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Identification of a Novel Tetragonally Compressed Six-Coordinate Copper(II) Complex: Preparation and Characterization of a 3-Chloroanilinium Copper Chloride Complex, (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$

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A monomeric hexachlorocuprate(II) ion has been found in the compound (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$, $CuC_{48}H_{56}Cl_{18}N_8$. The compound crystallizes in the triclinic space group $P\bar{1}$, with unit cell dimensions a = 8.5488 (16) Å, b = 13.964 (6) Å, c = 14.273 (7) Å, α = 90.46 (4)°, β = 107.82 (3)°, and γ = 102.11 (3)° with Z = 1. The coordination about the discrete [CuCl$_6$]$^{4-}$ ion is that of a tetragonally compressed octahedron with bond distances Cu–Cl(1) = 2.2773 (11) Å, Cu–Cl(2) = 2.6061 (18) Å, and Cu–Cl(3) = 2.6086 (20) Å. The two short bond distances are of the order frequently seen for copper–chloride bonds, but the remaining four bond distances are remarkably long for in-plane 4 + 2 coordination. The Cl(1)–Cu–Cl(1a), Cl(2)–Cu–Cl(2a), and Cl(3)–Cu–Cl(3a) angles are strictly 180°, and the 12 remaining Cl(i)–Cu–Cl(j) angles differ from 90° by 0.4–1.0°. The EPR spectrum of a powdered sample is of the "reversed" nature indicative of a ^{2}A ground state with $g_{\parallel}$ = 2.06 and $g_{\perp}$ = 2.19. Magnetic susceptibility data provide evidence for antiferromagnetic interactions between the hexachlorocuprate cations, since there is a maximum in the magnetic susceptibility near 10 K. The data may be approximated by Heisenberg chain theory with J = −5.6 cm^{-1} and g = 2.00 and an interchain exchange parameter J' = −2.1 cm^{-1}.

Introduction

Substituted anilinium cations form an interesting and novel series of complexes with chlorocuprates. Many of these have very unusual properties. For example, the parent member of the series bis(anilinium) tetrachlorocuprate(II) is ferromagnetic[2] as a result of orthogonal superexchange interactions in the extended planar array of bridged (CuCl$_4$) units. In the structure of bis(anilinium) tetrachlorocuprate(II),[3] there are four short copper–chloride bond distances of 2.3 Å and two long copper–chloride bond distances of 2.9 Å, with two of the short bonds being normal to the rectangular lattice. The anilinium ions are perpendicular to the chlorocuprate layers, with the phenyl rings of the anilinium ions also being mutually perpendicular. The $-NH_3$ groups are hydrogen bonded to the out-of-plane chloride ligands, and the interplanar separations are determined by substituents on the phenyl ring.[2]

Compounds with unusual formulations have been encountered in this research,[2] and studies described here on the title compound, (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$, revealed the presence of a discrete $CuCl_6^{4-}$ complex. Characterization of this new, unexpected complex by single-crystal X-ray diffraction studies and by magnetic methods are discussed in this article.

Experimental Section

Synthesis. To 15.2 mL (0.15 mol) of 3-chloroaniline (Aldrich Chemical Co.) and 28.73 g (0.17 mol) of copper(II) chloride dihydrate were added approximately 150 mL of distilled water and 350 mL of concentrated hydrochloric acid. The resulting solution was heated, with stirring, to the boiling point. The solution was then allowed to cool, and copious quantities of yellow crystals deposited. The crystals were collected on a glass-frit funnel and were washed with anhydrous diethyl ether. Anal. Calcd for $C_{48}H_{56}Cl_{18}CuN_8$: C, 39.85; H, 3.90; Cl, 44.11; Cu, 4.39; N, 7.75. Found: C, 39.78; H, 3.88; Cl, 44.61; Cu, 4.32; N, 7.60. The compound decomposes slowly with one product being a black material.

