

**384.** *Metallic Derivatives of 2-Nitroso-5-methoxy- and of 3-Chloro-2-nitroso-5-methoxy-phenol.*

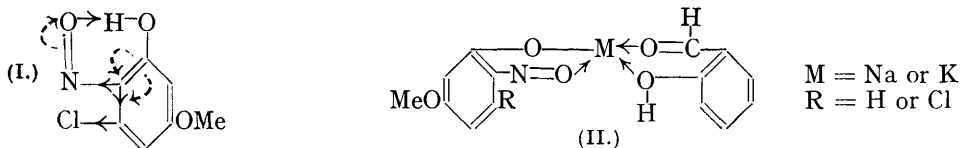
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2-NITROSO-5-METHOXYPHENOL apparently exists in the nitroso-form in benzene solution, since it always separates therefrom in green crystals, but it very readily changes into the quinoneoxime tautomeride, even on mere dissolution in alcohol, and the latter form appears to be of greater stability generally. This view is supported by properties such as the very slight volatility in steam and the moderate solubility in water. The 3-chloro-derivative, however, differs strikingly from the parent substance in being readily volatile in steam, from which it condenses in olive-green plates, and in always separating from alcohol, benzene, ether, and light petroleum in similar olive-green crystals, and so far no other coloured form has been obtained; further, its sparing solubility in water and ready solubility in benzene appear to indicate a high degree of chelation. The inductive ( $-I$ ) effect of the chlorine atom, therefore, which so materially improves the stability of 3-chloro-2-nitroso-5-methoxyphenol that it can be kept for months without deterioration, likewise prevents transition to the quinonoid form: the formula (I) appears to represent the facts.

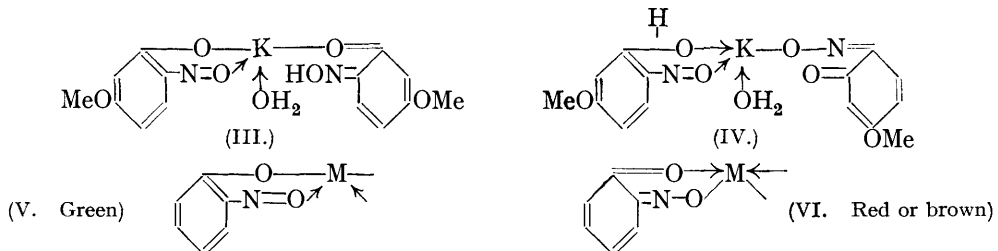
Of the metallic compounds which have now been prepared from 2-nitroso-5-methoxyphenol and from its 3-chloro-derivative, those with mercury, aluminium, tin, iron, cobalt, and nickel were found to be soluble in such organic solvents as benzene and chloroform, and those containing sodium, potassium, silver, zinc, cadmium, lead, manganese, and uranium were insoluble. The former products appear, therefore, to be co-ordination com-

pounds; the latter are probably normal salts. No metallic derivatives could be obtained from the nitroso-compounds and aqueous solutions of stannous or stannic chloride or of salts of chromium, aluminium, antimony, and titanium.

The normal sodium and potassium salts readily form addition compounds with one molecule of salicylaldehyde, and in so doing lose their bright green colour and turn yellow. This is evidence of the formation of a chelate compound (II) as in the products of Sidgwick and Brewer (J., 1925, 127, 2379). The 3-chloro-compound, however, reacts the more slowly, thereby indicating the ( $-I$ ) inductive effect of the chlorine substituent. The addition compounds from both nitroso-compounds appear to be more stable than the corresponding substances of Sidgwick and Brewer (*loc. cit.*), inasmuch as they can be purified by repeated washing with ether.



A potassium compound of 2-nitroso-5-methoxyphenol is described by Lifschitz (*Ber.*, 1914, 47, 1876) as having the formula  $KC_7H_6O_3N, C_7H_7O_3N, H_2O$  and being red-brown in colour, which would suggest the structural formulæ (III) and (IV) for the respective resonance forms.



Similarly the green and the red (or brown) co-ordinated compounds described below are depicted by the structures (V) and (VI), which are resonance forms, representing a single molecule. This, however, can partake of the characters of the two forms to a different extent, which may vary with the nature of the substituents. The reasonable assumption is made that the colour of the compound is evidence of the predominant form, those which approach (V) more nearly being green, and those which approach (VI) being red or brown.

#### EXPERIMENTAL.

*Preparation of the Metallic Compounds.*—(A) The nitrosophenol, dissolved in alcohol or acetone, is added dropwise to a very dilute aqueous solution of the mineral acid salt (chloride, nitrate, or sulphate) or of the acetate. Usually the co-ordination complex is precipitated immediately, whereas the normal salt separates gradually. It is necessary, however, to guard against mistaking precipitated reagent for the desired metallic compound. The cases of ferrous and cobalt salts require special attention, since, to obtain pure products, it is necessary to allow oxidation; this is facilitated by atmospheric exposure; also the solutions must be moderately dilute, otherwise the precipitates are unduly dark. Mild heating is an advantage in the preparation of the nickel salt.

(B) The chlorostannic and chloroaluminic compounds must be formed in dry benzene; the precipitate is of better texture when the nitrosophenol is added to the salt solution. The product must be rapidly washed with dry benzene and dried in a vacuum.

(C) For the preparation of the copper and the alkali-metal derivatives, the nitroso-compound is dissolved in alcohol or acetone, copper acetate in acetone, and the alkali hydroxide in alcohol.

