Synthesis and characterization of Cu$_2$ZrCl$_6$: a thermochromic, van Vleck paramagnet

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Received 14 November 2001; accepted 29 January 2002

Abstract

The solid state reaction of CuCl and ZrCl$_4$ yields the pale yellow crystalline solid of composition Cu$_2$ZrCl$_6$. This material crystallizes in the trigonal space group $P\bar{3}m1$ ($\#164$) at room temperature with lattice constants $a=10.9092(4)$ and $c=6.1517$, $Z=3$. The structure is shown to be related to ZrCl$_4$, where every other Zr site has been replaced with Cu atoms that partially occupy the six tetrahedral interstices surrounding the now vacant octahedral interstice. At room temperature, two copper atoms are disordered about three crystallographically distinct sites. Two thermochromic transitions are observed for this material at 120 and 673 K, which appear to be related to the movement of copper from the center of a tetrahedral interstice to a trigonal planar face. A second-order Jahn–Teller distortion accounts for this structural variation. This along with the insertion of the empty Zr-4d orbitals into the already small copper (I) based HOMO–LUMO gap afford significant mixing between ground and excited states resulting in notable van Vleck paramagnetism.

Keywords: Metal halide compounds; Crystal structure; X-ray diffraction; Neutron diffraction; Magnetic measurements

1. Introduction

The chemistry of copper (I) is unique among transition metals because of its distinctive electronic configuration. With respect to reactivity, the high lying and filled 3d-orbitals allow reactivity with electrophiles; at the same time the low lying and empty 4s- and 4p-orbitals provide a site for nucleophilic attack. This relatively small HOMO-LUMO gap is also responsible for the wide range of coordination geometries observed for Cu(I) [1]. Though this d$^{10}$-metal may have a crystal field preference for a tetrahedral geometry, a second-order Jahn–Teller mixing between the filled d- and empty s- and p-orbitals stabilizes two and three coordination [2]. In addition to unique structure and reactivity, the electronic configuration of Cu(I) has profound implications with respect to optical and luminescent properties [3], as well as with respect to mobility in ionic conductors [4]. In the course of our continuing investigation of the structure and reactivity of Cu(I) centers in Lewis acidic metal halide lattices, we have been interested in the possible construction of open frameworks from the phosphate-like [CuCl$_4$]$^{3–}$ building blocks with the Lewis acidic ZrCl$_4$ [3,5]. Unlike our prior work with the group 13 Lewis acids (Al and Ga), the introduction of Zr(IV) into the cuprous halide lattice is expected to further narrow the band gap of these wide band gap semiconductors by inserting the t$_{2g}^*$-type zirconium 4d-orbitals into the already narrow gap between the Cu 3d- and 4s,p-orbitals. In prior reports we have described the synthesis and characterization of ((C$_6$H$_5$)$_2$Cu)$_2$ZrCl$_6$ [6] and [H$_2$NMe$_2$]$_2$CuZrCl$_6$ [7]. We here describe the synthesis and characterization of the parent compound Cu$_2$ZrCl$_6$. We further demonstrate that the interaction between the d$^{10}$-Cu(I) and d$^{4}$-Zr(IV) is responsible for the observed thermochromism, and provides a system in which to probe the nature of van Vleck paramagnetism.

2. Experimental

2.1. General procedures

All reactions were performed under an inert atmosphere of dry N$_2$ in a glove box or using Schlenk line techniques.
ZrCl₄ (99.99%) was used as received from Aldrich. The CuCl was prepared from Cu metal and CuCl₂ (Aldrich) according to literature methods and further purified by sublimation [8]. Powder X-ray diffraction measurements were obtained using an Enraf-Nonius Guinier camera and were indexed with respect to a silicon standard. Diffuse reflectance spectra were taken using a Cary 3e UV–Vis spectrometer equipped with an integrating sphere and measured with respect to a pressed polytetrafluoroethylene powder standard. Reflectance spectra are plotted as the remission function $F(R) = (1 - R)^2 / 2R$, based on the Kubelka–Munk theory of diffuse reflectance [9]. Differential scanning calorimetry (DSC) data were collected on a Perkin-Elmer DSC 7 at a heat/cool rate of 10 °C/min. Samples were placed into stainless steel, high-pressure pans and hermetically sealed with gold foil caps. Magnetic susceptibility measurements were performed on a Quantum Design MPMS-5S SQUID magnetometer with a 5 T magnet in fused silica magnetic susceptibility containers and in DELRIN sample holders.

2.2. Preparation of Cu₂ZrCl₆

A sample of 0.200 g of ZrCl₄ (0.858 mmols) and 0.140 g of CuCl (1.72 mmols) was ground together in a mortar and pestle, then transferred into a fused silica tube (6 mm× 8 cm I.D.). The reaction vessel was evacuated and sealed with a torch. The reaction was heated to 450 °C in a box furnace for 1 day, and then cooled at 1.0 °C/min to room temperature. A small temperature gradient in the furnace caused the Cu₂ZrCl₆ to crystallize on the cool end of the tube. The bulk material was characterized by powder X-ray diffraction, DSC, magnetic susceptibility and diffuse reflectance spectroscopy.

2.3. X-ray structure determination of Cu₂ZrCl₆ at 298 K

A pale yellow single crystal (0.24×0.22×0.12 mm) covered in silicone grease was mounted in a Pyrex capillary and sealed under a N₂ atmosphere. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer at 298 K using MoKα radiation ($\lambda = 0.71073$ Å). Lattice constants for the trigonal cell, $a = 10.9892(4)$ Å, $c = 6.1517(2)$ Å, were determined from a symmetry-constrained fit of 24 well-centered reflections between $33° < 2\theta < 36°$ and their Friedel pairs. A unique quadrant $h, k, ±l$, was collected with 2429 independent reflections by $\omega$-scans for $0° < 2\theta < 60°$. These data were scaled to three intensity check reflections using a five-point smoothing routine. An empirical absorption correction was applied using psi scan data. Systematic absences were found to be consistent with the space group $P3\bar{3}m1$, which was subsequently confirmed by the structural solution refined using the NRCVAX suite of programs [10]. All zirconium and chlorine atoms were located by direct methods using the SIR92 program [11]. One copper site (Cu(1)) was also observed in the initial direct methods solution. Subsequent difference maps identified two additional sites that are partially occupied by copper atoms. All atoms were refined anisotropically. A full matrix least squares calculation using the 452 unique reflections ($I > 2.5\sigma(I)$) gave a final refinement with $R$ factors of $R = 0.053$ and $R_w = 0.087$.

