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PYRIDINE COMPLEXES OF COPPER (II)-POLYTHIONATES
AND THEIR ANALYTICAL APPLICATION

Gerhard Heinze

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(From German)

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SUMMARY

The tetrapyridine-copper (II)-salts of tri-, tetra- and pentathionic acid are well crystallised compounds, stable when cold, which are distinguished by crystal form and solubility, and to some extent also by their colour (violet to blue). The most stable of them, and at the same time the one which dissolves with greatest difficulty, is the tetrathionate complex.

Only tri- and pentathionate are precipitated as slightly soluble luteo compounds by $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ from the three polythionic acids; in the supernatant solution it is then possible to precipitate $[\text{Cu}(\text{NC}_5\text{H}_5)_4]\text{S}_4\text{O}_6$. Thus it is possible to obtain a good qualitative determination of $\text{S}_4\text{O}_6^{2-}$ in the presence of the other polythionic acids and thio-sulphuric acid, which has hitherto been impossible.

Moreover, $[\text{Cu}(\text{NC}_5\text{H}_5)_4]\text{S}_4\text{O}_6$, with its Cu content of only 10.5%, is suitable for the gravimetric determination of even small amounts of copper. A method is indicated for the rapid and accurate determination of amounts of copper down to 5 mg, using the normal analysis apparatus (accuracy $\frac{1}{2}\%$).

Although the polythionates of various divalent heavy metals, e.g. zinc, manganese, nickel and cobalt, are fairly stable if there is no dampness in the atmosphere, it is almost impossible to obtain stable, defined copper (II)-polythionates. Thus, v. DEINES and CHRISTOPH [1]*, who described the preparation of numerous tetra- and penta-thionates from heavy metals, were only able to produce the corresponding copper salts very transitorily, as extremely unstable substances. In a work on the even more sensitive heavy metal salts of trithionic acid MEUWSEN and HEINZE [2] were also unsuccessful in obtaining from copper, in contrast to some other heavy metals, even one stable trithionate. Even under the most careful conditions, sulphide separation occurred during the attempt to procure its isolation. Stabilisation of CuS_3O_6 was only possible by the formation of complexes; after the addition of pyridine to its diluted, aqueous solution, the crystalline, violet complex salt $[\text{Cu}(\text{NC}_5\text{H}_5)_4]\text{S}_3\text{O}_6$ (abbreviated to $[\text{CuPy}_4]\text{S}_3\text{O}_6$), which is very stable.

The very slight solubility and low copper content of this compound led to the investigation of its suitability for a separation and weighable form of copper. With this object, the complex tetrathionate $[\text{CuPy}_4]\text{S}_4\text{O}_6$, which had already been described by CALZOLARI [3] as very slightly soluble blue needles, was again prepared and tested. Contrary to expectations, a pentathionate with the formula $[\text{CuPy}_4]\text{S}_5\text{O}_6 \cdot \text{H}_2\text{O}$ was also obtained and, this distinct from tri- and tetrathionates, contains water of crystallisation. The material consists of blue flakes which dissolve without too much difficulty, remaining stable for a few weeks but only if preserved in a cool situation.

* For references, see end.

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MORGAN and BURSTALL [4], after many fruitless experiments with the object of preparing copper (II)-diethylenediaminepentathionate, came to the conclusion that the existence of such complex pentathionates was not possible, on account of the effect of nitrogen bases on $S_5O_6^{2-}$. V. DEINES and CHRISTOPH [1] also question the possibility of obtaining these compounds, because, through the alkalinity of nitrogeneous complex-forming substances, such as pyridine or ethylene diamine, the pentathionate would decompose to the tetrathionate with the separation of elemental sulphur.

Contrary to the statements of these authors, however, when ethylene diamine or pyridine is added to dilute solutions of entirely pure pentathionate, there is no appearance of turbidity through the precipitation of sulphur. Thus, the addition of pyridine to the aqueous solution of $CuSO_4$ and $K_2S_5O_6$ results in the precipitation of the pure, complex copper pentathionate. On the other hand, the violet crystals which were separated by adding alcohol to a solution of CuS_5O_6 which contained ethylene diamine, were always mixtures of tetra- and pentathionates. The substantially higher alkalinity of the aqueous solution of ethylene diamine ($K_b = 8.5 \cdot 10^{-5}$ compared with $1.7 \cdot 10^{-9}$ for pyridine at room temperature) obviously causes partial decomposition of the pentathionate, although no separation of sulphur can be observed.

