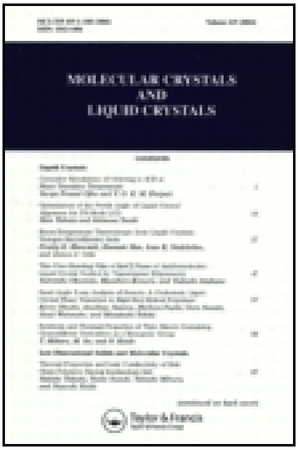

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STRUCTURAL AND MAGNETIC INVESTIGATION OF BIS (QUINOLINIUM) BIS (MALEONITRILE DITHIOLATO) CUPRATE(II) - $(Quin)_2Cu(mnt)_2$

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Abstract The title compound $(Quin)_2Cu(mnt)_2$ was synthesized by metathesis of the sodium salt of $Cu(mnt)_2^{2-}$ with quinoline hydrochloride, and its structural and magnetic properties were examined. The X-ray crystal structure reveals the segregated stacking of the $Cu(mnt)_2^{2-}$ anions and the quinolinium cations and indicates anisotropic properties. The magnetic susceptibility studies show that the exchange interaction is very weak as the Curie-Weiss fit holds down to 2.5K. The dynamics of the exchange interaction as probed by EPR linewidth analysis yield detailed information about the strengths of the various magnetic interactions.

INTRODUCTION

Considerable interest has been focused on square-planar transition metal complexes because of their ability to form stacked crystal structures exhibiting low-dimensional cooperative behavior.[1] Complexes with 1,2-dithiolato ligands,[1,2] $[M(S_2C_2X_2)_2]^{n-}[R^+]_n$, possess a number of characteristics which make them particularly attractive candidates for forming low dimensional charge-transfer complexes--overall planar geometry, large delocalization of the highest occupied molecular orbital of π-symmetry, ability to undergo reversible electron transfer reactions, and chemical variability by changes in the metal M, ligand substituent X, or counter ion R^+ to study systematic influences of the molecular features on the solid state properties.

For $Cu(mnt_2)^{2-}$ (X=CN) one observes different magnetic interactions among the d^9, S = 1/2 anions depending on R^+ (Table 1).

In the search for new structural motifs and magnetic properties we have used several planar cations with different size, symmetry, and abilities of electron transfer. In this paper we report the X-ray crystal structure, magnetic susceptibility and electron paramagnetic resonance of the quinolinium compound.

EXPERIMENTAL

$(Quin)_2Cu(mnt)_2$ was prepared according to standard methods,[4] and the reddish brown crystals for X-ray and EPR studies were grown from an acetonitrile solution by slow evaporation.

3169 unique reflections ($2\theta < 60°$, MoKα) with $F_{obs} > 2\sigma$ were used for the structure determination. Atomic positions were found by direct methods and difference maps. The full matrix least-squares refinement of 194 parameters gave R = 0.063. (For programs used see reference 5).

The magnetic susceptibility measurements were performed on a PAR vibrating sample magnetometer and the data collected between 2.5 and 300K.

The EPR studies were carried out at X-band on a Varian E-3 spectrometer and on a home assembled instrument at Q-band.

Table I. Properties of several $R_2Cu(mnt)_2$ salts.

Cation, R^+	(Antiferro-magnetic exchange parameter) J_o	Remarks	Reference
$N(ethyl)_4{}^+$	$\approx 1\ cm^{-1}$	Semiconductor with $\rho = 10^3\ \Omega$ cm at 300K.	3a
$N(n\text{-}propyl)_4{}^+$	$<0.0002\ cm^{-1}$	Insulating and virtually isolated paramagnetic metal chelate units.	3b
$N(n\text{-}butyl)_4{}^+$	$0.007\ cm^{-1}$	Exchange parameter comparable to copper hyperfine interaction; complicated EPR spectra allow determination of J_o from EPR line positions.	3c
N-methyl Phenazinium$^+$	$\approx 0.1\ cm^{-1}$	Mixed donor-acceptor-donor stack with weak exchange interaction.	3d
Methylene Blue$^+$	$2.6\ cm^{-1}$	Dimerized non-planar metal chelate units; weak dimer-dimer interaction detected by EPR.	3e

RESULTS AND DISCUSSION

I. CRYSTAL STRUCTURE

The title compound is triclinic, P1, with unit cell parameters, a = 7.404 (3)Å, b = 7.452 (3)Å, c = 13.090 (5)Å, α = 106.71 (2)°, β = 109.99 (3)°, γ = 91.19 (3)°, z = 1 molecule/cell.

