nation number, and $\beta = \exp(-\Delta A/RT)$, where ΔA defines the energy of ion pair-formation, by

$$K_1 = Z(\beta - 1) \qquad (6)$$

As the plot of log γ *vs.* R_{KX} shows no dependence on $(R_{KX})^2$, we may deduce that $K_2 \simeq K_1/2$. The deviations from a straight line which could be observed in each case at high values of R_{KX} were related to the appearance of AgX liquid and a slight evaporation of this compound which was much more pronounced for AgI than for AgBr. Thus, these deviations from a straight line are artifacts not related to association in solution. The values of K_2 and K_{12} are also shown in Table I.

Assuming a value of $Z = 4$, *i.e.*, the coordination number for sulfates in the solid state, we calculated the corresponding association energies. A crude comparison with the values derived from the model proposed by Flood and co-workers may also be made. Considering the equilibrium

$$^1/_2Ag_2SO_4 + KX \rightleftharpoons AgX + {}^1/_2K_2SO_4$$

and using the data of Table II,[13] we calculated the value of $\Delta A \cong \Delta H/2$, where ΔH designates the enthalpy change for the above reaction, assuming that the sums of the heat capacities of the reactants and products are the same. The two sets of values are also shown in Table I, and, considering the assumptions made, the agreement is satisfactory.

TABLE II

THERMODYNAMIC DATA FOR CALCULATION OF ΔH^{13}

Compd	Heat of formation of solid, ΔH_{298}, kcal/mole	Heat of fusion, ΔH_f, kcal/mole
K_2SO_4	−342.66	10.7
Ag_2SO_4	−170.50	5.9
AgBr	−23.78	2.18
AgCl	−30.36	3.16
AgI	−14.91	3.72
KBr	−93.73	7
KCl	−104.17	6.1
KI	−78.31	(8)[a]

[a] Estimated value.

Conclusions

The association constants for silver with bromide and iodide ions in sulfate melts have been calculated. Including the results of Woolner and Hill for the chloride, the values of K_1 follow the general trend $K_{1AgI} > K_{1AgBr} > K_{1AgCl}$ observed for these salts with other solvents.

However, the temperature dependence for these association constants is not correctly described by the quasi-lattice model, which is strictly valid for mixtures containing only monovalent monatomic ions. This indicates that the entropy of association in the sulfate melt contains contributions in addition to the configurational entropy of association calculated from the quasi-lattice theory.

Acknowledgments.—We express appreciation to Dr. Milton Blander of North American Aviation for many fruitful discussions and for suggesting this work and to NATO for a postdoctoral fellowship.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
WASHINGTON STATE UNIVERSITY, PULLMAN, WASHINGTON 99163

The Electronic Absorption Spectra of Monomeric Copper(II) Chloride Species and the Electron Spin Resonance Spectrum of the Square-Planar $CuCl_4^{2-}$ Ion

BY ROGER D. WILLETT, O. L. LILES, JR.,[1] AND CHRISTIAN MICHELSON[2]

Received October 8, 1966

The electronic absorption spectra of several monomeric copper(II) chloride species have been measured in the solid state. In both the square-planar and tetrahedral species, the positions of the charge-transfer bands are quite similar. It is found that the position of the absorption band for the d–d transitions is critical in distinguishing between these two possible geometries. This band occurs at 12,800 cm^{-1} in the square-planar species while it is located in the 5500–9000-cm^{-1} range in the tetrahedral species, the exact value of the maximum depending on the amount of distortion in the latter. At the low temperature, a phase transition occurs in the square-planar complexes, changing from a light yellow to a pale green. This involves a change in surroundings of the square-planar ion so that the symmetry of the complex changes from D_{4h} to C_{4v}. Spectral studies indicate only slight changes (<500 cm^{-1}) in the positions of the major absorption bands. The esr spectra of single crystals of the square-planar ions were investigated. Analysis of these data indicates that approximately 50% of the unpaired electron is delocalized onto the ligand.

