Single-Molecule Magnets

Synthesis and Characterization of a Cobalt(II) Single-Molecule Magnet[**]

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Single-molecule magnets (SMMs) provide a tantalizing glimpse of the future possibilities for data storage technology.[1] The well-defined molecular size of SMMs has also proved ideal for the observation of quantum effects such as tunneling of the magnetization.[2] The requirements for SMM behavior are well established: the presence of a large-spin ground state (S) and an Ising-type magnetic anisotropy ($D < 0$) leads to an energy barrier (ΔE) to reorientation of the magnetization, where $\Delta E = S^2 D$ for integer-spin ground states. Consequently, if the available thermal energy is small compared to the barrier height, slow magnetic relaxation can occur. The prototype SMM $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]$ still possesses the largest energy barrier of 66 K due to its $S = 10$ ground state and large negative D parameter.[3] Thus, many current routes to SMMs culminate in manganese(III) containing complexes, to exploit the associated large single-ion anisotropy.[4] Another promising candidate ion for the isolation of SMMs with a large anisotropy is cobalt(II). Despite this, there is only one report of a cobalt(II) cluster which displays slow magnetic relaxation.[5] Slow magnetic relaxation has been observed in a one-dimensional chain compound, which comprises cobalt(II) ions and nitronyl nitroxide radicals.[6]

We have developed a route to nickel(II) spin clusters using the citrate ligand ($cit^{4-} = [C(O^-)(CO_2^-)(CH_2CO_2^-)_2]$).[7] A nickel(II) citrate cluster, which contains 21 metal centers, displays SMM behavior as shown by the appearance of frequency-dependent out-of-phase signals in the ac susceptibility below 800 mK.[8] To isolate spin clusters with a larger

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magnetic anisotropy, and thus higher blocking temperatures, we have extended our synthetic approach to cobalt(II). Herein, we report the synthesis and characterization of a new hexanuclear cobalt(II) SMM.

Slow diffusion of ethanol into a neutral aqueous solution containing Co^{II} and citrate ions in the presence of NMe_4^+ and Na^+ ions gives pale-pink rodlike crystals of $[(NMe_4)_3Na\{Co_4(cit)_4[Co(H_2O)_5]_2\}]\cdot 11\,H_2O$ (**1**$\cdot$11 H_2O; see Experimental Section). The single-crystal X-ray structure of **1**$\cdot$11 H_2O reveals a hexanuclear cluster based on a $\{Co_4O_4\}$ core, where each oxygen atom is derived from a tridentate citrate alkoxide group (Figure 1).[9] The four citrate ligands are tetradeprotonated, in contrast to previously reported mono- and dinuclear cobalt(II) complexes which contain the trideprotonated ligand $Hcit^{3-}$.[10] The three carboxylate groups of each ligand cap the Co^{II} centers bridged by the alkoxide group. Each cobalt(II) center within the core is hexacoordinated, and displays a twisted trigonal-prismatic geometry. Two of the ligands are each bonded to a further octahedral Co^{II} center,[11] through carboxylate groups in an *anti–syn* bridging mode; this is the first time this bonding motif has been observed for the citrate ligand. The bonding mode of the two citrate ligands which bridge three metal centers (e.g., Co1-Co2-Co6) has been identified in nickel and iron complexes.[7,12] Water molecules complete the coordination sphere of Co3 and Co5; the $\{Co(O_2CR)Co(H_2O)_5\}$ fragment is unusual but has been observed in $[Co_2(H_2O)_5(pdc)_2]$ (H_2pdc is pyrdidine-2,6-dicarboxylic acid).[13] One Na^+ and three NMe_4^+ ions balance the overall negative charge on the cluster.

