Thermochromism and Structure of Piperazinium Tetrachlorocuprate(II) Complexes

Mark J. Riley,* Debora Neill, Paul V. Bernhardt, Karl A. Byriel, and Colin H. L. Kennard

Department of Chemistry, University of Queensland, Brisbane, 4072 Queensland, Australia

Received December 29, 1997

The tetrachlorocuprate(II) ion can crystallize in two different structures with the piperazinium dication ($pipzH_2$). Both structures contain discrete $CuCl_4^{2-}$ species. A yellow compound ($pipzH_2$)[$CuCl_4$]·$2H_2O$ (**1**) is monoclinic ($C2/c$, $Z = 4$, $a = 10.538(3)$ Å, $b = 7.4312(5)$ Å, $c = 17.281(4)$ Å, $\beta = 111.900(10)°$) and contains the $CuCl_4^{2-}$ ion as a distorted tetrahedron. A green compound ($pipzH_2$)$_2$[$CuCl_4$]·Cl_2·$3H_2O$ (**2**) is triclinic ($P\bar{1}$, $Z = 2$, $a = 9.264(3)$ Å, $b = 10.447(2)$ Å, $c = 11.366(2)$ Å, $\alpha = 68.38°$, $\beta = 82.86(2)°$, $\gamma = 83.05(2)°$) and contains the $CuCl_4^{2-}$ ion with a square planar geometry. This latter compound shows thermo/photochromism, changing from green to yellow upon heating or laser irradiation.

1. Introduction

Photochromic reactions based on a photoinduced geometry, rather than a chemical, change of a molecule are attractive for optical memory storage applications.[1] Major disadvantages of photochemical reactions in this role include either irreversibility or exhaustion after repeated write/erase photochemical cycles. In the present paper we investigate a photochromic reaction based on the geometry change of the $CuCl_4^{2-}$ ion. The change of geometry results in a yellow to green color change in the crystal.

The $CuCl_4^{2-}$ ion does not have a regular tetrahedral geometry due to the Jahn−Teller theorem. The predominant geometry is that of compressed tetrahedron. However, it is also possible for $CuCl_4^{2-}$ to adopt a centrosymmetric square planar geometry with D_{4h} symmetry.[2] To date there have been only four compounds reported[3−6] with the square planar geometry compared with the huge number of distorted tetrahedral complexes. In these four cases, the counterion is a large organic monocation that is thought to stabilize the square planar geometry by a hydrogen-bonding network. The present work reports the fifth structure of a square planar tetrachlorocuprate(II) complex. It is the first with a dication and also has an extensive hydrogen-bonding network. However, it has recently been found[7] that the square planar geometry is also adopted by $CuCl_4^{2-}$ doped into Cs_2ZrCl_6. Here the hydrogen bonding is absent, so this requirement does not appear to be necessary in doped crystals where presumably the host lattice stabilizes the square planar geometry.

Strict square planar $CuCl_4^{2-}$ ions with no axial coordination have very characteristic electronic absorption spectra. As the geometry of the $CuCl_4^{2-}$ ion changes from a D_{2d} distorted tetrahedron to the D_{4h} square planar geometry, the d−d absorption bands gradually shift to higher energy.[8] The green color of the square planar $CuCl_4^{2-}$ ion is partly due to the d_{z^2} orbital being depressed in energy by mixing with the 4s orbital which has the same symmetry in the D_{4h} point group.[9] As well as being shifted to higher energy, the d−d absorption bands of the square planar complex also characteristically show extensive vibration fine structure at low temperature.

A series of tetrahalocuprates with the piperazinium dication has previously been prepared.[10] One of the tetrachloro compounds was reported as having both yellow and green forms. The green form suggests that it may have a $CuCl_4^{2-}$ ion with a square planar geometry. The aims of this study was to first determine the geometry of $CuCl_4^{2-}$ ion in these crystals and then to investigate the possibility of a thermal or photoinduced geometry change in the $CuCl_4^{2-}$ ion. Thermochromism has previously been seen in copper(II) complexes with N,N-substituted ethylenediamines.[11] Here the thermochromism is not thought to result from a gross geometry change of the Cu(II) chromophore as in the present case, but rather a variation of the ligand field strength due to a change in the ethylenediamine conformation with temperature.