Introduction

Recently the study of the structure and spectra of copper(II) halide complexes has received considerable attention again. The existence of the distorted tetrahedral $CuCl_4^{2-}$ ion has been known for some time in solids such as Cs_2CuCl_4.[3] The spectra of this com-

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(1) Taken in part from the M.S. thesis of O. L. Liles, Jr., Washington State University, Pullman, Wash., Aug 1966.

(2) Undergraduate NSF recipient.

(3) L. Helmholz and R. F. Kruh, *J. Am. Chem. Soc.*, **74**, 1176 (1952).

pound[4,5] and of the isomorphous bromide salt[6] have been analyzed in detail. The bonding has been theoretically studied[7] and recently a detailed esr study[8] has elucidated details of the antibonding molecular orbitals. This model has been used to interpret the spectra of copper chloride complexes in various solvents.[9-12] Recently, however, in this laboratory, the existence of a square-planar $CuCl_4^{2-}$ ion has been shown in the yellow complexes $(NH_4)_2CuCl_4$ and $(C_2H_5NH_3)_2CuCl_4$.[13-15] These compounds are thermochromic, changing to a pale green at low temperature.

The Cu–Cl framework present in the structure of $(NH_4)_2CuCl_4$ is illustrated in Figure 1. Adjacent $CuCl_4^{2-}$ ions are arranged so as to give each copper(II) ion a pseudo-octahedral coordination. In reality, the interionic Cu–Cl distance of 2.79 A (2.98 A in $(C_2H_5NH_3)_2CuCl_4$[14]) is so long that no covalent bonding can be considered to be present. Estimates of the d_{z^2}–3pσ overlap integral (R = 2.98 A) indicate it has a value of less than 0.01 and that it is less than 10% of the $d_{x^2-y^2}$–3pσ overlap integral (R = 2.30 A). In addition, a calculation of the interionic Cu–Cl distance based on packing considerations indicates that a distance of 2.77 A is anticipated if this distance is determined by van der Waals interactions between chlorine atoms. Thus these compounds represent the first set of thoroughly documented square-planar $CuCl_4^{2-}$ ions. This will be further confirmed by the spectral and esr data presented in this paper although the thermochromic properties of these compounds (*vide infra*) indicate that some ionic interactions between the square-planar species do exist. It will be shown that the thermochromic change involves a rearrangement of the $CuCl_4^{2-}$ ions with respect to each other so that some of the long Cu–Cl interactions are broken.

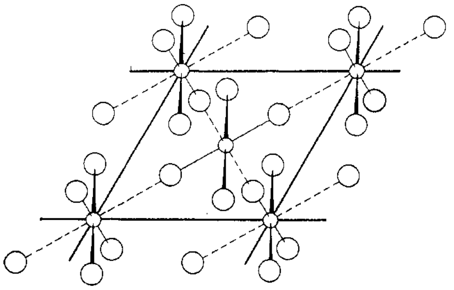

Figure 1.—Illustration of the arrangement of $CuCl_4^{2-}$ ions in $(NH_4)_2CuCl_4$.

Because of the unusual opportunity to study a simple metal–ligand system in a variety of coordination geometries, a study of several monomeric copper(II) chloride complexes was undertaken. Results of spectral studies of several tetrahedral and square complexes and of an esr investigation of the square-planar complex are reported here. In addition, the spectral properties of the thermochromic transitions are reported. Details of the spectral properties of polymeric copper chloride species will be published in a subsequent paper.

Experimental Section

Preparation of Compounds.—The preparations of all of the compounds studied have been reported by Remy and Laves.[16] The compounds in this study include $(CH_3NH_3)_2CuCl_4$, $(C_2H_5NH_3)_2CuCl_4$, $[(CH_3)_2NH_2]_2CuCl_4$, $[(CH_3)_2CHNH_3]_2CuCl_4$, and $[(CH_3)_4N]_2CuCl_4$.

