861. *Rhenium Complexes with a Tritertiary and a Tetratertiary Arsine.*

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Tris-(*o*-diphenylarsinophenyl)arsine, QAS, and bis-(*o*-diphenylarsino phenyl)phenylarsine, TAS, form complexes with rhenium(II) of the type $[ReX_2(QAS)]$ (X = Cl or Br) and $[ReX_2(TAS)]$ (X = Cl, Br, or I), respectively. All these are resistant to oxidation. The five-co-ordination of the TAS complexes is apparently unique for rhenium(II).

Complexes $[ReOX_3(TAS)]$ (X = Cl or Br) are formed by reaction between rhenium trihalides and the triarsine. Oxidation from rhenium(III) to rhenium(V) appears to take place during the reaction. It is not certain whether these complexes are six- or seven-co-ordinate.

The reaction between rhenium trichloride and the tetra-arsine gave a complex thought to be $[ReCl_2(QAS{\cdot}O)]Cl$, where the QAS·O represents QAS with one arsenic atom oxidized to arsine oxide.

The quadridentate ligand, tris-(*o*-diphenylarsinophenyl)arsine, QAS, gives stable complexes with the Group VIII metals ruthenium,[1] palladium,[2] and platinum.[3] In every case the oxidation state of the metal ion is +2, and thus the electronic configurations of the metal ions are d_6, d_8, and d_8, respectively. The formation of stable complexes of transition-metal ions in this oxidation state with ligands containing arsenic donor atoms is believed to be due partly to back-donation of electrons from metal *d*-orbitals to vacant ligand orbitals. This donation depends on the presence of filled metal *d*-orbitals of suitable energy, and it was therefore decided that the behaviour of rhenium(II) should be studied, since it has a smaller number of available *d*-electrons. Also, whereas the complexes of d_8-ions with the tetra-arsine could be oxidized to those of the corresponding d_6-ions,[2,3] those of d_6-ions could not be oxidized.[1] Since the resistance towards oxidation of the tetra-arsine complexes of d_6-ions could have been due either to the inertness characteristic of this electronic configuration or to some mechanistic factor, we wished to know whether the d_5-rhenium(II) complexes could be oxidized, thus allowing us to decide which of the two factors was more important in determining resistance towards oxidation.

The tridentate ligand, bis-(*o*-diphenylarsinophenyl)phenylarsine, TAS, was also used for the preparation of complexes.

Rhenium(II) *complexes*. Prolonged refluxing of potassium perrhenate, the organic ligand, and hydrogen halide in tetrahydrofurfuryl alcohol gave a product only when the tetra-arsine and hydrogen chloride were used, this being $[ReCl_2(QAS)]$. This complex was also obtained by reaction of the arsine with $[ReO(OEt)Cl_2(Ph_3P)_2]$. Replacement of the phosphine is accompanied by reduction, possibly by the liberated phosphine. The corresponding bromo-complex was produced from the reaction between the tetra-arsine and either rhenium tribromide or the phosphine complex $[ReO(OEt)Br_2(Ph_3P)_2]$.

The complexes $[ReX_2(TAS)]$ (X = Cl, Br, or I) were obtained by refluxing the complexes $[ReO(OEt)X_2(Ph_3P)_2]$ with the triarsine in chlorobenzene or bromobenzene.

Attempts to prepare iodo-complexes by direct combination of rhenium tetra-idodide with either arsine were unsuccessful, as were exchange reactions between chloro-complexes and sodium iodide, and the reaction between the tetra-arsine and the complex $[ReO(OEt)I_2(Ph_3P)_2]$.

In Table 1 are listed the new complexes characterized, with the physical measurements performed on them.

The infrared spectra of all the rhenium(II) complexes in the region 4000—600 cm.$^{-1}$

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[1] Hartley and Venanzi, *J.* 1962, 182.

[2] Savage and Venanzi, *J.*, 1962, 1548.

[3] Brewster, Savage, and Venanzi, *J.*, 1961, 3699.