2. Experimental Section

2. Preparation of the Complexes. Piperazinium dihydrochloride ($pipzH_2Cl_2$) was precipitated by adding concentrated hydrochloric acid to an ethanolic solution of piperazine. An ethanolic solution of $CuCl_2$·$2H_2O$ was added slowly with stirring to an aqueous solution of ($pipzH_2Cl_2$) resulting in a fine, light green powder. This was recrystallized in acidic aqueous solution over several days, resulting in a mixture of large yellow and green crystals. Recrystallization using the minimum amount of acid maximized the formation of the green crystals. Both crystals formed were hygroscopic and also deteriorated by dehydration. The green crystals changed to yellow and lost their clarity at 45−48 °C. Both crystals decomposed at ∼115 °C.

2.2. X-ray Crystal Structure Analyses. Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections measured on an Enraf-Nonius CAD4 four-circle

---

* To whom correspondence should be addressed.

(1) Parthenopolous, D. A.; Tentzepis, P. M. *Science* **1989**, *245*, 843.
(2) McDonald, R. G.; Hitchman, M. A. *Inorg. Chem.* **1986**, *25*, 3273.
(3) Harlow, R. L.; Wells W. J.; Watt, G. W.; Simonsen, S. H. *Inorg. Chem.* **1974**, *13*, 2106.
(4) Udupa, M. R.; Krebs, B. *Inorg. Chim. Acta* **1979**, *3*, 241.
(5) Nelson, H. C.; Simonsen, S. H.; Watt, G. W. *J. Chem. Soc., Chem. Commun.* **1979**, 632.
(6) Antolini, L.; Benedetti A.; Fabretti, A. C.; Giusti, A. *Inorg. Chem.* **1988**, *27*, 2192.
(7) Masters, V. M.; Riley, M. J.; Hitchman, M. A. *Chem. Phys. Lett.* **1998**, *228*, 743.
(8) McDonald, R. G.; Riley, M. J.; Hitchman, M. A. *Inorg. Chem.* **1988**, *27*, 894.
(9) Riley, M. J. *Inorg. Chim. Acta* **1997**, *268*, 55.
(10) Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *Inorg. Chem.* **1976**, *15*, 2333.
(11) Grenthe, I.; Paoletti, P.; Samström, M.; Glikberg, S. *Inorg. Chem.* **1979**, *18*, 2687.

S0020-1669(97)01612-1 CCC: $15.00

Table 1. Crystal Data

	1 $(pipzH_2)[CuCl_4]\cdot 2H_2O$	**2** $(pipzH_2)_2[CuCl_4]Cl_2\cdot 3H_2O$
color	yellow	green
size, mm	0.67 × 0.67 × 0.50	0.24 × 0.18 × 0.12
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
formula	$C_4H_{16}Cl_4CuN_2O_2$	$C_8H_{30}Cl_6CuN_4O_3$
a, Å	10.538(3)	9.264(3)
b, Å	7.4312(5)	10.447(2)
c, Å	17.281(4)	11.366(2)
α, deg		68.38(2)
β, deg	111.90(1)	82.86(2)
γ, deg		83.05(2)
V, Å^3	1255.6(5)	1011.3(4)
ρ_{calcd}, g cm^{-3}	1.743	1.664
fw	329.53	506.60
Z	4	2
μ, cm^{-1}	25.65	18.86
temp, °C	23	23
λ, Å	0.710 73	0.710 73
N	1112	3563
N_o ($F_o > 2\sigma$)	1050	2869
$2\theta_{max}$, deg	50	50
parameters	93	322
goodness of fit	1.137	0.971
residual extrema, e Å^{-3}	0.4, −0.3	0.3, −0.4
$R(F_o)^a$, $wR_2(F_o^2)^b$	0.0246, 0.0628^c	0.0231, 0.0618^d

