XXXIII.—*The Co-ordination Valency of Aluminium in its Salicylato-derivatives.*

By George Joseph Burrows and Ian William Wark.

Various complex aluminium compounds have been described in the literature. In some, the co-ordination number of aluminium is 4, as in $Na[AlCl_4]$ and the alkali aluminates generally, which Heyrovský (J., 1920, **117**, 1013) concluded were derivatives of $H[Al(OH)_4]$. In others, it is 6, as in cryolite. Various aluminium compounds containing residues of organic acids have been described, *viz.*, three types of oxalato-derivatives (all prepared from aluminium hydroxide): $R[Al(C_2O_4)_2]$, $R_2[Al(C_2O_4)_2(OH)]$, and $R_3[Al(C_2O_4)_3]$* (Rosenheim, *Z. anorg. Chem.*, 1896, **11**, 189); aluminium salts of various organic acids, in particular aluminium hydrogen tartrate, $Al(C_4H_5O_6)_3$, and sodium aluminotartrate, $Na_6[Al(C_4H_3O_6)_3]$ (Goldman, *Biochem. Z.*, 1922, **133**, 459); compounds with pyrocatechol to which are assigned formulæ such as $[Al(C_6H_4O_2)_3]K_2H$, $[Al(C_6H_4O_2)_2]K,C_6H_4(OH)_2,2C_2H_4O_2,9H_2O$ (Weinland and Benzel, *Ber.*, 1914, **47**, 2753).

A study of other complex aluminium compounds seemed desirable for various reasons. Aluminium oxide apparently gives rise to two stable hydroxides with 1 and $3H_2O$, respectively, which may be regarded as $H[Al(OH)_4]$ and $H_3[Al(OH)_6]$. The first would conform to the low atomic number of the metal and to its position in the periodic table, from which one might expect co-ordination compounds resembling those of boron, whilst in the second aluminium shows its resemblance to iron and chromium, and this resemblance is further exemplified by the ease of preparation and stability of the normal oxalato-derivatives, $R_3[Al(C_2O_4)_3]$, which are isomorphous with the corresponding ferri- and chrom-oxalates. This work was therefore undertaken with the view of ascertaining whether in its salicylato-derivatives aluminium resembles chromium and iron, or boron.

Furthermore, at the time this investigation was commenced it was hoped that some asymmetric aluminium compounds would be isolated which could be resolved into optical antipodes; but such a resolution has now been effected by Wahl (*Ber.*, 1927, **60**, 399).

Weinland and Zimmermann (*Arch. Pharm.*, 1917, **255**, 204) have studied the iron salicylato-compounds, and Barbieri (*Atti R. Accad. Lincei*, 1915, **24**, i, 605) has prepared various chromium compounds.

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* In all our attempts to prepare compounds of these three types from aluminium hydroxide we have succeeded in isolating only compounds of the type $R_3[Al(C_2O_4)_3]$. The oxalato-compounds will be discussed in a subsequent communication.

The latter are of particular interest, since chromisalicylic acid is $H[Cr(C_7H_4O_3)_2],3H_2O$ and salts of the type $R[Cr\{(C_7H_4O_3),NH_3\}_2$ were obtained, in which R is an alkali metal. In both these cases the ratio of chromium to salicylic acid is 1 : 2, and the complex ion is accordingly univalent.

The borosalicylates have been shown by Böeseken and his co-workers to be derivatives of $H[B(C_7H_4O_3)_2]$; and by obtaining the *d*- and *l*-strychnine salts, Böeseken and Meulenhoff (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 174) have definitely established the stereochemistry of these compounds.

