

bromic acid molecules. In the case of alkyl substitutions, this equilibrium of forces is disturbed so that molecular combination can take place.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

### SALTS OF HELIANTHINE.

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From recent studies by one of us with methyl orange<sup>1</sup> and with other colored solutes,<sup>2</sup> the conclusion was drawn that color changes in solutions are largely or wholly independent of ionic<sup>3</sup> concentrations. An hypothesis, interpreting such color changes and embracing the following propositions,<sup>4</sup> was indicated:

(1) The colored solute forms *additive compounds* with acids, with bases, or with "indifferent" solvents.

(2) Solutions of such additive compounds are more or less transformed by the solvent, yielding either simple *chromoisomeric equilibria* or polychromic equilibria.

(3) The *intrinsic susceptibility* of the additive compound to the transforming influence of the solvent is the important factor of color changes in solutions.

(4) Heat<sup>5</sup> and probably other physical conditions have secondary influences on color changes.

This paper will concern itself largely with the first proposition—that the colored solute forms additive compounds. It will be shown that helianthine forms salts with great ease and that all of these salts can be interpreted as additive compounds.

Prior to this only salts of sodium, ammonium, pyridine,<sup>6</sup> and hydrochloric acid<sup>7</sup> have been described. This paucity of described salts is remarkable, when it is observed that helianthine forms salts with the readiness of a strong acid, uniting with all classes of bases whether organic or inorganic.

Owing to its amphoteric nature, helianthine also forms salts with acids, but it was found that these salts cannot be prepared pure<sup>7</sup> in aqueous solutions. However, if the isomerizing influence of water is avoided, that is, if anhydrous conditions are observed, violet-red salts, compounded

<sup>1</sup> THIS JOURNAL, 39, 1348, 1377 (1917).

<sup>2</sup> *Ibid.*, 36, 846 (1914); 39, 1338, 1381, 1392, 1399 (1917).

<sup>3</sup> *Ibid.*, 39, 1357, 1390, 1396 (1917).

<sup>4</sup> *Ibid.*, 39, 1376, 1380, 1403 (1917).

<sup>5</sup> *Ibid.*, 36, 845 (1914); 39, 1374, 1391 (1917).

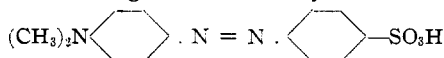
<sup>6</sup> Hantzsch, *Ber.*, 46, 1538 (1913).

<sup>7</sup> Hantzsch, *Ibid.*, 41, 1192 (1908).

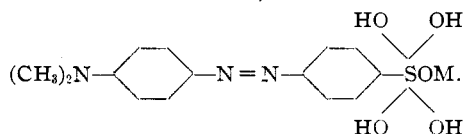
of so weak acids as phenol, the cresols, etc., can be prepared with ease. These salts also were found to be additive compounds.

Salts of helianthine, prepared in aqueous solutions with inorganic bases always contain water of crystallization, and always two molecules of water to one molecule of helianthine. In other words, such salts of helianthine always possess the following forms:  $C_{14}H_{14}N_3SO_3 \cdot M \cdot 2H_2O$ ;  $(C_{14}H_{14}N_3SO_3)_2 \cdot M \cdot 4H_2O$ ;  $(C_{14}H_{14}N_3SO_3)_3 \cdot M \cdot 6H_2O$ . From these types it is observed that helianthine always unites with all of the base, plus one or more molecules of water.

If we assume the following structure for yellow helianthine



it is easy to understand how *two molecules of water* are always present with each molecule of the helianthine, as showed in the formula



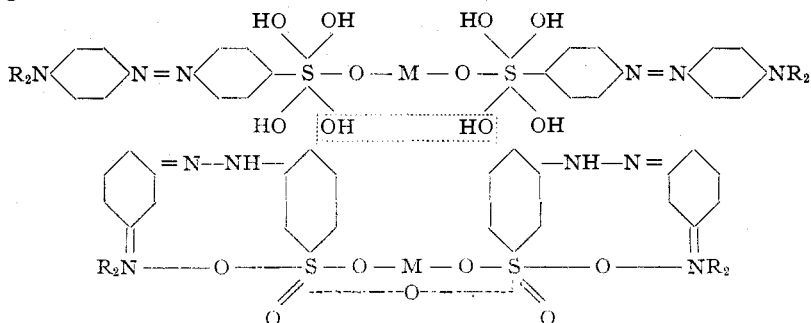
Interesting facts are brought out in connection with the color of helianthine salts.

