Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Ralf Feyerherm, Takayuki Ishida, Takashi Nogami & Michael Steiner (1999): Single Crystal Magnetic Susceptibility of 1-D $[PM{\cdot}Cu(NO_3)_2{\cdot}(H_2O)_2]_n$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 335:1, 235-244

To link to this article: http://dx.doi.org/10.1080/10587259908028868

*Mol. Cryst. and Liq. Cryst.*, 1999, Vol. 335, pp. 235-244
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# Single Crystal Magnetic Susceptibility of 1-D $[PM{\bullet}Cu(NO_3)_2{\bullet}(H_2O)_2]_n$

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Single crystal studies of the magnetic susceptibility of the chain compound $[PM{\bullet}Cu(NO_3)_2{\bullet}(H_2O)_2]_n$ (PM = pyrimidine) show that it is a good example of a uniform $S = 1/2$ antiferromagnetic Heisenberg chain, characterised by a single exchange parameter $|2J|/k_B = 36$ K. The Cu $g$-tensor principal values are $g_{\parallel} = 2.34(2)$ and $g_{\perp} = 2.05(2)$. In the low-$T$ region a divergent contribution to the susceptibility (Curie tail) is observed that exhibits a pronounced anisotropy. This Curie tail cannot be reconciled assuming chain defects or impurities as its origin. It rather appears intrinsic to the chains and associated with the relative canting of the local $g$-tensors of neighbouring Cu ions and the Dzialoshinski-Moriya interaction. Our study constitutes evidence for a staggered contribution to the susceptibility which has been predicted theoretically recently.

*Keywords:* Magnetic susceptibility; Heisenberg chain; anisotropic Curie tail

## INTRODUCTION

Magnetic chain compounds have attracted the interest of chemists and physicists for more than three decades. Chains of magnetic ions with low spin ($S$ = ½, 1) are of specific interest, because they exhibit pronounced quantum effects. Well known examples are the gapless continuum of spin excitations in the uniform $S$ = ½ antiferromagnetic (AFM) Heisenberg chain[1] and the appearance of the Haldane gap in the integer spin AFM chain[2] . The theory of the ideal $S$ = ½ antiferromagnetic Heisenberg chain is well established and

usually describes the observed properties in real systems very well. Recently, the theoretical prediction of magnetic-field-dependent incommensurate low energy modes could be verified by neutron scattering on copper benzoate[3]. However, specific heat measurements revealed the opening of a spin-excitation gap in the external magnetic field[3]. This behaviour is not consistent with the uniform Heisenberg chain model. It was shown theoretically that it arises from the relative canting of local $g$-tensors of neighbouring copper ions and the Dzialoshinski-Moriya (DM) interaction[4], leading to an effective staggered magnetic field. This mechanism was also predicted to cause a staggered contribution to the magnetic susceptibility, which diverges at $T \rightarrow 0$. Although such a contribution appears to be present in previously reported data on $S = ½$ AFM chains, it has never been recognised as intrinsic effect, but was usually associated with chain defects or impurity spins.

In this work we present single crystal studies of the magnetic susceptibility in the chain compound $[PM{\cdot}Cu(NO_3)_2{\cdot}(H_2O)_2]_n$, which has been synthesised recently[5]. It crystallises in the monoclinic structure, space group C2/c, with lattice constants $a$ = 12.404 Å, $b$ = 11.511 Å, $c$ = 7.518 Å, $\beta$ = 115.0°. As depicted in Figure 1, uniformly spaced chains of crystallographically equivalent Cu ions ($d_{Cu\text{-}Cu}$ = 5.737 Å) extend along the *ac* diagonal, bridged by N-C-N bonds, which constitute the intrachain magnetic exchange pathway. The Cu co-ordination is an elongated octahedron, built from an N-O-N-O equatorial plane and two O in the axial positions. The octahedral axis is tilted from the *ac* plane by ±29.4°. Due to the two-fold symmetry, for a pair of Cu neighbours along the chain these axes exhibit a relative canting of 58.8°, i.e., the $g$-tensor principal axis alternates along the chain. The polycrystalline susceptibility of $[PM{\cdot}Cu(NO_3)_2{\cdot}(H_2O)_2]_n$ exhibits Curie-Weiss behaviour with $\theta_{CW}$ = −17.8 K, pointing to a significant antiferromagnetic intrachain coupling.

