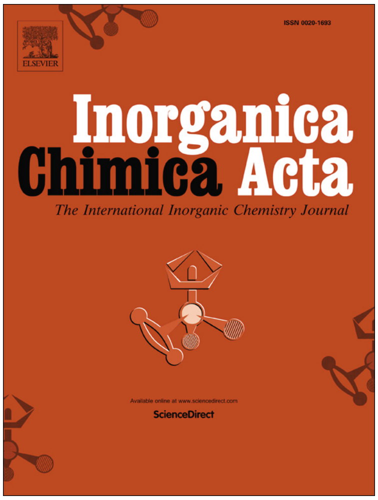

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Delineating factors that dictate the framework of a bulky phosphate derived metal complexes: Sterics of phosphate, anion of the metal salt and auxiliary N-donor ligand

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Abstract

A bulky phosphate, 2,6-dibenzhydryl-4-methylphenyl dihydrogen phosphate (**L^1H_2**) is synthesized from the reaction of 2,6-dibenzhydryl-4-methylphenol with $POCl_3$ followed by hydrolysis. **L^1H_2** reacts with metal nitrates, $M(NO_3)_2{\cdot}xH_2O$ in methanol under ambient conditions to afford mononuclear complexes, $[M(L^1H)_2(CH_3OH)_4]$ (M = Co (**1**), Cu (**2**), Zn (**3**)) which contain the phosphate group in mono-deprotonated form. On the other hand, when acetate rather than nitrate salt of cobalt is used, a one dimensional (1D) polymer, $[Co(L^1)(CH_3OH)_4]_n$ (**4**) is obtained wherein the phosphate ligand is in the doubly-deprotonated form. When the reaction of $Co(OAc)_2{\cdot}4H_2O$ and **L^1H_2** is carried out in the presence of a mono-*N*-donor ligand, pyridine, it results in the formation of a tetranuclear D4R cubane, $[Co_4(L^1)_4(Py)_4]$ (**5**). However, when the same reaction is carried out in the presence of a chelating di-*N*-donor ligand, 2,2′-bipyridine, a dinuclear complex with S4R core, $[Co_2(L^1)_2(bipy)_2(CH_3OH)_4]$ (**6**) is formed. The ligand and the complexes were structurally characterised through a single crystal X-ray diffraction study and depending on the type of compound further characterised by spectroscopic (IR, NMR and EPR), analytical (CHN), thermoanalytical (TGA) and magnetic techniques. This study shows how the steric bulk of the phosphate, nature of the anion in the metal salt as well as the nature of the *N*-donor ligand influence the framework of the products.

Keywords: Bulky phosphate; Cobalt acetate; Cobalt nitrate; One-dimensional polymer; Pyridine.

1. Introduction

The chemistry of metal phosphates and phosphonates has been extensively investigated due to their structural resemblance to secondary building unit of zeolites and other porous

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