XLVII.—*Co-ordinated Compounds of the Alkali Metals. Part III.*

By Frederick Mason Brewer.

In a previous paper (Sidgwick and Brewer, J., 1925, **127**, 2379) the existence of several co-ordinated compounds of the alkali metals was established and their formulation discussed. For two reasons it was considered desirable to extend those researches to cover compounds of all the alkali metals. First, these elements show much less variation in chemical character than those of any other group. Any variation in properties can therefore be attributed almost entirely to physical characteristics of the atom, such as size or distribution of charge, rather than to any definite variation in the distribution of the valency electrons. Secondly, the co-ordination compounds of this series offer practically the only opportunity of studying the properties of these elements in compounds in which ionisation is precluded, as the alkali metals have far too strong a tendency towards ionisation (where this is possible) to form covalencies. Since the chemistry of these elements, as it is known at present, is almost entirely that of their ions, any further information as to the behaviour of the un-ionised atom is to be welcomed.

The immediate points of interest are (i) the number of covalent links which can be established for any member of the series, and (ii) the relative stability of compounds of different co-ordination number. In addition, some points have been observed in the preparation and analysis of these compounds, particularly those of rubidium and cæsium, which are noteworthy in view of the scanty information on these subjects.

The series chosen for investigation was that of the salicylaldehyde derivatives. Although these have not the great solubility in non-polar solvents which characterises, for instance, many of the hydrates of organic sodium derivatives, they have the advantage that the co-ordinated molecule is formed by the addition of molecules of the parent substance to the simple alkali derivative. This avoids complications due to the presence of two or more types of organic molecule in the complex, each of which might influence the co-ordinating power of the alkali metal in its own way. Also, in previous experiments, salicylaldehyde had been found to be the most generally efficient molecule for chelate co-ordination.

EXPERIMENTAL.

Materials.—The salicylaldehyde was always purified shortly before use by conversion into the bisulphite compound. The regenerated aldehyde was then fractionally distilled under reduced pressure, and the main fraction submitted to fractional crystallisation.

Rubidium carbonate. This was prepared from a sample of rubidium alum kindly given by Mr. K. M. Chance of the British Cyanides Company. The preparation was substantially that outlined by Sidgwick and Gentle (J., 1922, **121**, 1837). To prevent the progressive precipitation of aluminium hydroxide which their method involves, the aluminium was first precipitated by the addition of concentrated ammonium hydroxide. All crystallisations and precipitations were followed spectroscopically. In this way it was found that the repeated washing of alumina and barium sulphate precipitates is not sufficient to remove rubidium carried down with them, but once the precipitates have been ignited, the rubidium salts are easily removed by a single treatment with hot water. In converting rubidium hydrogen tartrate to carbonate, the yellow colour, which usually persists after ignition and even after recrystallisation of a large quantity of material, was avoided by gentle ignition for several hours in an open quartz dish over a ring burner. The product was quite colourless and needed only one recrystallisation.

Cæsium carbonate. Finely powdered pollucite was repeatedly extracted with concentrated hydrochloric acid, and the cæsium precipitated as cæsium antimony chloride, $Cs_3Sb_2Cl_9$, by the addition of a concentrated solution of antimony chloride in hydrochloric acid. The antimony was precipitated by stirring the double salt into concentrated ammonium hydroxide and washing the precipitate with ammonium hydroxide until all the cæsium had been extracted. The mixed cæsium and ammonium chlorides were evaporated with the requisite quantity of sulphuric acid, converted to carbonate by treatment with baryta and carbon dioxide, and the cæsium freed from sodium and potassium by precipitation as hydrogen oxalate. Ignition and recrystallisation gave pure cæsium carbonate.

Analysis.—The main analytical work consisted in determining the alkali metals as sulphate. This is possible with lithium, sodium, and potassium by evaporation of the compound with a few drops of concentrated sulphuric acid. With rubidium and cæsium, however, this method gives a product with an acid reaction, and further ignition over a blowpipe gives inconsistent results due to volatilisation and decomposition. In order to avoid this, a small quantity of "redistilled" ammonium hydroxide was added to the acid sulphate, and the ammonium sulphate so formed dissociated at a comparatively low temperature and left pure alkali sulphate.

