Brief Communications

Competing ferro- and antiferromagnetic interactions in (manganese,sodium)phenylsilsesquioxane with metal oxide fragments

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Magnetic measurements of individual (manganese,sodium)phenylsilsesquioxane containing eight Mn^{II} ions were performed. The magnetic arrangement of manganese ions in this cage-like compound was investigated. The magnetic moment of the cage molecule equals 21 μ_B (at 300 K), that is a consequence of the mutual antiferromagnetic compensation of four Mn^{II} ions, whereas the other four Mn^{II} ions have aligned spins. Hence, this metallasiloxane is a promising compound for the chemical design of molecular nanomagnets. At low temperatures, the antiferromagnetic coupling causes a decrease in the effective magnetic moment (to 16 μ_B at 40 K).

Key words: metallasiloxanes, manganese(II), metal oxide clusters, magnetic measurements, magnetic moment, exchange interaction.

In recent years, high-spin molecules having unique physical properties have attracted great attention.[1—18] These compounds are naturally not abundant. They generally contain transition metal atoms and about ten unpaired electron spins and have a diamagnetic shell formed by organic ligands. This shell shields intermolecular exchange interactions between electrons, which makes the molecule magnetically isolated. Hence, these compounds are referred to as single-molecule magnets (SMMs).[19]

Among this type of compounds studied up to date, manganese acetate, acylate, and benzoate complexes containing manganese ions in different oxidation states as paramagnetic centers are most promising: $[Mn^{IV}_4Mn^{III}_8O_{12}(O_2CCH_3)_{16}(H_2O)_4]\cdot 4H_2O\cdot 2CH_3CO_2H$,[1—7] $[Mn^{IV}_4Mn^{III}_8O_{12}(O_2CC_2H_5)_{16}(H_2O)_3]\cdot 4H_2O$,[8—11] $[Mn^{IV}_4Mn^{III}_8O_{12}(O_2CPh)_{16}(H_2O)_4]\cdot 4H_2O$,[12—14] $Mn^{IV}Mn^{III}_3O_3Cl(O_2CCH_3)_3[PhC(O)CH{=}CPhCO]_3$,[15] $[Mn^{IV}_4Mn^{III}_8O_{12}(O_2CC_6H_4Me\text{-}p)_{16}(H_2O)_4]\cdot$

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 197—200, January, 2012.
1066-5285/12/6101-200

$\cdot(HO_2CC_6H_4Me\text{-}p)$,[16] $Mn^{II}_{16}Mn^{IV}_{14}O_{24}(OH)_8(O_2CCH_2Bu^t)_{32}(H_2O)_2(MeNO_2)_4$,[17] $Mn^{II}_6Mn^{IV}_6O_{12}(O_2CC_6H_4X\text{-}2)_{16}(H_2O)_4$ (X = Br, Cl),[3] and $Mn_{12}O_{12}(O_2CMe)_8(O_2PPh_2)_8(H_2O)_4(CH_2Cl_2)_2$.[18]

In these clusters, intramolecular exchange coupling is often a combination of exchange interactions having different signs for different groups of electrons. As a result, the total spin of the molecule generally does not correspond to the number of unpaired electrons. For example, the number of unpaired electrons in the compound $[Mn^{IV}_4Mn^{III}_8O_{12}(O_2CCH_3)_{16}(H_2O)_4]\cdot 4H_2O\cdot 2CH_3CO_2H$ is 44, whereas the total spin is only 10. These compounds are intermediate between macroscopic magnets and single atoms with a spin, *i.e.*, mesoscopic magnets. Hence, the synthesis of new types of high-spin compounds opens up the possibilities for investigating the nature of exchange interactions and quantum properties at the level of a countable number of spin.

Experimental

The synthesis and structure of the (manganese,sodium)phenylsilsesquioxane (MSPS) under study have been reported earlier.[20] The crystal structure of this compound is shown below.

