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Simple Mononuclear Cobalt(II) Complex: A Single-Molecule Magnet Showing Two Slow Relaxation Processes

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Supporting Information

ABSTRACT: Complex $[Co(PPh_3)_2Br_2]$ possesses intermediate magnetic anisotropy, $D/hc = -13$ cm^{-1}. It displays superparamagnetic behavior either in the absence of the magnetic field or in fields of $B_{dc} = 0.05$, 0.1, 0.15, and 0.2 T. At $B_{dc} = 0.1$ T, the barrier to spin reversal $U/k_B = 37$ K and the extrapolated relaxation time $\tau_0 = 9.4 \times 10^{-11}$ s confirm its classification as a single-molecule magnet. At $B_{dc} = 0.2$ T, two relaxation processes are evidenced.

The class of single-molecule magnets (SMMs; including single-chain and single-ion magnets) has been enriched in the past decade by a number of different architectural compounds.[1] Research moved from the assembly of 3d metal complexes in the earlier stages (like the well-known Mn_{12} or Fe_8 platelike complexes) to 4f systems and mixed 3d−4f systems more recently.[2] Among these investigations, a prominent role has been played by dysprosium(III) complexes (mononuclear, polynuclear, and heterometallic) because of the strong magnetic anisotropy that has a key role in creating an efficient barrier to spin reversal.[3] Less attention is paid to mononuclear 3d metal complexes of the iron group. Some of them are SMMs, for instance, iron(II), iron(III),[4] cobalt(II),[5] and manganese(III)[6] complexes.

Herein we report single-molecule magnetism in a well-known mononuclear complex, $[Co(PPh_3)_2Br_2]$ (**1**). Its structure was determined in the past (CCDC code BIHGII),[7] and its magnetic properties were reinvestigated recently.[8a] There are neither hydrogen bonds nor short contacts in the crystal structure, so that the compound consists of insulated molecules.

The magnetic data presented below were measured with a SQUID apparatus (MPMS-XL7, Quantum Design) using the RSO mode of detection; ca. 22 mg of the sample was encapsulated in a gelatin sample holder. The molar susceptibility χ_{mol} taken at $B = 0.1$ T was corrected for underlying diamagnetism. The alternating-current (ac) susceptibility measurements were done with an oscillating field $B_{ac} = 0.38$ mT for 14 frequencies; 10 scans were averaged for each temperature−frequency point. The external magnetic field was $B_{dc} = 0$, 0.05, 0.1, 0.15, and 0.2 T.

The magnetic functions of **1** are displayed in Figure 1. The room-temperature value of the effective magnetic moment amounts to $\mu_{eff} = 4.08\ \mu_B$; the high-temperature limit $\mu_{eff}(HT)/\mu_B = g_{iso}[S(S+1)]^{1/2}$ is recovered by $g_{iso} = 2.11$. Upon cooling, the effective magnetic moment decreases gradually, but below 30 K, it drops rapidly; this indicates a sizable zero-field splitting.

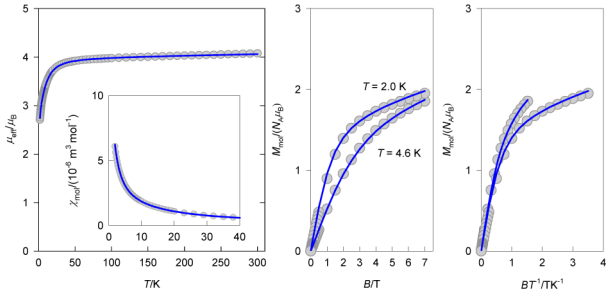

Figure 1. Magnetic functions for **1**. Left: Temperature dependence of the effective magnetic moment (inset: temperature dependence of the molar magnetic susceptibility). Center and right: Field dependence of magnetization per formula unit. Lines: fitted.

The magnetization per formula unit $M_1 = M_{mol}/N_A\mu_B$ rises gradually with the applied field, and at $T = 2.0$ K and $B = 7$ T, it is only $M_1 = 2.1$, as opposed to the theoretical limit of $M_1 = g_{Co}S_{Co} > 3$.

