Pyridine-Derived Tetrapodal Ligands with NO_4 and NN_4 Donor Sets

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Template Reaction, Tetrapodal Pentadentate Ligand, Pentaamine, Hydrobromide

The Mg^{2+} assisted synthesis of a pyridine-derived tetraalcohol ligand with an NO_4 donor set is described. 2,6-Diethylpyridine reacts cleanly with aqueous formaldehyde solution in the presence of 1 equivalent of $MgSO_4$ hydrate in a pressurised vessel to give the quadruply hydroxymethylated product 2,6-$C_5H_3N[CMe(CH_2OH)_2]_2$ (**1**) as a crystalline solid. Two alkali/alkaline earth metal perchlorate adducts of **1** have been structurally characterised, *viz.* [(**1**)$_2$ • $LiClO_4$] (**6**) and [(**1**)$_2$ • $Ba(ClO_4)_2$] (**7**). The ligand adopts a bridging coordination mode in both **6** (distorted tetrahedral coordination of Li^+) and **7** (square prismatic coordination of Ba^{2+}). The further derivatization of **1** leads to the tetratosylate (**2**) and the tetraazide (**3**), both of which have been obtained in pure form for the first time. Reduction of **3** gives the pentaamine ligand 2,6-$C_5H_3N[CMe(CH_2NH_2)_2]_2$ (**4**), isolated as the tetrakis(hydrobromide) salt **4** • 4 HBr. The presence of four ammonio substituents and an unprotonated pyridine nitrogen atom in the solid state has been unequivocally established by an X-ray structural analysis.

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