Zuschriften

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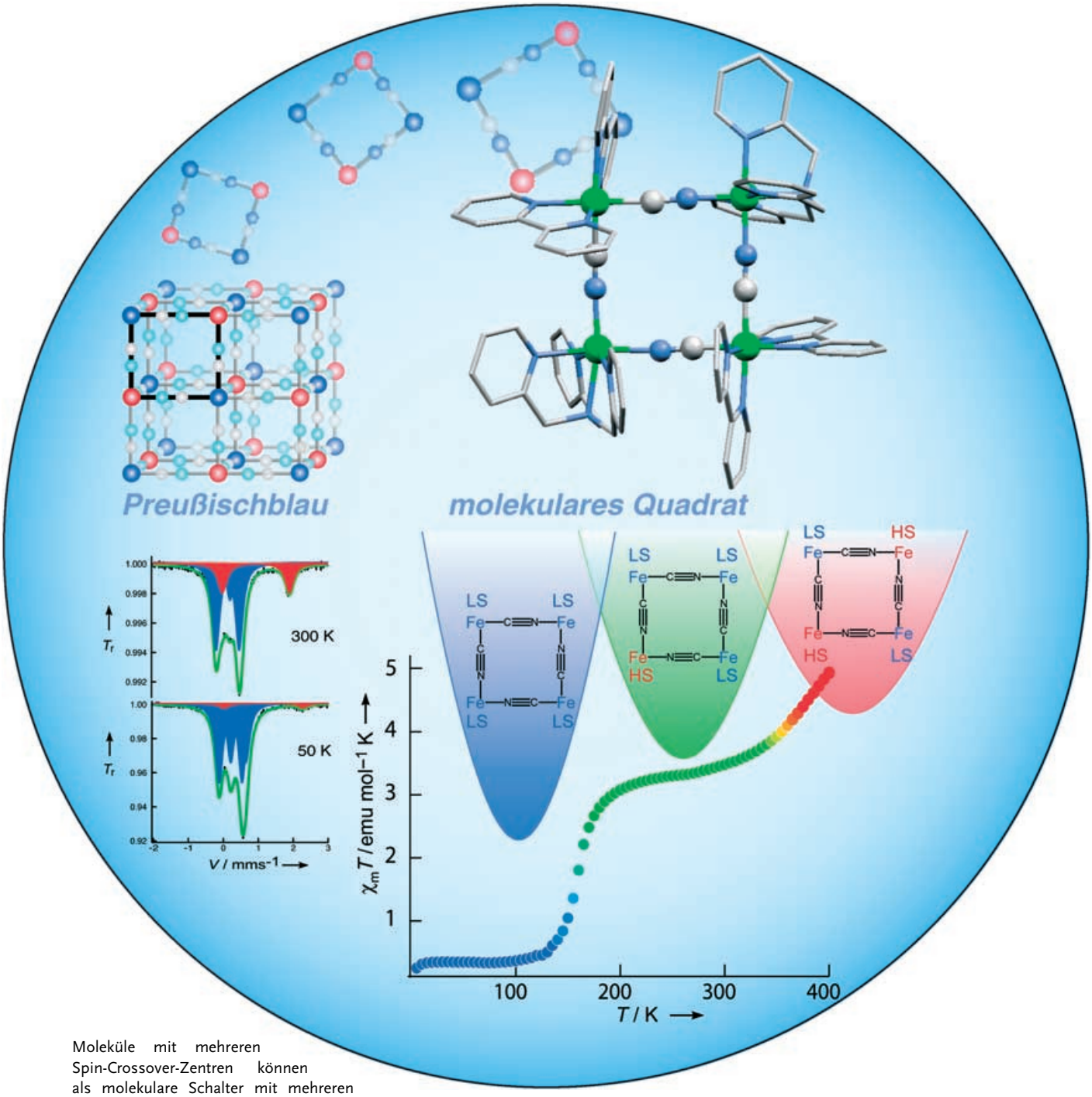

Moleküle mit mehreren Spin-Crossover-Zentren können als molekulare Schalter mit mehreren Zuständen angesehen werden. Das CN-verbrückte molekulare Quadrat $[Fe^{II}_4(\mu\text{-}CN)_4(bpy)_4(tpa)_4](PF_6)_4$ (bpy = 2,2′-Bipyridin; tpa = Tris(2-pyridylmethyl)amin), ein Preußischblau-Analogon, zeichnet sich durch einen thermisch induzierten zweistufigen Spinübergang aus. Näheres finden Sie in der Zuschrift von H. Oshio und Mitarbeitern auf den folgenden Seiten.

