

Synthesis and Characterization of Solid-Coordination Compounds $\text{Cu}(\text{AP})_2\text{Cl}_2$

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The solid state reaction of 2-aminopyrimidine ($\text{C}_4\text{H}_5\text{N}_3$, abbreviated as AP) with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in the molar ratio of 2:1 results in the formation of $\text{Cu}(\text{AP})_2\text{Cl}_2$ at room temperature. The solid product, which was unstable in solvents or at higher temperatures, can only be synthesized by solid state reaction, so it was called a solid-coordination compound. It was characterized by means of XRD, DTA, UV, IR, and ESR. © 1995 Academic Press, Inc.

INTRODUCTION

Recently, a series of complexes of transition metals with organic ligands such as 8-hydroxyquinoline, phenanthroline, salicyladoxime, bipyridyl, and aminobenzoic acid has been synthesized in our laboratory by solid state reactions at room temperature (1–4). The synthesis of some mixed ligands and intermediate compounds has great significance in both studies on solid state reactions of coordination compounds and preparation of new materials (5, 6).

Pyrimidine and its derivatives are known to be biologically important compounds (7). A complex $\text{Cu}(\text{AP})\text{Cl}_2$ of 1:1 coordination ratio was easily prepared by mixing the solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 2-aminopyrimidine (abbreviated as AP) (7). Research in the literature was mostly focused on its structure and thermal properties (8, 9). By solid state reactions, not only did we obtain the same product at 1:1 molar ratio, but also a new complex $\text{Cu}(\text{AP})_2\text{Cl}_2$ when the molar ratio was changed to 1:2. In contrast to other 1:2 complexes of Cu(II) with AP that can be synthesized in solution, for example, $\text{Cu}(\text{AP})_2\text{Br}_2$, $\text{Cu}(\text{AP})_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}(\text{AP})_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (7), $\text{Cu}(\text{AP})_2\text{Cl}_2$ is unstable in solvents. Similar products were reported for the solid state reaction of NiCl_2 with $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$ (10, 11), and observed during our research on other reaction systems. So we called these solid products solid-coordination compounds, which could only exist stably in the solid state and would change to other compounds when washed by solvents.

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In this paper, we report the preparation and characterization of the solid-coordination compound $\text{Cu}(\text{AP})_2\text{Cl}_2$ in order to provide new methods for the studies of solid state reactions.

EXPERIMENTAL

(1) Reagents and Apparatus

Both $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 2-aminopyrimidine are Analar grade. The complex $\text{Cu}(\text{AP})\text{Cl}_2$ from solution was prepared according to a literature method (8).

The contents of elements C, H, and N were measured by using a Perkin–Elmer Model 240C elemental analyzer; the Cu content was measured by means of iodimetry. XRD patterns were recorded on a Shimadzu Model XD-3A X-ray diffractometer with Cu target. Infrared and far-IR spectra were recorded on a Nicolet FTIR-170SX spectrophotometer with KBr pellets. A Shimadzu UV-240 spectrophotometer was used to record the UV diffuse reflectance spectra. DSC analyses were measured on a Perkin–Elmer DSC-2C analyzer with scanning rate of $20.0^\circ/\text{min}$. ESR spectra were recorded for powder samples with a German Bruker ER 200-D-SRC 10/12 spectrometer at room temperature.

(2) Synthesis by Solid State Reactions

$\text{Cu}(\text{AP})\text{Cl}_2$. Accurately weighed $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 2-aminopyrimidine in a 1:1 molar ratio were mixed and ground in an agate mortar in order to get the best possible homogeneity. The color of the mixture immediately turned from blue to yellow-green at room temperature. After 5 min, the product was washed with anhydrous methanol and acetone several times and air-dried. The bright yellow-green powder was obtained with a yield of 95%. The elementary analysis showed the composition C (20.83%), H (2.23%), N (18.09%), and Cu (27.22%) versus the calculated values C (20.93%), H (2.20%), N (18.30%), and Cu (27.68%).

$\text{Cu}(\text{AP})_2\text{Cl}_2$. The same procedure was done to the mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with 2-aminopyrimidine in a molar

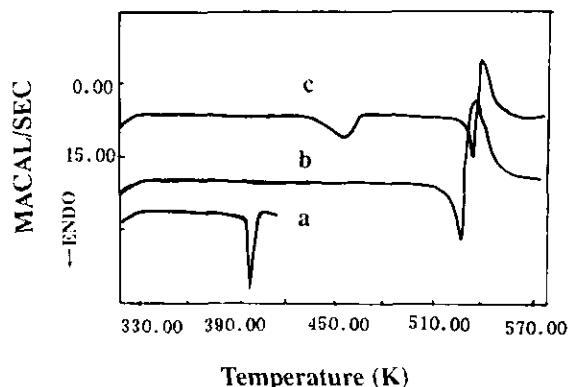


FIG. 1. DSC curves of (a) 2-aminopyrimidine, (b) $\text{Cu}(\text{AP})\text{Cl}_2$, and (c) $\text{Cu}(\text{AP})_2\text{Cl}_2$.

ratio of 1 : 2. The same phenomenon was observed as for the above 1 : 1 reaction at the first stage. Then the reaction continued till the color deepened to grass-green after 10 min. By keeping the reaction mixture at 40°C to an unchanged weight for 24 hr., a 9.77% mass loss was measured corresponding to two H_2O , calculated as 9.98%.

