

CCXXXV.—*Metallic Derivatives of Nitrophenolic Compounds. Part II. Some Nitrotolyloxides of Metals of Group II.*

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IN the present communication, a study has been made of the salts derived from the 1 : 2 : 3-, 1 : 3 : 4-, 1 : 4 : 3-, and 1 : 3 : 6-nitro-cresols, together with some compounds of dinitro-*o*-cresol. By comparing these with the alkaline-earth nitrophenoxides (Goddard, this vol., p. 1161), the change in solubility and in colour due to the influence of the methyl group is dealt with, and since the thalliumdialkyl nitrotolyloxides (Goddard, this vol., p. 1310) resemble the alkali compounds, they have also been alluded to in tracing similarities in solubility. All the substances now described were made by treating the nitrocresols in aqueous solution with the hydroxides or carbonates of the metals. The following hydrated barium salts have now been isolated: the 3-nitro-*o*-tolyloxide (+ 2H₂O); the 4-nitro-*m*-tolyloxide (+ 1H₂O); the 6-nitro-*m*-tolyloxide (+ 6H₂O), together with their anhydrous salts and the anhydrous 3-nitro-*p*-tolyloxide. The anhydrous salts were obtained by heating the hydrated forms at temperatures ranging from 120—160°. In the three cases, where the nitro- and hydroxyl

groups are in the *ortho*-position to one another, the deepest colour is observed, this reaching a maximum in the compound having $\text{CH}_3 : \text{OH} : \text{NO}_2 = 1 : 2 : 3$. The difference, however, in colour between the compounds containing these groups in positions 1 : 3 : 4 and 1 : 4 : 3 is not so marked as in the corresponding thalliumdialkyl compounds, and all the salts are darker than barium *o*-nitrophenoxide.

Although the last-named salt has never been obtained with water of crystallisation, it is noticeable that two of the above salts have water of hydration, which may be associated in some way with the presence of the methyl group. Barium 3-nitro-*o*-tolyl-oxide is the most soluble of the three compounds, and more so than barium *o*-nitrophenoxide, but it is much more insoluble than the thalliumdialkyl derivatives. The 6-nitro-*m*-tolyl-oxide having its nitro- and hydroxyl groups in the *para*-position is comparable with barium *p*-nitrophenoxide, and it has almost the same solubility in organic solvents.

In the case of the strontium salts, the following were obtained : the 3-nitro-*o*-tolyl-oxide ($+ 2\text{H}_2\text{O}$); the 4-nitro-*m*-tolyl-oxide ($+ 4\text{H}_2\text{O}$); the 3-nitro-*p*-tolyl-oxide ($+ 4\text{H}_2\text{O}$), and their corresponding anhydrous derivatives, also the anhydrous 6-nitro-*m*-tolyl-oxide. A noticeable feature of the strontium salts is the differently coloured solutions they give when heated with the various solvents, this not being so marked with the barium and calcium compounds. They are more soluble in ethyl acetate than the barium salts, and the greatest solubility is again shown by the derivative of 1 : 2 : 3-nitrocresol. When the nitro- and hydroxyl-groups in these compounds are in the *ortho*-position, their colour shows much more of the red and less of the yellow than strontium *o*-nitrophenoxide, and the yellow of the 1 : 3 : 6 salts is deeper than that of strontium *p*-nitrophenoxide.

In dealing with nitrophenoxides, it was shown that the calcium compounds usually contain more water of crystallisation than those of barium or strontium, but this has not been found to prevail in the present case. The undermentioned and their anhydrous derivatives are now described : the 3-nitro-*o*-tolyl-oxide ($+ 2\text{H}_2\text{O}$); the 4-nitro-*m*-tolyl-oxide ($+ 3\text{H}_2\text{O}$); the 3-nitro-*p*-tolyl-oxide ($+ 1\text{H}_2\text{O}$); and the 6-nitro-*m*-tolyl-oxide ($+ 2\text{H}_2\text{O}$). The anhydrous compounds of the first three are differentiated from the barium and strontium analogues by their greater solubility in alcohol, but the 4-nitro-*m*-tolyl-oxide is decidedly the most insoluble in organic solvents. The 6-nitro-compound resembles very closely calcium *p*-nitrophenoxide, being insoluble in most organic media.

