CCCXVIII.—*Complex Metallic Ammines. Part IX. The Introduction of Nitrophenol Radicals into Cobaltammine Complexes. Distinctive Behaviour of Mononitrophenoxides.*

By JAMES COOPER DUFF and EDWIN JOHN BILLS.

IN Part VIII (J., 1923, **123**, 561) it was shown that sodium salts of carboxylic acids react with aquopentamminocobaltic nitrate to give acidopentamminocobaltic salts. The sodium derivatives of several nitrophenols have now been found to react similarly with aquopentamminocobaltic nitrate and with bisaquobisethylenediamminocobaltic salts. Mono-, di-, and tri-nitrophenols have been used to examine as far as possible the influence of the number and the orientations of the nitro-groups. The unexpectedly varying nature of the series of compounds obtained is discussed below.

Previously the only nitrophenol which had been found to give cobaltammine derivatives was picric acid. Morgan and King (J., 1922, **121**, 1723) have described the reactions which occur between several cobaltammine salts and certain nitro-dyes. They found that sodium picrate reacts with aquopentamminocobaltic chloride to give aquopentamminocobaltic picrate, and suggested that nitro-dyes such as picric acid and dinitronaphthol do not, in their reactions with cobaltammines, become implicated in the cobalt complex, thus differing noticeably from the *o*-quinoneoxime (nitrosonaphthol) dyes examined similarly by Morgan and Smith (J., 1921, **119**, 704). The latter found that the quinoneoxime radical, although univalent as regards principal valency, functions as a chelate group in the complex, being linked to cobalt through a principal valency (electro-valency) and a residual valency (co-valency). Morgan and King further suggest (*loc. cit.*) that the lack of residual valency shown by the picrate radical may be taken as evidence corroborating its *p*-quinonoid structure. In no case did they find that the picrate radical became part of the cobalt complex. It has now been found that nitrophenoxide radicals can be induced to form part of the complex, particularly in the tetrammine type. In most cases, the nitrophenoxide radicals were linked through a principal valency, but two outstanding examples have been obtained in which a complete molecule of nitrophenol appears to be implicated in the complex through residual valency.

The mononitrophenoxides have yielded results which indicate a structural difference between *m*-nitrophenol and the *o*- and *p*-isomerides, the quinone structure probably applying to the last two but not to the first. The evidence supports the views of Hantzsch (*Ber.*, 1907, **40**, 330) and of Hewitt, Johnson, and Pope (J., 1913, **103**, 1626) on these compounds.

Conductivity measurements have been used in the present work as the best method available for determining whether a nitrophenoxide radical is within the complex ion or not. It was recorded in Part VIII (*loc. cit.*) that during conductivity measurements with dilute solutions, the platinum-black of the electrodes was capable in the case of compounds of the type $[Co(NH_3)_5X]NO_3$ ($X =$ a dibasic acid radical) of causing internal hydrolysis, changing the acido-salt into an aquo-salt. Examples of this effect have again been encountered (see Experimental), although the compounds concerned are different in type from those in Part VIII. There has also been found in the case of a *p*-nitrophenol derivative (p. 2373) an example where the platinum-black apparently induces the displacement of water from the complex by a nitrophenoxide radical. This is the only case where a fall in the value for μ has been found to occur as the result of the catalytic influence of platinum-black. It should be noted that neither type of change due to the platinum-black requires any current to be passing between the electrodes. As a further check on the value of the conductivity figures those of the corresponding sodium nitrophenoxides are given at the end of this paper.

The Pentammine Compounds.

Sodium mono- and di-nitrophenoxides form alkaline aqueous solutions which complicate the reactions with aquopentamminocobaltic nitrate. In each case there was liberation of nitrophenol and no cobaltammine compound containing *o*- or *m*-nitrophenol could be separated. The reaction in these two cases was nearly quantitatively that of the equation $[Co(NH_3)_5,H_2O](NO_3)_3 + NaO{\cdot}C_6H_4{\cdot}NO_2 = [Co(NH_3)_5(OH)](NO_3)_2 + NaNO_3 + HO{\cdot}C_6H_4{\cdot}NO_2$.

