

- (40) While there are no data which conclusively determine the number of ethylenes in $\text{Cu}_2(\text{C}_2\text{H}_4)_n$,²³ it is evident that the maximum is most likely four, based solely on a steric argument. If a tris(ethylene)metal complex is the outcome of a steric effect (see ref 41 for an MO description), with further coordination of ethylene highly unfavored, then replacing one ethylene by another $\text{M}(\text{C}_2\text{H}_4)_2$ fragment is not likely to relieve the strain sufficiently to permit a higher coordination number around each copper atom. On the basis of the cobalt work of the present study, we would like to ascribe the stoichiometry as $\text{Cu}_2(\text{C}_2\text{H}_4)_{1.2}$. Confirmation by $^{12}\text{C}_2\text{H}_4/^{13}\text{C}_2\text{H}_4$ studies will be necessary to establish this point.
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Characterization of Some Mixed-Halide Copper(II) Dimers of the General Formula $[\text{Cu}_2\text{X}_n\text{X}'_{6-n}]^{2-}$ ($\text{X} = \text{Cl}^-$ and $\text{X}' = \text{Br}^-$): Evidence for the Preference of Chloride Bridges in the Mixed-Halide Species

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Magnetic and spectral properties are reported for several halogen-bridged dimeric copper(II) clusters of the general form $\text{A}_2\text{Cu}_2\text{X}_n\text{X}'_{6-n}$ where $\text{A} = (\text{C}_6\text{H}_5)_4\text{P}^+$, $(\text{C}_6\text{H}_5)_4\text{Sb}^+$, or $(\text{C}_6\text{H}_5)_3(\text{C}_6\text{H}_5)_3\text{P}^+$, $\text{X} = \text{Cl}^-$, and $\text{X}' = \text{Br}^-$. All of the compounds exhibit ferromagnetic exchange coupling between pairs of copper(II) ions with $2J$ values ranging from 5.4 to 112 cm^{-1} . Infrared data and the magnitudes of the exchange interactions suggest that chloride bridges are preferred in the mixed-halide complexes. An analysis of the electron paramagnetic resonance data and the low-temperature magnetization data suggests that deviations from the simple pair model for the exchange interactions can be attributed to zero-field splittings of the triplet states instead of to interdimer exchange.

Introduction

The existence of ferromagnetic intracenter exchange in paramagnetic transition-metal cluster complexes has been documented only within the last decade.¹⁻³ Although the number of ferromagnetically coupled cluster complexes of known crystal structure is still relatively small, examples are being found at a rapidly increasing rate as a result of careful, systematic studies of magnetic and structural properties.^{4,5} For several comprehensive reviews of this field see ref 4-8. Since the available theoretical methods for treating the spin-spin coupling problem are unmanageable for a large number of interacting spins, the use of small clusters of well-isolated interacting systems as models for the larger, more complicated magnets is of considerable importance.⁹⁻¹¹ With the model approach it should be possible to more fully understand the various magnetic and structural features which are necessary for the ultimate realization of insulating magnets.^{12,13}

The rich variety of cluster complexes of the d^9 copper(II) ion make these systems especially attractive for magnetic and structural studies. Although large numbers of compounds containing oxygen bridges between copper(II) ions have been fully characterized,⁴⁻⁸ only a few dimeric clusters containing halogen bridge atoms have been studied.^{4,14-18} A general class of halocuprates(II) represented by the general formula ACuX_3 (where $\text{X} = \text{Cl}^-$ or Br^- and A is an alkali metal or monovalent organic cation) are of particular interest since structures of this type are known to vary from simple bimetallic clusters as in $[(\text{C}_6\text{H}_5)_4\text{AsCuCl}_3]_2$ ^{16a} to complicated arrays of dimers joined into chains as in KCuCl_3 .¹⁹ Apparently, the geometry about the $\text{Cu}_2\text{X}_6^{2-}$ ion is dictated by the size and packing requirements of the cation. Thus, with small cations these complexes possess complicated structures loosely based on the quasi-planar dimeric $\text{Cu}_2\text{X}_6^{2-}$ moiety, but with very large organic cations, the structures lose their quasi-planar nature and become isolated bimetallic clusters consisting of two distorted tetrahedra sharing an edge.^{16a,17a}

Shortly after the initial discovery of the ferromagnetically coupled $\text{Cu}_2\text{Cl}_6^{2-}$ dimers in the tetraphenylarsonium tri-

chlorocuprate(II),¹⁶ Textor et al.^{17a} showed that the tetraphenylphosphonium analogue was isomorphous and very nearly isostructural to the $\text{Ph}_4\text{AsCuCl}_3$ ($\text{Ph} = \text{C}_6\text{H}_5$) salt. One of the more important differences between the structures was a decrease in the $\text{Cu}-\text{Cl}_6-\text{Cu}$ bridge angle from 93.7 (1) to 93.3 (1)°. Since earlier work on an extensive series of hydroxo-bridged copper(II) dimers has shown that the magnitude and sign of the exchange coupling constant are very sensitive to small changes in the bridging geometry,¹³ we expected to find analogous behavior in halide-bridged copper(II) systems. To study this problem we have prepared and characterized the dimeric Ph_4P^+ complexes of mixed halides. In addition, two other complexes with the cations tetraphenylstibonium and triphenyl-*n*-propylphosphonium have been prepared as their chloride salts. The results of these studies are described in this paper.

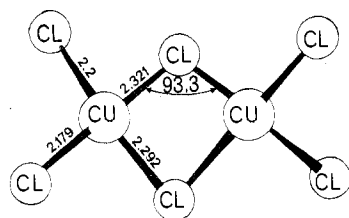
Experimental Section

Tetraphenylphosphonium chloride and bromide were obtained from Columbia Organic Chemicals, Inc. (Columbia, S.C.). Triphenyl-*n*-propylphosphonium bromide was obtained from Aldrich Chemical Co. (Atlanta, Ga.) and converted to the chloride salt via ion-exchange chromatography. Tetraphenylstibonium chloride was prepared and purified after the method of Doak et al.²⁰ Reagent grade $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and CuBr_2 were obtained from J. T. Baker Chemical Co. (Phillipsburg, N.J.) and used without additional purification.

Preparation of the Complexes. The complexes containing only one type of halide per formula unit were synthesized by adding equimolar amounts of the cation and the appropriate copper(II) halide in warm methanol or absolute ethanol. The orange-red ($\text{Cu}_2\text{Cl}_6^{2-}$) or maroon-black ($\text{Cu}_2\text{Br}_6^{2-}$) complexes were readily recrystallized from methanol or dichloromethane. The mixed-halide complexes of the Ph_4P^+ cation ($\text{Ph} = \text{C}_6\text{H}_5$) were prepared by the following method: Carefully weighed stoichiometric amounts of the phosphonium bromide and copper(II) chloride dihydrate were dissolved in separate amounts of warm absolute ethanol. These solutions were quickly mixed and allowed to cool until crystallization occurred. The precipitated mixed-halogen complexes were separated by filtration and air-dried. These compounds could not be recrystallized even from inert organic solvents such as dichloromethane since the process always led to preferential crystallization of a pure-halide compound. Analytical

Table I. Analytical Data

complex	% C		% H	
	calcd	found	calcd	found
(C ₆ H ₅) ₄ SbCuCl ₃	48.04	48.24	3.36	3.50
(CH ₃ CH ₂ CH ₂) ₃ (C ₆ H ₅) ₃ PCuCl ₃	53.07	52.79	4.67	4.48
(C ₆ H ₅) ₄ PCuCl ₃	56.60	56.41	3.96	3.08
(C ₆ H ₅) ₄ PCuBr ₃	44.85	44.73	3.14	3.09
(C ₆ H ₅) ₄ PCuBr ₂ Cl	48.19	48.01	3.37	3.29
(C ₆ H ₅) ₄ PCuBrCl ₂	52.05	52.06	3.64	3.70

**Figure 1.** View of the dimeric nature of [(C₆H₅)₄P]₂Cu₂Cl₆.

data for the compounds are listed in Table I. All microanalyses were performed by Integral Microanalytical Labs, Raleigh, N.C.

