

CLXXXVIII.—*The Constitution of Some Organic Derivatives of Thallium.*

By NEVIL VINCENT SIDGWICK and LESLIE ERNEST SUTTON.

THE majority of the known metallic alcoholates are salt-like substances; they are non-volatile, insoluble in organic solvents such as benzene, and they often combine with the parent alcohol. Examples of this type are the alcoholates of the alkali metals, the alkaline-earth metals (Chablay, *Compt. rend.*, 1911, **153**, 953; de Forcrand, *ibid.*, 1912, **154**, 1441; Doby, *Z. anorg. Chem.*, 1903, **35**, 93), zinc, magnesium (Tolkatscheff, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 469; Szarvasy, *Ber.*, 1897, **30**, 806), and lead (Chablay, *loc. cit.*). Aluminium is exceptional in that, though its methoxide decomposes on heating, its ethoxide melts at 135° and boils at 234—235°/23 mm., the propoxide and the amyloxyde being similar (Hillyer, *Amer. Chem. J.*, 1897, **19**, 597; Hillyer and Crooker, *ibid.*, p. 37). With the exception of the methoxide these may be regarded as esters of aluminic acid and as being analogous to the esters of boric acid.

Thallos ethoxide belongs to neither of these types; it is a colourless oil at room temperature (m. p.  $-3^{\circ}$ ) which is miscible with benzene, only partially with ethyl alcohol, but has no appreciable vapour pressure at temperatures up to 80°, where it decomposes. It is readily decomposed by water or carbon dioxide. The *n*-propoxide, the *n*-butoxide, and the *isobutoxide* have also been made and appear to be of the same type (Lamy, *Ann. Chim. Phys.*, 1863, **67**, 395; 1864, **3**, 373; Kahlbaum, Roth, and Siedler, *Z. anorg. Chem.*, 1902, **29**, 177), but the methoxide and *cyclohexanyloxyde* (Lamy, *loc. cit.*; de Forcrand, *Compt. rend.*, 1923, **176**, 20) are white microcrystalline solids which do not melt, but decompose above 110°. The phenoxide (de Forcrand, *loc. cit.*) and some of the substituted phenoxides (Christie and Menzies, *J.*, 1925, **127**, 2373) are stable white solids which can be recrystallised from water and have definite melting-points, but are soluble in benzene (see later), while the ethylene glycolate and glycerate (de Forcrand, *loc. cit.*) are yellow crystalline solids. It therefore seemed that some, at least, of these alcoholates were covalent, but, from their non-volatility, were associated.

In the present investigation, the molecular weights of the methoxide, the ethoxide, the *cyclohexanyloxyde* and the benzyloxyde in benzene solution were determined at the freezing point, those of the methoxide and the ethoxide also being determined in their parent alcohols at the boiling points. In addition, the molecular weights of several phenoxides and of ethyl thallicoacetate were measured

in boiling benzene, while finally the solubilities of the ethoxide in ethyl alcohol and of the methoxide in methyl alcohol and in benzene were determined.

#### EXPERIMENTAL.

*Preparation of Materials.*—*Thallos ethoxide.* This was the starting material for all the thallium derivatives used. Some of it was very kindly supplied to us by Dr. R. C. Menzies and more was made by Lamy's method in an apparatus similar to one described to us by Dr. Menzies, wherein thallium, rolled into ribbon, was subjected to the combined action of boiling, dry ethyl alcohol and dry oxygen. The thallos ethoxide dropped into the ethyl alcohol as it was formed, being subsequently withdrawn and filtered through a plug of cotton-wool into a receptacle. It kept best if a layer of alcohol was allowed to remain over it but, in any case, it decomposed in time with the formation of a black colloidal precipitate which could not be removed by filtration. We found that it could then readily be purified by dissolving it in boiling, dry ethyl alcohol, filtering the solution and allowing it to cool, and separating the two liquid layers. Specimens so purified kept considerably better than the crude ones. Ethyl alcohol is soluble in the ethoxide, though only to a small extent (Lamy, *loc. cit.*), so the last traces of it were removed from small quantities of ethoxide, as required, by keeping them for 24 hours over metallic sodium in a vacuum desiccator.