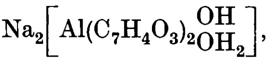
It was expected that aluminium compounds would be obtained corresponding to one or other of the acids $H[Al(C_7H_4O_3)_2]$ and $H_3[Al(C_7H_4O_3)_3]$. Our endeavours to prepare these compounds, however, were unsuccessful, and although we obtained evidence of the existence of the compound $Na_3[Al(C_7H_4O_3)_3]$ and the corresponding ammonium salt, we failed to isolate either in a pure condition. The salts isolated all contain sodium (or its equivalent), aluminium, and salicylic acid in the ratio 2 : 1 : 2, together with solvent of crystallisation. *Aluminosalicylic acid*, obtained from neutral solutions of alum and sodium or ammonium salicylate, on drying in a vacuum has the composition $HAl(C_7H_4O_3)_2,2H_2O$, differing from the chromisalicylic acid of Barbieri (*loc. cit.*) in containing $2H_2O$ instead of $3H_2O$. This would suggest the formula $H[Al(C_7H_4O_3)_2],2H_2O$, corresponding to the ordinary valency of aluminium, and a co-ordination number of 4. Experiment showed, however, that this acid requires 2 equivalents of sodium hydroxide for complete neutralisation (and solution), and this fact, together with the nature of the salt so formed and the effect of drying, leads to the conclusion that the acid is dibasic. This can be reconciled with the valency of aluminium by regarding the acid as $H_2\left[Al(C_7H_4O_3)_2{}^{OH}_{OH_2}\right]$, in which the co-ordination valency of aluminium is 6. Derivatives of this acid were prepared (*a*) by neutralising the free acid with the desired base, (*b*) by treating salicylic acid with freshly precipitated aluminium hydroxide and adding the calculated amount of the base, and (*c*) by double decomposition. In all cases the ratio metal (univalent) : aluminium : salicylic acid was 2 : 1 : 2.

Attempts to replace the hydroxyl and the aquo-group by another molecule of salicylic acid, or to introduce another atom of sodium into the molecule, were unsuccessful. No compound of the type $R_3[Al(C_7H_4O_3)_3]$ or $R[Al(C_7H_4O_3)_2]$ could be isolated from aluminium hydroxide and salicylic acid or alkali salicylates.

This result may possibly be due to the formation of the ion

$[Al(C_7H_4O_3)_3]'''$ and its subsequent hydrolysis by water. It was therefore decided to prepare analogous compounds in anhydrous alcohol from aluminium methoxide (or ethoxide), salicylic acid, and sodium methoxide (or ethoxide). Although the molecular proportions were varied, the salt which separated from solution invariably had the same molecular ratio as before and in addition contained alcohol. These salts could be recrystallised from anhydrous methyl alcohol, in which they dissolved with a noticeable evolution of heat.

The solution of aluminosalicylic acid formed from aluminium methoxide and salicylic acid was strongly fluorescent when cold, a fact which recalls the conclusions of Waterman (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 581) as to the possibility of tautomerism in salicylic acid and its salts.

From an exhaustive analytical study of the *sodium* salt obtained from aluminium methoxide, salicylic acid, and sodium methoxide, we are led to the conclusion that salts obtained in this way and those obtained in aqueous solution from aluminium hydroxide are derivatives of the same acid. Thus the *salt* prepared in methyl-alcoholic solution is  $Na_2\left[Al(C_7H_4O_3)_2\substack{OH \\ OH_2}\right],2CH_3{\cdot}OH$. Variation in the relative amounts of aluminium, salicylic acid, and sodium methoxide was without effect on the composition of the salt which separated from solution.

It is difficult to explain the presence of hydroxyl and aquo-groups in compounds prepared in the absence of water. In view of the precautions taken to render our reagents anhydrous, we feel certain that water was not introduced in this manner, and that these groups result from one of the reactions involved in the preparation.

Attempts to prepare from aluminosalicylic acid and weak bases salts conforming to the type $R_3[Al(C_7H_4O_3)_3]$ were also unsuccessful. No definite ammonium or pyridinium salt could be obtained, and the strychnine salt prepared in alcoholic solution was of the same type as the sodium salt.