Physical Measurements. Electron paramagnetic resonance (EPR) spectra were obtained with a Varian E-3 X-band (~9.5 GHz) spectrometer. The magnetic field of the E-3 was calibrated by NMR techniques using a Magnion G-502 gaussmeter and a Hewlett-Packard 5340A precision frequency counter, and the klystron frequency was measured directly with the frequency counter. Finely ground polycrystalline samples were run in 3 mm i.d. quartz tubes at room temperature (298 K) and at liquid-nitrogen temperature (77 K). The spectra recorded at 77 K were obtained with an insertion Dewar made by Varian. The free radical DPPH ($g = 2.0036$) was used as a frequency marker in all cases.

Mull (transmission) electronic spectra were obtained with a Cary 17 spectrometer.²¹ Far-infrared spectra were obtained with a Perkin-Elmer 621 spectrometer from Nujol mulls pressed between cesium iodide plates.

Magnetic susceptibility and magnetization measurements were obtained using a Princeton Applied Research vibrating-sample magnetometer (VSM) operating at field strengths of 10 kOe. The VSM was calibrated vs. the saturation moment of ultrapure (99.9999%) Ni metal²² and against the susceptibility of (NH₄)₂Mn(SO₄)₂·6H₂O,²³ the two calibrations agreed to within 2%. Finely ground polycrystalline samples typically weighing 150 mg were housed in precision-milled Lucite sample holders. Temperatures were measured with a calibrated Ga-As diode.²³ The output data were corrected for the diamagnetism of the sample holder and for the underlying diamagnetism of the constituent atoms using Pascal's constants.²⁴ A value of 60×10^{-6} emu/mol was assumed for the temperature-independent paramagnetism (TIP) due to Cu(II) ions.

All curve fitting was performed using either the nonlinear least-squares program DIMER²⁵ or a SIMPLEX function minimization program.²⁶ The function minimized was $F = 1/n[(\chi_{\text{obsd}}(T) - \chi_{\text{calcd}})^2/T^2 + \chi_{\text{obsd}}^2/T^2]$ where χ_{obsd} and χ_{calcd} are the observed and calculated susceptibilities, T is the observed temperature, and n is the number of observed data.

Results

A sketch of the dimeric Cu₂Cl₆²⁻ anion found in (C₆H₅)₄PCuCl₃ is shown in Figure 1.^{17a} The distorted nature of the edge-sharing tetrahedra is quite apparent since the terminal chlorides are bonded at much shorter distances (~2.2 Å) than the bridging ions (~2.3 Å). The similarity between (C₆H₅)₄P⁺^{17a} and (C₆H₅)₄As⁺^{16a} salts of the Cu₂Cl₆²⁻ anion is emphasized by the values of the two types of copper-chlorine bond distances: Cu-Cl terminal distances of 2.200 and 2.179 Å vs. 2.215 and 2.198 Å; Cu-Cl bridge distances of 2.321 and 2.292 Å vs. 2.333 and 2.305 Å. Perhaps the most significant difference between the two compounds is a decrease of the Cu-Cl₅-Cu angle from 93.7° ((C₆H₅)₄As⁺) to 93.3° ((C₆H₅)₄P⁺). Since superexchange interactions are known to be extremely sensitive to the geometry of the bridge ar-

Table II. Electronic Spectra (Mull Transmission)^a

complex	band position, nm	ref
(C ₆ H ₅) ₄ AsCuCl ₃	1150, 900 sh, 460, 400, 313	27
	1120, 820	16a ($T = 77$ K)
(C ₆ H ₅) ₄ PCuCl ₃	1250, 900 sh, 460, 410, 310	27, this work
(C ₆ H ₅) ₄ SbCuCl ₃	1050, 940 sh, 460, 410 sh	this work
<i>n</i> -Pr(C ₆ H ₅) ₃ PCuCl ₃	1000 br, 450, 400 sh	this work
(C ₆ H ₅) ₄ PCuBr ₃	1450 br, 975, 600 sh, 550	this work
(C ₆ H ₅) ₄ PCuBr ₂ Cl	1300, 900, 500 sh	this work
(C ₆ H ₅) ₄ PCuBrCl ₂	1250, 850, 625 sh, 550 sh	this work

^a sh = shoulder, br = broad.

angement,⁴⁻¹³ this difference was expected to be of utmost importance in understanding the differences in the magnetic properties of the two compounds. It is also of interest to note that in both cases the dimeric Cu₂Cl₆²⁻ ions are well separated in the materials with the closest copper-copper distances between clusters being about 9.3 Å along the *a* axis. Furthermore, the closest contacts between chloride atoms from one cluster to those of a neighbor are about 6.7 Å along the *a* axis. Finally, Textor et al.^{17a} have found that the (C₆H₅)₄PCuBr₃ complex is not isomorphous with its chloro analogue while Chow et al.^{16d} have found that the (C₆H₅)₄AsCuBr₃ complex is isomorphous with its chloro analogue.

The solid-state electronic spectra of the complexes are listed in Table II. There is excellent agreement between this work and the bands found earlier by Ludwig and Textor²⁷ for the (C₆H₅)₄PCuCl₃ compound. In general, all of the pure chloride complexes show at least one broad band in the near-infrared region centered near 0.8–0.9 μm^{-1} with a shoulder near 1.10 μm^{-1} . The spectrum of the (C₆H₅)₄PCuBr₃ shows an expected shift to lower energies of the near-infrared and visible bands, and these maxima are now centered at about 0.7–1.02 μm^{-1} . The spectra of the mixed-halide species, CuCl₄Br_{3-n}²⁻, are found to exhibit bands at energies which are intermediates between those of the two parent compounds. Owing to the marked similarity of the electronic spectra in the near-infrared and visible regions and the positions of the higher energy charge-transfer maxima (see Table II) it seems quite reasonable to suggest that the observed electronic transitions arise from copper(II) ions in a distorted tetrahedral environment.^{19,28}

