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# 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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**A neutral molecular complex, $Zn(ZnCl_4)_2(Cho)_2$, has been isolated from the well-known choline chloride/$ZnCl_2$ deep eutectic system (DES) and its crystal structure has been determined. The structure demonstrates the possibility of isolating unusual coordination complexes from DES which departs from the well-established observation of such systems being formed from large, ionic metal complexes or oligomers.**

Although high melting points are considered a characteristic trait of ionic compounds, an ever-increasing range of ions have been used to make low melting salts, otherwise called ionic liquids (ILs).[1] In many cases this is due to the ability of monatomic ions to form larger polyatomic complexes. Metal ions can coordinate to anions to form anionic metal complexes with low charge, as in the well-known halometallate ILs,[2] but examples of highly charged metal complexes forming ILs are known when the complex is sufficiently large, such as $[Ln(NO_3)_6]^{3-}$,[3,4] $[Ln(SCN)_6]^{3-}$,[5] and a very recent example of the Zintl anion $[Sb_{11}]^{3-}$.[6] Complexes of metal ions with neutral ligands give rise to larger cationic complexes which can form ILs,[7] sometimes in spite of very high charges.[8] Metal-free ions can also oligomerize, particularly through hydrogen bonds between ions and their neutral conjugate acids or bases,[9] a technique which is useful for lowering the melting points of salts where covalent modification of the ion is not acceptable, as is the case for pharmaceutical molecules.[10] The formation of new polyatomic or oligomeric ions in these systems can be confirmed because the bonds (dative ligand–metal bonds or exceptionally strong hydrogen bonds) are measurable by techniques such as spectroscopy (which can measure the bonds themselves or probe the symmetry of the ion) or crystal structure analyses (where the distance between atoms can be interpreted as proof of a bond).

Deep eutectic systems (DES) are low melting compounds made by combining a salt with either a neutral molecule or another salt.[11] DES are useful because they can be made easily from innocuous starting materials, and DES made from salts of choline ($[Cho]^+$), a B-vitamin for humans, are especially well studied. These DES share many properties with ILs and are used in many of the same applications as ILs, including, for example, electrodeposition,[12] biopolymer dissolution,[13] and catalysis.[14]

It is difficult to even begin defining DES as chemicals. IL-forming combinations of salts, such as $FeCl_3$ or $AlCl_3$ and imidazolium halides,[15,16] form polyatomic ions quantitatively, while DES-forming combinations (*e.g.*, [Cho]Cl and $ZnCl_2$)[17] behave as mixtures of species. Some of these systems, such as the well-studied [Cho]Cl–urea DES,[18] do not have components that are capable of reacting in the conventional sense. However, unlike normal eutectics, which are truly mixtures, the radical change in physical properties of DES compared to their components suggests new species are forming. Observations such as the fact that alkali metal salts do not readily form DES[19] suggest the phenomenon is tied to the ability of components to form chemically distinct species, as is the case with ionic transition metal complexes. Even the exclusively noncovalent forces in metal-free DES can facilitate charge transfer and fundamentally change or weaken cation–anion interactions.[20] Still, while a certain amount can be inferred from which systems do or do not form DES, the new species that actually form have proven elusive towards isolation.

DES composed of [Cho]Cl and $ZnCl_2$ were first described by Abbot *et al.* in 2001 with a reported freezing point of 23–25 °C.[17] This system has found application as a solvent for reactions including acetylation of cellulose,[21] esterification of soybean oil,[22] and aminations,[23] as a catalyst for Friedel–Crafts reactions,[24] and in the electrodeposition of Zn metal.[25] In 2005, it was reported that different kinds of low melting crystals could be grown from

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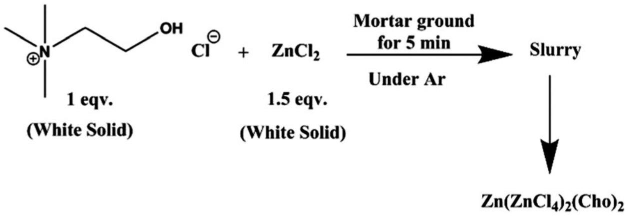

Scheme 1 Crystallization of $Zn(ZnCl_4)_2(Cho)_2$.

$[Cho]Cl/ZnCl_2$ DES at different compositions.[26] A combined DSC and XAFS study on this system led to the assignment of the liquid as containing chlorozincate anions hydrogen bonded to $[Cho]^+$ cations,[27] but the structure of the solid phase was never characterized.

Here, we report the crystal structure determination of $Zn(ZnCl_4)_2(Cho)_2$, crystallized from a 2 : 3 mol/mol combination of [Cho]Cl and $ZnCl_2$. The $[Cho]Cl/ZnCl_2$ eutectic was made by combining solid [Cho]Cl (50.0 mg) and solid $ZnCl_2$ (73.1 mg) at 2 : 3 molar ratio with *ca.* 5 min of grinding in an Ar-filled glove bag (Scheme 1). This resulted in the formation of a slurry from which crystals grew in a period of 1–2 weeks.

