Preparation and Properties of Some Osmium Nitrosylammines

By **F. Bottomley** * and **S. B. Tong**, Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada

$[Os(NH_3)_5I]I_2$ and NO gave a mixture of $[Os(NH_3)_5NO]I_3$ and $[OsI(NH_3)_4NO]I_2$, which was converted to $[Os(NH_3)_5NO]I_3$ in liquid ammonia. $[Os(NH_3)_5NO]X_3,H_2O$ (X = Cl, Br, or I) and OH^- gave $[OsNH_2(NH_3)_4NO]X_2$ reversibly, and under more vigorous conditions, *trans*-$[OsOH(NH_3)_4NO]X_2$. $[OsOH(NH_3)_4NO]X_2$, when refluxed with HX, gave $[OsX(NH_3)_4NO]X_2$. The physical properties of the complexes are reported and compared with the analogous ruthenium complexes. The complexes were unreactive to nucleophilic attack at the NO^+ group, though $[Os(NH_3)_5NO]^{3+}$ gave $[Os(NH_3)_5N_2]^{2+}$ on refluxing with hydrazine.

IN previous papers [1-3] we have described reactions of nitrosylpenta-ammineruthenium(II) with nucleophiles. It was desirable to extend these investigations to osmium for comparison between the reactivity of the ruthenium and osmium nitrosyl groups. Apart from a brief reference to nitrosylpenta-ammineosmium(III), $[Os(NH_3)_5NO](ClO_4)_3$,[4] osmium nitrosylammines have not been reported. We present here the preparation and properties of $[Os(NH_3)_5NO]X_3,H_2O$; amidotetra-amminenitrosylosmium(II), $[OsNH_2(NH_3)_4NO]X_2$; hydroxotetra-amminenitrosylosmium(II), $[OsOH(NH_3)_4NO]X_2$; and halogenotetra-amminenitrosylosmium(II), $[OsX(NH_3)_4NO]X_2$ (X = Cl, Br, or I).

Our original aim has been thwarted, since the complexes are unreactive towards attack at the nitrosyl group; only hydrazine, of those reagents which react with $[Ru(NH_3)_5NO]^{3+}$, reacts, and then only under reflux, giving $[Os(NH_3)_5N_2]^{2+}$.[5]

RESULTS AND DISCUSSION

It was shown that the reaction of nitric oxide with $[Ru(NH_3)_5A]^{n+}$ ($A = NH_3$, $n = 3$; $A = Cl$, $n = 2$) occurred by bimolecular electrophilic substitution, and from NO and $[Ru(NH_3)_5Cl]^{2+}$ essentially equal quantities of $[Ru(NH_3)_5NO]^{3+}$ and $[RuCl(NH_3)_4NO]^{2+}$ were obtained.[4] By analogy, the preferred starting material for the preparation of $[Os(NH_3)_5NO]^{3+}$ would be $[Os(NH_3)_6]^{3+}$. However, the lengthy procedure and low yields in preparing $[Os(NH_3)_6]^{3+}$ [6] made an indirect synthesis attractive. The procedure given, (see Experimental section) whereby a mixture of $[Os(NH_3)_5NO]I_3$ and $[OsI(NH_3)_4NO]I_2$, obtained by passing NO through the readily accessible $[Os(NH_3)_5I]I_2$,[5] was converted to $[Os(NH_3)_5NO]I_3$ in liquid ammonia, was relatively rapid and gave high yields of the desired product $\{(NH_4)_2OsCl_6$ to $[Os(NH_3)_5NO]I_3,H_2O$, 51%$\}$. Attempts to shorten the procedure further by passing NO through a

---

[1] F. Bottomley and J. R. Crawford, *Chem. Comm.*, 1971, 200.

[2] F. Bottomley and J. R. Crawford, *J.C.S. Dalton*, 1972, 2145.

[3] F. Bottomley and J. R. Crawford, submitted for publication.

[4] J. N. Armor, H. A. Scheidegger, and H. Taube, *J. Amer. Chem. Soc.*, 1968, **90**, 5928.

[5] A. D. Allen and J. R. Stevens, *Chem. Comm.*, 1967, 1147.

[6] G. W. Watt, E. M. Potrafke, and D. S. Klett, *Inorg. Chem.*, 1963, **2**, 868.

solution of $[Os(NH_3)_5I]I_2$ in liquid ammonia were not successful, the conversion rate being very low.