In an attempt to identify the bridging unit in the mixed-halide compounds [(C₆H₅)₄P]₂Cu₂X_{*n*}X'_{*n*'}²⁻ (X = Cl⁻, X' = Br⁻), far-infrared spectra were examined in the region of the Cu-Cl stretching frequencies. The spectra in the region 200–400 cm⁻¹ are shown in Figure 2. The spectra of all of the chloride-containing compounds were found to be quite similar with a sharp pair of bands centered near 325 and 300 cm⁻¹ and with a much weaker band at lower energy near 255 cm⁻¹. These band positions are in excellent agreement with those obtained by Ludwig and Textor²⁷ for the (C₆H₅)₄PCuCl₃ and (C₆H₅)₄AsCuCl₃ compounds. Furthermore, these authors observed only one broad band near 380 cm⁻¹ in CH₂Br₂ solutions of the (C₆H₅)₄PCuCl₃ and (C₆H₅)₄AsCuCl₃ compounds, which are known to contain bridging chloride ions. This result, along with the magnetic data discussed below, leads us to conclude that the bands near 300 and 255 cm⁻¹ arise from the stretching frequencies of bridging chloride ions in these complexes. It is of interest to note that work on the planar Cu₂Cl₆²⁻ species present in KCuCl₃ and NH₄CuCl₃ suggests that the terminal chloride stretches are centered near 300 cm⁻¹ while the bands near 280 and 230 cm⁻¹ are due to bridging chlorides.^{19,29}

The electron paramagnetic resonance spectra of polycrystalline samples of *all* of the compounds reveal a rich and wide variety of triplet-state ($S = 1$) transitions.³⁰ In general the Cu₂Cl₆²⁻ ions in the (C₆H₅)₄P⁺, (C₆H₅)₄Sb⁺, and (*n*-Pr)(C₆H₅)₃P⁺ complexes show X-band spectra which range from low-field forbidden ($\Delta M_s = \pm 2$) transitions near

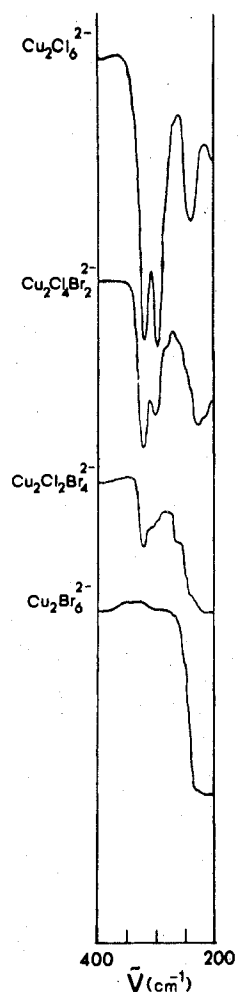


Figure 2. Infrared spectra in the copper-halogen stretching region.

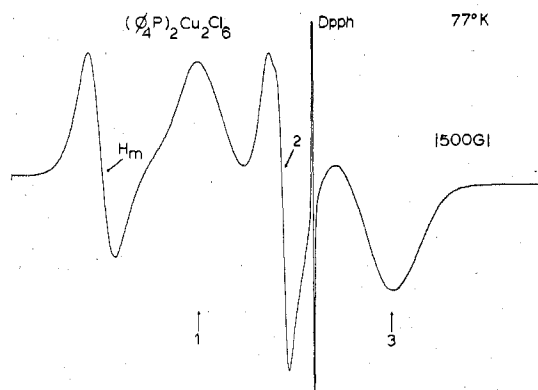


Figure 3. Observed EPR spectrum of $(\text{C}_6\text{H}_5)_4\text{PCuCl}_3$ at 77 K. The numbers indicate the resonance fields which could be unambiguously assigned.

1300–1600 G, which are exceptionally intense, to higher field resonances of medium intensity. These latter bands range from about 2000 to about 4700 G. In addition, broad overlapping resonances are observed at room temperature, and cooling the samples to 77 K results in considerable sharpening and resolution as well as large increases in the relative intensities of the lines. The observed spectra for these chloride salts are shown in Figures 3–6. Spectra were observed for the mixed-halide complexes of $(\text{C}_6\text{H}_5)_4\text{P}^+$; but upon increasing the number of bromide ligands in the $\text{Cu}_2\text{Cl}_n\text{Br}_{6-n}^{2-}$ structure, the EPR lines became progressively broader and the resonances in the forbidden region moved to lower fields while the other resonances showed a pronounced shift to higher fields. Thus,

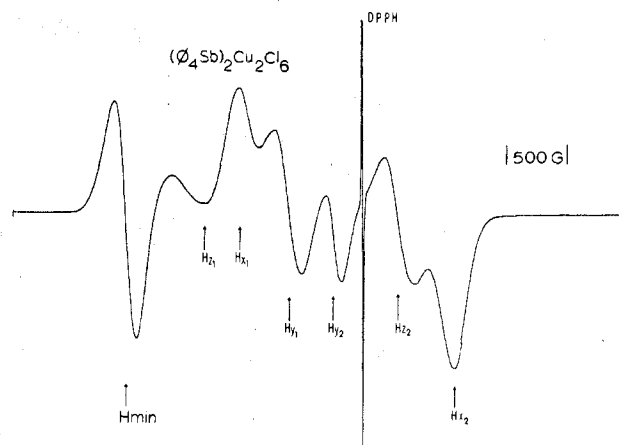


Figure 4. The 77 K EPR spectrum of $(\text{C}_6\text{H}_5)_4\text{SbCuCl}_3$. The assignments indicated yield the parameters listed in Table III (see text for a discussion).

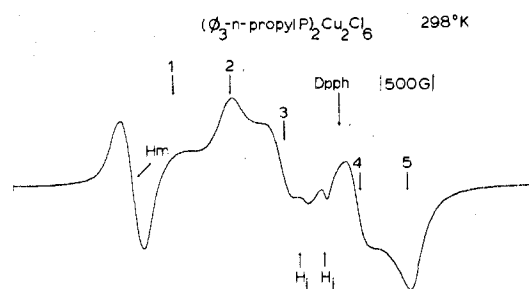


Figure 5. Room-temperature EPR spectrum of $(\text{C}_6\text{H}_5)_3(n\text{-Pr})\text{PCuCl}_3$. The weak lines labeled H_1 arise from minute amounts of a monomeric impurity.

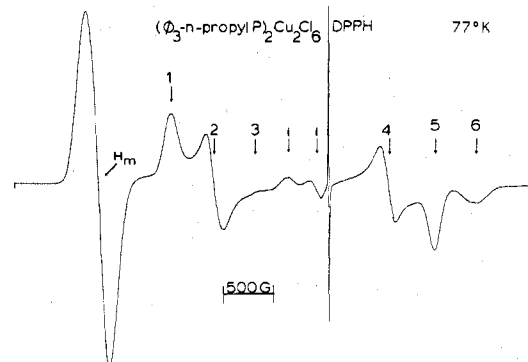


Figure 6. The 77 K EPR spectrum of $(\text{C}_6\text{H}_5)_3(n\text{-Pr})\text{PCuCl}_3$. The numbers indicate the triplet-state transitions and the lines labeled i are assigned as impurities. See text for a discussion of the assignments.

in $(\text{C}_6\text{H}_5)_4\text{PCuCl}_2\text{Br}$ two very broad, weak, low-field lines appear at ~ 600 and 1100 G while a very intense and very broad (~ 800 G) pair of resonances appear at 2100 and 3000 G. These lines are followed by a weak, broad resonance at 4900 G. Due to severe broadening, the compounds containing four and six bromide ligands per dimer yielded little more than qualitative information. However, for all of the bromide-containing complexes, we observed a dramatic increase in the intensities of the resonances upon cooling to 77 K. This effect is most apparent in the "half-field" $\Delta M_s = \pm 2$ lines such as those in the spectra of Figures 5 and 6.

