471. *Diarsine Complexes of Quadrivalent-metal Halides.*

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Titanium tetrachloride and titanium tetrabromide with *o*-phenylenebisdimethylarsine (Diarsine) form adducts of the type TiX_4,Diarsine and TiX_4,2Diarsine (X = Cl or Br). In the latter complexes the metal atom is eight-co-ordinated, being bound to four chlorine and to four arsenic atoms. Their structure is that of the $[Mo(CN)_8]^{4-}$ ion, *i.e.*, that predicted for d^4sp^3-hybridization. Zirconium, hafnium, and vanadium tetrachlorides also form complexes of the type MCl_4,2Diarsine, isostructural with TiX_4,2Diarsine, but no complexes of the type MCl_4,Diarsine could be isolated with these halides. The titanium and vanadium bis-Diarsine complexes are the first examples of complexes in which a first-transition-series element possesses eight-co-ordination.

PREVIOUS investigations of the transition-metal complexes of *o*-phenylenebisdimethylarsine[1] (Diarsine), $o\text{-}C_6H_4(AsMe_2)_2$, have been concerned primarily with metals in the second half of the transition series. Here the metal–arsenic bond has been considered to possess both σ- and π-character, the latter arising from back-donation of the "non-bonding" *d*-electrons of the metal to the empty *d*-orbitals on the arsenic atoms. It was therefore of interest to investigate the reactions of this arsine with Group IV (d^0) and Group V (d^1) elements, because in these cases π-bonding can be of little or no significance.

The only previous work with the d^0 elements and the Diarsine was by Sutton,[2] who isolated complexes TiX_4,Diarsine (X = Cl or Br). We have prepared these compounds by the simpler method of addition of the Diarsine at a 1 : 1 molar ratio to a solution of the halide in an inert solvent.[3] They are diamagnetic non-electrolytes (see Table 1) and are

TABLE 1.

Compound	Colour	Mol. conductivity in $Ph\cdot NO_2$ at 20°				
(D = Diarsine)		(cm.² ohm^{-1} mole^{-1})	Concn. (10^{-3}M)	ρ (g./c.c.)	$10^6\chi_g$	μ_{eff} (B.M.)
$TiCl_4$,D	Yellow-orange	0·5	5·0	—	−0·426	0·0
$TiBr_4$,D	Orange	0·9	1·1	—	−0·282	0·0
$TiCl_4$,2D	Orange-red	0·9	2·3	1·80	−0·423	0·0
$TiBr_4$,2D	Brown	0·7	1·5	—	−0·344	0·0
VCl_4,2D	Orange	—	—	1·80	1·149	1·74 *
$ZrCl_4$,2D	White	—	—	1·86	−0·533	0·0
$HfCl_4$,2D	Pale pink	—	—	2·04	−0·419	0·0

* Diamagnetic correction = 390 c.g.s.u.

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[1] Chatt and Mann, *J.*, 1939, 610.

[2] Sutton, *Austral. J. Chem.*, 1959, **12**, 122.

[3] Clark, Lewis, Nyholm, Pauling, and Robertson, *Nature*, 1961, **192**, 222.

therefore typical octahedral complexes of Ti^{IV}. Their infrared spectra have been recorded. The reflection spectrum of powdered $TiCl_4$,Diarsine shows a single peak at 21,400 $cm.^{-1}$ (Fig. 1). The absorption spectrum of this complex in polar solvents also shows a single peak at this frequency (*e.g.*, 21,600 $cm.^{-1}$ in acetonitrile); in non-polar solvents it occurs at slightly higher frequencies (*e.g.*, 22,300 $cm.^{-1}$ in benzene). The band (ϵ ~3000) is undoubtedly a charge-transfer band such as is typically found in other Diarsine complexes.[4] The agreement between the reflection and the absorption spectra of $TiCl_4$,Diarsine indicates that this is also the species absorbing in solution. The spectra of the bromide are rather more complex, but the same general situation prevails. The lowest-energy band of $TiBr_4$,Diarsine occurs at 20,000 $cm.^{-1}$ in both reflection and absorption (benzene solution), although in absorption a second band is resolved at 22,500 $cm.^{-1}$ (Fig. 2). As for the chloride, the bands are shifted by ~500 $cm.^{-1}$ to lower energies on passing from non-polar to polar media. The two mono-Diarsine complexes are not isomorphous with each other or with $SnCl_4$,Diarsine (originally prepared by Allison and Mann [5]).