TABLE 1.

Colour, decomposition points, conductivities, and magnetic moments of complexes of rhenium with tris-(*o*-diphenylarsinophenyl)arsine (QAS) and bis-(*o*-diphenylarsinophenyl)phenylarsine (TAS).

			Molar conductivity (mhos) at 22°		
Formula	Colour	Decomp.	Nitromethane	Nitrobenzene	μ_{eff} (B.M.)
$[ReCl_2(QAS)]$	Orange	278—280°	Insol.	1·3	1·16
$[ReBr_2(QAS)]$	Orange	266—267	,,	2·1	1·15
$[ReCl_2(TAS)]$	Red	235—237	22·4	—	1·60
$[ReBr_2(TAS)]$	Red	239—241	42·0	7·9	1·67
$[ReI_2(TAS)]$	Purple-black	175—178	23·9	5·9	1·74
$[ReOCl_3(TAS)]$	Green	284—285	6·3	0·4	Diamag.
$[ReOBr_3(TAS)]$	Yellow-green	275—276	42·0	1·8	,,
$[ReCl_2(QAS{\cdot}O)]Cl$	Green	245—247	93·3	Insol.	2·34

contained only bands present also in the spectrum of the spectrum of the tetra-arsine, there being no evidence of bands assignable to Re–O, As–O, Re–H, or O–Et vibrations.

Nitrobenzene solutions of the complexes $[ReCl_2(QAS)]$ and $[ReBr_2(TAS)]$ were treated with an excess of methyl iodide. Even after 24 hours there had been no appreciable rise in conductivity. A sharp rise would have been observed if there had been one or more unattached arsenic atoms, owing to the formation of an arsonium ion. It appears, therefore, that all the arsenic atoms are co-ordinated to the central atom.

Although the complexes $[ReX_2(QAS)]$ have molecular solubilities which are too low to allow molecular-weight determinations, they are assumed to be monomeric. They are non-electrolytes in nitrobenzene and we conclude that the rhenium has co-ordination number six. They may have a very distorted octahedral structure.

The low values for the magnetic moments of the products $[ReCl_2(QAS)]$ and $[ReBr_2(QAS)]$ call for comment. Since the bivalent rhenium complexes contain a metal ion with d_5-configuration, an octahedral stucture (for a strong-field case) should lead to a spin-only value for the magnetic moment equivalent to one unpaired electron. Distortion of the molecule should not affect this value. According to Kotani,[4] the moments of d_5-ions in regular octahedral environments are little affected by spin–orbit coupling, but in the highly irregular environment of these complexes this may no longer be so.

The complexes $[ReX_2(TAS)]$ (X = Cl, Br, or I), particularly $[ReBr_2(TAS)]$, were dissociated to some extent in nitromethane and rather less so in nitrobenzene. This could be attributed to the equilibria:

$$[ReX_2(TAS)] \rightleftharpoons [ReX(TAS)]^+ + X^-$$

$$2[ReX_2(TAS)] \rightleftharpoons [ReX(TAS)]^+ + [ReX_3(TAS)]^-$$

Both these equilibria would be shifted to the left on changing from nitromethane to the less polar nitrobenzene.

Molecular-weight determination for the complex $[ReBr_2(TAS)]$ in bromoform solution gave a mean value of 1084 (calc., 1109). Thus the complex was not present in solution as a six-co-ordinate dimer.

This suggests that the complexes $[ReX_2(TAS)]$ are monomeric and five-co-ordinate in non-ionizing solvents. The structure of the complexes is not known, two possibilities being a trigonal bipyramid and a square pyramid. In either case one would expect the presence of one unpaired electron, and the observed moments are in good agreement with those then expected.

The spectra of the rhenium(II) complexes with both arsines show marked similarities, despite the difference in co-ordination number (see Figs. 1 and 2 and Table 2). However,

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[4] Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293.

TABLE 2.

Visible and ultraviolet spectra of rhenium–arsine complexes.

