HYDROTHERMAL PREPARATION OF SOME COPPER SALTS

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ABSTRACT

Reactions of $Cu_2(OH)_3X(s)$ with $NH_4X(5 M, aq)$ ($X = Br$ or Cl) have been carried out in sealed tubes in an autoclave at temperatures between 100 and 300 °C, for times between 6 and 48 h. Crystal growth of the starting material was observed. as well as the formation of single crystals of $CuBr_2 \cdot 2NH_4Br \cdot 2NH_3$, $Cu(NH_3)_4(CuBr_2)_2$ and $CuBr \cdot \frac{1}{2}NH_3$ in the bromide system, and $CuCl_2 \cdot 2NH_4Cl \cdot 2NH_3$, $CuCl_2 \cdot NH_4Cl \cdot 2NH_3$, $Cu(NH_3)_4(CuCl_2)_2 \cdot H_2O$ and $CuCl \cdot \frac{1}{2}NH_3$ in the chloride system. The stoichiometry of the compounds produced was established by a combination of chemical analyses, X-ray measurements of unit cell dimensions and determinations of the densities of the solids. A brief discussion of some of the thermodynamic properties of the systems is given.

INTRODUCTION

Our original interest in the structures of basic copper salts arose as a result of a series of observations on the precipitation of basic compounds of various metals (Bi. Sb. Fe. Cr. Ni, Al, Cu, Cd, Pb, Co) when NaOH was added to dilute aqueous solutions of neutral compounds[1]. Typical of the reactions which occurred was the following:

$$X^{n-} + 2nCu^{2+} + 3n(OH^-) \rightarrow Cu_{2n}(OH)_{3n}X\downarrow$$

Some of these compounds have been observed previously as naturally occurring materials, and a number of crystal structures have been determined (atacamite[2], Gerhardite[3], brochantite[4], botallackite[5]). Interesting bridging structures have been found in these materials. and it seemed of value to attempt to prepare single crystals of other basic salts in order to investigate their solid state structures.

However, an immediate difficulty arose in that these basic salts are relatively insoluble and so the growth of single crystals of them posed serious problems. A number of techniques, which included homogeneous precipitation by means of urea hydrolysis[6], slow diffusion of a basic solution into the salt solution, and continued refluxing with a solvent, were tried in an effort to obtain single crystals of sizes convenient for X-ray studies. but these were not satisfactory. Finally, hydrothermal methods[7] were tried. In these experiments, basic salts of Cu^{II} were prepared as finely divided crystalline material and were sealed in pyrex tubes with solutions which

contained the ammonium salt of the anion of the basic salt, and were then heated for varying times and at varying temperatures in an autoclave.

Some crystal growth was observed, but in addition, a number of chemical reactions occurred. Ammonia is a mild reducing agent, and as the temperature and times of reactions were increased, it was found that the Cu^{II} salts were transformed, first into crystals of complex types such as $CuX_2 \cdot aNH_4X \cdot bNH_3$, then to materials of mixed valencies such as $Cu(NH_3)_4^{2+}(CuX_2^-)_2$ and finally to cuprous salts, $CuX \cdot 1\frac{1}{2}NH_3$.

The results seemed interesting for several reasons. First, improvement in crystal size seemed likely for at least some of the basic salts treated by this hydrothermal technique. Second, single crystals of a wide variety of complex salts were produced as a result of the reactions that occurred in these sealed vessels, and the preparations appeared to be reproducible and simple to carry out. Third, quite unstable Cu^I compounds could be prepared in this way and kept until their crystals could be examined. Fourth, mixed valency compounds were produced, and these materials may be of potential value because of the possibility of their having unusual solid state properties. Fifth, interesting growth and intergrowth patterns were observed for these materials as they were produced. Sixth, the entire method itself seemed of potential interest not only for the preparation of Cu compounds, but for what might occur if other metal salts were treated in a similar manner.

Clearly, not all of these areas could be investigated at once, so it was decided to observe first what changes in products were caused by variations in time and temperature of the autoclave for starting materials of closely related structures, $Cu_2(OH)_3Br$ and $Cu_2(OH)_3Cl$, and to determine what crystalline materials were produced.

