

118. *Covalency, Co-ordination, and Chelation. Part III.*

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The changes in covalency on passing from quadrivalent platinum through trivalent gold to bivalent mercury are discussed with reference to the derived organometallic pseudo-atoms and ions and the additive compounds of some of the latter with amines. The further changes on proceeding to trivalent thallium, quadrivalent lead, and bismuth are outlined.

Similar changes passing down sub-groups IIIB, IVB, and VB to the same metals are also discussed. A few illustrative experiments are described.

THE co-ordination numbers (C.N.) characteristic of the elements from Os (76) to Po (84) in their highest valency states are now well established in inorganic compounds, and pass from a maximum of 8 at osmium (as in OsF_8) through 6 (IrF_6 , $[\text{PtCl}_6]''$) to a minimum of 4 in gold, *e.g.*, $(\text{Au en}_2)\text{Br}_3$, and in mercury, *e.g.*, $[\text{HgI}_4]''$. Beyond this point the maximum C.N. remains at 6 for the next three elements, as shown by the thalli-, plumbi-, and bismuthi-chloride ions, rising finally to 8 again in the acetylacetonate derivative of polonium (Servigne, *Compt. rend.*, 1933, 196, 264).

In lower-valency states a minimum of 2 is found in the same place, as illustrated by $[\text{Au}_2\text{CS}(\text{NH}_2)_2]\text{Cl}$, and by the fact that mercurous chloride does not add pyridine, but is decomposed by it, giving mercury and the pyridine complex of mercuric chloride (Lang, *Ber.*, 1888, 21, 1578).

Definite organo-metallic compounds of osmium and iridium have not yet been described, although Lichtenwalter (Thesis, Iowa State College, 1939, pp. 59, 60) obtained small amounts of amorphous material containing carbon and metal when the trichlorides were treated with phenylmagnesium bromide.

In all its compounds, inorganic, organic and complex, quadrivalent platinum has a co-ordination number of 6, the bonds being directed to the corners of an octahedron (Werner, *Vierteljahrsschrift Naturf. Ges., Zurich*, 1917, 62, 553). Where one atom of quadrivalent platinum appears to be surrounded by less than six other atoms or groups, as in the trimethylplatinum halides (Part I, *J.*, 1933, 1292), association always occurs. Again trimethylplatinum acetylacetonate, the single formula for which suggests a co-ordination number of 5 for the metal, was shown (*J.*, 1928, 565) to be bimolecular in benzene, as were later the ethyl acetoacetate and dipropionylmethane derivatives (*J.*, 1933, 21). Another example of the same behaviour has now been provided by the new monopyridine derivative of trimethylplatinum iodide (Gibson, Ewens, and Foss, *Nature*, 1948, 162, 693), which is also bimolecular in benzene.

The 6-co-valency of quadrivalent platinum, in three dimensions, and the stability of its methyl compounds and of its co-ordination compounds with β -diketones, with ammonia, and with organic amines, are all well established, both organic and organometallic compounds being built on the same plan.

The work of Gibson and his school on the organic derivatives of gold, summarised in his Presidential Address to the British Association (Cambridge, 1938), has established that trivalent gold is 4-co-ordinate in its inorganic, organic, and complex compounds, the metal lying at the centre of a square and the other atoms or groups at the four corners. Brain and Gibson, in particular (*J.*, 1939, 765), attempted, but failed, to prepare a stable compound containing 5-co-ordinate auric gold. All that has been said about quadrivalent platinum and the octahedron may, with equal truth, be said about trivalent gold and the square. Moreover, within the framework of the above, both gold and platinum in both their inorganic and organometallic compounds form well-defined and stable compounds with β -diketones and with amines, the stability of their derivatives with ethylenediamine having been again demonstrated by Gilman and Wood's preparation (*J. Amer. Chem. Soc.*, 1948, 70, 550) of bistrimethylgold-ethylenediamine, decomposing at 94–98°, while their trimethylgold from which it is derived decomposes below –40°.

