[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA]

Cupric Pyrophosphate and Ethylenediamine

BY THOMAS P. MCCUTCHEON AND SAMUEL RAYMOND

It is well known that compounds of copper coordinate with different amounts of addenda, such as: ammonia, ethylenediamine, etc. ($CuCl_2 \cdot 2NH_3$, $CuCl_2 \cdot 4NH_3$, $CuCl_2 \cdot 2$ en) depending on the experimental conditions.[1]

We have prepared the following four, well-defined crystalline compounds of copper pyrophosphate with ethylenediamine (= en) and water of hydration, including one in which zinc replaced half the copper.

I. $Cu_2P_2O_7 \cdot 2$ en$\cdot 2$ H_2O; dark blue, nearly cubical crystals
II. $Cu_2P_2O_7 \cdot 3$ en$\cdot 6$ H_2O; lustrous blue plates
III. $Cu_2P_2O_7 \cdot 4$ en$\cdot 6$ H_2O; purple, felted needles
IV. $CuZnP_2O_7 \cdot 2$ en$\cdot 2$ H_2O; blunt purple needles, insoluble in water

Sodium hydroxide did not precipitate copper hydroxide from cold solutions of I, II or III; hydrogen sulfide precipitated copper sulfide immediately. These reactions indicate a low concentration of copper ion in solutions of these complex salts.

Experimental

$Cu_2P_2O_7 \cdot 2$ en$\cdot 2$ H_2O (I).—Copper pyrophosphate was prepared by adding a dilute solution of the sulfate of the metal to a dilute, boiling solution of sodium pyrophosphate. The product was a microcrystalline precipitate, which was easily filtered and washed. The reverse addition caused precipitation of a gelatinous mass, which was very difficult to handle. Three and eighty-seven hundredths grams of this substance was dissolved in 22 ml. of 5% ethylenediamine. The slight excess of pyrophosphate was filtered off and the solution was allowed to crystallize on the steam-bath. The dark blue, nearly cubical crystals were washed with cold water. Additional material, of the same composition, was obtained as a crystalline powder, by diluting the filtrate with ethanol.

Anal. Calcd. for: CuO, 34.9; en, 26.3. Found (crystals): CuO, 34.9; en, 26.3. Found (powder): CuO, 35.1; en, 26.3.

The formula [Cu$\cdot$2 en][CuP_2O_7] for compound (I) was supported by the following reactions:

(1) Soluble complexes, containing a copper-pyrophosphate anion, are readily prepared by the action of excess of sodium pyrophosphate on a copper sulfate solution.[2,3]

Silver nitrate precipitates the copper quantitatively, as a silver copper pyrophosphate, from such solutions. The precipitate is a crystalline powder, having a characteristic appearance under the microscope.

The same compound was precipitated from a solution of (I) by silver nitrate. All of the pyrophosphate and about half of the copper was precipitated, thus identifying a $CuP_2O_7^{=}$ ion. The filtrate, on evaporation, and recrystallization of the residue from ethanol, gave a significant yield of [Cu$\cdot$2 en]$\cdot(NO_3)_2 \cdot 2H_2O$,[4] identified by color, crystal form, and mixed melting point 213–216°, thus establishing the presence of the ion $[Cu \cdot 2\text{ en}]^{++}$.

(2) A solution of potassium thiocyanate, when added to a solution of (I), precipitated immediately [Cu$\cdot$en]$(SCN)_2 \cdot 2H_2O$, identified by its color, crystal form, and melting point 148–149°. The compound to be expected [Cu$\cdot$2 en]$(SCN)_2 \cdot 2H_2O$ is also stable but more soluble; hence the precipitation of the compound with one en is not surprising.

$Cu_2P_2O_7 \cdot 3$ en$\cdot 6H_2O$ (II).—A solution of 1 g. each of I and III (see below) in 20 ml. of water was heated and 10 ml. of ethanol added. The precipitate was re-dissolved and re-precipitated, giving 1 g. of shining, blue plates.

Anal. Calcd.: CuO, 27.1; en, 30.6. Found: CuO, 27.4; en, 30.7.

$Cu_2P_2O_7 \cdot 4$ en$\cdot 6H_2O$ (III).—A solution of 3.57 g. of cupric pyrophosphate (dihydrate) in 15 g. of 20% en was evaporated to one-fourth its volume, when incipient crystallization was observed. The addition of 3 volumes of ethanol gave a quantitative yield of purple, felted needles.

Anal. Calcd.: CuO, 24.5; en, 37.0. Found: CuO, 24.7; en, 36.4.

$CuZnP_2O_7 \cdot 2$ en$\cdot 2H_2O$ (IV).—To a solution of 1.4 g. of III in 30 ml. of water, 0.76 g. of zinc pyrophosphate was added. The latter dissolved gradually on boiling, and was replaced by a purple precipitate. This was recrystallized from dilute ammonia, yielding blunt, purple needles. It was insoluble in both cold and hot water.

Anal. Calcd.: CuO, 17.35; ZnO, 17.7; en, 26.1; H_2O, 7.85. Found: CuO, 17.35; ZnO, 17.4; en, 26.1; H_2O, 7.95.

This substance when heated to 80° lost the two molecules of water of hydration (loss in weight: calcd. 7.85, found 7.95), without apparent change in crystal form, but underwent a striking color change from deep purple to pinkish red. This change was reversible, and the compound regained its original color and weight, when allowed to stand in the air.

Summary

It has been shown that one molecule of copper pyrophosphate combines with two, three or four molecules of ethylenediamine, depending on experimental conditions, forming well-defined, crystalline compounds.

PHILADELPHIA, PENNA. RECEIVED SEPTEMBER 18, 1946

---

[1] Chattaway and Drew, *J. Chem. Soc.*, 947 (1937).

[2] Fleitmann and Henneberg, *Ann.*, **65**, 387 (1848).

[3] A. Pahl, *Oefrers. Vet. Fors.*, **7**, 1873.

[4] Grossman and Schuck, *Z. anal. Chem.*, **50**, 1 (1906).