$[Os(NH_3)_5NO]^{3+}$ was unreactive to attack at the NO^+ group. Hydroxide ion, ammonia, hydroxylamine, and hydrazine, all of which act as nucleophiles towards $[Ru(NH_3)_5NO]^{3+}$,[1-3] acted as simple bases towards $[Os(NH_3)_5NO]^{3+}$ at room temperature in aqueous solution. Refluxing $[Os(NH_3)_5NO]Cl_3,H_2O$ in a solution of hydrazine hydrate gave $[Os(NH_3)_5N_2]Cl_2$,[5] and reduction of $[Os(NH_3)_5NO]Br_3,H_2O$ with zinc in ammoniacal solution gave an as yet uncharacterized product containing no nitrosyl group, but no other reactions of the NO^+ group were found. As judged by the spectra (see below) of the osmium complexes in comparison with those of ruthenium, osmium is a better π-electron donor towards NO^+ than ruthenium. This would make the NO^+ group less susceptible to nucleophilic attack,[2,7] and may explain the lack of reactivity.

In aqueous alkaline solution, at room temperature, $[Os(NH_3)_5NO]^{3+}$ was in equilibrium with $[OsNH_2(NH_3)_4NO]^{2+}$. The equilibrium constant (determined spectroscopically at an ionic strength of 0·020 mol l^{-1}) for the reaction:

$$[Os(NH_3)_5NO]^{3+} + H_2O \rightleftharpoons [OsNH_2(NH_3)_4NO]^{2+} + H_3O^+$$

was $1{\cdot}2 \times 10^{-11}$ mol l^{-1}. On refluxing, alkaline solutions of $[Os(NH_3)_5NO]^{3+}$ gave $[OsOH(NH_3)_4NO]^{2+}$. $[OsOH(NH_3)_4NO]Cl_2$ had an *X*-ray powder pattern closely similar to *trans*-$[RuOH(NH_3)_4NO]Cl_2$, whose structure is known from a single crystal determination.[8] Therefore, we assign $[OsOH(NH_3)_4NO]^{2+}$ the *trans*-configuration also. $[OsOH(NH_3)_4NO]^{2+}$ was converted into $[OsX(NH_3)_4NO]^{2+}$ by prolonged refluxing in HX. The rate of substitution was very low. Since $[Os(NH_3)_5NO]^{3+}$ is itself a weak acid, it is likely that $[OsH_2O(NH_3)_4NO]^{3+}$ (which we have not observed) is an extremely strong acid, and hence, even in concentrated acid, substitution of OH^- by X^- may be occurring. This is likely to be slow.

TABLE 1

Some i.r. bands and analytical data of the complexes

				Calc.		Found	
		νNO/cm^{-1}	νOsN or δOsNO/cm^{-1}	N	X	N	X
$[Os(NH_3)_5NO]X_3,H_2O$	X = Cl	1893s, 1871s	614m	19·55	24·7	19·4	24·7, 23·7
	Br	1893s, 1876s	611m	14·95	42·6	15·0	42·7, 43·4
	I	1892s, 1879s	605m	11·95	54·1	11·9	55·0
$[Os(NH_3)_4(OH)NO]X_2$	X = Cl	1806s	633w, 613w, 582s	18·6	18·8	18·5	17·8
	Br	1808s	635w, 612w, 582s	15·05	34·4	15·25	35·1, 33·5
	I	1817s	632w, 609m, 580s	12·55	45·4	12·5	47·4, 46·3
$[Os(NH_3)_4(NH_2)NO]X_2$	X = Cl	1785s, 1764s	608w, 572m	22·4	18·9	22·3	17·8
	Br	1791s	615sh, 606w, 567m	18·1	34·4	17·85	33·5, 32·7
	I	1800s	617w, 603sh, 593w, 562m	15·05	45·5	14·9	45·0
$[Os(NH_3)_4(X)NO]X_2$	X = Cl	1832s	620sh, 612w, 591w	17·75	26·9	18·0	25·1
	Br	1842s, 1830sh	610sh, 601w	13·25	45·4	13·55	45·8
	I	1844s	594sh, 586w	10·45	56·9	10·3	57·1

The complexes isolated from the above reactions were characterized by spectroscopy (Tables 1 and 2), conductivity, magnetic moments (in representative cases), and partial analysis (Table 1). Great difficulty was experienced in obtaining reproducible halide analyses, even with materials recrystallized several times and with reproducible spectra. The reason for this is unknown.

