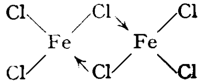
172. *Studies in Co-ordination Chemistry. Part III. Complexes of Iron with a Ditertiary Arsine.*

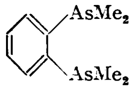
By R. S. Nyholm.

Complexes of ferric and ferrous halides with the chelating group *o*-phenylenebisdimethylarsine have been prepared and studied. Ferric chloride and bromide give rise to highly coloured salt-like compounds in which the univalent cation contains two halogen atoms and two molecules of the chelate group bound to the iron atom. The anion may be a halide ion or the ions $[FeCl_4]^-$ or $[FeBr_4]^-$. The tetrabromoferrate ion is converted readily into the bromide ion by treatment with water in acetone solution. Magnetic measurements have established that the cation has an effective magnetic moment which corresponds to one unpaired electron and it is concluded that the bonds to the iron are covalent, forming an octaheral complex; in the anions $[FeCl_4]^-$ and $[FeBr_4]^-$ a magnetic moment corresponding to five unpaired electrons is observed and in these ions the binding is thus ionic. The perchlorates have been prepared, and studies of their magnetic susceptibility support the above conclusions. When treated with iodides, the chloride complex is reduced to a diamagnetic ferrous compound which is formulated as a non-ionic octahedral complex with covalent bonds. The corresponding diamagnetic ferrous bromide and ferrous thiocyanate complexes have been prepared and studied. The implications of the magnetic measurements are discussed. Attempts to isolate halogen-bridged octahedral complexes were unsuccessful.

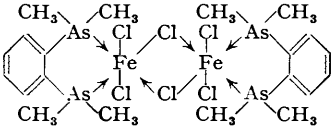
The complexes of iron halides with a ditertiary arsine have been studied as part of an investigation of Group VIII elements in various valency states with tertiary arsines. The chelating group *o*-phenylenebisdimethylarsine was chosen for this investigation for two reasons. Earlier investigations using diphenylmethylarsine had yielded complexes of ferric chloride which dissociated so readily in solution that it was possible only to speculate as to their structure (Nyholm, *J. Proc. Roy. Soc. N.S.W.*, 1944, **78**, 229) and a much more powerful ligand was needed. Jensen (*Z. anorg. Chem.*, 1936, **229**, 282) has reported that triethylphosphine, a stronger ligand than triethylarsine as a rule, does not co-ordinate with ferrous iron, and for this investigation the chelating group used was chosen because Chatt and Mann (*J.*, 1939, 1622) had shown that it forms very strong bonds, at least with bivalent palladium; it was also chosen in an attempt to isolate halogen-bridged complexes of ferric iron.



(I.)



(II.)



(III.)

Ferric chloride in the solid state has a layer structure with the ferric atom surrounded octahedrally by six chlorine atoms (Wooster, *Z. Krist.*, 1932, **83**, 35) but it sublimes readily at 285°, and below 440° its vapour pressure corresponds to the formula Fe_2Cl_6. In organic solvents like ether, alcohol, acetone, and pyridine, ferric chloride is monomeric but there is evidence for dimerisation in solvents like carbon disulphide, chloroform, and benzene (Wells, " Structural Inorganic Chemistry," Oxford, 1945, p. 139). These results have led to the general aceptance of a halogen bridge structure (I) for this dimer. The properties of ferric chloride make it inconvenient for a study of the properties of the bridge because of the ease with which it undergoes hydrolysis, but it was hoped that by using a chelate group the bridge could be stabilised with the formation of an octahedral complex as in (III). Tertiary arsines, and tertiary phosphines, are specially convenient for investigations of this nature, for their complexes are usually soluble in organic solvents and so permit of determination of molecular weights; furthermore, these ligands have not the troublesome consequences which often arise from the basic nature of ammonia and amines.

