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Solid state synthesis of a new compound $Cu(HQ)Cl_2$ and its formation reaction

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Abstract

The title compound was synthesized by the direct reaction of two solids, $CuCl_2.2H_2O$ and 8-hydroxylquinoline in 1:1 molar ratio. The reaction proceeds in two steps: $Cu(HQ)Cl_2$ hydrate is formed at the first stage, then the hydrate dehydrates. The heats of the two reactions have been measured.

Keywords: Cu(II) complex; DSC; 8-Hydroxylquinoline; Solid state reaction; Solid state synthesis

1. Introduction

Solid state chemistry is central to solid state science because it provides a number of useful materials. The materials are usually prepared through direct reactions of solid reactants in the solid state at high temperatures, often 1000–1500°C [1]. Since reactions at such high temperatures can only lead to thermodynamically stable products, there is now an increasing tendency to lower the reaction temperature so that some useful metastable phases can be obtained. It is important that the reactions can be kinetically controlled during this process [2]. Towards this, it was found that a knowledge of coordination chemistry is helpful to the understanding of the reactions [3].

Obviously, studies on coordination reactions in the solid state match this trend because they usually take place at room temperature or at low heating temperatures [4,5], and because they are also easily controlled to obtain intermediates [6].

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For example, the reactions of metal chloride hydrates with 2,2′-bipyridyl or *o*-phenanthroline in the solid state proceed in a step-wise manner, and every possible product can be obtained if the starting materials are mixed in the stoichiometric ratio of the metal to the ligand in the target product [6]. To extend this study, new kinds of ligands that have Brønsted acidity have been used to investigate the effect of their protons and the possible new structures to which they may lead.

8-Hydroxylquinoline is an excellent ligand, and has been widely used in analytical chemistry. Its copper(II) complexes have also been used in industrial applications because of their ability to protect wood and textiles from rot-producing fungi [7]. Accordingly, its coordination chemistry has been studied extensively in solutions, and this has now been extended into solid state chemistry [8-12].

In methanol or aqueous solution, the reaction of copper chloride (hydrate or anhydrate) with 8-hydroxylquinoline produces CuQCl and CuQ_2 under different conditions [13]. This paper reports the solid state reaction of $CuCl_2.2H_2O$ and 8-hydroxylquinoline in 1:1 molar ratio, which produces a new intermediate, $Cu(HQ)Cl_2$.

2. Experimental

2.1. Apparatus

XRD patterns were measured on a Shimadzu XD-3A diffractometer with Cu K_α radiation and a Be filter. The calorimeter used was a Setaram DSC with closed cells, using Al_2O_3 as a reference, and with 1 μW sensitivity. IR spectra were recorded on a Nicolet FTIR-170sx with KBr discs. Elemental analyses were performed on a 240 C microanalyser. TG/DTA curves were recorded on a TG/DTA apparatus manufactured by the Shanghai Analytical Apparatus Factory, China.

2.2. Reagents

Both $CuCl_2.2H_2O$ and 8-hydroxylquinoline were analytical reagents purchased from the Shanghai Chemical Factory. They were used after being ground and passed through a 180-mesh sieve.

CuQCl was prepared according to the literature method [13]. Calculated (%) values for $Cu(C_9H_6NO)Cl$ were: C, 44.35; H, 2.46; N, 5.75. Found: C, 44.04; H, 2.57; N, 5.66.

2.3. Preparation of $Cu(HQ)Cl_2$

A homogenized mixture of $CuCl_2.2H_2O$ and 8-hydroxylquinoline accurately weighed in a 1:1 molar ratio was ground in an agate mortar at room temperature. The mixture soon changed in color from pale blue to yellow green, then to tan with the mixture aggregating. In about 2 h, all the reactants were exhausted as indicated by the XRD pattern of the reaction mixture (Table 1). After the product was dried in a desiccator, its XRD pattern was measured again. It was found that the latter is

Table 1
XRD *d*-intensity values

$Cu(HQ)Cl_2.xH_2O$		$Cu(HQ)Cl_2$		β-CuQ_2		α-CuQ_2		CuQCl	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
		12.8	100	10.4	50	12.1	100	10.3	100
9.8	87	10.3	28	7.42	80	7.31	40	7.8	30
		8.6	39	6.72	70	6.67	90	6.7	16
		7.6	28	5.76	20				
		6.4	19	5.31	15				
				4.62	15				
				4.44	15	4.32	15	4.4	25
				4.27	15				
				3.90	10			4.0	9
3.6	75	3.6	56	3.76	15	3.76	50	3.8	16
				3.66	15	3.64	20		
				3.32	100	3.38	10	3.3	34
3.2	100	3.2	72	3.25	10	3.31	75	3.2	28
				3.19	30	3.20	75		
				3.14	10	3.05	10	2.9	19

different from the former. Since it was found that the aggregated product partly decomposed if it was washed with acetone, the dried product was analyzed without further treatments. Calculated (%) values for $Cu(C_9H_7NO)Cl_2$ were: C, 38.57; H, 2.50; N, 5.00. Found: C, 38.14; H, 2.57; N, 4.95.

