# Resonance in the Nonlinear Susceptibilities of $Co_3BTCA_2(H_2O)_4$, a Molecular-Based Magnet

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IN DEDICATION TO THE LATE PROFESSOR OLIVIER KAHN FOR HIS PIONEERING CONTRIBUTIONS TO THE FIELD OF MOLECULAR MAGNETISM

The linear and nonlinear magnetic responses of the molecular-based magnet $Co_3BTCA_2(H_2O)_4$ have been studied as a function of frequency and temperature. The out-of-phase component of the linear susceptibility and the nonlinear susceptibilities all show maxima at the critical temperature of 23 K while displaying a novel resonance in their frequency dependence. The existence of the resonance in the out-of-phase component demonstrates the absence of dynamic scaling in this magnetic system. © 2001
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## 1. INTRODUCTION

Magnetic materials based upon discrete molecular units (1) are being developed with ever-increasing critical temperatures. Compounds consisting of transition-metal ions bridged by cyanide groups have recently been found to order with spontaneous moments at 315 K (2), while mixed valence chromium cyanide thin films have been found in which the critical temperature (as high as 270 K) can be electrochemically shifted (3). Although most of the magnets based upon organic molecules order at less than 50 K (4), the amorphous ferromagnet $V/TCNE \cdot 0.5(CH_2Cl_2)$ (TCNE = tetracyanoethylenide) has a critical temperature that exceeds 350 K (5). The rapid advances in this field are due to the utilization of the enormous versatility of organic chemistry.

$Co_3BTCA_2(H_2O)_4$ is a member of a new family of magnetic materials based upon the BTCA trianionic molecule (neutral $BTCAH_3$ = 1,3,5 benzenetricarboxylic acid). BTCA was selected as a ligand since it has the geometry and connectivity to produce a magnetically frustrated lattice, such as the Kagomé. A number of transition-metal coordination complexes that contain the BTCA ligand in various states of protonation and demonstrate its potential for constructing interesting magnetic lattices have been reported recently (6).

The curious magnetic properties of $Co_3BTCA_2$ $(H_2O)_4$, (7) include long relaxation times, hysteresis, irreversibilities (such as a difference between the field-cooled and zero field-cooled susceptibilities), and aging phenomena. Much of this behavior resembles that of frustrated systems such as spin glasses. However, the transition occurring at 23 K in $Co_3BTCA_2(H_2O)_4$ is unlike that occurring in spin glasses or any other known disordered systems. Static scaling analysis of the dc magnetization (7) yields critical exponents not consistent with any known universality class. It has been concluded that the unique behavior is likely due to the presence of both multiple sources of disorder (random anisotropy and random exchange), as well as to the frustration provided by the geometry of the BTCA ligand. In this paper, we report the unusual dynamics of $Co_3BTCA_2(H_2O)_4$ near 23 K, specifically the linear and nonlinear ac susceptibilities.

## 2. EXPERIMENTAL

$Co_3BTCA_2(H_2O)_4$ was prepared as follows. $Co(ClO_4)_2 \cdot 6H_2O$ (1.41 g, 3.85 mmol) was dissolved in 30 mL of water. 1, 3, 5-Benzenetricarboxylic acid (0.5 g, 2.38 mmol) and KOH (0.5 g, 8.9 mmol) were dissolved in 20 mL of water and both solutions were heated to near boiling ($T = 98°C$). The hot $H_3BTCA$ solution was added to the cobalt solution and a purple precipitate formed immediately. The hot mixture was filtered and the precipitate washed with water followed by acetone. The precipitate was then

dried for 4 h at 130°C to give dark purple $Co_3BTCA_2(H_2O)_4$ (80–95%). Combustion analysis confirmed the stoichiometry of the product. Measurements were made using both a Lake Shore and a similar homebuilt ac susceptometer. The ac technique uses two coils, a primary, and a pick-up, which are wound such that their mutual inductance is zero. The sample is placed within these concentric coils, and a small oscillating field is applied via the primary coil, thus producing a response in the sample. This response is measured via a lock-in amplifier tuned to the driving frequency. The fundamental response of the sample, occurring at the same frequency as the ac driving field, can be written as the sum of two components, the in-phase susceptibility, $\chi_1'$, and the out-of-phase susceptibility, $\chi_1''$, as follows: $\chi_1 = \chi_1' + i\chi_1''$. By multiplying the reference frequency to the lock-in by either a factor of 3 or 5, the third and fifth harmonics can be measured. These harmonic responses can be related to the nonlinear susceptibilities via the following expansion of the magnetization, $M = \chi_1 H + \chi_3 H^3 + \chi_5 H^5 + \cdots$, where $\chi_3, \chi_5 \cdots$ are the nonlinear susceptibilities. Under an ac driving field, $H(t) = h\sin(\omega t)$, the time-dependent magnetization becomes