The reactivity of aluminium alkyloxides towards salicylic acid, together with the ease of obtaining pure derivatives by using this material as the starting point, induced us to study the action of ethyl and methyl salicylates on aluminium ethoxide and methoxide, respectively. In this way crystalline *products* were obtained the compositions of which are represented by $Al(C_9H_9O_3)_3$ and $Al(C_8H_7O_3)_3$ respectively. In view of the fact that phenol yields a crystalline derivative, it appeared possible that these compounds were simply salts of tervalent aluminium. However, experiments in which other esters, *e.g.*, ethyl malonate and benzoate, were caused to react with aluminium ethoxide lead to the conclusion that these compounds are co-ordination compounds of aluminium, and that not only is the hydrogen of the phenolic group reactive in this connexion, but that co-ordination also takes place through the ketonic oxygen of the ester. We are thus of the opinion that the constitution of the ester products is correctly represented by the formulæ given, in which the co-ordination valency of aluminium is 6.

The ethyl malonate compound, like the aluminium salicylic esters, was isolated in a crystalline condition, and analysis indicates that it is aluminium malonic ester, $[Al\{CH(CO_2Et)_2\}_3]$, identical with that prepared by Titschenko (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 694, 784); the extraordinary solubility of this compound in liquids of low dielectric constant indicates that it is not an aluminium salt.

The ethyl benzoate compound has not yet been obtained in a crystalline condition sufficiently pure for further investigation.

It is our intention to study the action of certain aldehydes on the aluminium alkyloxides.

EXPERIMENTAL.

Aluminosalicylic Acid, $H_2\left[(C_7H_4O_3)_2Al\genfrac{}{}{0pt}{}{OH}{OH_2}\right]$.—(*a*) On mixing hot aqueous solutions of potash alum (1 mol.) and of sodium or ammonium salicylate (2 mols.), a violet-pink solution was obtained from which fine, pink needles gradually separated. The product contained varying amounts of free salicylic acid, which was removed by washing with alcohol. *Aluminosalicylic acid* is only sparingly soluble in water, but on being moistened on litmus paper it gives an acid reaction. The acid requires 2 equivs. of sodium hydroxide for complete solution; further alkali renders the solution alkaline to litmus. On drying in an oven at 100°, the acid readily loses 1 molecule of water, a second being driven off only with difficulty (Found: Al, 7·8. $C_{14}H_{13}O_8Al$ requires Al, 8·0%).

(*b*) The same compound was obtained by mixing hot aqueous solutions of aluminium chloride (1 mol.) and salicylic acid (2 mols.) and washing the crystalline precipitate with alcohol (Found: Al, 7·8%).

(*c*) On adding an aqueous-alcoholic solution of salicylic acid (2 mols.) to a cold suspension of freshly precipitated aluminium hydroxide, the latter dissolved, but a pink crystalline precipitate of aluminosalicylic acid slowly separated (Found: Al, 7·8%).

(*d*) A solution of salicylic acid (2 mols.) in anhydrous alcohol (dehydrated with metallic calcium or aluminium) was added to a suspension of aluminium ethoxide (1 mol.) in anhydrous alcohol.

On warming, a clear purple solution was obtained having a blue fluorescence. No precipitate was formed, but on concentration in a vacuum desiccator, a pink, crystalline product was obtained which was dried over sulphuric acid (Found : Al, 7·9%).

In preparing the aluminium alkyloxides used in this work the procedure was as follows. The alcohol was first dehydrated by refluxing it with fine calcium turnings, or with very fine aluminium foil together with an extremely small quantity of mercuric chloride, and then distilling it, calcium chloride guard tubes being used throughout. A known weight of aluminium foil was then heated under reflux with dry alcohol and a trace of mercuric chloride until the aluminium was completely converted into alkyloxide. (In this operation it was found advantageous to add the alcohol very gradually—the reaction apparently proceeding most rapidly when metallic aluminium is exposed to alcohol vapour.) A solution of salicylic acid in anhydrous alcohol was then added.