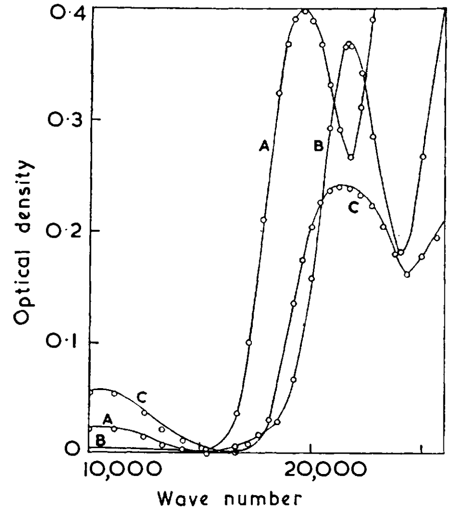

FIG. 1. Spectra of Diarsine complexes of titanium tetrachloride.

A, Reflection spectrum of $TiCl_4$,2Diarsine. B, Absorption spectrum of $TiCl_4$,2Diarsine in acetonitrile. C, Reflection spectrum of $TiCl_4$,Diarsine.

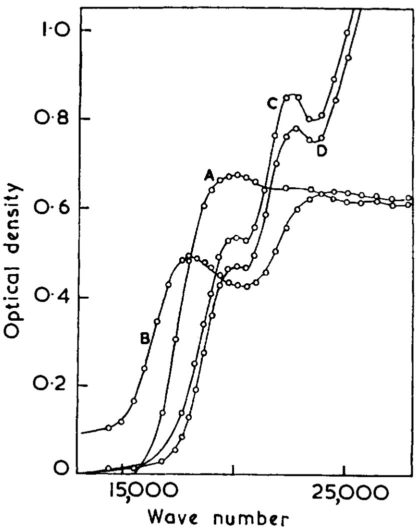

FIG. 2. Spectra of Diarsine complexes of titanium tetrabromide.

Reflection spectra of (A) $TiBr_4$,Diarsine and (B) $TiBr_4$,2Diarsine. Absorption spectra of (C) $TiBr_4$,Diarsine and (D) $TiBr_4$,2Diarsine in benzene.

Titanium tetrachloride reacts with an excess of Diarsine in an inert solvent, a red compound being precipitated; analytical data for this compound correspond with the formula $TiCl_4$,2Diarsine. The compound is diamagnetic and therefore contains Ti^{IV}. The strong infrared bands at 884, 846 (CH_3 rocking modes), and 741 $cm.^{-1}$ (CH deformation mode) [6] of the free Diarsine are absent from the infrared spectrum of the complex, but corresponding bands some 20 $cm.^{-1}$ to higher frequencies are present (Table 2). This frequency shift is characteristic of the chelated Diarsine molecule, but not of the molecule when it functions as a monodentate ligand. For the monoquaternary salt, o-$AsMe_2{\cdot}C_6H_4{\cdot}AsMe_3{}^+Cl^-$, the infrared bands in this region can be correlated with the presence of both tertiary and quaternary arsenic (*e.g.*, bands at both 762 and 744 $cm.^{-1}$

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[4] Dunn, Nyholm, and Yamada, *J.*, 1962, 1564.
[5] Allison and Mann, *J.*, 1949, 2915.
[6] Bellamy, " The Infra-Red Spectra of Complex Molecules," Methuen, London, 1958, p. 65.

Table 2.

Infrared frequencies (900—700 cm.$^{-1}$), for Nujol mulls.