Electronic Spectra.—The spectra was obtained over the range of 2000–25,000 A on a Cary Model 14. When single crystals were used, they were mounted on black paper in the sample compartment. A piece of black paper with a hole equal to the crystal size was placed in the reference compartment. When mulls were used, a thin layer of the mull was placed between two quartz plates, each 1/8 in. thick. Unfortunately the crystal structures and morphology of the square-planar compounds make it impossible to undertake single-crystal spectral investigations with polarized light since the extremely thin crystals had the C_4 axes of adjacent $CuCl_4^{2-}$ ions oriented at right angles to each other.

The spectra of $(CH_3NH_3)_2CuCl_4$ and $(C_2H_5NH_3)_2CuCl_4$ in their low-temperature thermochromic forms were obtained on the Cary 14 through the use of a special cold-temperature cell. This is a block metal frame mounted on the end of a cold finger. The cold finger fits into a glass T, the ends of which are quartz plates. The metal frame is adjusted so that crystals mounted in the frame may have spectra taken by passing the beam of light through the quartz plates and the center of the opening of the metal frame. The following symbols are used in Tables I–III to indicate the general form of the spectrum: "sm" indicates a sharp distinct maximum; "b" indicates a broad band—probably containing more than one transition, the number given is the maximum point and not necessarily the center of the band; "sh" indicates a shoulder.

Table I

Spectra (cm^{-1}) of the Tetrahedral $CuCl_4^{2-}$ Species

		Cs_2CuCl_4[a]	$((CH_3)_4N)_2CuCl_4$	$((CH_3)_2NH_2)$-$CuCl_4$
Charge transfer				
σ	$a_1 \longrightarrow b_2$	41,500	43,500 sm	44,500 sm
	$a_1(\pi) \longrightarrow b_2$	34,500		
	$e(\sigma, \pi) \longrightarrow b_2$	34,000	36,000 b	34,500 b
π	$e(\pi, \sigma) \longrightarrow b_2$	29,000		
	$e(N) \longrightarrow b_2$	24,800		
	$a_2(N) \longrightarrow b_2$	23,000	25,000 sm	22,000 sm
d–d transition				
	$d_{z^2} \longrightarrow d_{xy}$	9,000	9,000 b	9,000 b
	$d_{x^2-y^2} \longrightarrow d_{xy}$	7,900	6,000 b	
	$d_{xz} \longrightarrow d_{xy}$	5,500		6,000 b
	$d_{yz} \longrightarrow d_{xy}$	4,800		

[a] Reference 4.

Electron Spin Resonance Spectra.—For the esr spectra, small single crystals of the appropriate compound were mounted inside quartz tubes with styrofoam mounts. The crystals were aligned optically prior to insertion into the cavity and then spectra were recorded every 10° while rotating about the appropriate

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(7) (a) G. Felsenfeld, *Proc. Roy. Soc.* (London), **A236**, 506 (1956); (b) L. L. Lohr, Jr., and W. M. Lipscomb, *Inorg. Chem.*, **2**, 911 (1963); (c) P. Ros and G. C. A. Schuit, *Theoret. Chim. Acta*, **4**, 1 (1966).

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(13) R. D. Willett, *ibid.*, **41**, 2243 (1964).

(14) J. P. Steadman and R. D. Willett, submitted for publication.

(15) The corresponding complex with ethylenediamine dihydrochloride, $[(CH_2NH_3)_2]CuCl_4$, has been prepared by B. Zaslow, Arizona State University, private communication.

(16) H. Remy and G. Laves, *Ber.*, **66**, 401 (1933).

TABLE II

SPECTRA (CM^{-1}) OF THE SQUARE-PLANAR $CuCl_4^{2-}$ SPECIES

	$Pt(NH_3)_4$-$CuCl_4$[a]	$(CH_3NH_3)_2CuCl_4$	$(C_2H_5NH_3)_2CuCl_4$
Charge transfer			
$\sigma \longrightarrow d_{x^2-y^2}$		49,000 sm	49,000 sm
		38,500 b, sh	38,500 b, sh
$\pi \longrightarrow d_{x^2-y^2}$		33,300 b	33,300 b
$\pi(N) \longrightarrow d_{x^2-y^2}$	24,900	24,000 sm	24,000 sm
d–d transition			
$d_{xz,yz} \longrightarrow d_{x^2-y^2}$	14,300	13,000 b	12,800 b
$d_{xy} \longrightarrow d_{x^2-y^2}$	13,100		
$d_{z^2} \longrightarrow d_{x^2-y^2}$	10,900	10,700 sh	10,500 sh

[a] Reference 17.