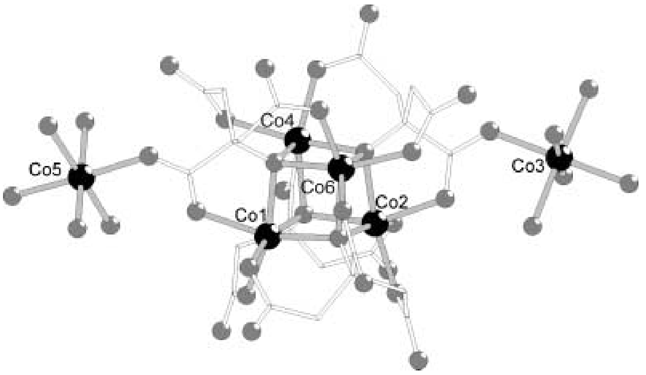

Figure 1. The structure of the anion in **1** (Co, black sphere; O, gray sphere; C, rods; H omitted for clarity). Bond length ranges [Å; average esd = 0.006 Å] Co-O: 2.075–2.142 (citrate O^-), 2.055–2.157 (citrate CO_2^-); bond angle ranges [°; average esd = 0.2°] Co-O-Co: 95.9–100.3.

If the synthesis is carried out in the absence of Na^+ ions, small needlelike crystals of **2**$\cdot$16 H_2O are obtained. These were found to be unsuitable for single-crystal X-ray diffraction due to multiple twinning. However, IR data and elemental analysis of **2**$\cdot$16 H_2O are consistent with a compound, which contains the $\{Co_6\}$ cluster found in **1**$\cdot$11 H_2O with the charge balanced by four NMe_4^+ ions, that is, $[(NMe_4)_4\{Co_4(cit)_4[Co(H_2O)_5]_2\}]\cdot 16\,H_2O$ (see Experimental Section and Supporting Information).

For a fully solvated sample, **1**$\cdot$11 H_2O, at 300 K $\chi T = 17.5\ cm^3\,mol^{-1}\,K$, consistent with six noninteracting Co^{II} centers with $S_i = 3/2$ and an average g value of 2.5 (Figure 2, ○).[14] χT reaches a local minimum at 20 K, then increases to reach a value of $16.5\ cm^3\,mol^{-1}\,K$ at 10 K, before dropping sharply to $13.2\ cm^3\,mol^{-1}\,K$ at 1.8 K. At 1.8 K, the magnetization $M/N\mu_B$ is not saturated in a field of 5 T and reaches a value of 11.2 (Figure 2, inset). For a fully solvated sample (**2**$\cdot$16 H_2O), χT (Figure 2, +) and $M/N\mu_B$ are practically identical to those of **1**$\cdot$11 H_2O. The magnetic behavior of partially desolvated samples **1**$\cdot$7 H_2O and **2**$\cdot$6 H_2O is shown in Figure 3.[15] The behavior is very similar to the fully solvated samples between 300 K and 50 K, (compare with Figure 2). Below 50 K there are slight differences, in particular the maximum in χT found in the fully solvated samples is no longer observed. As found for solvated samples, $M/N\mu_B$ is not saturated in a field of 5 T at 1.8 K (Figure 3, inset). It is difficult to perform a quantitative analysis of magnetic susceptibility data obtained for polycrystalline cobalt(II) compounds due to the large orbital contribution. At very low temperatures, each Co^{II} center may be treated as an effective spin $S' = 1/2$ center with anisotropic g values.[16] Using this approximation, the values obtained for $M/N\mu_B$ in all the four samples, are consistent with an effective value for

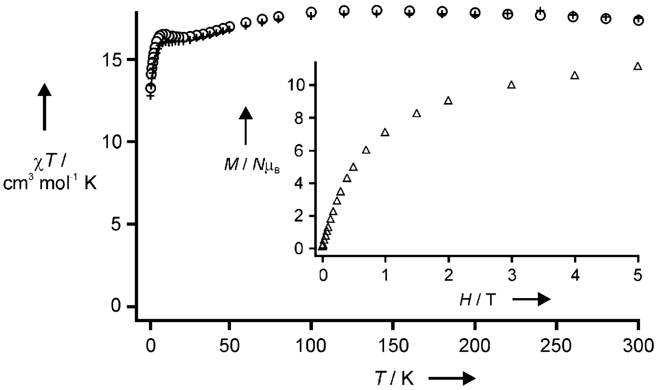

Figure 2. Temperature dependence of χT for **1**$\cdot$11 H_2O (○) and **2**$\cdot$16 H_2O (+). Inset shows the field dependence of the magnetization for **1**$\cdot$11 H_2O at 1.8 K.

