518. *Seven Co-ordinate Complexes of Niobium*(V) *and Tantalum*(V)

By R. J. H. CLARK, D. L. KEPERT, and R. S. NYHOLM

The addition of *o*-phenylenebisdimethylarsine (Diarsine) to solutions of niobium and tantalum pentachlorides and pentabromides in dry non-hydroxylic solvents yields 1 : 1 complexes of the type MX_5,Diarsine. These compounds are isomorphous, diamagnetic, monomeric, and non-conducting, and are therefore seven co-ordinate. Water or oxygen as impurities in the solvent result in the displacement of halogen with the formation of the oxo-compounds $NbOX_3$,Diarsine and ($NbCl_4$,Diarsine)$_2$O.

FAIRBROTHER *et al.* have shown that niobium and tantalum pentachlorides and pentabromides form 1 : 1 addition compounds with diethyl ether,[1] dimethyl sulphide, and diethyl sulphide.[2] There was evidence of further solvation at low temperatures, and in one instance a 1 : 2 complex was isolated ($TaCl_5,2Me_2S$). With tetrahydrothiophen, 1 : 2 complexes were always obtained.[2] Fowles *et al.*[3] have obtained the addition compounds $TaCl_5,Et_3N$ and $NbCl_5,2Me_3N$. These compounds are very unstable to oxygen and water, and the important measurements of conductivity and molecular weight were not carried out.

We have prepared 1 : 1 addition compounds with the bidentate ligand *o*-phenylenebisdimethylarsine (Diarsine),[4] and have shown them to be monomeric non-electrolytes and therefore seven co-ordinate. Some oxo-compounds have also been prepared, where some of the chlorine has been replaced by oxygen.

Addition Compounds.—The addition of the Diarsine to dry, non-hydroxylic solutions of the pentahalides precipitates the 1 : 1 compounds, MX_5,Diarsine. The chloro-compound $NbCl_5$,Diarsine and the isomorphous $TaCl_5$,Diarsine are most conveniently precipitated

---

[1] A. Cowley, F. Fairbrother, and N. Scott, *J.*, 1958, 3133.
[2] F. Fairbrother and J. F. Nixon, *J.*, 1962, 150.
[3] G. W. A. Fowles and C. M. Pleass, *J.*, 1957; 2078; P. J. H. Carnell and G. W. A. Fowles, *J.*, 1959, 4113.
[4] J. Chatt and F. G. Mann, *J.*, 1939, 610.

from carbon tetrachloride. Niobium and tantalum pentabromides are insoluble in carbon tetrachloride, and $NbBr_5$,Diarsine and $TaBr_5$,Diarsine are most conveniently prepared by prolonged reaction of slurries in diethyl ether. They are isomorphous with the chloro-complexes. The iodo-complexes could not be prepared because of the insolubility of NbI_5 and TaI_5; in sealed tubes, NbI_5 is reduced whereas TaI_5 does not react.[5]

The compounds are diamagnetic, or virtually diamagnetic as expected for d^0 niobium(v) and tantalum(v) compounds. $NbCl_5$,Diarsine and $TaCl_5$,Diarsine are monomeric in freezing nitrobenzene.

Solutions of all these compounds in nitromethane, nitrobenzene, and acetonitrile have a significant conductivity, about half that expected for a 1 : 1 electrolyte at 10^{-3}M, and increase sharply on dilution. This conductivity could be due to either: (*a*) very weak monomeric electrolytes, for example $(NbCl_4,Diarsine)^+Cl^-$, or fairly weak electrolytes, for example $(NbCl_4,2Diarsine)^+(NbCl_6)^-$ or $(NbCl_4,Diarsine)^+(NbCl_6,Diarsine)^-$. The last two formulæ can probably be eliminated since in fairly concentrated solutions (0·01—0·03M), where the conductances are low, the compounds are monomeric. The complexes $ANbCl_6$ (A = K or Ph_4As) have been prepared and isolated, but they do not react with Diarsine under our conditions.

(*b*) Non-electrolytes, but their reaction with the solvent, or impurities in the solvent, form conducting products. The pentahalides themselves form conducting solutions in the same solvents and we have shown elsewhere[6] that this conductivity is completely due to decomposition by oxygen and water impurities in the solvent.

