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Crystal Structure, Magnetism, and Electronic and EPR Spectroscopies of Bis(2-aminopyrimidinium) Tetrachlorocuprate(II): A Square-Planar $CuCl_4^{2-}$ Anion with Semicoordinated Cationic Ligands

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The crystal structure of $(C_4N_3H_9)_2CuCl_4$ [monoclinic, space group $P2_1/c$, $a = 7.136$ (2) Å, $b = 13.418$ (3) Å, $c = 7.705$ (2) Å, $\beta = 97.65$ (2)°, $Z = 2$] has been determined to contain neutral isolated $CuCl_4L_2$ species (L = 2-aminopyrimidinium). The 4 + 2 coordination sphere contains four chloride ions in a planar configuration and is completed by the formation of semicoordinate bonds to a ring nitrogen of each of the two pyrimidinium cations. The Cu–Cl distances average 2.324 Å, and the Cu···N distances are 2.676 Å. Magnetic susceptibility measurements indicate the presence of low-dimensional antiferromagnetic interactions, presumably through Cl···Cl contacts of 3.990 Å between $CuCl_4^{2-}$ ions related by unit cell translations parallel to the *c* axis. Analysis in terms of a 1d model yields $-J/k = 7.3$ K ($J = -5.2$ cm^{-1}). The *g* values obtained from single-crystal EPR spectra are $g_1 = 2.045$ (1), $g_2 = 2.076$ (1), and $g_3 = 2.313$ (1) with g_1 and g_2 approximately parallel to the Cu–Cl bonds and g_3 parallel to the semicoordinate bonds. Analysis of the broadening of the EPR lines due to the overlap from inequivalent magnetic sites yields a value of $J' = 3.2 \times 10^{-4}$ cm^{-1} for the coupling between those sites. The electronic spectrum in the near-IR region shows the existence of four d–d transitions in the 9600–12500 cm^{-1} region, and assignments are made on the basis of AOM parameters.

Introduction

The spectroscopy of $CuCl_4^{2-}$ ions continues to be of interest both experimentally and theoretically. This arises in large part because this anion is stereochemically nonrigid, exhibiting a more or less continuous range of geometries from square-planar (*trans*-Cl–Cu–Cl angle, θ, equal to 180°) to the Jahn–Teller distorted tetrahedral species of D_{2d} symmetry ($\theta \sim 125$–130°).[1-5] Many studies have examined the relationship between the energies of the d–d transitions and the *trans*-Cl–Cu–Cl angle, from either experimental[6-10] or theoretical[11] points of view. More recent investigations have focused on such aspects as the vibrational structure in the d–d bands,[12] the nature of the charge-transfer transitions,[13] and the intensities of the d–d transitions.[14] In spite of this, a number of questions remain unresolved including, for example, detailed experimental studies in the region of the expected crossover of the ^2E and $^2B_1$ states (see Figure 4 in ref 14).

Since there are few simple examples of $CuCl_4^{2-}$ anions with θ values between 150 and 170°, we have been seeking additional examples of isolated species with geometries within this range. Visually it is observed that $CuCl_4^{2-}$ anions with $\theta \sim 140°$ are yellow-green at room temperature, with the color shifting to a deeper green as θ increases and toward orange as θ decreases. However, planar $CuCl_4^{2-}$ anions with very weak semicoordinate bonds defining a very elongated 4 + 2 square-bipyramidal geometry (Cu···Cl > 3.0 Å) also exhibit a green coloration.[15-18] The variation of the strength of the semicoordinate interactions in the planar $CuCl_4^{2-}$ species is expected to lead to systematic variations in spectral properties. In particular, the energy splittings between the ground-state $^2B_{2g}$ level and the excited $^2A_{1g}$ and ^2E_g states are

Table I. Crystal Data

compd name: bis(2-aminopyrimidinium) tetrachlorocuprate(II)
empirical formula: $C_8H_{12}Cl_4CuN_6$
mol wt: 398.4
space group: $P2_1/c$ (monoclinic)
lattice consts:
$a = 7.136$ (2) Å
$b = 13.418$ (3) Å
$c = 7.205$ (2) Å
$\beta = 97.55$ (2)°
$Z = 2$
$\mu = 23.8$ cm^{-1}
abs: $T = 0.239$–0.822
$R = 0.047$ (3σ); 0.061 (all)
$R_w = 0.049$ (3σ); 0.064 (all)