2.4. X-ray structure determination of Cu₂ZrCl₆ at 157 K

The crystal used for the room temperature data collection was removed from the capillary under a flow of argon, covered in silicone grease, placed on the end of a glass fiber, and immediately transferred to the diffractometer where it was cooled to 157 K under a stream of dry nitrogen. Data were then collected on an Enraf-Nonius CAD4-Mach diffractometer with monochromated Mo(Kα) radiation. Lattice constants for the trigonal cell, $a = 10.906(2)$ Å, $c = 12.234(1)$ Å, were determined from a symmetry-constrained fit of 24 well-centered reflections between $33° < 2\theta < 36°$ and their Friedel pairs. A unique quadrant $h, k, ±l$, was collected with 2429 independent reflections by $\omega$-scans for $0° < 2\theta < 60°$. These data were scaled to three intensity check reflections using a five-point smoothing routine. An empirical absorption correction was applied using psi scan data. Systematic absences were found to be consistent with the space group $P3\bar{3}c1$, which was subsequently confirmed by the structural solution refined using the NRCVAX suite of programs. In spite of the doubled $c$-axis and change of space group, refinement of the low temperature data yielded essentially the same structure solution as that found for the room temperature data, with a similar distribution of the disordered copper atoms but a small variation in certain atom positions. All atoms were refined anisotropically. A full matrix least squares calculation on 877 unique reflections [$I > 1.5\sigma(I)$] gave a final refinement of $R = 11.1$ and $R_w = 10.8$.

2.5. Neutron powder diffraction

Cu₂ZrCl₆ (6.0 g, 0.014 mol) was sealed in a vanadium container of length 50 mm and diameter 6.0 mm (I.D.) inside a dry, He-filled glove box. Data were collected at room temperature, and at 100 K using a closed-cycle He refrigerator for temperature control. Neutron powder diffraction data were collected using the BT-1 32 detector neutron powder diffractometer at the NIST Center for Neutron Research reactor, NBSR. A Cu(311) monochromator with a 90° take-off angle, $\lambda = 1.5402(2)$ Å, and in-pile collimation of 15 min of arc were used. Data were collected over the range of 3–168° 2θ with a step size of...
0.05°. The instrument is described in the NCNR web site (http://www.ncnr.nist.gov).

The structure was also evaluated by the Rietveld refinement of the room temperature neutron diffraction data using GSAS [12]. Lattice constants and atom positions obtained from the CAD-4 data were utilized as starting positions for the refinement. Doubling of the c-axis was also considered, but it did not improve the overall fit of the data. The full profile refinement parameters include the zero point, 12 background parameters, three profile parameters plus the structural parameters. The refined structural parameters include two lattice parameters, the 15 atomic position parameters not dictated by special positions, the three isotropic thermal parameters for the chlorides, and the three fractional occupancies for the copper positions. Pseudo-translational symmetry led to a high correlation of the metal thermal parameters, and thus, they were all fixed to \( U_{iso} = 0.03 \). The final agreement factors are \( R_p = 6.04\% \), \( wR_p = 7.07\% \) for the full profile.

3. Results

3.1. Solid-state structure

The solid-state structure of \( \text{Cu}_2\text{ZrCl}_6 \) was determined by single crystal X-ray diffraction at room temperature and at 157 K, and by Rietveld refinement of room temperature neutron powder diffraction data. A summary of these crystallographic data is presented in Table 1 and the difference function of the Rietveld refinement of the neutron powder diffraction data is given in Fig. 1. Atomic positions and selected bond distances and bond angles from the room temperature single crystal refinement are given in Tables 2–4, respectively. (The corresponding data for the low temperature and neutron refinements are available from the author.) ORTEP drawings describing the local structure around each of the three copper sites are given in Fig. 2. The structure of \( \text{Cu}_2\text{ZrCl}_6 \) consists of a complex network based on a hexagonal close-packed chloride sublattice. Two crystallographically distinct zirconium cations reside on \( 3m \) and \( 3m \) sites, respectively, together filling 1/6 of the octahedral interstices. The \( \text{Zr}–\text{Cl} \) distances around the \( 3m \) site, \( \text{Zr}(1)–\text{Cl}(1) = 2.481(3) \) Å × 3 and \( \text{Zr}(1)–\text{Cl}(3) = 2.478(3) \) Å × 3, and the \( 3m \) site, \( \text{Zr}(2)–\text{Cl}(6) = 2.481(3) \) Å × 3

Table 1

<table>
<thead>
<tr>
<th>Crystallographic data for ( \text{Cu}_2\text{ZrCl}_6 ) at 298 K and 157 K (single crystal X-ray), and 293 K (powder neutron)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
</tr>
<tr>
<td><strong>Formula weight (g/mol)</strong></td>
</tr>
<tr>
<td><strong>Crystal dimensions (mm)</strong></td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
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<tr>
<td><strong>Temperature (K)</strong></td>
</tr>
<tr>
<td><strong>Space group (No.)</strong></td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
</tr>
<tr>
<td><strong>V (Å³)</strong></td>
</tr>
<tr>
<td><strong>Z</strong></td>
</tr>
<tr>
<td><strong>R-merge</strong></td>
</tr>
<tr>
<td><strong>( \rho_{calc} ) (mg cm⁻³)</strong></td>
</tr>
<tr>
<td><strong>( \lambda(\text{Mo Kα}) ) (Å)</strong></td>
</tr>
<tr>
<td><strong>( \mu ) (cm⁻¹)</strong></td>
</tr>
<tr>
<td><strong>No. reflns measured</strong></td>
</tr>
<tr>
<td><strong>No. reflns unique</strong></td>
</tr>
<tr>
<td><strong>( R_p )</strong></td>
</tr>
<tr>
<td><strong>( R_p )</strong></td>
</tr>
<tr>
<td><strong>GOF</strong></td>
</tr>
</tbody>
</table>

