35. *Some Ruthenium*(II) *Complexes with a Tetratertiary Arsine.*

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Tri-(*o*-diphenylarsinophenyl)arsine, QAS, reacts with nitrosylruthenium compounds to form complexes of the type [RuX$_2$(QAS)] (X = Cl, Br, I, CNS,* or NO$_3$). These are monomeric, diamagnetic, and non-electrolytes in nitrobenzene. Six-co-ordination appears to be preserved despite the stringent steric requirements of the chelating agent.

Brewster *et al.*[1] recently described the preparation and properties of some complexes of platinum(II) with the tetratertiary arsine tri-(*o*-diphenylarsinophenyl)arsine As(C$_6$H$_4$·AsPh$_2$-*o*)$_3$ (QAS). These complexes, [PtX(QAS)]Y (X = halogen, Y = anion), have trigonal bipyramidal co-ordination at the platinum atom.[2]

The fairly rigid structure of the polydentate ligand QAS and its preferred trigonal symmetry raise the problems: will QAS form complexes with d^6-metal ions which form exclusively octahedral complexes? and, if so, what will their structure be? We therefore attempted the preparation of some complexes of ruthenium(II) with this ligand. Considerable difficulty was encountered. The action of the ligand on [RuI$_2$(CO)$_2$]$_x$ gave polymeric compounds which still contained carbon monoxide (see below). Ruthenium trichloride and the ligand, when refluxed in high-boiling solvents, gave small amounts of products which proved difficult to characterize. The most convenient method found is to treat nitrosylruthenium compounds with the ligand in a high-boiling hydroxylic solvent. By this method compounds of the type [RuX$_2$(QAS)] (X = Cl, Br, or NO$_3$) were obtained. Two other derivatives of the same type (X = I or CNS) were obtained by a double exchange from the chloro-complex and the sodium salt of the desired anion. The products are reported in Table 1. The infrared spectra of the complexes confirm the absence of nitric oxide. In fact, apart from additional bands due to the anions in the case of the nitrato- and thiocyanato-complexes, the spectra of the ruthenium compounds differ only slightly from the spectrum of the free ligand.

Table 1.

Complexes of ruthenium(II) with tri-(*o*-diphenylarsinophenyl)arsine (QAS).

Complex	Colour	Decomp. pt.	χ_M (10^6)	Λ_M * (ohm^{-1})	Mol. wt. Found †	Mol. wt. Calc.
[RuCl$_2$(QAS)]	Pale yellow	>380°	+94	0	1150	1162
[RuBr$_2$(QAS)]	Yellow orange	>380	+133	0	—	—
[RuI$_2$(QAS)]	Orange	170—180	+171	0	—	—
[Ru(CNS)$_2$(QAS)]	Yellow	355—360	+159	0	—	—
[Ru(NO$_3$)$_2$(QAS)]	Yellow	340—345	+176	0	1180	1215

* In nitrobenzene. † In phenol.

The loss of nitric oxide during the reaction was unexpected as nitrosyl derivatives of ruthenium are known to retain it very tenaciously. The formation reaction, however, could be written as:

$$K_2[RuX_5(NO)] + QAS = \underset{\text{(unstable)}}{[RuX(NO)(QAS)]X_2} + 2KX$$

$$[RuX(NO)(QAS)]X_2 = [RuX_2(QAS)] + NOX$$

It is possible that displacement of nitric oxide in the complex is the result of lability induced by the *trans*-effect of the arsenic donors.

To test the stability of the bonds between ruthenium and arsenic in these compounds, a nitrobenzene solution of the complex [RuI$_2$(QAS)] was treated with methyl iodide.

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* Here written as thiocyanato-compounds, but we are uncertain whether they are *N*- or *S*-bonded.

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

[2] Mair, Powell, and Venanzi, *Proc. Chem. Soc.*, 1961, 170.

Any weakly held tertiary arsine group would give a quaternary compound under these conditions and so afford a conducting solution: $R\cdot AsPh_2 + MeI = [R\cdot AsPh_2Me]^+I^-$. Since no change in conductivity was observed in 24 hours, it is concluded that all the arsenic donors were strongly bonded to the ruthenium atom.

The visible and ultraviolet absorption spectra of dichloromethane solutions of the complexes described here are given in Fig. 1 and Table 2. They consist of a very intense band at about 380 mμ (ε 4—10 × 10^3) and a shoulder at about 270 mμ. Related complexes, $[RuX_2\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ and *trans*-$[RuX_2\{C_2H_4(PMe_2)_2\}_2]$, have been reported by Nyholm and Sutton,[3] and Chatt and Hayter,[4] respectively. Nyholm and Sutton do not record the spectra of their complexes, and those of the phosphine complexes differ from ours in two major ways: (1) the long-wavelength bands in our complexes are shifted by about 50 mμ towards shorter wavelength; (2) the extinction coefficients in our complexes are 100 times larger. Thus, unlike the long-wavelength bands of the phosphine complexes, our 380 mμ bands cannot be assigned to Laporte-forbidden t_{2g}–e_g transitions.

