data as a whole, a good description of the solution coordination chemistry of terbium complexes with two chiral hydroxycarboxylic acids, gluconic and saccharic acid, can be made. The Tb(GA) 1:1 complex exists as a monomeric unit throughout the pH range 2 to 12. Minor perturbations in the Tb(III) intensity and lifetime data in the low to moderate pH range may be attributed to some quenching due to the -OH stretching mode in the GA species. The Tb(GA) 1:5 complex exists as a monomeric unit from pH 2 to 10 whereupon it tends to become self-associated into an oligomeric species, possibly hydroxy bridged dimers. Above pH 10 the binding of the GA ligand enhances the Tb(III) intensity and lifetime associated with the Tb(III) luminescence (compared to the aquo-ion).

In the Tb(NTA)(GA) complex, a doubling of the initial Tb(III) emission intensity between pH 3 and 8 indicates a stable, monomeric species is formed in this region. An additional increase in Tb(III) emission intensity between pH 8 and 12 suggests either self-association into oligomeric complexes and/or conformational effects due to the chiral hydroxy groups. The latter effect is most likely due to the steady decrease in Tb(III) emission lifetime throughout the pH range 2-12 probably resulting from -OH group vibrational frequencies in the achiral ligand which may quench the excited state as new conformations are being formed. In the Tb(HEDTA)(GA) species a uniform Tb(III) emission intensity throughout the pH range 3 to 12 indicates the existence of a monomeric complex. However, a significant decrease of a major inflection of the Tb(III) lifetime intensity at pH 5 to much lower levels at pH 8 and 10 suggests the existence of conformational effects becoming predominant above pH 7. A sign change in the CPL data for this complex above pH 9 supports the idea. In the Tb(EDTA)(GA) species the Tb(III) emission intensity remains monomeric throughout the entire pH range, 2 to 12. However, a significant decrease of a major inflection point of the Tb(III) lifetime intensity of this complex at pH 3 to significantly lower levels at higher pH values suggests here, also, the existence of conformational effects beginning to occur somewhere above pH 4. The existence of a CPL signal only between pH 6 and 12 gives support to this notion.

The Tb(SA) 1:1 complex exists as a monomeric species between pH 3 and 9 and as a conformationally altered species between pH 10 to 12. A very strong Tb(III) emission intensity region between pH 3 to 9 and a less intense region between pH 10 and 12 in combination with two Tb(III) lifetime enhancement regions (between pH 8 to 9 and again between pH 10 to 11) and a sign change in the CPL spectrum at pH 7 gives support to the existence of either self-associated oligomeric species or a bidentate coordination of the SA ligand to the Tb(III) ion at the two higher pH regions. In the Tb(SA) 1:5 complex a similar effect occurs only with a shifting to a lower pH (3 and 7) of either the self association or bidentate coordination effects where Tb(III) lifetime emission enhancement occurs. CPL spectral changes over similar pH ranges support this idea.

Effects of the achiral stabilizing ligands on the bonding activity of the chiral SA ligand parallel somewhat that observed for GA. In Tb(NTA)(SA) two strong Tb(III) emission intensity regions between pH 3 to 4 and 5 to 8 suggest uni- and bidentate coordination of SA followed by conformationally altered species in the pH 8 to 12 region. Again, In the Tb(HEDTA)(SA) species a uniform Tb(III) emission intensity throughout the pH range 2 to 12 indicates the existence of a monomeric complex. Also, the presence of minor inflection points of the Tb(III) lifetime emission of this complex at pH 4 and 11 in association with an initial CPL signal at pH 4 and sign changes at pH 9 and 11 support this suggestion. In addition, in the Tb(EDTA)(SA) complex the Tb(III) emission intensity displays a strong band between pH 3 and 7 leveling off to another less intense region from pH 7 to 12. However, a significant decrease of a major inflection point of the Tb(III) lifetime intensity of this complex at pH 2 to significantly lower levels at higher pH values suggests here, also, the existence of conformational effects beginning to occur somewhere above pH 3 The existence of a CPL signal beginning at pH 6, changing sign between pH 8 and 9 also supports this notion.

5. References

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ACS News

continued from page 6

treating occupations (including registered nurses) and among health technologists and technicians.