The bulk magnetic properties of all of the compounds are very unusual. Examination of the inverse susceptibilities reveals that all of the compounds show a $(T - \Theta)^{-1}$ dependence from which positive temperature intercepts, Θ , can be obtained (see Figure 7). However, if one inspects the effective magnetic moments (μ_{eff}) vs. temperature or the product of the sus-

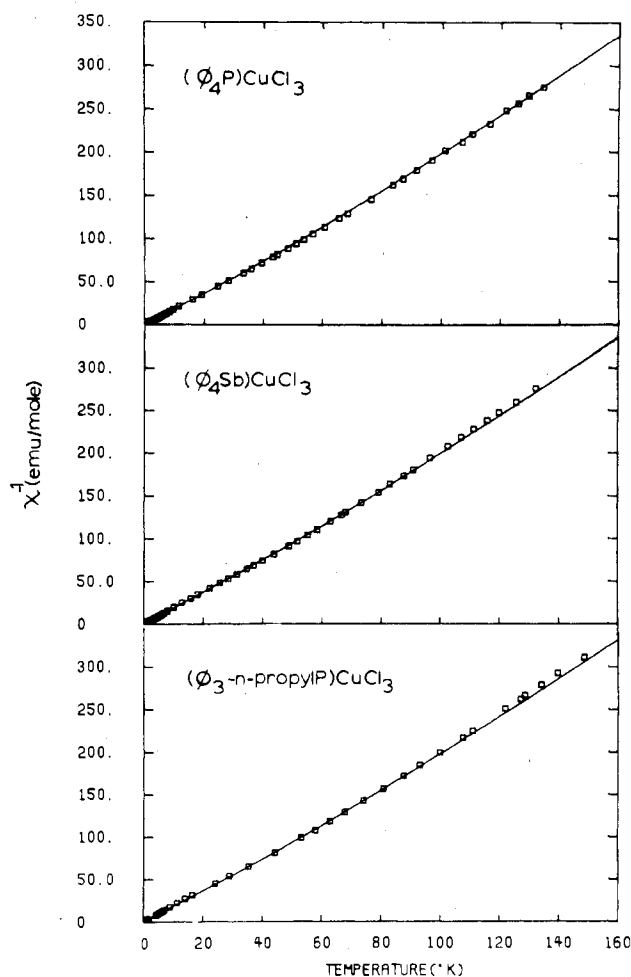


Figure 7. Inverse susceptibility as χ_m^{-1} for the three $Cu_2Cl_6^{2-}$ complexes. The solid curves are the best-fit parameters from eq 14. See Table IV and text for discussion.

ceptibility and temperature vs. temperature ($\chi_m T$ vs. T), a better indication of the deviation from the Curie law in eq 1 is possible.^{16a} Thus, a negative deviation from (1) will result

$$\chi = Ng^2\beta^2 S(S+1)/3kT \quad (1)$$

in a strictly decreasing μ_{eff} value as the temperature decreases, while a positive deviation will reveal a strictly increasing μ_{eff} value; furthermore, neither curve will show a singularity; i.e., there is no maximum or minimum. All of the compounds reported herein show a positive deviation from eq 1 such that μ_{eff} rises from about 1.95 ± 0.05 at 130 K to about $2.05 \pm 0.04 \mu_B$ at lower temperature. All of the complexes showed a maximum in μ_{eff} followed by a rapid decrease down to the lowest temperatures, ~ 1.5 K. For example, in $[(n\text{-Pr})-(C_6H_5)_3P]_2Cu_2Cl_6$, μ_{eff} rises from $1.95 \mu_B$ (148 K) to a maximum value of $2.09 \mu_B$ (16 K) and then falls rapidly to a value of $1.96 \mu_B$ near 1.5 K. In general, the compounds containing chlorides showed similar behavior with differences being noted in the temperatures of the maximum. It is of considerable importance to note that $[(C_6H_5)_4P]_2Cu_2Br_6$ shows qualitatively similar behavior, but the effective moments are significantly lower since μ_{eff} ranges from $1.90 \mu_B$ (106 K) to a maximum of $2.04 \mu_B$ (10 K) and then falls to a value of $1.82 \mu_B$ (2 K) (compare Figures 8 and 9). Clearly, the copper ions in these complexes are coupled by an exchange interaction. Furthermore, the triplet-state EPR data and the bulk susceptibility suggest that this interaction must be positive, i.e., ferromagnetic coupling. However, the low-temperature susceptibility data also show unequivocally that it is not solely

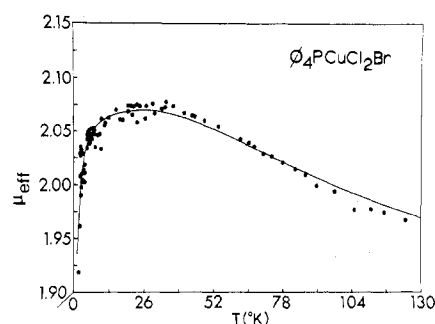


Figure 8. Effective magnetic moments in Bohr magnetons vs. temperature for $(C_6H_5)_4PCuCl_2Br$. The solid curve is the best fit to eq 7.

the ferromagnetic exchange which determines all of the properties of these compounds. It is immediately apparent that another weaker interaction is superimposed upon the stronger coupling mechanisms which becomes significant only at low temperatures ($T < 30$ K).

Discussion

Magnetic Theory. The most general form of the zero-field Hamiltonian appropriate to a dimeric cluster of $S = 1/2$ ions is given by eq 2.^{5-8,32} The first term in (2) represents the usual

$$H = -2J\hat{S}_1 \cdot \hat{S}_2 + d_{12}[\hat{S}_1 \times \hat{S}_2] + \hat{S}_1 \cdot \Gamma_{ij} \cdot \hat{S}_2 \quad (2)$$

isotropic Heisenberg exchange interaction with J being the exchange coupling constant which is positive for parallel (ferromagnetic) coupling and negative for antiparallel coupling (antiferromagnetic). The second and third terms represent the antisymmetric (Dzyaloshinsky-Moriya) and anisotropic exchange interactions, respectively.³² Thus, the antisymmetric exchange, d_{12} , tends to align S_1 and S_2 perpendicular to each other and to the vector d_{12} , and the anisotropic exchange Γ_{ij} tends to align the coupled spins along the maximum principal axis of Γ_{ij} .³² Both of these terms give rise to a splitting of the triplet state in zero field since the antisymmetric exchange mixes the $|1,0\rangle$ and $|0,0\rangle$ states of the total spin while the anisotropic exchange lifts the degeneracy of the triplet without mixing in the spin-singlet state. It is of importance to note that the antisymmetric exchange may exist only for certain crystal symmetries and is rigorously forbidden if an inversion center relates the two spins in question. Order of magnitude estimates of these two interactions are given by

$$d_{12} \approx \left(\frac{g-2}{2}\right)J, \quad \Gamma_{ij} \approx \left(\frac{g-2}{2}\right)^2 J \quad (3)$$

where g is the g value and J is the isotropic exchange coupling constant.

