

**300.** *Covalency, Co-ordination, and Chelation.*

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THE easy formation and stability of trimethylplatinum and dialkylthallium derivatives of  $\beta$ -diketones and  $\beta$ -keto-esters have recently been recorded (J., 1928, 565, 1288; 1932, 2604, 2734; 1933, 21). Attempts in 1928 to prepare methylmercury acetylacetonone and

triethyl-lead acetylacetonate were unsuccessful. These failures do not, of course, prove that the compounds in question cannot be made, but as they were carried out under conditions which gave the platinum and thallium compounds easily and in good yield, they do indicate that they are less stable.

At first sight unconnected with these facts, is Krause and Dittmar's observation (*Ber.*, 1930, **63**, 1956) that while the lower dialkylthallium halides are insufficiently soluble in benzene for molecular-weight determinations (in itself an indication of molecular association), di-*n*-hexyl thallifluoride and diamyl thallifluoride are both highly associated in this solvent. In the same paper these authors show that triphenyl-lead chloride is unimolecular in benzene. Again, Werner (*Z. anorg. Chem.*, 1897, **15**, 27, 31) showed that methylmercury chloride and iodide are unimolecular in ethyl sulphide and in methyl sulphide. This somewhat scanty information suggested the generalisation that in the organo-metallic derivatives of the elements from platinum to lead inclusive, stability of the acetylacetonates (and similar compounds) and polymerisation of the corresponding organo-metallic halides in benzene solution were connected phenomena. Further experiments have confirmed this generalisation. Trimethylplatinum iodide is polymerised in boiling benzene; methylmercury iodide is unimolecular in freezing benzene, as are triethyl-lead chloride at room temperature (Barger's capillary method) and triethyl-lead bromide in freezing benzene.

These observations can be correlated by a consideration of the valencies and of the effective co-ordination numbers of the metals in question.

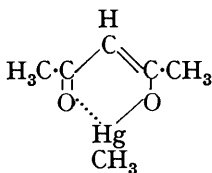
The relationships which were suspected, and which it is the object of this paper to confirm and explain, are conveniently displayed in the subjoined table:

	Me <sub>3</sub> Pt-	Et <sub>3</sub> Au-	MeHg-	(Alk) <sub>2</sub> Tl-	Et <sub>3</sub> Pb-
Valency .....	4	3	2	3	4
Effective co-ordination number .....	6	4	2	4-6	4
Formation (+) or non-formation (-) of compounds with diketones .....	+	+	-	+	-
Molecular association of halides .....	2·3-4·5	2	1	Up to 8	1

It will be noticed that compounds with diketones have only been made in those cases where the effective co-ordination number is greater than the valency functioning, and also that the organo-metallic halides are associated in those cases only.

The ready solubility of methylmercury iodide in organic solvents, and its volatility at room temperature, suggest that the attractive forces between the constituent atoms are completely or almost completely satisfied within the molecule, and this is confirmed by the observation (see p. 1292) that it is unimolecular in benzene. It may be recalled that volatility and solubility in organic solvents are characteristic of compounds in the molecules of which both the ordinary valencies and the co-ordination capacities of the constituent atoms are internally satisfied, and that chelation is only one way in which this may be brought about. Chelation, indeed, is only possible when the number of the ordinary covalencies functioning in the non-chelated enolic form is less than the potential co-ordination number. In the stable beryllium and aluminium acetylacetonates, for instance, the ordinary covalencies functioning are 2 and 3 respectively, whereas the effective co-ordination numbers are 4 and 6. In the methylmercury derivatives both are only 2, and both are already exercised in the enolic form of methylmercury acetylacetonate; subsequent change into the chelate form indicated by the dotted line would raise the covalency to 3 and apparently does not occur, the ready decomposition into a substance giving analytical figures approximating to those required for methylmercury acetate indicating an instability approaching that of sodium acetylacetonate. The functioning of mercury with a stable covalency of 2 in compounds of this type is also emphasised by Ghira's observation that dimethyl- and diethylmercury are unimolecular in the vapour state and that diphenylmercury is unimolecular in benzene solution (*Gazzetta*, 1894, **24**, 312).

