1054. *Complexes of Titanium, Vanadium, and Tin Tetrahalides with the Ligand* o-*Phenylenebisdiethylarsine*

By R. J. H. Clark

Titanium tetrachloride and tetrabromide, vanadium tetrachloride, and tin tetrachloride and tetrabromide react with the bidentate arsine, *o*-phenylenebisdiethylarsine (L), to yield six-co-ordinate adducts of the type MX_4,L. The physical properties, electronic and infrared spectra (4000—200 cm.$^{-1}$), and magnetism of the complexes are reported. Reaction of the complexes with excess of ligand failed to yield eight-co-ordinate adducts MCl_4,2L, such as are formed with the corresponding methylarsine. Reasons for the difference in behaviour of the two arsines are discussed.

Since the syntheses of the first eight-co-ordinate derivatives of titanium and vanadium tetrahalides [1,2] with the bidentate arsine, *o*-phenylenebisdimethylarsine [3] (I), many other bidentate ligands have been made to react with these halides. All such ligands, which include bidentate nitrogen-,[4] phosphorus-,[5] oxygen- and sulphur-donor [6] ligands have

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[1] R. J. H. Clark, J. Lewis, R. S. Nyholm, P. J. Pauling, and G. B. Robertson, *Nature*, 1961, **192**, 222.

[2] R. J. H. Clark, J. Lewis, and R. S. Nyholm, *J.*, 1962, 2460.

[3] J. Chatt and F. G. Mann, *J.*, 1939, 610.

[4] R. J. H. Clark, *J.*, 1963, 1377.

[5] J. Chatt and R. G. Hayter, *J.*, 1963, 1343.

[6] R. J. H. Clark, W. Errington, and R. S. Nyholm, *Inorg. Chem.*, to be published.

yielded six-co-ordinate complexes of the type MX_4L but no eight-co-ordinate complexes. In view of the apparent peculiarity of the original arsine towards stabilisation of eight-co-ordinated metal complexes, the corresponding ethylarsine [7] (II) has been synthesised

$C_6H_4(AsMe_2)_2$-o (I) $C_6H_4(AsEt_2)_2$-o (II) $C_6H_4(PEt_2)_2$-o (III)

and treated with titanium and tin tetrachlorides and tetrabromides and also with vanadium tetrachloride. The effect of the alkyl groups on the donor properties of the two arsines can thereby be investigated, and futhermore a direct qualitative comparison of the donor properties of the ligand (II) with those of the corresponding phosphine (III) [5] can be drawn by using the metal tetrahalides as probes.

RESULTS

The ligand (II) (L) reacts immediately in an inert solvent with titanium and tin tetrachlorides and tetrabromides and also with vanadium tetrachloride to yield 1 : 1 adducts of the type MCl_4,L. The adducts are all readily hydrolysed in moist air, especially the vanadium derivative for which special handling techniques are required. The adducts are all non-electrolytes in nitrobenzene solution, the small residual conductance being attributed to traces of hydrolysis in solution. The methiodide and ethiodide of ligand (II) have also been synthesised, and both these derivatives behave as 1–1 electrolytes in nitrobenzene solutions ($\Lambda \sim 26$ cm.^{2} ohm^{-1} mole^{-1}). These data, together with the magnetic properties of the complexes, are summarised in Table 1.

TABLE 1

Complexes of *o*-phenylenebisdiethylarsine (L)

		Molar conductivity *		Magnetism †	
Compound	Colour	Λ cm.^{2} ohm^{-1} mole^{-1}	Concn. 10^{-3}M)	$10^6\chi_g$. (c.g.s.u.)	$\mu_{eff.}$ (B.M.)
$TiCl_4$,L	Red	0·65	4·10	−0·534	0·0
$TiBr_4$,L	Maroon	2·2	2·24	−0·431	0·2
VCl_4,L	Brown-black	3·2	8·36	1·90	1·76 ‡
$SnCl_4$,L	White	2·4	4·45	−0·588	0·0
$SnBr_4$,L	Pale yellow	2·6	8·50	−0·511	0·0
CH_3I,L	Very pale yellow	25·5	3·86	—	—
C_2H_5I,L	Very pale yellow	26·9	3·84	—	—

* In nitrobenzene at 20°. † Diamagnetic correction for the ligand is taken as 197 c.g.s.u. ‡ Owing to difficulties in packing this compound in a Gouy tube, the magnetic moment is only accurate to ~0·1 B.M.

