

MS32-P19 Oleanolic Acid: A Case Study of the Control and Suppression of Solvate Crystals and its Potential for Chiral Resolution

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Oleanolic Acid (OA-H) a natural triterpene of pharmaceutical interest has been found to form solvate crystals from a wide range of solvents.[1][2] The control of solvate versus anhydrous phase formation is demonstrated for a variety of alcohols, with characterization by pXRD, TGA and single-crystal XRD. It appears that the product formation can be correlated to the temperature of crystallization.

OA-H has also demonstrated the ability to form diastereomeric salts with various amines, in particular the formation of diastereomeric salts of OA-H with racemic amines for the purpose of chiral resolutions have been studied. Following on from the solvate phases prepared and the potential of OA-H to form cocrystals with other chiral compounds, the potential of OA-H as a resolving agent for a variety of chiral alcohols has also been explored with promising results.

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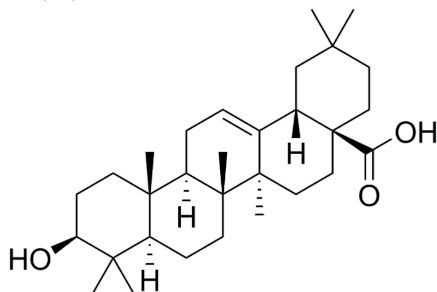


Figure 1. Oleanolic Acid Structure

Keywords: Solvates, cocrystals, chiral resolution

MS32-P20 From 0D to 3D - The structural diversity of polyoxometalate catalysts

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Polyoxometalates (POMs) are metal oxo clusters which are preferably formed by W, Mo and V in their high oxidation states. Among their remarkable spectrum of potential applications, POMs have widely been investigated as homogeneous and heterogeneous catalysts for organic reactions and as catalysts for artificial photosynthesis.[1] It was shown that the extent of Co/W disorder in the transition metal core of Co/Bi-sandwich type POMs based on the lacunary precursor $\text{Na}_9[\text{B}-\alpha\text{-BiW}_9\text{O}_{33}]$ is a key feature for their activity as water oxidation catalysts (WOCs).[2] In order to understand the origin of the catalytic activity, POMs were prepared from $\text{Na}_9[\text{B}-\alpha\text{-BiW}_9\text{O}_{33}]$ in the presence of Mn(II), Co(II), and Cu(II) cations. Efforts were made to prepare compounds with a specific composition of the transition metal core. Single crystal X-ray diffraction studies of the new transition metal containing POMs have revealed a large structural diversity of polyanions, which is due to α - β isomerization and partial decomposition of the lacunary precursor. Cross-linking of polyanions via supplementary d- or f-block counter cations resulted in the formation of 1D, 2D, and even 3D networks.[3] The polyanion $[\text{Cu}_4(\text{H}_2\text{O})_4(\text{B}-\beta\text{-BiW}_{10}\text{O}_{32})]^{10-}$ crystallized with a 2D structure in the presence of Na^+ and K^+ cations, while Rb^+ cations favored the crystallization of the 0D structure $\text{Na}_6\text{Rb}_4[\text{Cu}_3(\text{H}_2\text{O})_3(\text{B}-\alpha\text{-BiW}_9\text{O}_{33})_2]$ from the same reaction mixture. The importance of the counter cations as structure-directing parameter could thus be highlighted.

The negative charge of polyanions can be exploited to prepare new compounds with interesting properties by introducing of a transition metal complex as the counter cation. Crystals could be grown from $[\text{Mn}_3(\text{H}_2\text{O})_3\{\text{As}_5\text{W}_{18}\text{O}_{66}\}]^{8-}$ as a potential WOC and the photoensitizer cation $[\text{Ru}(\text{bpy})_3]^{2+}$. Crystal structure determination confirmed the formation of $[\text{Ru}(\text{bpy})_3]_4[\text{Mn}_3(\text{H}_2\text{O})_3\{\text{As}_5\text{W}_{18}\text{O}_{66}\}]$ from which crucial structural details could be deduced.

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