Molecular Switches

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Two-Step Spin Conversion in a Cyanide-Bridged Ferrous Square**

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An important route to the development of switches for advanced molecular devices involves changes in magnetic properties at the molecular level.[1] Spin crossover in transition-metal complexes, in which spin-state conversions occur as a result of heat, pressure, or light irradiation, is a key phenomenon for designing molecular switches.[2] Because cyanide-bridged complexes are relatively easy to synthesize and have rich magnetic properties, they have become the focus of this area of research. Prussian blue, which is a ferromagnet with a Curie temperature (T_C) of 5.6 K,[3] and some heterometal analogues that are high-T_C magnets with an ordering temperature up to 372 K are examples of well-known cyanide-bridged metal complexes.[4] Metal ions in cyanometalates typically adopt a low-spin configuration. However, introduction of ligands with weak ligand-field strengths and combinations of heterometal ions afford interesting magnetic properties such as spin crossover,[5] photoinduced magnetism,[6] and superparamagnetism.[7] Furthermore, molecules with more than one spin-crossover site can be used as multistepped molecular switches. Recently, some thermally induced, two-step spin-crossover complexes were reported.[8] However, the number of such systems is still small.[9] We have studied cyanide-bridged molecular squares, $[Fe_2M_2(\mu\text{-}CN)_4(bpy)_8]^{n+}$ (M = late first-row transition-metal ion; bpy = 2,2′-bipyridine), in which cyanide ions bridge four metal ions to form the macrocyclic tetranuclear core.[10] We found that by replacing bpy with tris(2-pyridylmethyl)amine (tpa), the ligand-field strength on the Fe^{II} centers is weakened and the resulting ferrous square, $[Fe^{II}_4(\mu\text{-}CN)_4(bpy)_4(tpa)_2](PF_6)_4$ (**1**-$(PF_6)_4$), showed two-step spin conversion.

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The reaction of $[Fe(CN)_2(bpy)_2]\cdot 3H_2O$[11] with $FeCl_2\cdot 4H_2O$, tpa,[12] and NH_4PF_6 in methanol afforded the tetranuclear complex **1**$(PF_6)_4$.[13] X-ray crystal structure analyses were performed at 100, 200, and 300 K, and the molecular structure of $\mathbf{1}^{4+}$ at 200 K is shown in Figure 1.

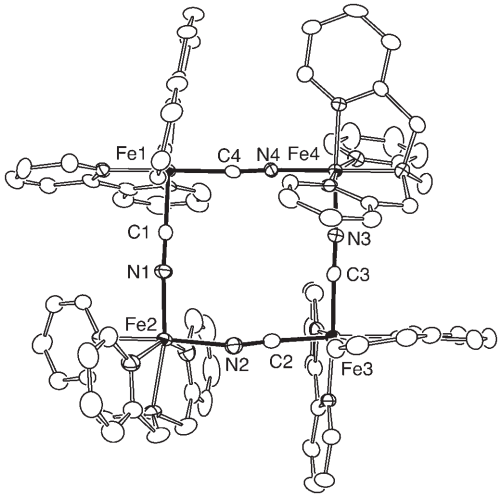

Figure 1. ORTEP diagram of $\mathbf{1}^{4+}$ at 200 K. Average coordination bond lengths [Å] about Fe^{II} ions at 100 K: Fe1 1.958, Fe2 1.976, Fe3 1.958, Fe4 1.963; at 200 K: Fe1 1.954, Fe2 2.154, Fe3 1.955, Fe4 1.965; and at 300 K: Fe1 1.954, Fe2 2.165, Fe3 1.959, Fe4 1.968.

