17. *Cobalt Phosphates. Part II.*[1] *Phase-diagram Studies of Some Cobalt*(III) *Ammine Phosphates.*

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Studies of the systems $[Co(NH_3)_6]_2O_3$–P_2O_5–H_2O at 25° and $[Co(NH_3)_5H_2O]_2O_3$–P_2O_5–H_2O at 0° and 25°, have shown a similarity between them which indicates that tervalent cations are present in each.

The diaquotetrammine phosphates behave differently. Their solutions in aqueous phosphoric acid were unstable and the complex decomposed if the phosphoric oxide content was less than 18% and the solutions were too viscous for a solid phase to separate if more than 35% of phosphoric oxide was present. Between these limits a solid phase separated which was best represented by the components $[Co(NH_3)_4(HPO_4)]_2O$–P_2O_5–H_2O, and evidence is presented to show that under these conditions phosphatotetrammine ions, with a bidentate phosphato-group, are present in both liquid and solid phases.

IN Part I,[1] where previous work on amminecobalt(III) phosphates and amminephosphatocobalt(III) complexes was reviewed, it was shown that, whilst phosphatotetramminecobalt(III) compounds could be separated from aqueous solution, yet all attempts to prepare phosphatopentamminecobalt(III) complexes yielded aquopentamminecobalt(III) phosphates instead. The tetrammine complexes appeared to contain a bidentate phosphate group, which might account for their having greater stability than the pentamine complexes where the phosphate would be present as a unidentate group. Evidently, if such a unidentate group is introduced it is readily displaced by water molecules from the solvent. Hence it seemed of interest to ascertain if the reverse process could be achieved, namely, the displacement of water molecules from the co-ordination sphere by phosphate groups, by the use of concentrated solutions of phosphoric acid.

A convenient method of approach was offered by the study of the systems aquopentamminecobalt(III) oxide–phosphoric oxide–water and the corresponding diaquotetrammine system, from which evidence might be obtained of the stage at which replacement of aquo- by phosphato-groups occurred. The corresponding hexammine system was studied at the same time for comparison. These systems are presumably thermodynamically unstable,[2] but, except for one region of the diagram for the tetrammine system at 25°, metastable states were encountered of sufficient stability for solid phases of definite compositions to persist in contact with solutions for many weeks.

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[1] Part I, Daniel and Salmon, *J.*, 1957, 4207.

[2] Taube, *Chem. Rev.*, 1952, **50**, 69.

EXPERIMENTAL

Starting Materials.—Hexamminecobalt(III) phosphate dihydrate was prepared from the corresponding chloride by a method similar to that used for the aquopentammine phosphate (method no. 3a in Part I [1]). The aquopentammine and diaquotetrammine phosphates were prepared as before: [1] it was unnecessary to purify the *cis*-chloroaquotetramminecobalt(III) sulphate used in the latter preparation.

Phase Diagrams.—The methods used were those of Jameson and Salmon.[3] The solutions of both the aquopentammine and the diaquotetrammine phosphate were prepared at the appropriate temperature by addition, to solutions of phosphoric acid, of portions of the starting material until an undissolved residue remained. With the hexammine phosphate some saturated solutions prepared at 40—50° deposited a solid phase on cooling; otherwise the method just described was used.

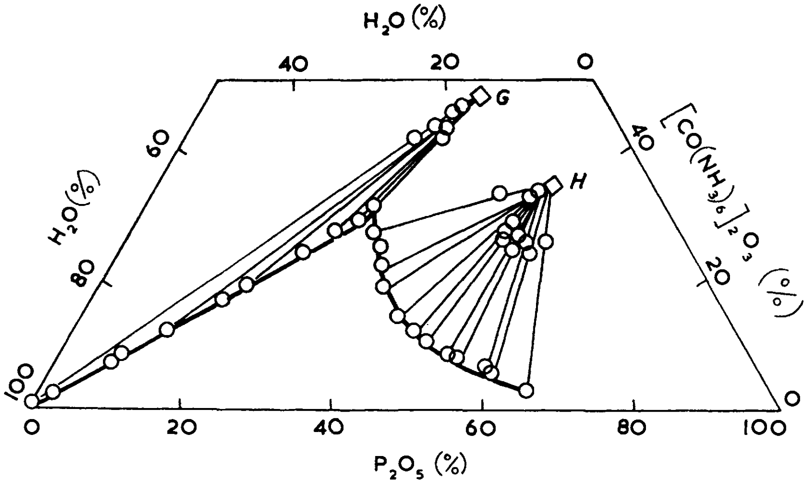
Analytical Methods.—These were described in Part I.[1]

