

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99163, and Battelle-Northwest, Richland, Washington 99352

Thermochromism in Copper(II) Chlorides. Coordination Geometry Changes in CuCl_4^{2-} Anions

R. D. WILLETT,* J. A. HAUGEN, J. LEBSACK, and J. MORREY

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Two types of thermochromic copper(II) chloride salts are reported. In $[(\text{C}_2\text{H}_5)_2\text{NH}_2]_2\text{CuCl}_4$ and $[(\text{CH}_3)_2\text{CHNH}_2]_2\text{CuCl}_4$, distinct phase transitions occur, as evidenced by dta, ir, and nmr studies, which involve a change in coordination geometry. In $[(\text{CH}_3)_2\text{NH}_2]_3\text{CuCl}_5$ and $(\text{RNH}_3)_2\text{CuCl}_4$ salts, the thermochromism results from the variation in the line widths of the electronic absorption bands with temperature.

Introduction

An intriguing feature of many copper(II) chloride complexes is their thermochromic behavior in the solid state. Typically, these compounds are yellow to yellow-orange at room temperature (or slightly above) and turn pale green upon cooling. This ability to change color with a change in temperature is unusual among inorganic compounds but not unknown.¹ This is a phenomenon which naturally attracts a coordination chemist, because of the relationship between color and structure in complex ions. We have investigated a number of copper(II) chloride salts of organic ammonium ions over the past several years and report our results in this paper. We have restricted our study to anhydrous complexes in which the color changes are reversible.

Two basic types of thermochromic behavior have been observed. For one class, experimental evidence points to the existence of a phase transition in which there is a change in the coordination geometry around the copper ion. This causes a shift in the energy of the electronic transitions that lie in the visible region and hence are responsible for the thermochromic effect. The driving force for these changes is associated with changes in the $\text{N-H} \cdots \text{Cl}$ hydrogen-bonding scheme caused by the thermal motion of the organic cation. For the other class of compound, which is much less interesting chemically, the thermochromism is associated only with the temperature dependence of the line widths of the electronic absorption bands. This, presumably, is due to the presence of vibronic coupling.

Experimental Section

The method of preparation of most of the compounds studied was reported by Remy and Laves.² In general, the method simply consists of mixing stoichiometric amounts of the appropriate amine hydrochloride and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in aqueous or alcoholic solution and allowing the solution to evaporate until precipitation or crystallization occurs. Analyses of pertinent compounds are given in Table I.

The electronic spectra were recorded on a Cary Model 14-R spectrometer. Temperature control was obtained with a special dewar flask with a range of 78–373°K or with an Air Products cryostat with range of 4.5–300°K. Samples were prepared by melting the compound between quartz or glass plates or by allowing a solution of the compound to crystallize between the plates.

The far-ir spectra were recorded on a Perkin-Elmer Model 521 (down to 200 cm^{-1}) or a Beckman Model 11 (down to 33 cm^{-1}) at room temperature. Samples were petroleum gel mulls spread between NaCl or polyethylene plates.

Differential thermal analysis data were collected on a Perkin-Elmer Model DSC-1B differential scanning calorimeter with a temperature range of 173–773°K. Broad-line nmr data were collected at 16 MHz with a locally constructed instrument.

* To whom correspondence should be addressed at Washington State University.

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Structural and Spectral Correlations in Discrete CuCl_4^{2-} Species

The crystal structure analyses on a large number of salts which contain discrete CuCl_4^{2-} ions have been reported in the literature.^{3–9} These are listed in Table II along with certain pertinent structural parameters. When no possibility of hydrogen bonding exists between the cation and the CuCl_4^{2-} anion, the trans Cl–Cu–Cl angle is always less than 132°. When $\text{N-H} \cdots \text{Cl}$ hydrogen bonding exists, the trans Cl–Cu–Cl angle is greater than 132° and becomes larger as the extent of hydrogen bonding increases. Indeed, for $(\text{RNH}_3)_2\text{CuCl}_4$ structures,¹⁰ the trans Cl–Cu–Cl angle becomes so large that the ion can assume its familiar 4 + 1 or 4 + 2 coordination. Also, in $\text{Pt}(\text{NH}_3)_4\text{CuCl}_4$, the CuCl_4^{2-} ion is apparently planar.¹¹

