376. *Ammineruthenium*(III) *Phosphates.*

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A number of ammineruthenium(III) complex compounds containing phosphate have been isolated and their compositions established by analysis, conductivity measurements, ion-exchange methods, and dehydration studies, as $[Ru(NH_3)_6]PO_4,2H_2O$, $[Ru(NH_3)_4PO_4],2H_2O$, $[Ru(NH_3)_4(H_2O)_2]PO_4$, $[Ru(NH_3)_5(OH)]HPO_4,H_2O$, and $[Ru(NH_3)_4(NO)(OH)]HPO_4,H_2O$. Attempts to introduce the phosphate group as ligand into the hexammine, pentammine, and triammine have failed. Only one phosphatotetrammine complex was obtained and this had properties different from those of the isomeric diaquotetetrammine phosphate.

Although several oxo-complexes of ruthenium(III) with various ligands, such as oxalate and acetylacetone, are known, no phosphato-complexes have been reported. Accordingly it seemed of interest to extend the work of Daniel and Salmon,[1] who showed that in cobalt(III)-ammine complexes the phosphate group can apparently act as a bidentate, but not as a unidentate, ligand, to studies of phosphatoruthenium(III)-ammine complexes.

The isolation of ruthenium phosphate from solutions of ammineruthenium(III) complexes was attempted by using as starting materials the known ammineruthenium(III) chlorides. Compounds in the series from the hexammine to the tetrammine were used.

Experimental and Results

Starting Materials.—The compounds $[Ru(NH_3)_6]Cl_3$ (ref. 2), $[Ru(NH_3)_5Cl]Cl_2$ (ref. 3) as $[Ru(NH_3)_5OH]Cl_2$ (ref. 4), $[Ru(NH_3)_4Cl_2]Cl$ (ref. 4), and $[Ru(NH_3)_4(NO)(OH)]Cl_2$ (ref. 5) were prepared essentially by the methods given in the references. Except for $[Ru(NH_3)_5OH]Cl_2$ which was used in aqueous solution, they were isolated and on analysis were found to be pure.

Phosphate Complexes.—The phosphates were prepared by treating an aqueous solution of the corresponding ammine chloride with one of disodium hydrogen or sodium dihydrogen phosphate. The precipitates were collected, washed with dilute aqueous ammonia, and allowed to dry in the air. They were sparingly soluble in water and organic solvents. Compounds A, B, and C described below were insoluble even in strong acids; compounds D and E dissolved in dilute mineral acids.

Analytical Methods.—The following procedures were used for both starting materials and products: (1) Ruthenium, gravimetrically as metal after reduction with hydrogen; compounds containing only volatile components apart from ruthenium were directly ignited with hydrogen; those also containing phosphate were first decomposed by boiling sodium hydroxide solution, to give ruthenium hydroxide which was filtered off and then reduced to the metal. (2) Chloride, gravimetrically as silver chloride. (3) Ammonia, by evolution and absorption in an excess of standard acid. (4) Nitrosyl group, as ammonia after reduction with Devarda's alloy. (5) Phosphate, gravimetrically as ammonium phosphomolybdate. (6) Water and hydroxyl group, by difference.

Hexammineruthenium Phosphate Dihydrate (*Compound A*).—Hexammineruthenium chloride (3 g.) was dissolved in the minimum amount of water, and a solution of disodium hydrogen phosphate dihydrate (1·2 g.) in water (10 ml.) was added in the cold, giving an immediate precipitate. The pale yellow *complex* was collected after some time {Found: Ru, 30·2; NH_3, 30·05; PO_4, 28·6; H_2O, 12·3. $[Ru(NH_3)_6]PO_4,2H_2O$ requires Ru, 30·3; NH_3, 30·45; PO_4, 28·1; H_2O, 10·95%}.

Phosphatotetrammineruthenium Dihydrate (*Compound B*).—To *cis*-dichlorotetrammineruthenium chloride (3 g.) in water (50 ml.) a solution of sodium dihydrogen phosphate dihydrate (1·2 g.) in water (10 ml.) was added in the cold, followed by dilute aqueous ammonia (5 ml.).

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[1] Daniel and Salmon, *J.*, 1957, 4207; 1961, 86.

[2] Lever, Ph.D. Thesis, London, 1955.

[3] Gleu and Cuntze, *Z. anorg. Chem.*, 1938, **237**, 187.

[4] Gleu and Breuel, *Z. anorg. Chem.*, 1938, **237**, 335.