$$M(H, t) = \left[\chi_1 + \frac{3}{4}\chi_3 h^2 + \frac{5}{6}\chi_5 h^4 + \cdots\right] h\sin(\varpi t)$$
$$- \left[\frac{1}{4}\chi_3 + \frac{5}{16}\chi_5 h^2 + \frac{21}{64}\chi_7 h^4 + \cdots\right] h^3 \sin(3\varpi t)$$
$$+ \left[\frac{1}{16}\chi_5 + \frac{7}{64}\chi_7 h^2 + \cdots\right] h^5 \sin(5\varpi t) + \cdots.$$
[1]

The terms in even powers of the field vanish due to time-reversal symmetry. The terms inside the square brackets represent the amplitudes of the harmonic responses. An explicit field dependence is present for each harmonic. In the limit of small fields, the higher terms in each bracket will be insignificant and the expression for the in-phase component of the magnetization reduces to

$$M(\omega) = \chi_1' h\sin\omega t - \frac{1}{4}\chi_3' h^3 \sin 3\omega t + \frac{1}{16}\chi_5' h^5 \sin 5\omega t + \cdots.$$
[2]

The third harmonic thus measures $-\frac{1}{4}\chi_3 h^3$ while the fifth harmonic measures $\frac{1}{16}\chi_5 h^5$. Similar expressions hold for the absorption $\chi''$

All susceptibilities are reported in molar units, where a mole refers to one formula unit with three $Co^{2+}$ ions. Corrections for diamagnetism were made but corrections for demagnetization were always less than 2% and have been ignored. (Their small size is due in part to the large molecular weight per spin-carrying unit.) Data were recorded at various frequencies using a one Oe ac field and

zero dc field (with the exception of the uncompensated component of the Earth's field). The dependence upon the amplitude of the exciting field of both the linear and nonlinear responses was checked and found to be linear beyond the field of 1 Oe used in these experiments. The phases of the instruments had been checked by studying nonabsorbent paramagnetic materials and are correct for the linear response. However, due to some remaining uncertainty about the phases of the higher harmonic contributions, the nonlinear responses are reported only as absolute magnitudes, as calculated by $\chi_n^2 = \chi_n'^2 + \chi_n''^2$.

## 3. RESULTS AND DISCUSSION

Figures 1 and 2 display the absolute magnitudes of $\chi_3$ and $\chi_5$ for a sample of $Co_3BTCA_2(H_2O)_4$. A broad maximum
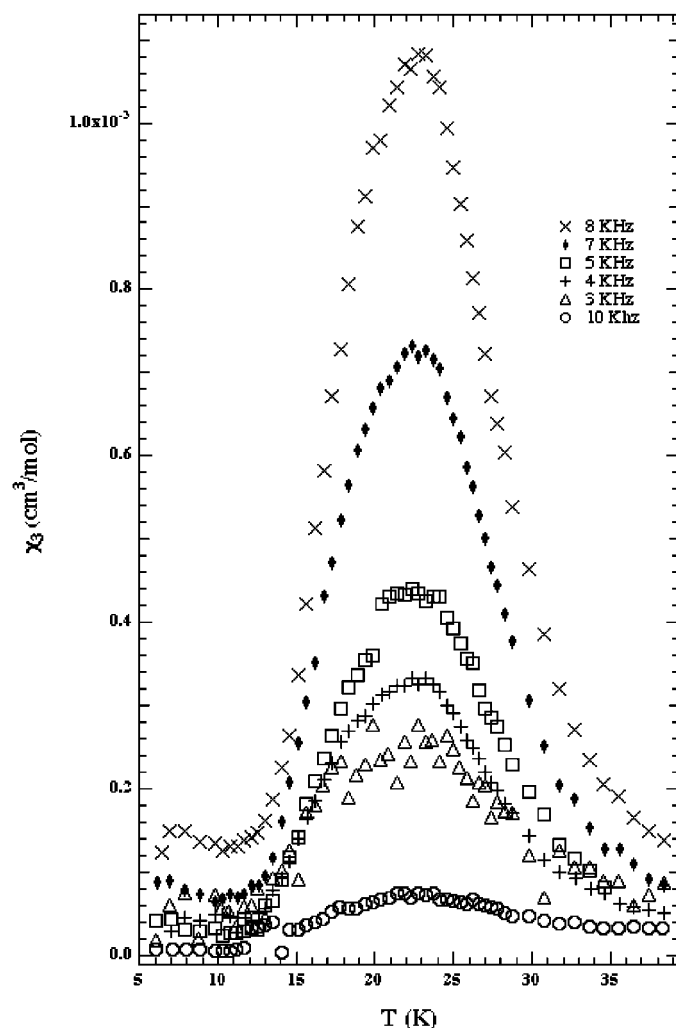