TABLE III

SPECTRA (CM^{-1}) OF THE LOW-TEMPERATURE THERMOCHROMIC FORM

	$((CH_3)_2CHNH_3)_2$-$CuCl_4$	$(CH_3NH_3)_2CuCl_4$	$(C_2H_5NH_3)_2CuCl_4$
	48,000 sm	50,000 sm	51,000 sm
σ transition	44,500 sh	41,500 b, sh	41,500 b, sh
	33,300 b	30,000 b	29,500 b
π transition	24,500 sm	24,500 sm	24,500 sm
d–d transition	13,300 b	13,100 b	13,100 b

axis. A single broad resonance was observed in each instance, with no hyperfine interaction resolved. For $((CH_3)_2CHNH_3)_2$-$CuCl_4$ two resonance signals were observed due to the orientation of the copper chloride complexes within the crystal. Because of the phase transitions, no attempt was made to run spectra at temperatures below room temperature. The resonances had half-widths ranging from 75 to 100 gauss, depending on the orientation of the crystal. The results are summarized in Table IV. The relative narrowness of the resonances, plus the existence of only one signal even though there are two magnetically inequivalent ions in the crystal, indicates the presence of relatively strong exchange interactions.

TABLE IV

ESR RESULTS

Compound	Orientation[a]	g(max)[b]	g(min)[b]	$g_{\parallel}$	$g_{\perp}$
$(CH_3NH_3)_2CuCl_4$	001	2.143 (parallel to 100)	2.046 (parallel to 010)	2.238	2.046
$(CH_3NH_3)_2CuCl_4$	011	2.141 (parallel to 100)	2.047 (parallel to 011)	2.235	2.047
$(C_2H_5NH_3)_2CuCl_4$	011	2.137 (parallel to 100)	2.044 (parallel to 011)	2.230	2.044
$[(CH_3)_2CHNH_3]_2CuCl_4$	100	2.175	2.047	...	...

[a] Axis about which crystal was rotated is given. [b] Axis parallel to magnetic field is given.

Discussion of Electronic Spectra of Solids

Tetrahedral Species.—The qualitative molecular orbital diagram for the tetrahedral copper(II) chloride species has been given by Ferguson[4] and the assignments, made on the spectra of Cs_2CuCl_4, are shown in Table I. Next to it are listed the spectra of two other compounds which were examined. Those areas listed as broad bands in our data were resolved by Ferguson into individual transitions through the use of polarized spectra.

The region from 6000 to 9000 cm^{-1} is one large band with slight maxima at the indicated numbers. The numbers listed below 5000 cm^{-1} are due to absorption by the organic ligands. These are probably covering the d–d transition which Ferguson identified.

A major reason for asserting that the anions of these compounds are distorted tetrahedrons like Cs_2CuCl_4 is their relative equal positioning of the large band centered in the 6000–7000-cm^{-1} region. This band has been shown to be caused by transitions within the d orbitals. It is larger and shifted to a longer wavelength than are the d–d bands of the other geometric species (*vide infra*).

