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Two New Copper(II) Hydroxoiodides*

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As evidenced by X-ray diffraction, two new hydroxoiodides of copper have been synthesized and their compositions were deduced from analytical data of their mixtures. One of the compounds, with Cu/I = 4 represented by the formula $Cu_4(OH)_7I(2.5H_2O)$, *had a fcc structure with* a = *9.43 Å, and the other with Cu/I = 2.5, represented by* $Cu(OH)_{1.4}(O)_{0.2}(I)_{0.1}(I_3)_{0.1}(0.74H_2O)$ *appeared to have a hexagonal (or pseudo-hexagonal) structure with* a *= 3.78 and* c *= 6.61 Å. The newly found Cu(II) hydroxoiodides constitute, together with* $Cu_2(OH)_3I$, *the only known instances in which the ions Cu(II) and* I^- *are present in compounds.*

Introduction

In the course of research on ractions of interest in the development of thermochemical cycles for the decomposition of water into its elements [1] experiments were performed which involved the equilibration, at room temperature, of copper(I) oxide with aqueous solutions of iodine and potassium iodide. The reaction resulted in the aqueous phase containing copper(I) as a soluble complex iodide anion and green or brownish precipitates that did not consist of copper iodate. Four dominant species were identified in the precipitate by X-ray diffraction analysis. These species occurred in varying amounts; sometimes only two were present. The latter were new compounds: a face-centered cubic (fcc) phase and a hexagonal phase. Other phases identified were unreacted copper(I) oxide and iodobotallackite, $Cu_2(OH)_3I$ [2]. Attempts to prepare pure samples of either of the two new compounds, or to separate their mixtures, were not successful. However, the analyses of these mixtures together with estimates of the relative amounts of the fcc and the hexagonal phase in each, based on intensities of the major X-ray diffraction lines, were utilized to calculate plausible stoichiometries for each compound.

Experimental

Initial experiments were performed using commercially available reagent grade materials, Cu_2O (96%, Matheson, Coleman and Bell) and KI and I_2 (Fisher Scientific Co.). Typically 24 millimol of Cu_2O were stirred in 600 ml of solution containing 50 millimol I_2 and 1200 millimol KI under flowing argon to avoid CO_2 contamination. Since subsequent experiments indicated no carbonate was present in the compounds when equilibrations were conducted in air, use of an inert atmosphere was discontinued. After varying periods of time the suspensions were filtered through glass frits. The filtrates on dilution with water (1:~10) produced a fine yellowish precipitate that was identified by X-ray diffraction as γ-CuI. The solids were washed with an aqueous solution of KI of the same concentration as the equilibration solution, with water, and, finally, with acetone. They were dried on the filter by passage of clean air.

Samples were examined by powder X-ray diffraction using Cu Kα radiation. Copper and iodine contents were determined by neutron activation, potassium by flame spectrophotometry, and water content by the Karl Fischer method. The data from the latter were used only qualitatively to demonstrate the presence of hydroxyl and water because the effect of the reagent on the compounds could not be easily ascertained. The "copper valence" was determined by thiosulfate titration of the iodine liberated when the solids were contacted with an acidified solution of KI [3]. Weight loss of ignition in air was determined and the residues were identified as CuO by X-ray diffraction.

In order to obtain product mixtures free of unreacted Cu_2O equilibration times up to 20 days were used with commercial Cu_2O. These attempts were unsuccessful even though the aqueous solution of I_2 and KI was renewed several times. Equilibration at 60 °C did not yield the fcc phase but converted the Cu_2O into CuO. Additionally, it was found that di-

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TABLE I. Powder X-Ray Diffraction Patterns.

Face-Centered-Cubic Phase

$Cu_4(OH)_7I(2.5\ H_2O$, adsorb?)

d_{exp} (Å)	I/I_1 (estimated from film)	hkl	a_0 (Å)
5.450	20	111	9.44
4.725	2	200	9.45
3.330	20	220	9.42
2.847	100	311	9.44
2.720	100	222	9.42
2.356	25	400	9.42
2.163	10	331	9.43
2.107	10	420	9.42
1.925	2	422	9.43
1.815	20	333,511	9.43
1.666	30	440	9.42
1.591	15	531	9.41
1.572	2	600,442	9.43
1.437	2	533	9.42
1.420	25	622	9.42
1.361	2	444	9.43
1.320	2	711,551	9.43
1.227	10	731,553	9.42
1.179	5	800	9.43
etc.			
			9.43 ± .01

no systematic absences, beside f.c.c
(δx-ray = 3.96 g/cm^3)

"Hexagonal" Phase (C6 Type?)