**FIG. 1.** The absolute magnitude of the nonlinear susceptibility $\chi_3$ as a function of temperature $T$, at various measuring frequencies for $Co_3BTCA_2(H_2O)_4$.
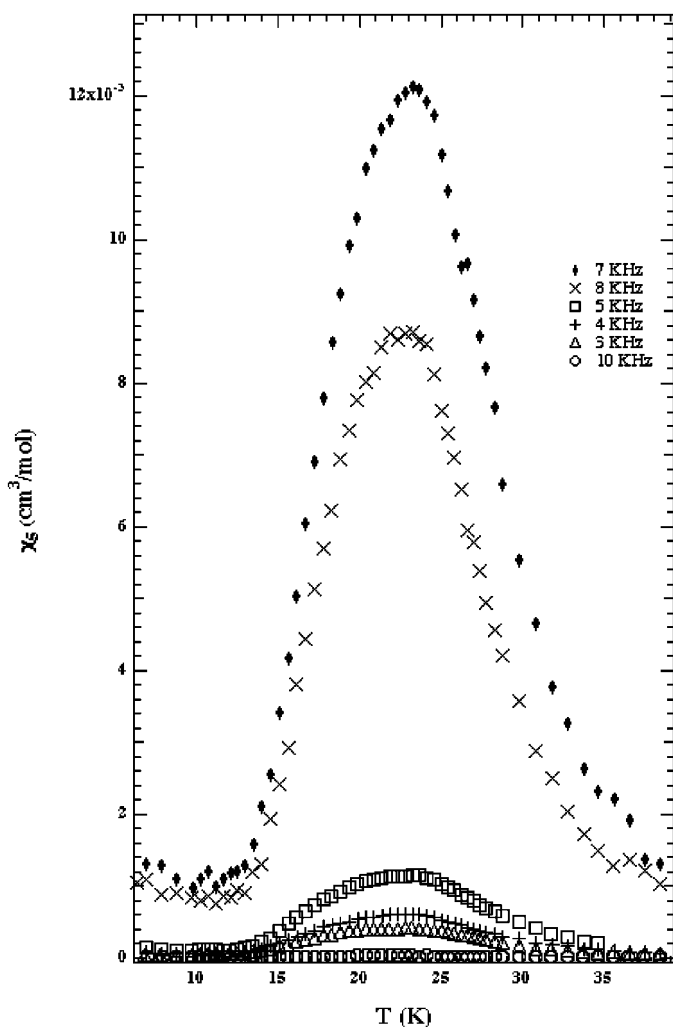
**FIG. 2.** The absolute magnitude of the nonlinear susceptibility $\chi_5$ as a function of temperature $T$, at various measuring frequencies for Co$_3$BTCA$_2$(H$_2$O)$_4$.

the first three terms for the expansion for the frequency-dependent magnetization (Eq. [2]) at 23 K and at 7 kHz reveals the magnitude of the nonlinear contributions at $T_c$. In the 1-Oe exciting field, the first three coefficients are 2.5, $1.08 \times 10^{-3}$, and $8.8 \times 10^{-3}$, respectively. Thus, relative to the linear term, the third harmonic and fifth harmonics are one part in 2300 and one part in 285, respectively. These nonlinear terms are significant but not overwhelming at $T_c$. These ratios of the coefficients are at $T_c$ somewhat larger than those seen in other nonlinear systems (8–10) but our system is unique in that the $5\omega$ term contributes more than the $3\omega$ term.

The temperature range over which a significant nonlinear response is observed is unusually broad. Defining the relative width as $\Delta T/T_c$ (the temperature width $\Delta T$ is the full-width at half-maximum) yields a relative width for these studies near 0.55. Previous nonlinear studies on spin glasses (8–10) found considerably narrower responses with relative widths less than 0.15. The broad response observed in the Co$_3$BTCA$_2$(H$_2$O)$_4$ compound is consistent with the large critical region revealed by the dc scaling analysis (7).