Sodium Aluminosalicylate.—(a) *The monohydrate,*

$$Na_2\left[(C_7H_4O_3)_2Al\begin{matrix}OH\\OH_2\end{matrix}\right],H_2O.$$

Aluminosalicylic acid was dissolved in the minimum quantity of aqueous sodium hydroxide. The deep yellow solution was warmed, filtered from excess of the acid (trace), and the filtrate concentrated on the water-bath under diminished pressure. The yellowish-pink needles that separated on cooling were filtered off and washed with alcohol. More of the salt was obtained from the mother-liquor by the addition of alcohol. The salt is extremely soluble in water and fairly readily soluble in methyl alcohol. An aqueous solution is alkaline to litmus (Found : Loss at 120°, 9·0; Al, 6·8; Na, 11·6; $C_7H_4O_3$, 67·2. $C_{14}H_{13}O_9AlNa_2$ requires Al, 6·75; Na, 11·5; $C_7H_4O_3$, 68·0; $2H_2O$, 9·0%).

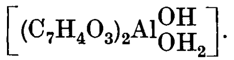
(b) *The dimethyl-alcoholate*, $Na_2\left[(C_7H_4O_3)_2Al\begin{matrix}OH\\OH_2\end{matrix}\right],2CH_3OH$. A solution of salicylic acid (2 mols.) in anhydrous methyl alcohol was added to aluminium methoxide (1 mol.) in methyl alcohol. On refluxing for some time, a clear solution was obtained, and to this was added a solution of sodium methoxide (2 mols.) in methyl alcohol. On cooling the yellow solution so obtained, the salt separated in cream-coloured needles; it was recrystallised from methyl alcohol and air-dried. In the process of crystallisation from methyl alcohol, the dissolution of the salt was strongly exothermic, and, on cooling, the separation of the salt was remarkably sudden, suggesting the possibility of the process being one of alcoholysis followed by recombination to form the salt. On drying at 100° the salt lost 14·7%, corresponding to 2 molecules of methyl alcohol. Owing to the difficulty of carrying out combustions with compounds of this type, several analyses were made, both of the air-dried salt and of the salt from which the alcohol had been expelled in the oven. Furthermore, combustions were effected in moist oxygen and also by the "wet" chromic acid method. In every case the results were concordant (Found : C, 43·3; H, 4·6; Al, 6·2; Na, 10·4; $C_7H_4O_3$, 60·6. $C_{16}H_{19}O_{10}AlNa_2$ requires C, 43·3; H, 4·3; Al, 6·1; Na, 10·4; $C_7H_4O_3$, 61·2; 2MeOH, 14·5%). The same salt is apparently obtained by using aluminium ethoxide and sodium ethoxide in place of the corresponding methoxides and recrystallising the product from methyl alcohol (Found : Al, 6·0; Na, 10·2%).

(c) *The dihydrate*, $Na_2\left[(C_7H_4O_3)_2Al{}^{OH}_{OH_2}\right],2H_2O$. This salt was obtained from the preceding by dissolving 5 g. in 20 c.c. of water at 40° and adding 100 c.c. of ethyl alcohol. The solution was kept at 40° for 2 hours and then allowed to stand over-night; a copious, cream-coloured, crystalline precipitate thus separated (Found : Al, 6·6; Na, 11·0. $C_{14}H_{15}O_{10}AlNa_2$ requires Al, 6·5; Na, 11·1%).

Barium Aluminosalicylate, $Ba\left[(C_7H_4O_3)_2Al{}^{OH}_{OH_2}\right],H_2O$.—This salt was obtained by adding an aqueous solution of sodium aluminosalicylate dihydrate to an aqueous solution of barium chloride, both at 40°. After a few minutes, a cream-coloured, crystalline precipitate separated. After 2 hours, this was removed by filtration and washed with water, in which the salt is only sparingly soluble. On drying in a desiccator over sulphuric acid, there was a slight change in colour, the final product being pale yellow (Found : Al, 5·6; Ba, 27·9. $C_{14}H_{13}O_9AlBa$ requires Al, 5·5; Ba, 28·1%). The same compound was obtained from a solution of sodium aluminosalicylate dimethyl-alcoholate at 40° by addition of barium chloride solution.

Ammonium Aluminosalicylates.—Several attempts were made to prepare definite salts by passing dry ammonia into an alcoholic solution of aluminosalicylic acid prepared from aluminium ethoxide and salicylic acid in ethyl alcohol. Although crystalline products were obtained, these always liberated the free aluminosalicylic acid on attempts at recrystallisation from methyl alcohol, and the analyses of such compounds indicated that the substance which originally separated in the preparation was invariably a mixture of aluminosalicylic acid and ammonium aluminosalicylate.

