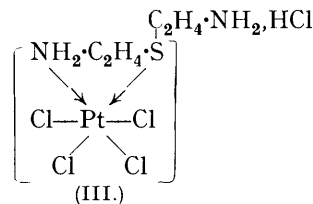
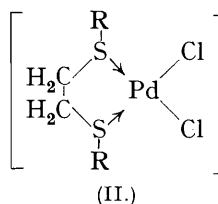
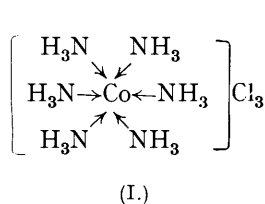


**366.** *The Constitution of Complex Metallic Salts. Part III. The Parachors of Palladium and Mercury in Simple and Complex Compounds.*

By FREDERICK G. MANN and DONALD PURDIE.

THE electronic theory of valency leaves little doubt that in the complex metallic amines the nitrogen of the ammonia molecule is bound to the central metallic atom by a co-ordinate link, and that the structural formula of hexamminocobaltic chloride is correctly represented by (I). It is significant that in all complex salts of the ammine type, *e.g.*, those formed by the co-ordination of ammonia or of organic amines, sulphides, selenides, tertiary phosphines, arsines, stibines, etc., the co-ordinating atom of the ammonia or the organic molecule possesses a complete octet of electrons before co-ordination, and that this octet always contains at least one pair of unshared electrons, by means of which the co-ordinate link to the metallic atom can be made; moreover, the formation of any other type of linkage would in all such cases produce an unstable electronic distribution around the co-ordinating non-metallic atom, which would therefore exhibit an abnormal (and, indeed, hitherto unknown) valency.



To obtain experimental evidence for the presence of co-ordinate links in complex salts, Bennett, Mosses, and Statham (J., 1930, 1668) prepared several non-ionic compounds of type (II) (wherein the two sulphur atoms become asymmetric by co-ordination with the palladium), but failed to separate them into racemic and *meso*-forms. More decisive evidence was obtained by Mann (*ibid.*, p. 1745), who prepared tetrachloro-( $\beta\beta'$ -diamino-diethyl sulphide monohydrochloride)platinum (III), and isolated the *d*-form having  $[M]_{5461} + 1070^\circ$ . The optical activity is here again due to the sulphur atom having become asymmetric by co-ordination, and thus electronically and stereochemically equivalent to the sulphur atom in the dissymmetric sulphoxides and sulphinic esters: the resolution of this platinum compound leaves very little doubt that a co-ordinate link joins the sulphur to the metal.

Sugden (J., 1929, 318) determined the parachors of aluminium and beryllium acetylacetonates, etc., and considered that the results showed the presence of singlet links joining the organic molecules to the metal: this interpretation is invalidated by a factor which was not recognised in his work but has become evident in the present investigation and will be discussed later.

To obtain further physical data to supplement the stereochemical evidence, the parachors of complex salts of the ammine type have been investigated. The neutral non-ionic derivatives of 4-covalent palladium of type  $[a_2\text{Pd}b_2]$  were used, partly because no complication from *cis-trans*-isomerism would arise, since in the palladium (as distinct from the platinum) compounds only the very stable *trans*-compounds normally occur, and partly because the high solubility of the palladium compounds in organic solvents would

enable the parachors to be determined in solution by Hammick and Andrew's method (J., 1929, 754).

A homologous series of dialkyl sulphide derivatives of palladous chloride, of formula  $[(R_2S)_2PdCl_2]$ , was prepared, and the members found to be fusible without decomposition; an accurate determination of their parachors could therefore be made directly with the fused material. The results [Table I (A)] were quite unexpected: the parachor of palladium in each compound is calculated by subtracting from the experimental molecular parachor the sum of the parachors of all elements except the metal, and is found to fall from 36 for the methyl compound to -7 for the *n*-amyl. (For this purpose, a revised list of atomic parachors was kindly provided by Prof. Sugden. The new values, which will be shortly published, in general differ only slightly from the earlier ones: those concerned in the present investigation are: C, 7.2; H, 16.2; O, 20.0; Cl, 53.5; Br, 68.0; S, 48.5; P, 37; As, 51; Hg, 69; co-ordinate link, 0; singlet link, -10.) The atomic parachor of palladium is unknown. Since, however, that of molybdenum (at. no. 42) is approximately 80 and that of silver (at. no. 47) 63 (Sugden, "Parachor and Valency," 1930, Chap. IX), and since only small fluctuations occur in the known parachors through adjacent members of the transitional series, it is probable that the parachor of palladium (at. no. 46) lies between these two values, and probably close to the latter. If the palladium parachors in the dialkyl sulphide series are extrapolated backwards, a value for palladium in its dichloride of 55-60 is obtained, in agreement with the expected value. It would appear, therefore, that the steady fall in the parachor of palladium on ascending the sulphide series is dependent chiefly on the size of the sulphide molecule, and not upon the co-ordinated structure as such. Moreover, the change in the parachor is not due to any progressive change in the general structure of the compounds (*e.g.*, by association, etc.), for the sulphide compounds show normal molecular weights in benzene solutions.

To determine whether the abnormal parachors were peculiar to the sulphide complex compounds, similar homologous series were prepared with tertiary phosphines and arsines, and these compounds also were found to be fusible without decomposition. The results [Table I, (B) and (C) respectively] are strictly parallel with those of the sulphides: as each series is ascended, the apparent parachor of the palladium falls steadily to a negative value. Moreover, in all three series, the m. p.'s of the homologous compounds also fall steadily, the tri-*n*-amylarsine compound, in particular, being liquid at room temperature.

TABLE I.

*Parachors of Complex Palladium Derivatives.*

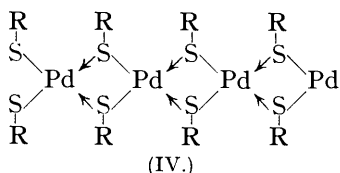
Compound.	M. p.	[P], obs.	$\Sigma[P]^*$	Parachor of Pd.	Compound.	M. p.	[P], obs.	$\Sigma[P]^*$	Parachor of Pd.
<i>Dichlorides.</i>					(C) Trialkylarsines, $[(R_3As)_2PdCl_2]$ .				
(A) Dialkyl sulphides, $[(R_2S)_2PdCl_2]$ .					R = Me	235°	—	—	—
R = Me	130°	463	427	36	Et	116	793	781	12
Et	81	613	586	27	<i>n</i> -Pr	55	1014	1019	— 5
<i>n</i> -Pr	59	760	744	16	<i>n</i> -Bu	54	1243	1257	— 14
<i>n</i> -Bu	32	906	902	4	<i>n</i> -Am	10-11	1467	1494	— 27
<i>n</i> -Am	41	1054	1061	— 7	<i>Dibromides.</i>				
<i>iso</i> -Bu	97	914	902	12	(D) Dialkyl sulphide, $[(R_2S)_2PdBr_2]$ .				
(B) Trialkylphosphines, $[(R_3P)_2PdCl_2]$ .					R = Et	103	638	615	23
R = Et	139	775	753	22	(E) Trialkylphosphine, $[(R_3P)_2PdBr_2]$ .				
<i>n</i> -Pr	96	994	991	3	R = <i>n</i> -Bu	73	1243	1258	— 15
<i>n</i> -Bu	66	1217	1229	— 12	(F) Trialkylarsine, $[(R_3As)_2PdBr_2]$ .				
<i>n</i> -Am	47	1452	1466	— 14	R = <i>n</i> -Pr	49	1040	1048	— 8

\*  $\Sigma[P]$  represents the sum of the parachors of all the elements except palladium.

Further, the abnormal parachors are not peculiar to the complex dichlorides, for in certain of the dibromides [Table I, (D), (E), (F)] the parachor of the palladium atom is almost identical with that derived from the corresponding dichlorides.

To decide whether the links co-ordinating the non-metallic atoms to the palladium determined the abnormal parachor values, fusible compounds of palladium devoid of co-ordinate links were sought, and for this purpose the palladium derivatives of the

aliphatic thiols, Pd(SR)<sub>2</sub>, were investigated. The ethyl, *n*-propyl, *n*-butyl, and *n*-amyl members were crystalline, but only the last two could be fused without decomposition; in these compounds the palladium atoms [Table II (A)] showed low parachor values almost



identical with those derived from the corresponding dialkyl sulphide compounds. It is not certain, however, that these palladium mercaptides are devoid of co-ordinate links. They are certainly not salts, since Prof. Sugden has kindly investigated the conductivity of the fused *n*-amyl derivative and reports: "It is a non-conductor in the fused state, the resistance of the cell filled with the liquid

substance being too large to measure. An upper limit for the conductivity is  $\kappa < 4 \times 10^{-6}$  at 95°." On the other hand, both the *n*-butyl and the *n*-amyl compound showed considerable association (4—7-fold) even in non-associating solvents such as ethylene dibromide and bromoform, and it is possible that the sulphur atoms of one molecule co-ordinate to the palladium of other molecules, giving a chelated structure such as (IV).

TABLE II.

*Parachors of Palladium and Mercury Mercaptides.*

Compound.	M. p.	[P], obs.	$\Sigma[P]$ .*	Parachor of metal atom.	Compound.	M. p.	[P], obs.	$\Sigma[P]$ .*	Parachor of metal atom.
(A) Palladium mercaptides, Pd(SR) <sub>2</sub> .									
R = <i>n</i> -Bu	142°	452	446	6	R = <i>n</i> -Am	83°	531—524†	525	6 to — 1
(B) Mercury mercaptides, Hg(SR) <sub>2</sub> .									
R = Et	77	334	288	46	R = <i>n</i> -C <sub>6</sub> H <sub>13</sub>	58	620	605	15
<i>n</i> -Pr	67	402	367	35	<i>n</i> -C <sub>7</sub> H <sub>15</sub>	75	692	684	8
<i>n</i> -Bu	85	475	446	29	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	71	772	763	9
<i>n</i> -Am	66	545	525	20					

\*  $\Sigma[P]$  represents the sum of the parachors of all the elements except the metal atom.