[5] Werner, *Ber.*, 1907, **40**, 2614.

The mixture was kept cold and the bright yellow crystals of *complex* were filtered off after a few days {Found: Ru, 33·65; NH_3, 22·2; PO_4, 31·9; H_2O, 12·6. $[Ru(NH_3)_4]PO_4,2H_2O$ requires Ru, 33·8; NH_3, 22·6; PO_4, 31·6; H_2O, 12·0%}.

Diaquotetrammineruthenium Phosphate (*Compound C*).—This *salt* was prepared in a similar manner to compound B except that the mixture was boiled with ammonia for an hour after mixing. It may also be prepared by boiling a suspension of compound B in aqueous ammonia {Found: Ru, 33·6; NH_3, 22·4; PO_4, 32·1; H_2O, 11·9. $[Ru(NH_3)_4(H_2O)_2]PO_4$ requires Ru, 33·8; NH_3, 22·6; PO_4, 31·6; H_2O, 12·0%}.

Hydroxotetramminenitrosoruthenium Phosphate Hydrate (*Compound D*).—$[Ru(NH_3)_4(NO)(OH)]Cl_2$ (3 g.) was dissolved in water (25 ml.) and a solution of disodium hydrogen phosphate (1·5 g.) in water (15 ml.) was added. The mixture was heated and set aside for crystallization. An orange-yellow *complex* was precipitated {Found: Ru, 30·75; NH_3, 20·35; PO_4, 29·4; H_2O, 5·25; NO, 8·85; OH, 5·4. $[Ru(NH_3)_4(NO)(OH)]HPO_4,H_2O$ requires Ru, 30·6; NH_3, 20·6; PO_4,29·1; H_2O, 5·45; NO, 9·1; OH, 5·15%}.

Hydroxopentammineruthenium Phosphate Hydrate (*Compound E*).—$[Ru(NH_3)_5Cl]Cl_2$ (3 g.) was heated with dilute aqueous ammonia until dissolved. This treatment converted it into $[Ru(NH_3)_5OH]Cl_2$. A solution of sodium dihydrogen phosphate dihydrate (1·2 g.) in water (10 ml.) was added and the mixture kept cold. The yellow precipitated *complex* was filtered off {Found: Ru, 31·9; NH_3, 26·55; PO_4, 30·55; H_2O, 5·65; OH, 5·3. $[Ru(NH_3)_5(OH)]HPO_4,H_2O$ requires Ru, 31·85; NH_3, 26·8; PO_4, 30·3; H_2O, 5·55; OH, 5·4%}. When chloropentammineruthenium chloride was treated with a solution of disodium phosphate or phosphoric acid no precipitation occurred in the cold, and no homogeneous product was isolated after heating.

When $[Ru(NH_3)_4(OH)]Cl_2$ was treated with phosphoric acid, the formation of $[Ru(NH_3)_4PO_4]$ was expected, similar to that of $[Ru(NH_3)_4C_2O_4]Cl$ under similar conditions. However, no pure product was obtained.

Dehydration.—The loss in weight of the products was studied by drying them over calcium chloride or concentrated sulphuric acid. Compounds A and B lost 2 mol. of water; compounds D and E lost 1 mol.; compound C lost none.

Ion-exchange.—A method similar to that described by Osborn [6] was used to ascertain whether the phosphate group is ionized in the sparingly soluble complexes. The compound (0·2—0·3 g.) was shaken in water (100 ml.) with DeAcidite FF (2—3 g.; Cl^- form) for a few hours. Gradual dissolution, due to formation of the soluble chloride, indicated the presence of ionized phosphate. Compound B was unchanged after this treatment; compounds A, C, D, and E dissolved.

Conductivity Measurements.—Because of the low solubility of the compounds only their saturated solutions were used for the experiments. The measurements, on fresh and aged solutions, were carried out at 25° with the use of a conventional conductivity cell with an AC Wheatstone bridge circuit. Measurements were also taken on solutions of ammineruthenium(III) chlorides for comparison. In calculating the molar conductance values (Table), it was assumed that the molecular weights were those required by the formulæ assigned.

Conductivity measurements.

