3D
interlaced

Magnetic order at 2.7 K

X 10

2D

Magnetic order at 0.25 K

SMM

Highlighting research from the laboratories of Larry Falvello and of Fernando Palacio at the University of Zaragoza and Spanish National Research Council (ICMA/ISQCH).

A symmetric, triply interlaced 3-D anionic MOF that exhibits both magnetic order and SMM behaviour

A ten-fold increase in the magnetic ordering temperature is observed on going from a layered square 2-D polymer of Co(II)-bridged $[Co_4(citrate)_4]^{8-}$ SMM cubane units in a molecular solid to an interlaced diamondoid 3-D structure.

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A symmetric, triply interlaced 3-D anionic MOF that exhibits both magnetic order and SMM behaviour†

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A newly prepared 3-D polymer of cobalt citrate cubanes bridged by high-spin Co(II) centres displays both single-molecule magnet (SMM) behaviour and magnetic ordering. Triple interpenetration of the 3-D diamondoid polymers yields a crystalline solid with channels that host cations and free water molecules, with the SMM behaviour of the Co_4O_4 cores preserved. The octahedrally coordinated Co(II) bridges are implicated in the onset of magnetic order at an experimentally accessible temperature.

The lure of potential applications in various fields – hydrogen and solvent storage, separations, sensors and catalysis,[1–6] *inter alia* – continues to drive efforts to prepare new metal–organic frameworks and other coordination polymers. In a specific line of development, for polymers whose basic link is a magnetically active centre, it is conceivable that their bulk magnetic properties can be tuned by variations of other components of the structure – small molecules in channels or magnetically active linkers – as well as by modulation of the porosity of the material with its concomitant effect on the distance between magnetic centres.[7]

Magnetic centres, and particularly single-molecule magnets (SMMs), have their own appeal as the potential basis of future applications, including in information storage, where the unending quest for further size reduction leads naturally to the molecular regime. The arrangement of SMMs into superstructures such as MOFs advances the suggestion, as yet unrequited in practice, of addressing individual nodes in the structure, a vital aspect of any storage device. The proximity of magnetic centres within polymers can affect their SMM properties and also the collective behaviour of the material,[8] facilitating the modification[9–11] or extinction of the SMM behaviour. Interestingly, orderly arrangements of SMMs have displayed new behaviours, such as the coexistence of magnetic order and slow magnetic relaxation in a 2D polymer of Co_4citr_4 cubane units[12] (H_4citr = citric acid, $C_6H_8O_7$) and in a single chain magnet (SCM) with three-dimensional magnetic order.[13]

From recent results using MOFs based on SMMs,[7,8] only a few of which possess 3-dimensional structures,[8,14,15] it may be surmised that such systems offer a promising alternative for the preparation of high-temperature magnets and multifunctional materials.

We report herein a new magnetic material based on the known Co_4citr_4 SMM subunit and paramagnetic Co(II) bridges. In the solid the complex is an anionic polymer with a diamondoid topology. The 3D nets are triply interpenetrated, giving a compact structure separated by channels that accommodate the cations (K^+) and free water molecules. It is a MOF and has the potential for displaying properties, such as ion exchange, typical of porous systems.[16] The Co_4citr_4 subunits retain their SMM behaviour; and magnetic order appears below the blocking temperature, at 2.7 K, a temperature accessible to commercial cryostats and indeed about 10 times higher than that observed for the aforementioned 2D polymer of Co citrate cubanes.[12]

$K_{4n}\{[\mu\text{-}Co(H_2O)_4]_2[Co_4citr_4]\}_n \cdot 8nH_2O$ (**1**), with the tetragonal space group $I4_1/a$, has a cobalt/citrate ratio of 6 : 4.¶ The asymmetric unit comprises a quarter of the cubane, on a (−4) symmetry element, half of a $Co(II)(H_2O)_4$ bridging unit, on an inversion center, two free water molecules, and one K^+ (Fig. 1 shows a full cubane unit plus its four attached linkers). The Co(II) bridges describe a tetrahedron around the cube with central angles in the range of 101.5–113.6°. This tetrahedron is nearly regular (distortion parameter $\lambda_{tet.}$ and variance 1.0097, 39.358 deg^2).[17] The S_4 axis of the cube coincides with the (−4)