† [P], obs., falls as the temperature of determination rises.

To obtain further evidence on this point, the alkyl mercaptides of mercury were investigated: these are fusible without decomposition, and have the great advantage that the parachor of the metal itself is accurately known. Various observers, *e.g.*, Brown (*Phil. Mag.*, 1928, 6, 1044), have determined the parachor of metallic mercury to be 69, and the same value was obtained by Cavell and Sugden (*J.*, 1929, 2572) for its parachor in diphenylmercury: the parachor in diethyl- and di-*n*-amyl-mercury has now been found to be 66 and 61 respectively. It is clear, therefore, that in ascending the homologous dialkylmercury series, the parachor of the mercury atom falls only very slightly from its value in the metallic state. In the homologous mercury mercaptides, however [Table II, (B)], this parachor falls to 46 for the ethyl compound and then continuously to a constant value of 8—9 for the *n*-heptyl and the *n*-octyl compound. These mercury mercaptides show normal molecular weights in dilute benzene solution, and therefore stable association, such as that shown in (IV), does not occur: hence the abnormal parachor values are independent of co-ordinate links.

A remote possibility that the abnormal parachor values in the above mercaptides might be a particular property of the group —S—X—S—, where X is an atom of another element joined to the sulphur atoms by covalent links, was disproved by determining the parachors of the bisethylmercaptols of acetone and of methyl ethyl ketone, CR'R'(SEt)<sub>2</sub>. For the first compound, [P], obs. = 402.3 (calc., 406.6) and for the second, [P], obs. = 439.7 (calc., 446.2). Since a correction of — 3 or — 4 for the *gem.*-dialkyl groups (Sugden, *J.*, 1929, 316; Mumford and Phillips, *ibid.*, p. 2118) has to be applied to each of the calculated parachors, it follows that no abnormality is associated with the above dithio-group.

It is clear from the foregoing results that in certain series of organometallic compounds, both simple and complex, the metal atom shows an apparent parachor which falls steadily as the homologous series is ascended, and may ultimately reach a constant value. Sugden (*op. cit.*, Chap. VII) has determined the parachors of certain ketonic derivatives of thallium,

beryllium, and aluminium, and finds that the average parachor of the metal, calculated on the basis of the commonly accepted constitution of these compounds, in which the ketonic oxygen is joined by a co-ordinate link to the metal, has a low (and frequently a negative) value : if, however, the organic molecule is assumed to be co-ordinated to the metal by the aid of singlet links (each having the earlier value  $[P] = -11.6$ ), higher average values for the parachor of the metal, agreeing well with those in simpler compounds, are obtained (Table III).

TABLE III.  
*Parachors of Thallium, Beryllium, and Aluminium Derivatives.*

Compound.	Formula.	[P], obs.	Normal formulæ.			Singlet formulæ.		
			[P], calc.	[P] for metal.	Mean.	[P], calc.	[P] for metal.	Mean.
Thalious ethoxide...	TlOC <sub>2</sub> H <sub>5</sub> *	177.3	115.1	62.2	65.5	272.0	60.2	62.4
Thalious formate ...	TlHCO <sub>2</sub>	150.3	80.3	70.0				
Thalious acetate ...	TlC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	183.5	119.3	64.2				
Thalious acetoacetic ester .....	Tl(C <sub>6</sub> H <sub>9</sub> O <sub>3</sub> )	332.2	295.2	37.0	39.2	459.1	64.6	62.4
Dimethylthallium benzoylacetate	Me <sub>2</sub> Tl(C <sub>10</sub> H <sub>9</sub> O <sub>2</sub> )	523.7	482.3	41.4				
Beryllium acetyl- acetate .....	Be(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub>	470.4	472.4	- 2.0	- 8.6	504.0	35.0	37.8
Beryllium propionyl- acetate .....	Be(C <sub>6</sub> H <sub>9</sub> O <sub>2</sub> ) <sub>2</sub>	539.0	550.4	- 11.4				
Basic beryllium propionate .....	OBe <sub>4</sub> (C <sub>3</sub> H <sub>5</sub> O <sub>2</sub> ) <sub>6</sub>	985.4	1035.2	- 12.4				
Aluminium acetyl- acetate .....	Al(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub>	680.5	708.6	- 28.1	- 32.8	756.0	32.0	38.6
Aluminium propi- onylacetate ...	Al(C <sub>6</sub> H <sub>9</sub> O <sub>2</sub> ) <sub>3</sub>	788.0	825.6	- 37.6				
Aluminium bromide	Al <sub>2</sub> Br <sub>6</sub>	457.6	419.6	19.0				

\* Considered as the simple compound, although subsequently shown by Sidgwick and Sutton (J., 1930, 1461) to be the polymeride, (TlOEt)<sub>4</sub>: this polymerisation would, however, probably not affect the parachor of the unit molecule.

Inspection of these results shows, however, that the phenomenon discovered in the present investigation occurs also in many of Sugden's compounds, but was not recognised because only two members of each homologous series were studied. For instance, the parachor of thallium falls markedly from the formate to the acetate, and is again much lower in the ketonic derivatives; the parachors of both beryllium and aluminium also decrease markedly in passing from their acetyl- to their propionyl-acetonates. There is no doubt that this fall would continue on further ascension of the homologous series, and that an average value based solely on two members of the series has no significance, and cannot be used as evidence for singlet links. In the absence of this evidence, that for the presence of co-ordinate links provided by the resolution of the platinum compound (III) stands unchallenged.

It is clear, however, that the experimental data are still insufficient for a detailed theoretical interpretation of these anomalous parachor values. Pearson and Robinson (J., 1934, 740) have found that the considerable variation in the parachor of hydrogen in the simple hydrides depends apparently on the electrochemical nature and the size of the second atom, since this parachor has a minimum value in the halogen hydrides (10.28 in hydrogen fluoride), a normal value in the neutral hydrides (16.96 in methane), and a maximum value in the metallic hydrides (19.20 in bismuthine). Clearly, no similar explanation can be applied to the parachor values of palladium or mercury in a *homologous* series of compounds. Mumford and Phillips (*loc. cit.*) have recalculated the average value of many atomic parachors, and consider that Sugden's original value of 39 for the methylene group should be *increased* to 40. (In the present paper, Sugden's amended value of 39.6 is used.) To obtain a constant value for palladium in each homologous series given in Table I, the value for the methylene group must, however, be greatly *decreased*. For instance, in the sulphide compounds (A) an increase

of 16 methylene groups from the methyl to the *n*-amyl member gives a decrease of 43 units (from 36 to -7) in the apparent parachor of palladium, or a mean value of 2.7 per methylene group; in the phosphine and the arsine series [Table I, (B) and (C)], mean decreases of 2.0 and 2.2 respectively are similarly found for each methylene group. If, therefore, in calculating the sum of the parachors of all elements except palladium, the parachor of the methylene group is reduced throughout by 2.3 units to 37.3, a constant value for palladium in each of the three series is obtained, *viz.*, 43 for the sulphide series (A), 48 for (B), and 40 for (C). Against this proceeding, however, it must be urged (i) that the value for the methylene group is remarkably constant in organic compounds, and is extremely unlikely to undergo so large a decrease in derivatives of aliphatic sulphides, phosphines, and arsines; (ii) a similar decrease applied to the palladium mercaptides [Table II (A)] gives a much lower value for palladium, which would not be sensibly changed by association of the molecule; and (iii) no such adjustment of unit parachors can explain the change in the value for mercury in its mercaptides [Table II (B)] where the change itself is falling to zero as the homologous series is ascended.

Mumford and Phillips (*loc. cit.*) have applied "strain factors" to the calculated parachors of certain classes of organic compounds in order to obtain close agreement with the observed values, and find that electronegative groups, such as Cl, CN, CO<sub>2</sub>R, have negative strain factors; *e.g.*, the groups or molecules CHCl<sub>2</sub>, CCl<sub>3</sub>, and CCl<sub>4</sub> have strain factors of -3, -6, and -9 respectively,\* whilst the corresponding bromo-groups have negative factors about 1.5 times larger. These negative strain factors are considered to represent a definite diminution in the molecular volume, caused either by a close and general packing of the atoms or groups within the molecule, or by a decrease in the effective size of certain of the constituent atoms. The negative strain factor of the chlorinated methanes is considered to be due to the second of these causes, *i.e.*, to a progressive decrease in the effective size of the carbon atom.

Hammick and Wilmut (J., 1934, 22; this vol., p. 207) have shown that "strain factors" cannot account quantitatively for the negative parachor anomaly shown by several organic compounds, which is of "a variable kind unassociated with any particular structure," but often appears to be connected with the accumulation of certain negative atoms or groups in the molecule, and also with the size of these substituting groups. Freiman and Sugden (J., 1928, 263) have shown that sulphonal, CMe<sub>2</sub>(SO<sub>2</sub>Et)<sub>2</sub>, and trional, CMeEt(SO<sub>2</sub>Et)<sub>2</sub>, have negative parachor anomalies of -11.7 and -22.4 respectively, which (it is now shown) are absent from the corresponding mercaptols, but the singlet link explanation applied by these authors to their sulphonal compounds cannot be applied to many of the compounds cited by Hammick and Wilmut.