The conductivity of these compounds has therefore been studied in some detail and three experimental techniques have been used. The results discussed here are those for $NbCl_5$,Diarsine, although similar results have been obtained for the other analogues (see Experimental section).

(*a*) The usual and most convenient experimental procedure is to prepare the compound in the apparatus on the vacuum line, then in a nitrogen-filled dry-box, and transfer the compound to a vacuum manifold. Samples are then removed and dissolved, and the conductivity determined, all operations being carried out in the dry-box. Typical results are shown in Table 1.

TABLE 1

Conductance of $NbCl_5$,Diarsine

	Concn.	Λ (cm.^{2} ohm^{-1} mole^{-1})			Concn.	Λ (cm.^{2} ohm^{-1} mole^{-1})	
Solvent	(10^3M)	Found	Calc.*	Solvent	(10^3M)	Found	Calc.*
Nitromethane...	3·00	31	70—80	Nitrobenzene ...	1·85	10	25—35
	1·17	39	70—80		1·57	12	25—35
	1·10	37	70—80	Acetonitrile ...	1·68	58	150—200
	0·64	44	70—80		1·26	82	150—200

* For a 1 : 1 electrolyte.

(*b*) The solid sample from the manifold can be dissolved under more completely anhydrous conditions on the vacuum line and the conductivity determined as a function of concentration (Figures 1 and 2).[6] It can be seen that at low concentrations the increase in conductivity with dilution is greater than that expected for a simple electrolyte. The data obtained are similar to those for $NbCl_5$,[6] which is known to be decomposed by water impurities in the solvent.

(*c*) As both the above methods of determining the conductivity involve manipulations in the dry-box, it is possible that reaction with water or oxygen impurities occurs at this stage. The isolation of the solid phase was therefore omitted and all operations carried out on the vacuum line. The conductivity of solutions of $NbCl_5$ and Diarsine in separate compartments of a sealed all-glass apparatus was determined; the solutions were mixed and the conductivity redetermined. An experimental disadvantage with this apparatus

---

[5] R. J. H. Clark, D. L. Kepert, J. Lewis, and R. S. Nyholm, *J.*, 1965, 2865.
[6] D. L. Kepert and R. S. Nyholm, preceding Paper.

is the difficulty of adding stoicheiometric quantities of the Diarsine to the niobium pentachloride. The results are shown below.

Nitromethane as solvent:	(i)	$NbCl_5$	+ 0·95 Diarsine →	$NBCl_5$, Diarsine
Concn. (M)		$66·6 \times 10^{-3}$	0·23	$51·8 \times 10^{-3}$
Λ (cm.^{2} ohm^{-1} mole^{-1})		12·0	0·02	15·4
	(ii)	$NbCl_5$	+ 0·88 Diarsine →	$NbCl_5$, Diarsine
Concn. (M)		$22·5 \times 10^{-3}$	0·11	$19·2 \times 10^{-3}$
Λ (cm.^{2} ohm^{-1} mole^{-1})		12·4	0·04	14·5
Acetonitrile as solvent:	(i)	$NbCl_5$	+ 2·45 Diarsine →	$NbCl_5$, Diarsine
Concn. (M)		$14·4 \times 10^{-3}$	0·11	$12·2 \times 10^{-3}$
Λ (cm.^{2} ohm^{-1} mole^{-1})		65·9	2·2	72·9
	(ii)	$NbCl_5$	+ 1·02 Diarsine →	$NbCl_5$, Diarsine
Concn. (M)		$29·9 \times 10^{-3}$	0·10	$22·7 \times 10^{-3}$
Λ (cm.^{2} ohm^{-1} mole^{-1})		52·1	0·40	58·0

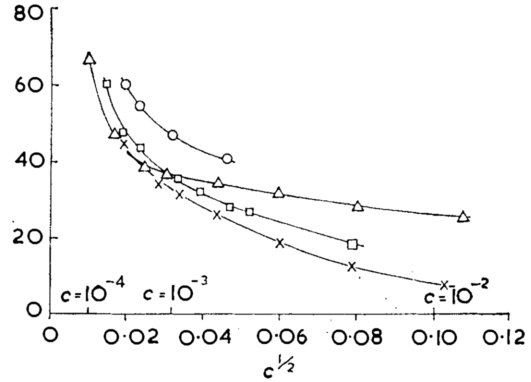

FIGURE 1. Conductance Λ (cm.^{2} ohm^{-1} mole^{-1}) of $NbCl_5$,Diarsine and $TaCl_5$,Diarsine in nitromethane as function of concentration

