suppression at the PEG resonance (70 dB), a 200 ms mixing time, 32 scans, and 512 increments.

The solution-state NMR titration between hexaethylene glycol and **1** was carried out at room temperature by monitoring the inner aromatic proton of the spacer unit. The results showed that the stoichiometry corresponds approximately to a 1:1 binding model.

Galactosyl beads: 1,2:3,4-Di-*O*-isopropylidene-D-galactopyranose (ca. 50 equiv with respect to the loading of Argogel-Cl) was treated with sodium hydride (ca. 100 equiv) in tetrahydrofuran. After filtration of the mixture, the filtrate was added to ArgoGel-Cl (0.41 – 0.45 mmol g^{-1}) and shaken for 2 days. The resulting beads were washed and deprotected with a mixture of trifluoroacetic acid and water (9:1, 2 mL). Washing the beads with tetrahydrofuran, methanol, and chloroform afforded the galactosyl beads.

2: A solution of a rigid porphyrin dimer[6] (50 mg) and palladium on carbon (50 mg) in tetrahydrofuran (25 mL) was stirred under hydrogen for 24 h. Filtration of the mixture through celite and removal of the solvent afforded a flexible porphyrin dimer. A mixture of ArgoGel-NH$_2$ (13 mg, 0.41 – 0.45 mmol g^{-1}), flexible porphyrin dimer (30 mg), TBTU (4 mg), and diisopropylamine (3 mg) in a mixture of *N*,*N*-dimethylformamide (1 mL) and dichloromethane (0.5 mL) was shaken for 4 days. The solvent was then removed by filtration and the beads were washed extensively with dichloromethane and methanol.

3: A mixture of the flexible porphyrin dimer (22 mg), TBTU (5 mg), and diisopropylamine (3 mg) in chloroform (1 mL) was added to a mixture of **1** (12 mg) and ArgoGel-NH$_2$ (15 mg) in chloroform (1 mL). The resulting mixture was shaken for 1 day. The solvent was then removed by filtration and the beads were washed extensively with dichloromethane and methanol.

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Cobalt(II)-Nitronyl Nitroxide Chains as Molecular Magnetic Nanowires[**]

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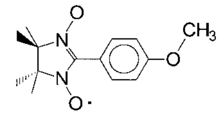
The observation of slow magnetic relaxation in molecular clusters is now considered as one of the most important achievements of molecular magnetism of the last few years.[1] In fact systems like Mn12, Fe8 have provided unique opportunities for the investigation of molecular magnetic hysteresis,[2] quantum tunneling of the magnetization,[3, 4] and of phase interference (Berry phase).[5] All these features depend on slow magnetic relaxation.

While clusters can be considered as zero-dimensional materials, in principle slow relaxation of the magnetization can also be expected in one-dimensional (1D) materials, as suggested by Glauber in 1963.[6] However, to date, it has not been possible to observe this behavior because no suitable experimental system has been produced. In fact the conditions to be met to observe slow magnetic relaxation in 1D materials are rather stringent: 1) the ratio of the interaction within the chain, *J*, and that between chains, *J'*, must be rather high, larger than 10^4; 2) the material must behave as a 1D Ising ferro- or ferrimagnet.

We have now found that slow relaxation of the magnetization and hysteresis effects which are not associated with three-dimensional (3D) order can be observed in [Co(hfac)$_2$(NITPhOMe)] (**1**; hfac = hexafluoroacetylacetonate, NITPhOMe = 4'-methoxy-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide). We want to show that these findings provide an experimental confirmation of Glauber's prediction.



