111. *Studies in Co-ordination Chemistry. Part XVIII.* Complexes of Osmium with a Di(tertiary Arsine).*

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Complexes of bivalent, tervalent, and quadrivalent osmium halides with the di(tertiary arsine) chelate group *o*-phenylenebisdimethylarsine have been prepared and studied. The bivalent osmium complexes are diamagnetic, sexicovalent non-electrolytes of the type $[Os(Diarsine)_2X_2]^0$ and are similar to the compounds formed by iron(II) and ruthenium(II). Oxidation of these osmium(II) complexes with halogens yields osmium(III) salts of the type $[Os(Diarsine)_2X_2]X$. The magnetic moments of these are in the range 1·7—2·0 B.M., indicating one unpaired electron. Treatment of these osmium(III) compounds with concentrated nitric acid yields, as with nickel and iron, quadrivalent osmium compounds. The magnetic moments of the osmium(IV) derivatives are only about 1·2 B.M., as observed previously for compounds such as K_2OsCl_6. Electrical-conductivity and molecular-weight measurements where possible have been carried out.

In this paper we complete the discussion of the complexes of the Fe, Ru, Os triad by describing the compounds of osmium. Some earlier work[1] with dimethylphenyl- and methyldiphenyl-arsine led to the isolation of complexes of the types $[Os^{II}X_2,4AsR_3]^0$ and $[Os^{III}X_3,3AsR_3]^0$ but the magnetic properties were not investigated. No compounds of osmium(IV) were described. As with ruthenium, the investigation of the di(tertiary arsine) complexes of osmium was initiated partly in order to attempt to stabilise less common valency states but also to compare the magnetic properties of the complexes of the various valency states with those of the other transition metals. Special interest attaches to osmium(IV) complexes because they usually have moments even less than those corresponding with the two spins expected on Pauling's theory; thus the moment of K_2OsCl_6 is only 1·4 B.M. at room temperatures.

Bivalent Osmium Compounds.—These were prepared simply by treating the osmium(IV) hexahalide anions with excess of di(tertiary arsine) in alcohol. Reduction to the tervalent state first took place, but further heating yielded the insoluble osmium(II) compounds. The chloride, bromide, iodide, and thiocyanate were prepared, and their properties are given in the Table. They are diamagnetic and non-electrolytes in nitrobenzene, in which solvent they are also monomeric. No evidence for two forms of the iodide as observed with ruthenium was obtained. The two halogen atoms are probably *trans*, but *X*-ray investigations are needed to determine this.

Tervalent Osmium Compounds.—These were conveniently prepared by oxidising the corresponding osmium(II) compounds with the appropriate halogen. They are all salt-like compounds having the general formula $[Os(Diarsine)_2X_2]X$. The molecular-weight measurements in nitrobenzene show that they are highly dissociated, and the molecular conductivities show that they are uni-univalent electrolytes in this solvent. Magnetic susceptibilities indicate the presence of one unpaired electron, as expected for the tervalent state. It may also be shown by potentiometric titration of the chloride ion that only one of the three halogen atoms in the compound $[Os(Diarsine)_2Cl_2]Cl$ is ionised. The properties of the tervalent complexes are summarised in the Table.

Quadrivalent Osmium Compounds.—Compounds of tervalent nickel of the type $[NiCl_2(Diarsine)_2]Cl$ and the corresponding iron(III) cation can be oxidised by 15N-nitric acid to yield compounds in which the metal is quadrivalent. This method has now been applied to obtain osmium(IV) di(tertiary arsine) complexes after it had been found that commoner oxidising agents such as the permanganate and cerate ions in water failed to achieve this. Compounds of the type $[Os^{IV}X_2(Diarsine)_2][ClO_4]_2$ (where X = Cl, Br, I)

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* Part XVII, preceding paper.