The organometallic compounds of mercury (*e.g.*, diphenylmercury, alkylmercury halides) do not form stable compounds with either β -diketones or amines, although they are soluble in pyridine and ethylenediamine, from which they are recovered unchanged. Evidence of combination is, however, provided by Maynard and Howard's observation (*J.*, 1923, **123**, 963) that the conductivity of an aqueous solution of methylmercury acetate was increased by the addition of pyridine. This suggests co-ordinate combination of the pyridine and the methylmercury group and extrusion of the acid radical as an ion, leaving the C.N. of mercury unchanged. There is yet no evidence that mercury in its organometallic derivatives ever has a higher covalency than 2.

Both valency and co-ordination number of organometallic compounds thus decrease on approaching mercury, and on passing beyond it a new and different structure appears, of which the strongly alkaline nature of the thallos and dialkylthallium hydroxides is an early indication, as is the reactivity of the third alkyl group in the trialkylthallium compounds. These changes resemble those found on passing towards and beyond an inert gas (*cf.* Berry and Lowry, *J.*, 1928, 1765; Hartmann, *Z. Naturforsch.*, 1947, **2**, a, 489). The mercury atom and the thallos ion are related as are argon and potassium, and the mercury dialkyls to the dialkylthallium ions as methane to the ammonium ion.

The alkylmercury halides and the dialkylthallium ions differ from the trialkyl derivatives of platinum and from the dialkyl derivatives of gold, but resemble each other, in not forming stable compounds with pyridine or with ethylenediamine; both, however, are soluble in these solvents. In the compounds of platinum and gold, the forces attaching these addenda to the molecule are of a higher order than those between solvent and solute. In the compounds of mercury, thallium, and lead, they are of the same order, organometallic lead complexes with pyridine and ammonia being unstable; thus diphenyl-lead dibromide forms a compound with four molecules of pyridine which is described as being stable in a pyridine atmosphere, and also with two molecules of ammonia, which can be removed by the passage of air (Pfeiffer, Truskier, and Disselkamp, *Ber.*, 1916, **49**, 2448). This is a contrast to the behaviour of the dipyriddy derivative of trimethylplatinum iodide, which, as described in Part II (Lile and Menzies, *J.*, 1949, 1168), is unattacked by boiling with dilute acetic or hydrochloric acid, 2N-ammonia, or sodium hydroxide. This decrease of the power of attachment is general. Tetramethylplatinum, for instance, is unaffected by iodine, but the tetra-alkyl derivatives of lead are readily decomposed by it. The trialkylbismuths are spontaneously inflammable in air.

Tetramethylplatinum, again, has no melting point, and is tetrameric in the solid state. Diphenylmercury, trimethylthallium, tetraethyl-lead, and triphenylbismuth are all unimolecular (Ghira, *Gazzetta*, 1894, **24**, 312; Abbott, Doctoral Thesis, Iowa State College, 1942, p. 28; Menzies and Overton, *J.*, 1933, 1292; Challenger and Goddard, *J.*, 1920, **117**, 771; see also p. 620).

Although Challenger and Parker (*J.*, 1931, 1462) and Challenger and Richards (*J.*, 1934, 409) have prepared pyridine derivatives of phenylthallium dihalides, and Molnikoff and Gratschewa (*J. Russ. Phys. Chem. Soc.*, 1935, **67**, 1768) those of ethylthallium dibromide, it is shown below that not only methylmercury iodide, but also dimethyl- and diethyl-thallium halides are recovered unchanged on adding water to their solutions in pyridine or ethylenediamine. It is also shown that diphenylmercury, triphenyl-antimony and -bismuth, and tetraphenyl-lead separate unchanged from their solutions in organic solvents containing also ethylenediamine, *i.e.*, under conditions which convert the trimethylplatinum and dialkylgold compounds into stable complexes. If thallium resembles mercury and differs from platinum and gold in not forming stable compounds with organic amines in its dialkyl and diaryl derivatives, it resembles them in forming the stable dialkylthallium derivatives of β -diketones (Menzies, Sidgwick, Cutcliffe, and Fox, *J.*, 1928, 1288). Here, as often, carrying a charge helps both initial attachment and subsequent co-ordination, the familiar arrow being electrically supported near the target. These stable, volatile compounds display both the stable combination leading to definite and reproducible composition, and the less stable form involving forces of the same order as those involved in solution. Their association in benzene depends on the concentration (*J.*, 1932, 2734). The corresponding platinum compounds display double molecular weights in benzene at all concentrations.

