Electronic Supplementary Information

Crystal Structure of $Zn(ZnCl_4)_2(Cho)_2$: The Transformation of Ions to Neutral Species in a Deep Eutectic System

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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.[1] Samples for which single crystals could not be isolated were not characterized further.

Synthesis of $Zn(ZnCl_4)_2(Cho)_2(OH_2)_2$: 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 S1. Different molar combinations of $ZnCl_2$ and [Cho]Cl.

[Cho]Cl	**$ZnCl_2$**	**Molar Ratio**	**Condition**	**Observation**
50.0 mg	48.8 mg	1:1	In Air	Transparent Liquid, uncharacterized
50.0 mg	97.6 mg	1:2		Mixture of crystalline [Cho]Cl and liquid
50.0 mg	73.1 mg	2:3		Gel like material with crystals of [Cho]Cl
76.81 mg	50.0 mg	3:2		Polycrystalline material uncharacterized
50.0 mg	48.8 mg	1:1	Under Argon Atmosphere	Polycrystalline material uncharacterized
50.0 mg	97.6 mg	1:2		Crystals of [Cho]Cl and uncharacterized polycrystalline solids
50.0 mg	73.1 mg	2:3		Crystals of $Zn(ZnCl_4)_2(Cho)_2$* and unidentified solid phases.
76.81 mg	50.0 mg	3:2		Polycrystalline material uncharacterized.

* 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 N_2 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.[2] 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. $Zn(ZnCl_4)_2(Cho)_2$ was solved with the *SIR92*[3] program. $Zn(ZnCl_4)_2(Cho)_2(OH_2)_2$ was solved by direct methods using the Bruker SHELXTL software suite.[4] Both structures were refined by full-matrix least squares methods on F^2 using *SHELXL2014*.[5]

Structural Description of $Zn(Cho)_2(ZnCl_4)_2(OH_2)_2$: For the $Zn(ZnCl_4)_2(Cho)_2(OH_2)_2$ complex, the SCXRD data were collected at -100 °C. This complex crystallized in the space group $P2_1/c$, 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 $[ZnCl_4]^{2-}$ ions, and two trans water ligands. The water molecules, choline ligand, and chlorine atoms interact via O-H···Cl hydrogen bonding both intra- and intermolecularly.

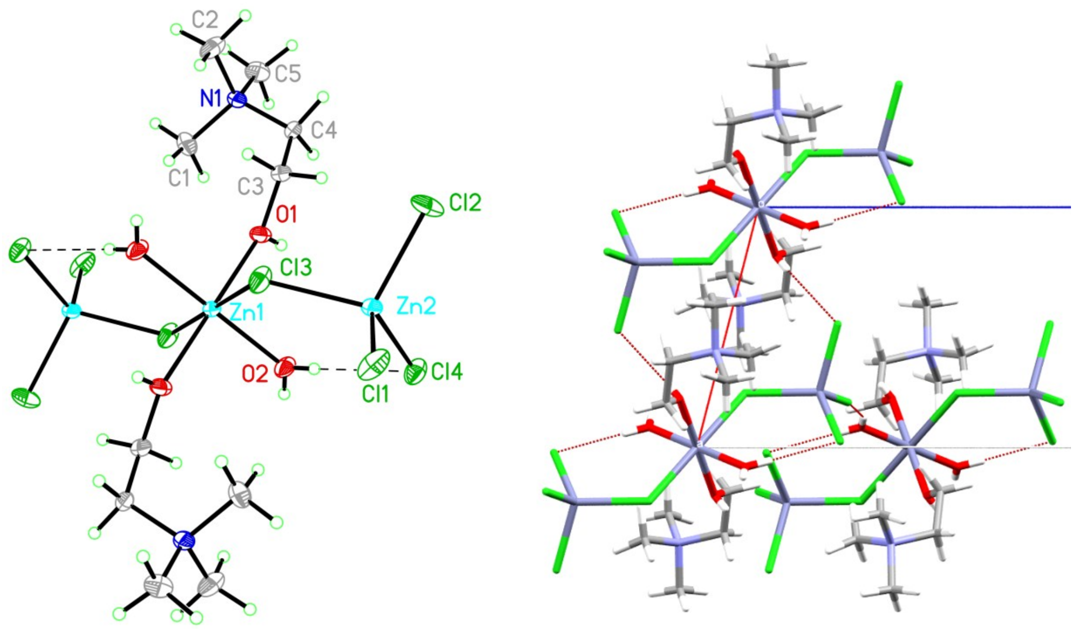


Figure S1. *Left* – 50% probability ellipsoid plot of the formula unit of $Zn(ZnCl_4)_2(Cho)_2(OH_2)_2$, unlabeled atoms are symmetry equivalents of labelled ones. *Right* – unit cell packing diagram viewed down *b*; dashed red lines indicate strong hydrogen bonds.

Melting point determination of $Zn(ZnCl_4)_2(Cho)_2$: 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 $ZnCl_2$/[Cho]Cl: The bulk material from which the crystals of $Zn(ZnCl_4)_2(Cho)_2$ 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 become 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 $Zn(ZnCl_4)_2(Cho)_2$ 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.

