

HEXANUCLEAR PIVALATE IRON(III) CLUSTER WITH A FUNCTIONALIZED SALICYLALDEHYDE

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In the last two decades there is a continuing search for new synthetic methods that can yield new polynuclear molecular species with unusual or novel magnetic properties. In this paper, we describe the use of aldehyde-based chelate ligand, 3-formylsalicylic acid, for the synthesis of new Fe clusters. From a structural point of view, this ligand could be compared with salicylaldehyde, which is further substituted by a carboxylic group in metha position to the hydroxy group. The approach we employed was the use of trinuclear species that have proven previously to be excellent starting points for the synthesis of high nuclearity iron(III) clusters.

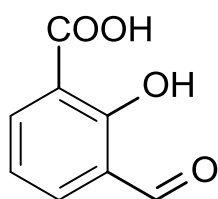


Fig.1. 3-formylsalicylic acid

Reaction of oxotrinuclear iron(III) pivalate $[\text{Fe}_3\text{O}(\text{piv})_6(\text{H}_2\text{O})_3]$ with 3-formylsalicylic acid (H_2L^1) yields a new hexanuclear cluster $[\text{Fe}_6\text{O}_2(\text{OH})_2(\text{L}^1)_2(\text{H}_2\text{O})_2(\text{piv})_8] \cdot \text{MeCN}$ (**1**). The X-ray analysis revealed that the unit cell of **1** consists of two independent hexanuclear clusters and two solvate MeCN molecules. All iron atoms adopt distorted octahedral coordination geometry and are in the +3 oxidation state. Each hexanuclear cluster with the $\{\text{Fe}_6\text{O}_2(\text{OH})_2\}$ core is formed of one μ_3 -oxotrinuclear cluster and its symmetry equivalent cluster ($\text{Fe}-\text{O}_{\mu_3}$ - 1.882-1.956 Å) linked by two μ_2 -OH groups ($\text{Fe}-\text{O}_{\text{OH}}$ - 1.991-1.998 Å) and two bridging pivalate ligands ($\text{Fe}-\text{O}_{\text{carb.}}$ - 2.025-2.067 Å) (Fig. 2).

The peripheral ligation of metal ions in **1** is completed by six pivalate molecules and two aldehyde ligands which are in their monoanionic ($(\text{CH}_3)_3\text{CCO}_2^-$) and dianionic forms (L^{2-}), respectively ($\text{Fe}-\text{O}_{\text{Lcarb}}$ - 1.996-2.006 Å; $\text{Fe}-\text{O}_{\text{ald}}$ - 2.081-2.088 Å). The two L^{2-} ligands are coordinated in the $\mu_1:\mu_2:1$ mode, their hydroxy groups bridging two iron ions within each $[\text{Fe}_3(\mu_3\text{-O})]^{7+}$ unit ($\text{Fe}-\text{O}_{\text{OH}}$ - 2.031-2.058 Å). The latter are located on opposite sides of the plane of the molecule, thus the structural core of **1** displays the *trans* conformation. The deprotonated state of the carboxylic group of the ligand is evident from the short C=O bond length 1.231-1.237 Å. The pivalate groups adopt the syn,syn- $\mu_1:\mu_1:\eta$ coordination mode with two of them bridging two edges of the triangular $[\text{Fe}_3(\mu_3\text{-O})]^{7+}$ units and the remaining six linking Fe atoms within the latter.

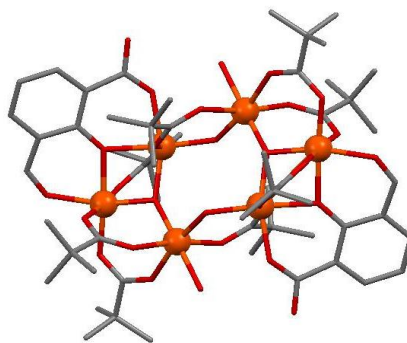


Fig.2. The molecular structure of complex $[\text{Fe}_6\text{O}_2(\text{OH})_2(\text{L}^1)_2(\text{H}_2\text{O})_2(\text{piv})_8]$

Previously the same synthetic strategy, where a benzaldehyde derivative and carboxylate act cooperatively as multiply bridging ligands, was reported for manganese(II) ions and led to formation of helical chains [1].

References

[1] G. Dulcevscaia, Sh-X. Liu, J. Hauser, K. W. Krämer, G. Frei, A. Möller, and S. Decurtins. *Cryst. Growth Des.* 2013, 13, 4138–4144.