This behavior can be readily rationalized. Lohr and Lipscomb¹² have shown that no potential barrier exists in the potential surface for the CuCl_4^{2-} ion as it distorts from a tetrahedral geometry to a square-planar configuration. Indeed, the minimum in the surface depended upon the extent of Cu 4s and 4p participation in the bonding: with no 4s and 4p participation, crystal field stabilization dominated and the minimum occurred at the planar configuration (a trans Cl–Cu–Cl angle of 180°), and when they were included, ligand–ligand repulsions dominated and the minimum occurred well toward a tetrahedral structure at a trans Cl–Cu–Cl angle of 120°. Thus, hydrogen bonding, in effectively removing charge from the chlorine atoms, reduces the electrostatic repulsions between the chlorine atoms and allows the CuCl_4^{2-} ion to move toward a square-planar geometry.

The electronic absorption spectra have been recorded for only a limited number of salts which contain strictly four-coordinate CuCl_4^{2-} species. The spectra of Cs_2CuCl_4 ,¹³

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(13) J. Ferguson, *J. Chem. Phys.*, **40**, 11 (1964).

Table I. Analyses of Compounds

Compd	% Cu		% Cl		% C		% N		% H	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[(C_2H_5)_2NH_2]_2CuCl_4$	17.97	17.82	40.10	40.12	27.17	27.11	7.92		6.84	7.00
$[(CH_3)_2CHNH_2]_2CuCl_4$	27.63	27.80	46.24	46.33	15.69		6.09		4.35	
$[(CH_3)_2NH_2]_3CuCl_5$	16.78	16.69	46.80	46.85	19.00	19.21	11.09	11.06	6.33	6.26

Table II. N-Cl Hydrogen-Bonding Distances and $CuCl_4^{2-}$ Geometry

Compd	N-Cl, Å	Trans Cl-Cu-Cl (av), deg
$Cs_2CuCl_4^3$		124
$[(CH_3)_4N]_2CuCl_4^4$		128
$[C_{12}H_{14}N_2]CuCl_4^5$		129
$[(C_6H_5)_3NCH_3]_2CuCl_4^6$		132
$[(CH_3)_2NH_2]_3CuCl_4 \cdot Cl^7$	3.13, 3.24	136
$[(C_2H_5)_3NH]_2CuCl_4^8$	3.11	137
$(C_{13}H_{19}N_2OS)_2CuCl_4^9$	3.14, 3.14	143
$Pt(NH_3)_4CuCl_4^{11}$	Not known	180

$[C_6H_5CH_2N(CH_3)_3]_2CuCl_4^{14}$, $(C_6H_5)_4AsCuCl_3^{15}$ and $Pt(NH_3)_4CuCl_4^{11}$ have been reported in the literature and we have recorded the spectrum of $[(CH_3)_2NH_2]_3CuCl_5$ (henceforth $(DMA)_3CuCl_5$) as part of this study. The unpolarized d-d spectra of these salts at liquid nitrogen temperature are characterized by the presence of two strong and quite well-resolved absorption bands in the near-ir region. The energy of these bands¹⁶ (except for the $C_6H_5CH_2N(CH_3)_3^+$ salt¹⁷) is plotted as function of the trans Cl-Cu-Cl bond angle in Figure 1. As can be seen, a relatively smooth correlation between these two quantities is obtained. It thus appears that the geometry of the $CuCl_4^{2-}$ species present can be predicted with fair accuracy from the energy of the d-d bands at 77°K.