EXPERIMENTAL

Reagents

The starting materials that were used included Mallinckrodt Reagent Grade ammonium bromide, ammonium chloride, and urea and Baker Reagent Grade cupric bromide, cupric chloride, hydrobromic acid and hydrochloric acid. All were used without further purification. The solutions required were prepared from distilled water further purified by passage through an Illco–Way ion exchange column. Prepurified bottled nitrogen, obtained from the Air Reduction Company, Inc., was employed to provide an inert atmosphere in an IR^2 glove bag for the manipulation of unstable compounds. Copper hydroxybromide, $Cu_2(OH)_3$ Br and copper hydroxychloride, $Cu_2(OH)_3Cl$ were prepared by the hydrolysis of urea in a solution of the appropriate cupric salt. The precipitated copper hydroxy-salts were washed with deionized water and dried at $120^\circ C$ before further use.

Equipment

The autoclave used in these preparations was a Magne Dash MFT-1000 electrically heated device manufactured by Autoclave Engineers, Inc. The mixing

components were removed in order to increase the internal space available. Operating temperatures were controlled and monitored with a Model 105C4 Brown Pyr-O-Vane indicating millivoltmeter controller and an iron–constantin thermocouple located in a temperature well in the autoclave body.

Sample tubes were constructed from 1 mm wall pyrex tubing. Various inside diameters from 5 to 15 mm were tested while the dimensions of the autoclave necessitated an overall tube length of less than 24 cm. The desirability of the increased sample size possible with larger capacity sample tubes was offset by the larger number of failures which occurred at high temperatures and pressures when large diameter tubes were employed. The best compromise was found with tubes constructed from 7 or 8 mm i.d. pyrex tubing. The tubes were sealed at the bottom and the necks drawn to a diameter of approximately 2 mm before filling. After filling, the tops were sealed with an oxygen torch. The sample tubes so constructed each had a capacity of 8 to 10 ml and were capable of withstanding a pressure differential of approximately 6 atm. Some sample tube failures were encountered due to overfilling the tubes. The volume of nitrogen generated during reactions at high temperatures and the expansion of the solution were such that a fill of less than 50% was necessary in order to prevent rupture of the sample tubes from internal pressures.

$Cu_2(OH)_3Br–NH_4Br–H_2O$ system

Samples which consisted of 0.5, 1.0 and 1.5 g of $Cu_2(OH)_3Br$ and 2–5 ml of 5 M $NH_4Br(aq)$ solution were sealed in pyrex tubes and placed in the autoclave which was partially filled with water in order to reduce pressure differences between the interior and exterior of the sample tubes at elevated temperatures. Experiments were carried out at temperatures which ranged from 100 to 300°C. Reaction times varied from 6 to 48 h measured from the start of the heating cycle to the time the autoclave heaters were turned off (thus, this time included the time needed to bring the autoclave to operating temperature, approximately 1 h, but did not include the cooling-off period of 6 to 10 h).

Between 100 and 150°C the major change which occurred in the reaction tubes was crystal growth of $Cu_2(OH)_3Br$. The original crystals were small hexagonal flat plates with a maximum dimension of 0.1 mm. The largest crystals obtained from the autoclave experiments, $3 \times 8 \times 0.1$ mm, were grown when the temperature was cycled between 100 and 150°C eight times in 48 h.

A small number of dark green, almost black, crystals of $CuBr_2 \cdot 2NH_4Br \cdot 2NH_3$ were obtained between 100 and 150°C. Most of these crystals were highly branched needle-like crystals with projections perpendicular to a central needle. A second crystal habit was in the form of branched needle-like crystals with projections at an angle to the central needle. If the central needle is considered to have the direction of the (1,1,1) diagonal of a cube, these branches occurred in the ($\bar{1}$,1,1), (1,$\bar{1}$,1), and (1,1,$\bar{1}$) directions.

Between 150 and 225°C, $Cu(NH_3)_4(CuBr_2)_2$ was produced in the form of purple needles. Some $Cu_2(OH)_3Br$ remained in all samples, the amount depended

upon the temperature, time and the quantity of $Cu_2(OH)_3Br$ originally present in the sample. Approximately the same amount of $Cu(NH_3)_4(CuBr_2)_2$ was formed in the 0.5, 1.0 and 1.5 g samples at each temperature and reaction time.