^{a} $R(F_o) = \sum||F_o| - |F_c||/\sum |F_o|$. ^{b} $wR_2(F_o^2) = (\sum w(F_o^2 - F_c^2)/\sum wF_o^2)^{1/2}$. ^{c} $w^{-1} = (\sigma^2(F_o^2) + (0.0399P)^2 + 0.90P)$. ^{d} $w^{-1} = (\sigma^2(F_o^2) + (0.0431P)^2 + 0.38P)$, where $P = {}^1/_3 \max(F_o^2, 0) + {}^2/_3 F_c^2$.

diffractometer employing graphite monochromated Mo Kα radiation and operating in the $\omega-2\theta$ scan mode. Data reduction and empirical absorption corrections (ψ scans) were applied with the XTAL package.[12] The structures were solved by heavy atom with SHELXS86[13] and refined by full-matrix least-squares analysis with SHELXL93.[14] All non-H atoms were refined with anisotropic thermal parameters, whereas H atoms located from difference maps and refined isotropically. Crystal data are assembled in Table 1, and the atomic nomenclature is defined in Figures 1 and 2 drawn with the program PLUTON.[15]

2.3. Electronic Absorption Spectroscopy. Absorption spectra were measured on a CARY-17D spectrometer interfaced to a computer. The sample was mounted on a copper foil mask and held in contact with a copper block of a Leybold closed-cycle cryostat. The temperature was measured and controlled by two calibrated silicon diodes located both in the cooling block and next to the sample. The absolute temperature was checked by also making the measurements using a helium flow tube. The transitions of the yellow compound were too intense to be measured as single crystals, and these were grown as a polycrystalline film between two microscope slides.

3. Results and Discussion

3.1. Crystal Structures. The yellow $(pipzH_2)[CuCl_4]\cdot 2H_2O$ (**1**) crystals belong to the space group $C2/c$ with four formula units in the monoclinic unit cell. The views of the unit cell projected onto the (100) and (010) crystal faces are shown in Figure 1. Crystallographic details are given in Table 1. The copper atoms lie on sites of C_2 symmetry. As given in the caption to Figure 1, the independent Cu−Cl bond lengths, 2.2358(7) Å and 2.2649(7) Å, and the two θ_{trans} angles of the flattened tetrahedron, 130.5° and 137.6°, are both substantially different. This reduces the idealized flattened tetrahedron of D_{2d} symmetry to C_{2v}. The slight twist of the Cl(2)$^{\#1}$−Cu−Cl(2) and Cl(1)$^{\#1}$−Cu−Cl(1) planes from perpendicular further reduces the symmetry to the C_2 site symmetry. The piperazinium dication adopts a chair conformation. Figure 1a and 1b gives views of the unit cell which clearly show the approximate D_{2d} geometry of the $CuCl_4^{2-}$ ions and the chair conformation of the piperazinium ion.