Results

Thermochromism of $[(C_2H_5)_2NH_2]_2CuCl_4$. This compound (henceforth $(DEA)_2CuCl_4$) provides the most striking example we have observed on the copper(II) chloride complexes of thermochromism involving a phase change. The compound forms bright green crystals at room temperature. When heated above 43°, the compound suddenly turns yellow. The color change is reversible, although supercooling occasionally occurs. Two preliminary reports on this salt have been given.¹⁸

The experimental evidence supports the interpretation of this thermochromic behavior as the result of a phase transition involving a change in coordination geometry. The dta data, given in Figure 2, show an endothermic peak initiating at 43° which is nearly as large as the peak at the melting point. In Figure 3, the near-ir spectral regions at temperatures immediately above and below the transition temperature are shown. As can be seen, the d-d transitions shift dramatically to longer wavelengths, indicating a pronounced change in coordination geometry. A pronounced shoulder at 4500 Å also appears on the charge-transfer band in the visible region. The spectrum of the low-temperature form is similar to the square-planar $CuCl_4^{2-}$ ion in $Pt(NH_3)_4CuCl_4$ while the high-temperature spectrum is typical of a com-

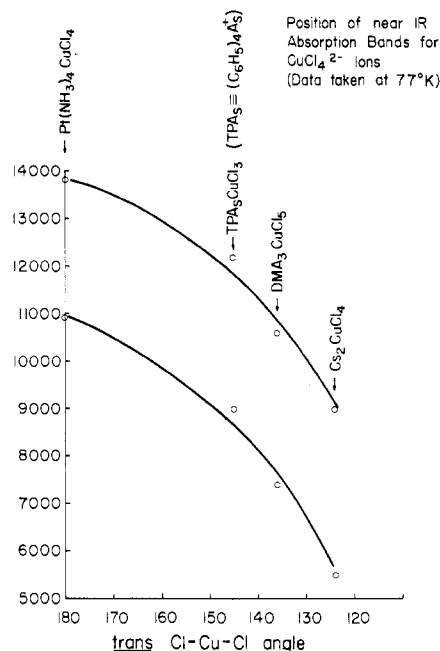


Figure 1. Correlation of $CuCl_4^{2-}$ geometry with observed d-d transition.

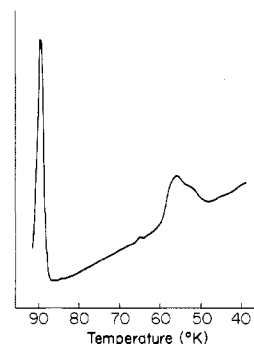


Figure 2. Differential thermal analysis data for $[(C_2H_5)_2NH_2]_2CuCl_4$.

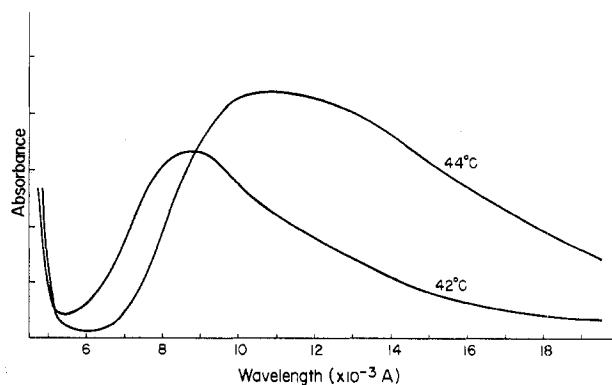


Figure 3. The d-d spectrum of the $CuCl_4^{2-}$ ion in $[(C_2H_5)_2NH_2]_2CuCl_4$ immediately above and below the phase transition.

pressed tetrahedral coordination (compare with Figure 7, *vide infra*).

(14) C. Furlani, E. Cervone, F. Calzona, and B. Balanza, *Theor. Chim. Acta*, **7**, 375 (1967).

(15) R. D. Willett and C. Chow, *Acta Crystallogr., Sect. B*, **30**, 207 (1974).

(16) Three transition energies are reported for $Pt(NH_3)_4CuCl_4$. The two high-frequency transitions are close together, and the average of those two was used to define the upper point for this compound.

(17) Inexplicably, the data for this salt do not fall on this plot.

(18) R. D. Willett, Symposium on Advances in Inorganic Stereochemistry, Banff, 1968; D. R. Hill and D. W. Smith, in press.