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters for $(2\text{-aminopyrimidinium})_2CuCl_4$

atom	*x*	*y*	*z*	*U*, Å
Cu	0	0.5	0	0.0254 (2)
Cl(1)	0.2426 (1)	0.44474 (6)	0.2164 (1)	0.0294 (3)
Cl(2)	−0.1672 (1)	0.55010 (6)	0.2447 (1)	0.0309 (3)
N(1)	−0.1942 (4)	0.3292 (2)	−0.0061 (4)	0.0329 (10)
C(2)	−0.1230 (5)	0.2379 (2)	−0.0306 (4)	0.0232 (9)
N(3)	−0.2193 (3)	0.1541 (2)	0.0031 (4)	0.0329 (10)
C(4)	−0.3939 (6)	0.1588 (3)	0.0550 (5)	0.0346 (11)
C(5)	−0.4750 (6)	0.2497 (3)	0.0745 (5)	0.0330 (11)
C(6)	−0.3677 (6)	0.3335 (3)	0.0421 (5)	0.0299 (10)
N(7)	0.0452 (5)	0.2314 (2)	−0.0891 (5)	0.0329 (10)

Table III. Bond Distances (Å) and Angles (deg) for $(2\text{-aminopyrimidinium})_2CuCl_4$

Cu–Cl(1)	2.295 (1)	C(2)–N(7)	1.326 (5)
Cu–Cl(2)	2.353 (1)	N(3)–C(4)	1.349 (6)
Cu–N(1)	2.676 (2)	C(4)–C(5)	1.365 (5)
N(1)–C(2)	1.347 (4)	C(5)–C(6)	1.397 (5)
C(2)–N(3)	1.356 (5)	C(6)–N(1)	1.333 (5)
Cl(1)–Cu–Cl(2)	89.7 (1)	C(2)–N(3)–C(4)	121.3 (3)
C(6)–N(1)–C(2)	117.0 (3)	C(3)–C(4)–C(5)	119.3 (4)
N(1)–C(2)–N(3)	121.5 (3)	C(4)–C(5)–C(6)	116.9 (4)
N(1)–C(2)–N(7)	118.3 (3)	C(5)–C(6)–N(1)	123.9 (3)
N(3)–C(2)–N(7)	120.2 (3)		

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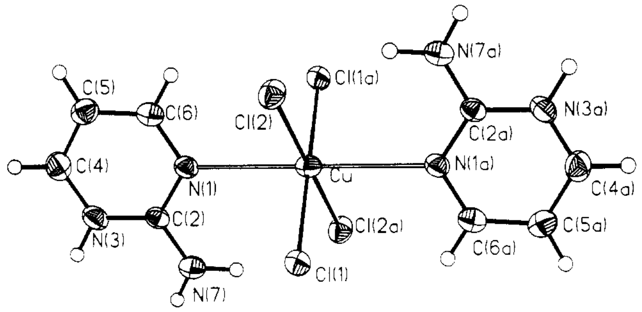

Figure 1. Illustration of the (2-aminopyrimidinium)$_2$CuCl$_4$ species.

expected to decrease as the axial interaction increases.[19,20] For the EPR spectrum, increased axial interaction should lead to less efficient quenching of the orbital angular momentum and hence give higher g values.[1] As part of a study of copper halide salts with planar organic cations,[10,22,23] both green and yellow salts of 2-aminopyrimidine were isolated. The green salt proved to be (2-aminopyrimidinium)CuCl$_3$·H$_2$O.[21] The crystal structure of the yellow salt, (2-aminopyrimidinium)$_2$CuCl$_4$, which contains coordinated cations, is reported here, along with the spectral, magnetic, and EPR properties of the elongated 4 + 2 square-bipyramidal species contained therein.

Experimental Section

The compound bis(2-aminopyrimidinium) tetrachlorocuprate(II) was prepared by dissolving a 2:1 mole ratio of 2-aminopyrimidine and CuCl$_2$·2H$_2$O in a minimum amount of hot, concentrated hydrochloric acid. Concentration of the hot solution yielded the yellow product. Controlled evaporation produced large, yellow platelets several mm on edge and 0.1–0.2 mm thickness. At low temperatures, or in more dilute HCl solutions, green crystals of 2-aminopyrimidinium aquotrichlorocuprate(II) were obtained.

