Structural and Mechanistic Studies of Co-ordination Compounds. Part 30.[1] Synthesis and Characterization of Some Octahedral Halogenoamine Complexes of Osmium(III)

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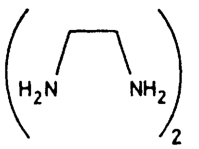
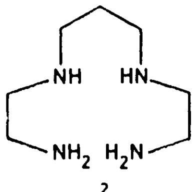
A series of osmium(III) amine complexes of the types *trans*-[OsLCl$_2$]$^+$ [L = L^1, bis(ethane-1,2-diamine); L^2, 3,7-diazanonane-1,9-diamine; L^3, 4,7-diazadecane-1,10-diamine; L^4, 1,4,8,11-tetra-azacyclotetradecane; or L^5, 1,4,8,12-tetra-azacyclopentadecane], *trans*-[OsLBr$_2$]$^+$ (L = L^3, L^4, or L^5), and *trans*-[OsL^{3}I$_2$]$^+$ has been prepared and characterized. All these complexes are low-spin monomeric species. The general synthetic methods and the electronic and i.r. absorption spectra of these complexes are discussed.

As part of our programme to study the photochemical, electrochemical, and thermal substitution reactions of Group 8 transition-metal amine complexes, we have reported the synthesis and thermal substitution reactions of some iron(III) [2,3] and ruthenium(III) [1,4-7] complexes of the type *cis*- and *trans*-[MLX$_2$]$^+$ where M represents either iron(III) or ruthenium(III), L either two bidentate or one quadridentate amine, and X a unidentate anionic ligand. It is our intention to extend the studies to osmium(III) systems. However, relatively little is known about osmium(III) amine complexes, probably because a general and convenient synthetic route for the synthesis of these complexes has not yet been fully developed. Dwyer and Hogarth [8,9] first reported the synthesis of [Os(NH$_3$)$_5$X]$^{2+}$ (X = Cl or Br) by treating the corresponding [NH$_4$]$_2$[OsX$_6$] with ammonia under pressure at *ca.* 290 °C. However, the overall yield was poor. Following the discovery [10,11] of stable dinitrogen complexes of ruthenium and osmium, Allen and Stevens [12] were able to synthesize [Os(NH$_3$)$_5$X]$^{2+}$ and *cis*- and *trans*-[Os(NH$_3$)$_4$X$_2$]$^+$ (X = Cl, Br, or I) in high yields starting with either [Os(NH$_3$)$_5$(N$_2$)]$^{2+}$ or [Os(NH$_3$)$_4$(N$_2$)$_2$]$^{2+}$ as appropriate. Although this method may appear very useful for the synthesis of ammine complexes, it is not a general method applicable to other amine systems. Recently, Coelho and Malin [13] reported the synthesis of *trans*-[OsL^{1}X$_2$]$^+$ [L^1 = bis(ethane-1,2-diamine); X = Cl or Br] by treating *trans*-[OsL^{1}H$_2$]$^{2+}$ with the corresponding HX. Once again, the overall yield, taking into account the large number of steps involved, was poor and the method was time-consuming and inconvenient. This paper describes a general method for the synthesis of some osmium(III) amine complexes of the types, *trans*-[OsLCl$_2$]$^+$ [L = L^1, L^2 (3,7-diazanonane-1,9-diamine), L^3 (4,7-diazadecane-1,10-diamine), L^4 (1,4,8,11-tetra-azacyclotetradecane), or L^5 (1,4,8,12-tetra-azacyclopentadecane)], *trans*-[OsLBr$_2$]$^+$ (L = L^3, L^4, or L^5), and *trans*-[OsL^{3}I$_2$]$^+$.



