COMPLEXES OF FERRIC CHLORIDE WITH TERTIARY ARSINES.

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The ease with which trivalent arsenic in tertiary arsines passes to the four-covalent state is well exemplified by the various complexes which arsines form with metallic salts. Complexes of several of the metals in Group VIII have already been described. Thus, Dwyer and Nyholm (1942-4) have studied the arsine complexes of the halides of rhodium and iridium, Burrows and Parker (1934) those of platinum, and finally Mann and Purdie (1936) similar compounds of palladium. The iron complexes described in this paper have been investigated in view of their expected similarity to the halogen bridge structures formed by rhodium and iridium.

Two series of compounds have been isolated, of empirical formulae, \( \text{FeCl}_6 \cdot 2 \text{Arsine (I)} \) and \( 2\text{FeCl}_3 \cdot 3 \text{Arsine (II)} \), but all attempts to isolate compounds of ferrous iron have proved fruitless. The outstanding property of the compounds was their ease of dissociation in water and acids. Because of this they were prepared from alcohol solution. Recrystallisation was often not possible, either because of the tendency for the compound to be thrown out as oil or to dissociation.

The complexes of diphenylmethylarsine were most closely investigated but similar compounds with other arsines were obtained. The compounds with the di-alkyl arsines took many weeks to crystallise out and were very difficult to purify. Owing to solubility relationships and ease of dissociation with other arsines, the two different complexes, (I) and (II), were obtained only with diphenylmethylarsine.

Compound (I), \( 2\text{FeCl}_3 \cdot 4\text{Ph}_2\text{AsMe} \), was obtained by treating an alcoholic solution of ferric chloride with excess of the arsine and purifying as below. The compound was only slightly soluble in water, the solution giving only a faint opalescence with silver nitrate but on boiling or treating the solution with nitric acid dissociation of the compound occurred with precipitation of all the chlorine. The substance was also less soluble in solvents and possessed a higher melting point (213°) than (II).

Compound (II), \( 2\text{FeCl}_3 \cdot 3\text{Ph}_2\text{AsMe} \), was much less stable than (I). It was prepared as for (I) using less arsine. This compound was readily soluble in water to form an electrically conducting solution, presumably due to structural breakdown, for the aqueous solution reacted readily with silver nitrate to precipitate silver chloride. Further, progressive dilution of the solution gave a reddish solution indicating hydrolysis of the ferric chloride. The substance was also more soluble in solvents and lighter in colour than (I).

The weakness of the arsenic-metal bond in these compounds is not unusual. Burrows (1940), in a reference to arsine co-ordinated complexes of metallic salts, mentions that in some cases it was impossible to recrystallise the compounds without loss of arsine, while with others merely washing with ether caused loss of arsine.

The formula attributed to the complex (I) is to be expected since ferric chloride is frequently dimeric in organic solvents and the formulation merely involves the completion of the co-ordination number of six for ferric iron by the
addition of four molecules of arsine to the Fe$_2$Cl$_4$ nucleus. The formula given to (II) is again necessary to complete the co-ordination number of six for iron. Previous examples of compounds in which four metal atoms have been joined by

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Fe} \\
\text{Ars.} & \quad \text{Cl} \\
\text{Ars.} & \quad \text{Ars.}
\end{align*}
\]

(I)

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Fe} & \quad \text{Fe} & \quad \text{Fe} & \quad \text{Fe} & \quad \text{Fe} \\
\text{Ars.} & \quad \text{Ars.} & \quad \text{Ars.} & \quad \text{Ars.} & \quad \text{Ars.} & \quad \text{Ars.}
\end{align*}
\]

(II)

\[
\begin{align*}
\text{Cl} & \quad \text{Fe} & \quad \text{Fe} & \quad \text{Fe} & \quad \text{Fe} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Ars.} & \quad \text{Ars.} & \quad \text{Ars.} & \quad \text{Ars.} & \quad \text{Ars.}
\end{align*}
\]

Boil in alcohol with FeCl$_3$ at 110°.

halogen bridges include the polynuclear complexes of rhodium and tin with arsines, described by Dwyer and Nyholm (1942b), which were also characterized by their ease of dissociation. The ease of conversion of (I) to (II) by boiling with ferric chloride emphasizes their closely related formulae.
Experimental.

