

CCXVII.—*Copper Hydride and its Crystal Structure.*

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Two definite compounds of copper with hydrogen are described in the literature, *viz.*, CuH and CuH_2 . The subject of this paper is the isolation of these products and the elucidation of their crystal structures.

Cuprous Hydride.

By the interaction of hypophosphorous acid and copper sulphate, Wurtz (*Compt. rend.*, 1844, **18**, 702; *Pogg. Ann.*, 1844, **63**, 476; *Ann. Chim. Phys.*, 1844, **11**, 25) first prepared a copper hydride for which he suggested the formula CuH (Cu_2H , in the original nomenclature), although his analysis gave better agreement with the less likely formula Cu_4H_3 (Cu_8H_3). The existence of this compound was doubted by Berthelot (*Compt. rend.*, 1879, **89**, 1005, 1097), but was supported by the work of Firth and Myers (*J.*, 1911, **99**, 1329). A copper-hydrogen compound has been used to bring about organic reductions (Chiozza, *Compt. rend.*, 1853, **36**, 632; Vorländer and Meyer, *Annalen*, 1902, **320**, 143; Wohl and Mylo, *Ber.*, 1912, **45**, 328) and on the intermediate formation of this compound was based an analytical method for the determination of copper (Mawrow and Muthmann, *Z. anorg. Chem.*, 1896, **11**, 268), but as far as we know no other analytical attempt has been made to establish the formula CuH . After a stoichiometric study of the reaction between hypophosphorous acid and copper salts, Sieverts (*Z. anorg. Chem.*, 1909, **64**, 56) concluded that the only hydride which could be produced as an intermediate stage in this reaction was CuH .

We prepared the copper hydride according to Wurtz's method and analysed it by the methods described later. The percentage of hydrogen in different samples varied from 1.0 to 1.3 (theoretical value, 1.55). Higher concentrations of hypophosphorous acid did not increase the percentage of hydrogen. The following method gives a purer product but very meagre yields. 3 G. of crystallised copper sulphate are dissolved in 100 c.c. of water free from oxygen and 6 g. of hypophosphorous acid (30%) are added. The solution is heated slowly to 50—55° in an atmosphere of hydrogen, and, after the formation of the brown hydride, is cooled with ice-water, the evolution of gas bubbles being thus prevented. The precipitate is filtered off, washed with water, alcohol, and ether, and dried and analysed as soon as possible, all operations being performed in an atmosphere of hydrogen. The precipitate is very finely divided and a small part runs through the filter. The filtrate still contains a large portion of the copper as sulphate. The copper hydride,

prepared by this method, when completely dry reacts with air and cannot be kept in an evacuated desiccator without spontaneous disintegration.*

The products obtained were analysed by a method analogous to Schiff's nitrogen determination. The hydride was filled into a small and narrow glass tube, which was put into an ordinary combustion tube. After the air had been replaced by carbon dioxide, the hydrogen was liberated by heating and driven into a nitrometer. If the copper hydride is very dry, the evolution of gas occurs vigorously and it is advisable to mix it with silica powder. The copper remaining may be weighed as such, but as it oxidises slightly in air it is preferably dissolved and determined by an ordinary analytical method; if it has been mixed with silica, this procedure is essential. By filling the copper into a tube instead of using a boat, one prevents the interaction of hydrogen with carbon dioxide under the catalytic influence of copper. Another method (compare Sieverts, *Z. physikal. Chem.*, 1907, **60**, 145; Sieverts and Loessner, *Z. anorg. Chem.*, 1912, **76**, 5), which allows one to determine also the water absorbed, was used to control these results. The substance was heated in a current of nitrogen, the water evolved being absorbed by a phosphorus pentoxide tube; the gases were then passed into a second furnace, filled with copper oxide, where the hydrogen was converted into water and absorbed by a second phosphorus pentoxide tube. The results obtained by both methods show an agreement within the limits of experimental error :