Industrial demand for BS chemists hinges on market conditions and the increased technological sophistication. Because of increasing complexity of chemical technology, those with BS degrees are likely to be called on increasingly to fill technician positions.

The Bureau of Labor Statistics estimates that in the next 15 years employment for technicians will grow by over 30%, most of them to be in service-oriented jobs, probably in the health services industry. This growth is likely to be faster than that in chemists' jobs, which is projected at about 16% in the next 15 years.

Salary statistics for 1992 show that median salaries for technicians increase from $ 21,000 for those with less than 1 year experience to $36,000 for those with 25-29 years experience. Significantly, those with more than 30 year experience have a lesser median salary of $33,000. This compares with corresponding salaries for B.S. industrial chemists of $30,000 (0-1 year since BS) to $64,000 (40+ years).

Predictions for the year 2000 are that the average company will be smaller and have fewer employees. Instead of the traditional vertical hierarchy, there will be a horizontal structure, based on the individuals' specialties. Business will move from making a product to providing a service. Companies will be shifting to an applied focus and getting products to market more quickly.

Because of this shift in emphasis from research to production, more technicians will be needed for production and quality control and for applied research. There may be less job stability and less upward mobility.

A copy of the complete 5-page report, which includes notes and references, may be obtained from: Workforce Studies American Chemical Society Office of Professional Services 1155 Sixteenth St., NW Washington, DC 20036 ◇

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Historical Notes

Again we are publishing brief biographies of chemists and chemical engineers whose deaths have not been recorded here previously. We thank members of the Northeastern Section and families of the deceased for their help in assembling the needed data. The alphabetical listing will be continued in a later issue.

Joseph L. Barrett, S.J., 84, died on November 22, 1993. He was a Boston native who obtained the B.S. degree from Boston College in 1931. He joined the Society of Jesus that year and while studying for the priesthood obtained the M.S. degree in chemistry at Holy Cross College. After his ordination in 1942 he taught chemistry at Boston College and at Fairfield College until 1956 at which time he began a 30-year career as professor of logic in the philosophy department at Boston College. At the time of his death he was a resident of the Campion Center in Weston, Mass. Rev. Barrett was a very popular figure on the B.C. campus and shared with his students a great interest in Boston College football.

Marie A. (Dobbrow) Barton, 91, died on October 26, 1993. A Connecticut native, she earned the B.S. and M.S. degrees in chemistry at Mount Holyoke College, then served as a chemist at Watertown Arsenal for many years. During the World War II years she served as a volunteer driver for the American Red Cross in the Boston area. Until 1979 she was also involved in the management of *The Nautilus,* a popular vacation resort in Chatham on Cape Cod.

Stacy Lloyd Bragdon, 97, died on September 14, 1993. He was a native of Westbrook, Maine and a graduate of Gorham High School. After serving with the AEF in France for 13 months during World War I he obtained the B.S. degree in chemistry at the University of Maine. He subsequently obtained the M.Ed. degree at Harvard.

Mr. Bragdon's career was teaching and administration at the secondary school level in Wellesley, Mass. He not only taught chemistry and biology but also introduced audio-visual teaching aids, was director of the summer and evening extension courses, served for a time as school principal, photographer, editor of the community publication "Your Schools," town meeting member and church deacon. He was president of the Massachusetts Teachers Association and a director of the National Education Association. Extensive obituaries of Mr. Bragdon were published in the *Boston Globe* and in the *Wellesley Townsman* for September 16, 1993.

Priscilla Carter, 74, a retired research chemist at Harvard's Huntington Laboratories, died on October 21, 1993 after a long illness. She was a New Bedford native and obtained the B.S. and M.S. degrees in chemistry from Wellesley College. Her hobby was photography, which she pursued at her homes in Newton and Dartmouth, Mass.

