Thermal and Pressure-Induced Spin Crossover in a Cobalt(II) Imide Complex

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We report the thermal- and pressure-induced spin-crossover (SCO) in the Co(II) imide complex [$Co^{II}(dpzca)_2$] using magnetic susceptibility measurements and high-pressure Raman spectroscopy. This complex displays thermally-induced reversible, complete, abrupt and hysteretic SCO, with $T_{1/2}\downarrow = 168$ K upon cooling and $T_{1/2}\uparrow = 179$ K upon heating with a thermal hysteresis of ~11K and a pressure-induced reversible high spin (HS) $\rightleftarrows$ low spin (LS) transition at ~0.3 GPa at room temperature.

1. Introduction

Spin-crossover (SCO) phenomena are known for their bistability of high-spin (HS) and low-spin (LS) electronic configuration [1]. The ground state of these materials may in principle be reversibly interchanged under external stimuli like temperature, stress, magnetic field or electromagnetic radiation. This property makes this class of material a potential candidate for applications in display and memory devices and as molecular switches.

SCO has been observed for d^4-d^7 transition metal ions with Fe(II) and Fe(III) complexes the most common [2]. A small number of Co(II) based compounds have been reported to show SCO [3] but most of them display gradual, incomplete or two-step thermally-induced spin transition [4-6]. Moreover, in contrast to the Fe(II) complexes, very few are reported to undergo pressure-induced SCO for Co(II) complexes [3]. For any technological application it is desirable to develop a complex which can show SCO which is abrupt, complete and hysteretic both by thermal and pressure stimuli. Here we report a mononuclear Co(II) complex which displays thermally-induced SCO satisfying these requirements.

2. Sample preparation

The Co(II) amide $\{Co[C_{10}H_6N_5O_2]_2\}$ samples were prepared both in powder and single-crystalline forms. The synthesis and characterisation of this Co(II) complex are provided elsewhere [8]. The variable temperature magnetic susceptibility measurements were carried out in a Quantum design MPMS SQUID magnetometer. The high-pressure Raman measurements were carried out at room temperature with a piston-cylinder type diamond anvil cell (DAC) with 700 μm culet diamonds. A stainless-steel gasket with a 200 μm hole was loaded with the sample along with ruby chips. A methanol-ethanol mixture in 4:1 ratio was used as a pressure medium. In order to compare the magnetic measurement at low temperature, which showed a HS-LS transition, we carried out low-temperature Raman measurements with a liquid nitrogen flow-through cryostat at ambient pressure. All the Raman measurements were carried out with a Horiba LabRam micro Raman spectrometer with a 514 nm Ar-ion laser as excitation source. An 1800 lines/mm grating was used to provide a spectral resolution of 1 cm^{-1}. Scattered light was collected in the backscattering geometry and the power of the laser reaching the sample was kept at 10 mW.

3. Results and discussion

3.1 Magnetic measurements

Fig. 1 shows the variable-temperature magnetic susceptibility measurements performed on the crystalline and powder samples. At 300 K the χT product of the sample is 2.3 cm^3 K mol^{-1} (4.3 μ_B) indicating a g value of 2.22, consistent with high-spin cobalt(II) in an octahedral environment. Upon cooling an abrupt spin transition, centred at $T_{\frac{1}{2}}\downarrow$ = 170 K, is observed. At 50 K the χT product decreased to 0.49 cm^3 K mol^{-1} (1.97 μ_B) and 0.35 cm^3 K mol^{-1} (1.67 μ_B) for the crystalline and powder samples respectively, in good agreement with the spin only value of 0.38 cm^3 K mol^{-1} (1.73 μ_B) expected for a cobalt(II) centre in the low-spin state (S = ½). For the powder sample this value stays relatively constant down to 2 K, whereas for the crystalline sample an increase in the χT product (0.65 cm^3 K mol^{-1}, 2.3 μ_B) is observed at 10 K possibly due to alignment of the crystals with the magnetic field (as this behaviour is not observed in the powder sample).