The resonant phenomena occurring in the nonlinear susceptibility is of great interest. Rather than showing a monotonic dependence on frequency, both $\chi_3$ and $\chi_5$ have maximum responses at unique frequencies. The resonance frequency is found to be near 8 KHz for $\chi_3$ and 7 KHz for $\chi_5$. For a given temperature, a change of frequency of 2 KHz from $f_{\text{res}}$ reduces the response by roughly half. The frequency dependence of the nonlinear susceptibilities has been previously reported for spin glasses (11), ferromagnets (12), and canted spin systems (13), but no resonant behavior was observed.

A resonance similar to that observed in the nonlinear susceptibilities is observed as well in the out-of-phase component of the linear susceptibility. Figure 3a displays the out-of-phase component of the linear susceptibility as a function of temperature and measuring frequency for the same compound discussed above. These data were obtained under the same conditions as the nonlinear susceptibilities. Again, a resonance is observed, in which the magnitude of the response is maximized at 8 KHz.

The data in Fig. 3a demonstrate the failure of dynamic scaling to apply to this compound. A recent method of dynamic scaling (14) has expressed the $\chi''T$ product as scaling with a function $\tilde{f}$, which is linear in the reduced temperature $t = (T - T_c)/T_c$:

$$\chi''T \sim \varpi^{\frac{\beta}{\nu}} \tilde{f}\left(\frac{t}{\varpi^{1/z\nu}}\right). \qquad [3]$$

This new form permits the determination of $\beta/2\nu$, $z\nu$, snf $T_c$ independently of each other and has recently been used to redetermine the critical exponents of Cd$_{0.6}$Mn$_{0.4}$Te. Since

centered at 23 K is observed in both $\chi_3$ and $\chi_5$ for all frequencies measured (between 3 and 10 kHz). At the frequency for which the strongest response is obtained, the susceptibility at $T_c$ is an order of magnitude greater than its value at $1.5T_c$. The temperature of the greatest response at any frequency (23 K) is the same as the critical temperature determined previously (7) by dc measurements.

Comparison of Figs. 1 and 2 reveals that the peak value of $\chi_5$ is significantly larger than that of $\chi_3$ at the transition temperature. At 23 K, $\chi_3$ reaches $4.3 \times 10^{-3}$ cm$^3$ Oe$^{-2}$ mol$^{-1}$ at 8 kHz while at the same temperature the peak magnitude of $\chi_5$ is 0.19 cm$^3$ Oe$^{-4}$ mol$^{-1}$ at 7 kHz, more than 40 times larger. Previous studies [7] of the frequency dependence of the linear susceptibility $\chi_1$ at 23 K show it to approach a value near 2.5 cm$^3$ mol$^{-1}$ as $f \to 0$ and near 2.0 cm$^3$ mol$^{-1}$ as $f \to 7$ kHz. Comparing the coefficients of
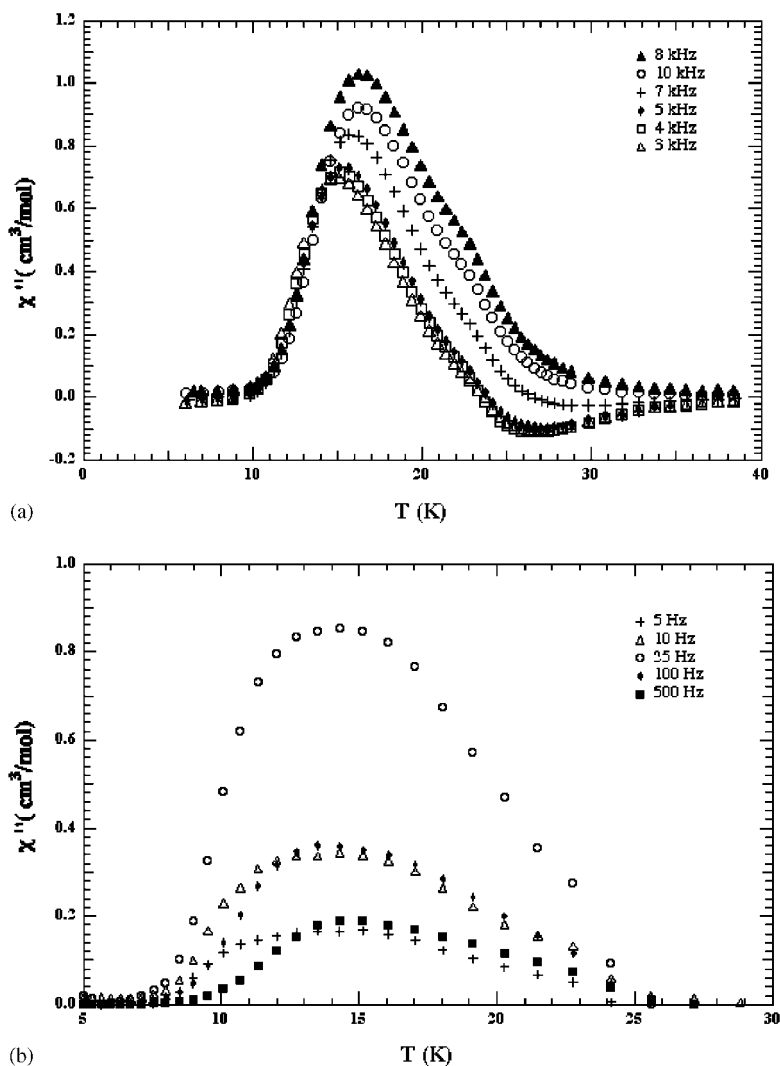
**FIG. 3.** The out-of-phase component of the complex ac susceptibility $\chi_1''$, as a function of temperature $T$, for (a) $Co_3BTCA_2(H_2O)_4$ and (b) the same compound after three months in a gel cap.