The tetranuclear macrocycle $\mathbf{1}^{4+}$ is composed of four cyanide-bridged Fe^{II} ions, and the overall geometry is almost square. In the square, two $\{Fe(bpy)_2\}^{2+}$ centers and two $\{Fe(tpa)\}^{2+}$ centers are alternately bridged by four CN^- groups with the carbon atoms coordinated to the Fe^{II} ions in $\{Fe(bpy)_2\}^{2+}$. The Fe^{II} ions have octahedral coordination geometry, and four of the coordination sites are occupied by nitrogen atoms from one tpa or two bpy ligands. The two remaining *cis* positions are coordinated by either carbon or nitrogen atoms from the cyanide groups. The carbon and nitrogen atoms of the cyanide ligands act as π acceptors and σ donors, respectively, and because the cyanide carbon atom has a stronger ligand-field strength,[14] the Fe^{II}–C(cyanide) bond distances become shorter than the Fe^{II}–N(cyanide) distances. The average Fe–C(cyanide) bond length in the $\{Fe(bpy)_2\}^{2+}$ units is 1.916 Å, and the average Fe–N(cyanide) bond length in the $\{Fe(tpa)\}^{2+}$ units is 1.950 Å. Because the coordination bond lengths about Fe^{II} ions differ between the low-spin (LS) and high-spin (HS) states (Δd = 0.2–0.3 Å), the average bond lengths are related to the spin state of the Fe^{II} ions. At 100 K, the average coordination bond lengths involving the Fe^{II} ions are between 1.958 and 1.976 Å in both $\{Fe(bpy)_2\}^{2+}$ and $\{Fe(tpa)\}^{2+}$, and these values are characteristic of LS Fe^{II} ions. At 200 and 300 K, three of the Fe^{II} centers (Fe1, Fe3, and Fe4) stay in the LS state with average Fe^{II} bond lengths the same as the values at 100 K. One of the Fe^{II} ions (Fe2) in the $\{Fe(tpa)\}^{2+}$ moieties forms longer bonds to the ligands (d_{Fe2-N} = 2.154–2.165 Å), characteristic of a HS Fe^{II} ion.

Magnetic susceptibility measurements for **1**-$(PF_6)_4$ were carried out in the temperature range of 5–400 K, and a $\chi_m T$

versus temperature plot is shown in Figure 2. X-ray crystal structure analyses suggest that four Fe^{II} ions in the square are in a LS state below 100 K. The $\chi_m T$ values below 100 K were constant (0.3 emu mol^{-1} K), and the nonzero $\chi_m T$ values are

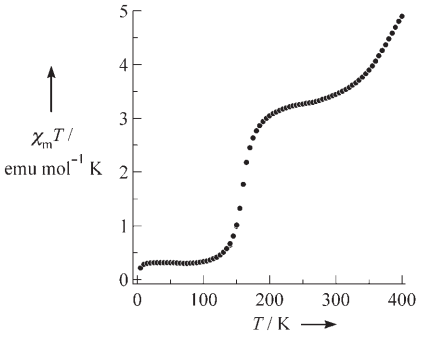

Figure 2. $\chi_m T$ versus T plot for **1**-$(PF_6)_4$.

due to a paramagnetic impurity corresponding to 2.5% of the HS Fe^{II} ($S=2$) species. As the temperature was raised to 200 K, the $\chi_m T$ values increased and reached a plateau value at 3.2 emu mol^{-1} K, which is close to the value (3.0 emu mol^{-1} K) expected for a free HS Fe^{II} ion. The plateau has a width of approximately 100 K and is centered at about 240 K. Upon increasing the temperature, another spin conversion occurred. However, the $\chi_m T$ values did not reach the plateau value (6.0 emu mol^{-1} K) expected for two uncorrelated HS Fe^{II} ions, even at 400 K. The $\chi_m T$ value at 400 K is 4.9 emu mol^{-1} K, which corresponds to 57% of the Fe4 ion being in the HS state. The magnetic susceptibility measurements clearly show the occurrence of a two-step spin conversion in **1**-$(PF_6)_4$. Notably, no hysteresis was observed in temperature-dependence measurements of the $\chi_m T$ values.

Reflectance spectra for a single crystal of **1**-$(PF_6)_4$ were measured on the (001) plane at 100 and 300 K with unpolarized light (Figure 3). The spectrum at 100 K consists of one sharp (2.13 eV) and two broad (2.3 and 2.6 eV) bands, and a new peak at 1.47 eV appeared with a decrease in the broad bands at 300 K. Absorption data for component molecules were used to assign the reflectance spectra. The LS Fe^{II} ion in $[Fe(CN)_2(bpy)_2]$ showed a d–d band at 570 nm (=2.17 eV),[15] whereas d–d bands for the LS and HS Fe^{II} ions in $[Fe(tpa)(L)_2]^{2+}$ (L = CH_3CN, CH_3OH) were observed at 516 (=2.40 eV) and 914 nm (=1.34 eV), respectively.[16] MLCT bands for the LS Fe^{II} species appeared in the high-energy region above 3.3 eV.[15,16] The sharp (2.13 eV) and broad (2.3 and 2.6 eV) bands in the reflectance spectrum at 100 K were, therefore, assigned to d–d transitions for the LS iron(II) ions in $\{Fe(bpy)_2\}^{2+}$ and $\{Fe(tpa)\}^{2+}$ moieties, respectively, and the new band (1.47 eV = 838 nm) at 300 K is due to d–d transitions for HS Fe^{II} species in the $\{Fe(tpa)\}^{2+}$ moiety. The observed changes in the reflectance spectra are in accord with the magnetic and Mössbauer data.

