New members of the [Mn_6/oxime] family and analogues with converging [Mn_3] planes.

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Rok wydania

2016

Czasopismo

Journal of Coordination Chemistry

Numer woluminu

69

Strony

826-840

DOI

10.1080/00958972.2016.1152359

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The synthesis, structural, and magnetic characterization of five new members of the hexanuclear oximate [Mn^{III}_6] family are reported. All five clusters can be described with the general formula [$Mn^{III}_6O_2$(R-sao)$_6$(R′-CO_2)$_2$(sol)$_x$(H_2O)$_y$] (where R-saoH_2 = salicylaldoxime substituted at the oxime carbon with R = H, Me and Et; R′ = 1-naphthalene, 2-naphthalene, and 1-pyrene; sol = MeOH, EtOH, or MeCN; x = 0–4 and y = 0–4). More specifically, the reaction of $Mn(ClO_4)_2$·$6H_2O$ with salicylaldoxime-like ligands and the appropriate carboxylic acid in alcoholic or MeCN solutions in the presence of base afforded complexes **1**–**5**: [Mn_6O_2(Me-sao)$_6$(1-naphth-CO_2)$_2$(H_2O)(MeCN)]·4MeCN (**1**·4MeCN); [Mn_6O_2(Me-sao)$_6$(2-naphth-CO_2)$_2$(H_2O)(MeCN)]·3MeCN·0.1H_2O (**2**·3MeCN·0.1H_2O); [Mn_6O_2(Et-sao)$_6$(2-naphth-CO_2)$_2$(EtOH)$_4$(H_2O)$_2$] (**3**); [Mn_6O_2(Et-sao)$_6$(2-naphth-CO_2)$_2$(MeOH)$_6$] (**4**) and [Mn_6O_2(sao)$_6$(1-pyrene-CO_2)$_2$(H_2O)$_2$(EtOH)$_2$]·6EtOH (**5**·6EtOH). Clusters **3**, **4,** and **5** display the usual [Mn_6/oximate] structural motif consisting of two [Mn_3O] subunits bridged by two $O_{oximate}$ atoms from two R-sao^{2-} ligands to form the hexanuclear complex in which the two triangular [Mn_3] units are parallel to each other. On the contrary, clusters **1** and **2** display a highly distorted stacking arrangement of the two [Mn_3] subunits resulting in two converging planes, forming a novel motif in the [Mn_6] family. Investigation of the magnetic properties for all complexes reveal dominant antiferromagnetic interactions for **1**, **2,** and **5**, while **3** and **4** display dominant ferromagnetic interactions with a ground state of S = 12 for both clusters. Finally, **3** and **4** display single-molecule magnet behavior with U_{eff} = 63 and 36 K, respectively.

Słowa kluczowe

Mn(III) oximate complexes, single-molecule magnets, converging [Mn3] planes, magnetic properties