The copper atom occupies the inversion center at (0,0,0) and hence the CuS_4 core is strictly planar. The complex, however, is not planar, the ligand framework forming an angle of 7.3° with the CuS_4 plane (Fig.1).

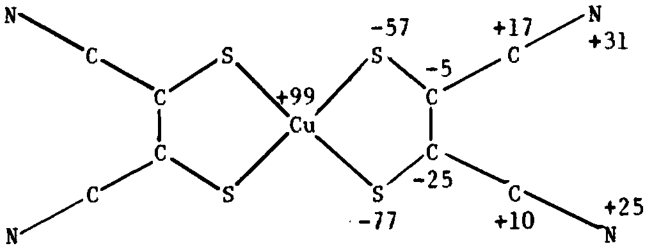

FIGURE 1 The $Cu(mnt_2)^{2-}$ unit with deviations from the least squares plane for each atom (Angstroms x 10^3).

There are only two other examples in the literature with a non-planar $Cu(mnt)_2^{2-}$ unit: 1. (Methylene Blue)$_2$Cu(mnt)$_2$[3e] where the dihedral angle between the ligand planes is 47°. 2. (Methyl$_4$N)$_2$Cu(mnt)$_2$[6] where the ligand planes make an angle of 20°. The essentially planar quinolinium cation is not exactly parallel to the metal chelate plane, but at an angle of 10.1°. Bond distances and angles in both the anion and the cation compare well with those found in other compounds with these units.

Although there are some short contacts between atoms of the anion and the cation, there is no significant lateral overlap between these units, thus showing that there is at best very weak charge transfer interaction.

Each $Cu(mnt)_2^{2-}$ is surrounded by twelve quinolinium ions, of which four lie in nearly the same plane as the complex. Two of these form hydrogen bonds to cyano-nitrogen in the anion (see Fig. 2).

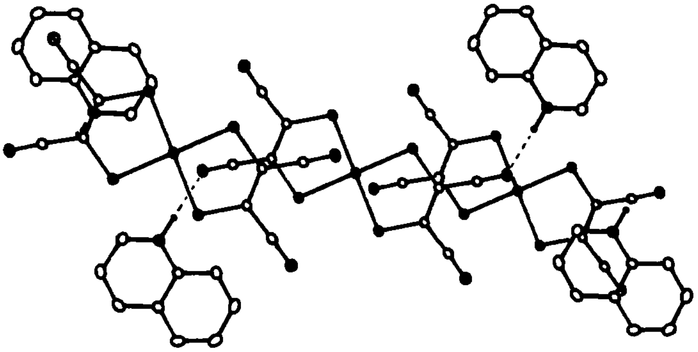

FIGURE 2 A view perpendicular to the $Cu(mnt)_2^{2-}$ plane showing three neighboring anions along the *a* axis and four quinolinium cations in the plane of the center anion. (Dashed lines: Hydrogen bonds).

Fig. 3 shows the stacking of the anions and the cations in the *ab* plane. Due to the tilt of the anionic molecular plane with respect to the crystal axes, the perpendicular distances between the best planes of the units separated along *a* and *b* are quite different: 3.17 Å along *a* and 6.36 Å along *b*. One could therefore imagine the S = 1/2 copper units to be stacked in a chain along *a* with the major magnetic exchange in this direction. Fig. 2, a view

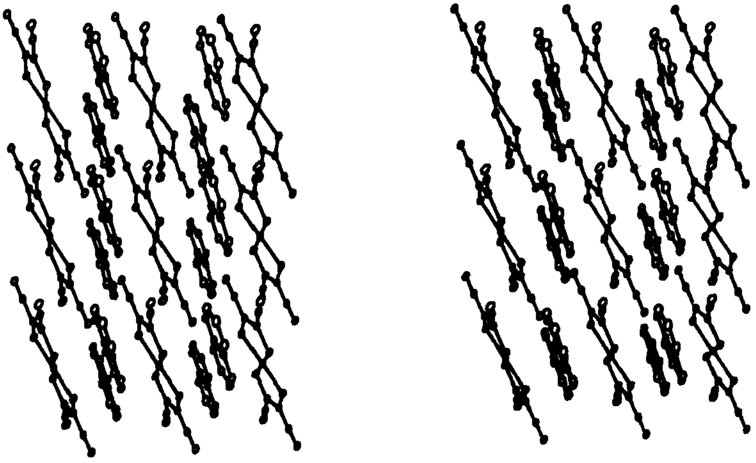

FIGURE 3 Stereoscopic view (*a* vertical, *b* horzontal) *showing the stacking of the anions and cations.*

perpendicular to the $Cu(mnt)_2^{2-}$ plane, showed three neighboring units along *a* and the lateral overlap of the complexes.