Magnetic and Spectral Measurements. Magnetic susceptibility data from 4.4 to 22 K were collected by using a Princeton Applied Research Model 155 Foner vibrating sample magnetometer in procedures that have been described earlier.[4] The magnetometer was calibrated with HgCo(NCS)$_4$.[5,6] Samples of the standard and the compound under study were contained in precision-milled Lucite sample holders. Approximately 150 mg of each was used. The magnetic susceptibility at room temperature was determined by the Faraday method by using procedures described earlier.[7] A correction for the diamagnetism of the constituent atoms were estimated from Pascal's constants.[8,9]

Table I. Crystallographic Data

$CuC_{48}H_{56}Cl_{18}N_8$	fw = 1446.71
a = 8.5488 (16) Å	space group: $P\bar{1}$
b = 13.964 (6) Å	$T \approx$ 20 °C
c = 14.273 (7) Å	λ = 0.709 30 Å
α = 90.46 (4)°	ρ_{calcd} = 1.519 g cm^{-3}
β = 107.82 (3)°	μ = 1.15 mm^{-1}
γ = 102.11 (3)°	transm coeff = 0.740–0.743
V = 1581.2 (10) Å^3	extinction coeff = 0.024 (28)
Z = 1	$R(F)^a$ = 0.044
	$R_w(F)^b$ = 0.053

$^a R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w(F) = \sum w(|F_o| - |F_c|)^2/\sum wF_o^2$.

Electron paramagnetic resonance spectra at X-band frequency of single-crystal and powdered samples were recorded with Varian Instruments E109 and E3 EPR spectrometers. The microwave frequency was monitored with a 5340 A Hewlett Packard frequency counter, and diphenylpicrylhydrazyl (DPPH) was used as the field marker.

Crystallographic Data Collection. X-ray diffraction data were collected by using an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator and by using molybdenum radiation at room temperature. Cell dimensions were obtained by least-squares fitting from 25 reflections with 2θ in the range 30.00–35.00°. Of the 5510 unique reflections recorded in the range 2° < 2θ < 50°, 3825 reflections having $I > 2.5\sigma(I)$ were used in the structure determination. Data were corrected for Lorentz, polarization, and absorption effects.

Refinement of the Structure. The positions of the copper and chlorine atoms were determined by direct methods after which the other atoms were located from difference syntheses. The structure was refined by full-matrix least-squares techniques; scattering factors were obtained[10] and corrected for anomalous dispersion. In the final cycles, a weighting scheme based on counter statistics was applied. All the non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in calculated positions and assigned isotropic thermal parameters based on the atom to which they were attached. An isotropic secondary extinction correction was made. Attempts to refine the structure in space group $P1$ lead to no improvement in the agreement factors, indicating that $P\bar{1}$ was the correct choice. All calculations were made using the NRCVAX suite of programs.[11] Pertinent crystal data, details of data collection, and refinement parameters are summarized in Tables I and SI (supplementary material). Atomic positions, bond lengths, and bond angles are given in Tables II–IV and SIII–SVI.

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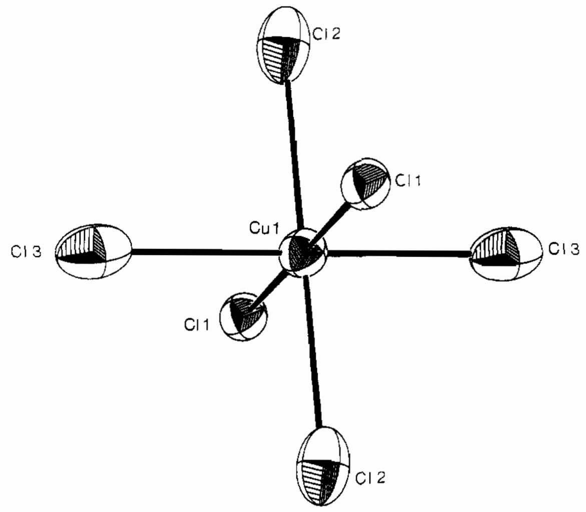

Figure 1. Ortep diagram of the $CuCl_6^{4-}$ anion. The compressed axis is composed of the Cl(1)–Cu–Cl(1a) bonds.

