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U.S.-Russia Cooperative Research: Designing Gold(I) Complexes for New Materials

Alice E. Bruce
Principal Investigator; University of Maine, Orono, abruce@maine.edu

Mitchell Bruce
Co-Principal Investigator; University of Maine, Orono, mbruce@maine.edu

Dmitri Lemenosvsii
Co-Principal Investigator; Moscow State University

Victor Dyadchenko,
Co-Principal Investigator; Moscow State University

Final Report for Period: 07/1998 - 01/2004 **Submitted on:** 02/16/2005

Principal Investigator: Bruce, Alice E. **Award ID:** 9810077

Organization: University of Maine

Title:

US-Russia Cooperative Research: Designing Gold(I) Complexes for New Materials

Project Participants

Senior Personnel

Name: Bruce, Alice

Worked for more than 160 Hours: Yes

Contribution to Project:

Name: Bruce, Mitchell

Worked for more than 160 Hours: Yes

Contribution to Project:

Mitchell Bruce, who is a co-PI for the project, is a faculty member in the Chemistry Dept. at the University of Maine. He is involved in the discussions of research progress and will be a co-author on any publications that are written. He did not receive a stipend from this grant.

Name: Lemenovskii, Dmitri

Worked for more than 160 Hours: Yes

Contribution to Project:

Dmitri Lemenosvsii is the co-PI at Moscow State University in Russia. He directs the personnnel who are working on this project at MSU.

Name: Dyadchenko, Victor

Worked for more than 160 Hours: Yes

Contribution to Project:

Victor Dyadchenko is a professor of chemistry at Moscow State University who also helps to direct students who are involved in the project at MSU. During the first year of the project, Victor traveled to the University of Maine twice, once for 6 weeks and then for 2.5 months. He has synthesized a number of new complexes containing gold and has helped to teach Scott Larkin several synthetic methods.

Post-doc

Graduate Student

Name: Larkin, Scott

Worked for more than 160 Hours: Yes

Contribution to Project:

Scott Larkin is a first year graduate student in our research lab. He began working on the project in February, 1999. He has made a number of new complexes containing gold, including several ligands which were not commercially available.

Name: Aksenov, Kirill

Worked for more than 160 Hours: Yes

Contribution to Project:

Kirill Aksenov is a graduate student at Moscow State University. He spent 2 months at the University of Maine this summer working on the project. He continues to work on it at MSU. Kirill has also made a number of new complexes containing gold.

Name: Makarov, Mikhail

Worked for more than 160 Hours: Yes

Contribution to Project:

Undergraduate Student

Technician, Programmer

Other Participant

Research Experience for Undergraduates

Organizational Partners

Moscow State University

Other Collaborators or Contacts

Professor Mohamad Omary at the University of North Texas
Professor Eric Scharrer at the University of Puget Sound

Activities and Findings

Research and Education Activities: (See PDF version submitted by PI at the end of the report)

Findings:

see file attached in step 1 - activities

Training and Development:

During the grant period, three chemists from Moscow State University made extended visits to UMaine, including a professor and two of his graduate students. One of the graduate students, M. Makarov, also attended two four-week sessions at the Intensive English Institute at the University of Maine in order to improve his English and his understanding of American culture. A Ph.D. student at UMaine who has worked on this project is nearing completion of his degree. Several undergraduates have been involved in various aspects of the synthesis and optical testing.

Outreach Activities:

The optical testing instrument and photos of liquid crystalline textures have been featured in a number of tours of our lab by middle school girls (during the annual Expanding Your Horizons program), prospective undergraduate students, their parents, State Legislatures, and administrators at the University of Maine System (including the Chancellor).

I have also made several presentations about growing cyrstals and using micrsoscopes to children at the local elementary school.

Journal Publications

Books or Other One-time Publications

Web/Internet Site

URL(s):

Description:

Other Specific Products

Contributions

Contributions within Discipline:

We have developed a method for preparation of thiol complexes of gold in high yield involving direct auration under phase transfer conditions.

Contributions to Other Disciplines:

Contributions to Human Resource Development:

This project has provided opportunities for students and faculty at the Univeristy of Maine and Moscow State University to further their research experience. The exchange aspect of the project has so far provided Moscow State University faculty and students direct exposure to an American university and has allowed them to experience living and working in Maine. Faculty and students in the Chemistry Dept. at the University of Maine have gained in understanding of Russian science and culture by interacting with visiting scientists from Moscow State University.