TABLE 2.

Spectra of complexes of ruthenium(II) with QAS.

	Solution *			Solid		Solution *			Solid
	$\lambda_{max.}$ (mμ)	$E_{max.}$ (cm.$^{-1}$)	$\varepsilon_{max.}$	$\lambda_{max.}$ (mμ)		$\lambda_{max.}$ (mμ)	$E_{max.}$ (cm.$^{-1}$)	$\varepsilon_{max.}$	$\lambda_{max.}$ (mμ)
$RuCl_2(QAS)$	250	40,000	sh	—	$Ru(CNS)_2(QAS)$	255	39,200	sh	—
	375	26,700	6400	385		355	28,200	9500	365
$RuBr_2(QAS)$	255	39,200	sh	—		445	22,500	sh	—
	382	26,200	6100	390	$Ru(NO_3)_2(QAS)$	260	38,500	sh	—
$RuI_2(QAS)$	260	38,500	sh	—		385	26,000	4500	393
	394	25,400	5600	410					

* In dichloromethane solution. sh = shoulder.

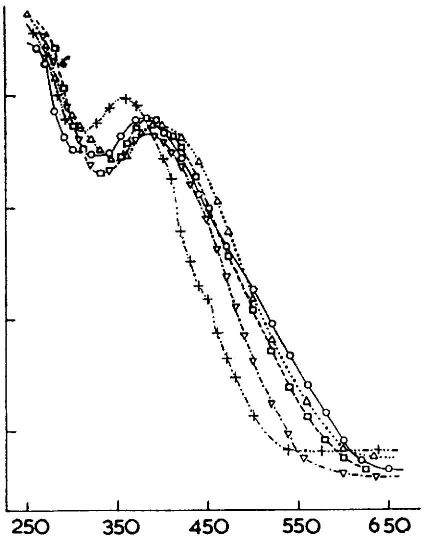

FIG. 1. Visible and ultraviolet spectra of the complexes $[RuX_2(QAS)]$.
X = Cl (○), Br (△), I (□), NO_3 (▽), CNS (+).

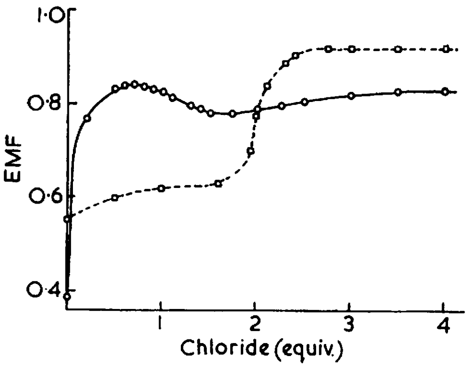

FIG. 2. Potentiometric titration of QAS complexes.
(□) [PtCl(QAS)]Cl. (○) $[RuCl_2(QAS)]$.

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[3] Nyholm and Sutton, *J.*, 1958, 567.

[4] Chatt and Hayter, *J.*, 1961, 772.

It is possible that the bands we observe are of charge-transfer type and that these overlap the weaker *d–d* transitions.

To check that no structural changes occurred in our complexes on dissolution, the spectra of the finely divided solids were measured in the region 324—1000 mμ (see Table 2). The bands at about 380 mμ are somewhat broader and shifted towards longer wavelength by 10—20 mμ. These changes are of the size normally associated with a change of physical state, and do not indicate structural change.

The behaviour of our compounds to oxidation is interesting. The complex $[RuCl_2(QAS)]$ is not oxidised by chlorine in dichloromethane at 0°. This is confirmed by a potentiometric titration of this complex with chlorine (see Fig. 2). It can be contrasted with two other results: (1) Nyholm and Sutton[3] report that the oxidation of the complex $[RuCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ gave a stable tervalent green derivative, $[RuCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}_2]Cl$, and the redox-potential deduced for the couple was 0·64 v; (2) the complex $[PtCl(QAS)](ClO_4)$[1] is oxidized smoothly under our experimental conditions to the corresponding platinum(IV) derivative (see Fig. 2). However, when the ruthenium complex is oxidised at —40° a green solution is obtained that reverts to yellow at 0° or on addition of precipitating agents.

The evidence, therefore, supports a six co-ordinate structure for the complexes of ruthenium(II) with our arsine both in solution and in the solid state.

Molecular models show that considerable distortion of bond distances and angles in the complexes is necessary in order to form compounds in which the co-ordination at the central atom can be considered as approaching an octahedral configuration. Such distortion would be expected to lead to instability. The high thermal stability of most of the complexes described here and their failure to react with methyl iodide are in contrast with this.

