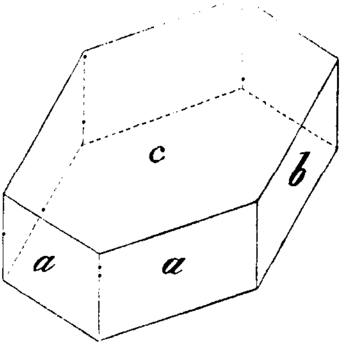
The specimens were found in Red Cañon, about four miles from the Colorado Central Railroad, and seven miles from Bristol, Colorado, a post office on the Colorado Central Railroad, thirty miles south of Cheyenne.

The crystals were all more or less weathered and stained with a red ferruginous matter, which, no doubt, accounts to some extent, for the foreign substances revealed in the analysis.

The largest crystal measures one inch in height and three inches in shortest diameter. The most perfect of the specimens is represented in its natural size in the following figure :



The form resembles a combination of a rhombic prism, *a*, brachy diagonal pinakoid, *b*, and basal pinakoid, *c*. The angle $a \wedge a$ measured 129°; the angle $a \wedge b$ measured within a fraction of a degree of the calculated value, 115° 30′.

The chemical composition of the mineral is, according to analysis, as follows :

| | |
|---|---|
| $CaCO_3$ | 95.30 |
| $MgCO_3$ | 1.19 |
| $Fe_2O_3$ | 2.18 |
| Silicious matter | 0.87 |

Ill. Ind. University, March, 1879.

## Upon the Oxidation of Quinine by means of Potassium Permanganate.

By S. HOOGEWERFF and W. A. VAN DORP. Berl. Ber. 12, 158.

Translated by Geo. A. Prochazka, Ph. D.

In the same manner as aniline and toluidine (Berl. Ber. X, 1936, XI, 1202), we have, also, oxidized quinine ; only, to accelerate the reaction, in place of the water bath, we have employed a chloride-of-calcium bath, which permits the liquid to be heated to boiling in the oxidation flask.

The quinine was employed as sulphate; for the quantitative experiments, it was previously dried to constant weight at 120°; 8.5–9.5 gms. potassium permanganate, and 16 gms. dried sulphate of quinine, were used. The oxidation of portions of 20 gms. took about 12 hours.

The quantity of oxalic acid obtained, varied between 22 and 26 p. c. of the quantity that might have been obtained, if the total carbon had been oxidized to oxalic acid.

The yield of ammonia in three different operations amounted to 41.2, 41.5, 43.4 p. c. of the quantity that might have formed, if the total nitrogen of the quinine had been converted into ammonia. The ammonia was isolated in the known manner, and determined by ignition of the platinum double salt. The amount of platinum found, at the same time demonstrates the absence of other amines.

Although the figures obtained suggest, that in the oxidation of the quinine one-half of the nitrogen appears as ammonia, yet we have not succeeded in approaching any nearer the figure of 50 p. c., demanded by this supposition. The cause seems to be, that a small portion of the quinine escapes decomposition. From the filtered manganese-oxides, at least, we could obtain a small quantity of a substance, which, according to all appearances, seems to be quinine.

These results necessarily directed our attention principally to the form in which the other half of the nitrogen appears in this oxidation of the quinine.

After several experiments, we succeeded in finding a nitrogenous acid, which was isolated in the following manner.

The oxidation liquid, after filtering off the manganese-oxides, was neutralized by sulphuric acid, and most of the potassium sulphate, besides a small quantity of potassium oxalate, removed by concentration. To the filtrate an excess of barium chloride was added, the voluminous precipitate exactly decomposed by dilute sulphuric acid, and the liquid concentrated after removal of the barium sulphate. The solid mass thus obtained contains the acid and large quantities of inorganic salts and oxalic acid. By extraction with ether-alcohol the acid is obtained in solution. After removal of the solvent, the acid, by boiling with water and barium carbonate, is converted into the barium salt, which dissolves with difficulty in water. This, after being well washed, upon decomposition with dilute sulphuric acid, filtration and concentration to a small bulk, yields the new acid in well developed plates. It generally contains a small quantity of oxalic acid, which may be easily removed by re-crystallization.