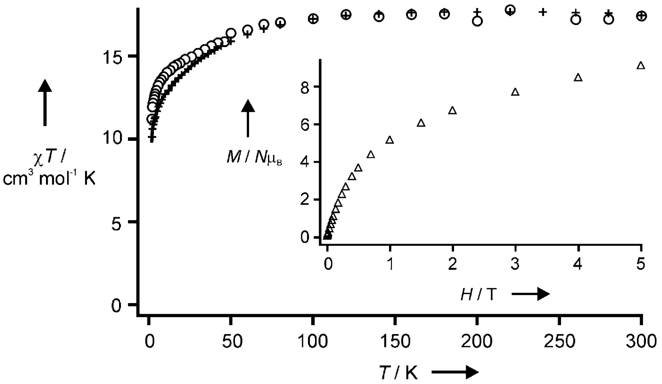

Figure 3. Temperature dependence of χT for partially solvated samples: **1**$\cdot$7 H_2O (○) and **2**$\cdot$6 H_2O (+). Inset shows the field dependence of the magnetization for **1**$\cdot$7 H_2O at 1.8 K.

S'_{cluster} of 3 and an average g value >3 for the new $\{Co_6\}$ cluster.

In ac susceptibility measurements, fully solvated samples $\mathbf{1}\cdot 11\,H_2O$ and $\mathbf{2}\cdot 16\,H_2O$ show the onset of a frequency-dependent out-of-phase ac signal (χ'') below 6 K, although no χ'' peaks are observed above 1.8 K. In contrast, for the partially desolvated samples, well-resolved peaks for χ'' are observed. Figure 4 shows the in-phase and out-of-phase components of the ac susceptibility of $\mathbf{1}\cdot 7H_2O$ and $\mathbf{2}\cdot 6H_2O$, measured at three different frequencies. An Arrhenius analysis yields the parameters: $\Delta E/k_B = 26$ K (18 cm^{-1}) and $\tau_0 = 8.2\times10^{-9}$ s for $\mathbf{1}\cdot 7H_2O$ and $\Delta E/k_B = 32$ K (22 cm^{-1}) and $\tau_0 = 2.1\times10^{-9}$ s for $\mathbf{2}\cdot 6H_2O$.[17] The magnitude of χ'' compared to χ' at the peak position, and the values obtained for $\Delta E/k_B$ and τ_0 are entirely consistent with SMM behavior. Hence, the $\{Co_6\}$ cluster found in compounds **1** and **2**, is a new example of a cobalt(II) SMM. Furthermore, the energy barriers obtained for $\mathbf{1}\cdot 7H_2O$ and $\mathbf{2}\cdot 6H_2O$ are the highest energy barriers found for a non-manganese based SMM (compared with $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$, $S=10$, $\Delta E/k_B = 24.5$ K, tacn = triazacyclononane; determined from ac susceptibility measurements).[18]

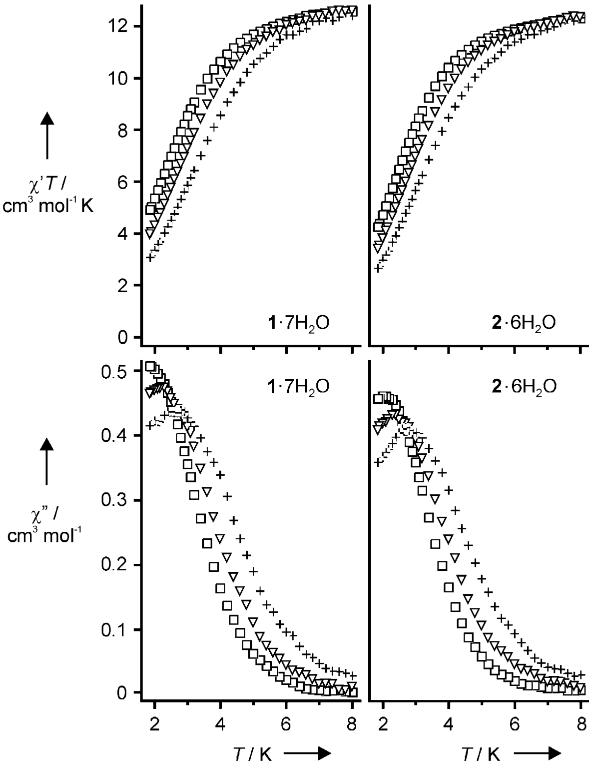

Figure 4. The in-phase and out-of-phase components of the ac susceptibility shown as $\chi'T$ versus T and χ'' versus T measured at 48 (□), 248 (△), and 1302 Hz (+) for samples of $\mathbf{1}\cdot 7H_2O$ and $\mathbf{2}\cdot 6H_2O$.