The crystal structure was determined by standard techniques utilizing diffraction data collected on a Nicolet R3m/E diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation. The salt belongs to the monoclinic crystal class, space group $P2_1/c$, with a = 7.136 (2) Å, b = 13.418 (3) Å, c = 7.205 (2) Å, and β = 95.55 (2)°. The preliminary phases were determined with the direct-methods routine SOLV in the SHELXTL system.[24] All atoms, including hydrogen atoms, were resolved on subsequent E maps and difference syntheses. Least-squares refinement of structural parameters (including isotropic thermal parameters on the hydrogen atom, but not their positions) led to final values of R equal to 0.047 and R_w equal to 0.049.[25] Crystal data are given in Table I. Final positional parameters are listed in Table II and interatomic distances and angles are given in Table III.

The EPR spectra of (2-aminopyrimidinium)$_2$CuCl$_4$ were recorded with a Bruker ER200 spectrometer at X-band frequency equipped with a standard Bruker apparatus down to liquid nitrogen temperatures. EPR-suitable single crystals of the title compound were found to have well-developed (100) and ($\bar{1}$00) faces. Magnetic susceptibility measurements were made on a powdered sample (106.3 mg) on a PAR vibrating sample magnetometer (H = 5000 Oe) at Montana State University. Visible spectra were measured on a Perkin-Elmer 1700 FT-NIR spectrometer of a sample melted between glass plates and of a single crystal through the (100) face.

Structure Description and Discussion

The structure consists of square-planar CuCl$_4^{2-}$ anions, which are further coordinated by two of the organic counterions. Protonation of the 2-aminopyrimidine molecule occurs at one of the ring nitrogen atoms. The two semicoordinate positions of the CuCl$_4^{2-}$ anion are occupied by the unprotonated ring nitrogen atoms from two 2-aminopyrimidinium cations, as seen in Figure 1. The planar, centrosymmetric CuCl$_4^{2-}$ ions show significant distortions from D_{4h} symmetry with Cu–Cl(1) = 2.295 (1) Å and Cu–Cl(2) = 2.353 (1) Å. The semicoordinate Cu···N(1) distances are 2.676 (2) Å, making the Cl···N contacts 0.2 Å greater than the sum of the van der Waals radii. This semicoordinate distance is similar to or shorter than the length of the Cu···N or Cu···O distances found in numerous compounds containing planar Cu$_2$X$_6^{2-}$ species.[26-30] (Cu···O = 2.627 Å in (morpholinium)$_2$Cu$_2$Cl$_6$,[26] and Cu···O = 3.128 Å in (ethanolammonium)$_2$Cu$_2$Cl$_6$[29]). Distances within the pyrimidinium system are normal.

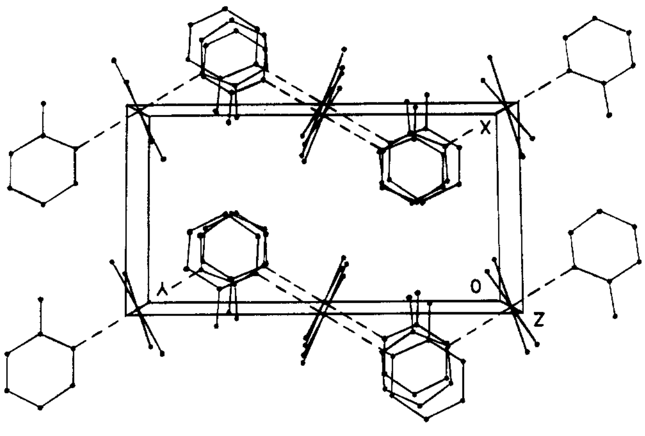

Figure 2. Unit cell packing diagram of (2-aminopyrimidinium)$_2$CuCl$_4$. The semicoordinate Cu···N bonds are shown as dashed lines.

The Cu–Cl distances (2.324 Å, average) are quite long. In isolated square-planar CuCl$_4^{2-}$ anions,[31-34] the Cu–Cl distances average 2.270 Å (excluding the structure[34] in which abnormally large thermal motion is present). In the layer perovskite salts, which have a 4 + 2 coordination due to formation of semicoordinate bridges between the CuCl$_4^{2-}$ anions, the Cu–Cl distances average 2.290 Å, independent of the semicoordinate Cu···Cl distance.[16] Thus, the combination of relatively short semicoordinate distances and long equatorial distances lead to a smaller than usual degree of tetragonality for the CuCl$_4$L$_2$ chromophore.