In all cases the following precautions are noteworthy. Rapid heating to a high temperature should be avoided, for this causes carbon to separate in a graphitic form which is very resistant to oxidation. Initial evaporation in an air-bath with a little dilute acid prevents separation of carbon. The presence of carbon is invariably accompanied by the production of alkali sulphides which are comparatively volatile, and furnish an additional reason for ignition at the lowest possible temperature.

Compounds of Lithium.—In Part II of this series the dihydrate of the lithium derivative of salicylaldehyde was described. This had all the properties of a substance formed exclusively by covalent and co-ordinate links, and was the only hydrate among the salicylaldehyde derivatives. In order to produce a molecule in which co-ordination was effected by salicylaldehyde instead of water, dry lithium hydroxide was added to the aldehyde, and the mixture warmed gently. The yellow solid then separating was recrystallised from pure salicylaldehyde, and washed with ether. The product was the "double molecule" containing 4-covalent lithium (Found: Li, 2·68. $C_7H_5O_2Li,C_7H_6O_2$ requires Li, 2·78%). This *compound* gives a yellow solution in toluene, in contrast to that of the dihydrate, which is colourless. The solid is pale yellow, and on heating gives off salicylaldehyde vapour. If any appreciable amount of water is present in the reaction mixture, the dihydrate is formed at the expense of the co-ordinated aldehyde. This behaviour is peculiar to lithium in this group.

Compounds of Sodium.—Hantzsch (*Ber.*, 1906, **39**, 3089) prepared the compound $C_7H_5O_2Na,C_7H_6O_2$ by the action of sodium ethoxide upon the aldehyde. This "acid salt," as he called it, was stable even in the presence of excess of sodium ethoxide.

Many experiments were carried out in the present research to make (*a*) hydrates of the simple sodium derivative and (*b*) compounds containing two co-ordinated molecules of salicylaldehyde, *i.e.*, with 6-covalent sodium. In all cases these gave negative results. Ettling (*Annalen*, 1840, **35**, 252) describes a compound $C_7H_5O_2Na,C_7H_6O_2,\frac{1}{2}H_2O$, but its precise formulation is not clear.

Compounds of Potassium.—A similar result was obtained by Hantzsch with potassium, with the exception that excess of potassium ethoxide reacted with the co-ordinated aldehyde and so destroyed the complex molecule.

As in the case of sodium, attempts to prepare hydrates of the simple potassium derivative failed (see, however, Ettling, *loc. cit.*). On the other hand, the compound containing 6-covalent potassium was prepared in the following way. Concentrated potassium hydroxide solution was added to salicylaldehyde, and the resulting solid, which was a mixture of the simple potassium derivative and the 4-covalent compound mentioned above, was dissolved in a mixture of alcohol and salicylaldehyde. The alcohol was necessary to prevent the temperature from rising above about 80°, for at higher temperatures there is considerable condensation between the excess aldehyde and the alkali derivatives. After crystallisation, the *product* was washed with alcohol (Found : K, 9·48. $C_7H_5O_2K,2C_7H_6O_2$ requires K, 9·68%). The crystals are very pale yellow and feathery. They dissolve to some extent in toluene in the cold, but are readily decomposed on warming the solution. If allowed to remain in the air, they rapidly become green and ultimately black, presumably owing to hydrolysis by moisture in the air and subsequent oxidation or condensation of the aldehyde. (This behaviour was noticed by Cajar, *Ber.*, 1898, **31**, 2804, with the sodium derivative.) In a dry atmosphere dissociation proceeds slowly, the vapour of the aldehyde being given off, indicating that the 6-covalent state is not particularly stable for this element.

Compounds of Rubidium.—When powdered rubidium carbonate was dropped into warm salicylaldehyde there was considerable evolution of carbon dioxide, and a clear yellow solution was obtained. From this was deposited a mass of almost colourless crystals, which later experiments showed to be a mixture of the compounds containing 4- and 6-covalent rubidium. On being heated under reduced pressure, this product gave off salicylaldehyde, and left a residue of a typically saline character (Found : Rb, 40·3. $C_7H_5O_2Rb$ requires Rb, 41·4%), which hydrolysed to give the aldehyde and an alkaline solution. The same result was obtained by repeatedly treating the product with boiling toluene and finally washing it with ether (Found : Rb, 40·95%). It is therefore evident that the residue was essentially the simple *rubidium salicylaldehyde*, which has not hitherto been prepared, and that the excess of aldehyde was co-ordinated as in the case of the other alkali elements.

