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Tetranuclear and Octanuclear Cobalt(II) Citrate Cluster Single Molecule Magnets

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In a follow-up study of the cobalt(II) member **1** of a family of isostructural cubane clusters of type $[C(NH_2)_3]_8[M^{II}_4(cit)_4]\cdot 8H_2O$ (cit = citrate, M = Mg, Mn, Fe, Co, Ni, Zn) by measuring AC magnetic susceptibilities, as a function of frequency, this compound clearly displays behaviour typical of magnetization reversal and slow magnetic relaxation ($\Delta E = 13.1$ K, $\tau_o = 8.4 \times 10^{-7}$ s). A related octanuclear cluster $[Co_8(C_4O_7)_4(H_2O)_{12}]\cdot 24H_2O$ (**2**) that contains a $[Co_4(C_4O_7)_4]$ cubane moiety, behaves likewise ($\Delta E = 20.5$ K, $\tau_o = 1.0 \times 10^{-7}$ s).

Introduction

Single-molecule magnetism in cobalt(II) clusters is much less well known than it is in manganese(II)/(III)/(IV) clusters. Indeed, there is some controversy as to whether some of the reported examples are true single-molecule magnets (SMMs) or whether they are examples of spin glass or superparamagnetic-like molecular materials. Octahedrally coordinated Co^{II} single ions have an orbitally degenerate $^4T_{1g}$ ground state, and this, when combined with intra-cluster ferromagnetic coupling within Co^{II} cluster species to yield a large ground-state spin S_T, as well as negative magnetoanisotropy (i.e. a negative zero-field splitting parameter, D_{mol}, occurs for the polynuclear molecule), provide the criteria for SMM behaviour. The first reported Co^{II} cluster SMM, $[Co_4(hmp)_4(MeOH)_4Cl_4]$, in which hmp^- is the anion of 2(hydroxymethyl)pyridine, displayed a cubane geometry, with S_4 site symmetry, an $S_T = 6$ coupled spin ground state and a negative D_{mol} value, the latter originating from positive values of the single ion D_{Co} values.[1] Steps were noted in the magnetization hysteresis loop obtained on a single crystal, M values being measured with H parallel to the easy-axis, under different scanning rates at temperatures between 0.04–1.1 K, by means of a micro-SQUID device, and these data provided one of the key observables for SMM behaviour. Oshio and Nakano subsequently made angular overlap model (AOM) calculations of single-ion D values for d^1 to d^9 octahedral ions, in cubane clusters, and predicted SMM behaviour by means of designing clusters that have D_{mol} negative, the latter originating from either the individual D_{ion} tensors being positive and aligned orthogonal to the hard (radial)-axis of the cube or the individual D_{ion} tensors (negative) being aligned collinear with the easy-axis.[2a] Experimentally, they obtained Fe^{II} (d^6) SMMs by such designs when combined with careful chemical variations in alkoxo-bridging Schiff base chelates.[2b]

As well as the cobalt(II) cluster SMMs just described (and others summarized in Table 1, below), there are a number of mononuclear cobalt(II)-{organic radical} compounds known that clearly exhibit SMM properties. In these cases intermolecular interactions were eliminated by preparing and measuring the samples in frozen solution, the radicals often being formed, in situ, upon light irradiation.[3]

In a recent paper describing a family of anionic, isostructural cubane clusters, with S_4 symmetry, of type $[C(NH_2)_3]_8[M^{II}_4(cit)_4]\cdot 8H_2O$, where cit^{4-} is the citrate tetraanion, $^-OC(CO_2^-)(CH_2CO_2^-)_2$, M^{II} = Mg, Mn, Fe, Co, Ni, Zn, we observed weak intra-cluster antiferromagnetic coupling in the Mn, Fe and Co cases and weak ferromagnetic coupling in the Ni case by means of DC susceptibility and magnetization studies.[4] The Co case had us intrigued because of (i) the orbital degeneracy of the single ions and the effect, after perturbation by spin-orbit coupling and low-symmetry ligand fields upon magnetic anisotropy and SMM features, (ii) the general paucity of reports of slow relaxation of magnetization being observed in Co^{II} clusters and those that showed slow relaxation had high S_T values (see Table 1), (iii) a prior report of SMM behaviour in a Co^{II}_6-citrate cluster that contained within it the cubane moiety described here, appended to two $[Co(H_2O)_5]^{2+}$ cations.[5] We therefore made in-phase (χ'_M) and out-of-phase (χ''_M) AC susceptibility measurements, as a function of