The planar organic cations lie essentially in the ab plane with the exo-C–N bond nearly parallel to the b axis. The normal to the plane of the pyrimidinium ring makes an angle of 31.4° with the Cu–Cl(1) bond direction. Cations related by c-glide operations form stacks parallel to the c axis, as illustrated in Figure 2. The –NH$_2$ moiety forms one intramolecular hydrogen bond to Cl(2) with a N–Cl distance of 3.297 (2) Å. Each pyrimidinium cation also forms two intermolecular hydrogen bonds to an adjacent CuCl$_4^{2-}$ anion with N(7)–Cl(1) = 3.171 (2) Å and N(3)–Cl(2) = 3.361 (2) Å. This hydrogen bonding ties the structure together into layers that lie parallel to the bc plane, and is consistent with the morphology, as described in the Experimental Section, in which the 100 and $\bar{1}$00 faces are strongly developed.

Electronic Spectroscopy

The electronic spectrum of a polycrystalline mull at 78 K in the near-IR region (5000–15000 cm^{-1}) consists of two partially resolved bands centered at 10200 and 11900 cm^{-1}. The two bands appear to have comparable widths. An unpolarized spectrum of the (100) face at room temperature further resolved these bands

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into a set of four at 9600 (shoulder), 10 800 (shoulder), 11 600, and 12 500 cm^{-1}. The latter two were of the same width and intensity. In this orientation, the Cu–Cl(1), Cu–Cl(2), and Cu–N bond directions (defining, roughly, the local *x*, *y*, and *z* directions) make angles of 41.6, 59.8, and 59.1° with the beam direction (the crystal a^* direction).

The observed d–d transitions can be interpreted with the aid of the angular overlap model (AOM) approach to parametrization of the energies of the d orbitals in a ligated complex.[35] For a complex of D_{4h} symmetry, the appropriate expressions for the d–d transition energies are[36]

$$E(^2A_{1g} \leftarrow {}^2B_{1g}) = 2e_\sigma(xy) + 2e_\sigma'(z)$$

$$E(^2E_g \leftarrow {}^2B_{1g}) = 3e_\sigma(xy) - 2e_\pi(xy) - 2e_\pi(z)$$

$$E(^2B_{2g} \leftarrow {}^2B_{1g}) = 3e_\sigma(xy) - 4e_\pi(xy)$$

where the *e* parameters describe the effects of the σ and π bonding for the equatorial (*xy*) and axial (*z*) ligands, and

$$e_\sigma'(z) = e_\sigma(z) - 2e_{ds}$$

where e_{ds} represents a mixing of the Cu 4s orbital with the $3d_{x^2-y^2}$ orbital. These expressions assume a π-bonding interaction that is effectively axially symmetric, which is reasonable for the equatorial (Cl$^-$) ligands, and is probably satisfactory for the coordinated pyrimidinium ion, since the plane of the cation cuts roughly across the diagonals of the $CuCl_4^{2-}$ ion.

This parametrization procedure has been applied to an extensive series of $CuCl_4^{2-}$ species with approximate D_{4h} symmetry with a wide range of axial interactions.[3,37-39] The values obtained in these previous studies may be used to estimate parameters for the $CuCl_4N_2$ chromophore in this study. Values for $e_\sigma(xy)$ and $e_\pi(xy)$ of 5285 and 885 cm^{-1} were reported for isolated $CuCl_4^{2-}$ anions[37] (Cu–Cl = 2.261 Å, average) and of 4800 and 820 cm^{-1} for the 4 + 2 anion in (cyclamH$_4$)CuCl$_6$ (Cu–Cl = 2.296 Å, average).[39] The decrease in the $e_\sigma(xy)$ and $e_\pi(xy)$ parameters as the Cu–Cl distance increases is anticipated.[40] For (2-aminopyrimidinium)$_2$CuCl$_4$, the average Cu–Cl distance is 2.324 Å. Thus, values for $e_\sigma(xy)$ and $e_\pi(xy)$ in the range 4300–4600 and 760–790 cm^{-1} might be anticipated.

