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Synthesis and Structure of Heterospin Compounds Based on the $[Mn_6(O)_2Piv_{10}]$-Cluster Unit and Nitroxide

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Reaction of $[Mn_6(O)_2Piv_{10}(Thf)_4]\cdot Thf$ with 2,4,4,5,5-pentamethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxyl (NIT-Me) produces different heterospin compounds depending of the solvent used in the synthesis. Among the latter a new molecular magnet $[Mn_6(O)_2Piv_{10}(Thf)_2(NIT\text{-}Me)Mn_6(O)_2Piv_{10}(Thf)(CH_2Cl_2)(NIT\text{-}Me)]$ with $T_c = 3.5$ K has been found.

Manganese oxocarboxylate clusters $[Mn^{II}_xMn^{III(IV)}_yO_z]$ belong to the group of extensively studied compounds. More than 250 oxocarboxylate species with nuclearity 3, 4, 6−14, 18, and 30 manganese atoms have been structurally characterized.[1] Mixed-valent manganese compounds attract strong interest as potential models for the oxygen-evolving complexes of photosystem II.[2] Moreover, for some of these metal clusters, atypical magnetic behavior with slow relaxation of magnetization at low temperatures has been found, and a specific family of single-molecule magnets (SMMs) has been created. SMMs are of great current interest because they represent nanoscale magnetic domains of sharply defined size that offer, among other things, the potential of access to the ultimate high-density information storage devices.[3] However, when "interdomain" interaction in SMMs is antiferromagnetic, the total magnetic moment of the system generally tends to zero at reduced temperatures. This can be avoided by linking the polynuclear fragments of $[Mn^{II}_xMn^{III(IV)}_yO_z]$ with an additional paramagnetic bridge whose spin differs from that of $[Mn^{II}_xMn^{III(IV)}_yO_z]$. We attempted to design heterospin structures by using stable nitronyl nitroxide (2,4,4,5,5-pentamethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxyl, NIT-Me) as a bridge between the cluster nuclei of $[Mn_6(O)_2Piv_{10}]$, where Piv is the trimethylacetate anion. We also note that inside the $[Mn_6(O)_2Piv_{10}]$ cluster nucleus, the two "central" Mn atoms are in the oxidation state III, and the other four terminal Mn atoms are in the oxidation state II.[4c,11b] Unexpectedly, we revealed that reaction of $[Mn_6(O)_2Piv_{10}(Thf)_4]\cdot Thf$ (**1**), where Thf is a tetrahydrofuran molecule, with NIT-Me is insensitive to the initial **1**/NIT-Me ratio and produces essentially different products depending of the solvent used in the synthesis.

Cluster **1** was prepared by using the method described elsewhere[4a] with a slight modification.[5] The choice of **1** was

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(5) Modifications have been made: KPiv was used in the synthesis instead of NaPiv. An excess of KPiv was not introduced in the reaction. In the course of synthesis, the reaction mixture was intermittently heated, and evaporated MeOH was added to keep the volume of the mixture at a constant level of ∼20−30 mL. After recrystallization of the crude product, **1** was obtained in a nearly quantitative yield and as perfect single crystals. The structure of **1** was described elsewhere;[5] *R*-factor 5.95%. We succeeded in growing single crystals of slightly better quality (*R*-factor 3.59%). In the CCDC, the data are stored under CCDC 227585.

(6) Synthesis of **2**: A solution of **1** (0.028 mmol) in heptane (or CCl_4) (7 mL) was carefully poured through a filter down the flask wall into a solution of NIT-Me (0.056 mmol) in heptane (or CCl_4) (7 mL). After a day, dark-blue crystals suitable for X-ray diffraction studies were collected. Yield: >40%. Anal. Calcd for $C_{66}H_{120}Mn_6N_4O_{26}$: C 46.21, H 7.05, N 3.27. Found: C 45.78, H 7.31, N 3.21. Synthesis of **3**: To a solution of **1** (0.028 mmol) in CH_2Cl_2 (3 mL) was added a solution of NIT-Me (0.056 or 0.112 or 0.280 mmol) in CH_2Cl_2 (2 mL). The solvent was gradually evaporated; after a day, X-ray quality dark-red crystals formed. Yield: >50%. Anal. Calcd for $C_{129}H_{236}Cl_2Mn_{12}N_4O_{51}$: C 45.71, H 7.02, N 1.65. Found: C 45.33, H 6.87, N 1.63. Synthesis of **4**: To a solution of **1** (0.028 mmol) in warm EtOAc (3 mL) was added a solution of NIT-Me (0.056 or 0.112 mmol) in EtOAc (2 mL). Yellow crystals suitable for X-ray diffraction studies were obtained by slow evaporation for 1 day. Yield: 45%. Analysis was performed for the desolvated product. Calcd for $C_{108}H_{195}Mn_{12}N_2O_{46}$: C 44.47, H 6.74, N 0.96. Found: C 44.91, H 6.92, N 0.96. NIT-Me was synthesized by the classical approach.[7]