L^1



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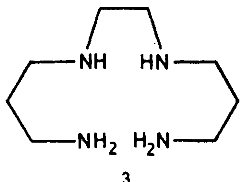

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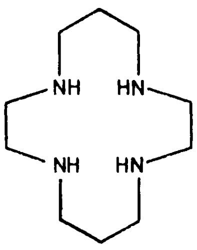
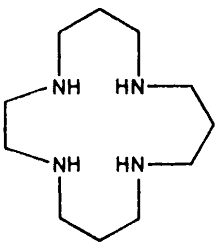


L^4



L^5

EXPERIMENTAL

trans-*Dichloro(tetra-amine)osmium*(III) *Perchlorate, trans*-[OsLCl$_2$][ClO$_4$] (L = L$^{1-5}$).—These complexes were prepared by essentially the same method which is described in detail below for L = L^4.

A methanolic solution (150 cm^3 A. R. grade solvent) of Na$_2$[OsCl$_6$] (1 g, from Johnson Matthey) was first refluxed on its own with vigorous stirring for *ca.* 10 min. The compound $Na[H_2PO_2]$ (1.5 g) was added and the refluxing was continued for another 5 min (NB. *this refluxing step before the addition of amine should be strictly followed*!). A methanolic solution of L^4 (0.5 g in 230 cm^3 A.R. grade solvent) was then added dropwise to the refluxing solution. When the addition was about $\frac{2}{3}$ complete, another portion of $Na[H_2PO_2]$ (1 g) was added and the entire addition process required *ca.* 5 h. After the addition of L^4, another portion of $Na[H_2PO_2]$ (1 g) was added and the solution was refluxed overnight. This was acidified with dilute HCl and was then filtered whilst hot. The resulting brown solution was evaporated to dryness. The yellowish brown residue was dissolved in the minimum volume of hot dilute HCl (2 mol dm^{-3}). Addition of excess of $Na[ClO_4]$ to the filtered hot solution slowly precipitated out some yellow solids which were collected and washed with a small quantity of ice-cold water and ethanol–diethyl ether. The product so obtained might have been contaminated with some partially dehydrogenated products. In fact, the yellow solid might appear dark brown or reddish brown. Therefore, the following reductive purification is essential.

The crude product was first dissolved in warm HCl (50 cm^3, 3 mol dm^{-3}) at *ca.* 90 °C. Several pieces of zinc were added whilst the solution was kept heating on a hot-plate. Hydrogen was generated to reduce the dehydrogenated components, if any, and the reduction process was continued until the solution appeared light brown. This usually took *ca.* 0.5 h. Excess of $Na[ClO_4]$ was added to the filtered hot solution. On cooling, some light brown microcrystalline solids deposited, which were collected, washed with ethanol, diethyl ether, and finally dried *in vacuo* at 78 °C (yield 50%).

The colour of the other complexes was pale yellow for L = L^1, L^2, and L^3, but light brown for L = L^5. The yield of the above procedure ranges from 10 to 50%, being highest for L = L^4 and L^5 and lowest for L = L^1. Elemental analytical data of all new complexes are collected in Table 1.

TABLE 1

Analytical data, magnetic moments, and molar conductivities of some osmium(III) complexes of the type *trans*-$[OsLX_2][ClO_4]$

		Analysis [a]/%				$\mu_{eff.}$ [b]/B.M.	Λ [c]/S cm^2 mol^{-1}
L	X	C	H	N	X		
L^1	Cl	10.2	3.50	11.5	22.2	2.05	105
		(10.0)	(3.30)	(11.7)	(22.2)		
L^2	Cl	16.1	3.60	10.6	20.4	2.10	101
		(16.1)	(3.80)	(10.8)	(20.5)		
L^3	Cl	18.0	4.20	10.6	19.9	2.10	102
		(18.0)	(4.10)	(10.5)	(19.9)		
	Br	15.6	3.70	9.20	5.70 [d]	2.11	104
		(15.4)	(3.50)	(9.00)	(5.70)		
	I	13.5	2.90	7.80	35.3	1.90	110
		(13.4)	(3.10)	(7.80)	(35.4)		
L^4	Cl	21.3	4.20	9.90	19.2	2.11	101
		(21.4)	(4.30)	(10.0)	(19.0)		
	Br	18.6	3.60	8.70	24.8	2.12	106
		(18.5)	(3.70)	(8.60)	(24.6)		
L^5	Cl	22.7	4.60	9.80	18.4	2.10	102
		(23.0)	(4.50)	(9.70)	(18.5)		
	Br	20.0	3.70	8.40	24.2	2.08	107
		(19.9)	(3.90)	(8.40)	(24.1)		

