

CLXII.—*Researches on Residual Affinity and Coordination. Part II. Acetylacetonates of Selenium and Tellurium.*

By GILBERT T. MORGAN and HARRY DUGALD KEITH DREW.

THE acetylacetonate derivatives of the metals, metalloids, and non-metals may be classified into three main groups.

I. Metallic acetylacetonates, in which the principal valencies of the metal are completely satisfied by the univalent acetylacetonate radicle,  $C_5H_7O_2$ , such as the thallos, glucinum, cupric, zinc, scandium, aluminium, chromic, ferric, and thorium derivatives, and numerous others. In many instances acetylacetonate has given wings to the metals, for certain of these compounds are volatile without decomposition (Combes, *Compt. rend.*, 1894, **117**, 1222; Kurovski, *Ber.*, 1910, **63**, 1078; T., 1913, **103**, 81; 1914, **105**, 189).

II. Acetylacetonates of the non-metals and metalloids, in which the principal valencies of the element are only partly satisfied by the univalent acetylacetonate radicle. Such are the compounds of boron, silicon, and titanium,  $B(C_5H_7O_2)_2Cl$ ,  $Si(C_5H_7O_2)_3Cl$ , and  $Ti(C_5H_7O_2)_3Cl$ , which function as metallic chlorides giving rise to remarkable double salts (Dilthey, *Annalen*, 1905, **344**, 326).

III. Acetylacetonates of sulphur, which behave as true organic derivatives of sulphur, carbon being attached directly to this non-metal and not through the intermediary of oxygen, as in the two preceding classes (Angeli and Magnani, *Gazzetta*, 1893, **23**, ii, 415; 1894, **24**, i, 342; Vaillant, *Compt. rend.*, 1894, **119**, 647).

There is also a transition group of metallic acetylacetonates between the main groups I and II, in which the principal valencies of the metal are only partly satisfied by the acetylacetonate complex. This

transition group includes the complex acetylacetonates of platinum (Werner, *Ber.*, 1901, **34**, 2584) and the cobaltic acetylacetonate compounds of the general type  $[C_5H_7O_2Co\ en_2]X_2$  (Werner, *Helv. Chim. Acta*, 1918, **1**, 78), where  $en =$  ethylenediamine. The latter series of acetylacetonate derivatives exhibits optical activity and the existence of enantiomorphous pairs of isomerides affords definite information as to the arrangement of the acetylacetonate nucleus in these substances, and justifies the belief that the univalent group  $CH_3 \cdot CO \cdot CH : C(CH_3) \cdot O \cdot$  functions as two associating units,\* forming a ring structure in which the metallic atom is implicated.

The research described below, which is still in a preliminary stage, shows that the interactions of acetylacetonate and the tetrachlorides of selenium and tellurium lead to products differing considerably in type from those classified above. Although there are many points of difference between the various members of the three main groups of acetylacetonate derivatives, they possess one attribute in common, namely, the univalent acetylacetonate radicle, of which one or more are present in the molecule of every one of these derivatives hitherto described. In the acetylacetonates of selenium and tellurium these metalloids are found to be associated with a bivalent radicle,  $C_5H_6O_2''$ .

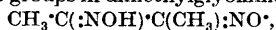
Selenium tetrachloride and acetylacetonate interact in ethereal solution in accordance with the following equation:



the products being *selenium acetylacetonate*, a well-defined, pale yellow, crystalline compound, chloroacetylacetonate, and hydrogen chloride. This selenium acetylacetonate, which is bimolecular in benzene solution, is readily decomposed by concentrated hydrochloric acid and by reducing agents, such as the alkali hydrogen sulphites. The former of these decompositions takes place readily, giving rise to elemental selenium and chloroacetylacetonate,



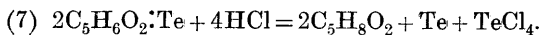
\* The adjective "chelate," derived from the great claw or "chela" ("chely") of the lobster and other crustaceans, is suggested for these caliper-like groups which function as two associating units and fasten on to the central metallic atom so as to produce heterocyclic rings. Among the compounds which, by virtue of their residual affinity, function as chelate groups are ethylenediamine ( $en$ ), propylenediamine,  $\alpha\alpha$ -dipyridyl and dimethylethylene sulphide (T., 1912, **101**, 1798). Many unsaturated radicles also function as chelate groups, partly owing to their principal valencies and partly owing to residual affinity, for example, the acetylacetonate and oxalate groups, and the univalent groups in dimethylglyoxime,