Selected ^{57}Fe Mössbauer spectra of **1**-$(PF_6)_4$ are shown in Figure 4. The Mössbauer spectrum at 50 K is dominated by two LS doublets (four lines in blue), whose Mössbauer parameters (LS1: $\delta=0.21$ and $\Delta E_Q=0.66$ mm s^{-1}; LS2: $\delta=0.43$ and $\Delta E_Q=0.43$ mm s^{-1}) are characteristic of LS Fe^{II}

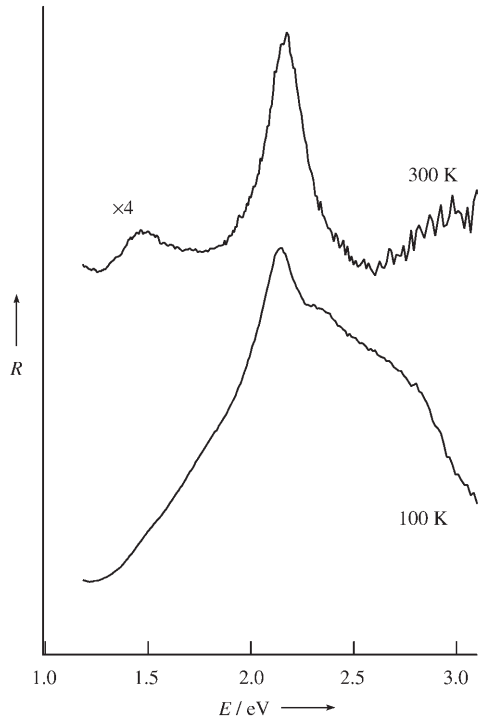

Figure 3. Reflectance spectra of **1**-$(PF_6)_4$ at 100 and 300 K. R = reflectivity, E = photon energy.

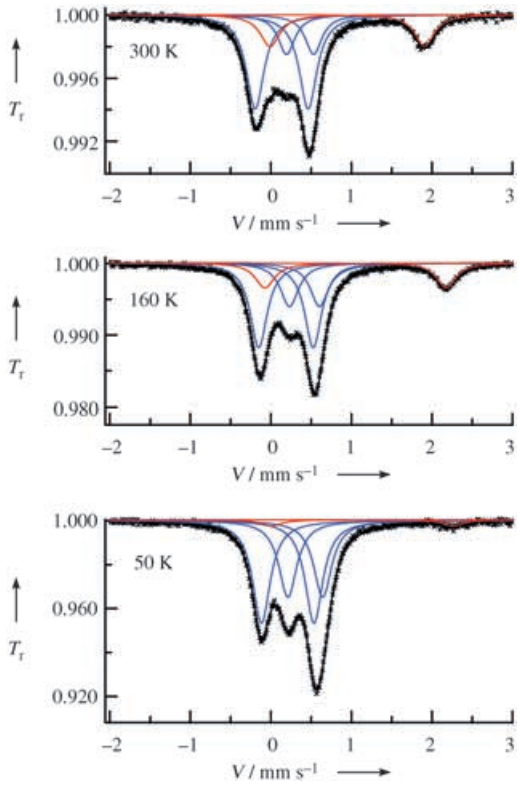

Figure 4. Selected ^{57}Fe Mössbauer spectra of **1**-$(PF_6)_4$. Velocity (V) is relative to iron metal. Low-spin pairs in blue and high-spin pair in red. T_r = relative transmission.