Additional Examination of the Solid Phases.—The solid was freed as completely as possible from the solution adhering to it after filtration, either by washing with water (if the stability of the compound permitted) or by pressing between filter-papers. Solutions of known concentration were then prepared for spectrophotometric and, if possible, conductivity measurements.

TABLE 1. *System* $[Co(NH_3)_6]_2O_3$–P_2O_5–H_2O *at* 25°.

Solution (%)		Solid (%)		Solution (%)		Solid (%)	
$[Co(NH_3)_6]_2O_3$	P_2O_5	$[Co(NH_3)_6]_2O_3$	P_2O_5	$[Co(NH_3)_6]_2O_3$	P_2O_5	$[Co(NH_3)_6]_2O_3$	P_2O_5
0·663	0·533	40·95	30·80	24·11	34·88	32·25	49·88
2·269	3·036	44·24	33·28	21·24	36·35	32·89	50·92
6·85	8·03	43·68	32·48	18·12	38·60	32·35	50·10
7·95	8·78	43·50	32·88	13·79	42·36	28·67	50·02
11·53	13·01	44·98	33·80	11·85	45·41	27·00	49·60
16·20	18·21	44·23	33·22	9·98	47·90	25·45	50·09
18·50	19·97	42·60	32·51	8·34	51·33	26·41	51·74
23·48	24·90	45·90	34·45	7·68	53·16	23·98	52·23
26·88	27·13	46·00	34·51	6·23	57·71	25·66	53·10
28·46	29·90	42·21	34·12	5·33	58·77	23·46	54·41
30·75	30·62	40·86	34·86	2·60	65·04	25·40	55·94
26·63	32·54	32·74	49·19				

FIG. 1. *The system* $[Co(NH_3)_6]_2O_3$–P_2O_5–H_2O *at* 25°.



Results.—*Hexamminecobalt*(III) *system.* The following new *compounds* (which for convenience have been designated by letters, following on from Part I) were found as solid phases at 25° (Table 1, Fig. 1): *G* $[Co(NH_3)_6]_2O_3,2P_2O_5,7H_2O$, as orange needles, and

H $[Co(NH_3)_6]_2O_3,4P_2O_5,9H_2O$,

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[3] Jameson and Salmon, *J.*, 1954, 4013; 1955, 360.

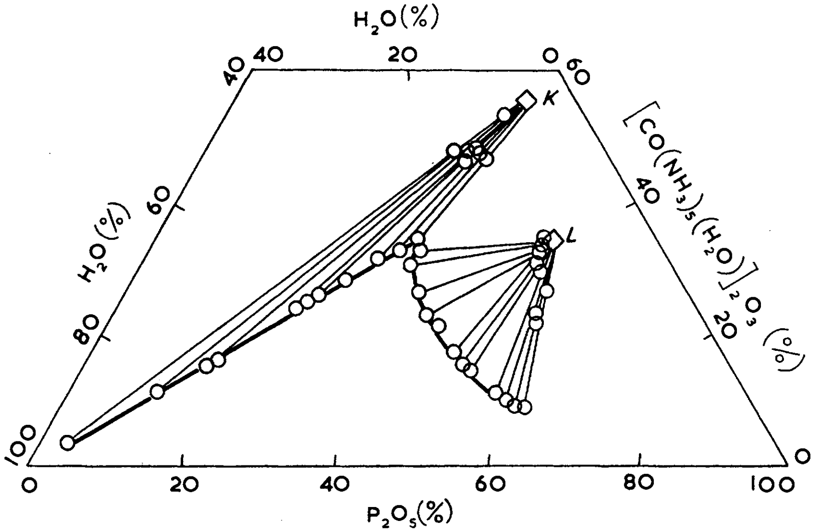
as red, water-soluble crystals which slowly disintegrated on exposure to air. If the solutions which had been in contact with these solid phases were filtered and diluted and the acid present neutralized with aqueous ammonia, a third new *compound*, *J*, separated as fine insoluble orange crystals {Found: Co, 18·2; NH_3, 32·6; PO_4 (total, all ionizable), 44·6. $2[Co(NH_3)_6]_2O_3,3P_2O_5,6H_2O$ requires Co, 18·2; NH_3, 32·1; PO_4, 44·7%}.