The titanium and tin derivatives are diamagnetic, as expected for d^0 and d^{10} complexes, respectively, whereas the vanadium derivative has a magnetic moment corresponding to the presence of one unpaired *d*-electron per vanadium atom.

The proton n.m.r. spectrum of the complex $TiCl_4$,L in dichloromethane solutions indicates an appreciable modification of the CH, CH_2, and CH_3 chemical shifts of the ligand on co-ordination, and since only one type of CH, CH_2, and CH_3 group is present in the complex, the ligand must be bidentate. The complex is thus a six-co-ordinate monomer, and this conclusion is supported by the comparatively high solubility of the compound in organic solvents and the lack of any evidence for bridging TiCl stretching frequencies in the infrared spectrum of the compound (see below). As the infrared spectra (4000—400 cm.$^{-1}$) of all the complexes are virtually identical with the spectrum of the complex $TiCl_4$,L (see below), it is concluded that all the complexes are six-co-ordinate monomers.

The complexes MX_4,L are not isomorphous with one another, nor with the corresponding complexes [2,3] of the methylarsine (I). Unfortunately a satisfactory *X*-ray powder photograph of the complex VCl_4,L could not be obtained as the complex is almost amorphous. It becomes green in air owing to the formation of the vanadyl species but the hydrolysis does not appear to halt at the stage $VOCl_2$,L in the way that has been outlined for the adducts of vanadium tetrachloride with 2,2′-bipyridyl and *o*-phenanthroline.[4]

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[7] W. Cochran, F. A. Hart, and F. G. Mann, *J.*, 1957, 2816.

TABLE 2

Proton n.m.r. results (τ av) *

	$C_6H_4(AsEt_2)_2$	$TiCl_4,C_6H_4(AsEt_2)_2$
Aromatic CH	2·47	2·13
CH_2	8·28	7·52
CH_3	8·88	8·55

* Chemical shifts are relative to tetramethylsilane, in p.p.m., for dichloromethane solutions at ~0·2M.

TABLE 3

Absorption spectra of titanium complexes in CCl_4 solutions

Compound	Absorption peak (cm.$^{-1}$)	ε	Compound	Absorption peak (cm.$^{-1}$)	ε
$TiCl_4$,L *	21,900	3300	$TiBr_4$,L † ...	19,950	4100
	27,000	3400		23,100	5900
	35,200	~7000		26,900	6800
				31,600	~14,000

* $TiCl_4$,D has a band [2] at 22,200 cm.$^{-1}$ in benzene (ε ~3000). † $TiBr_4$,D has bands [2] at 20,000 and 22,500 cm.$^{-1}$ in benzene solutions.

L = *o*-Phenylenebisdiethylarsine. D = *o*-Phenylenebisdimethylarsine.

Electronic Spectra and Diffuse Reflectance Spectra.—The solution spectra of the titanium derivatives were recorded in carbon tetrachloride in which the complexes are slightly soluble. The band maxima and extinction coefficients are listed in Table 3. The extinction coefficients are high (3000—14,000), and the bands thus correspond to change-transfer transitions from filled molecular orbitals essentially located on the ligands to the lowest unoccupied orbitals (the metal *d*-orbitals). The absorption bands suffer slight solvents shifts ~500 cm.$^{-1}$ to lower frequencies in more polar solvents than carbon tetrachloride, *e.g.*, in dichloromethane and nitrobenzene, and the intensities of the low-frequency bands in these solvents are lowered relative to the high-frequency transitions. The diffuse reflectance spectra of the powdered solids have also been recorded, but owing to the high intensities of the transitions involved and the consequent difficulties in the removal of the specular component to the reflected radiation,[8] the resolution of the bands are poor. However, they have the same general appearance as the solution spectra apart from a shift of 900—1600 cm.$^{-1}$ to lower frequencies compared with their positions in carbon tetrachloride solutions. Thus the same chemical species (*i.e.*, the six-co-ordinate monomer) are believed to exist in both solution and the solid state.