Sodium *p*-nitrophenoxide, in addition to yielding some free *p*-nitrophenol, gave a fair yield of p-*nitrophenoxopentamminocobaltic* p-*nitrophenoxide* [I; X = *p*-$C_6H_4(NO_2)\cdot O\cdot$].

$$[Co(NH_3)_5X]X_2 \qquad [Co(NH_3)_5,H_2O]X_3 \qquad \left[Co(NH_3)_5X\right]\begin{matrix}X\\OH\end{matrix}$$

(I.) (II.) (III.)

It is of interest that of the three nitrophenols only the *p*-isomeride is capable of combining with the corresponding sodium derivative; this may account for the subsequent production of a pentammino-derivative in this case, and explain the lack of success with *o*- and *m*-nitrophenols. By using the double compound of sodium *p*-nitrophenoxide and *p*-nitrophenol, a better yield of the compound (I) is obtained.

The sodium derivatives of 2 : 4- and 2 : 6-dinitrophenols gave simple aquopentammino-salts [II; X = $C_6H_3(NO_2)_2\cdot O\cdot$]. Sodium picrate yielded *picratopentamminocobaltic picrate* [I; X = $C_6H_2(NO_2)_3\cdot O\cdot$]; its relation to the aquo-picrate prepared by Morgan and King (*loc. cit.*) is considered in the experimental part. When picric acid reacts with carbonatopentamminocobaltic nitrate, two compounds can be obtained. If the carbonato-salt is used in excess, there is produced a basic salt (III), otherwise the normal compound (I) is again obtained.

The two compounds of special interest in this section are those of *p*-nitrophenol and of picric acid (III). Both these undergo a change of conductivity in the Kohlrausch cell with platinised electrodes at the ordinary temperature; this only ceases when an aquo-salt has resulted in each case :

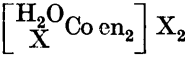
$$[Co(NH_3)_5X]X_2 + H_2O \longrightarrow [Co(NH_3)_5,H_2O]X_3$$

Thus for the *p*-nitrophenol compound μ (for $v = 1024$) changes from 177·7 to 322·5 in 24 hours, accompanied by a colour change, while the stock solution shows but little hydrolysis after 3 months in a stoppered flask. The solutions which have been catalytically hydrolysed in the cell remain permanently hydrolysed.

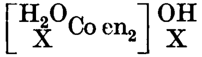
The Bisethylenediammine Compounds.

The sodium derivatives of all the nitrophenols examined react with bisaquobisethylenediamminocobaltic bromide to give crystalline compounds containing nitrophenol groups. The resulting compounds showed unusual differences. Sodium picrate gave *aquopicratobisethylenediamminocobaltic picrate* (IV; X = picrate radical) and sodium 2 : 4-dinitrophenoxide gave a similar compound (as IV), whilst the 2 : 6-isomeride yielded a basic salt (V; X = 2 : 6-dinitrophenoxide radical).

(IV.)



$$\left[\begin{matrix}H_2O\\X\end{matrix}\mathrm{Co\,en_2}\right]X_2$$

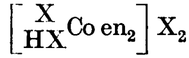


$$\left[\begin{matrix}H_2O\\X\end{matrix}\mathrm{Co\,en_2}\right]\begin{matrix}OH\\X\end{matrix}$$

(V.)

The outstanding results in this section were obtained from the mononitrophenoxides. One circumstance common to all three isomerides was that the resulting cobaltammine compounds contained a molecule of nitrophenol in addition to three nitrophenoxide radicals. The manner in which this nitrophenol molecule occurs in the compound is different in each case. Sodium *m*-nitrophenoxide produced a molecular compound between *bis*-m-*nitrophenoxobisethylenediamminocobaltic* m-*nitrophenoxide* and *m*-nitrophenol (VI; X = *m*-nitrophenoxide radical), in which the latter molecule is outside the complex.

(VI.) $[\mathrm{Co\,en_2}\,X_2]X,HX$

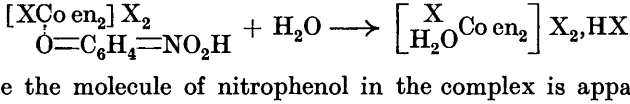


$$\left[\begin{matrix}X\\HX\end{matrix}\mathrm{Co\,en_2}\right]X_2$$

(VII.)