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(10) The magnetic measurements were carried out on a SQUID Quantum Design magnetometer. Molar magnetic susceptibility was measured in a magnetic field of 5000 Oe.

10.1021/ic049859y CCC: $27.50

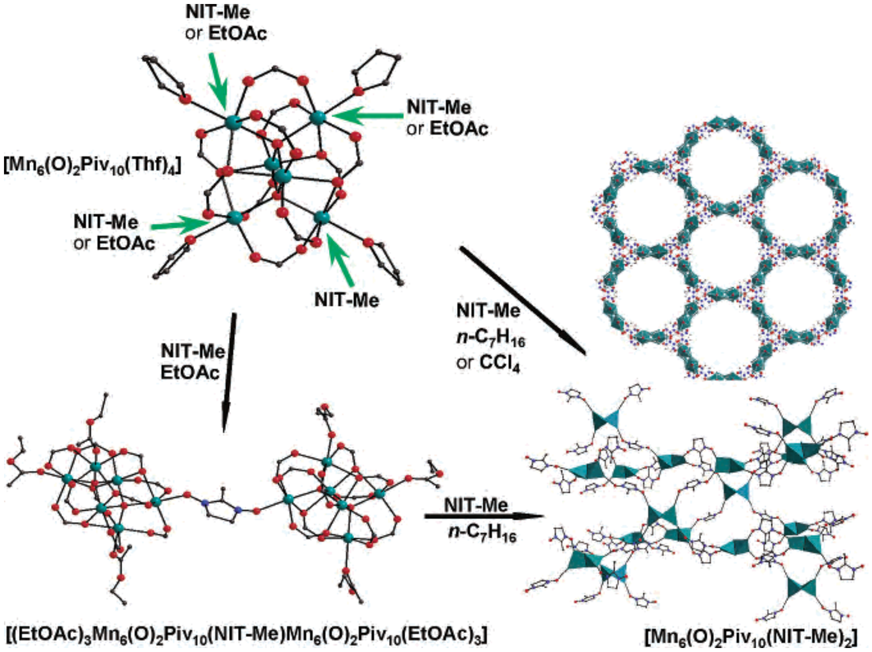

Figure 1. Formation of 3D diamond-like frame **2** and dumbbell-like molecules **4** (CH_3 and $(CH_3)_3C$ groups of ligands are omitted for clarity).

dictated by the fact that this compound has four monodentate terminal Thf molecules (in Figure 1, their coordination sites are marked by green arrows), and we hoped to be able to replace them by nitroxide. In other words, we would like to use [$Mn_6(O)_2Piv_{10}$] as a tectonic fragment with connectivity 4. At the same time, monodentate terminal Thf has to act as molecules weakly bonded to the cluster nuclei [$Mn_6(O)_2$-Piv_{10}] which is favorable for the replacement of Thf by poor donor NIT-Me. It seemed undesirable to use other structurally defined hexanuclear pivalates, [$Mn_6(O)_2Piv_{10}Py_4$][4b] and [$Mn_6(O)_2Piv_{10}$(t-BuC(O)OH)$_4$],[4c,d] as starting reagents, because Py molecules are difficult to replace and the presence of an acid in the reaction system provokes disproportionation of NIT-Me.[7]

Indeed, the reaction of **1** with NIT-Me in heptane (or CCl_4) led to substitution of all four coordinated Thf molecules and formation of [$Mn_6(O)_2Piv_{10}$(NIT-Me)$_2$] (**2**),[6] possessing a diamond-like frame structure (Figure 1). For clarity, Figure 1 presents the structure as a combination of Mn polyhedra and nitroxide, and it also shows the structure projected on the (001) plane, clearly demonstrating the honeycomb motif. The latter is formed from 60-membered rings based on the least perimeter (Figure 1).