The positions of the absorption bands are within 600 cm.$^{-1}$ of the corresponding peaks in the absorption spectra of the analogous complexes of the methyldiarsine (I). Furthermore, the extinction coefficients of corresponding bands in the spectra of analogous complexes of both diarsines are very similar (Table 3).

The complex VCl_4L is not sufficiently stable in solution for reliable electronic spectra to be recorded, but the diffuse reflectance spectrum has bands at 14,700m, 18,750m, and 21,550s cm.$^{-1}$. Presumably both charge-transfer and ligand-field spectra are overlapping in the 20,000 cm.$^{-1}$ region, and no estimate of 10*Dq* is thus possible.

The tin derivatives also have very similar colours to those of the corresponding derivatives of the methylarsine (II).

Infrared Spectra.—The infrared spectra of all the complexes have been recorded in the 4000—200 cm.$^{-1}$ region. The spectra of the complexes above 800 cm.$^{-1}$ are virtually identical with one another; the data below 800 cm.$^{-1}$ are given in Table 4. It is clear that the out-of-plane CH deformation mode of the free ligand is split on co-ordination in rather a complicated manner. The metal-halogen stretching frequencies are clearly evident below 400 cm.$^{-1}$, the frequencies in each case being characteristic of six-co-ordinate metal complexes.[9]

The ratio $\nu(MBr)/\nu(MCl)$ for a given metal is also consistent with previous findings.[10]

Reactions with Excess of Ligands (I) *and* (II).—In order to investigate the possibility that the ethylarsine (II) raises the co-ordination number of titanium and vanadium to eight in the

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[8] R. J. H. Clark, *J. Chem. Educ.*, 1964, **41**, 488.

[9] R. J. H. Clark, Symposium in Inorganic Chemistry, Bratislava, Czechoslavakia, Sept. 2, 1964; *Spectrochim. Acta*, 1965, **21**, 955; I. R. Beattie, G. P. McQuillan, L. Rule, and M. Webster, *J.*, 1963, 1514.

[10] R. J. H. Clark and T. M. Dunn, *J.*, 1963, 1198; M. A. Bennett and R. J. H. Clark, *Chem. and Ind.*, 1963, 861; *J.*, 1964, 5560.

TABLE 4

Infrared spectra (800—200 cm.$^{-1}$) of relevant complexes

	ν(CH) out of plane ring vibration							ν(MX)		
$C_6H_4(AsEt_2)_2$	—	—	745vs	563m	550w	437m	354m	—	—	—
$TiCl_4,C_6H_4(AsEt_2)_2$	764s	760sh	736vs	575m	552wm	438wm	393m	364vs		
$TiBr_4,C_6H_4(AsEt_2)_2$	757s		737vs	578m	559w	445m	381w	313s	291w	275s
$VCl_4,C_6H_4(AsEt_2)_2$	787m	758m	734vs	578m	555w	439wm	392w	348vs	278w	
$SnCl_4,C_6H_4(AsEt_2)_2$	762s		739vs	584m	557w	440m	377w	322m	303s	
$SnBr_4,C_6H_4(AsEt_2)_2$	763s	745sh	739s	585m	558w	441m	379w	209s		

same manner as is known to occur for the methylarsine (I), reactions of the complexes $TiCl_4$,L, $TiBr_4$,L and VCl_4,L with excess of the ligand under a variety of conditions have been investigated. However, in no circumstances was another molecule of the ligand attached to a six-co-ordinate complex. This is particularly surprising in the case of the vanadium adduct, because with the methylarsine (I), (D), the *only* product of its reaction with vanadium tetrachloride is the eight-co-ordinate derivative [2] VCl_4,2D—all attempts to prepare a six-co-ordinate species VCl_4,D being unsuccessful. Thus a remarkable difference in behaviour of the two ligands is apparent.