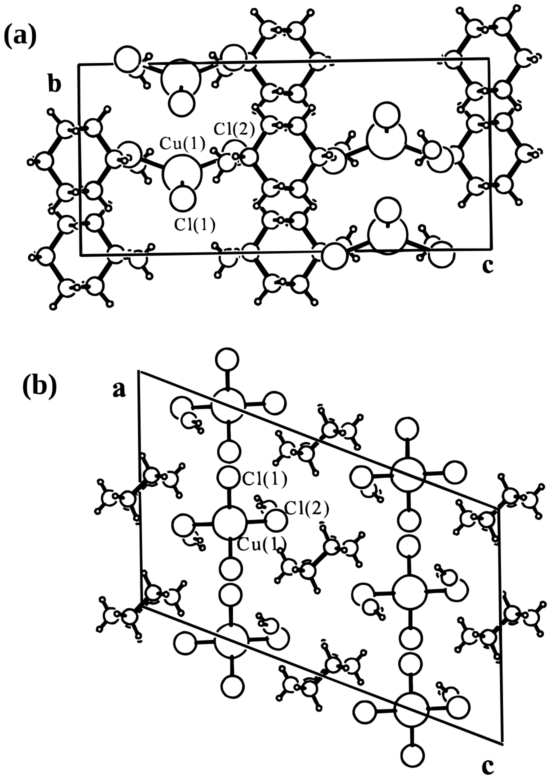

Figure 1. Projections of the unit cell of $(pipzH_2)CuCl_4\cdot 2H_2O$ (**1**) onto the (a) (100) and (b) (010) faces. Selected bond lengths and angles are Cu(1)−Cl(2) = 2.2358(7) Å, Cu(1)−Cl(1) = 2.2649(7) Å; Cl(2)$^{\#1}$−Cu(1)−Cl(2) = 137.65(4)°, Cl(2)$^{\#1}$−Cu(1)−Cl(1)$^{\#1}$ = 100.04(2)°, Cl(2)−Cu(1)−Cl(1)$^{\#1}$ = 97.35(2)°, Cl(1)$^{\#1}$−Cu(1)−Cl(1) = 130.55(3)°.

The green $(pipzH_2)_2[CuCl_4]\cdot Cl_2\cdot 3H_2O$ (**2**) crystals belong to the space group $P\bar{1}$ with two formula units in the triclinic unit cell. A view of the unit cell is given in Figure 2. The piperazinium dication also adopts the chair conformation in this structure. However, in this case each copper atom lies on a site with inversion symmetry and the $CuCl_4^{2-}$ ion is therefore strictly planar. The $CuCl_4^{2-}$ ions are unrelated by symmetry, one has the independent bond lengths 2.2570(8) Å and 2.2790(7) Å while the other has the independent bond lengths 2.2750(8) Å and 2.3489(8) Å. This longer bond is between Cu(2) and Cl(21). This chloride ion Cl(21) is the nearest atom in the axial position of Cu(1) at a distance of 3.792 Å. The Cu(1)···Cl(21) direction makes an angle of 11° with the normal of the $CuCl_4^{2-}$ plane. The long contact between Cu(2)−Cl(21)···Cu(1) results in linear chains of $CuCl_4^{2-}$ ions along (011) as shown in Figure 2b.

The other $CuCl_4^{2-}$ ion also has a long axial contact with a nonbonded Cl(31) ion. Here the Cu(2)···Cl(31) makes an angle of 7° with the normal to the $CuCl_4^{2-}$ plane at a distance of 3.189 Å. For comparison, the long bonds in tetragonally elongated six-coordinate $CuCl_6^{4-}$ complexes are ∼2.85 Å as determined by both low-temperature crystallography and EXAFS studies.[16] In the present case, in each of the independent sites the $CuCl_4^{2-}$ ion can be considered four-coordinate.

---

(12) Hall, S. R., Flack, H. D., Stewart, J. M., Eds. *The XTAL3.2 User's Manual*; Universities of Western Australia, Geneva and Maryland: Nedlands, Western Australia, 1992.

(13) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(14) Sheldrick, G. M. *SHELXL97: Program for Crystal Structure Determination*; University of Göttingen: Germany, 1993.

(15) Spek, A. L. *PLUTON 92*; University of Utrecht: The Netherlands, 1992.

