The Comparative Coordination Chemistry of Some Polyamines and Polyaminoacids

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by

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I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or institution.

(Signed)

E. N. Wilkes

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Abstract

This thesis describes the metal-templated synthesis of a number of macrocyclic ligands bearing pendant carboxylate groups and their coordination to a selection of first-row transition metal ions. Their structural and physical properties are compared to analogous macrocycles bearing pendant amine groups. The first chapter reviews the various methods of producing macrocyclic ligand using formaldehyde also employed in this thesis, as part of the cyclization process.

The second chapter describes the synthesis of a series of polyaza macrocyclic ligands bearing a single carboxylate pendant through the copper(II)-templated condensation of diethylmalonate and formaldehyde with a series of linear tetraamines, producing 13-, 14-, 15- and reinforced 15-membered macrocycles. The physical properties of the copper complexes of the intermediate acid ester pendant species were compared with the analogous complexes bearing a pendant nitro group. The X-ray crystal structure of the complex (ethyl 1,5,9,13-tetraazabicyclo[1.1.2.2]heptadecane-7-carboxylate)copper(II) perchlorate hydrate is described and compared with analogous structures. Zinc / acid reduction of the copper complexes led to the production of the metal-free hydrochloride salts of the macrocycles which were isolated and characterised using NMR and infrared spectroscopy. The protonation constants for the free ligands were determined by potentiometric titration.

The synthesis and characterisation of the Co(III) and Ni(II) complexes of the ligands 1,4,8,12-tetraazacyclopentadecane-10-carboxylic acid and 1,5,9,13-

tetrazabicyclo[1.1.2.2]heptadecane-7-carboxylic acid form the subject of Chapter 3. The equivalent complexes for the known amine pendant analogues were also synthesised for comparison. The X-ray crystal structures for the complexes (1,5,9,13-tetrrazabicyclo[1.1.2.2]heptadecane-7-carboxylate)-nickel(II) perchlorate and *trans*-(1,4,8,12-tetraazacyclopentadecane-10-carboxylate)aquacobalt(III) perchlorate hydrate are described. Base hydrolysis kinetics of the family chlorocobalt(III) complexes are reported.

By controlling the stoichiometry of the stepwise additions of diethyl malonate and then nitroethane in the presence of formaldehyde and base and using bis(ethanediamine)copper(II) as a template, the cyclam analogue 6-methyl-6-nitro-1,4,8,11-tetraazacyclotetradecane-13-carboxylic acid, which has both a pendant nitro group and carboxylic acid group was prepared. Zinc / acid reduction of the copper(II) complex of this macrocycle yields the hydrochloride salt of the ligand 6-methyl-1,4,8,11-tetrazatetradecane-6-amine-13-carboxylic acid (acammac). Two geometric forms of this ligand are produced, one with pendants on the same side of the macrocyclic plane (*cis*) and the other with the pendants on opposite sides of the macrocyclic plane (*trans*). Chapter 4 describes the synthesis and characterisation of this ligand and reports the poorly defined X-ray crystal structure of the copper(II) complex of the nitro precursor. The synthesis of the analogous macrocycle with two carboxylate pendants (diacmac) is also reported.

Chapter 5 describes the complexation of both the *cis* and *trans* forms of acammac to a range of first row transition metal ions. Their physical and structural properties are compared with those for the complexes of the analogous macrocycle bearing two pendant amines, diammac, and the reported complexes of diacmac. The X-ray crystal structures of the complexes cis-(*trans*-6-methyl-1,4,8,11-tetraazacyclotetradecane-6-amine-13-carboxylic acid)chlorocobalt(III) perchlorate hydrate, (*trans*-6-methyl-1,4,8,11-tetraazacyclotetradecane-6-amine-13-carboxylate)cobalt(III) perchlorate hydrate and (*cis*-6-methyl-1,4,8,11-tetraazacyclotetradecane-6-amine-13-carboxylate)nickel(II) perchlorate are described. Also described are the X-ray crystal structures of the cobalt complexes of diacmac, (*trans*-1,4,8,11-tetraazacyclotetradecane-6,13-dicarboxylate)cobalt(III) perchlorate and *trans*-aqua(*cis*-1,4,8,11-tetraazacyclotetradecane-6-carboxylate-13-carboxylic acid)cobalt(III) perchlorate. The formation constants for a selection of labile metal ions with diacmac and acammac are also reported and compared with the known values for diammac.