Repeated attempts to prepare co-ordinated derivatives of definite composition indicated clearly that there were two distinct substances to be isolated. Recrystallisation from alcohol in the presence of a large quantity of aldehyde gave a voluminous crop of pale yellow feathery crystals like those containing 6-covalent potassium. Recrystallisation from alcohol alone gave principally starred clusters of yellow needles. The separation of the individual *compounds* was finally effected as follows.

4-*Covalent rubidium.* To rubidium carbonate, dissolved in the minimum of hot water, salicylaldehyde containing a small quantity of alcohol was added, and the whole warmed until there was no further evolution of carbon dioxide. (The alcohol prevented the temperature from rising, the only product at high temperatures being a red resinous mass.) The crystals which separated on cooling were recrystallised from pure alcohol and washed with a little ether. They darkened rapidly in air, were readily hydrolysed by water, and melted indefinitely with decomposition. They dissolved slightly in toluene to give a yellow solution (Found : Rb, 25·93. $C_7H_5O_2Rb,C_7H_6O_2$ requires Rb, 26·02%).

6-*Covalent rubidium.* After recrystallisation from alcohol as above, the rubidium derivative was (*a*) allowed to stand in salicylaldehyde for several hours in the cold, and (*b*) recrystallised from the aldehyde containing the minimum of alcohol necessary to effect solution below 100°. The result in both cases was a crop of almost colourless feathery crystals, which were washed with a little alcohol [Found : (*a*) Rb, 19·17; (*b*) Rb, 19·05. $C_7H_5O_2Rb,2C_7H_6O_2$ requires Rb, 18·99%]. The same *product* was obtained by recrystallising the simple derivative described above from excess of the aldehyde (Found : Rb, 18·99%). Although these crystals eventually darkened in moist air, they showed much greater stability and permanence than the corresponding compound containing 4-covalent rubidium, and were also rather more soluble in toluene, but like the 4-covalent compound they were decomposed by hot toluene.

Compounds of Cæsium.—The preparation of these compounds was parallel to that of the rubidium compounds, but it was found advisable to carry out the initial reaction without alcohol, for this dissolves cæsium carbonate (but not rubidium carbonate). Recrystallisation from this solvent did not therefore completely remove any unused cæsium carbonate from the product. Sufficient water was used to keep any excess of carbonate in solution, and the product filtered and washed with water. After this substance had been kept for several hours in the aldehyde, filtered, and washed with alcohol, the 6-covalent *compound* was obtained (Found : Cs, 26·40. $C_7H_5O_2Cs,2C_7H_6O_2$ requires Cs, 26·68%).

If the initial product was (*a*) washed with ether until it began to show signs of discoloration, or (*b*) precipitated from an alcoholic solution by ether, the 4-covalent *compound* was obtained [Found : (*a*) Cs, 35·35; (*b*) Cs, 35·20, 35·35. $C_7H_5O_2Cs,C_7H_6O_2$ requires Cs, 35·34%]. The compounds described are both pale yellow crystalline solids, similar in behaviour to the corresponding rubidium compounds. On heating, the 6-covalent compound gives off salicylaldehyde vapour; the 4-covalent compound melts with decomposition in the neighbourhood of 165°.

Conclusions.

In the series of compounds studied, lithium alone appears to be able to form a true co-ordinated hydrate. It is of interest in this connexion that hydration is common with lithium and sodium ions but not with the ions of potassium, rubidium, or cæsium. The case of the ions is covered by Fajans' rule (see Sidgwick, "Electronic Theory of Valency," Oxford, 1927, p. 104). It would also appear that an increase in size of the co-ordinating molecule corresponds in effect to an increase in anion size, enabling the higher alkalis to co-ordinate with a comparatively large organic molecule when they fail to do so with water. The definite preference of lithium for co-ordinated water molecules must then be explained by considerations of atomic volume.