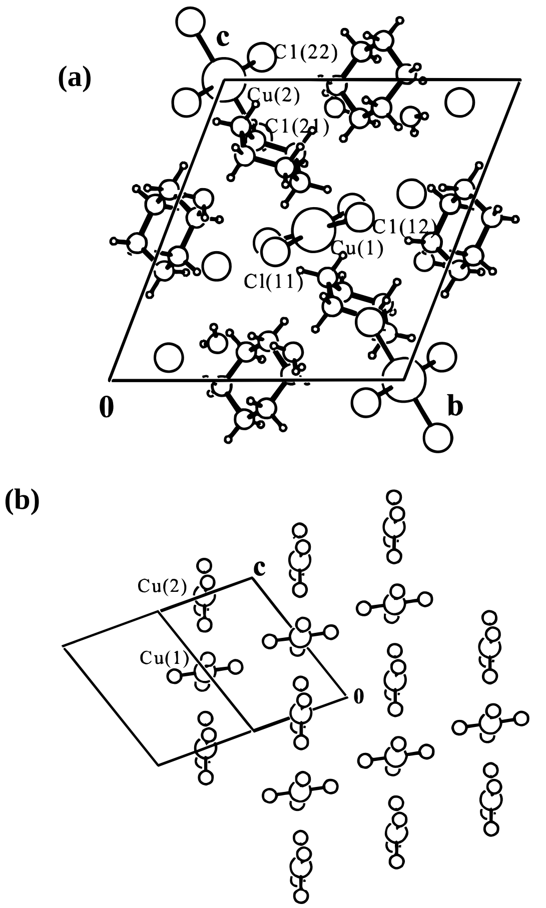

Figure 2. (a) Projection of the unit cell of $(pipzH_2)_2[CuCl_4].Cl_2{\cdot}3H_2O$ (**2**) onto the (100) crystal face. (b) Extended plane through the crystal which contains the approximate linear chains of the $CuCl_4^{2-}$ ions in the [011] direction. Selected bond lengths and angles are Cu(1)−Cl(12) 2.2570(8) Å, Cu(1)−Cl(11) 2.2790(8) Å, Cu(2)−Cl(22) = 2.2750(8) Å, Cu(2)−Cl(21) = 2.3489(8) Å; $Cl(12)^{\#1}$−Cu(1)−Cl(12) = 180.0°, $Cl(12)^{\#1}$−Cu(1)−Cl(11) = 90.39(3)°, Cl(12)−Cu(1)−Cl(11) = 89.61(3)°, $Cl(22)^{\#2}$−Cu(2)−Cl(21) = 89.85(3)°, Cl(22)−Cu(2)−Cl(21) = 90.15(3)°, Cl(21)−Cu(2)-$Cl(21)^{\#2}$ = 180.0°.

Table 2. Bond Lengths and Totally Symmetric Stretch Vibrations of the Planar $CuCl_4^{2-}$ Ion

cation	NmpH[a]	metH	creat	2-abt	$pipzH_2$ (**2**)[b]
bond lengths, pm	228.1[3]	228.33[5]	226.83[4]	227.1[6]	225.6
	224.8	225.3	223.3	226.9	227.9
					227.6
					234.8
$\nu(a_{1g})$, cm^{-1}					
ground state	276[17]	275[2]	290[2]	275[18]	
excited state	265	265		266	269

[a] Cation abbreviations: NmpH, *N*-methylphenethylammonium; metH, methadonium; creat, creatinium; 2-abt, 2-aminobenzothiazolium. [b] This work.

Table 2 compares the bond lengths found in the present case with those of other known planar tetrachlorocuprates. It has been suggested that to stabilize a tetrachlorocuprate ion at a square planar geometry, some hydrogen bonding between the cation and the copper tetrachloride ion is necessary. This is also found in the present compounds. In both crystal forms, the piperazinium dication forms a bifurcated hydrogen bond between two of the Cl atoms of the $CuCl_4^{2-}$ ion and the ammonium hydrogens at each end of the bridging dication in the trans position. The other two ammonium hydrogens are hydrogen bonded to water molecules.