In the reaction of **1** with NIT-Me in CH_2Cl_2, only some of the coordinated Thf molecules are substituted. Irrespective of the initial **1**/NIT-Me ratio, the reaction always leads to crystallization of [$Mn_6(O)_2Piv_{10}$(Thf)$_2$(NIT-Me)$Mn_6(O)_2$-Piv_{10}(Thf)(CH_2Cl_2)(NIT-Me)] chain polymer (**3**), in which half of all coordination sites are occupied by Thf and CH_2-Cl_2 molecules (Figure 2). Although they have Thf and CH_2-Cl_2 molecules and long Mn−O$_{Thf}$ and Mn−Cl distances (2.615−2.797 and 3.685 Å, respectively), single crystals **3** do not decay when stored in a refrigerator for a long time.

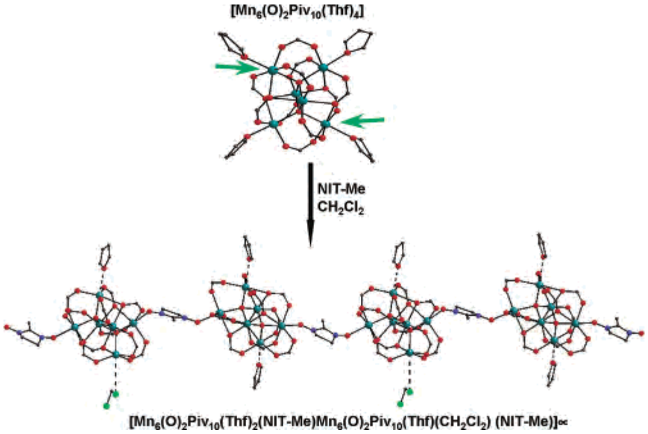

Figure 2. Structure of chain **3** (CH_3 and $(CH_3)_3C$ groups of ligands are omitted for clarity).

The interaction of **1** with NIT-Me in ethyl acetate leads to crystallization of nanosized (∼30 Å along the molecular axis) dumbbell-like [(EtOAc)$_3Mn_6(O)_2Piv_{10}$(NIT-Me)$Mn_6(O)_2$-Piv_{10}(EtOAc)$_3$] molecules (**4**), in which the two [$Mn_6(O)_2$-Piv_{10}] cluster fragments are linked by one NIT-Me bridging molecule, and the other six coordination sites are occupied by ethyl acetate molecules (Figure 1). Since the initial **1**/NIT-Me ratio is irrelevant to the formation of **4**, as in the case of the compounds discussed above, the solvent used is evidently the critical factor determining the product of the reaction of **1** with NIT-Me. This is also indicated by the fact that treatment of **4** with an excess of NIT-Me in heptane leads to frame compound **2** (Figure 1).

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Inside the [$Mn_6(O)_2Piv_{10}$] fragment, the Mn_6O_2 group is generally defined as two [Mn_4O] tetrahedra sharing a Mn−Mn edge.[4] In **2**−**4**,[8] the length of this edge (2.801−2.828 Å) is much smaller than the lengths of all other edges (3.101 Å). The Mn−O distances to the O atom at the center of the tetrahedron are 1.874(6)−1.918(8) Å for the Mn atoms of the common edge and 1.942(4)−2.191(3) Å for the terminal Mn atoms. The environment of the Mn atoms of the common edge is completed to a distorted octahedron by the O atoms of the pivalate ligands. For the terminal Mn atoms, four equatorial positions are occupied by the O atoms of the bridging pivalates, and the sixth vertex of the octahedron is filled by the O atom of NIT-Me, Thf, or EtOAc or the Cl atom of the CH_2Cl_2 molecule. For Piv ligands, the Mn−O_{Piv} bond lengths are from 2.203(5) to 2.310(6) Å, whereas for monodentate ligands bonded to the [$Mn_6(O)_2Piv_{10}$] fragments, the Mn−$O_{(NIT-Me,Thf,EtOAc)}$ bonds are slightly longer, 2.316(4)−2.338(7) Å. In **2**-**4**, the [$Mn_6(O)_2Piv_{10}$] fragment does not change its structural characteristics. The same holds for NIT-Me, except that in the coordinated paramagnetic ligand the N−O bonds are slightly longer compared to free NIT-Me (1.279(2) Å in free NIT-Me[9] versus 1.27(1)−1.33(1) Å for N−O in the coordinated NIT-Me groups in the compounds under study).