RESULTS AND DISCUSSION

(1) DSC Analysis

The DSC curves of the ligand AP and the solid products $\text{Cu}(\text{AP})\text{Cl}_2$ and $\text{Cu}(\text{AP})_2\text{Cl}_2$ (Fig. 1) show that 2-aminopyrimidine melts at 398 K (125°C) corresponding to the strong endothermal change (12), while the solid products remain without thermal changes before the melting point of ligand. A wide endothermal band, which appears in the curve of the 1 : 2 product (Fig. 1c) from 418 ~ 460 K ($145 \sim 187^\circ\text{C}$) but does not exist in that of the 1 : 1 product (Fig. 1b), displays the decomposition of $\text{Cu}(\text{AP})_2\text{Cl}_2$. By thermogravimetric analysis, we find that one ligand is released from $\text{Cu}(\text{AP})_2\text{Cl}_2$ at $140 \sim 180^\circ\text{C}$ and $\text{Cu}(\text{AP})\text{Cl}_2$ is obtained, which is confirmed by XRD.

(2) XRD Characterization

In the XRD patterns of the products (Fig. 2), neither the diffraction pattern of the ligand nor that of the reactant $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ appears. The new pattern of the 1 : 1 solid product (Fig. 2c) is not the addition of the patterns of two reactants, but almost the same as that of the solution product. However, the pattern of the 1 : 2 solid product (Fig. 2d), which is different from the patterns of both the 1 : 1 product and the solution product, shows that it must be a new complex. When the solid state reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with AP in a 1 : 3 molar ratio was carried out, the XRD pattern of the mixture was identical to that of the 1 : 2 product and surplus ligand. For these reasons,

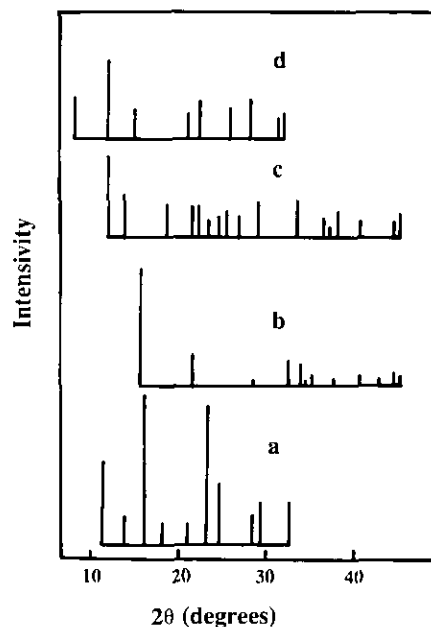


FIG. 2. XRD patterns of (a) ligand AP, (b) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, (c) solid product in a 1 : 1 molar ratio, (d) solid product in a 1 : 2 molar ratio.

we draw the conclusion that $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ reacts with 2-aminopyrimidine in a 1 : 2 molar ratio to produce the new complex $\text{Cu}(\text{AP})_2\text{Cl}_2$, in contrast to the reaction in solution.

(3) IR Spectra Study

The infrared spectra of the products measured in the range of $200\text{--}4000\text{ cm}^{-1}$ (Table 1) display many differences between $\text{Cu}(\text{AP})\text{Cl}_2$ and $\text{Cu}(\text{AP})_2\text{Cl}_2$. The shifts of some particular IR absorptions show that coordination of AP occurs through one of the ring nitrogen atoms and the

TABLE 1
Assignments of Part of the Infrared Absorptions of Ligand and Solid Products (cm^{-1})

Compound	$\nu_s(\text{NH}_2)$	$\nu(\text{C}=\text{N})$ ring vibration	$\beta(\text{NH}_2)$
2-aminopyrimidine	3170	1559	1478
Product from solution $\text{Cu}(\text{AP})\text{Cl}_2$	3248 3215	1579	1505
Product by solid state reaction at a 1 : 1 molar ratio $\text{Cu}(\text{AP})\text{Cl}_2$	3247 3214	1580	1505
Product by solid state reaction at a 1 : 2 molar ratio $\text{Cu}(\text{AP})_2\text{Cl}_2$	3124	1588 1566	1493

amino nitrogen atom in both solid product (8, 9), but the patterns of coordination are different. The former displays an octahedral structure, a copper–chlorine chain with each copper(II) having four bonds to chlorine atoms, giving the formula CuCl₂, and with the AP ligand attached above and below the planes of the CuCl₂ chain to two adjacent copper atoms (9) through the lone pairs of electrons on nitrogen atoms. As for the latter, because of the different coordination ratio, AP is considered as a bidentate ligand coordinating to one Cu(II) instead of to two adjacent ones to form another structure. Absorption bands of 322 ~ 326 cm⁻¹ (ν Cu–N) and 260 cm⁻¹ (ν Cu–Cl) in far-infrared spectra clearly confirm the patterns of coordination in the two solid products.