## EXPERIMENTAL

Single crystals of the title compound have been grown by slow evaporation of the equimolar aqueous solution of $Cu(NO_3)_2$ and pyrimidine. A crystal of about 40mg mass was mounted on a special sample holder, allowing for rotation of the sample around the crystallographic b-axis. Susceptibility and magnetisation measurements were carried out on an MPMS Squid magnetometer (Quantum Design) at temperatures $T$ between 1.8 and 300 K in varying magnetic fields $H$ up to 55 kOe and for a number of different orientations. $M/H$ values were constant in a wide field range and thus can be set equal to the susceptibility $\chi = \partial M/\partial H|_{H=0}$. The $\chi$ data were corrected for small diamagnetic and sample holder contributions that were determined experimentally by extrapolation of the high temperature susceptibility data as $1/T \rightarrow 0$.

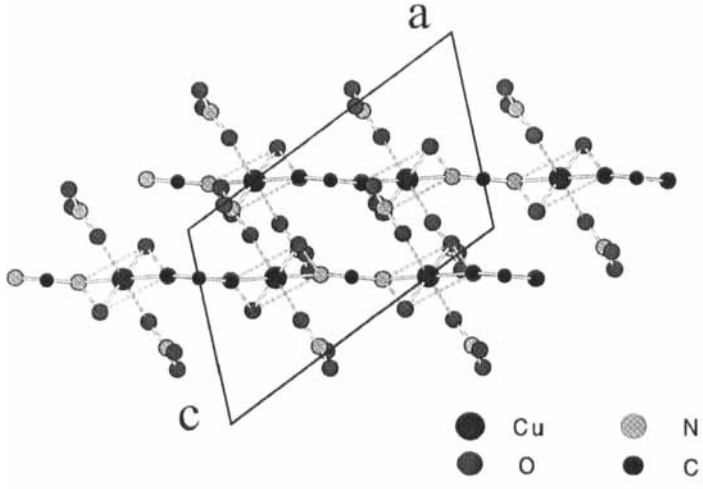


FIGURE 1 Crystal structure of $[PM{\cdot}Cu(NO_3)_2{\cdot}(H_2O)_2]_n$, viewed along the $b$ axis. The equatorial planes around Cu are marked.

## RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the magnetic susceptibility $\chi$ for $H$ parallel to the unique crystallographic $b$-axis (perpendicular to the chains). It exhibits the general features expected from the uniform $S = ½$ antiferromagnetic Heisenberg chain, as calculated first by Bonner and Fisher[6], with a characteristic maximum at 23 K and non-zero susceptibility as $T \rightarrow 0$. The upturn below 5 K points to some additional contribution that is not expected from the ideal chain.

The observed temperature dependence of $\chi$ can be well described by a sum of a Bonner-Fisher curve and a Curie tail (CT):

$$\chi(T) = g^2 (N_A \mu_B^2 / 4k_B) F(2J/k_B T)/T + C_{CT}/T , \qquad (1)$$

where $g$ is the Cu $g$-factor and $F(2J/k_BT)$ is an empirical rational function[7].

