MERS-CoV occurred before 2012 because diagnostic tests were not yet available. The only way to answer this question would be to screen archived samples of human blood to determine when a cross-species zoonotic transmission from camels to humans occurred.

Controversy over the rights to the MERS-CoV. The growth of the MERS epidemic has been slow, but it has not been without controversy. When Zaki provided the coronavirus (which was isolated in the laboratory in Saudi Arabia) to Fouchier for testing, he handed over the sovereign and intellectual property rights to the first diagnostic tests or treatments based on the viral sequencing results to the Erasmus Medical Center in the Netherlands. The Erasmus Medical Center thus had control over requests by researchers to access samples of the virus through material transfer agreements (MTAs) related to patent applications. This created tensions among Zaki, the Saudi Ministry of Health authorities, and other researchers. The hospital authorities terminated Zaki's contract, and he left to work as a microbiologist in Cairo, Egypt. Dutch researchers have fulfilled the MTA requests by other laboratories, but they have placed certain restrictions on experiments with and applications of the new coronavirus. Unfortunately, this controversy has led to conflicts of political and commercial interests that may hamper the global community in its quest to develop a suitable vaccine or treatment.

Outlook. Regardless of the legal controversy involving the MERS-CoV, the main goal of scientists has been to stop the spread of the MERS illness. So far, the disease has been confined to areas of the Arabian Peninsula. A few travel-associated cases occurred in Europe and the United States. Most recently, two health-care workers who traveled to Indiana (April 2014) and Florida (May 2014) from Saudi Arabia became ill. A health-care worker taking care of the patient with MERS in the Florida hospital also became ill. Coordinated efforts were in place to identify contacts and prevent the spread of MERS. After the hospital worker in Florida became ill, the WHO held an emergency meeting on MERS to discuss public health response efforts.

For background information *see* CAMEL; CLINICAL MICROBIOLOGY; DISEASE ECOLOGY; EPIDEMIC; EPIDEMIOLOGY; INFECTIOUS DISEASE; RESPIRATORY SYSTEM; RESPIRATORY SYSTEM DISORDERS; VIRUS; VIRUS CLASSIFICATION; ZOONOSES in the McGraw-Hill Encyclopedia of Science & Technology.

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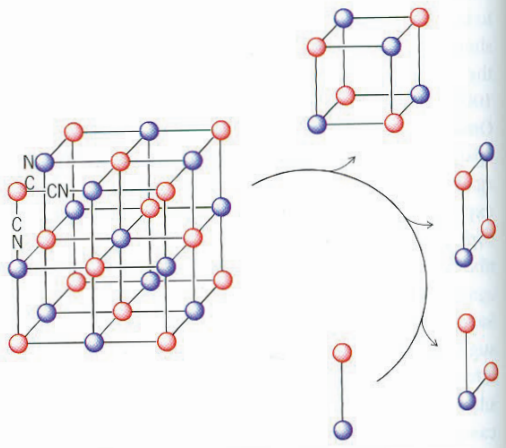
Molecular magnets

Over the past 2 decades, considerable worldwide attention has focused on the development of superparamagnetic complexes, known collectively as single-molecule magnets (SMMs). These molecular species belong to a class of magnetic materials that can be easily prepared, tuned, and studied via a range of spectroscopic and magnetic characterization techniques. The most celebrated of these are those containing transition-metal centers linked via oxo- and carboxylate bridges, with $\{Mn_{12}O_{12}(O_2CMe)_{16}(OH_2)_4\}$ (**1**) receiving the most attention (**Fig. 1**). These soluble, single-domain clusters generally display large spin ground states ($S_T = 10$, 20 unpaired electrons for **1**) due to efficient antiferromagnetic interactions between the Mn^{IV} ($S = {}^3/_2$, •) and Mn^{III} ($S = 2$, •) spin centers. Owing to a nearly parallel alignment of the Jahn-Teller axes (elongated) at the Mn^{III} sites, magnetic anisotropy is generated (where $D < 0$ with small E for the Hamiltonian: $H = DS_{T,z}^2$), which leads to the observation of slow magnetic relaxation at cryogenic temperatures (for example, below about 10 K; Fig. 1). Under ideal circumstances, these and other magnetic complexes