Our experiments, however, do not allow us to predict the arrangement of the donor atoms around the central ruthenium atom. Further discussion of their structure must be postponed until the results of *X*-ray structural investigations are available.

Reaction between QAS *and* $[RuI_2(CO)_2]$. When these reactants were refluxed in high-boiling solvents the ruthenium complex dissolved and a pale yellow solid was isolated from the solution. This product, which still contained carbon monoxide (as shown by its infrared spectrum), appeared to have the approximate composition $RuI_2(CO)_x(QAS)$. Its molecular weight in dimethyl sulphoxide was about 4500 and it had a molar conductance of 17 in nitrobenzene solution. In ethanol it reacted with silver nitrate and silver perchlorate, with precipitation of silver iodide. The solutions, on evaporation under reduced pressure, darkened gradually, leaving a black residue, presumably containing metallic ruthenium. Addition of potassium thiocyanate to these solutions, filtration of the silver thiocyanate formed, and evaporation left yellow intractable oils.

Reaction of $[RuI_2(CO)_2]_x$ with triphenyl-phosphines and -arsines[5] gives monomeric products of the type $[RuI_2(CO)_2L_2]$, and carbon monoxide is not displaced by an excess of these reagents. Thus, it is concluded that the tenacity with which carbon monoxide is bound to the ruthenium atom prevents the attachment of more than two arsenic atoms of our arsine and leads to the formation of polymeric products. These results are surprising in view of the stability of the complexes $[RuX_2(QAS)]$.

EXPERIMENTAL

Tri-(*o*-diphenylarsinophenyl)arsine (QAS) was prepared as described previously.[6]

The Complex $[RuCl_2(QAS)]$.—A stream of dry hydrogen chloride was passed for 1 hr. through a suspension of the salt $K_2[Ru(OH)(NO_2)_4(NO)]$[7] (0·83 g.) in tetrahydrofurfuryl alcohol (30 c.c.), heated on a water bath. An insoluble violet solid, presumably $K_2[RuCl_5(NO)]$, was obtained.

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[5] Irving, *J.*, 1956, 2879; Hieber and Heusinger, *J. Inorg. Nuclear Chem.*, 1957, **4**, 179.

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

[7] Joly and Vezes, *Compt. rend.*, 1889, **109**, 668.

To this suspension the ligand arsine QAS (2 g.) was added and the mixture refluxed for 4 hr., then evaporated. The residue was washed with tetrahydrofuran (to dissolve the unchanged ligand) and then with water and dried *in vacuo*. The *complex* (1·3 g.) was purified by repeated precipitation of a dichloromethane solution with ethanol (Found: As, 25·8; Cl, 6·2; Ru, 8·75%; *M*, in 2% phenol solution, 1155. $C_{54}H_{42}As_4Cl_2Ru$ requires As, 25·8; Cl, 6·1; Ru, 8·7%; *M*, 1164).

The Complex $[RuBr_2(QAS)]$.—The ligand (0·5 g.) in tetrahydrofurfuryl alcohol (30 c.c.) was refluxed for 4 hr. with the salt $K_2[RuBr_5(NO)]$,[8] (0·3 g.), brown fumes being evolved. The red solution was evaporated *in vacuo* and the residue extracted (Soxhlet) with ethylene dibromide. The *complex* (0·4 g.) was reprecipitated by addition of light petroleum (b. p. 100—120°) and precipitated from dichloromethane by methanol (Found: C, 51·8; H, 3·5; As, 23·7; Ru, 8·0. $C_{54}H_{42}As_4Br_2Ru$ requires C, 51·1; H, 3·4; As, 23·9; Ru, 8·1%).

The Complex $[Ru(CNS)_2(QAS)]$.—The chloro-complex (0·3 g.) in cyclohexanone (40 c.c.) was refluxed for 12 hr. with sodium thiocyanate (0·05 g.). The yellow solution was filtered from the white solid (presumably sodium chloride) and evaporated under reduced pressure. The crude *product* (0·3 g.) was purified in the same way as its chloro-analogue (Found: C, 55·2; H, 3·4; As, 24·7; Ru, 8·6; S, 5·1. $C_{56}H_{42}As_4N_2RuS_2$ requires C, 55·7; H, 3·5; As, 24·8; Ru, 8·4; S, 5·3%).

The *complex* $[RuI_2(QAS)]$ was prepared in 70% yield in the same way as the thiocyanato-complex and purified in the same way as the bromo-complex (Found: C, 48·3; H, 3·2; As, 22·1; Ru, 7·6%. $C_{54}H_{42}As_4I_2Ru$ requires C, 48·2; H, 3·15; As, 22·3; Ru, 7·5%).

