Spin-Crossover and Slow Magnetic Relaxation in a Mononuclear Cobalt(II) Complex with Square Pyramidal Geometry

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Introduction

Although a great number of single-ion magnets (SIMs) and spin-crossover (SCO) compounds were found, multifunctional materials with the combination of SCO and SIM properties are extremely scarce [1-3]. Here a mononuclear, five-coordinate cobalt(II) complex [Co(3,4-lut)$_4$Br]Br (**1**) with a square pyramid displays the spin transition with a small hysteretic loop and field-induced slow magnetization relaxation. The work presents the first instance of the five-coordinate mononuclear cobalt(II)-based SIM exhibiting the thermally induced complete SCO with a small hysteretic loop.

Experimental

Complex **1** was prepared according the modified method in literature [4]. High Frequency EPR measurements were done on a home-built homodyne instrument and its 17 T SC magnet at NHMFL.

Results and Discussion

For **1**, The coordination sphere of Co(II) is a square-pyramidal geometry, in which four nitrogens of four 3,4-lutidine molecules form the basal plane whereas one bromide ion locates at the apex (**Fig.1 a**). A small increase of the N−Co−N angles in the basal plane accompanying with the marked reduction of the apical Br−Co−N angles were observed on going from 296 to 123 K, which could be the reason of spin-crossover as observed in **Fig.1 c**.

Upon application of external dc field, the frequency-dependent χ_M'' maxima peaks appear in the applied frequencies (**Fig.1 b**). The χ_M'' magnetic susceptibility exhibits the strong frequency- and temperature-dependence, indicating the occurrence of slow dynamics of magnetization, which is character of field-induced SMMs. EPR spectra of microcrystalline powder sample of **1** at 4 K with the frequency of 302.4 GHz (**Fig.1 d**) is satisfactorily simulated as an S = 1/2 spin system, yielding the g-factors of g_1= 2.3986(5), g_2= 2.3857(5), and g_3 = 2.0063(5). The average g value (g_{av} = [(g_1+g_2+g_3)/3] = 2.26) is in accord with the g_{iso} value (2.23) determined from fitting the magnetic susceptibility.

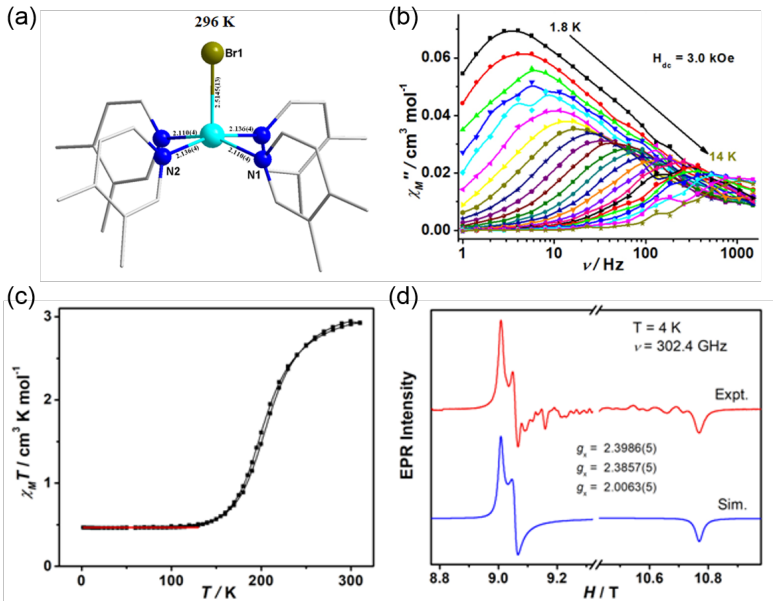

Fig.1 Structure, AC susceptibility, AC susceptibility, and HF-EPR.

Conclusions

We have reported here the structure and magnetic properties of the mononuclear complex [Co(3,4-lut)$_4$Br]Br (**1**). The magnetization study confirms that both the abrupt SCO with a small hysteretic loop and slow magnetic relaxation behaviors were simultaneously observed in **1**. Interestingly, the slow relaxation arises from the low-spin state (S = 1/2) of Co(II) with the spin-orbit coupling. This work provides a new avenue to construct multifunctional molecular materials. Future effort along this line will focus on the current material displaying both the SCO and SMMs behaviors.

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