In spite of the latter's criticism of the quantitative application of strain factors, it is probable that the general explanation of negative parachor anomalies put forward by Mumford and Phillips applies also to the palladium and the mercury compounds now described. In order to demonstrate clearly the progressive negative anomaly shown by the homologous series of these metals (Tables I and II), this anomaly has been calculated as if it were due entirely to the constituent metallic atom. Actually, however, it is extremely unlikely to be due to a progressive decrease in the effective size of the metallic atom itself (in view of the negative parachor which the metallic atom sometimes shows), but to a decrease in the size of the molecule as a whole, *i.e.*, to the first of the two causes put forward by Mumford and Phillips. It must be remembered that the parachor is a measure of the molecular volume at constant surface tension, *i.e.*, under conditions where normally the intermolecular forces are constant. Its remarkably additive nature, when applied to most organic compounds, is due to the fact that the molecules of these compounds consist essentially either of chains or rings, which in the liquid state can lie compactly together, no abnormal intermolecular forces being involved. The complex compounds listed in Table I, by virtue primarily of their *trans*-uniplanar configuration,

\* The negative anomaly of this particular series arises when the theoretical parachors are calculated on Mumford and Phillips's constants, but almost disappears if Sugden's revised constants are used. This does not apply, of course, to many of the compounds possessing negative anomalies cited by Mumford and Phillips.

will apparently not fit compactly together in the liquid state, and hence an abnormally high intermolecular compression throughout the series is required to maintain the constant surface tension, and the complete molecule is thus showing a correspondingly small volume. The same factor probably determines the low parachor values of the mercury mercaptides, for if these values were determined solely by a decrease in the effective volume of the mercury atom when linked to the two electronegative sulphur atoms, the negative anomaly would probably be almost constant throughout the series; on the other hand, if the molecules as a whole were undergoing general compression, due to their inability to fit compactly in the liquid state, it would be expected that, as the homologous series was ascended, this compression would at first steadily increase, but later, as the organic nature of the molecule became more pronounced, would ultimately reach a constant value, further increase in the methylene chain having no perceptible additional effect on the change in the intermolecular forces. It is probable that the negative anomaly shown by the palladium compounds in Table I would also ultimately attain a constant value, but the point at which this occurred would be considerably further up the series than in the simpler mercury mercaptides. To obtain further evidence on this subject, a detailed investigation is now being made of the complex aurous and cuprous derivatives of the phosphines, arsines, etc., of type  $R_3P \rightarrow AuCl$  and  $R_3P \rightarrow CuI$ , in which the metal shows a co-ordination number of 2. These compounds, which represent the simplest type of complex derivatives, are fusible without decomposition, and their parachors also exhibit marked negative anomaly.

Several points of considerable interest, apart from the parachor results, have arisen in this investigation. No evidence of *cis-trans*-isomerism has been detected in any of the compounds whose parachors are given in Table I, and the assumption that they are all the stable *trans*-compounds is strongly supported by the dipole moments of the three ethyl compounds of the chloro-series, *viz.*, 2.27, 1.05, 1.04 ( $\times 10^{-18}$ ) for the sulphur, phosphorus, and arsenic compounds respectively. The symmetrical *trans*-compounds should have a dipole moment closely approaching zero, whereas the *cis*-isomerides should have very high moments. The higher moment of the first compound, compared with those of the other two, is probably due to the co-ordinated phosphorus and arsenic atoms being each at the centre of a tetrahedron, which therefore rotates symmetrically about the co-ordinate link joining these elements to the palladium, whereas the sulphur atom is at the apex of the tetrahedron, which therefore rotates unsymmetrically about this link; moreover, as suggested by Dr. L. E. Sutton, the two ethyl sulphide molecules may rotate relative to one another about the axis formed by the two *trans*-co-ordinate links, and so set up a moment similar in cause to that of *s*-dichloroethane. The bistrimethylarsinepalladium dichloride, whose *m. p.* is too high for parachor measurements to be made, may, however, have the exceptional *cis*-configuration. It is significant that this methyl compound is pale yellow, whereas all the higher homologues prepared were deep orange; \* moreover, the crystals of the trimethylarsine compound possess strong pyro- and piezo-electric effects, which are usually absent from symmetrical *trans*-compounds. This compound, whose configuration is being fully investigated, is of further interest because it separates from solution in enantiomorphous crystals: the optical activity is due, of course, to the arrangement of the molecules in the crystal, and disappears on dissolution.

The tri-*n*-amylarsine compound (Table I) is the first pure palladium compound, liquid at room temperature, to be discovered, although there is evidence that the higher members of the sulphide and phosphine series are also liquid. The phosphine compounds have the novel property of being volatile at atmospheric pressure, and can be freely distilled in a high vacuum without decomposition. The arsine compounds decompose on heating, even in a high vacuum, and the nature and constitution of the very interesting products thus obtained will be discussed later.

\* Triethylarsine readily co-ordinates with platinous chloride to give the white and the yellow isomeric form of  $[(Et_3As)_2PtCl_2]$  (Cahours and Gals, *Compt. rend.*, 1870, **71**, 208), yet repeated attempts by one of us (F. G. M.) to prepare similar isomerides of  $[(Me_3As)_2PtCl_2]$  have given solely the white form, which, by analogy with similar platinum compounds (cf. Cox, Saenger, and Wardlaw, *J.*, 1934, 182), has presumably the *cis*-configuration.

An homologous series of dialkylsulphidepalladium dinitrites,  $[(R_2S)_2Pd(NO_2)_2]$ , which has also been prepared, is in one respect in marked contrast with the corresponding dichlorides, for the methyl compound has m. p.  $138^\circ$ , whilst the ethyl, *n*-propyl, *n*-butyl, and *n*-amyl compounds have m. p.'s  $161^\circ$ ,  $164^\circ$ ,  $165^\circ$ , and  $163^\circ$  respectively. This remark-

able constancy in m. p. is presumably due to the co-ordinate link in the  $\overset{\text{O}}{\nearrow}N=O$  group, although it is not clear why the co-ordinate link in this position, as distinct from that joining the sulphide molecules to the palladium atoms, should arrest completely the steady fall in m. p. which is a normal feature of the three homologous dichloride series (Table I).

Palladium diphenylmercaptide, of empirical formula  $Pd(SPh)_2$ , was prepared in order to extend the series given in Table II (A) : it proved to be a bright vermilion, amorphous powder, which on heating darkened and finally decomposed, giving a residue of metallic palladium, and was therefore useless for parachor measurements. It has, however, considerable analytical value. It is precipitated quantitatively when thiophenol is added to an aqueous solution of potassium chloropalladite, and the precipitate can be washed, dried, and ignited, the palladium being thus directly estimated as the metal; it can also be used for the micro-estimation of palladium, for an aqueous solution of a palladochloride containing even 0.5 part of palladium per million gives a pronounced coloration, which can be matched against that produced by a standard solution. Moreover, no similar colour is developed when thiophenol is added to aqueous solutions of complex or simple salts of silver, gold, rhodium, platinum, or iridium, and the reagent can therefore be used both to detect and to estimate palladium in the presence of these metals, although micro-estimation cannot be carried out in the presence of excess of their coloured salts. The mercaptide is insoluble in all the usual organic liquids, and is precipitated when thiophenol is added to alcoholic or acetone solutions of many of the palladium compounds (particularly the sulphide derivatives) described in this paper. This remarkable ability to decompose these very stable compounds and to precipitate the mercaptide, coupled with its insolubility and high decomposition point, shows that the mercaptide almost certainly has not the simple formula  $Pd(SPh)_2$ , but that considerable and very stable association, probably of the type shown in (IV), occurs, giving a compound of high molecular weight.

#### EXPERIMENTAL.

The names of solvents used for recrystallisation are given in parentheses immediately after the name of the substance concerned. Unless otherwise stated, molecular-weight determinations were cryoscopic and benzene was used as solvent.

The crystallographic and dipole data were provided by Dr. Nora Wooster (Cambridge University Crystallography Department) and Mr. A. E. Finn (The Dyson Perrins Laboratory, Oxford University) respectively, and are gratefully acknowledged.

The preparation and properties of the organic sulphides, mercaptans, phosphines, and arsines are given first, followed by those of their metallic derivatives.

Surface tensions were determined throughout by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27) in Pyrex-glass apparatus. For surface-tension determinations upon liquids at room temperature (and for some of the earlier metallic derivatives at higher temperatures) Sugden's usual apparatus, maintained at constant temperature in a thermostat or oil-bath, was used. For the remainder of the determinations, a similar apparatus was used, but to its body was fused a glass jacket having inlet and outlet tubes at the top and bottom respectively, a thermometer being fitted in the annular space. The vapour of a suitable liquid (*e.g.*, acetone; alcohol; water; *s*.-tetrachloroethane, b. p.  $145^\circ$ ; *o*-chlorotoluene, b. p.  $157^\circ$ ) was then blown vigorously through this space, and the molten substance was thus rapidly brought to a constant temperature: repeated tests showed that this was attained within 5 mins. of fusion. Each instrument was regularly recalibrated upon pure benzene, but the constants were found not to vary by more than 0.2% over a long period. Duplicate determinations, made with various of the metallic compounds, and in the jacketed apparatus most frequently employed, gave surface-tension values which varied by less than 0.3%; but similar duplicate determinations in both forms of the apparatus gave values having a maximum variation of 0.7%.

Densities of liquids were determined by means of ordinary pycnometers, those of molten solids by Sugden's graduated U-shaped pycnometer (J., 1924, 125, 1171); the arms of the latter (for all but the earlier determinations) were securely fitted at the top through a cork, so that the lower portion could be held in a flask through which the vapour of a boiling liquid could again be blown. The densities could thus be determined at temperatures identical with those used for the surface-tension measurements, and a density equation was therefore not required. Two such pycnometers were used: duplicate determinations with either pycnometer alone gave results having a maximum variation of 0.1%, and with both pycnometers a maximum variation of 0.15%.