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Table 1. Values of ΔE and τ_o for cobalt(II) clusters and cobalt(II) mononuclear-radical complexes obtained from AC χ''_M vs. T data (t.w. this work, n.a. not available, s.s. see script).

Complex	ΔE [K]	$10^7\tau_o$ [s]	S_T	Ref.
1	13.1	8.4	6 s.s.	t.w.
2	20.5	1.0	n.a.	t.w.
$[Co_4(hmp)_4(MeOH)_4Cl_4]$	n.a.	n.a.	6	[1]
$[Co_6(cit)_4(H_2O)_{10}]^{4-}$[a]	26.0	0.08	3[f]	[5]
$[Co_8(phosphonate)_{10}]$[b]	84.0	0.00003		[12,13]
$[Co_{12}(bm)_{12}(NO_3)]$[c]	82.0[d]	–	6[f]	[14]
$[Co_{20}(OH)_6(OAc)_{22}(HL)_4]$[e]	n.a.	n.a.	4?	[15]
$[Co^{II}_4Co^{III}_3(HL')_6(NO_3)_3]$[g]	n.a.	n.a.	2[f]	[16]
$[Co_7(bzp)_6(N_3)_9(OMe)_3]^{2+}$[h]	n.a.	n.a.	7/2[f]	[17]
$[Co(NCO)_2(4NOPy)_4]$[i,j]	50.0	1.8	5/2[f]	[3b]
$[Co(NCS)_2(4PPC)_4]$[j,k]	89.0	0.0023	n.a.	[3a]
$[Co(p\text{-tolsal})_2(cD5py)_2]$[j,l]	72.0	0.02	21/2	[3c]

[a] Full formula $(Me_4N)_3Na[Co_6(cit)_4(H_2O)_{10}]\cdot 11H_2O$. [b] Full formula $(Et_3NH)[Co_8(chp)_{10}(O_3PPh)_2(NO_3)_3(Hchp)_2]$, Hchp = 6-chloro-2-hydroxypyridine. [c] Full formula $[Co_{12}(bm)_{12}(NO_3)(O_2CMe)_6(EtOH)_6](NO_3)$, Hbm = (1*H*-benzimidazol-2-yl)methanol. [d] Deduced using $\Delta E = U = S_T^2|D|$. [e] Full formula $[Co_{20}(\mu_3\text{-}OH)_6(O_2CMe)_4(\mu_2\text{-}O_2CMe)_{12}(\mu_3\text{-}O_2CMe)_6(HL)_4(dmf)_2]\cdot 2H_2O\cdot 1.6dmf$ where $HL^{3-} = pyC(O^-)(OH)pyC(O^-)_2py$. [f] Assumes Co^{II} ions have $S_{eff} = 1/2$. [g] Full formula $[Co^{II}_4Co^{III}_3(HL)_6(NO_3)_3(H_2O)_3](NO_3)_2\cdot 9MeOH\cdot 4.5H_2O$ where $H_3L' = H_2NC(CH_2OH)_3$. [h] Full formula $[Co_7(bzp)_6(N_3)_9(OMe)_3](ClO_4)_2\cdot 2H_2O$, bzp = 2-benzoylpyridine. [i] 4NOPy is 4-(*N*-*tert*-butyl-*N*-oxylamino)pyridine radical. [j] In frozen solution. [k] 4PPC = (4-pyridyl)phenylcarbene. [l] cD5py is a cyclopentadiazo-pyridine derivative that forms a carbene after irradiation.