[1] Dwyer, Nyholm, and Tyson, *J. Proc. Roy. Soc. N.S.W.*, 1948, **81**, 272.

have been prepared and their properties investigated. In nitrobenzene solution they behave as bi-univalent electrolytes, but as they are only sparingly soluble in this solvent it was not possible to determine molecular weights. The magnetic moments expected for a d_ϵ^4 configuration (Os^{IV}) on the basis of Hund's rule is 2·83 B.M. However, values much less than this are observed; in these complexes values from 1·16 to 1·25 B.M. were obtained. Kotani [2] has explained this behaviour by examining the effect of the large nuclear charge of the Os^{IV} atom upon the spin-orbit interaction, and concludes that as the temperature decreases the paramagnetism should steadily decrease, μ_{eff} being proportional to $\sqrt{T}$ at room temperature. This has been confirmed for K_2OsCl_6 by Johannsen and Lindberg [3] and for some other osmium(IV) complexes by Figgis and Nyholm.[4] A more detailed interpretation of the results on these and other osmium complexes will be presented in due course. For a more detailed discussion, see Earnshaw *et al.*[5]

Properties of osmium–diarsine complexes.

		Molecular conductivity in $PhNO_2$ at 25°		Magnetic susceptibility at 20°				
Compound *	Colour	Λ_M	Concn. (10^{-3}M)	$\chi_g \times 10^{-6}$	$\chi_M \times 10^{-6}$	Diamag. corrn.	χ_M (corr.) $\times 10^{-6}$	μ_{eff} (B.M.)
$[OsD_2Cl_2]$	Pale yellow	0·7	1·33	−0·22	−184	426	—	0·0 †
$[OsD_2Br_2]$	Pale brown	0·4	1·45	−0·22	−205	447	—	0·0 †
$[OsD_2I_2]$	Dark brown	0·4	0·87	−0·22	−221	467	—	0·0 †
$[OsD_2(SCN)_2]$	Light brown	1·3	0·40	−0·20	−176	439	—	0·0 †
$[OsD_2Cl_2]Cl$	Purple-red	21·4	1·62	1·136	985	449	1434	1·85
$[OsD_2Cl_2]ClO_4$	Purple-red	22·7	0·86	1·07	998	456	1454	1·86
$[OsD_2Br_2]Br$	Purple-blue	21·8	2·0	1·02	1022	482	1504	1·88
$[OsD_2Br_2]ClO_4$	Purple-blue	23·3	1·18	1·04	1063	477	1540	1·91
$[OsD_2I_2]Br$	Blue-green	25·8	0·35	1·00	1096	502	1598	1·93
$[OsD_2I_2]ClO_4$	Blue-green	23·2	1·18	0·99	1083	497	1580	1·93
$[OsD_2(SCN)_2]ClO_4$	Blue	22·5	0·50	1·05	1027	469	1496	1·88
$[OsD_2Cl_2][ClO_4]_2$	Blue-black	43·2	0·83	0·173	178	486	664	1·25
$[OsD_2Br_2][ClO_4]_2$	Black	42·2	0·56	0·109	122	507	629	1·22
$[OsD_2I_2][ClO_4]_2$	Brown-black	44·2	0·66	0·038	46	527	573	1·16

* D = *o*-Phenylenebisdimethylarsine.

† These moments are regarded as formally zero. The small net paramagnetism after making the diamagnetic correction is attributed to small amounts of impurity and/or Van Vleck paramagnetism.

Many attempts to prepare compounds containing a trisdiarsineosmium ion, *i.e.*, [Os(Diarsine)$_3$]$^{n+}$, were unsuccessful. As before, we attribute this to the reluctance of osmium to accept too large a negative charge.

EXPERIMENTAL

*Dichlorodi-(*o*-phenylenebisdimethylarsine)osmium*(II).—Ammonium hexachloro-osmate (0·25 g.) in water (5 ml.) was added to ethanol (50 ml.) and diarsine (0·34 g.), one phase being obtained. The mixture was heated under reflux, and after a few minutes the colour changed from orange to cherry-red as the [Os(Diarsine)$_2$Cl$_2$]$^+$ ion was formed. After a further ½ hr. the colour had

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

[3] Johannsen and Lindberg, *J. Amer. Chem. Soc.*, 1954, **76**, 5349.

[4] Figgis, Thesis, N.S.W., 1955.