To estimate the accuracy of the final molecular parachor values, Sugden's equation  $[P] = M\gamma^{1/2}/D$  must be considered. Clearly, if the maximum error in the density values is taken as  $\pm 0.1\%$ , and in the surface tension as  $\pm 0.5\%$ , that in the final molecular parachor is  $\pm 0.2\%$ , although all these are generous estimates. It follows that for a typical metallic derivative having a parachor of about 1000 (e.g., bistri-*n*-propylphosphinepalladium dichloride,  $C_{18}H_{42}Cl_2P_2Pd$ ), the maximum experimental variation is 4–5 units. The maximum error in the calculated value is rather greater, for the value for the  $CH_2$  group has probably a maximum error of 0.2 unit, and that for the chlorine, phosphorus, and arsenic atoms an error of 0.5 unit: hence the total error in the calculated parachor of such a compound is 5–6 units. The maximum error in the difference between the calculated parachors of two consecutive members of any of the homologous series is very much less; this difference now involves only 2, 4, or 6 methylene groups (according to the series concerned) and the maximum error is only 1–2 units. The observed difference in the parachor of palladium or mercury in two such consecutive members is usually about 9 units, and is thus considerably outside the experimental and calculated error.

All parachors of the following organic liquids, unless otherwise stated, were determined at 24°.

*Sulphides.* Kahlbaum's preparations of the diethyl, the dimethyl, and the methyl ethyl compound were carefully rectified to constant b. p. Other aliphatic sulphides were prepared by a modification of Winssinger's method (*Bull. Soc. chim.*, 1887, 48, 109), the corresponding pure alkyl bromide (2 mols.) being added slowly to a boiling mixture of powdered anhydrous sodium sulphide (2.5–3.0 mols.) and rectified spirit. After 3–4 hours' further boiling, the alcohol was distilled off on a water-bath. The lower sulphides volatilised in the alcohol and were isolated by addition of water to the distillate; the higher sulphides remained in the distilling flask and were isolated by addition of water and extraction with ether, distillation of the dried ethereal solution giving the almost pure sulphide. All liquid sulphides were subsequently fractionated until pure: *n*-propyl (Winssinger, *loc. cit.*), b. p. 139°,  $d^* 0.84315$ ; isopropyl (Beckmann, *J. pr. chem.*, 1878, 17, 459), b. p. 120°; *n*-butyl (Grabowsky and Saytzeff, *Annalen*, 1874, 171, 253), b. p. 185.0–185.5°,  $d 0.8352$ ;  $\gamma$  (dynes/cm.) 26.45,  $[P] 395.5$  (Calc.: 397.7); isobutyl, b. p. 174°,  $d 0.8301$ ,  $\gamma 24.90$ ,  $[P] 392.8$  (Calc.: 397.7); *n*-amyl, b. p. 108–109°/15 mm. (Found: S, 18.5.  $C_{10}H_{22}S$  requires S, 18.4%),  $d 0.8408$ ,  $\gamma 27.60$ ,  $[P] 474.8$  (Calc.: 476.9). *Di-n*-amylsulphoxide was prepared by adding the sulphide (10 g.) to cold nitric acid ( $d 1.42$ ; 40 c.c.), an oily layer separating on the surface. The mixture was ultimately diluted with water, and the oil extracted with ether. Distillation of the dried extract gave the sulphoxide, b. p. 163–164°/16 mm., m. p. 60° after recrystallisation from light petroleum (Found: S, 16.9.  $C_{10}H_{22}OS$  requires S, 16.8%).

The *n*-hexyl sulphide had b. p. 136–138°/20 mm.,  $d 0.8447$ ,  $\gamma 27.83$ ,  $[P] 549.2$  (calc., 550.4). *n*-Heptyl bromide was obtained by adding phosphorus tribromide (110 g., 1.2 mols.) to pure *n*-heptyl alcohol (110 g., 3 mols.), the mixture being mechanically stirred for 1 hr. below 10° and for 1 hr. at room temperature; after being kept over-night, it was poured into ice-water (1 l.), 30% sodium hydroxide solution (100 c.c.) added, and the bromide steam-distilled; when dried and fractionated, it had b. p. 178–179°; yield, 110 g. (65%). The *n*-heptyl sulphide (Winssinger, *Bull. Acad. Roy. Belg.*, 1887, 14, 760) had b. p. 164°/20 mm.,  $d 0.8402$ ,  $\gamma 28.61$ ,  $[P] 633.6$  (Calc.: 635.3); and *n*-octyl sulphide (prepared from the bromide, b. p. 198–200°; Möslinger, *Annalen*, 1877, 185, 59) had b. p. 184–185°/20 mm.,  $d 0.8409$ ,  $\gamma 29.10$ ,  $[P] 713.5$  (Calc.: 714.5).

*Phenyl n-butyl sulphide.* Thiophenol (8.2 g., 1 mol.) and *n*-butyl iodide (13.8 g., 1 mol.) were added in turn to a solution of sodium (1.8 g., 1 atom) in absolute alcohol (75 c.c.), and the mixture boiled for 3 hrs. under reflux. Distillation removed the alcohol and then gave the sulphide as a colourless liquid, b. p. 137–139°/12 mm. (Found: S, 19.2.  $C_{10}H_{14}S$  requires S,

\* Here and elsewhere,  $d$  is the  $D$  of the parachor equation above.



19.1%),  $d$  0.9792,  $\gamma$  34.02,  $[P]$  409.7 (Calc. : 411.8). The iso-isomeride, prepared similarly, was a colourless liquid, b. p. 126—127°/12 mm. (Found : S, 19.3%). Diphenyl sulphide, prepared by Boeseken's sulphur monochloride method (*Rec. trav. chim.*, 1905, **24**, 217), was a colourless oil, b. p. 153°/12 mm.,  $d^{12.5}$  1.1212,  $\gamma^{12.5}$  44.21,  $[P]$  428.1 (Calc. : 425.9).

$\alpha\gamma$ -Bis(phenylthio)propane,  $\text{CH}_2(\text{CH}_2\cdot\text{SPh})_2$ , was prepared by adding thiophenol (11 g., 2 mols.) and trimethylene dibromide (10.1 g., 1 mol.) in turn to a solution of sodium (2.3 g., 2 atoms) in absolute alcohol (100 c.c.); the solution was boiled for 2 hrs., the alcohol distilled off, and the residue extracted with benzene. The dried benzene solution on fractionation gave the dithio-compound as a pale yellow (almost colourless) oil, b. p. 264°/12 mm. (Found : S, 25.0.  $\text{C}_{15}\text{H}_{16}\text{S}_2$  requires S, 24.6%).

$\alpha\alpha'$ -Bis(phenylthio)acetone,  $\text{CO}(\text{CH}_2\cdot\text{SPh})_2$ , prepared similarly from  $\alpha\alpha'$ -dichloroacetone, formed colourless crystals, b. p. 256—260°/12 mm., m. p. 43° after recrystallisation from alcohol (Found : C, 65.5; H, 4.84.  $\text{C}_{15}\text{H}_{14}\text{OS}_2$  requires C, 65.7; H, 5.1%).

Acetone bisethylmercaptol (Baumann, *Ber.*, 1885, **18**, 887) had b. p. 84.5—85.0°/20 mm.,  $d$  0.9441,  $\gamma$  28.67,  $[P]$  402.3 (Calc. : 406.6; or, after allowance of — 3 for the *gem*-dialkyl group, 403.6). Methyl ethyl ketone bisethylmercaptol, similarly prepared, was a colourless liquid, b. p. 99—100°/18.5 mm. (Found : S, 35.8.  $\text{C}_8\text{H}_{18}\text{S}_2$  requires S, 35.9%),  $d$  0.9446,  $\gamma$  29.63,  $[P]$  439.7 (Calc. : 446.2; or 443.2 after allowance as before).

*Thiols*.—The following general method of preparation was adopted : the pure alkyl bromide (0.7 mol.) was added to a solution of sodium (1 atom) in absolute alcohol, previously saturated with hydrogen sulphide, and the mixture kept over-night. For the lower thiols, the mixture was distilled, and the thiol, which volatilised with the alcohol, was isolated by dilution of the distillate with water. For the higher thiols, the reaction product was largely diluted with water, and the thiol extracted with a little ether. In all cases, the dried product was carefully fractionated. It is noteworthy that on ascending the homologous thiol series, atmospheric oxidation to the disulphide becomes negligible after the  $\text{C}_4$  member, whilst the odour decreases sharply after the  $\text{C}_5$  member, the *n*-hexyl derivative having only a faint smell.

*n*-Propylthiol (Roemer, *Ber.*, 1873, **6**, 784) had b. p. 61—63°; *n*-butylthiol, b. p. 97—97.5°; and *n*-amylthiol (Pexsters, *Bull. Acad. Roy. Belg.*, 1906, 796) b. p. 124.5—125°,  $d$  0.8414,  $\gamma$  22.69,  $[P]$  280.6 (Calc. : 278.9). The *n*-hexyl member was prepared by the series of reactions  $n\text{-C}_5\text{H}_{11}\text{Br} \rightarrow n\text{-C}_6\text{H}_{13}\cdot\text{OH} \rightarrow n\text{-C}_6\text{H}_{13}\text{Br} \rightarrow n\text{-C}_6\text{H}_{13}\cdot\text{SH}$ : into *n*-amylmagnesium bromide (1 mol.; prepared from the bromide, 80 g., magnesium, 13 g., and dry ether, 230 c.c.) was blown the vapour obtained by heating paraformaldehyde (27 g., 1.7 mols.) (cf. Ziegler, *Ber.*, 1922, **55**, 3406); after 1 hr., the reaction mixture was decomposed with ice and dilute sulphuric acid, the ethereal layer separated, and the aqueous layer extracted with ether. The united ethereal extracts were dried and distilled, and the *n*-hexyl alcohol thus obtained (b. p. 153.5—154.5°/768 mm.) was converted by the general method into the bromide (b. p. 154°) and thence into the thiol, b. p. 146—147° (Henry, *Bull. Acad. Roy. Belg.*, 1905, 158), a colourless, almost odourless liquid.

*n*-Heptylthiol (Winssinger, *loc. cit.*) had b. p. 66—67°/20 mm., 171—172°/760 mm.,  $d$  0.8384,  $\gamma$  27.35,  $[P]$  360.3 (Calc. : 358.1); it was almost odourless. *n*-Octylthiol had b. p. 86°/15 mm.,  $d$  0.8393,  $\gamma$  28.02,  $[P]$  400.2 (Calc. : 397.7).