$NbCl_5$,Diarsine: ×, $TaCl_5$,Diarsine: ○, run 1; △, run 2; □, run 3

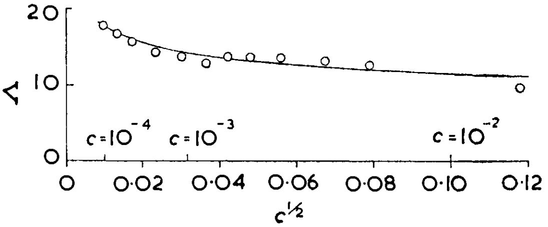

FIGURE 2. Conductance Λ (cm.^{2} ohm^{-1} mole^{-1}) of $NbCl_5$,Diarsine in nitrobenzene as function of concentration

In each case the small increase in conductivity is close to that expected simply from the dilution of the niobium pentachloride solution; that is, the addition of the Diarsine does not alter the conductivity of the niobium pentachloride. Since it has already been shown that niobium pentachloride should be regarded as a non-electrolyte in perfectly dry, oxygen-free solvents, the same can be claimed for $NbCl_5$,Diarsine.

Oxo-compounds.—Compounds in which some of the chlorine has been replaced by oxygen were invariably obtained during attempts to recrystallise $NbCl_5$,Diarsine. It was found that prolonged heating of $NbCl_5$,Diarsine solutions caused complete decomposition and produced two crystalline compounds, the less soluble $NbOCl_3$,Diarsine and the more soluble ($NbCl_4$,Diarsine)$_2$O. The $NbOBr_3$,Diarsine has similarly been obtained, and it is isomorphous with the chloro-analogue.

The diffuse reflectance spectra and solution spectra of the two oxy-chloro-compounds are virtually identical with those of $NbCl_5$,Diarsine (Table 2). The compounds are either diamagnetic or have a small temperature independent paramagnetism as expected for d^0 niobium(V) compounds.

TABLE 2

Visible spectra niobium chloride–diarsine compounds (mμ)

	Reflection	Nitromethane	Nitrobenzene	Acetonitrile
$NbCl_5$,Diarsine	496	498 ($\varepsilon = 360$)	499 ($\varepsilon = 350$)	496 ($\varepsilon = 370$)
$NbOCl_3$,Diarsine	497	497 ($\varepsilon = 410$)	497 ($\varepsilon = 420$)	497 ($\varepsilon = 390$)
$(NbCl_4$,Diarsine$)_2O$ *	500	497 ($\varepsilon = 360$)	497 ($\varepsilon = 390$)	—

* Extinction coefficients based on niobium concentration.

The infrared spectra of these compounds are also very similar, with the addition of strong absorption bands at 967 cm.$^{-1}$ for $NbOCl_3$,Diarsine (951 cm.$^{-1}$ for $NbOBr_3$,Diarsine), and at 765 cm.$^{-1}$ for $(NbCl_4$,Diarsine$)_2O$. These bands are characteristic for a Nb=O stretching frequency and a Nb–O–Nb stretching frequency, respectively, as indicated by the infrared spectra of the following compounds containing similar structural units.[7]

$NbOCl_3$	–Nb–O–Nb–	769 cm.$^{-1}$	$NbO(NO_3)_3$	Nb=O	906 cm.$^{-1}$
$K_2Cr_2O_7$	Cr–O–Cr	762 cm.$^{-1}$	$NbOF_6^{3-}$	Nb=O	922 cm.$^{-1}$
			$NbOF_5 \cdot H_2O^{2-}$ ...	Nb=O	927 cm.$^{-1}$

The molecular weight in freezing nitrobenzene shows that $NbOBr_3$,Diarsine is monomeric, and $(NbCl_4$,Diarsine$)_2O$ is also monomeric (that is, contains two niobium atoms).

