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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

Karl Jürgen Shaffer

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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.
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<tbody>
<tr>
<td>Acac</td>
<td>Acetylacetonate</td>
</tr>
<tr>
<td>BODIPY</td>
<td>Boron dipyrromethene</td>
</tr>
<tr>
<td>&quot;Bu</td>
<td>Normal butyl group</td>
</tr>
<tr>
<td>&quot;Bu</td>
<td>Tertiary butyl group</td>
</tr>
<tr>
<td>CBD</td>
<td>Chronic beryllium disease</td>
</tr>
<tr>
<td>CCSD</td>
<td>Cambridge crystal structure database</td>
</tr>
<tr>
<td>Cg</td>
<td>Centroid</td>
</tr>
<tr>
<td>COSY</td>
<td>Correlation spectroscopy</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DMAD</td>
<td>Dimethylacetylene dicarboxylate</td>
</tr>
<tr>
<td>DMAE</td>
<td>Dimethyaminoethanol</td>
</tr>
<tr>
<td>DMAN</td>
<td>1,8-Bis(dimethylamino)naphthalene</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>Dppe</td>
<td>1,2-Bis(diphenylphosphino)ethane</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron spin resonance</td>
</tr>
<tr>
<td>-Et</td>
<td>Ethyl group</td>
</tr>
<tr>
<td>GIAO</td>
<td>Gauge including atomic orbital</td>
</tr>
<tr>
<td>HEPA</td>
<td>High efficiency particulate air</td>
</tr>
<tr>
<td>Hfac</td>
<td>Hexafluoroacetylacetonate</td>
</tr>
<tr>
<td>HMQC</td>
<td>Heteronuclear multiple quantum coherence</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>-Me</td>
<td>Methyl group</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectroscopy</td>
</tr>
<tr>
<td>NBS</td>
<td>N-Bromosuccinimide</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>-OAc</td>
<td>Acetoxy group</td>
</tr>
<tr>
<td>-Ph</td>
<td>Phenyl group</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>SERS</td>
<td>Surface enhanced Raman spectroscopy</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin layer chromatography</td>
</tr>
<tr>
<td>TMS</td>
<td>Tetramethysilane</td>
</tr>
<tr>
<td>TOF</td>
<td>Time of flight</td>
</tr>
<tr>
<td>UV-Vis</td>
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