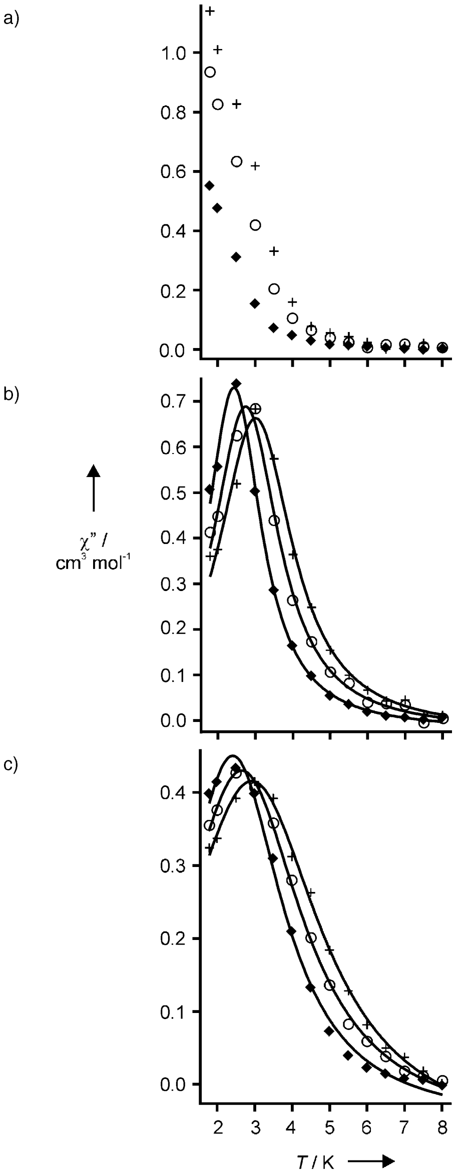

Figure 5. The out-of-phase component of the ac susceptibility χ'' versus T measured at 124 (◆), 496 (○), and 1302 Hz (+) for samples of **2**: a) fully solvated; b) dried in vacuo for 15 min; c) dried in vacuo for 3 h. Solid lines are least-squares fits to the data, yielding the following parameters: b) $\Delta E/k_B = 29$ K, $\tau_0 = 8.0\times10^{-9}$ s; c) $\Delta E/k_B = 32$ K, $\tau_0 = 2.1\times10^{-9}$ s.

Figure 5 shows the effect of solvent loss upon the out-of-phase ac component for **2**. Fully solvated samples show the onset of a frequency-dependent out-of-phase signal below 6 K (see Figure 5 a). Figure 5 b shows that after drying in vacuo for 15 min, peaks are observed for χ''. An Arrhenius analysis yields the parameters $\Delta E/k_B = 29$ K (20 cm^{-1}) and $\tau_0 = 8.0\times10^{-9}$ s, comparable to those found for samples of $\mathbf{1}\cdot 7H_2O$ and $\mathbf{2}\cdot 6H_2O$ after drying for 3 h. The shift in position of the χ'' signals for both **1** and **2** when moving from fully, to partially solvated samples is interesting. A similar shift in position of χ'' with respect to the amount of lattice solvent has been noted for manganese-based SMMs.[19] Upon solvent loss from the lattice, distortions in the cluster geometry will occur. This may be especially important at the two outer cobalt centers, which are each bonded to the central tetranuclear core by a monodentate carboxylate oxygen donor. Structural changes can affect the activation energy ΔE in two ways. We see from Figure 1 that the $\{Co_6\}$ cluster does not have axial symmetry. A change in the cluster geometry can therefore affect both the barrier height and the tunneling probability. Slightly different molecular geometries thus account for the difference in the $\Delta E/k_B$ parameters obtained for **1**·7 H_2O and **2**·6 H_2O.

In conclusion, we have synthesized a new hexanuclear cobalt(II) spin cluster using the tetradeprotonated form of the proligand citric acid. Magnetic measurements show that this cluster behaves as a single-molecule magnet, displaying the largest energy barrier to reorientation of the magnetization for a non-manganese based SMM. Hence, this study highlights the potential for creating improved SMMs by using cobalt(II) ions as metal centers.