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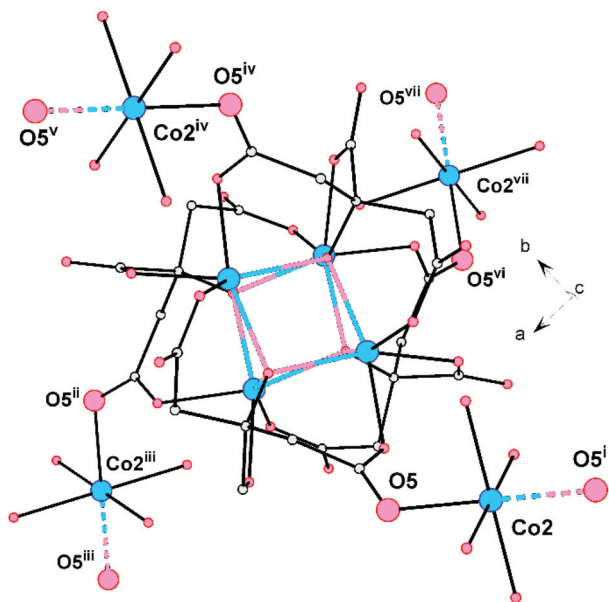
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Fig. 1 A cubane unit of compound **1** and the four bridging Co(II) units showing the propagation of the polymer (broken bonds).

Fig. 2 $\chi_m T$ versus T for compound **1**, measured at 500 Oe. Inset: ZFC–FC cycle measured at 50 Oe.

crystallographic symmetry element. The 3D net has a point symbol 6^6.

Triply interlaced, translation-related anionic diamondoid nets (Fig. S3†) form channels parallel to the *c*-axis, in which two-fold disordered potassium cations and two independent water molecules are located. The two partially occupied K$^+$ sites, at 0.722(6) Å from each other, are surrounded by six oxygen atoms each; in each case one of the O atoms is a peripheral citrate oxygen atom from a cubane, one is from an aqua ligand bound to bridging Co2, and the remaining four O atoms are from free water (Fig. S6†). It is conceivable that a change of the cation in the channel could cause the re-orientation of the octahedron about Co2, with important changes in the interaction between this center and the cubane. In the present structure, the Co2–O5 bond is inclined 68.5° to the principal (−4) axis of the cube.