Upon heating, $T_{\frac{1}{2}}\uparrow$ = 175 K, giving a hysteresis loop with $\Delta T_{\frac{1}{2}}$ = 5 K. Three consecutive thermal cycles were performed showing that the magnetic behaviour, including the hysteresis loop, is reproducible and hence fully reversible.

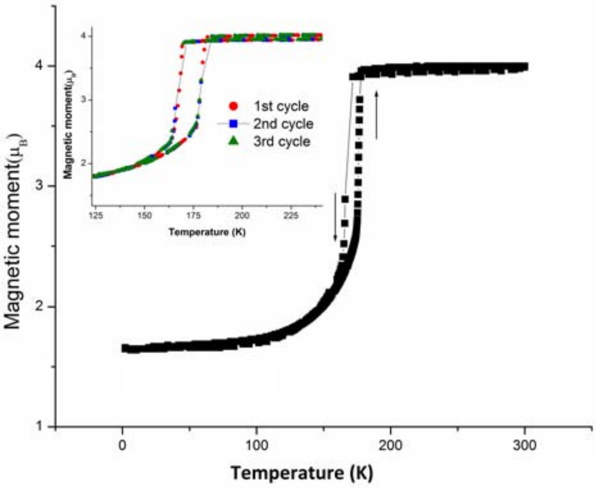

Fig. 1. Magnetic susceptibility measurements at low temperature and ambient pressure for Co(II) powder samples. The inset shows the reversibility of the hysteresis loop after three consecutive cycles.

3.2 Low-temperature Raman Measurements

Fig. 2 displays the variable-temperature measurements in the Co(II) compound for 600 cm^{-1} to 1700 cm^{-1} on cooling from room temperature to 100 K. Most of the Raman modes in this range remain the same for both HS and LS states. However, at 175 K close to the spin-transition temperature, as measured in the magnetic measurements, the Raman modes at 1264 cm^{-1} and 1284 cm^{-1} show changes indicative of an abrupt spin transition at that temperature. In contrast the mode at 635 cm^{-1} is more gradual with a split beginning at 175 K. On reheating the complex completely reverts back to the room-temperature HS state as can be seen from the spectra at 325 K.

3.3 High-pressure Raman measurements

Fig. 3 displays the high-pressure Raman spectra of Co(II) compound. The ambient pressure spectra are shown in red. The modes at 635, 1281, and 1303 cm^{-1} shown in Fig. 3(a) initially shift under compression at 0.25 and 0.28 GPa to lower wave number but eventually split at a pressure of 0.5 GPa. The mode at 635 cm^{-1} splits to 628 and 642 cm^{-1} and at a further elevated pressure of 1.9 GPa the former mode displays a red shift to 631 cm^{-1} and the latter a blue