From sodium *o*- and *p*-nitrophenoxides it was possible to obtain *nitrophenolnitrophenoxobisethylenediamminocobaltic nitrophenoxide* (VII; X = *o*- or *p*-nitrophenoxide radical). This is a new type of compound because the complete molecule of *o*- or *p*-nitrophenol is linked by residual valency (co-valency) in the same manner as a molecule of water in the case of aquocobaltammine salts. Formula (VII) is supported by the facts that (1) unlike all other compounds in this series, the aqueous solutions of the two salts concerned can be acidified without discharging the yellow or red colour, respectively, of the *p*- or *o*-nitrophenol compound, and (2) the aqueous solutions of these two salts when heated and then cooled and acidified have their colour discharged, yet the heating has caused no change in the values for molecular conductivity. This means that the substances hydrolyse in hot solutions, but only to the extent of having the molecule of nitrophenol displaced by a molecule of water, as in (IX):

(VIII.)



$$\begin{matrix}[\mathrm{XCo\,en_2}]X_2\\ \vdots\\ O{=}C_6H_4{=}NO_2H\end{matrix} + H_2O \longrightarrow \left[\begin{matrix}X\\H_2O\end{matrix}\mathrm{Co\,en_2}\right]X_2,HX.$$

(IX.)

Since the molecule of nitrophenol in the complex is apparently concerned in the colour of the cold acid solution, it would appear reasonable to attribute to this complete nitrophenol molecule in the complex the corresponding *o*- or *p*-quinonoid structure (VIII), especially as the red and yellow colours of the respective compounds correspond to those of *o*- and *p*-quinones. An important point in this connexion is the fact that no free *o*-, *m*-, or *p*-nitrophenol was present at the beginning of the preparation of these compounds. The nitrophenol was liberated in each case during the reaction between the sodium derivative and the bisaquocobaltammine salt, the probable reaction being as follows :

$$[\mathrm{Co\,en_2\,(H_2O)_2}]\mathrm{Br_3} + \mathrm{NaO{\cdot}C_6H_4{\cdot}NO_2} \longrightarrow \left[\substack{\mathrm{H_2O}\\ \mathrm{HO}}\mathrm{Co\,en_2}\right]\mathrm{Br_2} + \mathrm{NaBr} + \mathrm{HO{\cdot}C_6H_4{\cdot}NO_2}.$$

The foregoing results suggest that whilst sodium *m*-nitrophenoxide is not quinonoid in structure, yet the *o*- and *p*-nitrophenoxides probably are; and further, when these are decomposed as in the above equation, the newly-liberated nitrophenol has the quinonoid structure and is linked up in this form in the complex in place of water.

Whilst only one cobaltammine compound of this series could be isolated from each of the *o*- and *m*-nitrophenoxides, the *p*-nitrophenoxide was found capable of producing three others in addition to (VII); by use of its addition compound with *p*-nitrophenol, $\mathrm{NaC_6H_4O_3N,C_6H_5O_3N,2H_2O}$, two compounds represented by (IV) and (IX) were obtained by varying the conditions of reaction. In dilute aqueous solution, particularly in the presence of platinum-black, both these compounds undergo change, a nitrophenoxide radical entering the complex and displacing water :

$$\left[\substack{\mathrm{X}\\ \mathrm{H_2O}}\mathrm{Co\,en_2}\right]\mathrm{X_2,HX} \longrightarrow [\mathrm{Co\,en_2\,X_2}]\mathrm{X,HX} + \mathrm{H_2O}.$$

On attempting to recrystallise compound (IX) from hot water, some nitrophenol is liberated, yet from the solution it is possible to obtain crystals of the molecular compound *bis*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide*–p-*nitrophenol* (as VI), corresponding to that obtained from *m*-nitrophenol.

EXPERIMENTAL.