Analysis of the Paramagnetic Resonance Spectra. If one considers the spin Hamiltonian appropriate to a randomly oriented $S = 1$ species, then Wasserman et al.³⁰ have shown that the spin Hamiltonian may be written

$$H_{ss} = \beta\hat{H} \cdot \mathbf{g} \cdot \hat{S} + D(S_z^2 - 2/3) + E(S_x^2 - S_y^2) \quad (4)$$

where \hat{H} is the applied magnetic field, \mathbf{g} is the \mathbf{g} tensor, and D and E are the zero-field splitting parameters of the triplet state. In the case of uniaxial anisotropy, E must vanish, but for lower symmetries, full rhombic anisotropy will obtain, i.e., $E \neq 0$. In general the zero-field splittings of the triplet state of a coupled pair of $S = 1/2$ ions arises from the combined effects of the anisotropic and antisymmetric exchange and from the classical dipole-dipole interaction.^{16b,33} With the restriction that the \mathbf{g} and \mathbf{D} tensors have the same principal axes, Wasserman et al.³⁰ have shown that the resonance fields for a system of randomly oriented triplets are given by eq 5,

$$\begin{aligned}
 H_{x_1}^2 &= (g_e/g_x)^2[(H_0 - D' + E')(H_0 + 2E')] \\
 H_{x_2}^2 &= (g_e/g_x)^2[(H_0 + D' - E')(H_0 - 2E')] \\
 H_{y_1}^2 &= (g_e/g_y)^2[(H_0 - D' - E')(H_0 - 2E')] \\
 H_{y_2}^2 &= (g_e/g_y)^2[(H_0 + D' + E')(H_0 + 2E')] \\
 H_{z_1}^2 &= (g_e/g_z)^2[(H_0 - D')^2 - E^2] \\
 H_{z_2}^2 &= (g_e/g_z)^2[(H_0 + D')^2 - E^2]
 \end{aligned} \quad (5)$$

where $H_0 = h\nu/g_e\beta$, $D' = D/g_e\beta$, $E' = E/g_e\beta$, and g_e is the free-electron g value, 2.0023. Thus, for a randomly oriented $S = 1$ species in which the zero-field splittings are smaller than the measuring quantum, $h\nu > D > 3E$, six allowed lines ($\Delta M_s = \pm 1$) may be observed. In addition to the six allowed lines, an intense isotropic "forbidden" line ($\Delta M_s = \pm 2$) is often observed in the $g \approx 4$ region.³⁴ Since the expressions in eq 5 form a self-consistent set, it is necessary to solve them by repeated iteration using all six equations to obtain the parameters of interest, namely, g_i ($i = x, y, z$), D , and E .³⁵ Although the solutions to (5) cannot yield the absolute signs of D and E , their relative signs are of considerable importance since this information allows the correct ordering of the assigned resonance fields when significant g -tensor anisotropy is present. For the situation in which the symmetry of the cluster is uniaxial, the E terms in eq 5 vanish and the resonance fields ($|D| \ll h\nu$) are given by eq 6.³⁶

$$\begin{aligned}
 H_{\parallel 1} &= g_e/g_z(H_0 - D') \\
 H_{\perp 1}^2 &= (g_e/g_{\perp})^2 H_0(H_0 - D') \\
 H_{\perp 2}^2 &= (g_e/g_{\perp})^2 H_0(H_0 + D') \\
 H_{\parallel 2} &= g_e/g_z(H_0 + D')
 \end{aligned} \quad (6)$$

The EPR spectrum of $[(C_6H_5)_4P]_2Cu_2Cl_6$ may be analyzed in terms of pseudoaxial symmetry within the errors associated with a powdered sample of a pure complex. Unfortunately, severe dipolar broadening prevented the resolution of all four allowed ($\Delta M_s = \pm 1$) lines. The spectrum observed at room temperature (298 K) was nearly identical with that at 77 K (see Figure 2). This is in contrast to the behavior of the $[(C_6H_5)_4As]CuCl_3$ ^{16b} analogue since in that case only the 77 K spectrum qualitatively resembles that of the phosphonium analogue. By assigning the lowest and highest field $\Delta M = \pm 1$ lines, labeled 1 and 3 in Figure 3, to the low- and high-field parallel resonances, repeated iteration yields $g_{\parallel} = 2.12$ and $|D| = 0.0917 \text{ cm}^{-1}$. Assignment of the perpendicular resonances are not possible and the g_{\perp} value of 2.12 is too low for a pseudotetrahedral chromophore.^{16b,19} The combined effects of severe broadening and the known limitations of powder data have prevented us from obtaining an analysis of the triplet-state EPR of $(C_6H_5)_4PCuCl_3$. Of course, one possible explanation may involve a situation in which the g and D tensors do not share the same principal axis; if this is the case, then the method of Wasserman et al.³⁰ cannot be used. We find some evidence for this situation since the low-temperature susceptibility data (vide infra) suggest that the isotropic exchange is about a factor of 2 larger than that observed for $[(C_6H_5)_4As]CuCl_3$. Thus, one expects the anisotropic exchange and its contribution to the D tensor to be substantially larger and perhaps diagonal in a different coordinate system.³⁷⁻³⁹

The observed resonance spectra of $[(C_6H_5)_4Sb]CuCl_3$ (Figure 4) and $[(C_6H_5)_3-nPrP]CuCl_3$ (Figures 5 and 6) both show unusually well-resolved rhombic g -tensor anisotropy in their triplet-state spectra. The relatively large rhombic character of the $[(C_6H_5)_4Sb]CuCl_3$ compound is quite surprising since a change of only a slightly larger cation with identical geometry would hardly be expected to be such a significant perturbation on the electronic structure of the cluster. Thus, it is clear that the $(C_6H_5)_4SbCuCl_3$ complex

Table III. Triplet-State EPR Parameters

complex	$D, \text{ cm}^{-1}$	$E, \text{ cm}^{-1}$
$(C_6H_5)_4AsCuCl_3^a$	± 0.11	∓ 0.009
$(C_6H_5)_4PCuCl_3^{b,c}$	~ 0.09	-
$(C_6H_5)_4SbCuCl_3^c$	± 0.1043	∓ 0.0216
$(C_6H_5)_3(n-pr)PCuCl_3^{b,c}$	$\sim \pm 0.15$	$\sim \mp 0.02$
$(C_6H_5)_4PCuCl_2Br^{c,d}$	≥ 0.3	-
$(C_6H_5)_4PCuBr_2Cl^{c,d}$	> 0.3	-
$(C_6H_5)_4PCuBr_3^{c,d}$	-	-

^a Reference 16b, single-crystal study. ^b Resonance could not be assigned assuming coaxial g and D tensors. ^c This work, powder study. ^d Ill-resolved, severely broadened lines.

is not isomorphous with its phosphonium and arsonium analogues. The EPR spectrum of $[(C_6H_5)_4Sb]CuCl_3$ can be readily assigned by using eq 5, and the appropriate triplet-state parameters are $g_z = 2.40$, $g_y = 2.29$, $g_x = 2.11$, $D = \pm 0.1043$, and $E = \pm 0.0216$. Likewise, the spectrum of $[(C_6H_5)_3-nPrP]CuCl_3$ also shows remarkably well-resolved rhombic anisotropy, but we were unable to obtain reasonable parameters by assuming that eq 5 was appropriate.