	Solution *			Solid		
Complex	$\lambda_{max.}$ (mμ)	$E_{max.}$ (cm.$^{-1}$)	$\varepsilon_{max.}$	$\lambda_{max.}$ (mμ)	$E_{max.}$ (cm.$^{-1}$)	" D "
[$ReCl_2(QAS)$]	270	37,000	sh			
	360	27,800	3080	365	27,400	1·36
	430	23,300	sh	440	22,700	sh
[$ReBr_2(QAS)$]	270	37,000	sh			
	370	27,000	2950	390	25,600	1·60
	450	22,200	sh	460	21,700	sh
[$ReCl_2(TAS)$]	270	37,000	sh			
	365	27,400	3800	370	27,000	1·59
	470	21,300	sh	480	20,800	sh
				895	11,200	0·39
[$ReBr_2(TAS)$]	270	37,000	sh			
	350	28,600	sh	350	28,600	sh
	380	26,300	5740	390	25,600	1·56
	500	20,000	sh	500	20,000	sh
				960	10,400	0·51
[$ReI_2(TAS)$]	290	34,500	sh			
	360	27,800	5840	360	27,800	sh
				390	25,600	1·64
	520	19,200	5950	520	19,200	1·71
	600	16,700	sh	600	16,700	sh
	675	14,800	sh			
[$ReOCl_3(TAS)$]	280	35,700	sh			
	350	28,600	sh	350	28,600	1·41
	550	18,200	sh			
	600	16,700	83			
	660	15,200	sh	650	15,400	0·49
				840	11,900	0·39
[$ReOBr_3(TAS)$]	280	35,700	sh			
	355	28,200	6800	350	28,600	sh
				370	27,000	1·49
	625	16,000	42			
	675	14,800	42	690	14,500	0·60
				850	11,800	0·51

* In dichloromethane. sh = shoulder.

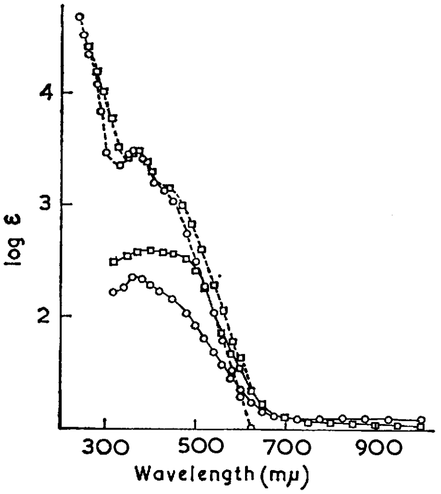

FIG. 1. Absorption and reflection spectra of QAS complexes of rhenium(II): [$ReCl_2(QAS)$] (○ - - - ○) in CH_2Cl_2 and (○——○) solid; [$ReBr_2(QAS)$] (□ - - - □) in CH_2Cl_2 and (□——□) solid.

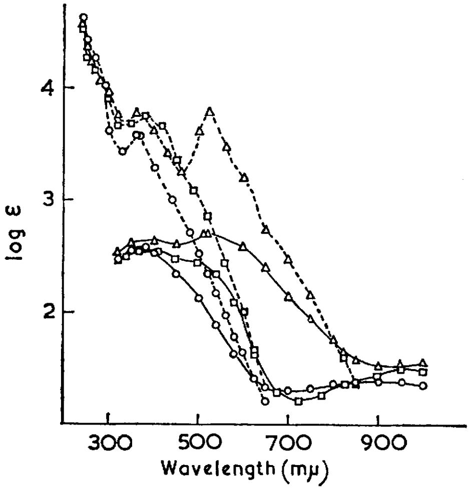

FIG. 2. Absorption and reflection spectra of TAS complexes of rhenium(II): [$ReCl_2(TAS)$] (○ - - - ○) in CH_2Cl_2 and (○——○) solid; [$ReBr_2(TAS)$] (□ - - - □) in CH_2Cl_2 and (□——□) solid; [$ReI_2(TAS)$] (△ - - - △) in CH_2Cl_2 and (△——△) solid.

none of the bands observed can be attributed to *d–d* transitions because of their high extinction coefficients. Since no other information appears to be available on the spectra of similar complexes an interpretation has not been attempted.