The i.r. spectra of the complexes were similar to those of the analogous ruthenium complexes. Table 1 lists the bands associated with the osmium-nitrosyl group. The frequency of νNO was *ca.* 30 cm^{-1} lower than for the analogous ruthenium complexes,[2,9,10] reflecting increased π-electron donation by osmium to NO^+. The value of νNO for $[OsNH_2(NH_3)_4NO]X_2$ indicated this complex probably has a *trans*-structure. Bands in the regions expected for νOs–N (of the NO^+ ligand) and δOsNO were observed. There has been some controversy in the assignment of such bands.[9-11] Cleare and Griffith [9] presented good evidence for their assignments in ruthenium complexes analogous to those of osmium prepared in this work, but there was not a one to one correspondence between the bands for the osmium and ruthenium complexes, and we prefer, therefore, not to give a definite assignment.

The electronic spectra of the complexes are given in Table 2. Schreiner and co-workers have recently analyzed the electronic spectra of a variety of ruthenium nitrosyls,[12] and a similar analysis can be made for osmium complexes (Table 2). The spectra of the analogous ruthenium and osmium complexes were very similar, with both the *d–d* and charge transfer absorption bands occurring at frequencies 10—15% higher for osmium than ruthenium, as may be expected on going from the second to the third row of the Periodic Table.[13]

---

[7] J. Masek and H. Wendt, *Inorg. Chim. Acta*, 1969, **3**, 455.

[8] N. A. Parpiev and G. B. Bokii, *Zhur. neorg. Khim.*, 1959, **4**, 2452.

[9] M. J. Cleare and W. P. Griffith, *J. Chem. Soc.* (*A*), 1969, 372.

[10] M. B. Fairey and R. J. Irving, *Spectrochim. Acta*, 1966, **22**, 359.

[11] J. R. Durig and D. W. Wertz, *Appl. Spectroscopy*, 1968, **22**, 627.

[12] A. F. Schreiner, S. W. Lin, P. J. Hauser, E. A. Hopcus, D. J. Hamm, and J. D. Gunter, *Inorg. Chem.*, 1972, **11**, 880.

[13] F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, second edition, Interscience, New York, 1966, p. 680.

TABLE 2

Electronic spectra[a] of $[Os(NH_3)_4(NO)L]^{n+}$ ($n = 3$ for $L = NH_3$; $n = 2$ for other L)

L	Anion	$\nu_{max.}$ (cm^{-1})	ε (mol^{-1} cm^{-1})	Assignment[b]	Ruthenium[c] analogue (ε)
NH_3[d]	Cl^-	22,600	51	I	22,000 (15)
		35,200	274	II	32,800 (56)
Br^-	Br^-	23,300	39	I	21,100 (17)
		33,200	116	II	26,900 (87)
		41,300	8340	III	36,500 (3700)
NH_2^-[f]	I^-	25,000	186	I	
		31,500	1560	II	
OH^-	Cl^-	26,500	59	I	23,300 (25)
		34,200	203	II	29,900 (211)
		49,500	8950	III	43,900 (5750)
I^-	ClO_4^-	35,000	6580	III	
		44,400			
		50,000			
Cl^-	Cl^-	23,700	41	I	22,700 (17)
		33,600	76	II_A	30,300 (264)
		35,700	72	II_B	
		45,700	7540	III	41,200 (4220)

[a] Unless otherwise stated, the spectra were determined in neutral aqueous solution. [b] I is $^1A_1 \longrightarrow {}^3\Gamma(^3T_1, {}^3T_2)$ and $t_{2g} \longrightarrow \pi^*NO$; II is $^1A_1 \longrightarrow {}^1T_1$; II_A is $^1A_1 \longrightarrow {}^1E$ $(^1T_1)$; II_B is $^1A_1 \longrightarrow {}^1A_2$ $(^1T_1)$; III is $p\pi L \longrightarrow (x^2 - y^2, z^2)Os$. [c] Ref. 12. [d] In 0·00137M HCl. [e] Weak shoulder. [f] In *ca.* 7·4M KOH.

EXPERIMENTAL

$(NH_4)_2OsCl_6$ was obtained from Johnson, Matthey and Mallory, Montreal, and used as received. All other materials were reagent grade. Dinitrogenpenta-ammineosmium dichloride and di-iodide, $[Os(NH_3)_5N_2]X_2$, were prepared by the literature method.[5] Their electronic and i.r. spectra agreed with the literature.[5,14,15]

Iodopenta-ammineosmium Di-iodide, $[Os(NH_3)_5I]I_2$.—Concentrated HI (3 drops) was added to a solution of $[Os(NH_3)_5N_2]I_2$ (2·365 g) in hot water (90 ml). Iodine (1—2 equivalents) was added until no more gas evolution was observed. The excess of iodine was filtered off, HI added to the filtrate, and the resultant orange-yellow precipitate of $[Os(NH_3)_5I]I_2$ removed by filtration, then washed with 95% ethanol and ether and air dried. A further quantity was obtained by evaporating the filtrate. Yield 2·666 g (96%). The crude product was recrystallized from water and dried *in vacuo* (P_2O_5) (Found: H, 2·2; N, 10·9. Calc. for $H_{15}I_3OsN_5$: H, 2·3; N, 10·7%. The product was a 2 : 1 electrolyte.