The susceptibility and magnetization data were fitted simultaneously using a conventional spin Hamiltonian for an $S = {}^3/_2$ system. It was found that this complex possesses an intermediate magnetic anisotropy measured by the axial zero-field-splitting parameter $D/hc = -13$ cm^{-1} ($g_z = 2.161$; g_x and $g_y = 2.006$).[8a] These magnetic parameters could be considered as typical for distorted tetrahedral cobalt(II) complexes.[8b] Analogous complex $[Co(PPh_3)_2Cl_2]$ possesses $D/hc = -11.6$ cm^{-1}, as obtained from combined direct-current (dc) susceptibility and magnetization studies[8a] and confirmed also by HF/HF-EPR (-14.8 cm^{-1}),[9] whereas CASSCF/CASPT2/RASSI calculations gave -16.7 cm^{-1}.[5a] It is generally accepted that the negative value of the D parameter is a prerequisite of the SMM behavior.

The ac susceptibility measurements for complex **1** are displayed in Figure 2 for 14 frequencies of the alternating field ranging between $\nu = 1$ and 1512 Hz and temperature interval $T = 1.9$−4.2 K. It can be seen that the out-of-phase component of the molar magnetic susceptibility exhibits temperature-dependent maxima with the onset at 4 K ($\nu = 1512$ Hz). These data refer to an applied external field of $B_{dc} = 0.1$ T. The frequency dependence of the maxima at the out-of-phase component of the magnetic susceptibility confirms a superparamagnetic behavior and possible single-molecule magnetism.

A plot of the magnetic data as a function of the frequency at constant temperature is given in Figure 3. A one-component Debye model was used in interpreting the frequency dependence

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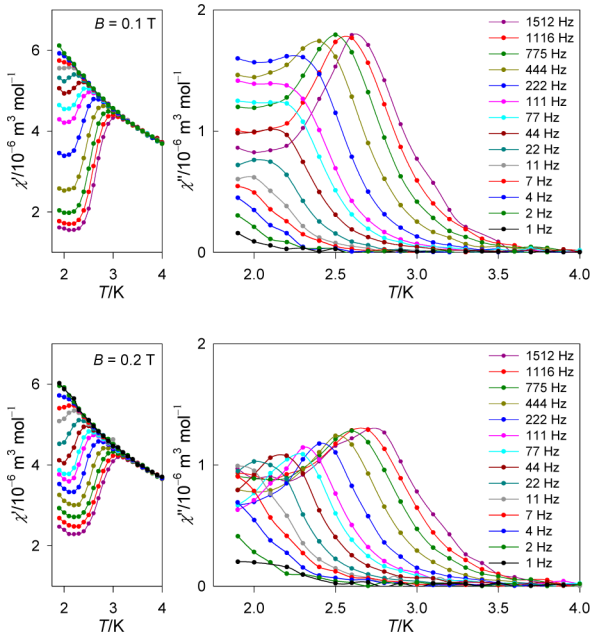

Figure 2. In-phase χ' and out-of-phase χ'' molar susceptibility (SI units) for **1** at the applied external field B_{dc} = 0.1 and 0.2 T, respectively. Lines serve as guides for the eyes.

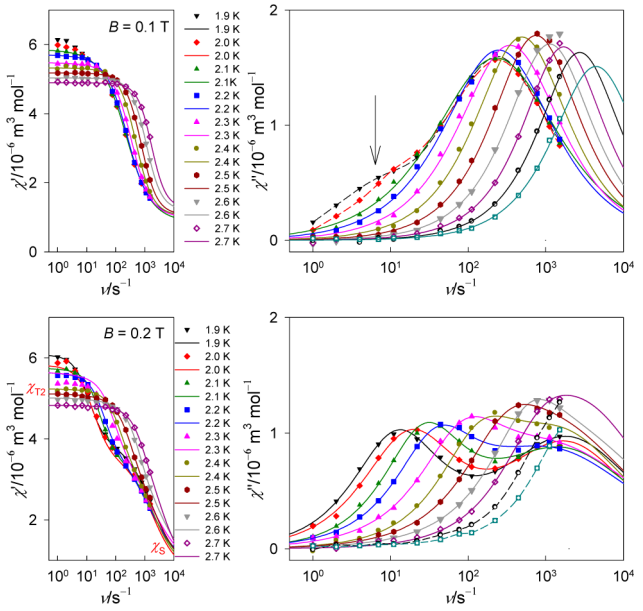

Figure 3. Frequency dependence of the ac susceptibility for **1** at B_{dc} = 0.1 and 0.2 T, respectively. Left: In-phase component. Right: Out-of-phase component. Solid lines: Fitted.

