# **843.** *Cobalt Phosphates. Part I. The Orthophosphate Group as Ligand in Some Cobalt*(III) *Ammine Complexes.*

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Attempts to prepare phosphatopentamminocobalt(III) complex salts by various methods all yielded aquopentamminocobalt(III) phosphates, whilst every attempt to obtain a phosphato-complex from triamminocobalt(III) complexes gave cobalt(II) compounds.

Only in the tetrammine series were two compounds with the properties expected for phosphato-complexes obtained. The first, $[Co(NH_3)_4PO_4],2H_2O$, had properties quite distinct from those of the isomer $[Co(NH_3)_4(H_2O)_2]PO_4$ which was also prepared. The second appeared to be $[Co(NH_3)_4HPO_4]_3PO_4$, but its constitution could not be established with certainty. The properties of the neutral complex indicated that in it the phosphate is a chelate group.

Although several hexammino-, aquopentammino-, and diaquotetrammino-cobalt(III) orthophosphates are known,[1] few cobalt(III) complexes containing a phosphato-group as ligand have been described. Duff [2] reported the preparation of the complex compounds $[Co(NH_3)_5PO_4],2H_2O$ and $[Co(NH_3)_5HPO_4]H_2PO_4,2H_2O$, and Duval and Duval [3] described an anhydrous compound $[Co(NH_3)_5PO_4]$, but only one phosphatotetrammino-complex $[Co(NH_3)_4PO_4],nH_2O$ ($n = 2$ or 3) appears to have been reported.[4]

The preparation of the hydrated phosphatopentamminocobalt(III) compound described by Duff was disputed by Klement,[4] and that of the corresponding anhydrous compound [3] is not described in sufficient detail for the method to be repeated. The neutral phosphatotetrammino-complex was not prepared directly, but was isolated from the complex products—containing both cobalt(II) and cobalt(III) compounds—of the reaction between sodium phosphate and either dichlorodiaquodiammino- or dichloroaquotriamminocobalt(III) compounds.[4]

There was, therefore, little evidence relating to the direct introduction of the phosphato-group into cobalt(III) ammine complexes. Less was known of the properties of the phosphato-groups as a ligand in such complexes than of those of the carbonato- or sulphato-groups, which can apparently occupy either one or two co-ordination positions.[5] We have therefore studied the preparation of phosphatocobalt(III) ammine complexes and their properties.

## Experimental and Results

*Starting Materials.*—The following compounds used in attempts to prepare phosphatocobalt(III) complexes were prepared by methods given in the references: $[Co(NH_3)_5Cl]Cl_2$,[6] $[Co(NH_3)_5H_2O]Cl_3$,[7] $[Co(NH_3)_5CO_3]NO_3$,[8] $[Co(NH_3)_5NO_3](NO_3)_2$,[9] $[Co(NH_3)_4CO_3]NO_3$,[10] *cis*-$[Co(NH_3)_4(H_2O)Cl]SO_4$,[11] $[Co(NH_3)_4(H_2O)_2]Cl_3$,[10] $[Co(NH_3)_3(H_2O)_3]Cl_3$,[12] and $[Co(NH_3)_3(NO_2)_3]$.[13] In every case the product was completely analysed. Apart from the carbonatopentamminocobalt(III) nitrate, which appeared to contain a little of the tetrammino-salt, all were pure. The " aquo-complexes " were prepared immediately before use.

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[1] Mellor, " Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1935, Vol. XIV, p. 856.

[2] Duff, *J.*, 1923, **123**, 560.

[3] Duval and Duval, *Compt. rend.*, 1929, **189**, 537.

[4] Klement, *Z. anorg. Chem.*, 1926, **156**, 237.

[5] Martell and Calvin, " Chemistry of the Metal Chelate Compounds," Prentice Hall, New York, 1952, p. 134.

[6] King, " Inorganic Preparations," George Allen and Unwin, London, 1950 (revised edn.), p. 106.

[7] Ref. (6), p. 109.

[8] Werner and Goslings, *Ber.*, 1903, **36**, 2378.

[9] Palmer, " Experimental Inorganic Chemistry," Cambridge Univ. Press, Cambridge, 1954, p. 535.

[10] Ref. (6), p. 110.

[11] Ref. (9), p. 545.

