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Unusual Magnetic Behaviour of Polyferro(phenyl)siloxanes

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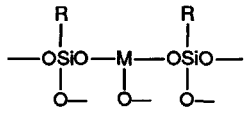
Polyferro(phenyl)siloxanes are paramagnetic when the iron content is low, *e.g.* at a ratio Fe:Si < 2.0, but when Fe:Si > 2.0 the effective magnetic moment of the Fe^{III} atom increases with increase of the Fe:Si ratio and it also increases as the temperature decreases; this unusual magnetic behaviour may be explained in terms of spin frustration in polynuclear oxo-ferric polymer clusters.

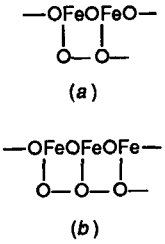
During our investigation of the new magnetic materials, organometallic ferromagnetics,[1] we have synthesized poly(ferro)- and poly(cobalt)-organosiloxanes by the polycondensation of trisodium *cis*-1,3,5-triphenylcyclotrisiloxane-1,3,5-triolate with metal chlorides. The products are network polymers containing the structural fragments **1**.[2]



1; R = Ph, CH_2=CH—
M = Fe, Co

The most interesting of these polymers are the polyferro(phenyl)siloxanes (PFPS). At low Fe:Si ratio the FeO_3 fragments are isolated and distributed statistically in a branched macromolecular chain. However, as this ratio increases, atomic pairs [Fig. 1(*a*)], triplets (*b*) *etc.* should appear along with the isolated Fe atoms. *I.e.*, polynuclear iron clusters are formed, in which exchange spin-aligning interactions occur between the Fe^{III} atoms *via* the oxo-bridges.

These polynuclear clusters seem to increase in both number and size as the Fe:Si atomic ratio increases and, consequently, they should manifest themselves in the magnetic behaviour of PFPS. Hence, we synthesized samples of PFPS with a high Fe:Si ratio (1.8–3.0), measured their magnetization using the Faraday method and determined the effective magnetic moment of an Fe atom.



(*a*)

(*b*)

Fig. 1

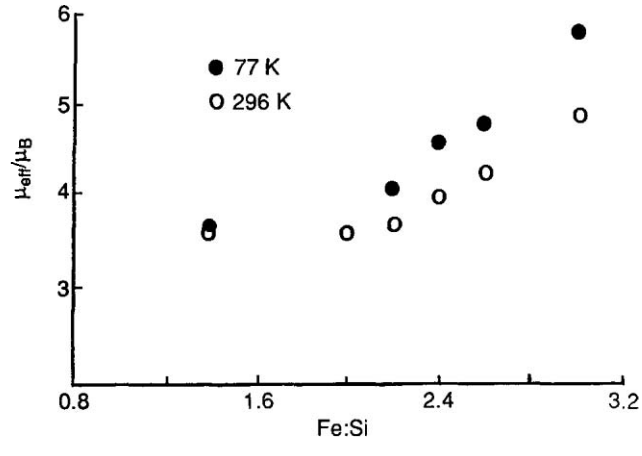


Fig. 2 μ_{eff} as a function of the Fe:Si atomic ratio

The magnetization of all PFPS polymers is a linear function of the magnetic field (up to 10 kG), which is evidence of their paramagnetism. However, the magnetic moment μ_{eff} for polymer samples with Fe:Si ratios of 1.8 and 2.1 is 3.6 ± 0.1 μ_B (Fig. 2). This corresponds to the effective spin $S = 3/2$ of an Fe^{3+} ion and is considerably lower than the theoretical value of 5.9 μ_B expected for the high spin state of this ion with $S = 5/2$. The magnetic susceptibility of PFPS with Fe:Si ratio 1.8 and 2.1 strictly obeys the Curie law, *i.e.* the magnetic moment does not depend on temperature.

The low values of μ_{eff} and the spin of the Fe^{3+} ion in PFPS suggest a considerable covalent contribution to the bonding of the Fe^{3+} ion in the FeO_2 fragments, in contrast to inorganic salts of Fe^{3+} with purely ionic bonding.