The three pyridine complexes are insoluble in methyl alcohol, ethyl alcohol and ether; their solubility in water decreases from the pentathionate, through the trithionate to the tetrathionate. Apart from this the latter is also the most stable compound and at room temperature it persists for months without decomposing.

By means of the copper-pyridine-polythionates it is possible to fill a gap which exists in the qualitative analysis of the polythionic acids. While there are good indicator reactions for the tri- and pentathionate, the reactions which are known for the tetrathionate also affect the pentathionate equally. The presence of $S_4O_6^{2-}$ can, even if only relatively small amounts of $S_5O_6^{2-}$ are also present, be determined only by indirect means, i.e. by a series of quantitative determinations; qualitative determination has not yet been found possible [5][6]. The systematic investigation of microcrystal precipitations by CHAMOT and BRICKENKAMP [7] particularly, likewise brought no substantial progress in the case of tetrathionate analysis.

Although the relatively easily soluble pentathionate is not suitable for indication, the violet crystals of $[CuPy_4]S_5O_6$ may possibly be used for identifying trithionic acid, assuming, of course, the absence of certain anions. A special interest, however, attaches to the blue needles or oblong prisms of the copper pyridine tetrathionate, because they permit direct indication of tetrathionic acid, even in the presence of other polythionic acids and thio-sulphuric acid. If the greater part of these disturbing ions be eliminated beforehand as very slightly soluble luteo compounds with $[Co(NH_2)_6]Cl_2$, which gives no precipitate with tetrathionate, it is possible to carry out the process of its identification in the remaining solution as $[CuPy_4]S_4O_6$ without any special difficulty.

Owing to the slight solubility of this complex tetrathionate in excess solution of reagent and its low copper content (10.5%), it can also be considered for the quantitative determination of copper. The precipitates obtained under analytical conditions exhibit a composition in conformity with the formula; persistent moisture can be eliminated rapidly with alcohol and ether, thus removing the tedious drying process at elevated temperatures. This method has been proved successful in the case of many other weighable substances of similar composition, as has been shown by SPACU and collaborators. We are familiar with determinations of divalent zinc, manganese, cobalt, nickel, cadmium and copper as tetrapyridine, or dipyridinerhodanide, e.g. $[NiPy_4](SCN)_2$ [8] or $[CuPy_2](SCN)_2$ [9], which combine accuracy with speed; their low specificity however, is an obstacle to a wider application of these procedures.

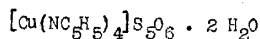
Since, by contrast with copper, even moderately concentrated solutions of zinc, manganese, cobalt and nickel form no sparingly soluble complex salts in pyridine and tetrathionate-containing solution, it seemed appropriate to use $[CuPy_4]S_4O_6$ for a rapid determination of copper, which could be applied even in the presence of these ions. Unfortunately, however, the accompanying metals become involved to a greater or lesser degree, even in hot conditions. By adhering to definite working conditions, it is possible to carry out only the determination of copper in the presence of manganese; the zinc, nickel and cobalt content of the solution may amount to a maximum of a few per cent of the amount of copper.

On the other hand the separate operation for copper determination was very satisfactory as regards the degree of precision. Owing to its speed and very low conversion ratio ($F = 0.1052$), the determination as $[CuPy_4]S_4O_6$ may be advantageous in certain cases. Thus, amounts of copper as low even as 5 mg can be determined accurately, to $\pm 1\%$, using the normal analytical balance and ordinary apparatus. It will also be possible to make accurate determinations of small quantities of precipitated copper sulphide, after ignition and treatment with potassium pyrosulphate, as $[CuPy_4]S_4O_6$, where the process of weighing as copper oxide would give most unreliable results, owing to the quantity being too small or on account of impurities.

