Understanding the Effects of Ionicity in Salts, Solvates, Co-Crystals, Ionic Co-Crystals, and Ionic Liquids, Rather than Nomenclature is Critical to Understanding Their Behavior

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Content:
1. General
2. Experimental
Commercially available chemicals were used as received. Morpholine, maleic acid, succinic acid, and salicylic acid were obtained from Acros Organics (Geel, Belgium). Acetic acid, 1,2-dimethylimidazole, 1-methylimidazole, and cesium carbonate were obtained from Sigma Aldrich (Milwaukee, WI). Anhydrous ethanol was obtained from AAPER (Shelbyville, KY). Deionized (DI) water was obtained from a commercial deionizer (Culligan, Northbrook, IL) with specific resistivity of 17.25 MΩ cm at 25 ºC.

**Synthesis of [Mor][OAc]:** Acetic acid (1.000 g, 16.6 mmol) was added to deionized water (1 mL). Morpholine (1.4536 g, 16.7 mmol) was slowly added to the solution and a water bath was used to keep exothermic reaction cooled, giving a pale yellow solution. Evaporation of this solution in a vacuum oven (40 ºC for one week) yielded colorless crystalline plates, one of which was used for SCXRD.

**Synthesis of [Mor][HMal]:** Maleic acid (1.006 g, 8.67 mmol) was dissolved in deionized water (1 mL). Morpholine (0.757 g, 8.69 mmol) was slowly added resulting in a transparent solution. Evaporation of this solution in a vacuum oven (40 ºC for one week) yielded colorless, irregularly-shaped crystals, one of which was used for SCXRD.

**Synthesis of [Mor]2[Succ]·H2Succ:** Succinic acid (1.008 g, 8.53 mmol) was added to deionized water (1 mL). Morpholine (0.7468 g, 8.57 mmol) was slowly added, resulting in the dissolution of the initially insoluble succinic acid and evolution of heat to give a transparent solution. Evaporation in a vacuum oven yielded a mass of colorless, intergrown crystalline plates, a fragment of which was used for SCXRD.
**Synthesis of [HDmim][Cl]-Dmim:** To a solution of 1,2-dimethylimidazole (9.6 g, 0.1 mol) in ethanol (30 mL), cooled in an ice-water bath, was added concentrated HCl (7.7 mL) with care. The reaction mixture was then allowed to warm to room temperature and was stirred overnight. The solvent was removed by rotary evaporation under reduced pressure at 50 °C to yield a viscous, colorless liquid which began to crystallize on cooling to and standing at room temperature. Large, colorless blocky crystals suitable for SCXRD were isolated from the crystallized product.

**Synthesis of [Tmim][H(Sal)₂]:** [Tmim][H(Sal)₂] was synthesized from commercially available 1,2-dimethylimidazole, dimethyl sulfate, cesium carbonate, and salicylic acid in two steps. First, dimethyl sulfate (47.3 mL, 0.499 mol) was carefully added to a solution of dimethylimidazole (48.1 g, 0.500 mol) in 100 mL of toluene with continuous stirring. The reaction proceeded with heat evolution followed by eventual precipitation of the product, 1,2,3-trimethylimidazolium methylsulfate, which was isolated as a brown to pink solid by filtering and drying with heat. Next, 4.2009 g of this product (0.0189 mol) was reacted with cesium carbonate (4.7185 g, 0.0090 mol) by stirring for 30 minutes in anhydrous ethanol. The mixture was allowed to sit overnight and any solids were filtered out. Salicylic acid (2.1602 g, 0.0189 mol) was added to the solution. Removal of the solvent with heat yielded a brown liquid which crystallized on cooling. A colorless platelet was analyzed by SCXRD, revealing it to be the compound [Tmim][H(Sal)₂].
X-ray Crystallography: Data collection for [Mor][OAc], [Mor][HMal], and [Mor]$_2$(Succ)·H$_2$Succ was conducted on a diffractometer equipped with a Siemens PLATFORM 3-circle goniometer and a Bruker Apex II CCD detector using graphite-monochromated Mo-K$_\alpha$ radiation. Crystals were cooled to -100 °C under a cold nitrogen stream using an LT-2 cryostat. A hemisphere of data was collected for each crystal using a strategy of omega scans with 0.5° frame widths. Indexing, data integration, scaling, and absorption correction were performed using the Apex2 software suite from Bruker.$^1$

Data collection for [Mor]$_2$(Succ)·H$_2$Succ was conducted on a small and weakly diffracting fragment, resulting in a poor ratio of observed to total data and an unusually high R$_{int}$ value for the monoclinic crystal system. However, the systematic absences were consistent with the space group P2$_1$/n, indicating that the poor R$_{int}$ value was due to data quality and not an incorrect choice of crystal system. A smaller unit cell could not be found by indexing, and transforming the unit cell by cutting it in half along any of its axes did not result usable data. PLATON ADDSYM$^2$ was unable to find additional symmetry apart from transforming the cell into P2$_1$/c.

The material was recrystallized by slow evaporation under ambient conditions from several different solvents (water, methanol, ethanol, ethyl acetate, and mixtures of these) in order to grow better crystals, but these yielded either syrups or crystals of equally low quality.

Data collection for [HDmim][Cl]-Dmim and [Tmim][H(Sal)$_2$] was conducted on a Siemens diffractometer equipped with a SMART CCD detector using graphite-monochromated Mo-K$_\alpha$ radiation. Crystals were cooled to -100 °C under a cold nitrogen stream using an LT-2 cryostat. A hemisphere of data was collected for each crystal using a strategy of omega scans. Cell determination and data collection were done using the SMART$^3$ software package. Integration and data reduction was done using SAINTPlus.$^4$ Absorption corrections and scaling were
applied using SADABS. All non-hydrogen atoms were anisotropically refined and all hydrogen atoms were located using difference Fourier maps and were isotropically refined.

Structure solution, refinement, and generation of ORTEP diagrams for all crystals were conducted using the SHELXTL-97 software suite from Bruker. Short contact analysis and generation of packing diagrams were conducted using Mercury from the Cambridge Crystallographic Data Center (CCDC). Crystal structures from the literature were found by searching the Crystal Structure Database with the program Conquest from the CCDC.

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1 APEX 2 AXScale and SAINT, version 2010; Bruker AXS, Inc.: Madison, WI.
3 SMART (2002) Bruker molecular analysis research tool, v.5.626. Bruker AXS, Madison, WI.