LVI.—*A New Series of Mixed Sulphates of the Vitriol Group.*

By ALEXANDER SCOTT, M.A., D.Sc.

THE new series of sulphates described in this paper were discovered in the following manner. A sample of copper carbonate was set in an examination for candidates to describe the action of heat on it. Several asserted that it gave off nitrous fumes (being misled by the brown dust of copper oxide carried away by the evolved carbon dioxide), and consequently came to the conclusion that the powder was copper nitrate. On applying the ordinary ferrous sulphate test for nitrates to the solution of the powder in sulphuric acid, no traces of nitrate could be detected, and finally the whole was shaken up and the test-tube allowed to stand. When next looked at, a deposit of fine, reddish-brown crystals was found at the bottom of the test-tube, these crystals being soluble in water, and reducing potassium permanganate readily.

Solutions of copper sulphate and of ferrous sulphate were now separately treated with strong sulphuric acid, but neither gave any reddish precipitate. On mixing fresh solutions and then adding strong sulphuric acid, a brown precipitate was easily obtained. As a general

rule, about equivalent quantities of the two sulphates were dissolved, so as to produce an approximately saturated solution in the cold, and about an equal volume of pure, strong sulphuric acid added, the precipitate rapidly washed two or three times with sulphuric acid diluted with its own volume of water, then with absolute alcohol, then with a mixture of absolute alcohol and dry ether, and finally with dry ether, and dried over strong sulphuric acid in a vacuum.

The general formula of these salts is $(M,N)SO_4 + H_2O$, M and N being metals of the group which give the sulphates known as vitriols.

At present, only salts containing two metals have been prepared and analysed, and of these the most interesting is that first prepared, namely, monhydrated cupric ferrous sulphate $(Cu,Fe)SO_4 + H_2O$. To prepare it, 100 grams of ferrous sulphate, $FeSO_4 + 7H_2O$, 90 grams of copper sulphate, $CuSO_4 + 5H_2O$, and 200 c.c. of water were employed; after filtering the solution, 170 c.c. of strong sulphuric acid were added. Analysis of the salt showed it to consist of

Cu.	Fe.	SO ₄ .	H ₂ O (diff.).	
11.68	22.20	55.75	10.37	per cent.
1838	3965	5803	5756	atomic proportions.

This clearly shows the sulphate to be of the form given above, and is almost $CuSO_4 \cdot 2FeSO_4 + 3H_2O$. It is not a mixture of the two salts precipitated together, but is homogeneous, each crystal having its own yellow-brown colour under the microscope. $FeSO_4 + H_2O$ is easily prepared in the above manner, but I have not succeeded in obtaining $CuSO_4 + H_2O$ in the same way, all attempts yielding a sulphate with more nearly $2H_2O$, as shown by Thorpe and Watts (*Chem. Soc. Journ.*, 1880, 37, 104).

The iron is easily estimated by permanganate solution in the ordinary way, and is undoubtedly in the ferrous condition. The salt is not cuprous ferric sulphate. The crystals have not yet been obtained large enough for measurement, but if the precipitate is allowed to settle, and the very hot liquid at once poured off, it deposits well defined crystals of a yellow-brown colour when it cools. The crystals are not hygroscopic in ordinary air, but take up water in a warm atmosphere saturated with water. The hydration begins in spots, like colonies of bacteria, and this goes on much more readily if the crystals are previously finely ground up in a mortar.

To test the variation in the composition of the salt produced by different proportions of the mother substances, the following quantities were taken: 200 grams of $FeSO_4 + 7H_2O$, 90 grams of $CuSO_4 + 5H_2O$, 300 c.c. of water, and 250 c.c. of strong sulphuric acid. The salt produced had the following composition.

Cu.	Fe.	SO ₄ .	H ₂ O.	
8.15	24.89	56.33	10.63	per cent.
13	45	59	59	atomic proportions.

It was perhaps a little lighter in colour, but otherwise was much like the other above described.

The next salt with double the original quantity of copper is much lighter in colour, and presents some anomalies which require further investigation. It undoubtedly contains a yellowish brown salt with a small quantity of some white crystals of a different shape, which are most probably $\text{CuSO}_4 + 2\text{H}_2\text{O}$. The point, however, which is puzzling is that the amount of acid is not sufficient for the bases present. A repetition of the analysis confirmed the previous one. The results of the analysis are

Cu.	Fe.	SO ₄ .	H ₂ O.	
18.40	16.31	50.34	14.95	per cent.
29	29	52	83	atomic proportions.