Results

Description of the Structure. The structure of (3-chloroanilinium)$_8$[$CuCl_6$]Cl_4 consists of discrete 3-chloroanilinium cations, discrete $CuCl_6^{4-}$ anions shown in Figure 1, and uncoordinated chloride ions. The cations have no unique structural features, and the bond angles and bond distances are given in Tables SIV and SV. The substituted phenyl ring is nearly perfectly planar, as shown by the torsional angles in Table SVI (supplementary material), and the chloro substituent and the nitrogen atom of the protonated amino group lie in the plane. A stereoview of the packing of the chloroanilinium ions, the $CuCl_6^{4-}$ ions, and the uncoordinated chloride ions is given in Figure 2.

The coordination about the discrete $[CuCl_6]^{4-}$ ion in (3-chloroanilinium)$_8$[$CuCl_6$]Cl_4 is that of a tetragonally compressed octahedron with bond distances Cu–Cl(1) = 2.2773 (11) Å, Cu–Cl(2) = 2.6061 (18) Å, and Cu–Cl(3) = 2.6086 (20) Å. The Cl(1)–Cu–Cl(1a), Cl(2)–Cu–Cl(2a), and Cl(3)–Cu–Cl(3a) angles are strictly 180°, and the remaining Cl(i)–Cu–Cl(j) angles differ from 90° by only 0.4–1.0°. See Figure 1 for the labels for the atoms and Tables III and IV for detailed metrical data that confirm the characterization of the $CuCl_6^{4-}$ ion as being a tetragonally compressed octahedron.

Magnetic Susceptibility. Magnetic susceptibility data were collected at room temperature and as a function of temperature in the range 4.4–22 K. The latter data are shown in Figure 3. The magnetic moment was found to be 1.8 μ_B at 290 K, 1.3 μ_B at 20 K and 0.6 μ_B at 4.4 K. There is a maximum in the magnetic susceptibility near 10 K. These data indicate that there are antiferromagnetic interactions in the compound. Since the material is magnetically dilute (1 spin/1447 amu) and the vibrating sample magnetometer is not exceptionally sensitive, the accuracy