*Phosphines*.—These were obtained by the Grignard reaction, triethylphosphine by the method of Hibbert (*Ber.*, 1906, **39**, 161), and the others by those of Davies and Jones (J., 1929, **33**) and Davies, Pearce, and Jones (*ibid.*, p. 1262). The ethyl member had b. p. 127°, the *n*-propyl, b. p. 85.5—87.0°/24 mm., and the *n*-butyl, b. p. 129—130°/22 mm., 136—137°/32.5 mm.

From 78 c.c. of *n*-amyl bromide, Davies and Jones obtained only 9 g. of tri-*n*-amylphosphine as a liquid, b. p. 185.5°/50 mm., but we have regularly obtained yields of 17—18 g., b. p. 165—166°/19 mm., m. p. 29°; this is the lowest tertiary phosphine to be solid at room temperature. Unless the phosphine is kept in a sealed tube, it is readily oxidised, first becoming liquid, and then depositing long, very deliquescent needles of tri-*n*-amylphosphine oxide, m. p. 59° (Found : C, 69.5; H, 12.3.  $\text{C}_{15}\text{H}_{33}\text{OP}$  requires C, 69.2; H, 12.7%).

Triethyl phosphite, prepared in excellent yield by the method of Milobendzki and Sachnowski (*Chem. Polski*, 1917, **15**, 34), had b. p. 55°/19 mm., 154.5—155.5°/755 mm.,  $d$  0.9604,  $\gamma$  24.10,  $[P]$  382.9 (Calc. : 383.2).

*Arsines*.—These were prepared by the method of Dyke and Jones (J., 1930, 2426). The compounds used had the following constants : trimethyl, b. p. 51—52°; triethyl, b. p. 138—139°; tri-*n*-propyl (not recorded by Dyke and Jones), b. p. 85—86°/18.5 mm. (41 g. were obtained from 115 g. of the iodide); *n*-butyl, b. p. 133°/23 mm. [Dyke and Jones obtained 10 g.

of this arsine from 69 g. of bromide, but 23 g. have now been obtained from the equivalent quantity (92.7 g.) of iodide]; *n*-amyl, b. p. 162°/14.5 mm., 164°/16 mm.

*Metallic Derivatives.*—For certain of the earlier compounds (notably the sulphide derivatives) a number of density determinations were made, and an equation deduced in order to determine the densities at the various temperatures at which the surface tensions were measured. For most compounds, however, the densities and surface tensions were determined at the same temperatures (in the vapour-jacketed apparatus): in such cases the various temperatures ( $t^\circ$ ) are given first, followed by the densities, surface tensions, and parachors at these temperatures. Unless otherwise stated, the m. p. of the compound and parachor determinations was never more than 0.5° below that of the original sample.

*Bis(dialkylsulphide)palladium Compounds.*—*Dichlorides*,  $[(R_2S)_2PdCl_2]$  [Table I (A)]. Ardel (Diss., Lund, 1896; *Z. anorg. Chem.*, 1897, **14**, 143) prepared the methyl, ethyl, *isobutyl*, and *iso*-amyl compounds, and recorded m. p.'s of 130°, 78°, 95°, and 95° respectively: the other members are new. In the general method of preparation, a mixture of the sulphide (2 mols.) and an aqueous solution of ammonium chloropalladite (1 mol.) was vigorously shaken mechanically for 2—3 hrs.; the lower sulphides co-ordinated rapidly, but the higher members required prolonged shaking to ensure complete reaction. The solid product was separated, thoroughly washed with water, dried, and crystallised. All the aliphatic sulphide compounds were deep orange-red. The dimethyl compound ( $R = Me$ ) formed deep red prisms from acetone, and hexagonal plates from benzene, m. p. 130° (Found: C, 15.9; H, 3.7; S, 21.5;  $M$ , in 1.618% solution, 284; in 3.836% solution, 292. Calc. for  $C_4H_{12}Cl_2S_2Pd$ : C, 15.9; H, 4.0; S, 21.2%;  $M$ , 302);  $t$  143°, 156°;  $d$  1.677, 1.658;  $\gamma$  43.53, 42.80;  $[P]$  462.1, 463.2; mean, 463;  $[P]_{Pd} = 36$ .

The *methyl ethyl* compound ( $R_2 = Me, Et$ ) (ether, and then acetone) had m. p. 67° (Found: C, 21.6; H, 4.85.  $C_6H_{16}Cl_2S_2Pd$  requires C, 21.8; H, 4.8%); it slowly decomposed on heating, and parachor measurements could not be made.

The *diethyl* compound ( $R = Et$ ) (petrol containing a little acetone) had m. p. 81° (Found: C, 26.8; H, 5.4; Pd, 29.5;  $M$ , in 1.592% solution, 348. Calc. for  $C_8H_{20}Cl_2S_2Pd$ : C, 26.8; H, 5.6; Pd, 29.8%;  $M$ , 358);  $d^{88^\circ}$  1.459,  $d^{96^\circ}$  1.452,  $d^{103^\circ}$  1.447,  $d^{111^\circ}$  1.440,  $d^{118^\circ}$  1.433,  $d^{135^\circ}$  1.419; whence  $d^t = 1.464 - 0.00085(t - 82)$ ;  $t$  99°, 102°, 119.5°, 129°;  $d$  1.450, 1.447, 1.432, 1.424;  $\gamma$  38.24, 37.72, 36.14, 35.70;  $[P]$  613.5, 612.8, 612.7, 614.3; mean, 613;  $[P]_{Pd} = 27$ .

*Dipole measurement on ethyl compound in benzene at 25°.*

$f_2$ .	$d$ .	$\epsilon^{25^\circ}$ .	$n_{5461}^{25^\circ}$ .	$P_2$ .	$eP_2$ .
0.004917	0.8825	2.3146	2.2650	192.28	87.77
0.006574	0.8854	2.3298	2.2669	194.18	86.94
0.007939	0.8877	2.3413	2.2678	193.87	85.59
0.01043	0.8921	2.3623	2.2707	192.82	85.18

$\infty P_2$ , 193.29 c.c.;  $eP_2$ , 86.38 c.c.;  $\infty P_2 - eP_2 = 106.91$  c.c.;  $\mu = 2.27 \times 10^{-18}$  e.s.u. The symbols have their usual significance.

The *di-n-propyl* compound ( $R = Pr^a$ ) (acetone and then petrol) had m. p. 59° (Found: C, 34.6; H, 6.7; S, 15.2.  $C_{12}H_{28}Cl_2S_2Pd$  requires C, 34.8; H, 6.8; S, 15.4%);  $d^{72^\circ}$  1.318,  $d^{81^\circ}$  1.310,  $d^{90^\circ}$  1.302,  $d^{104^\circ}$  1.291,  $d^{114^\circ}$  1.284,  $d^{121^\circ}$  1.279; whence  $d^t = 1.323 - 0.00079(t - 64)$ ;  $t$  65.5°, 88°, 120°;  $d$  1.322, 1.304, 1.279;  $\gamma$  34.72, 33.35, 29.90;  $[P]$  760.2, 762.7, 756.9; mean, 760;  $[P]_{Pd} = 16$ .

The *diisopropyl* compound ( $R = Pr^b$ ) (acetone and then ether) had m. p. 163°, which was too high for accurate parachor measurement (Found: Pd, 25.9;  $M$ , in 1.759% solution, 404; in 2.882% solution, 414.  $C_{12}H_{28}Cl_2S_2Pd$  requires Pd, 25.85%;  $M$ , 414).

The preparation of the *di-n-butyl* compound required 12 hrs.' shaking, and the mixture was then cooled in ice-water to ensure solidification of the red globules of crude material. The latter, when collected, washed, and dried, was twice recrystallised from a minimum of anhydrous methyl alcohol, the solution being chilled in ice-salt; m. p. 32° (Found: C, 40.9; H, 7.7; Pd, 22.9.  $C_{16}H_{36}Cl_2S_2Pd$  requires C, 40.85; H, 7.7; Pd, 22.8%);  $t$  56°, 77°, 98°;  $d$  1.243, 1.223, 1.204;  $\gamma$  32.64, 30.97, 29.37;  $[P]$  903.7, 906.3, 908.8; mean, 906;  $[P]_{Pd} = 4$ ;  $d^t = 1.265 - 0.00093(t - 32)$ . It was very soluble in most organic liquids, but least so in methyl and ethyl alcohol.

The *diisobutyl* compound (ether and then alcohol) had m. p. 97° (Found: C, 40.95; H, 7.4; S, 13.3. Calc. for  $C_{16}H_{36}Cl_2S_2Pd$ : C, 40.85; H, 7.7; S, 13.6%);  $d^{107^\circ}$  1.180,  $d^{116^\circ}$  1.173,  $d^{119^\circ}$  1.170,  $d^{135^\circ}$  1.157,  $d^{144^\circ}$  1.150; whence  $d^t = 1.188 - 0.00081(t - 96)$ ;  $t$  102°, 119°, 130°;  $d$  1.183, 1.170, 1.161;  $\gamma$  27.98, 26.73, 26.20;  $[P]$  913.4, 913.0, 915.6; mean, 914;  $[P]_{Pd} = 12$ .

The *di-n-amyl* compound was prepared in a similar manner to the *di-n-butyl* compound,

which it closely resembled in properties; thrice recrystallised from a small quantity of methyl alcohol, with ice-water cooling, it had m. p.  $41^\circ$  (Found: C, 45.4; H, 8.35; Pd, 20.1.  $C_{20}H_{14}Cl_2S_2Pd$  requires C, 45.65; H, 8.4; Pd, 20.3%);  $t$   $56^\circ$ ,  $77^\circ$ ,  $99^\circ$ ;  $d$  1.171, 1.156, 1.141;  $\gamma$  30.39, 28.77, 27.27;  $[P]$ , 1054, 1054, 1053; mean, 1054;  $[P]_{Pd} = -7$ ;  $d^\circ = 1.186 - 0.00071(t - 35)$ .

