

Citation:

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Chemistry. -- "*On Complex Salts of Ferri-Malonic-Acid*". By
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(Communicated in the meeting of June 30, 1917.)

§ 1. For certain purposes connected with the investigations into PASTEUR'S principle as made in this laboratory, it appeared desirable to prepare optically-active complex salts of trivalent *iron* with the radicals of *bivalent* carboxylic acids.

Such salts are already known derived from *oxalic acid*; some of them derived from *malonic acid* were prepared by SCHOLZ¹⁾, but in a not very recommendable way. The data given by this author concerning the content of crystallisation-water in these salts, do *not* agree with our numbers, moreover.

There exist in reality several series of hydrates here, as may become clear in the following paragraphs.

Moreover, analogous complex salts may be obtained, as we found, from *tartronic acid*, and from some *substituted tartronic acids*, as we shall demonstrate later-on.

§ 2. All attempts made by us with the purpose of resolving these racemic salts into their optically-active components, never gave really positive results, neither with derivatives of *oxalic*, nor with those of *malonic acid*.

In the case of the complex *malonates* the fission was attempted by means of the *strychnine*-, *brucine*-, and *cinchonine*-salts. These last gave sirupy, very viscous liquids, which did not crystallise. The *strychnine*- and *brucine-ferri-malonates* crystallise in small, greenish-yellow crystals, but after fractional crystallisation and elimination of the alcaloids from the salts obtained, no optically active solutions were obtained. The *tri-strychnine*-salt whose constitution, from analysis, could be established to be: $\{Fe(C_2H_2O_4)_3\} Str_3 + 6 H_2O$, showed a rotation corresponding about to the amount of *strychnine* present in it.

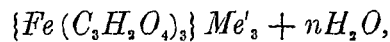
After the base had been removed by means of *KI*, the potassium-salt obtained appeared to be optically *inactive*, probably by very rapid racemisation. No attempts made with the purpose of prevent-

¹⁾ A. SCHOLZ, Monatshefte f. Chemie 29. 439. (1908).

ing this autoracemisation by experimenting in liquids containing much acetone and by working very fast, gave any better results. Analogous experience was gathered in the case of the *brucine*-salts.

In the same way we prepared the *tri-strychnine-ferri-oxalate*, which, from analysis, was seen to have the composition: $\{Fe(C_2O_4)_3\} Str_3 + 2 H_2O$, and here also several attempts were made to resolve it into its antipodes. The result was always negative, and the same occurred with: *Diammonium-strychnine-ferri-oxalate*, *diammonium-quinine*-, *diammonium-cinchonine*- and *diammonium-morphine-ferri-oxalates*. Only from the solution of the *strychnine*-salt a green substance was obtained, which, however, did not show an activity other than that corresponding to the amount of *strychnine* present. The corresponding salts of *hydroxylamine* did not give a positive result either.

§ 3. In this paper only racemic salts of the type:



are described in which Me' is replaced successively by K , (NH_4) , Na , Rb , Cs , and Tl . The Ba -salt could also be prepared, from which other salts could be obtained by interchange with soluble sulphates. The *sodium*-salt crystallises badly, and its description is therefore omitted here.

From warm solutions often *pale* green salts are obtained, possessing *rhombic* symmetry, and containing $1 H_2O$, not $2 H_2O$ as SCHOLZ¹⁾ believed. The corresponding K -salt crystallises badly, and the results obtained, although pointing in any case to a distinct isomorphism with the other salts, have therefore not been separately given here.

The most common K -salt, however, is a *triclinic* salt, crystallising with $4 H_2O$. Of the Rb -salt we obtained, besides the rarely occurring *rhombic* crystals ($+ 1 H_2O$), also darkly coloured *triclinic* crystals, containing only $1 H_2O$ too, but not well measurable. At least there must, therefore, be *three* series of hydrates possible here: *rhombic* and *triclinic* with $1 H_2O$, and *triclinic* ones with $4 H_2O$. But in no case we met with the crystals indicated by SCHOLZ, containing $2 H_2O$. A systematical investigation of the eventually possible hydrates, is very desirable.

