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Abstract

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PREPARATION, STRUCTURE, AND COLOR OF SALTS OF VIOLURIC AND 2-THIOVIOLURIC ACIDS

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The description of the preparation and structure of violurates given in the works of Hantzsch, Isherwood, and Isayacs (1) is presented in the most general form, and the salts themselves have not been studied sufficiently systematically. The preparation and properties of salts of 2-thiovioluric acid are likewise described only very briefly in the work of Lal and Dutt (2). At the same time, study of the structure of these salts and of the relationship between their structure and color is of very great interest, since the different coloration of salts of violuric acid gave Hantzsch (3) occasion to introduce the concept of phenomena of a special kind of isomerism—chromoisomerism and pantochromism. These phenomena have still not been given a satisfactory explanation, and they are mentioned as cases of a special isomerism (4), probably because a sufficiently detailed and systematic study of the preparation and structure of the indicated salts has not yet been undertaken. Therefore, in the present work we have studied in detail various methods leading to the preparation of violurates and 2-thiovioluates of different structure.

For the preparation of potassium and sodium violurates and 2-thioviolurates, we developed a known route of direct nitrosation of barbituric and 2-thiobarbituric acids by the action of nitrites in aqueous solutions (5). In addition, potassium and sodium violurates and 2-thioviolurates were obtained by us by the action of alkalis on the corresponding acids in aqueous and aqueous-alcoholic solutions, and also by the action of violuric and 2-thiovioluric acids on carbonates and bicarbonates of alkali metals. Further, potassium and sodium violurates and 2-thioviolurates were obtained by the action of alcoholic solutions of violuric and 2-thiovioluric acids on alcoholic solutions of potassium and sodium alcoholates.

We have established that the use of the above-mentioned methods makes it possible to obtain violurates and 2-thioviolurates of different structure. Thus, when nitrites in aqueous solutions act on barbituric and 2-thiobarbituric acids, monosubstituted salts are obtained, and upon addition of an equimolecular amount of violuric and, correspondingly, 2-thiovioluric acid, acid salts are formed containing one molecule of acid per one molecule of monosubstituted salt. In this case the monosubstituted salts obtained by the indicated method contain two molecules of water of crystallization, while the acid salts contain four molecules of water.

When caustic alkalis in equimolecular amounts act on violuric and 2-thiovioluric acids in aqueous solutions, monosubstituted salts with the same content of water of crystallization are obtained, while with an excess of alkali, disubstituted salts containing one molecule of water of crystallization are obtained. If the preparation of salts by this method is carried out in aqueous-alcoholic solutions, the same mono- and disubstituted salts are formed, but containing only half the amount of water of crystallization. In addition, in aqueous-alcoholic solutions, by the action of corresponding excesses of caustic alkalis, trisubstituted salts of violuric and 2-thiovioluric acids can also be obtained.

It was further established that such trisubstituted salts are especially conveniently obtained by the action of sodium and potassium alcoholates on violuric and 2-thiovioluric acids in alcoholic solutions. By the same method one can obtain mono- and disubstituted salts that do not contain water of crystallization. It was also established that, in the interaction of violuric and 2-thiovioluric acids with carbonates and bicarbonates in aqueous solutions, acid and monosubstituted salts can be obtained, containing, respectively, four and two molecules of water in the composition of the crystalline hydrate.

All the methods described make it possible to obtain potassium and sodium salts of violuric and 2-thiovioluric acids of various degrees of substitution, including the previously undescribed trisubstituted salts, which indicates the presence in violuric and 2-thiovioluric acids of three hydrogen atoms capable of salt formation. Table 1 gives the results of analyses of various sodium and potassium violurates and 2-thiovioluric acids, dehydrated at 110°.

