

Synthesis of pyridinium transition metal tetrachlorides counter-ions as starting materials for coordination of organic ligands

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Pyridinium counter-ions are an old class of compounds in which the *N*-protonated pyridine can form hydrogen bonds with different anions, such as tetrachloroferrate. In the past, they have been studied as potential single molecule magnets and normally exhibit antiferromagnetic coupling at very low temperatures (< 10 K). Inspired by the last ACA meeting (2016) where the Cahill group demonstrated that 4-bromo-pyridine could be used as linear linker in crystal engineering, we explored the use of pyridinium tetrachlorometalates to coordinate organic ligands such as *N*-2-pyridylimido-2-pyridylamidine (**1**) and *N*-2-pyrimidylimido-2-pyrimidylamidine (**2**). This resulted in four complexes of **1** and **2** with the metal in a different coordination site than previous reports. Subsequently, pyridinium tetrachloroferrate(III), pyridinium trichloromanganate(II) monohydrate, and dipyridinium tetrachlorocobaltate(II) were reproduced, along with the new compounds dipyridinium tetrachloroferrate(II) (**3**), 2,6-diaminopyridinium tetrachloromanganate(II) monohydrate (**4**) and 2,6-diaminopyridinium tetrachlorocobaltate(II) (**5**). The unit cell of **3** indicates that it is a polymorph of other similar dipyridinium tetrachlorometalates with the refcodes EWAXIJ, PYDMNC and WOHFII. The crystal structure of **5** exhibits strong intermolecular interactions between the cation and the tetrachlorocobaltate(II) anions, in which each 2,6-diaminopyridinium cations are coordinating to the tetrachlorocobaltate in a pincer-like fashion consisting of three hydrogen bonds, two in the amino groups and one in the protonated pyridine. The results of these studies will be presented, as well as our efforts towards exploration of these pyridinium counterions in the synthesis of metallic complexes with various organic ligands in the pursuit of metallic clusters.