Similar compounds with *n*-heptyl and *n*-octyl sulphides were prepared as oils which crystallised only when chilled to about  $0^\circ$ : their liquid condition was undoubtedly due primarily to their low m. p., and not to impurities. Because of the difficulty of complete purification, and the high value of their parachors, these were not determined.

The compound ( $R = CH_2CH_3$ ) from vinyl sulphide was prepared as an orange powder, which decomposed at room temperature whilst being dried in a vacuum. The *phenyl n-butyl* compound ( $R_2 = Ph, n-Bu$ ), prepared by shaking together aqueous and alcoholic solutions of ammonium chloropalladite (1 mol.) and phenyl *n*-butyl sulphide (2 mols.) respectively, and recrystallised from alcohol, formed orange needles, m. p.  $118^\circ$  (Found: C, 46.6; H, 5.4.  $C_{20}H_{28}Cl_2S_2Pd$  requires C, 47.0; H, 5.5%). The *isobutyl* isomeride, similarly prepared and recrystallised, had m. p.  $96^\circ$  (Found: C, 46.8; H, 5.7%).

The *diphenyl* compound ( $R = Ph$ ), recrystallised from boiling acetone, in which it is only slightly soluble, formed orange needles, m. p.  $170^\circ$  (decomp.) (Found: C, 52.5; H, 3.6; Pd, 19.2.  $C_{24}H_{20}Cl_2S_2Pd$  requires C, 52.4; H, 3.6; Pd, 19.4%); and the *dibenzyl* compound ( $R = CH_2Ph$ ) (alcohol and then acetone), prepared as the phenyl butyl analogue, formed orange needles, m. p.  $154^\circ$  (Found: C, 55.7; H, 4.5; S, 10.7;  $M$ , in 2.011% solution, 620.  $C_{28}H_{28}Cl_2S_2Pd$  requires C, 55.5; H, 4.6; S, 10.6%;  $M$ , 606). No parachor determinations were made with the last four compounds.

*Dibromide*,  $[(Et_2S)_2PdBr_2]$  [Table I (D)]. Ammonium chloropalladite (5 g., 1 mol.) was added to a solution of potassium bromide (20 g., 4.8 mols.) in water (80 c.c.); after 2 hrs.' shaking, diethyl sulphide (3.3 g., 2.1 mols.) was added, and after a further 3 hrs.' shaking, the precipitate was filtered off, washed with water, and dried. Bis(diethylsulphide)palladium dibromide (alcohol, then acetone) separated as deep red prisms, m. p.  $103^\circ$  (Ardell, *loc. cit.*, gives m. p.  $98^\circ$ ) (Found: C, 21.8; H, 4.5. Calc. for  $C_8H_{20}Br_2S_2Pd$ : C, 21.5; H, 4.5%);  $t$ ,  $109^\circ$ ;  $d$  1.7312;  $\gamma$  37.30;  $[P]$  637.8;  $[P]_{Pd} = 23$ .

The di-iodide,  $[(Et_2S)_2PdI_2]$ , similarly prepared from potassium iodide, recrystallised from alcohol as purple-brown plates, m. p.  $107-108^\circ$  (decomp.), which slowly decomposed on exposure to air and were not further investigated.

*Dinitriles*,  $[(R_2S)_2Pd(NO_2)_2]$ . Ardell (*loc. cit.*) claimed to have prepared the methyl, ethyl, and *isobutyl* members, having m. p.'s  $45^\circ$ ,  $145^\circ$ , and  $155^\circ$  respectively, but the m. p.'s of the first two compounds differ so markedly from those now determined that the identity of his compounds is unknown.

In the general method of preparation, the corresponding dichloride was ground in a mortar with a saturated aqueous solution of 2—3 times its weight of sodium nitrite until the colour changed to a pale yellow. The product was kept for 2 hrs., and then collected, washed with water, dried, and recrystallised. All the members are pale yellow crystalline solids: *dimethyl* compound ( $R = Me$ ) (acetone), m. p.  $137-138^\circ$  (decomp.) (Found: C, 15.0; H, 3.9.  $C_4H_{12}O_4N_2S_2Pd$  requires C, 14.9; H, 3.7%); *diethyl* compound (acetone), m. p.  $161-163^\circ$  (slight decomp.) (Found: C, 25.6; H, 5.35; Pd, 28.2;  $M$ , in 1.371% solution, 392.  $C_8H_{20}O_4N_2S_2Pd$  requires C, 25.4; H, 5.3; Pd, 28.2%;  $M$ , 379); *di-n-propyl* compound (alcohol), m. p.  $163-164^\circ$  (Found: C, 33.5; H, 6.6; Pd, 24.6.  $C_{12}H_{28}O_4N_2S_2Pd$  requires C, 33.2; H, 6.45; Pd, 24.6%); *di-n-butyl* compound (alcohol), m. p.  $165-166^\circ$  (Found: C, 38.9; H, 7.1; Pd, 21.7.  $C_{16}H_{36}O_4N_2S_2Pd$  requires C, 39.1; H, 7.4; Pd, 21.75%); *di-n-amyl* compound (methyl alcohol, then petrol), m. p.  $163^\circ$  (Found: C, 44.1; H, 7.8; Pd, 19.45.  $C_{20}H_{44}O_4N_2S_2Pd$  requires C, 43.9; H, 8.1; Pd, 19.5%).

It is noteworthy that the lower members of this homologous series are moderately soluble in hot water; on ascending the series, the solubility in water decreases rapidly, whilst that in most organic liquids increases considerably. The lower members decompose on melting, and parachor measurements were not possible: it is probable that such measurements could be made with the higher members.

*Bis(trialkylphosphine)palladium Compounds*,  $[(R_3P)_2PdX_2]$ .—*Dichlorides* [Table I (B)]. Cahours and Gals (*Compt. rend.*, 1870, 70, 897) prepared the ethyl compound; the others are new. The general method of preparation was precisely similar to that for the dialkyl sulphide series, except that the triethyl compound was prepared by adding triethylphosphine (2.5 mols.) to a solution of ammonium chloropalladite (1 mol.) in cold, freshly boiled water. A mixture of the

yellow dichloride and some brown scum separated and was filtered off; cautious addition of dilute ammonium chloropalladite solution to the clear colourless filtrate gave a further small crop of the yellow dichloride. The two crops were united and recrystallised from alcohol, in which the brown scum largely reverted to the dichloride.

The triethyl compound ( $R = Et$ ,  $X = Cl$ ), m. p.  $139^\circ$ , sublimes readily without decomposition in a high vacuum at  $140^\circ$  (Found:  $M$ , in 1.273% solution, 399; in 3.098% solution, 399. Calc. for  $C_{12}H_{30}Cl_2P_2Pd$ :  $M$ , 414);  $t$   $157^\circ$ ;  $d$  1.226;  $\gamma$  27.71;  $[P]$  775;  $[P]_{Pd} = 22$ .

*Dipole measurement of triethyl compound in benzene at  $25^\circ$ .*

$f_2$	$d$	$\epsilon^{25^\circ}$	$n_D^{25^\circ}$ <sub>5461</sub>	$P_2$	$eP_2$
0.005058	0.8820	2.2865	2.2640	130.76	107.62
0.006794	0.8848	2.2911	2.2659	130.31	107.38
0.007570	0.8862	2.2927	2.2671	129.45	107.68
0.009841	0.8897	2.2994	2.2697	130.81	107.66

$$\infty P_2, 130.33 \text{ c.c.}; eP_2, 107.59 \text{ c.c.}; \infty P_2 - eP_2 = 22.74 \text{ c.c.}; \mu = 1.05 \times 10^{-18} \text{ e.s.u.}$$

The *tri-n-propyl* compound (alcohol) had m. p.  $96^\circ$ , b. p.  $183^\circ/3 \times 10^{-3}$  mm. (Found: C, 43.45; H, 8.4; Pd, 21.5.  $C_{18}H_{42}Cl_2P_2Pd$  requires C, 43.4; H, 8.5; Pd, 21.4%);  $t$   $100^\circ$ ,  $145^\circ$ ,  $157^\circ$ ;  $d$  1.1439, 1.1095, 1.1006;  $\gamma$  27.40, 24.03, 23.15;  $[P]$  995.6, 993.5, 993.2; mean, 994;  $[P]_{Pd} = 3$ ;  $d^v = 1.1469 - 0.00076(t - 96)$ . It formed pale yellow, monoclinic, flattened parallelepipeds; extinction direction inclined about  $16^\circ$  to the  $c$  axis;  $d$  (by flotation) 1.273. It showed no pyroelectric effects. Oscillation photographs showed the cell dimensions to be  $a = 8.8$ ,  $b = 17.6$ ,  $c = 8.8 \text{ \AA}$ ,  $\beta = 83^\circ$ , hence there are 2 molecules per unit cell.

The *tri-n-butyl* compound (alcohol), m. p.  $66^\circ$ , b. p.  $198^\circ/3 \times 10^{-3}$  mm., was very soluble in most other solvents (Found: C, 49.6; H, 9.3;  $M$ , in 1.408% solution, 572; in 3.733% solution, 572.  $C_{24}H_{54}Cl_2P_2Pd$  requires C, 49.5; H, 9.35%;  $M$ , 582);  $t$   $78^\circ$ ,  $99^\circ$ ,  $145^\circ$ ,  $157^\circ$ ;  $d$  1.0939, 1.0782, 1.0430, 1.0325;  $\gamma$  27.41, 25.76, 22.44, 21.72;  $[P]$  1218, 1216, 1215, 1217; mean 1217;  $[P]_{Pd} = -12$ . The *tri-n-amyl* homologue, when thrice recrystallised from alcohol, had m. p.  $47^\circ$ , b. p.  $211^\circ/78 \times 10^{-4}$  mm. (Found: C, 54.35; H, 10.3; Pd, 16.4.  $C_{30}H_{66}Cl_2P_2Pd$  requires C, 54.05; H, 10.0; Pd, 16.0%);  $t$   $99^\circ$ ;  $d$  1.025;  $\gamma$  24.92;  $[P]$  1452;  $[P]_{Pd} = -14$ .