First, helianthine salts compounded of ammonia or of volatile organic bases when heated give free helianthine. This was observed by Hantzsch with the pyridine salt.

Second, those containing the colored ions  $Cr^{+++}$ ,  $Cu^{++}$ ,  $Co^{++}$ ,  $Ni^{++}$ ,  $Fe^{++}$  and  $Fe^{+++}$  give no evidence of the presence of these ions if they are judged only by their color. All of these helianthine salts are practically identical in color and this color is almost uniformly that of methyl orange (sodium helianthate).

Third, when dehydrated, all helianthine salts containing the bivalent and trivalent metals, but not the monovalent elements, tend to form the color of helianthine itself.

This color transformation is satisfactorily accounted for by the following indicated dehydrations and isomerizations:



That is, dehydration between hydroxyls on two different sulfonic acid groups leaves *one* or *three* hydroxyls on each sulfonic acid group; then dehydrating and isomerizing give the quinoid form.

Salts of organic bases, prepared under anhydrous conditions, contain, of course, no water of crystallization, but these salts are always additive compounds of the type  $C_{14}H_{14}N_3SO_3H$ .Base.

From the foregoing and the data given below, the conclusion is drawn that *helianthine salts are always additive compounds*.

#### Methods of Preparation of Helianthine Salts.

Different methods were employed by us for the preparation of helianthine salts; some salts were best prepared by one method and other salts by another method. In all cases the isomerizing influence of heat and of water was recognized and, as far as possible, was avoided. Since typical salts of helianthine with bases are yellow, while helianthine itself and its salts with acids are violet-red, compounds of intermediate colors were assumed to be mixtures containing traces of free helianthine. The analyses usually proved this assumption to be true.

The following 4 methods yielded helianthine salts compounded with bases.

I. Helianthine and a water solution containing the free base were heated at about  $80^\circ$  or were boiled for some time. After filtering and cooling, crystals of the salt separated. When the salts were partially or completely decomposed by hot water, the lower temperature was maintained. If the precipitated salts contained a trace of free helianthine, such trace was indicated by the color of the salt or by the presence of mixed crystals. Proof of the character of such mixtures was obtained by analysis. This method yielded most of the contributed salts of inorganic bases.

II. When equimolecular quantities of methyl orange and a salt of some organic base were brought together in water, the less soluble new helianthine salt precipitated. After filtering and washing, dissolving in hot water and filtering, this helianthine salt separated as well-defined crystals. The color of the salt was usually indicative of its purity. This method gave good results with the sulfates of alkaloids, with a few other organic bases and with ferrous sulfate.

III. Helianthine was added to an excess of the pure liquid base<sup>1</sup> and was shaken or was heated until the salt was formed. The precipitates were filtered off and dried on clay plates or washed with anhydrous ether to remove the excess of the free base. A variation of this method involved the addition of anhydrous ether to a solution of helianthine in an

<sup>1</sup> Hantzsch employed this method for the preparation of pyridine helianthate, *Ber.*, 46, 1538 (1913).

excess of the base. Salts of aniline, pyridine, quinoline and the toluidines were satisfactory prepared by this method.

IV. Pure helianthine was treated with an excess of the base dissolved in absolute ether. Violet-red helianthine was slowly replaced by its brilliant orange salts. In this manner, in the course of number of weeks' standing and shaking, piperidine helianthate was prepared pure.

The following method yielded helianthine salts compounded with acids. Pure helianthine was dissolved in an excess of warm acidic solvents capable of uniting chemically with it, such as phenol, the cresols, etc. On adding absolute ether to the cooled solution, the salt precipitated and the excess of the acidic solvent was washed out with ether.

### Metallic Salts of Helianthine.

Aluminium helianthate.—Golden rhombic plates.