The parameter $e_\sigma'(z)$ contains two contributions: $e_\sigma(z)$, which is expected to be zero for the isolated $CuCl_4^{2-}$ anion and to increase as the semicoordinate Cu···L interaction is turned on, and e_{sd}, which will be zero for an octahedral complex and a maximum for the isolate square-planar species. The result is that $e_\sigma'(z) = -3055$ cm^{-1} for the isolated $CuCl_4^{2-}$ anion, and increases as the Cu···Cl axial interaction increases,[39] with $e_\sigma'(z)$ and Cu···Cl values found of −2050 cm^{-1} and 3.257 Å [Pt(NH$_3$)$_4$CuCl$_4$], −1650 cm^{-1} and 3.175 Å [(cyclamH$_4$)CuCl$_6$], and −750 cm^{-1} and 3.04 Å [(C$_3$H$_7$NH$_3$)$_2$CuCl$_4$]. Correcting for differences in radii, the Cu···N distance of 2.676 Å found in this study is still relatively shorter than the 3.04 Å distance in the latter salt. Thus, the expected value of $e_\sigma'(z)$ can be −500 cm^{-1} or even smaller. The values of $e_\pi(z)$ have generally found to be small (<100 cm^{-1}), and that value may be taken as an upper limit for this study.

A trial and error process leads to following "best" values of $e_\sigma(xy) = 4600$ cm^{-1}, $e_\pi(xy) = 790$ cm^{-1}, $e_\pi(z) = 75$ cm^{-1}, and $e_\sigma(z) = -300$ cm^{-1}. This yields predicted transition energies for a D_{4h} species of

$^2E_g \leftarrow {}^2B_{1g}$	12 050 cm^{-1}
$^2B_{2g} \leftarrow {}^2B_{1g}$	10 640 cm^{-1}
$^2A_{1g} \leftarrow {}^2B_{1g}$	9 800 cm^{-1}

in reasonable agreement with the observed peaks at 11 900 and 10 200 cm^{-1}. Due to the inequivalence of the Cl(1) and Cl(2) distances, the $^2E_g \leftarrow {}^2B_{1g}$ transition is expected to be split into two separate bands of equal intensity. This difference in bond lengths will lead to different effective $e_\sigma(xy)$ (and $e_\pi(xy)$) values for the *x* and *y* directions. The bond-length difference of over 0.05 Å could easily lead to shifts in the $e_\sigma(xy)$ and $e_\pi(xy)$ values of ±3%. Substituting this into the $^2E_g \leftarrow {}^2B_{1g}$ energy expression gives an estimate of 12 450 and 11 650 cm^{-1}. This gives a consistent set of AOM parameters and a very reasonable fit of the observed spectrum. The spectral assignment leads to the ordering of energy levels as $^2B_{1g} < {}^2A_{1g} < {}^2B_{2g} <$ ^{2}Eg for the tetragonal distortion in this species. It should be noted that the reduced values of the $e_\sigma(xy)$, $e_\pi(xy)$, and $e_\sigma'(z)$ parameters are consistent with the smaller degree of tetragonality deduced from the structural parameters.

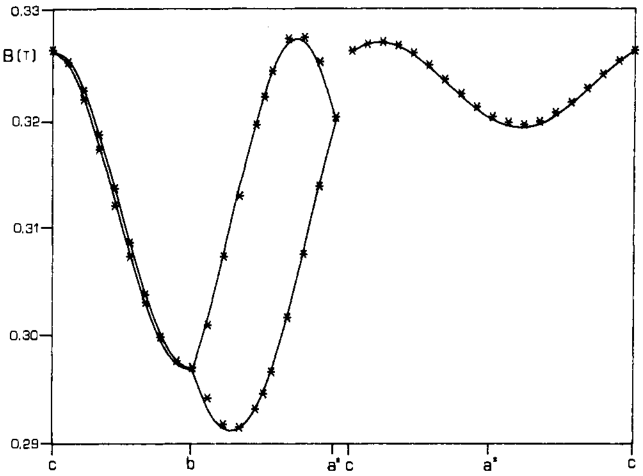

Figure 3. Angular dependence of the transition fields in the *cb*, *ba**, and *a*c* planes for (2-aminopyrimidinium)$_2$CuCl$_4$ at X-band frequency and room temperature.

Table IV. Principal Values and Direction of the **g** Tensor for (2-aminopyrimidinium)$_2$CuCl$_4$[a]

$g_1 = 2.046$ (1)	$g_2 = 2.076$ (1)	$g_3 = 2.313$ (1)
−0.71 (1)	0.56 (1)	−0.420 (2)
0.322 (7)	−0.269 (7)	−0.907 (1)
−0.62 (1)	−0.78 (1)	0.087 (3)

[a] The direction cosines are referred to the *a**, *b*, *c* reference frame.