The EPR data for the mixed-halide complexes of $(C_6H_5)_4P^+$ are very unusual. Since both $(C_6H_5)_4PCuCl_2Br$ and $(C_6H_5)_4PCuBr_2Cl$ show spectra with lines appearing from about 500 to 6000 G, it is apparent that the zero-field splitting must be at least comparable to, or larger than, the X-band measuring quantum ($\sim 0.3 \text{ cm}^{-1}$). The various EPR parameters for all the compounds studied here are collected in Table III.

Low-Temperature Bulk Magnetic Properties. Within the usual formalism of the isotropic Heisenberg exchange interaction, the susceptibility of a pair of copper(II) ions is given by (7) where χ_m is given per mole of $S = 1/2$ ions and TIP

$$\chi_m = [Ng^2\beta^2/3k(T - \Theta)][1 + 1/3 \exp(-2J/kT)]^{-1} + \text{TIP} \quad (7)$$

is the temperature-independent paramagnetism. The molecular field parameter, Θ , representing the intercluster exchange is given by (8) where z is the number of nearest

$$J' = 3k\Theta/2zS'(S' + 1) \quad (8)$$

neighbors per cluster and S' is the effective spin of the dimer ($S' = 1$).

We have fitted the observed susceptibilities of these halocuprates to eq 7 and 8. As we noted in the Introduction, the use of additional weak interactions in addition to the pairwise exchange was found to be necessary to describe the lowest temperature data. Using this model, the best-fit values which were obtained for the singlet-triplet splitting, the average g value, and the intercluster exchange parameter (Θ value) are collected in Table IV and compared with the analogous arsonium compounds. Of particular interest is the observation that all of the chloride-containing compounds in our series ($Cu_2Cl_6^{2-}$, $Cu_2Cl_4Br_2^{2-}$, and $Cu_2Br_4Cl_2^{2-}$) have very similar $2J$ values centered about $2J \approx +90 \text{ cm}^{-1}$ while the pure bromide compound has $2J \approx +54 \text{ cm}^{-1}$. Thus, on the basis of the magnetic data and the Cu-X infrared data, it appears that the chloride ions are the bridging units in the mixed-halide complexes, i.e., $Cu_2Cl_4Br_2^{2-}$ and $Cu_2Cl_2Br_4^{2-}$. However, we note that in the analogous arsonium series this apparently is not the case.^{16c,d} Moreover, for this situation to obtain, one must assume that all of the members of the $[(C_6H_5)_3-nPrP]_2Cu_2X_nX'_{6-n}$ are isomorphous and isostructural; and Textor et al.^{17a} have shown that $(C_6H_5)_4PCuCl_3$ and $(C_6H_5)_4PCuBr_3$ are not isomorphous in contrast to their arsonium analogues.^{1b} We note that $2J$ varies from $+80$ to $+40 \text{ cm}^{-1}$ in going from $(C_6H_5)_4PCuCl_3$ to $(C_6H_5)_4AsCuCl_3$ with an accompanying change in the Cu-Cl-Cu' bridge angle from 93.7 (1) to 93.3

(1)°. It is apparent that the magnitude of the exchange is very sensitive to minute structural changes.¹⁵

In order to fit the low-temperature data ($T < 30$ K), the use of eq 7 and 8 implies that there must be *intercluster* exchange interactions ranging from about -0.03 to -0.12 cm⁻¹. To understand this we must examine the known structural data of (C₆H₅)₄AsCuCl₃^{16a} and (C₆H₅)₄PCuCl₃. The closest copper-copper contacts between clusters are about 9.3 Å, the shortest Cl-Cl' contacts are 6.7 Å, and the shortest Cl-C vectors from a given cluster to an intervening organic cation are about 3.5 Å. If one assumes that the supposed cluster-cluster interaction is transmitted via a superexchange interaction, then the enormous distances between clusters and the absence of a readily discernible hydrogen-bonding network make the assignment of the superexchange pathway difficult. The only other example of a well-isolated, chloride-bridged copper(II) dimer, the Cu₂Cl₈²⁻ cluster present in [Co^{III}-(NH₂CH₂CH₂NH₂)₃]₂[Cu₂Cl₈]Cl₂·2H₂O, has been extensively characterized by single-crystal susceptibility and resonance techniques.⁴⁰ In this structure the shortest copper-copper distances are 8.617 Å, the closest Cl-Cl' contacts are 5.108 Å, and a water molecule lies between two clusters such that relatively short O-Cl contacts of 4.99 and 4.63 Å occur. Although the intracenter exchange is small ($2J = -14.5$ cm⁻¹), an *intercluster* exchange interaction of about -0.08 cm⁻¹ is sufficiently strong enough to completely average out the zero-field line structure in the EPR at high temperatures ($T > 77$ K) where the triplet state is highly populated. By essentially reversing the logic of the observed behavior in the Cu₂Cl₈²⁻ system, one would expect *intercluster* exchange values on the order of those necessary to fit the observed data for the Cu₂Cl₆Br_{6-n}²⁻ compounds to completely average the triplet fine structure. Since the exchange energy is positive ($2J > 0$) for these complexes, the low-temperature EPR should be more effectively averaged. Precisely the opposite effects have been observed experimentally for these systems (vide post).

Since we have observed very distinct triplet-state EPR with the accompanying fine structure due to a moderate zero-field splitting, a more attractive explanation of the low-temperature data can be obtained by assuming that the deviation from the simple pair model (eq 7, $\theta = 0$) results from a zero-field splitting of the triplet state. Thus, by assuming that the **g** and **D** tensors share the same principal axis, one may calculate the magnetization and the zero-field susceptibility of a dimeric copper(II) cluster by solving the Hamiltonians (9) and

$$H = 2JS_1 \cdot S_2 + g_{\parallel} \beta H \cdot \hat{S}_z + D[S_z^2 - \frac{1}{3}S(S+1)] \quad (9)$$

(11),⁴¹⁻⁴³ where the first term represents the isotropic Heisenberg exchange which couples the two copper(II) spins, the second term is the usual Zeeman term, and the third term represents the zero-field splitting of the triplet state with the *z* axis as the axis of quantization. Thus, the solutions to (9) are readily shown to be

$$\begin{aligned} E_{1,1} &= -J/2 + D/3 + g_{\parallel} \beta H \\ E_{1,0} &= -J/2 - 2D/3 \\ E_{1,-1} &= -J/2 + D/3 - g_{\parallel} \beta H \quad E_{0,0} = +3J/2 \end{aligned} \quad (10)$$

In a similar fashion, the perpendicular energies of eq 11 can be calculated.

$$H_{\perp} = -2JS_1 \cdot S_2 + \frac{g_{\perp} \beta H}{2}(S^+ + S^-) + D \left[S_z^2 - \frac{S(S+1)}{3} \right] \quad (11)$$

$$\begin{aligned} E_1 &= \frac{(J + D/3) + (D^2 + 4g_{\perp}^2 \beta^2 H^2)^{1/2}}{2} \\ E_2 &= -J/2 + D/3 \\ E_3 &= \frac{(J + D/3) - (D^2 + 4g_{\perp}^2 \beta^2 H^2)^{1/2}}{2} \\ E_4 &= +3J/2 \end{aligned} \quad (12)$$