The quinolinium units stack as dimers with an interplanar distance of 3.64 Å but with little lateral overlap. The distance between the quinolinium and the metal chelate planes is 3.4 Å but again with little lateral overlap. A quinolinium molecule lies nearly halfway between two neighboring metal chelate units along the *b* axis.

II. MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility (Fig. 4) shows Curie-Weiss $\chi = C/(T-\theta)$ behavior almost down to the lowest temperature measured with a slightly negative Weiss constant $\theta \approx -1°K$ implying a small antiferromagnetic exchange interaction. However, the magnitude of the exchange constant J cannot be determined accurately without going to lower temperatures.

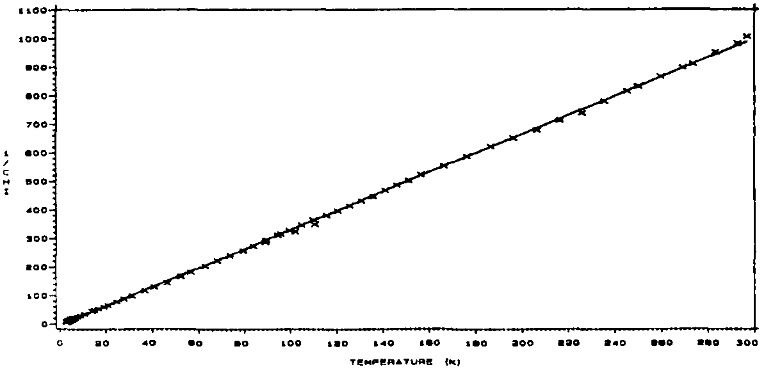

FIGURE 4 Plot of χ_m^{-1} vs temperature with Curie-Weiss fit (solid line).

III. ELECTRON PARAMAGNETIC RESONANCE

A single EPR line is observed at all orientations in both X- and Q-bands, in accordance with the fact that there is only one orientation of the $Cu(mnt)_2^{2-}$ unit in the crystal. The g tensor values agree well with those reported for the diamagnetically diluted $(NBu_4)_2Cu/Ni(mnt)_2$ with $g_{xx} = 2.023$ $g_{yy} = 2.022$ $g_{zz} = 2.091$, and their direction cosines match within ~3° those calculated from the crystal structure.

Angle and frequency dependence of linewidth and lineshape yield a detailed picture of the various cooperative magnetic phenomena in solids such as dipolar and exchange interaction. The loss of hyperfine structure and the observation of a single Lorentzian line indicates a lower bound of the exchange interaction of about 0.05 cm^{-1}.

The linewidths did not show any change on going from X band frequency to Q band frequency. This insensitivity of linewidth to Zeeman frequency can occur in two limiting situations: i) exchange frequency $\omega_e \approx J/h >> \omega_{Zee}$ or ii) $\omega_e << \omega_{Zee}$. From the susceptibility results the latter situation must prevail, and an upper bound for the exchange interaction is therefore 0.3 cm^{-1} (X-band frequency), i.e., $0.05 \leq J < 0.3\ \mathrm{cm}^{-1}$.

The general theories of magnetic resonance in exchange coupled systems[7] start with a zero order Hamiltonian

$$\mathcal{H}_o = \mathcal{H}_{Zee} + \mathcal{H}_{ex} \quad , \qquad (1)$$

with local dipolar and hyperfine fields being treated as a perturbation to $\mathcal{H}_o$ leading to small deviations $\Delta\omega$ from deviations $\omega_o (\Delta\omega << \omega_o)$. The local field correlation function[8]

$$\psi(\tau) = \langle \Delta\omega(\tau)\Delta\omega(0)\rangle \qquad (2)$$

is related to the relaxation function

$$\phi(t) = \exp[-\int_0^t (t-\tau)\psi(\tau)d\tau] \qquad (3)$$

and the resonance absorption is given by the frequency Fourier transform of $\phi(t)$. For strong exchange narrowing, the peak to peak derivative linewidth ΔH_{pp} is given as

$$\Gamma = \frac{3}{2}\Delta H_{pp} = \int_0^\infty \psi(\tau)d\tau \qquad (4)$$

We have used the method outlined by Soos *et al.*[9] to obtain, from the angular and frequency dependence of linewidth, the Fourier components of the spin correlation function for kT >> J with the knowledge of the local field magnitudes.