Method of preparation.	Method of analysis.	Cu : H (found).
(1) After Wurtz	Combustion.	1 : 0.82
(2) " "	Nitrometer.	1 : 0.86
(3) Authors' (but not washed with alcohol and ether)	Combustion.	1 : 0.92
(4) Authors' method	"	1 : 0.97
(4a) " "	Nitrometer.	1 : 0.97

X-Ray diagrams were taken from each of these samples. The Debye powder method was used and the apparatus was as described by Bradley (*Phil. Mag.*, 1924, **47**, 657). The products prepared without careful exclusion of air showed two spectra superimposed, a weaker one corresponding to that of ordinary copper and a stronger one corresponding to an atomic arrangement of the hydride. Only in the case of (4), in which the atomic ratio of Cu : H is nearly 1 : 1, could no copper lines be traced. The interference lines always appear at the same angles and are independent of the water content,

* The product described by Vanino ("Handbuch der Präparativen Chemie," 1913, p. 402) exhibits these phenomena only to a very small extent. Nevertheless its crystal structure is found to be the same (compare also Wohl and Mylo, *loc. cit.*).

the amount of which was negligible in the last case. Thus it is evident that we are dealing, not with alloys or a hydrate (Berthelot, *loc. cit.*), but with a definite hydride of the composition CuH . Owing to its nearly colloidal state, the broadness ("Halbwertsbreite," compare Scherrer, Zsigmondy's "Kolloidchemie," 1920, p. 394) of the lines is comparatively great and this accounts for the fact that the intensities of the lines at bigger glancing angles are underestimated.

The following table gives the mean values from four photographs taken with the $\text{K}\alpha$ line of a copper anticathode, the β -radiation being absorbed by a nickel screen; lines due to copper are omitted.

θ (obs.).	$\frac{1}{\sin \theta}$	<i>hkl.</i>	a (calc.) * Å.U.	Intensities.	
				(calc.).	(obs.).†
17.86°	3.264	100	2.895	6	<i>s</i>
19.45	3.003	001(2)	2.892	8	<i>m w</i>
20.42	2.866	101	2.892	36	<i>s s</i>
26.88	2.212	102	2.892	12	<i>m w</i>
32.07	1.883	110	2.890	24	<i>m</i>
36.02	1.700	103	2.900	36	<i>w w</i>
37.9	1.63	100(2)	2.89	6	?
38.85	1.593	112	2.891	48	<i>w w</i>
39.5	1.572	201	2.895	36	<i>w w</i>

* *I.e.*, for a value of $c = 1.595$.

† *s* = strong, *m* = moderate, *w* = weak.

In the case of copper hydride, it is evident that the diffracting power of hydrogen will be comparatively small and that the interference spectrum will only indicate the position of the copper atoms. We have the case of a "simple substance regarding which no reliable crystallographic data exist," referred to by Hull and Davey (*Physical Rev.*, 1921, 17, 549). The spacings observed were compared with Hull and Davey's half-logarithmic graphs and were found to match the hexagonal close-packing graph at an axial ratio of between 1.59 and 1.60. The values for the length of the side of the unit rhomb, calculated from

$$a = \frac{\lambda}{2 \sin \theta} \sqrt{\frac{4}{3}(h^2 + hk + k^2) + \frac{c}{a^2}}$$

are given in the fourth column and have a mean of 2.89 Å.U. The observed intensity shows agreement with the calculated values if allowance is made for the increasing "Halbwertsbreite," which also prevented a more accurate determination of a . The lattice of copper in copper hydride may be considered as that of hexagonal close-packed spheres which are compressed by 2.2% in the direction of the c -axis. The density calculated from these data is 6.38. It is remarkable that the volume of the hydride exceeds that of copper

by an amount equivalent to 5.1 \AA.U.^3 per atom,* which shows the fundamental difference between the homopolar copper hydride and the heteropolar lithium hydride, the density of which is greater than that of metallic lithium (Bijvoet and Karssen, *Proc. K. Akad. Wetensch. Amsterdam*, 1923, **25**, 27). Attention should be drawn to the point that lithium, in forming the hydride, assumes the electron-shell structure of the preceding rare gas, but that in copper hydride the copper (which is not next to an inert gas) seems to take up the finished outer-electron shell of zinc, thus attaining the hexagonal symmetry of this element (compare Stoner, *Phil. Mag.*, 1924, **48**, 719; Sommerfeld, *Physikal. Z.*, 1925, **26**, 71).