When the diarsine (II) reacts with anhydrous ferric chloride dissolved in alcohol or benzene a red colour immediately develops and a crimson precipitate is obtained. The presence of a little water does not affect the reaction, which is very sensitive, the red colour being formed with only traces of ferric chloride, and under the right conditions precipitation of the ferric iron is almost quantitative. The *compound* has the empirical formula $FeCl_3,C_6H_4(AsMe_2)_2$; it melts at 219°, and dissolves readily in nitromethane, acetone, and nitrobenzene. The molecular weight was determined ebullioscopically in acetone and cryoscopically in nitrobenzene and some association was observed, x in the formula $[FeCl_3,C_6H_4(AsMe_2)_2]_x$ being found to vary between 1·1 and 1·4 according to the solvent and the concentration. The compound is stable in air and does not react with moisture unless dissolved in acetone and treated with a fairly large amount of water, whereupon hydrolysis takes place. The corresponding *bromide* has been prepared and has a deep chocolate-brown colour; it melts at 209° and has properties similar to those of the chloride except that it is very much less stable to water, which converts it very readily into the green *salt* $[FeBr_2,2C_6H_4(AsMe_2)_2]^+$ Br^-. The facts that both the chloride and the bromide melted and dissolved in certain organic solvents at first seemed to exclude a salt-like structure, and a bridged structure (III) seemed likely since dissociation of halogen bridges in the solvents used for the molecular weights is not uncommon. However, it was not possible to split the bridge with such co-ordinating groups as pyridine, triethylarsine, or *p*-toluidine, and the magnetic measurements were difficult to interpret on such a hypothesis.

Magnetic-susceptibility measurements showed that both the chloride and the bromide were strongly paramagnetic, with an effective magnetic moment of about 4·6 Bohr magnetons both in the solid state and in acetone solution. This value would correspond to between three and four unpaired electrons if it is assumed that the whole of the moment may be attributed to spin alone. Pauling (" Nature of the Chemical Bond," N.Y., 1945, 2nd edition, p. 115) predicts that a moment of 1·73 B.M. should be found for octahedral covalent complexes of ferric iron using d^2sp^3 bonds, owing to the presence of one unpaired electron in the $3d$ shell; an example of this type of complex is potassium ferricyanide, for which the moment of 2·33 B.M. has been reported, the larger value being accounted for by orbital contribution. On the other hand, ionic complexes of ferric iron have a predicted magnetic moment of 5·92 B.M. due to the presence of five unpaired electrons; an example of this type of complex is the salt $(NH_4)_3FeF_6$ for which a moment of 5·9 B.M. has been reported. In Table I are shown the electronic arrangements and calculated magnetic moments for various types of ferrous and ferric complexes. The most unusual value of 4·6 B.M. for the complexes described above would be found in compounds in which both covalent and ionic binding were present, and with this idea in mind alternative methods for formulating these complexes were examined.

TABLE I.

Calculated magnetic moments for various types of iron complexes.

Complex.	Electronic arrangement.			Calculated * magnetic moment (μ).
	3*d*.	4*s*.	4*p*	
Ferric covalent octahedral (d^2sp^3 bonds)	↓↑ ↓↑ ↓ ↓↑ ↓↑	↓↑	↓↑ ↓↑ ↓↑	1·73
Ferric ionic, octahedral or tetrahedral ...	↓ ↓ ↓ ↓ ↓	☐	☐ ☐ ☐	5·92
Ferric covalent planar (dsp^2 bonds)	↓↑ ↓ ↓ ↓ ↓↑	↓↑	↓↑ ↓↑ ☐	3·88
Ferrous covalent octahedral (d^2sp^3 bonds)	↓↑ ↓↑ ↓↑ ↓↑ ↓↑	↓↑	↓↑ ↓↑ ↓↑	0·00
Ferrous ionic, octahedral or tetrahedral	↓↑ ↓ ↓ ↓ ↓	☐	☐ ☐ ☐	4·90
Ferrous covalent planar (dsp^2 bonds)......	↓↑ ↓↑ ↓ ↓ ↓↑	↓↑	↓↑ ↓↑ ☐	2·83

* These values are calculated on the assumption that the whole of the moment is due to spin alone. Usually, there is a small orbital contribution which increases these values slightly; its effect is most marked with the lower values.