Table II. Atomic Parameters x, y, z, and B_{iso}

	x	y	z	B_{iso}, Å^2
Cu(1)	0	0	0	2.79 (3)
Cl(1)	0.26796 (12)	0.00195 (7)	0.00183 (7)	2.77 (4)
Cl(2)	−0.03272 (14)	−0.18135 (10)	0.04728 (8)	4.55 (6)
Cl(3)	0.11512 (15)	0.06467 (9)	0.18576 (10)	4.71 (6)
Cl(4)	0.35229 (15)	0.91226 (8)	0.74527 (8)	4.00 (5)
Cl(5)	0.53238 (15)	0.24580 (8)	0.92576 (8)	3.96 (6)
Cl(11)	1.01872 (25)	0.41516 (10)	0.88578 (12)	7.26 (10)
N(11)	1.1605 (5)	0.7921 (3)	0.8889 (3)	3.99 (19)
C(11)	0.9901 (6)	0.5236 (3)	0.8316 (4)	4.3 (3)
C(12)	1.0873 (6)	0.6120 (3)	0.8816 (3)	3.70 (22)
C(13)	1.0620 (5)	0.6965 (3)	0.8369 (3)	3.24 (20)
C(14)	0.9450 (8)	0.6950 (4)	0.7461 (4)	5.7 (3)
C(15)	0.8541 (9)	0.6049 (5)	0.6991 (4)	7.4 (4)
C(16)	0.8740 (7)	0.5191 (4)	0.7415 (4)	5.7 (3)
Cl(21)	0.49084 (20)	0.36603 (11)	0.55581 (11)	6.08 (7)
N(21)	0.6597 (5)	0.1066 (3)	0.7981 (3)	3.97 (19)
C(21)	0.5615 (6)	0.2591 (3)	0.5840 (3)	3.93 (21)
C(22)	0.5865 (5)	0.2284 (3)	0.6786 (3)	3.29 (20)
C(23)	0.6365 (5)	0.1417 (3)	0.6985 (3)	3.19 (19)
C(24)	0.6637 (6)	0.0854 (4)	0.6277 (4)	4.28 (23)
C(25)	0.6396 (7)	0.1180 (4)	0.5350 (4)	5.1 (3)
C(26)	0.5896 (7)	0.2043 (4)	0.5124 (3)	4.9 (3)
Cl(31)	0.13042 (18)	0.11746 (10)	0.42803 (9)	5.18 (7)
N(31)	0.2027 (5)	0.0929 (3)	0.7967 (3)	4.08 (20)
C(31)	0.1124 (6)	0.1607 (3)	0.5381 (3)	3.53 (20)
C(32)	0.1627 (5)	0.1101 (3)	0.6210 (3)	3.43 (20)
C(33)	0.1509 (5)	0.1462 (3)	0.7076 (3)	3.33 (19)
C(34)	0.0912 (6)	0.2296 (3)	0.7133 (3)	4.21 (24)
C(35)	0.0409 (7)	0.2777 (4)	0.6287 (4)	4.7 (3)
C(36)	0.0525 (6)	0.2438 (3)	0.5407 (3)	4.28 (24)
Cl(41)	0.20774 (21)	0.54335 (11)	0.59506 (11)	6.81 (8)
N(41)	0.5981 (4)	0.7879 (3)	0.8834 (3)	3.98 (18)
C(41)	0.3545 (6)	0.5691 (3)	0.7116 (3)	4.12 (22)
C(42)	0.4168 (6)	0.6653 (3)	0.7488 (3)	3.58 (21)
C(43)	0.5347 (5)	0.6853 (3)	0.8416 (3)	3.45 (20)
C(44)	0.5896 (7)	0.6122 (4)	0.8969 (4)	4.9 (3)
C(45)	0.5252 (8)	0.5161 (4)	0.8573 (4)	5.8 (3)
C(46)	0.4087 (7)	0.4943 (3)	0.7653 (4)	5.4 (3)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table III. Bond Lengths (Å) about Copper[a]

Cu(1)–Cl(1)	2.2773 (11)	Cu(1)–Cl(2a)	2.6061 (18)
Cu(1)–Cl(1a)	2.2773 (11)	Cu(1)–Cl(3)	2.6086 (20)
Cu(1)–Cl(2)	2.6061 (18)	Cu(1)–Cl(3a)	2.6086 (20)

[a] Atoms designated by "a" are related by the $\bar{1}$ operation.

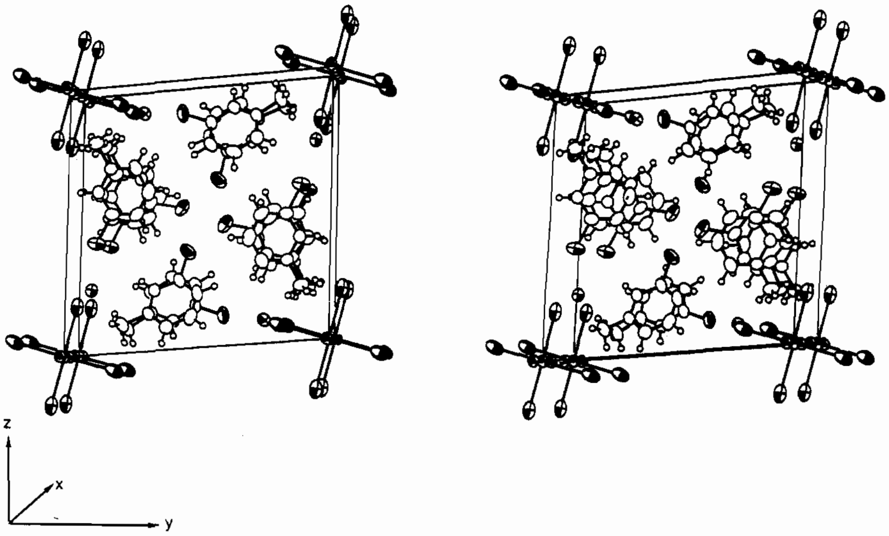

Figure 2. Stereoview that shows the packing of the ions in the unit cell.

