The Many Moods of the 3-Aminopyridinium Chlorocuprate(II) System

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Our group has previously reported the structure of bis(3-aminopyridinium) tetrachlorocuprate(II) (as a possible correction to the published structure, CSD refcode: PATMUT). This compound was serendipitously obtained as red crystals from acetonitrile using a thermal gradient technique on a green solid that in turn was obtained by evaporation of a 6 M HCl solution of 3-aminopyridine and CuCl2.2H2O in a 2:1 molar ratio. We have since made a more systematic study, first by thermal gradient crystal growth with green crystals of 3-ammoniumpyridinium tetrachlorocuprate(II) (SAGJIT, grown by the method of Willett et al. JACS (1988), 110, 8639) as the source material in a variety of organic solvents. Growth in acetonitrile yielded crystals of SAGJIT. However, growth in 1-proponal yielded green crystals of a new compound, bis(3-aminopyridinium)dichlorodi-μ-chlorodicuprate(II), consisting of an asymmetrically bridged dimer. This is in contrast to red crystals of the symmetrically bridged analog (GAGNOR) reported by Blanchette and Willett (Inorg. Chem. (1988), 27, 843), but similar to their reported asymmetrically bridged bromide dimer (GAGNUX). Crystal growth in methylethylketone yields an extremely dark solution and a dark solid mass containing lighter crystals of 3-ammoniumpyridinium chloride and a darker, as yet undetermined solid, while crystal growth in tetrahydrofuran has proceeded very slowly. The green source crystals of SAGJIT were then also ground together with a stoichiometric amount of 3-aminopyridine. This yielded a red solid which was loaded into thermal gradient tubes. Growth in acetonitrile yielded red crystals of the desired bis(3-aminopyridinium) tetrachlorocuprate(II), consisting of isolated CuCl42- flattened tetrahedral. Growth in 1-proponal yielded orange crystals of the same stoichiometry, but formulated as 3-aminopyridinium (3-aminopyridinium)tetrachlorocuprate(II). This new compound contains isolated 5-coordinate complexes, each containing a coordinated 3-aminopyridinium cation, which are separated by 3-aminopyridinum counterions The complex assumes a geometry intermediate between tbp and sp, with the 3-aminopyridinium cation axial and basal, respectively, and forming a trans N-Cu-Cl angle of 178°. The three basal chlorides have a Cu-Cl bond lengths of ~2.3 Å, with a trans Cl-Cu-Cl angle of 154°, and an apical Cu-Cl bond length of 2.54 Å.

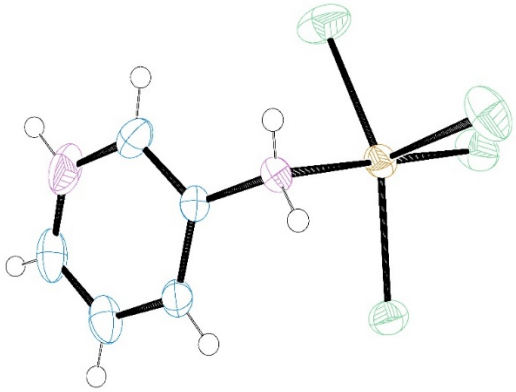

Figure 1