both frequency and temperature, on $[C(NH_2)_3]_8[Co^{II}_4(cit)_4]\cdot 8H_2O$ (**1**). To our great surprise, slow relaxation behaviour was clearly evident and we describe the results here together with data on another of our recently reported cubane-containing Co^{II} clusters, $[Co_8(C_4O_7)_4(H_2O)_{12}]\cdot 24H_2O$ (**2**).[6] The ligand in **2**, a trisubstituted methoxide, $^-OC(CO_2^-)_3$, was obtained in situ, when cobalt(II) salts were reacted with dihydroxyfumaric acid. Preliminary results have been presented.[7]

Results and Discussion

The structures of **1** and **2** are shown in Figure 1, the cubane unit of **1** having Co^{II} centres with geometry between octahedral and trigonal prismatic, S_4 cube symmetry and all Co atoms equivalent (Co···Co = 3.22 and 3.17 Å; Co–O–Co = 97–99°).[4] Each cubane cluster is separated from neighbours by numerous hydrogen-bonding interactions involving guanidinium cations and lattice water molecules. Details of chiral aspects of the citrate ligands and the cubane clusters have been given. Because of the shorter "reach" of the ligand chelating arms in **2**, the Co^{II} geometry [M(1)] in the $Co_4(C_4O_7)_4^{\,4-}$ moieties of the cluster is close to trigonal prismatic.[6]

The DC magnetic moments for **1** were reported by us previously,[4] and were of magnitude ca. 9.25 μ_B per Co_4 (χ_MT = 10. 71 $cm^3\,mol^{-1}\,K$) between 300 and ca. 50 K but with a very broad maximum at ca. 100 K of 9.35 μ_B. They then decreased rapidly to reach 7.67 μ_B (χ_MT = 7.35 $cm^3\,mol^{-1}\,K$) at 4.5 K. Such behaviour was interpreted to mean that a small degree of orbital degeneracy remained in the single-ion states arising from the distorted octahedral Co^{II} geometries and the rapid decrease at low temperatures was due to weak antiferromagnetic coupling combined with zero field splitting effects.[4] Any effects of crystallite torquing upon the μ_{eff}/temperature data, a possibility to be aware of in anisotropic Co^{II} systems, were eliminated by measuring these and all the magnetic studies on a Vaseline-dispersed sample. When a $S = 3/2$ single-J tetranuclear model was used[4] it gave a reasonable fit of the μ_{eff} data (in H = 1 T) for $g = 2.42$, $J = -0.09\ cm^{-1}$, the model of course being approximate for such a system since orbital contribution and anisotropic exchange effects[8] were not included. We have re-fit the data using the two-J model,[1] as we did for $[C(NH_2)_3]_8[Ni^{II}_4(cit)_4]\cdot 8H_2O$[4] and obtained a marginally better fit than for the single-J model when using $g = 2.42$, J_{12} (equivalent to J_0 in ref [1]) of $-0.1\ cm^{-1}$ and J_{13} (J_1) of $-0.3\ cm^{-1}$. Use of positive J's did not improve matters