It was also found that the above mixture experienced a loss of 11.2% total weight when it was put in a thermostat at 40°C until constant weight was obtained. This is well-matched with a loss of 2 molecules of water.

2.4. DSC measurements

At 24°C and 70% relative humidity, accurately weighed 1 mmol each of $CuCl_2.2H_2O$ and HQ were carefully mixed in an agate mortar by grinding as lightly as possible to prevent deep reaction, then rapidly transferred into a cell of the calorimeter. Reference Al_2O_3 of approximately the same specific heat was placed in another cell. Both cells were the same, i.e. closed and with an effective volume of 1 cm^3. The temperature scan rate was 0.5°C min^{-1} up to 90°C, and then changed to 0.8°C min^{-1} to make cyclic scans, e.g. see Fig. 2.

The integration of the peak area was carried out on the computer of the calorimeter, which has an error of about 5%.

2.5. TG/DTA measurements

TG/DTA was used to investigate the thermal stability of dried $Cu(HQ)Cl_2$, which showed that it is stable even when heated up to 250°C.

3. Results and discussion

3.1. The characterization of the product

The empirical formula of the dried product is Cu(HQ)Cl_2. Since the XRD pattern of the product contains no peaks of the starting materials, and is also different from that of the two known compounds, CuQCl and CuQ_2 [14] (Table 1), it is a new compound.

The FTIR curve of Cu(HQ)Cl_2 suggests that it is an anhydrate. It is also different from that of CuQCl. Fig. 1 shows the far-IR spectra. Table 2 gives some important absorptions and their assignments for the related compounds. It is important to point out that there is an absorption at 1111 cm^{-1}, which is evidence for bidentate coordinated 8-hydroxylquinoline [15], and there are also absorptions attributed to

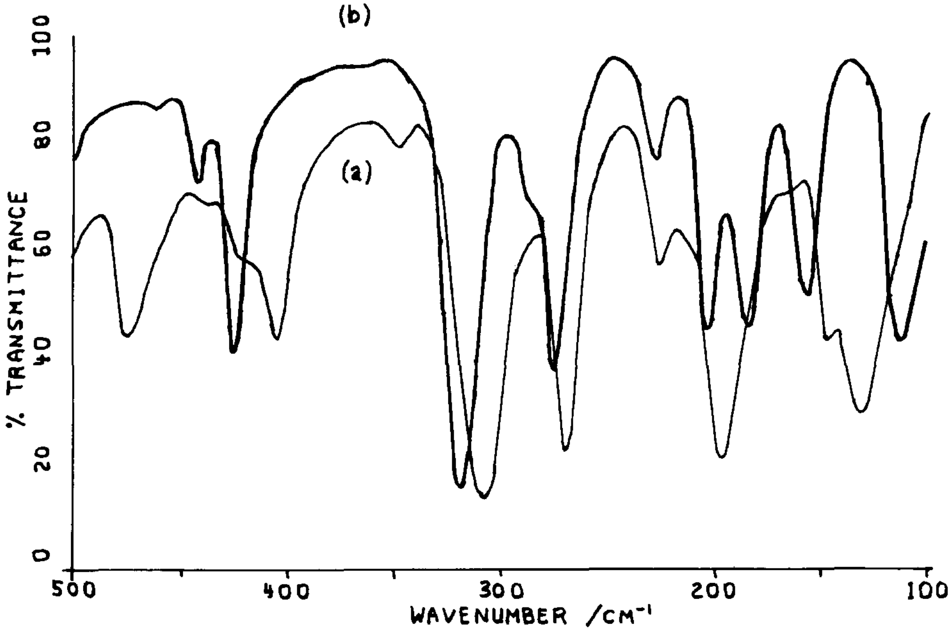
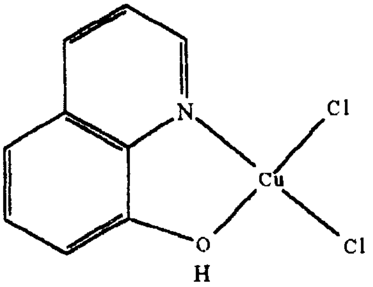


Fig. 1. Far-IR spectra of (a) Cu(HQ)Cl_2 and (b) CuQCl.