Strychnine Aluminosalicylate, $C_{21}H_{22}O_2N_2,H\left[(C_7H_4O_3)_2Al{}^{OH}_{OH_2}\right]$.—From the composition of the various salts isolated in this work, we were led to conclude that the constitution of the complex ion is



$$\left[(C_7H_4O_3)_2Al\genfrac{}{}{0pt}{}{OH}{OH_2}\right].$$

Since the hydroxyl and the aquo-group are obviously in the 1 : 6 positions, such an ion is asymmetric and should be capable of resolution into optical antipodes. So far, we have failed to carry out such a resolution. We have, however, isolated definite crystalline alkaloidal salts such as the strychnine, brucine, quinine, and narcotine compounds. Of these only the strychnine salt was analysed; it was prepared by adding the calculated amount of the alkaloid, dissolved in hot chloroform, to a hot alcoholic solution of aluminosalicylic acid, and cooling the solution. Although the molecular proportion of strychnine was varied, the composition of the salt did not change. Attempts to separate the optical isomerides by fractional crystallisation from alcohol or mixtures of alcohol and chloroform were unsuccessful (Found : Al, 4·0. $C_{35}H_{34}O_{10}N_2Al$ requires Al, 4·0%).

Aluminium Methyl Salicylate, $(C_8H_7O_3)_3Al$.—This compound was obtained by adding freshly distilled methyl salicylate (3 mols.) to an alcoholic solution of aluminium methoxide (1 mol.). The solution became pink, and after refluxing for 2 hours was kept over-night, whereupon well-formed, lustrous, brown crystals separated. These were washed with a small quantity of alcohol and then with ether, and dried in a desiccator. They did not melt sharply on heating, but apparently underwent decomposition (Found : C, 60·0; H, 5·3; Al, 5·6. $C_{24}H_{21}O_9Al$ requires C, 60·0; H, 4·4; Al, 5·6%).

Aluminium Ethyl Salicylate, $(C_9H_9O_3)_3Al$.—This compound was prepared in an analogous manner to the preceding. The crystals obtained were similar in appearance to those of the previous compound (Found : C, 61·1; H, 5·4; Al, 5·0. $C_{27}H_{27}O_9Al$ requires C, 62·1; H, 5·2; Al, 5·2%).

Aluminium Ethyl Malonate, $(C_7H_{11}O_4)_3Al$.—This compound was obtained by Titschenko (*loc. cit.*) by acting on aluminium with ethyl malonate in the presence of a trace of mercuric chloride. In the present work, it was obtained in a manner similar to that adopted for the preparation of the aluminium salicylic esters, *i.e.* by the interaction of ethyl malonate and aluminium ethoxide in the presence of ethyl alcohol. It is readily decomposed by water, and is remarkably soluble in all organic liquids. In fact, we had great difficulty in recrystallising the compound from any solvent and finally had to allow a solution in ether partly to evaporate in order to obtain a pure crystalline product (Found : C, 49·8; H, 6·6; Al, 5·4. Calc. : C, 50·0; H, 6·5; Al, 5·4%).

Summary.

1. Several derivatives of aluminosalicylic acid,

$$H_2\left[(C_7H_4O_3)_2Al{}^{OH}_{OH_2}\right],$$

have been prepared from aqueous and alcoholic solutions. It has not been possible to prepare alkali-metal derivatives of $H[Al(C_7H_4O_3)_2]$ or of $H_3[Al(C_7H_4O_3)_3]$.

2. An attempt to resolve the strychnine, brucine, quinine, and narcotine salts of the above acid into optical isomerides was unsuccessful.

3. Reactions between aluminium alkyloxides and certain esters, *e.g.*, methyl salicylate and ethyl malonate, produce complexes of the type $Al[(C_8H_7O_3)_3]$ and $[Al\{CH(CO_2Et)_2\}_3]$.

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