Calc. for  $(C_{14}H_{14}N_3SO_3)_3Al.6H_2O$ : Al, 2.59;  $H_2O$ , 10.32. Found: Al, 2.78;  $H_2O$ , 10.29.

Ammonium helianthate.<sup>1</sup>—Large gold-red rhombic plates.

Calc. for  $C_{14}H_{14}N_3SO_3.NH_3$ : S, 9.98. Found: S, 9.90;  $H_2O$ , 0.2.

Barium helianthate.—Gold-brown rhombic plates.

Calc. for  $(C_{14}H_{14}N_3SO_3)_2Ba.4H_2O$ : Ba, 16.79;  $H_2O$ , 8.81. Found: Ba, 16.73, 16.54, 16.76;  $H_2O$ , 10.76.

Cadium helianthate.—Gold-red rhombic plates.

Calc. for  $(C_{14}H_{14}SO_3)_2Cd.4H_2O$ : Cd, 14.18;  $H_2O$ , 9.09. Found: Cd, 14.64;  $H_2O$ , 8.41.

Calcium helianthate.—An orange mixture of long needles and rhombic plates.

Calc. for  $(C_{14}H_{14}N_3SO_3)_2Ca.4H_2O$ : Ca, 5.56;  $H_2O$ , 10.00. Found: Ca, 5.33, 5.34;  $H_2O$ , 9.63, and 9.88.

Chromium helianthate.—Gold-brown rhombic plates.

Calc. for  $(C_{14}H_{14}N_3SO_3)_3Cr.6H_2O$ : Cr, 4.85;  $H_2O$ , 10.08. Found: Cr, 4.74;  $H_2O$ , 10.19.

Cobalt helianthate.—Gold-red hexagonal and rhombic plates.

Calc. for  $(C_{14}H_{14}N_3SO_3)_2Co.4H_2O$ : Co, 7.95;  $H_2O$ , 9.99. Found: Co, 7.83;  $H_2O$ , 9.88.

Copper helianthate.—Light gold-brown rhombic plates.

Calc. for  $(C_{14}H_{14}N_3SO_3)_2Cu.4H_2O$ : Cu, 8.54;  $H_2O$ , 9.46. Found: Cu, 8.72;  $H_2O$ , 9.15.

Ferrous helianthate.—Gold-brown rhombic plates.

Calc. for  $(C_{14}H_{14}N_3SO_3)_2Fe.4H_2O$ : Fe, 7.58;  $H_2O$ , 9.79. Found: Fe, 7.68;  $H_2O$ , 9.22.

Ferric helianthate.—Red-gold irregular and rhombic plates.

<sup>1</sup> Though given in the literature, the composition of the ammonium salt is not described.

Calc. for  $(C_{14}H_{14}N_3SO_3)_2Fe \cdot 6H_2O$ : Fe, 5.19;  $H_2O$ , 10.04. Found: Fe, 5.18, 5.21;  $H_2O$ , 10.83.

Lead helianthate.—Brown masses and irregular plates.

Calc. for  $(C_{14}H_{14}N_3SO_3)_2Pb \cdot 4H_2O$ : Pb, 23.33;  $H_2O$ , 8.12. Found: Pb, 23.92;  $H_2O$ , 7.99.

Magnesium helianthate.—Red-gold, hexagonal and rhombic plates.

Calc. for  $(C_{14}H_{14}N_3SO_3)_2Mg \cdot 4H_2O$ : Mg, 3.45,  $H_2O$ , 10.22. Found: Mg, 3.44;  $H_2O$ , 10.17.

Manganese helianthate.—Large, light red-gold, irregular and rhombic plates.

Calc. for  $(C_{14}H_{14}N_3SO_3)_2Mn \cdot 4H_2O$ : Mn, 7.48;  $H_2O$ , 9.80. Found: Mn, 7.34, 7.50;  $H_2O$ , 9.18, 11.32.

Silver helianthate.—Dull brown-red needles.

Calc. for  $C_{14}H_{14}N_3SO_3Ag \cdot 2H_2O$ : Ag, 24.06;  $H_2O$ , 8.04. Found: Ag, 23.98;  $H_2O$ , 8.24.