Attempts to prepare pure hydride by means of electrolysis proved unsuccessful in so far as the interference spectrum indicated admixture with metal. With solutions of $N/20$ – $N/100$ -copper sulphate we obtained nearly 25% of copper hydride at a platinum cathode. That electrolysis causes the formation of a hydride and not of a new modification (Mylius and Fromm, *Ber.*, 1894, **27**, 630, where the older literature is summarised) may be deduced from the identity of the hydride lines obtained from an electrolytical product with those from Wurtz's hydride. Moreover, the addition of even a weak oxidising agent like ammonium nitrate largely prevents the formation of the hydride. It was surprising that the product which contained most hydride had a deep black colour, although copper hydride prepared by chemical means is red, a fact which may explain the older view that copper hydride was not formed by electrolysis.

Cupric Hydride.

A surprisingly stable hydride of the composition CuH_2 is described by Bartlett and Merrill (*Amer. Chem. J.*, 1895, **17**, 185). They obtained it by the action of hypophosphorous acid on copper oxide and copper sulphate and by the reduction of copper oxide with molecular hydrogen at higher temperatures. The existence of this compound was disputed by Sieverts (*loc. cit.*) and we can confirm his observations in so far as we could not pump any appreciable amount of hydrogen out of this product at a bright red heat. The X-ray spectra of the products prepared with hypophosphorous acid exactly in accordance with Bartlett and Merrill's method show a mixture of lines corresponding to cuprite (W. H. and W. L. Bragg, "X-Rays and Crystal Structure," 1924, p. 145) and copper. By

* From a paper of Yamada (*Phil. Mag.*, 1923, **45**, 241) dealing with the crystal structure of palladium hydrogen alloys, we calculate the space occupied by one hydrogen atom to be 4.9 \AA.U.^3 , which is nearly the same as in the case under consideration.

careful reduction of copper oxide with hypophosphorous acid at 50—70°, it is even possible to obtain pure cuprous oxide. The reduction product of copper oxide with molecular hydrogen gives a spectrum which indicates only copper with the normal crystal structure. The analytical method described by Bartlett and Merrill did not allow them to distinguish between a mixture of copper with a small amount of cuprous oxide and the product they expected to obtain. The fact that their products exhibit the same properties as finely-divided crystalline copper, taken in conjunction with the results of Sieverts and the evidence of X-ray analysis, must throw considerable doubt on the existence of the hydride CuH_2 .*

Summary.

The copper hydride of Wurtz has the atomic ratio of unity for Cu : H. Under certain conditions, it may be formed when a dilute solution of a copper salt is electrolysed. Its crystal structure may be considered as hexagonal close-packed with an axial ratio of 1.59 to 1.60, the side of a unit rhomb being 2.89 Å.U. By obtaining one electron from hydrogen, the substance assumes the hexagonal symmetry of zinc, the size of the elementary hexagon of which ($a = 2.67$ Å.U.) is slightly smaller than that of copper hydride. The space occupied by one hydrogen atom is nearly the same as that corresponding to the lattice-expansion of palladium-hydrogen alloys.

Evidence is submitted that the cupric hydride described by Bartlett and Merrill consists of a mixture of finely-divided copper and cuprous oxide.

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* Stock and Kuss (*Ber.*, 1914, **47**, 819) describe a very unstable copper-hydrogen compound, obtained by interaction of potassium hypoborate with copper sulphate, the hydrogen content of which lies between that of CuH and CuH_2 . This product gives off hydrogen at room temperature and cannot be identical with Bartlett and Merrill's product.