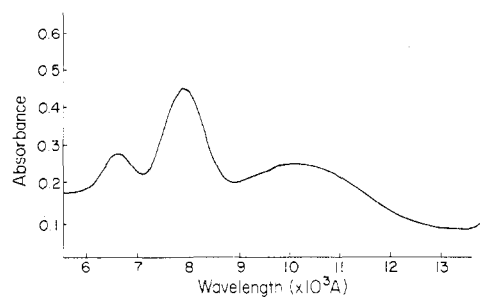


Figure 4. The d-d spectrum of the CuCl_4^{2-} ion in $[(\text{C}_2\text{H}_5)_2\text{NH}_2]_2\text{CuCl}_4$ at 9.2°K .

Assuming that no polymerization occurs, the geometry of the two forms can be predicted from the observed positions of the d-d transitions and Figure 1. The low-temperature form absorbs at 9900 and $12,900\text{ cm}^{-1}$ (plus a weak absorption at $15,300\text{ cm}^{-1}$) at 9.2°K . This is illustrated in Figure 4. Thus we predict trans Cl-Cu-Cl angles of $162 \pm 5^\circ$. The high-temperature spectrum has been fit to two gaussian bands at 7300 and $10,200\text{ cm}^{-1}$. This corresponds to trans Cl-Cu-Cl angles of $133 \pm 5^\circ$. Thus the thermochromic transition from the high-temperature (yellow) form to the low-temperature (green) form involves the compression of the CuCl_4^{2-} ion from a recognizably tetrahedral ion to an ion with distorted square-planar geometry. This then represents what is certainly a rarity in transition metal chemistry: a distinct difference in coordination geometry between two solid phases of the same compound.

Thermochromism of $[(\text{CH}_3)_2\text{CHNH}_3]_2\text{CuCl}_4$. This compound (henceforth $\text{IPA}_2\text{CuCl}_4$) was reported to be thermochromic in 1933 by Remy and Laves, who noted that the green crystals obtained at room temperature were yellow at 60° . Above that temperature, the compound crystallizes as flat yellow platelets. The crystal structure of the green needles obtained at room temperature has been determined.^{10b} Three chemically distinct CuCl_4^{2-} ions are found in the structure: one with rigorous planar geometry, one with a moderate tetrahedral distortion (the average trans Cl-Cu-Cl angle being 159°), and the third with a somewhat larger distortion (the average trans Cl-Cu-Cl angle being 152°). Through bridging with adjacent ions, the first type assumes an elongated "octahedral" coordination through bridging; the last two form pseudo five-coordinate species.

The dta results, shown in Figure 5, definitely indicate a first-order phase transition at 56° . Below this temperature, the d-d bands occur in the range $11,000$ – $13,000\text{ cm}^{-1}$.¹⁹ Above that temperature, the bands shift to shorter wavelengths, with the band maximum at $10,000\text{ cm}^{-1}$. This red shift is indicative again of a distortion toward tetrahedral geometry. The corresponding mixed halide, $\text{IPA}_2\text{CuCl}_3\text{Br}$, has an identical d-d spectrum, which is illustrated in Figure 6. The spectrum is almost identical with that observed in the high-temperature phase of $(\text{DEA})_2\text{CuCl}_4$. Thus, the high-temperature form of $(\text{DEA})_2\text{CuCl}_4$ and $(\text{IPA})_2\text{CuCl}_4$ must contain CuCl_4^{2-} ions of almost identical geometry. Again, the existence of a change in coordination geometry of the CuCl_4^{2-} ion during the phase transition is confirmed.

Compounds with No Structure Changes. In this section, the discussion will concentrate on $(\text{DMA})_3\text{CuCl}_5$, a compound where there is little or no evidence of a structural change associated with the thermochromism. Mention will also be made of the thermochromism of the class of com-

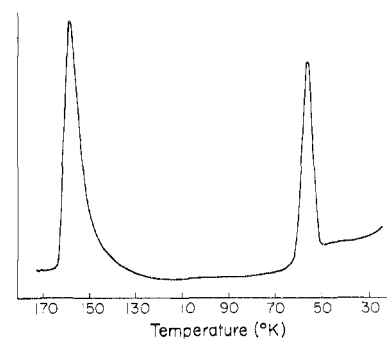


Figure 5. Differential thermal analysis data for $[(\text{CH}_3)_2\text{CHNH}_3]_2\text{CuCl}_4$.