DESCRIPTION OF EXPERIMENTS

Starting materials: $K_2S_3O_6$ was obtained according to RASCHIG [10] by introducing SO_2 into a solution of $Na_2S_2O_3$ and $NaHSO_3$ in the presence of arsenite and precipitation with KCl . $Na_2S_4O_6 \cdot 2H_2O$ and $K_2S_4O_6$ were prepared according to KURTENACKER and LASZLO [11] and KURTENACKER and FLUSS [12] from SO_2 and $Na_2S_2O_3$ with arsenite as catalyst. For obtaining $K_2S_5O_6 \cdot \frac{3}{2}H_2O$ As(III) was similarly used as a catalyst to assist the conversion of thio-sulphuric acid into pentathionic acid in the method of STAMM, SEIPOLD and GOEHRING [13]. All the salts were quite pure after one recrystallisation.

Copper (II)-tetrapyrindine pentathionate: 2.50 g (= 10.0 mmol) $CuSO_4 \cdot 5H_2O$ and 5.40 g (= 15.0 mmol) $K_2S_5O_6 \cdot \frac{3}{2}H_2O$ are dissolved in 400 ml water. 15 ml pyridine is added and immediately stirred vigorously; rapid separation of a blue deposit consisting of thin crystal flakes is produced. This is separated without delay, washed with water, and after treatment with alcohol and ether it is dried over silica gel in the evacuated desiccator. The yield is about 5.0 g = 75% of the theoretical



Calculated	Cu 9.5	S 23.8	C 35.7	H 3.6	N 8.3
Found	9.6, 9.6	24.0, 23.9	36.4	3.7	8.6

Copper (II)-tetrapyrindine trithionate and copper (II) tetrapyrindine tetrathionate: By a simplification of the methods of preparation referred to [2, 3], the two complex salts can be obtained in an analogous manner to the pentathionate. Instead of $K_2S_5O_6$ use is made of 2.80 g (= 10.4 mmol) $K_2S_3O_6$ or 3.20 g (= 10.4 mmol) $Na_2S_4O_6 \cdot 2H_2O$. The yield of $[CuPy_4]S_3O_6$ is about 4.0 g = 70% of $[CuPy_4]S_4O_6$ about 5.7 g = 95% of the theoretical.

Distinction between $S_3O_6^{2-}$ and $S_4O_6^{2-}$: A micro-drop (0.01 ml) of the solution to be tested is mixed on the object slide with an equal volume of the reagent solution (0.85 g $CuCl_2 \cdot 2H_2O$ + 8.0 g pyridine/100 ml); if spontaneous crystallisation does not occur, this can be stimulated by scratching with a sharp-edged glass rod. If $S_3O_6^{2-}$ (= 0.02 molar) is present, rectangular, violet crystals appear (Figure 1). Limit of detection: $40 \gamma S_3O_6^{2-}$; limit concentration: 1:250.

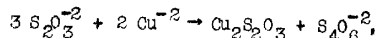
In the case of the tetrathionate (≥ 0.02 m) there is immediate separation of needles or elongated prisms (Figure 2), which, in contrast to the trithionate crystals, show a pure blue coloration. Limit of detection: $12 \gamma S_4O_6^{2-}$; limit concentration: 1:850. With lower concentrations down to 0.005 m scratching with a needle is necessary to produce the crystals.

The blue crystals of the pentathionate (Figure 3) appear only from a fairly concentrated solution; they have almost no significance for the identification of $S_5O_6^{2-}$.

Determination of $S_4O_6^{2-}$ together with the other polythionates and other disturbing anions: When $S_4O_6^{2-}$ and tri- or pentathionate are present simultaneously, there is always formation of peculiar growth forms of mixed crystals with a predominating tetrathionate content. For perfect identification of $S_4O_6^{2-}$, therefore, the greater part of the other polythionates must be removed, a procedure which is possible by precipitation with cobalt (III)-hexammine chloride.

A few drops of the experimental solution are gradually mixed in the pointed capillary tube with small amounts of extremely finely ground $[Co(NH_3)_6]Cl_3$; each time the precipitation of the luteo salts is brought about by vigorous trituration with a glass rod, and the solid reagent is added until the solution is coloured yellow by the excess. Centrifuging is then performed and a drop removed with the capillary tube; this is then tested, by the addition of copper chloride-pyridine reagent and seeding, for $S_4O_6^{2-}$. With very low concentrations, the crystals do not appear before 5-10 minutes.

