Structure and spectroscopy of CuH prepared *via* borohydride reduction

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Abstract

INTRODUCTION

In 1844 Adolphe Würtz reported to the Académie des Sciences (France), that the action of hypophosphorous acid on copper salts resulted in the formation of a copper hydride (Würtz, 1844). Copper (I) hydride, (cuprous hydride, CuH), was the first binary metal hydride to be discovered and is singular in that it is synthesised in solution, at ambient temperature. It is also unusual in that it adopts the Würtzite structure (space group $P6_3mc$, no. 186) (Goedkoop & Andersen, 1955); binary metal hydrides usually have the same crystal structure as the pure metal, (Fukai, 1993) thus for CuH a face centred cubic (fcc) structure might be expected. An fcc CuH is known but it is only stable above 12.5 GPa (Burtovyy & Tkacz, 2004). A second high pressure phase, Cu_2H, is formed at pressures above 18.6 GPa (Donnerer *et al.*, 2013). This compound exhibits an anti-CdI_2-type structure (space group P-$3m1$, $P\overline{3}m1$ no. 164), where hydrogen atoms are proposed to occupy every second layer of octahedral interstitial sites.

Würtz prepared CuH by the reduction of acidic, aqueous copper sulfate with hypophosphorous acid. This remains the most often used route to CuH (Warf, & Feitknecht, 1950; Fitzsimons *et al.*, 1995), although other routes have been developed including a sonochemical synthesis (Hasin & Wu, 2012), precipitation of the hydride from pyridine solutions of CuI and LiAlH$_4$ (Dilts & Shriver, 1968) and reduction of aqueous Cu^{2+} by borohydride ion (Dasgupta & Mahanti, 2010) (Eq. 1).

$$2Cu^{2+}_{(aq)} + 2BH_4^{-}_{(aq)} + 6H_2O \rightarrow 2CuH_{(ppt)} + 2B(OH)_{3(ppt)} + 2H^{+}_{(aq)} + 5H_{2(g)} \tag{1}$$

While the products from the Würtz and the pyridine methods have been extensively investigated (Korzhavyi *et al.*, 2012; Soroka *et al.*, 2013; Auer & Kohlmann, 2014; Bennett *et al.*, 2015) that produced *via* Eq. 1 has been much less studied. Synthesis results in an insoluble form of CuH ("CuH/BH$_4$"), in this case the precipitate is coffee-coloured rather than the rust-red obtained from the Würtz synthesis. This form also appears to be more stable than the others because it is stated that it survives in boiling water, whereas the products from the other routes decompose. The CuH/BH$_4$ product is reported to show an infrared band at 521 cm^{-1}, which was assigned to a Cu··H··Cu··H bridge structure (Dasgupta & Mahanti, 2010). However, CuO is a common decomposition product of CuH and it exhibits a strong infrared band at 537 cm^{-1} (Kliche & Popovic, 1990) and this is a more reasonable assignment. CuH/BH$_4$ was recently studied by X-ray and neutron powder diffraction (Auer & Kohlmann, 2014). The aims of this paper are to use a combination of structural and spectroscopic methods to provide further insight into the nature of CuH formed *via* the borohydride route.

EXPERIMENTAL

Synthesis. CuH/BH$_4$ was prepared by a variation of the literature (Dasgupta & Mahanti, 2010) synthesis based on Eq. 1. In a two-necked 1 L round bottom flask, CuSO$_4$.5H$_2$O (40 g, 160.2 mmol, Aldrich, 99.995%) was fully dissolved in a minimum of 2 M H$_2$SO$_4$. The aqueous mixture was degassed with argon for 2 h and warmed slowly to 30°C upon which a solution of NaBH$_4$ (6.06 g, 160.2 mmol, Aldrich, 99%) was added slowly. The vigorous exothermic reaction instantaneously resulted in coffee coloured particles of CuH and flecks of copper metal. Under an inert argon atmosphere the reaction vessel was then sealed with rubber septa and stirred at 30°C for 2 h. The mixture was then filtered through a sintered glass vacuum filter with a medium porosity (G02)

