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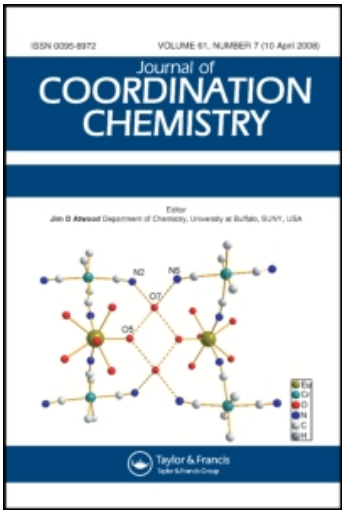

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One-Dimensional Magnetic Behavior in N,N'-Bis(Trifluoroacetylacetone)ethylenediimine Copper(II)

Harry C. Allen Jr.[a]
[a] Department of Chemistry, Jeppson Laboratory, Clark University, Worcester, Massachusetts, U.S.A.

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SHORT COMMUNICATION
One-Dimensional Magnetic Behavior in N,N'-Bis(Trifluoroacetylacetone)ethylenediimine Copper(II)†

HARRY C. ALLEN, Jr.

Department of Chemistry, Jeppson Laboratory, Clark University, Worcester, Massachusetts 01610, U.S.A.

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In view of the current interest[1–7] in one-dimensional magnetic materials, preliminary results of a EPR linewidth study on N,N'-bis(trifluoroacetylacetone)ethylenediimine copper(II) [Cu(tfacac)$_2$en] are reported in this note. Although a complete crystal structure of the copper chelate is not available, preliminary results[8] indicate it is very closely related to the structure of the corresponding Nickel(II) chelate that has been completely determined. The space group for both crystals in $P_{2\,1/c}$. The unit cell dimensions for the copper chelate are a = 10.40 A, b = 16.23A, c = 9.06 Å, $\beta = 98.08°$ and there are four molecules per unit cell. The nearly planar [Ni(tfacac)$_2$en] molecules crystallize in stacks forming a chain of Ni^{+2} ions along the c-axis with a Ni-Ni separation of about 4.0 Å. The bulky ligands separate the chains by about twice this distance. The similarity in the x-ray spot distributions indicates that the [Cu(tfacac)$_2$en] has a similar structure. Studies of the copper chelate[9] doped into the diamagnetic nickel chelate indicate that two of the principal g-values and the ion chain lie in the ac-plane.

With the crystal mounted so that it could be rotated about the b-axis with respect to the magnetic field, the peak-to-peak linewidth of the EPR signal was measured as a function of the angle between the axis of the ion-chain and the applied field in the ac plane. The results are shown in Figure 1.

The linewidth for one-dimensional spin-diffusional dynamics has been found to be[1,7]

$$\Delta H_{pp} = C\,\frac{(M_{2d} + M_{2h})^{2/3}}{H_e^{1/3}} \qquad (1)$$

M_{2d} is the dipole-dipole second moment of Van Vleck and M_{2h} is the second moment due to the hyperfine interaction between the unpaired electrons and the copper nuclear spin[6,7], i.e.,

$$M_{2h} = \frac{\frac{5}{4}\,[A_{\parallel}^2 g_{\parallel}^2 \cos^2\varphi + A_{\perp}^2 g_{\perp}^2 \sin^2\varphi]}{g_{\parallel}^2 \cos^2\varphi + g_{\perp}^2 \sin^2\varphi}.$$

C is a constant that is essentially unity.

The dominant angular dependence of M_{2d} is $(3\cos^2\vartheta - 1)^2$ except where ϑ is near 54° when there is a small contribution from the non-secular part of the Hamiltonian.[1] The angle of maximum g-value in the ac-plane indicating the molecular magnetic $g_{\parallel}$ direction does not coincide with the chain axis. This is the first crystal studied in which this non-coincidence has been reported. The angular relationship is $\varphi \sim \vartheta + 25°$. It is this fact that causes the asymmetry in the angular dependence of the linewidth in the range 0°–180°. The dotted curve in Figure 1 is the curve to be expected if the only contribution to the linewidth is M_{2d}.