of the ac magnetic susceptibility[1] $\hat{\chi}(\omega) = \chi_S + (\chi_T - \chi_S)/[1 + (i\omega\tau)^{1-\alpha}]$, where the relaxation time (τ) and distribution parameter (α) occur along with the isothermal susceptibility (χ_T) and the adiabatic susceptibility (χ_S); $\omega = 2\pi\nu$. This equation decomposes into two components, χ' and χ'', as shown in the Supporting Information (SI). The fitting procedure was based on minimization of functional $F = w_1R(\chi') + w_2R(\chi'')$, which accounts for the relative errors of both data sets ($R < 0.01$). The results in numerical form are listed in Table 1. It can be concluded that the resulting parameters vary systematically with temperature (see also Figure S1 in the SI). Data for T = 1.9 and 2.0 K was not processed by the fitting procedure because there is

Table 1. Parameters of the One-Component Debye Model for 1 Using Data Taken at B_{dc} = 0.1 T[a]

T/K	χ_S	χ_T	α	$\tau \times 10^{-6}$ s
2.1	0.85	5.86	0.283	693
2.2	1.01	5.71	0.220	642
2.3	0.98	5.47	0.178	459
2.4	1.02	5.32	0.125	322
2.5	1.06	5.18	0.093	212
2.6	1.16	5.03	0.058	143
2.7	1.26	4.89	0.050	93.7
2.8	1.23	4.78	0.053	58.1
2.9	0.67	4.66	0.068	30.7

[a]SI units for the molar magnetic susceptibilities (adiabatic, χ_S; isothermal, χ_T) [10^{-6} m^3 mol^{-1}].

an indication for the presence of a second relaxation process (follow the arrow in Figure 3), which will be discussed later.

The final parameters were used in generating extrapolation/interpolation lines for frequencies between ν = 1 and 10^4 Hz, which are displayed in Figure 3. When χ'' versus χ' for a set of fixed temperatures was plotted, the Cole–Cole (Argand) diagram was constructed (Figure 4). This, in fact, refers to an

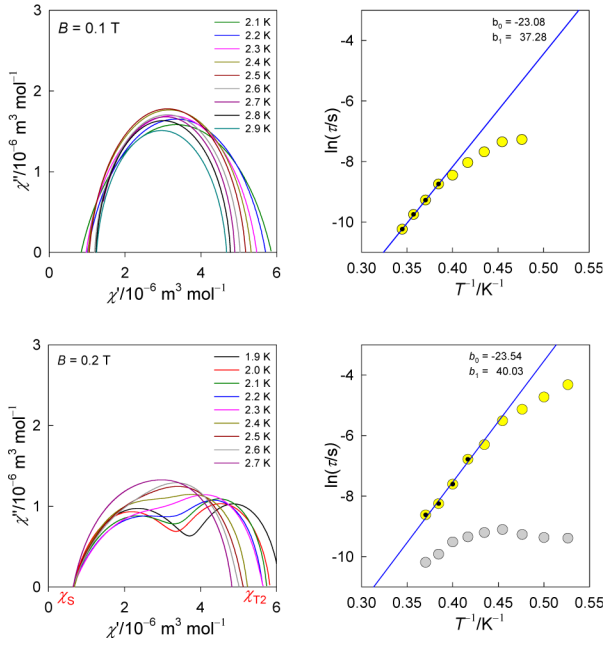

Figure 4. Fitted ac susceptibility data for **1** at B_{dc} = 0.1 and 0.2 T, respectively. Left: Cole–Cole plot (fixed temperature). Lines: Calculated for ν = 1–10^4 Hz based upon the fitted parameters. Right: Arrhenius-like plot. Coefficients of the linear regression: $b_0 = \ln \tau$ and $b_1 = U/k_B$.