under a flowing argon blanket. The filtrate was blue due to the presence of unreacted aqueous Cu(II) sulfate. The CuH cake was washed with degassed room temperature H_2O to remove any remaining soluble starting materials, followed by 60°C H_2O to remove free boric acid crystals that form upon cooling. After being filtered and washed, the product and the sintered glass filter was transferred into a sealed argon filled glove bag. It was then weighed (7.8 g) and loaded into the sample holders for neutron characterisation (TOSCA and SANDALS). A small amount (<0.3 g) was taken and treated with ether, then dried under argon aspiration to obtain a dry powder which could be loaded into a 1 mm quartz capillary for XRD analysis.

The remaining CuH product (≈ 3.5 g) was then taken and stirred for ≈ 12 h in D_2O under an argon atmosphere. The mixture was filtered, dried *via* vacuum filtration and loaded into the sample holders for neutron studies.

Note that exclusion of air is essential. *Caution: the dried product may decompose explosively.*

Neutron diffraction. Time-of-flight neutron diffraction measurements were performed using the diffractometer, SANDALS (SANDALS, 2015) at ISIS (ISIS, 2015). The CuH sample was loaded into flat-plate 40 mm diameter cells of 1 mm or 2 mm thickness made of the null scattering alloy Ti(52.5%)Zr(47.5%). A full set of experimental corrections and an absolute normalisation were made using the standard Gudrun software (Gudrun, 2015).

X-ray diffraction. X-ray diffraction (XRD) measurements were made using a Panalytical X'Pert Pro Multi-purpose Diffractometer in capillary mode, with a silver anode source (wavelength 0.560885 Å).

Inelastic neutron scattering (INS) spectroscopy. INS spectroscopy is a complementary form of vibrational spectroscopy (Mitchell *et al*., 2005). The scattering intensity depends on the incoherent inelastic scattering cross section and the amplitude of vibration. For ^1H both of these are large, consequently the scattered intensity is dominated by hydrogenous motion. Neutrons are highly penetrating, so the spectra are representative of the bulk rather than just the surface. INS spectra were recorded with the high resolution spectrometer TOSCA (Parker *et al*., 2014) at ISIS. The CuH samples were either loaded (in a glovebag) into sealed aluminium cans or the SANDALS samples in the TiZr cans were loaded into a closed cycle cryostat, cooled to ∼20 K then the spectra were recorded for 8 – 12 h.

RESULTS AND DISCUSSION

The synthesis of CuH *via* the borohydride route has not been extensively studied. Eq. 1 requires a 1:1 stoichiometry of $CuSO_4$ to $NaBH_4$, however, it was clear from the deep blue colour of the filtrate that the limiting factor in this reaction is the $NaBH_4$. It is also worth noting that increasing the quantity of the reactants (*i.e*. 160.2 mmol → 400.5 mmol) in the hope of increasing the mass yield, gave rise to filtering and aspiration problems.

The vigorous, effervescent and exothermic reaction that occurs upon addition of the $NaBH_4$ generates sufficient localised heating to allow small amounts of decomposition to copper metal. Minute, but visible, amounts of copper metal can been seen in the reaction mixture and in the dried product, as well as visible crystals of $B(OH)_3$. The literature (Dasgupta & Mahanti, 2010) states that

full removal of this free boric acid can be achieved by boiling the crude CuH product (after filtration) in boiling water for 1 h. Addition of 70-75°C H_2O (deionised and degassed) instantly resulted in CuH decomposition (effervescence), thus 1 h in boiling would result in complete decomposition, with the most likely product being CuO. The coffee colour of the product can be ascribed to it being a mixture of CuH and Cu metal. XRD of the washed product, Figure 1, confirms the presence of CuH and a substantial quantity of Cu metal.
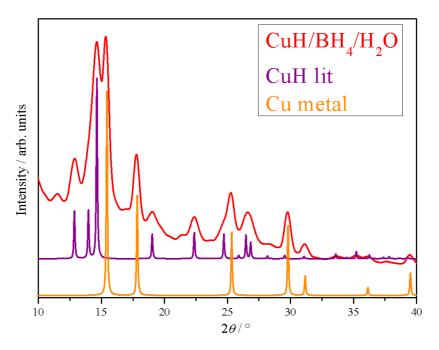

Figure 1. Comparison of XRD pattern of CuH as prepared by the borohydride method (red) and simulated patterns of Cu metal (orange) and CuH (purple).

