Uniaxial Pressure Effect on the Magnetic Properties of the Metal-Organic Hybrid Compound Co\textsuperscript{II}(H\textsubscript{2}O\textsubscript{6})\textsubscript{pyromellitate}

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Abstract. A uniaxial pressure technique is developed to study the dependence of the magnetization up to 12 kbar using a SQUID magnetometer. The technique has been tested for the magnetic properties of a Metal-Organic Framework, Co(H\textsubscript{2}O\textsubscript{6})(C\textsubscript{10}H\textsubscript{4}O\textsubscript{8}), where C\textsubscript{10}H\textsubscript{4}O\textsubscript{8} is benzene-1,2,4,5-tetracarboxylate, along three orthogonal axes of single crystals. It displays anisotropic paramagnetic properties between 2 and 300 K without any phase transition. The isothermal magnetizations at 5 K show decrease with pressure when the field is applied along the \textit{b}-axis but an increase along the \textit{a}- and \textit{c*}-axes. The results are interpreted as a change in the g-value tensor as a function of pressure due to compression along the Jahn-Teller distorted axis.

1. Introduction

The major advances in the field of Metal-Organic Framework (MOF) have lead to a wide variety of magnetic materials and among them cobalt(II) containing compounds show more complexities, such as canting, metamagnetism and unusual magnetic hardness even for antiferromagnets.[1] These are believed to be due to the orbital contribution via the spin-orbit coupling to the magnetic properties. A consequent of this is the large magnetic anisotropy which gives rise to considerable magnetic hardness.[2] This range of behaviors is due firstly to the different coordination geometries that can be adopted the cobalt ion and accompanying electronic effects.[3] Secondly, the stabilization of an effective \textit{S}=1/2 at low temperatures with a very large anisotropy gives rise to very unusual low temperature effects such as the commonly observed canted-antiferromagnetism and also brings about large magneto-crystalline anisotropy which gives rise to magnetic hardness, that is coercive field that can exceed 5 Tesla.[2,4] Thirdly, the presence of competing ferromagnetic and antiferromagnetic interactions within the same compounds, may it be one-, two- or three-dimensional, has some interesting subtle balances between ground states.[1] In order to understand these effects further, a better understanding of the magnetism of the isolated ion is of utmost importance. For example a study of the magnetic properties through the continuous variation of the geometry and the orientation dependence on single crystals can be very useful.

Most studies of the magnetism in the field of MOF are carried out on polycrystalline samples due to the lack of large single crystals.[1,5] The successful growth of large single crystals of Co(H\textsubscript{2}O\textsubscript{6})(C\textsubscript{10}H\textsubscript{4}O\textsubscript{8}),[6] consisting of non-interacting cobalt ions with an almost octahedral geometry, provided the opportunity to explore the anisotropy of the magnetic properties as well as studying the
uniaxial pressure effects up to 12 kbar in an attempt to elucidate the geometry related parameters that govern the magnetic properties of Co(II). Here, we present some preliminary experimental results.

2. Experimental

Co(H$_2$O)$_6$(C$_{10}$H$_4$O$_8$) was synthesized by hydrothermal synthesis using a Teflon lined stainless steel cell working under autogenous pressure.[6] Cobalt chloride hexahydrate, CoCl$_2$.6H$_2$O (1.2 g) was added to a neutralised solution of pyromellitic acid, C$_{10}$H$_6$O$_8$ (0.63 g) and potassium hydroxide, KOH (0.28 g) in 10 ml water and the solution was placed in the cell and kept at 120°C for 12 hours. Some large single crystals were obtained in the presence of two other phases and these are separated under a microscope by their colors and sizes. Single crystals and a piece of pure lead as pressure sensor were first orientated on strips of overhead projector slide along the appropriate axes. These were then fixed in a cylinder made of Stycast 1226 so as to be aligned along the three crystal axes, $a$- and $b$-axes, and perpendicular to $ab$-plane. The cylinder is 3 mm in diameter and 6 mm in length. The view of the cylindrical samples is schematically shown in figure 1. For the magnetic properties measurements of the sample under pressure, as shown in figure 1, both the magnetic field and the pressure are applied along the cylindrical direction of the sample.

![Figure 1. Schematic feature of the sample preparation for the measurements and the relation to both magnetic field and pressure, where some single crystals are arranged so as to align the crystal axis and fixed with Stycast 1226.](image)

The magnetization of the sample under pressure was measured by using a home-built Cu-Be pressure cell for a SQUID magnetometer, QD-MPMS. The sample was pressurized up to 12 kbar and the pressure on the sample was determined by using the pressure dependence of the superconducting transition of the lead. The obtained data are corrected for the background of the pressure cell which has been previously recorded under the same conditions.