[12] Ref. (6), p. 111.

[13] Ref. (9), p. 539.

*Analytical Methods.*—The following methods were used for both starting materials and products: (a) *Chloride.* Gravimetrically as silver chloride. (b) *Ammonia.* By evolution and absorption in excess of standard acid. (c) *Nitrite* (*nitro-groups*) *and* (d) *nitrite.* By evolution as ammonia after reduction with Devarda's alloy. (e) *Total phosphate.* Gravimetrically as ammonium phosphomolybdate. (f) *Ionisable phosphate.* Gravimetrically by precipitation as silver phosphate from cold aqueous solution. (g) *Cobalt.* The complex was decomposed by boiling with a slight excess of sodium hydroxide solution; the precipitate thus formed was dissolved by addition of the minimum quantity of dilute hydrochloric acid and warming; 50 ml. (*i.e.*, excess) of a standard solution (approx. M/100) of disodium ethylenediaminetetraacetate were added, and the solution neutralised with ammonia, boiled for 2 min., and cooled; 2 or 3 drops of 2N-ammonia were then added, and the excess of edta was determined by titration with standard (*ca.* M/100) zinc sulphate solution, with Eriochrome Black-T as indicator; the presence of phosphate in the amounts occurring in our samples did not interfere. (h) *Carbonate and* (j) *water.* Both determined by difference.

*Conductivity Measurements.*—Because of the very low solubility in water of the compounds containing phosphate, measurements were made on their saturated solutions in conductivity water, and their concentrations were then obtained from a determination of cobalt content. Measurements were made on fresh solutions at 25° by use of a conventional conductivity cell with an A.C. Wheatstone bridge circuit. The molar conductances, shown in Table 1, were calculated on the assumption that the molecular weights were identical with the formula weights.

TABLE 1. *Molar conductances at 25°.*

| Compound | Dilution (l. mole$^{-1}$) | Molar conductance * (ohm$^{-1}$ cm.$^2$ mole$^{-1}$) | No. of ions indicated |
|---|---|---|---|
| C | 2564 | 409 | 4 |
| D | 2337 | 318 | 3—4 |
| E | 2033 | 47 | 0 |
| F | 1953 | 225 | 2—3 |

* Calculated on the assumption that the molecular weight is given by the formula weight.
† For key to letters, see details of preparations.

*Absorption Spectra.*—These were determined in the range 3000—8000 Å by use of apparatus of commercial design. Solutions of approximately M/100-concentration were of suitable optical density for use with 1 cm. cells. Those of compounds containing phosphate were obtained by use of M/100-phosphoric acid as solvent; those of the other compounds used as reference substances were aqueous solutions. All measurements were made on fresh solutions. The extinction coefficients given in Table 2 were calculated on the assumption that the molecular weights were given by the formula weights.

TABLE 2. *Absorption spectra for visible and ultraviolet regions.*

| | Values of $\lambda_{max.}$ (Å) and $\varepsilon_{max.}$ | | | | | |
|---|---|---|---|---|---|---|
| Compound | $\lambda_{max.}$ | $\varepsilon_{max.}$ | $\lambda_{max.}$ | $\varepsilon_{max.}$ | $\lambda_{max.}$ | $\varepsilon_{max.}$ |
| D * | 3420 | 43 | 4850 | 48 | — | — |
| $[Co(NH_3)_5(H_2O)]Cl_3$ † | 3450 | 47 | 4940 | 48 | — | — |
| $[Co(NH_3)_5Cl]Cl_2$ † | 3570 | 43 | 5300 | 42 | — | — |
| C * | 3620 | 46 | 5100 | 54 | — | — |
| E * | 3650 | 23 | 5220 | 37 | 6950 | 61 |
| F * | 3520 | 38 | 5100 | 50 | — | — |
| $[Co(NH_3)_4(H_2O)_2]Cl_3$ † | 3560 | 38 | 5270 | 48 | — | — |
| $[Co(NH_3)_4CO_3]NO_3$ † | ‡ | — | 5260 | 57 | 7040 | 26 |

* Solvent, M/100-$H_3PO_4$. † Solvent, water. ‡ Strong peak at *ca.* 3500 Å.