Neutron total scattering using the SANDALS diffractometer allows direct observation of the characteristic Cu–H distance of 1.78 Å. As shown in Figure 2, there is clearly a negative-going peak at 1.76 Å confirming the presence of CuH. There is also a substantial peak at ~1.05 Å due to an X–H distance. We will discuss this later in the paper.
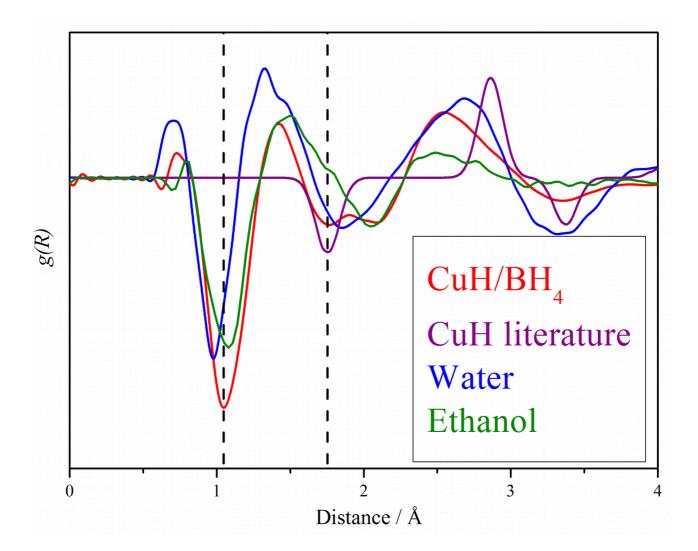
Figure 2. Comparison of radial distribution functions for CuH prepared by the borohydride route (red), liquid water (blue), liquid ethanol (olive) and that calculated from the literature structure for CuH (purple). The dashed vertical lines are at 1.048 and 1.75 Å.

INS spectroscopy allows the Cu–H vibration to be observed. Figure 3 shows a comparison of the CuH product after isolation and subsequent exchange with D_2O, a reference spectrum of D_2O ice I_h and the difference spectrum. The difference spectrum shows a strong peak at 1070 cm^{-1} and a weaker peak at 2080 cm^{-1}. These are assigned as the $0 \rightarrow 1$ and $0 \rightarrow 2$ transitions of CuH (Bennett *et al.*, 2015). Comparison of the spectra of solid D_2O with the exchanged product, clearly shows the presence of D_2O ice I_h in the CuH product but also that the CuH has not exchanged. This strongly supports a core-shell model of a CuH core and a water shell.
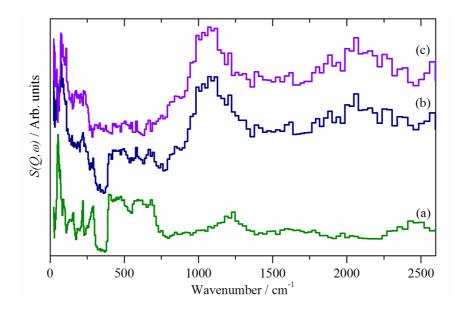
Figure 3. INS spectra recorded on TOSCA at 20 K of: (a) D_2O, (b) D_2O exchanged CuH/BH$_4$ and (c) the scaled difference spectrum. (a) is plotted on a different ordinate scale to that of (b) and (c).