$[Co(NH_3)_6]Cl_3$ is also the means of removing the disturbing ions I^- , $S_2O_6^{2-}$ and $S_2O_3^{2-}$. The iodide would later give the insoluble CuI with the reagent. In a moderate concentration (≥ 0.1 m) dithionate with $CuCl_2$ and pyridine would produce a precipitate similar to the $S_5O_6^{2-}$, which would make it more difficult to recognise the $[CuPy_4]S_4O_6$ crystals. Special care must be taken to ensure that thio-sulphate is completely eliminated as regards its use as a luteo salt because, in accordance with



it would give, with the reagent solution, exactly the substance to be determined, $S_4O_6^{2-}$.

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With the precipitation of fairly large amounts of luteo salts the solution loses some $S_4O_6^{2-}$, so that the sensitivity given for the separate determination of tetrathionate is not quite achieved. In tests with 0.02 M $S_4O_6^{2-}$ solutions the determination was still quite successful, even with the 20-fold molar excess of the acids mentioned, especially too, the pentathionic acid; corresponding blank determinations always produced negative results. Cl^- , Br^- , NO_3^- , SO_4^{2-} have no effect on the determination and similarly, ammonium salt up to a 0.5 molar concentration does not influence the sensitivity at all.

Separate determination of copper: For quantitative precipitation of copper a concentration of about 1 g tetrathionate and 4 ml pyridine in 100 ml precipitation volume is sufficient. An excess is not harmful. In a still solution the complex salt is only precipitated slowly; by stirring either more or less vigorously it is possible to produce at will either fine or coarse crystals. In all cases the deposit is very readily filterable and washable and does not adhere to the glass wall. The method was checked by means of a $CuSO_4$ solution with a content of exactly 1 mg Cu/ml, the titration standard of which was verified electro-gravimetrically. Cu determinations as $[CuPy_4]S_4O_6$ were carried out as follows:

The neutral, or very weakly acid solution, which should contain 15-50 mg Cu, is diluted to about 80 ml, mixed with pyridine to a dark blue coloration first, and then with another 4 ml. More strongly acid solutions are first almost neutralized with NaOH. On the addition of 1 g sodium or potassium tetrathionate (dissolved in a few ml water) the precipitate appears either at once or - in the case of small amounts of copper - after stirring. After some minutes, complete precipitation of the complex salt will be effected, by stirring with a glass rod and then, when the supernatant solution is no longer blue in colour, cooling is carried out by standing for half an hour in ice-cold water; with frequent vigorous stirring. The solution is then filtered at a pump on an A 2 porcelain filter crucible or a 1 G 4 glass filter crucible. For transferring the remainder of the precipitate into the crucible, the filtrate is used, or if this is not permissible, a similarly cooled solution of equal reagent-concentration (= 1 g tetrathionate + 4 ml pyridine/100 ml). The outside of the crucible is well wiped and the precipitate is dried by washing three times at the pump with 1-2 ml absolute alcohol to which pyridine has been added in the amount 3 ml to 100 ml. Each time, the suction is stopped, and the alcohol allowed to run down the whole crucible wall by means of a thin glass rod, and is then pumped off. There follow 5-10 washings (according to the amount of precipitate) with a micro-wash-bottle using small portions of absolute ether, containing pyridine (100 ml ether + 15 drops of pyridine). The crucible is then rinsed again outside and evacuated in a desiccator charged with silica gel. After 10-15 minutes weighing is carried out. $F = 0.1052$, $\log F = 0.02188 - 1$. Time required: 1 determination takes about 60 minutes, 4 determinations about 90 minutes including the cleansing and weighing of the empty crucible.

