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COVER SHEET FOR TRIP REPORTS SUBMITTED TO THE OFFICE OF ENERGY RESEARCH

Destination(s) and Dates for Which Trip Report Being Submitted: Porto, Portugal 08/28-09/03/88
Turin, Italy 09/05-09/10/88

Name of Traveler: Gerard F. Payne

Joint Trip Report ☐ **Yes**
☒ **No**

If so, Name of Other Traveler(s): ____________________

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ORNL
FOREIGN TRIP REPORT

ORNL/FTR-3033

DATE:

SUBJECT: Report of Foreign Travel of Gerard F. Payne, a Research Chemist in the Chemistry Division

TO: Alexander Zucker

FROM: Gerard F. Payne

PURPOSE: To participate in the XXVI International Conference on Coordination Chemistry in Porto, Portugal and also to participate in the XIII International Conference on Organometallic Chemistry in Turin, Italy.

SITES VISITED:

08/28-09/03 XXVI International Conference on Coordination Chemistry, Porto, Portugal

Principal persons contacted at conference:

Alan Bond	Division of Chemical and Physical Sciences University of Deakin Geelong, Victoria 3217 Australia
Sigeo Kida	Department of Chemistry Faculty of Science Kyushu University, Hakozaki 812 Fukuoka Japan
Janos Mink	Institute of the Isotopes Hungarian Academy of Sciences P.O. Box 77 H-1525 Budapest Hungary
Franz Dickert	Institute of Physics and Theoretical Chemistry Egerlandstr. 3 D-8520 Erlangen Federal Republic of Germany

Principal persons contacted at conference (continued):

Elaine Armstrong
Chemistry Department
University of Manchester
Oxford Road
M13 9PL Manchester
United Kingdom

09/05-09/10-88 XIIIth International Conference on Organometallic Chemistry, Turin, Italy

Principal persons contacted at conference:

Craig Forsyth
Department of Chemistry
Monash University
Clayton, Victoria 3168
Australia

Tobin Marks
Department of Chemistry
Northwestern University
Evanston, Illinois 60201
USA

Diane Burns
Dept. of I.P.I. Chem.
University of Liverpool
P.O. Box 147
Liverpool L69 3BX
United Kingdom

Giovanni DePaoli
Dip. Chim. Inorg. Metall.- Univ. of Padova
Via Loredan 4
35131 Padova
Italy

Nikos Psaroudakis
Dept. of Chemistry - Univ. of Athens
Frantzi 10
114 73 Athens
Greece

Thomas Rauchfuss
School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801
USA

ABSTRACT:

The traveler attended the XXVI International Conference on Coordination Chemistry and presented some work entitled "An Investigation of the Perchlorate Complexation of Europium(III) in Benzonitrile and Dimethylsulphoxide Using an Ion Exchange Technique." Papers of particular interest concerned electrochemistry in nonaqueous solvents (in particular, using electrodes of submicron dimensions that could be applicable to the later actinides); Raman spectroscopy as applied to coordination chemistry, and solution chemistry in nonaqueous solvents with emphasis on identifying the species in solution. The traveler also attended the XIII International Conference on Organometallic Chemistry in Turin, Italy and presented work entitled "Synthesis and Characterization of Some Divalent and Trivalent Samarium Organometallic Complexes." Papers of particular interest were given in a complete session on organometallic chemistry of the f-elements. Other papers useful to our work concerned d-transition metals where phosphine, arsine, and stibine ligands were used (in order to compare and contrast the behavior with the work we have done on this type of ligand with europium) and phosphide and sulphur bridged type species applicable to both d-transition and f-transition metals.

SUMMARY OF ACTIVITIES:

Alan Bond

Alan Bond is a Professor at the University of Deakin in Australia. His major interest lies in electrochemistry, in particular, using electrodes of submicron dimensions. With a normal electrode, because of its shape and size, the primary process is planar diffusion. However, if in theory you have an electrode which is one atom, the primary process is radial diffusion because in effect you have a point source. Bond has taken this theory and attempted to put it into practice with submicron electrodes. He has stated that he can get 99% radial diffusion using such electrodes with properties that vary dramatically from say a Pt electrode on the bulk scale. Such changes in properties include:

1. A steady state response can be achieved in milliseconds.
2. A supporting electrolyte is unnecessary when working in certain solvents (e.g., hexane).
3. Microelectrodes can be used to look at virtually any compound since it has been found that the working range can be from up to -4.5V to +4.5V before the solvent is destroyed.