The crystals were found to be highly deliquescent and were quickly coated with Paratone oil before analysis by single crystal X-ray diffraction (SCXRD) under a stream of cold nitrogen (−50 °C). The deliquescence may explain why the crystal structure has never been determined, although the crystals have been observed before.[26] The melting point of the crystals, $Zn(ZnCl_4)_2(Cho)_2$, was determined visually (see ESI†) to be 55–57 °C. Different molar combinations of [Cho]Cl and $ZnCl_2$ were also attempted using the same procedure (see ESI†) which either resulted in gel-like substances or formation of [Cho]Cl crystals.[28] We were also successful in getting a new structure of $Zn(ZnCl_4)_2(Cho)_2(OH_2)_2$ as a result of moderate exposure to humid air (see ESI†), but were not able to reproduce it. Surprisingly, powder X-ray diffraction (PXRD) measurement of the bulk material from which $Zn(ZnCl_4)_2(Cho)_2$ was isolated showed a series of peaks which could not be matched to $Zn(ZnCl_4)_2(Cho)_2$ or [Cho]Cl (Fig. S2, ESI†). SCXRD photographs of a crystal at −50 °C and 0 °C show a large difference in the diffraction pattern, suggesting that the crystal structure may be of a low temperature phase (Fig. S3, ESI†). The higher temperature structure could not be indexed to a single phase and was not determined. This may be related to polymorphism in ILs, which is correlated with their low melting point and stems from the conformational flexibility of large organic ions.[29] This high degree of structural flexibility also seems to be a general trait of $ZnCl_2$, as seen from the recently published structures of its varied hydrates.[30]

The neutral compound $Zn(ZnCl_4)_2(Cho)_2$ (Fig. 1, left) crystallized in the space group $P2_1/n$ with half of a unique formula unit per asymmetric unit. This trinuclear, zwitterionic complex has a central $Zn^{2+}$ ion, residing on a crystallographic center of inversion, with an octahedral environment composed of four bridging chlorine atoms from two tetrahedral $[ZnCl_4]^{2-}$ ions and two coordinated $[Cho]^+$ ions. There are no intramolecular interactions present; instead the $[Cho]^+$ cations act donate strong hydrogen bonds through their −OH groups to $Cl^-$ ligands on neighboring molecules. These hydrogen bonds organize the complexes into infinite layers which stack perpendicular to the *ac* diagonal (Fig. 1, right).

Perhaps the most striking feature of the $Zn(ZnCl_4)_2(Cho)_2$ complex is that it is overall neutral. It is generally understood that melting point reduction in ILs and DES made from metal salts occurs because larger, more weakly coordinating ions are being formed and possibly interconverting with each other through dynamic equilibrium. Such a phenomenon reduces the stability of a crystalline lattice relative to the liquid state, but does not change the overall ionic nature of the compound. The possibility of forming significant amounts of neutral complexes such as $Zn(ZnCl_4)_2(Cho)_2$ suggests melting point depression in

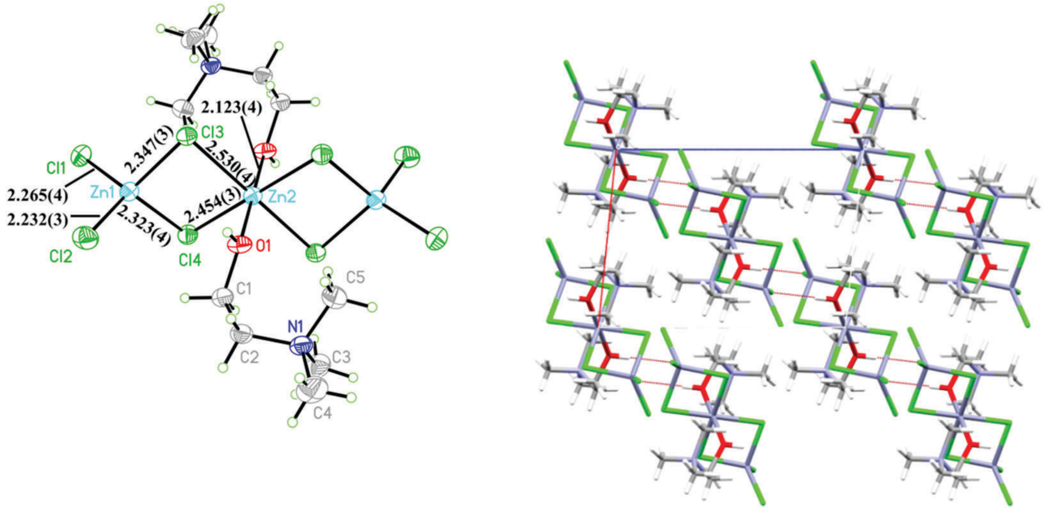

Fig. 1 Left – 50% probability ellipsoid plot of the formula unit of $Zn(ZnCl_4)_2(Cho)_2$ (unlabeled atoms are symmetry equivalents of labeled ones) with Zn–ligand bond distances in Å. Right – 1.5 × 1.5 × 1.5 unit cell packing diagram viewed down *b*; dashed red lines indicate strong hydrogen bonds (axes are color coded: red = *a*, blue = *c*).

