Asian Journal of Chemistry Vol. 20, No. 4 (2008), 2781-2784

Solid-State Synthesis and Characterization of a Copper(II) Complex with *o*-Vanillin

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The complex, $[Cu(C_8H_7O_3)_2H_2O]$, has been synthesized by the solid-state reaction of copper acetate and *o*-vanillin ($C_8H_8O_3$) ligand. The complex was characterized by X-ray powder diffraction, elemental analysis, FTIR spectra and TG-DTG. The elemental analyses indicate 1:2 (metal:ligand) stoichiometry for the complex. The spectral studies show that the ligand acts as a bidentate ligand with the phenolic-CO and carbonyl group as coordinating donor sites and the H_2O was coordinated with Cu(II) ion. The suggested coordination number is five in this complex.

Key Words: Solid-state synthesis, *o*-Vanillin, Copper(II) complex.

INTRODUCTION

Compared with the reactions in solutions, reactions in solid state have their own characteristics, which are shown in the direct synthesis of compounds[1,2]. Studies show that the solid state reactions are simple, rapid, high yield, high election, no used organic solvents, low pollution[3]. Few studies on the synthesis of coordination compounds at low temperatures or even at room temperature have been reported so far. Recently, a series of complexes of transition metals with organic ligands such as 8-hydroxyquinoline, 1,10-phenanthroline, salicyladoxime, 2,2′-bipyridyl and aminobenzoic acid have been synthesized by solid state reactions at room temperature[1,2,4-8]. Bullock *et al.*[9] reported the synthesis of two complexes $Cu(C_8H_7O_3)_2$ and $Cu(C_8H_7O_3)_2\cdot 2H_2O$ from *o*-vanillin in solution. The structure of the complex $[Ni(C_8H_7O_3)_2(C_5H_5N)_2]\cdot 2H_2O\cdot C_5H_5N$ prepared in ethanol solution was also reported[10]. In this paper, we describe the solid state synthesis, X-ray powder diffraction of Cu(II) complex $[Cu(C_8H_7O_3)_2H_2O]$ with *o*-vanillin (2-hydroxy-3-methoxybenzaldehyde).

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EXPERIMENTAL

All reagents were AR grades and used without further purification. Reaction was carried out in air. XRD was taken on a Phillips PW3040/ 60X'pert Pro X-ray diffractometer with graphite-monochro-matized Cu Kα radiation (λ = 1.540560 Å). FTIR spectra were recorded on a Nicolet NEXUS 670 FTIR spectrophotometer using KBr discs in the range of 4000-400 cm^{-1}. The copper content was determined by EDTA complexometric titration after decomposition a known amount of the complex with concentrated nitric acid. Elemental analysis (C, H) was performed on CHN elemental analyzer, Elementar Vario EL III. A Mettler Toledo thermal analyzer TGA/SDTA 851e was used to carry out the thermoanalytical analysis with a heating rate of 10 ºC min^{-1} from 30 to 900 ºC in air atomsphere.

Synthesis of the complex: $Cu(OAc)_2 \cdot H_2O$ (0.1996 g, 10 mmol) and *o*-vanillin (3.0430 g, 20 mmol) were weighed accurately and mixed carefully in agate mortar. The mixture was ground for 0.5 h and placed in air at room temperature for 24 h to ensure the completeness of reaction. After further grinding at room temperature, the mixture was washed with alcohol (95 %) and air-dried, in Yield 95 %. Anal. calcd. (%) for $C_{16}H_{16}O_7Cu$: C, 50.06; H, 4.20; Cu, 16.55. Found (%): C, 49.91; H, 4.36; Cu, 16.70.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the $Cu(OAc)_2 \cdot H_2O$, *o*-vanillin and the complex. It can be seen that the X-ray powder diffraction pattern of the product shows great difference from those of the copper acetate and *o*-vanillin

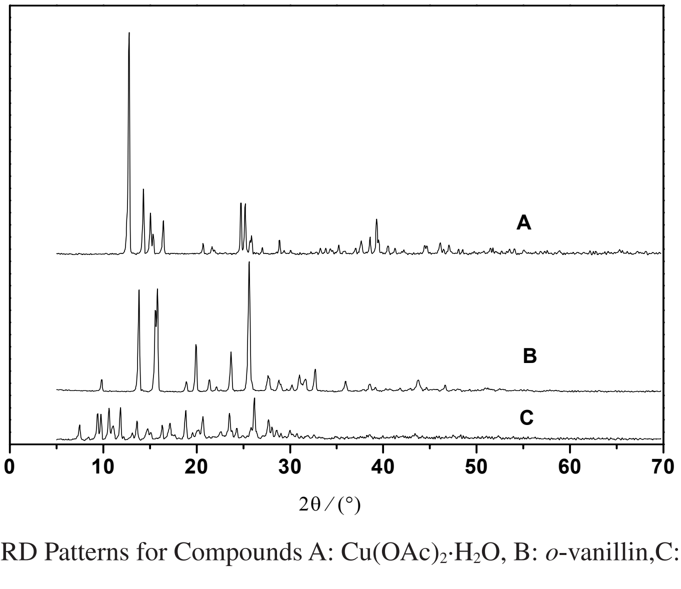

Fig. 1. XRD Patterns for Compounds A: $Cu(OAc)_2 \cdot H_2O$, B: *o*-vanillin,C: product