Scheme 1. Dimensional reduction of an idealized Prussian blue structure into discrete polynuclear complexes. (*Adapted from P. Ferko and S. M. Holmes, Curr. Inorg. Chem., 3:172–193, 2013*)

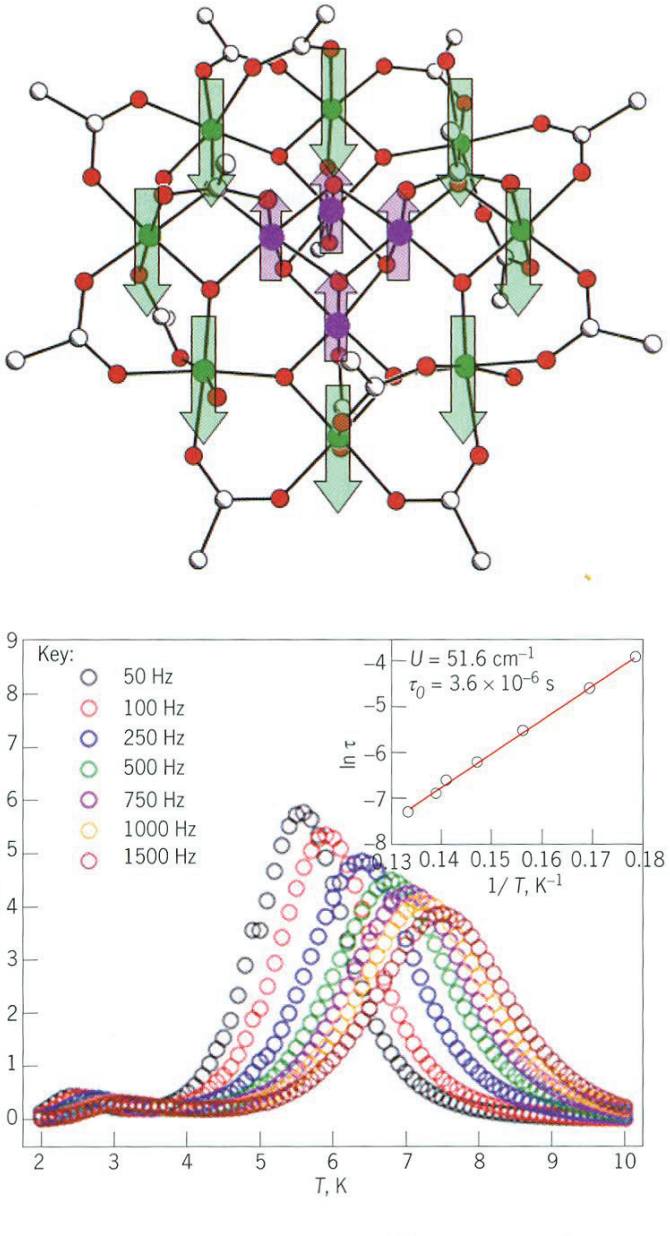


Fig. 1. (*a*) X-ray structure and magnetic interactions between Mn^{III} (↑, green) and Mn^{IV} (↑, purple) unpaired spins. (*b*) Structure and magnetic data for $\{Mn_{12}O_{12}(OAc)_{16}(OH_2)_4\}$. Inset: Arrhenius data show that magnetic relaxation is thermally activated. (*Adapted from D. Ruiz et al., Angew. Chem., Int. Ed., 37:300–302, 1998 and R. Sessoli and D. Gatteschi, Angew. Chem., Int. Ed., 42:268–297, 2003*)

exhibit sizable energy barriers to magnetization reversal, where $\Delta \sim |D|S_T^2$ or $\Delta = |D|(S_T^2 - {}^1/_4)$ for integer or half-integer S_T values, respectively.