NITPhOMe

Complex **1** consists of alternating Co(hfac)$_2$ and radical moieties arranged in 1D arrays with a helical structure arising from the trigonal crystallographic

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lattice (Figure 1).[7] Similar structures have been reported for manganese(II) analogues,[8] and the role of supramolecular interactions for determining the helical arrangement were discussed.[7] The temperature dependence of χT of **1**, (Figure 2), gives clear indications of 1D behavior, presumably of ferrimagnetic nature. The rapid increase of χT below 100 K suggests strong intrachain interactions as observed in 1D ferro- and ferrimagnets. Antiferromagnetic coupling between cobalt(II) and the NITPhOMe radical is suggested by the temperature dependence of the magnetic susceptibility of the mononuclear complex $[Co(hfac)_2(NITPhOMe)_2]$,[9] in which the coordination of the central cobalt ion is essentially the same as in the chain compound. At low temperature the spin of octahedral cobalt(II) centers can be handled as an effective $S = 1/2$ spin with anisotropic g values significantly different from 2. The chains therefore behave as 1D ferrimagnets, because of the noncompensation of the magnetic moments of the cobalt(II) center and the radical.

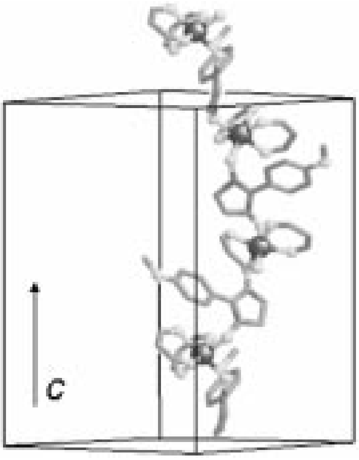

Figure 1. A simplified view of the content of the unit cell of **1**. Large dark spheres represent the metal ions. For the sake of clarity the hydrogen, fluorine, and most of the methyl carbon atoms are omitted. Compound **1** crystallizes in the $P3_1$ space group with $a = b = 11.294$ Å and $c = 20.570$ Å. The trigonal space group leads to stacking interactions between the phenyl ring of the radical and two adjacent hfac molecules thus giving an asymmetric "sandwich structure" with the planes forming angles of 10.1/9.6° and distances of 3.6/3.9 Å. Each trigonal chain is surrounded by other six equivalent chains with 11.289 Å and 10.345 Å being the shortest interchain Co^{II}–Co^{II} and the shortest NO–NO contacts, respectively.

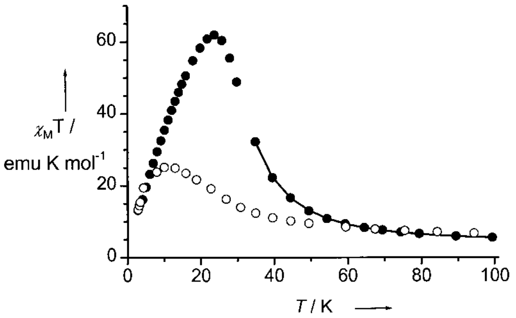

Figure 2. Temperature dependence of the ratio between magnetization and magnetic field (indicated for simplicity as a susceptibility) multiplied by the temperature and measured in 1 kOe external field parallel to the chain direction (●) or perpendicular to it (○). The solid line corresponds to the calculated value using the alternating spins 1D Ising model (see text). The decrease observed below 30 K is field dependent and is caused by the rapid approach to saturation because of strong short-range correlation.

The susceptibility below 50 K is strongly anisotropic, as shown in Figure 2, with the trigonal axis corresponding to the easy axis of magnetization and therefore to Ising-type anisotropy. A first estimation of the exchange coupling has been obtained through a fit of the temperature dependence of χT with an Ising model, which gives $J/k_B = 220$ K, $g_{Co} = 7.4$, $g_{rad} = 2$, where the Hamiltonian is given by Equation (1). The large value of J is in agreement with the values in the manganese(II) and nickel(II) analogues.[7, 10]

$$\mathcal{H} = \sum_i J(\mathbf{S}^z_{2i}\mathbf{S}^z_{2i+1} + \mathbf{S}^z_{2i}\mathbf{S}^z_{2i-1}) - \mu_B H^z \sum_i (g_{Co}\mathbf{S}^z_{2i} + g_{rad}\mathbf{S}^z_{2i-1}) \tag{1}$$