*Loss of Water from Products.*—The loss in weight of samples of the compounds containing cobalt(III) and phosphate when heated to (*a*) 70°, (*b*) 90°, and (*c*) 110° was studied. At the conclusion of the experiments the samples were analysed for both cobalt and ammonia to ascertain the loss of ammonia, if any, and the loss of water was obtained by correction for this. The losses in water and ammonia from the various compounds when heated at three different temperatures are shown in Table 3. The rates at which compounds E and F lost weight when heated at 110° are given in Table 4.

*Attempts to prepare Phosphate Complexes.*—The various methods given below were tried.

Any solid products obtained were collected on a Büchner funnel and washed with either water or dilute aqueous ammonia (whichever had been used as solvent originally) to remove any unchanged starting material, then with alcohol or acetone. The product was then left to dry first in the air and, finally, for a short time in a desiccator ($CaCl_2$). All were very sparingly soluble in water, alcohol, or acetone, but dissolved readily in dilute solutions of mineral acids.

(1*a*) Duff's method "for salts derived from aquopentamminocobaltic nitrate."[2] Red crystals of the *aquopentammino-phosphate* (Compound A) were obtained {Found: Co, 21·29; $NH_3$, 31·02; $PO_4$ (total and ionisable), 34·35; $H_2O$, 13·34. $[Co(NH_3)_5H_2O]PO_4,H_2O$ requires Co, 21·43; $NH_3$, 30·97; $PO_4$ (total and ionisable), 34·53; $H_2O$, 13·10%}.

TABLE 3. *Loss of water from compounds on heating.*

| | Loss of weight (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | at 70° * | at 90° * | at 110° † | | | Calc. for loss of $H_2O$: | |
| Compound | (total) | (total) | (total) | ($NH_3$) | ($H_2O$) | of crystn. | total |
| A | 1·43 | — | 6·98 | 2·79 | 4·19 | 6·55 | 13·10 |
| B | — | — | 7·23 | 2·86 | 4·37 | 6·55 | 13·10 |
| C | — | — | 16·29 | 12·97 | 3·32 § | 0 | 0 |
| D | 3·14 | 3·36 | 11·07 | 2·09 | 8·98 | 12·30 | 18·45 |
| E | 14·03 | 16·47 ‡ | 20·35 | 6·81 | 13·54 | 13·96 | 13·96 |
| F | 0·45 | 1·27 | 12·74 | 2·25 | 10·49 | 0 | 13·96 |

* Samples heated to constant weight (5—7 days); no loss of ammonia except in case of compound E at 90°.
† Loss of weight after 15 days recorded.
‡ Loss due to ammonia, 2·58%.
§ Presumably due to some conversion of acid phosphate groups into pyrophosphate.

TABLE 4. *Rate of loss of weight at* 110°.

| Time (hr.) ......... | | 3 | 6 | 24 | 48 | 72 | 96 | 360 |
|---|---|---|---|---|---|---|---|---|
| Wt. loss * (%) ... | E | 19·96 | 20·02 | 20·19 | 20·30 | 20·34 | 20·35 † | 20·35 † |
| | F | 2·66 | 2·87 | 3·51 | 4·22 | 5·45 | 6·12 | 12·74 |

* Loss required for removal of $2H_2O$ = 13·96%.
† Loss required for removal of $2H_2O + 1NH_3$ = 20·56%.

(1*b*) As method 1*a*, but applied to carbonatotetramminocobalt(III) nitrate. However, on the addition of nitric acid (initially) crystals of the diaquotetramminocabalt(III) nitrate separated.

(2*a*) Duff's method "for salts derived from carbonatopentamminocobaltic nitrate,"[2] but, since in no case did concentration of the final solution yield a crop of crystals (even on standing), this solution was concentrated and then neutralised with dilute sodium hydroxide solution before addition of a solution (20 ml.) of $Na_2HPO_4,12H_2O$ (6·7 g.) and NaOH (0·75 g.); in an attempt to minimise any tendency for aquo-complexes to be formed, the temperature to which the solution containing the carbonato-complex and phosphoric acid was heated was changed from 60° (as in ref. 2) to 45°, but without any effect on the nature of the product; red crystals (Compound B) which were identical with those of Compound A were obtained.