H_e in eqn (1) is the exchange field and is normally determined from susceptibility measurements. Unfortunately, it has not yet been determined for [Cu(tfacac)$_2$en]. Linewidth measurements at both X-band and K-band frequencies agree within experimental error indicating that H_e is either much larger or smaller than the observation field so it does not complicate the analysis.

The solid line in Figure 1 was obtained from the theory by a curve fitting method. The value of M_{2d} and M_{2h} were calculated and normalized to their maximum value. The parameters used to calculate M_{2h} are those obtained from studies on magnetically dilute samples.[9] The quantity $(aM_{2h} + M_{2h})^{2/3}$ was calculated for various values of a and scaled to the observed maximum linewidth to obtain a best fit with the experimental values.[6] The solid line is calculated for a value of $a = 2.5$ and $\psi = \vartheta + 25°$. The fit could probably be improved by including higher corrections to M_{2h}. The theoretical curve reproduces the observed linewidth very well and in particular, in the region of $90° < \vartheta < 180°$, where M_{2h} is small the observed linewidth closely approximates the

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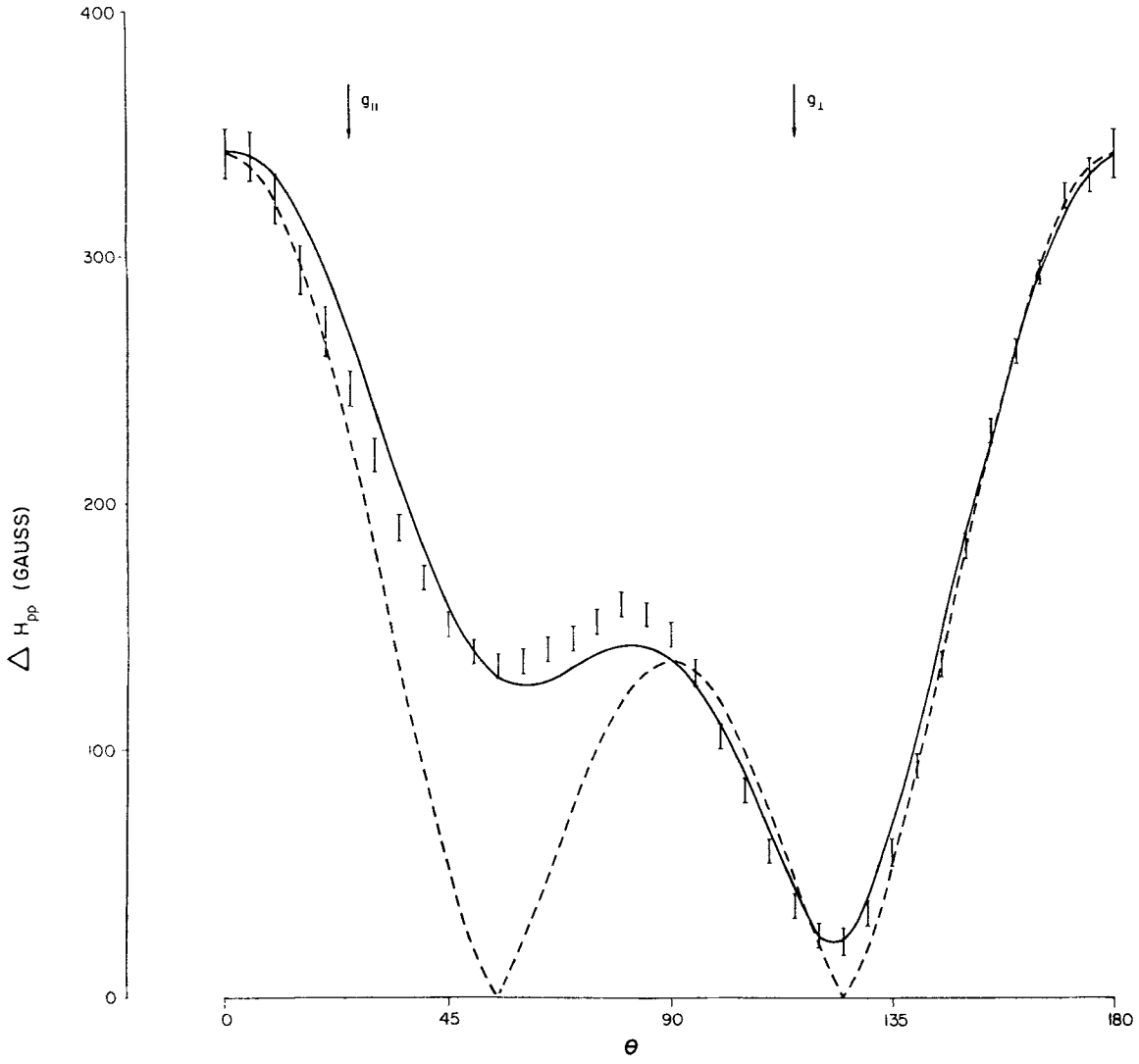