[5] Earnshaw, Figgis, Lewis, and Nyholm, *Nature*, 1957, **179**, 1121.

become pale orange. The heating was stopped after another ½ hr., the reduction being complete. On standing, a pale yellow precipitate settled out. The latter (0·16 g.) was separated by centrifuging, washed with ethanol, and dried in a vacuum. The *complex* is oxidised readily by permanganate, dichromate, chlorine or bromine when suspended in ethanol, acetone, or dioxan. It was stable to above 360° (Found: Cl, 8·30; Os, 22·5%; *M*, cryoscopic in 0·12% solution in nitrobenzene, 750. $C_{20}H_{32}Cl_2As_4Os$ requires Cl, 8·5; Os, 22·8%; *M*, 833). Potentiometric titration of this compound in acetone solution with dichromate and use of a platinum electrode showed that E_0 for oxidation to the osmium(III) complex is approx. 0·6—0·7 v.

*Dibromodi-(*o*-phenylenebisdimethylarsine)osmium*(II).—Ammonium hexabromo-osmate(IV) (0·36 g.), together with diarsine (0·28 g.) and ethanol to form one phase, were heated under reflux as above. Reduction first produced in solution the purple blue $[Os(Diarsine)_2Br_2]^+$ ion, but heating was continued until a brownish-pink colour had developed. A further ½ hr. was allowed to ensure completion of reduction, and separation of the fawn-brown crystalline solid (0·2 g.) was carried out as for the chloride. When heated, the *compound* did not decompose below 360° (Found: Br, 17·1; Os, 20·4%; *M*, cryoscopic in 0·14% solution in nitrobenzene, 820. $C_{20}H_{32}Br_2As_4Os$ requires Br, 17·35; Os, 20·6%; *M*, 922).

*Di-iododi-(*o*-phenylenebisdimethylarsine)osmium*(II).—Ammonium hexabromo-osmate(IV) (0·42 g.) and sodium iodide (2 g.) in water together with diarsine (0·3 g.) were refluxed in sufficient ethanol as before. The reaction was carried beyond the bluish stage, $[Os(Diarsine)_2I_2]^+$ formation, until a light cinnamon-brown precipitate had formed, and then continued for a further ½ hr. The fine crystalline solid (0·25 g.) which separated was washed free from impurities and dried as before. Owing to extremely low solubility in suitable solvents, recrystallisation was not practicable. The *complex* is very slightly soluble in methanol, giving a pale yellow solution; it did not decompose below 360°. Molecular-weight determinations were not possible owing to the low solubility in all solvents (Found: I, 24·4; Os, 18·5. $C_{20}H_{32}I_2As_4Os$ requires I, 25·0; Os, 18·7%).

*Dithiocyanatodi-(*o*-phenylenebisdimethylarsine)osmium*(II).—Ammonium hexabromo-osmate(IV) (0·9 g.), together with ammonium thiocyanate (3 g.) in water (5 ml.) and diarsine (0·75 g.), was refluxed in ethanol (50 ml.). The original orange colour changed to bluish-green after 15 min. and to a dull yellow after 1 hr. On standing, a light brown, powdery precipitate settled out. The complex (0·4 g.) was washed, and dried in a vacuum as already described. The substance is soluble in methanol, but almost insoluble in other common organic solvents. Like the corresponding halides, the *complex* did not decompose below 360°. Molecular-weight determination was not possible owing to the low solubility in nitrobenzene (Found: CNS, 13·1; Os, 21·3. $C_{22}H_{32}N_2S_2As_4Os$ requires CNS, 13·22; Os, 21·6%).

*Dichlorodi-(*o*-phenylenebisdimethylarsine)osmium*(III) *Chloride*.—The osmium(II) complex $[Os(Diarsine)_2Cl_2]^0$ (0·1 g.) was suspended in methanol (150 ml.) at 40°, and chlorine bubbled through until there was no solid left in suspension, the solution becoming red. After filtering, a saturated solution of calcium chloride in ethanol (10 ml.) was added, followed by 25 ml. of water. Red monoclinic crystals of the tervalent osmium *complex* were precipitated. These were removed by centrifuging, washed with a little dilute ethanol to remove calcium chloride, and dried in a vacuum. The substance was recrystallised from acetone–1 : 4-dioxan. The red crystals decomposed at 255° (Found: Cl, 12·3; Os, 21·9%; *M*, in 0·13% solution in nitrobenzene, 360. $C_{20}H_{32}Cl_3As_4Os$ requires Cl, 12·3; Os, 21·9%; *M*, 868). As a check on the valency state of the osmium, a solution of the complex was treated with aqueous potassium iodide, and the liberated iodine titrated with 0·1N-sodium thiosulphate solution. The titre agreed closely with the calculated volume for the liberation of 1 equiv. of iodine.

