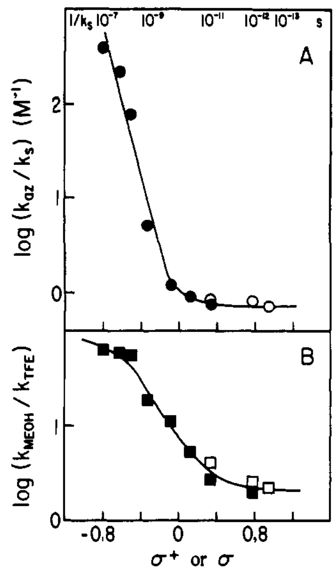

Figure 1. (A) Logarithmic plot of the product selectivity k_{az}/k_s (M^{-1}), determined by HPLC analysis, for reaction of $XArC(Me)_2Y$ in 50:50 (v/v) TFE/H_2O at 25 °C and ionic strength 0.50 ($NaClO_4$) against σ_x^+: (●), Y^- = substituted benzoate leaving groups; (○), Y^- = chloride leaving group. (B) Logarithmic plot of the product selectivity k_{MeOH}/k_{TFE}, determined by HPLC analysis, for reaction of $XArC(Me)_2Y$ in 5:45:50 (v/v/v) MeOH/TFE/H_2O at 25 °C and ionic strength 0.50 ($NaClO_4$) against σ_x^+: (■), Y^- = substituted benzoate leaving groups; (□), Y^- = chloride leaving group.

≈ 2 shows that the nucleophilicity of an associated solvent molecule has little effect on the rates of internal return and reaction to give solvolysis products.

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Supplementary Material Available: Table of the effect of added azide ion on first-order rate constants for reaction of 4-methoxy- and 4-methylcumyl *p*-nitrobenzoates and 4-nitro- and 3,5-bis(trifluoromethyl)cumyl chlorides in 50:50 (v/v) TFE/H_2O at 25 °C and ionic strength 0.50 ($NaClO_4$) (1 page). Ordering information is given on any current masthead page.

Alternating Current Susceptibility, High Field Magnetization, and Millimeter Band EPR Evidence for a Ground $S = 10$ State in $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$

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Molecular magnetism is passing from the investigation of the paramagnetic properties of isolated molecules to the design and synthesis of materials exhibiting spontaneous magnetization below a critical temperature.[1] In particular clusters of increasing complexity are synthesized, and their magnetic properties have shown unusual features.[2]

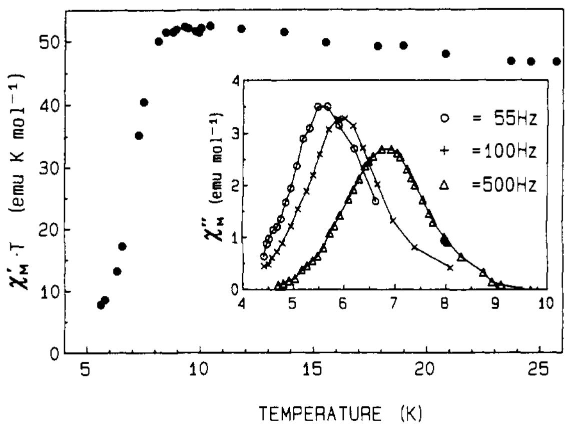

Figure 1. Temperature dependence of the real part of the magnetic susceptibility of a powdered sample of **2** in the form $\chi_M \cdot T$. In the inset is reported the imaginary part of the ac susceptibility at three frequencies.

High nuclearity spin clusters stabilize high-spin ground states. $[Mn(hfac)_2(NITPh)]_6$, which comprises[3] six manganese(II), $S = 5/2$, and six nitronyl nitroxide radicals, $S = 1/2$, has a ground $S = 12$ state, while $[Mn_{12}O_{12}(PhCOO)_{16}(H_2O)_4]$, **1**, which comprises[4] four manganese(IV) and eight manganese(III), has a ground $S = 14$ state.