arc. The positions of the maxima ν_{max}'' enter the Arrhenius-like equation of the thermal activation process, i.e., $\ln \tau = \ln(1/2\pi\nu_{max}'')$ versus $1/T$. Then the linear fit for high-temperature points yields the parameters of the SMM at B_{dc} = 0.1 T: barrier to spin reversal U/k_B = 37 K and the extrapolated relaxation time $\tau_0 = 9.4 \times 10^{-11}$ s. There is some curvature in the Arrhenius plot for the first relaxation process when the lowest temperatures of the experiment are approached. This could be associated with the onset of the tunneling mechanism.

The application of a small field (B_{dc} = 0.1 T) is essential in suppression of the magnetic tunneling mechanism, which gives a

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much faster relaxation process. When the field was switched off, the out-of-phase susceptibility is oddly resolved and not passing through a maximum in the range of frequencies limited by the actual hardware (see Figure S2 in the SI).

The dependence of the out-of-phase susceptibility on the applied external field at T = 1.9 K is shown in Figure S2 in the SI for a number of frequencies.

The results of the applied field of B_{dc} = 0.2 T are qualitatively different compared to those of B_{dc} = 0.1 (Figures 3 and 4) because two relaxation processes are well evident. The data analysis is based upon a two-component Debye model (see Table S1 in the SI). The fitting procedure offers two primitive components, giving rise to the convolution curve displayed in the Cole−Cole diagram (Figure 4). The maxima of the primitive curves (not of the convolution curve) were used in the Arrhenius-like plot displayed in Figure 4, right. One of the relaxation processes can be considered as an analogue of that found at B_{dc} = 0.1 T; its parameters are $U^{(1)}/k_B$ = 40.0 K and $\tau^{(1)}_0 = 5.98 \times 10^{-11}$ s. The presence of the second, faster and field-induced process is really a challenge. The corresponding data plotted in Figure 4 as gray circles refer to a primitive curve resulting from the fitting procedure; they possess some scattering so that no further processing was made. Notice that not only is the thermal activation (Orbach) process in the play but also the "direct" and Raman processes could apply.[10] Some recent results on analogous systems are presented in Table 2.

Table 2. Parameters of the Arrhenius-like Equation for Cobalt(II) SMM

chromophore	B_{dc}/T	(D/hc)/cm^{-1}	(U/k_B)/K	τ_0/s	ref
$\{CoBr_2P_2\}$	0.10	−12.5	37.3	9.44×10^{-11}	this work
	0.20		40.0	5.98×10^{-11}	this work
$\{CoCl_2P_2\}$	0.10	−16.2[a]	37.1	1.2×10^{-10}	5a
$\{CoCl_2P_2\}$	0.10	−14.4[a]	35.0	2.1×10^{-10}	5a
$\{CoCl_2P_2\}$	0.10	−15.4[a]	29.9	6.0×10^{-9}	5a
$\{CoClN_3\}$	0.15	+12.7	35 (24 cm^{-1})	2×10^{-10}	5b
$\{CoCl_2N_3\}$	0.06		28	1.07×10^{-6}	5c
	0.56		4	7.44×10^{-2}	
$\{CoN'_2N_3\}$	0.06		17	5.85×10^{-6}	5c
	0.56		3	0.11	
$\{CoN'_2N_3\}$	0.2	−40.5	16	3.6×10^{-6}	5d
$\{CoN'_2N_3\}$	0.2	−40.6	24	5.1×10^{-7}	
$\{CoS_4\}$	0, 0.1	−70	30 (21 cm^{-1})	1.0×10^{-7}	5e

[a]Calculated.

The behavior of **1** under study approves its classification as a SMM. The presence of two relaxation processes in such a simple system with the absence of any intermolecular short contacts, however, remains unexplained so far.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and figures/tables referring to the magnetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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