The corresponding tantalum complexes could not be characterised. The easier formation of niobium oxy-compounds is one of the main chemical differences between niobium and tantalum, for example:

(i) the classical method of separation of niobium and tantalum is the formation of the more soluble fluoroxyniobates $(NbOF_5,H_2O)^{2-}$ in 2% hydrofluoric acid solutions, compared[8] with the less soluble fluorotantalates $(TaF_7)^{2-}$.

(ii) reaction of niobium and tantalum pentahalides with the higher alcohols form, for example, $NbO(OBu^t)_3$ and $Ta(OBu^t)_5$, respectively.[9]

It has been established that niobium and tantalum form the seven-co-ordinate complexes $NbCl_5$,Diarsine, $(NbCl_4$,Diarsine$)_2O$, $NbBr_5$,Diarsine, $TaCl_5$,Diarsine and $TaBr_5$,Diarsine. For this co-ordination number, there is no simple arrangement of ligands such that all nearest neighbours are at an equal distance apart, and the most notable feature is that although the structures of few compounds have been determined, a number of stereochemistries have been reported. These are:

(i) pentagonal bipyramid or " 1 : 5 : 1 " stereochemistry (symmetry D_{5h}). This structure has been reported for $K_3UO_2F_5$,[10] K_3UF_7, $(NH_4)_3ZrF_7$, $(NH_4)_3HfF_7$, and K_3ZrF_7.[11]

(ii) octahedral monopyramid or " 1 : 4 : 2 " stereochemistry (symmetry C_{2v}), can be considered to be formed if a seventh atom is placed outside a rectangular face of a distorted trigonal prism, and has been reported for K_2NbF_7 and K_2TaF_7,[12] and for $Mn_3(HY)_2,10H_2O$ (where H_4Y is ethylenediaminetetra-acetic acid), where the four atoms in the central plane are puckered.[13]

(iii) decahedron or " 1 : 3 : 3 " stereochemistry (symmetry C_{3v}), can be considered to be formed if a seventh atom is placed outside a triangular face of a distorted octahedron, and has been reported for K_3NbOF_6.[14]

(iv) enneahedron or " 4 : 3 " stereochemistry (symmetry C_s), which has been observed for $Se_2Fe_3(CO)_9$,[15] $Ph_4C_4 \cdot Fe(CO)_3$,[16] and $(Me_4C_4 \cdot NiCl_2)_2$.[17]

---

[7] B. D. Field and C. J. Hardy, *Proc. Chem. Soc.*, 1963, 11.

[8] J. C. Marignac, *Ann. Chim. Phys.*, (4), 1866, **8**, 6.

[9] D. C. Bradley, W. Wardlaw, and S. Whitley, *J.*, 1956, 1139; D. C. Bradley, B. N. Chakravarti, and W. Wardlaw, *J.*, 1956, 4439.

[10] W. H. Zachariasen, *Acta Cryst.*, 1954, **7**, 783.

[11] W. H. Zachariasen, *Acta Cryst.*, 1954, **7**, 792.

[12] J. L. Hoard, *J. Amer. Chem. Soc.*, 1939, **61**, 1252.

[13] S. Richards, B. Pederson, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, 1964, **3**, 27.

[14] M. B. Williams and J. L. Hoard, *J. Amer. Chem. Soc.*, 1942, **64**, 1139.

[15] L. F. Dahl and P. W. Sutton, *Inorg. Chem.*, 1963, **2**, 1067.

[16] R. P. Dodge and V. Schomaker, *Nature*, 1962, **186**, 798.

[17] J. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, 1962, **45**, 647.

There is not much that can be said about the stereochemistry of the Diarsine compounds at this stage, except that the more irregular structures (for example, the " 1 : 4 : 2 " stereochemistry) may be preferred, as the different ligands may be expected to take advantage of any increased stabilisation which may occur by the alteration of bond lengths (without loss of symmetry).

