384. *Even and Odd Co-ordination Numbers.*

By R. C. Menzies.

It is a commonplace that an important condition for the stability of any molecule is the attainment by the constituent atoms of effective atomic numbers (E.A.N.) (calculated by Sidgwick's rules, " Electronic Theory of Valency," pp. 163—164) equal to those of the inert gases. In particular, the stability of the grouping of 86 electrons (radon) appeared to explain the two-fold molecular weight in benzene of trimethylplatinum acetylacetone (J., 1928, 565) and of the ethyl acetoacetate and the dipropionylmethane derivative (J., 1933, 21).

This idea was strengthened by the stability of the lead tetra-alkyls (E.A.N. again 86) and of the dialkylthallium chelate derivatives of β-diketones (J., 1928, 1288). Again, the four-fold and two-fold molecular weight of thallous ethoxide and of thallous ethyl acetoacetate respectively in benzene are both explained by Sidgwick and Sutton (J., 1930, 1471) as due to the completion of octets by the gain of 5 electrons, one from each covalency and two from each co-ordinate link, making the atomic number of the metal, 81, up to 86.

The determination of the molecular weights of a number of dialkylthallium chelate compounds (Wiltshire and Menzies, J., 1932, 2734) was therefore undertaken in the expectation that all these compounds would prove unimolecular in benzene, in conformity with the above conclusions; that they were actually found to be associated (*loc. cit.*, p. 2737) was surprising. The possibility that the E.A.N. of the thallium had exceeded 86 led to the observation that many related compounds exist in which the metallic atom does not have an E.A.N. of 86 but of 82, 84, and 88, and the generalisation that these other groups can also result in stable compounds when the central atom possesses an *even* covalency was suggested by the easy preparation of the acetylacetonates of trimethylplatinum (*loc. cit.*), diethylgold (Gibson and Simonsen, J., 1930, 2531), and dialkylthallium, in all of which the stable co-ordination number is probably even, and by the failure to obtain acetylacetone derivatives of methylmercury and triethyl-lead, the formulæ of which require co-ordination numbers of 3 and 5 respectively (Menzies and Overton, J., 1933, 1290). In this paper additional evidence for the above generalisation is summarised (cf. Berry and Lowry, J., 1928, 1764).

Substances possessing an E.A.N. of 82 are comparatively stable when the co-ordination number is 2; *e.g.*, the mercury dialkyls and diaryls, and the univalent dialkylthallium ions, the hydroxides of which are much stronger bases than those of methylmercury or triethyl-lead. The last two ions both require an odd covalency for the metallic atom, and the hydroxides appear to ionise with difficulty (Hein and Meininger, *Z. anorg. Chem.*, 1925, **145**, 95).

Undissociated diethylgold and auric bromides both require in the unassociated formula an E.A.N. of 82 for the metal, with an odd covalency. Gibson and Simonsen (*loc. cit.*) have shown that the former is bimolecular in benzene, and the prediction (Gibson and Colles, J., 1931, 2409) that the latter would also be bimolecular in this solvent has now been verified (Burawoy and Gibson, this vol., p. 862, footnote).

The bimolecular formula in both cases requires an E.A.N. of 84 for the metal and a covalency of 4, both the same as required for gold in chloroauric acid and its salts. Although these compounds are comparatively stable, the much greater solubility of the aurichlorides than of the platinichlorides (E.A.N. 86, co-ordination number 6) is an indication that the gold is co-ordinately unsaturated.

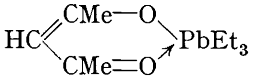
The hypothetical monoethylthallium would also have in its co-ordinated form an E.A.N. of 82, with a co-ordination number of unity. It has been shown by Menzies and Cope (J., 1932, 2864) that, under conditions where its formation might be expected, triethylthallium and metallic thallium are obtained instead. Both the stable diethylthallium ion and the above ethylthallium have the same E.A.N.; hence the difference in stability is apparently connected with the even and odd co-ordination numbers of 2 and 1.

Compounds with the E.A.N. of 84 are very unstable, with odd covalencies. They include the violently reactive triethylthallium (Groll, *J. Amer. Chem. Soc.*, 1930, **52**, 2999) and the monomeric undissociated dialkylthallium halides, which have been shown to be polymerised in the few cases in which their solubility in benzene permits of their molecular-weight determination (Krause and Dittmar, *Ber.*, 1930, **63**, 1956).

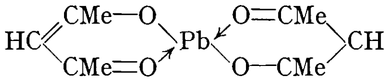
The simple formula for trimethylplatinum acetylacetone also requires an effective atomic number of 84 with a covalency of 5. Polymerisation into double molecules raises this to 86 and 6 respectively. Osmium tetroxide, however, which on the formula $Os(=O)_4$ requires an E.A.N. of 84 for the metal, shows no tendency to polymerise either as vapour (Deville and Debray, *Ann. Chim. Phys.*, 1859, **56**, 403) or, as shown below, in benzene solution.

The stable lead tetra-alkyls have also E.A.N. of 86 and co-ordination numbers of 4, as have the dialkylthallium derivatives of β-diketones in the non-polymerised state, but the latter, as already pointed out, have a tendency to polymerise, suggesting that the E.A.N. may increase above 86, although this increase is unstable. Stability thus appears to depend both on the E.A.N. and on the co-ordination number, being greatest when the former is 86 and the latter is even.