Sodium helianthate.—A stock sample contained only a little water of crystallization.

Calc. for  $C_{14}H_{14}N_3SO_3Na \cdot 2H_2O$ :  $H_2O$ , 9.92. Found:  $H_2O$ , 1.41.

Nickel helianthate.—Light gold-red hexagonal and rhombic plates.

Calc. for  $(C_{14}H_{14}N_3SO_3)_2Ni \cdot 4H_2O$ : Ni, 7.94;  $H_2O$ , 9.75. Found: Ni, 7.97;  $H_2O$ , 9.66.

TABLE I.—SOLUBILITIES AND MELTING POINTS.

Salt of:	Composition.	Solubility 1000 cc. $H_2O$ .		Heated.		Melts.	Color. Heated 120°.
		Salt.	Hel.	Colors or decom- poses.	Does not melt.		
Al.....	$Hel_3Al \cdot 6H_2O$	0.092	0.08	200°	280°		brown-gold
$NH_4$ .....	$Hel \cdot NH_3 \cdot 2H_2O$	.....	6.00	.....	.....	225°	
Ba.....	$Hel_2Ba \cdot 4H_2O$	0.201	0.15	280°	280°		brown
Cd.....	$Hel_2Cd \cdot 4H_2O$	.....	0.07	296°	296°		bronze-brown
Ca.....	$Hel_2Ca \cdot 4H_2O$	0.177	0.15	290°	290°		gold-brown
Cr.....	$Hel_3Cr \cdot 6H_2O$	0.176	0.15	270°	270°		bronze-brown
Co.....	$Hel_2Co \cdot 4H_2O$	0.036	0.03	280°	280°		purple-brown
Cu.....	$Hel_2Cu \cdot 4H_2O$	0.122	0.10	290°	300°		bronze-brown
$Fe''$ .....	$Hel_2Fe \cdot 4H_2O$	0.109	0.10	.....	.....	209°	purple-brown
$Fe'''$ .....	$Hel_2Fe \cdot 6H_2O$	0.118	0.10	280°	300°		gold-bronze
Pb.....	$Hel_2Pb \cdot 4H_2O$	0.111	0.08	.....	300°		
Mg.....	$Hel_2Mg \cdot 4H_2O$	0.035	0.03	267°	280°		gold-brown
Mn.....	$Hel_2Mn \cdot 4H_2O$	0.060	0.05	270°	280°		brown
Ni.....	$Hel_2Ni \cdot 4H_2O$	0.072	0.06	235°	275°		bronze-brown
K.....	$Hel \cdot K \cdot 2H_2O$	4.368	3.50	280°	.....	300°	
Ag.....	$Hel \cdot Ag \cdot 2H_2O$	0.292	0.20	200°	230°		black-brown
Na.....	$Hel \cdot Na \cdot 2H_2O$	.....	.....	.....	.....	224°	
Sr.....	$Hel_2Sr \cdot 4H_2O$	0.126	0.10	.....	300°		orange
U.....	$Hel_2U \cdot 4H_2O$	0.300	0.25	250°	280°		brown
Zn.....	$Hel_2Zn \cdot 4H_2O$	0.098	0.08	.....	.....	241°	bronze-brown

Potassium helianthate.—This salt formed a blood-red, ropey colloidal solution that filtered with great difficulty. The crystals were orange hexagonal plates.

Calc. for  $C_{14}H_{14}N_8SO_3K \cdot 2H_2O$ : K, 10.31;  $H_2O$ , 9.69. Found: K, 10.22;  $H_2O$ , 2.25.

Strontium helianthate.—Brilliant orange rhombic plates and needles.

Calc. for  $(C_{14}H_{14}N_8SO_3)_2Sr \cdot 4H_2O$ : Sr, 11.41;  $H_2O$ , 9.38. Found: Sr, 11.25 and 11.44;  $H_2O$ , 9.01 and 9.24.

Uranium helianthate.—Orange-red rhombic plates.

