Towards Selective Small Cation Chelation

A thesis presented
in partial fulfilment of the requirements
for the degree of
Doctor of Philosophy in Chemistry
at Massey University, Palmerston North

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2010

Acknowledgements

First and foremost I would like to thank my supervisor Paul Plieger who was always friendly and supportive throughout my study. He encouraged me to put my own twist on the thesis and this has fostered the development of my independent research and problem-solving abilities.

I would like to thank Anthony Burrell and Mark McCleskey for hosting me when I visited the Los Alamos National Laboratory to conduct the beryllium coordination chemistry aspects of this thesis. Whilst there, Himashinie Diyabalanage provided much insight regarding the particular aspects of conducting this challenging field of chemistry.

Ross Davidson deserves a special mention for providing a wealth of knowledge on the inorganic chemistry and computational aspects of this thesis. Marco Wenzel must be thanked for taking time away from his own research to run most of my crystals on the diffractometer.

I would also like to acknowledge the New Zealand Government for providing financial support in the form of a Top Achiever Doctoral Scholarship.

Finally, I wish to thank my parents for supporting my efforts to pursue a PhD.

Abstract

This thesis sought to identify ligands which could be used in sensing or sequestering applications for the toxic element beryllium. The overall aim was to search for ligands with tight binding cavities and those capable of fully encapsulating the small Be(II) cation. Please refer to the foldout at the end of this book for ligand descriptions.

Proton sponge ligands **L1** – **L13** were synthesised and evaluated for their use as simple bidentate small cation chelators. An efficient modified route to **L1** was developed. The derivatisation and properties of these unexplored ligands were investigated. X-ray crystallography gave insight into the structures of these unique molecules. Ligands of type **L1** had an ideal size-fit for the small cation B(III), used as a structural analogue for Be(II), as indicated by the crystal structure of the boron complex. Due to their high basicity they were unsuitable for coordination to Be(II) in aqueous systems due to competition for protonation. The larger Cu(II) cation was a poor fit for these ligands and a rare crystal structure showed large distortions of the metal ion from the ligand plane. The Cu(II) complexes were unstable and hydrolysed readily.

A fundamentally new type of tetra-coordinate ligand, **L14**, was synthesised and while untested in this thesis offers promise as an ideal Be(II) chelator.

The ligands **L15** – **L21** were evaluated for use as fully encapsulating Be(II) chelators and those containing three oxygen donors were found to be most suitable. The rigidity imparted by the locking of certain conformations of the ligands **L18** and **L19** upon Be(II) coordination gave rise to fluorescence. The ligands containing carboxylic acid groups (**L17** and **L18**) enabled good water solubility and **L18** in particular showed the most promise as a ligand for beryllium sensing or sequestering applications.

Contents

List of Abbreviations

Acac	Acetylacetonate
BODIPY	Boron dipyrromethene
-^{n}Bu	Normal butyl group
-^{t}Bu	Tertiary butyl group
CBD	Chronic beryllium disease
CCSD	Cambridge crystal structure database
Cg	Centroid
COSY	Correlation spectroscopy
DFT	Density functional theory
DMAD	Dimethylacetylene dicarboxylate
DMAE	Dimethyaminoethanol
DMAN	1,8-Bis(dimethylamino)naphthalene
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
Dppe	1,2-Bis(diphenylphosphino)ethane
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
ESR	Electron spin resonance
-Et	Ethyl group
GIAO	Gauge including atomic orbital
HEPA	High efficiency particulate air
Hfac	Hexafluoroacetylacetonate
HMQC	Heteronuclear multiple quantum coherence
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
-Me	Methyl group
MS	Mass spectroscopy
NBS	N-Bromosuccinimide
NMR	Nuclear magnetic resonance

-OAc	Acetoxy group
-Ph	Phenyl group
RT	Room temperature
SERS	Surface enhanced Raman spectroscopy
TLC	Thin layer chromatography
TMS	Tetramethylsilane
TOF	Time of flight
UV-Vis	Ultraviolet-Visible spectroscopy

List of Figures, Tables and Reaction Schemes