Pentamminecobalt(III) *system*. For the range of solutions up to 60% of P_2O_5 at 0° the following new *compounds* were indicated (Table 2, Fig. 2): *K* as fine, insoluble, red crystals $5[Co(NH_3)_5H_2O]_2O_3,9P_2O_5,12H_2O$; *L* as large, irregular, red, water-soluble crystals $[Co(NH_3)_5(H_2O)]_2O_3,4P_2O_5,9H_2O$. The latter are unstable when dry.

TABLE 2. *System* $[Co(NH_3)_5H_2O]_2O_3$–P_2O_5–H_2O *at* 0°.

Solution (%)		Solid (%)		Solution (%)		Solid (%)	
$[Co(NH_3)_5H_2O]_2O_3$	P_2O_5	$[Co(NH_3)_5H_2O]_2O_3$	P_2O_5	$[Co(NH_3)_5H_2O]_2O_3$	P_2O_5	$[Co(NH_3)_5H_2O]_2O_3$	P_2O_5
3·795	3·59	47·95	32·57	30·41	35·23	33·72	51·38
11·54	11·31	53·11	36·40	26·53	38·48	33·08	51·85
15·21	16·26	36·73	33·42	22·98	41·20	33·86	52·07
16·12	16·70	48·02	35·34	21·31	43·13	33·12	51·42
24·00	23·20	48·14	35·00	17·56	47·32	32·47	51·63
25·10	24·33	48·52	35·35	15·36	49·60	30·62	51·91
26·30	25·48	46·86	34·96	14·21	50·91	31·51	52·03
28·30	27·91	48·40	35·35	11·47	56·00	29·60	52·85
31·40	31·67	46·78	35·01	9·98	57·82	23·13	55·51
32·70	32·68	47·79	36·37	8·87	59·85	21·64	56·10
34·20	34·27	46·72	37·58	8·92	60·97	26·38	55·23
32·88	35·12	33·99	51·72				

FIG. 2. *The system* $[Co(NH_3)_5(H_2O)]_2O_3$–P_2O_5–H_2O *at* 0°.



For the same system at 25° (Table 3, Fig. 3) a new *compound M*,

$$[Co(NH_3)_5H_2O]_2O_3,2P_2O_5,3H_2O$$

and compound *L* were found as solid phases. If, after they had been separated from the solid phases, the supernatant solutions were diluted and an excess of aqueous ammonia added to them crystals of compound A^1 separated {Found: Co, 21·3; NH_3, 31·1; PO_4 (total, all ionized), 34·4. Calc. for $[Co(NH_3)_5H_2O]PO_4,H_2O$: Co, 21·4; NH_3, 31·0; PO_4, 34·5%}.

Tetramminecobalt(III) *system*. At 25° decomposition of the tetramminecobalt(III) ion occurred with solutions containing less than 15% of P_2O_5, and no solid could be made to separate from solutions containing more than 35% of P_2O_5. For the solutions in the range 15—35% of P_2O_5 (total) it proved possible to represent the analytical data in terms of the components $3[Co(NH_3)_4(HPO_4)]_2O$–P_2O_5–H_2O (Table 4, Fig. 4) when the dark purple crystals of the solid phase were identified as compound *N*, $3[Co(NH_3)_4(HPO_4)]_2O,P_2O_5,24H_2O$ (a hydrate of compound *C*, ref. 1), but not in terms of the components $[Co(NH_3)_4(H_2O)_2]_2O_3$–$P_2O_5$–$H_2O$. On addition of dilute aqueous ammonia to solutions which had been in contact with compound *N*, compound *C* was obtained {Found: Co, 23·2; NH_3, 26·85; total PO_4, 49·7; ionized PO_4, 14·0; H_2O, 0·2. Calc. for $[Co(NH_3)_4(HPO_4)]_3PO_4$: Co, 23·1; NH_3, 26·7; total PO_4, 50·1; ionized PO_4, 12·5%}. Addition of dilute aqueous ammonia to the solutions containing over 35% of