Carolus Melville Cobb, 71, died on September 21, 1993. A native of Lynn, he majored in chemistry at M.I.T. where he obtained the S.B. degree in 1944 and later the Ph.D. in physical chemistry. He was employed on the atomic bomb project at Oak Ridge during World War II, then at Ionics, Inc. in Cambridge and at the Allied Research Associates in Boston. In 1959 Cobb was a cofounder of American Science and Engineering, Inc. in Cambridge and served as chief chemist and vice president until his retirement. He became interested in the discovery of techniques for the detection of cervical cancer, including one using radioactive gallium. At the time of his death he was seeking patent protection for his discoveries. ◇

To be continued

Calendar

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Michael Rubner (M.I.T)
"Layer by Layer Molecular Assembly of Electroactive Polymers"
UMass Lowell, North Campus, Olney Science Center, Room 428 at 3:30

April 15

Prof. David A. Evans (Harvard Univ.)
"Approaches to the Synthesis of Vancomycin and Related Peptide Antibiotics"
Boston College, Room 127
Merkert Chemistry Center at 4:00 pm

Paolo Lombardi (Menarini Ricerche Sud S.p.A)
"Designs and Synthesis of Irreversible Inhibitors of the Enzyme Aromatase (Estrogen Synthetase)"
Boston University, Room 107 Metcalf Center for Science and Engineering at 3:00 pm

April 18

Prof. Albert Meyers (Colorado State Univ.)
"The Chemistry of Chiral Oxazolines"
Harvard University
12 Oxford Street, Mb-23 at 4:15 pm

April 19

Prof. Peter J. Stang (Univ. of Utah)
"Polyvalent Iodine Chemistry: a Renaissance"
Boston College, Room 127
Merkert Chemistry Center at 4:00 pm

April 20

Christopher J. Turner (Francis Bitter Magnet Lab, M.I.T.)
"The Determination of the Three Dimensional Structure of the Ragweed Allergen *ambrosia trifida* V by Homonuclear 3D NMR"
Boston University, Science Center Auditorium, SCI 107 at 4:00 pm

April 21

Prof. Giacinto Scoles (Princeton Univ.)
"Interfacial Self-Assembly of Long-Chain Molecules"
Harvard University, 12 Oxford Street, Room Mb-23 at 5:00 pm

Dr. Terry M. Phillips (The George Washington Univ. Medical Ctr.)
"High Performance Immunoaffinity Chromatography for Protein Analysis"
Northeastern University
Room 129 Hurtig Hall at 4:00 pm

April 22

Wayne Guida (Ciba-Geigy Corp.)
"Protein Modeling and X-ray Crystallography in Drug Design"
Boston University,
Room 107 Metcalf Center for Science and Engineering at 3:00 pm

April 25

Prof. William Armstrong (Boston College)
"Polynuclear Manganese Complexes for the Photosystem-II Water Oxidase"
Boston University, Science Center Auditorium, SCI 107 at 4:00 pm

Dr. Adrian Parsegian (Physical Sciences Lab, DCRT)
TBA
Brandeis University
Room 122 Gerstenzang at 4:00 pm

April 26

Dr. Jay Troutman (AT&T Bell Labs)
"Imaging, Spectroscopy, and Dynamics of Single Molecules"
Massachusetts Institute of Technology
Room 2-105 at 4:00 pm

April 27

Dr. Mary Mandich (AT&T Bell Labs-N.J.)
"Semiconductor Clusters Fill Which Gap?"
Harvard University
12 Oxford Street, Mb-23 at 4:00 pm

April 28

Prof. Dennis P. Curran (Pittsburgh Univ.)
"Recent Applications of Radical Reactions in Organic Synthesis"
Boston College, Room 127
Merkert Chemistry Center at 4:00 pm

Russell Gaudiana (Polaroid Corp.)
"Control of Emission Wavelengths in Electroluminescent Polymers"
UMass Lowell, North Campus, Olney Science Center, Room 428 at 3:30 pm

April 29

James P. Snyder (Istituto di Recerche Biologia Molecolari)
"Virus Deactivation Strategies"
Boston University, Room 107 Metcalf Center for Science and Engineering at 3:00 pm

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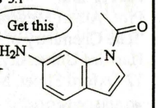
Get this → 

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April 1

Annette Doherty (Parke-Davis Pharmaceutical Research)
"Vasoactive Peptides and Their Modulation"
Boston University, Room 107 Metcalf Center for Science and Engineering at 3:00 pm

April 4

Prof. Barbara Seaton (Boston Univ. School of Medicine)
"Annexin V, a Caldium-Dependent Membrane-Binding Protein: Crystal Structure and Solution Studies"
Boston University, Science Center Auditorium, SCI 107 at 4:00 pm