In SMMs the creation of an energy barrier (Δ) between two thermodynamically equivalent $m_S = \pm S$ configurations allows the possibility that slow relaxation dynamics may be seen (**Fig. 2***a*). Using a variety of magnetization measurements, below a critical temperature (the so-called blocking temperature, T_B,), the available thermal energy is insufficient to overcome Δ and the spin becomes trapped in one of two possible configurations. Application of large external magnetic fields (H) saturate the magnetization (M) of the sample and, upon removal of this dc field ($H_{dc} = 0$), M slowly decays toward zero (becomes demagnetized) with a characteristic relaxation time (τ). The relaxation time usually exhibits temperature-dependent (or thermally activated) behavior and can be measured by following magnetization (M) as a function of time or the frequency (ν) dependence of the ac susceptibility. At very low temperatures (Fig. 2*b*), quantum tunneling of the magnetization (QTM, also known as short-cut) can be seen, where magnetic relaxation occurs at a faster

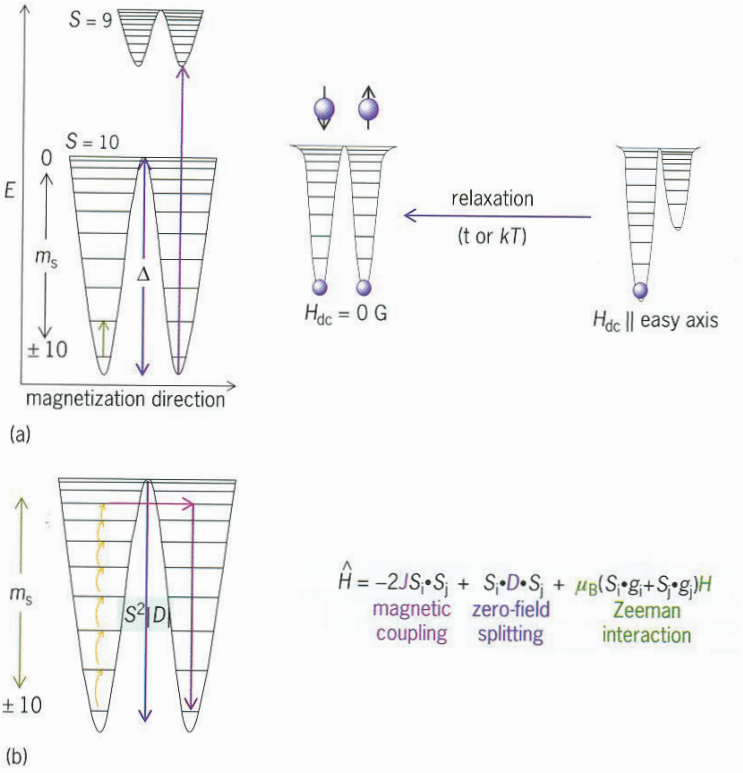


Fig. 2. (*a*, left) Idealized energy-level diagram for $\{Mn_{12}O_{12}(OAc)_{16}(OH_2)_4\}$. (*a*, right) Idealized magnetic relaxation from saturated to equilibrium state with time and/or thermal energy. (*b*, left) Pictorial representation of quantum tunneling of the magnetization. (*b*, right) General design considerations for tuning magnetic properties in polynuclear SMMs. (*Adapted from R. Sessoli and D. Gatteschi, Angew. Chem., Int. Ed., 42:268–297, 2003*)

rate than thermally activated pathways allow, thus bypassing the energetic costs associated with climbing the potential-energy barrier (Δ). With sufficiently large spin-reversal energy barriers, slow magnetization relaxation can be observed at low temperatures when QTM is slow. Of known analogs, $[Mn^{III}{}_6O_2(Et\text{-}sao)_6(O_2CPhMe_2)_2(EtOH)_6]$ displays the highest spin-reversal barrier ($\Delta = 86$ K) for this class of SMMs.