Lead in its trialkyl and triaryl derivatives usually displays a co-ordination number of 4. In addition to new examples given below, Ghira (*loc. cit.*, p. 320) found tetraethyl-



lead to be unimolecular in ethylene dibromide. The effective valency is also 4, so that the non-formation of triethyl-lead acetylacetonate may be explained in the same way as the unsuccessful attempt to prepare methylmercury acetylacetonate.

Quadrivalent platinum usually displays a stable covalency of 6. The enolic formula for trimethylplatinum dipropionylmethane or ethylacetoacetate requires a covalency of 4. This is raised to 5 by chelation, and finally to 6 by formation of the stable double molecules recently described (J., 1933, 21). The polymerisation of trimethylplatinum iodide (described below) is to be explained similarly by co-ordination between atoms in adjacent molecules. Trimethylplatinum iodide is, moreover, much less soluble in benzene than methylmercury iodide, and is not volatile, both indicating greater attraction between adjacent molecules.

Tervalent gold is commonly 4-covalent, and the preparation of diethylgold acetylacetonate and the observation that diethylgold bromide is bimolecular in benzene solution (Gibson and Simonsen, J., 1930, 2531) are both in agreement with the generalisation now discussed.

In thallic compounds, the ordinary valency is again 3, while the effective co-ordination number may vary from 4 to 6. Powell and Crowfoot (*Nature*, 1932, 130, 131) have shown that the alkyl chains in the dialkylthalliums are attached at an angle of 180°. This makes the packing of four other atoms round the central thallium atom easy, and may explain the tendency for the co-ordination number to exceed 4. The polymerisation of the dialkyl halides and the formation and subsequent association of the chelate derivatives of this element resemble the behaviour of the corresponding platinum compounds, and are to be explained in the same way.

*Molecular weights, cryoscopic in benzene.*

(Concn. = mols. per 100 g. of benzene.)

Formula.	Concn.	M.	Formula.	Concn.	M.
CH <sub>3</sub> HgI	0.00858	341.2	Hg(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	{ 0.0064*	342 }
(342.5)	0.01952	338.5	(354.7)	{ 0.0142*	391 }
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> PbBr	0.00923	264	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> Pb	0.00463	305
	0.0177	315	(323.4)	0.0118	362
(374.2)	0.0202	355		0.0175	351
	0.0250	327		0.0198	343
	0.0830	380	(in C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub> )	{ 0.01057*	328 }
				{ 0.00482*	306 }

\* Calculated from Ghira's figures.

These results show that mercury is 2-covalent and lead 4-covalent in compounds of the type under discussion.

*Molecular weights of trimethylplatinum iodide.*

(CH<sub>3</sub>)<sub>3</sub>PtI, formula weight 367.2.

Orange variety.			White variety.		
Concn.	M.	a.*	Concn.	M.	a.*
Cryoscopic in benzene.					
0.001	1565	4.26	0.001017	935	2.55
0.00203	1592	4.34	0.002159	930	2.53
0.00304	1587	4.32			
Ebullioscopic in benzene.					
0.0222	1639	4.46	0.0114	852	2.32
0.03205	1671	4.55	0.0156	846	2.30
0.0371	1685	4.56			
0.0407	1639	4.46			

\* a, here and throughout, represents degree of association.

EXPERIMENTAL.

*Molecular Weights by Barger's Method.*—The capillary method of molecular-weight determination mentioned above is that due to Barger (J., 1904, 85, 286). It is of special value for substances of low solubility, or where the total quantity available is very small. Essentially it consists in the comparison of the vapour pressures exerted by solutions in the same solvent of a standard substance and of the substance whose molecular weight is required. Alternate

drops of the two solutions are introduced into a capillary tube which is afterwards sealed at both ends. The drops are then measured, using a microscope fitted with a micrometer eyepiece which carries an arbitrary scale, in this case of 50 divisions. The tube is kept for 1—24 hours, and the drops again measured. Those of the solution having the greater vapour pressure decrease, whilst the others increase in size. This gives an indication of which solution has the higher molecular concentration. A series of experiments with standards of varying concentration furnishes limits for the molecular weight.