*Test for the Sensitivity of the Iron Coloration.*—3 Drops of a 1% solution of the nitrosophenol in acetone were added to 10 c.c. of  $N/10^8$ -aqueous ferrous sulphate, and the well-stirred mixture compared with a similar one made with 1% potassium ferricyanide solution. Initially the colour change with the nitrosophenol was at least three times as intense as that with the ferri-

cyanide, but after 24 hours the colours of both solutions were of approximately equal intensity. The yellow-brown colour given by ferric iron was not visible at dilutions below  $N/10^5$ .

Wool mordanted with ferrous salts is dyed a blue-green shade when padded with nitroso-phenol solutions; the colour lake is decolourised by acids, restored by ammonia, and destroyed by stannous chloride.

*Description of the Metallic Compounds.*—For brevity, the analyses are expressed in the form : Radical, % found (% required); e.g., Hg, 40.0 (39.7).  $X = C_7H_6O_3N$  and  $Y = C_7H_5O_3NCl$ .

*Probable co-ordination compounds.* These are all more or less soluble in benzene and chloroform. *Mercury* :  $HgX_2$  crystallises from benzene in short, deep red micro-prisms, m. p.  $201^\circ$  [Hg, 40.0 (39.7)].  $HgY_2$  crystallises from benzene or chloroform in bright red micro-grains [Cl, 12.2 (12.3)]. *Aluminium* :  $AlXCl_2$ , light yellow micro-crystals from chloroform, which darken in air [Cl, 28.2 (28.4)].  $AlYCl_2$ , very light yellow prisms from chloroform; the colour deepens on heating [Total Cl, 37.2 (37.4); ionic Cl, 25.1 (25.0)]. *Tin* :  $SnXCl_3$ , red-orange micro-plates from chloroform, m. p.  $147^\circ$  [Cl, 28.3 (28.2)].  $SnYCl_3$ , brown-red plates from chloroform; the colour deepens on heating [Total Cl, 34.3 (34.5); ionic Cl, 25.7 (25.9)]. *Iron* :  $Fe(OH)X_2$ , dark green micro-needles from chloroform, which are also soluble in pyridine, naphthalene, acetone, benzene, and alcohol [Fe, 14.9 (14.8)].  $FeX_3$ , brown micro-crystals from benzene [Fe, 11.0 (10.9)].  $Fe(OH)Y_2$ , dark green needles from chloroform [Cl, 15.6 (15.9)].  $FeY_3$ , brown micro-crystals from benzene [Cl, 17.0 (17.3)]. *Cobalt* :  $CoX_3$ , red microprisms from chloroform, which are also soluble in benzene, chloroform, alcohol, and acetone (slightly) but insoluble in light petroleum [Co, 11.2 (11.4)].  $CoY_3$ , bright red micro-grains from chloroform [Cl, 17.1 (17.2)]. *Nickel* :  $NiX_2$ , micro-needles from chloroform, resembling the dimethylglyoxime compound in colour, and the cobalt compound in solubility [Ni, 16.4 (16.2)].  $NiY_2$ , bright red microcrystals like the cobalt compound [Cl, 16.5 (16.5)]. *Sodium* : Double compounds with salicylaldehyde : light yellow crystals.  $NaX, C_7H_6O_2$  [Na, 7.8 (7.7)].  $NaY, C_7H_6O_2$  [Na, 7.0 (6.9)]. *Potassium* : Double compounds with salicylaldehyde : light yellow crystals.  $KX, C_7H_6O_2$  [K, 12.0 (12.4)].  $KY, C_7H_6O_2$  [K, 11.5 (11.2)].

*Non-co-ordinated salts.* These are insoluble in organic solvents. *Sodium* :  $NaX$ , bright green crystals [Na, 13.3 (13.1)].  $NaY$ , bright green crystals [Na, 11.2 (11.0)]. *Potassium* :  $KX$ , bright green crystals [K, 20.0 (20.4)].  $KY$ , bright green crystals [K, 17.1 (17.3)]. *Silver* :  $AgX$ , red-brown micro-needles [Ag, 41.6 (41.5)].  $AgY$ , brown micro-needles [Cl, 12.0 (12.0)]. *Zinc* :  $ZnX_2$ , light yellow-brown, flat prisms [Zn, 17.9 (17.6)].  $ZnY_2$ , light yellow prisms [Cl, 16.4 (16.2)]. *Cadmium* :  $CdX_2$ , flat maroon macro-prisms [Cd, 26.6 (26.8)].  $CdY_2$ , maroon plates [Cl, 14.6 (14.6)]. *Lead* :  $PbX_2$ , dark yellow-brown micro-crystals [Pb, 40.2 (40.5)].  $PbY_2$ , dark brown micro-crystals [Cl, 12.2 (12.2)]. *Manganese* :  $MnX_2$ , minute brown prisms [Mn, 15.1 (15.3)].  $MnY_2$ , long, dark brown prisms [Cl, 16.9 (16.6)]. *Uranium* :  $UO_2X_2$ , yellow-brown micro-plates [U, 42.0 (41.5)].  $UO_2Y_2$ , russet micro-crystals [Cl, 11.2 (11.0)].

The silver and mercury compounds described by Kietaibl (*Monatsh.*, 1898, **19**, 544) as given by 2-nitroso-3-ethoxyphenol are really those of 2-nitroso-5-ethoxyphenol and homologous with the corresponding compounds described above.

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