*Thallos methoxide.* This was prepared as described by de Forcrand (*loc. cit.*) by double decomposition between the ethoxide and an excess of dry acetone-free methyl alcohol (kindly supplied by the Balliol and Trinity College Laboratories). Owing to its instability, small quantities were made as required and purified by recrystallisation from dry benzene. The time during which the filtered solutions were exposed to the air was kept as short as possible, and, with care, specimens could be obtained which gave very clear benzene solutions in the molecular-weight determinations. When quite free from methyl alcohol, the methoxide was very unstable; these solutions would begin to deposit a black precipitate even at 25–30°.

Thallos methoxide has no melting point; the solid begins to decompose above 120°.

*Thallos cyclohexanyloxyde.* This was prepared in a similar way, thallos ethoxide being added to an excess of a dry, ethereal solution of cyclohexanol which had twice been distilled in a vacuum to remove most of the water in it. It was washed with a small quantity of pure dry ether and recrystallised from benzene. It has no melting point, but begins to decompose above 110°.

*Thallous benzyloxyde* was also prepared in this way, but, owing to its greater solubility in ether, the reaction mixture was well cooled in a freezing-bath. The product crystallised in colourless shining plates, which were filtered off, washed with a small quantity of well-cooled ether, and kept over potash. It was finally recrystallised from ligroin (b. p. 60—80°). The removal of the last traces of benzyl alcohol from small samples of this substance was difficult, owing to the limited solubility in ligroin of the alcohol and the relatively great solubility of the benzyloxyde.

This compound, m. p. 74—78°, has not been previously described. It decomposes slowly on keeping, is very sensitive to moisture, and is readily soluble in benzene or ether [Found: Tl, estimated as iodide, (1) 65.9, (2) 65.1.  $C_7H_7OTl$  requires Tl, 65.6%].

Dr. T. V. Barker and Mr. R. C. Spiller kindly made a micro-crystallographic examination of this substance. The crystals were regular octagonal plates which, under crossed Nicols, exhibited straight extinction. Normal to the plate was the acute bisectrix of a positive biaxial figure with medium axial angle. The system was possibly orthorhombic, certainly not cubic, tetragonal, hexagonal or rhombohedral.

*Thallous phenoxide, m-tolyloxyde, o-methoxyphenoxide, m-methoxyphenoxide, thallous salicylaldehyde, and the thallous derivative of o-vanillin.* These were all made by double decomposition of the ethoxide with an excess of an ethereal solution of the appropriate phenol. They were filtered off, washed with ether, and recrystallised by solution in either boiling benzene or pyridine and precipitation with ligroin (b. p. 60—80°). The m. p.'s of the first five substances were higher than those reported by Menzies and Wilkins (J., 1924, 125, 1148) and Christie and Menzies (*loc. cit.*), who recrystallised them from alcohol or water.

|                                    |                                   |            |
|------------------------------------|-----------------------------------|------------|
| Thallous phenoxide .....           | M. p. 233—235° (C. & M. 231—235°) |            |
| „ <i>m</i> -tolyloxyde .....       | 196°                              | (187°)     |
| „ <i>o</i> -methoxyphenoxide ..... | 164°                              | (160°)     |
| „ <i>m</i> -methoxyphenoxide ..... | 148°                              | (146—148°) |
| „ salicylaldehyde .....            | 197° decomp.                      | (186°)     |
| „ <i>o</i> -vanillin .....         | 142° decomp.                      |            |

The last *compound* is new. After purification it was obtained as fine yellow crystals which kept well (Found: Tl, determined as iodide, 58.2.  $C_8H_7O_3Tl$  requires Tl, 57.5%); the crude product eventually turned brown or black. It was sufficiently soluble in boiling benzene for its molecular weight to be determined (thallous salicylaldehyde is not).

*Determination of Molecular Weights in Benzene by the Beckmann Freezing-point Method.*

For these determinations the solvent had to be thoroughly dry and the solutions had to be protected against wet air during the course of the experiments, owing to the ease of hydrolysis of the solutes.

The benzene was purified in the usual manner, by repeated fractional freezing and by shaking with sulphuric acid. It was distilled, in a stream of dry air, into a reservoir from which, by the closing of an air by-pass tap, it could be blown direct into the Beckmann tube. Throughout the experiment a slow stream of dry air was passed. It left the apparatus through the stirrer sleeve, which was provided with the usual buffer space to prevent wet air being drawn in by the movement of the stirrer. The air appeared to be sufficiently saturated with benzene in passing through the distilling flask, for no drift of readings, which could be ascribed to evaporation of benzene from the Beckmann tube, was observed. The efficiency of the apparatus in this form was once tested by observing the freezing point of some benzene over a period of 6 hours. The first and the last reading differed by  $0.003^{\circ}$ , the former being  $0.001^{\circ}$  above and the latter  $0.002^{\circ}$  below the mean of the whole series. In view of this and the fact that the alcoholates gave perfectly clear solutions, the drying was considered satisfactory.