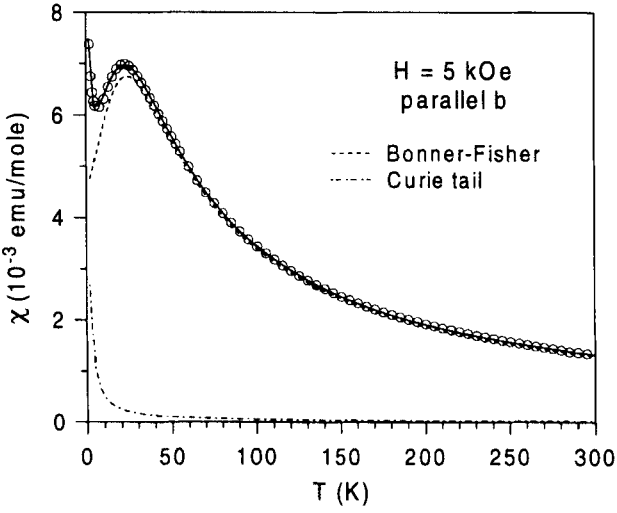


FIGURE 2 Temperature dependence of $\chi$ for $H$ along the $b$ axis. The fit (solid line) is a fit of eq. (1) to the experimental data.

From fits of this function to the experimental data the parameters $J$, $g$ and $C_{CT}$ are determined. For $H$ parallel $b$ we find $|2J|/k_B$ = 36.0(5) K, $g_b$ = 2.11(2), and $C_{CT}$ = 0.0050(3) emu K/mol. The interchain coupling is assumed to be small because of the larger distance of the respective Cu ions ($d$ = 6.874 Å) and the missing magnetic exchange path. Low-temperature specific heat measurements show linear $T$ dependence with the expected[6] slope $C/T(T\rightarrow 0) = 0.7R/|2J| =$ 0.162 J/molK$^2$ and exhibit no indications for three-dimensional long-range ordering down to 0.38 K[8]. We conclude that $[PM{\cdot}Cu(NO_3)_2{\cdot}(H_2O)_2]_n$ is a good example of a uniform antiferromagnetic Heisenberg chain, with the interchain interaction by at least a factor of $10^{-2}$ smaller than the intrachain interaction. However, preliminary ESR measurements exhibit relatively narrow resonance lines, showing that some moderate interchain interactions are present[9].

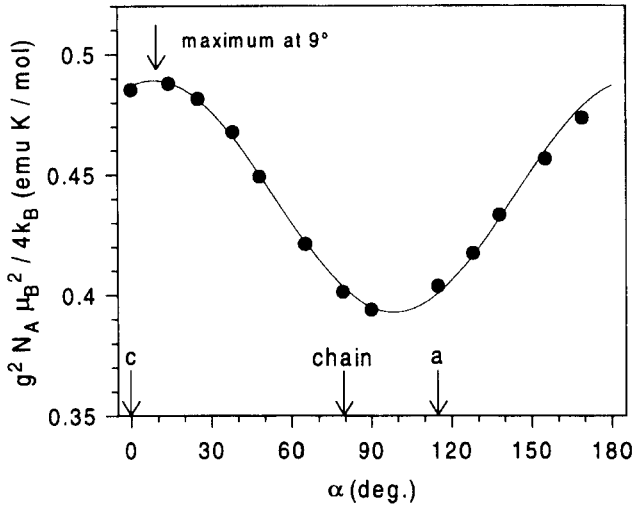


FIGURE 3 Angular dependence of $C_{BF} = g^2 (N_A\mu_B^2/4k_B)$ in $ac$ plane.