Contributions to Resources for Research and Education:

Contributions Beyond Science and Engineering:

Categories for which nothing is reported:

Any Journal

Any Book

Any Product

Contributions: To Any Other Disciplines

Contributions: To Any Resources for Research and Education

Contributions: To Any Beyond Science and Engineering

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Final Report for NSF CHE-9810077
P.I.: Alice E. Bruce
January 31, 2005

A. Activities – research and education

There were two principle objectives of the grant: (1) the synthesis and structural investigation of new types of organogold compounds based on calamitic (rod-shaped) molecules, and (2) physical investigation of their liquid crystalline properties. As the project developed, the objectives were broadened to include the synthesis of dinuclear gold(I) complexes and calamitic ferrocenomesogens. The project was carried out through a cooperative research program involving chemists and physicists at the University of Maine and Moscow State University.

During the grant period, three chemists from Moscow State University made extended visits to UMaine, including a professor and two of his graduate students. A Ph.D. student at UMaine who has worked on this project is nearing completion of his degree. Several undergraduates have been involved in various aspects of the synthesis and optical testing. Two presentations and two publications have appeared; one manuscript has been submitted and two more are in preparation. Significant project delays occurred as a result of difficulties encountered by Russian scientists in obtaining visas as well as major renovations in the Chemistry Dept. at UMaine. Several no-cost extensions were requested and granted.

Optical testing of materials was initially carried out in Professor James McClymer's lab in the Physics Department at UMaine. Purchase of a Nikon Polarizing microscope with an attached digital camera was made possible as part of an NSF-MRI grant (#0115832). This microscope, together with a home built hotstage has put us in a good position to conduct the optical testing in our own lab. As a result we are now involved in two additional collaborations with Professor Eric Scharrer at the University of Puget Sound and Professor Mohammad Omary at the University of North Texas. Several presentations have resulted from these collaborations and two manuscripts are being written up. Overall, given the limited funds available for this collaboration, the results to date have been excellent.

B. Project Summaries

Three types of complexes were prepared during the course of this project: (1) phosphine gold(I) complexes incorporating promesogen organic ligands, (2) ferrocenyl complexes containing promesogen molecules attached to one Cp ring and (3) dinuclear phosphine gold(I) complexes containing biphenyl. Progress in these areas is described below.

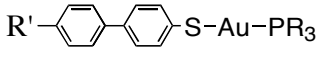


Figure 1. Target organogold compounds; R' = H, OC_nH_{2n+1} (n = 1. 8, 12, 14); R = CH_3, C_6H_5.

(1) We are in the process of completing the testing of the phosphine gold(I) complexes shown above for liquid crystalline behavior. The free thiol ligands are also being tested. For optical testing, we are employing a Nikon polarizing microscope with an attached digital camera and a home-built hotstage. Our results to date indicate that several of the gold-thiolate complexes with n > 1 show interesting mesogenic behavior upon melting, but they also show irreversible decomposition after formation of the isotropic phase (Figure 2). A crystal structure of the trimethylphosphine gold(I) complex with n = 8 has been obtained showing three different types of intermolecular interactions: between gold atoms, between long chain aliphatic regions and between aromatic rings.

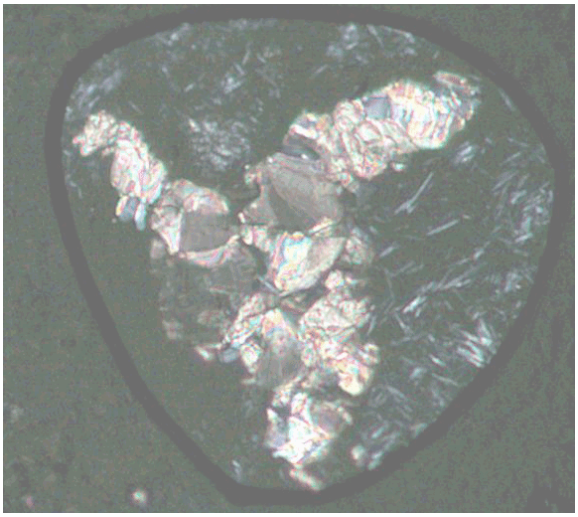


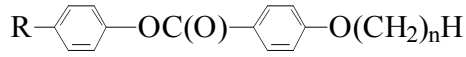
Figure 2. Polarized optical microscopy of compressible phase of Ph_3PAuSR ($R = (C_6H_4)_2OC_{14}H_{29}$) at 90°C.