There remained the possibility that the complex $TiCl_4$,L may add a molecule of the methylarsine (D) to form an eight-co-ordinate derivative $TiCl_4$,L,D. However, the product of this reaction was the eight-co-ordinate derivative $TiCl_4$,2D, *i.e.*, not only does the methylarsine co-ordinate to the complex $TiCl_4$,L but it completely displaces the ethyl ligand in favour of the insoluble $TiCl_4$,2D. An exactly analogous reaction takes place with the bromo-complex, *i.e.*,

$$TiBr_4,L + D(excess) \longrightarrow TiBr_4,2D + L$$

These results seem to indicate that the methylarsine forms stronger complexes with metal halides than does the ethylarsine.

DISCUSSION

Considerations of molecular models of ligands (I) and (II) suggest that there would be little if any more steric hindrance in a bisadduct of the ethylarsine with titanium tetrachloride than in the corresponding (known) adduct of the methylarsine. However, loss of free rotation about the arsenic–carbon bonds could be an important factor. Hence, while steric effects cannot be completely excluded, it may be that the difference in behaviour of the two arsines is electronic in origin, *i.e.*, the methyl groups on the arsenic atoms render their lone pairs of electrons more available for formation of σ-bonds with electron-acceptor molecules than is the case with ethyl groups. This is an important result, because it suggests that the ethylphosphine (III), which evidently only forms a six-co-ordinate adduct with titanium tetrachloride,[5] may do so not because tertiary phosphines are intrinsically poorer ligands to titanium than tertiary arsines, but because the different alkyl groups on the donor atoms significantly affect the donor properties of the ligand.

Further investigations on the reactions of closely related ligands with metal tetrahalides are in progress.

EXPERIMENTAL

Spectra.—Electronic spectra were recorded on a Unicam S.P. 500 spectrophotometer, 1 cm. silica cells being used. Diffuse reflectance spectra were recorded by using the standard attachment to the above instrument, and magnesium carbonate as reference reflector. Infra-red spectra were recorded on Grubb–Parsons double-beam grating spectrophotometers, type GS2A for the region 4000—400 cm.$^{-1}$ and type DM2 for the region 455—200 cm.$^{-1}$. The region 4000—400 cm.$^{-1}$ was also scanned on a Perkin-Elmer 337 instrument. The compounds were made into mulls with both hexachlorobutadiene and Nujol and the mulls supported between sodium chloride, potassium bromide, and Polythene plates for the appropriate frequency regions.

Magnetic Measurements.—The magnetic susceptibilities of the complexes were determined by the Gouy method using a permanent magnet of ~7000 gauss. The Gouy tube was calibrated against mercury cobalt thiocyanate.

Conductivity.—The equivalent conductances of the complexes were determined by breaking a tared ampoule of the solid, under nitrogen, into a glass apparatus containing the anhydrous and deoxygenated solvent. The electrodes were incorporated in the apparatus.

Powder Photographs.—*X*-Ray powder photographs were taken with a Phillips Debye-Scherrer camera of 114·8 mm. diameter and copper-K_α-radiation with a nickel filter. The complexes were sealed in Lindemann glass capillaries.

Synthesis of Ligand.—The ligand *o*-phenylenebisdiethylarsine was synthesised by addition of ethylmagnesium iodide [Mg (7·9 g.) in diethyl ether (150 ml.) and ethyl iodide (50 g.)], to a solution of *o*-phenylenebisdichloroarsine [30 g. in diethyl ether (100 ml.)], in moisture- and oxygen-free conditions. The complex was hydrolysed with ammonium chloride (60 g.) in water (200 ml.) with ice-cooling and stirring. The upper (ether) layer was collected, dried over a molecular sieve, and distilled. The required ligand, b. p. 116—118°/0·3 mm. (lit.,[7] 116·5—117°/0·3 mm.), is colourless with an odour resembling that of the analogous methyl arsine.

Preparation of Compounds.—British Oxygen Company's "white spot" nitrogen was deoxygenated by being passed through an activated copper column at 280° and dehydrated by being passed through a three-feet-long column containing molecular sieves. All operations were carried out in an all-glass vacuum system, and this purified nitrogen used.