$Cu(OH)_{1.4}(O)_{0.2}(I)_{0.1}(I_3)_{0.1}(0.74\ H_2O$ absorb?)

d_{exp} (Å)	I/I_1 (estimated from film)	hkl	d_{calc} (Å)
6.53	100	00.1	6.61
3.30	100	00.2(10.0?)	3.305(3.275)
2.93	100	10.1	2.934
2.32	40	10.2	2.324
2.176	50	00.3	2.177
1.816	50	11.1	1.817
1.642	40	11.2	1.640
1.591	20	20.1	1.590
1.468	30	20.2(10.4?)	1.467(1.475)
1.428	10	11.3	1.434
1.311	30	20.3	1.314
etc.			

a = 3.78 Å
c = 6.61 Å
(δx-ray = 2.91 g/cm^3)

valent copper in the form of freshly precipitated $Cu(OH)_2$ and commercial CuO did not react at room temperature with the aqueous solution of I_2 and KI. It was then decided to use freshly prepared and more reactive Cu_2O.

One variety of Cu_2O designated here "Cu_2O-S" was prepared [4] by reducing a complex cupric chloride solution with Na_2SO_3 and precipitation with KOH, the solutions being cooled rather than heated to avoid formation of large crystallites. Another type of Cu_2O, designated here "Cu_2O-I", was prepared by a method in which no alien anionic species ($SO_4^=$, Cl^-, $SO_3^=$) were introduced. In this procedure, CuI was dissolved in concentrated KI solution, the solution was filtered, and, then, Cu_2O was precipiated by addition of KOH. This product consisted of very small crystallites (<1500 Å) which oxidized rapidly in air.

After equilibration of "Cu_2O-I" in I_2–KI solution for two days, a brown precipitate formed. X-ray diffraction showed the presence of a fcc phase with *a* = 9.43 Å (found earlier with "CuO-S" preparations) and a larger proportion of a phase earlier thought to be an impurity. This new phase appears to be hexagonal (*a* = 3.78; *c* = 6.61 Å), *i.e.* most probably of the C6 type of structure identified by Oswald and Feitknecht [5] for various compounds $M_2(OH)_3Cl$, where M = Ni, Mg, Co, Fe and Mn. The *d* spacings and intensities for the fcc and hexagonal compounds found in these experiments are given in Table I. For purposes of comparison $Cu_2(OH)_3I$ was synthesized [2] and the differing diffraction pattern (monoclinic, botallackite type of structure) and chemical analysis were confirmed (a similar preparation, but with elemental iodine added, also produced pure $Cu_2(OH)_3I$). Attempts to separate the fcc and hexagonal phases by selective dissolution, or to convert one phase into the other by equilibration with KI solutions at various pHs were not successful (the nature of the system precluded making significant changes in pH without changing the reactants). It was found, however, that equilibration time had a marked effect on the relative amounts of the phases present; thus, starting with "Cu_2O-I", two days' equilibration yielded a mixture of about 50% each of monoclinic $Cu_2(OH)_3I$ and fcc (sample #19, Table II) while equilibration for twelve days yielded a mixture of 10% monoclinic $Cu_2(OH)_3I$, 55% fcc and 35% hexagonal phases (sample #10, Table II).

TABLE II. Experimental Conditions and Analytical Results of Mixtures Copper(II) Hydroxoiodides.