FIGURE 1 A plot of the peak-to-peak linewidth in plane 1 to b axis as a function of the angle between the chain axis and the applied magnetic field. The dotted curve is the dipole-dipole dependence for one-dimensional diffusive behavior scaled to the maximum linewidth; $[3\cos^2\vartheta - 1]^{4/3}$. The solid line is the combined dipole-dipole and hyperfine linewidth.

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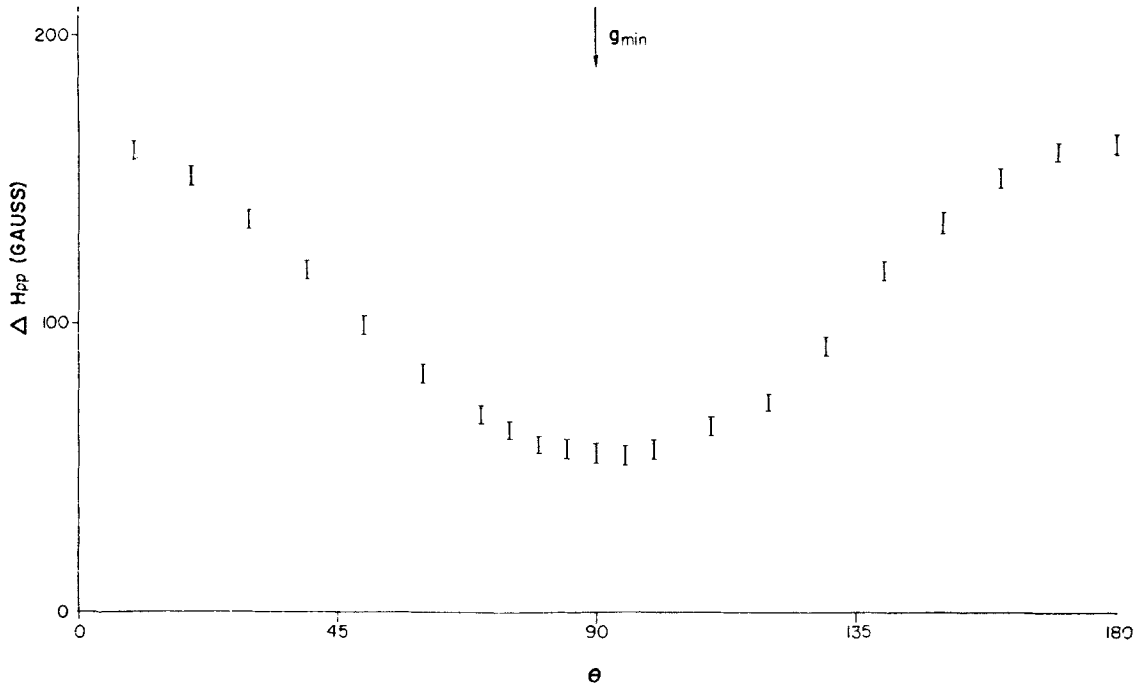

FIGURE 2 Linewidth angular dependence in plane perpendicular to the chain axis.

$(3\cos^2\vartheta - 1)^{4/3}$ dependence expected for one dimensional spin-diffusional dynamics.

Further evidence for the one-dimensional behavior may be seen in Figure 2. Here the linewidth dependence is shown in a plane perpendicular to the ion-chain. In this plane the linewidth dependence seems to be dominated by M_{2h}.

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