The compounds were prepared by dissolving the appropriate halide (~1 g.) in an inert solvent (usually carbon tetrachloride, ~25 ml.) and adding the ligand, in slight excess, to this solution. The complexes, which were precipitated immediately and quantitatively, were filtered off under nitrogen and dried in vacuum. When dry, the complexes were sealed in glass manifolds under vacuum.

The compounds are appreciably more soluble in organic solvents than the corresponding adducts of the methylarsine (I).

Analyses.—Metals were determined by ignition to the oxides or by oxidation-reduction titrations. The halogen was determined by the Carius method, and the carbon, hydrogen, and arsenic analyses were determined at the Max Planck Institut für Kohlenforschung, Mulheim, Germany.

Results were as follows:

Tetrachloro-(o-*phenylenebisdiethylarsine*)*titanium*(IV). The diarsine was added to a solution of titanium tetrachloride in carbon tetrachloride solution. The red *complex* precipitated immediately, had m. p. 160—165° (Found: C, 31·9; H, 5·0; As, 28·3; Cl, 26·7; Ti, 9·1. $C_{14}H_{24}As_2Cl_4Ti$ requires C, 31·6; H, 4·6; As, 28·2; Cl, 26·7; Ti, 9·0%).

Tetrabromo-(o-*phenylenebisdiethylarsine*)*titanium*(IV). Similarly prepared, this maroon *complex* had m. p. 165—170° preceded by some preliminary darkening (Found: C, 23·7; H, 3·4; As, 21·3; Br, 45·0; Ti, 6·8. $C_{14}H_{24}As_2Br_4Ti$ requires C, 23·7; H, 3·4; As, 21·1; Br, 45·0; Ti, 6·7%).

Tetrachloro-(o-*phenylenebisdiethylarsine*)*vanadium*(IV). When this *complex* was similarly prepared, extreme care was taken to avoid the formation of vanadyl complexes (Found: C, 32·1; H, 4·5; As, 29·8; Cl, 27·3; V, 9·5. $C_{14}H_{24}As_2Cl_4V$ requires C, 31·4; H, 4·5; As, 28·0; Cl, 26·5; V, 9·5%).

Tetrachloro-(o-*phenylenebisdiethylarsine*)*tin*(IV). Addition of the diarsine to a solution of stannic chloride in carbon tetrachloride resulted in immediate precipitation of a white *complex*, m. p. 203—206° (decomp.) with some preliminary darkening (Found: C, 28·0; H, 3·8; As, 24·8; Cl, 23·5; Sn, 19·6. $C_{14}H_{24}As_2Cl_4Sn$ requires C, 27·9; H, 4·0; As, 24·9; Cl, 23·5; Sn, 19·7%).

Tetrabromo-(o-*phenylenebisdiethylarsine*)*tin*(IV). Owing to the low solubility of tin tetrabromide in non-polar solvents, the reaction of this halide was carried out at 40°, *i.e.*, above the melting point of the halide (31°); the *product* had m. p. 174—180° (decomp.) with preliminary softening (Found: C, 21·7; H, 3·1; As, 19·1; Br, 41·1; Sn, 14·1. $C_{14}H_{24}As_2Br_4Sn$ requires C, 21·5; H, 3·1; As, 19·2; Br, 40·9; Sn, 15·2%).

Methyl iodide derivative of o-*phenylenebisdiethylarsine*. The ligand was added to methyl iodide and the excess of the latter allowed slowly to evaporate. Very pale yellow, almost colourless, *crystals* were deposited (Found: C, 37·3; H, 5·7; As, 30·7. $C_{15}H_{27}As_2I$ requires C, 37·2; H, 5·6; As, 30·9%).

Ethyl iodide derivative of o-*phenylenebisdiethylarsine*. Prepared similarly the very pale yellow crystals were deposited only after almost complete removal of the ethyl iodide (Found: C, 38·5; H, 5·9; As, 29·9. $C_{16}H_{29}As_2I$ requires C, 38·6; H, 5·9; As, 30·1%).

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William Ramsay and Ralph Forster Laboratories,
University College, London W.C.1.

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