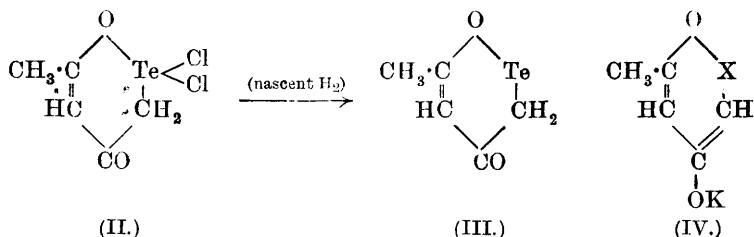
nitroso- $\beta$ -naphthol,  $O : C_{10}H_8 : NO \cdot$ , and many other lake-forming complexes. In the present communication the bivalent radicle,  $C_5H_6O_2''$ , functions as a chelate group entirely owing to its principal valencies.



Tellurium acetylacetonone differs from the selenium analogue in its decomposition with cold concentrated hydrochloric acid (compare equation 2); it yields acetylacetonone and half the tellurium as the tetrachloride:



These reactions support the view that tellurium acetylacetonone dichloride (II) and tellurium acetylacetonone (III) may be represented respectively by the following formulæ:



Selenium and tellurium acetylacetones function as weak acids and dissolve in aqueous alkali hydroxides. It is therefore evident that they may have an alternative enolic configuration (IV), which would correspond with that of their unstable alkali salts.

#### EXPERIMENTAL.\*

##### *Selenium Acetylacetonone, [C<sub>5</sub>H<sub>6</sub>O<sub>2</sub>:Se]<sub>2</sub>.*

Selenium tetrachloride was prepared by passing dry chlorine in excess over coarsely powdered selenium at the ordinary temperature, the dark red monochloride being formed as an intermediate phase. The pale yellow, crystalline tetrachloride (14.3 grams) suspended in 140 c.c. of dry ether was treated at the ordinary temperature with 13 grams of acetylacetonone (2 mols.) dissolved in 30 c.c. of the same solvent. Hydrogen chloride was forthwith evolved, the solution reddened, the tetrachloride slowly passed into solution, while a yellow precipitate appeared and redissolved in about thirty minutes to a transparent, pale red, fuming lachrymatory solution, which was evaporated rapidly at the ordinary temperature in a current of air. Hydrogen chloride, ether, and chloroacetylacetonone were thus removed; the residue, a pale red oil, solidified on stirring. The product (10 grams, yield 90 per cent.) crystallised from benzene in pale primrose-yellow, glistening plates or lath-like needles, giving yellow solutions in organic media; on exposure to light for prolonged periods its surface became thinly coated with pink selenium.

\* The authors are indebted to Dr. Scott for a gift of pure tellurium, and to Professor Ling for specimens of this metalloid and of selenium.

During this incipient decomposition the odour which at first was pleasing and farinaceous became faintly nauseating, a result which was due probably to liberation of traces of hydrogen selenide. The substance reddened at about  $140^{\circ}$ , and subsequently melted and decomposed at  $175^{\circ}$ . In a sealed capillary tube heated from  $150^{\circ}$  it melted to an orange-red liquid at  $185^{\circ}$ .

The selenium was determined by heating the weighed substance with 5 c.c. of fuming nitric acid in a flask with ground-in air condenser. Oxidation being completed, the solution was boiled with excess of hydrochloric acid until all nitrous compounds were destroyed, the metalloid, precipitated as the red modification, transforming into the dark grey variety on warming with sodium sulphite or aqueous sulphurous acid, was collected and weighed. Carbon and hydrogen estimations were made in combustion tubes charged with fine copper oxide, a long length of lead chromate, and a spiral of copper oxide, a little of this oxide being also placed in the porcelain boat. In the combustion of selenium and tellurium derivatives more accurate results were obtained by burning with oxygen alone than with air followed by oxygen (Found, C=34.23, 33.74; H=3.45, 3.72; Se=44.10, 44.17.  $(C_5H_6O_2Se)_n$  requires C=33.86; H=3.41; Se=44.68 per cent.).

Molecular determinations by the ebullioscopic method in benzene gave 316, 312 (0.65 and 1.18 grams per 100 c.c. respectively), thus indicating association:  $n=1$  or 2 requires 177 or 354.