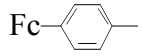
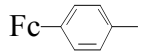
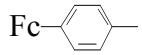
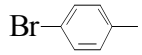
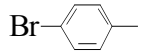
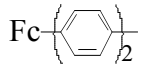
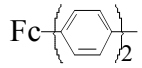
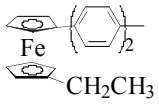
We are continuing to study these complexes to confirm preliminary results as well as to continue the effort to design complexes with lower melting points. One problem that is hampering progress is the presence of small amounts of an impurity (1-2%) in some samples that makes it difficult to reproduce optical textures and identify mesophases. Alternative synthetic routes for the complexes are being employed to help identify the specific nature of this problem. The Ph.D. student at the University of Maine who has worked on this project is in the process of completing his experimental work and writing his thesis. One publication has appeared from his thesis project and two other manuscripts are in preparation.

(2) We have also synthesized 4′-ferrocenyl-1,1′-biphenyl-4-yl 4-alkoxybenzoates $Fc\text{-}(C_6H_4)_2\text{-}OC(O)\text{-}C_6H_4\text{-}O\text{-}C_nH_{2n+1}$ (n = 8, 10, 12) (**4a-c**) representing a new class of ferrocene-containing thermotropic mesogens (Table 1). Two synthetic approaches were used: reaction of 4′-ferrocenyl-1,1′-biphenyl-4-ol (**3**) with 4-alkoxybenzoylchlorides and cross-coupling of *tris*(4-ferrocenylphenyl)-boroxine (**5**) with the corresponding halobenzene. Cross-coupling was also applied for the synthesis of terphenyl-containing mesogens $Fc\text{-}(C_6H_4)_3\text{-}OC(O)\text{-}C_6H_4\text{-}O\text{-}C_nH_{2n+1}$ (n = 10, 12) (**7a,b**) and $(C_2H_5C_5H_4)Fe[C_5H_4\text{-}(C_6H_4)_3\text{-}OC(O)\text{-}C_6H_4\text{-}O\text{-}C_{10}H_{21}]$ (**12**). The latter compounds also form nematic phases.

The mesophases formed by the mesogens **7a,b** exist in broader thermal intervals than mesophases of their biphenyl-containing counterparts **4b,c**. The most pronounced mesomorphism was displayed by compound **12**: its nematic phase exits between 141 and 253 °C.

Table 1. Thermal properties[a] of compounds **4a-c**, **6a-c**, **7a,b** and **12** with general formula



Compound	R	n	Phase transition and its temperature/°C	Interval of mesophase existence ΔT/°C	Enthalpy of transition ΔH/kJ·mol^{-1}
4a		8	K 156 N[b] N 163 I[b]	7	46.7 2.1
4b		10	K 148 N N 155 I	7	
4		12	K 133 N N 148 I	15	
6a	I	12	K 85 I I (84 S_A)[c,d] K	–	–
6b		10	S_A[e] 205 I	–	–
6c		12	S_A[e] 201 I	–	–
7a		10	K 204 N N 270 I	66	
7b		12	K 202 N N 262 I	60	
12		10	K 141 N N 253 I	112	

[a] All phase transition temperatures were determined by polarized optical microscopy.
[b] Transition temperatures were established by DSC and agreed with those, found in optical investigations.
[c] Monotropic transition.
[d] This compound was prepared previously[8].
[e] Mesophase exists up to room temperature.

