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CLIV.—Researches on Residual Affinity and Coordination. Part XVIII. Interactions of Zirconium Salts and β-Diketones.

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THE earliest attempt to bring about chemical change between zirconium hydroxide or carbonate and acetylacetone in aqueous or alcoholic solution led to amorphous, ill-defined products (Mandl,

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Z. anorg. Chem., 1903, 37, 252), but in the following year Biltz and Clinch obtained decahydrated zirconium tetra-acetylacetone, $Zr(C_5H_7O_2)_4$,10H₂O, and converted this hydrate into anhydrous zirconium acetylacetone by repeated crystallisation from absolute alcohol (*ibid.*, 1904, 40, 218). The existence of this tetra-acetylacetone derivative brings zirconium into line with its higher homologues of the fourth periodic group, namely, cerium and thorium, since these metals form similar compounds with acetylacetone.

By combining with four chelate acetylacetone groups, each of which functions as two associating units round the central metallic atom, the three metals manifest a similar co-ordination number of eight and in the case of zirconium this co-ordination index is confirmed by the composition of such inorganic compounds as the following: $ZrX_4,8NH_3$ (X = Cl, Br or I). Other inorganic derivatives of zirconium point, however, to a lower co-ordination number, namely, six, as indicated in the most stable type of zirconifluorides, R'_2ZrF_6 , and this value is also displayed in the organic compounds $ZrCl_2(O\cdot C_6H_4\cdot CO_2Me)_2$ and $ZrCl_2(O\cdot C_6H_4\cdot COH)_2$, where the univalent radicals derived respectively from methyl salicylate and salicylaldehyde function as chelate groups. It is therefore evident that with zirconium the capacity for combining with associating units varies in different types of combination between the co-ordination values of six and eight.

On attempting to combine the homologues of acetylacetone with zirconium nitrate in acidic aqueous solutions partly neutralised by sodium carbonate, the method adopted by Biltz and Clinch, it was not found possible to obtain definite crystalline products analogous with zirconium tetra-acetylacetone. Interaction with higher aliphatic diketones in aqueous solution was tried without success and double decomposition between sodium benzoylacetone and zirconium nitrate or oxychloride led to zirconyl bisbenzoyl-acetone, [ZrO($C_{10}H_9O_2$)₂]₃.

Since these reactions in presence of water proved to be unpromising, experiments were then made with anhydrous zirconium tetrachloride and the β -diketones in dry media. In this way, a different mode of interaction was discovered which was shown to be general by applying it to the three typical cases of dibenzoylmethane, benzoylacetone, and acetylacetone. By operating in dry chloroform or benzene with zirconium tetrachloride and either of the foregoing β -diketones, three of the chlorine atoms of the tetrachloride are replaced by three chelate β -diketonic radicals, hydrogen chloride being evolved in accordance with the following general equation, where A \overline{c} signifies the univalent diketonic chelate group : $ZrCl_4 + 3HA\overline{c} = [ZrA\overline{c}_3]Cl + 3HCl.$

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Excess of the diketone and prolonged heating does not lead to complete substitution of diketonic radicals for the chlorine atoms, the compound formed in each case being zirconium tris- β -diketone chloride. It is, however, evident that the complexity of the β -diketone plays an important part in conducing to the stability of the product.

Zirconium trisdibenzoylmethane chloride (I), the most stable member of the series, can be preserved indefinitely in the dry state; it gives rise to crystallisable double salts such as the *ferrichloride* (III), *chloroaurate* (III), and *chloroplatinate* (II).

Zirconium trisbenzoylacetone chloride (IV) comes next in order of stability; its molecular weight corresponds with the graphic formula, and it gives rise to double chlorides with ferric chloride, auric chloride, and platinic chloride which, however, are oily and non-crystallisable.

$$(IV.) \left[Zr \left(< \stackrel{O \cdot C(C_{6}H_{5})}{O:C(CH_{3})} > CH \right)_{3} \right] Cl \left[Zr \left(< \stackrel{O \cdot C(CH_{3})}{O:C(CH_{3})} > CH \right)_{3} \right] Cl (V.)$$

Zirconium trisacetylacetone chloride (V) is the most readily hydrolysable of the series, but in the absence of moisture it is so stable that it may be crystallised unchanged from hot acetylacetone, thus showing that hydrolytic substitution of hydroxyl for the chlorine anion is an essential prelude to any change in the configuration of the co-ordination complex.

In the presence of water and sodium acetylacetone, however, this hydrolysis occurs and zirconium trisacetylacetone chloride is thus converted forthwith into the decahydrated zirconium tetraacetylacetone.

