Terephthalate Salts of Dipositive Cations

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Introduction

Purified terephthalic acid (PTA, 1,4-benzenedicarboxylic acid) is the primary raw material for the polyester used to make a myriad of consumer and industrial products. From time to time, terephthalate salts of catalyst and corrosion metals are isolated from commercial process streams. Understanding the natures of these structures will lead to process insights and improvements. We have undertaken a program to prepare pure materials (instead of the mixtures isolated commercially). The isostructural magnesium, manganese, iron, and cobalt(II) terephthalate dihydrate complexes have been characterized by solving the structure of the magnesium salt using synchrotron powder data.

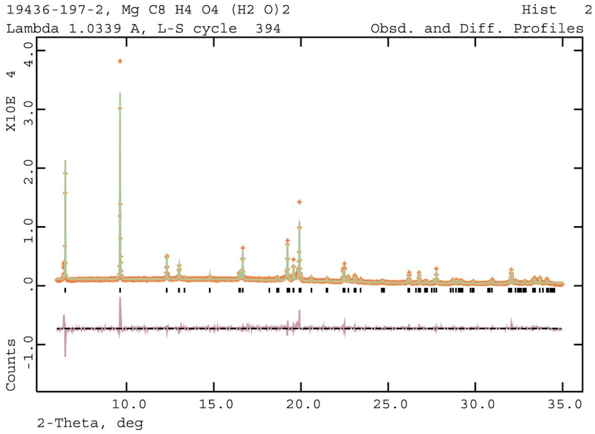

FIG. 1. Observed, calculated, and difference powder patterns of magnesium terephthalate dihydrate, measured on beamline ID-10.

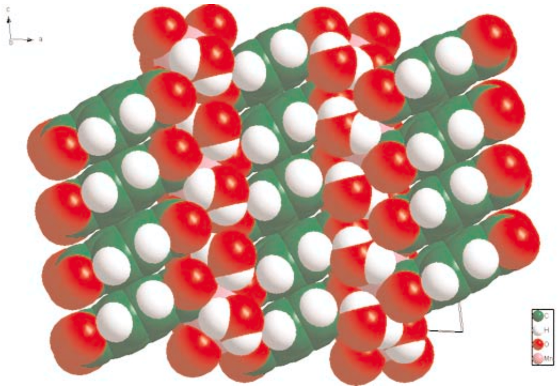

FIG. 2. Crystal structure of $M(C_8H_4O_4)(H_2O)_2$, viewed down the monoclinic b-axis.

Methods and Materials

Magnesium terephthalate dihydrate was prepared by mixing solutions of magnesium acetate tetrahydrate and diammonium terephthalate in water, letting the resulting clear colorless solution evaporate partially, and filtering the resulting slurry. The powder pattern (Fig. 1) could be indexed on a *C*- centered monoclinic unit cell having a = 18.5055(3), b = 6.5351(1), c = 7.3179(1) Å, and β = 99.675(1)%. The systematic absences were consistent with space groups *C2/c* or *Cc*. To obtain a reasonable density, Z = 4. Space group *C2/c* was selected, and confirmed by successful solution and refinement of the structure. A terephthalate anion was built and minimized in Cerius^2,[1] and fixed at the origin. The orientation of the anion was determined using Monte Carlo simulated annealing techniques as implemented in the STRUCTURE_SOLVE module of InsightII.[2] With Z = 4, the Mg cation also occupies a special position. The only special position which yielded a reasonable coordination geometry was degrees 0, and the position of the coordinated water molecule could be deduced easily. The Rietveld refinement was carried out using GSAS.[3] The C_6H_4 terephthalate core was described as a rigid body, and soft constraints were applied to the carboxylate bond distances and angles. The final refinement of 69 variables using 19056 observations (two synchrotron patterns and laboratory data) yielded the residuals R_{wp} = 0.1637, R_p = 0.1054, and R(F) = 0.0702. The largest errors represent incomplete description of the profile shapes. The final hydrogen positions were determined by quantum chemical calculations using the Cambridge Serial Total Energy Package (CASTEP).[4]

Results and Discussion

The structure (Fig. 2) consists of alternating layers (perpendicular to a) of terephthalate anions and octahedrally-coordinated metal cations. The octahedra are isolated; the equatorial coordination consists of four terephthalate oxygens, and there are two axial water molecules. The Mg cation valence, calculated from the sum of bond valences, is 2.04. The deviations of the O-M-O angles from the ideal octahedral values are small.

None of the terephthalate anions is completely planar; the carboxylates are rotated approximately 10% out of the ring plane. Aromatic carboxylates are more-flexible than is commonly believed. These rotations result in only a small energy penalty (~3 kJ/mole),[5] and result in more-favorable coordination geometries. Both water molecule hydrogens participate in normal-strength hydrogen bonds to carboxylate oxygens.

The stacking of the aromatic rings is relatively "tight," the shortest intermolecular C···C and C···H distances fall in the range 3.2-3.3 Å. The angle between successive ring planes in the stack is 8.0%. The density of these complexes is not exceptionally high, and the "side-to-side" packing of the terephthalates is relatively "loose." There is significant volume which could be occupied by a probe of 0.8-1.0 Å radius. Apparently, coordination interactions are more important than the packing of the aromatic anions in determining the crystal structure. The terephthalate packing does not fit into the pattern of aromatic hydrocarbons, in contrast to that in terephthalates of monopositive cations.[6]

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