Over the past 20 years several successful synthetic strategies have been developed for the preparation of polynuclear complexes with higher spin ground states. The majority of oxo- and carboxylate SMMs contain first-row transition-metal ions and generally exhibit small zero-field splitting terms ($D \sim -0.1$ to 0.2 cm^{-1}) because orbital angular momentum contributions to their magnetic ground states are nearly quenched by the low-symmetry environment of the paramagnetic metal ions. Several research groups have attempted to tune this behavior by systematically inserting a variety of organic molecules (ligands) into a given structure, so that the total spin state and zero-field splitting may be maximized (and thus Δ; Fig. 2). Unfortunately, as a general trend, when the overall spin ground state of polynuclear complexes increases, the uniaxial magnetic anisotropy $|D|$ becomes proportional to S_T^{-2}, thus leading to lower SMM energy barriers which generally scale as a function of S_T^0 rather than S_T^2. Over the past 20 years many analogs that display high spin ground states have been known, but Δ is generally found to be lower than predicted, due to insufficient magnetic anisotropy control and rapid QTM.

Mononuclear single-molecule magnets. In an effort to further tune the magnetic properties of these complexes, increasing worldwide attention has turned toward the exploitation and insertion of metal centers with greater orbital contributions to their spin ground states. Significant efforts to control the magnetic properties of these complexes have been explored, with most concerned with the systematic alteration of the zero-field splitting term exhibited by these complexes; the general approach exploits selective substitution of transition metals in existing structural archetypes in favor of those with even greater single-ion anisotropy (**Fig. 3**). These interactions fall into two general categories, in-state and out-of-state orbital contributions, where the former concern symmetry-allowed mixing of degenerate spin states (for example, that are related by rotation, substantial first-order orbital angular momentum contributions) or by the latter, where low-energy excited states with orbital contributions are allowed to mix electronically with the lower-energy ones; simultaneously and preferentially orienting the resulting single-ion anisotropy tensors is highly important and can often be controlled by choosing the right ligand(s). For example, through the use of sterically demanding polydenate ligands, preferential orientation of the Jahn-Teller axes and/or single-ion anisotropy tensor orientations during the self-assembly can give complexes that display dramatically different magnetic properties for a given number of paramagnetic centers present.

More recent approaches exploit heavy-metal ions as a route for systematically introducing centers with large orbital contributions to their magnetic ground states. As spin–orbit coupling is generally a relativistic effect (scales with atomic number), several SMM analogs containing paramagnetic *f* elements have been explored, given that their orbital contributions are significant and often remain unquenched by the ligand field. Several lanthanide and actinide derivatives are known, and many of these polynuclear complexes afford degenerate spin ground states (and high magnetic anisotropy). These hybrid *d*-*f* compounds can, under ideal circumstances, display higher spin-reversal energy barriers than their 3*d* analogs, but systematic control of their single-ion tensors still remains a difficult synthetic chemistry challenge.

Given that control of single-ion anisotropy tensors is a difficult feature inherent to many SMM systems, and that the energy barriers for spin reversal are not dramatically changed with increasing spin values, a logical approach has investigated how reducing the numbers of paramagnetic ions to a few or a single anisotropic metal center may circumvent