When zirconium trisdibenzoylmethane chloride (I) is heated with excess of acetylacetone, the three aromatic diketonic residues are completely replaced by acetylacetone radicals and zirconium trisacetylacetone chloride (V) is obtained.

So long as these reactions are performed in anhydrous solvents the type of co-ordination complex remains unchanged and in these tris- β -diketonic derivatives zirconium displays a striking analogy with its lower homologues, titanium and silicon, the tetrachlorides of which elements have been shown by Dilthey to interact in a similar way with β -diketones in anhydrous solvents. With silicon tetrachloride the general type is $[SiA\overline{c}_3]Cl$ and the analogy extends to the double chlorides, $[SiA\overline{c}_3]FeCl_4$, $[SiA\overline{c}_3]AuCl_4$, and $[SiA\overline{c}_3]_2PtCl_6$. So close is the similarity that analogous derivatives are found to contain the same solvent of crystallisation; $[Zr \ Dibenz_3]FeCl_4$ was found to crystallise with chloroform of crystallisation (compare [Si Dibenz_3]AuCl_4, CHCl_3, Dilthey, *Ber.*, 1903, **36**, 1598).

With titanium tetrachloride, the initial products with the diketone have the empirical general formula $\text{Ti}A\overline{c}_2\text{Cl}_2$, but Dilthey showed that the substances are really trimeric $[\text{Ti}A\overline{c}_3]_2\text{Ti}\text{Cl}_6$ by converting them into the double chlorides $[\text{Ti}A\overline{c}_3]_2\text{FeCl}_4$, $[\text{Ti}A\overline{c}_3]\text{AuCl}_4$, and $[\text{Ti}A\overline{c}_3]_2\text{PtCl}_6$. This comparison shows that silicon and zirconium behave similarly in regard to the constitutions of the tris- β -diketone chlorides and of their double chlorides, and that as regards the latter series of salts this analogy may be extended to titanium.

Moreover, in its combinations with acetylacetone, zirconium shows its transitional position between the metals and non-metals of the fourth periodic group. In its capacity as metal it resembles cerium and thorium in yielding the tetra-acetylacetone derivative; as a metalloid it resembles titanium and silicon in giving rise to the trisacetylacetone type of combination.

EXPERIMENTAL.

I. Interaction of Zirconium Tetrachloride and β-Diketones in Anhydrous Media.

Preparation of Anhydrous Zirconium Tetrachloride.—The starting materials employed in the following experiments were Brazilian zirkite in the form of rock or pebbles ("favas") supplied by Messrs. Trost Bros., of Coventry, in two grades of 80 and 90 per cent. ZrO_2 , and zirconia (97 per cent. ZrO_2 , Messrs. Johnson and Matthey).

The finely powdered zirkite (passing through a 90-mesh sieve) was converted to the sulphate by evaporation with concentrated sulphuric acid and the impurities, ferric and titanium chlorides, were removed by crystallisation of the oxychloride, $ZrOCl_2,8H_2O$, from concentrated hydrochloric acid. The tartaric acid method of Dittrich and Pohl (Z. anorg. Chem., 1905, 43, 236) was also used as an alternative for the separation of iron.

Hevesy (Chem. and Ind., 1923, 42, 929) states that Brazilian zirkite contains approximately 1 per cent. of hafnium, and shows that hafnium ammonium fluoride and hafnium ammonium sulphate are more soluble than the corresponding zirconium double salts. Accordingly, a further purification of zirconium sulphate was effected by evaporating over sulphuric acid a solution containing 10 grams of zirconium sulphate dissolved in 20 c.c. of water and 14 grams of ammonium sulphate (3 mols.) in 25 c.c. of water. The double zirconium ammonium sulphate, $(NH_4)_4[Zr_4(OH)_8(SO_4)_6],14H_2O$, crystallised out (Rosenheim and Pinsker, Z. anorg. Chem., 1919, **106**, 10), and afforded also a ready separation from last traces of iron, which were converted into the more soluble ferric ammonium alum.

Anhydrous zirconium tetrachloride was prepared from purified zirconia by heating this dioxide in a stream of chlorine and carbon tetrachloride at $550-600^{\circ}$, the yield of tetrachloride being quantitative (Lely and Hamburger, Z. anorg. Chem., 1914, 87, 209; Venable and Bell, J. Amer. Chem. Soc., 1917, 39, 1598).

