

and conveniently eluted by placing both ends of each curved strip on filter-paper soaked in eluent. Capillary action concentrates the adsorbate in the centre of the strip, whence it may be drawn off on paper or by capillary pipette.

A study of modified types of filter-paper in particular separations will be discussed more fully elsewhere.

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<sup>1</sup> Brown, W. G., *Nature*, **143**, 377 (1939).

<sup>2</sup> Consden, R., Gordon, A. H., and Martin, A. J. P., *Biochem. J.*, **38**, 224 (1944).

<sup>3</sup> Hopf, P. P., *J. Chem. Soc.*, 785 (1946).

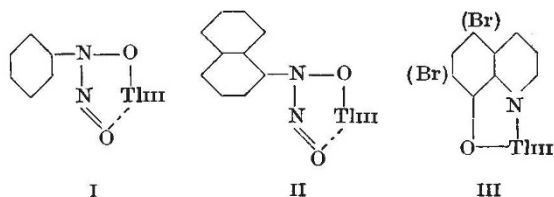
<sup>4</sup> Dent, L. E., Stepka, W., and Steward, F. C., *Nature*, **160**, 682 (1947).

### Inner-Complex Salts of Trivalent Thallium

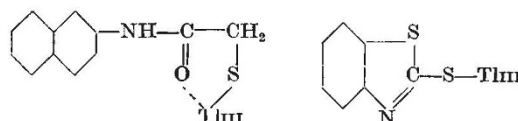
HITHERTO it has seemed that thallium was the only heavy metal with but slight tendency to form water-insoluble normal and inner-complex salts with organic compounds of acid character. Monovalent thallium gave insoluble salts with the mercaptans thioglycolic acid-anilid, thioglycolic acid- $\beta$ -aminonaphthalid ('Thionalid')<sup>1</sup> and mercaptobenzthiazole<sup>2</sup>. Of these compounds only the first and second can be considered as inner-complex salts. Since thallium belongs to the same group in the Periodic Table as the inner-complex-forming metals gallium and indium, the existence of inner-complex salts of trivalent thallium was to be expected; and it has now been found that inner-complex salts of trivalent thallium with nitrosophenylhydroxylamine,  $\alpha$ -nitrosophenylhydroxylamine, 8-hydroxyquinoline, 5,7-brom-8-hydroxyquinoline and 'Thionalid' can be obtained in the following manner.

Sufficient tartaric acid, citric acid or sulphosalicylic acid is added to a solution of thallium (Tl III) sulphate, bromide, etc., in order to avoid, by formation of complex thallic ions, precipitation after addition of ammonia. To the ammoniacal solution thus obtained, a solution of the complex-forming organic compound in alcohol or ammonia is added. Immediately precipitates of the respective thallic inner-complex salts are formed. The precipitations are quantitative, as in the filtrates no thallium can be detected by the usual tests.

Precipitates with nitrosophenyl- and nitrosophenylhydroxylamine (white amorphous products) are also obtainable from mineral acids, non-masked thallic solutions. In this case the precipitate is mixed with the precipitant. The precipitates with 8-hydroxyquinoline and 5,7-brom-8-hydroxyquinoline (orange-coloured crystalline products) can also be formed from non-masked, acetate-buffered thallic solutions with alcoholic solutions of the reagents. The composition and constitution of the above inner-complex salts correspond to co-ordination formulæ I-III.



The precipitation with 'Thionalid', from ammoniacal-masked thallic solution, is white, whereas thallic 'Thionalid' is yellow. When precipitated with mercaptobenzthiazole, a yellow product (thallic compound) is formed, which in a few minutes is transformed into white thallic mercaptobenzthiazole and the disulphide of the mercaptan. The different behaviour of mercaptobenzthiazole and 'Thionalid' is obviously based on the fact that only the latter forms an inner-complex salt with trivalent thallium. Through chelate-ligation (IV) the trivalent thallium as well as the oxidizable mercaptan are stabilized. In the case of the normal mercaptobenzthiazole-salt V there is no stabilization by chelate-ligation, and therefore a redox reaction occurs, forming thallic mercaptobenzthiazole and the disulphide of the mercaptan.



IV. Stable inner-complex salt

V. Unstable normal salt

It seems that certain inner-complex salts of trivalent thallium can serve as a basis for new methods for the detection and determination of thallium.

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<sup>1</sup> Berg, R., and Roebing, O., *Ber.*, **68**, 403 (1935); *Z. angew. Chem.*, **48**, 430 (1935).

<sup>2</sup> Spacu, G., and Kuraš, M., *Z. anal. Chem.*, **102**, 24 (1935); **104**, 88 (1936).

### Order of Stability of Metal Complexes

IN a recent communication<sup>1</sup> it was pointed out that the order of stability of a series of internal metal complexes is substantially the same whether the metals are combined with bidentate chelate molecules like salicylaldehyde, glycine or 8-hydroxyquinoline. There is evidence from the results of other workers<sup>2,3</sup> that the same order is to be found with complex cations and with internal complexes formed with quadridentate chelate molecules. Cations containing ethylenediamine have been studied by Bjerrum<sup>2,4</sup> and Carlson, McReynolds and Verhoek<sup>3</sup>. From the accompanying table, which shows the overall stability constants for salicylaldehyde and ethylenediamine complexes, the similarity of order in the two cases is evident.

Bivalent Metal	log $K_{sal}$	log $K_{en}$
Pd	14.8	26.9(a)
Cu	13.3	19.6(c)
Ni	9.2	18.6(b), 18.1(c)
Co	8.3	13.8(b)
Zn	8.1	12.9(d), 12.1(c)
Cd	7.8	12.3(d), 12.1(c)
Fe	7.6(a)	9.5(b)
Mn	6.8(a)	5.7(b)
Mg	6.8	—

Abbreviations: sal = salicylaldehyde; en = ethylenediamine. (a) Recent measurements by the authors; (b) measurements by Bjerrum, ref. 2; (c) measurements by Carlson, McReynolds and Verhoek, ref. 3; (d) measurements by Bjerrum and Anderson, ref. 4. The figures for Cu and Pd in the right-hand column refer to complexes containing two molecules of ethylenediamine; all the other metals listed combine with three molecules of ethylenediamine.