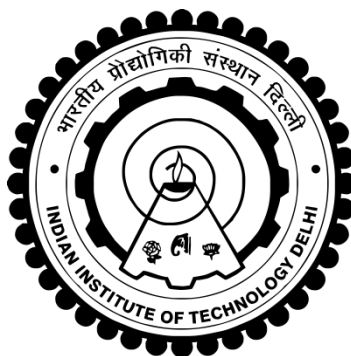


**COINAGE METAL(I) HALIDE COMPLEXES
STABILIZED THROUGH GERMYLENES AND
GERMANECHALCOGENONES**

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**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
AUGUST 2016**

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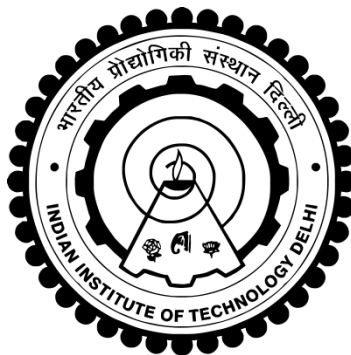
Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of

Doctor of Philosophy

to the



Indian Institute of Technology Delhi

August 2016

Dedicated to My Parents

Certificate

This is to certify that the thesis entitled “**Coinage Metal(I) Halide Complexes Stabilized through Germylenes and Germanechalcogenones**” being submitted by **Mr. Dhirendra Yadav** (Entry No.: 2009CYZ8173) to **Indian Institute of Technology Delhi**, for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by him. **Mr. Dhirendra Yadav** has worked under my supervision and has fulfilled all the requirements for the submission of his PhD thesis, which to my knowledge has reached the requisite standard and is worthy of consideration for the award of PhD degree.

The work embodied in this thesis has not been submitted, in part or full, to other University or Institute for the award of any degree or diploma.

Date: 24-08-2016

Place: New Delhi

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Abstract

The thesis entitled “*Coinage Metal(I) Halide Complexes Stabilized through Germylenes and Germane chalcogenones*” presents the details about the study of various aminotroponimate (ATI) ligand stabilized Ge(II) and Ge(IV) compounds as ligands for the group 11 metal(I) halides. The thesis is divided into the six chapters. A brief description about each chapter is given below:

Chapter 1: This chapter gives a brief overview about metallylenes, their isolation, and reactivity. Under the reactivity, the use of metallylenes as ligands for the stabilization of metal complexes is focussed. Subsequently, the aim of the thesis is mentioned.

Chapter 2: In this chapter, methods of drying solvents used in synthesis and NMR spectroscopic studies are mentioned. Commercial sources and synthetic methodology for various starting materials are provided. Details regarding the synthetic techniques, apparatus, instruments used for analyses, crystallographic software, structure visualization software, chemical structure drawing program, and theoretical studies are also discussed.

Chapter 3: The use of aminotroponimato(chloro)germylene [(*i*-Bu)₂ATIGeCl] (**3a**) (ATI = aminotroponimate) as a ligand to stabilize copper(I) iodide complexes is presented. The reaction of compound **3a** with CuI in acetonitrile, afforded an aminotroponimato(chloro)germylene stabilized copper(I) iodide complex [{(*i*-Bu)₂ATIGeCl}₂(Cu₄I₄)(CH₃CN)₂] (**3b**) with a tetrameric distorted cubane type Cu₄I₄ core. The reaction of compound **3a** in dichloromethane with CuI in the presence of two equivalents of pyridine resulted in the first germylene stabilized copper(I) iodide complex [{(*i*-Bu)₂ATIGeCl}(CuI)(C₅H₅N)₂] (**3c**) with a monomeric CuI core. A reaction of compound **3a** with equimolar amounts of CuI and pyridine in