Experimental Section

Addition of citric acid monohydrate (1.518 g, 7.2 mmol) to an aqueous solution (10 mL) of $CoSO_4$·7 H_2O (2.030 g, 7.2 mmol) gave a solution with pH 1.46. The pH value was raised to 7.0 using NMe_4OH·5 H_2O (4.65 g, 25.7 mmol). 0.2 mL aliquots of this solution were taken, mixed with a solution of Na_2SO_4 (0.01 g in 0.2 mL H_2O) and layered with EtOH (1.6 mL). After one month, well-formed rodlike crystals of **1**·11 H_2O could be isolated. Yield per aliquot: 4 mg (16 % based on Co); elemental analysis (after drying for 3 h in vacuo) calcd(%)for **1**·7 H_2O ($C_{36}H_{86}Co_6N_3NaO_{45}$): C 26.08, H 5.23, N 2.53; found: C 26.25, H 5.02, N 2.36. Selected IR data (KBr): $\tilde{\nu} = 3434$ (s), 1573 (s), 1489 (m), 1385 (m), 1292 (w), 1242 (w), 1087 (w), 1057 (w), 950 (w), 920 (w), 850 (w), 689 (w), 648 cm^{-1} (w). For the synthesis of **2**, 0.2 mL aliquots of the solution at pH 7.0 were taken, mixed with H_2O (0.2 mL) and then EtOH (1.9 mL) and kept in sealed sample tubes. After two weeks needlelike crystals of **2** could be isolated: elemental and thermogravimetric analysis on fully solvated samples are consistent with 16 water molecules of crystallization. Yield per aliquot: 8 mg (29 % based on Co); elemental analysis (after drying for 3 h in vacuo) calcd(%) for **1**·6 H_2O ($C_{40}H_{96}Co_6N_4O_{44}$): C 28.41, H 5.72, N 3.31; found: C 28.59, H 5.76, N 3.27. Selected IR data (KBr): $\tilde{\nu} = 3437$ (s), 1577 (s), 1489 (m), 1384 (m), 1289 (w), 1241 (w), 1094 (w), 1057 (w), 950 (w), 922 (w), 850 (w), 689 (w), 650 cm^{-1} (w).

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[9] Crystal structure analysis: Intensity data were collected using a Bruker AXS SMART CCD area detector attached to Station 9.8 at the CCLRC Daresbury synchrotron radiation source ($\lambda = 0.6932$ Å). The structure was solved by direct methods using the SHELXS-97 program. The refinement and all further calculations were carried out using SHELXL-97. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. After the location of three tetramethylammonium cations and two possible positions for the sodium cation (occupancy 0.5 each site), giving four cations in all, the SQUEEZE routine in PLATON was used (488 electrons for a volume of 1660.8 Å). The disordered solvent of crystallization was equated to 11 water molecules per molecule of complex (per asymmetric unit). The crystal structure was refined in the noncentrosymmetric space group $Pna2_1$ as a racemic twin, refined x factor = 0.409(19). Crystal data for **1**·11 H_2O: 0.14 × 0.02 × 0.02 mm; $C_{36}Co_6H_{94}N_3NaO_{49}$, $M_r = 1729.10$; orthorhombic, space group $Pna2_1$, $a = 23.093(3)$, $b = 14.3843(18)$, $c = 21.691(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 7205.2(16)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.595$ g cm^{-3}, $T = 150$ K, $1.66 < \theta < 24.06°$; $F(000) = 3504$. Refinement by full-matrix least-squares methods gave final $R_1(F_o) = 0.0565$, $wR_2(F_o^2) = 0.1590$ for 9701 reflections with $I > 2\sigma(I)$ and 632 parameters; max/min residual electron density 0.662/−0.681 e Å^{-3}. CCDC-209085 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[14] Variable-temperature magnetic measurements were recorded using a SQUID magnetometer (Quantum Design). Crushed single crystals were restrained between the two halves of a gelatine capsule by inverting the top half.

[15] After drying in vacuo at ambient temperature for three hours, samples analyzed as **1**·7 H_2O and **2**·6 H_2O.

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