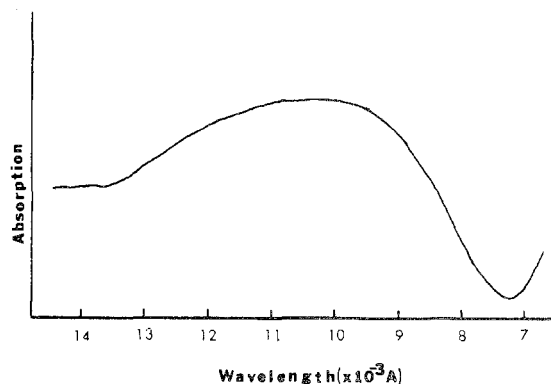


Figure 6. The d-d spectrum of the $\text{CuCl}_3\text{Br}^{2-}$ ion in $[(\text{CH}_3)_2\text{CHNH}_3]_2\text{CuCl}_3\text{Br}$.

pounds $(\text{RNH}_3)_2\text{CuCl}_4$, where $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$, etc. The thermochromism of these compounds involves a gradual change in color from gold to yellow to light green as the temperatures are lowered from 100° down to liquid nitrogen temperature.

The crystal structure of $(\text{DMA})_3\text{CuCl}_5$ has been determined at room temperature and contains discrete CuCl_4^{2-} ions. Each CuCl_4^{2-} ion has nearly D_{2d} symmetry with Cu-Cl distances of 2.230 (7) Å, trans Cl-Cu-Cl angles of 135.8 (5) $^\circ$, and cis Cl-Cu-Cl angles of 98.1 (7) $^\circ$. The crystal structure analysis revealed that one of the dimethylammonium ions and the remaining chloride ion are disordered.

A series of electronic absorption spectra in the near-ir region for $(\text{DMA})_3\text{CuCl}_5$ as a function of temperature are shown in Figure 7. As can be seen, the only variation in the spectrum as the temperature is lowered is a gradual but pronounced sharpening of the two resolved bands. A similar sharpening is observed in the charge-transfer bands at 4000 Å and below. The far-ir shows absorption bands at 80 and 130 cm^{-1} (Cu-Cl bending modes) as well as 230 and 295 cm^{-1} (Cu-Cl stretching modes). These are characteristic of a tetrahedral CuCl_4^{2-} species.²⁰ Thermal population of these vibrational levels provides a mechanism for this variation in line width and intensity *via* vibronic coupling.

Examination of the long-wavelength tail of the spectrum of 77°K leads one to believe that a resolved band is contained therein, and, indeed, this is confirmed by analytical curve fitting. If the structure was unknown, this would be an important clue in the structure assignment of the copper chloride species, since the two large peaks are reminiscent of the absorption spectrum of the trigonal-bipyramidal CuCl_5^{3-} anion where only two bands are allowed (actually two pairs

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(20) D. M. Adams and P. J. Lock, *J. Chem. Soc. A*, 620 (1967).

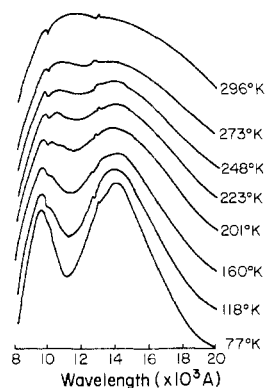


Figure 7. Temperature dependence of the d-d transitions of the CuCl_4^{2-} ion in $[(\text{CH}_3)_2\text{NH}_2]_3\text{CuCl}_5$.

of closely spaced transition when spin-orbit coupling is considered).

The dta data gave no indication of any major phase change (other than at the melting point at 123°). Two small endothermic peaks which occur at -23 and $+3^\circ$ are too small to be caused by a major structural change in the crystal. We feel these are associated with the onset of thermal motion of the dimethylammonium ion and chloride ion which were observed to be disordered in the structure. Evidence that the disorder of the DMA^+ ion is of a dynamic nature (and thus that of the Cl^- also, since they are bound together by hydrogen bonding) was obtained from a broad-line nmr study. At 78°K , the spectrum consists of a single line with no structure, indicating that at that temperature the methyl groups are undergoing hindered rotation. As the temperature is increased, the line shows pronounced narrowing at 184 and 243°K , both of which correspond to the onset of additional modes of thermal motion of the DMA^+ ion in the crystal including, presumably, the hopping between the two equivalent sites occupied by the disordered DMA^+ ion.