Nitrosylpenta-ammineosmium, $[Os(NH_3)_5NO]X_3,H_2O$ (X = I, Br, *or* Cl).—Nitric oxide was passed through a slurry of $[Os(NH_3)_5I]I_2$ (1·0 g) in a mixture of water (130 ml) and concentrated HCl (7 ml) for three days. The iodine deposited was removed by filtration * and the filtrate evaporated to half volume. Concentrated HI (57%, 20 ml) was added and the resultant yellow precipitate filtered off, washed with absolute ethanol and ether and air dried. Yield 0·706 g.

The i.r. spectrum showed the product was a mixture of $[OsI(NH_3)_4NO]I_2$ and $[Os(NH_3)_5NO]I_3,H_2O$. This mixture (0·706 g) was dissolved in liquid ammonia. The orange solution was maintained at −70 °C (' dry ice '-methanol) for 2 days. The ammonia was evaporated off and the resultant yellow residue of $[Os(NH_3)_5NO]I_3$ dissolved in cold water (15 ml). The solution was filtered and concentrated HI (57%) added dropwise until precipitation was complete. The yellow *needles* of $[Os(NH_3)_5NO]I_3,H_2O$ were removed by filtration, washed with absolute ethanol and ether and air dried. A further crop of crystals was obtained by evaporating the filtrate to a small volume. Yield 0·736 g [51%, based on $(NH_4)_2OsCl_6$].

The product was recrystallized by dissolving in warm water, filtering, and reprecipitating by adding several drops of concentrated HI. The crystals were filtered off, washed with absolute ethanol and ether, and dried *in vacuo* (P_2O_5).

$[Os(NH_3)_5NO]Br_3,H_2O$ and $[Os(NH_3)_5NO]Cl_3,H_2O$ were prepared metathetically from the iodide salt using aqueous HBr and HCl respectively. Yields, based on $[Os(NH_3)_5NO]I_3,H_2O$: bromide, 81%; chloride, 81%. The complexes were 3 : 1 electrolytes. The iodide salt was diamagnetic, $\chi = -0{\cdot}350 \times 10^{-6}$ (c.g.s.u.) at 25 °C.

Reaction of $[Os(NH_3)_5NO]Cl_3,H_2O$ *with Hydrazine Hydrate*.—$[Os(NH_3)_5NO]Cl_3,H_2O$ (0·070 g) was refluxed in a mixture of hydrazine hydrate (85%, 6 ml) and water (4 ml) for 2 h. Potassium chloride was added and the resultant pale yellow precipitate of $[Os(NH_3)_5N_2]Cl_2$ removed by filtration, washed with ethanol and ether, and air dried. Yield 0·022 g (36%). The product was recrystallized from hot water. Its electronic and i.r. spectra agreed with those of a sample prepared by literature methods.[5,14,15]

Amidotetra-amminenitrosylosmium, $[OsNH_2(NH_3)_4NO]X_2$ (X = I, Br, *or* Cl).—A solution of $[Os(NH_3)_5NO]I_3,H_2O$ (0·20 g) in 0·880 ammonia (20 ml) was set aside at 0 °C for a few minutes. Potassium iodide was added and the resultant yellow precipitate of $[OsNH_2(NH_3)_4NO]I_2$ removed by filtration, washed with 95% ethanol and ether and air dried. Yield 0·13 g (82%). The product was recrystallized from cold concentrated ammonia and dried *in vacuo* (P_2O_5).

The bromide and chloride salts were prepared similarly using the appropriate nitrosyl and potassium salts. Yields: bromide salt, 79%; chloride, 65%. The bromide salt was diamagnetic, $\chi = -0{\cdot}27 \times 10^{-6}$ (c.g.s.u.) at 25 °C.

Reaction of $[OsNH_2(NH_3)_4NO]I_2$ *with* HI.—To a solution of $[OsNH_2(NH_3)_4NO]I$ (0·0337 g) in a minimum quantity of cold water (6 ml) was added concentrated HI (1 ml). The resultant yellow crystals of $[Os(NH_3)_5NO]I_3,H_2O$ were removed by filtration, washed with absolute ethanol and ether, and air dried. Yield 0·0394 g (93%).