[a] Calculated values are given in parentheses. [b] At 25.0 °C. 1 B.M. = 9.274×10^{-24} A m^2. [c] In deionized water at 20.0 °C. [d] Chlorine analysis.

trans-*Dibromo*(*tetra-amine*)*osmium*(III) *Perchlorate, trans*-$[OsLBr_2][ClO_4]$ (L = L^{3-5}).—A hot aqueous solution of crude *trans*-$[OsLCl_2][ClO_4]$ (0.5 g in 50 cm^3) was treated with excess of NaBr (7 g) and the resulting solution was heated on a steam-bath for *ca.* 5 h. A deep reddish brown solution was obtained, which was filtered whilst hot and then acidified with HBr. Addition of excess of $Na[ClO_4]$ precipitated out some deep reddish brown solids which were collected and purified by the same reductive method as described above for *trans*-$[OsLCl_2][ClO_4]$ except that HBr was used instead of HCl. The recrystallized product appears brownish yellow in powdered form but deep reddish brown in needle crystals. The yield of the preparation varies between 60 and 70%.

trans-(4,7-*Diazadecane*-1,10-*diamine*)*di-iodo-osmium*(III) *Perchlorate*.—This complex was prepared by essentially the same method as that of *trans*-$[OsL^3Br_2][ClO_4]$ except that NaI was used instead of NaBr. The crude dark violet solid was purified by dissolving it in hot toluene-*p*-sulphonic acid (50 cm^3, 1.5 mol dm^{-3}, at *ca.* 90 °C). Several pieces of amalgamated zinc were added and the solution was heated on a hot-plate for *ca.* 0.5 h. Toluene-*p*-sulphonic acid was added during the course of the reaction, if necessary, to ensure a continuous production of H_2. The solution was then filtered whilst hot and NaI (1 g) was added to the filtrate. On further addition of excess of $Na[ClO_4]$ followed by cooling overnight, dark violet-red needle-shaped crystals deposited. These were collected, washed with a little ice-cold water and ethanol–diethyl ether, and dried *in vacuo* at 78 °C (yield 60%).

Physical Measurements.—Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer 577 spectrophotometer (200—4 000 cm^{-1}). Electronic absorption spectra of freshly prepared solutions were measured with a Beckman Acta CIII spectrophotometer. Magnetic susceptibilities of solid samples were measured by the Gouy method using mercury tetrathiocyanatocobaltate(II) as the calibrant.[14]

