

PREPARATION AND THERMAL STABILITY OF BIS(2,6-DIMETHYLPYRIDINE)SILVER(I) NITRATE

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ABSTRACT.— Bis(2,6-dimethylpyridine) silver(I) nitrate has been prepared directly from solid silver nitrate and 2,6-dimethylpyridine and from aqueous systems. In contrast to previous reports, the compound is slightly light sensitive and decomposes at temperatures significantly below its melting point. Observations on the thermal stability of this compound are presented.

Recently there have been several studies on complexes of 2,6-dimethylpyridine with ions of copper, nickel, and manganese (Allen, et. al., 1964, 1965). These compounds lose part or all of the 2,6-dimethylpyridine on heating. Several other complexes containing this ligand have also been prepared (Zavari and Datar, 1964; Buffagni, Vallarino, and Quagliano, 1964). Peard and Pflaum (1958) reported the preparation of bis(2,6-dimethylpyridine)silver(I) nitrate from aqueous silver nitrate and alcoholic 2,6-dimethylpyridine. However, these authors reported a melting point of 141-151°C for the silver complex without decomposition, and did not report an elemental analysis for the complex. The purpose of this communication is to describe two alternate methods of preparing bis(2,6-dimethylpyridine)silver(I) nitrate and report some observations on its thermal stability.

EXPERIMENTAL

Reagent grade silver nitrate (5.1 g, 0.030 mole) was treated with 10 ml of Eastman White Label 2,6-dimethylpyridine (9.4 g, 0.088 mole). The reaction does not start immediately at room temperature but begins when the mixture is heated to 50-60°C. The silver nitrate crystals wet by the amine have a translucent appearance. As the reaction begins,

the crystals swell very rapidly and take on a white opaque appearance. The mixture becomes quite warm and the entire mass appears solid. The fluffy white product was washed several times with benzene and dried by warming in air. The dried product melts at 202-204°C. Calculated for $\text{AgNO}_3 \cdot 2\text{C}_7\text{H}_9\text{N}$: Ag, 28.08%; C, 43.76%; H, 4.69%; N, 10.93%. Found: Ag, 28.17%; C, 43.57%; H, 4.68%; N, 10.56%.

In the second method, 5 ml of 2,6-dimethylpyridine (4.7 g, 0.044 mole) was added dropwise to a well-stirred solution of 2.55 g of silver nitrate (0.015 mole) in 50 ml of water. After all the amine was added, the foamy white suspension was stirred for about 15 min and filtered. The product was washed several times with cold water followed by acetone and air dried. The product melts at 202-204°C. Found: Ag, 27.90%; C, 43.50%; H, 4.68%; N, 10.21%.

Thermal stability studies were made by heating several individual samples in an oil bath at $130 \pm 0.2^\circ\text{C}$. Samples heated for long periods of time were heated in an oven at $130 \pm 2^\circ\text{C}$.

DISCUSSION

Bis(2,6-dimethylpyridine)silver(I) nitrate can be prepared easily and rapidly by either of the methods described. Since this compound is somewhat soluble in water, the first method is particularly useful. As previously reported (Peard and Pflaum, 1958), the compound is slightly soluble in cold water and is appreciably soluble in hot water. Both of these methods should be applicable to the preparation of other silver amine complexes as well.

Peard and Pflaum (1958) reported a melting point of 141-151° for the silver complex. This rather broad range indicates either gradual decomposition or

an impure compound. An elemental analysis for the complex was not given in their report. The analysis of the compounds prepared by the above methods indicates a relatively high purity, and this is reflected in the much higher melting point and the much narrower melting range than obtained previously (Peard and Pflaum, 1958). Peard and Pflaum reported that the compound melted without decomposition. Other complexes of this ligand do not behave in this way (Allen, et. al., 1964, 1965). Stability studies carried out by heating the silver complex at 130° show that this compound eventually lost weight corresponding to complete loss of the 2,6-dimethylpyridine. FIGURE 1 shows

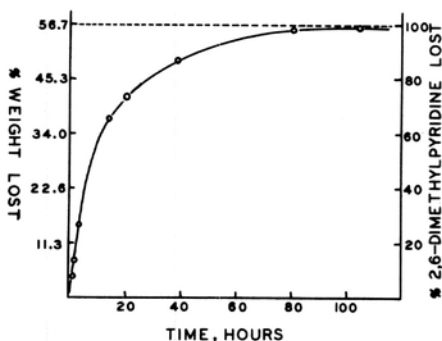


FIGURE 1. Weight loss of bis(2,6-dimethylpyridine)silver(I) nitrate heated at 130°C.

the weight loss curve for the complex heated at 130°. Continued heating produced no additional weight loss. Samples of bis(2,6-dimethylpyridine)silver(I) nitrate prepared by either method behaved similarly. A sample of silver nitrate heated for the same time lost less than 0.5% of its weight. It is apparent from these observations that bis(2,6-dimethyl-

pyridine)silver (I) nitrate not only does not melt without decomposition, but that it can be completely decomposed into the amine and silver nitrate at temperatures as low as 130°. This is similar to the behavior of other complexes of this ligand (Allen, et. al., 1964, 1965). The compound also darkens slowly when exposed to light in contrast to previous information (Peard and Pflaum, 1958).

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