this form of the scaling function is linear in reduced temperature $t$, all dependence upon $t$ vanishes at the critical temperature and the $\chi''T$ product at $T_c$ is predicted to scale with frequency as a simple power law, with exponent $\beta/2\nu$. The observed resonance in the frequency dependence is inconsistent with this prediction and demonstrates that $Co_3BTCA_2(H_2O)_4$ is not described by conventional dynamics.

Previous studies (15) have shown that the hydration state of the compound affects its magnetic properties. In general, the glassy-like nature of the compound is enhanced as its hydration state is decreased. Enhanced behavior includes increases in the low-temperature relaxation times, increases in the magnitude of the low-temperature $\chi T$ product, and increases in the strength of the dc coercive fields. Interestingly, the 23-K transition temperature does not change with

hydration state (15). The hydration state itself is affected by either the initial synthesis of the compound or subsequent exposure to an aqueous environment, such as the humidity of the air or the moisture in a gel capsule. Figure 3b displays data obtained after the sample used in Fig. 3a had been exposed to the moisture of a gel cap for a period of three months. The resonance now occurs near 25 Hz. The conclusion that the hydration state has changed as the sample ages is supported by the fact that the sample begins to change color from dark purple to pink as it is exposed to the moisture of the gel cap over time. This particular color change in a $Co^{2+}$ ion is indicative of an increasing hydration state.