\( R = \sum(F_2 - F_1)/F_2 \)

\( R_p = \left[ \sum(w(F_2^2 - F_1^2))^{1/2} \right] / \sum(F_2^2)\)

\( GOF = \left[ \sum(w(F_2^2 - F_1^2)) / (\text{No. of reflns.} - \text{No. of parameters}) \right]^{1/2} \)

\( R_p = \sum(F_2^2 - F_1^2) / \sum(F_2^2) \)

\( wR_p = \sqrt{(M/\sum F_2^2)} \)
Table 2
Atomic coordinates and isotropic displacement parameters for Cu\textsubscript{2}ZrCl\textsubscript{6} (1) at 298 K

<table>
<thead>
<tr>
<th>Occupancy</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B\textsubscript{iso}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(1)</td>
<td>1.0</td>
<td>1/3</td>
<td>2/3</td>
<td>0.0283(2)</td>
</tr>
<tr>
<td>Zr(2)</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0.0323(6)</td>
</tr>
<tr>
<td>Cu(1)</td>
<td>0.52(5)</td>
<td>0.2279(3)</td>
<td>0.7721(3)</td>
<td>0.4344(6)</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>0.32(1)</td>
<td>0.1083(4)</td>
<td>0.8917(4)</td>
<td>0.9121(1)</td>
</tr>
<tr>
<td>Cu(3)</td>
<td>0.17(1)</td>
<td>0.4242(8)</td>
<td>0.5758(8)</td>
<td>0.609(2)</td>
</tr>
<tr>
<td>Cl(1)</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0.2539(4)</td>
</tr>
<tr>
<td>Cl(2)</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0.2716(4)</td>
</tr>
<tr>
<td>Cl(3)</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0.7958(4)</td>
</tr>
</tbody>
</table>

Table 3
Bond distances (Å) for the room temperature structure of Cu\textsubscript{2}ZrCl\textsubscript{6}

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(1)–Cl(1)</td>
<td>2.481(3)×3</td>
</tr>
<tr>
<td>Zr(1)–Cl(3)</td>
<td>2.478(3)×3</td>
</tr>
<tr>
<td>Zr(2)–Cl(2)</td>
<td>2.474(2)×6</td>
</tr>
<tr>
<td>Cu(1)–Cl(1)</td>
<td>2.308(3)×2</td>
</tr>
<tr>
<td>Cu(1)–Cl(2)</td>
<td>2.511(6)</td>
</tr>
<tr>
<td>Cu(1)–Cl(3)</td>
<td>2.223(4)</td>
</tr>
<tr>
<td>Cl(2)–Zr(2)–Cl(2)</td>
<td>180.0(1)×3</td>
</tr>
</tbody>
</table>

Cl(2)=2.474(2) Å×6 are essentially equivalent. The copper cations reside in slightly distorted tetrahedral interstices and are disordered over three crystallographically distinct sites with occupancies of Cu(1)=52(5)%, Cu(2)=32(1)%, and Cu(3)=17(1)% (Occupancies of 46%, 29%, and 16% were found for Cu(1), Cu(2), and Cu(3), respectively, when the thermal parameters were fixed at B\textsubscript{iso}=0.08). (Refinement of the neutron powder data yielded occupancies of Cu(1)=41(2)%, Cu(2)=24(2)%, and Cu(3)=21(2)%). Copper atoms 1 and 3 in particular are distorted toward a trigonal face of the interstice with three short Cu–Cl distances of 2.2–2.3 Å and one long distance, Cu(1)–Cl(2)=2.511(6) Å and Cu(3)–Cl(1)=2.71 Å. The bond distances around Cu(2) are more regular, ranging from 2.21(1) to 2.35(1) Å. All attempts to refine the structure in lower symmetry space groups in order to accommodate a stoichiometric occupancy of the copper sites resulted in the same structural solution with the symmetry of the original space group P\textsuperscript{3}m1. Neither Weissenberg nor axial photographs indicated the presence of a non-merohedral twin. Flack’s method of left coset decomposition was utilized to determine the possible twin laws for a merohedral twin [13]. Information about each possible twin law for the Laue group \( \text{3m1} \) [14] was incorporated into the structure model using the twin refinement options provided by SHELXL97 [15]. None of the possible twin laws led to an improvement of the structure refinement.

Low-temperature single crystal X-ray diffraction (157 K) and X-ray and neutron powder diffraction (100 K) data were obtained to examine the temperature dependence of the copper site occupancy. The 157 K single crystal X-ray data gave evidence for a doubling of the \( c \) lattice constant (and thus a change in the space group), however, the
of about 2.9 eV. A second broad maximum in the absorption spectrum is observed at around 35 000 cm$^{-1}$. By way of comparison, the diffuse reflectance spectrum of the colorless $[\text{H}_2\text{NMe}_2]\text{CuZrCl}_6$, and CuCl, which has a band gap of 3.2 eV [16], are also given in Fig. 4b and c, respectively. The other starting material, ZrCl$_4$, has a band gap in the vacuum ultraviolet; beyond the limits of our instrumentation. These spectra further provide no evidence for the presence of any copper (II) chloride (onset of absorption at 16 000 cm$^{-1}$). Due to our instrumental limitations it has not been possible to obtain spectroscopic data for either the high-temperature or low-temperature phases.

The thermochromic and structural phase transitions were further quantified by differential scanning calorimetry (DSC) measurements shown in Fig. 5. Two sharp endotherms are observed at 673 and 735 K upon heating a sample of Cu$_2$ZrCl$_6$ from room temperature to 773 K at a rate of 10$^\circ$/min. These correspond to the temperatures of the high-temperature thermochromic (and structural) phase transition, and the melting point, respectively. Cooling at the same rate finds that both transitions supercool by about 20 $^\circ$. These same transitions were observed on multiple heat–cool cycles confirming that no decomposition takes place under these conditions. However, the material will sublime at the elevated temperatures, thus requiring the use of hermetically sealed, high-pressure DSC pans. Low temperature DSC measurements were made from room temperature to 93 K at a cooling rate of 10$^\circ$/min. However, these data are essentially featureless, given the sensitivity of our instrument.