The method used is applicable to any exchange coupled system with magnetically equivalent sites and provides a direct test for theoretical models of the spin correlation function. The individual contributions to ΔH_{pp} are obtained as the product of that particular second moment with the corresponding Fourier component of the auto-correlation function C(t),

$$\frac{\sqrt{3}}{2}\,\Delta H_{pp} = M_2^{(0)}\, f(0) + M_2^{(1)}\, f(\omega_o) + M_2^{(2)} f(2\omega_o) + a^{(0)}\, g(0) + a^{(1)} g(\omega_o) \qquad (5)$$

$$g(\omega) = 1/2\int_{-\infty}^{\infty} e^{i\omega t}\, c(t)dt;\ f(\omega) = 1/2\int_{-\infty}^{\infty} e^{i\omega t}\, c^2(t)dt$$

$M_2^{(0)}$ and $a^{(0)}$ are the secular, and $M_2^{(1)}$, $M_2^{(2)}$ and $a^{(1)}$ the non-secular dipolar ($\Delta m = \pm 1$, $\Delta m \pm 2$) and hyperfine second moments, respectively.

By solving equation (5), using a nonlinear least-squares procedure, for measured ΔH_{pp} and computed second moments, the five unknowns are evaluated as

$g(0) = 9.2 \times 10^{-4} G^{-1}$ $f(0) = 8 \times 10^{-4}\ G^{-1}$

$g(\omega_o)$, $f(\omega_o)$, and $f(2\omega_o) < 5 \times 10^{-5} G^{-1}$.

Figure 5 shows the fit obtained with the final parameters.

We can extract the exchange parameter from these Fourier components using the Blume-Hubbard form of the auto-correlation function,[10]

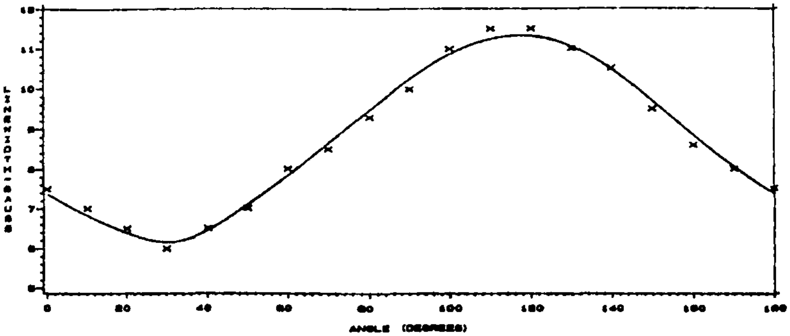

FIGURE 5 Experimental EPR linewidth (x) in the *ab** plane and calculated linewidth (solid line) using theoretical second moments and Fourier components.

$$C_{B\cdot H}(t) = \cosh^{-2}(1/2\ Jt) \tag{6}$$

which yields,

$$g_{B\cdot H}(\pi\omega/J) = \frac{2}{J}\ \frac{\pi\omega/J}{\mathrm{Sinh}(\pi\omega/J)}\ ;\ g_{B\cdot H}(0) = \frac{2}{J}$$

$$f_{B\cdot H}(\pi\omega/J) = \frac{4}{3J}\ \frac{\pi\omega/J}{\mathrm{Sinh}(\pi\omega/J)}\left[1+\frac{\omega^2}{J^2}\right];\ f_{B\cdot H}(o) = \frac{4}{3J} \tag{7}$$

From the secular components, $J \approx 1900$ G or 0.18 cm^{-1} is obtained. The very small non-secular terms are in keeping with the independence of linewidth with Zeeman frequency. J thus obtained is the root mean square of all pairwise exchange interactions, and if we assume two nearest neighbors (as seen from the crystal structure) the exchange parameter between two sites is estimated to be 1340 G or 0.124 cm^{-1}.

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