Due to symmetry, the $b$ axis is a principal axis of the bulk susceptibility tensor. To determine the orientation of the other two principal axes and the associated $g$-factors we measured $\chi(T)$ for a number of different orientations of $H$ in the $ac$ plane. Figure 3 shows the angular dependence of the coefficient of the Bonner-Fisher term $C_{BF} = g^2(N_A\mu_B^2/4k_B)$ for these data. The maximum $g$-factor, $g_{c'} = 2.27(2)$, is observed at $\alpha = 9°$ (± 5)°, close to the projection of the local octahedral axes onto the $ac$-plane ($\alpha = 14°$). The minimum $g$-factor is $g_{a'} = 2.05(2)$. Within the experimental uncertainty, our values are in agreement with ESR data ($g_{a'} = 2.074$, $g_b = 2.151$, $g_{c'} = 2.290$)[9]. From the canting angle of the octahedral axis from the ac plane we estimate the axial $g$-factor $g_{\parallel} = 2.34(2)$, while $g_{\perp} = 2.05(2)$. The $g$-value anisotropy is consistent with the usual behaviour of $Cu^{2+}$ ions in an elongated octahedral environment. The value of $2J$ is isotropic within the experimental uncertainty (± 2%).

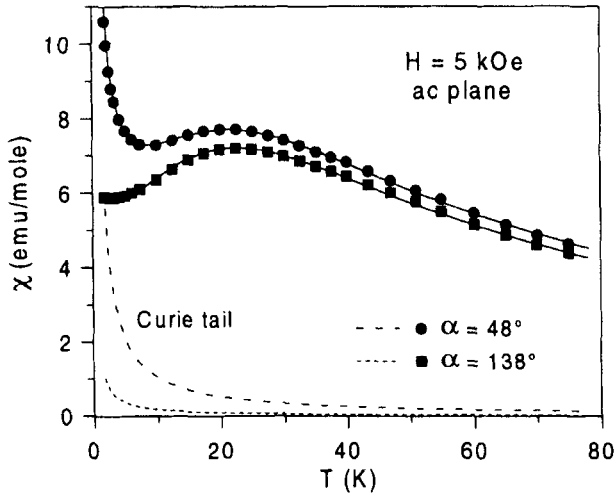


FIGURE 4 Temperature dependences of $\chi$ for the two orientations of maximum and minimum low-temperature Curie tail.

The Curie tail shows unusual behaviour in being highly anisotropic. This is demonstrated in Figure 4 which shows $\chi(T)$ for the two orientations of $H$ in the $ac$ plane for which $C_{CT}$ is extremal. The Curie tail, being very pronounced for the one direction almost vanishes for the perpendicular direction. Figure 5 shows the angular dependence of $C_{CT}$ in the $ac$ plane. It varies by a factor of six. The maximum is observed at an angle 48° with respect to the $c$-axis. This direction appears to be unrelated to the chain direction and the octahedral axis.

We confimed on separately synthesised crystals that this strong anisotropy is quantitatively reproducible. We also verified by magnetisation measurements at $T$ = 1.8 K in fields between 1 and 55 kOe that the Curie tail behaves like of paramagnetic origin[10] and is not due to any ferro- or ferrimagnetic impurities. The Curie tail coefficient $C_{CT}$ is constant in fields up to 30 kOe and shows an only weak saturation effect above.

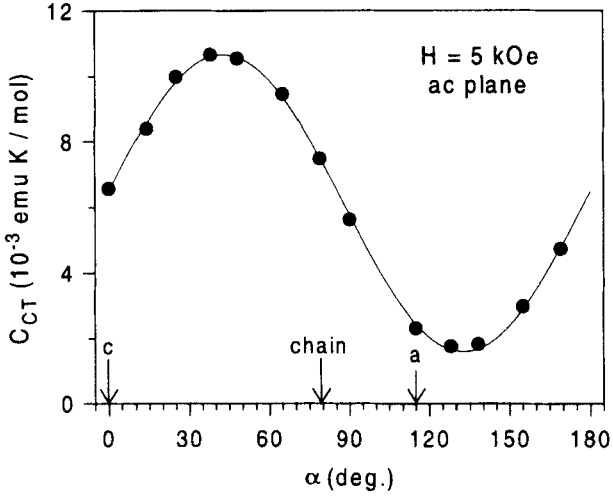


FIGURE 5 Angular dependence of the Curie tail coefficient $C_{CT}$ in the $ac$ plane. The maximum is located at $\alpha = 48°$.