3.2. Color and thermochromism

At room temperature, Cu$_2$ZrCl$_6$ exhibits a pale yellow color. Upon cooling the sample in liquid nitrogen (77 K) it becomes colorless, but returns to its original color upon warming. Upon heating to 673 K the sample exhibits a sharp thermochromic transition to a burnt red color before it is observed to melt at 735 K. The room temperature diffuse reflectance spectrum of Cu$_2$ZrCl$_6$, shown in Fig. 4, with the onset of absorption at approximately 21 000 cm$^{-1}$ is consistent with the yellow color and an optical band gap of about 2.9 eV. A second broad maximum in the absorption spectrum is observed at around 35 000 cm$^{-1}$. By way of comparison, the diffuse reflectance spectrum of the colorless $[\text{H}_2\text{NMe}_2]\text{CuZrCl}_6$, and CuCl, which has a band gap of 3.2 eV [16], are also given in Fig. 4b and c, respectively. The other starting material, ZrCl$_4$, has a band gap in the vacuum ultraviolet; beyond the limits of our instrumentation. These spectra further provide no evidence for the presence of any copper (II) chloride (onset of absorption at 16 000 cm$^{-1}$). Due to our instrumental limitations it has not been possible to obtain spectroscopic data for either the high-temperature or low-temperature phases.

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3.3. Magnetic susceptibility

A series of magnetic measurements were made to confirm that the yellow color in Cu$_2$ZrCl$_6$ was not due to a Cu(II) impurity. In the absence of a paramagnetic impurity, we further wanted to investigate the van Vleck paramagnetism of this material with a relatively small
HOMO-LUMO gap between the high-lying d$^{10}$-orbitals of Cu(I) and the low-lying d$^{0}$-orbitals of Zr(IV). Measurement of the magnetization was made both as a function of temperature and of the applied field. Because any magnetic response from this material would be expected to be quite small, measurements were made in both fused silica and DELRIN sample holders to verify that the observed responses were not artifacts of the sample holder. Parallel measurements were also made on materials from different synthetic preparations to control for possible impurities introduced in the synthesis.

A plot of the magnetic susceptibility, $\chi$, as a function of temperature at applied field strengths of 0.05, 0.5, 1.0 and 5.0 T is given in Fig. 6. A diamagnetic core correction of $1.9 \times 10^{-3}$ emu mol$^{-1}$, taken from tabulated values [17], was applied to this data. A weak and nearly temperature independent susceptibility is observed, albeit surprisingly dependent upon the magnitude of the applied field. A pronounced step is observed in the magnetic susceptibility data at around 120 K, which apparently corresponds to the low-temperature thermochromic transition. This transition is most pronounced in the low-field measurements, and tends to be masked at higher applied fields. A plot of the magnetization as a function of the applied field is given in Fig. 7. These data demonstrate a paramagnetic susceptibility at low applied fields. However at an applied field of greater than about 0.1 T the paramagnetism saturates and the diamagnetic susceptibility dominates. While the slope of the high field response of the $M$ vs. $H$ curve (the diamagnetic susceptibility) is approximately constant over the temperature range examined, the $y$ intercept increases with decreasing temperature due to a temperature dependence of the paramagnetic contribution. A parallel set of measurements was made on the related compound [H$_2$NMe$_2$]CuZrCl$_6$, which was made from the same CuCl$_2$ and ZrCl starting materials. No step in the susceptibility at 120 K was observed in the [H$_2$NMe$_2$]CuZrCl$_6$ measurements, and the known hydrogen-bond induced structural phase transition at 210 K [7] is not apparent in the magnetic data. Although about half the magnitude, the $M$ vs. $H$ data for [H$_2$NMe$_2$]CuZrCl$_6$ similarly exhibit a paramagnetism at low applied field that saturates above an applied field of about 0.1 T. Unlike Cu$_2$ZrCl$_6$ the $y$ intercept of the slope of the high field data is temperature independent for [H$_2$NMe$_2$]CuZrCl$_6$, suggesting that both paramagnetic and diamagnetic components of the later material are temperature independent.

4. Discussion

4.1. Understanding the structure of Cu$_2$ZrCl$_6$

The complex network structure of Cu$_2$ZrCl$_6$ can most readily be understood by a comparison to the structure of ZrCl$_3$. The c lattice constant in these materials is virtually identical; 6.13 Å for ZrCl$_3$ and 6.15 Å for Cu$_2$ZrCl$_6$, consistent with the hcp chloride sublattice common to both materials. In the $a$-$b$ plane, the unit cell of Cu$_2$ZrCl$_6$ represents a $\sqrt{3} \times \sqrt{3}$ expansion of the ZrCl$_3$ unit cell as shown in Fig. 8a and b. In ZrCl$_3$, the face-sharing octahedral chains, Fig. 8c, reside on the 6$_3$-axis, which also correspond to the edges of the unit cell. In Cu$_2$ZrCl$_6$, half of the Zr atoms are removed and are replaced by Cu atoms that are distributed throughout tetrahedral interstices surrounding the now vacant octahedral interstice. If the zirconium atom at $z=0.5$ is removed, the symmetry of this broken chain is lowered to 3$m$ and all six tetrahedral interstices surrounding this site are equivalent; this is the site of Cu(2) in Cu$_2$ZrCl$_6$. By contrast if the zirconium atom at $z=0.0$ is removed, the symmetry of the broken chain is lowered to 3$m$. Now two crystallographically distinct sets of tetrahedral interstices surround the vacant octahedral interstice providing the sites for Cu(1) and
Cu(3) in Cu₆ZrCl₆. Independently, the Cu(1) and Cu(3) sites form rings of three corner shared tetrahedra which in turn are capped by an octahedral zirconium chloride unit creating the Cu₂ZrCl₁₂ adamantane-type building blocks. These adamantane-type building blocks are then stacked into chains pointing in the +c direction for occupation of the Cu(1) site and in the −c direction for occupation of the Cu(3) site, Fig. 2a and c, respectively. By contrast, the Cu(2) sites surrounding a 3m octahedral interstice form chains of bicapped trigonal antiprisms equivalent to the superposition of the two adamantane-type chains formed by Cu(1) and Cu(3). Unlike the structure of ZrCl₃ where the chains are isolated by van der Waals contacts, occupation of the tetrahedral copper sites link these chains into three dimensional networks through inter-chain Cu−Cl bonds. These external Cu−Cl bonds that are elongated in Cu₂ZrCl₁₂, likely the result of a second-order Jahn–Teller trigonal pyramidal distortion commonly observed in cuprous chlorides [2].