Expt.	Initial Conditions[a]				Analysis of Precipitate					Wt % hexagonal phase in precipitate calculated[b]	Comments[c]
	Cu_2O/I_2	I_2/KI (Molar ratios)	KI/H_2O		Final pH	Wt % Cu	Wt % I_2	Wt % loss on ignition	Millimol of I_2 evolved per g of precipitate in acidified KI solution		
1	0.60	0.04	0.04	Commercial, 20d	–	47.18	21.58	38.36	–	–	Cu_2O and $Cu_2(OH)_3I$, green
2	0.62	0.04	0.04	Cu_2O-S, 5d	–	45.94	24.58	40.44	3.726	13.3	green
3	0.59	0.04	0.04	Cu_2O-S, 1d	6.90	46.22	25.26	43.77	3.743	17.5	green
4	0.15	0.16	0.04	Cu_2O-I, 3d	6.75	41.37	32.38	47.10.	–	–	bcc with $a = 6.6$ Å, brown
5	0.12	0.16	0.04	Cu_2O-I, 20 hr	6.65	42.76	29.62	45.50	3.889	67.4	brown–green
6	0.13	0.16	0.04	Cu_2O-I, 20 hr	7.10	44.09	28.68	45.50	3.737	53.6	brown–green
7	0.13	0.16	0.04	Cu_2O-I, 20 hr	7.10	43.03	28.42	44.90	3.879	56.9	brown–green
8	0.12	0.16	0.04	Cu_2O-I, 6d	6.85	41.95	31.43	46.26	–	85.1	brown
9	0.12	0.16	0.04	Cu_2O-I, 6d	7.00	41.04	28.64	47.21	–	69.0	brown–green
10	0.13	0.16	0.04	Cu_2O-I, 6d	6.95	41.52	29.19	46.72	–	70.7	brown–green
11	0.15	0.15	0.04	Cu_2O-S, 3d	–	44.10	27.00	44.95	3.701	40.7	green
12	0.05	0.46	0.04	Cu_2O-S, 3d	–	44.00	27.30	45.58	–	43.5	green
13	0.07	0.54	0.03	Cu_2O-S, 6d	6.83	41.28	26.90	45.22	3.779	54.0	green
14	0.05	0.47	0.04	Cu_2O-I, 4d	–	45.40	26.31	41.67	–	–	$Cu_2(OH)_3I$, green
15	0.60	0.04	0.04	Cu_2O-I, 4d	–	45.80	25.24	44.63	–	–	$Cu_2(OH)_3I$, green
16	0.38	0.55	0.01	Cu_2O-S, 6d	6.51	42.74	28.16	48.72	–	–	$Cu_2(OH)_3I$, green
17	0.12	0.20	0.04	Cu_2O-I, 4d	7.27	42.20	29.98	44.37	3.781	73.0	brown–green
18	0.24	1.49	0.01	Cu_2O-I, 4d	6.05	–	–	45.94	3.279	0.0	$Cu_2(OH)_3I$, green[d]
19	1.64	0.02	0.02	Cu_2O-I, 2d	7.25	42.14	30.34	41.64	–	0.0	$Cu_2(OH)_3I$, green[e]
20	1.64	0.02	0.02	Cu_2O-I, 12d	–	41.51	26.72	42.57	–	34.1	10% $Cu_2(OH)_3I$, green

[a] Source of Cu_2O and length of equlibration. [b] Calculation based on analytical results and assuming fcc: $Cu_4(OH)_7I(2.5\ H_2O)$ and hexagonal; $Cu(OH)_{1.4}(O)_{0.2}(I)_{0.1}(I_3)_{0.1}$-(0.74 H_2O), the complement to 100%, unless indicated in the next column is the fcc phase. [c] Additional phases present beside fcc and color. [d] Solid I_2 was present during equilibration, no fcc was present. [e] No hexagonal phase was obtained, the precipitate consisted of 53 wt % fcc and 47 wt % $Cu_2(OH)_3I$.

Because we were unable to synthesize each phase separately, the relative amounts present in the mixtures obtained could be estimated only roughly by visual comparison of the intensities of the principal lines of the X-ray diffraction patterns. These estimates together with the chemical analyses of the mixtures and the experimental (initial) conditions are shown in Table II.

Although the color of the mixtures could not be taken as a definitive indication of the phases that were present, in general it can be stated that, when Cu_2O was absent, the brown color could be associated with the presence of 50% or more of the hexagonal phase. The green colored mixtures varied in shade, the lighter and more yellowish tint almost always indicated that presence of 10% or more of monoclinic $Cu_2(OH)_3I$. We speculated that the brown color might be indicative of the presence of copper in two valence states; therefore, the "copper valence" was determined. Surprisingly, the average valence of copper as measured by iodometry appeared to be greater than Cu(II). These results were taken into account to deduce, as described in the Discussion, the apparent stoichiometry of the hexagonal phase.