Only two magnesium hydrates and their anhydrous salts have been investigated, namely: the 4-nitro-*m*-tolylloxide ($+ 4\text{H}_2\text{O}$) and the 3-nitro-*p*-tolylloxide ($+ 3\text{H}_2\text{O}$). These are the most soluble compounds yet described, and their corresponding nitrophenoxides are at present under investigation. Their colour tends more towards orange than is the case with the barium, strontium, and calcium salts. Staedel (*Annalen*, 1883, **217**, 159) describes barium dinitro-*o*-tolylloxide ($+ 3\text{H}_2\text{O}$), and Cazeneuve (*Bull. Soc. chim.*, 1897, [iii], **17**, 204) a barium salt ($+ 2\text{H}_2\text{O}$) and also a calcium derivative ($+ 1\text{H}_2\text{O}$) (*Compt. rend.*, 1897, **124**, 1130), but no investigator seems to have described the strontium salt. It has now been obtained along with its hydrate ($+ 6\text{H}_2\text{O}$), and is much more soluble than the mononitro-compound and is orange in colour.

Passing to the second vertical series of group II, the colours change from brilliant orange in the magnesium dinitrotolylloxide, through orange-yellow of the zinc salt to brilliant yellow in the cadmium salt. This points to the colour change being due to the metal itself, and not to any acquisition of a quinonoid structure. The following hydrates and their anhydrous derivatives have now been obtained: magnesium dinitro-*o*-tolylloxide ($+ 3\text{H}_2\text{O}$); the zinc and cadmium salts containing ($+ 2\text{H}_2\text{O}$) and ($+ 6\text{H}_2\text{O}$) respectively. Their solubility in organic solvents increases with increasing molecular weight. The solubilities of all compounds have been tested in alcohol, ether, acetone, chloroform, carbon tetrachloride, toluene, light petroleum, ethyl acetate, and pyridine.

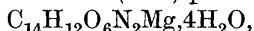
EXPERIMENTAL.

Derivatives of 3-Nitro-o-cresol.— $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ba}\cdot 2\text{H}_2\text{O}$, bright red needles, which darken in toluene, carbon tetrachloride, or chloroform [Found: N = 5.88 (5.84)*; Ba = 28.70 (28.72); H_2O = 7.62 (7.54) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ba}$, deep red [Found: N = 6.36 (6.33); Ba = 31.10 (31.07) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Sr}\cdot 2\text{H}_2\text{O}$, orange-red needles, which become deep red in pyridine or alcohol and darken in acetone or ethyl acetate [Found: Sr = 20.93 (20.45); H_2O = 8.47 (8.41) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Sr}$, brownish-red [Found: Sr = 22.87 (22.33) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ca}\cdot 2\text{H}_2\text{O}$, slender, orange-yellow needles becoming red in chloroform, carbon tetrachloride, or toluene [Found: N = 7.21 (7.36); Ca = 10.57 (10.52); H_2O = 9.54 (9.46) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ca}$, red [Found: N = 7.97 (8.12); Ca = 11.69 (11.62) per cent.].

Derivatives of 4-Nitro-m-cresol.— $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ba}\cdot 1\text{H}_2\text{O}$, red needles

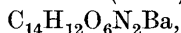
* The figures in the brackets denote the theoretical percentages.

[Found : N = 6.08 (6.08); Ba = 29.71 (29.85); H_2O = 3.82 (3.91) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ba}$, deeper red [Found : N = 6.33 (6.33); Ba = 30.89 (31.07) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Sr}, 4\text{H}_2\text{O}$, shining, rhomboidal, orange plates, becoming red in carbon tetrachloride or chloroform [Found : Sr = 19.20 (18.86); H_2O = 15.63 (15.51) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Sr}$, dark red [Found : Sr = 22.76 (22.33) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ca}, 3\text{H}_2\text{O}$, golden-yellow needles darkening in toluene or ethyl acetate [Found : N = 7.04 (7.02); Ca = 10.83 (10.04); H_2O = 12.76 (13.55) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ca}$, deep yellow [Found : N = 8.07 (8.12) per cent.].



pale orange [Found : Mg = 6.03 (6.06); H_2O = 17.84 (17.96) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Mg}$, pale orange [Found : Mg = 7.33 (7.41) per cent.].