$TiCl_4$,2Diarsine	898	861	757	$HfCl_4$,2Diarsine	904	864	759
VCl_4,2Diarsine	904	869	761	$TiBr_4$,2Diarsine	899	863	754
$ZrCl_4$,2Diarsine	903	864	759	Diarsine	884	846	741

occur). We conclude that all four arsenic atoms of $TiCl_4$,2Diarsine are bound to the metal atom. The reflection spectrum of the powdered solid shows a single peak at 19,600 cm.$^{-1}$ (Fig. 1). A nitrobenzene solution of the complex is non-conducting, indicating the absence of ionic chloride in solution and thus eliminating other possible structures such as $[TiCl_2,(\text{Diarsine})_2]^{2+}2Cl^-$.

The absorption spectrum of the compound shows a single peak at 21,600 cm.$^{-1}$ in polar solvents (*e.g.*, nitrobenzene) and at 22,300 cm.$^{-1}$ in benzene, *i.e.*, at frequencies identical with those of $TiCl_4$,Diarsine. We interpret this to mean that the bis-Diarsine complex dissolves by virtue of its dissociation into the mono-Diarsine complex and free Diarsine. The latter cannot be detected directly by physical methods. The lability of the second Diarsine molecule is demonstrated by the following interconversions which proceed quantitatively:

$$TiCl_4,\text{Diarsine} + (\text{excess})\ \text{Diarsine} \longrightarrow TiCl_4,2\text{Diarsine}$$

$$TiCl_4,2\text{Diarsine} + (\text{excess})\ TiCl_4 \longrightarrow 2TiCl_4,\text{Diarsine}$$

Titanium tetrabromide also reacts with excess of Diarsine, to form the brown complex $TiBr_4$,2Diarsine. It is diamagnetic and isomorphous with $TiCl_4$,2Diarsine and its infrared spectrum is almost identical with that of the latter. The lowest-energy band of its reflection spectrum (Fig. 2) occurs at 17,900 cm.$^{-1}$, but its absorption spectrum in benzene solution is identical with that of $TiBr_4$,Diarsine. This result is interpreted to mean that $TiBr_4$,2Diarsine dissolves by dissociating into $TiBr_4$,Diarsine and free Diarsine. A nitrobenzene solution of the complex is non-conducting. The bromo-complexes are interconvertible in the same manner as the chloro-complexes.

Furthermore, zirconium and hafnium tetrachlorides (in acetone solutions) and vanadium tetrachloride (in carbon tetrachloride) each react almost immediately with the Diarsine, to precipitate insoluble bis-Diarsine complexes, which are isomorphous with the titanium analogues TiX_4,2Diarsine. The infrared spectra of all five bis-Diarsine complexes are almost identical (Table 2), and their densities vary in the manner expected for an isomorphous series (Table 1). The zirconium and hafnium complexes are diamagnetic; the vanadium complex has a magnetic moment of 1·74 B.M. as expected for a d^1-complex. Physical measurements on solutions of these complexes were not possible owing to the extremely low solubilities. Attempts to prepare mono-Diarsine derivatives of these halides were unsuccessful. This is perhaps significant, for if they exist, one would expect the bis-Diarsine derivatives of these halides to be rendered soluble by the same dissociation mechanism as that employed by the titanium complexes. The reflection spectrum of VCl_4,2Diarsine is shown in Fig. 3. The splitting of the *d*-electron orbital levels of metal ions by a strong dodecahedral crystal field has been given by Griffiths *et al.*[7] It is possible that the weak band at 13,250 cm.$^{-1}$ in Fig. 3 is a ligand field band of V^{IV}.