Discussion

As can be seen in Table II, the estimates of the relative weights of each phase have considerable uncertainties; however, within their range and using an iterative method, it was possible to calculate plausible stoichiometries for the hexagonal and fcc phases. In these calculations only those mixtures were considered where no additional phases besides the fcc and the hexagonal were present. The calculation was started assuming that, by analogy with the other $M_2(OH)_3Cl$ compounds with C6 type of structure, the hexagonal phase had the same composition as iodobotallackite, $Cu_2(OH)_3I$. Then, by difference, the composition (wt % of copper and iodine) of mixtures rich in fcc phase (samples #2 and 3) was computed. The result gave a Cu/I ratio and weight percent of copper and iodine in the fcc phase. The copper was assumed to be divalent in these compounds, since it seemed improbable that trivalent copper could have formed and be stable in concentrated KI solution. Potassium was either absent or present at a level of less than 500 ppm; therefore, hydroxyl ions were used to balance the charges. Additionally, a certain amount of water was estimated to be associated with the compound. The amount was that required to match (together with the I_2 evolved by ignition) the observed weight losses on ignition. This estimated stoichiometry of the fcc compound was then used to calculate similarly the stiochimetry of the hexagonal compound (Sample #8). Although the limits of uncertainty assigned to the estimated proportion of each phase were large, the calculation could be repeated until the Cu/I ratios converged within a variation of 4%. The results obtained indicated that the fcc compound (a_o = 9.43 Å) had the stoichiometry, probably with four formula weights per unit cell.

$$Cu_4(OH)_7I\,(2.5\ H_2O), \qquad (A)$$

The hexagonal phase a = 3.78 and c = 6.61 Å could be represented by

$$Cu_5(OH)_8I_2\,(3.7\ H_2O)$$

probably containing statistically one fifth of this formula per unit cell. Since the valence of copper was thought to be (II), and since the iodimetric determinations of "copper valence" exceeded (II) as the proportion of hexagonal phase was greater, it was postulated that the hexagonal phase contained iodine in some oxidation state higher than I^-. Thus, the hexagonal phase was represented as

$$Cu_5(OH)_{8+2x}(I^-)_{2-2x}(I_2)_x\cdot[(3.7-2x)H_2O],$$

in which the difference of several hydrogen atoms has an insignificant effect upon formula weight. Since on reaction with an acidic iodide solution one mol of fcc compound would evolve 2 mol of I_2 and one mol of hexagonal compound would evolve (2.5 + x) mol of I_2, the I_2 evolved on titration was used to calculate x. The results from six samples gave an average x = 0.54 ± 0.19 (90% confidence level). Thus, the hexagonal compound was inferred to have the stoichiometry

$$Cu^{2+}_{10}(OH^-)_{18}(I^-)(I_3^-)\,(5.4\ H_2O) \qquad B)$$

Both general formulas A and B best represented all the data; however, as in similar compounds involving OH^- and H_2O,* the presence of O^{2-} cannot be ruled out, *e.g.*, per unit cell without water,

$$Cu^{2+}_{1.0}(OH^-)_{1.4})\,(O^{2-})_{0.2}(I^-)_{0.1}(I_3^-)_{0.1} \qquad (B')$$

Additionally, the possibility exists that, in the hexagonal compound, all of the iodine was present as I_3^-. This would be compensated by the presence of Cu(I), *e.g.*,

$$Cu(II)_{14}Cu(I)(OH)_{21}(O)_3(I_3)_2\,(11.1\ H_2O) \qquad (B'')$$

or per unit cell, without water,

$$Cu(II)_{0.933}Cu(I)_{0.067}(OH)_{1.4}(O)_{0.200}(I_3)_{.133}$$

No analytical procedure was employed which might provide the basis for selecting a formula from among B, B′ and B″. However the latter two are to be preferred because the C6 (CdI_2) type of structure contains only twice as many anionic as cationic sites; in formula B, even without the water, not 20 but 18 + 1 + 3 = 22 (OH) and I would have to be placed on

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*Presently we have no information about the state of association of the water.