To test this, an attempt was made to prepare the benzoylacetone derivative $C_{10}H_9O_2Rb,C_{10}H_{10}O_2$. In this series of compounds, hydration takes place in the case of lithium and sodium (Sidgwick and Brewer, *loc. cit.*; Weygand and Forkel, *J. pr. Chem.*, 1927, **116**, 293) and also with potassium, but in this case it is doubtful from the description of its properties recorded by Weygand and Forkel whether the hydrate is a true co-ordination compound. With none of these elements could a " double molecule " be prepared. If the benzoylacetone derivatives resembled the salicylaldehyde compounds, there was a possibility that with the higher elements in the group the double molecule might be stable. Rubidium carbonate was therefore dissolved in excess of molten benzoylacetone, with liberation of carbon dioxide, and the product recrystallised from hot toluene. It proved to be essentially the hitherto unprepared simple *rubidium benzoylacetone* (Found: Rb, 35·2. $C_{10}H_9O_2Rb$ requires Rb, 34·7%), which formed bright yellow plates melting to a red liquid at 131°. The solubility of this compound in toluene containing the parent substance (compare the behaviour of the sodium derivative of ethyl acetoacetate; Sidgwick and Brewer, *loc. cit.*) indicates the formation of the required complex molecule in solution.

All the alkali metals will co-ordinate with salicylaldehyde, the following covalency numbers having been established: lithium, 4; sodium, 4; potassium, 4 and 6; rubidium, 4 and 6; cæsium, 4 and 6. Only in the case of rubidium does the 6-covalent compound appear to be definitely the more stable. With potassium, the 6-covalent compound is formed only with difficulty; with cæsium there is little difference in stability between the 4- and the 6-covalent compound.

The 4-covalent compounds of sodium and potassium are much the most stable of all the compounds investigated, the sodium compound being stable even in the presence of excess of sodium ethoxide.

It is quite clear that there must be three influences at work in determining the stability of these compounds. (1) Increasing atomic number carries with it increasing electropositiveness and ease of ionisation: this diminishes the tendency to co-ordinate. (2) The increasing distance of the nucleus from the co-ordinating electrons with increasing atomic volume makes it less likely that additional electrons will be held with ease. (3) On the other hand, there is an increase in the maximum co-ordination number with the elements of higher atomic number. These factors are in keeping with a maximum of stability for the 4-covalent compounds occurring with the element sodium, and in the case of the 6-covalent compounds with rubidium. The change in chemical character through the group is not sufficient to affect the general result, and the formation of co-ordinated compounds with these elements may therefore be considered as a useful standard for measuring the co-ordinating power of chelate groups.

The following table of those co-ordinated compounds of the alkali metals whose formulæ have been established summarises the co-ordinating power of the metals themselves.

HB = Benzoylacetone, HA = acetylacetone, HE = ethyl acetoacetate, HQ = $\frac{1}{2}$ quinizarin, HM = methyl salicylate, HS = salicylaldehyde, HNp = *o*-nitrophenol, HNc = *o*-nitrocresol, HIn = *ψ*-indoxyl*spirocyclo*pentane.

Metal.	4-Covalent.	6-Covalent.
Lithium	LiB,$2H_2O$ [1]	None.
	LiM,$2H_2O$ [1]	
	LiS,$2H_2O$ [1]	
	LiS,HS [2]	
	LiQ,HS [1]	
	LiIn,HIn [3]	
Sodium	NaB,$2H_2O$ [1]	NaB,$4H_2O$ [5]
	NaE,$2H_2O$ [1]	NaQ,2HS [1]
	NaA,$2H_2O$ [1]	
	NaS,HS [4]	
	NaNp,HS [1]	
	NaNc,HS [1]	
	NaIn,HIn [3]	
Potassium	KA,$2H_2O$ [1]	KQ,2HS [1]
	KS,HS [4]	KS,2HS [2]
	KNp,HS [1]	
	KIn,HIn [3]	
Rubidium	RbS,HS [2]	RbS,2HS [2]
Cæsium	CsS,HS [2]	CsS,2HS [2]

[1] Sidgwick and Brewer, *loc. cit.*

[2] This paper.

[3] Sidgwick and Plant, J., 1925, **127**, 209.

[4] Hantzsch, *loc. cit.*

[5] Weygand and Forkel, *loc. cit.* These authors also describe a trihydrate of sodium benzoylacetone, and a monohydrate of potassium benzoylacetone. They are not responsible for the formulation of the tetrahydrate put forward above.

In conclusion, I should like to express my thanks to Dr. N. V. Sidgwick, F.R.S., for the interest he has taken and the suggestions he has made during the course of this research.

UNIVERSITY MUSEUM, OXFORD.

[*Received, December* 30*th,* 1930.]