Single crystals of $TiCl_4$,2Diarsine have been examined by P. Pauling and G. B. Robertson by *X*-ray diffraction methods and the results will be published separately in detail. They unequivocally demonstrate that the co-ordination polyhedron around the titanium atom is a dodecahedron, with eight vertices, consisting of four equivalent arsenic atoms and four equivalent chlorine atoms (Fig. 4). The point symmetry of the titanium atoms is $\bar{4}2m$, with all the atoms in the molecule except the methyl groups lying on mirror planes. The titanium–arsenic distance is 2·71 ± 0·02 Å, the bonds being at 36·3° ± 0·2° to the tetragonal axis. The titanium–chlorine distance is 2·46 ± 0·02 Å, these bonds being

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[7] Griffiths, Owen, and Ward, *Proc. Roy. Soc.*, 1953, *A*, **219**, 526.

at 72·8° ± 0·3° to the tetragonal axis. The compound has the same molecular symmetry as the $[Mo(CN)_8]^{4-}$ ion in the solid state,[8] *i.e.*, that predicted by Racah [9] for d^4sp^3-hybridization. {Note, however, that the Raman spectrum of an aqueous solution of $K_4Mo(CN)_8$ has been interpreted to imply that in solution the symmetry of the $[Mo(CN)_8]^{4-}$ ion is raised to D_{4d}.[10]} For this scheme, the sum of the bond strengths reaches a maximum when the eight bonds are split into two sets of four, the first set making an angle of 34° 33′ with the tetragonal axis (strength 2·995) and the second set of 72°47′ with this axis (strength 2·968). The $TiCl_4$ tetrahedron obviously fits the second set of hybrid orbitals. The arsenic–titanium tetragonal-axis angle is 1·8° greater than that strictly demanded by the first set of hybrid orbitals. However, the carbon–carbon–arsenic angle (117°) is 3° less than the ideal trigonal angle. Hence the arsenic–arsenic distance is a compromise between that demanded by the d^4sp^3- and by the sp^2-hybridization schemes.

The reaction between an acetic acid solution of $TiCl_3,6H_2O$ and the Diarsine has been reported [2] to yield the complex $[TiCl_3,Diarsine,H_2O]$. We have repeated the above preparation but our infrared, *X*-ray, analytical, and magnetic results indicate that we have obtained only $TiCl_4$,2Diarsine as product.

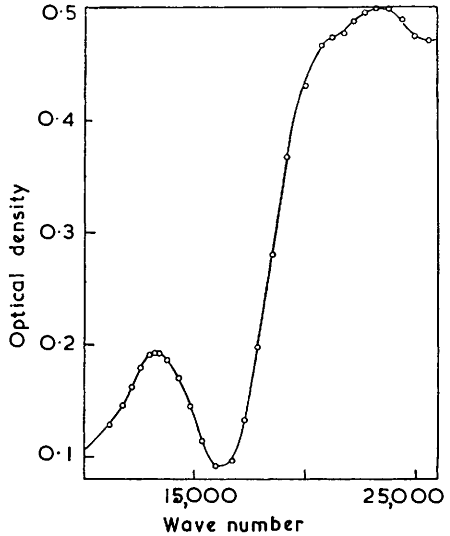

FIG. 3. Reflection spectrum of VCl_4,2Diarsine.

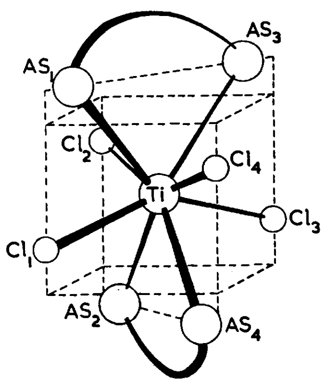

FIG. 4. Structure of $TiCl_4$,2Diarsine. (The phenyl rings are represented diagrammatically.)

$\angle Cl_1TiCl_3 = \angle Cl_2TiCl_4 = 145·6°$.
$\angle As_1TiAs_3 = \angle As_2TiAs_4 = 72·6°$.

There is no indication of reaction between silicon, germanium, or thorium tetrachlorides with the Diarsine. Stannic chloride which is known to form a 1 : 1 adduct with the Diarsine [5] does not appear to add a further molecule of the ligand.