Since the methoxide and the *cyclohexanyloxyde* gave maximum lowerings of only  $0.08^{\circ}$  and  $0.05^{\circ}$  respectively, considerable care was necessary in working with them. Whenever possible, freezing-point readings were taken until four successive values differing by not more than  $0.005^{\circ}$  had been obtained, and the mean value taken. If greater fluctuations persisted, the mean of six readings was taken.

We confirmed the observation of Jones and Bury (J., 1925, 127, 1947) that dry benzene is difficult to supercool, and, moreover, at first we experienced difficulty in avoiding caking of the fine benzene crystals on the walls of the tube. This occurred less in the case of the solutions than with the pure solvent, so the conditions under which the "convergence temperatures" (Wildermann, *Proc. Roy. Soc.*, 1896, 59, 251) were reached were different in the two cases, and a zero error resulted. This difficulty was overcome by using an air space round the Beckmann tube of at least 8 mm. and by supercooling about  $1^{\circ}$  for all readings.

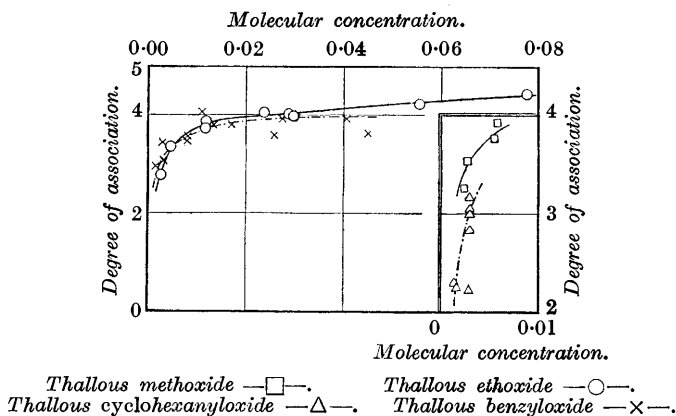
The methoxide, ethoxide, or *cyclohexanyloxyde* was introduced through the side tube of the Beckmann apparatus, and, after the readings had been taken, some of the solution was withdrawn through a curved tube which was passed through the side tube,

filtered through a plug of cotton-wool, weighed, and then shaken with a definite volume of water, which was shown to remove the whole of the thallium. The concentration of the solution in the Beckmann tube was altered by adding more benzene from the reservoir to make it up roughly to its original volume, and the cycle of operations repeated. The thallos hydroxide in the aqueous layers was titrated with *N*/50-hydrochloric acid (methyl-red indicator) and the concentration of the original benzene solution could then be calculated. The benzyloxyde was weighed into the Beckmann tube.

The degrees of association of the thallos compounds were calculated (the cryoscopic constant of the benzene being taken as 53.1

FIG. 1.

*Association curves in freezing benzene.*



from the results of calibration experiments with naphthalene as solute) and plotted against the "simple molecular concentrations," *i.e.*, the quotient of the weight of solute per 100 g. of solvent divided by its simple molecular weight. The curves obtained are shown in Fig. 1 and the data from which they are constructed are tabulated below. The error in the associations of the sparingly soluble substances could be expected to be 5%, allowing an error of 0.002° in the depression of freezing point and of 0.05 c.c. in the titrations. For most points it is actually less.

*Molecular Weights in Benzene, Ethyl and Methyl Alcohols by the Cottrell-Washburn Boiling-point Method.*

The apparatus used for the measurements with benzene and ethyl alcohol was an adaptation of that described by Cottrell (*J. Amer. Chem. Soc.*, 1919, **41**, 721; see also Washburn, *ibid.*, p. 729) so designed

TABLE I.