$\text{Bu})_2\text{ATiGe}\}_2\text{O})_2(\text{Cu}_3\text{I}_3)]$ (**5c**) with a Cu_3I_3 core, and $[\{(i\text{-Bu})_2\text{ATiGe}\}_2\text{O}(\text{Cu}_2\text{I}_2)(\text{C}_5\text{H}_5\text{N})_2]$ (**5d**) with a butterfly type Cu_2I_2 core. The reactions of compound **5a** with AgI and AuI produced $[\{(i\text{-Bu})_2\text{ATiGe}\}_2\text{O})_2(\text{Ag}_4\text{I}_4)]$ (**5e**) with a Ag_4I_4 octahedral core and $[\{(i\text{-Bu})_2\text{ATiGe}\}_2\text{O}(\text{Au}_2\text{I}_2)]$ (**5f**) with a Au_2I_2 core, respectively. The presence of metallophilic interactions in these compounds is shown through the single crystal X-ray diffraction and Atoms in Molecules (AIM) studies.

Chapter 6: The potential of germane chalcogenones $[\text{ATi}(\text{Ge}=\text{E})(\text{Ph})]$ ($\text{E} = \text{S}$ **6a**, Se **6b**) to function as ligands has been demonstrated through the isolation of their coinage metal(I) iodide complexes $[\{(t\text{-Bu})_2\text{ATiGe}(\text{E})\text{Ph}\}_2(\text{M}_2\text{I}_2)]$ ($\text{E} = \text{S}$, $\text{M} = \text{Cu}$ **6c**; $\text{E} = \text{Se}$, $\text{M} = \text{Cu}$ **6d**; $\text{E} = \text{S}$, $\text{M} = \text{Ag}$ **6e**; $\text{E} = \text{Se}$, $\text{M} = \text{Ag}$ **6f**; $\text{E} = \text{Se}$, $\text{M} = \text{Au}$ **6g**). Crystallographic studies reveal the presence of cuprophilic (**6c**, **6d**), argentophilic (**6f**) interactions in these complexes. Crystallographic data reveals the presence of a strong argentophilic interaction (2.950(1) Å) in complex **6f**, but is inconclusive in complex **6e** (3.470(1) Å). Using theoretical studies, proof for the presence and absence of argentophilic interactions in complexes **6f** and **6e** was obtained, respectively. Further, it is disclosed that the donor ability of the chalcogen atoms in the $\text{Ge}=\text{E} \rightarrow \text{Ag}-\text{I}$ moieties dictate the $\text{Ag} \cdots \text{Ag}$ interaction in the complexes **6e-f**.

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List of Symbols and Abbreviations

ATI	aminotroponimate	K	kelvin
%	percentage	Kcal	kilocalorie
°	degree	LUMO	lowest unoccupied molecular orbital
°C	degree centigrade	<i>m/z</i>	mass-to-charge ratio
Å	angstrom	Me	methyl
AIM	atoms in molecules	mg	milligram
Anal	analysis	MHz	megahertz
au	atomic unit	min.	minute
bcp	bond critical point	mL	milliliter
bs	broad singlet	mmol	mill mole
Calcd	calculated	MO	molecular orbital
cm	centimeter	Mp	melting point
Cp*	pentamethylcyclopentadienyl	NBO	natural bond orbital
Cp	cyclopentadienyl	NHC	<i>N</i> -heterocyclic carbene
DCM	dichloromethane	nm	nanometer
dd	double doublet	NMR	nuclear magnetic resonance
deg	degree	NPA	natural population analysis
DFT	density functional theory	<i>J</i>	coupling constant
Et	ethyl	NHGe	<i>N</i> -heterocyclic germylene
Me	methyl	g	gram
Ph	phenyl	Ph	phenyl
<i>n</i> -Pr	<i>normal</i> -propyl	ppm	parts per million
h	hour	Py	pyridyl
HOMO	highest occupied molecular orbital	Pz	pyrazolyl
Hz	Hertz	rcp	ring critical point
<i>i</i> -Bu	<i>iso</i> -butyl	rt	room temperature
<i>i</i> -Pr	<i>iso</i> -propyl	<i>t</i> -Bu	<i>tertiary</i> -butyl

THF	tetrahydrofuran	WBI	Wiberg bond index
TLC	thin layer chromatography	δ	(delta) chemical shift
NRT	natural resonance theory	ΔG	change in free energy
OTf	triflate	ΔH	change in enthalpy
TMS	trimethylsilyl	λ	(lambda) wavelength