Full occupancy of any one copper site would result in the formation of one of the three different lattices shown in Fig. 9a−c; each with the same Cu₆ZrCl₆ stoichiometry. The set of zirconium and chloride positions are equivalent in each figure. When the Cu(1) site is fully occupied, Fig. 9a, the lattice consists of chains of Cu₂ZrCl₁₂ building blocks running along the +c direction, which are connected laterally along a and b by chloride bridges to isolated Zr(2)Cl₆ octahedra. Each Zr(2)Cl₆ octahedron links six different chains through long, apical Cu(1)−Cl(2), 2.511(6) Å, bonds. Full occupancy of the Cu(3) site, Fig. 9c, results in analogous chains that are oriented in the −c direction and are connected to each other by the bridging Cl(1), which is apical to the adamantine-type building block of one chain, Cl(1)−Cu(3)=2.71(2) Å, and inner to a similar building block of a neighboring chain, Cl(1)−Cu(3)=2.20(1) Å. While adjacent chains are connected by bridging halides, in this lattice model the Zr(2)Cl₆ octahedra are completely isolated in channels constructed from the network of chains. By contrast, when only the Cu(2) sites are fully occupied, as shown in Fig. 9b, three chains of bicapped trigonal anti-prisms are linked to Zr(1)Cl₆ octahedra through chloride bridges, Cu(2)−Cl(3)=2.35(1) Å. This connectivity also leaves three terminal Zr(1)−Cl(1) contacts in the network.

The structural solution described above suggests the possibility of a variable copper stoichiometry, up to Cu₆ZrCl₆. However, off composition loadings exhibit no discernable change in lattice constants, thus providing no evidence of any significant variation in stoichiometry. Copper rich compositions (Cu₂+,ZrCl₆), or even occupation of only the Cu(2) site by greater than 0.5 would require quite close copper–copper contacts, ~2.3 Å. While such edge shared tetrahedral linkages are known for cuprous chlorides, connectivity through sharing tetrahedral corners is much more common. The requirement of such close copper–copper contacts in the lattice resulting from the full occupation of the Cu(2) site leads us to suspect that this structure is energetically unfavorable. Nevertheless, we find no reason why one of the ordered lattices resulting from the complete occupancy of either Cu(1) or Cu(3) is not energetically favored over the observed...
disordered structure. Careful examinations of the diffraction data provide no evidence for the twinning of crystals with different copper site occupancies. To consider the possibility of the in-registry growth of crystallite domains, each with a unique copper site occupation, the calculated powder patterns for the three lattices obtained by the occupation of individual copper sites (Fig. 10b–d) were compared with the observed powder diffraction (Fig. 3). For each of these calculated patterns the (100) reflection is observed to exhibit significant intensity. But this reflection is absent in the observed room temperature powder and single crystal data. Notably, the (100) reflection is also absent from the diffraction pattern calculated for the model based on the fractional occupancy of all three copper positions (Fig. 10a). By contrast, the 100 K X-ray powder diffraction data (Fig. 3b) exhibits a reflection at $Q = 0.59 \, \text{Å}^{-1}$ that may be related to a (100)-type reflection. This reflection is calculated to be less intense in the neutron diffraction given the difference between X-ray and neutron scattering factors, and as a result is not observed in the low temperature neutron data. The appearance of this low $Q$ reflection along with the splitting of the other reflections is suggestive of a lower symmetry model in which the Cu atoms are possibly localized in certain of the tetrahedral interstices at low temperature. Nevertheless, we conclude that at room temperature any ordering of copper atoms into domains with specific site occupancies does not occur over distances of larger than at most a few unit cells. Given the apparently insignificant difference in energetic preference for the three copper site occupancies, we speculate that the copper atoms have significant mobility throughout this lattice. By contrast, at low temperature, the copper atoms are likely localized in specific sites.

### 4.2. Color and thermochromism

The pale yellow color observed for Cu$_2$ZrCl$_6$ at room temperature is a result of the onset of absorption at around 20,000 cm$^{-1}$ (500 nm) as seen in Fig. 4a. This absorption originates from the insertion of the empty zirconium d-orbitals into the copper centered (Cu-d$^{10}$ to Cu-$s^2$) band gap of cuprous chloride. We previously demonstrated that the electronic localization caused by alternation of Al (III) and Cu (I) in CuAlCl$_3$ flattens the valence and conduction bands and shifts the absorption deeper into the UV than is observed for the binary CuCl [3]. The lowest energy absorption in CuAlCl$_3$ was also clearly shown to be due to the Cu-d$^{10}$ to Cu-d$^5s^5$ transition. Here we assign the broad absorption maximum at 35,000 cm$^{-1}$ to the copper centered transition in Cu$_2$ZrCl$_6$. (The Cl-lone pair to Zr-4d transition in ZrCl$_4$ is in the vacuum UV.) Unlike Al(III), however, the octahedral Zr(IV) introduces the low-lying and empty t$_{2g}$-type non-bonding orbitals to the system. Under the $C_{3v}$ symmetry of the Cu$_2$ZrCl$_{12}$ adamantane cage-type units the zirconium nonbonding orbitals transform with $a_1$ and $e$ symmetry, and, the set of copper d-based Cu–Cl $\sigma^*$ orbitals transform as two orbitals of $a_1$ symmetry, one $a_2$ orbital and three sets of orbitals with $e$ symmetry. Several transitions between the Cu-d$^{10}$ to the Zr-d$^0$ are allowed, and sufficient orbital overlap is possible given the Cu–Zr distance of only 3.2 Å, such that this metal-to-metal charge transfer is responsible for the low energy band edge, and thus the color at room temperature. These assignments are further supported by Extended Hückel calculations, in which the projected DOS clearly shows a majority of Cu and Cl character with a small amount of Zr in the valence band, whereas the much narrower conduction band is localized on the non-bonding Zr d-orbitals. [18]