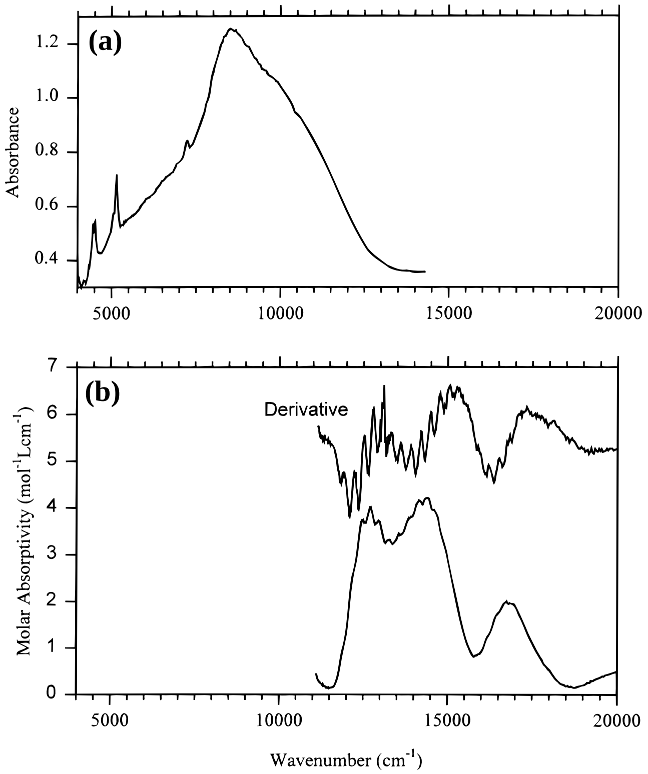

Figure 3. Absorption spectrum of (a) **1** and (b) **2** measured at 10 K. The inset to (b) gives the derivative of the spectrum to make the vibrational structure more apparent.

Table 3. Observed Electronic Transition Energies (cm^{-1})

D_{2d} $CuCl_4^{2-}$ (**1**)		D_{4h} $CuCl_4^{2-}$ (**2**)	
transition	energy/cm^{-1}	transition	energy/cm^{-1}
$^2B_2 \rightarrow {}^2E$	6 000	$^2B_{1g} \rightarrow {}^2B_{2g}$	12 600
$\rightarrow {}^2B_1$	8 700	$\rightarrow {}^2E_g$	14 300
$\rightarrow {}^2A_1$	11 000	$\rightarrow {}^2A_{1g}$	16 850

3.2. Electronic Absorption Spectra. The low-temperature electronic absorption spectra are shown in Figure 3a and b for compounds **1** and **2**, respectively. Compound **1**, which contains the D_{2d} distorted tetrahedral $CuCl_4^{2-}$ complex has several broad overlapping bands in the near-IR and extending into the red part of the visible spectrum. Superimposed on these electronic transitions are several sharp features corresponding to vibrational overtones of N−H stretches. The spectrum of **2**, which contains the D_{4h} square planar $CuCl_4^{2-}$ ion, is much weaker and is shifted to higher energy. The three broad absorption bands all have vibrational fine structure, most clearly seen in the derivative spectrum of Figure 3b. The spectra were deconvoluted using Gaussian functions, and the observed transition energies are given in Table 3.

The spectra of both compounds were measured with unpolarized light. With compound **1**, this is because it is grown as a polycrystalline thin film. The structure of compound **2** has an intrinsic packing problem. As seen in Figure 2, it is not possible to separate the *xy*- and *z*-polarized molecular spectra. Crystals of **2** undergo an exothermic phase transition at ∼227 K, as observed in differential scanning calorimetry measurements. However, the vibrational fine structure at 10 K indicates that the $CuCl_4^{2-}$ species remains square planar below this transition.

---

(16) Ellis, P. J.; Freeman, H. C.; Hitchman, M. A.; Reinen, D.; Wagner, B. *Inorg. Chem.* **1994**, *33*, 1249.

