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Microidentification of Cupric and Perchlorate Ions as Cupric Pyridine Perchlorate.

By

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With 2 figures.

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Experiments with $Cu(C_5H_5N)_4(ClO_4)_2$ indicate that this compound would serve as a basis for a superior microchemical identification of both cupric and perchlorate ions. *Weinland, Effinger,* and *Beck*[1] prepared and characterized it macroscopically, while *Zwikker*,[2,3] *Wagenaar*,[4] and *Steenhauer*[5] report the use of the cupric pyridine complex in the chemical identification of certain organic substances. The present contribution gives somewhat different special methods of preparation calculated to produce perfect crystals of a flat, platy type suitable for edge or profile angle measurement as the principle means of identification.

Procedure.

Preparation of the Reagent. The reagent is prepared by adding to 30 ml. of an approximately 2 per cent aqueous solution of cupric nitrate, one or two drops excess pyridine above that required to just form the deep-blue color of the complex.

Preparation of the Cupric Pyridine Perchlorate. To one milliliter of this reagent is added an equal volume of a dilute aqueous solution of a perchlorate, approximating the strength of a saturated water solution of potassium perchlorate. The resulting mixture is agitated violently

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[1] *R. Weinland, K. Effinger, V. Beck,* Arch. Pharmaz. Ber. dtsch. pharmaz. Ges. **265**, 352 (1927).

[2] *J. J. L. Zwikker,* Pharmac. Weekbl. **68**, 975 (1931).

[3] *J. J. L. Zwikker,* Pharmac. Weekbl. **70**, 551 (1933).

[4] *M. Wagenaar,* Mikrochem. (N. S.) **5**, 132 (1932).

[5] *A. J. Steenhauer,* Pharmac. Weekbl. **72**, 667 (1935).

until crystallization takes place. A few drops of the solution containing the crystals are then transferred to a slide and "ring blotted". This is done by folding a filterpaper into a strip which is then wrapped around the finger in the form of a ring, the circumference of which is adjusted to, and applied at, the edge of the drop of solution on the slide. The liquid is thus drawn evenly away from the crystals causing a uniform distribution on the slide. The remaining mother liquor is absorbed by direct gentle application of a folded filterpaper to the preparation. The crystals are then examined and measured by methods previously described by *Shead.*[6]

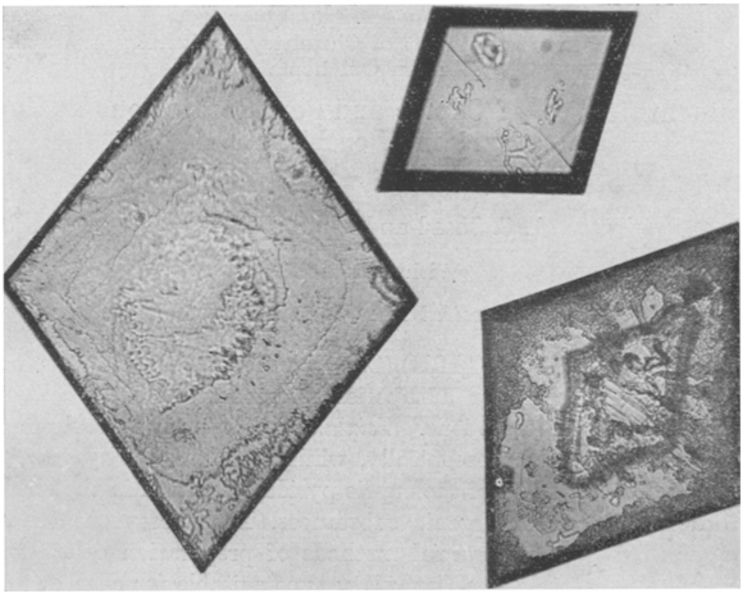

Fig. 1. Cupric Pyridine Perchlorate.

Characterization of Cupric Pyridine Perchlorate. The cupric pyridine perchlorate as above prepared is violet, lavender, or blue depending upon the thickness of the individual crystals. It forms sharply defined, platy, rhombic, parallelograms as shown in Fig. 1. The average of 95 different measurements on ten different crystals showed an obtuse angle of *Shead* and *Bailey* 107,0 ± 0,2 degrees.[7]

Dr. *Clifford A. Merritt* of the *Department of Geology* at the *University of Oklahoma* is to be thanked for supplying the following optical data

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[6] *A. C. Shead,* Ind. Engng. Chem., Analyt. Edit. **9**, 496 (1937).

[7] *A. C. Shead,* Ind. Engng. Chem., Analyt. Edit. **10**, 662 (1938).

for the crystals: Color-lavender to blue. Pleochroism-none. Extinction-symmetrical, lies in the diagonals of an equilateral parallelogram (Fig. 2).

Analysis of the Cupric Pyridine Perchlorate. The compound was prepared by the same method as described above except on a larger scale. It was washed with dilute pyridine-water in which it was slightly soluble, and dried at 100° C., at which temperature it proved stable. Five closely agreeing electrolytic copper determinations gave an average of 11,17 per cent copper. Representative check determinations are 11,11 and 11,21 per cent Cu respectively. The theoretical percentage for $Cu(C_5H_5N)_4(ClO_4)_2$ is 10,99 per cent copper. These results agree with the formula reported by *Weinland*[8] et al.

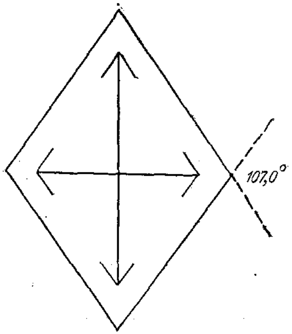

Fig. 2. Crystal of Cupric Pyridine Perchlorate Showing Obtuse Angle and Symmetrical Extinction.

Discussion.

The effect of anions was briefly studied. Sulfate, chloride, and acetate of copper were substituted for the nitrate recommended above. The results were not quite so good as in the case of the nitrate. Crystals of the resulting cupric pyridine perchlorate were smaller in the presence of the acetate ion. Insufficiency or a large excess of pyridine, alike, result in the failure of the test. Concentrations of perchlorates should be kept low; ionic concentrations approximating those of a saturated, aqueous solution of $KClO_4$ are satisfactory. A 3 to 5 per cent solution of magnesium perchlorate trihydrate gave excellent results. One or two drops of 72 per cent perchloric acid in 2 ml. of approximately 2 per cent cupric nitrate solution on also proved satisfactory. Precipitation from hot solution sometimes gives better results with $KClO_4$ but is not necessary with $Mg(ClO_4)_2$. Recrystallization of the complex perchlorate from water, pyridine, or a mixture of the two, is inadvisable.

Summary.

A microchemical test involving the formation of $Cu(C_5H_5N)_4(ClO_4)_2$ in perfect crystals, the edge or profile angles of which can be accurately measured, is proposed for the cupric and perchlorate ions. Some properties, including the values of the angles mentioned, are described, and an analysis of cupric pyridine perchlorate is presented.

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[8] *A. J. Steenhauer*, Pharmac. Weekl. **72**, 667 (1935).