Derivatives of 6-Nitro-m-cresol.— $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ba}, 6\text{H}_2\text{O}$, bright yellow plates, which become deep yellow in carbon tetrachloride, chloroform, or light petroleum [Found : N = 4.93 (4.92); Ba = 24.97 (24.12); H_2O = 19.78 (22.49) per cent.].

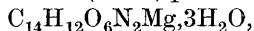


golden-yellow [Found : N = 6.14 (6.33); Ba = 31.10 (31.07) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Sr}$, bright yellow granules [Found : Sr = 22.28 (22.33) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ca}, 2\text{H}_2\text{O}$, bright yellow granules, which become deep yellow in toluene [Found : Ca = 10.40 (10.52); H_2O = 9.64 (9.46) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ca}$, deep yellow [Found : Ca = 11.50 (11.62) per cent.].

Derivatives of 3-Nitro-p-cresol.— $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ba}$, red shining plates [Found : N = 6.34 (6.33); Ba = 31.27 (31.07) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Sr}, 4\text{H}_2\text{O}$, scarlet plates, which become deep red in toluene or chloroform and darken in carbon tetrachloride or light petroleum [Found : N = 6.12 (6.03); Sr = 19.17 (18.86); H_2O = 15.21 (15.51) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Sr}$, deep red [Found : N = 7.39 (7.14); Sr = 22.61 (22.33) per cent.].



slender, orange-yellow needles, becoming yellow in chloroform and red in toluene [Found : N = 7.79 (7.72); Ca = 11.07 (11.04); H_2O = 4.64 (4.97) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ca}$, red [Found : N = 8.16 (8.12); Ca = 11.61 (11.62) per cent.].

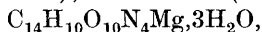


flat, orange needles, which become red in toluene [Found : N = 7.23 (7.32); Mg = 6.77 (6.35); H_2O = 14.08 (14.07) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Mg}$, red [Found : N = 8.42 (8.51); Mg = 7.39 (7.41) per cent.].

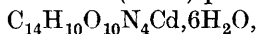
Derivatives of Dinitro-o-cresol.— $\text{C}_{14}\text{H}_{10}\text{O}_{10}\text{N}_4\text{Sr}, 6\text{H}_2\text{O}$, brilliant yellow needles, becoming orange in ether or chloroform and darken-

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ing in toluene [Found : N = 9.56 (9.49); Sr = 14.67 (14.84); H_2O = 17.82 (18.31) per cent.]. $\text{C}_{14}\text{H}_{10}\text{O}_{10}\text{N}_4\text{Sr}$, deep orange [Found : N = 11.70 (11.61); Sr = 17.90 (18.17) per cent.].



golden-yellow needles, becoming orange in carbon tetrachloride or toluene [Found : Mg = 5.11 (5.14); H_2O = 11.65 (11.42) per cent.]. $\text{C}_{14}\text{H}_{10}\text{O}_{10}\text{N}_4\text{Mg}$, brilliant orange [Found : Mg = 5.78 (5.81) per cent.]. $\text{C}_{14}\text{H}_{10}\text{O}_{10}\text{N}_4\text{Zn}, 2\text{H}_2\text{O}$, orange-yellow granules [Found : N = 11.42 (11.29); Zn = 13.55 (13.17); H_2O = 7.29 (7.26) per cent.]. $\text{C}_{14}\text{H}_{10}\text{O}_{10}\text{N}_4\text{Zn}$, orange-yellow [Found : N = 12.30 (12.18); Zn = 14.60 (14.21) per cent.].



brilliant yellow plates, becoming orange in toluene or chloroform [Found : Cd = 18.30 (18.27); H_2O = 17.82 (17.57) per cent.]. $\text{C}_{14}\text{H}_{10}\text{O}_{10}\text{N}_4\text{Cd}$, orange yellow [Found : Cd = 21.75 (22.16) per cent.].

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