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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY
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LVI.—SALTS OF DINITRO- α -NAPHTHOL WITH VARIOUS METALLIC BASES.

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THE preparation and study of the following compounds were undertaken with the view of ascertaining whether in addition to the few salts of dinitro- α -naphthol thus far known, there might not be other combinations with metallic bases possessing a greater degree of solubility than the commercial calcium salt (Manchester yellow, Martius Gelb) now so largely used, or more especially showing distinct variations in the color imparted to animal and vegetable fibers. The results showed that in the latter respect the metal present is practically without influence on the tinctorial properties of dinitro- α -naphthol, the tint yielded in each individual case being essentially that imparted by the free phenol or by its calcium salt.

The salts of dinitro- α -naphthol thus far examined and analyzed are those with sodium,¹ potassium,¹ ammonium,² barium,³ strontium,² calcium,³ and silver.¹

The dinitro- α -naphthol used was prepared by precipitating

¹ Hübner: *Ann. Chem. (Liebig)*, 208, 332.

² Martius: *J. prakt. Chem.*, 102, 443.

³ Darmstädter and Wichelhaus: *Ann. Chem. (Liebig)*, 157, 201; Liebermann: *Ann. Chem. (Liebig)*, 183, 249; Martius: *Vide supra*.

the concentrated aqueous solution of the commercial calcium salt by dilute sulphuric acid, washing the precipitate thoroughly with water, drying, and extracting the liberated phenol by boiling alcohol. The finely crystallized product thus obtained possessed the melting-point of 138° .

LITHIUM DINITRO- α -NAPHTHOLATE, $C_{10}H_7(NO_2)_2OLi$.

This salt is obtained in solution by boiling an excess of dinitro- α -naphthol with an aqueous solution of lithium carbonate and filtering. On evaporation it is deposited in the form of a brilliant crimson powder, which is amorphous and anhydrous. The salt, on being heated to 295° , explodes before melting. It is soluble in ninety-six parts of water at 19° , in fourteen parts of boiling water, in fifty parts of cold alcohol, in fifteen parts of boiling alcohol, and in 300 parts of ether. It is insoluble in carbon disulphide and in benzene. The temperature of solutions, unless otherwise noted, is $18^{\circ}C$.

The salt, dried between sheets of bibulous paper, lost no weight on heating to 105° . The analyses were made by adding concentrated sulphuric acid to weighed amounts in a platinum crucible, evaporating to dryness and ignition as lithium sulphate. Care is necessary to avoid spattering.

I. 0.246 gram of the dry salt gave 0.0535 gram lithium sulphate, equal to 0.0069 gram of lithium, or 2.80 per cent.

II. 0.256 gram gave 0.0535 gram lithium sulphate, equal to 0.0068 gram of lithium, or 2.88 per cent.

	Calculated for $C_{10}H_7N_2O_5Li$.	I.	Found.	II.
Lithium	2.87	2.80		2.88

MAGNESIUM DINITRO- α -NAPHTHOLATE, $[C_{10}H_7(NO_2)_2O]_2Mg$.

This salt is prepared by boiling in water a mixture of magnesium carbonate with an excess of the naphthol. It crystallizes slowly from the filtered solution in the form of reddish needles, grouped in rosettes. It is anhydrous, the salt dried between sheets of bibulous paper, losing no weight when heated to 105° . It is soluble in 792 parts of water at 20° , in 154 parts of boiling water, in 436 parts of cold alcohol, in 144 parts of boiling alcohol, and in 260 parts of ether. It is insoluble in benzene and carbon disulphide.

The first three analyses were made by igniting the substance in a platinum crucible, in which a smaller inverted crucible was wedged so as to prevent as much as possible mechanical loss by explosive decomposition, and weighed as magnesia.

In the fourth analysis the substance was strongly heated in a sealed tube. After cooling, the tube was opened, its contents were dissolved in dilute nitric acid, and the solution was evaporated to dryness, ignited, and weighed likewise as magnesia.

I. 0.035 gram of the salt dried at 105° gave 0.0025 gram magnesium oxide, equal to 0.0015 gram magnesium, or 4.28 per cent.

II. 0.1557 gram gave 0.0113 gram magnesium oxide, equal to 0.067 gram magnesium, or 4.35 per cent.

III. 0.1552 gram gave 0.012 gram magnesium oxide, equal to 0.0072 gram magnesium, or 4.64 per cent.

IV. 0.0623 gram gave 0.0039 gram magnesium oxide, equal to 0.0023 gram magnesium, or 3.77 per cent.

	Calculated for ($C_{10}H_8N_2O_8$) ₂ Mg.	I.	Found. II.	III.	IV.
Magnesium.....	4.87	4.28	4.35	4.64	4.77

ZINC DINITRO- α -NAPHTHOLATE, $[C_{10}H_8(NO_2)_2O]Zn$.