*Dibromide.* The *tri-n-butyl* compound [Table I (E)] was prepared precisely as the diethyl sulphide compound and twice recrystallised from alcohol; m. p.  $73^\circ$  (Found: C, 42.9; H, 8.1.  $C_{24}H_{54}Br_2P_2Pd$  requires C, 42.9; H, 8.1%);  $t$   $78^\circ$ ,  $99^\circ$ ;  $d$  1.2405, 1.2221;  $\gamma$  28.04, 26.12;  $[P]$  1245, 1241; mean 1243;  $[P]_{Pd} = -15$ .

*Di-iodide.* The *tri-n-butyl* compound (alcohol, then acetone) formed magnificent dark orange plates, m. p.  $64-65^\circ$  (Found: C, 37.8; H, 7.1;  $C_{24}H_{54}I_2P_2Pd$  requires C, 37.6; H, 7.1%); it decomposes slowly just above its m. p., and parachor measurements were valueless.

*Dinitrites.* Aqueous sodium nitrite solution, when cold, has no appreciable action on the above phosphine dichlorides, but when mixed with an alcoholic solution of the dichloride and boiled, it soon converts it into the dinitrite, which may then be obtained by cooling and dilution with water. The *tri-n-propyl* compound (acetone) formed white crystals having a faint yellow tint, m. p.  $167-168^\circ$  (partial decomp.) (Found: C, 41.7; H, 7.8; Pd, 18.5.  $C_{18}H_{42}O_4N_2P_2Pd$  requires C, 41.6; H, 8.1; Pd, 18.3%).

*Bis(trialkylarsine)palladium Salts.*—*Dichlorides* [Table I (C)]. The triethyl compound was prepared by Cahours and Gals (*loc. cit.*); the others are new. The general method of preparation resembled that of the corresponding sulphur and phosphorus compounds, ice being added, however, to the crude reaction mixture for the tripropyl and the tributyl compound towards the end of the shaking, to ensure complete solidification. Special precautions are required for the triamyl compound (*q.v.*). The trimethyl compound is pale yellow, the others deep orange.

The *trimethyl* compound (alcohol containing a little acetone) had m. p.  $235^\circ$ , so no parachor measurements could be made (Found: C, 17.5; H, 4.5.  $C_6H_{18}Cl_2As_2Pd$  requires C, 17.2; H, 4.35%). It formed fine golden-yellow crystals, 2—3 mm. long, many in the form of five-sided prisms terminated by a single pyramidal face, others in irregular truncated pyramids. Goniometer measurements showed them to be triclinic, and enantiomorphous; very large variations (sometimes more than  $1^\circ$ ) occurred in the angles, although the crystals were perfect in appearance and very sharp images were usually obtained. An easy but imperfect cleavage occurred parallel to (112). The pyro- and piezo-electric effects were very strong. The refractive indices, measured through naturally occurring prisms, varied from 1.820 to 1.678 for green light; dispersion was high—through the prism it was 1.722 for blue, 1.680 for green, and 1.675 for yellow (Hg lines). The slow direction made an angle of about  $22^\circ$  with the prism edge. Pleochroism was marked: slow direction deep yellow, fast almost colourless.

The lattice was found by *X*-rays, using oscillation and Weissenberg photographs, to have the following dimensions:  $a = 8.84$ ,  $b = 11.89$ ,  $c = 6.33 \text{ \AA}$ . ( $\pm 0.05$ ),  $\alpha = 90^\circ$ ,  $\beta = 70^\circ$ ,  $\gamma = 91^\circ$ ;  $d$  (by flotation) 2.14. Therefore there are two molecules per unit cell. The lattice is so nearly monoclinic that it is reasonable to treat it as such. Since (0*k*0) is halved, the space group is  $P2_1$ . No decisive evidence for the configuration can be adduced.

The triethyl compound (alcohol, thrice) had m. p.  $116^\circ$ ;  $t$   $128^\circ$ ,  $156^\circ$ ;  $d$  1.483, 1.455;  $\gamma$  30.18, 27.96;  $[P]$  792.5, 792.9; mean, 793;  $[P]_{Pd} = 12$ .

*Dipole measurement on triethyl compound in benzene at 25°.*

$f_2$ .	$d$ .	$\epsilon^{25^\circ}$ .	$n_D^{25^\circ}$ .	$P_2$ .	$\epsilon P_2$ .
0.005421	0.8874	2.2882	2.2657	135.19	113.49
0.007525	0.8927	2.2943	2.2684	135.26	112.81
0.008746	0.8958	2.2982	—	135.77	—
0.01317	0.9067	2.3103	2.2765	135.06	112.88

$$\infty P_2, 135.32 \text{ c.c.}; \epsilon P_2, 113.06 \text{ c.c.}; \infty P_2 - \epsilon P_2 = 22.26 \text{ c.c.}; \mu = 1.04 \times 10^{-18} \text{ e.s.u.}$$

The *tri-n-propyl* homologue (alcohol, thrice) had m. p.  $55^\circ$  (Found: C, 36.8; H, 7.0;  $M$ , in 1.567% solution, 568; in 3.904% solution, 580.  $C_{18}H_{42}Cl_2As_2Pd$  requires C, 36.9; H, 7.2%;  $M$ , 586);  $t$   $77^\circ$ ,  $98^\circ$ ;  $d$  1.349, 1.332;  $\gamma$  29.72, 28.10;  $[P]$ , 1014, 1013; mean, 1014;  $[P]_{Pd} = -5$ . The *tri-n-butyl* compound (alcohol, thrice) had m. p.  $54^\circ$  (Found: C, 43.3; H, 8.05.  $C_{24}H_{54}Cl_2As_2Pd$  requires C, 43.0; H, 8.1%);  $t$   $77^\circ$ ,  $99^\circ$ ;  $d$  1.236, 1.219;  $\gamma$  27.70, 26.25;  $[P]$  1243, 1244; mean, 1243;  $[P]_{Pd} = -14$ .

The *tri-n-amyl* compound separated as an orange-red oil when ammonium chloropalladite was shaken with the arsine. This oil was extracted with ether, the solution dried over sodium sulphate, filtered, and the solvent evaporated in a vacuum. The oil was then crystallised from a small quantity of absolute methyl alcohol with ice-salt cooling. The orange crystals were then separated in a chilled filter, and dried in a vacuum desiccator at  $0^\circ$  for 48 hrs.; m. p.  $10-11^\circ$  (Found: C, 47.7; H, 8.5; Pd, 14.2.  $C_{30}H_{66}Cl_2As_2Pd$  requires C, 47.7; H, 8.8; Pd, 14.15%);  $t$   $24^\circ$ ,  $77^\circ$ ,  $99^\circ$ ;  $d$  1.217, 1.170, 1.149;  $\gamma$  31.29, 26.64, 26.24;  $[P]$  1466, 1464, 1472; mean, 1467;  $[P]_{Pd} = -27$ .

*Dibromide.* The *tri-n-propyl* member [Table I (E)], prepared as the other bromide and twice recrystallised from alcohol, formed orange prisms, m. p.  $49^\circ$  (Found: C, 32.2; H, 6.1.  $C_{18}H_{42}Br_2As_2Pd$  requires C, 32.0; H, 6.3%);  $t$   $56^\circ$ ,  $78^\circ$ ;  $d$  1.5442, 1.5210;  $\gamma$  32.07, 30.23;  $[P]$  1040, 1040;  $[P]_{Pd} = -8$ .

*Dinitrite.* The *triethyl* compound was prepared in a parallel manner to that of the phosphine dinitrite, and recrystallised from alcohol; m. p.  $176-177^\circ$  (no decomp.) (Found: C, 27.4; H, 5.4.  $C_{12}H_{30}O_4N_2As_2Pd$  requires C, 27.5, H, 5.8%).

*Palladium Mercaptides*,  $Pd(SR)_2$  [Table II (A)].—Hofmann and Rabe (*Z. anorg. Chem.*, 1897, 14, 294) prepared the ethyl compound; the others are new. Finely powdered ammonium chloropalladite (1 mol.) was covered with chloroform, and a chloroform solution of the thiol (2.1 mols.) added; the solvent became orange and hydrogen chloride was evolved. After 12 hrs., the solution was filtered, the chloroform carefully volatilised, and the residue purified. All aliphatic members are deep reddish-orange in colour.

For the ethyl derivative, the crude residue was warmed with dioxan, which dissolved impurities; the product so obtained decomposed without melting at *ca.*  $250^\circ$ , and was not further investigated.

The *n-propyl* derivative (acetone then dioxan) formed small, needle-shaped, red crystals, m. p.  $209-210^\circ$ , freely soluble in chloroform and benzene, sparingly soluble in alcohol, acetone, and petrol (Found: C, 28.1; H, 5.45.  $C_6H_{14}S_2Pd$  requires C, 28.0; H, 5.45%). The high m. p. precluded parachor measurements. The crystals exhibited pleochroism, the slow direction, which is parallel to the needle axis, being orange-yellow, the fast direction yellow. The refractive index, measured by means of a naturally occurring prism, was 1.794 for yellow and 1.807 for green light;  $d$  (by flotation) 1.751.

Oscillation and Weissenberg photographs showed that the lattice was triclinic, the cell dimensions being  $a = 14.3$ ,  $b = 10.3$ ,  $c = 11.3 \text{ \AA}$ .,  $\alpha = 98^\circ$ ,  $\beta = 113.5^\circ$ ,  $\gamma = 101^\circ$ . There are therefore 6 molecules in the unit cell.