Electrical Conductivity Measurements.—The method of measurement recorded in Part VII (J., 1922, **121**, 453) was adopted. Since most of the compounds were only moderately soluble, measurements were limited to $v = 1024$ and 2048 at 25°, at which temperature all determinations were made. Fresh solutions were made for each. The Kohlrausch cell constant was 0·2117 and the resistances measured did not greatly exceed 5000 ohms. Where conductivity changes due to the platinised electrodes were found, these were checked on new solutions. To find the extent to which change occurred it was usually necessary to leave the cell solution and the stock solution for 24 hours in the thermostat and then redetermine μ for each. No attempt was made to compare the rates at which changes occurred, as it was noted that these only took place in the neighbourhood of the electrodes. Samples of solutions which had undergone change in this way were kept in closed tubes for 3 months and again examined. In no case had there been any tendency to revert to the original form. With unplatinised electrodes practically no catalytic effect was noticeable.

The Pentammine Series.

The Cobaltammine Reagent.—5 G. of carbonatopentamminocobaltic nitrate, 30 c.c. of water, and 20 c.c. of 2*N*-nitric acid were maintained at 45° until effervescence ceased. The solution was neutralised with 2*N*-sodium hydroxide. For the following compounds, this reagent was mixed at 45° with a solution of the corresponding sodium derivative (3 mols.) in the minimum amount of water. Except in the case of the picrate it was necessary to extract the washed precipitate with alcohol and ether to remove free nitrophenol or dinitrophenol. The product was then crystallised from water at 65°.

Sodium *o*- and *m*-nitrophenoxides produced only a precipitate of free nitrophenol. On addition of sufficient alcohol to retain this in solution, long red needles slowly separated; these were identified by analysis and reactions as hydroxopentamminocobaltic nitrate (see equation, p. 2366).

The following compounds are all easily decomposed by dilute acid or alkali. In the crystalline form and in solution, they begin to decompose at 70—80°.

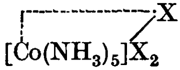
p-*Nitrophenoxopentamminocobaltic* p-*nitrophenoxide* (as I; with $3H_2O$) was obtained in minute, orange, oblong plates (Found: Co, 9·34; NH_3, 13·76; nitrophenoxide, 67·8; H_2O, 8·21. $C_{18}H_{27}O_9N_8Co,3H_2O$ requires Co, 9·64; NH_3, 13·88; nitrophenoxide, 67·64; H_2O, 8·82%). By the use of the addition compound of sodium *p*-nitrophenoxide and *p*-nitrophenol, the same compound was obtained in better yield (Found: Co, 9·24; nitrophenoxide, 65·77%); $\mu_{1024} = 177·7$ and $\mu_{2048} = 189·2$; 24 hours later the cell solution had $\mu_{1024} = 322·5$ and $\mu_{2048} = 322·2$, whilst the stock solution had $\mu_{1024} = 181·2$ and $\mu_{2048} = 189·4$. The cell solution had become greenish-yellow, whilst the flask solution remained golden-yellow. The solutions were kept sealed for 3 months, and the two cell solutions then had $\mu_{1024} = 340·5$ and $\mu_{2048} = 342·8$, and the stock solutions $\mu_{1024} = 208·4$ and $\mu_{2048} = 245·3$. A few minutes in the cell caused a greater change than 3 months in the stock flask.

Aquopentamminocobaltic 2 : 4-*dinitrophenoxide* (as II; with $3H_2O$) was obtained as an orange, sandy, crystalline powder (Found: Co, 7·72; NH_3, 11·11; dinitrophenoxide, 71·88; H_2O, 8·86. $C_{18}H_{26}O_{16}N_{11}Co,3H_2O$ requires Co, 7·71; NH_3, 11·11; dinitrophenoxide, 71·76; H_2O, 9·41%); $\mu_{1024} = 284$ and $\mu_{2048} = 291·6$.

Aquopentamminocobaltic 2 : 6-*dinitrophenoxide* (as II) was obtained as an orange-red, microcrystalline powder, only sparingly soluble in water (Found: Co, 8·29; NH_3, 12·20; dinitrophenoxide, 77·68. $C_{18}H_{26}O_{16}N_{11}Co$ requires Co, 8·29; NH_3, 11·95; dinitrophenoxide, 77·21%); $\mu_{2048} = 318{\cdot}4$.

