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Inspiration from old molecules: field-induced slow magnetic relaxation in three air-stable tetrahedral cobalt(II) compounds†

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We have investigated the dynamics of the magnetization of three four-coordinate mononuclear cobalt(II) compounds, which are synthesized conveniently and are air stable. Slow magnetic relaxation effects were observed for the compounds in the presence of a dc magnetic field.

Single-molecule magnets (SMMs) displaying slow relaxation of the magnetic moment upon removal of a magnetizing field have aroused widespread interest, due to their potential applications in quantum computing, spintronics, and high-density storage devices.[1] As more and more accurate control of the synthetic process is achieved, new systems with unprecedented and fascinating magnetic phenomena are being produced. The field of SMMs is experiencing very fast evolution. Scientists' main attention has shifted from the synthesis of giant clusters with the highest possible ground-state spin (S) and negative axial magnetic anisotropy (D) to the search for smaller and smaller SMMs.[2] Especially, the design and synthesis of single-ion magnets (SIMs), which refer to mononuclear compounds with a single slow relaxing metal centre, is a new emerging trend in molecular magnetism. They could be considered as the smallest SMMs and the simplest models for fundamental research on magnetic relaxation. Since the first publication of slow magnetic relaxation in double-decker compound Tb(III)Pc_2 by Ishikawa *et al.* in 2003,[3] more and more mononuclear compounds based on anthanides[4] or actinides[5] metal ions exhibiting SIM behaviour have been reported. In 2010, Chang and Long *et al.* proved that slow relaxation can also be possible for mononuclear transition-metal compounds.[6a] Thereafter intensive research interest and considerable effort has been devoted to the design of SIMs based on transition-metal ions, but to date, this still remains a challenge and the number of such species is still limited.[6,7]

Usually, when designing a mononuclear 3d metal compound with the expectation of a slow magnetic relaxation effect, a low coordination number is favourable. The reason lies in the fact that for a 3d metal compound the first-order orbital angular momentum is largely quenched by the ligand field so that the spin–orbit coupling may be compensated.[6b,7c,8] A low coordination number can afford a relatively weak ligand field and prevent the quenching effect up to a certain point. However, for a low coordinated compound the synthetic environment may be critical and the compound itself may be air-sensitive. By accident, we turned our attention to the field of late transition metal polymerization catalysis, and to our surprise, there is a rich variety of such mononuclear 3d metal compounds with a low coordination number.[9] We believe that many of them could be used in probing slow magnetic relaxation behaviour or give us some inspiration at least. It will certainly enlarge the scope of SIMs with first-row transition metal ions.

Here we report the dynamics of the magnetization of three very simple molecules, $[Co(PPh_3)_2Cl_2]$ (**1**), $[Co(DPEphos)Cl_2]$ (**2**) and $[Co(Xantphos)Cl_2]$ (**3**) (where PPh_3, DPEphos, and Xantphos represent triphenylphosphine, 2,2′-bis(diphenylphosphino) diphenyl ether, and 9,9-dimethyl-4,5-bis(diphenylphosphino) xanthenes, respectively), which had been reported as highly selective catalysts for the hydrovinylation of styrene.[10,11] Compared to many other SIMs based on 3d metal reported previously, they are synthesized conveniently and are air-stable. Their molecular structures are shown in Fig. 1. The Co^{2+} centers in the three compounds are coordinated by two P atoms and two Cl anions, forming slightly distorted tetrahedral geometry. There are subtle differences in their bond angles of P–Co–P, P–Co–Cl, and Cl–Co–Cl (Table S2, ESI†). The mononuclear units are well isolated from each other, the shortest intermolecular Co–Co distance being 8.253 Å, 9.127 Å,

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Fig. 1 Crystal structures of the three tetrahedral compounds. Blue, green, pink, and gray spheres represent Co, Cl, P, and C atoms, respectively; H atoms are omitted for clarity.

and 9.011 Å for **1**, **2**, and **3**, respectively. No short intermolecular exchange pathway is apparent in **2** and **3**, while compound **1** may favor an intermolecular Co–Cl…Cl–Co superexchange path (Fig. S1–S3, ESI†).[12]