The tetra- and tri-arsine complexes differ from the *o*-phenylenebisdimethylarsine (DAS) complexes of Curtis, Fergusson, and Nyholm,[5] in the difficulty of oxidation from rhenium(II) to rhenium(III). The complexes [ReX_2(QAS)] and [ReX_2(TAS)] were oxidized by halogens only under conditions which led to decomposition. Potentiometric titration of the material [$ReCl_2$(QAS)] was unsuccessful, the readings obtained suggesting merely that the chlorine was polarizing the platinum electrode. Also the tetra-arsine, when refluxed with perrhenate, hydrochloric acid, and hypophosphorous acid gives the bivalent rhenium compound [$ReCl_2$(QAS)], whereas the diarsine gives the tervalent rhenium compound [$ReX_2(DAS)_2$]X.[5] The difference may be due to the weaker electron-donor capacity of the arsenic atoms in complexes of the tetra- and tri-arsine. The methyl groups in the diarsine will have an inductive effect increasing the donor capacity of the arsenic lone pair, while in the tetra- and tri-arsine these alkyl groups are replaced by phenyl groups.[2] The greater concentration of negative charge on the metal ion in the diarsine complexes should lead to easier oxidation.

When one compares the tetra-arsine complexes of rhenium with those of other metals, a similarity is noticeable between rhenium and ruthenium.[1] Both form six-co-ordinate complexes [MX_2(QAS)] which resist oxidation to the tervalent state. In contrast, the tetra-arsine complexes of platinum and palladium are five-co-ordinate, have trigonal-bipyramidal structure, and are easily oxidized.[2,3]

The co-ordination number of five in the triarsine complexes is unusual for this ligand and apparently unique for bivalent rhenium. Since Tronev and Bondin[6] claim that bivalent rhenium forms square-planar complexes with ammonia and pyridine similar to those of platinum, one might have expected the triarsine complexes of bivalent rhenium to be like those of platinum, which are of the type [PtX(TAS)]Y and are believed to be square-planar. In fact, there is a resemblance between the triarsine complexes of rhenium and those of palladium, since [PdI_2(TAS)] is five-co-ordinate in the solid state and in benzene solution but four-co-ordinate in methanol solution, and has a molar conductance of 9 mhos in nitrobenzene.[2] However, in the case of the tetra- and tri-arsine complexes there is no similarity between rhenium and platinum.

Quinquevalent Triarsine Complexes.—Refluxing rhenium trihalides with the triarsine in 1,2-dimethoxyethane affords the complexes [$ReOX_3$(TAS)] (X = Cl or Br). The change in colour that occurs as the solutions of the trihalides are warmed suggests that oxidation may occur at this stage. Reduction of these complexes with stannous halides in glacial acetic acid gave products containing tin.

An attempt to prepare a complex [$ReO(CNS)_3$(TAS)] by refluxing [$ReOCl_3$(TAS)] with sodium thiocyanate in cyclohexanone resulted in decomposition.

Apart from bands due to the organic ligand, the complexes [$ReOX_3$(TAS)] showed one additional intense band, at 980 (X = Cl) and 971 cm.$^{-1}$ (X = Br). Similar bands were found by Chatt and Rowe[7] for the complexes [$ReOX_3(Ph_3P)_2$], at 969 (X = Cl) and 958 cm.$^{-1}$ (X = SCN) and were assigned by them to the Re–O stretching frequency. Direct analysis showed one atom of oxygen in the complexes [$ReOX_3$(TAS)], and we therefore assigned the extra band to Re–O.