TABLE 3. *System* $[Co(NH_3)_5H_2O]_2O_3$–P_2O_5–H_2O *at* 25°.

Solution (%)		Solid (%)		Solution (%)		Solid (%)	
$[Co(NH_3)_5H_2O]_2O_3$	P_2O_5	$[Co(NH_3)_5H_2O]_2O_3$	P_2O_5	$[Co(NH_3)_5H_2O]_2O_3$	P_2O_5	$[Co(NH_3)_5H_2O]_2O_3$	P_2O_5
22·30	22·87	44·91	35·61	34·42	35·60	50·32	39·28
23·07	23·12	29·05	26·29	35·87	37·23	46·29	39·37
23·96	24·34	27·89	26·64	35·67	38·67	36·98	50·12
27·92	27·60	49·02	38·19	29·42	42·09	31·85	49·09
27·84	28·48	48·97	38·21	22·99	47·93	31·93	52·82
29·98	30·30	32·63	31·70	18·21	54·64	31·17	53·79

TABLE 4. *System* $[Co(NH_3)_4HPO_4]_2O$–P_2O_5–H_2O *at* 25°.

Solution (%)		Solid (%)		Solution (%)		Solid (%)	
$[Co(NH_3)_4HPO_4]_2O$	Free P_2O_5	$[Co(NH_3)_4HPO_4]_2O$	Free P_2O_5	$[Co(NH_3)_4HPO_4]_2O$	Free P_2O_5	$[Co(NH_3)_4HPO_4]_2O$	Free P_2O_5
56·68	4·11	68·63	6·03	55·74	14·72	67·27	9·21
56·13	5·28	70·94	6·42	56·18	16·88	68·31	9·56
56·72	6·52	65·20	6·51	57·86	17·45	61·11	15·03
55·79	8·43	68·97	2·78	57·35	19·62	64·43	12·18
55·98	8·92	65·83	7·08	58·49	20·83	64·62	13·02
56·68	11·86	69·20	7·31	58·57	22·57	68·07	12·15
55·63	12·66	68·24	8·28				

FIG. 3. *The system* $[Co(NH_3)_5(H_2O)]_2O_3$–P_2O_5–H_2O *at* 25°.

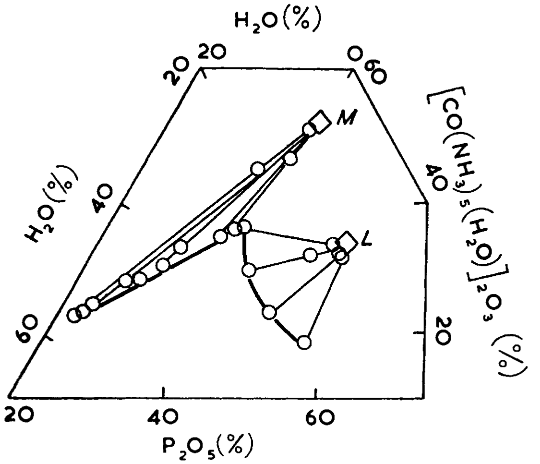
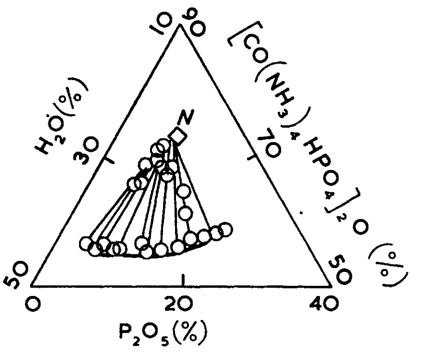


FIG. 4. *The system* $[Co(NH_3)_4(HPO_4)]_2O$–P_2O_5–H_2O *at* 25°.



