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

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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 3*d* 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_2**L1** systems, where the coordination of the 6-coordinate 3*d* metal centres were accompanied by the coordination of either water, solvent, counterion or a combination of these.

Contents

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Abbreviations

Chemical

A.R	Analytical reagent
Ac_2O	Acetic anhydride
Boc	*Tert*-butyloxycarbonyl protecting group
$(Boc)_2O$	Di-*tert*-butyl dicarbonate
$CDCl_3$	Deuterated chloroform
ClO_4^-	Perchlorate
$Co(CH_3COO)_2 \cdot 4H_2O$	Cobalt acetate tetrahydrate
$Co(ClO_4)_2 \cdot 6H_2O$	Cobalt perchlorate hexahydrate
CT	Creutz Taube
DME	Dimethoxyethane
DMF	Dimethylformamide
DMSO-d_6	Deuterated dimethyl sulfoxide
Et_2O	Diethyl ether
EtOAc	Ethyl acetate
Fc	Ferrocene
$Fe(ClO_4)_2 \cdot 6H_2O$	Iron perchlorate hexahydrate
HOMO	Highest occupied molecular orbital
HSAB	Hard-soft acid-base
IPA	Issopropyl alcohol
LDA	Lithium diisopropylamide
m-CPBA	*Meta*-chloroperoxybenzoic acid
MeOH-d_4	Deuterated methanol
$Mn(ClO_4)_2 \cdot 6H_2O$	Manganese perchlorate hexahydrate
$Mn(NO_3)_2 \cdot 4H_2O$	Manganese nitrate tetrahydrate
$Na_2S_2O_5$	Sodium metabisulfite
NBu_4ClO_4	Tetrabutyl ammonium perchlorate
O_3	Ozone
OsO_4	Osmium tetroxide
$Ph_3P{=}O$	Triphenylphosphine oxide
$(Ph_3PCH_2OCH_3)Cl$	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 *et al*. (**X** = letter code)
FC^{X}	Complexes as published by Shen *et al*. (**X** = letter code)
JL	Ligands as published by Hausmann *et al*.
JC	Complex as published by Hausmann *et al*.
RL	Ligands as published by Hogue *et al*.
RC#	Complexes as published by Hogue *et al*. (**#** = number code)