By using the standard formula for the magnetization of an ensemble obeying Boltzmann statistics, eq 13, and the solutions to (9) and (11), the molar magnetizations per copper(II) ion are given by⁴⁴

$$M = \frac{NkT}{z} \left(\frac{\partial z}{\partial H} \right) \quad (13)$$

where *z* is the partition function. The components of *M* are

$$M_{\parallel} = g_{\parallel} \beta N \sinh(g_{\parallel} \beta H / kT) / \{ \exp[(-2J + D/3)/kT] + \exp(D/kT) + 2 \cosh(g_{\parallel} H / kT) \} \quad (14a)$$

$$M_{\perp} = \{ 2g_{\perp}^2 \beta^2 H N / (D^2 + 4g_{\perp}^2 \beta^2 H^2)^{1/2} \} \{ \sinh[(D^2 + 4g_{\perp}^2 \beta^2 H^2)^{1/2} / 2kT] / \{ \exp[(-4J - D/3)/kT] + \exp(-D/2kT) + 2 \cosh[(D^2 + 4g_{\perp}^2 \beta^2 H^2)^{1/2} / 2kT] \} \} \quad (14b)$$

$$M_{av} = \frac{1}{3} M_{\parallel} + \frac{2}{3} M_{\perp} \quad (14c)$$

where *M*_{av} is the powder average of the anisotropic components of the magnetization. The use of the magnetization instead of the zero-field susceptibility was necessary since our measurements were carried out in applied fields (*H*) of 10 kOe in which case $H \gg D/g\beta$.

We have compared the constant-field magnetization of the halocuprates and have discovered some very interesting results. The data for the complexes containing only chloride ions ((C₆H₅)₄PCuCl₃, (C₆H₅)₄SbCuCl₃, and (C₆H₅)_{3-n}PrCuCl₃) were easily described by eq 14, and the results obtained were in excellent agreement with the EPR data (see Table IV). For example, (C₆H₅)₄SbCuCl₃ yielded $2J = +104 \pm 12$ cm⁻¹, $\langle g \rangle = 2.06 \pm 0.02$, and $D = -0.117 \pm 0.005$ cm⁻¹ while the EPR *D* value was $D = \pm 0.1043$ cm⁻¹ (ignoring the small rhombic term, *E*). *D*, of course, has both magnitude and sign,⁴⁵ and one can uniquely specify the *sign* of *D* from the magnetization data but not from the EPR experiment. By defining a susceptibility as $\chi^{-1} = H/M$, we show the best-fit curves for the Cu₂Cl₆²⁻ compounds in Figure 7 (parameters $2J$, $\langle g \rangle$, and *D* are listed in Table IV). It is unfortunate that none of the magnetic models available (eq 7, eq 14, or the Ising chain^{16d}) are particularly sensitive to the *J* value for $J > 0$; furthermore, the effect of additional terms such as zJ' or *D* tend to show similar net effects thus making a choice of models difficult.^{45,46}

Attempts to describe the magnetization of the mixed-halide compounds and the pure bromide complex with eq 14 were not very informative (see Table IV). In general, it was possible to obtain $2J$ values in reasonable agreement with those obtained from the dimer model with molecular field corrections (eq 7). However, the remaining parameters, $\langle g \rangle$ and *D*, either converged to unrealistically low values for $\langle g \rangle$ or yielded values for the zero-field splitting which were too high. The EPR spectra of the mixed-halogen compounds were consistent with a substantially larger *D*⁴⁸ than those of pure chloro complexes, but these spectra could not be assigned by assuming coaxial **g** and **D** tensors. This may be responsible in part for the inability of eq 14 to describe the magnetization data. Alternatively, a potentially more serious drawback results from the fact that in using eq 14 to fit the powder data with a reasonable number of parameters we have assumed that *g*_∥ and

Table IV. Bulk Magnetic Parameters

complex	dimer model with molecular field correction				dimer model with zero-field splitting			ref
	$2J$, cm ⁻¹	$\langle g \rangle$	Θ , K	$J'(z=4)$, cm ⁻¹	$2J$, cm ⁻¹	$\langle g \rangle$	D , cm ⁻¹	
(C ₆ H ₅) ₄ PCuCl ₃	80.2 ± 8.8	2.12 ± 0.005	-0.19 ± 0.13	-0.025	86.8 ± 10.0	2.08 ± 0.02	+0.317 ± 0.08	this work
(C ₆ H ₅) ₄ PCuCl ₂ Br	97.8 ± 12.0	2.08 ± 0.02	-0.21 ± 0.03	-0.027	112 ± 15	1.89 ± 0.04	-0.096 ± 0.010	this work
(C ₆ H ₅) ₄ PCuClBr ₂	94.4 ± 10	2.06 ± 0.02	-0.52	-0.068	97.8 (fixed)	2.07 ± 0.005	+1.01 ± 0.30	this work
(C ₆ H ₅) ₄ SbCuCl ₃	89.7 ± 14.4	2.09 ± 0.006	-0.17 ± 0.02	-0.022	97 ± 15	1.82 ± 0.2	+0.79 ± 0.2	this work
[(C ₆ H ₅) ₃ C ₃ H ₇ P]CuCl ₃	93 ± 11.0	2.09 ± 0.03	-0.11 ± 0.01	-0.014	94.4 (fixed)	1.99 ± 0.1	+1.46 ± 0.5	this work
(C ₆ H ₅) ₄ AsCuCl ₃	39	2.17			104 ± 12	2.06 ± 0.02	-0.117 ± 0.005	this work
(C ₆ H ₅) ₄ AsCuCl ₂ Br	45	2.12		-0.30	96 ± 13	2.08 ± 0.02	-0.202 ± 0.006	16c
(C ₆ H ₅) ₄ AsCuBr ₃	31	2.08		-0.41				16d (Ising model)
(C ₆ H ₅) ₄ PCuBr ₃	54.2 ± 9.0	2.08 ± 0.02	-0.99 ± 0.03	-0.13	58 ± 7	2.03 ± 0.02	+0.55 ± 0.02	16d (Ising model) this work

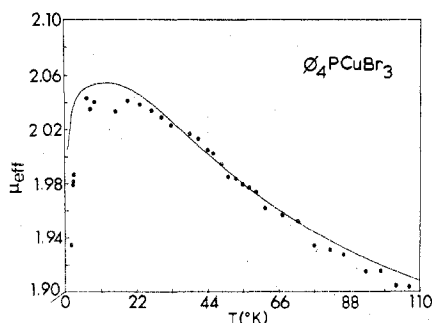


Figure 9. Effective magnetic moments vs. temperature for (C₆H₅)₄PCuBr₃. The solid curve is the best fit to eq 7.

g_{\perp} may be replaced by $\langle g \rangle$; this is known to be quite reasonable for Ni(II) complexes⁴⁶ but may not be valid for dimeric Cu(II) compounds. Of course, this unknown can readily be removed by single-crystal work once structural information has been obtained for these compounds. Thus, the simple dimer model with molecular field corrections apparently provides an adequate description of the interactions present in the mixed-halide and Cu₂Br₆²⁻ compounds (Figures 8 and 9 show the best fits to eq 7 for two examples).