(2*b*) Attempts to use method (2*a*) with carbonatotetramminocobalt(III) nitrate as starting material led to the precipitation of cobalt(III) oxide during the concentration of the acid solution; the method was modified as follows: 5 g. of the tetrammino-nitrate were heated with 30 ml. of 1M-phosphoric acid at 45°; when effervescence had ceased, the solution was cooled and excess of acid was neutralised with 2N-sodium hydroxide before the addition of a solution (20 ml.) of $Na_2HPO_4,12H_2O$ (6·7 g.) and NaOH (0·75 g.); violet crystals (3·5 g.) of the *Compound* C separated {Found: Co, 23·66; $NH_3$, 26·46; $PO_4$, 49·36 (total), 14·49 (ionisable); $H_2O$, 0·50. $[Co(NH_3)_4HPO_4]_3PO_4$ requires Co, 23·06; $NH_3$, 26·74; $PO_4$, 50·11 (total), 12·53 (ionisable); $H_2O$, 0%}.

(2*c*) As method (2*a*), but with triaquotriamminocobalt(III) chloride (5 g.) or trinitrotriamminocobalt(III) (5 g.) as starting material; it was necessary to avoid heating the acid solution otherwise the complex was decomposed; however, on neutralisation of the free acid present with sodium hydroxide, cobalt(II) ammonium phosphate separated.

(3*a*) To a solution obtained by warming to 60° 5 g. of either chloropentamminocobalt(III) chloride or nitratopentamminocobalt(III) nitrate with 100 ml. of 30% aqueous ammonia, a second solution (25 ml.) containing 4·8 g. of $Na_2HPO_4,12H_2O$ and 0·5 g. of NaOH was added, and the mixed solution cooled; red crystals (3 g.; Compound D) separated {Found: Co, 19·95; $NH_3$, 29·03; $PO_4$, 32·38 (total and ionisable); $H_2O$, 18·64. Calc. for $[Co(NH_3)_5H_2O]PO_4,2H_2O$: Co, 20·11; $NH_3$, 29·05; $PO_4$, 32·41 (total and ionisable); $H_2O$, 18·45%}; when left in a desiccator over concentrated sulphuric acid, this aquopentamminocobalt phosphate dihydrate lost one molecule of water.

(3*b*) To a solution of 5 g. of a tetrammino-salt in 50 ml. of water a solution (25 ml.) of 2·64 g. of $(NH_4)_2HPO_4$ was added, and the mixed solution kept at 0° for 2 days; when carbonatotetramminocobalt(III) nitrate was used as starting material, purple crystals (2·5 g.; Compound E) separated slowly {Found: Co, 22·54; $NH_3$, 27·55; $PO_4$, 36·24 (total), 0 (ionisable); $H_2O$, 13·27. Calc. for $[Co(NH_3)_4PO_4],2H_2O$: Co, 22·84; $NH_3$, 26·38; $PO_4$, 36·81 (total), 0 (ionisable); $H_2O$, 13·96%}; both molecules of water were lost when this phosphatotetramminocobalt dihydrate was left in a desiccator over concentrated sulphuric acid. When *cis*-chloraquotetramminocobalt(III) sulphate was the starting material, a red-purple powder (4 g.) of the compound F separated rapidly as soon as the solution was cooled {Found: Co, 22·30; $NH_3$, 26·66; $PO_4$, 36·85 (total and ionisable); $H_2O$, 14·19. Calc. for $[Co(NH_3)_4(H_2O)_2]PO_4$: Co, 22·84; $NH_3$, 26·38; $PO_4$, 36·81 (total and ionisable); $H_2O$, 13·96%}.

(3*c*) The method just described, when applied to 5-g. quantities of the triammino-complexes, triaquotriamminocobalt(III) chloride or trinitrotriamminocobalt(III) yielded in each case cobalt(II) ammonium phosphate.

(4) The action of heat (at 70°, 90°, or 100°; see Table 3) on the aquopentamminocobalt(III) phosphates (Compounds A and D) or diaquotetramminocobalt(III) phosphate (Compound F) did not achieve complete removal of water before loss of ammonia commenced.

(5) Attempts to effect the oxidation of cobalt(II) phosphate in the presence of ammonium phosphate and of free ammonia, either by atmospheric oxygen or by hydrogen peroxide under conditions suggested by consideration of refs. 6. 9, 10, 11, and 13, gave cobalt(II) ammonium phosphate.