In the present determinations the standard substance was naphthalene, and the solvent benzene. Each tube contained 7 drops arranged thus :

1	2	3	4	5	6	7
$C_{10}H_8$	$x$	$C_{10}H_8$	$x$	$C_{10}H_8$	$x$	$C_{10}H_8$

Drops 2, 3, 4, 5, and 6 were about 1 mm. in length. Drops 1 and 7, which were not measured, were about 3—4 mm., in order to minimise changes in concentration produced by overheating when the tubes were sealed. Even with this precaution, the changes in drops 2 and 6 are occasionally irregular, but the behaviour of the inside drops (3, 4, 5) does not appear to be subject to this source of error.

An illustration of the method is given in the following account of its application to trimethylplatinum chloride. The solubility of this in benzene is so small that the most concentrated solution obtainable contained only 0.188% w/v (0.00078 g.-mol. per 100 g. of benzene). Figures are given for the comparison of this solution with 0.0035*N*- and 0.004*N*-solutions of naphthalene. Drops 1, 3, 5, 7 were of the standard; 2, 4, 6 of trimethylplatinum chloride.

Standard.	Change in length of drops (in tenths of a division).					Time.
	2	3	4	5	6	
0.0035 <i>N</i>	+ 54	- 29	+ 18	- 70	+ 150	After 21 hours.
0.004 <i>N</i>	+ 7	+ 9	- 38	+ 22	- 36	After 19 hours.

These changes show that the solution of trimethylplatinum chloride was between 0.0035*N* and 0.004*N*; whence the molecular weight must be less than 537, but greater than 470. The formula weight is 275.6, so that the degree of association is 1.71—1.95.

Other results obtained by this method include :

*White trimethylplatinum iodide* ( $M = 367.2$ ). Concn., 0.00249; normality \* found, between 0.010 and 0.008;  $M$ , found, 800—1000;  $\alpha$ , 2.18—2.72. When drops of this solution were alternated with drops of 0.009*N*-naphthalene solution, there was no definite variation in the size of either, indicating that they had the same molecular concentration, giving a molecular weight for the iodide of 890, and hence an association of 2.42.

*Yellow trimethylplatinum iodide*. This sample was recovered from the b. p. determination referred to above. Concn., 0.00312; normality found, between 0.0085 and 0.008;  $M$ , found, 1176—1250;  $\alpha$ , 3.20—3.40.

*Triethyl-lead chloride* ( $M = 329.8$ ). Concn., 0.00347; normality found, between 0.040 and 0.025;  $M$ , found, 250—400;  $\alpha$ , 0.76—1.21. This solution showed no variation in the drops when compared with 0.03*N*-naphthalene, indicating a molecular weight of 333, and an association of 1.01.

Methylmercury iodide was prepared by exposing mercury and methyl iodide to occasional sunlight for some days; it was recrystallised from methyl alcohol, and that used for molecular-weight determination from light petroleum. Its volatility is well shown by placing a drop of its solution in benzene on a glass slide. On evaporation of the solvent the iodide crystallises, but after 2 hours at room temperature it sublimes, leaving no trace (Found: C, 3.65, 3.68; H, 1.08, 0.92. Calc.: C, 3.5; H, 0.88%).  $M. p. 144.4^\circ$ .

*Attempted preparation of methylmercury acetylacetonone*. 8.1 G. of methylmercury iodide were treated in hexane with 5.9 g. (1 mol.) of thallos ethoxide, and 2.36 g. of acetylacetonone added, following a procedure which easily gives the trimethylplatinum and dialkylthallium acetylacetonones in good yield. After separation of the precipitated thallos iodide and concentration of the solution, 1 g. of a crystalline product was obtained (Found: C, 15.61; H, 2.27. Methylmercury acetylacetonone requires C, 22.8; H, 3.2%. Methylmercury acetate requires C, 13.11; H, 2.2%).

