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New Synthetic Route toward Heterometallic 3d–3d′ and 3d–4f Single-Molecule Magnets. The First Co^{II}–Mn^{III} Heterometallic Complex

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Supporting Information

ABSTRACT: Four tetranuclear heterometallic complexes, $[Co^{II}_2Mn^{III}_2(dpm)_4(MeO)_6]$ (**1**) and $[Ln^{III}_2Mn^{III}_2(dpm)_6(MeO)_6(MeOH)_n]$, where Ln = Gd (**2**, *n* = 2), Tb (**3**, *n* = 2), and Dy (**4**, *n* = 0), have been obtained following the same general synthetic route, namely, the one-pot reaction between 2,2,6,6-tetrametil-3,5-heptanodione (Hdpm), $MnCl_2$ and $CoCl_2$ or $Ln(NO_3)_3$ in the presence of sodium methoxide. Within the four compounds, the metal ions bridged by methoxide ligands display a defect-diheterocubane core. Compounds **1**, **3**, and **4** show slow relaxation of the magnetization below 4 K.

Multimetallic coordination compounds based on β-diketonate ligands present a rich variety of nuclearities and structures.[1] Numerous compounds of this family are particularly important in the field of molecular magnetism because they display slow relaxation of the magnetization and quantum effects at low temperatures.[2] These complexes, known as single-molecule magnets (SMMs), are potential candidates for applications in high-density information storage or quantum computing.[3] Since the discovery of the first SMM in 1993,[4] considerable efforts have been made in order to increase the blocking temperature, that is, to increase the energy barrier for magnetization reversal. Recently, it has been shown that SMMs can be chemically grafted on conductive surfaces, maintaining their SMM properties and confirming the possibility of using them in devices where they can be connected to noninnocent metals.[5] The height of the energy barrier arises from a molecular uniaxial anisotropy associated with a nonzero spin ground state. One of the strategies to achieve this goal is the use of metal ions with a strong uniaxial magnetic anisotropy, e.g., Mn^{III}, Co^{II}, Tb^{III}, Dy^{III}, and Ho^{III}. Such nanomagnets contain at least one of these ions or combinations of them, as illustrated by classical examples reported previously.[6] Herein we report the syntheses, crystal structures, and magnetic behavior of four tetranuclear heterometallic complexes with a Mn_2M_2 core: $[Co^{II}_2Mn_2^{III}(dpm)_4(MeO)_6]$ (**1**) and $[Ln^{III}_2Mn^{III}_2(dpm)_6(MeO)_6(MeOH)_n]$ where Ln = Gd (**2**, *n* = 2), Tb (**3**, *n* = 2), and Dy (**4**, *n* = 0). Compound **1** represents the first heterometallic complex containing Mn^{III} and Co^{II} ions. The four compounds have been obtained following the same synthetic strategy. The synthesis consists in a one-pot reaction, in which $MnCl_2$ and $CoCl_2$ or $Ln(NO_3)_3$ are reacted with 2,2,6,6-tetrametil-3,5-heptanodione (Hdpm) with the further addition of a 30% sodium methoxide solution (see the Supportig Information, SI). In these syntheses, the Mn^{II} ions are oxidized in situ to Mn^{III}. The crystal structure of four complexes consists of a M_2Mn_2 core, in which metal ions and the bridging methoxo groups describe a defect-diheterocubane topology. Table S1 in the SI contains a summary of data collection and refinement of the crystal structures of compounds **1**–**4**. Selected bond lengths and angles are listed in Table S2 (SI). In all of these complexes (Figure 1), Mn^{III} ions are located on the face shared between two defective cubanes. Each Mn^{III} ion lies on a distorted octahedral environment, being coordinated by one dmp^- and four methoxide ligands. Because of the Jahn–Teller distortion expected for d^4 metal ions, the bond lengths in the axial positions are longer than those observed for the equatorial ones in all compounds [for **1**, Mn1–O2 = 2.125(3) Å and Mn1–O4^i = 2.299(2) Å; for **2**, Mn1–O2 = 2.326(7) Å and Mn1–O9 = 2.08(1) Å; for **3**, Mn1–O1 = 2.317(6) Å and Mn1–O10 = 2.141(7) Å; for **4**, Mn1–O1 = 2.288(7) Å and Mn1–O10 = 2.151(7) Å]. It is important to stress that the Jahn–Teller axes of the Mn^{III} ions are parallel to each other in **1**–**4** and to the bridging methoxide plane. Although the molecular structures of the four compounds are similar, they differ when the coordination spheres of Co^{II} and Ln^{III} are compared. In **1**, the Co^{II} ions are pentacoordinated by one dmp^- ligand and by three