| $dT$ , obs.                         | G. solute per<br>100 g. solvent. | Simple mol.<br>conc. | $M$ . | Assocn. |
|-------------------------------------|----------------------------------|----------------------|-------|---------|
| Thallous ethoxide.                  |                                  |                      |       |         |
| 0.3095°                             | 5.90                             | 0.0237               | 1011  | 4.06    |
| 0.160                               | 2.92                             | 0.0117               | 967   | 3.88    |
| 0.070                               | 1.105                            | 0.00444              | 837   | 3.36    |
| 0.379                               | 7.14                             | 0.0287               | 999   | 4.01    |
| 0.165                               | 2.905                            | 0.0117               | 933   | 3.745   |
| 0.048                               | 0.628                            | 0.00252              | 694   | 2.785   |
| 0.924                               | 19.32                            | 0.0776               | 1108  | 4.45    |
| 0.690                               | 13.78                            | 0.05535              | 1058  | 4.25    |
| 0.396                               | 7.41                             | 0.02975              | 992   | 3.98    |
| Thallous methoxide.                 |                                  |                      |       |         |
| 0.076                               | 1.27                             | 0.00540              | 887   | 3.775   |
| 0.0385                              | 0.603                            | 0.002565             | 833   | 3.545   |
| 0.078                               | 1.335                            | 0.00568              | 907   | 3.86    |
| 0.038                               | 0.550                            | 0.00234              | 767   | 3.265   |
| Thallous <i>cyclohexanylo</i> xide. |                                  |                      |       |         |
| 0.050                               | 0.869                            | 0.00287              | 921   | 3.04    |
| 0.048                               | 0.867                            | 0.00286              | 957   | 3.16    |
| 0.040                               | 0.5055                           | 0.00229              | 670   | 2.21    |
| 0.050                               | 0.8535                           | 0.002815             | 905   | 2.985   |
| 0.037                               | 0.475                            | 0.00157              | 681   | 2.245   |
| 0.032                               | 0.4175                           | 0.00138              | 692   | 2.283   |
| 0.054                               | 0.872                            | 0.00288              | 856   | 2.825   |
| Thallous <i>benzylo</i> xide.       |                                  |                      |       |         |
| 0.024                               | 0.416                            | 0.00138              | 918   | 2.95    |
| 0.052                               | 0.938                            | 0.00302              | 956   | 3.075   |
| 0.119                               | 2.431                            | 0.00782              | 1083  | 3.483   |
| 0.043                               | 0.862                            | 0.00277              | 1062  | 3.415   |
| 0.118                               | 2.464                            | 0.00793              | 1170  | 3.56    |
| 0.235                               | 5.243                            | 0.0169               | 1183  | 3.805   |
| 0.183                               | 4.079                            | 0.0131               | 1181  | 3.800   |
| 0.379                               | 8.018                            | 0.0258               | 1121  | 3.604   |
| 0.658                               | 13.98                            | 0.04495              | 1126  | 3.62    |
| 0.142                               | 3.39                             | 0.0109               | 1265  | 4.06    |
| 0.369                               | 8.515                            | 0.0274               | 1223  | 3.93    |
| 0.538                               | 12.45                            | 0.0405               | 1226  | 3.94    |

that the solutions could be kept dry. The dry solvent was distilled in a stream of dry air into a reservoir from which it could be elevated into a burette, as required, by suction, and it could be run out from this direct into the actual boiling-point apparatus. A side tube, from the outlet, was connected with this so that a positive pressure of dry air could be maintained within it, but no stream of air went through. The end space of the burette was calibrated in order that it could be completely emptied, and risk of solvent slowly leaking through the tap, which could not be greased, was thus avoided. The actual boiling-point apparatus is shown in Fig. 2. The outer Pyrex tube was 5 cm. in diameter at the top, but only 2.5 cm. at the

bottom, in order to use less liquid. The cork A carried a Beckmann thermometer, B, the end of the burette, C, the leads to the spiral composition-tubing condenser, D, and the pressure supply tube, E. There was also a hole through which solution could be withdrawn. An inner tube, F, 2.5 cm. in diameter, slightly constricted at the bottom, was held on to the thermometer by means of a cork, and the Y-tube G, through which the mixture of liquid and vapour rose, rested on this constriction and was held central by a loop of nickel wire encircling the thermometer. The dimensions are important, and the diagram is therefore drawn to scale. Radiation, etc., was prevented by the asbestos jacketing, and the burner was shielded from draughts by a mica chimney.

The results of two trial runs with ethyl alcohol as solvent and benzil as solute are in Table II. The readings were steady to  $0.001^\circ$  and it will be seen that the method is satisfactory for elevations down to  $0.02^\circ$ .

For the ethoxide, as in the freezing-point measurements, successive solutions were made up in the tube, their boiling points were determined, and they were then withdrawn and analysed. The more stable phenoxides could be weighed into measured volumes of benzene.