		Fresh solutions		Solutions aged for 2 weeks	
Compound	Concn. (M)	Mol. conductance (ohm^{-1} $cm.^2$ $mole^{-1}$)	No. of ions indicated	Mol. conductance (ohm^{-1} $cm.^2$ $mole^{-1}$)	No. of ions indicated
A	$1·4 \times 10^{-3}$	248	2—3	250	2—3
B	$5·4 \times 10^{-4}$	67	0—2	228	2—3
C	$1·1 \times 10^{-3}$	238	2—3		
D	$4·2 \times 10^{-2}$	227	2—3		
E	$2·6 \times 10^{-2}$	235	2—3		

Spectrophotometric Measurements.—These were carried out on solutions of compounds D and E, in nitric acid only since the other phosphate compounds were too sparingly soluble even in acids. Solutions in the range of 0·01—0·05M gave suitable optical-density values with the use of 1 cm. cells. Compound D absorbed strongly around 3950 Å, resembling $[Ru(NH_3)_4(NO)(OH)]Cl_2$ which was studied for comparison. Compound E showed an absorption maximum in the range 3600 Å but a similar absorption peak was not found for $[Ru(NH_3)_5OH]Cl_2$.

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[6] Osborn, *Analyst*, 1953, **78**, 220.

Discussion

In each of the ammineruthenium(III) phosphates prepared there is only one phosphate group per ruthenium atom, and the same products were obtained whether the theoretical amount or an excess of phosphate was used in the preparation. It proved impossible to replace ammonia in any of the ammines although such replacement occurs with other ligands, *e.g.*, chloride and oxalate. Accordingly, the complex $[Ru(NH_3)_6]Cl_3$ yielded only one product, namely, compound A with the phosphate present as an ion.

Attempts to introduce the phosphate as ligand into the pentammines failed. Only one pentammine phosphate, compound E, with ionized phosphate was obtained (see Table). The analytical results allow its formulation as $[Ru(NH_3)_5OH]HPO_4,H_2O$ or $[Ru(NH_3)_5H_2O]PO_4,H_2O$. The latter seems to be improbable as the $[Ru(NH_3)_5H_2O]^{3+}$ ion is stable in strongly acidic solutions only, whilst compound E was precipitated from its solutions at pH ~ 9.

From the experimental evidence, compound D, too, may be represented as $[Ru(NH_3)_4(NO)(OH)]HPO_4,H_2O$ or as $[Ru(NH_3)_4(NO)(H_2O)]PO_4,H_2O$. The first alternative, however, seems to be more likely as the hydroxotetramminenitrosoruthenium(III) ion is very stable and not easily attacked; further, the aquotetramminenitroso-ion is formed only at low pH values, whilst compound D was prepared under slightly basic conditions.

Preparation of phosphato-complexes by heating the corresponding hydroxopentammine phosphate was not possible, as the latter decomposed before the dehydration was completed.

The two tetrammine phosphate complexes, compounds B and C, seem to be hydrate isomers according to the analytical data and dehydration studies. This is supported by their behaviour towards ion-exchange resins and by their conductivities. The molar conductance of compound C indicates the presence of 2—3 ions, whilst the low conductance of compound B suggests that it is non-ionic. The small conductance which is in fact observed with the freshly prepared solutions is evidently due to slow hydrolysis which converts compound B into compound C: $[Ru(NH_3)_4PO_4] + 2H_2O \longrightarrow [Ru(NH_3)_4(H_2O)_2]PO_4$. The conductivity of a solution of B rises steadily with time, becoming approximately the same as that of C after two weeks (Table).

The formation of compounds B and C from the same reagents may be explained by assuming that the phosphate may react with the ammineruthenium(III) solution by either of the two reactions:

$$(1)\quad [Ru(NH_3)_4Cl_2]^+ + HPO_4^{2-} \longrightarrow [Ru(NH_3)_4PO_4]^0 + 2Cl^- + H^+$$

or

$$(2)\quad [Ru(NH_3)_4Cl_2]^+ + 2H_2O \longrightarrow [Ru(NH_3)_4(H_2O)_2]^{3+} + 2Cl^-$$

$$[Ru(NH_3)_4(H_2O)_2]^{3+} + HPO_4^{2-} \longrightarrow [Ru(NH_3)_4(H_2O)_2]PO_4 + H^+$$

Thus, in case (1), the chlorides are directly replaced by the phosphate before hydrolysis occurs, whilst in case (2) the dichlorotetrammine ion is first converted into the diaquotetrammine ion, owing to the temperature rise, and precipitation of the corresponding phosphate follows. The easy conversion of compound B into C proves that of the two isomers the diaquo-complex is the more stable, recalling the behaviour of the similar amminecobalt(III) phosphate complexes.[1]

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