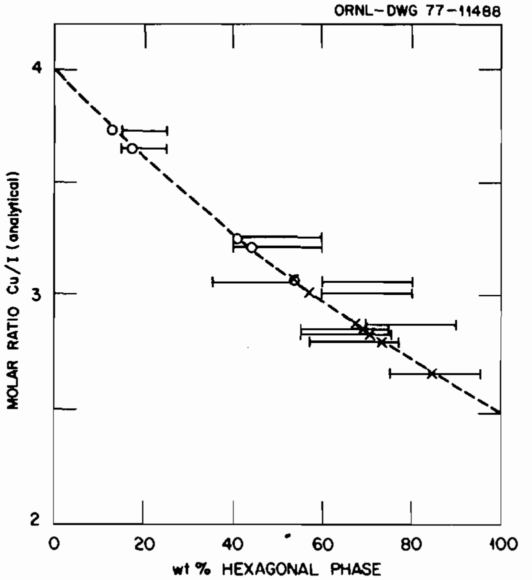

Figure 1. Cu/I molar ratio (analytical) in fcc and hexagonal copper hydroxoiodide mixtures *vs.* weight percent of hexagonal phase. Broken line calculated assuming species $Cu_4(OH)_7I(2.5H_2O)$ and $Cu(OH)_{1.4}(O)_{0.2}(I)_{0.1}(I_3)_{0.1}$ $(0.74\ H_2O)$. Open circles and crosses calculated with these stoichiometries indicate, respectively, the use of cuprous oxide of two different origins, "Cu_2O-S" and "Cu_2O-I". Horizontal bars are estimates based on X-ray diffraction.

anionic sites. Attempts to prove the presence of I_3^- by laser-Raman spectroscopy gave inconclusive results.

The theoretical weight percentages of copper and iodine for both A and B compounds, together with the corresponding analytical data from the obtained mixtures, were used to calculate the relative amounts of the fcc and hexagonal phases. These results are shown in Fig. 1 as the measured Cu/I molar ratio as a function of the calculated weight percent of the hexagonal phase. Also included are the values of weight % hexagonal phase based on visual interpretation of the X-ray diffraction line intensities. The agreement is encouraging.

Finally, the calculated weight % values of the two phases were used to test an independent determination, the measured weight loss by ignition in air. The difference between expected and found values were smaller than ±5%.

The deduced formulae can be rationalized by the following reactions leading to the formation of the hydroxoiodides. For the fcc compound:

$$7/2\ Cu_2O_{(s)} + 2I_{2(d)} + 6KI_{(d)} + 6H_2O_{(l)} = Cu_4(OH)_7I(2.5H_2O)_{(s)} + 3K_2CuI_{3(d)}$$

For the hexagonal compound:

$$9Cu_2O_{(s)} + 6I_{2(d)} + 16KI_{(d)} + 14.4H_2O_{(l)} = Cu_{10}(OH)_{14}(O)_2I(I_3)(7.4H_2O)_{(s)} + 8K_2CuI_{3(d)}$$

For $Cu_2(OH)_3I$:

$$3/2\ Cu_2O_{(s)} + I_{2(d)} + 2KI_{(d)} + 3/2\ H_2O_{(l)} = Cu_2(OH)_3I_{(s)} + K_2CuI_{3(d)}$$

where (s), (d) and (l) refer, respectively, to the solid, dissolved and liquid states.

The above equations indicate that the initial molar ratios of Cu_2O/I_2 and I_2/KI required to form either compound are not considerably different; *i.e.*, for the fcc phase, 1.75 and 0.333; for the hexagonal phase, 1.5 and 0.375; and for $Cu_2(OH)_3I$, 1.5 and 0.5. The similarity of these ratios may explain our inability to synthesize the compounds in a pure state by means of the above reactions.

From the relative amounts of each phase obtained with various ratios and concentrations of reagents, it is only possible to discern a general trend in the conditions that appear to favor the predominance of one phase over the others. The maximum proportion of hexagonal phase was obtained with Cu_2O/I about 0.12 and $I_2/KI = 0.16$. Maximum proportions of the fcc phase were obtained at Cu_2O/I of 0.07 and 0.6 and I_2/KI of 0.04 and 0.55. The large excess of KI was probably required to yield a concentrated solution which rapidly dissolved the CuI formed and prevented the latter from coating the Cu_2O. With solid iodine present and/or when the concentration of KI was lower than 1 *M*, the preparation resulted in either pure monoclinic $Cu_2(OH)_3I$ or a mixture with the fcc phase. Additionally, a difference in behavior was noted between "Cu_2O-S" and "Cu_2O-I", the latter yielding a higher proportion of hexagonal phase under similar experimental conditions. This may reflect only a difference in kinetics due to a difference in crystallite size.

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References

1 C. E. Bamberger and D. M. Richardson, *Cryogenics, April,* 197 (1976).
2 H. R. Oswald, Y. Jitaka, S. Locchi and A. Ludi, *Helv. Chim. Acta, 44,* 2103 (1961).
3 A. Yu. Prokopchik and P. K. Norkus, *Russ. J. of Inorg. Chem., 4,* 611 (1959).
4 G. G. Schlessinger, "Inorganic Laboratory Preparations", *11,* Chemical Publications Co. Inc., NY (1962).
5 H. R. Oswald and W. Feitknecht, *Helv. Chim. Acta, 47,* 272 (1964).