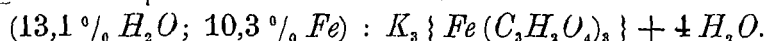
The different salts can be prepared from concentrated solutions of the *alkali-malonates* by adding the calculated amount of free *malonic acid*, heating on the water-bath, and by finally adding freshly precipitated and well-washed *ferri-hydroxide* prepared from

¹⁾ A. SCHOLZ, loco cit. p. 443. 445.

the calculated quantity of *ferrisulfate*. The beautifully green solutions, after evaporation on the water-bath, deposited crystals of the salts here described.

§ 4. POTASSIUM-FERRI-MALONATE.

Splendid, pale emerald-green, ordinarily flattened, very big and perfectly transparent crystals. They are well developed, but in the zone of the prism and that of the clinodoma they often show oscillations of the angular values to an amount of $\frac{1}{2}^\circ$. Analysis proved the composition to be



The salt possesses therefore $2 H_2O$ more than mentioned by SCHOLZ¹⁾.

Triclinic-pinacoidal.

$$a : b : c = 0,4924 : 1 : 0,4897.$$

$$A = 96^\circ 33' \quad \alpha = 98^\circ 5'$$

$$B = 103^\circ 43' \quad \beta = 104^\circ 30'$$

$$C = 84^\circ 41' \quad \gamma = 82^\circ 52\frac{1}{2}'$$

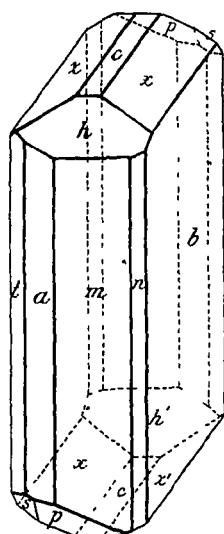


Fig. 1.
Potassium-Ferri-
Malonate
(+ 4 H₂O).

Forms observed: $b = \{010\}$, large and lustrous; $m = \{110\}$, and $a = \{100\}$, almost equally large; $p = \{120\}$, somewhat smaller than m ; $t = \{110\}$, narrow, but well reflecting; $o = \{111\}$, and $q = \{011\}$, well developed, and like $r = \{101\}$, giving perfect images; $c = \{001\}$, small; $s = \{021\}$, well-developed; $\omega = \{111\}$, as a narrow truncation of the edge $r:b$. The external habit is elongated parallel to the c -axis, and in most cases somewhat flattened parallel to $\{010\}$.

Angles: Observed: Calculated:

$a : b = (100) : (010) =^*$	95° 19'	—
$b : c = (010) : (001) =^*$	83 27	—
$c : a = (001) : (100) =^*$	76 17	—
$a : m = (100) : (110) =^*$	26 39	—
$b : q = (010) : (011) =^*$	59 13	—
$b : m = (010) : (110) =$	68 40	68° 40'
$c : q = (001) : (011) =$	24 14	24 14
$b : p = (010) : (120) =$	48 16	48 6 $\frac{1}{3}$
$p : m = (120) : (110) =$	20 34	20 33 $\frac{2}{3}$
$a : t = (100) : (110) =$	25 0	25 7
$t : b' = (110) : (010) =$	59 43	59 34

¹⁾ A. SCHOLZ, Monatshefte f. Chemie, 29. 445. (1908).

Observed: Calculated:

$c:s = (001) \cdot (0\bar{2}1) =$	47 30	47 $36\frac{1}{3}$
$s:b' = (0\bar{2}1) \cdot (0\bar{1}0) =$	48 59	48 $56\frac{2}{3}$
$b:o = (010) \cdot (\bar{1}11) =$	60 36	60 36
$o:r = (\bar{1}11) \cdot (\bar{1}01) =$	20 5	20 10
$r \cdot b' = (\bar{1}01) \cdot (0\bar{1}0) =$	99 20	99 14
$m:r = (110) \cdot (10\bar{1}) =$	59 59	60 0
$r:q = (\bar{1}01) \cdot (011) =$	52 38	52 45
$q \cdot m = (011) \cdot (\bar{1}\bar{1}0) =$	67 14	67 $15\frac{1}{2}$
$b \cdot o = (010) \cdot (111) =$	72 26	72 17
$a \cdot q = (100) \cdot (011) =$	80 26	80 24
$q \cdot o = (011) \cdot (111) =$	36 32	36 31
$o \cdot a = (111) \cdot (100) =$	43 44	43 53
$a' \cdot o = (\bar{1}00) \cdot (\bar{1}11) =$	54 42	54 $58\frac{1}{2}$
$o:q = (\bar{1}11) \cdot (011) =$	44 42	44 $37\frac{1}{2}$
$c \cdot o = (001) \cdot (111) =$	38 32	38 $20\frac{1}{2}$
$o:m = (111) \cdot (110) =$	35 34	35 $48\frac{1}{2}$
$m:c = (110) \cdot (001) =$	74 16	74 9
$p:q = (120) \cdot (011) =$	60 18	60 22
$a:r = (100) \cdot (10\bar{1}) =$	51 59	52 $3\frac{1}{2}$
$r \cdot c = (\bar{1}01) \cdot (001) =$	51 48	51 $39\frac{1}{2}$

No distinct cleavability could be found.

Distinctly dichroitic: on $\{010\}$ for vibrations parallel to the c -axis green, for those perpendicular to the former: yellow. On p and m the dichroism is only unappreciable.

On b and m is the angle of extinction about 27° , on p 44° with respect to the direction of the vertical axis. The plane of the optical axes intersects the edge $b:q$ on $\{010\}$ under an angle of about 21° .

AMMONIUM-FERRI-MALONATE.

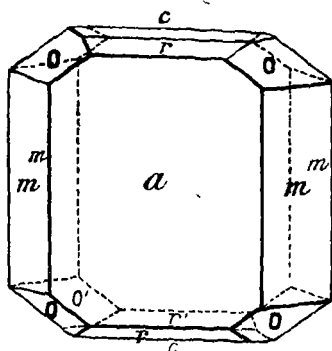
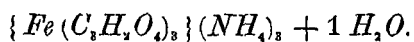


Fig. 2.
Ammonium-Ferri-Malonnate.



Pale green, flattened, very lustrous, small crystals.

Rhombic-bipyramidal.

$$a:b:c = 0,9407:1:0,6860.$$

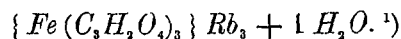
Forms observed: $a = \{100\}$, predominant, giving sharp reflexes; $m = \{110\}$, well-developed and highly lustrous; $o = \{111\}$, well-developed, and like $r = \{102\}$ yielding good reflexes; $s = \{101\}$, and $c = \{001\}$, very narrow and badly reflecting.

Angles:	Observed:	Calculated:
$a \cdot m = (100):(110) =^*$	$43^\circ 15'$	—
$a \cdot o = (100):(111) =^*$	$58 \ 59$	—
$o \cdot o = (111):(\bar{1}\bar{1}\bar{1}) =$	$62 \ 5$	$62^\circ 3'$
$m \cdot m = (110):(\bar{1}\bar{1}0) =$	$93 \ 31$	$93 \ 30$
$a \cdot s = (100):(101) =$	$54 \ 0$	$53 \ 54$
$s \cdot r = (101):(102) =$	$15 \ 53$	$16 \ 4$
$a \cdot r = (100):(102) =$	$69 \ 52$	$69 \ 58$
$r \cdot c = (102):(001) =$	$20 \ 8$	$20 \ 2$
$r \cdot o = (102):(111) =$	$32 \ 33$	$32 \ 48$
$m \cdot o = (110):(111) =$	$44 \ 59$	$44 \ 58$
$c \cdot o = (001):(111) =$	$45 \ 2$	$45 \ 2$
$o \cdot o = (111):(\bar{1}\bar{1}\bar{1}) =$	$57 \ 52$	$58 \ 0$
$o \cdot s = (111):(101) =$	$28 \ 56$	$29 \ 0$
$m \cdot o = (\bar{1}\bar{1}0):(\bar{1}\bar{1}\bar{1}) =$	$92 \ 30$	$92 \ 28\frac{1}{2}$

No distinct cleavability was observed.