The elements and groups attached to the heavy metals preceding mercury are more firmly held and in more definite positions than those following it, around which also the form taken by co-ordination is frequently different. 4-Covalent quadrivalent lead, for example is tetrahedral, but optically active lead compounds have not yet been described, racemisation after their attempted preparation possibly taking place on the lines suggested by Garner (*Proc.*,

1912, 28, 67). This loosening becomes apparent on approaching thallium, lead, and bismuth, both from above and from the left. Practical applications of this have been made by Challenger and Ridgeway and by Goddard and Goddard (*J.*, 1922, 121, 104, 256) who used triphenylbismuth as a phenylating agent for the earlier members of Group V, and for mercuric and thallic chlorides.

EXPERIMENTAL.

Action of Ethylenediamine and Pyridine on Methylmercury Iodide.—The ethylenediamine used for this and for the dialkylthallium halides was part of a consignment of 38½ lb. purchased from the Beresworth Laboratories of Framlingham, Mass., early in 1937 and kept since in stoppered bottles; in 1949 it had become light brown and had taken up a little water. It was kept for a few days over potassium hydroxide and then distilled twice from sodium wire. It then boiled at 116–117°/740 mm. and titration by *N*-sulphuric acid, with methyl-red as indicator, showed a purity of 98.7%. The pyridine used was distilled from a good commercial sample, the fraction of b. p. 114°/745 mm. being used. The methylmercury iodide was the same sample as that used in Part I; it melted at 142–145°, and after drying (P_2O_5), at 145–146°. A sample was dissolved in cold pyridine and reprecipitated by addition of water; after separation and drying (P_2O_5) it melted at 143–144°. A sample was then dissolved in the above purified ethylenediamine, the solution boiled, and water added; a little solid separated out, m. p., after drying over sulphuric acid, 142°. On adding hydrochloric acid to the filtrate, much more solid was again precipitated; m. p. (P_2O_5) 145°, mixed m. p. with original methylmercury iodide 145–146°.

Precipitation on adding water is apparently much more complete with solutions of methylmercury iodide in pyridine than with those in ethylenediamine.

Action of Ethylenediamine on Dialkyl- and Diaryl-thallium Halides.—In most cases mixed m. p.s of the substances before and after recovery afford sufficient evidence of identity, but since the dimethyl- and diethyl-thallium halides have no m. p.s, another means of identification is supplied by the unique and unexplained patterns formed by these substances on the surfaces of drops of their hot solutions cooled on a microscope slide (see *Nature*, 1931, 128, 907). All these halides are very soluble in anhydrous ethylenediamine, but in contrast to the behaviour of trimethylplatinic iodide they are reprecipitated by water, and even if the halides are boiled with the amine, on subsequent addition of water, the above patterns can be obtained just as if the amine had not been used, formation being occasionally facilitated in both cases by addition of a little of the corresponding alkali halide.

Diphenylthallium bromide does not form these patterns, but analysis of a sample dissolved in anhydrous ethylenediamine and then left until dry over sulphuric acid indicated that, apart from a little adhering ethylenediamine, it was recovered unchanged (Found : C, 33.9; H, 2.4; Br, 16.7; N, 0.68. Calc. for $C_{12}H_{10}TlBr$: C, 32.8; H, 2.3; Br, 18.24; N, 0%. Calc. for $C_{12}H_{10}TlBr \cdot NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$: N, 5.6%). The high carbon and low bromine figures are probably due to the presence of diphenylthallium chloride.

Pyridine has so long been used for recrystallisation of dialkyl- and diaryl-thallium halides that further evidence of their separating unchanged is unnecessary.

Action of Ethylenediamine on Triphenylantimony, Triphenylbismuth, Diphenylmercury, and Tetraphenyl-lead.—Triphenylantimony (m. p. 51°) was prepared by the action of phenylmagnesium bromide on freshly distilled antimony trichloride, b. p. 216–217° (Pfeiffer and Heller, *Ber.*, 1904, 37, 4621). The antimony was determined by heating with nitric and sulphuric acids, reduction by sulphur dioxide, boiling off excess of the latter, and iodometric titration (Found : Sb, 34.7, 34.5. Calc. for $C_{18}H_{15}Sb$: Sb, 34.5%). Triphenylbismuth (m. p. 78.5°) was similarly prepared from phenylmagnesium bromide and bismuth trichloride (Pfeiffer and Pletsch, *ibid.*, p. 4622). Tetraphenyl- and triphenyl-lead were prepared together by the action of phenylmagnesium bromide on lead chloride and separated by acetone, in which the latter is easily soluble, followed by recrystallisation from chloroform [Found, for triphenyl-lead : Pb, 47.5 (as sulphate). Calc. for $C_{18}H_{15}Pb$: Pb, 47.2%. Found, for tetraphenyl-lead : Pb, 39.1. Calc. for $C_{24}H_{20}Pb$: Pb, 40.2%].