In the temperature range 225–275 °C, thin, colorless to pale green flat plates of $CuBr \cdot \frac{1}{2}NH_3$ crystallized from solution, as well as purple needles of $Cu(NH_3)_4(CuBr_2)_2$. The two types of crystals often grew together with the needle axis of the purple crystals in the plane of the flat plates at an angle of forty-five degrees to the edges of the flat plates.
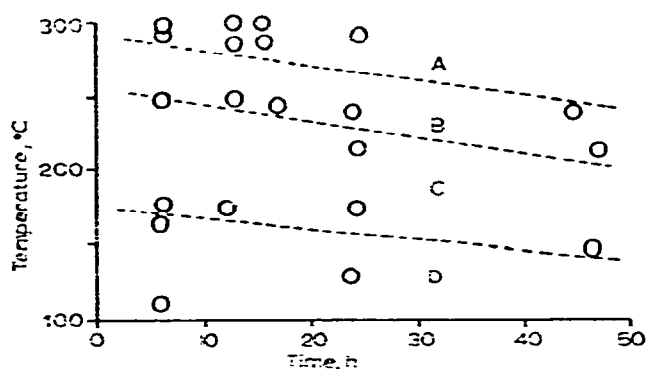

Fig. 1. Crystalline phases obtained in $Cu_2(OH)_3Br–NH_4Br–H_2O$ system. A, $CuBr \cdot \frac{1}{2}NH_3$; B, $CuBr \cdot \frac{1}{2}NH_3$, $Cu(NH_3)_4(CuBr_2)_2$, $Cu_2(OH)_3Br$; C, $CuBr_2 \cdot 2NH_4Br \cdot 2NH_3$, $Cu_2(OH)_3Br$; D, $Cu_2(OH)_3Br$.

Above 275 °C, only colorless flat plates of $CuBr \cdot \frac{1}{2}NH_3$ were formed. Fig. 1 summarizes the data regarding the crystalline phase obtained from the autoclave experiments for the $Cu_2(OH)_3Br–NH_4Br–H_2O$ systems.

$Cu_2(OH)_3Cl–NH_4Cl–H_2O$ system

Autoclave experiments were also carried out with $Cu_2(OH_3)Cl$ and 5 M $NH_4Cl(aq)$ solution. The samples were prepared and the experiments were carried out with a procedure similar to those described for the $Cu_2(OH)_3Br–NH_4Br–H_2O$ system.

Between 100 and 150 °C, some crystal growth of $Cu_2(OH)_3Cl$ was observed. The original crystals were very small, approximately 1×10^{-3} mm in their largest dimension. In one experiment in which the temperature was cycled between 100 and 150 °C eight times in 48 h, the crystals obtained were approximately 1×10^{-2} mm in their maximum dimension. No larger crystals of $Cu_2(OH)_3Cl$ were obtained in any other experiment.

A small number of light green crystals of two cubic salts was also formed between 100 and 150 °C. One was $CuCl_2 \cdot NH_4Cl \cdot 2NH_3$ which crystallized as small cubes, approximately 0.2 mm on each edge. The other compound was $CuCl_2 \cdot 2NH_4Cl \cdot 2NH_3$ which crystallized as highly branched needles that consisted of a central stem, with secondary needles growing in a threefold pattern from it. If

the main needle axis is labeled (1.1,1) (corresponding to the diagonal of a cube), the secondary needles grew along directions ($\bar{1}$.1,1), (1.$\bar{1}$,1) and (1.1,$\bar{1}$).

At temperatures between 150 and 300°C, thin flat plates of $CuCl \cdot \frac{1}{2}NH_3$ were formed even when the bulk of the $Cu_2(OH)_3Cl$ remained unreacted. The flat plates retained a blue tint until all $Cu_2(OH)_3Cl$ had reacted, after which they became colorless. In one experiment, at 250°C, 12 h, tetragonal prisms of $Cu(NH_3)_4(CuCl_2)_2 \cdot H_2O$ were formed. Fig. 2 summarizes the results obtained from the autoclave experiments for the $Cu_2(OH)_3Cl-NH_4Cl-H_2O$ system.
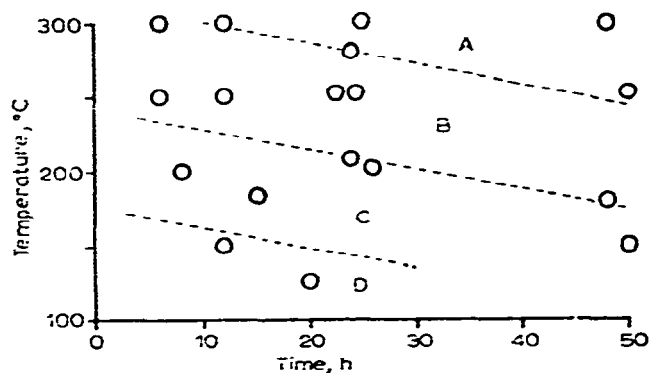
Fig. 2. Crystalline phases obtained in the $Cu_2(OH)_3Cl-NH_4Cl-H_2O$ system. A, $CuCl \cdot \frac{1}{2}NH_3$; B, $CuCl \cdot \frac{1}{2}NH_3$, $Cu(NH_3)_4(CuCl_2)_2 \cdot H_2O$, $Cu_2(OH)_3Cl$; C, $CuCl_2 \cdot NH_4Cl \cdot 2NH_3$, $CuCl_2 \cdot 2NH_3Cl \cdot 2NH_3$, $Cu_2(OH)_3Cl$; D, $Cu_2(OH)_3Cl$.