These complexes have an apparent co-ordination number of seven. The negligible conductivity of the chloro-complex in both nitrobenzene and nitromethane, and the slow rate of reaction with methyl iodide (shown by conductivity measurements in nitrobenzene solution), suggest that this complex might be seven-co-ordinate in solution. However, the bromo-complex, although non-conducting in nitrobenzene, has a molar

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[5] Curtis, Fergusson, and Nyholm, *Chem. and Ind.*, 1958, 625.
[6] Tronev and Bondin, *Doklady Akad. Nauk S.S.S.R.*, 1952, **86**, 87.
[7] Chatt and Rowe, *Chem. and Ind.*, 1962, 92.

conductivity of 42 in nitromethane, and also the rate of reaction with methyl iodide is much greater than that of the chloride, being almost identical with that of triphenylarsine. Hence there appears to be a co-ordination number of six in solution, with competition between bromide and one arsenic donor for the sixth place.

Both complexes are diamagnetic, as are other complexes of rhenium(V), *e.g.*,

$$[ReCl_4(DAS)_2](ClO_4)\ ^{8} \text{ and } [ReOCl_3(Ph_3P)_2].^{7}$$

The visible and ultraviolet spectra of the rhenium(V) complexes (see Fig. 3 and Table 2) show some interesting long-wavelength bands which could be attributed to *d*–*d* transition. However, in view of the uncertainty about the structure of these complexes and the lack of spectral data on related compounds their assignment has not been attempted.

The complexes [ReOX_3(TAS)] have no analogue in the chemistry of this ligand with other transition-metal ions. It is interesting that, in spite of the difficulty of oxidizing rhenium(II) complexes of the tetra- and tri-arsine, these rhenium(V) complexes should be so stable. The fact that rhenium(V) has only two *d*-electrons means that π-bonding by back-donation of electrons into empty ligand orbitals must be weak, and suggests that the rhenium–arsenic σ-bond may be stronger than might be expected at first sight.

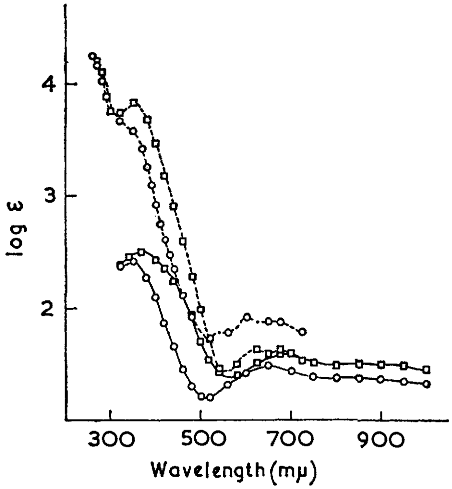

FIG. 3. Absorption and reflection spectra of TAS complexes of rhenium(V): [ReOCl_3(TAS)] (○ - - - ○) in CH_2Cl_2 and (○——○) solid; [ReOBr_3(TAS)] (□ - - - □) in CH_2Cl_2 and (□——□) solid.

Complexes containing a Ligand QAS·O.—Reaction between rhenium trichloride and the tetra-arsine in 1,2-dimethoxyethane gave a product believed to be [ReCl_2(QAS·O)]Cl, where QAS·O represents the tetra-arsine with one arsenic atom oxidized to arsine oxide. This complex shows two infrared bands other than those of the arsine, namely, at 838 and 813 cm.$^{-1}$. According to Phillips and Tyree,[9] complexes of triphenylarsine oxide with many metals show from one to four bands in this region, due to co-ordinated As–O groups. It is possible that a complex similar to [ReOCl_3(TAS)] is first formed, leaving one arsenic atom unco-ordinated. This may exchange oxygen with the rhenium, giving an arsine oxide complex of rhenium(III). The magnetic moment of 2·34 B.M. is much nearer to those of the complexes [ReX_2(DAS)$_2$](ClO$_4$) [5] than to the diamagnetism of the rhenium(V) complexes. The complex [ReCl_2(QAS·O)]Cl is a 1 : 1 electrolyte in nitromethane. Reduction of this complex with stannous chloride in glacial acetic acid gave the complex [ReCl_2(QAS)].