The attempt to replace the molecule of water by a sulphate of an alkali metal or of ammonium was not successful. Ammonium sulphate was used, but the only effect of its presence apparently was to give larger crystals having a higher colour, and a much diminished yield, only 46 grams instead of 79 being obtained.

The proportions used were: 100 grams of $\text{FeSO}_4 + 7\text{H}_2\text{O}$, 90 grams of $\text{CuSO}_4 + 5\text{H}_2\text{O}$, 100 grams of $(\text{NH}_4)_2\text{SO}_4$, 300 c.c. of water, and 250 c.c. of sulphuric acid. Analysis showed it to consist of

Cu.	Fe.	SO ₄ .	H ₂ O.	
14.42	19.89	56.69	9.0	per cent.
23	36	59	50	atomic proportions.

Here the water is somewhat deficient in quantity.

The cupric nickel salt was similarly prepared. It had a pale yellowish green colour and was apparently quite homogeneous. Analysis showed it to consist of

Cu.	Ni.	SO ₄ .	H ₂ O.	
16.90	17.13	54.87	10.77	per cent.
27	29	57	60	atomic proportions.

The cupric zinc salt looked pure white and the crystals seemed to be larger than most of the others, but of the same form. It gave on analysis:

Cu.	Zn.	SO ₄ .	H ₂ O.	
11.34	25.02	54.72	10.24	per cent.
18	38	57	57	atomic proportions.

The cupric magnesium salt has always given somewhat too high a quantity of water, as the following analysis shows.

Cu.	Mg.	SO ₄ .	H ₂ O.	
19·65	7·40	60·07	12·75	per cent.
31	30	62	71	atomic proportions.

It appears to be pure white, and no appearance of its being a mixture can be detected.

The cupric manganese sulphate has a pale buff-yellow tint and was well crystallised. It consisted of

Cu.	Mn.	SO ₄ .	H ₂ O.	
19·81	15·32	55·54	10·03	per cent.
31	28	58	56	atomic proportions.

The cupric cobalt sulphate had a fine pink tint, was well crystallised, and gave on analysis

Cu.	Co.	SO ₄ .	H ₂ O.	
13·03	22·10	54·18	10·90	per cent.
20	37	56	59	atomic proportions.

Ferrous zinc sulphate was, as might have been anticipated, pure white, and was well crystallised. It consisted of

Fe.	Zn.	SO ₄ .	H ₂ O.	
16·87	16·93	55·34	10·65	per cent.
31	26	57	59	atomic proportions.

Ferrous manganese sulphate was very like the last, but had the faintest pink tint. Analysis showed it to consist of

Fe.	Mn.	SO ₄ .	H ₂ O.	
16·18	16·06	56·33	10·33	per cent.
29	29	58	57	atomic proportions.

The ferrous chromous sulphate had a pale yellowish-green tint and seemed to be quite homogeneous, but perhaps hardly all the free acid had been washed out of it, as it was not as dry a powder as most of the others. It was made by using chromous acetate and an equivalent amount of sulphuric acid, then the quantity of ferrous sulphate in solution was added, and finally about an equal bulk of strong sulphuric acid. The results of analysis were not satisfactory, as the amount of bases found were short of the acid, the ratio of the H₂O to the SO₄ was, however, as 56 : 57.

The cobalt nickel salt which was first prepared, using equivalent quantities of the two sulphates, had a pretty pink colour, but not so rich as the copper cobalt salt above described. Its composition is

Co.	Ni.	SO ₄ .	H ₂ O.	
19·75	14·71	55·34	10·2	per cent.
33	25	57	57	atomic proportions.

Another specimen, using twice the proportion of nickel, was much paler in colour, but was still quite pink. It has not yet been analysed.

The zinc chromous sulphate was a purer green than the ferrous chromous salt. Both doubtless owe their green tints to a trace of adhering chromic salt. On analysis, it gave the following results :

Zn.	Cr.	SO ₄ .	H ₂ O.
23·10	11·31	54·60	10·99 per cent.
35	22	57	61 atomic proportions.

The simple ferrous salt, prepared from 100 grams of $\text{FeSO}_4 + 7\text{H}_2\text{O}$, 100 c.c. of water, 90 c.c. of strong sulphuric acid, gave an almost pure white salt with only the faintest greenish-yellow tint. On ignition, it gave 46·5 per cent. of ferric oxide. $\text{FeSO}_4 + \text{H}_2\text{O}$ should give 47·0 per cent.

Several other salts have been prepared, but have not yet been analysed ; amongst these may be mentioned a cupric beryllium, a chromous zinc, and a nickel cadmium sulphate. The atomic weights used in calculating all the above were those given by F. W. Clarke in the *Journal of the American Chemical Society*, 1896, 18, 197.

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