4. The technique can be used with extremely small amounts of material. Bond stated that he could do such measurements on the atomic level, the limiting factor being a statistical one rather than a matter of measuring such small currents.

Such a technique would therefore be ideal for an actinide program which deals with small scale syntheses, not just up to einsteinium, but fermium and beyond.

Alan Bond has promised to send some of his publications relating to this work. A future collaboration may also be a good idea.

Sigeo Kida

Sigeo Kida is from Kyushu University in Japan. Currently he is studying copper complexes which bind O_2 at low temperatures (-80 to -90°C). Since one of the areas I have been involved with is oxidation of cerium(III) species due to oxygen bubbling, this paper was of great interest. Kida has shown that by using resonance Raman he can assign certain peaks to the oxygen complex which are shifted when $^{18}O_2$ is used. This complex also showed a distinct band in the electronic spectrum at 472 nm which disappeared on Ar bubbling but reappeared when O_2 was used again. Although nothing has so far been published on this work, Kida has said he will send me a copy of his paper when it does go into print.

Janos Mink

Janos Mink is from the Hungarian Academy of Science in Budapest. Primarily he is involved with FT-IR and Raman studies as an aid to understanding coordination in solution. One of the topics under discussion in the paper that he gave was perchlorate vs chloride complexation of Fe(II) in aqueous solution. He stated that from far infrared data perchlorate was removed completely from coordination with the iron, although one and possibly two chlorides were still coordinated. Once again this was of primary interest because we have done some tentative studies on perchlorate vs chloride complexation for europium in aqueous solution. Mink also has done similar studies on uranyl and has said he will send that paper and also the complete data for the iron to me.

Franz Dickert

Franz Dickert is from the Institute of Physics and Theoretical Chemistry in the Federal Republic of Germany. Currently he is investigating M(II)-crown-ether (M=Ni,Co,Fe) complexes in nonaqueous solvents, using a 2 dimensional NMR technique. At temperatures above 60°C line broadening occurs which according to Dickert indicates a ligand exchange between free and coordinated macrocycles. Since crown ether and macrocycle complexes in general are well known for both lanthanides and actinides, this is another technique which would be ideal for f-element complexation studies in nonaqueous media.

Elaine Armstrong

Elaine Armstrong is a graduate student from the University of Manchester and at the moment is working on sulphur complexes of d-transition metals. Sulphur is known to coordinate to f-elements and along with phosphorus is a possible bridging group in hetero-bimetallic species between f and d elements. This is an area of great interest to me because of its possible applications in metal-metal bonded systems of the f-elements.

Elaine currently works for Dave Garner who is a leader in this particular field and someone I have known for a number of years. Professor Garner is an ideal contact for up-to-date information in this area of chemistry.

> After the XXVIth International Conference on Coordination Chemistry the traveler went to Turin, Italy to participate in the XIIIth International Conference on Organometallic Chemistry.

Craig Forsyth

Craig Forsyth is from Monash University in Victoria, Australia and like myself is presently carrying out studies on trivalent and divalent lanthanides, principally samarium. His "one pot" syntheses of divalent samarium complexes could be very applicable to the studies I hope to carry out on californium and americium. Forsyth also informed me that co-workers at Monash are presently engaged in some electrochemical studies and have tentatively identified Nd(II) in nonaqueous media. They are also collaborating with Alan Bond (see earlier) using submicron electrodes for similar types of studies.

Tobin Marks

Tobin Marks, a professor at Northwestern, works on uranium and thorium organometallic chemistry. He gave a plenary lecture in Turin on f-element reactivity, thermochemistry, and catalysis. Marks was interested in the work I am doing; and, using the theories he had talked about in his lecture, we discussed which of the organic ligands I am using could possibly give the best results in terms of stabilizing lower oxidation states of lanthanides and actinides.