Selenium acetylacetonone is not obtained unless the prescribed experimental conditions are followed closely in regard to temperature, concentration, proportion of reagents, and removal of the volatile products at the ordinary temperature. The proportion of two molecules of acetylacetonone to one of selenium tetrachloride has been found to give the optimum yield, whereas ratios of one or four molecules of the diketone do not give rise to any crystalline product. Experiments carried out in chloroform or with selenium dibromide,  $Se_2Br_2$ , and acetylacetonone in ether have led so far to elimination of selenium and to the production of lachrymatory oils. A preliminary experiment with benzoylacetonone and selenium tetrachloride in cold ether indicated the formation of a pale yellow selenium benzoylacetonone (m. p.  $212^{\circ}$ ) having similar properties to selenium acetylacetonone.

Selenium acetylacetonone, which has a faintly acidic, sweetish taste, dissolves slightly in hot water, the solution being distinctly acid; it is somewhat sparingly soluble in boiling ether, ethyl alcohol, acetone or chloroform, and dissolves more freely in hot glacial acetic acid. Its solubility in boiling benzene is about 1.5 grams in 100 c.c., but is ten times less in the cold.

Selenium acetylacetone dissolves readily in cold aqueous alkali hydroxides or ammonia to bright yellow solutions, which regenerate the compound if neutralised at once with dilute acid. The alkaline solutions speedily decompose, red selenium being precipitated, whilst a nauseating odour is developed. Although insoluble in aqueous sodium carbonate, prolonged treatment with this reagent leads to the foregoing decomposition. The organic product of these alkaline decompositions is an oil having a pleasant ketonic odour.

Dilute mineral acids are without effect on selenium acetylacetone, concentrated nitric and sulphuric acids have a destructive action, whereas cold concentrated hydrochloric acid decomposes it smoothly into red selenium and chloroacetylacetone, identified by its boiling point, lachrymatory properties, and green copper derivative.

Ferric chloride either in aqueous or alcoholic solution gives no red coloration with selenium acetylacetone even after two hours. In twenty-four hours an orange tint is discernible, and this coloration is developed more quickly on boiling, but selenium is set free simultaneously. When distilled with zinc dust, selenium acetylacetone loses selenium, evolves a nauseating vapour, and gives rise to an oil which, after rectification, gives a red coloration with ferric chloride and has a pleasant ketonic odour. Iodine in chloroform solution has no action on selenium acetylacetone, but chlorine in the same solvent gives selenium tetrachloride and chloroacetylacetone, whereas bromine yields lachrymatory products and a colourless, crystalline substance (m. p.  $180^{\circ}$ ). Aqueous hydrogen sulphide decomposes it slowly in the cold with liberation of sulphur and selenium. Hydroxylamine, phenylhydrazine, *p*-bromophenylhydrazine, *p*-nitrophenylhydrazine, and 6-chloro-3:4-tolylenediamine induce a more or less rapid elimination of selenium.

*By-products of the Formation of Selenium Acetylacetone.*—The amount of hydrogen chloride set free in the condensation was estimated and found to be equivalent to three-fourths of the chlorine originally present in the selenium tetrachloride. The chloroacetylacetone (b. p.  $148$ — $150^{\circ}$ ), of which more than two-thirds of the calculated amount were obtained in a purified condition, was further identified by conversion into its green copper derivative soluble in chloroform. These results support the view expressed by equation 2 (p. 1457).

*Quantitative Decomposition of Selenium Acetylacetone: Alkali Selenodithionates.*

Two grams of powdered selenium acetylacetone were added to 18 c.c. of water containing 3 grams of potassium metabisulphite ( $2\frac{1}{3}$  mols. of  $\text{KHSO}_3$  equivalent to 1 atom of Se), and the mixture

was shaken mechanically for one hour. A colourless, crystalline precipitate of potassium selenodithionate,  $K_2S_2SeO_6$ , was then collected, the filtrate extracted with ether to remove acetylacetone, and the aqueous layer mixed with alcohol to complete the deposition of the inorganic product (yield 3.5 grams = 97 per cent. of the theoretical). When separating rapidly from aqueous solution the selenodithionate appeared in lustrous scales or thin plates; when crystallising slowly it was obtained in long, transparent, silky needles.

Both forms of the salt were quite colourless and stable when exposed to air and light. On heating they commenced to redden at  $190^\circ$ , and at  $250^\circ$  the red selenium turned grey. Meanwhile sulphur dioxide was evolved, and finally a residue of potassium sulphate was left (Found, K = 24.59; S = 20.06, 20.58; Se = 25.06, 25.07. Calc., K = 24.63; S = 20.19; Se = 24.95 per cent.).