The pale green crystals are distinctly dichroitic: on {100} pale yellowish-green for vibrations parallel to the *c*-axis, for those perpendicular to them, pale green. The plane of the optical axes is {001}, with the *a*-axis as first bisectrix, probably of positive character. The birefringence is weak; the apparent axial angle is very small.

RUBIDIUM-FERRI-MALONATE.



Pale green, rhombical limited crystals.

Rhombic-bipyramidal.

$$a : b : c = 0,9442 : 1 : 0,6985.$$

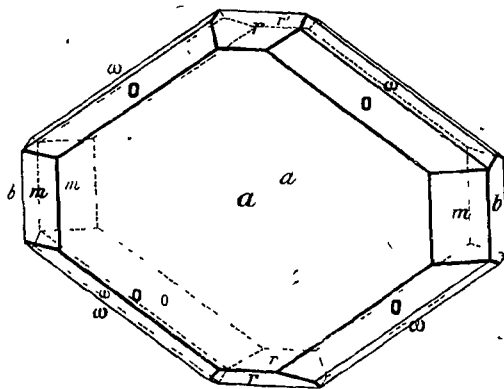


Fig. 3. Rubidium-Ferri Malonate (+ 1 H₂O).

¹⁾ This content of water of crystallisation is adopted because of the isomorphism with the other salts. The numbers of the analysis were unsatisfactory, the quantity of material at hand being too small.

Forms observed: $a = \{100\}$, strongly predominant and highly lustrous; $o = \{111\}$, and $r = \{102\}$, well-developed and yielding good reflexes, $m = \{110\}$, well reflecting; $b = \{010\}$, and $\omega = \{122\}$, narrow, built exactly measurable; $x = \{11\bar{2}\}$, small, often absent.

Angles:	Observed:	Calculated:
$a : o = (100) : (111) =$	$58^{\circ}46'$	—
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$58^{\circ}38'$	—
$o : \omega = (111) : (122) =$	14 14	$14^{\circ}22'$
$\omega : r = (122) : (102) =$	33 22	$33^{\circ}14\frac{1}{2}'$
$a : m = (100) : (110) =$	43 20	$43^{\circ}21\frac{1}{2}'$
$m : b = (110) : (010) =$	46 40	$46^{\circ}40\frac{1}{2}'$
$a : r = (100) : (102) =$	69 48	69 42
$r : r = (100) : (\bar{1}02) =$	40 24	40 36
$o : x = (111) : (11\bar{2}) =$	18'46	18 32
$\omega : \omega = (122) : (\bar{1}\bar{2}\bar{2}) =$	34 0	33 44

No distinct cleavage.

Noticeably dichroitic: on $\{100\}$ yellowish-white for vibrations parallel to the c -axis, for those perpendicular to them: pale green. The plane of the optical axes is $\{001\}$; the a -axis is first bisectrix. The apparent axial angle is very small.

No exact measurements could hitherto be made of the triclinic Rb -salt with $1 H_2O$, because of the bad crystals only at hand.

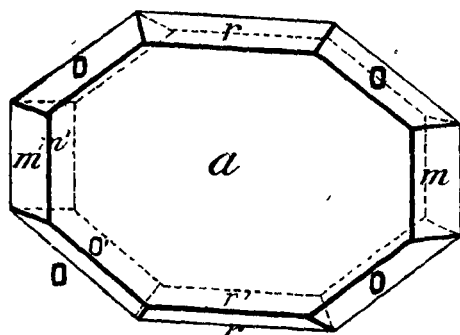
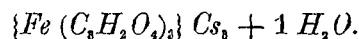


Fig. 4.
Caesium-Ferri-Malonate.