The *complex* $[Ru(NO_3)_2(QAS)]$.—This was prepared from the crude compound $[Ru(NO_3)_3(NO)]$ [9] (0·97 g.) and the arsine in the same way as the bromo-complex. The *product* was purified by washing it with tetrahydrofuran and precipitating it from dichloromethane by carbon tetrachloride (Found: As, 24·6; N, 2·1; Ru, 8·3%; *M*, 1180. $C_{54}H_{42}As_4N_2O_6Ru$ requires As, 24·65; N, 2·3; Ru, 8·4%; *M*, 1215).

Attempts were made to prepare the nitrito- and the cyano-complexes from $K_2[Ru(OH)(NO_2)_4(NO)]$ and $Na_2[Ru(CN)_5(NO)]$,[10] respectively. Residues consisting mainly of metallic ruthenium were obtained.

Reaction of the Complex $[RuI_2(CO)_2]_x$ *with the Arsine*.—The carbonyl complex[11] (1 g.) and the arsine QAS (2·4 g.) were refluxed for 6 hr. in anisole (100 c.c.). The dark red solution was filtered from a small amount of metallic ruthenium and evaporated under reduced pressure. The residue was dissolved in boiling acetone (200 c.c.) from which a yellow-brown solid (1·8 g.) was obtained on evaporation. This could not be recrystallised from hot solvents because it tended to give oils. Purification was by chromatography through alumina and repeated precipitation of acetone solutions with di-isopropyl ether. The pale yellow product decomposed at 153—156° (Found: C, 46·75; H, 3·3; As, 22·5; I, 20·0; Ru, 8·0%; *M*, in 1·5% dimethyl sulphoxide solution, *ca*. 4500).

Products with similar properties were obtained when the reaction was carried out in a sealed tube, or with other solvents such as tetrahydrofurfuryl alcohol, dimethylformamide, cyclohexanone, or isopentyl alcohol. Analogous products were obtained in the reaction of the carbonyl $[RuBr_2(CO)_2]$ [11] with the arsine.

Analytical.—Ruthenium was determined spectrophotometrically by DeFord's method.[12] The ruthenium was distilled off as tetroxide and collected in sodium hydroxide. The ruthenate formed was reduced to the dioxide with ethanol, and the solid centrifuged off and dissolved in hydrochloric acid. The metal was determined with thiourea as described by Sandell.[13]

Arsenic was determined by Maren's modification[14] of the molybdenum-blue of Magnusson and Watson.[15] Arsenic was distilled off as the pentabromide, and the colour developed by the addition of ammonium molybdate and hydrazine sulphate.

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[8] Gmelin, " Handbuch der anorganischen Chemie," Verlag Chemie, Berlin, 1938, Vol. LXII, " Ruthenium," pp. 63, 99.

[9] Werner, *Ber.*, 1907, **40**, 2620.

[10] Manchot and Düsing, *Z. anorg. Chem.*, 1933, **212**, 109.

[11] Manchot and König, *Ber.*, 1924, **57**, 2130.

[12] DeFord, U.S. Atomic Energy Commission Report NP-1104, 1948.

[13] Sandell, " Colorimetric Analysis of Traces of Metals," Interscience Publ. Inc., New York, 1959, p. 781.

[14] Maren, *Ind. Eng. Chem.*, *Anal. Edn.*, 1946, **18**, 521.

[15] Magnusson and Watson, *Ind. Eng. Chem.*, *Anal. Edn.*, 1944, **16**, 339.

Nitrogen was determined by a micro-Kjeldahl method; carbon, hydrogen, and iodine were determined by Dr. A Bernhardt (Mülheim).

Conductivity Measurements.—These were carried out with 10^{-3}M-solutions in nitrobenzene at room temperature, by means of a type E7566 Mullard conductivity bridge.

Determinations of Molecular Weights.—These were made by the cryoscopic method. The low solubility of the complexes required the use of solvents such as phenol and nitrobenzene.

Magnetic-susceptibility Measurements.—These were made by using a Faraday-type balance similar to that described by Milligan and Whitehurst.[16] The molecular susceptibilities, χ_M, were calculated from the room-temperature measurements. After correction for the diamagnetism of the component atoms (by means of the Pascal constants given by Selwood [17]) the compounds show a small residual paramagnetism; this appears to be common in complexes of ruthenium(II).[3]

Infrared Spectra.—These were recorded for Nujol mulls on a Perkin-Elmer 21 spectrophotometer fitted with a rock salt prism.

Visible and Ultraviolet Spectra.—These were recorded on a Unicam SP 500 spectrophotometer. The reflection spectra were recorded on the same instrument fitted with the diffuse reflection attachment SP 540.

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

[17] Selwood, "Magnetochemistry," Interscience Publ. Inc., New York, 1956, pp. 78, 92.