If it be assumed that the compounds are salts, the formulæ $[Fe\{C_6H_4(AsMe_2)_2\}_2][FeCl_6]$ and $[Fe\{C_6H_4(AsMe_2)_2\}_2Cl_2][FeCl_4]$ are possibilities. The former would contain the most unlikely square co-ordinated ferric iron, the cation having three and the anion five unpaired electrons (see Table I). The second formula, however, contains one octahedrally co-ordinated ferric atom, which would contain one unpaired electron if covalent bonds are present, and one ferric atom in which five unpaired electrons are expected; it will be shown that the susceptibility found is almost exactly that calculated for the second formula. This structure has also been confirmed by the preparation of the *perchlorate* of the cation. When an acetone solution of the *chloride* is treated with perchloric acid, a red precipitate is immediately formed, which has the formula $[Fe\{C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]$. This compound has a magnetic moment of 2·34 B.M., which indicates one unpaired electron if due allowance is made for the orbital contribution, and shows that the cation is an octahedrally co-ordinated complex of ferric iron with covalent bonds. The magnetic susceptibilities of the various compounds are shown in Table II.

TABLE II.

Experimental magnetic susceptibilities of iron complexes.

Compound.	$\chi_M \times 10^{-6}$ (20°).	Diamagnetic correction.	$\chi_M \times 10^{-6}$ corr. for diamagnetism.	Magnetic moment (μ) per Fe atom.
1. $[Fe(Diarsine)_2Cl_2][FeCl_4]$	16,950	523	17,470	4·55
2. $[Fe(Diarsine)_2Cl_2][ClO_4]$	1,860	461	2,320	2·34
3. $[Fe(Diarsine)_2Cl_2]^+$	1,890	431	2,320	
4. $[FeCl_4]^-$ [from (1)–(3)]	15,060	94	15,150	5·98
5. $[Fe(Diarsine)_2Br_2][FeBr_4]$	17,100	598	17,700	4·57

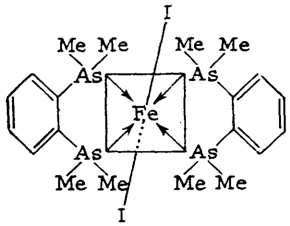
(The diamagnetic corrections used in this table were taken from Selwood, " Magnetochemistry," N.Y., 1943, p. 52.)

By subtracting the susceptibility of the chlorate ion from the susceptibility of the salt (2) (Table II), we obtain the susceptibility of the $[Fe(Diarsine)_2Cl_2]^+$ cation. If this value be then subtracted from the susceptibility of the compound (1) we obtain the susceptibility of the $[FeCl_4]^-$ ion and the magnetic moment calculated from this (μ = 5·98 B.M.) is in good agreement with that calculated for ferric iron with ionic bonds (μ = 5·92).

The behaviour of the ferric bromide *complex* (5) with water is readily explained from a consideration of its structure, for the first step one would expect is hydrolysis of the $[FeBr_4]^-$ ion; the product, $[Fe(Diarsine)_2Br_2]Br$, can be isolated because of its fairly low solubility in aqueous acetone. The corresponding chloride complex could not be isolated. The addition of a considerable amount of water to an acetone solution of the chloride (1) caused no change in colour or any immediate precipitate, although on long standing a brownish precipitate consisting chiefly of ferric hydroxide was obtained, which indicated complete breakdown of the compound. It is quite possible that the compound $[Fe(Diarsine)_2Cl_2]Cl$ is too soluble to be isolated under the conditions employed. The solubility of a salt like $[Fe(Diarsine)_2Cl_2][FeCl_4]$ in acetone, nitrobenzene, and nitromethane is explained by the high dielectric constants of these liquids; in spite of the large organic molecules which go to make up their structure, these compounds are quite insoluble in benzene and chloroform, and their solubility in such good ionising solvents as those mentioned above must be taken as a significant indication of their structure. The molecular weights which are found in nitrobenzene and acetone show that the molecules are largely ionised in these solvents.