Usually, the Curie tail is explained by an „impurity contribution" from uncoupled Cu ions due to chain defects[11]. The strong anisotropy observed in our data clearly rules out such an explanation. Elemental analysis by EDX show that no magnetic impurity atoms of other kind are present in our samples down to the 0.1% level. We therefore believe that the anisotropic Curie tail is an intrinsic property of the Cu chains in the present system and is associated with the alternating $g$-tensor principal axis. For that case, a staggered, divergent contribution to the susceptibility was predicted theoretically[4].

From the theory, a theoretical estimate of the magnitude of the maximum Curie tail contribution is given by $C_{CT}/C_{BF} = (\Delta g/g)^2$, where $\Delta g = |g_{\parallel} - g_{\perp}|$ is the $g$-factor anisotropy. In the present case, $C_{CT}/C_{BF} = 0.02$ is theoretically expected, in good agreement with the experimental value 0.023, which gives us confidence that the mechanism predicted in ref. [4] is responsible for the Curie tail in the present system.

Already in previously published data an anisotropic Curie tail is visible, e.g., on Cu-Benzoate[3,12]. In this compound, it is a relatively small effect, which might be associated with the smaller canting of only 20° between the local $g$-tensors. An example of a pronounced Curie tail in polycrystalline material is dichlorobis(thiazole)copper(II), where the $g$-tensor canting is 90°[7]. However, in the well-known $S = ½$ Heisenberg chain compounds dichlorobis(pyridine)copper(II)[13] and $Cu(NO_3)_2{\cdot}C_4H_4N_2$[14], in which no canting is present, no Curie tail can be identified in the susceptibility data. Therefore, we speculate that in a number of compounds in which a Curie tail in the susceptibility is reported, it might be intrinsic to the chain and not due to chain defects.

Now we discuss the fact that in $[PM{\cdot}Cu(NO_3)_2{\cdot}(H_2O)_2]_n$ the maximum Curie tail appears at an orientation that seems to be unrelated to the $g$-tensor principal axis. Incidentally it is located approximately at half angle between the

projection of the octahedral axis onto the *ac*-plane and the chain direction.

Therefore, due to symmetry reasons, the canting of the *g*-tensor alone cannot explain the observed behaviour but we have to assume another mechanism that induces effective staggered fields. This is most likely the DM interaction which was also invoked to quantitatively explain the observed anisotropy of the field-induced spin excitation gap in Cu-benzoate[3,4]. This interaction is also related to the *g*-factor anisotropy.

Due to symmetry, in $[PM{\cdot}Cu(NO_3)_2{\cdot}(H_2O)_2]_n$ the vector $\boldsymbol{D}$ characterising the DM interaction must lie in the ac plane. The maximum (minimum) effective staggered field is induced when the external field $\boldsymbol{H}$ is perpendicular (parallel) to $\boldsymbol{D}$[4]. This gives an estimate for the orientation of $\boldsymbol{D}$ approximately parallel to the orientation of the minimum Curie tail. Due to the lack of detailed theory, no quantitative analysis of the observed anisotropy of the Curie tail can be given to date.

In conclusion, we have given experimental evidence for a staggered contribution to the magnetic susceptibility in $[PM{\cdot}Cu(NO_3)_2{\cdot}(H_2O)_2]_n$ that is caused by the canting of the *g*-tensors of neighbouring Cu ions and the DM interaction. This constitutes a new mechanism for the occurence of (anisotropic) low-temperature Curie tails in $S = ½$ antiferromagnetic Heisenberg chains.

**Acknowledgements**

We greatfully acknowledge useful discussions with H. Shiba, O. Kahn, U. Schotte, and V. Eyert, as well as experimental support by M. Meschke and R. Sellmann (susceptibility measurements), D. Günther and M. Meißner (specific heat), I. Sieber (EDX), and B. Pilawa (ESR).

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