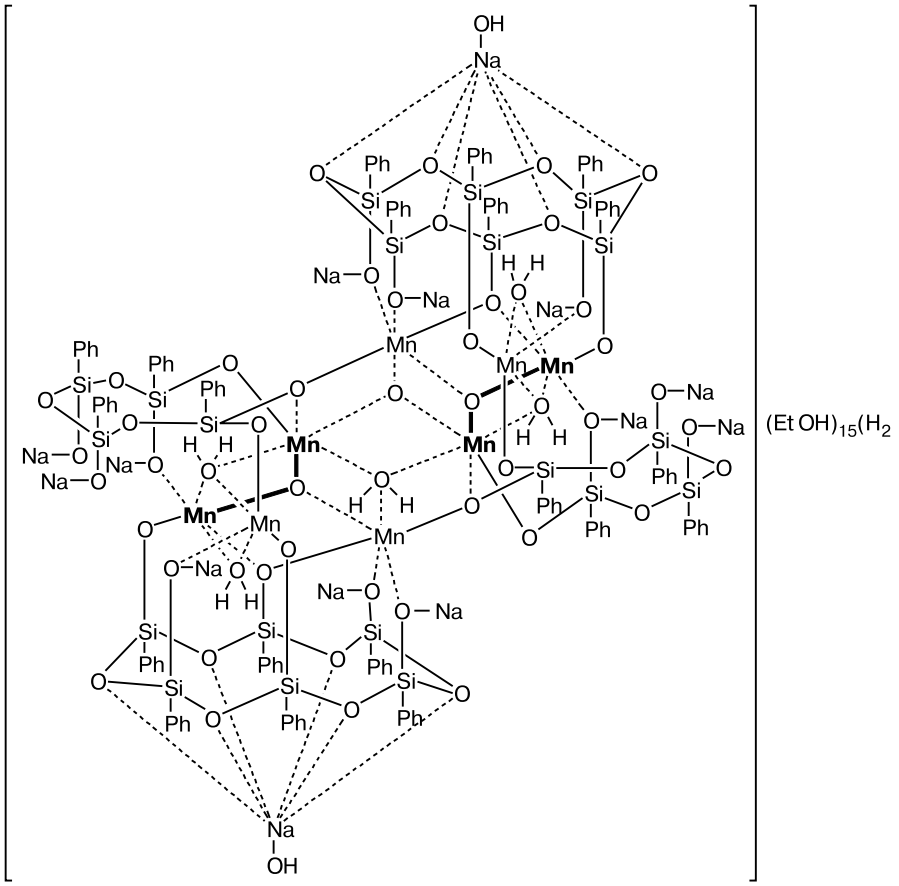
The UV spectra were recorded on a Specord M-40 spectrometer in the range of 300—600 nm (0.05 *M* solution in DMF).

Magnetic measurements were performed on a Quantum Design MPMS 5XL SQUID magnetometer. The temperature dependence of the magnetic moment was measured in the temperature range of 2—300 K in a constant magnetic field $H = 1$ kOe.

Results and Discussion

All the above-mentioned manganese complexes[1—18] are crystalline polynuclear complexes assembled through coordination bonds from single molecules containing one or two transition metal ions. For example, $[Mn^{IV}_4Mn^{III}_8O_{12}(O_2CCH_3)_{16}(H_2O)_4]\cdot 4H_2O\cdot 2CH_3CO_2H$ (see Ref. 1) is a coordination compound built of manganese acetate and acetate oxide molecules. In MSPS with the composition $(PhSiO_{1,5})_{20}(MnO)_8(NaO_{0,5})_{12}\cdot 2NaOH\cdot \cdot 15EtOH\cdot 11H_2O$ (empirical formula $C_{150}H_{214}Mn_8Na_{14}O_{72}Si_{20}$), which we have studied earlier,[20] all eight Mn^{2+} ions involved in the single silsesquioxane cage are, on the contrary, covalently bound.

The UV spectrum of MSPS represents bands at 431 and 527 nm assigned to d—d electron transitions in six-coordinate Mn^{II} complexes with O-containing ligands.[21]



MSPS

Therefore, unlike to the earlier-considered complexes, all manganese ions in MSPS are exclusively Mn^{II} ions and contain five unpaired d electrons each. The spin-orbit coupling between these ions is close to zero (1 cm^{-1}) and can be ignored in calculations of the effective magnetic moment.

