

Reinvestigation of the crystal structure of bis(3-aminopyridinium) tetrachloridocuprate(II)

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The structure of bis(3-aminopyridinium) tetrachloridocuprate(II) (PATMUT) was reported by Kumar, et al. (Cryst. Growth Des. (2005) 5, 651), along with the structure of the 2-aminopyridinium analog (YOPNAS01). Both structures belong to the same space group (triclinic P-1) with very similar lattice constants (within 0.4% of longest cell dimension)--and with atomic coordinates that closely overlay. The published ORTEP diagram for PATMUT also shows an anomalously large ellipsoid for the ring N atom (with this atom not involved in significant hydrogen bonding) and an anomalously small ellipsoid on the C atom ortho to the amino group, which led us to believe that atom mis-assignment had occurred during refinement of PATMUT. Furthermore, the proximity of the amino group to the ring N atom in 2-aminopyridine leads to a preference for mono-protonation in halidometallate systems--the di-protonated cation is unknown. For 3-aminopyridine, in contrast, the di-protonated cation is readily observed in 3-ammoniumpyridinium salts while the mono-protonated cation, when it occurs, is usually found to coordinate the metal through the amino group.

An attempt to grow crystals of bis(3-aminopyridinium) tetrachloridocuprate(II) by slow evaporation of a 2:1 molar ratio of 3-aminopyridine and CuCl₂ in a 6 M HCl solution yielded only green, thin, plate-like crystals of 3-ammoniumpyridinium tetrachloridocuprate(II). Recrystallization of these crystals from dry acetonitrile in a thermal gradient tube yielded only orange-red crystals initially, which then gradually re-dissolved to be replaced by green crystals of the 3-ammoniumpyridinium salt. Single crystal X-ray diffraction analysis at 295 K of an orange-red crystal yields the structure bis(3-aminopyridinium) tetrachloridocuprate(II) as triclinic P-1 with a c-axis ~1 Å longer than in PATMUT and very different unit cell angles, yet a cell volume only 0.5% smaller. The CuCl₄²⁻ anion in this structure has a flattened tetrahedral geometry that is more distorted than in PATMUT (trans-∠Cl-Cu-Cl = 138.81 and 140.29° versus 130.27 and 136.35°, respectively), while significant hydrogen bonding by the ring N atoms is now also found.

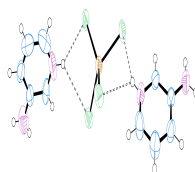


Figure 1