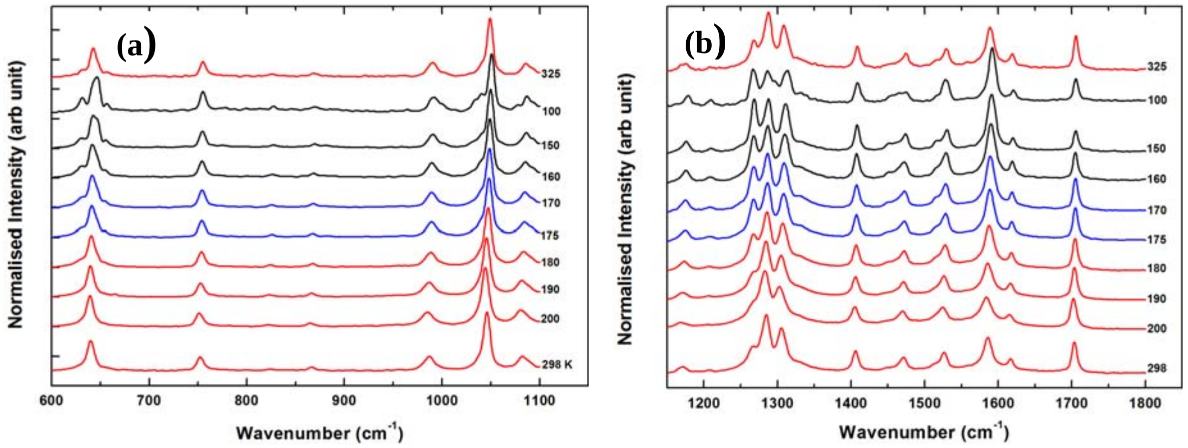

Fig. 2. Raman measurements at low-temperature and ambient pressure in the range (a) 600-1100 cm^{-1} and (b) 1150 – 1750 cm^{-1} showing cooling data from room temperature to 100 K and then warming back to 325 K. Red = HS state; black is mixed state of HS & LS; blue= LS state.

shift to 650 cm^{-1}. Similarly, modes at 1281 and 1303 cm^{-1} split into a stronger 1262 cm^{-1} mode accompanied by weak modes at 1278 and 1290 cm^{-1}. The relatively very weak intensity peak at 750 cm^{-1} becomes stronger and the peak at 984 cm^{-1} disappears above 0.28 GPa. One of the strong modes at 1043 cm^{-1} initially shifts at 0.28 GPa and above that it reverts back to its original state but with reduced intensity and almost disappears at 1.9 GPa. In the other range shown in Fig. 3(b), the peak at 1467 cm^{-1} broadens and above 0.28 GPa eventually splits at 0.5 GPa to two very weak peaks at 1458 and 1473 cm^{-1}. On the other hand the mode at 1700 cm^{-1} disappears above 0.28 GPa. The peak at 1583 cm^{-1} shows no transition up to 0.57 GPa but shows considerable shift to 1600 cm^{-1}at 1.9 GPa with a shoulder feature at 1591 cm^{-1}.

The unloading measurements from a peak pressure of 1.9 GPa show that the modes at 0.57 GPa were identical to those on loading at 0.5 GPa denoting that the sample is in the LS state at these pressures. However, at 0.32 GPa it shows a mixed state of both LS and HS features in both the ranges shown in Fig. 3(a) and (b) as discussed above and therefore indicative of the transition pressure because, upon complete unloading to ambient pressure, the sample switches to its original HS only state. This can be clearly seen in the figure where the spectra marked as UL-Amb and Amb are totally identical. Moreover a change of colour