The magnetic properties[10] of hexanuclear carboxylates of [$Mn_6(O)_2(RCOO)_{10}(L)_4$] type, where L is a monodentate diamagnetic ligand (Py, EtOH, CH_3CN) exhibiting spin frustration, are well documented.[11a−c] On the basis of the results of these studies, one would expect that at high temperatures the effective magnetic moment (μ_{eff}) of heterospin clusters with nitroxides will tend to the theoretical values of 10.86, 11.36, and 16.40 μ_B for **2**−**4**, respectively. In these calculations, it is assumed that, in the [$Mn_6(O)_2Piv_{10}$] cluster unit, the moments of the "inner" two Mn(III) ions lying at very short distances of ∼2.8 Å fully compensate each other as a result of a strong antiferromagnetic interaction[4c,11a,b] and that the moment of one of the odd electrons of the terminal Mn(II)[11d] is completely canceled by the odd electron of the coordinated NIT-Me again due to the antiferromagnetic interaction with the cluster nucleus. The calculated values of μ_{eff} obtained in this approximation are close to the experimental values of 10.8, 11.3, and 15.9, respectively (Figures 3 and 4). The decreased values of μ_{eff} at reduced temperatures indicate that antiferromagnetic exchange interactions prevail in all solid compounds under study. Compounds **2** and **4** are paramagnetic over the whole range of measurements, as confirmed by the field dependences of magnetization versus the magnetic field strength (Figure 3, inset). Compound **3**, however, shows a different behavior at low temperatures. Below 3.5 K, **3** exhibits antiferromagnetic ordering with a weak ferromagnetic effect (Figure 4, insets). The ordering temperature was evaluated from the magnetic susceptibility curve in a low magnetic field. The sample was subjected to zero-field cooling (ZFC). Magnetization above 200 Oe is defined by the function $\sigma = \sigma_s + \chi H$, where spontaneous magnetization σ_s at 2 K amounts to 2800 G·cm^3/mol or ∼0.5 μ_B (inset b, Figure 4). Analysis of the magnetization dependence $\sigma(H)$ did not reveal any hysteresis within the error of measurement. To the best of our knowledge, **3** is the first example of a molecular magnet based on a metal cluster unit and nitroxide.

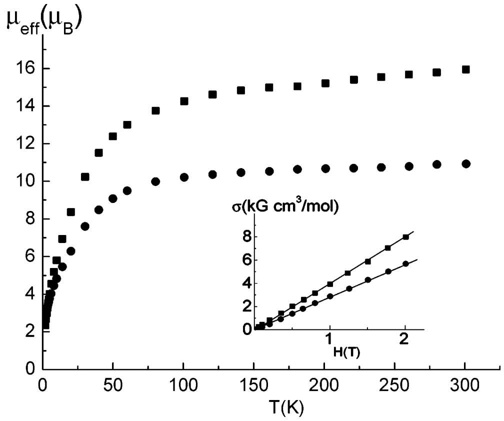

Figure 3. Dependences $\mu_{eff}(T)$ for **2** (●) and **4** (■). Inset: dependences $\sigma(H)$ for **2** (●) and **4** (■) at 2 K.

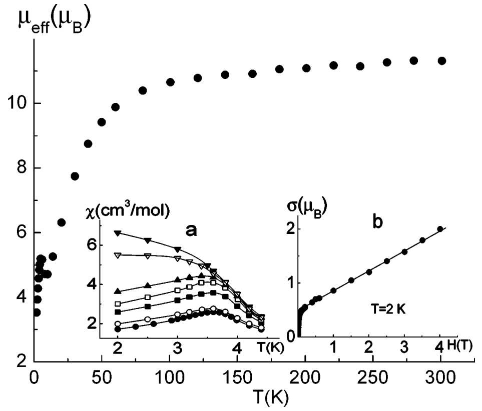

Figure 4. Dependence $\mu_{eff}(T)$ for **3** (●). Inset a: dependence $\chi(T)$ for **3** in different magnetic fields: 6 Oe (●), 14 Oe (○), 24 Oe (■), 44 Oe (□), 100 Oe (▲), 150 Oe (▽), and 200 Oe (▼). Inset b: magnetization curve for **3**.

Thus investigation of the products of the interaction of **1** with NIT-Me has revealed a group of heterospin compounds **2**−**4** differing in the composition and structure of the solids. The initial ratio of **1**/NIT-Me turned out to be irrelevant to the formation of definite compound. The solvent used is the critical factor determining the composition and structure of the solid product of the reaction of **1** with NIT-Me.

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Supporting Information Available: Structural determination parameters, crystal and structure refinement data, atomic coordinates, and isotropic displacement parameters for **1**−**4** (in CIF form). This material is available free of charge via the Internet at http://pubs.acs.org.

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