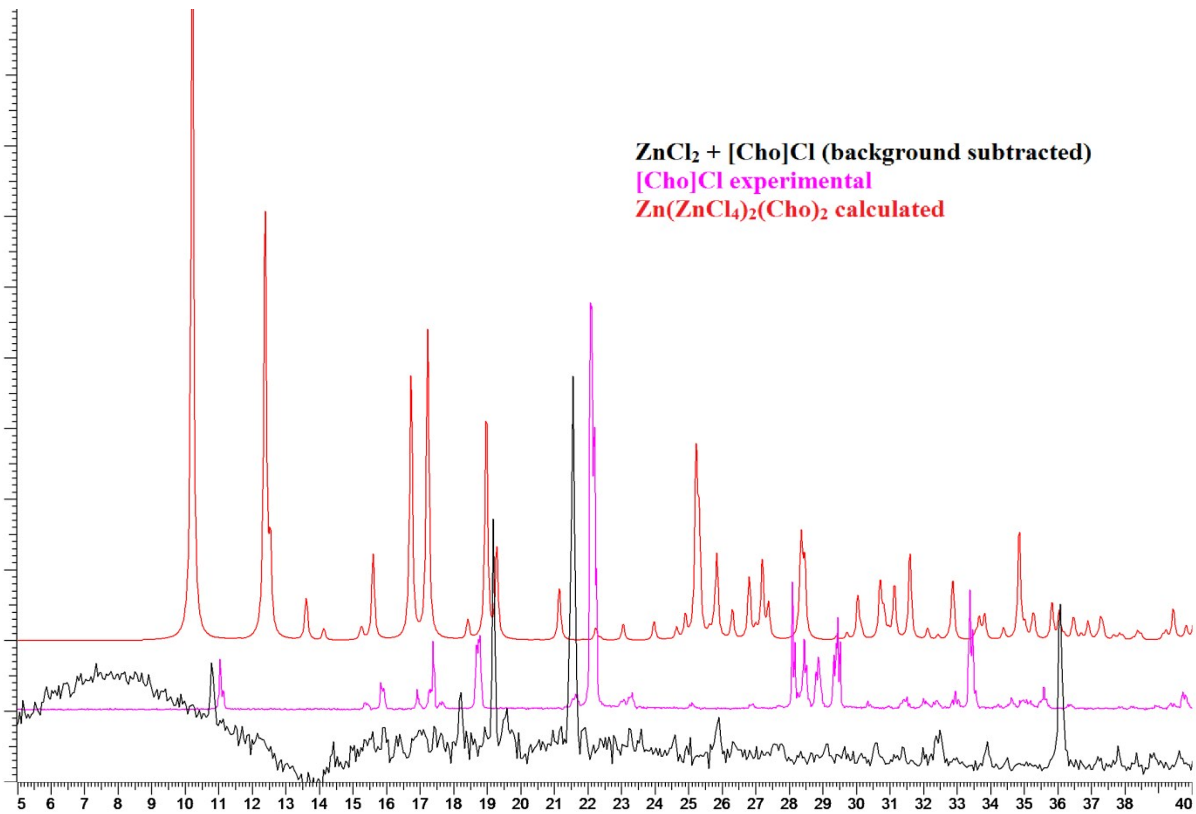
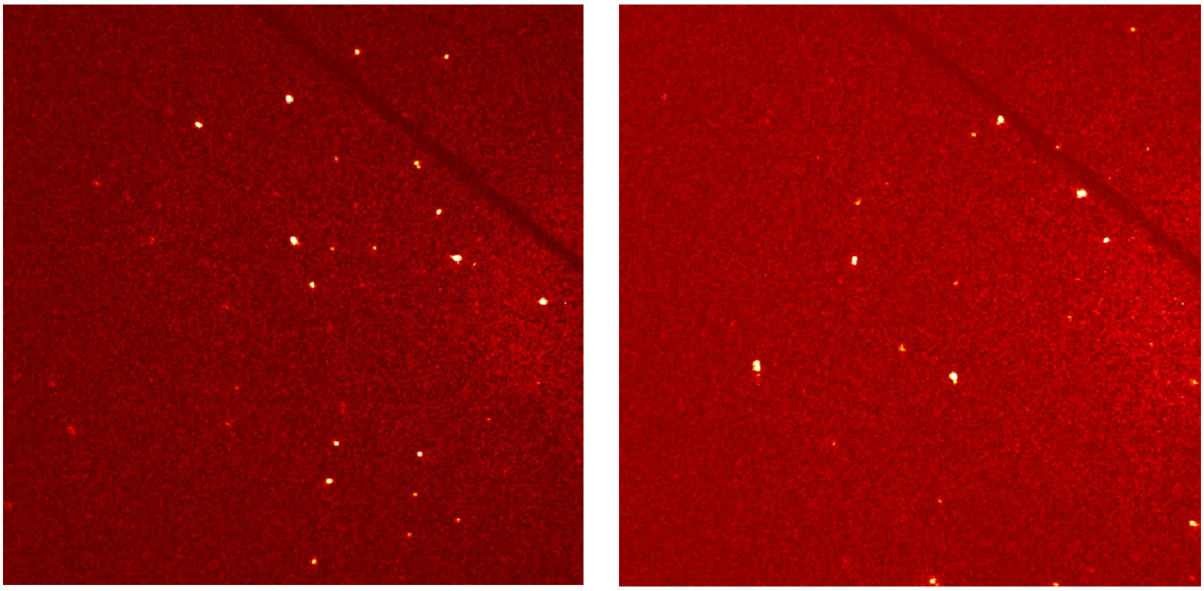


Figure S2: Comparison of measured powder patterns of bulk 3:2 $ZnCl_2$/[Cho]Cl (bottom), pure [Cho]Cl (middle), and simulated PXRD of $Zn(ZnCl_4)_2(Cho)_2$ (top).

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.



(a) **(b)**

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

[1] J. Hjortas, and H. Sorum, *Acta Cryst.,* 1971, **B27**, 1320.

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[3] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr*. 1994, **27**, 435.

[4] G. M. Sheldrick, (2001) SHELXTL, structure determination software suite, v.6.10. Bruker AXS Inc, Madison, WI.

[5] G. M. Sheldrick (2014), SHELXTL XLMP Crystal Structure Refinement Multi-CPU Version, v.2014/7, Bruker AXS Inc. Madison, WI.