CAESIUM-FERRI-MALONATE.



Pale green, kite-shaped crystals.

Rhombic-bipyramidal.

$$a : b : c = 0,9548 : 1 : 0,7089.$$

Forms observed:

$a = \{100\}$, predominant and giving good reflexes; $o = \{122\}$, well reflecting, and, like $r = \{102\}$, rather largely

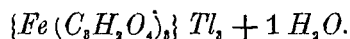
developed; $m = \{110\}$, narrow and smaller than r ; $b = \{010\}$, small but well measurable.

Angles:	Observed:	Calculated:
$a : o = (100) : (122) =$	$73^{\circ}9'$	—
$a : r = (100) : (102) =$	69 38	—
$o : o = (122) : (\bar{1}\bar{2}\bar{2}) =$	33 42	$33^{\circ}42'$
$r : r = (102) : (\bar{1}02) =$	40 46	40 44
$a : m = (100) : (110) =$	43 48	$43^{\circ}40\frac{1}{2}'$
$m : b = (110) : (010) =$	46 12	$46^{\circ}19\frac{1}{2}'$
$o : r = (122) : (102) =$	33 28	33 36
$o : o = (122) : (\bar{1}\bar{2}\bar{2}) =$	66 56	67 0
$o : b = (122) : (010) =$	56 30	56 24

No distinct cleavability could be found.

The crystals are dichroitic: on {100} greenish-yellow for vibrations parallel to the c -axis, for those perpendicular to them: pale green. The plane of the optical axis is {001}; the apparent axial angle is small, with the a -axis as first bisectrix. The birefringence is weak.

THALLO-FERRI-MALONATE.



Beautiful, pale green, flattened crystals with rectangular borders.

Rhombic-bipyramidal.

$$a : b : c = 0,9615 : 1 : 0,7050.$$

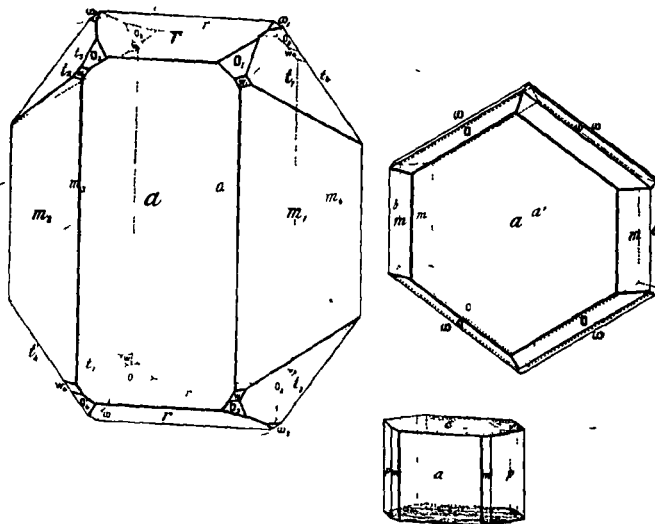


Fig. 5.

Thallo-Ferri-Malonate.

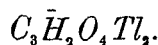
Forms observed: $a = \{100\}$, predominant and very lustrous; $r = \{102\}$, large and lustrous; $c = \{001\}$, commonly hardly visible, sometimes however well developed and striated parallel to $c \cdot a$; $m = \{110\}$, commonly well developed, very lustrous, occasionally narrow, while $p = \{120\}$, which form is ordinarily absent, is much broader in that case than m , but much duller; $o_1 = \{111\}$, well developed; $t = \{121\}$, also well-developed and lustrous; $w = \{221\}$, much smaller than o , but giving good reflexes; $\omega = \{122\}$, very narrow, but exactly measurable; $b = \{010\}$, very narrow.