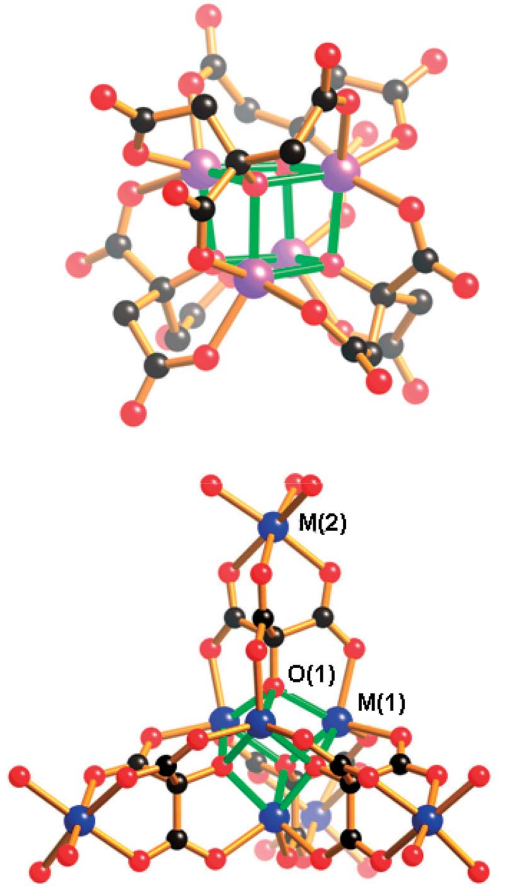

Figure 1. Cubane cluster structures of **1** and **2**. M(2) in **2** are the *fac*-chelated $Co(H_2O)_3$ ions with octahedral geometry, while M(1) have trigonal-prismatic coordination.

The magnetisation, M vs. H/T, plots on the Vaseline-dispersed sample of **1** are shown in Figure 2, (a) and (b), the latter as a +/–H loop, determined at the lowest temperature, 2 K. In part b of Figure 2, a plateau-like value of ca. 1.2 $N\beta$, per Co, (4.8 $N\beta$ per Co_4) is noted between 1–3 T followed by a gradual increase of M to reach 1.7 $N\beta$ (6.8 $N\beta$ per Co_4)

at 5 T and still rising. The increase above 3 T is indicative of the presence of low-lying excited states. This behaviour was mirrored in the negative field sweep and no hysteresis occurred in the rapidly changing, Curie-like region between 0 and ca. 1 T under the conditions of fixed field (held at fixed T for 90 s) used in the measurement. The same plateau/S-shape was seen at 3 and 4 K but not above 4 K (see also Figure S1).[4] The low value of M, per Co_4, obtained at the highest field (Figure 2, part a, of 6.8 $N\beta$, when compared to the value expected for four $S = 3/2$ Co^{II} ions, is indicative of spin-orbit coupling combined with ground state zero-field splitting and, perhaps, weak intra-cluster antiferromagnetic coupling. We had tried, unsuccessfully, to simulate the plateau region in M using single ion $^4T_{1g}$ states perturbed by spin-orbit coupling or using Brillouin functions assuming $S_{eff} = 1/2$, with large g values.[4] The ground S_T value, per Co_4, can not be zero as was inferred by the single, or double, negative J value fits.[4]

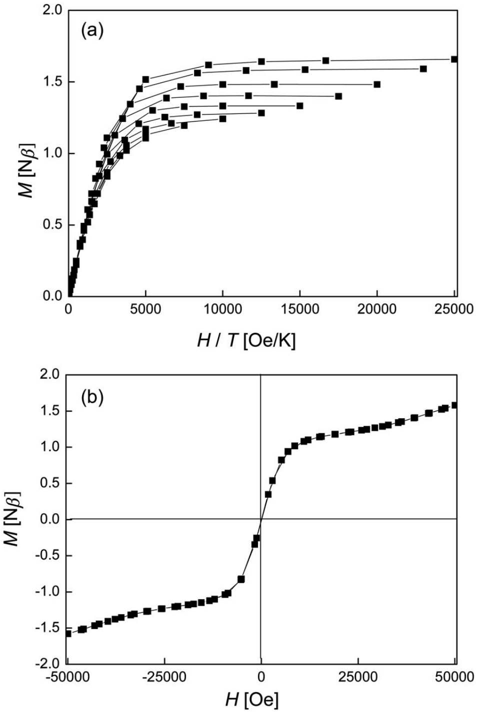

Figure 2. (a) Iso-field plots of magnetisation, M, per Co, vs. H/Oe, for **1** (top to bottom H = 5, 4.6, 4, 3, 2, 1.5, 1, 0.5, 0.1, 0.01 T; T = 20 to 2 K). (b) plot of M vs. +/–H [Oe] at 2 K. Solid lines are guides to the eye.