Figure 4 shows a comparison of the CuH product as initially isolated: *i.e.* after washing with ethanol, a reference spectrum of ethanol and the difference spectrum. In agreement with the spectra in Figure 3c, the difference spectrum shows a strong peak at 1070 cm^{-1} and a weaker peak at 2080 and 3020 cm^{-1}. These are assigned as the $0 \rightarrow 1$ and $0 \rightarrow 2$ transitions of CuH. The unexpected feature is that the isolated product shows no evidence for water, only ethanol is apparent. The difference spectrum, Figure 3c, shows a weak feature at 625 cm^{-1} that is assigned to a small amount of residual, strongly disordered water. This strongly suggests that the water shell present from the synthesis has been largely exchanged for ethanol by the washing process. This is the first example where it has been possible to exchange the outer shell of CuH prepared by an aqueous route for anything other than D_2O. This proposal is supported by the neutron diffraction data shown in Figure 2, the apparent 0.1 Å difference between the O–H distance in liquid water and the water in the shell of CuH is very difficult to rationalize, however, it is readily understandable if the peak in the CuH sample is due to ethanol, where the peak will be dominated by the C–H distance of ~1.1 Å, rather than the O–H distance of ~1.0 Å. In contrast to water, where the shell freezes to crystalline ice I_h, the ethanol shell remains amorphous, as shown by the broad methyl torsion at 275 cm^{-1} in both the reference spectrum and that of CuH.
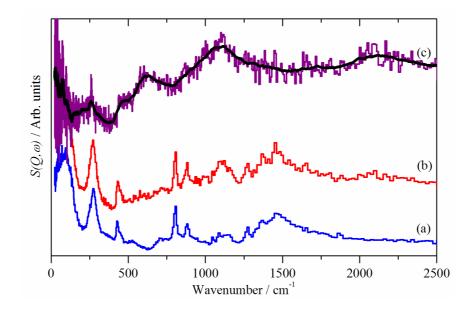
Figure 4. INS spectra recorded on TOSCA at 20 K of: (a) ethanol, (b) CuH prepared by the borohydride route and (c) the scaled difference spectrum. (a) and (b) are plotted on different ordinate scales, (c) is 10 times expanded relative to (b). The black line in (c) is the smoothed spectrum as a guide to the eye.

The identification of the difference spectra as being CuH is confirmed by comparison to the calculated INS spectrum of CuH shown in Figure 5. It is also clear that the CuH core is unchanged by modifying the shell by successive replacement of water with ethanol and D_2O.
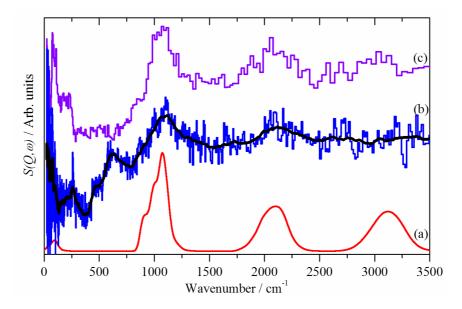

Figure 5. Comparison of INS spectra of: (a) CuH calculated using CASTEP and generated using a relaxed instrumental resolution function, (b) the initially isolated CuH prepared by the borohydride route after subtraction of ethanol and (c) the product in (b) after exchange with D_2O and subtraction of D_2O.

CONCLUSIONS

The combination of diffraction and vibrational spectroscopy studies clearly demonstrate that the CuH product resulting from synthesis by the borohydride route, Eq. 1, is the same as that generated by the traditional synthesis based on Würtz's 1844 method. This is in agreement with the most recent powder diffraction study (Auer & Kohlmann, 2014). In particular, the reported differences between the products (Dasgupta & Mahanti, 2010); the colour and its stability, are artefacts and are incorrect. The colour is due to a significant admixture of copper metal and our experience was that the product was no more stable than that produced by other routes *i.e.* it decomposed within a few days at room temperature.

We have shown elsewhere (Bennett *et al.*, ~~2014~~2015) that the difference between the products from the Würtz method and from the non-aqueous method is the nature of the surface termination of the CuH particles: chemically bound hydroxyls and coordinated pyridine respectively. The INS spectrometer used in this work does not allow observation of the hydroxyl O–H stretch, however, our previous computational studies show that the Cu–O–H deformation modes occur in the 500–800 cm^{-1} where there is a pronounced shoulder that is not predicted for CuH. Inspection of Figure 5b and 5c shows that CuH from the borohydride route also exhibits such a shoulder, consistent with the model that CuH produced from aqueous solution is hydroxyl terminated.

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