DES may occur because the actual number of free ions has decreased. Even transient interactions between cations and anions in ILs can lower the ionicity, a measurable property related to how strongly the ions respond to an electric field.[31] The crystallization of $Zn(ZnCl_4)_2(Cho)_2$ appears to be due to its ability to form charge-assisted hydrogen bonded chains rather than the type of charge-separated network that is found in virtually all crystalline ionic compounds (even those capable of hydrogen bonding).[32] Our group has also observed that, for organic acids and bases, those that form effectively neutral complexes rather than free ions tend to have greatly reduced melting points.[33] Previous investigations on the transport properties $ZnCl_2$/[Cho]Cl deep eutectics have found that the ions are too large to easily migrate through the bulk fluid,[34] so the ability of $Zn(ZnCl_4)_2(Cho)_2$ to form polymeric hydrogen bonds possibly through only rotation of the $[Cho]^+$ ligands and reorientation of the molecule may be what allows it to crystallize selectively.

Another feature of $Zn(ZnCl_4)_2(Cho)_2$ is that it captures a higher state of organization of the ions than is normally observed in ILs and DES. $ZnCl_2$ is able to abstract $Cl^-$ ions from [Cho]Cl to form polyatomic chlorozincate ions, as has been observed in other ILs based on $ZnCl_2$ and chloride salts.[35] However, these ions, as well as $[Cho]^+$, are further organized by coordination to the central $Zn^{2+}$ ion. The resulting complex thus has every component from the two starting salts, but with the original ionic bonding completely reorganized.

The key to this is the possibility of a cation–cation interaction between $[Cho]^+$ and $Zn^{2+}$. While $[Cho]^+$ complexes with metal ions are actually not that common (Cu[36] and Nd[37] are the only structurally characterized examples), the concept of tethering a metal-coordinating group to an IL cation is rather well-explored.[38] The structurally characterized complex formed between $Co^{2+}$ and a nitrile-functionalized imidazolium IL is one example.[39] The ability of $[Cho]^+$ to coordinate metal ions may be connected to its ability to form so many DES, and salts of cations with metal coordination groups (for instance, protonated basic amino acids) may be a useful family to screen for new DES.

It is also notable that $Zn(ZnCl_4)_2(Cho)_2$ is the first structurally characterized example of a molecule containing the trinuclear $[Zn_3Cl_8]^{2-}$ core. The Cambridge Structural Database[40] contains only three examples of $Zn^{2+}$ chlorometallates with a higher nuclearity than $[Zn_2Cl_8]^{2-}$. Among these structures two are infinite polymeric anions,[35,41] while the third is a cyclic cluster, $[Zn_4Cl_{10}]^{2-}$.[42] The $[Zn_3Cl_8]^{2-}$ core in $Zn(ZnCl_4)_2(Cho)_2$ is geometrically much different from the relatively common $[Hg_3Cl_8]^{2-}$ anion wherein the $Hg^{2+}$ centers have distorted tetrahedral geometries.[43] There is a structurally characterized metal complex which is isostructural to $Zn(ZnCl_4)_2(Cho)_2$, where two $[CdCl_4]^{2-}$ ions and two thiacrown, $\{K_2Calix[4]\text{-bis-monothiacrown}\}^{2+}$ ligands are coordinated to a central $Cd^{2+}$ ion.[44] Isolation of this unusual species suggests that DES, which are primarily used in application-based studies, have potential for exploring new fundamental inorganic chemistry.

The metal–ligand bonds of $Zn(ZnCl_4)_2(Cho)_2$ are nevertheless similar to those of other $Zn^{2+}$ structures (Fig. 1). The Zn–Cl bond distances of the central $Zn^{2+}$ atom are similar to those for other octahedral $Zn^{2+}$ centers with four chlorides,[45–47] while the $[ZnCl_4]^{2-}$ bond distances are similar to those in another structurally characterized complex with this moiety, $Zn(ZnCl_4)(dimethoxyethane)_2$.[48]

In conclusion, we have shown a well-characterized example of a new species formed in a DES which, though not necessarily establishing the speciation of the DES in its molten state, nevertheless proves such neutral structures can and do form from the ions in DES. The structure also presents a well-characterized example of a neutral species formed from the separate components of an IL, which are hypothesized to lead to low melting points in different classes of ILs. Whereas speciation changes in ILs are usually conceived of as equilibria between single-step additions or exchanges of protons or monatomic ion between the components, $Zn(ZnCl_4)_2(Cho)_2$ represents a more complex case where newly formed polyatomic ions are then further organized into a yet more elaborate structure. Both of these observations are tied to the ability of $[Cho]^+$ to act as an inner-sphere ligand. These findings have implications for detecting new species in DES (particularly those that are not ionic), selecting more classes of salts for DES formation, and the use of DES in fundamental inorganic chemistry.

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