The i.r. spectrum of the product was identical to that of $[Os(NH_3)_5NO]I_3,H_2O$ prepared as above.

Hydroxytetra-amminenitrosylosmium, $[OsOH(NH_3)_4NO]X_2$ (X = I, Br, *or* Cl).—A solution of $[Os(NH_3)_5NO]I_3,H_2O$ (0·358 g) in 0·880 ammonia (20 ml) was refluxed for 24 h. The solution was filtered, the filtrate evaporated to a small volume and cooled to 0 °C. The resultant yellow *crystals* of $[OsOH(NH_3)_4NO]I_2$ were removed by filtration, washed with 95% ethanol and ether, and air dried. A further quantity was obtained by adding KI to the filtrate. The combined products were recrystallized from water–ammonia (1 : 1) and dried *in vacuo* (P_2O_5). Yield 0·247 g (87%).

$[OsOH(NH_3)_4NO]Br_2$ was prepared similarly from $[Os(NH_3)_5NO]Br_3,H_2O$ (75% yield) and $[OsOH(NH_3)_4NO]Cl_2$ from $[Os(NH_3)_5NO]Cl_3,H_2O$ (60% yield).

Alternatively, $[OsOH(NH_3)_4NO]X_2$ (X = I, Br, or Cl)

---

* Better yields of the $[Os(NH_3)_5NO]I_3$–$[OsI(NH_3)_4NO]I_2$ mixture were obtained when NO was passed through the $[Os(NH_3)_5I]I_2$ slurry without prior degassing. Removal of I^- by oxidation to I_2 increased the solubility of $[Os(NH_3)_5I]^{2+}$.

[14] A. D. Allen, personal communication.

[15] H. A. Scheidegger, J. N. Armor, and H. Taube, *J. Amer. Chem. Soc.*, 1968, **90**, 3263.

were prepared by refluxing the $[Os(NH_3)_5NO]I_3,H_2O$–$[OsI(NH_3)_4NO]I_2$ mixture (see above) in 0·880 ammonia for 7 h, followed by the addition of the appropriate potassium halide. Yield: 0·195 g of the $[OsI(NH_3)_4NO]I_2$–$[Os(NH_3)_5NO]I_3,H_2O$ mixture gave 0·098 g $[OsOH(NH_3)_4NO]I_2$.

The complexes were 2 : 1 electrolytes. The iodide salt was diamagnetic, $\chi = -0{\cdot}25 \times 10^{-6}$ (c.g.s.u.) at 22 °C.

Halogenotetra-amminenitrosylosmium, $[OsX(NH_3)_4NO]X_2$ (X = Cl, Br, *or* I).—A solution of $[OsOH(NH_3)_4NO]I_2$ (0·213 g) in hydroiodic acid (57%, 10 ml) and water (3 ml) was refluxed for 23 h. The resultant orange-yellow precipitate was removed by filtration of the hot solution, washed with absolute ethanol and ether, and air dried. Yield 0·152 g (60%).

The product was purified by dissolving in minimum quantity hot water, filtering, and reprecipitating as orange *crystals* by adding several drops of hydroiodic acid. The sample was dried *in vacuo* (P_2O_5).

$[OsBr(NH_3)_4NO]Br_2$ was similarly prepared from $[OsOH(NH_3)_4NO]Br_2$ (Yield 74% after refluxing for 2 days) and $[OsCl(NH_3)_4NO]Cl_2$ from $[OsOH(NH_3)_4NO]Cl_2$ (Yield 84% after refluxing for 4 days). The complexes were 2 : 1 electrolytes. The iodo-complex was diamagnetic, $\chi = -0{\cdot}22 \times 10^{-6}$ (c.g.s.u.) at 27 °C.

I.r. spectra were measured as Nujol or hexachlorobutadiene mulls between potassium bromide or Polyethylene plates on a Beckman IR 12 instrument. Electronic spectra (aqueous solution) were recorded on a Hitachi–Perkin-Elmer EPS-3T instrument. Conductivities in aqueous solution, over the concentration range (5—60) $\times 10^{-5}$M were measured using a Beckman RC-18A conductivity bridge. Magnetic moments were by the Gouy method. Microanalyses were by A. Bernhardt, Mulheim, W. Germany.

We thank the N.R.C. of Canada and the University of New Brunswick Research Fund for financial support, and Johnson, Matthey and Mallory, Montreal, for a loan of osmium.

[2/1761 *Received, 27th July,* 1972]