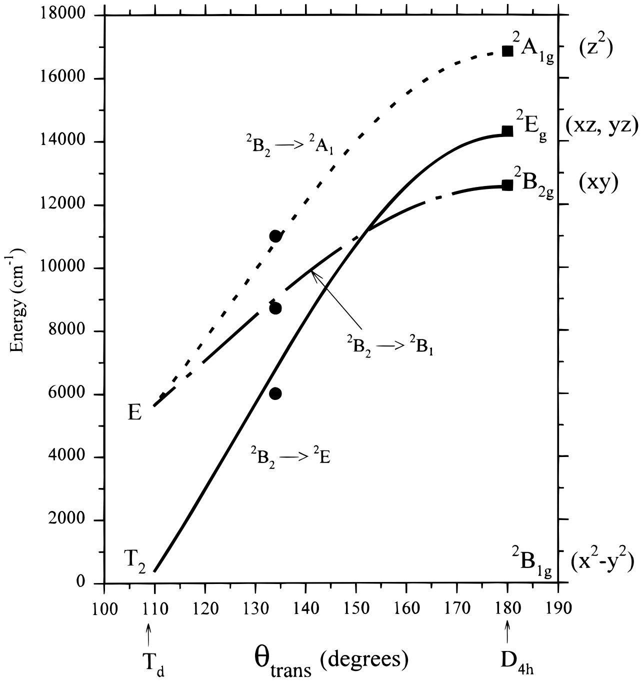

Figure 4. The d−d transition energies relative to the electronic ground state as a function of the trans Cl−Cu−Cl angle, θ_{trans}. The energies were calculated using the AOM parameters $e_\sigma = 5250$ cm^{-1}, $e_\pi = 800$ cm^{-1}, and $e_{ds} = 1550$ cm^{-1}. The filled circles and squares represent the observed energies of **1** and **2**, respectively. The left and right end points of the curves correspond to the T_d and D_{4h} limits, respectively, and the irreducible representations in these points groups are given.

The variation of the electronic energy levels of $CuCl_4^{2-}$ with the distortion of the angle θ_{trans} between the trans chloride ions is well-known. The three transitions can be fitted to σ- and π-bonding angular overlap model (AOM) parameters e_σ and e_π, respectively. In addition an extra parameter, e_{ds}, must be used to account for the 4s−3d mixing which becomes especially important for the square planar geometry.[9] Using the values $e_\sigma = 5250$ cm^{-1}, $e_\pi = 800$ cm^{-1}, and $e_{ds} = 1550$ cm^{-1}, one obtains the calculated energy levels shown in Figure 4. The experimental transition energies are also indicated in this figure, where an average value of $\theta_{trans} = 134°$ for the D_{2d} complex has been used. The agreement between calculation and experiment is excellent, indicating that the actual distortion away from the idealized D_{2d} and D_{4h} symmetry is small.

3.3. Vibrational Fine Structure. The spectrum of compound **2** is temperature dependent: the vibration fine structure disappears at above ∼80 K, and the intensity of the bands increase as the temperature is raised. This is typical of d−d transition of a centrosymmetric complex. Here the electronic transitions become allowed through vibronic coupling. In principle it is possible to obtain the energy of the vibration involved in the vibronic coupling by analyzing the temperature dependence of the absorption spectrum. However, in the absence of polarized data the results are only qualitative and do not differ from values previously found.[2,17,18]

The vibrational fine structure that appears in the spectrum of Figure 3 is due to a progression in the totally symmetric stretch of the $CuCl_4^{2-}$ ion. The vibrational energy is 270 ± 5 cm^{-1}, the same as that found in three of the four other known planar $CuCl_4^{2-}$ compounds (see Table 2).

The excited-state geometry can be obtained from fitting the observed Franck−Condon intensity pattern with that calculated from the overlap of vibrational wave functions in the harmonic approximation. The *n*th member of a vibrational progression which originates from the $n = 0$ ground-state vibrational level is given by

$$I_{0\rightarrow n} = \frac{D^{2n}}{2^n n!}\exp(-D^2/2) \qquad (1)$$

where D is a displacement of the excited-state potential energy surface with respect to the ground state in dimensionless units. This is related to simultaneous change in all four bond lengths Δr by

$$\Delta r = {}^1/_2 \times 580.6 \times D/\sqrt{\mu\bar{\nu}}\ \text{pm} \qquad (2)$$

Here μ is the reduced mass (of one chloride ligand in this case) in amu, and $\bar{\nu}$ is the frequency of the a_{1g} vibration in cm^{-1}. The most clearly resolved band in the absorption spectrum is the lowest-energy band. This is what would be expected in a spectrum with arbitrary polarization as the lowest energy $^2B_{1g}(x^2 - y^2) \rightarrow {}^2B_{2g}(xy)$ transition is not vibronically allowed in z polarization. All other transitions are vibronically allowed in both xy and z polarization, meaning that the superposition of the spectrum from each polarization, which is built on vibronic origins of different energy, would be expected to be broadened. The analysis of the intensities of the vibrational members of the $^2B_{1g}(x^2 - y^2) \rightarrow {}^2B_{2g}(xy)$ transition gives $D = 2.69$ and therefore an overall expansion of each Cu−Cl bond length in the excited state by 8.0 pm with respect to the ground state. This is typical of values found in the Franck−Condon analysis of other tetrachlorocuprates.[2,18]