Variable temperature dc susceptibility measurements were collected on powdered crystalline samples of the compounds at a field of 5000 Oe over the 2–300 K temperature range as shown in Fig. S7 (ESI†). At 300 K, the $\chi_M T$ value is 2.50 emu K mol^{-1}, 2.55 emu K mol^{-1}, and 2.54 emu K mol^{-1} for compounds **1**, **2**, and **3**, respectively. These values, while larger than the anticipated spin-only value for $S = 3/2$ of 1.88 emu K mol^{-1}, fall well in the range of 2.1–3.4 emu K mol^{-1} for experimentally observed highly anisotropic Co^{2+} centers.[13] The $\chi_M T$ values remain roughly constant at 100 K, 75 K, and 25 K for **1**, **2**, and **3**, respectively, before decreasing upon further cooling. The phenomenon is consistent with Curie-type behaviour of isolated Co^{2+} centers. The decrease at low temperature is possibly due to intrinsic magnetic anisotropy of the Co^{2+} ions, and for **1** the weak intermolecular antiferromagnetic interaction could make a certain contribution.

The field dependence of the magnetization for the compounds at 1.8 K is shown in Fig. S8 (ESI†). The magnetization at 50 kOe reaches 2.0$N\beta$, 2.3$N\beta$, and 2.5$N\beta$ for **1**, **2** and **3**, respectively. The lack of saturation for the compounds also suggests the presence of magnetic anisotropy. Low-temperature magnetization data at various applied dc fields for the compounds were also collected. The resulting plots of reduced magnetization, depicted in Fig. 2, Fig. S9 and S10 (ESI†), exhibit significant separation between the isofield curves, confirming the existence of magnetic anisotropy. Several attempts to fit the reduced magnetization data were unsuccessful. To estimate the nature of magnetic anisotropy of the ground state, the zero-field-splitting parameters were calculated using CASSCF/CASPT2/RASSI method. The calculation afforded $D = -16.2$ cm^{-1} and $E = 0.9$ cm^{-1} for **1**, $D = -14.4$ cm^{-1} and $E = 1.7$ cm^{-1} for **2**, $D = -15.4$ cm^{-1} and $E = 1.3$ cm^{-1} for **3**, respectively. The negative sign of D and their large magnitude indicate the large uniaxial anisotropy of the compounds and therefore the possibility of observing slow magnetic relaxation.

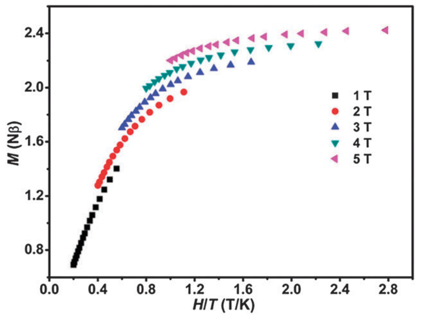

Fig. 2 Low-temperature magnetization data for **2** collected under various applied dc fields. The solid lines represent fits to the data.

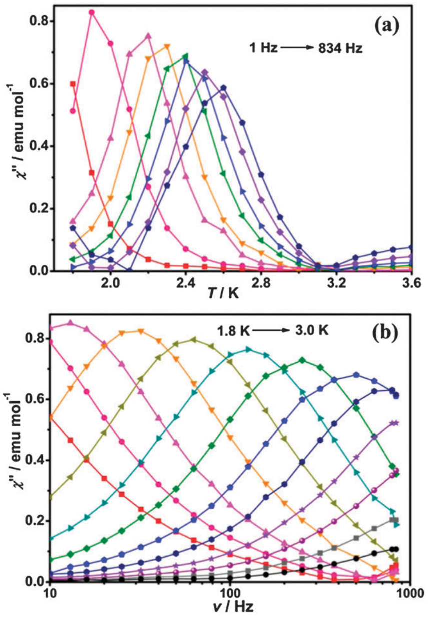

Fig. 3 (a) Temperature dependence of the out-of-phase (χ'') ac susceptibility component at different ac frequency for **2** (H_{ac} = 3 Oe and H_{dc} = 1000 Oe). (b) Frequency dependence of out-of-phase ac susceptibility from 1.8 to 3.0 K under 1000 dc field for **2**.

