

E0014

Crystal Structure and Charge Density Analysis of 1:1 Complex of 4-Nitrophenol and Ammonium 4-Nitrophenolate. Kenneth L. Martin¹, Madoka Hasegawa¹, and Edwin D. Stevens², ¹Dept. of Chemistry, Berry College, Mt. Berry, GA, ²Dept. of Chemistry, Univ. of New Orleans, New Orleans, LA.

A 1:1 complex of *p*-NO₂-C₆H₄OH and *p*-NO₂-C₆H₄ONH₄ was synthesized via addition of NH₃(aq) to aqueous 4-nitrophenol. An X-ray diffraction data set was collected at 150 K using a Bruker SMART-CCD single crystal diffractometer and MoK α radiation ($\lambda = 0.71073$ Å). The crystal structure is monoclinic (space group C2) with $a = 21.122(4)$ Å, $b = 3.6963(7)$ Å, $c = 10.765(2)$ Å, $\beta = 117.75(3)^\circ$. A cell volume of 743.8 Å³ and a cell weight of 644.549 g/mol (*p*-NO₂-C₆H₄OH·*p*-NO₂-C₆H₄ONH₄·2H₂O, $Z = 2$) yield a density of 1.439 g/cm³. The refinement led to $R(F) = 0.0489$ for 4589 reflns [$F_o > 4\sigma(F_o)$] and $S = 1.022$. Of particular interest is the disorder of H9, which makes the phenol indistinguishable from the phenolate.

The EDD of the complex has been modeled using the multipole formalism via XD^[1]. Before the κ 's and multipoles were refined, the atomic charges (determined by refinement of the monopoles) of the 4-nitrophenol moiety are as follows. Phenol OH: O = -0.37(2); H = +0.42(4) with an occupancy of 0.5. Nitro group: N = +0.38(2); O = -0.23(1). Ring: avg. C = -0.14(2); avg. H = +0.14(2). Refinement of κ 's and multipoles led to $R(F) = 0.0379$. The deformation map reveals electron density in the region where H9 is shared between the phenol and the phenolate ion.

[1] XD: *Computer Program Package for Multipole Refinement and Analysis of Electron Densities from Diffraction Data* (4.95), T. Koritsanszky, S.T Howard, Z. Su, P.R. Mallinson, T. Richter and N.K. Hansen.