The ethyl alcohol was first dried with quick-lime and then with calcium; the benzene was treated as before.

FIG. 2.

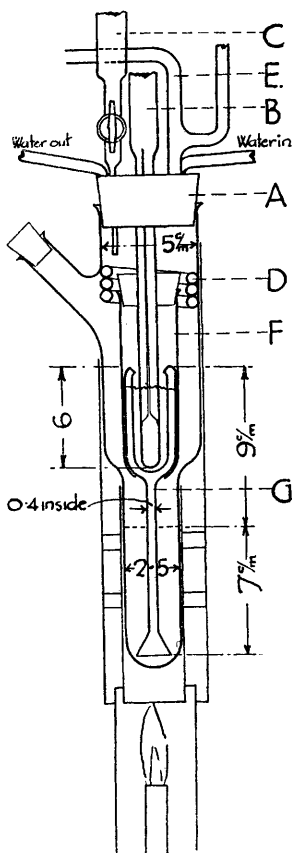


TABLE II.

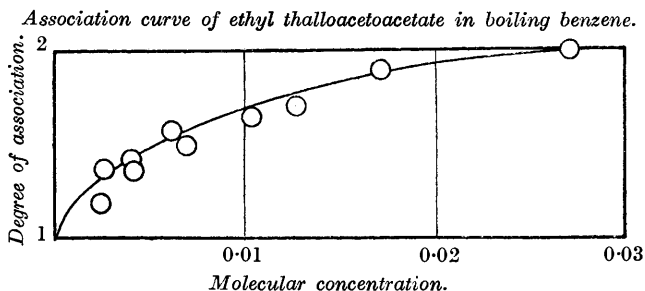
| $dT$ ,<br>obs. | G. solute per<br>100 g. solvent. | Ebullioscopic<br>const. | $dT$ ,<br>obs. | G. solvent per<br>100 g. solvent. | Ebullioscopic<br>const. |
|----------------|----------------------------------|-------------------------|----------------|-----------------------------------|-------------------------|
| $0.021^\circ$  | 0.3805                           | 11.59                   | $0.041^\circ$  | 0.764                             | 11.27                   |
| 0.052          | 0.9930                           | 11.00                   | 0.069          | 1.261                             | 11.50                   |
| 0.101          | 1.920                            | 11.05                   | 0.104          | 1.914                             | 11.41                   |
| 0.173          | 3.230                            | 11.25                   | 0.147          | 2.735                             | 11.29                   |

Methyl alcohol rapidly attacked the corks in the above simple type of apparatus, so an all-glass apparatus, similar to that of

Washburn (*loc. cit.*), originally designed for use with pyridine, was adapted for use with this solvent. The dimensions were essentially the same as in the other apparatus, the inner tube fitted into the outer one by means of a large ground joint, the thermometer was fixed in it by a small piece of rubber tube, and the Y-tube rested on two pairs of indentations and was kept central by a loop of wire, as before. It had a side tube with a condenser jacket, and the end of this was connected with the dry air supply, so that a small pressure could be maintained within the apparatus.

The methyl alcohol was supplied by the Balliol and Trinity College Laboratories and was dried with aluminium methoxide (from aluminium amalgam); the thallos methoxide was freshly made, and not recrystallised from benzene. The general procedure was like that for the ethoxide, the solutions being poured out through a small side tube after the boiling point had been determined.

FIG. 3.



The degrees of association are tabulated below, and those for ethyl thallicoacetate are shown, plotted against simple molecular concentration, in Fig. 3.

TABLE III.

*Molecular Weights in Ethyl Alcohol.*

| <i>d</i> T, obs.  | G. solute per 100 g. solvent. | Simple mol. conc. | <i>M</i> . | Assocn. |
|-------------------|-------------------------------|-------------------|------------|---------|
| Thallos ethoxide. |                               |                   |            |         |
| 0.140°            | 13.08                         | 0.0526            | 1065       | 4.28    |
| 0.066             | 5.15                          | 0.0207            | 890        | 3.57    |
| 0.040             | 2.65                          | 0.0106            | 755        | 3.03    |
| 0.113             | 9.09                          | 0.0365            | 917        | 3.685   |
| 0.116             | 9.79                          | 0.0393            | 963        | 3.865   |
| 0.079             | 6.14                          | 0.0247            | 887        | 3.56    |
| 0.039             | 2.86                          | 0.0115            | 836        | 3.36    |
| 0.156             | 13.69                         | 0.0550            | 1000       | 4.02    |
| 0.083             | 5.63                          | 0.0226            | 774        | 3.11    |
| 0.036             | 2.88                          | 0.0116            | 912        | 3.66    |
| 0.018             | 1.52                          | 0.0061            | 966        | 3.88    |

(Ebullioscopic constant taken as 11.4, mean value from Table II.)