As the source of heat, a small electric furnace was used 18 inches in length and the zirconia was heated in a silica tube of 1 inch internal diameter, joined to a glass receiving tube 2 feet in length and $1\frac{1}{4}$ inches in internal diameter. These tubes were connected by a bung made of asbestos and waterglass, a glass-wool filter being attached to the outer end of the condenser. A stream of dry chlorine was bubbled through carbon tetrachloride and the mixed gas and vapour were carried over the heated zirconia. The zirconium tetrachloride thus obtained in pure white, lustrous crystals was quickly transferred to stoppered bottles, which were sealed with paraffin wax.

Zirconium Trisdibenzoylmethane Chloride (I) .-- Zirconium tetrachloride (2.6 grams; 1 mol.) was heated under reflux in 50 c.c. of chloroform B.P. with 7.3 grams of dibenzovlmethane (3 mols.) until the evolution of hydrogen chloride ceased. To the filtered solution light petroleum was added and the liquid left for a few hours in a stoppered bottle, when yellow, complex, pyramidal crystals separated, m. p. 258° (yield 7.3 grams or 82 per cent.). The product was stable in air, insoluble in ether or light petroleum, sparingly soluble in alcohol, acetone, benzene, toluene, or chloroform, dissolving readily in glacial acetic acid. It crystallised best from the last solvent or from chloroform, the melting point rising to 262°. Hydrolysis occurred when the acetic acid solutions were exposed to air. The condensation was also effected in dry benzene, when 0.9 gram of zirconium tetrachloride and 2.7 grams of dibenzoylmethane were refluxed in 75 c.c. of this solvent until hydrogen chloride was no longer evolved. The product was isolated by adding light petroleum and by concentrating the solution in a vacuum (yield 1.6 grams) [Found : C = 67.32, 67.42; H = 4.31,Cl (grav.) = 4.38, 4.50; (vol.) 4.84, 4.50; Zr = 11.24, 4.38:11.17. $C_{45}H_{33}O_6CIZr$ requires C = 67.90; H = 4.15; Cl = 4.50; Zr = 11.20 per cent.].

Zirconium trisdibenzoylmethane chloride was also prepared by double decomposition between zirconium tetrachloride (2 mols.) and copper dibenzoylmethane (3 mols.) when 0.9 gram of the former reacted with 2.7 grams of the latter in 50 c.c. of chloroform B.P., the mixture being warmed for a few minutes on the waterbath and left for 2 hours at the ordinary temperature. Cupric chloride was removed and the filtrate concentrated in a vacuum (yield 82 per cent.). When heated in an ignition tube, zirconium trisdibenzoylmethane chloride decomposed, evolving hydrogen chloride and chlorodibenzoylmethane. Aqueous or alcoholic ferric chloride developed an immediate red coloration.

Zirconium Trisdibenzoylmethane Ferrichloride (III).-On adding 0.24 gram of anhydrous ferric chloride (1 mol.) to 1.72 grams of zirconium trisdibenzoylmethane chloride in 50 c.c. of chloroform B.P., a transient violet colour appeared and changed to yellow. The solution was heated under reflux, filtered, and diluted with light petroleum until an oil separated which subsequently crystallised in large, six-sided, orange-yellow prisms charring at 160° and melting at 163°. This preparation was soluble in warm alcohol, chloroform, or glacial acetic acid and dissolved in pyridine to a deep red solution. After a week in the desiccator the crystals became opalescent. When heated in an ignition tube, the product gave the odour of chloroform, and the presence of this substance was confirmed by applying the phenylcarbylamine reaction (Found : Zr = 8.83; Fe = 5.23; total oxides $ZrO_2 + Fe_2O_3 = 19.42$; Cl =20.43, 20.75. $C_{45}H_{33}O_{6}$ ZrFeCl_{4,2}CHCl₃ requires Zr = 8.74; Fe = 5.40; total oxides = 19.54; Cl = 20.54 per cent. A specimen heated for 3 hours at 90° lost 7.69. Theoretical loss for $\frac{2}{3}$ CHCl₃ = 7.61 per cent.). A larger portion of the ferrichloride containing chloroform was heated at 90° until of constant weight and the residue was analysed [Found: Zr = 9.07; Fe = 6.07; total oxides = 20.95; Cl = 14.67(Carius), 15.14 (hydrolysis). $C_{45}H_{33}O_6ZrFeCl_4$ requires Zr = 9.46; Fe = 5.83; total oxides = 21.15; Cl = 14.82 per cent.]. When crystallised from hot glacial acetic acid, the ferrichloride containing chloroform separated in well-defined, yellow, obliquely truncated prisms charring at 110°.