Square-Planar Species.—The qualitative MO diagram of square-planar copper(II) chloride species is shown in Figure 2. To the left are located the metal orbitals, to the right are located the ligand orbitals, and in the center are shown the MO's for the square-planar species. The ordering of the primarily 3d orbitals is difficult to predict for the square-planar species. It is easy to show that the highest orbital is the $2b_{1g}$ antibonding MO ($d_{x^2-y^2}$) but beyond that there is little agreement. Hatfield and Piper[17] have made crystal field calculations and obtained the ordering $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz,yz}$. On the other hand, Wolfsberg–Helmholz calculations by Schuit and Ros[7c] place the d_{z^2} orbital lowest. An extended Hückel MO treatment by Lohr and Lipscomb[7b] gave two different orderings dependent upon the involvement of the Cu 4s and 4p orbitals. This is expected since the 4s and $3d_{z^2}$ orbitals belong to the same irreducible representation in the point group D_{4h}. Thus mixing of these two metal orbitals can occur causing simple crystal field calculations to give incorrect answers. All three of the above calculations indicate that the three lowest antibonding levels ($2e_g$, $2a_{1g}$, $2b_{2g}$) all lie close together in energy. Howald and Keeton[18] have made "point bond" calculations but unfortunately fail to state the ordering they obtained.

Thus a series of three d–d transitions is expected in the square-planar complex. Unfortunately only a broad, rather featureless envelope was observed with a maximum at 12,800 cm^{-1} and a shoulder near 10,500 cm^{-1}. Because of the peculiarities of the crystal structure and morphology indicated previously, it was not possible to decipher further the enigma by the use of polarized spectra. The extinction coefficient for this band is approximately 20, in accord with the fact that the transitions are only vibronically allowed. This is a factor of 5 smaller than the extinction coefficient for the corresponding band of the tetrahedral species. It should be noted that the observed wavelength is considerably shorter than that predicted by Ros and Schuit[7c] (9300 cm^{-1}) and longer than that predicted by Lohr and Lipscomb[7b] ($\sim$30,000 cm^{-1}).

The assignment of the more intense charge-transfer

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(17) W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, **3**, 841 (1964). As pointed out by W. E. H., the reported order was a typographical error.

(18) R. A. Howald and D. P. Keeton, *Spectrochim. Acta*, **22**, 1211 (1966).

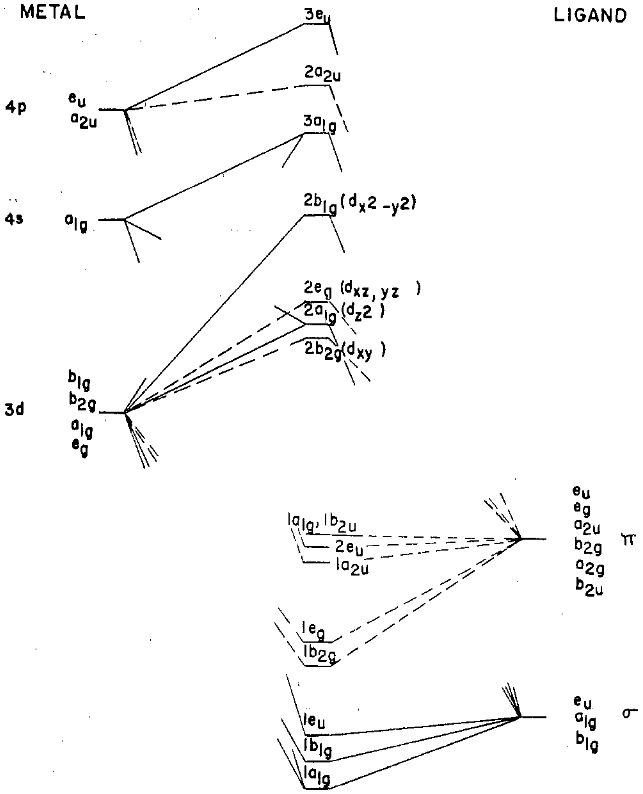

Figure 2.—Molecular orbital correlation diagram for the square-planar $CuCl_4^{2-}$ ion.

bands is made by analogy to the spectrum of the distorted tetrahedral $CuCl_4^{2-}$ ion. These are transitions from primarily ligand orbitals (bonding or nonbonding) to the highest antibonding d orbital. It is felt that the position of these bands should be relatively insensitive to actual coordination geometry as long as there is no drastic change in the nature of the bonding. Indeed it is found that there is little shift in the position of the charge-transfer bands in going from the tetrahedral to the square-planar configuration. It does appear that the only major difference between the spectra of the tetrahedral and square-planar species is the position of the d–d band. As expected, this band appears at lower energy (6000–9000 cm^{-1}) in the tetrahedral species than in the square-planar species (10,000–13,000 cm^{-1}).