The in-phase component of the linear susceptibility shows no evidence of a resonance, regardless of the hydration state of the compound. Figure 4 displays in-phase data for two
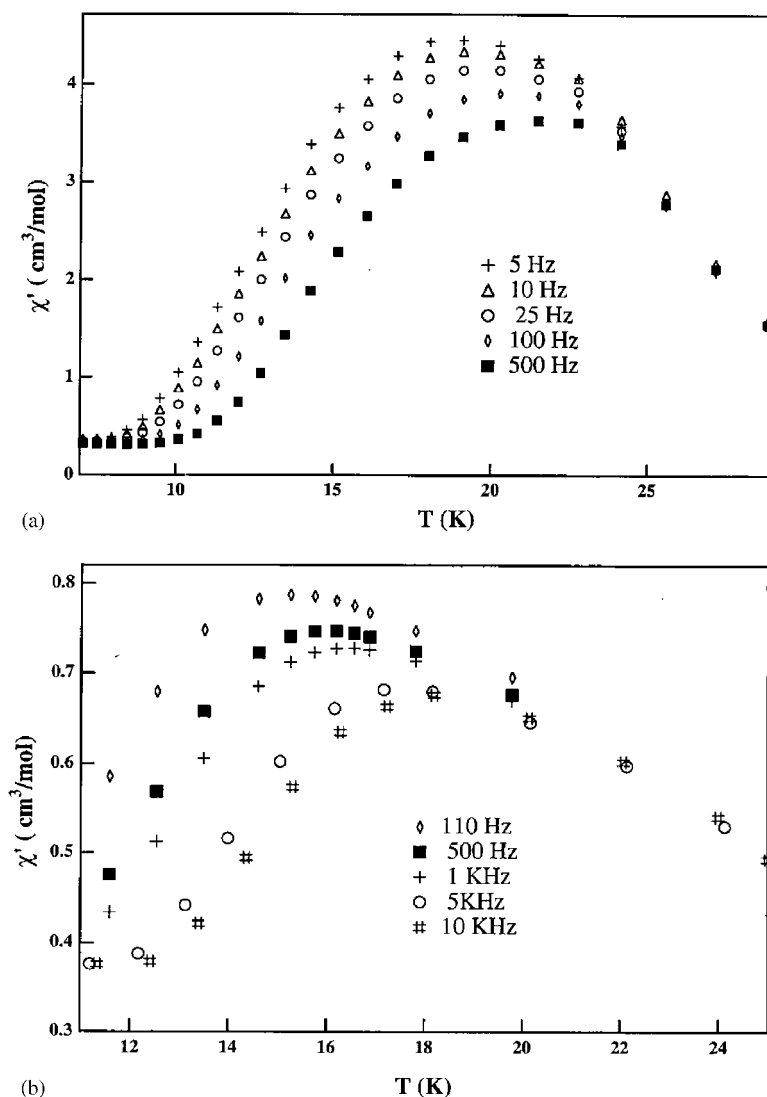
**FIG. 4.** The in-phase susceptibility $\chi'_1$, as a function of temperature $T$, as measured in various frequencies for (a) the Co$_3$BTCA$_2$(H$_2$O)$_4$ compound after three months in a gel cap and (b) a compound that was prepared at a reaction temperature (78°C) lower than that of the Co$_3$BTCA$_2$(H$_2$O)$_4$ compound, which was prepared at 98°C.

compounds with different hydration states. Figure 4a displays the in-phase susceptibility for the compound of Fig. 3b, while Fig. 4b displays data for a compound synthesized at a reaction temperature (78°C) lower than that of the compound in Fig. 3b, which was synthesized at 98°C. Previous studies (7, 15) have shown that a lower reaction temperature produces a compound with an increased hydration state. These studies have also shown that a decrease in reaction temperature (and thus an increase in hydration state) leads to a decrease in the overall magnitude of the susceptibility. This is consistent with the data in Fig. 4 and supports the conclusion that the compound in Fig 4b has an even higher hydration state. Note the frequency dependence, which begins near 23 K, shows no resonance

phenomena but instead shows a decrease in signal magnitude with increasing measuring frequency. The small upturn in susceptibility in Fig. 4b is due to the presence of a paramagnetic impurity phase, always found for samples prepared at lower temperatures.

In summary, the dynamics of the molecular-based magnet Co$_3$BTCA$_2$(H$_2$O)$_4$ are most unusual. The nonlinear susceptibilities $\chi_3$ and $\chi_5$ show distinct maxima at $T_c$; such maxima have been interpreted as demonstrating the existence of spin-glass transitions in other systems (8–10). However, we believe the transition at 23 K in Co$_3$BTCA$_2$(H$_2$O)$_4$ is more complex than a simple spin glass (15).

Studies of the frequency dependence of the compound reveal resonance phenomena in $\chi_3$, $\chi_5$, and $\chi''_1$, but not in $\chi'_1$.

Neither the linear nor nonlinear responses of the ac susceptibility near a spin-glass transition are predicted to behave in such a manner (16) and such behavior has not been previously reported. Furthermore, experimental studies of the linear ac susceptibility of other disordered systems, such as random anisotropy magnets (17), do not reveal such behavior. A superparamagnetic description (18) is also inapplicable.

The ultimate explanation of the behavior of $Co_3BTCA_2(H_2O)_4$ is certainly related to the BTCA ligand and the short-range structure it creates. This ligand was chosen because it has the geometry and connectivity to produce a frustrated lattice such as the Kagomé. It also has the ability to bind to a metal ion in several manners (chelating, monodentate, and bridging), allowing for a randomness in the exchange pathways. Furthermore, the highly anisotropic nature of the $Co^{2+}$ ion, coupled with the disordered nature of the material, should provide a randomness in the anisotropy. The combination of all these factors leads to a highly disordered system with many possible sources of frustration. Both the ac dynamics and the previously observed static properties are most probably linked to this highly disordered nature.

## ACKNOWLEDGMENT

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