*Dichlorodi-(*o*-phenylenebisdimethylarsine)osmium*(III) *Perchlorate*.—The chloride complex of bivalent osmium $[Os(Diarsine)_2Cl_2]^0$ (0·078 g.) was suspended in methanol (50 ml.) and chlorine passed through until all the complex had dissolved to form the red solution of the tervalent complex. After filtering, the solution was treated with perchloric acid (1 ml.) and evaporated carefully to about half its bulk; no precipitate was formed until water (15 ml.) was added; red powdery crystals of the *perchlorate* then settled out. The complex (0·07 g.) was separated and dried as for the corresponding chloride. The substance was soluble in methanol and dioxan–acetone, slightly soluble in ethanol and in acetone, very sparingly soluble in dioxan, and insoluble in chloroform, carbon tetrachloride, benzene, toluene, ether, and water. It decomposed explosively at 293° (Found: Cl, 12·0; Os, 20·4%; *M*, in 0·11% solution in nitrobenzene,

440. $C_{20}H_{32}O_4Cl_3As_4Os$ requires Cl, 11·4; Os, 20·4%; *M*, 933). Potentiometric titration with silver nitrate in acetone solution and use of a silver electrode established that only one chlorine atom is ionised.

*Dibromodi-(*o*-phenylenebisdimethylarsine)osmium*(III) *Bromide*.—The bivalent osmium complex (0·1 g.) was oxidised by bromine in methanol (100 ml.) at 40°. The bromine was added in alcoholic solution, excess being avoided. The purple solution which formed was filtered, and a solution of sodium bromide (0·2 g.) in methanol (5 ml.) added. On standing, purple-blue crystals (0·15 g.) of the tervalent *complex* were obtained. It decomposed at 304°, and was slightly soluble in ethanol, sparingly soluble in acetone and dioxan, and almost insoluble in benzene, carbon tetrachloride, chloroform, and ether. However, the substance dissolved very readily in dioxan–acetone (1 : 1) (Found: Br, 24·7; Os, 18·75%; *M*, cryoscopic in 0·12% solution in nitrobenzene, 506. $C_{20}H_{32}Br_3As_4Os$ requires Br, 24·0; Os, 18·96%; *M*, 1002). Potentiometric titration with silver nitrate in acetone solution with a silver electrode showed that only one bromine atom is ionised.

*Dibromodi-(*o*-phenylenebisdimethylarsine)osmium*(III) *Perchlorate*.—An alternative method of preparation directly from the hexabromo-osmate ion was used. To $(NH_4)_2OsBr_6$ (0·369 g.) in water (5 ml.), diarsine (0·3 g.) was added, and a homogeneous phase obtained by addition of ethanol. The solution was heated under reflux until a violet-blue colour had developed, and was then filtered, and perchloric acid (1 ml.) added to the filtrate. On standing, purple-blue crystals (0·21 g.) of the required *complex* settled out. These were washed with alcoholic ether to remove any diarsine and recrystallised from acetone–dioxan, in a vacuum. The complex decomposed at 302° with explosive violence (Found: Os, 18·8%; *M*, in 0·2% solution in nitrobenzene, 470. $C_{20}H_{32}O_4Br_2ClAs_4Os$ requires Os, 18·6%; *M*, 1022).

*Di-iododi-(*o*-phenylenebisdimethylarsine)osmium*(III) *Bromide*.—The osmium complex $[Os(Diarsine)_2I_2]^0$ (0·1 g.) was suspended in methanol (100 ml.), and the calculated proportion of bromine in methanol added cautiously with stirring. The solution was then filtered, and water (25 ml.) added. The blue-green precipitate (0·1 g.) which formed was separated by decantation and centrifuging, washed with dilute ethanol, and dried (H_2SO_4) in a vacuum-desiccator. The *complex* is soluble in acetone–dioxan to a bluish-green solution. On heating it decomposed at 288°. Owing to its low solubility in nitrobenzene its molecular weight was not measured (Found: Os, 17·3. $C_{20}H_{32}BrI_2As_4Os$ requires Os, 17·35%).