DC magnetic susceptibility was measured in the presence of a field of 500 Oe from room temperature to 1.8 K. At 300 K, $\chi_m T$ (Fig. 2) has a value of 17 cm^3 mol^{-1} K, consistent with six independent Co(II) ions ($S = 3/2$, $g = 2.4$). A Curie–Weiss fit above 200 K gives $g = 2.469(2)$ and $\theta = -6.9(3)$ K. From 300 K, the signal decreases slowly down to 65 K, a typical behaviour for Co(II) ions due to the depopulation of the higher energy Kramers doublets, where it reaches a value of 16 cm^3 mol^{-1} K. On cooling further, a peak of 114 cm^3 mol^{-1} K appears near 2.7 K. Below this temperature the signal decreases to a value of 82 cm^3 mol^{-1} K at 1.8 K. The existence of a peak and the decrease at lower temperatures is an indicator of the existence of magnetic ordering. In addition, the temperature of the peak in the $\chi_m T$ curve corresponds to that of an irreversible feature in a zero-field-cooled/field-cooled (ZFC–FC) cycle (inset, Fig. 2), revealing the magnetic order.
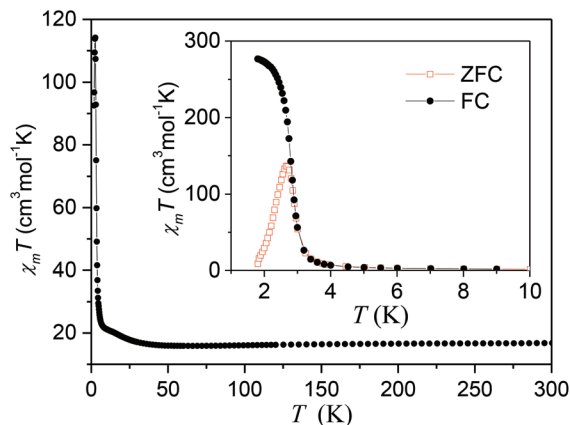
Magnetic order is also seen in the χ_{AC} measurements, in which a frequency independent peak appears near 2.7 K (Fig. 3). Below 6 K a frequency dependent peak appears. For this compound the blocking temperature, T_B, is considered to be the temperature at which the time needed for the magnetization to relax is 100 s, and is lower than the temperature at which magnetic ordering occurs.[18,19] The frequency dependent peak occurs at temperatures and frequencies similar to those seen for other Co(II) cubanes.[20–22]
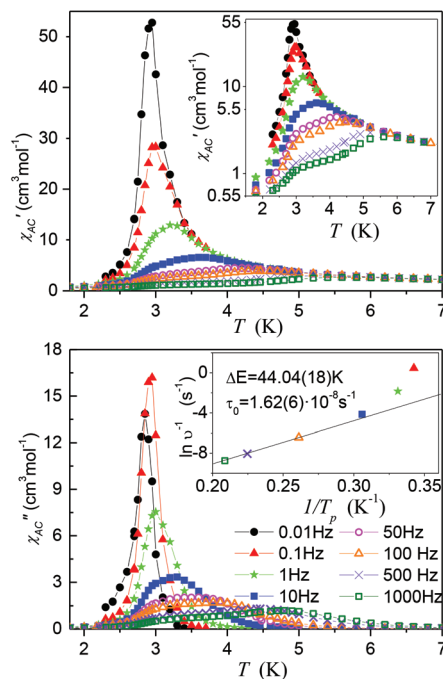

Fig. 3 AC susceptibility measurements at different frequencies for compound **1**. Top: In-phase χ' signal versus T; the inset on a logarithmic scale reflects the presence of two peaks, one frequency-dependent around 4 K at higher frequencies and one frequency-independent around 2.7 K. Bottom: Out-of phase χ'' signal versus T; the inset shows an Arrhenius fit of the peak at 4 K for frequencies higher than 100 Hz.

For frequencies below 100 Hz, the slow relaxation of the magnetization occurs at temperatures closer to T_c, and the blocking process occurs at temperatures higher than those predicted by an Arrhenius-law fit (inset Fig. 3 bottom). At those temperatures, intermolecular interactions may modify the relaxation process, as observed for isolated clusters joined through weak interactions.[9] This effect may be more pronounced in the present case, in which SMMs are covalently linked by paramagnetic Co(II) bridges, which can mediate exchange interactions. A fit to an Arrhenius law between 100 Hz and 1000 Hz gives an effective energy barrier of $\Delta_{eff} = 44.04(18)$ K and a pre-exponential factor of $\tau_0 = 1.62(6) \times 10^{-8}$ s^{-1}, in agreement with the values found for isolated SMM Co(II) cubanes.[20–23]

Heat capacity (HC) measurements show the onset of magnetic order at 2.7 K, where a λ peak appears (Fig. 4). At around 6 K, a dynamic process takes place; it was necessary to thermalise the sample for several minutes at each temperature and to reduce the amplitude of the heat pulse to allow the system to reach equilibrium. Heat capacity analysis for this kind of compound can present difficulties, and the Debye model needs to be extended.[24] An empirical fit to a cubic polynomial for the lattice contribution and a Schottky function for the blocking of the cluster were used to subtract all but the magnetic contribution (HC$_m$) from the total heat capacity, as in other networked SMM compounds.[11,25]