To investigate the potential for slow magnetic relaxation in the compounds, temperature dependence and frequency dependence of the ac susceptibility in the temperature range 1.8–4.0 K were determined. Under a zero dc field and a 3 Oe ac field oscillating at frequencies between 1 and 834 Hz, no out-of-phase ac susceptibility (χ'') signal was observed. However, when a 1000 Oe static dc field was applied, all the compounds displayed a temperature and frequency dependent signal as shown in Fig. 3 and Fig. S11–S18 (ESI†). These phenomena have been observed in most of the mononuclear transition metal SMMs reported previously. The absence of slow relaxation in the compounds under zero applied field can most likely be attributed to quantum tunneling of the magnetization (QTM) through the spin-reversal barrier.

Here for these three half integer spin systems, the mixing of the ground ±3/2 levels by transverse zero-field-splitting (E) is forbidden according to Kramer's theorem.[14] The observed QTM effect may stem from the mixing of ±3/2 levels *via* hyperfine interaction and dipolar interaction,[15] the relaxation processes mediated by which could be suppressed when a proper dc field is applied.

The magnetization relaxation time (τ) is derived from the frequency-dependence measurements and is plotted as a function of $1/T$ in Fig. 4; Fig. S14 and S18 (ESI†). The τ of each compound shows a strong temperature dependence and fits well with the Arrhenius equation, $\tau = \tau_0 \exp(E_a/k_B T)$,

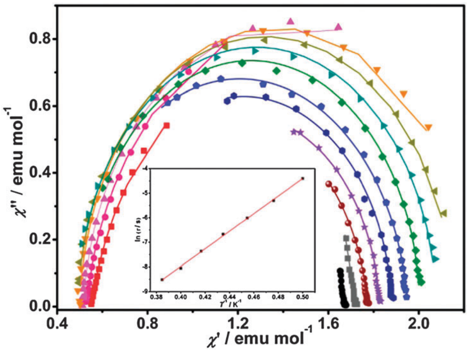

Fig. 4 Cole–Cole plot of **2** under 1000 Oe at temperatures between 1.8 K (red) and 3.0 K (black); the solid lines are the best fit obtained with a generalized Debye model (with α always smaller than 0.09). Inset: relaxation time of the magnetization ln(τ) *vs.* T^{-1} plot; the solid line corresponds to the Arrhenius law.

characteristic of a thermally activated mechanism. There is only one relaxation process for each compound and no quantum tunneling regime was observed, implying that the applied field of 1000 Oe is appropriate to suppress any QTM effect mediated by the hyperfine and dipolar mediated relaxation process. The calculated values of the pre-exponential factor $\tau_0 = 1.2 \times 10^{-9}$ s and the activation energy $E_a = 37.1$ K for **1**, $\tau_0 = 2.1 \times 10^{-10}$ s and $E_a = 35.0$ K for **2**, $\tau_0 = 6.0 \times 10^{-9}$ s and $E_a = 29.9$ K for **3** are consistent with those reported previously for the very few other Co^{2+}-based SIMs.

To inspect the distribution of the relaxation time, the Cole–Cole plots were scrutinized for the compounds (Fig. 4; Fig. S13 and S17, ESI†). The data can be fitted using a generalized Debye model with $\alpha < 0.02$ for **1**, $\alpha < 0.09$ for **2**, and $\alpha < 0.05$ for **3** (α indicates deviation from the pure Debye model),[16] respectively. These low degrees of disorder support the proposal that the present relaxation process can be considered with a single relaxation time for each compound.

In conclusion, we have probed SMM behaviour in three old mononuclear Co^{2+} compounds, which have been reported as highly selective catalysts for the hydrovinylation of styrene. They are air stable while the Co^{2+} centers are in a low four-coordinated environment. All of the compounds exhibit significant uniaxial anisotropy and slow magnetic relaxation behaviour has been observed under an applied field. The subtle difference in their tetrahedral geometry leads to slight variation in their magnetic anisotropy and activation energy. Further investigation into the variation of the donor characteristics in the easily replaceable anions is in progress. Our present work is only a start, and more efforts are demanded. Firstly, considering the limited number of mononuclear transition metal-based SIMs, more SIMs should be synthesized and characterized. We do believe that the field of late transition metal polymerization catalysis will give us much inspiration to design and probe SIMs. Most importantly, the pursuit of SMMs with high energy barrier to spin inversion and high blocking temperature will be our long-term objective.

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