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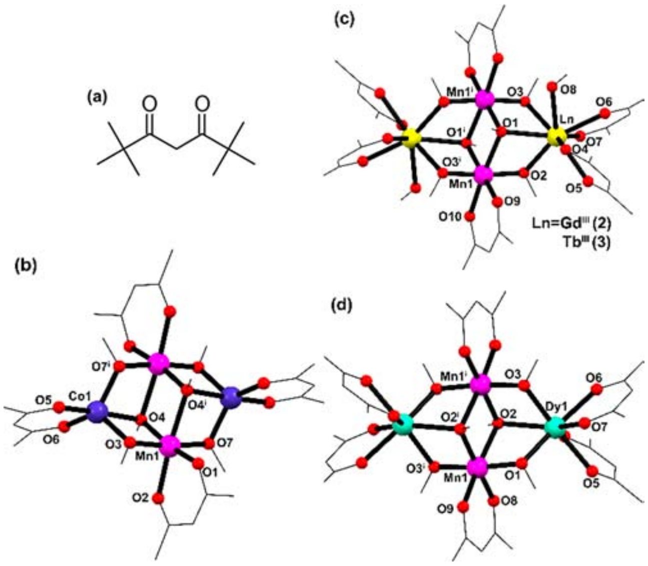

Figure 1. Hdpm (a) and the molecular structures of compounds **1** (b), **2** and **3** (c), and **4** (d). dpm⁻ methyl groups and hydrogen atoms were omitted for the sake of clarity (i: −*x*, −*y*, −*z*).

methoxide bridges. The value of the trigonality parameter (τ) is 0.4 and indicates that Co^{II} ions are in an intermediate geometry between square-pyramidal and trigonal-bipyramidal.[7] Within compounds **2** and **3**, the Ln^{III} ions are coordinated by two β-diketonate anions, one methanol molecule, and three bridging methoxide ligands. The lanthanide ions in **4** lie on a pentagonal-bipyramidal geometry, coordinated to two dmp⁻ ligands and bridged to the Mn^{III} ions through three methoxide ligands. Compounds **1**−**4** present three pairs of faces in the defect-diheterocubane framework with different bridging angles; the average angles Mn−O−M are 100.32(1)°, 105.90(3)°, 104.37(3)°, and 105.57(3)°, respectively for compounds **1**−**4**, while the Mn1−O−Mn1^{i} angles are slightly smaller, except for the Mn$_2$Co$_2$ derivative [102.4(1)° for **1**; 99.20(3)° for **2**; 99.30(3)° for **3**; 100.1(3)° for **4**]. Intramolecular hydrogen bonding between the alcohol hydroxyl group and the adjacent β-diketonate oxygen atom is present in compounds **2** and **3**, with distances between the donor (O8) and acceptor (O10^{ii} in **2**, ii: −*x*+2, −*y*+1, −*z*+1 and O10^{iii} in **3**, iii: −*x*, −*y*+1, −*z*) atoms of 2.737 Å and 2.692 Å, while the D−H···A angles are 131° and 168°, respectively.