The failure to obtain a stabilised halogen-bridge complex with this diarsine chelating group seems to indicate that such octahedral bridged complexes must be most unstable. The conditions used appeared most favourable for the formation of such a compound; if ferric chloride exists in benzene as a halogen-bridged molecule, then addition of the chelate might be expected to give the bridged octahedral complex readily, since addition of the diarsine would merely involve increasing the co-ordination number of the ferric atom from four to six without affecting the bridge.

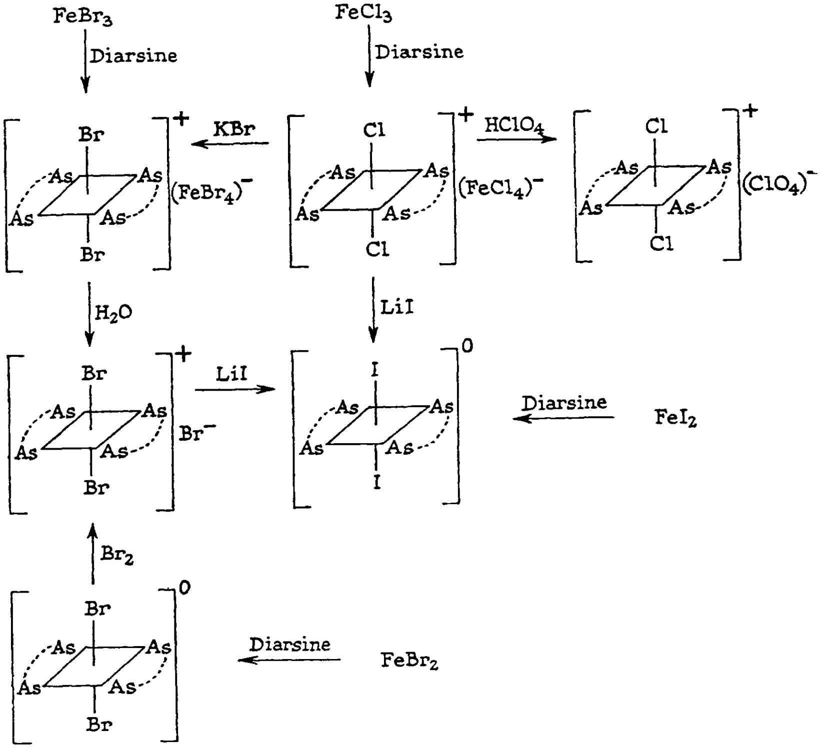
Attempts to isolate the ferric iodide salts resulted in the formation of a non-ionic complex of ferrous iron. The reaction between ferric iodide and the diarsine cannot be carried out directly owing to the instability of the former, so replacement of the chlorine from the compound $[Fe(Diarsine)_2Cl_2][FeCl_4]$ by the addition of lithium iodide in acetone solution was attempted. The dark solution quickly precipitated a yellow compound of empirical formula $Fe(Diarsine)_2I_2$ which was slightly soluble in acetone and chloroform, but solubilities were too low to enable one to carry out a molecular-weight determination. Since the compound is found to be diamagnetic, formulation as a planar four-covalent salt of the type $[Fe(Diarsine)_2]^{++}\ I^-{}_2$ is clearly excluded



(IV.)