Polymers with Fe:Si > 2.1 exhibit an unusual magnetic behaviour. Firstly, the magnetic moment of the Fe^{3+} ion increases as the Fe:Si ratio increases (Fig. 2). Secondly, the magnetic moment increases as the temperature decreases, the ratio of the magnetic moments at 77 and 296 K, $\mu_{eff}(77)/\mu_{eff}(296)$, being larger the higher the Fe:Si ratio. Such behaviour means that in iron-rich PFPS, in addition to the

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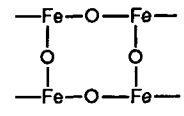
isolated Fe^{3+} ions in the FeO_3 fragments, clusters appear, as expected, consisting of one- and two-dimensional iron–oxygen chains and their combinations, in which exchange interaction takes place between the Fe^{3+} ions *via* the oxo-bridges. This interaction is not strong enough to ensure macroscopic ferro-antiferromagnetism, but it is sufficient to induce a change of spin and effective magnetic moment in the clusters.

The increase of the effective magnetic moment at low temperature indicates that the averaged spin density of the unpaired electron and the sum of the spins in the cluster increase at low temperature. *I.e.*, the ground state of a cluster is at least a high spin state, if not the highest.

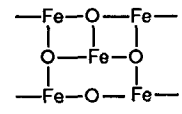
The simplest way to explain such magnetic behaviour is to assume that the exchange interaction is positive and affords a partial spin alignment in the clusters. However, it has been well-documented that in polyiron complexes pairwise Fe^{III}–Fe^{III} exchange interaction, when mediated by oxide, hydroxide and alkoxide bridges, is antiferromagnetic (see ref. 2) as in ferrooxides and oxyhydroxides. A low magnetic moment (3.6 μ_B for PFPS with Fe: Si = 1.8 and 2.2) is consistent with the conclusion that in these clusters the exchange interaction in the FeOFe fragments is also antiferromagnetic and, therefore, the magnetic moment is expected to decrease at low temperatures. This behaviour is characteristic of all known ferropolynuclear oxo- and hydroxo-complexes.[3,4]

The attainment of a high spin state *via* antiferromagnetic exchange interaction appears paradoxical, but this problem is not at all new. The problem of organic ferromagnetics was formulated in order to obtain ferromagnetism *via* antiferromagnetism.[1]

Unusual magnetic behaviour, similar to that described here, has recently been observed for a hexanuclear iron complex and $[Fe_6(O)_2(OH)_2(OAc)_{10}(C_{10}H_{13}N_4O)_2]\cdot CH_2Cl_2$,[3] explained in terms of spin frustration. This phenomenon occurs in molecular systems in which there are two or more competing routes for interatomic exchange interaction. For example, in a cluster such as **2** there is only one route for antiferromagnetic interaction transfer, along the Fe—O—Fe chains. The signs of the spin density alternate, and the total spin is equal to zero, the ground spin state of the cluster being singlet. However, if in clusters there are fragments with three-coordinated oxygen atoms, *e.g.* **3**, the routes of the antiferromagnetic exchange interaction are branched and the signs of the spin density on atoms do not alternate. Different routes transfer spin densities of a different sign and the sign compensation may be violated. For example, if in cluster **3** the Fe^{III}–Fe^{III} exchange interaction of the central atom is stronger along the inner Fe—O—Fe bonds than that along the peripheral bonds, the high spin state of cluster **3** is stabilized. In the opposite situation the cluster's low spin state is stabilized.



2



3

We believe that the unusual magnetic behaviour of PFPS provides evidence for the spin frustration of clusters and for the existence of three-coordinated oxygen bridges in PFPS. It is possible to use such cluster polymer structures as models of ferritin and other iron containing metallo-proteins. We are searching for ways to control the molecular topology of such clusters in order to increase their magnetization. We also anticipate unusual dynamic high frequency magnetic properties in such polymers.

All PFPS are soluble in organic solvents. We have measured the magnetization of PFFS with Fe: Si = 2.2 in 0.5% solution, in a mixture of acetone with $CHCl_3$ and n-butanol at 296 K and determined $\mu_{eff} = 3.7$ μ_B. This corresponds to μ_{eff} for a solid polymer with the same composition. This implies that the clusters remain unchanged in solution; however the conclusion requires verification for PFPS with Fe: Si > 2.2.

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