EXPERIMENTAL

Physical Measurements.—The starting materials and products were stored in vacuum manifolds. The preparation of complexes, and all measurements of conductance and spectra were carried out in a conventional vacuum line. " Oxygen-free " nitrogen and solvents were purified as described previously.[6] The methods used for determining conductances, magnetic susceptibilities, reflectance, and solution spectra have also been described.[6] The molecular weight of the Diarsine compounds was measured by the depression of freezing point of nitrobenzene (40—50 g.) in a specially designed apparatus on the vacuum line. The errors quoted for the determinations are based on an estimated uncertainty in the freezing point depression of 0·005°.

Halides.—Preparation and analyses for the halides have been described elsewhere.[5]

Pentachloro-(o-*phenylenebisdimethylarsine*)*niobium*(V).—Niobium pentachloride (1·51 g.) was dissolved in carbon tetrachloride (150 ml.) to give a clear yellow solution, a slight excess of Diarsine added (1·13 ml.) and the red precipitate filtered off, washed with carbon tetrachloride, and pumped dry (Found: C, 21·5; H, 3·4; As, 26·4; Cl, 31·5; Nb, 17·7. $C_{10}H_{16}As_2Cl_5Nb$ requires C, 21·6; H, 2·9; As, 26·9; Cl, 31·9; Nb, 16·7%). Identical compounds were also obtained by using diethyl ether or acetonitrile as solvents.

The magnetic susceptibility (χ) is $-0{\cdot}40 \times 10^{-6}$; therefore $\chi'_{Nb} = 30 \times 10^{-6}$ cgsu and $\mu_{eff} = 0{\cdot}3$ B.M. The compound is soluble in nitromethane, nitrobenzene, acetonitrile, and acetone, but insoluble in other common solvents. The molecular weight in freezing nitrobenzene at 0·0316M is 590 ± 20 (Calc. for monomer, 556).

Pentabromo-(o-*phenylenebisdimethylarsine*)*niobium*(V).—Niobium pentabromide (1·94 g.) was partly dissolved in hot diethyl ether (100 ml.) to give a red solution and slurry, presumably of $NbBr_5,Et_2O$. The stoicheiometric quantity of Diarsine was added (0·81 ml.) precipitating the brown complex. The slurry was kept hot with vigorous stirring for 1 hr. and then filtered; the residue was washed with ether and pumped dry (Found: C, 16·4; H, 2·7; As, 18·0; Br, 47·7; Nb, 12·3. $C_{10}H_{16}As_2Br_5Nb$ requires C, 15·4; H, 2·1; As, 19·2; Br, 51·3; Nb, 11·9%).

The magnetic susceptibility is $-0{\cdot}29 \times 10^{-6}$; therefore $\chi'_{Nb} = -70 \times 10^{-6}$ cgsu. The diffuse reflectance spectrum is complex, with shoulders at approximately 690, 550, and a peak at 504 mμ with further shoulders at lower wavelengths. In solution there are absorption peaks at approximately 515 and 545 mμ; in nitromethane and acetonitrile, $\varepsilon = 350$ and 390, respectively, and in nitrobenzene, $\varepsilon = 600$ for both peaks.

The solutions have a conductance similar to $NbCl_5$,Diarsine solutions:

Solvent	Nitromethane			Nitrobenzene		Acetonitrile
Concn. (M × 10^{-3})	5·70	3·41	1·21	1·31	1·21	1·95
Λ (cm.^{2} ohm^{-1} mole^{-1})	21	25	42	9	13	27

Pentafluoro-(o-*phenylenebisdimethylarsine*)*niobium*(V).—Niobium pentafluoride (0·39 g) was dissolved in carbon tetrachloride (200 ml.) and an excess of Diarsine added (0·52 ml.) precipitating the white complex which was filtered off, washed with carbon tetrachloride, and pumped dry. The analysis approximately corresponds to $NbO_{\frac{1}{4}}F_{4\frac{1}{2}},\frac{1}{4}Nb_2O_5$ (Found: C, 21·8; H, 3·6; As, 26·2; F, 15·3; Nb, 25·1%).