because the use of dsp^2 bonds would require the presence of two unpaired electrons, making the compound paramagnetic (see Table I). The *compound* is thus a six-covalent non-ionic octahedral complex of ferrous iron with d^2sp^3 bonds (IV). This compound is one of the few examples known of diamagnetic, octahedral, non-ionic ferrous complexes; salt-like diamagnetic complexes of ferrous iron included the well-known red tris-*o*-phenanthroline and trisdipyridyl compounds. This compound appears to arise from the self-oxidation and -reduction of the unstable salt [Fe(Diarsine)$_2$I$_2$]$^+$ I$^-$, for the solution at first turns black on treatment with lithium iodide and then lightens and precipitates the ferrous complex. This black colour is also observed when a suspension of [Fe(Diarsine)$_2$I$_2$] in alcohol is treated with iodine; a black precipitate is formed but the compound decomposed during attempts at its isolation. The ferrous complex may also be prepared by shaking together ferrous iodide and the diarsine in aqueous-alcoholic solution, the yellow ferrous iodide complex being quickly precipitated. The corresponding ferrous bromide complex may be prepared in a similar way and is also diamagnetic. When treated with bromine water, the ferrous bromide complex turns green immediately, with formation of the ferric salt [Fe(Diarsine)$_2$Br$_2$]$^+$ Br$^-$. The corresponding ferrous chloride complex was not isolated, but on shaking together a mixture of ferrous chloride and the diarsine in aqueous alcohol an immediate red colour was observed, and in the presence of air a copious precipitate of the ferric compound [Fe(Diarsine)$_2$Cl$_2$][FeCl$_4$] was formed in a short time. In attempts to prepare a ferric thiocyanate complex the ferrous *compound* [Fe(Diarsine)$_2$(CNS)$_2$]^0 was isolated and, like the bromide and iodide, this compound is also diamagnetic and clearly an octahedral covalent complex. As with the iodide, reduction took place, and this is not difficult to understand in view of the oxidation potentials of the halogens; the oxidation potential for the reaction 2CNS$^-$ ⟶ (CNS)$_2$ (+0·77 v.) is much less than that for the reaction 2Br$^-$ ⟶ Br$_2$ (+1·07 v.) and not much more than that for the reaction 2I$^-$ ⟶ I$_2$ (+0·53 v.). Thus

TABLE III.



the order of stability to oxidation of the ferrous complexes is iodide > thiocyanate > bromide > chloride, which is the order of increasing oxidation potentials of the halogens.

In Table III are shown the relationships between the various complexes of ferrous and ferric iron. In all cases the two halogen atoms are shown as *trans-* for convenience; this is probably the case but no attempt has been made to prove it.

EXPERIMENTAL.

o-*Phenylenebisdimethylarsine.*—This was prepared by the method of Chatt and Mann (*J.*, 1939, 610). From *o*-nitroaniline (414 g.) after the six steps a yield of 22·6 g. of the diarsine, b. p. 157°/14 mm., was obtained (Found: C, 42·2; H, 5·4. Calc. for $C_{10}H_{16}As_2$: C, 42·0; H, 5·6%) as a colourless oil of unpleasant odour; it was kept sealed. Unlike the trialkylarsines, it is not readily oxidised in air and is more stable to air than phenyldimethylarsine.