Fig. 3. [Dy5(μ Angew

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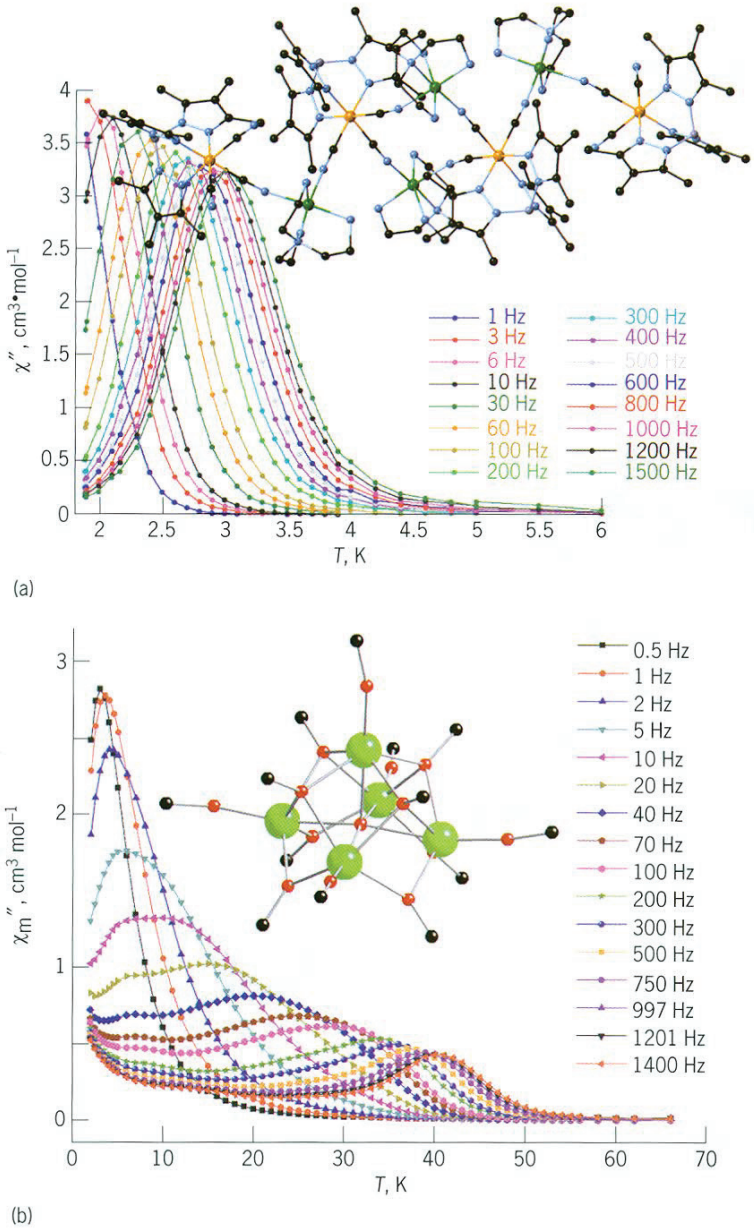
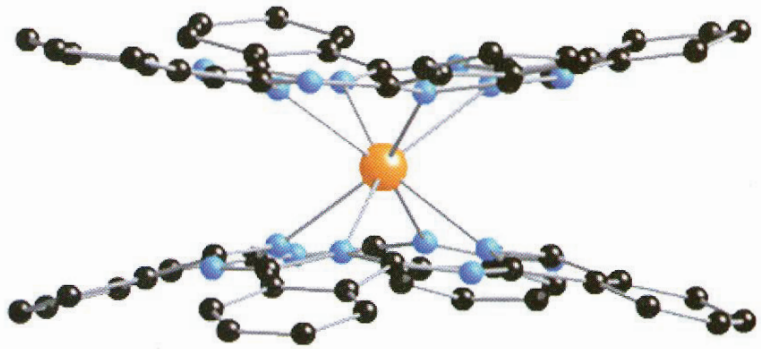


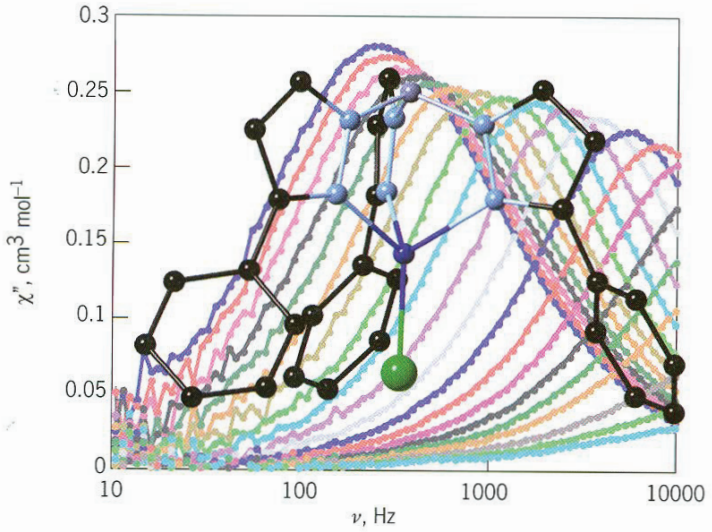
Fig. 3. X-ray structures and magnetic data for (*a*) octanuclear $[(Tp^*Me)Fe^{III}(CN)_3]_4[Ni^{II}(tren)]_4$ and (*b*) pentanuclear $[Dy_5(\mu\text{-}O)(OiPr)_{12}]$ complexes. (*Adapted from Y.-Z. Zhang et al., Chem. Commun., 46:4953–4955, 2010 and R. J. Blagg et al., Angew. Chem., Int. Ed., 50:6530–6533, 2011*)