According to the analyses shown in Table 1,* the method gives accurate results over a wide range, for equal additions of reagent and equal volumes of precipitate; with very low concentrations, however, the values come out too low. Accurate determination of copper is possible, however, as soon as work is carried out with the same reagent concentration in smaller volumes. If, for example, a solution containing only about 20 ml is precipitated with 1 ml pyridine and 0.25 g tetrathionate, then, if the procedure is followed without other modification, very accurate values are obtained, down to 5 mg copper. With still smaller copper contents the method becomes uncertain once more but, of course, on account of weighing errors the limit of application of ordinary analytical balances has then almost been reached. In Table 2 are shown the values for a series of determinations which, on account of the small volumes and amounts of precipitate, can be carried out particularly quickly. In this case single weighed amounts of pure $CuSO_4 \cdot 5H_2O$, measured out in the measuring flask, were analysed.

The presence of alkali salts has no effect on the accuracy of the determination; in the analyses in Table 1, up to 3 g KCl or $KHSO_4$ was added in some cases before precipitation. On the other hand, interference is caused by complex-forming substances such as NH_3 , tartrate, etc., which combine with Cu^{+2} to form stable complex ions. Ammonium salt also, even in moderate concentration, interferes in the quantitative separation of copper. For example, with the addition of 1 g NH_4Cl /100 ml the Cu-value came out too low by 1.0%, with the addition of 2 g NH_4Cl , 3.2%.

Separation of copper from manganese: Coprecipitation of manganese can be prevented to a high degree by precipitating the greater part of the copper in the presence of an approximately equal amount of tetrathionate and only then adding an excess. Purer precipitates are also obtained if, in addition to free pyridine, a little pyridinium salt is also added. The procedure is as follows:

* For Tables, see end.

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The neutral solution, which should be about 80 ml, is mixed first with 5 ml approximately normal HCl or 1 g KHSO_4 , then with 6 ml pyridine. 1 g tetrathionate is dissolved in 10 ml water and at first only 2 ml is taken for analysis. After allowing it to stand for a short time a precipitate is brought down by stirring and then the remaining 8 ml is added in small quantities during the course of some minutes; while this is happening the precipitate is agitated each time by vigorous stirring. It is then put into ice and the procedure which follows is the same as that for the separate determination of copper (Control analyses; Table 3).

When more than 5-10% of cobalt, nickel and especially zinc is present the values for the copper become too high; smaller amounts of the above foreign metals, on the other hand, hardly have any effect on the determination as $[\text{Cu}(\text{NC}_5\text{H}_8)_4]\text{S}_4\text{O}_6$.

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TABLE 1

EXP. NO.	STANDARD SOLUTION	WEIGHED AMOUNT [CuPy ₄]S ₄ O ₆ mg	COPPER/mg.		RELATIVE ERROR %
			CALCULATED	FOUND	
1	100.00 ml	953.2	100.00	100.24	+ 0.2
2	100.00	953.3	100.00	100.26	+ 0.3
3	50.00	475.1	50.00	49.97	- 0.1
4	50.00	475.4	50.00	50.00	-
5	50.00	473.9	50.00	49.84	- 0.3
6	50.00	475.3	50.00	49.99	-
7	25.00	236.8	25.00	24.90	- 0.4
8	25.00	237.2	25.00	24.95	- 0.2
9	25.00	237.7	25.00	25.00	-
10	25.00	237.9	25.00	25.02	+ 0.1
11	25.00	237.6	25.00	24.99	-
12	25.00	238.2	25.00	25.05	+ 0.2
13	20.00	190.9	20.00	20.08	+ 0.4
14	20.00	190.7	20.00	20.08	+ 0.3
15	20.00	190.7	20.00	20.08	+ 0.3
16	20.00	190.9	20.00	20.08	+ 0.4
17	20.00	190.9	20.00	20.08	+ 0.4
18	20.00	190.5	20.00	20.03	+ 0.2
19	15.00	142.2	15.00	14.95	- 0.3
20	15.00	142.5	15.00	14.99	- 0.1
21	15.00	142.1	15.00	14.94	- 0.4
22	15.00	142.5	15.00	14.99	- 0.1
23	15.00	142.5	15.00	14.99	- 0.1
24	15.00	142.1	15.00	14.94	- 0.4