Discussion.—Theoretical calculations have indicated that in the $[Mo(CN)_8]^{4-}$ ion the d_{xy}-orbital is considerably more stable than any other *d*-orbital. The diamagnetism of such d^2-complexes can be understood by assuming that the two *d*-electrons are paired in this orbital. It is apparent that only d^0-, d^1-, or d^2-configurations could give rise to the d^4sp^3-hybridization scheme, *e.g.*, the zirconium and hafnium atoms in K_2ZrF_6, K_2HfF_6 (ZrF_8 and HfF_8 units, respectively [11]), and the cerium atom in cerium tetrakisdibenzoylmethane.[12] The occurrence of the dodecahedral structure with Group IVa and Group Va elements is therefore not surprising, except that a co-ordination number of eight has not

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[8] Hoard and Nordsieck, *J. Amer. Chem. Soc.*, 1939, **61**, 2853.
[9] Racah, *J. Chem. Phys.*, 1943, **11**, 214.
[10] Stammreich and Sala, *Z. Elektrochem.*, 1960, **64**, 741.
[11] Bode and Tenfer, *Acta Cryst.*, 1956, **9**, 929.
[12] Wolf and Bärneghausen, *Acta Cryst.*, 1960, **13**, 778.

previously been reported for first-row transition elements. These had been considered to be too small to form effective bonds with eight atoms, but it is evident that the steric effects of this co-ordination number are not necessarily forbidding. It is worth noting that recently the structures of ethylenediaminetetra-acetatoaquoferrate(III)[13] and of an ethylenediaminetetra-acetato-complex of manganese(II)[14] have been determined, and are considered to contain seven-co-ordinate iron(III) and seven-co-ordinate manganese(II), respectively. The observed bond lengths, Ti–Cl = 2·46 Å and Ti–As = 2·71 Å, are rather longer than those expected[15] for d^2sp^3-hybridization (2·35 Å, 2·54 Å, respectively), indicating that the radius of the titanium atom in this higher co-ordination number is, as expected, closer to that in the metal (1·44 Å)[15] than to the octahedral radius (1·35 Å).

The eight donor atoms form two inter-penetrating tetrahedra, one flattened and one elongated about the four-fold axis. The former set (the chlorine atoms of MCl_4,2Diarsine) are in positions which are potentially double-bonding (*e.g.*, by π-electron donation to the empty d_{xy}-orbital on the metal). The arsenic atoms, which on the other hand are good π-electron acceptors, might have been expected to occupy these positions if the d_{xy}-orbital had been fully occupied.[16] However, it transpires that the geometry of the Diarsine molecule, and in particular, the arsenic–arsenic distance, is incompatible with that demanded by the flattened tetrahedron but compatible with that of the elongated tetrahedron (Found, 3·21 Å).

EXPERIMENTAL

All operations were carried out under highly purified nitrogen, with solvents that had been freshly distilled from suitable dehydrating agents. Metals were determined by ignition of the hydrolyzed compound to the oxide. Halogens were determined potentiometrically after destruction of the organic matter in the compound by alkali fusion. Solutions for absorption spectra and conductivity measurements were made up by breaking a tared ampoule of the complex into a cell containing a known volume of the anhydrous solvent held under nitrogen. The samples for the reflection spectral measurements were made up in a dry box by grinding the complex with a suitable amount of magnesium carbonate (a perfect reflector of visible radiation), and the spectra were recorded by using the diffuse-reflection attachment to the S.P. 500 Unicam spectrophotometer. Once prepared, the complexes were stored in glass manifolds under a vacuum to prevent hydrolysis.

Tetrachloro-(o*-phenylenebisdimethylarsine*)*titanium*(IV).—The diarsine was added to a solution of titanium tetrachloride in carbon tetrachloride up to a 1 : 1 mole ratio. The yellow-orange *complex* which was precipitated immediately could be recrystallized from benzene; it had m. p. 210° (decomp.) (Found: C, 25·1; H, 3·6; As, 31·3; Cl, 30·0; Ti, 10·1. $C_{10}H_{16}As_2Cl_4Ti$ requires C, 25·2; H, 3·4; As, 31·5; Cl, 29·8; Ti, 10·0%).