RESULTS AND DISCUSSION

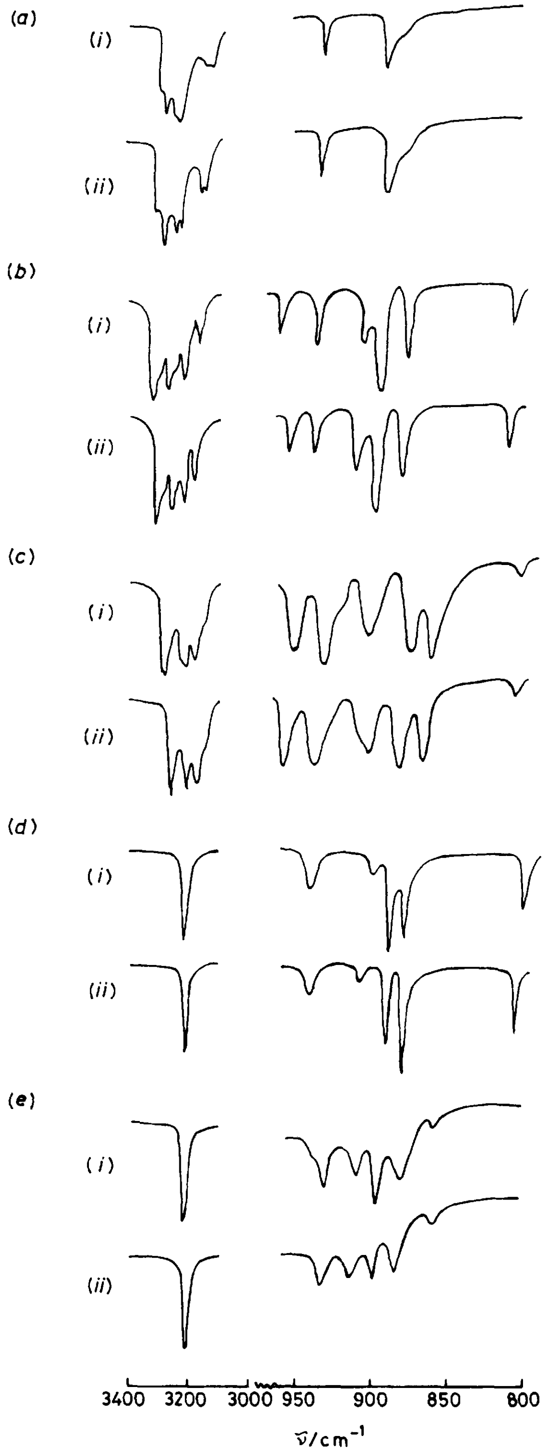
The synthetic method of controlled dropwise addition of amines to a boiling methanolic solution of $Na_2[OsCl_6]$ is reproducible as it has been checked by several independent workers of this laboratory. An important feature of this method is the use of methanol (or ethanol) as the reaction medium. Various other solvents, such as water, tetrahydrofuran, dimethyl sulphoxide, dimethylformamide, and acetonitrile, have been tried for the synthesis of these amine complexes, but in every case the reaction was either unsuccessful or proceeded inefficiently with many side-products. When $Na_2[OsCl_6]$ is refluxed in a basic medium of alcohol, a reactive hydrido-intermediate is probably formed. This idea was derived from the observation of Chatt and Shaw [15] that the reactions of tertiary phosphine metal halides of ruthenium, osmium, or rhodium with alcohols in the presence of a base gave very good yields of some hydrido-, carbonyl, or carbonyl hydrido-complexes. Although it has not been possible to detect the presence of any hydrido-species in the course of the synthetic reactions, the proposition is supported by the observation that the synthesis of *trans*-$[OsLCl_2]^+$ was facilitated by the addition of $Na[H_2PO_2]$. A number of other reducing agents, such as iodide, oxalic acid, and zinc have been tried, but in every case the reaction was either unsuccessful or very inefficient. The superiority of $Na[H_2PO_2]$ over other reducing agents might be due to its potential function as a hydride donor. As a matter of fact, the direct reaction between $[OsCl_6]^{3-}$, freshly generated by the zinc reduction of $[OsCl_6]^{2-}$, and some amines did lead to the formation of *trans*-$[OsLCl_2]^+$, but the course of the reaction was rather complicated with many side products. Furthermore, the synthesis of *trans*-$[OsL^1Cl_2]^+$ could not be achieved without the addition of $Na[H_2PO_2]$.