Table IV. Bond Angles (deg) about Copper

Cl(1)-Cu(1)-Cl(1a)	180.0	Cl(1a)-Cu(1)-Cl(3a)	89.60 (5)
Cl(1)-Cu(1)-Cl(2)	89.46 (5)	Cl(2)-Cu(1)-Cl(2a)	180.0
Cl(1)-Cu(1)-Cl(2a)	90.54 (5)	Cl(2)-Cu(1)-Cl(3)	91.04 (5)
Cl(1)-Cu(1)-Cl(3)	89.60 (5)	Cl(2)-Cu(1)-Cl(3a)	88.96 (5)
Cl(1)-Cu(1)-Cl(3a)	90.40 (5)	Cl(2a)-Cu(1)-Cl(3)	88.96 (5)
Cl(1a)-Cu(1)-Cl(2)	90.54 (5)	Cl(2a)-Cu(1)-Cl(3a)	91.04 (5)
Cl(1a)-Cu(1)-Cl(2a)	89.46 (5)	Cl(3)-Cu(1)-Cl(3a)	180.0
Cl(1a)-Cu(1)-Cl(3)	90.40 (5)		

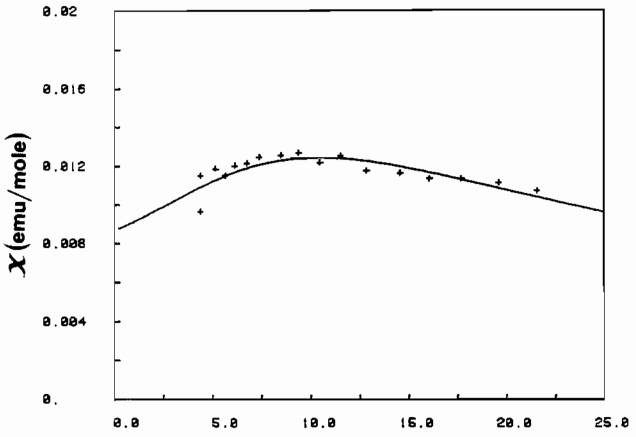

Figure 3. Magnetic susceptibility data in the range 4 to 22 K. Experimental data are given as +'s, and the solid line is the best fit of antiferromagnetic Heisenberg chain theory to the data with the parameters given in the text.

of the data is low. However, the data are adequate to assess the nature of the antiferromagnetic interactions and to reveal the low-dimensional character of those interactions.

Inspection of the structure reveals that the CuCl$_6^{4-}$ units are arranged into chains along the *a* axis with a copper-copper separation of 8.55 Å. The copper-chloride bond distance along this direction is 2.28 Å, and the chloride-chloride separation is 3.99 Å. While chloride-chloride separations of this length would normally be considered rather long in view of the van der Waals radius of Cl being 1.80 Å as given by Pauling,[12] Brown and co-workers[13] found Heisenberg chain properties with $J = -7.6$ cm^{-1} in chains of [CuCl$_2$(AdH$^+$)$_2$]Cl$_2$ (AdH$^+$ is protonated adenine) with a similar Cu-Cl···Cl-Cu superexchange pathway. The chloride-chloride separations in [CuCl$_2$(AdH$^+$)$_2$]Cl$_2$ are 3.76 Å. Also, Hatfield and Jones[14] have reported significant antiferromagnetic interactions in [Co(NH$_3$)$_6$][CuCl$_5$]. The chloride-chloride contacts between monomeric [CuCl$_5$]$^{3-}$ ions in this latter compound are 4.11 Å.