*Molecular Weights in Methyl Alcohol.*

## Thallos methoxide.

|       |       |        |       |      |
|-------|-------|--------|-------|------|
| 0-076 | 1-59  | 0-0068 | 186-5 | 0-79 |
| 0-088 | 2-043 | 0-0087 | 206-5 | 0-88 |
| 0-062 | 1-96  | 0-0083 | 281   | 1-20 |
| 0-080 | 2-07  | 0-0088 | 230-5 | 0-98 |

(Ebullioscopic constant taken as 8.9, mean of values in "Physikalische-Chemische Tabellen," Landolt-Börnstein.)

*Molecular Weights in Benzene.*

## Thallos phenoxide.

|       |       |         |      |       |
|-------|-------|---------|------|-------|
| 0-029 | 1-124 | 0-00378 | 1091 | 3-67  |
| 0-055 | 2-226 | 0-00749 | 1139 | 3-835 |
| 0-025 | 0-762 | 0-00257 | 858  | 2-89  |
| 0-048 | 1-288 | 0-00434 | 755  | 2-54  |
| 0-060 | 1-680 | 0-00566 | 787  | 2-65  |

Thallos *o*-methoxyphenoxide.

|       |       |         |      |      |
|-------|-------|---------|------|------|
| 0-026 | 1-113 | 0-00340 | 1223 | 3-74 |
| 0-045 | 1-900 | 0-00581 | 1188 | 3-63 |
| 0-080 | 3-650 | 0-01116 | 1283 | 3-92 |
| 0-135 | 5-910 | 0-01840 | 1232 | 3-77 |
| 0-036 | 1-818 | 0-00555 | 1420 | 4-34 |
| 0-055 | 2-672 | 0-00815 | 1367 | 4-17 |
| 0-086 | 4-075 | 0-01243 | 1333 | 4-07 |
| 0-123 | 5-490 | 0-01678 | 1256 | 3-84 |

Thallos *m*-methoxyphenoxide.

|       |       |         |      |       |
|-------|-------|---------|------|-------|
| 0-032 | 1-504 | 0-00460 | 1321 | 4-04  |
| 0-084 | 3-952 | 0-0121  | 1321 | 4-04  |
| 0-111 | 5-290 | 0-0162  | 1338 | 4-09  |
| 0-053 | 2-400 | 0-00734 | 1279 | 3-90  |
| 0-112 | 4-285 | 0-0131  | 1076 | 3-29  |
| 0-138 | 5-430 | 0-0166  | 1105 | 3-375 |

Thallos *o*-vanillin derivative.

|       |       |         |      |      |
|-------|-------|---------|------|------|
| 0-041 | 1-639 | 0-00463 | 1124 | 3-18 |
| 0-050 | 2-385 | 0-00674 | 1340 | 3-78 |
| 0-085 | 3-565 | 0-01007 | 1180 | 3-33 |

## Ethyl thalooacetate.

|       |       |         |       |       |
|-------|-------|---------|-------|-------|
| 0-055 | 0-864 | 0-00259 | 442   | 1-37  |
| 0-080 | 1-335 | 0-00401 | 469   | 1-41  |
| 0-109 | 2-028 | 0-00610 | 524   | 1-57  |
| 0-254 | 5-680 | 0-01705 | 629   | 1-89  |
| 0-382 | 8-990 | 0-0270  | 662   | 1-99  |
| 0-058 | 0-815 | 0-00245 | 395   | 1-185 |
| 0-086 | 1-384 | 0-00416 | 451   | 1-356 |
| 0-129 | 2-288 | 0-00687 | 498   | 1-495 |
| 0-177 | 3-440 | 0-01033 | 546   | 1-64  |
| 0-209 | 4-210 | 0-01263 | 566-5 | 1-70  |

(Ebullioscopic constant taken as 28.14, from calibration with benzil as solute.)