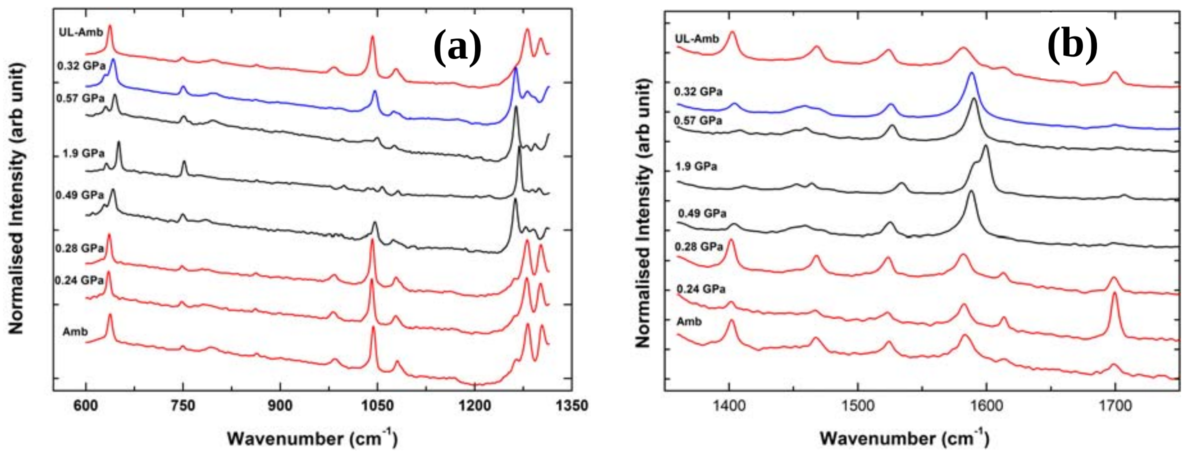

Fig. 3. High-pressure Raman measurements at room temperature in the range (a) 600-1350 cm^{-1} and (b) 1375 – 1750 cm^{-1}. Red = HS state; black is mixed state of HS & LS; blue= LS state.

from a brown to black is observed under a microscope when the sample undergoes a SCO from ambient to above 0.3 GPa.

The Raman band maxima were located by analysis after normalisation of the observed spectra at low temperature and high pressure. $\gamma_{HS}=I_{HS}/(I_{HS}+I_{LS})$ where I_{HS} and I_{LS} are the intensities of the selected HS and LS marked bands respectively [7]. Fig. 4 shows the variation of the spin fraction ratio as a function of (a) temperature and (b) pressure for the modes 1265 cm^{-1} and 1284 cm^{-1} respectively. At ambient pressure the HS Co(II) species could be transformed to the LS state with a SCO temperature of $T_{\frac{1}{2}} \approx 170$K. Under ambient temperature pressurization the SCO transformation begins around $P_{\frac{1}{2}} \approx 0.3$ GPa, where $T_{\frac{1}{2}}$ and $P_{\frac{1}{2}}$ are defined as the temperature and pressure for which $\gamma_{HS} = 1/2$.

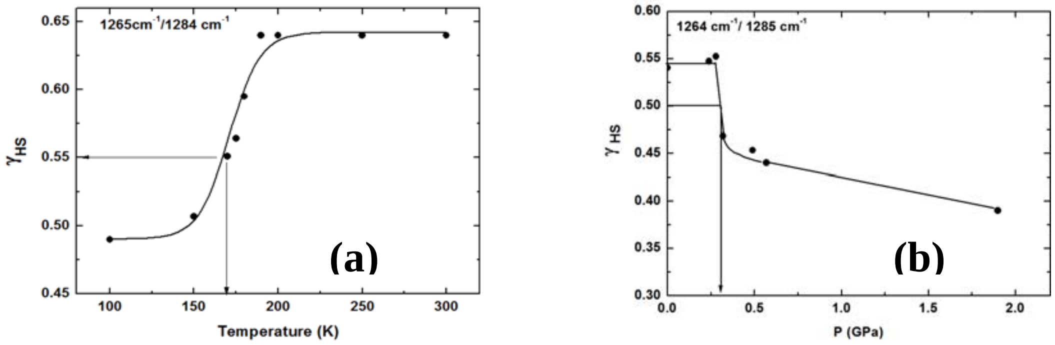

Fig. 4. (a) Temperature and (b) pressure dependent spin fraction and γ_{HS} in Co(II) imide complex.

4. Conclusions

Co(II) imide is the first cobalt complex to display abrupt hysteretic SCO. Both the pressure-induced transition and the thermally-induced transition are remarkably sharp and reversible suggesting a thermodynamic transition rather than a mere crossover. The observed hysteresis in the magnetic measurement could be due to a cooperative transition between the molecules. With thermally-induced SCO occurring at 175 K and a pressure-induced transition occurring at 298 K, the very large $dT_c/dP \approx 383$ K/GPa coefficient suggests a rather large volumetric change in the structure at the transition. The high pressure Raman measurements indicated that contraction of equatorial bonds in the low-spin state is more favourable under pressure. Further measurements of low-temperature and high-pressure Raman scattering and magnetic measurements are continuing to help understand the mechanism of the spin-crossover. This will also assist in the systematic development of related complexes.

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