Assuming isotropic exchange, the exchange Hamiltonian for a linear chain compound is

$$H_{ex} = -2J_{ij}\sum_{i\leq j}\mathbf{S}_i\cdot\mathbf{S}_j$$

with $S_i = S_j = {}^1/_2$. Bonner and Fisher[15] showed that the maximum magnetic susceptibility and the temperature at which it occurs are uniquely defined by

$$k_BT_{max}/|J| = 1.282$$

and

$$\chi_{max}|J|/Ng^2\mu_B^2 = 0.07346$$

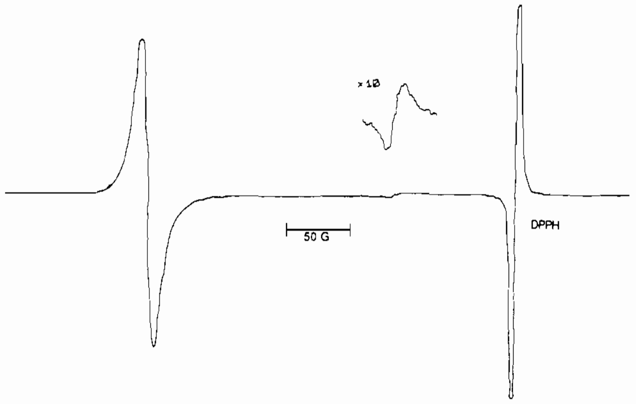

Figure 4. EPR spectrum of a single crystal of (3-chloroanilinium)$_8$CuCl$_{10}$ oriented with the *a* axis perpendicular to the magnetic field. The single crystal value of $g_\perp$ is 2.186. The feature observed in the 10-fold magnification is $g_\parallel$ (from misaligned fragments) of 2.062. The standard, DPPH radical, has a *g* value of 2.002.

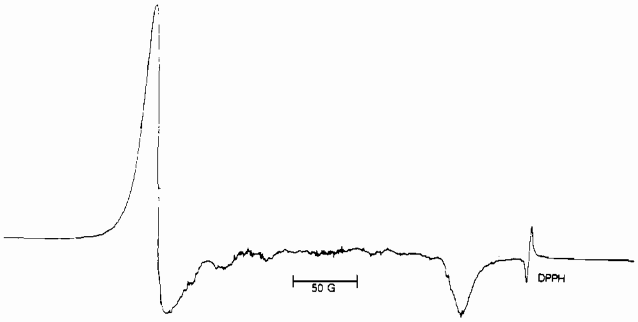

Figure 5. Powder EPR spectrum of (3-chloroanilinium)$_8$CuCl$_{10}$. The resonance arising from $g_\perp$ is at the lowest magnetic field with the resonance at the highest field arising from DPPH.

Hall[16] has provided the following analytical expression for the temperature variation of the magnetic susceptibility of antiferromagnetic Heisenberg chains with $S = {}^1/_2$

$$\chi_{BF} = (Ng^2\mu_B^2/k_BT)[A + Bx + Cx^2]/[1 + Dx + Ex^2 + Fx^3]$$

where $A = 0.25$, $B = 0.14995$, $C = 0.30094$, $D = 1.9862$, $E = 0.68854$, $F = 6.0626$, and $x = |J|/k_BT$. Interchain interactions were accounted for by inclusion of a molecular field correction term

$$\chi_{cor} = \chi_{BF}/(1 - 2zJ'\chi_{BF}/Ng^2\mu_B^2)$$

where J' is the interchain exchange parameter and *z* is the number of nearest neighbors. A least-squares fit of the magnetic susceptibility equation to the data using a nonlinear Simplex fitting routine[17,18] yielded $J = -5.6$ cm^{-1}, $g = 2.0$, and $J' = -2.1$ cm^{-1}. The solid line shown in Figure 3 was generated with these best-fit parameters. Although there are large experimental uncertainties in the *g* value and the interchain mean-field parameter J', the intrachain exchange coupling constant agrees well with that predicted from the expression $k_BT_{max}/|J| = 1.282$. When T_{max} is taken to be 10 K, a value for $|J|$ of 5.4 cm^{-1} results.