This is obtained by boiling together in water an excess of the naphthol with zinc carbonate. From a hot concentrated solution it crystallizes out in the form of handsome reddish-yellow needles, while more dilute solutions yield reddish crystals, possessing the shape of rhomboidal plates. In this respect the zinc salt resembles the calcium salt.¹

It is soluble in 960 parts of water at 20° , in 300 parts of boiling water, in 250 parts of cold alcohol, in 115 parts of boiling alcohol, and in 150 parts of ether. It is insoluble in benzene and carbon disulphide. The salt is anhydrous, crystals dried between sheets of bibulous paper losing no weight at 105° .

The explosive nature of the compound renders necessary in analysis the careful use of the two crucibles described above, small amounts being taken. Even with these precautions a small loss is unavoidable.

I. 0.123 gram of the salt dried at 105° gave 0.017 gram zinc oxide, equal to 0.0136 gram zinc, or 11.09 per cent.

¹ Liebermann: *Ann. Chem.* (Liebig), 183, 249.

II. 0.108 gram gave 0.016 gram zinc oxide, equal to 0.0128 gram zinc, or 11.89 per cent.

	Calculated for (C ₁₀ H ₅ N ₂ O ₅) ₂ Zn.	I.	Found.	II.
Zinc	12.22	11.09		11.89

COPPER DINITRO- α -NAPHTHOLATE, [C₁₀H₅(NO₂)₂O]Cu.

This salt is obtained by adding an excess of a concentrated solution of copper chloride to a cold aqueous solution of ammonium dinitro- α -naphthol. The chocolate-colored precipitate is washed with water until all traces of copper chloride are removed, and dried between sheets of bibulous paper. Thus prepared, it is an anhydrous, dark-brown, amorphous powder, the most insoluble of the salts of the naphthol thus far known.

It dissolves in 5,750 parts of water at 21°, in 2,165 parts of boiling water, in 1,007 parts of cold alcohol, in 954 parts of boiling alcohol, and in 2,615 parts of ether. It is insoluble in benzene and carbon disulphide.

The analyses were performed by gently heating the salt with concentrated nitric acid in a covered porcelain crucible, and finally igniting. As in the preceding cases, the explosive nature of the salt renders the utmost care necessary.

I. 0.2663 gram of the salt dried at 105° gave 0.036 gram cupric oxide, equal to 0.0287 gram copper, or 10.79 per cent.

II. 0.1665 gram gave 0.023 gram cupric oxide, equal to 0.0183 gram copper, or 11.03 per cent.

III. 0.3033 gram gave 0.0443 gram cupric oxide, equal to 0.0353 gram copper, or 11.67 per cent.

	Calculated for (C ₁₀ H ₅ N ₂ O ₅) ₂ Cu.	I.	Found.	II.	III.
Copper	11.97	10.79	11.03		11.67

SOLUBILITIES OF THE AMMONIUM AND CALCIUM SALTS.

No data existing on the solubilities of these two compounds, the following determinations were made :

Ammonium dinitro- α -naphtholate is soluble in 600 parts of water at 25°, in thirty-eight parts of boiling water, in 113 parts of cold alcohol, in 57 parts of boiling alcohol, and in 1,124 parts of ether.

Anhydrous calcium dinitro- α -naphtholate is soluble in 1,656

parts of water at 20°, in eighty-six parts of boiling water, in forty-seven parts of cold alcohol, in fifteen parts of hot alcohol, and in forty-five parts of ether.

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LVII. ON CERTAIN AMINE DERIVATIVES OF DINITRO- α -NAPHTHOL AND ITS CHLORINATION.

BY T. H. NORTON AND IRWIN J. SMITH.

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IN connection with a recent study of dinitro- α -naphthol derivatives,¹ the following salt of this phenol with various amines were prepared and analyzed. The dinitro- α -naphthol used was prepared from the commercial calcium salt by treatment with sulphuric acid and recrystallization from alcohol. It possessed the correct melting-point of 138°.²

TRIMETHYLAMINE-DINITRO- α -NAPHTHOLATE, $C_{10}H_7(NO_2)_2OH.N(CH_3)_3$.

This salt was prepared by boiling dinitro- α -naphthol with an excess of a thirty-three per cent. aqueous solution of trimethylamine. The product was crystallized from alcohol and obtained in the form of long, lustrous, red needles, which are anhydrous and melt at 190° (uncorr.). The salt is soluble in 909 parts of water at 18°, in fifteen parts at 100°, in 200 parts of cold alcohol, in 40 parts of boiling alcohol, and in 4,000 parts of ether. It is insoluble in carbon disulphide and in benzene. The temperature of solutions in all cases, when not otherwise noted, is 18° C.

Analysis: 0.2154 gram of the salt dried at 100° gave 0.0969 gram water or five per cent. of hydrogen, and 0.4193 gram carbon dioxide or 53.06 per cent. of carbon.

	Theory.	Found.
Carbon	53.24	53.06
Hydrogen	5.12	5.00

The yellow solutions of the salt resemble in tinctorial power those of dinitro- α -naphthol itself.

¹ Norton and Loewenstein: This Journal, 19, 923.

² Martius: *Ztschr. Chem.*, 1868, 80.