P_2O_5, from which no solid phase had separated, caused the precipitation of dark purple crystals of a new *compound* P {Found: Co, 19·0; NH_3, 22·4; total PO_4, 46·1; ionized PO_4, 16·6; H_2O, 12·5. $[Co(NH_3)_4(HPO_4)]_2,HPO_4,4H_2O$ requires Co, 19·2; NH_3, 22·1; total PO_4, 46·3; ionized PO_4, 15·4; H_2O, 11·7%}; Λ_{2478} = 312 for *P* indicates the probable presence of 3 ions in solution.

DISCUSSION

The Hexammine- and Pentammine-cobalt(III) *Systems*.—The marked similarity of these two systems (Figs. 1, 2, and 3) and of the solid phases separating from them leads us to infer that in each case the same type of ion (*i.e.*, a tervalent one) is present. The conclusion to be drawn is that, in the pentammine system, the ion present is the aquopentamminecobalt(III). Support is provided in the separation from the aqueous phase of this system of the previously known aquopentamminecobalt(III) phosphate (compound *A*, ref. 1) on addition of ammonia to the liquid. The similarity of the absorption spectra of compound *L* and of the aquopentammine phosphate (Table 5) also suggests that the same cation is present in each. It is evident that even at high concentrations of phosphate in solution (*e.g.*, up to 50% of P_2O_5, Tables 1—3) the phosphato-group is unable to displace the aquo-group from the pentammine complex.

The Tetramminecobalt(III) *System.*—This system differed from the other two in that attempts to represent it in terms of the same type of components [*i.e.*, on the assumption that the cation was the diaquotetramminecobalt(III) ion] led to tie lines that crossed irregularly without meeting at any given point. Trial and error showed that it could be satisfactorily represented by using the components $[Co(NH_3)_4(HPO_4)]_2O,P_2O_5$ and H_2O (Fig. 4). This indicates that, as soon as the solutions contain sufficient acid to stabilize the tetrammine ion, the two aquo-groups are displaced by a phosphate group. In support of this, the phosphate tetrammine compounds $[Co(NH_3)_4(HPO_4)]_3PO_4$ (compound *C*, ref. 1) and $[Co(NH_3)_4(HPO_4)]_2HPO_4$ (compound *P*) can be made to separate from aqueous phases of this system. A solution of compound *P* in 12M-phosphoric acid shows the strong peak at about 6950 Å that characterizes compound *E* ($[Co(NH_3)_4PO_4],2H_2O$, ref. 1) and the carbonatotetrammine ion, but like solutions of compound *C* it is rapidly hydrolyzed in M/100-phosphoric acid, and this peak does not appear in such solutions (Table 5).

TABLE 5. *Absorption spectra for visible and ultraviolet regions.*

Compound	$\lambda_{max.}$	*E*	$\lambda_{max.}$	*E*	$\lambda_{max.}$	*E*
* $[Co(NH_3)_5(H_2O)]_2O_3,4P_2O_5,9H_2O$ (compound *L*)	3450	42	4820	44	—	—
† $[Co(NH_3)_5H_2O]PO_4,2H_2O$ (compound *D*, ref. 1)	3420	43	4850	48	—	—
‡ $[Co(NH_3)_4(HPO_4)]_2HPO_4,4H_2O$ (compound *P*)	§	§	5260	73	6900	33·5
† $[Co(NH_3)_4(PO_4)],2H_2O$ (compound *E*, ref. 1)	3650	23	5220	37	6950	61
* $[Co(NH_3)_4(CO_3)]NO_3$	3500	§	5260	57	7040	26

* Solvent water. † Solvent M/100-H_3PO_4. ‡ Solvent 12M-H_3PO_4. § Not recorded.

Apparently, the ion containing the monohydrogen phosphate ligand $[Co(NH_3)_4(HPO_4)]^+$ is more susceptible to hydrolysis than the neutral complex $[Co(NH_3)_4(PO_4)]$, although there is no very obvious reason why this should be so.

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