The magnetic susceptibility is $-0{\cdot}23 \times 10^{-6}$; therefore $\chi'_{Nb} = 70 \times 10^{-6}$ cgsu and $\mu_{eff} = 0{\cdot}4$ B.M. The conductivity of niobium pentafluoride as a function of concentration in nitromethane is shown:

Concn. (M × 10^{-3})	112	64·3	41·6	29·5	20·3	13·3	8·2	5·7	4·4	3·3
Λ (cm.^{2} ohm^{-1} mole^{-1})	4·2	5·4	8·2	11·9	17·5	25·6	29·3	31·5	35·7	41·2

These figures for the conductance are very similar to those obtained for niobium pentachloride in nitromethane,[6] and it therefore appears that the pentafluoride should be regarded as a non-electrolyte, but reaction with water impurities in the solvent causes some decomposition.

Determination of the conductivity of the Diarsine complex in nitromethane without isolation of the complex by the method described for the pentachloro-complex shows that NbF_5,Diarsine is also a non-electrolyte:

	NbF_5	$+$ 1·39 Diarsine $\longrightarrow$	NbF_5,Diarsine
Concn. (M)	15·7 × 10^{-3}	0·094	12·8 × 10^{-3}
Λ (cm.^{2} ohm^{-1} mole^{-1})	65·5	0·10	70·7

Trichloro-oxo-(o-*phenylenebisdimethylarsine*)*niobium*(V).—Niobium pentachloride (2·1 g.) was dissolved in nitromethane (250 ml.) and the Diarsine added (1·2 ml.). The solution was boiled and slowly cooled during several days precipitating large red crystals in low yield. The diamagnetic compound was filtered off, washed with small quantities of nitromethane, and pumped dry (Found: C, 24·1; H, 3·1; As, 28·0; Cl, 22·0; Nb, 18·5. $C_{10}H_{16}OAs_2Cl_3Nb$ requires C, 24·0; H, 3·2; As, 29·9; Cl, 21·2; Nb, 18·5%).

The solutions are significantly conducting as before:

Solvent	Nitromethane	Nitrobenzene	Acetonitrile
Concn. (M × 10^{-3})	1·03	1·49	1·49
Λ (cm.^{2} ohm^{-1} mole^{-1})	39	13	64

The molecular weight in freezing nitrobenzene shows it to be monomeric (Found: *M*, 530 ± 30 at 0·0172M; 640 ± 50 at 0·0122M. Calc.: 501).

μ-*Oxo-di-*[*tetrachloro-*o-*phenylenebisdimethylarsineniobium*(V)].—The filtrate from the preparation of $NbOCl_3$,Diarsine was evaporated to a small volume, filtered off, washed, and pumped dry (Found: C, 22·5; H, 3·3; As, 28·0; Cl, 26·8; Nb, 17·9. $C_{20}H_{32}OAs_4Cl_8Nb_2$ requires C, 22·7; H, 3·0; As, 28·3; Cl, 26·8; Nb, 17·6%).

The magnetic susceptibility is $-0·15 \times 10^{-6}$ at 290·5, 113·0, and 81·0°K; therefore $\chi'_{Nb} = 130 \times 10^{-6}$ cgsu and μ_{eff} (290·5°K) = 0·6 B.M.

The complex is soluble in the same solvents as $NbOCl_3$,Diarsine and $NbCl_5$,Diarsine, but has intermediate solubility. Similar conductometric behaviour is also shown (if the concentration is expressed as niobium concentration); Nitromethane: Concn. = 1·13 × 10^{-3}M, Λ = 42 cm.^{2} ohm^{-1} mole^{-1}, nitrobenzene: Concn. = 1·17 × 10^{-3}M, Λ = 13 cm.^{2} ohm^{-1} mole^{-1}.

The molecular weight in freezing nitrobenzene shows it to be monomeric, although at these concentrations, some decomposition is expected (Found: *M* = 1060 ± 160 at 0·00550M; 1130 ± 140 at 0·00675M; 1260 ± 120 at 0·01065M, calc. for $(NbCl_4$,Diarsine$)_2O$: 1057).

Tribromo-oxo-(o-*phenylenebisdimethylarsine*)*niobium*(V).—Niobium pentabromide (2·06 g.) was dissolved in hot acetonitrile (40 ml.) and excess of Diarsine was added (1·05 ml.); the product was filtered off, washed with small quantities of acetonitrile, and pumped dry. $NbBr_5$,Diarsine remained in the filtrate (Found: C, 19·1; H, 2·5; As, 22·5; Br, 35·4; Nb, 14·0. $C_{10}H_{16}As_2OBr_3Nb$ required C, 18·9; H, 2·5; As, 23·6; Br, 37·8; Nb, 14·6%).