The alternating current (ac) magnetic susceptibility of **1** is strongly frequency dependent below 17 K. The in-phase susceptibility, χ', goes through a maximum, and the out-of -phase component, χ'', becomes different from zero also going through a maximum(Figure 3). These results indicate that the relaxation of the magnetization in this temperature range becomes slow on the time scale of the experiment (2 µs – 1 s). The frequency dependence rules out a 3D transition, and suggests a thermally activated mechanism. In fact, over the wide frequency range investigated (0.18 – 95 kHz) τ has exponential behavior [Eq. (2)] as observed in superparamagnets[11] and spin glasses.[12] The best-fit parameters are $\tau_0 = 3.0(2) \times 10^{-11}$ s, $\Delta/k_B = 154(2)$ K. The value of τ_0 is close to that expected for the relaxation time of octahedral cobalt(II) centers. The entire magnetization, of both the cobalt and radical sublattices, experience the same blocking temperature, as suggested in that χ' goes to zero for temperatures below the peak in χ'', and indeed χ' and χ'' almost describe a semicircle in the Cole – Cole plot.[13, 14]

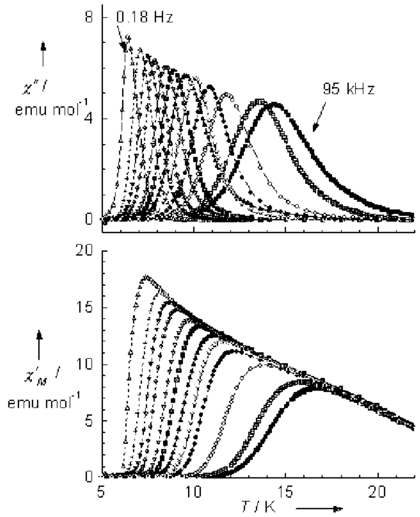

Figure 3. Temperature dependence of the real (bottom) and imaginary (top) component of the ac susceptibility measured in zero applied static field and with the oscillating field (0.5 – 2 Oe) applied along the chain direction. The frequency of the oscillating field varies in the range 0.18 – 95 kHz. The lines are only a guide.

$$\tau = \tau_0 \exp(\Delta/k_B T) \tag{2}$$

The strong frequency dependence of the relaxation time and the physically reasonable value of τ_0, without introducing any scaling factor, rule out the possibility that the system is a spin glass.[12] Further, since a spin glass demands the presence of disorder, this is difficult to reconcile with the single-crystal nature of the sample. The model developed by Glauber for Ising ferromagnetic chains predicts that the reversal of the spins becomes more difficult on lowering the temperature because the short-range correlation along the chain favors the parallel alignment of the spins.[6] An Arrhenius behavior is predicted for the relaxation time, with the height of the barrier corresponding to the nearest-neighbor exchange interaction J. The experimental barrier Δ/k_B, is indeed close to the J coupling constant estimated from analysis of the magnetic susceptibility using the Ising model.

Static measurements of the magnetization parallel to the trigonal axis, obtained by cooling in zero field and then applying a field, show the onset of irreversibility around 6 K. The field-cooled magnetization shows a plateau below this temperature typical of a complete freezing process. The isothermal magnetization has a hysteretic behavior when the external magnetic field is applied parallel to the trigonal axis (Figure 4) while no hysteresis can be observed when the field is applied in the trigonal plane.

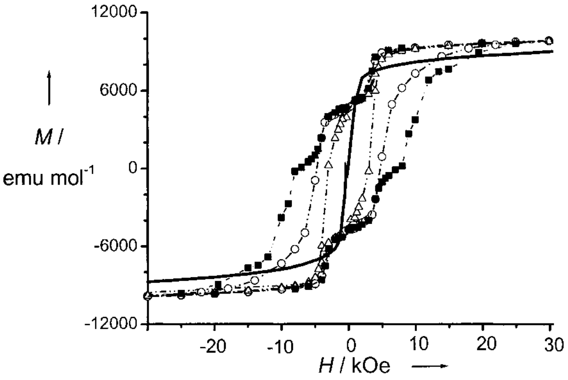

Figure 4. Hysteresis loops measured on a single crystal of **1** by applying the field parallel to the chain axis at 2.0 K (■), 3.0 K (○), 4.5 K (△), and at 2.0 K perpendicular to it (——).