Triethyl-lead acetylacetone (I) requires a co-ordination number of 5 and an E.A.N. of 88, and thus fulfils neither of the above conditions, and an attempt to prepare it failed. On the other hand, the diacetylacetone of bivalent lead (II) requires 4 and 88 respectively, so the latter condition is fulfilled but not the former; its preparation (see below) is therefore of interest as new evidence that the stability of co-ordinate compounds depends on both these factors.



(I.)



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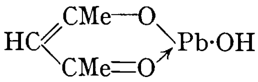

(III.)

Combes (*Compt. rend.*, 1887, **105**, 871) mentions a water-soluble lead acetylacetone, but gives no analyses, whilst Gach (*Monatsh.*, 1900, **21**, 114) refers to a basic lead acetylacetonate, insoluble in water, described by Fette ("Beiträge zur Kenntnis der 1–3 Diketonen," Diss., München, 1894): the thesis gives good analyses for the composition $Pb(OH)(C_5H_7O_2)$, but no other details. If the chelate form for the acetylacetone radical be assumed (III), the formula requires an E.A.N. of 86 for the lead and a covalency of 3, so in this case the former condition of stability is fulfilled but not the latter: in this compound the great stability of the 86 grouping apparently counteracts the instability of the odd covalency. No description of *lead diacetylacetone* could be found in the literature, but the above considerations suggested that its preparation should be possible.

EXPERIMENTAL.

Preparation of Lead Diacetylacetone.—22 G. of lead oxide were added to 20 g. of acetylacetone; the mixture became warm and much of the oxide caked. The whole was then boiled with toluene, which was partly distilled off until the distillate was no longer cloudy, to remove water formed by the reaction, the mixture was filtered, and on cooling, a solid separated (12 g.) [Found: C, 28·4, 28·5; H, 3·4, 3·3. $Pb(C_5H_7O_2)_2$ requires C, 29·6; H, 3·5%]. A quantity of white lumps remained; to this were added 10 c.c. of acetylacetone and some toluene, the mixture being boiled, and again filtered; the solid separating on cooling (8 g.) was recrystallised from toluene containing a little acetylacetone (yield 6 g.) (Found: C, 28·4, 28·5; H, 3·3, 3·4%). The solids were, in both cases, washed on the filter with toluene followed by hexane. The data indicate hydrolysis: a mixture of 92·5 parts of lead acetylacetone with 7·5 parts of lead acetate requires C, 28·49; H, 3·36%.

In order to minimise hydrolysis, granulated lead was heated under reflux with acetylacetone in dry toluene for about an hour, the solution filtered, and cooled. Well-defined crystals were obtained, resembling tetrathallium tartrate (Found: C, 29·1, 29·1; H, 3·4, 3·4%). A second crop was obtained by reheating the mother-liquor from the first crop under reflux with the lead [Found: C, 28·9, 28·7; H, 3·4, 3·4; Pb, 50·7, 51·0 (detmtns. by A. R. P. Walker). $Pb(C_5H_7O_2)_2$ requires Pb, 51·1%].

The substance on heating shows signs of volatilising. An outstanding property is its ease of hydrolysis. It is soluble in commercial absolute alcohol, but the solutions soon become cloudy.

Molecular Weight of Osmium Tetroxide in Benzene (with H. OVERTON).—0·0830 G. of the tetroxide was dissolved in 6·24 g. of benzene: the f. p. took a long time to become constant.

Time, minutes	15	35	50	65	90	105
Δt	0·258°	0·259°	0·276°	0·280°	0·279°	0·274°

The mean of last four readings, 0·277°, gives *M*, 245·9 (Calc.: 255·6).

More osmium tetroxide was then added, to a total of 0·1068 g.:

Time (minutes) after second addition	30	45	55
Δt	0·351°	0·352°	0·349°

The mean, 0·351°, gives *M*, 249·7. The solution was not stable, for after 110 minutes Δt had fallen to 0·336°, and after 22 hours to 0·324°. After the final determination, a black sediment was found, whilst some osmium tetroxide had volatilised up the tube. It thus seems probable that the inconstancy of the f. p. shown in the previous day's determinations was due to volatilisation and decomposition of the osmium tetroxide in solution.

SUMMARY.

It has been shown that the stability of a number of newer compounds of the heavier metals depends, not only on the tendency for the central atom to attain a rare-gas structure,

but also on the preference for even rather than for odd covalencies. The fulfilment of the latter condition alone indicated that lead diacetylacetone should be capable of existence, and this has been confirmed by its preparation.

Sidgwick's statement that the relation of an odd value to the next higher even value is that of unsaturation (*op. cit.*, p. **161**) and Bassett's explanation of the structure of a number of complex lithium compounds as determined by the need for the lithium atom to become either 2- or 4-co-ordinated (*Ann. Reports*, 1932, **29**, 78; *Sci. J. Roy. Coll. Sci.*, 1934, **27**) are both indications that this tendency towards even covalencies is displayed all through the periodic classification.

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