The magnetic susceptibility is $-0·24 \times 10^{-6}$; therefore $\chi'_{Nb} = 110 \times 10^{-6}$ cgsu and μ_{eff} = 0·5 B.M. The diffuse reflectance spectrum is similar to that of $NbBr_5$,Diarsine, with distinct shoulders at 440, 510, and 560 mμ. The molecular weight in freezing nitrobenzene shows it to be monomeric (Found: *M*, 690 ± 70 at 0·00857M. Calc.: 635).

Pentachloro-(o-*phenylenebisdimethylarsine*)*tantalum*(V).—Tantalum pentachloride (1·73 g.) was dissolved in carbon tetrachloride (150 ml.) to give a clear solution, an excess of Diarsine added (1·65 ml.) and the yellow precipitate filtered off, washed with carbon tetrachloride, and pumped dry (Found: C, 18·4; H, 2·5; As, 20·7; Cl, 27·2; Ta, 28·7. $C_{10}H_{16}As_2Cl_5Ta$ required C, 18·6; H, 2·5; As, 23·3; Cl, 27·5; Ta, 28·1%).

The magnetic susceptibility is $-0·42 \times 10^{-6}$; therefore $\chi'_{Ta} = 20 \times 10^{-6}$ cgsu and μ_{eff} = 0·2 B.M. The diffuse reflectance spectrum shows a single band at 413 mμ, which in nitromethane is at 414 mμ (ε = 450) and in nitrobenzene is at 429 mμ (ε = 380). $TaCl_5$,Diarsine dissolves to form significantly conducting solutions. Nitromethane: Concn. = 1·14 × 10^{-3}M, Λ = 28 cm.^{2} ohm^{-1} mole^{-1}, nitrobenzene: Concn. = 1·20 × 10^{-3}M, Λ = 10 cm.^{2} ohm^{-1} mole^{-1}. Determination of the conductivity in nitromethane without isolation of the complex by the method described for the corresponding niobium complex shows that $TaCl_5$,Diarsine is a non-electrolyte.

	$TaCl_5$	$+$ 0·97 Diarsine $\longrightarrow$	$TaCl_5$,Diarsine
Concn. (M)	20·9 × 10^{-3}	0·0127	18·0 × 10^{-3}
Λ (cm.^{2} ohm^{-1} mole^{-1})	33·3	0·25	39·0

The molecular weight in freezing nitrobenzene shows the complex to be monomeric (Found: *M*, 740 ± 130 at 0·00565M; *M*, 620 ± 30 at 0·0164M; *M*, 660 ± 30 at 0·0216M. Calc. 644).

Pentabromo-(o-*phenylenebisdimethylarsine*)*tantalum*(V).—Tantalum pentabromide (1·33 g.) was partially dissolved in hot diethyl ether (200 ml.) to give a yellow solution and slurry, presumably of $TaBr_5,Et_2O$. An excess of Diarsine (0·50 ml.) was added precipitating the bright yellow complex. The slurry was kept hot, stirred vigorously for 2 hr. and then filtered; the residue was washed with ether and pumped dry (Found: C, 12·9; H, 2·6; As, 16·3; Br, 42·9. $C_{10}H_{16}As_2Br_5Ta$ requires C, 13·9; H, 1·9; As, 17·3; Br, 46·0%).

The diffuse reflectance spectrum shows a single absorption at 451 mμ, which in nitromethane and nitrobenzene is at 450 mμ (ε = 710 and 810 mμ, respectively).

The conductivity of these solutions is given: Nitromethane: Concn. = 0·76 × 10^{-3}M, Λ = 32 cm.^{2} ohm^{-1} mole^{-1}, nitrobenzene: Concn. = 0·85 × 10^{-3}M, Λ = 9 cm.^{2} ohm^{-1} mole^{-1}.

We are indebted to E. I. du Pont de Nemours and Co., who provided financial support to one of us (D. L. K.).

William Ramsey and Ralph Forster Laboratories,
University College, Gower Street, London W.C.1. [*Received, September 2nd,* 1964.]