The magnetization at the highest field (60 kOe) and 1.8 K is 1.90 μ_B parallel to the trigonal axis and 1.72 μ_B perpendicular to it. These values seem to suggest that the anisotropy of the chains is small even if the slow dynamics are associated with the Ising anisotropy of the exchange interaction. In fact, the helical arrangement of the anisotropy tensors of the individual cobalt spins reduces the bulk anisotropy if the easy axis of the cobalt(II) ions is not parallel to the trigonal axis.[15] That the anisotropy axes of cobalt spins are not parallel to each other could also be responsible of the reversible steps in the hysteresis loop observed for $H \approx \pm 4$ kOe.

Molecular magnets are providing new types of magnetic behavior, which are not easily observed in traditional magnets. This is particularly true for nanosized species, because the presence of large nonmagnetic organic moieties can relatively easily provide confinement of the magnets in zero, one, and two dimensions.

The unique feature of **1**, its highly one-dimensional nature, allowed us to record for the first time the slow relaxation of the magnetization in the paramagnetic phase of a 1D compound, a process predicted theoretically almost forty years ago.[6] The different magnetic behavior of the manganese(II) derivative, which orders ferrimagnetically at 4.6 K,[7, 8] is because of the almost negligible anisotropy of the manganese(II) centers. The anisotropy of the cobalt–radical exchange interaction in the chain gives a barrier for the reorientation of the magnetization. This, combined with the smaller spin of cobalt(II) compared to manganese(II) centers, determines slow relaxation of the magnetization before the weak interchain dipolar interaction can induce three-dimensional magnetic order.

1D magnetic systems are well known to be able to show long-range order only at 0 K. The research in molecular magnetism of the last two decades therefore has been characterized by strong efforts to efficiently connect magnetic chains in 3D networks to observe bulk magnetism. We have shown here that magnetic bistability and the related *memory* effect can indeed be observed in a 1D material without requiring any interchain interaction.[16] These results may open exciting new perspectives including that of storing information in a single magnetic polymer as well as in the novel class of 1D materials where ionic structures are obtained inside carbon nanotubes.[17]

Experimental Section

Crystals of **1** were prepared as reported in ref. [7]. The crystals were checked on an Enraf Nonius CAD4 four-circle diffractometer. The axis of the helical chains is easily recognized as it corresponds to the elongation axis of the crystals, which have the shape of hexagonal rods. Magnetic measurements were performed by using a Cryogenic S600 SQUID magnetometer equipped with the ac option. High frequency ac susceptibility measurements have been performed on a home-built susceptometer. A single crystal of **1**, of approximate weight 1 mg, was used for the static magnetic measurements, while samples containing around 10 iso-oriented single crystals for a total weight of about 4–6 mg were employed for the ac susceptibility measurement.

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[15] In **1** the cobalt ion occupies a general position thus lacking the trigonal symmetry. Its easy axis of magnetization can therefore be at any angle from the trigonal axis and the comparison with the mononuclear compound[9] suggests that this angle can be as large as 50°.