Electron Paramagnetic Resonance Spectra. EPR spectra collected on a single crystal of (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$ as well as on a powdered sample of the compound are shown in Figures 4 and 5. To verify the identity of the crystal used for the EPR experiment, a small part of the crystal was cut away, and the unit cell of the fragment was determined to be identical with that of the crystal used for the X-ray structural determination. This experiment also confirms that the crystal used in the X-ray structural determination is characteristic of the bulk sample.

The single-crystal EPR spectra clearly are of the "reversed" nature expected for a compressed octahedron with a ^{2}A ground

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state. Analysis of the spectral features yield $g_\parallel = 2.06$ and $g_\perp = 2.19$. Although $g_\parallel$ should be equal to 2.0 for a tetragonally compressed six-coordinate copper(II) complex in a high-symmetry environment,[19] there are two mechanisms that contribute to the departure of $g_\parallel$ from 2.0 in (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$. The copper ion sits only on a center of inversion in this complex, and it is possible for excited states with orbital angular momentum to be mixed into the ground state. Since the departure of $g_\parallel$ from 2.0 is small, being only 0.06, the amount of admixture of excited states into the ground state must be small. The second mechanism that can cause a departure from $g_\parallel = 2.0$ involves the dynamic Jahn–Teller effect.[20]

The expression for $g_\perp$ (in high symmetry) is

$$g_\perp = 2.0023 - 6\lambda/\Delta E(\mathrm{d}_{z^2} \rightarrow \mathrm{d}_{xz},\mathrm{d}_{yz})$$

Although the $\mathrm{d}_{z^2} \rightarrow \mathrm{d}_{xz},\mathrm{d}_{yz}$ band was not identified in the electronic spectrum, it is expected to be at a low energy as a consequence of the long bond distances and resulting small ligand field splitting. Thus, $g_\perp$ is expected to depart substantially from the free electron value.

Discussion

In the course of research on substituted anilinium chlorocuprates,[2] compounds with unusual formulations have been encountered. For the most part, these have been only partially characterized, since the focus of prior research has been the identification of planar chlorocuprate networks with intercalated anilinium cations. The cations that had been studied were limited to those with substituents in the para position of the phenyl ring, since substituents in this position were thought to be most effective in modulating the interplanar separation.

Continuation of this research with anilinium cations having substituents in other ring positions have revealed a compound formulated, from analytical data, as (3-chloroanilinium)$_8$CuCl$_{10}$. The compound is not very stable. A sample stored on the bench top in a beaker covered with Parafilm began to turn black after several weeks. An EPR spectrum of a powdered sample collected several months after its synthesis revealed numerous additional lines from decomposition products.

A single-crystal X-ray structure determination on (3-chloroanilinium)$_8$CuCl$_{10}$ revealed the presence of 3-chloroanilinium ions, CuCl$_6^{4-}$ units, and uncoordinated chloride ions. A stereoview that shows the arrangement of these ions in the unit cell is given in Figure 2. The structure of the hexachlorocuprate(II) ions is of especial interest. In fact, it was thought for a long time that only large like-charged counterions could stabilize hexachlorometalates in the solid state,[21] although recent work has revealed such complexes with small cations.[22]

It is very common for hexacoordinated copper(II) complexes to exhibit 4 + 2 coordination as a result of the Jahn–Teller effect, with the distortion resulting in four short copper–ligand bonds and two long copper–ligand bonds. There are few examples of CuCl$_6^{q\pm}$ with axial compression,[23] one of those being the CuF$_6^{4-}$ ion in Ba$_2$CuF$_6$.[23] Burdett[23] notes that even the ZnF$_6^{4-}$ ion in Ba$_2$ZnF$_6$ is octahedrally compressed, and he attributes this, and the compression of the CuF$_6^{4-}$ ion in Ba$_2$CuF$_6$, to lattice forces and not to the Jahn–Teller effect. An early report[24] that K$_2$CuF$_4$ contained axially compressed hexafluorocuprate entities was later shown to be incorrect.[25]