Diane Burns

Diane Burns is from the University of Liverpool and is presently engaged in studies of phosphine complexes of d-transition metals (in this paper, iridium only). Because she is principally looking at electronic and steric effects of phosphine ligands, we discussed at great length what the effects of changing from a phosphine to an arsine or a stibine ligand would be. In general donor properties are thought to increase in the order P > As > Sb for d-elements; however, we have found the reverse for lanthanides. Burns was of the opinion that it would depend on the system being discussed because in some cases small changes in steric crowding can dramatically alter the structure of the complex and hence change the electronic effects and also vice versa. Because of this it is difficult to draw any hard conclusions about such a substitution.

Giovanni DePaoli

Giovanni DePaoli is from the University of Padova in Italy and like Diane Burns is looking at the influence electronic and steric effects have on structure. DePaoli is principally looking at one particular type of complex (i.e., $CpLnCl_2(THF)_3$) and how conformational changes may vary across the lanthanide period. He was interested in the work I was presenting because he wondered if changing the ligand from pentaphenylcyclopentadiene to cyclopentadiene, pentamethylcyclopentadiene or indene would change the conformation of the complexes so obtained. Unfortunately, as of yet I do not have any solid state data but I said I would send him the information if and when it becomes available.

Nikos Psaroudakis

Nikos Psaroudakis is from the University of Athens, Greece. Although primarily concerned with d-transition metals, he does some f-element chemistry. He was very interested in the work I was presenting. We talked at great length about the possible products and reaction mechanisms which are involved in the systems I am looking at and I found his insights especially helpful.

Thomas Rauchfuss

Thomas Rauchfuss is from the University of Illinois and is a leading expert in organometallic chemistry involving sulphur ligands. I have been in contact with Rauchfuss on previous occasions and his interesting approaches and insights into sulphur chemistry (multiple bonded systems, bridging, ligands, and cluster complexes) could be of great help in the future in possible metal-metal bond studies.

SUMMARY

The trip to Europe to attend the XXVIth International Conference on Coordination Chemistry in Porto, Portugal and the XIIIth International Conference on Organometallic Chemistry in Turin, Italy was extremely beneficial. It provided many opportunities to talk with people who have a similar research interest to myself but also the topics were broad enough to give me an insight into related fields. The trip also gave me a chance to make a number of contacts as well as maintain a number of not so new ones. Such contacts may lead to collaboration with scientists from some of the institutions mentioned in this report.

APPENDIX:

Itinerary

08/27-28/88	Travel to Portugal from U.S.
08/28-09/02/88	XXVIth International Conference on Coordination Chemistry (26th ICCC), Porto, Portugal
09/03/88	Travel to Italy
09/04-09/88	XIIth International Conference on Organometallic Chemistry (13th ICOC), Turin, Italy
09/10/88	Travel to U.S.

Persons With Whom Discussions Were Held

<u>26th ICCC</u>

Martin Anteberg	HOECHST AG Frankfurt, FRG
Elaine Armstrong	University of Manchester, Manchester, UK
Geoffrey Pilcher	
Nigel Powell	
David Benlian	Lab. Chimie de Coordination, Marseille, France
Alan Bond	University of Deakin, Victoria, Australia
John Cotton	University of Queensland, Queensland, Australia
Franz Dickert	Institute of Physics and Theoretical Chemistry, Erlangen, FRG
Julian Koe	University of Exeter, Exeter, UK
Nick Long	
Sigeo Kida	Kyushu University, Hakozaki, Japan
Janos Mink	Institute of the Isotopes, Budapest, Hungary

<u>13th ICOC</u>

Edward Abel	University of Exeter, Exeter, UK
Diane Burns	University of Liverpool, Liverpool, UK
Ann Dolby	
Stuart Kernaghan	
Suzanne Mulley	

Giovanni DePaoli	University of Padova, Padova, Italy
Craig Forsyth	Monash University, Victoria, Australia
Jurgen Graefe	Schering AG Bergkamen, FRG
Steven Howdle Richard Bates	University of Nottingham, Nottingham, UK
Brian Mann	University of Sheffield, Sheffield, UK
Tobin Marks	Northwestern University, Evanston, Illinois,USA
Nikos Psaroudakis	University of Athens, Greece
Thomas Rauchfuss	University of Illinois, Urbana, Illinois, USA

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