Zirconium Trisdibenzoylmethane Chloroaurate (III).—A chloroform solution (35 c.c.) of 0.128 gram of auric chloride hydrochloride, AuCl₃,2HCl (Johnson and Matthey) and 0.2684 gram of zirconium trisdibenzoylmethane chloride was heated for a few minutes under reflux, concentrated in a vacuum, and treated with light petroleum. An oil separated which gradually solidified to a yellow, crystalline powder. This chloroaurate charred at 150° and melted at 155— 156°; it was slightly soluble in cold chloroform, warm alcohol, acetone, or benzene. It dissolved with decomposition in hot glacial acetic acid, colloidal gold being set free; it was insoluble in ether or light petroleum (Found: Au = 17.96; Zr = 7.92; $Au + ZrO_2 = 28.68$; Cl = 13.27. $C_{45}H_{33}O_6ZrAuCl_4$ requires Au = 17.94; Zr = 8.24; $Au + ZrO_2 = 29.10$; Cl = 12.92 per cent.).

Zirconium Trisdibenzoylmethane Chloroplatinate (II).—A molecular proportion (0·1676 gram) of anhydrous chloroplatinic acid, H_2PtCl_6 (Johnson and Matthey), dissolved in a small quantity of glacial acetic acid, was added to 0·6510 gram (2 mols.) of zirconium trisdibenzoylmethane chloride in 30 c.c. of glacial acetic acid, when a pulverulent, orange-yellow, crystalline double salt separated. It charred and decomposed at 210—220° and was insoluble in water and organic media [Found : Pt = 10.09; Zr = 9.66; $ZrO_2 + Pt =$ 23.17; Cl = 11.45, 11.61. $(C_{45}H_{33}O_6Zr)_2PtCl_6$ requires Pt = 10.13; Zr = 9.40; $ZrO_2 + Pt = 22.85$; Cl = 11.05 per cent.].

Zirconium Trisbenzoylacetone Chloride (IV).—Zirconium tetrachloride (3·1 grams; 1 mol.) and 4·5 grams of benzoylacetone (3 mols.) in 50 c.c. of anhydrous benzene were heated under reflux for 2 hours; the solution was then filtered and concentrated in a vacuum, when pale yellow, rhomboidal prisms separated. Recrystallised from benzene, the product melted at $124-125^{\circ}$; it was soluble in alcohol, benzene, chloroform, or glacial acetic acid and was precipitated from these solvents on the addition of light petroleum. From benzene and petroleum, it crystallised in clusters of prisms, m. p. $126-127^{\circ}$ (Found : $C = 59\cdot47$; $H = 4\cdot61$; Cl = $5\cdot81$, $5\cdot89$; $Zr = 14\cdot47$; M = 614, cryoscopic method in benzene. $C_{30}H_{27}O_6ClZr$ requires $C = 59\cdot11$; $H = 4\cdot43$; $Cl = 5\cdot83$; Zr = $14\cdot55$ per cent.; $M = 609\cdot1$).

Zirconium trisbenzoylacetone chloride developed immediately a red coloration with aqueous ferric chloride; it was stable in the desiccator, but hydrolysed by moist air. An alcoholic solution of the tris-diketone chloride and silver nitrate gave an immediate precipitate of silver chloride.

Attempts were made to prepare double chlorides by warming this chloride with chloroplatinic acid, chloroauric acid, or ferric chloride in well-dried benzene, chloroform, or glacial acetic acid, but in each case the addition of light petroleum led to the separation of oily products.

Zirconium Trisacetylacetone Chloride (V).—Zirconium tetrachloride (2.5 grams; 1 mol.) and 4.5 grams of acetylacetone (4 + mols.) were heated under reflux with 30 c.c. of purified anhydrous chloroform until evolution of hydrogen chloride had ceased. The filtered solution on concentration in a vacuum desiccator yielded large, transparent, colourless prisms, which were hydrolysed by moist air, liberating hydrogen chloride and acetylacetone. The compound was soluble in water (with decomposition) and in alcohol, chloroform, acetone, glacial acetic acid, or warm benzene, but insoluble in ether or petroleum; an alcoholic solution developed a red coloration with aqueous ferric chloride. An alcoholic solution added to alcoholic silver nitrate gave an instant precipitate of silver chloride.

Zirconium trisacetylacetone chloride separated from dry benzene in colourless crystals and was recrystallised without change from warm acetylacetone, when well-defined, colourless prisms were obtained, m. p. 101—102° (Found : C = 41.93; H = 5.12; Cl =8.31, 8.36; Zr = 21.30, 21.36; M = 418, ebullioscopic method in benzene. $C_{15}H_{21}O_6ClZr$ requires C = 42.55; H = 4.96; Cl =8.38; Zr = 21.40 per cent.; M = 423).

