

(1 mole) in water (1000 ml) was mixed with an equimolar solution of sodium salicylate in water (750 ml). When the mixed solution was left to stand, pale blue needle crystals separated. They were recrystallized from water. *Analysis*: Calc. for $\text{Cu}(\text{C}_6\text{H}_4\text{.OH.CO}_2)_2 \cdot 4\text{H}_2\text{O}$: Cu, 15.5; C, 41.0; H, 4.4%. Found: Cu, 15.6; C, 41.0; H, 4.6%. The magnetic susceptibility 3.32×10^{-6} per gram of this sample determined by the Gouy method at room temperature (22 °C) gave a magnetic moment 1.92 B.M. (*N* modification, *N* standing for the normal moment), corrections being made for the molar diamagnetic susceptibilities of salicylic acid (-75×10^{-6}) and water (-13×10^{-6}). This indicates the presence of separate rather than paired copper atoms in crystals in agreement with the result of X-ray analysis.

Accordingly, we were led to suppose that there should be at least two magnetically different crystal modifications of copper(II) salicylate tetrahydrate unless Ploquin's value is incorrect. Unfortunately, Ploquin does not describe the method of preparation of his sample in detail. Therefore, we have tried various methods of preparation and finally succeeded in obtaining a sample differing from the *N* modification in color and crystal habit. The aforementioned copper(II) salicylate tetrahydrate and an equimolar amount of salicylic acid were dissolved in as small an amount of ethanol as possible. A small amount of water was added to it. (In cases when precipitates were formed, a minimum amount of acetone was added to dissolve them.) When the solution was cooled to 0 °C, blue-green plate crystals separated. Alternatively, the ethanol solution of salicylic acid and the aqueous solution of copper(II) acetate were mixed and cooled to obtain the same sample. *Analysis*: Calc. for $\text{Cu}(\text{C}_6\text{H}_4\text{.OH.CO}_2)_2 \cdot 4\text{H}_2\text{O}$: Cu, 15.5; H₂O, 17.6%. Found: Cu, 15.7; H₂O, 17.2%. This sample was fairly stable so long as it was kept in a refrigerator. However, it gradually lost water in atmospheric air. This preparation showed a subnormal magnetic moment 1.45 B.M. at room temperature (24 °C) suggesting the presence of dimer molecules similar to those found in copper(II) acetate monohydrate crystals (*S* modification, *S* standing for the subnormal moment).

The conversion of the *N* modification into the *S* modification can be achieved as described above. The reverse process is much simpler: the former can be obtained by the recrystallization of the latter from water.

The existence of two modifications of copper(II) salicylate tetrahydrate suggests the possible formation of *N* and *S* modifications for anhydrous copper(II) salicylate also. Therefore, we have tried its synthesis by use of solvents other than water and the dehydration

of the tetrahydrates. The first method was unsuccessful. The dehydration of the *S* tetrahydrate by gradual heating or over phosphorus pentoxide at room temperature yielded green powders of anhydrous copper(II) salicylate showing a subnormal magnetic moment 1.44 B.M. at room temperature (25 °C) (*S*-1 modification). *Analysis*: Calc. for $\text{Cu}(\text{C}_6\text{H}_4\text{.OH.CO}_2)_2$: Cu, 18.8; C, 49.7; H, 3.0%. Found: Cu, 18.8; C, 49.2; H, 3.3%. On the other hand, the *N* tetrahydrate gave two different anhydrous compounds depending on the method of dehydration. When the pale blue tetrahydrate was heated to 85 °C very slowly and maintained at the same temperature until no further weight decrease took place, blue-green anhydrous copper(II) salicylate was obtained. It showed a subnormal moment 1.41 B.M. at 25 °C (*S*-2 modification). *Analysis*: Calc. for $\text{Cu}(\text{C}_6\text{H}_4\text{.OH.CO}_2)_2$: Cu, 18.8; C, 49.7; H, 3.0%. Found: Cu, 19.0; C, 48.9; H, 3.3%. On dehydration of the same tetrahydrate sample by means of phosphorus pentoxide at room temperature or when it was heated rapidly to 85 °C, very hygroscopic brown anhydrous copper(II) salicylate was obtained. *Analysis*: Calc. for $\text{Cu}(\text{C}_6\text{H}_4\text{.OH.CO}_2)_2$: Cu, 18.8; C, 49.7; H, 3.0%. Found: Cu, 18.6; C, 49.2; H, 3.1%. The magnetic moment observed at 25 °C was 1.87 B.M. (*N* modification). Although chemical analysis indicated the anhydrous nature of these three samples, it is not certain whether they are free from contamination with magnetically different modifications. Despite slight differences in the observed moment and color between the *S*-1 and *S*-2 modifications, it is difficult to conclude that they represent two different types of crystallographically uniform modification, because the properties of the *S*-1 sample depended to some extent on the rate of dehydration in preparation. However, there is no doubt that both *N* and *S* modifications exist for anhydrous copper(II) salicylate.

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A redetermination of the orthorhombic IF₇ structure. A correction. By R. D. BURBANK, *Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.*

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In the paper of the above title (Burbank, 1962) there is a typographical error on p. 1213 in the φ coordinates of atoms 3,3' and 4,4' in the simplified four parameter description. These quantities should read $78.65 \pm 1.15^\circ$ and $180 - 78.65 \pm 1.15^\circ$ instead of $76.65 \pm 1.15^\circ$ and

$180 - 76.65 \pm 1.15^\circ$. I am indebted to Dr Andrew D. Liehr for calling this to my attention.

Reference

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