Tetrabromo-(o*-phenylenebisdimethylarsine*)*titanium*(IV).—The same procedure was used, with titanium tetrabromide instead of tetrachloride. The *product* had m. p. 176—179° (Found: C, 18·1; H, 2·7; As, 22·7; Br, 49·1; Ti, 7·4. $C_{10}H_{16}As_2Br_4Ti$ requires C, 18·4; H, 2·5; As, 22·9; Br, 48·9; Ti, 7·3%).

Tetrachlorodi-(o*-phenylenebisdimethylarsine*)*titanium*(IV).—Diarsine in excess of the 2 : 1 mole ratio was added to a solution of titanium tetrachloride in benzene. The slightly soluble orange-red precipitate, when recrystallized from benzene, had m. p. 174° (Found: C, 31·7; H, 4·2; As, 38·8; Cl, 18·6; Ti, 6·3. $C_{20}H_{32}As_4Cl_4Ti$ requires C, 31·5; H, 4·2; As, 39·3; Cl, 18·6; Ti, 6·3%). The same *compound* is obtained in about 50% yield by addition of the Diarsine to a solution of titanium trichloride in acetic acid.

Tetrabromodi-(o*-phenylenebisdimethylarsine*)*titanium*(IV).—This *compound,* prepared by the above procedure by substituting titanium tetrabromide for the tetrachloride, had m. p. 166—170° (decomp.) (Found: C, 26·0; H, 3·4; As, 31·4; Ti, 5·1. $C_{20}H_{32}As_4Br_4Ti$ requires C, 25·6; H, 3·4; As, 31·9; Ti, 5·1%).

Tetrachlorodi-(o*-phenylenebisdimethylarsine*)*vanadium*(IV).—Diarsine in excess of the 2 : 1 mole ratio was added to a solution of vanadium tetrachloride in carbon tetrachloride. The

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[13] Hoard, Lind, and Silverton, *J. Amer. Chem. Soc.*, 1961, **83**, 2770.

[14] Hoard, Pedersen, Richards, and Silverton, *J. Amer. Chem. Soc.*, 1961, **83**, 3533.

[15] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1960, pp. 403, 410.

[16] Orgel, *J. Inorg. Nuclear Chem.*, 1960, **14**, 136.

orange, precipitated *complex* was washed with fresh carbon tetrachloride, then having m. p. 134° (decomp.) (Found: C, 31·4; H, 4·4; As, 39·2; Cl, 18·2; V, 6·7. $C_{20}H_{32}As_4Cl_4V$ requires C, 31·4; H, 4·2; As, 39·2; Cl, 18·5; V, 6·7%).

Tetrachlorodi-(o-*phenylenebisdimethylarsine*)*zirconium*(IV).—Diarsine at a 2 : 1 mole ratio was added to a solution of zirconium tetrachloride in acetone. The white *complex* that was precipitated was washed with acetone before being dried in a vacuum. It decomposed from ~290° (Found: C, 30·1; H, 4·1; As, 37·2; Cl, 17·3; Zr, 11·5. $C_{20}H_{32}As_4Cl_4Zr$ requires C, 29·8; H, 4·0; As, 37·2; Cl, 17·6; Zr, 11·3%).

Tetrachlorodi-(o-*phenylenebisdimethylarsine*)*hafnium*(IV).—Hafnium tetrachloride was substituted for zirconium tetrachloride in the above preparation. The *product* decomposed from ~284° (Found: C, 26·5; H, 3·7; As, 33·9; Cl, 15·6; Hf, 20·0. $C_{20}H_{32}As_4Cl_4Hf$ requires C, 26·9; H, 3·6; As, 33·6; Cl, 15·9; Hf, 20·0%).

We are indebted to British Titan Products Ltd. for financial support (to R. J. H. C.) and to Magnesium Electron Ltd. for a sample of hafnium tetrachloride.

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[*Received, January* 16*th*, 1962.]