The abrupt color changes over small ranges in temperature at around 120 and 673 K, respectively, are characteristic of discontinuous thermochromic transitions and suggest that the thermochromism of Cu$_2$ZrCl$_6$ is due to either first- or second-order structural phase transitions. The low temperature DSC measurements provide no evidence for the phase transition, consistent with a very small and reasonably a continuous change in enthalpy across the phase transition. Thus the 20–30 °C temperature range over which the structural transformation appears to occur suggests that the low temperature transition is a second order phase transition. In addition to the proposed localization of the copper atoms into discrete sites, based on the low temperature diffraction data, we suspect that the copper atoms adopt a more ideal tetrahedral geometry at low temperature, analogous to the phase transition behavior we have previously reported for ((bz)Cu)$_2$ZrCl$_6$ [6] and [H$_2$NMe$_2$]CuZrCl$_6$ [7]. The movement of copper away from a tetrahedral face into the center of the interstice will result in a slight lowering of the Cu–Cl $\sigma^*$

![Fig. 10. Calculated powder X-ray diffraction patterns for the lattices of Cu$_2$ZrCl$_6$ (a) with a fractional occupancy of all three copper sites, (b) with complete occupancy of Cu(1), (c) with complete occupancy of Cu(2) and (d) with complete occupancy of Cu(3).](image-url)
HOMO (Scheme 1) thus shifting the absorption edge into the UV to give a colorless material.

A sharp endotherm at 673 K characteristic of a first-order phase transition is observed by DSC upon heating Cu$_2$ZrCl$_6$ prior to the melting endotherm at 735 K, as shown in Fig. 5. At this phase transition an abrupt color change from yellow to burnt-orange is observed. This phase transition is reversible as seen by the reverse color change and the exotherm in the DSC observed upon cooling. All attempts to obtain structural data for this high temperature phase have been complicated by the sublimation of the material out of the X-ray beam when at elevated temperatures. Undoubtedly at temperatures above this phase transition there will be increased disorder and/or mobility of the copper atoms. This high temperature phase transition may be related to the thermochromism observed in Ag$_2$Hgl$_4$ and Cu$_2$Hgl$_4$ [19]. In these materials the room temperature color is assigned to iodine-to-mercury charge transfer. The thermochromism has been assigned to an increased width of the iodine p-bands due to metal–iodine interactions above the phase transition temperature when copper or silver atoms are disordered over multiple tetrahedral sites. In Cu$_2$ZrCl$_6$, the HOMO (valence band) is not halide centered because the chlorine is much more electronegative than iodine. However, the Cu–Cl σ* orbitals (bands) have a substantial mix of both copper and chlorine character and thus will similarly be influenced by the copper distribution and site symmetry. As the copper atoms traverse between tetrahedral interstices, they must pass through either a trigonal face or two coordinate edge of the tetrahedron. It has been shown that such copper ion mobility is facilitated by a second-order Jahn–Teller distortion whereby the low-lying and empty copper 4s- and 4p-orbitals mix into the copper d-orbitals [2]. By moving the copper atom into a trigonal face between interstices, the t$_2$-type Cu–Cl σ* orbitals of the tetrahedral interstice are split such that an a$_g$ orbital is stabilized and an e set of orbitals are destabilized as described in Scheme 1. Such a destabilization of the HOMO by placing the copper into a site of trigonal coordination above the high temperature phase transition could account for the decrease in the band gap, and thus the yellow to burnt-orange thermochromism.

4.3. van Vleck paramagnetism

The magnetic susceptibility of materials with closed shell ground states (i.e. with no permanent magnetic moment) yet exhibit a temperature independent or van Vleck paramagnetism is a relatively understudied phenomenon. Initially described by van Vleck this temperature independent paramagnetism observed for close shell materials originates from the coupling of ground and excited states through a magnetic field if there is spin–orbital coupling [20]. As such, the magnitude of this effect is greatest for systems that exhibit low-lying excited states. The [MnO$_4$]$^{2-}$ and [CrO$_4$]$^{2-}$ anions are archetypal examples of van Vleck paramagnetism, although this phenomenon has been observed for numerous closed shell transition metal compounds [21]. Normally resulting from intramolecular interactions, van Vleck paramagnetism has also been measured for a series of charge transfer salts in which the magnitude of the paramagnetic susceptibility is inversely correlated to the energy of the charge transfer bands [22]. Recently, controversy has surfaced with regard to the possible van Vleck paramagnetism in In$_2$ZrBr$_6$, which was proposed to originate from an indirect electronic coupling between occupied In 5s- and empty Zr 4d-orbitals through the bromide bridges [23,24]. The challenge facing all of these studies is the deconvolution of the contribution of the diamagnetic core from any van Vleck paramagnetic susceptibility. In most cases, a diamagnetic susceptibility is measured that is smaller than that expected, based on Pascal’s constants for the diamagnetic core [17]. Paramagnetism is thus implied after subtraction of the diamagnetic core correction from the measured susceptibility. However, measurement of the magnetization as a function of the applied field and temperature allow us to separate the diamagnetic and paramagnetic components of the susceptibility.

Given the small magnitude of the observed magnetic response for Cu$_2$ZrCl$_6$, it is difficult to unequivocally distinguish an intrinsic effect of a material from a small magnetic impurity, although, the temperature independence of van Vleck paramagnetism is notably distinct from the behavior of a simple paramagnetic impurity. Thus, we must preface this part of the discussion with the possibility that the observed effects are due to some kind of magnetic impurity. Nevertheless, based on the following evidence we have attempted to rule out the likelihood that the observed effects are due to magnetic impurities: (1)
Equivalent data are obtained for samples originating from different sample preparations. (2) Equivalent data are obtained from samples sealed in fused silica and DELRIN sample holders, respectively. (3) Samples of \( \text{Cu}_2\text{ZrCl}_6 \) are EPR silent at room- and low-temperature. (4) Distinct, but related behavior is observed for multiple preparations of the related compound \([\text{H}_2\text{NMe}_2]\text{CuZrCl}_6\) that was prepared from the same CuCl and ZrCl\(_4\), starting materials. (5) The temperature effect on the \( M \) vs. \( H \) measurements are distinctly different for \( \text{Cu}_2\text{ZrCl}_6 \) and \([\text{H}_2\text{NMe}_2]\text{CuZrCl}_6\).