3.4. Photo/thermochromism. The heating or 20 mW of 514 nm laser irradiation of the green crystals of **2** caused a color change to yellow. This change cannot be a simple conversion to compound **2** to **1**, as these two compounds have different structural formulae. However, it is most likely that the green to yellow thermo/photochromic transition corresponds to a $D_{4h} \rightarrow D_{2d}$ distortion of the $CuCl_4^{2-}$ ion. This distortion is the same as the b_{2u} (a_1) vibrational coordinate in the D_{4h} and D_{2d} ions, respectively. This is a low-energy bending vibration capable of large amplitude motion. The stabilization of the square planar complex appears to be small and there is evidence that in the excited electronic states this stabilization may be even smaller.[19] For some square planar compounds it has been possible to perform a detailed temperature dependent study. The large red shift of the d−d transitions[19] combined with details in the change of vibrational fine structure,[20] imply that the excited electronic states can have a potential energy surface which is has a double minimum along the b_{2u} bending coordinate. Each minimum of the potential would correspond to an equivalent but opposite compressed tetrahedral geometry.

Therefore there may be two mechanisms for the $D_{4h} \rightarrow D_{2d}$ phase transition. Heating may provide enough thermal motion to overcome the stabilization of the D_{4h} geometry by hydrogen bonding. Alternatively, the transition may possibly occur by exciting the D_{4h} compound into an excited state in which the D_{2d} distortion is the preferred geometry. Radiationless relaxation at this geometry back to the ground electronic state may then disrupt the hydrogen bonding network allowing the $CuCl_4^{2-}$

---

(17) Hitchman, M. A.; Cassidy, P. J. *Inorg. Chem.* **1979**, *18*, 1745.

(18) Riley, M. J.; Boutchard, C.; Krausz, E. R.; Hitchman, M. A. *Chem. Phys. Lett.* **1996**, *254*, 403.

(19) Riley, M. J.; Hitchman, M. A. *Inorg. Chem.* **1987**, *26*, 3205.

(20) McDonald, R. G.; Riley, M. J.; Hitchman, M. A. *Chem. Phys. Lett.* **1987**, *142*, 529.

ion to relax further to the more favored D_{2d} geometry. It should be noted that this photoinduced phase transition has not been observed in other square planar $CuCl_4^{2-}$ compounds, and in the present case may be due to local heating.

Materials which show a photoinduced geometry change have great potential for two-photon recording in a memory storage device. Photochromism based on a geometry change rather than a photochemical reaction is inherently more robust and thus is of interest. The present compound, which it has been shown to exist as geometric isomers with the ability to interconvert, suffers from a lack of long-term stability. In addition, the induced geometry change appears to be only semireversible. After several cycles the crystals lose their clarity and remain yellow. However, the present study shows the potential of molecules which can be converted between different geometric isomers via a low-energy vibrational mode. This property is especially useful the geometry change is more easily accomplished in an excited electronic state. This can lead to a photoinduced geometry change. We are continuing to investigate the potential of the square planar $CuCl_4^{2-}$ system for this property.

4. Conclusions

The structures of two compounds of the $CuCl_4^{2-}$ ion and the piperazinium dication are reported. The compounds are yellow and green due to the $CuCl_4^{2-}$ ion being at a distorted tetrahedral and a square planar geometry, respectively. The square planar compound undergoes a green → yellow phase transition caused either by heating or light irradiation. The color change is shown to be due to a geometry change of the $CuCl_4^{2-}$ ion. Mechanisms for this geometry change and their potential applications have been given.

Supporting Information Available: Crystallographic data, in CIF format, are available on the Internet only. Access and ordering information is given on any current masthead page.

IC971612W