The magnetic properties have been investigated in the temperature range 2−300 K. The thermal dependences of the $\chi_M T$ product for the four compounds are presented in Figure 2. The room temperature values of $\chi_M T$ are 9.6 (for **1**), 21.7 (for **2**), 30.2 (for **3**), and 34.6 cm^3 mol^{-1} K (for **4**), close to the expected values for noninteracting ions (9.7, 21.7, 29.6, and 34.4 cm^3 mol^{-1} K, respectively). The match of the experimental and calculated $\chi_M T$ values for **1** confirms that Co^{II} ions are pentacoordinated because the orbital contribution is quenched as a result of a reduction of the symmetry compared with the octahedral geometry. Upon cooling, $\chi_M T$ remains constant and decreases at lower temperature, indicating predominant antiferromagnetic interactions and/or zero-field splitting (ZFS) effects. In order to characterize the magnetic coupling and the magnetic anisotropy of this compound, an isotropic spin Hamiltonian (eq 1) describing the exchange interactions within this spin topology[8,9] as well as the uniaxial anisotropy of Mn^{III} and Co^{II} ions was used:

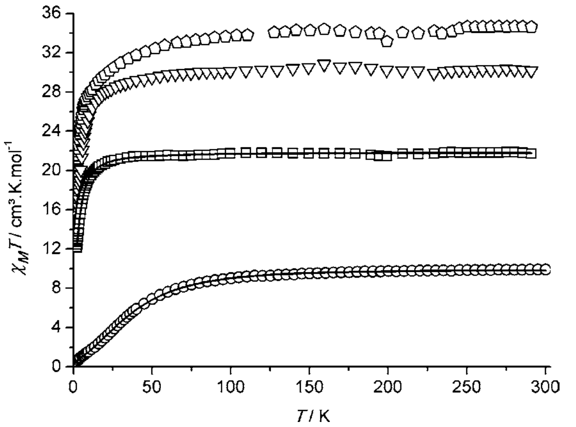

Figure 2. Thermal dependence of $\chi_M T$ product for **1** (circles), **2** (squares), **3** (triangles), and **4** (pentagons) at H = 0.1 T. The solid lines represent the best fit.

$$\hat{H} = -J_1(\vec{S}_{Mn1}\cdot\vec{S}_{Mn2}) - J_2(\vec{S}_{Mn1}\cdot\vec{S}_{Co1} + \vec{S}_{Mn1}\cdot\vec{S}_{Co2} + \vec{S}_{Mn2}\cdot\vec{S}_{Co1} + \vec{S}_{Mn2}\cdot\vec{S}_{Co2}) + D_{Mn}S_{Mn,z}^{\ 2} + D_{Co}S_{Co,z}^{\ 2} \tag{1}$$

where J_1 represents the Mn···Mn interaction and J_2 denotes the Mn···Co one. Calculations were performed with the *MagProp* routine, available under *DAVE*.[10] The solid line in Figure 2 shows the best fit for **1** found with g = 2.05, J_1 = 11.7 cm^{-1}, J_2 = −5.8 cm^{-1}, D_{Mn} = −3.6 cm^{-1}, and D_{Co} = −5.4 cm^{-1}. The J_1 value is within the range for Mn^{III}−Mn^{III} interactions reported for other similar tetranuclear compounds[8] and dinuclear complexes.[12] The fit made without taking into account the anisotropy leads to nonrealistic values of the J parameters. Recent magnetostructural correlations supported by density functional theory calculations for Mn^{III} dimers show that the nature and magnitude of the exchange interaction between alkoxo-bridged Mn^{III} dimers are strongly influenced by the following: (i) Mn−O−Mn angle; (ii) Mn−O distance; (iii) out-of-plane shift of the methyl group from the methoxide bridge; (iv) relative orientation of the Jahn−Teller axes of the two Mn^{III} ions.[12a] Compound **1** belongs to the type II structures within the classification made by Rajaraman and Jones.[a] For these compounds, the J values range from weakly antiferromagnetic to quite significant ferromagnetic interactions (J = 12.6 cm^{-1}). The D_{Mn} value falls within the range reported for related elongated six-coordinate high-spin Mn^{III} complexes.[13] Because Co^{II} ions are in a quite distorted geometry, intermediate between square-pyramidal and trigonal-bipyramidal ones, it seems difficult to compare the D_{Co} values found here; however, it is quite consistent with a recent semiquantitative estimation of the ZFS parameters for mononuclear first-row transition-metal complexes.[14] In the case of compound **2**, the Hamiltonian was slightly modified considering $S = {}^7/_2$ for Gd^{III} ions and anisotropy only for Mn^{III} ions. The best fit of the magnetic data was achieved with g = 2.01 (fixed), J_1 = 0.38 cm^{-1}, J_2 = −0.18 cm^{-1}, and D_{Mn} = −3.79 cm^{-1}. The obtained J_1 and J_2 values are in agreement with the reported ones for other similar tetranuclear compounds.[9] The isothermal field dependence of the magnetization for **1**−**4** does not show a hysteresis cycle.