*Dichlorodi-(*o*-phenylenebisdimethylarsine)iron*(III) *Tetrachloroferrate.*—Anhydrous ferric chloride (1·7 g.) was dissolved in purified spirit (75 ml.), and the solution filtered from traces of impurity and added with stirring to *o*-phenylenebisdimethylarsine (2·9 g.) dissolved in purified spirit (80 ml.). A crimson precipitate was immediately formed which was allowed to settle for about five minutes then filtered off and well washed with purified spirit, in which it was only very slightly soluble. An almost quantitative yield (4·5 g.) was obtained [Found: C, 26·6; H, 3·7; Cl, 23·5; Fe, 12·6%; *M* (cryoscopic) in 2·55% solution in nitrobenzene, 490; (ebullioscopic) in 2·76% solution in acetone, 536; in 3·87% solution in acetone, 637. $C_{20}H_{32}Cl_6As_4Fe_2$ requires C, 26·76; H, 3·6; Cl, 23·7; Fe, 12·46%; *M*, 897], m. p. 219° (decomp.). The *compound* was recrystallised from acetone–light petroleum. It dissolved readily in acetone, nitrobenzene, and nitromethane, was slightly soluble in alcohol and ethyl acetate, but completely insoluble in benzene, chloroform, ether, dioxan, and water. The compound was quite unaffected by water at room temperature. It could be prepared conveniently, also, by mixing solutions of the diarsine and ferric chloride dissolved in benzene, the crimson precipitate appearing immediately. The complex was stable indefinitely in air and no smell of arsine developed after many months' exposure to the atmosphere. Treatment of an acetone solution with silver nitrate solution caused decomposition of the compound, silver chloride being at once precipitated, and the colour changing from red to a deep blue which faded in about ½ hour. The substance responsible for this blue colour was not identified because of the rapid decomposition. When the acetone solution of the complex was treated with 1 mol. of pyridine, *p*-toluidine, or triethylarsine per iron atom there was no change in colour and the complex could be recovered unchanged by concentrating the solution. An acetone solution was not reduced by sulphur dioxde, but addition of perchloric acid to it gave an immediate precipitate of the perchlorate (see below).

Magnetic susceptibility. Magnetic susceptibilities were measured by the Gouy method on the magnet described by Baddar, Hilal, and Sugden (*J.*, 1949, 132). (*a*) The data for the powdered compound at 20° are in Table II; at 18·6°, $\chi = 18{\cdot}8 \times 10^{-6}$, whence, after correction as before, $\mu = 4{\cdot}52$; at 28·5°, $\chi = 18{\cdot}4 \times 10^{-6}$, whence, after correction, $\mu = 4{\cdot}55$.

(*b*) In acetone solution (M/25): at 23·8°, $\chi = 19{\cdot}7 \times 10^{-6}$, $\chi_M = 17{,}600 \times 10^{-6}$, and after correction, mean $\mu = 4{\cdot}61$; at 25·2°, $\chi = 20{\cdot}0 \times 10^{-6}$, $\chi_M = 18{,}000 \times 10^{-6}$, and after correction, mean $\mu = 4{\cdot}71$.

*Dibromodi-(*o*-phenylenebisdimethylarsine)iron*(III) *Tetrabromoferrate.*—*o*-Phenylenebisdimethylarsine (1·6 g.), dissolved in alcohol (100 ml.), was slowly added with rapid stirring to a freshly filtered solution of anhydrous ferric bromide (5 g.) dissolved in alcohol (30 ml.). (The ferric bromide was present in considerable excess and the order of addition given was followed to minimise formation of the green compound $[FeBr_2,2C_6H_4(AsMe_2)_2]Br$ described below.) A brown precipitate was formed immediately, and this was filtered off and washed many times with alcohol to remove excess of ferric bromide and any of the green compound, which is soluble in alcohol. The filtrate was finally very pale green owing to the presence of a small amount of the green compound formed by hydrolysis. The *tetrabromoferrate* (3·3 g., nearly quantitative) [Found: C, 20·8; H, 3·0; Br, 41·3; Fe, 9·7%; *M* (cryoscopic) in 2·73% solution in nitrobenzene, 692; (ebullioscopic) in 4·24% solution in acetone, 820; in 6·42% solution in acetone, 850. $C_{20}H_{32}Br_6As_4Fe_2$ requires C, 20·6; H, 2·58; Br, 41·25; Fe, 9·6%; *M*, 1164] was purified by recrystallisation from acetone–light petroleum. It dissolved readily in acetone, nitrobenzene, and nitromethane, forming a solution which was brown if dilute and red when concentrated. The compound formed brown shimmering crystals, m. p. 207° (decomp.), which under the microscope were seen to consist mainly of flat rhombs. The compound was completely insoluble in benzene, chloroform, ether, dioxan and organic solvents other than those mentioned above. Although it is insoluble in water it slowly hydrolysed to form the green salt $[FeBr_2(Diarsine)_2]Br$ and this green compound was also formed when water was added to a solution of the compound in acetone. An acetone solution of the complex reacted immediately with silver nitrate solution to precipitate silver bromide, the solution first turning green, then blue; the colour faded entirely in about 15 minutes.