$[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$, **2**, has a structure[5] very similar to **1**; and it is better suited to physical investigations because it has a tetragonal symmetry crystallographically imposed. Also the temperature dependence of the magnetic susceptibility of the two compounds is rather similar, but for the former no indication of the nature of the ground state has been given. Direct evidence of the nature and of the properties of the large spin ground states requires the use of several techniques, such as high field magnetization, high field EPR, and ac susceptibility measurements. The simultaneous use of these magnetic techniques provides evidence of an $S = 10$ ground state for **2** and of a magnetic behavior which resembles that of superparamagnets.

2 was prepared as previously described.[5] Single crystals are indefinitely stable, but when ground they lose 2 mol of acetic acid, as shown by elemental analysis. However the structure of the cluster is preserved, as shown by the similarity of the magnetic data of the crystals and of the powder.

Dc susceptibility measured with a Faraday susceptometer in the range 5–300 K confirmed that previously reported.[5] In order to avoid saturation and/or orientation effects associated with a strong external field, the ac susceptibility was measured in the range 4–25 K in zero applied field. For frequencies in the range 55–500 Hz, the real part of the susceptibility, χ', increases on lowering the temperature to 8 K, and the product χT, which is temperature dependent, reaches a plateau at 52.3 emu K mol^{-1} ($\mu_{eff} = 20.4\mu_b$) below 12 K, Figure 1. On lowering the temperature below 8 K, χ' decreases dramatically, while the imaginary component, χ'', becomes different from zero, reaches a maximum, and goes to zero again. The temperature at which the maximum in χ'' occurs is frequency dependent. These data indicate a frequency-dependent freezing temperature of the magnetization, analogous to that observed in superparamagnets[6] and spin glasses.[7]

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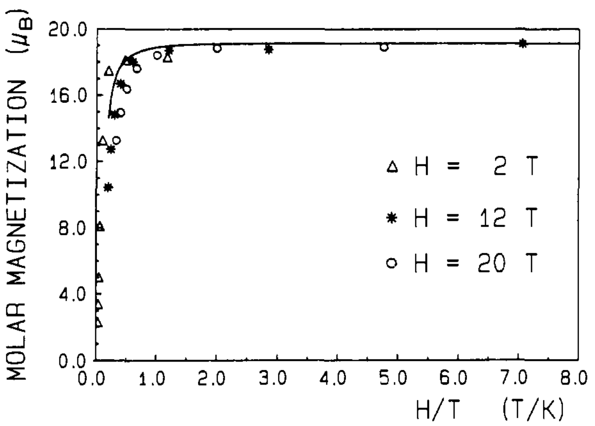

Figure 2. Molar magnetization of a powdered sample of **2** vs the ratio H/T. The measurements were performed varying the field between 0 and 20 T at eight temperatures in the range 1.7–60 K. The solid line represents the parallel magnetization calculated for $S = 10$ with $g = 1.9$ and $D = -0.5$ cm^{-1} at a field strength of 12 T.

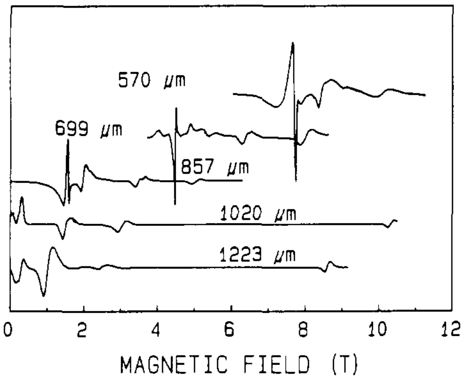

Figure 3. EPR spectra of a powdered sample of **2** recorded at different wavelengths.