The shapes of the isofield M vs. H/T plots for **1** (Figure 2, a), and their separations, are indicative of zero field splitting and are generally similar to those reported for $[Co_4(hmp)_4(MeOH)_4Cl_4]$, except that the hmp case had $M_{satd.}$ of 8.4 $N\beta$, per Co_4, for a powder sample and 10.1 $N\beta$ for a single crystal, at 2 K, assigned to a S_T ground state of 6, and with D_{mol} of –4 K.[1] The corresponding μ_{eff}/temperature data, at 1 T, was different in detail to that for **1**, with a narrower maximum in μ_{eff} of 9.96 μ_B noted at 15 K assigned to ferromagnetic coupling, and giving confirmation of one J being positive and the other negative when using an orthogonal hard-axis alignment spin Hamiltonian model for $S = 3/2$ centres, including the D term (see Introduction). Unfortunately, we do not have programs available to diagonalise a 256×256 matrix and calculate M values, required to incorporate the exchange, Zeeman and D terms in an Hamiltonian appropriate to the J and D terms being of similar magnitude in a tetranuclear model.[1,9] Thus we can not obtain the S_T, J and D values simultaneously and quantitatively. While it is possible that **1** has the same S_T value of 6 as in $[Co_4(hmp)_4(MeOH)_4Cl_4]$, probably with a larger D_{ion} (and D_{mol}) value being responsible for the lower $M_{satd.}$ value, we cannot prove this. The common practice of using an effective spin, S_{eff}, of 2, per cluster, and g_{eff} of 3.4 is compatible with the M value at 2 K and 5 T of 6.8 $N\beta$. The other practice of obtaining S_T by extrapolating the AC $\chi'_M T$ values (see below) to zero K gives a value closer to that expected for a ground state spin of 4. Indeed, the tiny best-fit J values, and the unusual magnetization data, could well suggest that the four Co^{II} centres are uncoupled with each displaying zero field splitting and with energy levels close to the ground level.

The AC susceptibility data for **1**, plotted in Figure 3 as $\chi'_M T$ and χ''_M, vs. T, with AC frequencies varied between 10 to 1500 Hz, show a close to horizontal dependence between ca. 5–8 K. Most importantly, we see the characteristic maxima in χ''_M at a blocking temperature of below 4 K, indicative of slow relaxation and an energy barrier, ΔE, to magnetization reversal. Fitting the linear plot of ln[1/frequency(max)] vs. $1/T$(max) (over T = 2–3 K) to an Arrhenius dependence $\tau(T) = \tau_o \exp(\Delta E/k_B T)$ gave the energy barrier, ΔE = 13.1 K and the pre-exponential factor τ_o of 8.4×10^{-7} s (Figure S2). Values of ΔE and τ_o for other recently studied Co^{II} clusters are given for comparison in Table 1 and discussed below. The present AC susceptibility data are better defined in terms of clearly observed maxima in the χ''_M plots than for most of the other systems listed, apart from the well resolved, frozen solution cobalt(II)-radical systems.[3] A Cole-Cole plot of χ'_M vs. χ''_M, measured at 2 K, shows an inverted hemispherical dependence indicative of a single relaxation process being operative in **1** (Figure S3). Plots of χ'_M/χ_M(total) and χ''_M/χ_M(total) vs. temperature yield maximum values of 0.5, at the highest AC frequency used (Figure S4) indicative of all the Co_4 molecules in **1** undergoing Arrhenius relaxation.[10] There is a difference in slope of the 5–8 K region of $\chi'_M T$ compared to that in the DC $\chi_M T$ plot. This is quite a common occurrence in SMM species[11] and it is largely due to Zeeman interaction/population differences within the lowest energy levels and thus will be different for the 1 T field used in the DC data and the ca. zero static field used in the AC measurements.