Magnetic susceptibility. At 20°, see Table II. At 27·3°, $\chi = 14{\cdot}3 \times 10^{-6}$, whence, after correction, mean $\mu = 4{\cdot}57$.

*Dibromodi-(*o*-phenylenebisdimethylarsine)iron*(III) *Monobromide.*—Anhydrous ferric bromide (2 g.) was dissolved in alcohol (30 ml.), and the solution filtered and added with vigorous stirring to a solution of *o*-phenylenebisdimethylarsine (1·0 g.) dissolved in alcohol (75 ml.). A green compound was precipitated in a dark solution and a small amount of the brown ferribromide complex was formed also. The green precipitate had a characteristic appearance as shimmering, finely divided crystals. The mixture was then treated with distilled water with vigorous stirring until the brown colour disappeared, leaving only a green precipitate in a green solution. The solution was filtered quickly and the compound washed several times, first with small quantities of aqueous alcohol and finally with water. The minimum quantity of alcohol had to be used because of the high solubility of the compound in this solvent. After a final washing with light petroleum, the *compound* was obtained as microcrystalline rods. Recrystallisation was difficult, for attempts at purification from acetone–light petroleum gave the brown ferribromide; also, contact with water for very long caused hydrolysis. The compound was nevertheless obtained fairly pure by starting with freshly filtered solutions and filtering rapidly after treatment with water. It probably still contained traces of ferric hydroxide formed by hydrolysis, as shown by the iron value (Found: C, 27·6; H, 3·7; Br, 27·3; Fe, 6·7. $C_{20}H_{32}Br_3As_4Fe$ requires C, 27·7; H, 3·7; Br, 27·7; Fe, 6·5%). The compound dissolved readily in alcohol, acetone, and warm water to a green solution. Boiling with insufficient alcohol to dissolve it caused some formation of the brown complex. It was practically insoluble in all other organic solvents. Treatment of an alcoholic solution with silver nitrate solution gave an immediate precipitate of silver bromide followed by development of a blue colour which faded rapidly.

Dichlorodi-(o*-phenylenebisdimethylarsine*)*iron*(III) *Perchlorate.*—The tetrachloroferrate (2·8 g.), prepared as above, was dissolved in acetone, and the solution filtered and treated at once with excess of perchloric acid (30%). The solution was well stirred and almost immediately a red crystalline precipitate of the *perchlorate* was obtained. This was filtered off after a few minutes and well washed with alcohol, in which it is practically insoluble. It was then dried in a vacuum desiccator, yield 2·0 g. [Found: C, 30·3; H, 4·3; Cl, 8·8; Fe, 7·0. $C_{20}H_{32}O_4Cl_3As_4Fe$ requires C, 30·1; H, 4·0; Cl, 8·9 (excluding Cl present in the ClO_4 ion), Fe, 7·0%]. It was slightly soluble in acetone and fairly soluble in nitrobenzene, but quite insoluble in water or organic solvents like chloroform or benzene. When heated the compound did not melt but decomposed violently about 210°.

Magnetic susceptibility. See Table II.

Di-iododi-(o*-phenylenebisdimethylarsine*)*iron*(II).—The tetrachloroferrate complex (1·35 g.), dissolved in acetone (70 ml.) and filtered from traces of impurity, was treated with lithium iodide (2 g.; excess) dissolved in acetone (30 ml.). The red solution immediately became dark brownish-red and finally brown. After 3 minutes' vigorous stirring, golden-yellow crystals were precipitated. These were filtered off, well washed with acetone, a little water, then finally with alcohol, and dried in a vacuum desiccator; yield 0·7 g. (Found: C, 27·2; H, 3·7; I, 29·3; Fe, 6·7. $C_{20}H_{32}I_2As_4Fe$ requires C, 27·2; H, 3·6; I, 28·8; Fe, 6·4%), a little more of the *complex* remaining dissolved in the acetone. In all other solvents the complex was quite insoluble. An acetone solution gave a precipitate with silver nitrate solution on warming. When heated the compound did not melt but began to darken at 250° and decomposed above 300°. This compound could also be prepared by shaking together for a few minutes an alcoholic solution of the arsine with an aqueous solution of ferrous iodide.