Integration of the curve HC$_m$/T gave a magnetic entropy of $\Delta S = 1.24R$ (inset Fig. 4). This value compares well to the sum of two magnetic species of effective spin 1/2 ($R \ln 2 = 0.69R$), attributed to the two linking Co(II) per polymer unit. We attribute the absence of a cubane contribution to the magnetic entropy, together with the dynamic anomaly at 6 K, to the blocking process of the SMM. The quality of the data in the critical region obviated the determination of the critical exponent for the transition. However, due to the high anisotropy of the Co(II) atoms, we expect **1** to behave as a 3D Ising system. The sign of the interaction between the magnetic

species can be extracted from data in the spin-wave region. For a 3D lattice, the spin-wave contribution of a ferromagnet varies as $T^{3/2}$, while the dependency is T^3 for an antiferromagnet. Data at temperatures below the critical temperature are well fitted by a T^3 relationship, revealing an antiferromagnetic interaction between the magnetic species.

Below 2.7 K, magnetic hysteresis appears (inset Fig. 5), confirming the existence of magnetic order. The coercive field at 1.8 K is 1340 Oe and the remanent magnetisation is $3.20\mu_B$.

In this range of temperatures linking Co(II) can be considered to have an isolated spin value of 1/2 with an experimental g value of $g = 4.6$, and a total spin S_T can be used to describe the cubane.[26] For similar cubane structures a ferromagnetic interaction between Co(II) in the cubane has been found, and the cubane itself has been described with an estimated $S_T = 2$,[20,27] and with a saturation magnetisation of roughly $8.4\mu_B$. According to this, the remanent magnetisation for **1** agrees with that expected for a model in which the cubanes and bridging Co(II) centers align antiferromagnetically ($8.4\mu_B - 2 \times 2.3\mu_B = 3.8\mu_B$).

In Fig. 5 the first magnetisation curve is shown for several temperatures (a detailed curve for low fields can be seen in Fig. S4†). Below T_N and for fields around 21 000 Oe an inflexion point appears, which could indicate the critical field at which the ferromagnetic order is destroyed. At 5 T, saturation is not reached. A saturation value larger than $13\mu_B$ ($8.4\mu_B + 2 \times 2.3\mu_B = 13\mu_B$) should be expected if the cubane and the bridging Co(II) become aligned with the field. Fitting with simplified models did not produce satisfactory results.

A thorough knowledge of the energy levels will be necessary for a complete analysis of the magnetic properties.

To our knowledge, this compound is the first 3D magnet built from Co(II) SMMs for which clear evidence of the existence of both SMM behaviour and magnetic order has been found. The proximity of a slow magnetic relaxation below 6 K and magnetic order at 2.7 K suggest the possibility of tuning
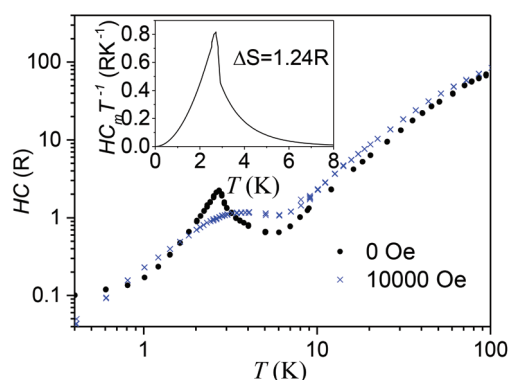

Fig. 4 Temperature dependence of the heat capacity of **1** measured in the absence of a magnetic field and with a field of 10 000 Oe. The inset shows the temperature dependence of the magnetic contribution normalized by T.
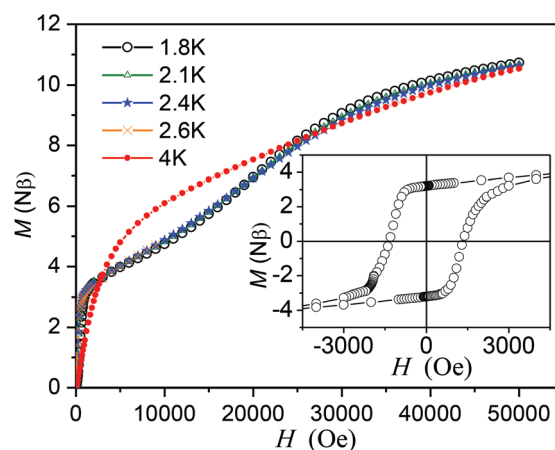

Fig. 5 Magnetization *versus* field at different temperatures for compound **1**. The inset shows a hysteresis cycle at 1.8 K.

the magnetic behaviour, for example by absorption of small species into the MOF, or by a change of the counterion.