Another important feature of this synthetic method is the controlled dropwise addition of the amine to a refluxing alcoholic solution of the metal complex. A previous report[5] on the synthesis of ruthenium(III) amine complexes suggested that, since $K_2[RuCl_5(OH_2)]$ was only sparingly soluble in methanol, the act of controlled dropwise addition of the amine was merely to provide a roughly stoicheiometric ratio of $[RuCl_5(OH_2)]^{2-}$ to amine in solution. If this was in fact the case it should not be necessary to maintain this dropwise addition of the amine for the synthesis of osmium amine complexes since $Na_2[OsCl_6]$ is quite soluble in alcohol. However, if the amine was not added dropwise, some dark brown solids were obtained. Infrared spectra of these solids showed the complete absence of ν(N–H) and ν(C–H) and no *trans*-$[OsLCl_2]^+$ could be isolated.. It would therefore appear that the rate of formation of the reactive hydrido-intermediate is slow and the dropwise addition of the amine to the reaction solution is to maintain a roughly stoicheiometric ratio of this hydrido-intermediate to amine. The starting complexes appeared to be unstable in basic solutions.

One of the major difficulties associated with the synthesis of the Group 8 amine complexes is the ease of metal-promoted dehydrogenation of the co-ordinated amine ligands.[16-20] Therefore, syntheses are best carried out under an inert atmosphere. In practice, it was found that the refluxing of the starting material in absolute methanol for *ca.* 15 min before the addition of the amine to start the synthetic reaction produced a satisfactory inert atmosphere. However, the initially prepared crude products were still sometimes contaminated with some partially dehydrogenated species and hence a reductive purification of the crude products was necessary to generate the pure microcrystalline complexes.

All the new chloro- and bromo-complexes prepared are light coloured but *trans*-$[OsL^3I_2][ClO_4]$ is dark violet-red. The complexes appear to be stable indefinitely in the solid state and in acidic solutions. However, in basic media, all these halogeno-amine complexes gradually turned dark brown. We have not yet been able to identify the nature of these dark brown species. The purity of the complexes was confirmed by the observation that the i.r. and electronic absorption spectra of the complexes were unaffected by repeated recrystallization and preparation. This was further confirmed by chromatography as described previously.[5] The magnetic moments and molar conductivities of these complexes (Table 1) confirm that they are low-spin monomeric species.

The assignment of *trans* configurations to these complexes was made on the basis of i.r. spectroscopy. Previous reports[1,2,5,21,22] state that the i.r. spectrum in



Infrared spectra of corresponding pairs of ruthenium(III) (*i*) and osmium(III) (*ii*) complexes of the type *trans*-$[MLCl_2][ClO_4]$, L = L^1 (*a*), L^2 (*b*), L^3 (*c*), L^4 (*d*), L^5 (*e*), in the 800—960 and 3 100—3 400 cm^{-1} regions the 790—950 cm^{-1} region is most useful in differentiating between *cis* and *trans* isomers of most tetra-amine complexes. The i.r. spectra in the 3 100—3 400 and 790—960 cm^{-1} regions for corresponding pairs of *trans*-[RuLCl$_2$][ClO$_4$] and *trans*-[OsLCl$_2$][ClO$_4$] (L = L$^{1-5}$) are shown in the Figure. It is clear that the i.r. spectra of the new [OsLCl$_2$][ClO$_4$] complexes are very similar to those of the corresponding *trans*-[RuLCl$_2$][ClO$_4$] complexes,[5] hence the assignment of a *trans* configuration to these osmium(III) complexes. The i.r. spectra of dibromo- and di-iodo-complexes in these regions are also very similar to their corresponding dichloro-analogues. The ν(Os–X) (X = Cl or Br) stretches were obtained by comparing the far-i.r. spectra of corresponding pairs of *trans*-[OsLX$_2$][ClO$_4$] with the same L. For the dichloro-complexes, the ν(Os–Cl) stretches showed a small splitting [L = L^2, 320s, 315s(sh); L^3, 322s, 315s(sh); L^4, 314s, 305s(sh); L^5, 322s, 315s(sh) cm^{-1}]. This splitting could arise from crystal packing effects. The corresponding ν(Os–Br) stretches, on the other hand, did not show any splitting for L^3 (225m) and L^5 (228m cm^{-1}) and are therefore consistent with a *trans* configuration. The far-i.r. spectrum of *trans*-[OsL^{4}Br$_2$]-[ClO$_4$] below 230 cm^{-1} was not well defined and we could not assign with confidence the ν(Os–Br) stretch of this complex. The ν(Os–I) stretch of *trans*-[OsL^{3}I$_2$][ClO$_4$] clearly falls below our instrumental limit of 200 cm^{-1} and it could not be determined in the present investigation.