these apparent engineering limitations. The smallest members contain 4*f* ions whose complexes of general $[LnPc_2]^n$ stoichiometry, where Ln = Tb, Dy, Ho (for $n = \pm 1, 0$) and Pc = phthalocyanine; alternative strategies explore structurally related mononuclear low-coordinate 3*d* complexes (**Fig. 4**). Astonishingly, owing to unquenched orbital angular momentum and well-isolated states, several of these two-coordinate 3*d* complexes display exceptionally high thermal barriers to magnetization reversal [$\Delta \sim 325(4)$ K, for Fe^I] and slow magnetic relaxation (up to about 29 K) is found. In these mononuclear iron complexes, spin-orbit interactions give rise to significant magnetic anisotropy, in addition to efficient coupling of the molecular vibrations to those of lattice phonon modes. Consequently, rapid QTM occurs even under an applied magnetic field.

Thermo- and photochromic materials. The systematic engineering of molecular complexes with atom-economical efficiency is an exciting area of worldwide research activity, as realization of this goal may afford a diverse array of materials suitable for molecule-based electronic applications. These materials are of interest owing to their potential use in a variety of high-density information storage, sensor, display, and device switching applications.



(a)



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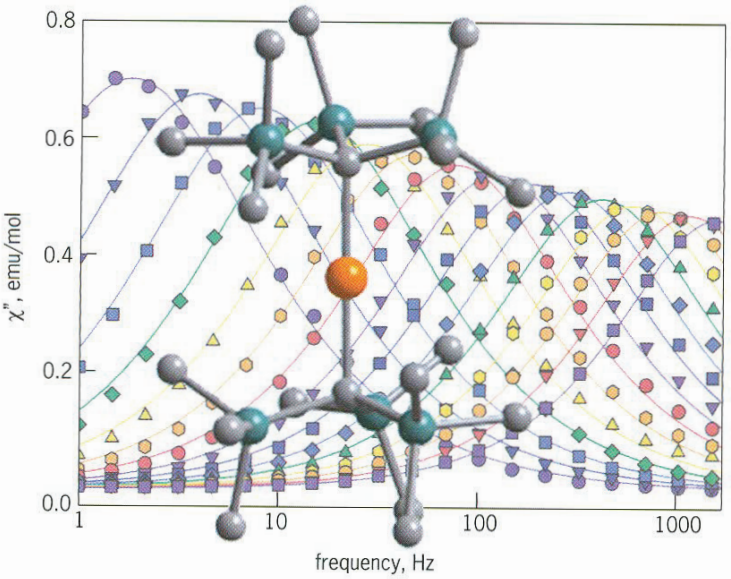

(c)

Fig. 4. Recent examples of mononuclear (*a*) $[NBu_4][TbPc_2]$, (*b*) [K(222-crypt)] $[Fe^{I}\{C(SiMe_3)_3\}_2]$, and (*c*) $(Tp^{Ph})Co^{II}Cl$ single-molecule magnets. (*Adapted from N. Ishikawa et al., J. Am. Chem. Soc., 125:8694–8695, 2003; P. J. Ferko et al., submitted; and J. M. Zadrozny et al., Nat. Chem., 5:577–581, 2013*)

