

Poster Presentation

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Tetraphenylphosphonium Salts for Small Molecule Capture

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Tetraphenylphosphonium salts are useful tools for capturing (and crystallizing) small molecules. The packing of the cations in such salts leads to channels or cavities suitable for trapping of the small molecule by the anion. For example, we have prepared the complex salts [PPh₄][SO₂X] (X = Cl, Br, I) through the exposure of solutions of [PPh₄]X to an atmosphere of SO₂. Churakov et al. have reported the preparation of [PPh₄]X·nH₂O₂ (X = Cl, Br; n = 0.98–1.90) after trapping hydrogen peroxide using the precursor halide salts (1). Envisioning a similar result, a concentrated solution of [PPh₄]CN·xH₂O was exposed to an atmosphere of CO₂. Colourless crystals were isolated and characterised as [PPh₄][NCCO₂] using crystallographic and spectroscopic techniques. The packing of the ions in the product, in the tetragonal space group I-4, is similar to that observed in many other simple [PPh₄]X salts, where X = Br, I, SCN, OCN, N(CN)₂, etc. Solution of the crystal structure was complicated by the high symmetry and disorder in the anion, with only three unique atoms being necessary for its characterization. Thus the utility of our chosen cation can also become a hindrance. Crystals can usually be grown and data obtained but structure solution is not a certainty. For example, the structures of [PPh₄]CN·xH₂O have not been reported, likely because of the rapid spinning of the anions in the cation framework, even though they are hydrogen bonded to the water which is clearly visible. Similarly, we have data collected for the products from a number of related reactions, [PPh₄][CN]·xH₂O + PhC(O)F, [PPh₄]F + SO₂, [PPh₄]X (X = Cl, Br, I, CN, N₃) + CS₂, and can clearly identify the cation in the unit cell. However, elucidation of the structures of the anions has not been possible. It is hoped that this presentation will engender discussion of possible solutions to the observed disorder problems.

[1] A.V. Churakov, P.V. Prikhodchenkoa, J.A.K. Howard, *Cryst. Eng. Comm.* (2005) 7, 664–669.

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