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Magneto-structural correlations of Iron-salicylaldoxime clusters.

A dissertation presented in partial fulfilment of the Requirements for the degree of

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New Zealand.

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ABSTRACT

The syntheses and characterisation of polynuclear metal clusters using a series of derivatised salicylaldoxime ligands are described in this thesis. The polynuclear iron clusters contain metallic cores consisting of oxo-centred triangles. It was found that slight modifications of the phenolic oxime ligands can lead to metal clusters with different nuclearities, thus producing a variety of magnetic properties within the materials. The predominant building block in the complexes is a triangular \([\text{Fe}_3\text{O(R-sao)}_3]^+\) (R = alkyl derivative, sao = salicylaldoxime) unit which can self-assemble into more complicated arrays depending on reaction conditions.

A number of ligands containing a single phenolic oxime unit has been synthesised. These ligands have been used to form di-iron (C1), hexairon (C2), and heptairon (C3) complexes.

A second series of ligands containing two double-headed phenolic oxime units linked by diamine straps has been synthesised and fully characterised. Two copper complexes C5 and C7 were crystallised and pyridine also took part in coordination to the copper centres. Three of the iron complexes formed with double-headed oxime ligands are heptairon compounds. The heptairon compounds were all analogous in their iron coordination environment. The hexairon complex (C8) formed from a double-headed oxime was analogous to the complex C2 formed from a single-headed oxime ligand in its iron coordination environment. The tri-iron complex (C10) also contains a metaborate ion. In each case of the heptairon complexes and the hexairon complex, the metallic skeleton of the cluster was based on a trigonal prism in which two \([\text{Fe}_3^{III}\text{O}]\) triangles are fastened together via three helically twisted double-headed oxime ligands. Each of these ligands is present as (L-2H) where the oximic and phenolic O-atoms are deprotonated and the amino N-atoms protonated, with the oxime moieties bridging across the edges of the metal triangles. The identity of the metal ion has a major impact on the nuclearity and topology of the resultant cluster.

The magnetic susceptibility measurements of these iron complexes suggest the presence of strong antiferromagnetic interactions between the metal centres and the Mössbauer analyses confirm the oxidation state of all the iron centres is 3+. The CHN analyses and
other general characterisation allowed verifying and / or modifying the formulae generated by the X-ray analyses.
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- International Conference of Coordination Chemistry (ICCC) held in Singapore in July 2014. *Poster presented.*
DECLARATION BY THE CANDIDATE

I do hereby declare that the work described in this thesis was carried out by me under the supervision of Associate Professor Paul Plieger and Professor David Harding and a report on this has not been submitted in whole or part to any university or any other institution for another Degree or Diploma. To the best of my knowledge it does not contain any material published or written by another person, except as acknowledged in the text.

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Date:

Signature:

DECLARATION BY THE SUPERVISORS

This is to certify that this dissertation is based on the work carried by Ms D.N.T. De Silva under our supervision. The dissertation has been prepared according to the format stipulated and is of acceptable standard.

Supervisor 1   Name: A/P Paul Plieger

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Signature:

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Signature:
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ABBREVIATIONS

AF Antiferromagnetic exchange
SMMs Single molecule magnets
SCMs Single chain magnets
ZFS Zero field splitting parameter ($D$)
M Magnetisation
H External magnetic field
$\chi$ Magnetic susceptibility
Tc Curie temperature
$T_N$ Néel temperature
VT Variable temperature
QTM Quantum tunnelling of magnetisation
QPI Quantum phase interference
MeOH Methanol
EtOH Ethanol
MeCN Acetonitrile
EtOAc Ethyl acetate
DMF Dimethylformamide
DMSO Dimethyl sulfoxide
Et$_2$O Diethylether
Et$_3$N Triethylamine
Py Pyridine
CDCl$_3$ Deuterated chloroform
T Temperature
RT Room temperature
MP Melting point
dc Direct current
br Broad
m Medium
s Strong
saoH$_2$ Salicylaldoxime
Me-saoH$_2$ Methyl salicylaldoxime
Et-saoH$_2$ Ethyl salicylaldoxime
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Ph-saoH₂</td>
<td>Phenyl salicylaldoxime</td>
</tr>
<tr>
<td>MRI</td>
<td>Magnetic resonance imaging</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>SQUID</td>
<td>Superconducting quantum interference device</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin layer chromatography</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>ESI-MS</td>
<td>Electrospray ionisation mass spectrometry</td>
</tr>
<tr>
<td>IR</td>
<td>Infra-red</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>TMS</td>
<td>Trimethylsilane</td>
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