Among more celebrated switchable molecule-based materials are those derived from cyanometalate anions. The first example, which belongs to the Prussian blue structural archetype, consists of a face-centered cubic array of metal centers that are linked via bridging cyanides to form Fe(μ-CN)Co units (scheme 1). In these three-dimensional-defect solids, diamagnetic $Fe^{II}_{LS}(\mu\text{-CN})Co^{II}_{LS}$ units are reversibly converted into paramagnetic $Fe^{III}_{LS}(\mu\text{-CN})Co^{II}_{HS}$ ones upon light exposure or with changes in temperature (**Fig. 5**); their behavior is highly dependent on the ligand-field environment (at Co) and presence of interstitial alkali metal cations.

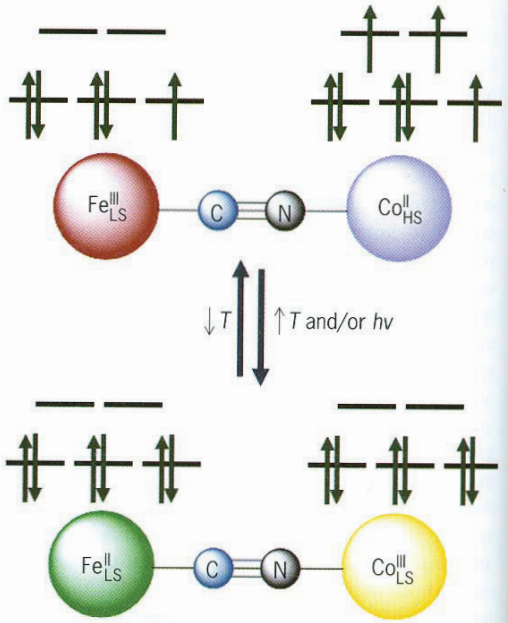

Fig. 5. Thermally and photoinduced electron transfer.

Using the concept of dimensional reduction, where capping ligands limit the number of cyanides available for forming linkages to adjacent metal centers, a variety of well-defined molecular clusters may be systematically prepared, whose optical and magnetic properties can be engineered to resemble those of Co/Fe Prussian blues (scheme 1). The optical and magnetic behavior of these Co/Fe valence tautomers may be systematically controlled as a function of ancillary ligand steric demand [various ligands such as 2,2′-bipyridines (bpy^R), pyrazolylborates (Tp^R), etc.], electron-density donation ability, and internuclear separation in the solid state (**Fig. 6**). It appears that tri-, tetra-, and hexanuclear complexes exhibit a wide temperature range over which their magnetic and optical properties may be switched; we were the first to demonstrate conclusively that the interconversion of the $Fe^{II}_{LS}(\mu\text{-CN})Co^{III}_{LS} \leftrightarrow Fe^{III}_{LS}(\mu\text{-CN})Co^{II}_{HS}$ states proceeds through a common intermediate and that their relaxation follows Arrhenius behavior. Current efforts are aimed at understanding structural and electronic factors responsible for these changes.

