Crystal Structure of Zn(ZnCl$_4$)$_2$(Cho)$_2$: The Transformation of Ions to Neutral Species in a Deep Eutectic System

Yogesh P. Patil,a Rajkumar Kore,a Steven P. Kelley,b Scott T. Griffin,a,c and Robin D. Rogersa,b*

a Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, USA  
b Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, QC H3A 0B8, Canada  
c Cytec Solvay Group, 1937 West Main St. Stamford, CT 06902

Table of Contents
1. Experimental procedure for combining [Cho]Cl and ZnCl$_2$..........................S1
2. Crystallographic and melting point characterization of Zn(ZnCl$_4$)(Cho)$_2$ ..........................................................S3
3. PXRD of bulk ZnCl$_2$/[Cho]Cl........................................................................S4
4. SCXRD photographs of Zn(ZnCl$_4$)$_2$(Cho)$_2$ ...................................................S5
5. References......................................................................................................S5

Experimental procedure for combining [Cho]Cl and ZnCl$_2$: ZnCl$_2$ (Sigma Life Science, St. Louis, MO) and [Cho]Cl (Reagent Grade, Amresco, Pelham, AL) were weighed onto weighing paper in the amounts listed in Table S1, transferred to an agate mortar and pestle, and ground by hand for 5 min. Both weighing and grinding were conducted in either in air or in an argon-filled (100% pure, Airgas, Tuscaloosa, AL) glove bag. The reactions done in air were then transferred to sample vials and kept in a refrigerator, while the reactions done in argon atmosphere were transferred to sample vials which were sealed tightly with Parafilm and kept at room temperature. All samples were examined for crystals under a Nikon Labphot POL optical polarizing microscope (Nikon Instruments, Meville, NY). Crystals were obtained in a few cases and were indexed as crystals of the known [Cho]Cl reported earlier. Samples for which single crystals could not be isolated were not characterized further.

Synthesis of Zn(ZnCl$_4$)$_2$(Cho)$_2$(OH)$_2$: The crystals for this compound were obtained from Zn(ZnCl$_4$)$_2$(Cho)$_2$ by adventitious absorption of moisture. Numerous attempts to reproduce these crystals were undertaken by doing the reaction in air with different ratios as mentioned in Table S1, but it was not possible to replicate its isolation.
<table>
<thead>
<tr>
<th>[Cho]Cl</th>
<th>ZnCl$_2$</th>
<th>Molar Ratio</th>
<th>Condition</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.0 mg</td>
<td>48.8 mg</td>
<td>1:1</td>
<td>In Air</td>
<td>Transparent Liquid, uncharacterized</td>
</tr>
<tr>
<td>50.0 mg</td>
<td>97.6 mg</td>
<td>1:2</td>
<td></td>
<td>Mixture of crystalline [Cho]Cl and liquid</td>
</tr>
<tr>
<td>50.0 mg</td>
<td>73.1 mg</td>
<td>2:3</td>
<td></td>
<td>Gel like material with crystals of [Cho]Cl</td>
</tr>
<tr>
<td>76.81 mg</td>
<td>50.0 mg</td>
<td>3:2</td>
<td></td>
<td>Polycrystalline material uncharacterized</td>
</tr>
<tr>
<td>50.0 mg</td>
<td>48.8 mg</td>
<td>1:1</td>
<td>Under Argon Atmosphere</td>
<td>Polycrystalline material uncharacterized</td>
</tr>
<tr>
<td>50.0 mg</td>
<td>97.6 mg</td>
<td>1:2</td>
<td></td>
<td>Crystals of [Cho]Cl and uncharacterized polycrystalline solids</td>
</tr>
<tr>
<td>50.0 mg</td>
<td>73.1 mg</td>
<td>2:3</td>
<td></td>
<td>Crystals of Zn(ZnCl$_4$)$_2$(Cho)$_2$* and unidentified solid phases.</td>
</tr>
<tr>
<td>76.81 mg</td>
<td>50.0 mg</td>
<td>3:2</td>
<td></td>
<td>Polycrystalline material uncharacterized.</td>
</tr>
</tbody>
</table>

* Present structure discussed in the paper.
Characterization with Single Crystal X-ray diffraction (SCXRD): SCXRD data were collected on a Bruker diffractometer equipped with a Platform 3-circle goniometer and an Apex II CCD area detector (Bruker-AXS, Madison, WI) using graphite-monochromated Mo-Kα radiation. Suitable single crystals were isolated under an optical polarizing microscope, mounted on a nylon loop, and cooled to the collection temperature under a stream of N2 gas using an Oxford N-helix cryostat (Oxford Cryosystems, Oxford, UK). A hemisphere of unique data was collected for each crystal using a strategy of 0.5° scans about omega and phi. Unit cell determination, data collection, integration, absorption correction, and scaling were done using the Bruker Apex2 software suite. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were fixed using a riding model. Hydrogen atoms on –OH groups were located from the difference map, their coordinates were refined freely, and their thermal parameters were constrained to ride on the carrier atoms. Zn(ZnCl4)2(Cho)2 was solved with the SIR92 program. Zn(ZnCl4)2(Cho)2(OH)2 was solved by direct methods using the Bruker SHELXTL software suite. Both structures were refined by full-matrix least squares methods on F2 using SHELXL2014.