TABLE 2

Visible and u.v. absorption spectra of some osmium(III) complexes of the type *trans*-[OsLX$_2$][ClO$_4$]

Complex	Solvent [a]	$\lambda_{max.}$ [b]/nm
[Os(NH$_3$)$_4$Cl$_2$]$^+$ [c]	H$_2$O	271 (4 810), 245 (1 290), 212 (1 610)
[OsL^{1}Cl$_2$]$^+$	HCl	284 (4 360), 250 (sh) (1 360), 235br (1 670), *ca.* 215br (sh) (1 850)
[OsL^{2}Cl$_2$]$^+$	HCl	291 (3 840), 251br (1 890)
[OsL^{3}Cl$_2$]$^+$	HCl	290 (3 330), 254br (1 920)
[OsL^{4}Cl$_2$]$^+$	HCl	298 (2 560), 265 (1 570), 250 (sh) (1 470)
[OsL^{5}Cl$_2$]$^+$	HCl	294 (2 860), 266br (1 840)
[Os(NH$_3$)$_4$Br$_2$]$^+$ [c]	H$_2$O	317 (4 690), 280 (870)
[OsL^{1}Br$_2$]$^+$ [d]	H$_2$O	330 (4 940)
[OsL^{3}Br$_2$]$^+$	HBr	338 (4 260), 289br (1 040)
[OsL^{4}Br$_2$]$^+$	HBr	346 (3 940), 293 (760)
[OsL^{5}Br$_2$]$^+$	HBr	343 (3 200), 294 (1 680)
[Os(NH$_3$)$_4$I$_2$]$^+$ [c]	H$_2$O	418 (4 920), 368 (860), 308 (245)
[OsL^{3}I$_2$]$^+$	tsa	502 (4 350), 429br (1 350), *ca.* 316 (sh) (2 890)

[a] 0.1—1.0 mol dm^{-3} HCl, HBr, or toluene-*p*-sulphonic acid (tsa). [b] Molar absorption coefficients (ϵ/dm^3 mol^{-1} cm^{-1}) are given in parentheses; br = broad, sh = shoulder. [c] Ref. 12. [d] Ref. 13; a bromide salt.

The electronic absorption spectra of the osmium(III) complexes (Table 2) are dominated by the intense ligand-to-metal charge-transfer transitions. This assignment is confirmed by the gradual red shift of the lowest-energy $\lambda_{max.}$ from dichloro- through dibromo- to di-iodo-complexes. Within the same series of *trans*-[OsLX$_2$][ClO$_4$] complexes (X = Cl or Br), $\lambda_{max.}$ gradually increases with increasing chelation about the central osmium(III) ion: $(NH_3)_4 < L^1 < L^2 \simeq L^3 < L^5 < L^4$. This gradual variation of $\lambda_{max.}$ was also observed for corresponding series of ruthenium(III) complexes.[5] A comparison between $\lambda_{max.}$ values of corresponding ruthenium(III) [5] and osmium(III) complexes indicates that the ruthenium(III) ion has a greater tendency to accept π electrons in to its t_{2g} orbitals, or is more electronegative, than the corresponding osmium(III) ion (for *trans*-[MLCl$_2$]$^+$, $\lambda_{max.}$ *ca.* 350 for M = Ru^{III} and *ca.* 290 nm for M = Os^{III}; for *trans*-[MLBr$_2$]$^+$, $\lambda_{max.}$ *ca.* 420 for Ru^{III} and *ca.* 340 nm for Os^{III}; and for *trans*-[MLI$_2$]$^+$, $\lambda_{max.}$ *ca.* 580 for Ru^{III} and *ca.* 500 nm for Os^{III}).

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