Chemical analysis

A sample of $Cu(NH_3)_4(CuBr_2)_2$ was dissolved in a slight excess of HBr and Cu^I precipitated as CuSCN. The precipitate was filtered through a weighed sintered glass crucible. The filtrate which contained Cu^{II} was treated with a solution of hydroxylamine hydrochloride, Cu^{II} was reduced to Cu^I, and precipitated as CuSCN in situ. This precipitate was filtered through a second weighed glass crucible. The two samples were dried at 120°C, cooled in a dessicator and weighed. The following results were obtained. Found: Cu^I 19.98; Cu^{II} 12.98; total 32.96. Calculated: Cu^I 21.97; Cu^{II} 10.99; total 32.96. Since Cu^I is quite unstable in air, low results for it and high results for Cu^{II} may be expected.

Analysis of $Cu(NH_3)_4(CuBr_2)_2$ for bromine and nitrogen was performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. The following results were reported. Found: Br 55.78, 55.53; N, 9.51, 9.63. Calculated: Br 55.28; N 9.07.

In addition to the preceding work, the analysis of one of the cuprous compounds prepared, $CuBr \cdot \frac{1}{2}NH_3$, was carried out by Galbraith Laboratories and in this laboratory. This was done because there is a large number of known compounds of composition $CuX \cdot aNH_3 \cdot bNH_4X$ where X represents a halogen and a and b are fractions or small whole numbers or zero. Any of these compounds was considered to be a possible product or the autoclave work. Samples were dissolved in a slight excess of concentrated nitric acid, treated with sodium thiosulphate and sulphuric

acid to remove excess nitrous acid, and the copper deposited electrically on platinum gauze electrodes. Triplicate determinations gave the following results. Found: Cu 41.86, 43.22, 43.77. Calculated: Cu 41.82. Nitrogen was determined as ammonia by means of a Stone thermogravimetric analyzer. A weight loss of 4.42% was recorded between 100 and 150°C. The results supplied by Galbraith Laboratories were. Found: Br 51.00, 51.26; N 3.93, 3.96. Calculated: Br 52.59; N 4.61.

The remaining compounds prepared in this work were not analyzed by conventional means, but a combination of X-ray methods and density measurements were used to determine their composition. This was done because the "wet analyses" were slow, time and sample-consuming, and suffered from inaccuracies that were difficult to avoid in some cases, since the oxidation of Cu^I to Cu^{II} occurred very readily.

X-ray measurements

Unit cell dimensions were determined from single crystals with precession photographs (Zr filtered, MoK_α radiation, $\lambda = 0.7107$ Å) for $Cu(NH_3)_4(CuBr_2)_2$, $CuCl_2 \cdot 2NH_4Cl \cdot 2NH_3$ and $Cu(NH_3)_4(CuCl_2)_2 \cdot H_2O$ and with a Syntex Autodiffractometer (oriented graphite monochromator, (002) reflection, MoK_α radiation, $\lambda = 0.7107$ Å) for the remaining compounds. The cell dimensions and estimated errors are given in Table I, as well as the calculated X-ray densities for comparison with the densities measured directly.