Conventional relaxation effects must be excluded because the measurements were performed in zero applied field.[8]

Isothermal magnetization measurements with a Bitter magnet[9] were performed in the range 4.2–60 K with external field up to 20 T. The isofield plots are shown in Figure 2. The magnetization saturates for H/T greater than 1 at the value expected for $S = 10$, in agreement with the ac susceptibility data above 12 K. The experimental data can be satisfactorily reproduced by the parallel component of the magnetization calculated for $S = 10$, $g = 1.9$, and $D = -0.5$ cm^{-1}, suggesting that the crystallites are almost completely aligned by the strong magnetic field.[10]

No EPR spectra were detected with a conventional spectrometer operating at X- and Q-band frequency. However polycrystalline powder spectra at 4.2 K with a high frequency spectrometer operating with a far infrared laser[11] at 17.5, 14.3, 11.7, 9.8, and 8.2 cm^{-1} show a large number of features; see Figure 3.

The spectra recorded at the lowest frequencies show some features close to zero field, which move regularly to higher fields on increasing frequency. This is a clear indication that they belong to transitions within a spin multiplet split in zero field. The presence of resonances close to zero field for B_0 in the range 11–8 T indicates that the levels are separated by roughly 10 cm^{-1} in zero field. Since only low field transitions are observed, the zero field splitting of the ground manifold must be such that the levels with the largest M components have the lowest energy. Similar conclusions were reached[4] from the analysis of the magnetization of **1**. If we assume that the lowest field transition corresponds to $M_s = -10 \rightarrow M_s = -9$, then D can be estimated to be ca. ≈ -0.5 cm^{-1}, in agreement with magnetization data.

The main evidence of a ground $S = 10$ state comes from the magnetization data. The ac susceptibility confirms this value and adds the puzzling observation of large frequency-dependent relaxation effects. It is tempting to attribute these to factors analogous to those observed in superparamagnets. Although the dimensions of the clusters are still much smaller than those observed in superparamagnets, the large magnetic anisotropy, which arises from the large spin and the fact that the $M_s = \pm 10$ levels lie lowest, determines large internal fields which give rise to the observed relaxation effects.

The reasons stabilizing this ground state compared to the $S = 14$ of **1** are currently under investigation. However it is interesting to notice that an $S = 10$ is compatible with all the manganese(III) spins up and the manganese(IV) spins down.

Acknowledgment. The financial support of the CNR, of the Progetto Finalizzato "Material Speciali per Tecnologie Avanzate", and of MURST is gratefully acknowledged.

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Novel Formal 3 + 2 Annulation Reaction Based on S-Propargyl Dithiocarbonates (Xanthates)

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We report a novel annulation reaction involving S-propargyl dithiocarbonates (xanthates) which we discovered accidentally while attempting to generate propargyl radicals. We had earlier found[1] that resonance-stabilized carbon-centered radicals can be easily generated from the corresponding S-alkyl xanthates **1** and captured by an electrophilic olefin such as **2a** as shown in Scheme I. The radical chain reaction is triggered by a combination of visible light and a catalytic amount of S-benzoyl O-ethyl xanthate. When we applied the same procedure to S-propargyl xanthate **1b**, the expected adduct **3b**, arising from addition of a propargyl radical to N-benzylmaleimide, was produced but only in low yield (5–10%). The major product, isolated in up to 45–50% yield, turned out to be the bicyclic derivative **4**.[2] Other highly electrophilic olefins also gave the corresponding cyclopentene derivatives in variable (unoptimized) yields (Table I). With less reactive olefins, such as methyl acrylate or even dimethyl fumarate, complex mixtures were obtained from which no useful products could be isolated.

At first, this unexpected transformation was thought to proceed through a hitherto unprecedented 5-endo-digonal radical cyclization step,[3] as indicated in Scheme II (path A). However, a number of observations compelled us to reject such a mechanism. For example, in the case of citraconimide **5**, two isomeric adducts **6** and **7** were obtained in an approximately 1:1 ratio (80% combined yield, see Table I; for structural confirmation purposes, the

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