(4) UV and ESR Spectra Studies

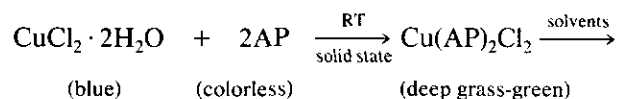
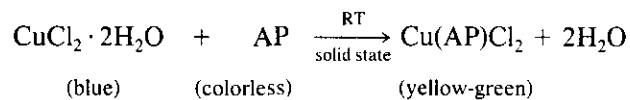
The solid reflectance spectra of these two complexes display strong absorptions at 300 ~ 400 nm which are obviously due to the 2-AP ligand and charge transfer band. The broad and asymmetric band at 550 ~ 850 nm is assignable to a *d*–*d* transition (²*E_g*–²*T_{2g}*) in a distorted octahedral field (8). However, the maxima of Cu(AP)₂Cl₂ shifts to a shorter wavelength by 20 nm with a higher intensity that is nearly twice than that of Cu(AP)Cl₂.

From the similar ESR spectra, the *g* values of the complexes are calculated:

$$\begin{aligned} \text{Cu(AP)Cl}_2 \quad g_{\parallel} &= 2.220, \quad g_{\perp} = 2.089; \\ \text{Cu(AP)}_2\text{Cl}_2 \quad g_{\parallel} &= 2.226, \quad g_{\perp} = 2.063. \end{aligned}$$

(5) Changes in the Solid-Coordination Compound Cu(AP)₂Cl₂ in Solvents

The equations of the solid state reactions are



various products (see Table 2).

The product Cu(AP)₂Cl₂ by solid state reaction is unstable in many solvents (Table 2).

(6) Discussion

If accurately weighed CuCl₂ · 2H₂O and 2-aminopyrimidine in a 1 : 1 molar ratio were mixed and ground to produce a yellow-green powder, and then another ligand was added and ground for 5 min a deep grass-green product with a 1 : 2 ratio was obtained. Based on the above phe-

TABLE 2
Changes of Cu(AP)₂Cl₂ in Solvents

Solvent	Phenomenon	Explanation
Ethanol, methanol, acetone, THF, CHCl ₃ , CH ₂ Cl ₂ , <i>n</i> -hexane	Not soluble, changing to yellow-green powder Cu(AP)Cl ₂ (confirmed by XRD)	Cu(AP) ₂ Cl ₂ is unstable in such solvents and transforms to Cu(AP)Cl ₂
H ₂ O	Soluble, changing to a light-blue solution	The complex decomposed to form aqueous Cu ²⁺ cation
DMF	Soluble, a yellow-green solution (just like the solution of Cu(AP)Cl ₂)	Cu(AP) ₂ Cl ₂ soluted in DMF and transformed to Cu(AP)Cl ₂
CH ₃ CN	Partially soluble, changing to light-blue powder	Decomposition of Cu(AP) ₂ Cl ₂ in CH ₃ CN

nomena, the solid state reaction leading to the 1 : 2 ratio is assumed to be stepwise. But the product could not be obtained by mixing the pure Cu(AP)Cl₂ with another part of AP, because the solid state reaction is dependent on H₂O released from reactants and on the crystal defects which can prompt the formation of Cu(AP)₂Cl₂.

The structure of the 1 : 1 complex Cu(AP)Cl₂ was determined (7), but the 1 : 2 complex cannot be prepared from solutions. The IR absorptions similar to other Cu(AP)₂X₂ (X = Br⁻, NO₃⁻, $\frac{1}{2}$ SO₄²⁻) (8) prepared from solutions prove that the copper atom is coordinated by two AP in this complex.

According to the chain structure of CuCl₂ · 2H₂O linked by bridging chlorine atoms (13), the ligand AP replaces the coordination site of water molecules when the solid state reaction is carried out at room temperature and the chain structure remains so that the product is stable both in solid state and in solutions. The product with a 1 : 2 coordination ratio of Cu/AP cannot be prepared unless the long chain is broken or AP plays the role of a monodentate ligand. Because of the solvent effect, it tends to form a 1 : 1 complex rather than a 1 : 2 complex in solution, even when the reactants are mixed in a 1 : 2 ratio. In contrast, some particular features of the solid state reaction make possible the formation of Cu(AP)₂Cl₂, which is unstable in solvents.

We hope to further investigate the structure and features of this solid-coordination compound.

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