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[8] Fergusson and Nyholm, *Chem. and Ind.*, 1958, 1555.

[9] Phillips and Tyree, *J. Amer. Chem. Soc.*, 1961, **83**, 1806.

EXPERIMENTAL

The tetra- and tri-arsine were prepared by the method of Howell *et al.*[10]

Preparation of Rhenium Halides.—Rhenium trichloride was obtained by chlorinating metallic rhenium and thermally decomposing the resulting pentachloride in a slow stream of nitrogen.[11] Rhenium tribromide was prepared by direct combination of rhenium and bromine vapour.[12] Rhenium tetra-iodide was prepared by the method of Peacock *et al.*,[13] perrhenic acid being obtained by passing a solution of potassium perrhenate through a cation-exchange resin and concentrating the resulting solution on a water-bath.

The complexes $[ReO(OEt)X_2(Ph_3P)_2]$ (X = Cl, Br, or I) and $[ReOX_3(Ph_3P)_2]$ (X = Cl or Br) were prepared and purified by the methods of Freni and Valenti,[14] who assign them the formulæ $[ReX_2(Ph_3P)_2]$ and $[ReX_3(Ph_3P)_2]$, respectively.

Arsine Complexes.—These were prepared by three main methods: (A) by refluxing potassium perrhenate, the arsine, concentrated halogen acid, and 50% hypophosphorous acid in tetrahydrofurfuryl alcohol; (B) by refluxing the appropriate rhenium halide with the arsine in a donor solvent; and (C) by refluxing the corresponding $[ReO(OEt)X_2(Ph_3P)_2]$ complex with the arsine in a high-boiling solvent. The quantities of reagent used, in the order mentioned, the reaction time, the yield of crude material, and the solvents used in the purification are given below for each compound.

(*a*) *Dihalogenotris-*(o-*diphenylarsinophenyl*)*arsinerhenium*(II). (i) The *dichloro-complex*, $[ReCl_2(QAS)]$: (A) 0·6 g., 2 g., 24 drops, 24 drops, 50 c.c., 6 hr., 27%, methylene chloride–light petroleum (b. p. 40—60°) (Found: As, 23·8; Re, 15·0. $C_{54}H_{42}As_4Cl_2Re$ requires As, 24·0; Re, 14·9%); (C) 0·5 g., 1·75 g., 6 hr., methylene chloride–light petroleum (b. p. 40—60°) (Found: As, 23·8; Re, 14·8%).

(ii) The *dibromo-complex*, $[ReBr_2(QAS)]$: method A gave only traces of product together with much unchanged ligand and some dark oil; (B) 0·55 g., 1·0 g., 1,2-dimethoxyethane (25 c.c.), 2 days, extraction of impurities with benzene, recrystallisation from ethyl methyl ketone (Found: As, 22·1; Re, 13·7. $C_{54}H_{42}As_4Br_2Re$ requires As, 22·4; Re, 13·9%); (C) 0·5 g., 1·75 g., bromobenzene, 50 c.c., 6 hr., free ligands extracted with benzene, methylene chloride–light petroleum (b. p. 40—60°) (Found: As, 22·2; Re, 13·6%).

In attempts to prepare the di-iodo-complex, method A gave much unchanged ligand and some brown oil. (B) Rhenium tetra-iodide and the ligand, when refluxed in 2-methoxyethanol, gave a brown solution from which most of the ligand was recovered unchanged. (C) On refluxing the reactants in bromobenzene decomposition occurred. A double-exchange experiment between the dichloro-complex and sodium iodide in cyclohexanone gave an oil from which no product could be obtained.

(*b*) *Dihalogenobis-*(o-*diphenylarsinophenyl*)*phenylarsinerhenium*(II). (i) The *dichloro-complex*, $[ReCl_2(TAS)]$: (C) 0·2 g., 0·6 g., chlorobenzene (25 c.c.), 6 hr., ethyl methyl ketone–light petroleum (b. p. 40—60°) (Found: As, 21·9; Re, 18·6. $C_{42}H_{33}As_3Cl_2Re$ requires As, 22·0 Re, 18·3%).