Picratopentamminocobaltic picrate (as I; with $3H_2O$) was obtained in glistening, golden leaflets (Found: Co, 6·53; NH_3, 9·53; picrate, 78·2; H_2O, 6·91. $C_{18}H_{21}O_{21}N_{14}Co,3H_2O$ requires Co, 6·68; NH_3, 9·63; picrate, 77·55; H_2O, 6·12%). The same compound resulted from the reaction between picric acid (3 mols.) and carbonatopentamminocobaltic nitrate (Found: Co, 6·35; NH_3, 9·28; picrate, 76·8%). For conductivity measurements it was difficult to obtain a solution for $v = 2048$ without heating to 60°, and this apparently caused some hydrolysis. At 25°, $\mu_{2048} = 304$, changing in the cell in 2 days to 359·1. In view of this somewhat high value for an acidopentammine salt, the compound described by Morgan and King (*loc. cit.*) was prepared and examined: at 25°, $\mu_{2048} = 288$, changing in 3 hours in the cell to 360, and over-night to 415·3, whilst the stock solution only changed to $\mu_{2048} = 299$; it was noticed that the cell solution had changed from golden-yellow to greenish-yellow. These changes suggest that Morgan and King's compound $[Co(NH_3)_5H_2O]X_3$ is not simply an aquopentammine salt, as they assert. The molecule contains $2H_2O$ less than our compound and differs in appearance, but it can be changed to our picrato-salt by crystallisation from a hot dilute solution of picric acid. A possible explanation may be that in the compound of Morgan and King one of the picrate radicals is linked to the cobalt by residual valency and to the complex by principal valency as in (X). This could account

(X.)



$$[Co(NH_3)_5]X_2 \cdots X$$

for the conductivity changes and the conversion by means of picric acid into our compound.

Picratopentamminocobaltic hydroxypicrate (III; with $2H_2O$) was obtained as a brown, microcrystalline powder by stirring powdered picric acid (1 mol.) into a concentrated solution of carbonatopentamminocobaltic nitrate at 60°. The product was recrystallised from water at 60° (Found: Co, 9·09; NH_3, 13·14; picrate, 69·85; H_2O, 5·18. $C_{12}H_{20}O_{15}N_{11}Co,2H_2O$ requires Co, 9·03; NH_3, 13·02; picrate, 69·83; H_2O, 5·51%); $\mu_{2048} = 203{\cdot}3$, changing in the cell in 12 hours to 352·2, while the stock solution remained at 203·3. The cell solution changed in colour from orange to greenish-yellow. After 3 months in a sealed tube, this solution gave $\mu_{2048} = 360$, whilst the stock solution gave 225·6. When the basic picrate was dissolved in hot dilute picric acid solution, the normal picrato-salt separated on cooling.

Bisethylenediammine Series.

The Cobaltammine Reagent.—5 G. of carbonatobisethylenediamminocobaltic bromide, 30 c.c. of water, and 20 c.c. of 2*N*-nitric acid were maintained at 50° until effervescence ceased. The solution was neutralised with 2*N*-sodium hydroxide. It was freshly made for each of the following preparations.

o-*Nitrophenol*-o-*nitrophenoxobisethylenediamminocobaltic* o-*nitrophenoxide* (as VII; with $1H_2O$) was prepared by mixing the cobaltammine reagent at 50° with 7·5 g. of sodium *o*-nitrophenoxide (3 mols.) in 70 c.c. of water. After alcohol and ether extraction, the product was crystallised from water at 70°, yielding dark red, minute, glistening plates (Found: Co, 7·83; nitrophenoxide, 73·34. $C_{28}H_{33}O_{12}N_8Co,H_2O$ requires Co, 7·86; nitrophenoxide, 73·60%). The aqueous solution is red and changes to a more scarlet tint on addition of dilute mineral acids, with separation of some nitrophenol. The acid solution becomes faintly pink on boiling. A fresh aqueous solution of the compound becomes yellow when immersed in boiling water, and subsequent addition of acid gives only the pink colour of aquocobaltammine inorganic salts. It is inferred from these reactions that a complete molecule of *o*-nitrophenol is within the complex and is only readily replaced by a molecule of water in hot solutions. Dilute alkali causes complete hydrolysis immediately. The compound is appreciably soluble in alcohol and in acetone, but not sufficiently soluble to serve for an accurate estimation of the molecular weight: values obtained ebullioscopically ranged from 780 to 900. $\mu_{1024} = 135·6$ and $\mu_{2048} = 142·2$. After the latter solution had been heated on the water-bath to change the colour from red to yellow, μ_{2048} became 140·2.

