

AROMATIC CARBOXYLATES. TRIMELLITATES

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Trimellitic acid (1,2,4-benzenetricarboxylic acid, $\text{H}_3\text{C}_9\text{H}_3\text{O}_6$) is of interest as a ligand in the preparation of nanoporous metal organic frameworks (MOFs). It is an impurity in the commercial synthesis of terephthalic acid and other aromatic acids, so characterization of its denser metal complexes is of interest from a purely practical viewpoint. The crystal structures of several new trimellitates have been determined using powder diffraction data, and the bonding has been examined using quantum chemical calculations.

$(\text{NH}_4)_2\text{HC}_9\text{H}_3\text{O}_6$ was prepared by recrystallizing the very hygroscopic solid obtained by the reaction of ammonia vapor and trimellitic acid from water. It crystallizes in $P2_1/a$, with $a = 13.8644(10)$, $b = 20.0654(12)$, $c = 3.7344(2)$ Å, $\beta = 96.947(6)^\circ$, $V = 1031.27(12)$ Å³, $Z = 4$, and $\rho = 1.573$ g/mL. There is a very strong intramolecular hydrogen bond between the 1- and 2-carboxyl groups, and an extensive network of intermolecular hydrogen bonds.

The new compound $\text{Ca}(\text{HC}_9\text{H}_3\text{O}_6)\text{H}_2\text{O}$ was prepared by reaction of aqueous solutions of trimellitic acid and calcium acetate monohydrate. It crystallizes in $P\bar{1}$, with $a = 6.9418(2)$, $b = 7.0404(2)$, $c = 10.4125(3)$ Å, $\alpha = 86.884(3)$, $\beta = 82.418(2)$, $\gamma = 69.531(1)^\circ$, and $V = 472.58(3)$ Å³. The complete synthesis, solution, and refinement was carried out in under one day! $\text{Ce}(\text{C}_9\text{H}_3\text{O}_6)(\text{H}_2\text{O})_4$ crystallizes in $P2_12_12_1$ with $a = 6.1541(12)$, $b = 9.7258(20)$, $c = 20.311(4)$ Å, and $V = 1215.7(4)$ Å³. It is isostructural to known Nd and Er analogs.

The structure of the new compound $[\text{Mn}(\text{HC}_9\text{H}_3\text{O}_6)(\text{H}_2\text{O})]\text{H}_2\text{O}$ was solved and refined using synchrotron powder data. It crystallizes in $P\bar{1}$ with $a = 6.41805(8)$, $b = 7.35044(7)$, $c = 10.87662(11)$ Å, $\alpha = 92.2118(9)$, $\beta = 100.9500(13)$, $\gamma = 99.9543(10)^\circ$, and $V = 494.829(10)$ Å³. The 1- and 2-carboxylate groups are rotated significantly out of the ring plane. One water molecule bridges two Mn, and the other lies in a channel along the a -axis, and is hydrogen bonded to the 4-carboxyl group, the 2-carboxylate group, and the coordinated water molecule.

$[\text{M}(\text{H}_2\text{C}_9\text{H}_3\text{O}_6)(\text{H}_2\text{O})_4](\text{H}_2\text{O})_2$ $\text{M} = \text{Co}$ and Ni are isostructural to the known Mn complex. $[\text{M}(\text{HC}_9\text{H}_3\text{O}_6)(\text{H}_2\text{O})](\text{H}_2\text{O})_2$ $\text{M} = \text{Mg}$ and Co are isostructural to the known Fe complex. The hydrogen bonding in these compounds and in $[\text{Cu}(\text{HC}_9\text{H}_3\text{O}_6)(\text{H}_2\text{O})_{1.5}](\text{H}_2\text{O})$ have been quantified using quantum calculations.