TABLE I

CRYSTAL DATA AND DENSITIES

Compound	Crystalline form, cell dimensions (Å)	X-ray density (g/ml)	Measured density (g/ml)
$Cu(NH_3)_4(CuBr_2)_2$	Tetragonal needles $a = b = 10.34(2)$ $c = 5.71(1)$	3.25(1)	3.22(2)[a]
$CuBr_2 \cdot 2NH_4Br \cdot 2NH_3$	Cubic needles $a = b = c = 4.070(1)$	2.790(2)	2.80(1)[b]
$CuBr \cdot 4NH_3$	Tetragonal plates $a = b = 4.049(1)$ $c = 15.340(4)$	4.023(4)	4.05(1)[a] 4.01(1)[c]
$CuCl_2 \cdot 2NH_4Cl \cdot 2NH_3$	Cubic needles $a = b = c = 3.91(1)$	1.90(1)	1.86(1)[b]
$CuCl_2 \cdot NH_4Cl \cdot 2NH_3$	Cubic $a = b = c = 3.901(1)$	2.059(2)	2.06(1)[b]
$CuCl \cdot 4NH_3$	Tetragonal plates $a = b = 3.868(1)$ $c = 14.637(4)$	3.258(3)	3.21(8)[b, d]
$Cu(NH_3)_4(CuCl_2)_2 \cdot H_2O$	Tetragonal prisms $a = b = 10.187(12)$ $c = 5.468(8)$	2.44(1)[g, c]	>2.17[b]

[a]Modified Berman method. [b]Flotation method. [c]Displacement method. [d] A wide range of densities of individual crystals were observed, probably due to crystal decomposition. [e]Only one sample of this material was obtained in the autoclave experiments. Identification was made from unit cell dimensions and chemical tests for Cu^I and Cu^{II}.

Densities of crystals

Several methods of density determinations were used in the determination of the densities of the various crystals used in this study. Whenever possible, the flotation method was used due to the relative speed and simplicity of the method and the small amount of sample that could be used. A discussion of each method used follows, and a tabulation of the results obtained is given in Table I.

(*a*) *Flotation method.* — In the flotation method, two miscible liquids, 1-bromo-butane ($d = 1.299$ g/ml) and 1,1,2,2-tetrabromobutane ($d = 2.965$ g/ml) were mixed in varying proportions until the crystals immersed in them neither rose nor sank, even under centrifugation. In a total volume of approximately 5 ml, the density of the mixture could be adjusted in increments of 0.5%, and this constituted a major error in the method. The density was determined by measurement of the weight of a 3 ml aliquot withdrawn with a class A pipette. A second major error, common to all of the density methods used, occurred whenever air or solvent pockets were present in the crystals. This was avoided as much as possible by careful selection by microscopic examination of the crystals that were used for the density determinations.

(*b*) *Displacement method.* — In the displacement method, the weight change due to the displacement of *n*-butyl phthalate by the crystals (at constant volume) was used to calculate the bulk density of the solid phase. The bulk density of the crystals was calculated by:

$$d_{solid} = d_{liquid} \ (wt._{solid}/wt._{displaced(liq.)})$$

The error in this method was estimated as $\varepsilon = \Delta w / S$ where Δw represented the accumulated weighing errors and S represented the weight of the sample.

(*c*) *Modified Berman method.* — In the Berman method[8] of density determination the weight loss of a sample weighed immersed in a liquid was compared to the weight of a sample weighed in air. The density was calculated by $d = W_a D_1 / (W_a - W_1)$ where W_a was the weight of the sample in air and W_1 was the weight of the sample immersed in liquid and D_1 is the density of the immersing liquid. The relative error was estimated as:

$$\varepsilon = (W \Delta D + D \Delta W) / (W_a - W_1)$$

A chain balance was modified by removing the balance pans and hanging a small glass boat from one arm of the balance and counter-balancing the other arm so that the balance was at approximately zero position while the boat was suspended in a light liquid (usually ethanol). The first "zero" position was found for the boat dry and suspended in air. The second "zero" position was found for the boat suspended in the liquid phase. The sample was first weighed in the dry boat, in air. It was then immersed (while still in the boat) in a side-arm test-tube containing the same liquid used with the balance. The test-tube was stoppered and a partial vacuum was drawn while the sample was gently agitated by shaking the test-tube. This procedure removed any trapped air from around the sample and was necessary to the success of the

method. The sample was then transferred to the balance and weighed while suspended in the liquid medium.

RESULTS AND DISCUSSION

Figs. 1 and 2 summarize the results obtained. The crystalline phases produced in the various experiments are identified on the figures, and the dotted lines serve to separate roughly the regions in which they were predominant. From the general downward slope of the lines, it seems possible that if the experiments were extended to much longer times, the essentially complete reduction of Cu^{2+} to Cu^+ would be observed in experiments at all temperatures.