Triphenylantimony, insoluble in hot aqueous ethylenediamine, dissolves readily in the anhydrous solvent. This solution, after addition of alcohol, was evaporated until solid separated; after recrystallisation from alcohol, this melted at 49–50° (mixed m. p. with triphenylantimony, 49–51°).

Action of Ethylenediamine on Other Phenyl-Metal Derivatives.—The compounds were dissolved in benzene, ethylenediamine added, and the solution evaporated to give a solid, as follows :

Compound.	Original.	M. p.	Product.	M. p.	Mixed m. p.
$Pb(C_6H_5)_4$	White needles	224°	White crystals	219°	221°
$Bi(C_6H_5)_3$	White needles	77–78	White needles	76	77–78
$Hg(C_6H_5)_2$	White needles	122–124	Rhombic plates	122–123	122–123

Ethylenediamine therefore does not appear to attack phenyl-metal derivatives in the absence of an acid group.

Triphenylantimony dibromide was made (13 g., 90% yield) by mixing solutions of triphenylantimony (10 g.) and a slight excess of bromine in light petroleum, filtration, and recrystallisation from the same solvent (charcoal); m. p. 214–215° (Michaelis and Reese, *Annalen*, 1886, 233, 48, gave m. p. 216°) (Found : Sb, 24.3. Calc. for $C_{18}H_{15}SbBr_2$: Sb, 23.8%). The high m. p. and consequent stability are in contrast with the properties of triphenylbismuth dibromide, which decomposes in boiling benzene.

Triphenylantimony dichloride was prepared similarly as long colourless needles (up to 8 cm. long); m. p. 143° (Found : Sb, 30.2, 29.9, 29.9. Calc. for $C_{18}H_{15}SbCl_2$: Sb, 28.8%).

Triphenylantimony sulphide was prepared (theoretical yield) by passing hydrogen sulphide into a

cooled alcoholic solution of triphenylantimony dibromide saturated with ammonia; m. p. 112° (Kaufmann, *loc. cit.*, p. 2765, gives m. p. 119—120°) (Found: Sb, 31.4. Calc. for $C_{18}H_{15}SbS$: Sb, 31.6%). The compound is apparently more soluble in alcohol than stated by Kaufmann, 3.7 g. dissolving readily in 30 c.c. of boiling alcohol. It crystallises in needles on cooling. The alcoholic mother-liquors, on cooling, deposit large, colourless, rhombic plates, m. p. 51°, evidently of triphenylantimony re-formed by decomposition of the sulphide. Similarly, a benzene-hexane solution deposits crystal of rhombic sulphur on standing for some days.

The similar treatment (Michaelis and Polis, *Ber.*, 1887, 20, 57) of triphenylbismuth dichloride or dibromide leads to formation of triphenyl bismuth, ammonium halide, and sulphur.

The molecular weights of three of the above compounds were determined cryoscopically in benzene, with the following results:

Compound.	Weight (g.).	Weight of benzene (g.).	Δ .	M , found.	M , calc.
$Sb(C_6H_5)_3$	0.7179	17.28	0.619°	348.4	} 352.9
	0.9894	16.16	0.893	351.1	
	1.7445	16.16	1.583	349.2	
$Sb(C_6H_5)_3Br_2$	0.9707	18.24	0.508	536.4	} 512.7
	1.4344	18.24	0.758	531.1	
	1.9257	18.24	1.019	530.8	
$Sb(C_6H_5)_3S$	0.2647	15.08	0.196	458.5	} 385
	0.4797	15.08	0.380	428.7 *	

* During this determination, some decomposition occurred, and the solution became milky.