Calc. for  $(C_{14}H_{14}N_8SO_3)_2U \cdot 4H_2O$ : U, 25.93;  $H_2O$ , 7.83. Found: U, 27.04;  $H_2O$ , 8.84.

Zinc helianthate.—Gold-brown rhombic plates.

Calc. for  $(C_{14}H_{14}N_8SO_3)_2Zn \cdot 4H_2O$ : Zn, 8.98;  $H_2O$ , 9.90. Found: Zn, 8.99;  $H_2O$ , 9.67.

### Salts of Organic Bases.

Aniline helianthate.—Gold-orange prismatic flakes and needles.

Calc. for  $C_{14}H_{15}N_8SO_3 \cdot C_6H_7N$ : S, 8.05. Found: S, 7.68.

Benzidine helianthate.—Gold-brown irregular and rectangular plates and prismatic needles.

Brucine helianthate.—Orange prismatic needles.

Calc. for  $C_{23}H_{36}N_2O_4 \cdot C_{14}H_{15}N_8SO_3 \cdot H_2O$ : S, 4.47;  $H_2O$ , 2.52. Found: S, 4.74;  $H_2O$ , 1.69.

Cinchonidine helianthate.—Light yellow prismatic needles and irregular plates.

Calc. for  $C_{19}H_{22}N_2O \cdot C_{14}H_{15}N_8SO_3$ : S, 5.35. Found: S, 5.74, 5.74.

Dimethylaniline helianthate.—Equimolecular quantities of helianthine and dimethylaniline gave no yellow color or apparent chemical change on standing for one month. On adding water and shaking, yellow crystals were formed immediately. After recrystallizing from hot water, long needles and hexagonal plates were obtained.

Methylaniline helianthate.—Thin, gold-brown prisms and rhombic and hexagonal plates.

Morphine helianthate.—Bright orange irregular plates and sheaves, and wart-like masses of prisms.

Calc. for  $C_{14}H_{15}N_8SO_3 \cdot C_{17}H_{19}NO_3$ : S, 5.43. Found: S, 5.40, 5.60.

$\alpha$ -Naphthylamine helianthate.—Dull-brown needles.

Calc. for  $C_{14}H_{15}N_8SO_3 \cdot C_{10}H_9N$ :  $C_{14}H_{15}N_8SO_3$ , 68.01. Found:  $C_{14}H_{15}N_8SO_3$ , 68.00.

$\beta$ -Naphthylamine helianthate.—Brown-yellow thin irregular plates.

Phenylhydrazine helianthate.—Orange needles and rectangular plates.

Calc. for  $C_{14}H_{15}N_8SO_3 \cdot C_6H_5N_2$ : S, 7.73. Found: S, 7.85.

$\alpha$ -Picoline helianthate.—Dark brown-red rectangular and octagonal plates.

Piperidine helianthate.—When an ether solution of piperidine was

treated with helianthine, the violet-red color of the latter, during a number of weeks, was gradually replaced by bright orange, coarse rectangular crystals of the salt. From hot water, octagonal and irregular plates were obtained.

Calc. for  $C_{14}H_{15}N_3SO_3 \cdot C_5H_9N$ : S, 8.22. Found: S, 8.19.

Quinine helianthate.—Orange amorphous masses.

Calc. for  $C_{14}H_{15}N_3SO_3 \cdot C_{20}H_{24}N_2O_2$ : S, 5.09. Found: S, 5.13.

Quinoline helianthate.—Orange-red prisms and octagonal plates.

Calc. for  $C_{14}H_{15}N_3SO_3 \cdot C_9H_7N$ : S, 7.38. Found: S, 7.42.

Strychnine helianthate.—Gold-orange prisms and rectangular and irregular plates.

Calc. for  $C_{14}H_{15}N_3SO_3 \cdot C_{21}H_{22}N_2$ : S, 5.02. Found: S, 5.43, 5.25;  $H_2O$ , 0.8.

*o*-Toluidine helianthate.—Orange-red prismatic needles.

Calc. for  $C_{14}H_{15}N_3SO_3 \cdot C_7H_9N$ : S, 7.77. Found: S, 8.38.

*m*-Toluidine helianthate.—Gold-yellow needles and irregular plates.

