

reduced by this reagent to salts of comparatively strong bases which are precipitated incompletely or not at all.

Zinc, cadmium, mercury, cobalt and nickel, when sufficiently concentrated, form difficultly soluble addition products with phenylhydrazine. With aniline, also, zinc, cadmium and mercury give similar compounds. The strongly basic elements, magnesium, barium, calcium, strontium, manganese and ferrous iron are not precipitated.¹

Beryllium, when present alone, is not precipitated by aniline, nor by phenylhydrazine, except from sulphate solutions. Actual separations were worked out as follows: titanium and zirconium from iron; titanium, zirconium and thorium from beryllium. The separation of aluminum from iron proposed by Campbell and Hess was studied more closely. A double precipitation is advisable in all these separations. The separations from ferrous iron depend upon the reducing power of phenylhydrazine as well as its weakly basic nature. Aniline can not be substituted for it here, but all the separations from beryllium may be done equally well with aniline.

(5) Phenylhydrazine will accurately separate minute quantities of alumina (and probably also the weaker bases) from large masses of iron.

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CHROM-MALONATES.

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COMPLEX salts of organic acids are little known. The chrom-oxalates have been thoroughly studied from the days of Mitscherlich on, and in more recent time the complex oxalates of the metals of the platinum group have been investigated by Joly, Leidié, Vèzes, and their pupils. Few, if any, other organic acids than oxalic have been examined from the standpoint of the formation of complex salts.

Several years ago a preliminary qualitative examination was made in this laboratory, by Mr. G. B. Capito and Mr. W. E. Davis, of the relations of chromium to a number of organic acids, and it

was found that several promised interesting results, among them malonic, tartronic, tartaric, racemic, lactic, and others.

Owing to pressure of other work, the investigation was laid aside until the past session, when Mr. G. R. Smiley spent some time studying the compounds of chromium with malonic acid. The investigation has now led in quite a different direction, and as there is no prospect that the chromium salts will be further studied in this laboratory, the results obtained by Mr. Smiley are published at this time.

The method used in the study of the chromium malonates was to prepare chromium hydroxide by the action of ammonium hydroxide upon a solution of pure chromium chloride, the green precipitate being washed by decantation until the wash-waters showed no further trace of soluble salts. This process took several weeks. This chromium "mud" was preserved in a moist condition. Definite quantities of the hydroxide were dissolved in solutions of malonic acid of varying strengths. When it was desired to form salts, an excess of malonic acid was used, and this excess neutralized by the base. The salts, with the exception of that of pyridine, do not crystallize well, and it was in most cases difficult to prepare enough of the pure salt for analysis.

Two chrom-malonic acids were found: $\text{HCr}(\text{Mal})_2 \cdot 2\text{H}_2\text{O}$ and $\text{H}_3\text{Cr}(\text{Mal})_3 \cdot 3\text{H}_2\text{O}$. These must undoubtedly be looked upon as true complex acids, and correspond to the chrom-oxalic acids. The pyridine salt of the monobasic chrom-malonic acid was obtained in fine crystals, as well as a very similar potassium salt, which probably has the same composition. Small quantities of a similar ammonium salt were obtained, but not enough for analysis. It was always accompanied by a salt, very different in appearance, consisting of thin blue plates. This blue salt reminds one of the tribasic chrom-oxalates. A single sample, appearing pure under the microscope and weighing 0.09 gram, gave 19.95 per cent. chromium, which would indicate that it was not a salt of the tribasic acid. A similar blue salt appeared in working with other acids and also with cobalt salts.

The cesium and rubidium salts obtained are unlike the pyridine and potassium salts, and unlike each other. They are not of a simple formula, and the amounts obtained were insufficient to determine the composition of the salts. The rubidium-chromium ratio was 4:5, and the cesium-chromium ratio 1:7. The rubidium

salt is orthorhombic and strongly pleochroic, while the cesium salt shows no pleochroism.

Work is at present being carried on in this laboratory on the double salts of cobalt with organic acids; the cobalt malonates prove to be easily oxidizable to cobalti-malonates.

Chrom-malonic Acid, Monobasic, $\text{HCr}(\text{Mal})_2 \cdot 2\text{H}_2\text{O}$.—Formed by the action of malonic acid solution on chromium hydroxide. Pink crystals, not pleochroic, rather insoluble in cold water, soluble in hot water. The solution is acid and the chromium is not precipitated by ordinary reagents. It forms salts on neutralization by alkalis.

	Calculated for $\text{HCr}(\text{Mal})_2 \cdot 2\text{H}_2\text{O}$.	Found. Per cent.
Chromium.....	17.74	18.08
Water.....	12.32	13.97

Chrom-malonic Acid, Tribasic, $\text{H}_3\text{Cr}(\text{Mal})_3 \cdot 3\text{H}_2\text{O}$.—Formed by warming chromium hydroxide with excess of malonic acid in solution. Fine, pale pink powder, soluble in water. Similar in properties to the monobasic acid.

	Calculated for $\text{H}_3\text{Cr}(\text{Mal})_3 \cdot 3\text{H}_2\text{O}$.	Found. Per cent.
Chromium.....	12.55	12.41
Water.....	13.00	12.98

Pyridine Chrom-malonnate, $\text{PyrCr}(\text{Mal})_2 \cdot 2\text{H}_2\text{O}$.—Formed by neutralizing a solution of chromium in excess of malonic acid, with pyridine. Monoclinic crystals, showing base, prism, clinopinacoid and pyramid; trichroic, exhibiting pink, salmon, and violet. Rather difficultly soluble in cold water, but easily soluble in hot water, from which the salt crystallizes readily.

	Calculated for $\text{PyrCr}(\text{Mal})_2 \cdot 2\text{H}_2\text{O}$.	Found.	
		I. Per cent.	II. Per cent.
Chromium.....	14.00	13.80	13.99

Potassium Chrom-malonnate.—This salt resembled, both in manner of formation and in properties, the pyridine salt, exhibiting the same pleochroism and the same crystallographic form. The chromium-potassium ratio in two analyses was found to be 1:1.05 and 1:0.93, and the chromium-water ratio in one analysis 1:1.75, making the probable formula of the salt $\text{KCr}(\text{Mal})_2 \cdot 2\text{H}_2\text{O}$, similar to that of the pyridine salt.