Cluster **2** also displays a series of maxima in the χ''_M vs. T plots when varying the AC frequency between 10 and 1500 Hz (Figure 4). The maxima occur at slightly higher temperature than in **1**. A good fit to the Arrhenius expression (Figure S5), given above, yielded the values of ΔE and τ_o listed in Table 1, the energy barrier to magnetization reversal being somewhat larger than for **1**. In contrast to the

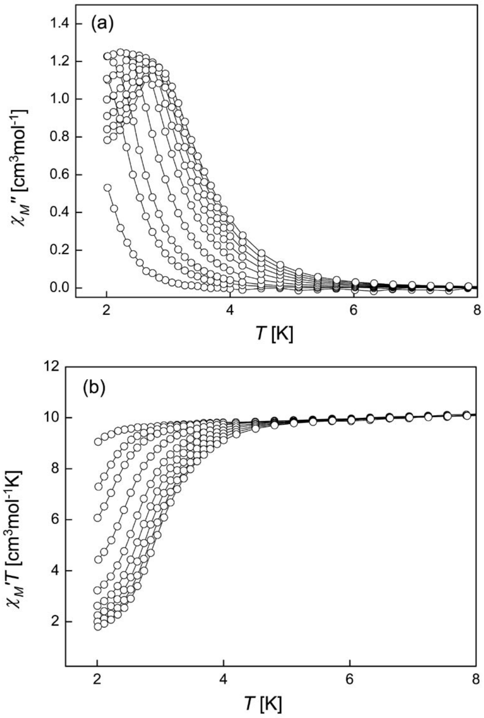

Figure 3. (a) Out-of-phase AC χ''_{M} values, per Co_4, vs. temperature for **1** at frequencies between 10 (left), 50, 100, 250, 500, 750, 1000, 1250, 1500 (right) Hz, (b) In-phase $\chi''_{\mathrm{M}}T$ values vs. temperature at 10 (top) to 1500 (bottom) Hz. DC field close to zero.

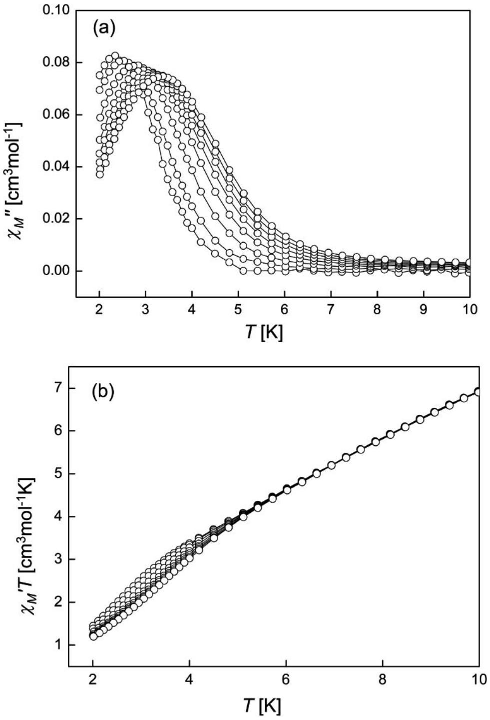

Figure 4. (a) Out-of-phase AC χ''_{M} values, per Co_8, vs. temperature for **2** at frequencies between 10 (left), 50, 100, 250, 500, 750, 1000, 1250, 1500 (right) Hz, (b) In-phase $\chi''_{\mathrm{M}}T$ values vs. temperature at 10 (top) to 1500 (bottom) Hz. DC field close to zero.