*Di-iododi-(*o*-phenylenebisdimethylarsine)osmium*(III) *Perchlorate*.—Ammonium hexabromo-osmate (0·36 g.), sodium iodide (0·16 g.), diarsine (0·25 g.), and ethanol (50 ml.) were refluxed together until a greyish-blue colour had developed. The mixture was then filtered, and the filtrate treated with perchloric acid (3 ml.). The green precipitate (0·15 g.) which formed was filtered and purified by recrystallisation from acetone–dioxan and dried in vacuum. The *perchlorate* decomposes on heating at 273° (Found: Os, 17·1%; *M*, in 0·1% solution in nitrobenzene 500. $C_{20}H_{32}O_4ClI_2As_4Os$ requires Os, 17·1%; *M*, 1115).

*Dithiocyanatodi-(*o*-phenylenebisdimethylarsine)osmium*(III) *Perchlorate*.—Ammonium hexabromo-osmate(IV) (0·31 g.), ammonium thiocyanate (0·4 g.), diarsine (0·23 g.), and ethanol 95% (50 ml.) were refluxed together until a light blue colour had developed, then filtered; perchloric acid (2 ml.) was added, and the solution evaporated to 25 ml. on a water-bath. Addition of water (25 ml.) yielded a precipitate of the *perchlorate* (0·16 g.). This was removed by centrifuging, washed with ether, and reprecipitated from acetone–dioxan. It decomposed with explosive violence at 265° (Found: Os, 19·2%; *M*, cryoscopic in 0·10% solution in nitrobenzene, 450. $C_{22}H_{32}O_4N_2ClS_2As_4Os$ requires Os, 19·4%; *M*, 977).

*Dichlorodi-(*o*-phenylenebisdimethylarsine)osmium*(IV) *Perchlorate*.—The red tervalent osmium complex $[Os(Diarsine)_2Cl_2]Cl$ (0·1 g.) was treated with 15N-nitric acid (3 ml.) with stirring until all had dissolved. A few drops of perchloric acid were then added to the green solution, and the mixture left in a refrigerator. After several hours, the blue-black crystals which had settled out were separated by centrifuging, shaken rapidly with three portions of cold anhydrous ether to remove any nitric or perchloric acids and any traces of products of oxidation, and dried in a vacuum [Found: Cl (total), 13·5; Os, 18·5. $C_{20}H_{32}O_8Cl_4As_4Os$ requires C, 13·75; Os, 18·5%]. When heated at 160° the *complex* decomposed, first turning red, the colour of the tervalent compound.

*Dibromodi-(*o*-phenylenebisdimethylarsine)osmium*(IV) *Perchlorate*.—The blue complex $[Os(Diarsine)_2Br_2]Br$ (0·1 g.) was treated with 15N-nitric acid as above, a green solution being formed. Addition of perchloric acid, and subsequent treatment as for the above chloro-complex, led to black shiny crystals (0·11 g.) (Found: Os, 17·2. $C_{20}H_{32}O_8Br_2Cl_2As_4Os$ requires Os, 17·0%). When heated, the *perchlorate* decomposed at 194°.

Di-iododi-(o*-phenylenebisdimethylarsine*)*osmium*(IV) *Perchlorate.*—The green compound $[Os(Diarsine)_2I_2]ClO_4$ (0·04 g.) was oxidised with concentrated nitric acid as before, and after the addition of perchloric acid and cooling, dark brown crystals of the osmium(IV) *complex* (0·04 g.) were precipitated from the golden-yellow solution. The complex was then washed with cold anhydrous ether and dried in a vacuum (Found: Os, 15·7. $C_{20}H_{32}O_8Cl_2I_2As_4Os$ requires Os, 15·6%). The compound decomposed on heating to 210°.

Potentiometric Titration: Oxidation–Reduction.—The yellow complex $[Os(Diarsine)_2Cl_2]$ (0·1580 g.) was dissolved in acetone (80 ml.) together with 5N-sulphuric acid (80 ml.), and the homogeneous mixture titrated with 0·01N-potassium dichromate solution from a microburette. The reaction was carried out in a carbon dioxide atmosphere, a sharp end-point being obtained after adding 1 equiv. of oxidising agent. E_0 was estimated at 0·6—0·7 v.

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