Bis-m-*nitrophenoxobisethylenediamminocobaltic* m-*nitrophenoxide* + m-*nitrophenol* (as VI; with $1H_2O$) was obtained when the cobaltammine reagent at 50° was mixed with 7·5 g. of sodium *m*-nitrophenoxide in 70 c.c. of water. The mixture was filtered at 25° and the solution left over-night. The desired compound was obtained in brownish-red nodules (Found: Co, 7·81; nitrophenoxide, 72·98. $C_{28}H_{33}O_{12}N_8Co,H_2O$ requires Co, 7·86; nitrophenoxide, 73·6%). The aqueous solution is yellow and addition of dilute acid renders it pink, with liberation of all the nitrophenol; $\mu_{1024} = 75·7$ and $\mu_{2048} = 71·5$. The former value is high because of hydrolysis during the preparation of the solution. After this solution had been heated on the water-bath for 30 minutes, μ_{1024} became 101·5.

p-Nitrophenol was found capable of yielding the compounds A, B, C, D, as follows.

A. p-*Nitrophenol*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* (as VII; with $3H_2O$). To obtain this compound it was necessary to use a solution of sodium *p*-nitrophenoxide freshly prepared from the nitrophenol: the use of the crystallised salt resulted in a mixture of A and C. The cobaltammine reagent at 50° was mixed with a solution of 6·5 g. of *p*-nitrophenol in 46·8 c.c. of *N*-sodium hydroxide and 40 c.c. of water. The precipitate, washed with alcohol and ether to remove *p*-nitrophenol, was crystallised from water at 70°. In this way, A was obtained in dark brown microcrystals which assumed a purple shade on dehydration at 90° (Found: Co, 7·30; nitrophenoxide, 69·45; H_2O, 6·72. $C_{28}H_{33}O_{12}N_8Co,3H_2O$ requires Co, 7·50; nitrophenoxide, 70·23; H_2O, 6·87%). The compound is appreciably soluble in alcohol and acetone. The aqueous solution is orange and when acidified retains a yellow colour for several minutes. If the solution is heated, then cooled and acidified, it becomes pink immediately. $\mu_{1024} = 130{\cdot}2$ and $\mu_{2048} = 139{\cdot}6$. After the latter solution had been heated for 15 minutes at 90° it had $\mu_{2048} = 125{\cdot}7$, changing in the cell to 91·0 after 24 hours and 78·8 after 48 hours. This indicates a change from A through C into D (p. 2374). The hydrated salt changes slowly in the solid state, passing into the compound C, since after 4 months it gave aqueous solutions which at once became pink on being acidified. The anhydrous form of the salt is more stable.

B. *Aquo*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* (as IV; with $2H_2O$) was obtained as a light brown, crystalline powder when the cobaltammine reagent was mixed at 70° with 15 g. of the double compound of sodium *p*-nitrophenoxide and *p*-nitrophenol in 200 c.c. of water. The precipitate was filtered immediately and free nitrophenol removed by ether extraction (Found: Co, 9·14; nitrophenoxide, 63·83. $C_{22}H_{30}O_{10}N_7Co,2H_2O$ requires Co, 9·11; nitrophenoxide, 63·98%). An aqueous solution is immediately decomposed by dilute acid, a distinction from A. On heating to 80°, the aqueous solution decomposes with separation of *p*-nitrophenol, yet the impure crystals which separate on cooling contain more than three equivalents of nitrophenoxide. There is evidently a tendency for B to pass into the more stable compound C. $\mu_{1024} = 115{\cdot}8$ and $\mu_{2048} = 122{\cdot}8$; the latter changes in the cell to 84·3.

C. *Aquo*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* + p-*nitrophenol* (as IX; with $1H_2O$) was obtained in orange-brown microcrystals by mixing the cobaltammine reagent with 15 g. of the double sodium salt in 200 c.c. of water at 40°, filtering the solution after 2 hours, and removing free *p*-nitrophenol by ether extraction (Found:. Co, 7·74; nitrophenoxide, 71·34; H_2O, 3·8. $C_{28}H_{35}O_{13}N_8Co,H_2O$ requires Co, 7·68; nitrophenoxide, 71·87; H_2O, 4·68%). In solution, C behaves similarly to B. $\mu_{1024} = 119·5$ and $\mu_{2048} = 118·8$; after 24 hours in the cell $\mu_{2048} = 70·1$ while the stock solution gave $\mu_{2048} = 117·9$. The results support the change of C into D as below.