3. Results and discussion

![Figure 2. Perspective views of the crystal structure showing the (a) 3D-packing of Co(H$_2$O)$_6$(C$_{10}$H$_4$O$_8$) and the layer arrangement of Co(H$_2$O)$_6$: Co(blue), C(black), O(red), H(cyan). Hydrogen bonds are shown as black and white dotted lines.](image)
Co(H$_2$O)$_6$(C$_{10}$H$_4$O$_8$) crystallizes in the monoclinic space group $P_2_1/m$, $a=6.4460(3)$, $b=9.9464(4)$, $c=6.4723(3)$ Å, $\beta=114.747(2)$ $^\circ$ and $V=376.86(3)$ Å$^3$ at 295 K.[6] The structure consists of layers of Co(H$_2$O)$_6$ separated by the pyromellitate dianions (Figure 2(a)). The cobalt are coordinated to six water molecules in an almost perfect octahedral geometry; the only distortion is a slight Jahn-Teller distortion of the Co-O bond along the $b$-axis resulting in Co-O distances of 2.048, 2.047 and 2.124 Å. The O-Co-O angles are nearly 90°. The Co-Co distances within the layers are 6.446 Å ($a$-axis), 6.472 Å ($c$-axis) and 6.965 Å (along the 101-axis). The Co-Co distance between layers is 9.946 Å (Figure 2(b)). Due to these long distances and also the absence of any connecting bonds between the cobalt atoms, the magnetic exchange interactions are expected to be very small and we may consider the ion to be isolated. This has been previously shown to be the case. Important for the discussion of our results of the magnetism are the presence of H-bonds between the oxygen of the carboxylate and the water molecules. Unfortunately the X-ray analyses do not locate the hydrogen positions but the O … O distances of 2.782, 2.786 and 2.813 Å within the expected angles suggest three hydrogen bonds per carboxylate group.

The application of pressure on such structures is supposed to have two effects. The first is the compression of the lattice at low pressures that will affect the packing of the molecular units and secondly at high pressures distortion of the coordination may take place. In the present case, we may expect an anisotropic compression due to the structure and the way the hydrogen bonds are oriented.

![Figure 3](image3.png)

**Figure 3.** Temperature dependence of the susceptibility, where the pressure and the magnetic field are applied along (a) $a$-axis and (b) $b$-axis, and perpendicular to (c) $ab$-plane.

![Figure 4](image4.png)

**Figure 4.** The magnetization as a function of field at 5 K, where the pressure and the magnetic field are applied (a) $a$-axis and (b) $b$-axis, and perpendicular to (c) $ab$-plane.

The temperature dependence in 2 kOe and field dependence at 5 K of the magnetization as a function of pressure for the three orthogonal orientations are shown in figures 3 and 4. The
susceptibility under all the conditions remains paramagnetic as has been reported.[6] Upon application of pressure we observe that the Curie constants along the three different axes remain constant with almost an isotropic value of 3.3(1) cm³ K/mol. However, the Weiss constant is quite different for the three axes; while it remains almost constant along the b-axis (+11±4 K) and perpendicular to ab-plane (+10±6 K), that along the a-axis is quite large and varies from −272 to -109 K on going from 0.97 kbar to 12 kbar. These values are for analyses of the data from 150 to 300 K. Further work will be needed to understand these results and presently, we can suggest that the apparent Weiss constant does not reflect the interaction between neighboring cobalt atoms but is due to electronic effect. One inference will be that pressure distorts the coordination around the cobalt atom and thus affect the Jahn-Teller distortion which consequently results in changes in the g-values. The isothermal magnetizations at 5 K also exhibit continuous trends that involve a decrease for field along the a-axis but increase along the other two orthogonal orientations. Both these observations are consistent with a change of g-values. The pressure dependence of the magnetization at 5 K and at 5 T for three crystal orientations, along a- and b-axes and perpendicular to ab-plane is shown in figure 5. The magnetization at 0 kbar for the three crystal orientations is rather different from each other, which means that the compound shows considerable anisotropy. Interestingly, the anisotropy tends to decrease as the pressure is increased.

Figure 5. Pressure dependence of the magnetization at 5 K and at 5 T for the three crystal orientations.

4. Conclusion
A preliminary study of the uniaxial pressure dependence of the magnetic properties of the isolated paramagnetic [Co(H2O)6]²⁺ in Co(H2O)₆(C10H4O8) with field applied along three orthogonal axes reveals Curie constant independent of pressure, large difference in Weiss constants which vary only along the JT axis and isothermal magnetization suggesting changes in the g-value tensor. Further theoretical analyses and X-ray analyses under the same pressure conditions will be required for a thorough understanding of the results.

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