## DISCUSSION

The analytical results show that none of the pentammino-compounds prepared (A, B, or D) contained the phosphate group as a ligand. In fact all three appear to be identical ($[Co(NH_3)_5H_2O]PO_4$,1 or $2H_2O$) except that Compound D contains an extra molecule of water of crystallisation. The inference that compound D is an aquopentamminocobalt(III) phosphate dihydrate is supported by a study of its absorption spectrum, which resembles that of aquopentamminocobalt(III) chloride (Table 2). Its molar conductance (Table 1), for which we found a rather higher value than that reported by Klement,[4] appears to accord rather better, however, with the formation of 3 or 4 ions in solution than with the formation of 2 (as required by the formula), but this might arise from the reactions

$$PO_4^{3+} + H_2O \rightleftharpoons HPO_4^{2-} + OH^- \qquad (1)$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^- \qquad (2)$$

The marked ease with which compounds A, B, and D lost ammonia on being heated (Table 3), together with the fact that this occurred even before all the water of crystallisation had been driven off, made it impossible to prepare the corresponding phosphato-complexes from them by the conventional method.[14]

From our results Klement's doubts [4] about Duff's report [2] of the formation of a phosphatopentamminocobalt(III) complex seem to be justified. From the failure of all the attempts to prepare them, it is evident that the phosphatopentamminocobalt(III) complexes must be extremely labile and be converted readily into the corresponding aquopentammino-phosphates $[Co(NH_3)_5H_2O]PO_4,nH_2O$ ($n = 1$ or 2).

Of the three tetrammino-compounds, E and F appear from the analyses, taken in conjunction with the conductometric (Table 1) and heating (Tables 3 and 4) experiments, to be the hydrate isomers $[Co(NH_3)_4PO_4],2H_2O$ and $[Co(NH_3)_4(H_2O)_2]PO_4$, both of which have been reported before,[4] although the direct preparation of the first of these from a

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[14] Emeléus and Anderson, " Modern Aspects of Inorganic Chemistry," Routledge and Kegan Paul, London, 1952 (revised edn.), p. 108.

tetrammino-complex had not been achieved previously. The essential differences between these compounds have now been clearly established from the studies of ionisable phosphate present, molar conductances (Table 1), absorption spectra (Table 2), and behaviour when heated (Tables 3 and 4).

The molar conductance of Compound F, like that of Compound D, is higher than expected for a compound giving two ions (Table 1), probably for the same reason (eqns. 1 and 2). However, the effect here is not so marked, possibly owing to interaction between the hydroxyl ions thus formed and the complex itself:

$$[Co(NH_3)_4(H_2O)_2]^{3+} + OH^- \rightleftharpoons [Co(NH_3)_4(OH)H_2O]^{2+} + H_2O \quad . \quad . \quad (3)$$

The small conductance found for Compound E might arise from a slight hydrolysis, which would convert it into Compound F. The very low solubility of this compound (even in the anhydrous state) in any suitable solvent makes the determination of its molecular weight by cryoscopic or similar methods impracticable. However, the following considerations suggest that as it exists in solution it should be assigned a monomeric structure with a four membered chelate ring (I).

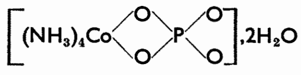
(1) The failure of both Klement[4] and ourselves to obtain pentammino-complexes containing a unidentate phosphate ligand, which would suggest that the phosphato-complexes are stable only when the phosphate group occupies two co-ordination positions; further, these must both be on the same cobalt atom, for if the formation of two co-ordinate links by the phosphate group, rather than chelation, were the important factor, then the formation of pentammino-complexes such as $[(NH_3)_5\text{-}Co\text{-}(PO_4)\text{-}Co\text{-}(NH_3)_5]^{3+}$ would be expected, but no evidence for these has been obtained.

(2) The general similarity of the absorption spectrum of Compound E to that of the carbonatotetramminocobalt(III) nitrate (Table 2) in which the carbonato-group is generally assumed to act as a chelate[15]—an assumption supported by the identification of the green anionic complex ion in the Field–Durrant solution as $[Co(CO_3)_3]^{3-}$;[16] the fact that the phosphato- and carbonato-tetrammino-complexes alone of all those studied possess strong absorption peaks at about 7000 Å (Table 2) strongly supports the assumption that they have similar structures.