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A Novel Polynuclear Gold–Sulfur Cube with an Unusually Large Stokes Shift[**]

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The luminescence properties of polynuclear transition metal complexes with a d^{10} closed-shell electronic configuration have attracted much attention over the past few decades.[1] In view of the wide applicability of d^{10} transition metal chalcogenides in semiconducting materials, photovoltaics, and nanomaterials, and their intriguing optical behavior, their spectroscopic and photophysical properties are worthy of exploration. With our recent success in making soluble polynuclear copper(I), silver(I), gold(I), zinc(II), cadmium(II) and mercury(II) complexes with unsubstituted chalcogenide and chalcogenolate ligands and rich luminescence behavior,[2] we hope that, by systematic variation of the metal, chalcogen, and ancillary ligands, insights into the spectroscopic properties, the nature of the excited states, and the structure–property relationship can be obtained. This is particularly important, as many of the transition metal chalcogenides and chalcogenolates are insoluble, and this renders their structures and photophysical properties less amenable to study. Owing to the recent growing interest in the aurophilic nature of gold(I) centers and the scantiness of gold(I) chalcogenide aggregates,[3–5] we launched a program to investigate this class of compounds. A number of soluble dodecanuclear and decanuclear gold(I) sulfido complexes with bridging diphosphane ligands have been successfully synthesized by us.[2c,d] These complexes have the formulas $[Au_{12}(\mu\text{-dppm})_6(\mu_3\text{-S})_4](PF_6)_4$ (dppm = bis(diphenylphosphanyl)methane) and $[Au_{10}\{\mu\text{-}Ph_2PN(n\text{Pr})PPh_2\}_4(\mu_3\text{-S})_4](PF_6)_2$ and possess novel structures and interesting photophysical behaviors. Here we report an unprecedented hexanuclear gold(I) sulfido complex with bridging diphosphane ligands, namely, **1**, which has unusual photophysical properties.

$[Au_6\{\mu\text{-}Ph_2PN(p\text{-}CH_3C_6H_4)PPh_2\}_3(\mu_3\text{-S})_2](ClO_4)_2$ **1**

Reaction of H_2S with a suspension of $[Au_2\{Ph_2PN(p\text{-}CH_3C_6H_4)PPh_2\}Cl_2]$ in ethanol/pyridine followed by metathesis reaction with $LiClO_4$ and recrystallization from acetone/dichloromethane/diethyl ether yielded **1** as colorless crystals in 50% yield. It was characterized by elemental analysis, positive-ion FAB mass spectrometry, positive- and negative-ion ESI mass spectrometry, and ^1H and ^{31}P NMR spectroscopy.[6]

The structure of the complex cation of **1** in the solid state was determined by X-ray crystallography.[7] The cation is hexanuclear, and the Au_6S_2 unit is arranged in a distorted heterocubane structure with the two sulfur atoms at opposite apices of the cuboid. Figure 1 shows a perspective drawing of the cation. Each sulfur atom is bonded to three gold(I) centers in a μ_3 bridging mode, and the two Au_3S units are interconnected by three diphosphanylamin ligands. Noticeable gold–gold interactions are present, and the Au···Au distances range from 2.939(3) to 3.3775(18) Å. The Au–S and Au–P bond lengths of 2.325(8)–2.346(8) and 2.256(9)–2.272(8) Å, respectively, and the P-Au-S angles of 168.4(3)–178.5(3)°, which are distorted from ideal linear geometry, are not uncommon.[2c–e, 8–10] The Au-S-Au angles at the μ_3-S atoms are in the range of 92.13–95.66° and thus deviate only slightly from the ideal 90° expected for bonding involving the sulfur 3p orbitals. The P-N-P angles are very close to 120°, indicative of sp^2 hybridization at the N center. Unlike other polynuclear gold(I) sulfido complexes with bridging diphosphane ligands,

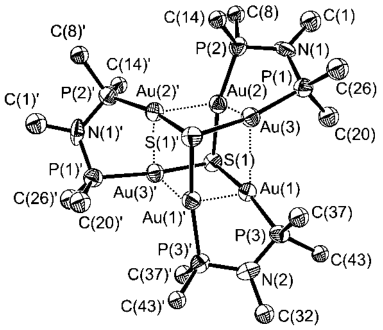

Figure 1. Perspective drawing of the structure of the complex cation of **1** in the crystal. Only the *ipso*-C atoms of the aromatic rings are shown for clarity. Thermal ellipsoids are drawn at the 30% probability level.

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