



THE UNIVERSITY
of ADELAIDE

**SYNTHESIS AND COORDINATION
CHEMISTRY OF POLYPYRIDYL
AMIDE LIGANDS**

A thesis submitted for the degree of
Doctor of Philosophy

by

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Abstract

This thesis provides an account of the synthesis and study of fifteen amide-containing polypyridyl ligands, eleven of which are new compounds. These ligands all possess at least one amide moiety, potentially capable of anion binding and one or more pendant pyridyl donor groups as the metal coordinating sites. A further evolution over previously reported compounds is that a majority of the amide compounds incorporate a pre-organised amide component that will constitute the anion binding region. The alkyl and phenyl spacers were utilised to confer flexibility to these compounds and to extend the spacing between the anion binding moiety and the pendant metal complexing groups. The compounds investigated in this work are divided into three categories; (i) unsymmetrical monoamide ligands that possess one amide functional group, one ester protected carboxylate and one external donor pyridyl moiety; (ii) symmetrical flexible amide ligands that possess two or more internal amide groups and two external pyridyl metal coordinating sites, and; (iii) symmetrical amide bridging ligands that incorporate two di-2-pyridylmethylamine chelating motifs.

The coordination chemistry and metallo-supramolecular chemistry of these ligands was investigated with a range of late transition metals including cadmium(II), copper(II), cobalt(II), silver(I), zinc(II) and palladium(II). Palladium(II) precursors, with a selection of monodentate or bidentate chelating ancillary blocking ligands, were utilised to form discrete mono- and dinuclear assemblies with a view to investigating anion complexation in solution. Other transition metal precursors were studied with a focus on the synthesis of coordination polymers that display anion coordinating pockets. Reaction of the monoamide ligands containing a pendant 3-pyridyl group with copper salts led to the formation of five very similar discrete planar and cleft-containing $[\text{Cu}_2\text{L}_2]$ dinuclear metallo-macrocyclic complexes. The monoamide compounds, lacking a methylene spacer between the amide and the pendant pyridyl ring, form near planar $[\text{Cu}_2\text{L}_2]$ dinuclear metallo-macrocyclic complexes; meanwhile introduction of a CH_2 spacer, by using a more flexible ligand, results in the formation of cleft-containing complexes. Reaction of the more flexible ligand with copper perchlorate results in a cleft-containing complex whereby encapsulation of a perchlorate anion in the cavity is stabilised by anion- π interactions. The flexible monoamide ligand with a pendant 4-pyridyl group forms 1-D coordination polymers based on a similar dinuclear metallo-macrocyclic

building block motif. Reaction of a related ligand with cadmium(II) nitrate and copper(II) acetate led to a formation of two 2-D coordination polymers, both prepared *via* a solvothermal approach. The 2-D coordination polymer obtained with cadmium(II) nitrate has small oval channels with the oxygen atoms of the nitrate anions and ligands lining the channels. This contrasts with the 2-D coordination polymer obtained with copper(II) acetate which is close-packed in the solid-state.

In a similar manner to studies on the monoamide ligands, the symmetrical flexible diamide ligands and tetraamide ligands were used to form discrete complexes and metallo-macrocyclic containing coordination polymers. Two mononuclear Pd(II) supramolecular cages were obtained from the reaction of flexible diamide ligand with pendant 3-pyridyl groups, while a mixture of Pd(II) supramolecular isomers was obtained with the analogue of this ligand. A crystal structure of a mononuclear palladium(II) complex showed specific anion interactions between the pre-organised NH donors and hexafluorophosphate anions in the solid-state. Similar interactions were observed in the majority of the coordination polymers obtained with the flexible diamide and tetraamide ligands. In the crystal structures of three isostructural dinuclear metallo-macrocyclic based coordination polymers containing the diamide ligand with pendant 3-pyridyl groups, the pre-organised NH donors are hydrogen bonded to the counterions, including nitrate and perchlorate. In addition to this interaction, the structures were stabilised by π -stacking interactions between the pendant pyridine groups and pyridyl cores. Reaction of the flexible diamide ligand containing pendant 4-pyridyl groups with cadmium(II) and zinc(II) nitrate provided access to two isostructural and isomorphous 1-D coordination polymers, while slow evaporation with cadmium(II) perchlorate gave 2-D coordination polymer. Reaction of the set of flexible tetraamide ligands containing pendant 4-pyridyl groups gave two coordination polymers that adopt semi-helical and close-packed structures in the solid-state. Only one coordination polymer was able to be obtained with the tetraamide ligands with pendant 3-pyridyl groups. The coordination chemistry of the chelating amide ligands with silver(I), cadmium(II) and palladium(II) salts were also studied and these ligands found to act as a bis(bidentate) ditopic bridge to connect two metal ions.

This study has revealed that the monoamide or unsymmetrical amide ligands in combination with copper(II) salts can form discrete anion cages potentially capable of interacting with anions *via* hydrogen bonding and anion- π interactions. The symmetrical and flexible diamide ligands also show potential to interact with anions in the solid-state and may be used for the development of materials suitable for anion separation or sequestration and

also as design elements of anion binding moieties for sensors. Unfortunately, the incorporation of more flexible amide ligands into metallo-supramolecular assemblies was not shown to increase the ‘size’ of the anion pocket of the assemblies but, due to the additional flexibility, results in the formation of more close-packed structures. It is also shown that self-association may limit the applicability of the tetraamide ligands to bind with either cations or anions in solution. The preliminary anion competition studies have shown that the coordination compounds derived from **L5** and **L6** tend to precipitate salts of either sulfate or, more likely based on the Hofmeister series, perchlorate anions under competitive conditions.

All compounds obtained in this work were characterised by a combination of ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, mass spectrometry, elemental analysis and X-ray crystallography. Simultaneous Thermal Analysis (STA) and Powder Diffraction X-ray Diffraction (PXRD) results for selected compounds are also described. In this thesis, crystal structures of seven ligands and twenty nine novel coordination compounds are described.

Declaration

NAME: Maisara Abdul Kadir

PROGRAM: Chemistry

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

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List of Abbreviations

DMSO	dimethyl sulfoxide
COSY	correlation spectroscopy
NOESY	nuclear Overhauser effect spectroscopy
DOSY	diffusion ordered spectroscopy
ES-MS	electrospray mass spectrometry
FTIR	Fourier transform infrared spectroscopy
DMF	<i>N,N'</i> -dimethylformamide
bipy	2,2'-bipyridine
en	1,2'-ethylenediamine
Ph	phenyl
Py	pyridine
PXRD	powder X-ray diffraction
TGA	thermal gravimetric analysis
STA	simultaneous thermal analysis
<i>m/z</i>	mass to charge ratio
L	ligand
1-D	one-dimensional
2-D	two-dimensional
3-D	three-dimensional