Tetrachloro-tetrakis-diphenylmethylarsine-μ-dichloro-di-ironIII. (I)

This compound is usually difficult to obtain free from (II). Ferric chloride hexahydrate (3 g.) in ethyl alcohol (25 ml.) was treated with diphenylmethylarsine (6 g.; i.e. excess arsine in the ratio 1 : 2½ mols) in alcohol (25 ml.) and the solution heated on the water bath for one hour, alcohol being gradually added to make up for evaporation. On cooling, the solution was left to stand and after some days brown crystals melting at 213° were obtained. Frequently compound (II) was co-precipitated, purification being effected by dissolving all in acetone and fractionally precipitating with alcohol, the required complex being precipitated first.

The compound was also conveniently prepared as follows: 1 g. of the compound 2FeCl₃. 3Ph₂AsMe (II) was heated for one hour at 110° on a watch glass. After melting a brown, vitreous residue was left which on cooling was recrystallised from acetone and alcohol. This reaction is of interest in that above the melting point, compound (II) dissociated with the splitting out of ferric chloride.

The pure compound crystallised in rods melting at 213°, and was only slightly soluble in water, the solution giving only a faint opalescence with silver nitrate until treated with nitric acid or boiled. It dissolved readily in acetone but was only slightly soluble in other organic solvents. A suspension of the complex in alcohol dissolved readily on boiling with ferric chloride solution due to change over to complex (II).

Found: Cl=16·4%, Fe=8·3%, As=21·7%.
Calculated for [2FeCl₃. 4(C₆H₅)₂AsCH₃]: Cl=16·4%, Fe=8·6%, As=23·0%.

Hexachloro - hexakis - diphenylmethylarsine - μ - dichloro - di - ironIII - μ - dichloro - di - ironIII. (II)

Ferric chloride hexahydrate (3 g.) and p-tolyl dimethylarsine (4·5 g.) (2 : 3 mols) in alcohol (25 ml.) and the solution heated on the water bath until about two-thirds of the alcohol had evaporated. The solution was then diluted to its original bulk and the process repeated. The solution was finally diluted to 50 ml. and allowed to stand. After two to three days yellow, cubic crystals were obtained and after washing with alcohol these were recrystallised from acetone and alcohol, the required compound being obtained as microcrystalline yellow plates melting at 93°. Often a small amount of compound (I) was first precipitated, for which reason the first fraction during recrystallisation was rejected.

The compound was extremely soluble in acetone, fairly soluble in glacial acetic acid and nitrobenzene and moderately soluble in alcohol; it dissolved slightly in, and could be recrystallised with difficulty from, benzene. It dissolved readily in water to form an electrically conducting solution indicating dissociation. On testing with hydrochloric acid and potassium ferricyanide, this compound and all others gave no blue colour, indicating that the iron was present wholly in the ferric state. Molecular weight determinations in nitrobenzene showed marked dissociation.

Found: Cl=19·9%, Fe=10·4%, As=19·9%.
Molecular weight (cryoscopic in nitrobenzene)=477,487.
Calculated for [2FeCl₃. 3(C₆H₅)₂AsCH₃]₂: Cl=20·1%, Fe=10·6%, As=21·3%.
Molecular weight=2,114.

Note.—On occasions this compound has crystallised out with alcohol of crystallisation which could be removed by recrystallisation from benzene. The alcohol was confirmed by the iodoform test.

Tetrachloro-tetrakis-o-tolyldimethylarsine-μ-dichloro-di-ironIII. (Type I)

This was the only compound similar to (I) obtained with a di-alkylarsine. After heating in the usual manner, o-tolyldimethylarsine (5 g.) and ferric chloride hexahydrate (3 g.) in alcohol (50 ml.) were allowed to stand. After some months brownish crystals melting at 115° were obtained which could not be recrystallised due to dissociation. The substance, although soluble
in water, did not precipitate silver chloride from silver nitrate till nitric acid was added, indicating similarity to compound (I). Sufficient compound for the Cl and As analyses only was obtained.

Found: Cl=19.2%, As=25.9%.
Calculated for [2FeCl₃·4C₄H₄As(CH₃)₂]: Cl=19.2%, As=27.0%.

Hexachloro-hexakis-di-p-tolylmethylarsineμ dichloro-di-iron(III)μ dichloro-di-iron(III). (Type II.)

Di-p-tolylmethylarsine (4·5 gm.) and ferric chloride hexahydrate (3 g.) were allowed to react in 50 ml. alcohol in the usual manner and the mixture allowed to stand. After some days cubic crystals melting at 148° were obtained. Properties were similar to those of the corresponding diphenylmethyarsine complex except that recrystallisation was more difficult and solubilities generally were lower. Attempts to prepare a complex of Type I from this arsine, directly or indirectly, have proved a failure.