(ii) The *dibromo-complex*, $[ReBr_2(TAS)]$: (C) 0·4 g., 1·2 g., bromobenzene (40 c.c.), 6 hr., ethyl methyl ketone–light petroleum (b. p. 40—60°) (Found: As, 20·0; Re, 17·0%; *M*, in 5×10^{-3}M-bromoform solution, 1084. $C_{42}H_{33}As_3Br_2Re$ requires As, 20·3; Re, 16·8%; *M*, 1109).

(iii) The *di-iodo-complex*, $[ReI_2(TAS)]$: (C) 0·2 g., 0·6 g., chlorobenzene (20 c.c.), 6 hr. The crude *product* was extracted with acetone and the residue after evaporation of the acetone recrystallized from ethyl methyl ketone–light petroleum (b. p. 40—60°) (Found: As, 18·3; Re, 15·8. $C_{42}H_{33}As_3I_2Re$ requires As, 18·7; Re, 15·5%).

(*c*) *Oxotrihalogenobis-*(o-*diphenylarsinophenyl*)*phenylarsinerhenium*(V). (i) The *trichloro-complex* $[ReOCl_3(TAS)]$: (B) 0·8 g., 1 g., 1,2-dimethoxyethane (25 c.c.), 1½ hr., 43%, nitromethane (Found: C, 47·0; H, 3·3; O, 1·6; As, 20·9; Re, 17·3. $C_{42}H_{33}As_3Cl_3ORe$ requires C, 47·1; H, 3·1; O, 1·5; As, 21·0; Re, 17·4%).

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[10] Howell, Pratt, and Venanzi, *J.*, 1961, 3167.

[11] Geilmann and Wrigge, *Z. anorg. Chem.*, 1933, **214**, 244.

[12] Hagen and Sieverts, *Z. anorg. Chem.*, 1933, **215**, 111.

[13] Peacock, Welch, and Wilson, *J.*, 1958, 2901.

[14] Freni and Valenti, *J. Inorg. Nuclear Chem.*, 1961, **16**, 240.

(ii) *The tribromo-complex,* [ReOBr$_3$(TAS)]: (B) 0·5 g., 1 g., 1,2-dimethoxyethane (25 c.c.), ½ hr., 42%, nitromethane (Found: C, 42·2; H, 2·8; O, 1·4; As, 18·5; Re, 15·3. $C_{42}H_{33}As_3Br_3ORe$ requires C, 41·9; H, 2·8; O, 1·3; As, 18·7; Re, 15·5%).

(iii) In attempts to prepare the tri-iodo-complex, method B gave some unchanged ligand and a trace of black powder.

(iv) In an attempt to prepare the thiocyanato-complex, refluxing the trichloro-complex (0·25 g.) and sodium thiocyanate (0·06 g.) in cyclohexanone (30 c.c.) caused decomposition.

(*d*) *Trihalogenobis* - (o - *diphenylarsinophenyl*) - (As - *oxido* - o - *diphenylarsinophenylarsine*) - *rhenium.* (i) The *trichloro-complex,* [ReCl$_2$(QAS·O)]Cl: (B) 0·75 g., 1 g., 1,2-dimethoxyethane (25 c.c.), 1½ hr., 60%, solution decanted and complex washed several times with dimethoxyethane and then twice with ether (Found: As, 22·9; Re, 14·5. $C_{54}H_{42}As_4Cl_3ORe$ requires As, 23·1; Re, 14·3%). (ii) An attempt to prepare the tribromo-complex by method B produced only a small yield of [ReBr$_2$(QAS)].