Helianthine phenolate.—Dark purple prisms.

Calc. for  $C_{14}H_{15}N_3SO_3 \cdot C_6H_5OH$ : S, 8.03. Found: S, 7.54.

TABLE II.—SOLUBILITIES AND MELTING POINTS.

Salt of:	Solubility 1000 cc. $H_2O$ .		Heated.		Color when heated, 130°.
	Salt.	Hel.	Colors or decomposes.	Melts.	
Aniline.....	0.262	0.20		211°	helianthine
Benzidine.....	0.082	0.05	194°	198°	
Brucine.....	0.245	0.11		224°	
Cinchonidine.....	0.196	0.10	146°	155°	orange
Dimethylaniline.....	0.700	0.50		...	helianthine
Methylaniline.....	0.541	0.40		167°	helianthine
Morphine.....	0.400	0.20		219°	
$\alpha$ -Naphthylamine....	0.132	0.09		211°	
$\beta$ -Naphthylamine....	0.103	0.07		209°	brown
Phenylhydrazine....	0.135	0.10		165°	black
$\alpha$ -Picoline.....	65.300	50.00	157°	180°	helianthine
Piperidine.....	....	....		223°	orange-brown
Quinine.....	0.185	0.09		158°	.....
Quinoline.....	0.854	0.60		194°	helianthine
Strychnine.....	0.481	0.23		254°	
<i>m</i> -Toluidine.....	0.162	0.12		202°	helianthine
<i>o</i> -Toluidine.....	0.270	0.20		203°	brown
Helianthine.....	....	....		234°	
Phenol.....	0.157	0.12		200°	helianthine

### Special Observations.

1. The contents of water in the above salts were determined by heating at 100–130° for one or more hours; heating to constant weight was not often possible, for the reason that the salts undergo secondary decomposi-

tion. This was especially marked in the case of the barium salt; tests for methyl alcohol and for dimethylamine gave negative results.

2. The solubility of pure helianthine in water is 0.02 g. per liter; the solubilities of all of its salts are greater than this. This can indicate that its salts are not completely hydrolyzed. Since solutions of its salts are partially or largely hydrolyzed, as shown in previous studies,<sup>1</sup> and these colors are not parallel to these solubilities, it may be concluded that the chromoisomerizations of helianthine are largely dependent upon the stabilities of the salts toward water.

3. No obvious conclusion can as yet be drawn from studies of the melting points of helianthine salts.

The formation of salts by other indicators will be studied.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR  
MEDICAL RESEARCH.]

## ON NITRO- AND AMINOARYL ARSONIC ACIDS.

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In the course of studies on the synthesis of organic arsenic compounds for therapeutic purposes it was found necessary to prepare a number of aminoaryl arsonic acids. It was therefore of importance to find methods which would furnish these substances in amounts sufficient for synthetic work. Of the methods available the application of the Béchamp synthesis, first used for the preparation of arsanilic acid, has rendered directly accessible only a limited number, mainly *p*-aminoaryl arsonic acids. In order to obtain *o*- and *m*-amino arsonic acids it has usually been necessary to employ indirect methods.

The most useful of these involves the preparation of the corresponding nitro compound, which is then reduced to the desired amino acid. In case the nitro acid is synthesized by direct nitration of an aryl arsonic acid, only the *m*-nitro compound can be obtained. More general, however, is Bart's excellent method<sup>2</sup> in which a diazo or isodiazo group is replaced by the arsonic acid residue. This reaction has greatly increased the availability of aromatic arsonic acids, many of which have been unobtainable by other means. Among the wide variety of examples given by Bart are enough to demonstrate the value of the method for the preparation of the nitro arsonic acids and his procedure was, in fact, used later in a few instances by others<sup>3</sup> for the same purpose.

In the present work we have found the method to be of exceptional

<sup>1</sup> THIS JOURNAL, **39**, 1373 (1917). See especially the potassium salt.

<sup>2</sup> Bart, D. R. P. 250,264.

<sup>3</sup> D. R. P. 266,944, 267,307; Bauer, *Ber.*, **48**, 1582 (1915).