<i>Angles :</i>	<i>Observed :</i>	<i>Calculated :</i>
$a:r = (100):(102) =^* 69\ 52'$		—
$a:o = (100):(111) =^* 59\ 4$		—
$r:r = (102):(\bar{1}02) = 40\ 16$		40°16'
$o\ \omega = (111):(122) = 14\ 6$		14 15
$\omega\ \omega = (122):(\bar{1}22) = 33\ 37$		33 22
$a:w = (100):(221) = 49\ 40$		49 41½'
$w.t = (221):(121) = 17\ 5$		17 19½'
$a:t = (100):(121) = 66\ 58$		67 1
$a.p = (100):(120) = 62\ 40$		62 31½'
$a:m = (100):(110) = 43\ 50$		43 52½'
$m:m = (100):(\bar{1}10) = 92\ 20$		92 15
$m.p = (110):(120) = 18\ 50$		18 39
$m:b = (110):(010) = 46\ 10$		46 7½'
$o:r = (111):(102) = 33\ 4$		33 6

No distinct cleavability.

The crystals are noticeably dichroitic: on {100} yellow-green for vibrations parallel to the *c*-axis, and pale green for those perpendicular to the former. The plane of the optical axes is {001}, with the *a*-axis as first bisectrix of positive character. The apparent axial angle is very small.

THALLO-MALONATE.



Crystallised from water, the salt is deposited in very big, transparent crystals; they are *anhydrous* (79.93% *Tl*; calc: 80%). The compound is very soluble, and crystallisation starts only in highly supersaturated solutions.

Monoclinic-prismatic.

$$a:b:c = 0,5707:1:1,0833:$$

$$\beta = 81^\circ 30\frac{1}{3}'$$

Forms observed: $c = \{001\}$, very lustrous; $b = \{010\}$, gives good reflexes; in the same way: $m = \{110\}$, and $o = \{111\}$; $s = \{\bar{1}01\}$, narrow and often badly measurable, $r = \{102\}$, not measurable, because the faces are either concave, or strongly curved. Besides the forms

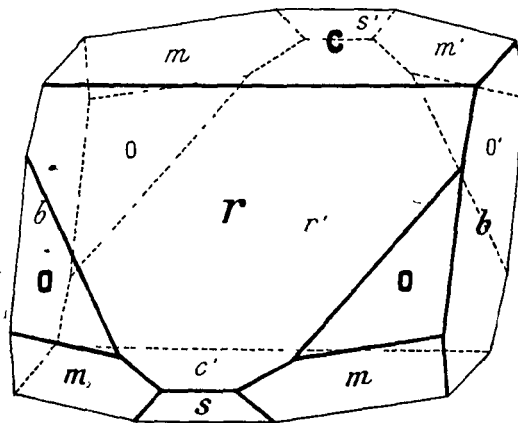


fig. 6

Anhydrous Thallo-Malonate.

reproduced in fig. 6, also plates parallel to {010} as a predominant form, are occasionally observed.

<i>Angles :</i>	<i>Observed : Calculated :</i>	
$c : m = (001) : (110) = *$	82°36 $\frac{1}{4}'$	—
$b : m = (010) : (110) = *$	60 33 $\frac{1}{2}$	—
$c : o = (001) : (111) = *$	59 21 $\frac{3}{4}$	—
$m : m = (110) : (\bar{1}\bar{1}0) =$	58 53	58°53'
$o : o = (111) : (\bar{1}\bar{1}1) =$	50 28	50 29
$b : o = (010) : (111) =$	64 46	54 45 $\frac{1}{2}$
$o : m = (111) : (110) =$	23 14 $\frac{1}{2}$	23 14 $\frac{1}{2}$
$m : s = (110) : (10\bar{1}) =$	40 49	40 42
$c : s = (001) : (\bar{1}01) =$	69 1	69 1 $\frac{1}{2}$

Very perfectly cleavable parallel to {001}.

According to HAUSHOFER ¹⁾ the corresponding *potassium*-salt crystallises with 1 H₂O, and is also *monoclinic*, but without distinct form-analogy with the *thallo*-salt here described. ($a : b : c = 1,4945 : 1 : 0,9174$; $\beta = 61^{\circ}15'$).

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¹⁾ K HAUSHOFER, Zeits. f. Kryst. u. Miner 6. 120 (1881).