Triethyl-lead chloride, prepared by the action of hydrogen chloride on crude tetraethyl-

\* "Normality" indicates mols. per litre as determined by comparison with the solutions of naphthalene of known strength.

lead made from lead chloride and ethylmagnesium iodide, was purified by solution in water and reprecipitation by addition of hydrochloric acid. Its volatility is indicated by the following analytical figures supplied by Dr. Ing. A. Schoeller: 4.979 Mg. dried for 5 days at room temperature in high vacuum over phosphoric oxide lost 1.302 mg. (Found: C, 21.89; H, 4.66%). 5.015 Mg. dried under identical conditions lost 1.429 mg. (Found: C, 21.92; H, 4.62%). 12.161 Mg. dried for 2 days under the same conditions lost 0.283 mg. (Found: Cl, 10.85%). None of these samples attained constant weight, yet all gave good analytical figures (Calc. for  $C_6H_{15}ClPb$ : C, 21.84; H, 4.59; Cl, 10.75%).

Triethyl-lead bromide was prepared from tetraethyl-lead ( $n_D^{20}$  1.5211; Grüttner and Krause, *Ber.*, 1916, 49, 1421, give  $n_D^{20}$  1.5218) (supplied by the British Drug Houses) by solution in ether, addition of solid carbon dioxide, and careful addition of bromine dissolved in ether at  $-70^\circ$  until the colour of the bromine was permanent (Grüttner and Krause, *loc. cit.*) (Found: C, 19.48, 19.45; H, 4.3, 4.31; Br, 21.36, 21.24. Calc. for  $C_6H_{15}BrPb$ : C, 19.24; H, 4.04; Br, 21.35%); m. p. 103—105° (decomp.).

*Attempted preparation of triethyl-lead acetylacetonone.* 0.93 G. of triethyl-lead chloride was treated for  $\frac{1}{2}$  hour in boiling ether with 0.77 g. of thallos acetylacetonone. After filtration from precipitated thallos chloride, and removal of the ether, a slightly viscous oil was obtained which slowly crystallised (Found: C, 23.37; H, 4.06. Triethyl-lead acetylacetonone requires C, 33.56; H, 5.64%. Triethyl-lead acetate requires C, 27.17; H, 5.14%. Diethyl-lead diacetate requires C, 25.05; H, 4.21%).

[With E. R. WILTSHIRE.]

Trimethylplatinum iodide, prepared by the action of ethylmagnesium iodide as described by Pope and Peachey (J., 1909, 95, 572) on dehydrated platinum chloride, is an orange-coloured sandy powder (Found: C, 10.09; H, 2.48; I, 35.15; Pt, 53.50, 52.55. Calc. for  $C_3H_9IPt$ : C, 9.80; H, 2.47; I, 34.56; Pt, 53.15%). Repeated recrystallisation does not make the orange iodide lighter in tint. A small quantity of a sparingly soluble orange deposit separated on the sides of the beaker during this recrystallisation {Found: C, 8.26; H, 1.92; I, 44.2.  $[(CH_3)_3Pt]_2I_3$  requires C, 8.36; H, 2.10; I, 44.2%}, but the agreement may be fortuitous, as a similar substance obtained as a by-product in another preparation contained C, 7.79; H, 1.6; I, 42.9%.

A colourless substance closely resembling Pope and Peachey's trimethylplatinum iodide was also obtained by dissolving trimethylplatinum acetylacetonone in aqueous acetic acid and adding potassium iodide to the solution. In two preparations, 5.28 g. (Found: C, 9.95; H, 2.43; I, 34.88, 34.61; Pt, 51.87, 51.65%) [theory for  $(CH_3)_3PtI$ , 5.23] and 1.31 g. (theory 1.34) were obtained respectively from 4.83 and 1.24 g. of trimethylplatinum acetylacetonone. Both the orange and the white compound crystallise from benzene in transparent (hexagonal) prisms indistinguishable under the microscope except in colour. On standing in air, both sets of crystals become opaque, the opacity beginning at two opposite faces and gradually extending inwards. When recrystallised from toluene the crystals remain transparent.

*Trimethylplatinum chloride.* Residues from molecular-weight determinations of chelate trimethylplatinum compounds were evaporated to dryness, dissolved in 30% glacial acetic acid, and after filtration, treated with dilute hydrochloric acid. The precipitate obtained on boiling was filtered off, washed, and dried (Found: C, 13.45, 13.34; H, 3.43, 3.32; Cl, 13.03, 12.78. Calc. for  $C_3H_9ClPt$ : C, 13.06; H, 3.29; Cl, 12.86%).

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