The acid presents transparent crystals which show a slight greenish coloration in reflected light, and begin to effloresce at 100° by the loss of water of crystallization. Heated in the capillary tube, they gradually become black beyond 190°, and melt at about 240° (uncorr.). At the same time, carbonic acid and, as it seems, water, are evolved. A crystalline, nitrogenous sublimate is obtained, which shows acid reaction. Before the acid melts it is, apparently, already decomposed, from which cause probably the melting point was found somewhat varying.

The acid dissolves pretty easily in hot, less so in cold water, pretty easily in spirits, very little in ether and benzol. With ferrous salts it gives a slightly red coloration.

We have examined the acid and several of its salts. By our analyses which we propose to publish elsewhere, the acid is tribasic, and corresponds to the formula $C_8H_5NO_6$. Air-dry, it contains 1.5 mol. crystal water which escapes slowly at 100°, as already mentioned, more rapidly at 120°.

The neutral barium salt $C_8H_2Ba_3NO_6$ is obtained either by precipitation of the acid solution, neutralized by ammonia, with barium acetate, or by precipitating the acid solution by the same reagent. It is almost insoluble in water, and is obtained in an amorphous condition by precipitation from the aqueous solution of the acid by barium acetate. By heating the precipitate together with the liquid, on the water bath, it is converted into small needles.

The neutral calcium salt $C_8H_2Ca_3NO_6$ was obtained by precipitating the acid solution by acetate of lime, or by boiling the acid with calcium carbonate and water. It dissolves with difficulty in water, and presents small, concentrically grouped needles.

The neutral silver salt $C_8H_2Ag_3NO_6$ is precipitated from the acid solution, neutralized by ammonia, by silver-nitrate, apparently in an amorphous condition.

An acid silver salt $C_8H_3Ag_2NO_6$ is precipitated from the acid solution by silver-nitrate, as an amorphous precipitate, which becomes crystalline.

The neutral potassium salt $C_8H_2K_3NO_6$ was prepared by neutralizing the aqueous acid solution with caustic potash solution, evaporating, redissolving the residue in little water, and cautiously adding spirits. The salt is thus obtained in the form of small white, very bright scales.

By precipitation of the acid solution, with copper acetate, a light blue, difficultly soluble, amorphous precipitate is obtained; acetate and basic acetate of lead yield white precipitates. The yield of the acid amounts to about 15 per cent. of the crystallized sulphate of quinine employed in the oxidation; small quantities, however, collect in the mother liquors, which are obtained in preparation of the barium salt.

The mother liquors probably contain also other nitrogenous oxidation products of quinine, the purification of which still engages our attention.

We call attention to the fact that Ramsay and Dobbie (Ber. XI, 324) have described an acid obtained in the oxidation of quinine by potassium permanganate, which shows many similarities to ours.

Quinidine (Conchinine of Hesse) and Cinchonine, on oxidation with potassium permanganate, apparently yield the same acid.

The analytical results obtained for the three acids, and the behavior of these acids to salt-solutions, are the same.

Our acid, which, as already mentioned, is tribasic, will probably have to be looked upon as Tricarbopyridinic acid, $C_5H_2N(COOH)_3$.

The observation that the lime salt, on distillation, with an excess of lime, yields an oil, the odor of which reminds of that of Dippel's bases, tends to confirm this view.

We are still engaged upon the further investigation of the acids and their derivatives.

ROTTERDAM, AMSTERDAM, January, 1879.

## Reports on Special Departments of Chemical Science.

### REPORT ON THE PROGRESS OF ANALYTICAL CHEMISTRY, JANUARY TO MARCH, 1879.

BY GIDEON E. MOORE, PH. D.

F. KESSLER (Zeits. f. anal. Chem., **18**, 1, 1) describes an improvement on his *method of determining manganese in alloys of iron* (idem, **11**, 255), whereby the method which, in its original form, was applicable only to alloys containing not more than 13 p. c. of manganese, is rendered applicable to alloys of every degree of richness. The principles on which the method is based, are: 1st, Precipitation of the iron as basic sulphate in the cold, by addition of sodium carbonate as long as the precipitate first formed dissolves on shaking, and addition of sodium sulphate. 2d, Precipitation of the manganese as dioxide, combined with zinc oxide, by the addition of zinc chloride,