*Solubility Measurements.*

These were made by the usual analytical method, the two phases being stirred together for various periods, after which the solutions were withdrawn, filtered, and analysed. All outlets were protected

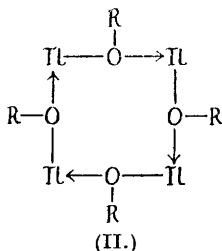
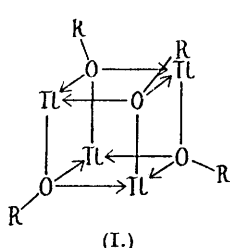
with sulphuric acid tubes, and a mercury-sealed stirrer was used, in order to prevent the ingress of moisture.

The observed solubilities at 25° were : thallos ethoxide in ethyl alcohol, 9.108 g./100 g.; thallos methoxide in methyl alcohol, 1.703 g./100 g.; thallos methoxide in benzene, 3.16 g./100 g.

These are the mean values of sets of readings which each included one result obtained by saturating for at least 11 hours.

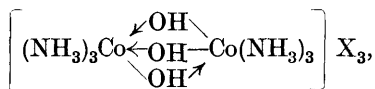
#### *Discussion of Results.*

Both the aliphatic and the aromatic alcoholates of thallium behave in water as salts, and their differences in such properties as ease of hydrolysis can be explained by the differing acidities of the parent alcohols. They all dissolve in benzene, however, as much as covalent compounds could be expected to do, which shows that they are covalent in benzene and therefore, presumably, in the solid state. In these solutions they are highly associated, fourfold association being already complete when the *actual* concentrations (of the polymeride) are only about  $N/20$  in the case of the four aliphatic compounds examined and the *o*- and *m*-methoxyphenoxides. The phenoxide and the *o*-vanillin derivative, at actual concentrations of  $N/100$ — $N/50$ , are already associated about three times, but their sparing solubility prevents measurements at higher concentrations. The ethoxide (but not the benzyloxyde) appears to undergo a slow further polymerisation in more concentrated solutions. Its complex is, moreover, stable in ethyl alcohol, but the methoxide is apparently unimolecular in methyl alcohol. Though both of these are more soluble in benzene than in their parent alcohols, the difference (at 25°) is less for the methoxide (benzene, 3.16 g./100 g.; methyl alcohol, 1.7 g./100 g.) than for the ethoxide (completely miscible with benzene; ethyl alcohol, 9.1 g./100 g.), which is probably connected with the difference of molecular states in the alcohols. From this it is evident that a fourfold polymeride exists which has a very considerable degree of stability and must, therefore, have a structure which explains why the alcoholates associate readily up to four times, and no further. One possibility is a cubic structure (I) and another is an eight-membered ring structure (II) :—



In the former structure the thallium, having gained one electron from the normal covalency and two from each co-ordinate link, has a complete octet 2, 3, 3, this including the two electrons which are inert in the normal thallos compounds. The oxygen atoms have each formed two co-ordinate links and so have completely shared octets as in basic beryllium acetate (Morgan and Bragg, *Proc. Roy. Soc.*, 1923, **104**, 437; Sidgwick, *Nature*, 1923, **111**, 808). The further polymerisation could be accounted for by assuming the formation of a co-ordinate link from a thallium atom in one molecule to one in another. In the ring structure each thallium atom has four shared electrons, having gained one by forming a covalency and two from the donor link, so it would probably have a shared quartet outside the core plus the "inert pair" (78) (2), 2, 2. Each oxygen has two ordinary covalencies and one co-ordinate link, as in the majority of its co-ordination compounds. Further polymerisation could occur either by the formation of a double bond between one or more pairs of thallium atoms in different molecules, or by the formation of a co-ordinate link from oxygen to thallium.

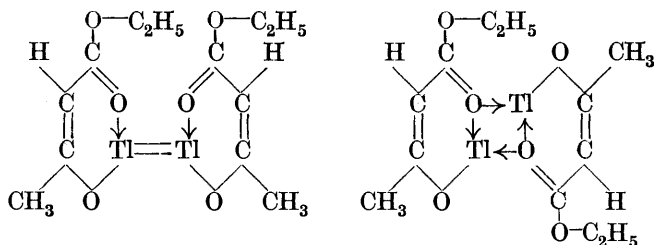
The main difficulty in the cubic structure is that it would certainly be highly strained, though a compound,