Magnetic susceptibility. $\chi = -0{\cdot}3 \times 10^{-6}$ whence $\mu = 0$.

Dibromodi-(o*-phenylenebisdimethylarsine*)*iron*(II).—Ferrous sulphate heptahydrate (0·6 g.) and sodium bromide (0·8 g.) were dissolved in air-free distilled water (20 ml.) containing one drop of 10N-hydrochloric acid and added to a solution of *o*-phenylenebisdimethylarsine (1·0 g.) dissolved in alcohol (20 ml.). Most of the arsine was immediately precipitated as an oil, and the solution developed a pale green colour owing to the presence of a little ferric salt. The mixture was well shaken in a 100-ml. stoppered flask for about ½ hour with frequent warming on the water-bath; most of the arsine had then dissolved and a yellow precipitate had started to form. After 24 hours with occasional shaking and heating, the residue was filtered off and well washed, first with alcohol and finally with distilled water until the washings gave no precipitate with silver nitrate. After a final washing with alcohol it was dried in the vacuum desiccator. The bright yellow *complex* (Found: C, 31·5; H, 4·6; Br, 20·5; Fe, 7·0. $C_{20}H_{32}Br_2As_4Fe$ requires C, 30·4; H, 4·1; Br, 20·2; Fe, 7·1%) was slightly soluble in alcohol and chloroform but could not be recrystallised. It was quite insoluble in all other common solvents. The alcoholic solution reacted with silver nitrate on warming. Bromine immediately oxidised the complex to the green ferric salt $[FeBr_2,2C_6H_4(AsMe_2)_2]Br$. On heating, the compound did not melt but decomposed near 300. It was diamagnetic but the susceptibility was not measured precisely because the yield (0·9 g.) was insufficient to fill the tube; the susceptibility was estimated at about $-0{\cdot}2 \times 10^{-6}$.

Dithiocyanatodi-(o*-phenylenebisdimethylarsine*)*iron*(II).—Anhydrous ferric chloride (1·6 g.) was dissolved in absolute alcohol (100 ml.), and the solution filtered and treated with a solution of ammonium thiocyanate (2·8 g.) in absolute alcohol (100 ml.). To the dark red solution was added *o*-phenylenebisdimethylarsine (2·9 g.) dissolved in absolute alcohol (50 ml.). The solution was well stirred and left for 5 minutes, a heavy purple powder being precipitated. This was filtered off and washed many times with absolute alcohol until the washings showed only a very pale green colour. After a final washing with water the *compound* was dried in the vacuum desiccator; yield, 3·1 g.; m. p. 293° (decomp.) (Found: C, 35·6; H, 4·4; N, 3·7; S, 8·6; Fe, 7·6. $C_{22}H_{32}N_2S_2As_4Fe$ requires C, 35·4; H, 4·3; N, 3·76; S, 8·6; Fe, 7·5%). This powder had a magnetic susceptibility of $+0{\cdot}17 \times 10^{-6}$ but after recrystallisation from chloroform and light petroleum this value fell to $0{\cdot}0 \times 10^{-6}$; the higher initial value was probably due to traces of ferric salt. The compound was slightly soluble in acetone and chloroform to a purple solution but was insoluble in water, benzene, light petroleum, and other common solvents. An acetone suspension reacted very slowly with silver nitrate to precipitate silver thiocyanate. When heated, the compound became lighter in colour above 200°. When finely divided the complex had a purplish-pink colour.

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