Thermochromic Square-Planar Species.—It has been noted that several of the square-planar $CuCl_4^{2-}$ complexes exhibit thermochromism in the solid state.[13–15] All three of the square-planar compounds examined in this study exhibited this property. The compounds crystallize as flat, yellow sheets above the transition temperature and as long, light green needles in the low-temperature phase. The transition temperature is near −40° for $(CH_3NH_3)_2CuCl_4$ and $(C_2H_5NH_3)_2CuCl_4$ but occurs at about +60° for $((CH_3)_2CHNH_3)_2CuCl_4$.[16] A dta study of $(C_2H_5NH_3)_2CuCl_4$[14] showed that the transition was very broad, covering a temperature range of nearly 50°.

The structural properties of both phases of all of the compounds are not known in detail. The high-temperature phase is presumed to be the same for all of them, containing the square-planar $CuCl_4^{2-}$ ion previously discussed. A structural investigation of the low-temperature phase of $((CH_3)_2CHNH_3)_2CuCl_4$ is currently underway in this laboratory. It appears that for two-thirds of the $CuCl_4^{2-}$ ions the phase change rearranges the immediate neighbors so that there is only one other $CuCl_4^{2-}$ ion in contact with it. This gives these copper atoms a square-pyramidal configuration but again with one atom outside the coordination sphere. The other third of the copper atoms remain unchanged in environment. Again, because of the similarity between physical properties, it is assumed that the other two compounds have the same structure in the low-temperature phase. Thus it appears that in the light green complexes we are dealing, at least in part, with copper in a square-pyramidal coordination.[19]

In general, as seen by comparison of Tables II and III, there are very slight changes in the positions of the absorption bands between the spectra of the two phases. In particular there is very little variation in the positions of the d–d transition, a small shift to shorter wavelength. This type of change has been observed to occur for a wide variety of square-planar copper complexes with organic ligands when molecules move in and out of the fifth and sixth coordination sites.[20] This substantiates the treatment of both the square-bipyramidal and square-pyramidal configurations as simple square-planar ions. For the charge-transfer bands, the largest charge is in the second band which increases in wavelength from 30,000 to 33,000 cm^{-1}. Further studies of the properties of these and other thermochromic phase transitions are underway.

Esr Spectra.—As indicated in Table IV, examination of the esr spectra of single crystals of the square-planar complexes gave g values that varied from 2.044 to 2.143, depending upon the orientation of the crystal. With the magnetic field applied perpendicularly to the a axis, the field is perpendicular to the fourfold axes of all of the $CuCl_4^{2-}$ ions. Thus $g_\perp$ can be obtained directly from the g(min) values given in column 4 of Table IV. With the magnetic field parallel to the a axis, half of the $CuCl_4^{2-}$ ions are oriented with their axes parallel to the field and half with their axes perpendicular to the field. Hence, $g(\max) = {}^1/_2(g_\parallel + g_\perp)$. In this manner the values of $g_\parallel = 2.234$ and $g_\perp = 2.046$ are obtained.

The crystal field spin Hamiltonian for a square-planar spin ${}^1/_2$ ion gives expressions for $g_\parallel$ and $g_\perp$

$$g_\parallel = 2.0023\left(1 - \frac{4\lambda}{E_{B_{2g}} - E_{B_{1g}}}\right)$$

$$g_\perp = 2.0023\left(1 - \frac{\lambda}{E_{E_g} - E_{B_{1g}}}\right)$$

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[19] These conclusions are substantiated by the behavior of complexes containing the $Cu_2Cl_6^{2-}$ dimer. The complexes are dichroic, appearing red when examined with polarized light parallel to the copper–copper direction. Perpendicular to this direction, the color depends on the nature of the coordination sphere of the dimer. In $LiCuCl_3 \cdot 2H_2O$ and $KCuCl_3$, where copper has a distorted (4 + 2) octahedral coordination, the color is yellow. In $[(CH_3)_2NH_2]CuCl_3$, where each copper has a square-pyramidal coordination, the color is green.