Reduction of the Complex [ReCl$_2$(QAS·O)]Cl.—The complex (0·5 g.) was refluxed with stannous chloride (0·3 g.) in glacial acetic acid (40 c.c.). After 3 hr. the solution was allowed to cool and the brown precipitate (0·3 g.) was filtered off and recrystallised from methylene chloride–light petroleum (Found: As, 23·8; Re, 14·6. Calc. for $C_{54}H_{42}As_4Cl_2Re$: As, 24·0; Re, 14·9%). This product is identical with [ReCl$_2$(QAS)] prepared by method A or C.

Analytical.—Rhenium. The organic matter in the complexes was destroyed by fusion with sodium peroxide (0·5 g.) in an alumina crucible. After neutralization of the solution of the mixture after fusion, a very slight excess of concentrated sulphuric acid was needed to redissolve precipitated alumina. The rhenium content of this solution was determined by the furil α-dioxime method of Meloche *et al.*[15] Owing to the presence of peroxide in solution, the development time for the violet colour was longer than that given by them. A time of 5 hr. was found to be satisfactory. The acetone solution of the dioxime gave low results if kept for >20 min. and was always used immediately on preparation. The calibration curve was obtained by using a solution of spectrographically pure potassium perrhenate.

Arsenic. This was determined by the Maren modification [16] of the heteromolybdenum method of Magnuson and Watson.[17] A 2 c.c. portion of the solution from the peroxide fusion, diluted with distilled water (13 c.c.), was used for the determination. The comparison solution was prepared by fusing sodium peroxide (0·5 g.) in the crucible, washing it out, neutralizing the solution, and making it up to 100 c.c. A 2 c.c. portion was then treated by the standard procedure.

Visible and Ultraviolet Spectra.—The reflection spectra of the powdered complexes were measured over the range 1000—320 mμ with a Unicam S.P. 500 spectrophotometer, fitted with a Unicam diffuse reflection attachment, S.P. 540, and a magnesium carbonate comparison disc. Solution spectra were obtained on the same spectrophotometer with 10^{-3}—10^{-5}M-solutions in methylene chloride in 1 cm. silica cells, the range covered being 1000—240 mμ.

Infrared Spectra.—These were recorded on a Perkin–Elmer model 21 spectrophotometer fitted with a rock-salt prism. The samples were examined in " Nujol " mulls.

Conductivity Determinations.—A cell with horizontal electrodes of bright platinum was used, with a type E 7566 Mullard conductivity bridge. The determinations were carried out on *ca.* 5 × 10^{-4}M-solutions of the complexes in nitrobenzene and nitromethane. The values were corrected for the conductivities of the solvents at the same temperature.

Quaternarization was carried out by adding an excess of methyl iodide to about 10^{-3}M-solutions of the complexes in nitrobenzene and measuring the change in conductivity during several days.

Magnetic-susceptibility Measurements.—These were carried out on a balance of Faraday type, similar to that described by Milligan and Whitehurst.[18] The molecular susceptibilities, χ_M, were calculated and then corrected for the diamagnetism of the component atoms by using Pascal's constants.[19] The corrected values were used to calculate the magnetic moments.

Molecular-weight Determination.—This was performed cryoscopically, with bromoform (cryoscopic constant 14·4) as the solvent.

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[15] Meloche, Martin, and Webb, *Analyt. Chem.*, 1957, **29**, 527.

[16] Maren, *Ind. Eng. Chem., Analyt.*, 1946, **18**, 521.

[17] Magnuson and Watson, *Ind. Eng. Chem., Analyt.*, 1944, **16**, 339.

[18] Milligan and Whitehurst, *Rev. Sci. Instr.*, 1952, **23**, 618.

[19] See Selwood, " Magnetochemistry," Interscience Publ., Inc., New York, 1956.

Potentiometric Titrations.—An apparatus of standard type was used. When a solution of the salt $[PtCl(QAS)]ClO_4$ in methylene chloride was titrated with chlorine in carbon tetrachloride a sharp end-point was obtained, but a similar titration on the complex $[ReCl_2(QAS)]$ gave no end-point. Titration of this complex with ferric chloride in cyclohexanone was unsuccessful.

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