near horizontal temperature dependence of $\chi'_{\mathrm{M}}T$ found for **1**, above 4 K, the values for **2** decrease almost linearly below 10 K and head towards 0.7 cm^3 mol^{-1} K at 0 K, with a small frequency dependent separation occurring below ca. 5 K. This is indicative of thermal depopulation of higher lying, closely spaced energy levels perhaps with a $S_T = 0$ ground state. The DC magnetic moment ($\chi_M T$) data, per Co_8, (in a field of 1 T) showed a slow decrease from 12.0 μ_B ($\chi_M T$ = 18.0 cm^3 mol^{-1} K) at 300 K to ca. 10.5 μ_B at 50 K, then more rapidly to reach 3.9 μ_B ($\chi_M T$ = 1.71 cm^3 mol^{-1} K) at 2 K, and still decreasing (Figure S6), the 2 K value being similar to the corresponding AC $\chi'_{\mathrm{M}}T$ value of ca. 1.4 cm^3 mol^{-1} K in Figure 4 (b). This behaviour is indicative of orbital degeneracy/spin-orbit effects combined with weak antiferromagnetic coupling, that is stronger than in **1**, but no clear maximum was seen in the χ_{M} plot at low temperatures (Figure S7). It is possible that the triple H-bonding that occurs between Co_8 clusters[6] is responsible for transmitting weak antiferromagnetic coupling. No such interactions occurred in **1**. The sizes of the χ''_{M} maxima for **2** are much less than the corresponding χ'_{M} values indicating that not all the octanuclear molecules in the sample are undergoing the same slow relaxation and magnetization reversal process, with the remaining molecules presumably showing faster relaxation. A similar situation was found recently in the Co_8-phosphonate cluster.[12,13]

Conclusions

The slow relaxation and magnetisation reversal observed in AC susceptibility studies of **1** and **2** originate from their being new examples of SMMs of cobalt(II). Their ΔE values are of similar size to that obtained for the related citrate cluster $[Co_6(cit)_4(H_2O)_{10}]^{4-}$[5] but lower by a factor of ca. 5 compared to those of the Co_8-phosphonate[12,13] and Co_{12}-bm[14] examples and of the mononuclear Co-radical compounds.[3] The present Co_8 complex **2** has a quite different cluster structure and mode of bridging than does the phosphonate cluster and is more structurally related to the Co_6-citrate. The Co_{12}-bm compound is made up of three Co_4 cubanes bridged by a μ_6 – nitrate, its larger ΔE probably being a result of using the relationship $\Delta E = U = S_T^2|D|$, with the S_T obtained by assuming each Co$^{\mathrm{II}}$ ion has the S_{eff} value of 1/2. More difficult to understand is the variation, by a factor of ca. 10^5 (Table 1), noted in the pre-exponential factor, τ_{o}. Those for **1** and **2** are normal for cluster SMMs for which the range 10^{-7}–10^{-9} s is common. The ca. 10^{-12} s value obtained for the Co_8-phosphonate was sample dependent[13] but not small enough to indicate spin glass behaviour.[9]

At the intra-cube level, when looking at the Co–O–Co bridging geometries and the distortion towards trigonal prismatic Co$^{\mathrm{II}}$ geometry in **1** (and more so in **2**)[4,6] compared to ca. octahedral in the hmp case, there will be subtle differences in bridge angles, nature of Co single-ion ground state (D_{3h} symmetry gives a different state, ^4E, than does O_h) and hence in the Co$^{\mathrm{II}}$ magnetic orbital involved. These will influence to some degree the size, and perhaps sign of the exchange coupling constants, being much weaker and close to zero in **1**. In turn, the D_{ion} and D_{mol} values will differ in size from those in the hmp cluster.

Finally, we note that studies on a 2×2 grid cluster (ca. D_{4h} symmetry), $[Co^{II}_4L_4]^{8+}$ (L = bis(pyridyl)pyrimidine),[8c] that showed intra-cluster antiferromagnetic coupling displayed some, but not all, features of the M vs. H plot of Figure 2 (b). Using S_{eff} of 1/2, per Co, they interpreted the lack of hysteresis and observation of "steps" in their field swept M vs. H data as being indicative of an "ideal quantum spin system" for four antiferromagnetically coupled S_{eff} = 1/2 ions. It would be most informative to know if this compound displayed the slow relaxation AC data of the kind observed here. If it did, such behaviour would originate from low-lying $S > 0$ levels.

Experimental Section

Complexes **1** and **2** were synthesized and structurally characterised as described earlier.[4,6] DC and AC susceptibility studies were made using Quantum Design MPMS5 and PPMS instruments as described earlier.[18]

Supporting Information (see also the footnote on the first page of this article): Figures S1 to S7 provide various DC and AC plots and the Arrhenius best fit plots for **1** and **2**.

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