*Sodium selenodithionate*,  $Na_2S_2SeO_6$ , was produced by adding selenium acetylacetone to a cold concentrated solution of sodium hydrogen sulphite ( $2\frac{1}{2}$  mols.), the mixture being shaken until the organic compound had dissolved, and precipitated, by adding alcohol, in colourless, lustrous anhydrous scales, readily soluble in water (Found, Na = 16.24.  $Na_2S_2SeO_6$  requires Na = 16.12 per cent.). Aqueous sulphur dioxide had a similar action on selenium acetylacetone, dissolving it in the cold to a colourless solution containing acetylacetone, extracted by ether, and selenodithionic acid, which slowly decomposed into selenium, sulphur dioxide, and sulphuric acid.

*Estimation of Acetylacetone.*—The acetylacetone set free in the foregoing decompositions was identified by conversion into its pale blue copper and colourless aluminium derivatives. It was estimated by coupling with sodium *iso-p*-nitrobenzenediazo-oxide.

Selenium acetylacetone (0.2 gram) was shaken for four hours with 0.25 gram of potassium metabisulphite and 3 c.c. of water. Potassium selenodithionate was precipitated by alcohol, and the filtrate treated with 0.23 gram of sodium *iso-p*-nitrobenzenediazo-oxide, ( $NO_2 \cdot C_6H_4 \cdot N_2 \cdot ONa, H_2O$ ). The pale orange-red precipitate of *p*-nitrobenzeneazoacetylacetone, after washing with dilute alcohol, weighed 0.2 gram (calc., 0.28 gram), and gave the correct melting point,  $219-222^\circ$ .

*Tellurium acetylacetone dichloride*,  $C_5H_6O_2 : TeCl_2$ .

Tellurium reacted with dry chlorine, evolving heat and forming tellurium tetrachloride as a yellowish-white liquid, in which excess of the metalloid dissolved to an almost black solution, probably containing the dichloride. With excess of chlorine the whole solidi-

fied to a yellow, crystalline mass of tetrachloride, which was purified by sublimation.

Sublimed tellurium tetrachloride (10.3 grams) was mixed with 7.6 grams of acetylacetone (2 mols.) in 55 c.c. of dry chloroform and the orange solution heated under reflux on the water-bath. The evolution of hydrogen chloride ceased after two hours' boiling; the solution was filtered from a heavy, dark grey oil, and concentrated over lime in a desiccator. Crystals of tellurium acetylacetone dichloride separated; the concentrated filtrates yielded further crops (yield 7 grams, or 62 per cent. calculated on  $\text{TeCl}_4$ ). The product was sparingly soluble in ether, benzene, or chloroform, rather more so in hot alcohol, and very readily soluble in cold acetone. It crystallised from alcohol or benzene in acicular forms, and separated slowly from acetone in large, transparent, hexagonal prisms often twinned. Both forms were colourless; they darkened at 155—160° and melted and decomposed between 169° and 173°, liberating tellurium and evolving hydrogen chloride and a lachrymatory oil, which developed a red coloration with aqueous ferric chloride. The tellurium was estimated by warming a weighed amount with fuming nitric acid (5 c.c.) in a reflux apparatus. After boiling with concentrated hydrochloric acid (25 c.c.) to remove nitrous compounds, the solution was evaporated to dryness. The residue dissolved in 15 c.c. of 10 per cent. hydrochloric acid was warmed with 10 c.c. of 15 per cent. hydrazine hydrochloride and 35 c.c. of saturated sulphurous acid gradually added, the liberated tellurium being dried at 107°. The chlorine was estimated by alkaline hydrolysis and precipitation as silver chloride; the combustions were carried out as in the case of selenium acetylacetone (Found, C=20.72; H=2.07; Cl=24.01, 23.95; Te=42.87.  $(\text{C}_5\text{H}_6\text{O}_2\text{Cl}_2\text{Te})_n$  requires C=20.24; H=2.04; Cl=23.92; Te=43.00 per cent.).

Molecular-weight determinations by the ebullioscopic method in acetone (1.846 and 4.207 grams per 100 c.c.) gave 241 and 255 ( $M=296.5$ ).

*Tellurium acetylacetone dichloride* does not become discoloured on exposure to light. It readily loses chlorine with hot water or aqueous acids or alkalis. Tellurium is not set free by boiling with aqueous potassium hydroxide. With aqueous ferric chloride a red coloration is developed only very slowly. When warmed with considerable excess of aqueous sulphurous acid this compound is decomposed completely, yielding tellurium and acetylacetone.