The *n-butyl* compound (acetone, dioxan, and again acetone) formed needles, m. p.  $142^\circ$ , freely soluble in benzene, chloroform, and ether, slightly soluble in cold alcohol and acetone; it can be recrystallised from petrol (Found: C, 33.5; H, 6.6; Pd, 37.4;  $M$ , in 1.276% benzene solution, 1204; in 3.198% solution, 1202; in 1.035% cyclohexane, 1995; in 2.854%, 1883;

in 0.800% bromoform, 936; in 2.216%, 1242.  $C_8H_{18}S_2Pd$  requires C, 33.7; H, 6.4; Pd, 37.5%;  $M$ , 285;  $t$  157°;  $d$  1.382;  $\gamma$  23.08;  $[P]$  452;  $[P]_{Pd} = 6$ . After the complete parachor determination, the m. p. had fallen to 124–130°, although no smell of disulphide, etc., was perceptible; the accuracy of the parachor value is therefore uncertain.

The *n*-amyl compound (acetone, thrice) formed needles, m. p. 83°, having solubilities similar to those of the lower homologue (Found: C, 38.2; H, 7.0; Pd, 34.2;  $M$ , in 1.196% benzene solution, 1361; in 2.595%, 1545; in 0.467% ethylene dibromide, 1574; in 1.319% cyclohexane, 2054; in 3.196%, 2024; in 0.414% bromoform, 1187; in 1.098%, 1345.  $C_{10}H_{22}S_2Pd$  requires C, 38.3; H, 7.0; Pd, 34.2%;  $M$ , 313;  $t$  143°, 157°;  $d$  1.3020, 1.2894;  $\gamma$  22.58, 21.89;  $[P]$  524.0, 524.9. Prof. Sugden kindly checked the parachor value, and obtained the following results:  $t$  95.2°, 104.1°, 111.7°, 124.9°;  $d$  1.3456, 1.3375, 1.3306, 1.3186;  $\gamma$  26.40, 25.62, 24.99, 23.91;  $[P]$  530.6, 529.6, 529.1, 528.3;  $d^c = 1.4321 - 0.0009091t$ . It is clear therefore that the parachor falls slightly but regularly with rising temperature.

*Diphenyl derivative.* Thiophenol (2.1 mols.) was added to a dilute aqueous solution of ammonium chloropalladite (1 mol.), and the mixture vigorously shaken. The vermilion amorphous compound rapidly separated (leaving the solution colourless), and was filtered off, washed with water and acetone, and dried. On heating, it decomposed, giving metallic palladium (Found: C, 44.25; H, 3.3; Pd, 32.9.  $C_{12}H_{10}S_2Pd$  requires C, 44.3; H, 3.1; Pd, 32.85%). This compound was formed when thiophenol was added to alcoholic or acetone solutions of any of the sulphide derivatives listed in Table I (A); the phosphine derivatives [Table I (B)] were, however, unaffected, whilst the arsine derivatives [Table I (C)] gave unstable, deep red products of undetermined composition.

*Mercury Derivatives.*—Diethylmercury (Gilman and Brown, *J. Amer. Chem. Soc.*, 1930, 52, 3314) had b. p. 53.7–53.8°/15 mm. (the b. p., 65–66°/18 mm., given by those authors is evidently an error);  $t$  24°;  $d$  2.4583;  $\gamma$  35.44;  $[P]$  256.8; whence  $[P]_{Hg} = 66.0$ .

Di-*n*-amylmercury, prepared by method of Jones, Evans, Gulwell, and Griffiths (this vol., p. 39), had b. p. 90.5°/1 mm., 144°/21 mm. The parachor was determined immediately after final rectification at the lower pressure, as the liquid slowly decomposes at room temperature, depositing mercury;  $t$  24°;  $d$  1.6433;  $\gamma$  30.37;  $[P]$  489.7; whence  $[P]_{Hg} = 61$ .

*Mercury Alkylmercaptides*,  $Hg(SR)_2$  [Table II (B)].—Claësson (*J. pr. Chem.*, 1877, 15, 205) and Otto (*Ber.*, 1882, 15, 125) prepared the ethyl compound, and Roemer (*Ber.*, 1873, 6, 784) the *n*-propyl compound; the others are new. The thiol (2 mols.) was added to finely divided dry mercuric oxide (1.2 mols.) covered with about 10 times its weight of alcohol. The mixture, which rapidly became warm, was occasionally shaken for 2–3 hrs., and was then heated under reflux on a water-bath for 1 hr. It was filtered hot, and the mercuric mercaptide, which crystallised on cooling, was recrystallised until pure. The solubility of the mercaptides in hot alcohol falls on ascending the series, and therefore after the amyl compound, benzene was used as a solvent in the preparation. All these compounds are white crystalline solids.

The ethyl compound (acetone) has m. p. 77°, becomes cloudy at 170°, and decomposes at ca. 210° (Found: C, 14.8; H, 3.0. Calc. for  $C_4H_{10}S_2Hg$ : C, 14.9; H, 3.1%);  $t$  78°, 99°;  $d$  2.391, 2.354;  $\gamma$  37.15, 35.85;  $[P]$  333.3, 335.5; mean, 334;  $[P]_{Hg} = 46$ . The molten material was very pale grey, suggesting that the reaction  $Hg(SET)_2 \rightarrow Hg + S_2Et_2$  had occurred to a very small extent; the liquid on cooling, however, gave a pure white solid, which after the parachor measurements had m. p. 75.5–77.0°. The other mercaptides gave completely colourless liquids and showed no sign of dissociation; their m. p.'s, unless otherwise stated, were unchanged after the measurements.

The *n*-propyl compound (acetone) had m. p. 67° (Found: C, 20.7; H, 3.6. Calc. for  $C_6H_{14}S_2Hg$ : C, 20.5; H, 4.0%);  $t$  77°, 99°;  $d$  2.063, 2.027;  $\gamma$  30.71, 29.54;  $[P]$  400.2, 403.4; mean, 402;  $[P]_{Hg} = 35$ ; the m. p. fell 0.5° during the determination.

The *n*-butyl homologue (acetone) had m. p. 85° (Found: C, 25.1; H, 4.8; S, 16.8;  $M$ , ebullioscopic, in 1.282% acetone solution, 396; in 2.367% benzene solution, 467; in 3.975%, 495.  $C_8H_{18}S_2Hg$  requires C, 25.4; H, 4.8; S, 16.9%;  $M$ , 379);  $t$  99°;  $d$  1.820;  $\gamma$  26.82;  $[P]$  475.0;  $[P]_{Hg} = 29$ . The m. p. fell 1° during the determination.

The *n*-amyl derivative (acetone, then benzene) had m. p. 66° (Found: C, 29.9; H, 5.45.  $C_{10}H_{22}S_2Hg$  requires C, 29.5; H, 5.5%);  $t$  77°, 99°;  $d$  1.695, 1.669;  $\gamma$  26.48, 25.30;  $[P]$  544.4, 546.6; mean, 545;  $[P]_{Hg} = 20$ .

The *n*-hexyl compound (benzene, thrice) had m. p. 58° (Found: C, 33.1; H, 5.9;  $M$ , in 0.507% bromoform solution, 422; in 1.151%, 447.  $C_{12}H_{26}S_2Hg$  requires C, 33.1; H, 6.0%;  $M$ , 435);  $t$  78°, 99°;  $d$  1.5805, 1.5551;  $\gamma$  25.51, 24.32;  $[P]$  618.4, 621.1; mean, 620;  $[P]_{Hg} = 15$ .

The *n*-heptyl derivative (benzene) had m. p. 75° (Found: C, 36.35; H, 6.5; S, 13.7.

$C_{14}H_{30}S_2Hg$  requires C, 36.3; H, 6.7; S, 13.8%;  $t$  77°, 99°;  $d$  1.499, 1.474;  $\gamma$  24.97, 24.02;  $[P]$  690.1, 694.5; mean 692;  $[P]_{Hg} = 8$ .

The *n-octyl* homologue (benzene) had m. p. 71° (Found: C, 39.4; H, 6.7; S, 13.1;  $M$ , ebullioscopic, in 1.548% benzene solution, 573; in 2.498%, 729; in 3.885%, 987; in 6.001%, 1560.  $C_{16}H_{34}S_2Hg$  requires C, 39.1; H, 7.0; S, 13.1%;  $M$ , 491);  $t$  77°, 99°;  $d$  1.424, 1.405;  $\gamma$  25.06, 24.01;  $[P]$  770.9, 773.1; mean, 772;  $[P]_{Hg} = 9$ .

Diethylsulphidemercuric chloride,  $[Et_2S, HgCl_2]$ , was prepared in the hope that the parachor of co-ordinated mercury could be measured, but this was not achieved. Loir (*Annalen*, 1853, 87, 369) and Abel (*Z. physiol. Chem.*, 1894, 20, 269) give m. p. 90° and 119° respectively; Wegscheider and Schreiner (*Monatsh.*, 1919, 40, 330) give m. p. 60—90° and composition  $Et_2S, 2HgCl_2$ . Diethyl sulphide (2.3 g., 1 mol.) was shaken with saturated aqueous mercuric chloride solution (100 c.c., *i.e.*, 7 g. or 1 mol.), and the white precipitate which immediately formed was collected and recrystallised from alcohol and then from acetone; m. p. 77.5—78.5°, easily soluble in hot alcohol, acetone, and benzene, sparingly in chloroform; yield 4.5 g. (Found: C, 13.2; H, 2.4. Calc. for  $C_4H_{10}Cl_2SHg$ : C, 13.7; H, 2.7%). On exposure to air at room temperature, diethyl sulphide was liberated and the m. p. rose; the decomposition was rapid on warming; *e.g.*, after 6 hrs. at 60°, m. p. 115—117°; after 12 hrs., m. p. 132—136°, and the substance no longer melted to a clear liquid; hence the diversity of recorded m. p.'s.

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