Structural Description of Zn(Cho)2(ZnCl4)2(OH)2: For the Zn(ZnCl4)2(Cho)2(OH)2 complex, the SCXRD data were collected at -100 °C. This complex crystallized in the space group P21/c, and the molecular structure is shown in Figure S1 (left). The asymmetric unit contains half of the formula unit. This complex is a zwitterionic, trinuclear zinc complex and contains two trans [Cho]+ ions, two trans [ZnCl4]2− ions, and two trans water ligands. The water molecules, choline ligand, and chloride atoms interact via O-H···Cl hydrogen bonding both intra- and intermolecularly.

Figure S1. Left – 50% probability ellipsoid plot of the formula unit of Zn(ZnCl4)2(Cho)2(OH)2, unlabeled atoms are symmetry equivalents of labelled ones. Right – unit cell packing diagram viewed down b; dashed red lines indicate strong hydrogen bonds.

Melting point determination of Zn(ZnCl4)2(Cho)2: Under Ar in a glove bag, the crystals were ground to a powder and transferred to a Pasteur pipette, sealed at one end. The other end was temporarily sealed with parafilm. The Pasteur pipette was then flame sealed and was tied via thread to a thermometer in an oil bath. The melting point was determined by constant heating of the oil bath and found to be 55-57 °C.
**Powder X-Ray Diffraction (PXRD) of Bulk ZnCl\textsubscript{2}/[Cho]Cl:** The bulk material from which the crystals of Zn(ZnCl\textsubscript{4})\textsubscript{2}(Cho)\textsubscript{2} were characterized was analyzed by PXRD as follows. The sample preparation for the PXRD experiment was done in the glove bag under argon atmosphere. The bulk material was ground in an agate mortar and pestle. On grinding the material became sticky and was placed as a thin layer on a silicon low background sample holder. The area covered by the sample on the holder was then sealed with Kapton tape (Southwestern Bag, Los Angeles, California). The PXRD pattern was then recorded on a Bruker D2 PHASER instrument with a Linxeye linear position-sensitive detector (Bruker-AXS, Madison, WI) using Ni-filtered Cu-Kα radiation. The diffraction data was measured across the 2θ range of 4° to 40° with 0.05 step size and 3s/step exposure. A background measurement was also done for the Kapton tape coated on the holder with the same parameters.

The comparison of the PXRD patterns (Fig. S2) shows that the pattern obtained at room temperature does not match with either the reactant [Cho]Cl or the simulated pattern of Zn(ZnCl\textsubscript{4})\textsubscript{2}(Cho)\textsubscript{2} which was recorded at -50 °C. This may be due to phase transition occurring due to grinding or the temperature change from -50 °C to room temperature.

![Comparison of PXRD patterns](image)

**Figure S2:** Comparison of measured powder patterns of bulk 3:2 ZnCl\textsubscript{2}/[Cho]Cl (bottom), pure [Cho]Cl (middle), and simulated PXRD of Zn(ZnCl\textsubscript{4})\textsubscript{2}(Cho)\textsubscript{2} (top).
SCXRD photographs of Zn(ZnCl$_4$)$_2$(Cho)$_2$: To validate further the possibility of a phase transition indexing of a crystal of Zn(ZnCl$_4$)$_2$(Cho)$_2$, coated with paratone oil, was done at both -50 °C and 0 °C. The SCXRD measurement was done with the same procedure as described earlier. The lower temperature diffraction indexed as the same unit cell as that of Zn(ZnCl$_4$)$_2$(Cho)$_2$ while at 0 °C the sample crystal show twin components [indexed individually as Zn(ZnCl$_4$)$_2$(Cho)$_2$] along with unindexed peaks (68 of 372 peaks). This difference is clearly visible in diffraction photographs shown in Fig. S3. The sample becomes liquid when the temperature is increased to room temperature. This indicates a phase transformation occurs at higher temperature.

Figure S3: Still diffraction photographs for the single crystal of Zn(ZnCl$_4$)$_2$(Cho)$_2$ of the first frame with the same parameters (a) at -50 °C; (b) at 0 °C.

References

2. APEX 2 AXScale and SAINT, version 2010; Bruker AXS, Inc.: Madison, WI.