While weak coupling between clusters can bias the quantum tunnelling effect and modulate the quantum behaviour of isolated Co_4 cubanes,[28] coupling through paramagnetic bridges in **1** gives rise to long range magnetic order. While in other networked SMM compounds[11] the interaction between clusters either does not affect the SMM behaviour, or gives rise to magnetic order or to a competition between blocking and ordering that leads to frustrated order, in **1** both phenomena – SMM behaviour and magnetic order – occur within a small temperature range.

One plausible explanation for the negligible contribution of the cubanes to the magnetic heat capacity near the transition at 2.7 K would be a ground state $S_T = 0$ for the cubane. Although in this case SMM behaviour would still be possible due to accessible excited levels with non-zero S_T,[22] this hypothesis can be discarded on the basis of the magnetisation measurements. The position of the cubanes in the structure and their links to the bridging Co(II) centres make it unlikely that they do not participate in the magnetic ordering. The most plausible explanation may be that the cubane is not in equilibrium. In the AC susceptibility measurements, due to the coexistence of magnetic order and SMM behaviour the relaxation time and the energy barrier become frequency dependent at low frequencies. As the critical temperature is approached, the relaxation time and the energy necessary to reverse the magnetisation increase. The boundary between DC and AC behaviour is not clearly defined in this frequency range. Therefore, on the time scale of the heat capacity measurements, the cubane is not in thermodynamic equilibrium. This is another example of the conflict between the experimental time domain and the relaxation time of an SMM.

In the previously reported 2D compound with blocking and ordering, in which Co_4citr_4 subunits are linked by Co(II) ions through the fragments Co–O–C–C–C–O–Co and Co–O–C–O–Co, the SMM behaviour of the clusters was similar, and magnetic order appeared below 250 mK.[12] In **1**, the Co(II) ions and cubanes are linked through two Co–O–C–O–Co arms and the polymers are interpenetrated, which increases the ordering temperature 10-fold to 2.7 K. Although the importance of dipolar interactions cannot be ruled out because the distance between a cubane and a Co(II) from a neighbouring net is 7.8 Å, the increase of the dimensionality of the lattice and the change in the exchange pathways may also play an important role in increasing the magnetic ordering temperature.

Assuming the ground state of the cubane to be the same as that of the cubanes in the previously reported 2D compounds, $S_T = 2$, we arrive at a magnetic model with two sublattices, one of cubanes and one of linking Co(II) ions, which align antiferromagnetically. Magnetisation measurements confirm this conclusion.

Compound **1** also presents an opportunity to test the influence of guest molecules on T_N by modifying the contents of the channels.

Acknowledgements

Notes and references

¶Crystal data, $K_{4n}\{[\mu\text{-Co}(H_2O)_4]_2[Co_4citr_4]\}_n \cdot 8nH_2O$, **1**: $(C_{24}H_{48}Co_6K_4O_{44})_n$, $M_r = 1550.6$, tetragonal, $I4_1/a$ (origin choice 1), $a = b = 20.7872(3)$ Å, $c = 11.3290(2)$ Å, $V = 4895.35(13)$ Å^3, $Z = 4$, $\lambda = 0.71073$ Å, $\theta_{max} = 30.74°$, $\theta_{full} = 27.50°$, 223 parameters, no restraints, $R_1 = 0.0294$, [for 3442 data with $I > 2\sigma(I)$], w$R_2 = 0.0734$ for all 3514 data, CCDC 1487245.

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