The molar magnetic susceptibility data for \( \text{Cu}_2\text{ZrCl}_6 \) at applied field strengths of 0.05±5.0 T (Fig. 6), are essentially temperature independent. However, when plotted on the expanded scale of Fig. 6 (two orders of magnitude less than a \( S=1/2 \) system), subtle temperature and field effects are observed. Immediately apparent is the field dependence of this data, and the jump in the susceptibility data at about 120 K. We note that at applied fields above about 1 T, the 'paramagnetic susceptibility' of \( \text{Cu}_2\text{ZrCl}_6 \) is only a result of the measured diamagnetic susceptibility being smaller than the diamagnetic core correction. However, a paramagnetic susceptibility is measured directly under applied fields of less than about 1 T. Data obtained on the related compound \([\text{H}_2\text{NMe}_2]\text{CuZrCl}_6\) exhibit a similar field dependence, however, no transition at 120 K is observed. Thus, we believe that jump in the susceptibility of \( \text{Cu}_2\text{ZrCl}_6 \) is a manifestation of the low temperature thermochromic, and structural phase transition. A similar conclusion was proposed by Dronskowski [23] to explain the observed magnetic response in \( \text{In}_2\text{ZrBr}_6 \). His conclusion was later contested by Jansen et al. [24]. However, when the data from the latter report are digitally scanned and expanded to the same scale as that reported in the former (as well as subtracting the diamagnetic core correction), the two sets of data are seen to be very similar, further supporting the idea that the structural phase transitions may be manifest in the van Vleck paramagnetism. Nevertheless, the impact of this phase transition on the susceptibility appears to be masked at higher applied field strengths, suggestive of a magnetic saturation.

To further probe the field dependence of this magnetic response, we have measured the magnetization as a function of applied field at several temperatures between 5 and 300 K for both \( \text{Cu}_2\text{ZrCl}_6 \) (shown in Fig. 7) and \([\text{H}_2\text{NMe}_2]\text{CuZrCl}_6\). These data exhibit a maximum in the magnetization at applied field strengths of about 0.1 T. A mixture of a ferromagnetic impurity and a diamagnetic compound might account for such data. However, while only \( 4.7 \times 10^{-5} \) g of iron (out of the total sample of 0.041 g) could account for a molar magnetization of \( 1 \times 10^{-4} \) emu mol\(^{-1} \), it seems unlikely that multiple preparations would yield the same very small amount of an iron impurity. Furthermore, while the \( M \) vs. \( H \) data for \( \text{Cu}_2\text{ZrCl}_6 \) exhibit a notable temperature dependence, inset of Fig. 7 (itself inconsistent with a ferromagnetic impurity), the equivalent data for \([\text{H}_2\text{NMe}_2]\text{CuZrCl}_6\) are temperature independent. Thus we believe that the observed response is intrinsic to these materials and not an impurity. The negative linear slope at high fields of the \( M \) vs. \( H \) data is equal to the diamagnetic susceptibility, \( \chi_{\text{dia}} \). The diamagnetic susceptibility of \( \text{Cu}_2\text{ZrCl}_6 \), extracted from the average of the linear fits of the − and +0.4 to 5.0 T data obtained at temperatures between 5 and 300 K, are plotted in Fig. 11, and are observed to be essentially temperature independent. The slight up-turn in this \( \chi_{\text{dia}} \) below 100 K may be a result of a small paramagnetic impurity. Similar behavior is observed for \([\text{H}_2\text{NMe}_2]\text{CuZrCl}_6\). The magnitude of the measured \( \chi_{\text{dia}} \), \(-1.6 \times 10^{-7} \) emu mol\(^{-1} \) for \( \text{Cu}_2\text{ZrCl}_6 \), and \(-1.7 \times 10^{-4} \) emu mol\(^{-1} \) for \([\text{H}_2\text{NMe}_2]\text{CuZrCl}_6\), are consistent with the values obtained from the sum of Pascal’s constants, \(-1.9 \times 10^{-4} \) emu mol\(^{-1} \) and \(-1.8 \times 10^{-4} \) emu mol\(^{-1} \), respectively. This diamagnetism can then be subtracted from the \( M \) vs. \( H \) data to yield Fig. 12, for example, which is presumably a picture of the field dependence of the van Vleck paramagnetism.

The saturation magnetization of this van Vleck paramagnetism, \( M_{\text{sat, \text{VV}}} \), can be readily determined from the \( y \)-intercept of the high field \( \chi_{\text{dia}} \) curve of Fig. 7, and is plotted as a function of temperature in Fig. 13. Only a small decrease in this \( M_{\text{sat, \text{VV}}} \) is observed for \([\text{H}_2\text{NMe}_2]\text{CuZrCl}_6 \) upon decreasing temperature from 300 to 20 K. A slight decrease in the \( y \)-intercept would be the expected effect of a small paramagnetic impurity (i.e. the measured slope, \( \chi_{\text{dia}} + \chi_{\text{impurity}} \), would be less negative resulting in a smaller \( y \)-intercept). By contrast the \( M_{\text{sat, \text{VV}}} \) of \( \text{Cu}_2\text{ZrCl}_6 \) is about twice the magnitude of that observed for \([\text{H}_2\text{NMe}_2]\text{CuZrCl}_6\) and exhibits a remarkable tempera-