[20] J. M. Waters and T. N. Waters, *J. Chem. Soc.*, 2489 (1964).

Using the free-ion spin–orbit coupling constant of -828 cm^{-1} and assuming $E_{E_g} - E_{B_{1g}} \approx 12{,}800$ cm^{-1} and $E_{B_{2g}} - E_{B_{1g}} \approx 10{,}500$ cm^{-1}, values of $g_{||}$ and $g_{\perp}$ equal to 2.631 and 2.130 are obtained, respectively. These values are too large. However, covalent bonding will cause a reduction in the spin–orbit coupling constant. Using a spin–orbit coupling constant of -305 cm^{-1}, a good agreement was obtained with the experimental values, $g_{||}(\text{calcd}) = 2.233$ and $g_{\perp}(\text{calcd}) = 2.048$. The large reduction of the spin–orbit coupling constant from the free-atom value of -828 cm^{-1} indicates considerable covalent bonding. This reduction is larger than that found by Hatfield and Piper[17] in the trigonal-bipyramidal ion and the ordering of energy levels is in contrast to the ordering predicted by their crystal field calculations. However the esr results do not give conclusive evidence with respect to the order of the levels since the correct inclusion of covalent bonding will introduce covalency factors into the equations for $g_{\perp}$ and $g_{||}$. An attempt which was made to reproduce the g values using the molecular orbital parameters obtained by Ros and Schuit[7c] gave discouraging results with $g_{||}(\text{calcd}) = 2.338$ and $g_{\perp}(\text{calcd}) = 2.068$ when both $E_{B_{1g}} - E_{B_{2g}}$ and $E_{B_{1g}} - E_{E_g}$ were assumed to be equal to 12,800 cm^{-1}. Poorer agreement was obtained if either transition energy was assumed to be equal to 10,500 cm^{-1}.

Since it was not possible to resolve the hyperfine interactions, owing to the effects of dipolar broadening and exchange narrowing, it was not possible to use the procedure of Maki and McGarvey[21] to obtain values of the molecular orbital parameters for the antibonding molecular orbitals. The equations for the parameters in the spin Hamiltonian in this case reduce to two equations in three unknowns and a unique solution obviously cannot be obtained. Solutions were attempted restricting the value of one of the parameters within reasonable limits. These solutions indicated that approximately 50% of the spin density of the σ (b_{1g}) electrons was delocalized onto the ligands while only around 20% of the spin density of the π electrons was delocalized. This amount of delocalization for the σ electron is unexpectedly high although an analysis of the hydrogen nmr data from $CuCl_2 \cdot 2H_2O$ in the antiferromagnetic state also indicated about 50% delocalization onto the chlorine atoms.[22] It should be noted that this amount of delocalization is consistent with the large reduction of λ from its free-ion value.

Summary

The electronic absorption spectrum of the square-planar $CuCl_4^{2-}$ species has been characterized in detail over the range of 5000–50,000 cm^{-1} for the first time. It is found that all three of the expected d–d transitions are located in one absorption band whose maximum is located at 12,800 cm^{-1}. Comparison of the charge-transfer spectra of several complexes of both the square-planar and the distorted tetrahedral $CuCl_4^{2-}$ ions revealed no significant shifts in any of the charge-transfer bands. However the d–d transitions in the distorted tetrahedral species are shifted out into the near-infrared region, covering the range 6000–9000 cm^{-1}. Thus, in attempting to determine the coordination geometry of the copper(II) halide species by spectral means, it is necessary to focus attention on the position of the d–d transitions. In the square-planar complexes studied, weak but significant interionic forces occur as exemplified by their thermochromic properties.

Acknowledgments.—This work was supported by the Washington State University Research Committee and by the Petroleum Research Fund, Grant No. 1592-A3.

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