Thus we conclude that no major phase or structural change involving the CuCl_4^{2-} ion occurs in $(\text{DMA})_3\text{CuCl}_5$ and that the thermochromism is simply a result of the variation in band width. This same conclusion carries over to a number of other salts. $(\text{DMA})_2\text{CuCl}_4$, for example, at room temperature shows two barely resolved peaks in the d-d region. Upon cooling, no abrupt shift occurs in the spectrum, but these bands become much better resolved and at 78°K occur at 5750 and 9200 cm^{-1} with a weaker peak now evident at $10,300\text{ cm}^{-1}$. This corresponds to a tetrahedral CuCl_4^{2-} ion with trans Cl-Cu-Cl angles of $\sim 125^\circ$. Hence, the thermochromism in this complex is of a similar nature.

Another group of compounds which fall in this category is the $(\text{RNH}_3)_2\text{CuCl}_4$ salts. We have commented in an earlier paper on their thermochromism and speculated this involved a change in coordination geometry. This was based on the observation of an endothermic transition in the dta curve of $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$ at -40° ^{10a} (roughly the same temperature as the onset of the color change) and on the behavior of $[(\text{CH}_3)_2\text{CHNH}_3]_2\text{CuCl}_4$ (*vide infra*). We have not been able to repeat the observation of this transition in the ethylammonium salt with our dta instrument. Also, no shift in the position of d-d transitions is observed as the temperature is lowered from room temperature to 77°K .²¹ Thus there is no evidence to support a structural change in these compounds, and we include them in this class.

Discussion

After the initial submission of this paper, the crystal structure analyses and electronic spectra of the high- and low-temperature phases of bis(*N*-methylphenethylammonium) tetrachlorocuprate(II) have been reported.²² The results are in complete agreement with our study. The room-temperature phase consists of isolated square-planar CuCl_4^{2-} ions. The compound undergoes a phase transition at 80° to a structure which contains irregular distorted tetrahedral ions with trans Cl-Cu-Cl angles of 138 and 123° . In the high-temperature phase, the N-H...Cl distances average 3.45 \AA , while in the low-temperature phase the average is 3.31 \AA . Thus, the planar geometry is considerably stabilized by hydrogen-bonding interactions as postulated in this paper. The electronic spectrum of the square-planar ion at 77°K consists of three bands at $16,900$, $14,300$, and $12,500\text{ cm}^{-1}$. The high-temperature phase shows a broad maximum centered near 9100 cm^{-1} . This is in good agreement with the data presented in Figure 1 and adds credence to the assignment of the geometry of the CuCl_4^{2-} ion based on its electronic absorption spectrum. In particular, comparison with the low-temperature spectrum of $(\text{DEA})_2\text{CuCl}_4$ confirms that the CuCl_4^{2-} ion in the latter salt must contain some distortion from planarity.

Acknowledgments. This work was supported in part by PRF Grant 3152-A3.

Registry No. $\text{DEA}_2\text{CuCl}_4$ (tetrahedral), 52003-08-4; $\text{DEA}_2\text{CuCl}_4$ (square planar), 52003-09-5; $\text{IPA}_2\text{CuCl}_4$, 52003-02-8; $\text{IPA}_2\text{CuCl}_3\text{Br}$, 52003-04-0; $\text{DMA}_3\text{CuCl}_5$, 52003-06-2; $\text{DMA}_2\text{CuCl}_4$, 52003-07-3.

(21) C. Furlani, E. Cervone, F. Calzona, and B. Baldanza, *Theor. Chim. Acta*, **7**, 375 (1967).

(22) R. L. Harlow, W. J. Wells, III, G. W. Watt, and S. H. Simonson, *Inorg. Chem.*, in press.