

The Relative Stability of Some Copper (II) Complexes*

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The existence of complex ions and complex compounds has long been of interest to chemists. Copper (II) is a strong complex former and usually exists as a complex ion in solution. Very little study has been made of the stabilities of the copper (II) complexes.

In view of this, a spectrophotometric study was made of the relative stabilities of some of the copper (II) complexes using a Beckman spectrophotometer to measure the transmittancy of various anions. Since each copper (II) complex has a characteristic hue discernible by transmittancy curves, it was possible to compare curves of individual anions with those of mixtures of anions and establish relative stabilities of the complexes.

In 1892, H. M. Vernon (3) studied the color of copper (II) salts using the sulfate, chloride, nitrate, and acetate. He used a colorimeter which consisted of 2 graduated glass tubes with flat bottoms, about 2.5 cm. in diameter. Vernon found that the difference in color between the chloride, nitrate, and sulfate was very slight.

French and Lowry (1) studied the absorption spectra and coordination of various copper (II) compounds, both organic and inorganic. They ascertained that the different behavior of various metallic derivatives, especially their different behavior toward solvents, could be attributed to the varying stability of the coordinated complexes, rather than to the presence or absence of coordination.

In 1927, Job (2) studied complex formations and their stabilities. He mixed sodium bromide with 3.92 *M.* copper (II) nitrate and found that the bromide complex was more stable than the nitrate complex.

Experimental Work

A stock solution of 0.1 *M.* copper (II) chloride complex was prepared by dissolving C.P. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 0.2 *M.* hydrochloric acid. The resulting solution was analyzed for copper by titration with a standard solution of sodium thiosulfate. Four tenths molar stock solutions were prepared of all anions to be studied. Throughout these studies, all solutions used were prepared on the assumption that copper has a coordination number of four.

Transmittancy measurements were made with a Beckman spectrophotometer using a slit width of less than 2 mm. A tungsten filament lamp served as the source of light. The transmittancy measurements were made in 1.000, \pm 0.002, cm. absorption cells at every 20 millimicron interval in wave length.

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The effect of each anion was measured in the presence of the chloride ion and the transmittancy curves compared to the curve for copper (II) chloride complex. These curves served as standards when

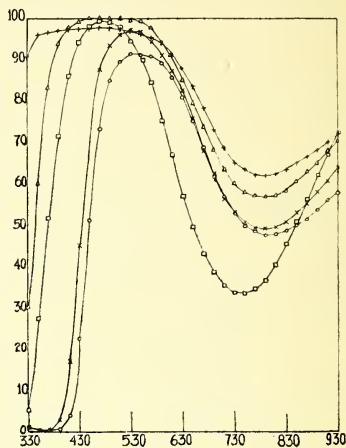
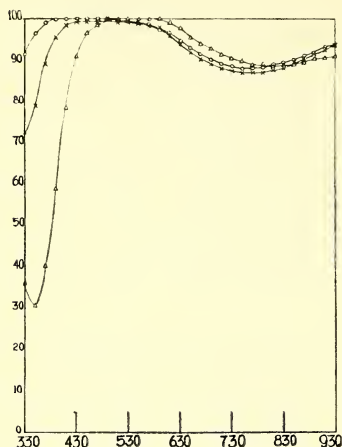


Fig. 1. Transmittancy curves for Copper (II) complexes of o) Oxalate ion (0.004 M); x) Oxalate and Thiocyanate ions; Δ) Thiocyanate ion (0.008M).

Fig. 2. Transmittancy curves for Copper (II) complexes of O) Thiocyanate ion (0.04M); x) Thiocyanate and Citrate ions; Δ) Citrate ion (0.013M); \square) Citrate and Acetate ions; +) Acetate ion (0.04M).

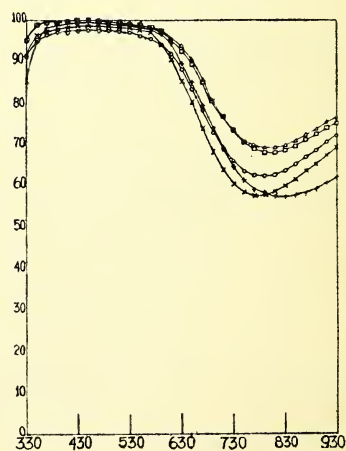
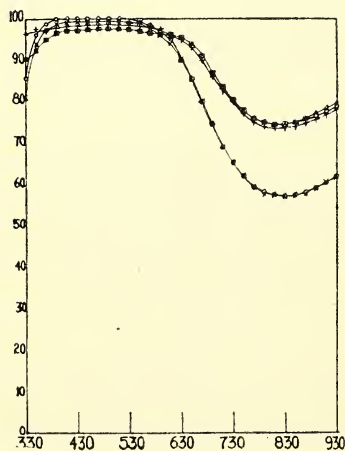


Fig. 3. Transmittancy curves for Copper (II) complexes of O) Acetate ion (0.04M); x) Acetate and Formate ions; Δ) Formate ion (0.04M); \square) Formate and Tartrate ions; +) Tartrate ion (0.02 M).

Fig. 4. Transmittancy curves for Copper (II) complexes of O) Tartrate ion (0.02 M); x) Tartrate and Bromide ions; Δ) Bromide ion (0.04 M); \square) Bromide and Phosphate ions; +) Phosphate ion (0.0133 M).

two anions were mixed to determine the stability of one with respect to the other. The chloride ion was selected as a standard because of its large instability constant.

Each anion was measured in the presence of every other anion and by comparing transmittancy curves the stability list was established. A solution of 0.01 *M.* in copper (II) chloride complex and 0.02 *M.* in sodium oxalate gave a voluminous precipitate. Consequently, it was necessary to use a solution of lower concentration which was 0.002 *M.* in copper (II) chloride complex and 0.004 *M.* in oxalate ion.

In figures 1, 2, 3, and 4, it is shown how the relative stability was established. In each figure the ordinate is the per cent transmittancy and the abscissa is the wave length in millimicrons.

The relative stability was established by comparing the transmittancy curve of a mixture of two anions being studied with the transmittancy curve of each anion. The curve of the anion that the mixture more nearly resembled was the curve of the more stable complex.

The use of a sodium, potassium, or ammonium salt for the addition of an anion has practically no effect upon the transmittancy values.

Figure 1 shows that the oxalate complex is more stable than the thiocyanate complex.

Figure 2 shows that the thiocyanate complex is more stable than the citrate complex and that the citrate complex is more stable than the acetate complex.

Figure 3 shows that the acetate complex is more stable than the formate complex which is more stable than the tartrate complex.

Figure 4 shows that the tartrate complex is more stable than the bromide complex and that the bromide complex is more stable than that with phosphate.

The transmittancy curves obtained for the phosphate and sulfate ions were very similar. The curve obtained for the mixture of the two anions was like both the phosphate and sulfate curves. Hence, they were placed together in the list of relative stability. The same situation existed in the case of the chloride and nitrate anions.

Results

The relative stability observed for the copper (II) complexes, the most stable being listed first, is as follows:

| | |
|-------------|--------------------|
| Oxalate | Tartrate |
| Thiocyanate | Bromide |
| Citrate | Phosphate, Sulfate |
| Acetate | Fluoride |
| Formate | Chloride, Nitrate |

Literature Cited

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3. Vernon, H. M., Chem. News, **66**:104, 114, 141, 152. (1892)