EPR Spectroscopy

The room-temperature single-crystal spectra of (2-aminopyrimidinium)$_2$CuCl$_4$ were recorded at X-band frequency at room temperature and at 100 K, with the static magnetic field in the *a*b*, *a*c*, and *bc* planes. No substantial shifts in resonance fields were observed upon cooling, and only a small narrowing of the lines occurred. The angular dependence of the transition fields is shown in Figure 3. Since the unit cell is monoclinic, two magnetically nonequivalent sites are expected to be present in the planes containing the *b* axis, and indeed two transitions are clearly observed in the *a*b* and *bc* planes. Standard least-squares fit yielded the **g** tensor principal values and directions reported in Table IV. The orientation of the **g** tensor is as expected for an elongated octahedral copper(II) complex, with the maximum *g* value, $g_3 = 2.313$ (1), observed in a direction perpendicular to the CuCl$_4$ plane, while the other two are, within experimental error, parallel to the equatorial bond directions, $g_1 = 2.045$ (1) making an angle of 3 (2)° with the Cu–Cl(1) bond and $g_2 = 2.076$ (1) at 5 (2)° from the Cu–Cl(2) direction. It is possible to give a reasonable qualitative explanation of the **g** anisotropy observed in the equatorial coordination plane due to the deviation of the actual geometry of the chromophore from D_{4h} symmetry: in fact, even if the Cl–Cu–Cl angles show only small variations with respect to the idealized geometry, the Cu–Cl(1) and Cu–Cl(2) bond distances have markedly different values, namely 2.295 (1) and 2.364 (1) Å respectively. The copper ion ground state can be mainly described as $d_{x^2-y^2}$ in a molecular reference frame having the *x* axis along the Cu–Cl(1) bond and the *z* axis perpendicular

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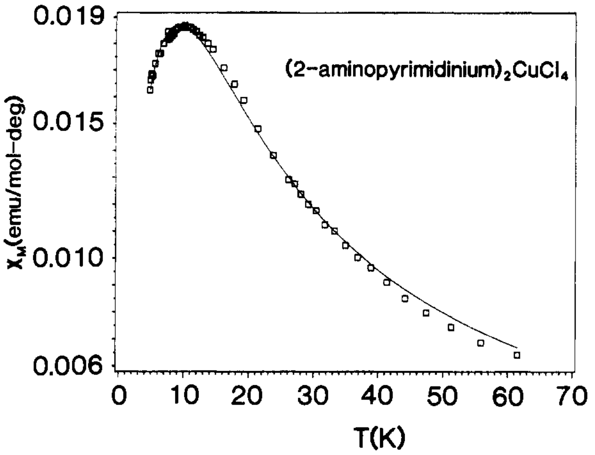

Figure 4. Plot of χ_m vs T for (2-aminopyrimidinium)$_2$CuCl$_4$.

to the equatorial plane. The Δg_i ($\Delta g_i = g_i - 2.0023$) values depend on the reciprocal of the energy gap, $\Delta E_{\text{ground/excited}}$, between the ground state and the excited states coupled into the ground level by the orbital angular momentum operators L_i.[41] Due to the shorter Cu–Cl(1) bond distance, the d_{xz} state will have a somewhat higher energy than the d_{yz} state, so that $\Delta E_{x^2-y^2,yz}$ is larger than $\Delta E_{x^2-y^2,xz}$. Since d_{xz} can be coupled to the ground state through L_y we can predict g_y to be larger than g_x, as experimentally observed.

The value of $g_3 = 2.313$ is substantially larger than the $g_\parallel$ values reported for other distorted octahedral chlorocuprate anions. Isolated $CuCl_4^{2-}$ anions have $g_\parallel$ values in the range 2.20–2.22,[1,3] $K_2PdCl_4(Cu^{2+})$ and $CdCl_2(Cu^{2+})$ give $g_\parallel = 2.232$ and 2.339, respectively,[44,45] and (cyclamH$_4$)CuCl$_6$ has $g_\parallel = 2.272$ (Cu···Cl = 3.175 Å),[39] while the series of $(RNH_3)_2CuCl_4$ layer perovskites gives $g_\parallel = 2.270$–2.285 for semicoordinate distances from 3.1 Å down to 2.9 Å.[16] The increase of $g_\parallel$ with decreasing tetragonality is clearly seen, and thus the EPR data again confirm the low degree of tetragonality in the 2-aminopyrimidinium complex reported here.