Table 2
Important IR bands and their assignments [15-17]

Compounds	ν_{Cu-N}	ν_{Cu-O}	ν_{Cu-Cl}	9-μ Band
Cu(HQ)Cl_2	269	307	404 (terminal)	1111
CuQCl	275	318	318 (bridging)	1113
α-CuQ_2	297.3	332.1		1118.1
β-CuQ_2	289.7	324.0		1111

ν_{Cu-N}, ν_{Cu-O}, $\nu_{Cu-Cl(terminal)}$ in the IR spectrum of $Cu(HQ)Cl_2$; therefore, the complex may have the following structure:



3.2. Reaction pathway

If there is one substance that can act as a base in solution, the total reaction of $CuCl_2$ and HQ may be either

$$CuCl_2 + HQ \rightarrow CuQCl + HCl \quad (1)$$

or

$$CuCl_2 + 2HQ \rightarrow CuQ_2 + 2HCl \quad (2)$$

However, the solid state reaction must proceed in a different way, since the product is $Cu(HQ)Cl_2$:

$$CuCl_2.2H_2O(s) + HQ(s) \rightarrow Cu(HQ)Cl_2(s) + 2H_2O(l) \quad (3)$$

DSC was employed to determine how the solid state reaction proceeds. The DSC curve of the reaction is composed of two parts: a sharp exothermic peak at 46°C, with a peak area of 16.3 ± 1.0 kJ mol^{-1}, and a wide endothermic peak at 74°C, with a peak area of 9.0 ± 0.2 kJ mol^{-1}. The latter does not come from the melting of HQ, because of its peak shape and its behavior in cyclic scans (Fig. 2).

Because spontaneous reactions in a condensed state are usually exothermic, the first exothermic peak must come from a reaction, and the second endothermic peak must come from a process such as dehydration.

In the synthetic reaction, there are indications that the initial products are aggregated due to water release; moreover, the XRD patterns of the product before and after it is dried are different. Since the dried product is an anhydrate, it must experience a process of dehydration when it is drying. In addition, because dehydration is usually endothermic, we can conclude that the pathway is: first, HQ reacts with $CuCl_2.2H_2O$ to produce $Cu(HQ)Cl_2.xH_2O$:

$$CuCl_2.2H_2O(s) + HQ(s) \rightarrow Cu(HQ)Cl_2.xH_2O(s) + (2-x)H_2O(l)$$

$$\Delta H = -16.3\,kJ\,mol^{-1}$$

second, $Cu(HQ)Cl_2.xH_2O$ is unstable and dehydrates:

$$Cu(HQ)Cl_2.xH_2O(s) \rightarrow Cu(HQ)Cl_2(s) + H_2O(l) \quad \Delta H = 9.0\,kJ\,mol^{-1}$$

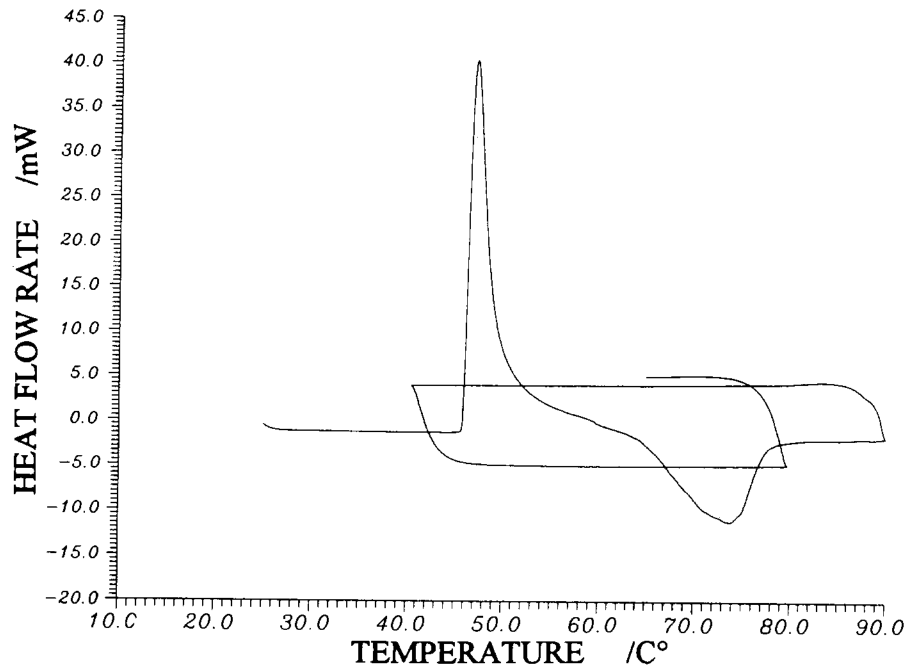


Fig. 2. DSC curve of the reaction, (a) Cu(HQ)Cl_2 and (b) CuQCl.

Similar processes can be found in the literature. It was reported that adducts are produced when $Cu(OH)_2$, $Ni(OH)_2$ [8], Tl_2CO_3 [9], $ZnCO_3$, and $CdCO_3$ [10] react with HQ.

It can be seen in the DSC curve that the reaction takes place after a long induction period. However, once the reaction occurs, it rapidly accelerates and completes. This may suggest that the reaction is autocatalytic. This is because copper chloride hydrate can dissolve in the water produced by the reaction. Since we know that the difficulty in solid state reactions is the diffusion of reactants, the dissolved and solvated $\{CuCl_2\}_n$ will help the diffusion, and thus increase the reaction rate. This is also supported by the reaction in the open system, which shows that when the mixture becomes aggregated, the color changes rapidly. This is vital evidence confirming a water-catalytic reaction.

Acknowledgement

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