(3) During the course of this project we also synthesized gold complexes containing a biphenyl ligand with two thiolate groups. As is typical for gold (I), this ligand forms complexes with two gold(I) phosphine moieties rather than acting as a chelating ligand. The dinuclear gold(I) complexes shown in Figures 3 and 4 were prepared by reaction of $ClAuPR_3$ (R = Ph, Me) and 1,1'-biphenyl-2,2'-dithiol in thf/CH_3OH under phase transfer conditions (Me_3BzNCl/K_2CO_3). In the PPh_3 complex, the Au-Au distance (3.9064 Å) is longer than the sum of the van der Waals radii for Au (3.4 Å) however the Au atoms appear to be drawn together, leading to a significant bending of the P-Au-S angles (170°). When the less bulky phosphine, PMe_3, is used the gold(I) complex crystallizes as a dimer of dinuclear units in which there are inter and intramolecular Au-Au interactions.

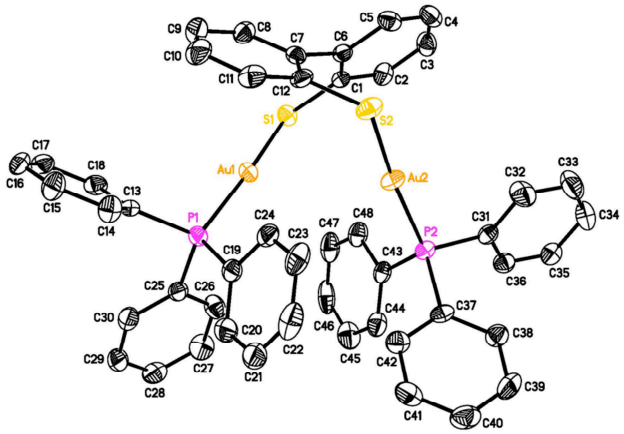


Figure 3. A view of the molecular structure of [1,1'-biphenyl]-2,2'-dithiolate bis(triphenylphosphine) gold(*I*). Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity. [Au1---Au2 = 3.9064 (3) Å, P-Au-S = 170.24 (5) and 169.52 (5)°] (*Acta Crystallographica*, *Section C: Crystal Structure Communications*, **2004**, *C60(9)*, m440-m44.)

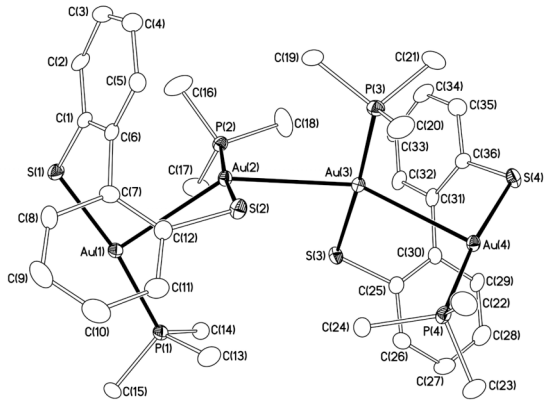


Figure 4. A view of the molecular structure of [1,1'-biphenyl]-2,2'-dithiolate bis(trimethylphosphine) gold(*I*). Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity. [Au1---Au2 = 3.1164 (6) Å, Au2---Au3 = 3.1196 (8) Å, Au3---Au4 = 3.0075 (7) Å.]

C. Publications

1. "μ-Biphenyl-2,2'-dithiolato- k2S:S'-bis[(triphenylphosphine- kP)gold(I)]." Larkin, Scott A.; Krause Bauer, Jeanette A.; Konoplev, V. E.; Dyadchenko, Victor P.; Lemenovskii, Dmitrii A.; Bruce, Mitchell R. M.; Bruce, Alice E. *Acta Crystallographica* , *Section C: Crystal Structure Communications*, **2004** ,*C60(9)*, m440-m44.
2. "Synthesis and Crystal Structure of Ferrocenyl Derivatives of Biphenyl." Lemenovskii, D. A.; Makarov, M. V.; Dyadchenko, V. P.; Bruce, A. E.; Bruce, M. R. M.; Larkin, S.; Averkiev, B. B.; Starikova, Z. A.; Antipin, M. Yu.; *Russian Chemical Bulletin*, **2003**, *52(3)* , 607-615.
3. "Liquid Crystals Based on Ferrocenylbiphenyl and Ferrocenylterphenyl." Makarov, M. V.; Lemenovskii, D. A.; Bruce, A. E.; Bruce, M. R. M.; Dyadchenko, V. P.; *Liquid Crystals*, submitted.