the existence of which was established by Werner (*Ber.*, 1907, **46**, 4834), would have approximately the same degree of strain per atom, if the metallic atoms in each be assumed to have their valencies normally at right angles, as is certainly the case for the cobalt and possibly for the thallium. If not, the strain would be about twice as great as in this other compound. There is, on the other hand, a strong *a priori* objection to the ring structure inasmuch as no eight-membered chelate rings, in the strict sense of the word, are definitely known to exist (Sidgwick, "Electronic Theory of Valency," p. 251), whereas six-membered chelate rings are very common, and, therefore, if a ring compound were to be formed by polymerisation, we should expect it to be a three-fold and not a four-fold complex. In both formulæ we postulated that the thallium should accept co-ordinate links, but it is remarkable that it does not appear to do this from pyridine or acetone; the thallos phenoxides can be precipitated unchanged from pyridine solutions by ligroin, or recrystallised from acetone. Moreover, the one type of thallos ammine reported (Biltz and Stollenwerk, *Z. anorg. Chem.*, 1921, **119**, 97) is only formed in liquid ammonia.

Ethyl thalooacetate was found not to be a simple co-ordin-

ation compound, but to be completely polymerised to a two-molecular complex in a solution  $N/8$  in *actual* concentration. This polymeride could be formed in either of two ways. First, by the formation of a double bond between the two thallium atoms, which was suggested as a way in which the eight-membered ring might polymerise; this would be analogous to the readiness of the inert pair of electrons to partake in the formation of a completely shared octet, which is so marked in lead.



Secondly, co-ordinate links from oxygen to thallium could be formed, so that the thallium would be given a mixed octet, as in the suggested cubic structure. In fact, the whole similarity of the two structures may be taken to support both. Thallous acetylacetonate was reported by Kurowski (*Ber.*, 1910, **43**, 1078) to be unimolecular in ethyl alcohol, but we could not confirm this; we obtained irregular results suggestive, possibly, of alcoholysis. We should expect the thallous derivative of *o*-vanillin to behave in the same way, but actually, as previously stated, it appears to be associated largely to the four-fold polymeride.

These results are of interest in their bearing on Sugden's deductions from the parachors of thallium compounds (*J.*, 1929, 316). He there claims to have shown that the parachor of thallium in ethyl thalloacetoacetate is approximately the same as in dimethylthalliumbenzoylacetone, whether we assume singlet or duplet linkages, and the same as in thallous ethoxide, formate, and acetate, if we assume singlet linkages in the first two, and duplet linkages in the last three substances. If we assume that no allowance has to be made for the tervalency of the oxygen, the eight-membered ring structure gives parachor values for thallium practically identical with those derived from the unimolecular formula, on either the singlet or the duplet link hypothesis (*ca.* 62 for duplet links, and 85 for singlet links). The cubic structure involves parachors for thallium of about 48 for duplet links and less than 30 for singlet links. In order to derive a parachor value of about 62 from ethyl thalloacetoacetate, which we now know to be bimolecular, we must assume that all the thallium linkages (including those uniting the two

simple molecules) are singlet links; all other assumptions give lower values. Thus, the difficulty of reconciling the various data for  $P_{Ti}$  is that we have to assume that the polymerisation arises from the formation of duplet links in the case of the ethoxide and singlet links in the case of the acetoacetic ester derivative.

We should expect that, if the cubic structure were the correct one, crystals of the alcoholates would be cubic. From the previously mentioned crystallographic examination of the benzyloxyde (the only derivative which gave suitably large crystals) this obviously was not so, but the cubic structure is not definitely ruled out as a consequence; carbon tetrabromide is cubic above  $46.68^\circ$ , but monoclinic below this temperature (Zirngiebl; compare Groth, "Chemische Krystallographie," Vol. I; [Leipzig, 1906], p. 229).

Though the structure of the four-molecular complex cannot be settled from the available evidence, its stable existence is interesting, since it shows that mono-covalent thallium, which could have a partially shared quartet (78), 2, 1, 1, or a shared pair outside the core plus the inert pair (78) (2), 1, 1 (compare the mercurous ion), although it can exist, is very unstable, and this may be correlated with the fact that no monoalkyl derivative of thallium has yet been isolated.

We should like to express our thanks to Dr. R. C. Menzies for his great kindness in supplying specimens of several thallos compounds and for his helpful advice regarding the preparations; also to Imperial Chemical Industries Ltd. for a grant towards the expenses of the research.

THE DYSON PERRINS LABORATORY,  
OXFORD.

[Received, May 13th, 1930.]

---