*Tellurium Acetylacetonate*,  $C_5H_6O_2 \cdot Te$ .

The foregoing dichloride (2.2 grams) when triturated for ten minutes with 1.8 grams of potassium metabisulphite (1 mol.) and 20 c.c. of water yielded a small amount of tellurium and 1 gram (yield 60—70 per cent.) of a yellow compound, which was purified by crystallisation from benzene or hot water. This product was also obtained with less liberation of tellurium by boiling the dichloride with a slight excess of aqueous sulphur dioxide (Found, C=27.14, 26.62; H=2.88, 2.92; Te=56.55.  $(C_5H_6O_2Te)_n$  requires C=26.61; H=2.68; Te=56.52 per cent.).

Molecular-weight determinations in boiling benzene and acetone (0.462 and 0.879 gram per 100 c.c.) gave respectively 262 and 185. M.W. for  $n=1$  is 225.6.

*Tellurium acetylacetonate* forms heavy, golden-yellow needles sparingly soluble in water, ether, chloroform, or alcohol, and decomposing indefinitely at 145—180°. In a sealed tube it melts to a yellow liquid, which partly sublimes in yellow needles, and on further heating decomposes with elimination of tellurium and production of an oil resembling acetylacetonate. Under reduced pressure the compound sublimes at about 160° in glistening, yellow needles.

Tellurium acetylacetonate resembles the selenium compound in its chemical reactions. It dissolves in cold aqueous potassium hydroxide to a bright yellow solution, from which immediate neutralisation with acid regenerates the original compound, but after a few minutes the alkaline solution deposits tellurium. Cold concentrated hydrochloric acid decomposes the compound with elimination of tellurium. Ferric chloride develops a red coloration, but only after a long time. Hydrogen peroxide decolorises immediately the yellow aqueous solution of tellurium acetylacetonate, giving a white precipitate; hydrogen sulphide produces at once a black deposit ( $TeS_2$  ?), alcoholic mercuric iodide yields a yellow precipitate, and warm aqueous sulphur dioxide reduces the compound with elimination of tellurium.

*Quantitative Decompositions of Tellurium Acetylacetonate.*

(a) *With Bisulphite*.—Tellurium acetylacetonate (0.4 gram) shaken for five hours with 0.4 gram of potassium metabisulphite and 3 c.c. of water yielded sulphur dioxide, 0.2 gram of tellurium, and 0.3 gram of potassium sulphate, the latter precipitated by alcohol after extracting the acetylacetonate with ether.

Warm aqueous sulphur dioxide brought about a similar reduction, yielding acetylacetonate, tellurium, and sulphuric acid.

(b) *With an Aluminium-Mercury Couple.*—Tellurium acetylacetone (0.4 gram) in 50 c.c. of hot water was shaken with an aluminium-mercury couple, and the solution, filtered from precipitated tellurium, was treated with sodium *iso-p*-nitrobenzenediazoxide (0.37 gram) in 8 c.c. of glacial acetic acid and 20 c.c. of absolute alcohol. After three hours the orange-red *p*-nitrobenzeneazoacetylacetone was collected (0.35 gram, yield 80 per cent.) and crystallised from glacial acetic acid; it then melted at 220°.

(c) *With Concentrated Hydrochloric Acid.*—A preliminary experiment showed that tellurium acetylacetone, unlike its selenium analogue, yielded acetylacetone and not chloroacetylacetone on decomposition with concentrated hydrochloric acid, a portion only of the tellurium being precipitated, whilst the remainder was left in solution as tellurium tetrachloride. Tellurium acetylacetone (0.1558 gram) was stirred with cold concentrated hydrochloric acid for several hours. The precipitated tellurium, which was then collected and washed successively with a little more concentrated acid and water, weighed 0.0432 gram. The filtrates were then treated with aqueous hydrazine hydrochloride saturated with sulphur dioxide. These reducing agents precipitated the remainder of the tellurium, which weighed 0.0427 gram (total amount of tellurium found = 0.0859 gram.; calc., 0.0880). These results confirm equation 7 (p. 1459).

The authors desire to express their thanks to the Advisory Council for Scientific and Industrial Research for grants which have partly defrayed the expenses of this investigation.

CHEMICAL DEPARTMENT,  
UNIVERSITY OF BIRMINGHAM,  
EDGBASTON.

[Received, October 25th, 1920.]