species. An additional small doublet (two lines in red, $\delta = 1.13$ and $\Delta E_Q = 2.26\ mm\,s^{-1}$) corresponds to a HS Fe^{2+} species, which is a paramagnetic impurity. The bpy ligand is a strong π acid, and the cyanide carbon atoms act as π acceptors. Furthermore, the LS Fe^{II} ions (Fe1 and Fe3) in the $\{Fe(CN)_2(bpy)_2\}$ centers have smaller isomer shifts than the Fe2 and Fe4 ions in $\{Fe(NC)_2(tpa)\}$ centers. Therefore, the LS1 and LS2 doublets were assigned to the Fe1/Fe3 and Fe2/Fe4 pairs, respectively. The peak-area ratio of the LS1, LS2, and HS doublets is 0.52:0.44:0.04 at 50 K, even though X-ray crystal structure analysis at 100 K showed that all Fe^{II} ions are in LS states. The deviation of the area ratio for LS1 and LS2 is caused by the different Lamb–Mössbauer factors for each LS species.

As the temperature was increased, the LS2 doublet lost intensity, and the HS doublet gained intensity. The ratios of the peak areas for LS1, LS2, and HS doublets became 0.53:0.29:0.18 and 0.56:0.22:0.21 at 160 and 300 K, respectively, meaning that either Fe2 or Fe4 is in a HS state at 300 K. The Mössbauer measurements and X-ray crystallographic analyses suggest the occurrence of a complete spin conversion on the Fe2 ion at 300 K. In summary, **1**-$(PF_6)_4$ exhibits a two-step spin conversion with the first step occurring on the Fe2 ion at $T_{sc} = 160$ K (T_{sc} = spin-conversion temperature) and the second step starting to occur on Fe4 at 300 K. Light-induced excited-spin-state trapping (LIESST) experiments are currently underway to explore the possibility of two-step spin conversion by irradiation.

Experimental Section

All procedures were carried out under a nitrogen atmosphere. $FeCl_2 \cdot 4H_2O$ (36 mg, 0.18 mmol) in methanol (6.5 mL) was added to a solution of $[Fe(CN)_2(bpy)_2] \cdot 3H_2O$ (86 mg, 0.18 mmol) in methanol (13.5 mL), followed by the addition of tpa (52 mg, 0.18 mmol). A methanolic solution (20 mL) of NH_4PF_6 (118 mg, 0.72 mmol) was added to the dark red solution by diffusion in an H tube to afford dark-red tablets of **1**-$(PF_6)_4$. Elemental analysis (%) calcd for $C_{80}H_{68}N_{20}F_{24}Fe_4P_4$: C 45.48, H 3.24, N 13.26; found: C 45.36, H 3.08, N 13.20.

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[13] Crystal data for **1** at 100 K: $C_{80}H_{68}N_{20}F_{24}Fe_4P_4$, dark red tablet ($0.2 \times 0.2 \times 0.2\ mm^3$), $M_r = 2112.82$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, triclinic $P\bar{1}$, $a = 14.426(2)$, $b = 15.042(2)$, $c = 22.272(3)$ Å, $\alpha = 77.270(3)$, $\beta = 83.486(3)$, $\gamma = 64.112(3)°$, $V = 4240(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.655\ Mg\,m^{-3}$, 20179 reflections collected, 12124 independent reflections ($R_{int} = 0.0435$), final refinement with 1189 parameters converged with agreement factors $R1 = 0.0531$, w$R2 = 0.1279$ using 1189 reflections with $I > 2\sigma$. Crystal data at 200 K: triclinic $P\bar{1}$, $a = 14.470(2)$, $b = 15.165(2)$, $c = 22.536(3)$ Å, $\alpha = 77.326(2)$, $\beta = 83.317(2)$, $\gamma = 63.709(2)°$, $V = 4324.7(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.622\ Mg\,m^{-3}$, 20649 reflections collected, 12371 independent reflections ($R_{int} = 0.0479$), final $R1 = 0.0600$, w$R2 = 0.1445$ using 1189 reflections with $I > 2\sigma$. Crystal data at 300 K: triclinic $P\bar{1}$, $a = 14.561(3)$, $b = 15.297(3)$, $c = 22.661(4)$ Å, $\alpha = 77.391(4)$, $\beta = 83.209(4)$, $\gamma = 63.602(4)°$, $V = 4411(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.591\ Mg\,m^{-3}$, 20765 reflections collected, 12553 independent reflections ($R_{int} = 0.0588$), final $R1 = 0.0689$, w$R2 = 0.1612$ using 1189 reflections with $I > 2\sigma$. CCDC 274454 (**1** at 100 K), 274455 (**1** at 200 K), and 274456 (**1** at 300 K) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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