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Cyclo- and Polyphosphazenes Containing 2-oxypyridine Moieties Coordinated to Selected Transition Metals

A thesis presented in partial fulfilment of the requirements for the degree of
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Man's mind, once stretched by a new idea, never regains its original dimensions.

Oliver Wendell Holmes

US author & physician (1809 - 1894)

(http://www.quotationspage.com/quotes/Oliver_Wendell_Holmes/accessed 18 June 2008)

Abstract

The phosphazene ligands spiro(biph)tetrakis(2-oxypyridine)cyclotriphosphazene (L^1), spiro(biph)tetrakis(4-methyl-2-oxypyridine)cyclotriphosphazene (L^2), and spiro(biph)tetrakis(6-methyl-2-oxypyridine)cyclotriphosphazene (L^3) have been synthesised and characterised as small molecule templates for the polymeric analogues. Complexes of each ligand with selected transition metals have been synthesised and characterised. Where X-ray crystal structures have been obtained, the predominant geometry is a five-coordinate trigonal bipyramidal (TBP) form, though variations exist. In solution, $[CuL^2Cl_2]$ retains the TBP form whereas $[CoL^2Cl_2]$ rearranges to a tetrahedral geometry. In order to elucidate this behaviour, diamagnetic complexes were synthesised and variable temperature NMR (VTNMR) studies conducted.

The complexes $[ZnL^2Cl_2]$, $[CdL^2Cl_2]$ and $[HgL^2Cl_2]$ exhibit fluxional behaviour as monitored by VTNMR studies. The X-ray structure of $[CdL^2Cl_2]$ contains three molecules in the unit cell that demonstrate what is thought to be the first evidence for a fluxional mechanism in phosphazene compounds. The complex $[ZnL^2Cl_2]$ exists at low temperature as discernable major and minor species.

Polyphosphazene analogues have been synthesised and complexed with selected transition metals. The polymer complexes display variations in solubility and stability which is postulated to be due to the ratio of side group substitution, position of the pyridyl methyl group and the nature of the complexing metal. A number of the polymers degrade prior to workup, possibly as a result of base-promoted attack on the backbone by the pyridyl nitrogen atoms. Electronic spectra reveal that where soluble, the Co(II) polymer complexes have a tetrahedral geometry, whereas the Cu(II) polymer complexes distort between TBP and square-based pyramidal dependent on the ratio of metal used. Polymer complexes with Zn(II) demonstrate fluxional behaviour.

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