Found: Cl=19.1%, Fe=10.0%, As=18.6%.
Molecular weight (cryoscopic in nitrobenzene)=650,750.
Calculated for [2FeCl₃·3(C₄H₄)₂AsCH₃]₂: Cl=18.7%, Fe=9.8%, As=19.7%.
Molecular weight=2,282.

Hexachloro-hexakis-dimethyl-p-tolylarsineμ dichloro-di-iron(III)μ dichloro-di-iron(III)μ dichloro-di-iron(III). (Similar to II.)

Ferric chloride hexahydrate (3 g.) and p-tolylidinethylarsine (4·5 g.) in alcohol (50 ml.) were heated as usual and allowed to crystallise. After some weeks yellow, monoclinic rods melting at 100-101° were obtained. This compound, as expected, was more difficult than with the di-aryl arsines to obtain pure and could not be recrystallised without passing to an oil. Even washing with ether tended to cause dissociation. The compound dissolved readily in solvents and gave the usual reaction with silver nitrate. It is of importance to note that if the original solution was too concentrated, heating caused the arsine to reduce the ferric chloride to ferrous chloride which was precipitated.

Found: Cl=23.8%, Fe=12.4%.
Calculated for [2FeCl₃·3C₄H₄As(CH₃)₂]: Cl=23.33%, Fe=12.27%.

ANALYSIS.

Chlorine was determined by the distillation method of Dwyer and Nyholm (1942b). Iron provided some difficulty, being finally estimated by careful ignition of the complex with excess concentrated sulphuric acid. The iron remained as ferric oxide, some difficulty being experienced in preventing partial reduction to Fe₂O₃ due to the reducing nature of other constituents, which tended to make results somewhat low.

Arsenic was determined by Kjeldahl decomposition of the complex with concentrated sulphuric acid and potassium sulphate and gravimetric estimation of the arsenic as As₂S₅. Results were usually low, due partly to volatility of the arsine and partly to loss of arsenic as arsenious chloride. This difficulty was also encountered by Burrows and Parker (1934), whose results indicate that loss of arsenic was marked with chloride complexes.

SUMMARY.

The complexes of ferric chloride with tertiary arsines have been described. Two types, of empirical formulæ FeCl₃·2 Arsine and 2FeCl₃·3 Arsine, have been isolated. Formulation of these complexes required halogen bridge structures if a covalency of six were assumed for iron. Similar structures have been ascribed to complexes of bivalent rhodium.
THE RESPONSE OF THE STEENAL INTEGUMENT OF TRICHOSURUS VULPEGVLA TO CASTATION AND TO SEX HORMONES.

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With Plate XIV.

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In a previous paper (Bolliger and Hardy, 1944) the highly glandular skin area over the sternum of Trichosurus vulpecula (the common Australian possum) and the distinctive brown hairs covering it, have been described and the significance of this region has been considered to be, mainly that of a male sex characteristic. This theory was found to be well supported after observing the effects of the following series of experiments on the sternal integument.

1. Castration of immature females and males.
2. Castration of sexually mature females and males.
3. Administration of female sex hormone to female and male castrates.
4. Administration of male sex hormones to female and male castrates.

1. The Effect of Castration on the Sternal Integument of Immature Possums.
   (a) Females. Three females were ovariecrotomised before they had reached sexual maturity. At the time of castration they were approximately 8 to 11 months of age and their sternal patches consisted either of exclusively grey hairs, or of grey with a small amount of light brown hair, or of grey with about an equal amount of light brown hairs. After castration these animals were observed for a period of 10 months, a period during which control animals of similar age changed from adolescence into sexual maturity, and developed the comparatively small but well defined sternal patch of the female. The results of these experiments were a retarded and incomplete change from the grey sternal hair of the immature animal to the brown coloured hair of the quite mature female. For example, in the animal depicted in Figure 1, the majority of the sternal hairs were a light grey colour at the end of the period of observation and only the shaft of a few discreet hairs took on a light yellow brown colour, while in controls the greater part of the grey sternal pellage had changed into a brown colour.

(b) Males. Three males were castrated at the age of about six months. Two of these were subsequently given some injections of oestrogen and will therefore be mentioned again in paragraph 3 when dealing with the administration of female sex hormones to male castrates. At this stage it may, however, be stated that in all three animals no large, evenly brown or red-brown and oily sternal patch developed as was seen in controls. Moreover, the castrated

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