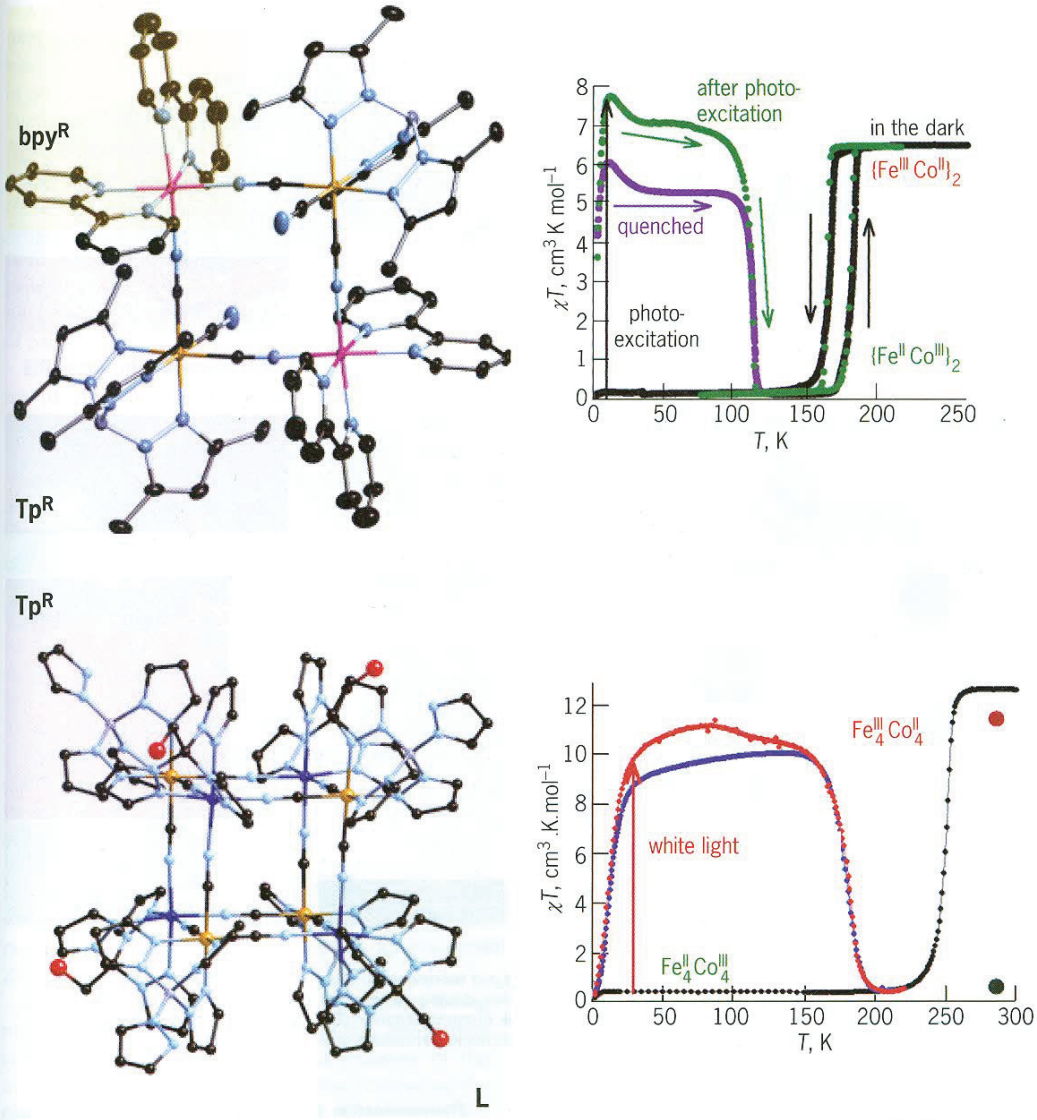

Fig. 6. (left) X-ray structure of thermo- and photochromic (top, left) tetranuclear and (top, right) octanuclear Co/Fe complexes. (bottom) Variable temperature magnetic data collected for both complexes in the presence and absence of light. (*Adapted from D.-F. Li et al., J. Am. Chem. Soc., 128:252–258, 2008 and Y.-Z. Zhang et al., Angew. Chem., Int. Ed., 49:3752–3756, 2010*)

For background information *see* ANTIFERROMAGNETISM; ATOM ECONOMY; CRITICAL PHENOMENA; CYANIDE; JAHN-TELLER EFFECT; LIGAND; MAGNETIC RELAXATION; MAGNETISM; MAGNETOCHEMISTRY; PARAMAGNETISM; PRUSSIAN BLUE in the McGraw-Hill Encyclopedia of Science & Technology.

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Nanostructured thermoelectric energy scavenging

Approximately 50–60% of the energy input that our society uses is eventually wasted as heat. Automobiles use only approximately 20–25% of the heat output of combustion, with about one-third of the remaining energy being rejected as heat through the exhaust pipe and another third being lost through