5. *Metallic Hydroxy-acid Complexes. Part VI. Complexes of Lead and Zinc.*

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THE complex salts of hydroxy-acids and copper have been described by I. W. Wark in a series of papers in this journal. Unrecorded attempts by him to resolve the alkaloid cuprisalicylates, after the manner of Böeseken's resolution of a borosalicylate (*Rec. trav. chim.*, 1921, **40**, 553), proved unsuccessful. Since the successful resolution of one of these metallic salicylates would definitely determine their configuration, a study of the complex salts of lead and zinc has been undertaken. These give colourless solutions more suitable for attempts at resolution than those of the copper complexes.

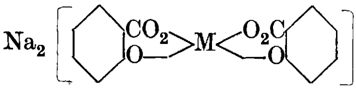
The complexes of lead and zinc hydrolyse more readily than those of copper. The simple tartrates dissolve in sodium hydroxide in a manner similar to copper tartrate, except that excess of sodium tartrate is necessary to prevent hydrolysis. All three tartrates—lead, zinc, and copper—appear to require 5/4 mols. of sodium hydroxide per mol. of tartrate to produce a complex, but whereas the sodium cupritartrate formed according to the equation (Packer and Wark, J., 1921, **119**, 1348)

$$5NaOH + 4CuC_4H_4O_6 \longrightarrow Na_3Cu_4C_{12}H_9O_{19} + Na_2C_4H_4O_6 + 4H_2O$$

is scarcely hydrolysed by water, and the sodium zincitartrate is slightly hydrolysed, yet the plumbitartrate is very highly so.

The monohydroxymonobasic acid complexes exhibit a similar range in stability. Sodium cuprilactate solution may be stabilised by sodium lactate (Wark, J., 1923, **123**, 1815), but it is quite impossible to stabilise the lead and zinc salts in this manner. To prevent hydrolysis of the copper complexes, recourse had to be made to working in anhydrous alcoholic solutions (Wark, J., 1927, 1753). The lead and zinc complexes, being less stable than that of copper, have likewise only been isolated from anhydrous alcoholic solutions. So readily hydrolysed are they that even a trace of moisture in the alcohol causes decomposition.

The general composition of these complexes is Na_2MA_2, where M signifies the metal, and A the acid radical. It is suggested, from an analogy with Böeseken's formula for the borosalicylates, that their constitution is



Difficulties attending the preparation and purification of the alkaloid salts of the complex salicylates have so far prevented any exhaustive attempts at resolution.

EXPERIMENTAL.

Complexes with Monohydroxymonobasic Acids.—Preparation. All the complexes were prepared by the action of sodium ethoxide or methoxide on the anhydrous simple salts, which were themselves best prepared by the interaction of aqueous solutions of the appropriate acid and zinc and lead acetate, other methods giving basic salts. These salts were then dehydrated, the lactates, glycollates, and mandelates by heating, and the salicylates, since they decompose on heating, by recrystallisation from an acetone solution by addition of benzene. All the salts, when treated with a standard solution of sodium ethoxide or methoxide in alcohol (the alcohol, whether ethyl or methyl, was dried over quicklime and then over aluminium ethoxide or methoxide), required two molecules of alkali to dissolve one molecule of simple salt. The salicylates were used in alcoholic solutions, and the immediate effect of the alkali was to give a white precipitate which dissolved on addition of further alkali. The other compounds were used in the solid state. On evaporation of the resultant solutions over sulphuric acid, the complex salt crystallised. This was freed from alkali by washing with alcohol and acetone.

Analysis. In each case the organic radical was destroyed by sulphuric acid. Zinc was determined electrolytically, and lead and sodium were weighed as sulphates. The results are tabulated below.

(a) Zinc Complexes.

Salt.	Zn, %.	Na, %.	Na/Zn.
Sodium zincimandelate, found	14·3	9·9	1·97
$Na_2Zn[C_6H_5\cdot CH(\bar{O})\cdot C\bar{O}_2]_2,C_2H_6O$ requires...	14·3	10·1	2·00
Sodium zincisalicylate, found	15·4	10·8	2·04
$Na_2Zn[C_6H_4(\bar{O})\cdot C\bar{O}_2]_2,CH_4O$ requires	15·7	11·1	2·00
Sodium zincilactate, found	17·9	12·5	1·98
$Na_2Zn[CH_3\cdot CH(\bar{O})\cdot C\bar{O}_2]_2,2CH_4O$ requires ...	18·6	13·1	2·00

(b) Lead Complexes.

Salt.	Pb, %.	Na, %.	Na/Pb.
Sodium plumbimandelate, found	34·9	7·9	2·04
$Na_2Pb[C_6H_5\cdot CH(\bar{O})\cdot C\bar{O}_2]_2,C_2H_6O$ requires...	34·6	7·7	2·00
Sodium plumbisalicylate, found	40·3	8·8	1·96
$Na_2Pb[C_6H_4(\bar{O})\cdot C\bar{O}_2]_2$ requires	39·5	8·8	2·00

Sodium zincilactate is so deliquescent that analyses were difficult to obtain; this accounts for the low zinc and sodium assays, but the Zn/Na ratio is satisfactory. Lead lactate is even more deliquescent and is, moreover, so soluble in water that it could not be isolated in a sufficiently pure and dry state for the successful formation of the complex sodium plumbilactate.

Neither zinc nor lead glycollate dissolves in either sodium ethoxide or sodium methoxide. They differ in this respect from the copper glycollate (Wark, *loc. cit.*).

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