(3) The direct formation of compound E from the carbonato-tetramminocobalt(III) nitrate in which the carbonato-group presumably occupies two *cis*-positions [see (2) above].

Our results for the absorption spectrum of the carbonatotetramminocobalt(III) nitrate accord with those of Yoneda and Kobayashi[17] with respect to the peaks at 3600 and 5250 Å. Our studies did not extend to the region of their peak at 2540 Å (since most of our solutions contained phosphate which absorbs strongly in this region) nor did theirs extend to the region of the peak at 7000 Å.

It is noteworthy that, whilst Compounds E and F are both prepared *by the same method* from complexes which both have a *cis*-structure, they are so different in constitution. A possible explanation lies in the fact that of the reactions

(I) 

$$[Co(NH_3)_4CO_3]^+ \xrightarrow{PO_4^{3-}} [Co(NH_3)_4PO_4] \quad . \quad (4)$$

$$[Co(NH_3)_4CO_3]^+ \xrightarrow{2H_2O} [Co(NH_3)_4(H_2O)_2]^{3+} \quad . \quad (5)$$

$$[Co(NH_3)_4(H_2O)Cl]^{2+} \xrightarrow{PO_4^{3-}} [Co(NH_3)_4PO_4] \quad . \quad (6)$$

$$[Co(NH_3)_4(H_2O)Cl]^{2+} \xrightarrow{H_2O} [Co(NH_3)_4(H_2O)_2]^{3+} \quad . \quad (7)$$

both (4) and (5) are two-stage processes, so that (5) is not more favoured than (4), whilst (7) is a single-stage substitution and is thus more favoured than the two-stage substitution of (6).

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[15] Bailar (Editor), "Chemistry of the Co-ordination Compounds," Reinhold Publishing Corp., New York, 1956, pp. 32, 33, 226.

[16] McCutcheon and Schuele, *J. Amer. Chem. Soc.*, 1953, **75**, 1845.

[17] Yoneda and Kobayashi, *J. Chem. Soc. Japan*, 1954, **75**, 1192.

Compound C, like Compound E, contains some non-ionisable phosphate and from the analyses (Table 1) appears to be $[Co(NH_3)_4HPO_4]_3PO_4$. Its molar conductance (Table 2) is also consistent with its yielding four ions; apparently any tendency for this to be increased by hydrolysis of the phosphate ion [equations (1) and (2)] is offset by ionisation of the proton on the phosphato-group:

$$[Co(NH_3)_4HPO_4]^+ + OH^- \rightleftharpoons [Co(NH_3)_4PO_4] + H_2O \quad . \; . \; . \quad (8)$$

The similarity of its absorption spectrum (Table 2) to that of the diaquotetramminocobalt(III) phosphate (Compound F) is surprising, but may be attributed to a rapid hydrolysis, which would convert it into Compound F, in the presence of the acid solvent used in the absorption-spectrum studies. It is evidently more stable in the neutral solutions in which the determinations of ionisable phosphate and conductivity measurements were made.

No triammino-complexes containing phosphato-groups were obtained from the reactions in solution, but the loss in weight in Compound E after prolonged heating at 110° corresponds closely to the loss of $2H_2O + NH_3$, which would indicate $[Co(NH_3)_3PO_4]$ as the product. It seems unlikely, however, that the phosphate group will cccupy three co-ordination positions and the product may be more complex.

Riley [18] attributed the greater tendency of carbonate than of sulphate to occupy two co-ordination positions to the lower effective charge on the central atom in the carbonate ion, which will lead to looser binding of the electrons on the oxygen atoms and hence to their more ready utilisation in co-ordination; with the higher effective charge on the sulphur in the sulphate ion the electrons on the oxygen atoms are more tightly held. If this simple treatment, which neglects both the state of hybridisation of the central atom and the bond type (*i.e.*, possible partial double-bond character), is accepted, then the phosphate ion should show properties between those of the other two—a deduction which is in general accord with our observations. However, with respect to its ability to occupy one co-ordination position on a cobalt atom phosphate is less effective than either carbonate or sulphate.

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[18] Riley, *J.*, 1928, 2985.