Prof. David Tirrell (UMass Amherst)
"Bioengineered Polymeric Materials"
Tufts University, Room 136, STC, 4 Colby St., Medford at 2:30 pm

Prof. Gerald Babcock (Mich. State Univ.)
"Dioxygen Activation in Cytochrome Oxidase—Spectroscopic Resolution of Steps in the O=O Bond Cleavage Chemistry"
Harvard University
12 Oxford Street, Mb-23 at 4:15 pm

Prof. Geoffrey Davies (Northeastern Univ.)
"Encapsulated Metal Catalysts?"
U Mass Lowell, North Campus, Olney Science Center, Room 428 at 2:30 pm

Dr. Steven Cooper (Mallincrodt)
"Inorganic Chemistry Meet Medicine: New Directions in Diagnosis and Therapy"
Brandeis University
Rm. 122 Gerzenzang at 4:00 pm

April 6

Prof. Michael Weiss (Univ. of Chicago)
"DNA Bending and Gene Regulation: The Chemical Basis of Male Sex Determination"
Harvard University
12 Oxford Street, Mb-23 at 4:00 pm

April 7

Prof. David Chandler (Univ. of California, Berkeley)
"The Mechanism for the Primary Charge Transfer in Photosynthesis"
Massachusetts Institute of Technology
Room 6-120 at 5:00 pm

Dr. T.V. Rajanbabu (DuPont Central Research)
"Electronic Effects in catalytic Asymmetric Synthesis"
Boston College, Room 127
Merkert Chemistry Center at 4:00 pm

Prof. William Stwalley (Univ. of Connecticut at Storrs)
"Revealing the Darkest and Outermost Secrets of Molecules by Multiple Resonance Laser Spectroscopy"
Northeastern University
Room 129 Hurtig Hall at 4:00 pm

Dale Spall (Los Alamos Nat'l Lab)
"Kinetic Model of Dishwashing"
UMass Lowell, North Campus, Olney Science Center, Room 423 at 3:30 pm

April 8

Alex Nadzan (Ligand Pharmaceuticals)
"Intracellular Receptors: Discovery of Novel Compounds Acting at Retinoid Receptor Subtypes"
Boston University, Room 107 Metcalf Center for Science and Engineering at 3:00 pm

April 11

Prof. Shaul Mukamel (Univ. of Rochester)
"Cooperative and Ultrafast Nonlinear Spectroscopy of Confined Excitons in Molecular Nanostructures"
Boston University, Science Center Auditorium, SCI 107 at 4:00 pm

Prof. Kris A. Berglund (Mich. State Univ.)
"Fluorescence Spectroscopy for the Study of Particle Formation from Solutions"
Tufts University, Room 136, STC, 4 Colby St., Medford at 2:30 pm

Dr. Samuel Fogel (Bioremediation Consulting, Inc.)
"Bioremediation of Groundwater"
UMass Lowell, North Campus, Olney Science Center, Room 423 at 2:30 pm

Prof. R.J.P. Williams (Oxford)
"Coupling Electron and Proton Transfer to Energy Capture using Proteins"
Harvard University
12 Oxford Street, Mb-23 at 4:15 pm

Prof. Steven Weinreb (Penn State Univ.)
"New Synthetic Methodology Utilizing electron Deficient Imines"
Brandeis University
Room 122 Gerstenzang at 4:00 pm

April 11–13

Prof. Rudy A. Marcus (California Inst. of Technology)
A.D. Little Lectures in Physical Chemistry
Massachusetts Institute of Technology
Room 6-120 at 4:00 pm

April 13

Dr. Phaedon Avouris (IBM—Yorktown, NY)
"Probing the Wave Properties of Electrons and Manipulating Atoms at Surfaces with STM"
Harvard University
12 Oxford Street, Mb-23 at 4:00 pm

Prof. David A. Evans (Harvard Univ.)
"Studies in Asymmetric Catalysis"
Boston College, Room 127
Merkert Chemistry Center at 4:00 pm

April 14

Prof. David A. Evans (Harvard Univ.)
"The Synthesis of Polypropionate Natural Products"
Boston College, Room 127
Merkert Chemistry Center at 4:00 pm

Dr. Gilda Barabino (Northeastern Univ.)
"Biomedical Engineering"
Northeastern University
Room 129 Hurtig Hall at 4:00 pm

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