Triphenylbismuth and its Dichloride.—By passing chlorine through a light petroleum solution of triphenylbismuth, the corresponding dichloride was obtained; m. p. 141° (Michaelis and Polis, *ibid.*, p. 56). Molecular weights were determined cryoscopically in benzene (the constant used was 51.15):

Compound.	Weight (g.).	Weight of benzene (g.).	Δ .	M , found.	M , calc.
$Bi(C_6H_5)_3$	0.5412	17.49	0.348°	455.3	} 440.1
	0.9334	17.49	0.602	453.9	
	1.6251	17.49	1.042	456.4	
$Bi(C_6H_5)_3Cl_2$	0.3756	16.63	0.238	485.9	} 511
	0.5956	16.63	0.379	484.0	
	0.7701	16.63	0.486	488.0	

Challenger and Goddard (*J.*, 1920, 117, 771) found 427 for the molecular weight of triphenylbismuth in benzene, but as their observed depression was only 0.153°, they were obviously using a more dilute solution. Their figure 498.5 for the molecular weight of the dichloride was calculated from an observed depression of 0.47° and agrees well enough with our value.

Action of Ethylenediamine on Triphenylantimony Dichloride.—The dichloride (4 g.) was dissolved in ether, and ethylenediamine (0.6 c.c., 1 equiv.) added. A white precipitate was produced. This was filtered off, washed with alcohol, and dried, forming minute white crystals, m. p. 206° (decomp. at 235°). The compound was analysed without further purification. The figures show the presence of nitrogen but do not indicate any definite compound (Found: Sb, 23.7; C, 44.4; H, 5.3; N, 6.6. Calc. for $C_{18}H_{15}SbCl_2 \cdot NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$: Sb, 24.2; C, 49.6; H, 4.8; N, 5.8%).

Triphenylantimony dichloride was stirred with aqueous ethylenediamine. The solid became curdy. It was filtered off and dried in a vacuum desiccator, but did not contain Cl or N; m. p. 208°; mixed m. p. with the corresponding compound from the dibromide, 210°. It is therefore presumably triphenylantimony dihydroxide.

Action of Ethylenediamine on Triphenylantimony Dibromide.—This dibromide is only slightly soluble in anhydrous ethylenediamine. Addition of ethylenediamine to a solution of the dibromide in alcohol-ether or in benzene gives a white precipitate. This white solid is very deliquescent, and extremely soluble in water, from which it cannot be crystallised; it does not melt below 280°. Heated in a test-tube, it leaves only a slight residue of carbon. It contains bromine and nitrogen, but less than 2% of antimony. With copper sulphate solution it gives the deep blue colour characteristic of ethylenediamine-copper complexes. It would seem, therefore, to be ethylenediaminium dibromide.

Triphenylantimony dibromide (4 g.) was suspended in water, and a few c.c. of ethylenediamine were added. The solid changed in appearance, forming hard cakes. These were broken up, filtered off, washed, and dried, giving a white solid, m. p. 210°, which did not contain either nitrogen or bromine [Found: Sb, 31.8, 33.3. Calc. for $C_{18}H_{15}Sb(OH)_2$: Sb, 31.5%. Calc. for $C_{18}H_{15}SbO$: Sb, 33.1%]; the dihydroxide has m. p. 212°.

Tetraphenyl-lead was heated under reflux with glacial acetic acid, and the diacetate formed was crystallised from dilute acetic acid; it was then dissolved in dilute acetic acid, and hydrogen sulphide passed through the cooled solution. The grey curdy precipitate was separated, extracted with benzene, and the solution crystallised, forming pale yellow prisms, m. p. 130° (decomp. above 90°) [Found: Pb (as sulphate), 51.05; S, 7.94. Calc. for $C_{12}H_{10}PbS$: Pb, 52.69; S, 8.16%]. The sulphur was determined as barium sulphate after fusion with potassium hydroxide and nitrate.

Molecular weights, determined cryoscopically in benzene, were as follows :

Compound.	Weight (g.).	Weight of benzene (g.).	Δ .	M , found.	M , calc.
Pb(C ₆ H ₅) ₃	0.2260	15.30	0.097°	780	} 438
	0.4757	15.30	0.201	792	
Pb(C ₆ H ₅) ₂ S	0.5540	23.08	0.120	1006	} 393
	0.5540	15.90	0.172	1019	

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