D. *Bis*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* + p-*nitrophenol* (as VI; with $2H_2O$) was obtained from C above by crystallising it from water at 70°, filtering the solution from liberated *p*-nitrophenol, and leaving it over-night; the salt separated in dark brown nodules (Found: Co, 7·73; nitrophenoxide, 71·9; H_2O, 5·23. $C_{28}H_{33}O_{12}N_8Co,2H_2O$ requires Co, 7·68; nitrophenoxide, 71·87; H_2O, 4·68%). The yellow colour of the aqueous solution is changed to pink immediately by dilute acid. $\mu_{1024} = 88·0$ and $\mu_{2048} = 70·1$; the high value for μ_{1024} is due to the fact that the solution had been prepared at 40°.

Aquo-2 : 4-dinitrophenoxobisethylenediamminocobaltic 2 : 4-dinitrophenoxide (as IV; with $1H_2O$) was prepared by mixing the cobaltammine reagent at 60° with 9·6 g. of sodium 2 : 4-dinitrophenoxide (3 mols.) in 200 c.c. of water. After being washed, finally with ether, the pure compound crystallised from water at 70° in orange-red microcrystals (Found: Co, 7·71; dinitrophenoxide, 70·55; H_2O, 4·13. $C_{22}H_{27}O_{16}N_{10}Co,H_2O$ requires Co, 7·72; dinitrophenoxide, 71·86; H_2O, 4·71%); $\mu_{2048} = 184·1$—it was necessary to warm to 60° to obtain this solution.

Aquo-2 : 6-dinitrophenoxobisethylenediamminocobaltic hydroxy-2 : 6-dinitrophenoxide (as V) was obtained in brown microcrystals by the analogous method (Found: Co, 10·02; dinitrophenoxide, 63·45. $C_{16}H_{25}O_{12}N_8Co$ requires Co, 10·17; dinitrophenoxide, 63·10%); $\mu_{2048} = 165·7$.

Aquopicratobisethylenediamminocobaltic picrate (IV; with $4H_2O$) was obtained in orange, flat needles from the cobaltammine reagent and 12 g. of sodium picrate in 200 c.c. of water by the method used for the two preceding compounds (Found: Co, 6·16; picrate, 72·7; H_2O, 9·69. $C_{22}H_{24}O_{22}N_{13}Co,4H_2O$ requires Co, 6·18; picrate, 71·77; H_2O, 9·44%). The same compound was produced by the action of excess of picric acid in solution on carbonatobisethylenediamminocobaltic bromide at 60° (Found: Co, 6·32; picrate, 70·84%); $\mu_{2048} = 251·7$, without change in the cell on standing.

Analysis.—In both series cobalt was determined directly as sulphate by heating the compounds with concentrated sulphuric acid. The nitrophenols were estimated by heating with excess of titanous chloride solution and titrating the excess with standard ferric alum solution: in the pentammine series this was done after precipitation of cobalt with sodium hydroxide, but in the bisethylenediammine series it was necessary to let the titanous chloride reduce both the cobaltic complex and the nitrophenol and subsequently to allow for the cobalt present. No estimation of ethylenediamine was made, since all the compounds in this series were found to yield the green *trans*-dichlorobisethylenediamminocobaltic chloride on evaporation with hydrochloric acid.

As standards for the conductivity values, the following values were determined (at 25°) for the various sodium derivatives of the nitrophenols :

	μ_{1024}.	μ_{2048}.
Sodium *o*-nitrophenoxide	82·0	92·9
Sodium *m*-nitrophenoxide	82·35	92·6
Sodium *p*-nitrophenoxide	86·35	90·0
Sodium 2 : 4-dinitrophenoxide	82·6	90·6
Sodium picrate	82·6	91·6

CENTRAL TECHNICAL COLLEGE,
BIRMINGHAM.

[*Received, July* 15*th,* 1927.]