TABLE 2

EXP. NO.	WEIGHT OF CuSO ₄ · 5 aq mg	WEIGHT OF [CuPy ₄]S ₄ O ₆ mg	COPPER/mg.		RELATIVE ERROR %
			CALCULATED	FOUND	
25	237.8 . 1/5	114.7	12.10	12.06	- 0.3
26	237.8 . 1/5	115.1	12.10	12.10	-
27	237.8 . 1/5	114.8	12.10	12.07	- 0.3
28	237.8 . 1/5	114.7	12.10	12.06	- 0.3
29	172.5 . 1/5	83.9	8.78	8.82	+ 0.5
30	172.5 . 1/5	83.7	8.78	8.80	+ 0.2
31	147.4 . 1/5	71.2	7.50	7.49	- 0.1
32	147.4 . 1/5	71.3	7.50	7.50	-
33	147.4 . 1/5	71.4	7.50	7.51	+ 0.1
34	147.4 . 1/5	71.2	7.50	7.49	- 0.1
35	122.9 . 1/5	59.1	6.26	6.22	- 0.6
36	122.9 . 1/5	59.5	6.26	6.26	-
37	122.9 . 1/5	59.2	6.26	6.23	- 0.5
38	104.1 . 1/5	50.5	5.30	5.31	+ 0.2
39	104.1 . 1/5	50.5	5.30	5.31	+ 0.2
40	104.1 . 1/5	50.5	5.30	5.31	+ 0.2
41	104.1 . 1/5	50.4	5.30	5.30	-

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TABLE 3

EXP.NO.	STANDARD SOLUTION ml	FOREIGN METAL mg	WEIGHT OF $[\text{CuPy}_4]_2\text{S}_4\text{O}_6$ mg	COPPER/mg		RELATIVE ERROR %
				CALCULATED	FOUND	
MANGANESE						
42	25.00	10.0	237.9	25.00	25.02	+ 0.1
43	25.00	25.0	237.7	25.00	25.00	-
44	25.00	25.0	238.0	25.00	25.03	+ 0.1
45	25.00	25.0	237.5	25.00	24.98	- 0.1
46	25.00	25.0	238.6	25.00	25.09	+ 0.4
47	25.00	35.0	238.7	25.00	25.10	+ 0.4
48	25.00	50.0	238.1	25.00	25.04	+ 0.2
49	25.00	50.0	238.7	25.00	25.10	+ 0.4
50	50.00	25.0	476.4	50.00	50.10	+ 0.2
51	50.00	50.0	476.0	50.00	50.06	+ 0.1
NICKEL						
52	25.00	1.0	238.8	25.00	24.90	- 0.4
53	25.00	2.0	238.3	25.00	25.06	+ 0.2
54	25.00	3.0	237.7	25.00	25.00	-
55	25.00	4.0	238.1	25.00	25.04	+ 0.2
56	25.00	5.0	239.2	25.00	25.16	+ 0.6
COBALT						
57	25.00	1.0	237.4	25.00	24.97	- 0.1
58	25.00	2.0	237.1	25.00	24.94	- 0.2
59	25.00	3.0	237.8	25.00	25.01	-
60	25.00	4.0	239.8	25.00	25.20	+ 0.8
61	25.00	5.0	240.3	25.00	25.27	+ 1.1
ZINC						
62	25.00	1.0	238.1	25.00	25.04	+ 0.2
63	25.00	2.0	239.1	25.00	25.15	+ 0.6
64	25.00	3.0	241.1	25.00	25.36	+ 1.4

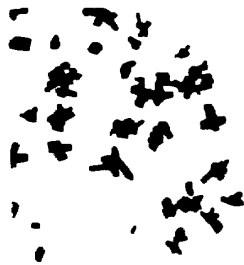


Fig. 1: Crystals of $[\text{CuPy}_4]\text{S}_5\text{O}_6$
(Magnified x 60)

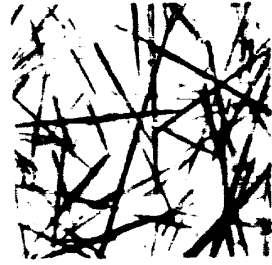


Fig. 2: Crystals of $[\text{CuPy}_4]\text{S}_4\text{O}_6$
(Magnified x 60)



Fig. 3: Crystals of $[\text{CuPy}_4]\text{S}_5\text{O}_6 \cdot 2\text{H}_2\text{O}$
(Magnified x 60)