Table 1

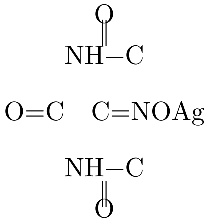
Gross formula	Metal content, % calculated	Metal content, % found	Gross formula	Metal content, % calculated	Metal content, % found
$C_4H_3O_4N_3 \cdot C_4H_2O_4N_3Na$	6.84	6.87	$C_4H_3O_4N_3 \cdot C_4H_2O_4N_3K$	11.10	11.31
$C_4H_2O_4N_3Na$	12.80	12.62	$C_4H_2O_4N_3K$	20.00	19.65
$C_4HO_4N_3Na_2$	22.90	22.40	$C_4HO_4N_3K_2$	33.50	33.20
$C_4O_4N_3Na_3$	30.95	30.71	$C_4O_4N_3K_3$	43.15	42.94
$C_4H_2O_3N_3SNa \cdot C_4H_3O_3N_3S$	6.25	6.08	$C_4H_2O_3N_3SK \cdot C_4H_3O_3N_3S$	10.15	9.97
$C_4H_2O_3N_3SNa$	11.80	11.50	$C_4H_2O_3N_3SK$	18.15	18.23
$C_4HO_3N_3SNa_2$	21.20	20.97	$C_4HO_3N_3SK_2$	31.30	31.11
$C_4O_3N_3SNa_3$	28.90	28.72	$C_4O_3N_3SK_3$	40.70	40.58

Most of the indicated methods are also applicable for obtaining violurates and 2-thioviolurates of alkaline-earth metals. In addition, for obtaining these same salts of barium, calcium, and magnesium, and especially for obtaining violurates and 2-thiovioIurates of heavy metals, we employed the reaction between potassium or sodium violurates in aqueous and aqueous-alcoholic solution and soluble inorganic salts of heavy metals. In this way, on interaction with silver nitrate, silver violurate and 2-thioviolurate are obtained; on interaction with zinc sulfate, the corresponding zinc salts; with cobalt chloride, the corresponding cobalt salts, etc.

However, this method of obtaining salts of heavy metals leads in certain cases to new derivatives of violuric and 2-thiovioluric acids. Thus, for example, upon interaction of equimolecular amounts of mercuric chloride and potassium or sodium violurate in aqueous solution, a weakly colored precipitate of mercurivioluric acid is obtained: $C_4HO_4N_3Hg$; calculated Hg 55.8%; found Hg 56.5%, identical with that described in Old' s work ([6]). This acid is capable of giving only a monosubstituted potassium salt, which indicates the following structure for it:

[structural formula: a violuric-acid ring with Hg in the ring and side group C=NOH] $\rightleftharpoons$ [tautomeric structu

whereas the violurates of heavy metals should be assigned the structure:



$$\begin{array}{c} O \\ \| \\ NH-C \\ O=C \quad C=NOAg \\ NH-C \\ \| \\ O \end{array}$$

Table 2 gives the results of analyses of some of the obtained violurates of alkaline-earth and heavy metals after their dehydration at 110°.

On the basis of the various methods developed, it proved possible to obtain salts of violuric and 2-thiovioluric acids with different degrees of substitution and with different contents of water of crystallization. It was established that the color of the salts in the solid state depends both on the degree of substitution and on the content of water of crystallization.

Table 2

Gross formula	Metal content, %, calculated	Metal content, %, found	Gross formula	Metal content, %, calculated	Metal content, %, found
$(C_4H_2O_4N_3)_2Mg$	7.14	6.92	$(C_4H_2O_4N_3)_2Co$	15.90	15.20

Gross formula	Metal content, %, calculated	Metal content, %, found	Gross formula	Metal content, %, calculated	Metal content, %, found
$(C_4H_2O_4N_3)_2Mg\cdot \frac{1}{2}C_4H_3O_4N_3$	5.80	5.21	$(C_4H_2O_4N_3)_2Cu$	17.00	16.25
$(C_4H_2O_4N_3)_2Ca$	11.35	11.40	$(C_4H_2O_4N_3)_3Al$	6.35	6.18
$(C_4H_2O_4N_3)_2Ca\cdot \frac{1}{2}C_4H_3O_4N_3$	9.27	9.24	$(C_4H_2O_4N_3)_3Pb$	39.50	38.50
$(C_4H_2O_4N_3)_2Ba$	30.50	30.90	$(C_4H_2O_4N_3)_2Zn$	17.25	16.87
$(C_4H_2O_4N_3)_2Ba\cdot \frac{1}{2}C_4H_3O_4N_3$	20.60	25.10			

The following comparison of the colors of monosubstituted sodium, potassium, and silver violurates gives an idea of the difference in colors caused by different contents of water of crystallization. The indicated colors of the solid salts change in accordance with changes in the content of water of crystallization (upon dehydration and recrystallization), and therefore the change in color in salts of one and the same metal and of the same substitution (Ganch' s pantochromism) is undoubtedly due to the influence of the water molecules participating in the formation of the crystal lattices of the indicated, differently colored salts.