The dynamic properties of compounds **1**−**4** were investigated by temperature- and frequency-dependent alternating-current (ac) magnetic susceptibility measurements in the ranges of 2−9 K and 10 Hz−10 kHz. Figure 3 shows the thermal dependence of the in-phase (χ') and out-of-phase (χ'') susceptibilities for **4**. The

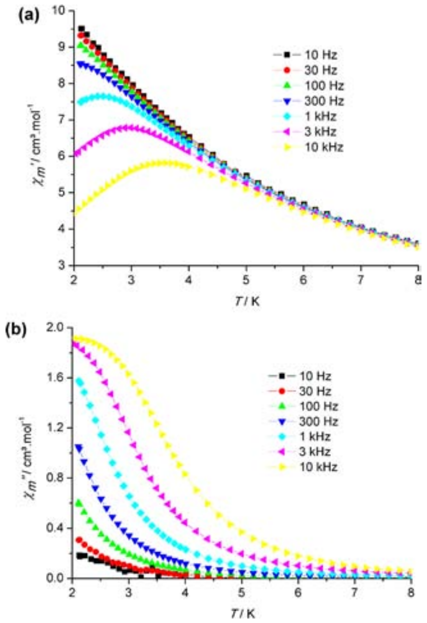

Figure 3. Thermal dependence of (a) the in-phase (χ') and (b) out-of-phase (χ'') susceptibility components for **4** at H_{dc} = 0 T.

respective thermal dependence for compounds **1**−**3** is depicted in Figure S2 in the SI. Compounds **1**, **3**, and **4** exhibit slow relaxation of its magnetization, with a clear frequency dependence in the in-phase (χ') and out-of-phase (χ'') susceptibilities, although no maximum in χ'' was observed down to 2 K. On the contrary, no frequency dependence was evidenced in **2**. It is well-known that in SMM the energy barrier responsible for the relaxation process can be tuned by a magnetic field. Therefore, the ac susceptibilities of **3** and **4** were measured under a static magnetic field (Figure S3 in the SI). For both compounds, the in-phase and out-of-phase signals moved to higher temperatures, which is a signature of quantum tunneling of the magnetization in zero field. Because the maxima of χ_M'' occur below 2.0 K, we could not go further in the analysis of the slow relaxation processes. The value of the relative variation of the χ' peak temperature (T_f) per decade frequency $\{K = \Delta T_f/[T_f\,\Delta(\log f)]\}$ for **4** is 0.27, typical for compounds with superparamagnetic behavior.[15]

In summary, we described here a new route that allows for the synthesis of tetranuclear heterometallic SMMs containing 3d−3d′ and 3d−4f ions. Compound **1** is, to the best of our knowledge, the first polynuclear compound containing both Mn^{III} and Co^{II} ions. Further work on other heterometallic complexes obtained following this strategy is in progress in our laboratory and will be reported in subsequent papers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, experimental section, crystallographic data information (Tables S1 and S2), asymmetric units of **1**−**4** (Figure S1) and ac magnetic data for compounds **1**−**4** (Figures S2 and S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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