The EPR data also give valuable information concerning magnetic exchange pathways. The very narrow line width, with a ΔB_{pp} not exceeding 12–13 G at room temperature, and the Lorentzian line shape, observed along crystallographic axes and in the a^*c and a^*b planes, indicate that an exchange-narrowing regime is operative. The exchange interaction is strong enough to produce a complete merging of the hyperfine splitting lines as is evident from the Lorentzian line shape, but it does not average the signals coming from the two magnetically nonequivalent sites. Assuming that the parallel hyperfine splitting is at least 100 × 10^{-4} cm^{-1}, the exchange coupling between equivalent sites must be at least 30 × 10^{-4} cm^{-1} to completely average it. The results clearly suggest that the exchange interaction between magnetically equivalent sites is much more efficient than that between inequivalent ones. This is substantiated by the magnetic results reported below.

The interaction between inequivalent sites is very small but not zero as shown by the fact that in the bc plane, where the two signals are close to each other, the experimental line shape cannot be fitted with two independent Lorentzian lines, especially in the central part of the spectra. This is a clear indication that the EPR lines coming from magnetically nonequivalent complexes are perturbed by mutual exchange interaction. Some years ago a simple model was proposed to reproduce the non-Lorentzian line shape of merged lines[5,42,43] coming from magnetically nonequivalent sites in the unit cell. We performed sample calculations with the reported formula, obtaining an improved fit of the experimental shape of the lines in the bc plane with an isotropic exchange integral $|J|$ of 3.2 (5) × 10^{-4} cm^{-1}. This value indicates that the principal g values and directions are practically unaffected by the merging effect of the lines[5] and confirms the dominant role of the chlorine–chlorine contacts in determining the exchange pathway.

Magnetic Properties

A plot of the molar magnetic susceptibility versus temperature is given in Figure 4. The data very clearly show the presence of a substantial antiferromagnetic coupling, as evidenced by the maximum in χ_m at ~10 K. This behavior is indicative of low-dimensional magnetic coupling, but the data by itself is not sufficient to distinguish between 1d and 2d behavior. As discussed in the following paragraph, the structure would indicate the presence of intermolecular Cl···Cl contacts leading to a 1d set of exchange pathways parallel to the c axis. Hence the data was fit to a 1d model, yielding $J/k = -7.3$ (1) K with $g = 2.24$ (1). The fit in the region of the maximum is not good, with the calculated maximum occurring at a temperature lower than the observed maxima. Thus, the actual value of J may be slightly larger than the calculated value.

The dominant antiferromagnetic coupling must occur between magnetically equivalent sites, since the EPR data demonstrates that only weak coupling exists between magnetically inequivalent sites. The shortest intermolecular contacts between magnetically equivalent complexes involve the chlorine atoms, with the Cl(1)–Cl(2^c) and Cl(2)–Cl(1^c) distances of 3.990 (3) Å and the Cl(1)–Cl(2^a) and Cl(2)–Cl(1^a) distances of 4.422 (3) Å (a and c indicate a unit cell translation along the a and c axes respectively). The Cl–Cl contacts are at a distance that may yield substantial antiferromagnetic exchange coupling ($|J_a/k| \leq 20$ K, $|J_c/k| \leq 2$ K);[46,47] however, the Cu–Cl···Cl bond angles deviate enough from linearity to reduce the expected values substantially.[48] Thus, the observed value of $J/k = -7.3$ K is consistent with the postulate that the magnetic chains run parallel to the c axes.

For magnetically nonequivalent sites, intermolecular contacts can be established via the 2-aminopyridinium ligands, through the overlap of π orbitals of the aromatic rings belonging to two different complexes, with an interplane distance of about 3.56 Å, as well as via Cl···H–N–H···Cl hydrogen-bonding pathways. The former would be expected to give an antiferromagnetic contribution to the exchange but should be extremely small since there is no direct delocalization of the unpaired electron density onto these axially coordinated ligands. The latter should be ferromagnetic,[49] but again will be small since the hydrogen bonding geometry is such that primarily p_π orbitals of the chlorine atoms are involved. Thus the very small value of $|J|$ may be due to a partial cancellation from these two pathways.

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Supplementary Material Available: Table 1s, listing all atom positions and thermal parameters, and Table 3s, giving the X-ray data collection and refinement parameters (4 pages); a table of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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