![Fig. 11. Lower plot: Diamagnetic susceptibility, \( \chi_{\text{dia}} \), extracted as the slope of the \( M \) vs. \( H \) data between 0.4 and 5.0 T, as a function of temperature. Upper plot: van Vleck paramagnetic susceptibility, \( \chi_{\text{VV}} \), extracted as the slope of the \( M \) vs. \( H \) data between ±200 T, as a function of temperature. (Note the order of magnitude difference in the scales of these respective plots.).](image-url)
magnetic susceptibility, $\chi_{\text{para, VV}}$, from the slope of the low field $M$ vs. $H$ data ($\pm 0.02$ T), although there is considerably more scatter to this data, thus any conclusions from it must be made cautiously. Nevertheless, these data, shown in Fig. 11, suggest a $\chi_{\text{para, VV}}$ of about $1.2 \times 10^{-3}$ emu mol$^{-1}$ above the thermochromic transition and a $\chi_{\text{para, VV}}$ of about $1.6 \times 10^{-3}$ emu mol$^{-1}$ below the phase transition. A value of $\chi_{\text{para, VV}} = 2 \times 10^{-3}$ emu mol$^{-1}$ is obtained for $[\text{H}_2\text{NMe}_2]\text{CuZrCl}_6$, although the magnetization begins to saturate and thus deviate from a linear response even by 0.01 T. Interestingly, both the colorless, low-temperature phase of $\text{CuZrCl}_6$ and the colorless $[\text{H}_2\text{NMe}_2]\text{CuZrCl}_6$ exhibit a larger $\chi_{\text{para, VV}}$ than is observed for the room-temperature phase of $\text{CuZrCl}_6$ that has the smaller band gap. These data are consistent with the above hypothesis that the low temperature phase of $\text{CuZrCl}_6$ exhibits a more ideal local tetrahedral coordination around Cu, analogous to that observed in $[\text{H}_2\text{NMe}_2]\text{CuZrCl}_6$. However, this trend in the $\chi_{\text{para, VV}}$ is inverse to that anticipated based on the band gap (i.e. $\chi_{\text{para, VV}}$ is anticipated to be inversely proportional to the band gap). While the optical band gap due to the Cu$\rightarrow$Zr transition increases as the copper moves into the center of a tetrahedral interstice, this motion also significantly reduces the second-order Jahn–Teller mixing of the Cu-3d and Cu-4s,p orbitals, which lowers the energy of the empty Cu-4s,p orbitals. Thus, while the Cu$\rightarrow$Zr band gap increases on going to the tetrahedral geometry, the Cu-3d$\rightarrow$Cu-4s band gap may decrease. Therefore, a combination of the copper centered and copper$\rightarrow$zirconium centered charge transfer likely account for the increase in the $\chi_{\text{para, VV}}$ and $M_{\text{sat, VV}}$ of $\text{Cu}_2\text{ZrCl}_6$ at low temperature.

5. Summary

The solid state reaction of CuCl and ZrCl$_4$ was shown to yield $\text{Cu}_2\text{ZrCl}_6$. The structure of this compound is most reasonably understood as a derivative of the ZrCl$_4$ structure-type. Here, every other metal site in a ZrCl$_4$ face-sharing octahedral chain is removed, and is replaced by copper(I) atoms, which partially occupy the six tetrahedral interstices surrounding the now vacant octahedral interstice. The multiple tetrahedral interstices provide three crystallographically equivalent sites over which the copper atoms are disordered at room temperature. The compound $\text{Cu}_2\text{ZrCl}_6$ is observed to undergo two thermochromic and structural phase transitions at 120 and 473 K, respectively. Copper-to-zirconium charge transfer, the energy of which is determined by the geometry of the copper coordination sphere, best accounts for the color and thermochromism. As the copper atoms move out of a more ideal tetrahedral interstice at low temperature toward a site in the trigonal face of the interstice at high temperature, the band gap is decreased and thus the absorption edge is red shifted into the visible range.

![Figure 12](image-url) Saturation of the van Vleck molar magnetization of $\text{Cu}_2\text{ZrCl}_6$ at 250 K as a function of the applied field.

![Figure 13](image-url) Plot of the $y$-intercept of the high field $M$ vs. $H$ curve (equal to $M_{\text{sat, VV}}$) as a function of temperature for $\text{Cu}_2\text{ZrCl}_6$ and $[\text{H}_2\text{NMe}_2]\text{CuZrCl}_6$. The line through the $[\text{H}_2\text{NMe}_2]\text{CuZrCl}_6$ is the least squares linear fit. The line through the $\text{Cu}_2\text{ZrCl}_6$ is simply to highlight the change as a function of temperature.
Coupling between the high-lying filled Cu–Cl* orbitals and the low lying and empty Zr 4d-orbitals (or to the low lying Cu 4s- and 4p-orbitals) provides a stage on which to investigate the temperature independent paramagnetism said to result from the field induced mixing of the ground and low-lying excited states described by van Vleck [20]. While one can never completely exclude the possibility that a weak magnetic response is due to impurities, the magnetic behavior of the closed shell materials Cu₂ZrCl₆ and [H₂NMe₂]₂CuZrCl₆ seem to provide new insights into the nature of van Vleck paramagnetism. As classically understood, the magnitude of the van Vleck paramagnetism is clearly dependent on the structure of the material as well as its band gap (or HOMO-LUMO gap). However, it is reasonable to assume that like spin-only magnetization, one must also consider saturation effects. The van Vleck paramagnetism exhibits saturation effects similar to that described by the Brillouin function for classic paramagnetic systems, though here saturation occurs at very low applied fields. As a result, most literature reported values for van Vleck paramagnetic susceptibility reflect the saturation magnetization. That the colorless (i.e. larger band gap) [H₂NMe₂]₂CuZrCl₆ and low temperature form of Cu₂ZrCl₂ can be accounted for if the less distorted tetrahedral Cu site provides more effective overlap between the ground and excited states, relative to the second-order Jahn–Teller distorted trigonal prismatic geometry. By contrast the M₆sat,νV is apparently doubled for Cu₂ZrCl₆ with respect to [H₂NMe₂]₂CuZrCl₆ because it has twice the number of copper atoms per formula unit. It is necessary to now reexamine a variety of other materials that are reported to exhibit van Vleck paramagnetism to firmly establish the saturation effects, and then develop a model consistent with the phenomenon.

Acknowledgements

The authors acknowledge Dr Paul Boyle for collecting the single crystallographic data, Dr Barbara Reisner, Dr Brian Toby, and Roger Sullivan for collecting and analyzing the neutron powder diffraction data. Neutron powder data were obtained with support from the National Institute of Standards general user program (award NIST-1965), and synchrotron powder X-ray diffraction data were obtained at the National Synchrotron Light Source via the DOE BES contract (DE-AC02-98CH10886). This work was supported by the National Science Foundation (DMR-9501370, DMR-0072828, DMR-9703419 and DMR-0108605) and instrumentation grants (CHE-9509532 and DMR-9601825). J.D. Martin is a Cottrell Scholar of the Research Corporation.

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