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**Synthesis and Characterisation of Pyrazine-
Based Ligands for the Analysis of Metal-Metal
Communication**

A thesis presented in partial fulfilment of the requirements for the degree of

Master of Science

in

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Pyrazine Pirate. Out.

Abstract

Pyrazine is an attractive molecule that has been incorporated as a bridging ligand between two metal centres. These complexes have been shown to exhibit both magnetic and electrochemical exchange between the metal centres through the pyrazine unit. Addition of functionality onto the 2 and 5 position of pyrazine can reinforce the coordination of $3d$ octahedral metal ions to the pyrazine ring.

The Schiff base condensation of **A1** with various primary amine reactants produced three unique ligand systems. The confirmed synthesis of these ligands was verified with a variety of characterisation techniques. A single crystal structure was generated for one ligand system (**L3**), which revealed both imine – π stacking interactions, as well as alkane hydrogen – pyridine interactions.

Several complexations were attempted with the three ligand systems synthesised. Manganese and cobalt complexes were successfully synthesised with **L3**, the single crystal structures generated showed cyclohelicate triangles, which were unique at the time. The electrochemical analysis of these complexes in MeCN showed similar redox processes as was seen in the electrochemical analysis of **L3**. Signs of possible metal-metal communication within the cyclohelicate triangles was also noticed, with oxidation (and reduction) processes present. Further analysis is necessary to verify these interpretations, including magnetic analysis. Complexations with identical metal salts and **L2** could not be characterised by SCXRD. Other techniques such as mass spectrometry and conductivity measurements indicated the likely formation of a polymorphic – potentially cyclohelical structure with this ligand. Complexations with **L1** incorporated the inclusion of a larger collection of metal salts. Unfortunately, due to time constraints, only three complexes were suitably characterised. From the various characterisation methods used,

it was deduced that all three complexes were likely simple M_2L_1 systems, where the coordination of the 6-coordinate $3d$ metal centres were accompanied by the coordination of either water, solvent, counterion or a combination of these.

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Abbreviations

Chemical

| | |
|---|--|
| A.R | Analytical reagent |
| Ac ₂ O | Acetic anhydride |
| Boc | <i>Tert</i> -butyloxycarbonyl protecting group |
| (Boc) ₂ O | Di- <i>tert</i> -butyl dicarbonate |
| CDCl ₃ | Deuterated chloroform |
| ClO ₄ ⁻ | Perchlorate |
| Co(CH ₃ COO) ₂ ·4H ₂ O | Cobalt acetate tetrahydrate |
| Co(ClO ₄) ₂ ·6H ₂ O | Cobalt perchlorate hexahydrate |
| CT | Creutz Taube |
| DME | Dimethoxyethane |
| DMF | Dimethylformamide |
| DMSO-d ₆ | Deuterated dimethyl sulfoxide |
| Et ₂ O | Diethyl ether |
| EtOAc | Ethyl acetate |
| Fc | Ferrocene |
| Fe(ClO ₄) ₂ ·6H ₂ O | Iron perchlorate hexahydrate |
| HOMO | Highest occupied molecular orbital |
| HSAB | Hard-soft acid-base |
| IPA | Isopropyl alcohol |
| LDA | Lithium diisopropylamide |
| <i>m</i> -CPBA | <i>Meta</i> -chloroperoxybenzoic acid |
| MeOH-d ₄ | Deuterated methanol |
| Mn(ClO ₄) ₂ ·6H ₂ O | Manganese perchlorate hexahydrate |
| Mn(NO ₃) ₂ ·4H ₂ O | Manganese nitrate tetrahydrate |
| Na ₂ S ₂ O ₅ | Sodium metabisulfite |
| NBu ₄ ClO ₄ | Tetrabutyl ammonium perchlorate |
| O ₃ | Ozone |
| OsO ₄ | Osmium tetroxide |
| Ph ₃ P=O | Triphenylphosphine oxide |
| (Ph ₃ PCH ₂ OCH ₃)Cl | Triphenylphosphine methoxymethyl ether |

| | |
|------------------|---------------------------|
| Pz | Pyrazine |
| S.M | Starting material |
| SeO ₂ | Selenium dioxide |
| THF | Tetrahydrofuran |
| TLC | Thin layer chromatography |

Equipment

| | |
|--------|--|
| ATR-IR | Attenuated total reflectance – infrared spectroscopy |
| CE | Counter electrode |
| CV | Cyclic voltammetry |
| HMQC | Heteronuclear multiple quantum coherence |
| HPLC | High performance liquid chromatography |
| IR | Infrared spectroscopy |
| KBr | Potassium bromide |
| M.W | Microwave |
| NMR | Nuclear Magnetic Resonance |
| RE | Reference electrode |
| SCXRD | Single crystal X-ray diffraction |
| SQUID | Superconducting quantum interference device |
| TGA | Thermogravimetric analysis |
| WE | Working electrode |

Units

| | |
|--------------------|----------------------------------|
| c | Concentration |
| μ_{eff} | Effective magnetic moment |
| χ | Magnetic susceptibility |
| κ | Measured conductivity of sample |
| κ_s | Measured conductivity of solvent |
| o/n | Overnight |
| rt | Room temperature |

Compound codes

| | |
|------------|--|
| A# | Aldehyde (# = number code) |
| K# | Ketone (# = number code) |
| L# | Ligand (# = number code) |
| C#X | Complex (# = number code, X = letter code) |

Literature compound codes

| | |
|-----------------------|--|
| FL^X | Ligands as published by Shen <i>et al.</i> (X = letter code) |
| FC^X | Complexes as published by Shen <i>et al.</i> (X = letter code) |
| JL | Ligands as published by Hausmann <i>et al.</i> |
| JC | Complex as published by Hausmann <i>et al.</i> |
| RL | Ligands as published by Hogue <i>et al.</i> |
| RC# | Complexes as published by Hogue <i>et al.</i> (# = number code) |