The expected effective magnetic moment of MSPS calculated by the equation $\mu_{eff} = \mu_B g[8s(s + 1)]^{0.5}$ ($g = 2.002$) for eight noninteracting atoms with the electron spins $s = 5/2$ is 16.73 μ_B. In the case of eight ferromagnetically coupled electron spins, the total spin of the molecule is $8 \cdot 5/2 = 20$, and the effective magnetic moment $\mu_{eff} = \mu_B g[s(s + 1)]^{0.5}$ should be 41 μ_B. Apparently, only spins in the quartet of ions are ferromagnetically coupled so that each molecule contains two independent fragments, each with the spin $s = 4 \cdot 5/2 = 10$. In terms of this model, $\mu_{eff} = \mu_B g[2s(s + 1)]^{0.5} = 29.3\ \mu_B$.

In the case of competing antiferromagnetic and ferromagnetic exchange interactions, different effective magnetic moments varying from 0 μ_B (all eight spins are antiferromagnetically coupled) to 31 μ_B (two antiferromagnetically coupled spins in one quartet and all ferromagnetically coupled spins in the other quartet) would be expected.

The measurements (Fig. 1) showed that at 300 K, the magnetic moment of the MSPS is 21 μ_B, which is similar to that for the model consisting of ferromagnetically coupled spins in one quartet of ions and antiferromagnetically coupled spins in the other quartet (in this case, the expected effective magnetic moment is 21 μ_B). At low temperatures, μ_{eff} monotonically decreases and reaches a minimum value of 16 μ_B at $T = 40$ K, which is close to the calculated value for a paramagnetic system with eight noninteracting spins. However, it is unlikely that a system, in which spins are exchange-coupled at 300 K, is paramagnetic at 40 K. Generally, the efficiency of the exchange coupling increases rather than decreases with decreasing temperature. Therefore, at high temperatures, the exchange coupling, apparently, arranges spins parallel and antiparallel to each other in two quartets of the cluster. The observed decrease in the effective magnetic moment as the sample is cooled can be attributed to the involvement of different spin states of the molecules with ferromagnetic and antiferromagnetic interactions having the corresponding Boltzmann populations. For example, at low temperatures, states with the spin $s = 2 \cdot 5/2 = 5$, which can exist in a spin quartet consisting of two antiferromagnetically and two ferromagnetically coupled spins, can have higher populations. The monotonous increase in the effective magnetic moment from 16 to 21 μ_B can be attributed to the competition between these states and a gradual thermal population.

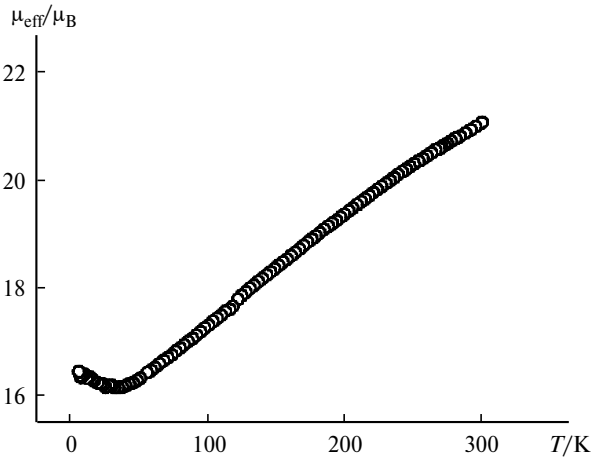


Fig. 1. Temperature dependence of the effective magnetic moment of MSPS.

The competition between ferro- and antiferromagnetic interactions in the cluster under consideration can be explained, for example, by a change in the molecular geometry (bond lengths and bond angles) with a change in the temperature.

To conclude, the MSPS studied is a cage compound with well-defined molecular architecture, which contains exchange-coupled paramagnetic centers. Hence, it holds promise for the chemical design of molecular nanomagnets.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 11-03-00646 and 10-03-00314).

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Received January 31, 2011;
in revised form October 4, 2011