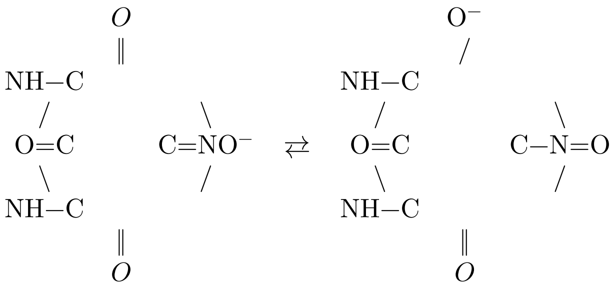
This is also confirmed by the fact that the various crystalline hydrates of the described potassium and sodium salts in aqueous solutions all give one and the same absorption spectrum.

Table 3

Gross formula	Color of crystals
$C_4H_2O_4N_3Na\cdot 2H_2O$	Dark red
$C_4H_2O_4N_3Na\cdot H_2O$	Bluish-pink
$C_4H_2O_4N_3Na$	Violet-red
$C_4H_2O_4N_3K\cdot 2H_2O$	Violet
$C_4H_2O_4N_3K$	Red
$C_4H_2O_4N_3Ag\cdot 3H_2O$	Grayish-blue
$C_4H_2O_4N_3Ag\cdot \frac{1}{2}H_2O$	Grayish-green
$C_4H_2O_4N_3Ag$	Greenish-brown

It was further established that violurates and 2-thiovioliurates of one and the same metal, but of different substitution, having different colors in the solid state, in aqueous solutions give practically the same or very close absorption maximum. For example, tri-, di-, and monopotassium and sodium violurates, acid potassium and sodium violurates, differently col-

dissociated in the solid state, give in aqueous solutions an absorption maximum between 525–535 mμ. At the same time, the absorption for solutions of these salts of one and the same concentration differs only in the intensity of absorption (at the maximum), which decreases as the substitution of the salt increases. From the observations made it follows that the difference in the coloration of salts of different metals and of different degrees of substitution (Hantzsch chromoisomerism) is probably due to the existence, in salts of violuric and 2-thiovioluric acids, of equilibrium desmotropic forms of the anions, for example, in the simplest case of monoviolurate:



(colorless) (colored)

The coloration of salts in the solid state changes depending on the state of such an equilibrium and on the presence of anions of a higher degree of ionization. This explanation is very close to that which was given by Lall and Datt (^{2}) for the coloration, in the simplest case, of monosubstituted 2-thioviolurates.

Upon dissolving the salts in water, practically complete hydrolysis is observed for the second and third degrees of substitution, and therefore the absorption spectrum of their solutions depends on the presence of anions of the first degree of dissociation. This conclusion is confirmed by determination of pK' for the different degrees of dissociation of violuric and 2-thiovioluric acids.

As a result of our work, various methods of preparation were studied and it was established that, depending on the method used, violurates and 2-thioviolurates of different degrees of substitution are formed (including the previously undescribed trisubstituted salts), with different contents of water of crystallization. The coloration of violurates and 2-thioviolurates in the solid state depends on the degree of substitution of the salt, and also on the content of water of crystallization. An explanation is proposed for Hantzsch pantochromism as a phenomenon caused by the presence of hydration water participating in the formation of the crystal lattice of crystal hydrates of one and the same salt. The difference in the coloration of different salts, including salts of different degrees of substitution (Hantzsch chromoisomerism), is explained by the presence of desmotropism of colored and colorless forms of the anions.

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Note: Figure translations are in progress. See original paper for figures.

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