Conclusion

The spectral data and magnetic properties of the dimeric halocuprates(II) with (C₆H₅)₄P⁺, (C₆H₅)₄Sb⁺, and (C₃H₇)(C₆H₅)₃P⁺ cations have revealed several interesting trends. From the magnitudes of the ferromagnetic exchange coupling constants ($2J$), electronic spectra and low-frequency infrared spectra suggest that all of the mixed halides of (C₆H₅)₄P⁺ have similar structures and hence may show preferential bridging by chlorides in the Cu₂Cl₇Br_{6-n}²⁻ species. Additionally, the ferromagnetic exchange in these compounds was found to be consistently larger than the previously studied (C₆H₅)₄As⁺ series.¹⁶ Finally, the EPR data of the two Cu₂Cl₆²⁻ ions with slightly different cations, (C₆H₅)₄Sb⁺ and (*n*-Pr)(C₆H₅)₃P⁺, exhibit the best resolved fully anisotropic triplet-state spectra of any polycrystalline complexes yet reported in the literature. It is rather surprising that the seemingly "insignificant" change of the size of the cation as in (C₆H₅)₄SbCuCl₃ should have such a profound effect on the electronic structure of the complex. Since it is rather likely that the larger rhombic character of the EPR of (C₆H₅)₄SbCuCl₃ results from a change in the immediate geometry about the Cu₂Cl₆²⁻ ion, it would be of considerable interest to compare the structure of this compound with its (C₆H₅)₄P⁺ and (C₆H₅)₄As⁺ analogues.

The agreement between the low-temperature magnetization and the EPR experiments strongly suggests that the deviations observed at very low temperatures are the result of *intracluster* interactions rather than *intercluster* exchange. This is es-

pecially true for the Cu₂Cl₆²⁻ species since the agreement of the zero-field splitting parameters obtained from EPR and magnetization experiments is excellent. However, the magnetization and EPR spectra of the mixed-halide and pure-bromide complexes of (C₆H₅)₄P⁺ could not be adequately described by the simplest model of intracluster interactions which assumes coaxial \mathbf{g} and \mathbf{D} tensors. The observed EPR spectra of these compounds are qualitatively consistent with a larger zero-field splitting which may arise from the combined effects of the anisotropic exchange and antisymmetric exchange. If the structure of the dimeric unit in the bromide-containing complexes is noncentrosymmetric, then the antisymmetric exchange will force a noncoaxial arrangement on the \mathbf{g} and \mathbf{D} tensors.⁵⁰ The fact that distinct though puzzling EPR spectra can be observed suggests that any intercluster exchange must be very small^{47,49} since only "doublet-like" spectra are seen in KCuCl₃, a compound in which the interdimer exchange is known to be rather strong.^{16d}

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Registry No. (C₆H₅)₄SbCuCl₃, 67597-60-8; (CH₃CH₂C-H₂)(C₆H₅)₃PCuCl₃, 67597-61-9; (C₆H₅)₄PCuCl₃, 50860-38-3; (C₆H₅)₄PCuBr₃, 67597-62-0; (C₆H₅)₄PCuBr₂Cl, 67577-03-1; (C₆H₅)₄PCuBrCl₂, 67577-05-3.

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Spin-Spin Coupling in the Nitrogen-Bridged Dimer Formed by Sodium (Glycylglycylglycinato)cuprate(II) Monohydrate

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The magnetic properties of the unique nitrogen-bridged dimer sodium (glycylglycylglycinato)cuprate(II) monohydrate ($\text{Na}_2[\text{Cu}(\text{ggg})\text{H}_2\text{O}]_2$) have been measured as a function of temperature (1.6–160 K) and magnetic field strength (10–50 kOe). The data indicate that the copper(II) ions are exchange coupled with the exchange coupling constant, J , being approximately -1.2 cm^{-1} . In addition, there are extensive intercluster interactions which are sensitive to the strength of the applied field and vary from -0.30 to -0.63 cm^{-1} (for $Z' = 4$). The EPR results indicate that an upper limit for the zero-field splitting of the triplet state is approximately $|D| = 0.27 \text{ cm}^{-1}$. The intra- and intercluster superexchange pathways are postulated from the available crystallographic data.

Introduction

Since copper(II) ions are widely distributed in biological systems,¹⁻⁴ a significant amount of current research has centered around the search for relatively simple copper(II) complexes which may display some of the properties of the metalloproteins.⁵⁻⁸ At least several native copper-containing proteins are known to contain more than one copper ion per enzyme unit.^{1,5,8} Furthermore, there is growing experimental evidence that suggests there may be cluster formation among copper(II) ions within these macromolecules. Since copper(II) ions are widely known to exist in small exchange-coupled clusters in "normal complexes", dimeric complexes of copper(II) with small peptides are of considerable interest. The properties of sodium (glycylglycylglycinato)cuprate(II) monohydrate, $\text{Na}_2[\text{Cu}(\text{ggg})\text{H}_2\text{O}]_2$, are of interest in this regard since Freeman et al.¹¹ have shown that the structure of this compound consists of dimeric clusters of copper(II) ions. Also, this compound is the only reported copper(II) dimer known to be bridged by nitrogen atoms. Results of spectral and magnetic studies on this unusual dimeric cluster are reported in this paper.

Experimental Section

Preparation of $\text{Na}_2[\text{Cu}(\text{ggg})\text{H}_2\text{O}]_2$. The preparations described in the literature^{11,12} were not adequate for our work, and, therefore, the procedure that we used is described in detail here.

Copper(II) chloride dihydrate was obtained from J. T. Baker Chemical Co. (ACS reagent grade) and used without further purification. Triglycine was obtained from Aldrich Chemical Co. and also used without additional purification.

To a stirred solution of 0.91 g (5 mmol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 75 mL of distilled water was added 0.99 g (5 mmol) of solid triglycine. The resulting light blue solution was stirred for several minutes and then filtered. The pH of this mixture was about 3.2 (Corning Model 7 pH meter). The pH of this mixture was then carefully adjusted to 9.3 by titration with 0.1 N NaOH. At this point the solution was deep bluish purple. The solution was then covered with Parafilm and allowed to evaporate slowly in a desiccator over solid NaOH. The pH of the mixture was checked periodically and readjusted when necessary. Crystals grew slowly over a period of several weeks, and the dark bluish purple prisms showed the morphology found earlier.¹¹ Anal. Calcd for $\text{Na}_2[\text{Cu}(\text{C}_6\text{H}_9\text{N}_3\text{O}_4)_2 \cdot \text{H}_2\text{O}]_2$: C, 24.79; H, 3.47; Cu, 21.86. Found: C, 24.41, 24.20; H, 3.50, 3.50; Cu, 21.28, 21.19. Carbon and hydrogen duplicate analyses were performed by Integral Microanalytical Laboratories, Inc. (Raleigh, N.C.). Copper analyses were determined by EDTA titrations using a SNAZOX indicator.¹³

Physical Measurements. Magnetization measurements at constant applied field (isoelectric) and susceptibility experiments (1.6–160 K) were carried out on a PAR Model 155 vibrating-sample magnetometer (VSM) operating at a field strength of 10 kOe. Temperatures were measured with a calibrated GaAs diode using techniques described in detail elsewhere.¹⁴ High-field isothermal magnetization measurements were obtained on a PAR Model 150-A VSM equipped with a Westinghouse superconducting solenoid capable of attaining 50 kOe.