Zirconium trisacetylacetone chloride was also prepared by double decomposition from zirconium tetrachloride (2 mols.) and copper acetylacetone (3 mols.) in dry benzene, but owing to sparing solubility in this solvent it had to be extracted with hot benzene from the by-product, cupric chloride.

Although zirconium trisacetylacetone chloride separated unchanged from warm dry acetylacetone, it was converted into decahydrated zirconium tetra-acetylacetone under the following conditions: 1.30 grams of $[ZrA\bar{c}_3]Cl$ were dissolved in 19.5 c.c. of water, 0.32 gram of acetylacetone was added with sufficient aqueous sodium carbonate to dissolve it, the solution remaining faintly acid; 0.7 gram of zirconium tetra-acetylacetone was obtained in the first crop of crystals [Found: Zr = 13.35. $Zr(C_5H_7O_2)_4,10H_2O$ requires Zr = 13.56 per cent.].

The decahydrated zirconium tetra-acetylacetone obtained in the preceding experiment and a similar specimen prepared by Biltz and Clinch's method from zirconium nitrate were recrystallised twice from acetylacetone. Both preparations were rendered anhydrous by this procedure; they melted at 193—195° and did not depress each other's melting points. The specimen prepared from zirconium trisacetylacetone chloride was analysed [Found: Zr = 18.51. $Zr(C_5H_7O_2)_4$ requires Zr = 18.62 per cent.].

Interconversion of Zirconium Tris- β -diketone Chlorides.—When zirconium trisdibenzoylmethane chloride was crystallised from the minimum quantity of acetylacetone, the product precipitated by light petroleum consisted of unchanged dibenzoylmethane derivative, a certain amount of zirconium trisacetylacetone chloride, and mixed crystals of the two salts. With excess of acetylacetone, the conversion was complete, and the product deposited by light petroleum consisted entirely of colourless, prismatic needles of zirconium trisacetylacetone chloride [Found : Cl = 8.29. $Zr(C_5H_7O_2)_3Cl$ requires Cl = 8.38 per cent.].

II. Interaction of Zirconium Salts and β-Diketones in Aqueous Solution.

Zirconium tetra-acetylacetone, $ZrA\bar{c}_{4},10H_2O$, prepared from zirconium nitrate by Biltz and Clinch's method, was obtained in similar yield and gave Zr = 13.42, 13.49, theory requiring Zr = 13.56per cent.; it was dehydrated completely by five crystallisations from alcohol or preferably by two crystallisations from acetylacetone.

Experiments were then made with varying concentrations of zirconium nitrate and alkali and with the following homologues of acetylacetone: 3-methylacetylacetone, propionylacetone, and *n*-butyrylacetone, but in no case was a crystalline analogue of zirconium tetra-acetylacetone produced.

Benzoylacetone being less readily soluble in alkali than acetylacetone, the procedure was modified in this instance by using sodium benzoylacetone. Aqueous solutions of zirconium nitrate and sodium benzoylacetone in various concentrations gave a white precipitate, deposited from the faintly acid solution. The product was more conveniently prepared by interaction with zirconium oxychloride, $ZrOCl_{2,8}H_2O$.

Zirconyl Bisbenzoylacetone.—To a solution of 3.6 grams of oxychloride in 100 c.c. of water, 4.2 grams of sodium benzoylacetone in 100 c.c. of water were slowly added with stirring. A white, granular precipitate was slowly deposited (1.4 grams) which was soluble in alcohol, benzene, or glacial acetic acid. A specimen deposited from benzene solution on addition of light petroleum melted at 194° [Found : Zr = 21.34, 21.21. ($C_{10}H_9O_2$)₂ZrO requires Zr = 21.14 per cent.]. Molecular-weight determinations in boiling benzene, although difficult owing to sparing solubility, indicated threefold association. M = 1213; theory requires M = 1284.

Note on the Analysis of Zirconium Tris- β -diketone Chlorides.

The foregoing zirconium compounds were readily hydrolysed by boiling aqueous potassium hydroxide, the chlorine-ion being estimated both gravimetrically and volumetrically in the filtrate from precipitated zirconium hydroxide, but in the exceptionally stable dibenzoylmethane derivative chlorine was estimated by the Carius method. Although zirconium trisacetylacetone chloride was a comparatively unstable, easily hydrolysed salt, it gave persistently low results in the carbon estimation until ignited copper oxide was mixed with the weighed substance in order to oxidise traces of carbon probably retained in the form of zirconium carbide. View Article Online RESIDUAL AFFINITY AND CO-ORDINATION. PART XIX. 1261

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