ligand. In the XRD pattern of the complex, neither the diffraction pattern of the ligand nor that of the copper acetate appears. The new pattern of the complex is not the addition of the patterns of two reactants, indicating that the solid-state chemical reaction between copper acetate and *o*-vanillin was generated. Finally, the title product was formed. In addition, acetic acid was evaporated from the mixture in the process of grounding. So, the reaction equation may be described as follow:

$$Cu(OAc)_2{\cdot}H_2O\ (s) + 2C_8H_8O_3\ (s) \longrightarrow Cu(C_8H_7O_3)_2H_2O\ (s) + 2HOAc\ (g)$$

The main stretching bands in the free ligand spectrum are those at 3452 s, 1655 s, 1257 vs, 1219 m cm^{-1} which are assigned to ν(OH), ν(C=O), ν(C-O) and ν(C-OMe), respectively. They were observed in the spectrum of the corresponding complex, too. However, some changes can be observed as a result of the coordination to Cu(II). The infrared spectrum of the complex exhibits a weak absorption at 3445 w cm^{-1} proving the presence of the -OH group, three absorption bands at 861, 649, 505 cm^{-1} supporting the coordination of water molecular[11]. The large red-shift of the ν(C=O) stretching vibration of the carbonyl of aldehyde from 1655 to 1605 cm^{-1} indicated the coordination of oxygen atom of carbonyl group. The ν(C-O) stretching vibration shifted from 1257 to 1250 cm^{-1} showed the complexation of oxygen atom phenolic -OH and the hydroxy of phenolic group was deprotonation. An absorption band at 1219 cm^{-1} has been attributed to ν(C-OMe) was not changed in complex where the methoxy group was not coordinated. A new band appears at 434 cm^{-1} in the complex which is assigned to the (Cu-O) bond.

The TG-DTG curves of the $Cu(C_8H_7O_3)_2{\cdot}2H_2O$ are shown in Fig. 2. The TG degradation of the compound reveals three decomposition stages, as predicted by the DTG curve and there are weight loss with maximum rate at 103.7, 261.3 and 323.7 ºC in the DTG curve. The first step of decomposition of the complex occurs from 81.4 to 153.0 ºC. The observed weight

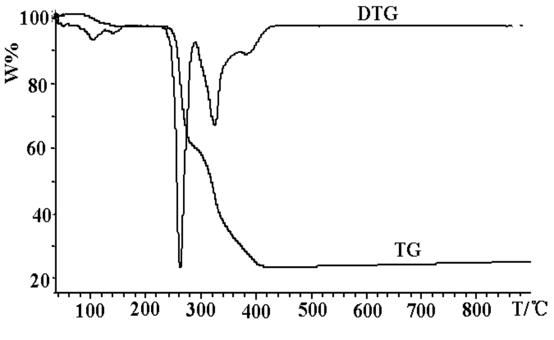

Fig. 2. TG-DTG curves of the complex

loss (4.41 %) corresponds to the loss of 1 mol water (theoretical loss is 4.69 %). The second step decomposition temperature is in the range of 230.7 - 288.3 ºC with a mass loss 37.13 % which corresponds to the loss of a *o*-vanillin ligand (theoretical loss is 37.29 %). The third weight loss 37.00 % (calc. 37.29 %) at 288.3-419.0 ºC, corresponds to the decomposition of the another *o*-vanillin ligand. Above 419.0 ºC no weight loss was observed and the final product is metal oxide CuO. This result is in good accordance with the composition of the complex.

Conclusion

From above, it is concluded that central ion Cu(II) in the complex coordinates with both two *o*-vanillin anion ligands *via* four oxygen atoms of phenol hydroxy groups, carbonyl groups and one oxygen atom of water molecular. Its coordination number is five. The suggested structure of the complex is shown in Fig. 3.

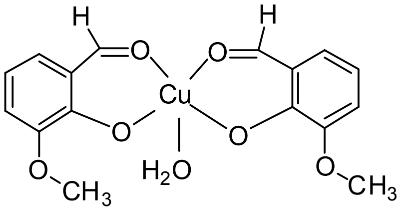

Fig. 3. Structure view of $Cu(C_8H_7O_3)_2 \cdot 2H_2O$

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(*Received*: 15 May 2007; *Accepted*: 7 January 2008) AJC-6179