Because of the elevated temperatures and pressures at which experiments were performed, the high concentrations of the salts present, and the general complexity of the systems studied, it does not seem possible to attempt any detailed thermodynamic treatment of the reactions which occurred. However, a qualitative discussion does seem in order because of the possible applicability of these techniques to other copper salts and to other metal compounds. In Table II are collected some

TABLE II

THERMODYNAMIC DATA FOR SPECIES INVOLVED IN HYDROTHERMAL EXPERIMENTS

Species	ΔG_f (kcal/mole)[a]	Species	$-logK_{sp}$[b]
Cu^{2+}(aq)	15.53	$Cu_2(OH)_3Br$	33.84
NH_4^+(aq)	−18.97	$Cu_2(OH)_3Cl$	34.58
$N_2(g)$	0.0	$Cu_4(OH)_6SO_4$	68.77
Cu^+(aq)	12.0		
H^+(aq)	0.0		

[a]Selected data from Refs. 10 and 11. [b]Average values from L.S. SILLEN and A.E. MARTELL, *Stability Constants of Metal-Ion Complexes, Spec. Publ. No. 17, The Chemical Society*, Burlington House, London, 1964.

thermodynamic data[10,11] for some of the species present in the system. The overall reaction for the reduction is:

$$3Cu^{2+}(a_1) + NH_4^+(a_2) \rightarrow \tfrac{1}{2}N_2(g,f) + 3Cu^+(a_3) + 4H^+(a_4)$$
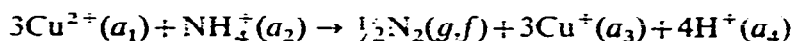
where a is the symbol for activity, f for fugacity. At equilibrium at T, P, the change in Gibbs free energy, ΔG, is zero.

$$\Delta G = 0 = +8400\ cal + RT \ln \frac{a_3^3 a_4^3 f^{1/2}}{a_1^3 a_2}$$

At room temperature, the pH of the initial and final solutions for the Br^- system was close to 7, the partial pressure of N_2 between 0.8 and 12 atm, and NH_4^+ between

5.0 and 4.5 M. If concentrations and pressures are used instead of activities and fugacity then a reasonable estimate of the ratio $[Cu^+]/[Cu^{2+}]$ at equilibrium is given by:

$$[Cu^+]/[Cu^{2+}] = 10^{7.5}$$

for $p(N_2) = 2$ atm and $[NH_4^+] = 5$ molal.

From the average pK_{sp} for $Cu_2(OH)_3Br$, $pK_{sp} = -33.84$, $[Cu^{2+}] = 10^{-6.7}$, if solid remains in equilibrium with the solution under these conditions. There appear to be wide discrepancies in the numerical values available for the various equilibria that involve Cu^{2+} and Br^- or Cl^- to form ions of the type $[CuX_n]^{(2-n)+}$. Their net effect, compared to systems which involve little-complexing ions such as SO_4^{2-} will be to enhance the solubility of the basic salts used as starting materials. Similarly, complexation of Cu^+ will assist the completeness of the reduction*. If the complexation is ignored, the reduction of Cu^{2+} to Cu^+ would be expected to be practically complete at room temperature for the systems studied.

CONCLUSION

In summary, it appears that the reduction of Cu^{2+} to Cu^+ via a series of intermediate crystalline products is possible, as well as the growth of satisfactory single crystals of them by hydrothermal experiments. The situation is complicated by the many equilibria possible, but thermodynamic data at room temperature serve as a reasonable guide to the occurrence of the desired reduction of Cu^{2+} to Cu^+. The production of specific products, and the sequence of reactions observed depend on many factors, including the complexing ability of the anions selected and the possibility of formation of mixed salts. The specific sequence of products formed appears to follow a regular pattern, as evidenced by the results illustrated in Figs. 1 and 2, but this may be due to favorable kinetics of the reactions rather than their thermodynamics. The extension to other metal salts may be possible (and available thermodynamic data should serve as a guide to what may be possible) but the specific systems tested will probably have to be chosen with care.

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*We have performed similar experiments with $Cu_4(OH)_6SO_4$. Some crystal growth of the starting material was observed, but the reduction gave Cu_2O without the appearance of intermediate crystalline products. This may be due in part to the inability of SO_4^{2-} to complex well with Cu^+, since in the crystals obtained with Cl^- or Br^- which contained Cu^+, tetrahedral units of stoichiometry $CuCl_3^-$ or $CuBr_3^-$ are present. The discussion of the crystal structures of these materials and their relation to the epitaxial growth observed will be reported elsewhere.

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