The magnetic orbital for the compressed octahedral copper(II) ion is d_{z^2}. The compressed copper–chloride bonds occur along the *a* axis of the crystal and are aligned one-dimensionally such that a Cu–Cl···Cl–Cu exchange pathway exists; see Figure 2 for the pathway and Figure 6 for the superexchange orbitals. This relatively long superexchange pathway allows the antiferromagnetic interactions between copper ions. The question arises as to whether the packing of the CuCl$_6^{4-}$ ions in the crystal structure leads to the axial compression. This appears to be unlikely since the chloride–chloride contact between CuCl$_6^{4-}$ ions of 3.99 Å is 0.23 Å longer than the chloride–chloride contact in [CuCl$_2$(AdH$^+$)$_2$]Cl$_2$, yet the copper–chloride separation of 2.29 Å in [CuCl$_2$(AdH$^+$)$_2$]Cl$_2$ is typical of copper–chloride bonds in tetrahedrally coordinated copper(II). For example, the average copper–chloride bond distance in the flattened tetrahedron CuCl$_4^{2-}$ in Cs$_2$CuCl$_4$ is 2.2 Å.[26,27]

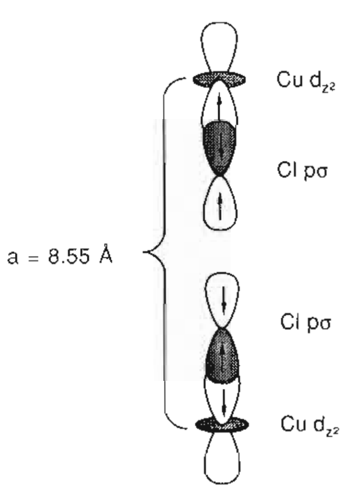

Figure 6. Superexchange orbitals in the Cu–Cl···Cl–Cu pathway.

The EPR spectra agree with tetragonal compression since the relative positions of $g_\perp$ and $g_\parallel$ are those expected for an axially compressed octahedron. These are reversed from those predicted and observed for tetragonal elongation normally seen in (4 + 2)-coordinated copper(II) systems. "Reversed" EPR spectra arising from d_{z^2} ground states occur in copper(II) complexes having trigonal-bipyramidal, tetragonally compressed octahedral, cis-distorted-octahedral, and rhombic-distorted-octahedral stereochemistries. Such reversed spectra may also arise for certain orientations of tetragonally elongated octahedral species where the observed crystal *g* values $g_\parallel'$ and $g_\perp'$ are related to the site *g* values by the relationships

$$g_\parallel'^2 = g_\perp^2$$

and

$$g_\perp'^2 = g_\perp^2 \cos^2\alpha + g_\parallel^2 \sin^2\alpha$$

where 2α is the angle between the tetragonal axes. Misalignment of molecular tetragonal axes will yield a unique perpendicular resonance occurring at high field and a more intense resonance at a lower field that is an average of molecular parallel and perpendicular *g* values. However, such is not the case for the CuCl$_6^{4-}$ ion in (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$. This a bona fide case of a "reversed" EPR spectrum arising from a d_{z^2} ground state in a tetragonally compressed octahedron.

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Supplementary Material Available: A figure showing the 3-chloroanilinium cation and tables of crystallographic data collection details (Table SI), anisotropic thermal parameters (Table SII), complete atomic parameters including hydrogen atom coordinates (Table SIII), complete bond angles (Table SIV), complete bond distances (Table SV), and phenyl ring torsion angles (Table SVI) (8 pages); a table of calculated and observed structure factors (Table SVII) (26 pages). Ordering information is given on any current masthead page.

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