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NEW OSMIUM NITROSYL COMPOUNDS

ANTONIO ARÀNEO, VENANZIO VALENTI and FRANCO CARIATI
Istituto di Chimica Generale dell' Università, C.N.R., Centro Naz. di Chimica dei Composti di Coordinazione, Via Venezian 21, (20133) Milano, Italy

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Abstract—Osmium nitrosyl derivatives, of formula $OsX_3(NO)L_2$ [$X = Cl$, Br, I; $L = P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$], are reported, addition to the very few nitrosyl compounds of osmium so far described. The structure of these new compounds is discussed on the basis of their i.r. and electronic spectra. The Os—L, Os—X, Os—NO bonds are discussed.

INTRODUCTION

THE PREPARATION and properties of the compound $OsCl_3(NO)[Sb(C_6H_5)_3]_2$ have previously been reported[1]; it is one of the very few osmium nitrosyl derivatives and the first non-ionic nitrosyl compound of osmium.

In this paper some halogenonitrosyl compounds of general formula $OsX_3(NO)L_2$ are described, X being Cl, Br, I, and L a neutral ligand as triphenylphosphine, -arsine, -stibine.

RESULTS AND DISCUSSION

The preparation of the osmium nitrosyl compounds was carried out according to the general reaction of this scheme

$$M_2OsX_6 + NO + 2L' \longrightarrow OsX_3(NO)L'_2 \qquad (1)$$

$$M_2OsX_6 + NO + 2L'' \longrightarrow OsX_3(NO)L''_2 \qquad (2)$$

$$M_2OsX_6 + 3L''' \longrightarrow OsX\,L'''_3 \xrightarrow{+NO} OsX_3(NO)L'''_2 \qquad (3)$$

$$M_2OsX_6 = Na_2OsCl_6,\ (NH_4)_2OsBr_6,\ (NH_4)_2OsI_6$$

$$L' = P(C_6H_5)_3;\ L'' = As(C_6H_5)_3;\ L''' = Sb(C_6H_5)_3.$$

Some properties of the products are reported in Table 1, in which the properties of $OsCl_3(NO)[Sb(C_6H_5)_3]_2$ [1] are also reported for comparison.

The halogenonitrosyl derivatives with $Sb(C_6H_5)_3$ as ligand were prepared by treating the corresponding halogenoosmate (VI) with triphenylstibine in aqueous alcohol solution, according to the procedure described previously[1]; the intermediate products of general formula $OsX_3\,L'''_3$ ($X = Cl$, Br, I) (see Experimental Section) were reacted with NO to give $OsCl_3(NO)L'''_2$ (VII) $OsBr_3(NO)L'''_2$ (VIII), $OsI_3(NO)L'''_2$ (IX).

In some case, the i.r. spectrum of the compound VIII showed, in addition to the stronger band at 1810 cm^{-1} (ν_{NO}), a weaker band at 1780 cm^{-1}, which we attributed to a small amount of a more soluble isomer, which we did not isolate.

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[1] A. Aràneo and C. Bianchi, *Gazz. Chim. Ital.* **97**, 885 (1967).

Table 1

	Compound	Colour	m.p. (°C)	ν_{NO} (cm^{-1})
I	$OsCl_3(NO)[P(C_6H_5)_3]_2$	yellow	~ 300°C	1850
II	$OsBr_3(NO)[P(C_6H_5)_3]_2$	yellow	~ 260	1840
III	$OsI_3(NO)[P(C_6H_5)_3]_2$	yellow	~ 300	1840
IV	$OsCl_3(NO)[As(C_6H_5)_3]_2$	red-orange	~ 300	1840
V	$OsBr_3(NO)[As(C_6H_5)_3]_2$	red-orange	~ 280	1840
VI	$OsI_3(NO)[As(C_6H_5)_3]_2$	red-orange	~ 300	1835
VII	$OsCl_3(NO)[Sb(C_6H_5)_3]_2$	red	~ 245	1805
VIII	$OsBr_3(NO)[Sb(C_6H_5)_3]_2$	red	~ 240	1810
IX	$OsI_3(NO)[Sb(C_6H_5)_3]_2$	red	~ 235	1830

The nitrosyl derivatives with $P(C_6H_5)_3$, I, II, III, were prepared by first treating the corresponding halogenoosmate (IV) in 2-methoxyethanol solution with NO and then with triphenylphosphine.

The compound $OsBr_3(NO)L'_2$(II) was formed together with other products in small yield, which remained in the mother-liquor and which we were not able to characterize.

The arsine derivatives IV, V, VI, were prepared analogously, by treating the halogenoosmate with NO and then with triphenylarsine.

By reacting Na_2OsCl_6 with NO and then with triphenylarsine, the compound $OsCl_3(NO)L''_2$ (IV) ($\nu_{NO} = 1840\,cm^{-1}$) was obtained as the main product, as orange red crystal, together with a yellow isomer ($\nu_{NO} = 1810\,cm^{-1}$). By column-chromatography of a benzene solution, we isolated from the first eluted fractions the yellow isomer, but it was impossible to recover the orange-red isomer; after deactivation of the column by ethanol, a new product was obtained which showed, in addition to a band at $1810\,cm^{-1}$, a broad band at around $860\,cm^{-1}$, that is normally the range of frequencies of the Os—O stretching[2]. The red isomer, almost free of the yellow isomer, could be prepared by reacting NO with the product (probably $OsCl_4L''_2$) derived from the reaction of Na_2OsCl_6 with triphenylarsine.

I.R. spectra

The N—O stretching frequencies of derivatives containing the same halogen [e.g. the chloroderivatives I, IV, VII, (Table 2)], decrease with variation of ligand L, $L' > L'' > L'''$, as found[3] in analogous ruthenium compounds. This may be principally attributed to the inductive effect of the ligand L.

In the series of phosphine (I, II, III) and arsine (IV, V, VI) derivatives, the N—O stretching frequencies decrease in the order Cl > Br > I. This may be attributed to the increasing polarizability of halogens accompanied by an increase in electron density on the metal atom.

[2] W. P. Griffith, *J. chem. Soc.* **A**, 211 (1969).

[3] M. B. Fairy and R. J. Irving, *J. chem. Soc.* **A**, 475 (1966).

Table 2. I.R. frequencies (cm^{-1}) in nujol

Compound	ν_{NO}	K_{NO} (mdine/A)	$\nu_{(OsNO)}$	$\nu_{(OsX)}$
$OsCl_3(NO)(PPh_3)_2$	1850 s	15·05	608 m	324 m 312 s 298 w
$OsBr_3(NO)(PPh_3)_2$	1840 s	14·89	596 m	236 s 214 s
$OsI_3(NO)(PPh_3)_2$	1840 s	14·89	589 m	
$OsCl_3(NO)(AsPh_3)_2$	1840 s	14·89	610 m	337 s 320 s 299 w
$OsBr_3(NO)(AsPh_3)_2$	1840 s	14·89	591 m	230 s
$OsI_3(NO)(AsPh_3)_2$	1835 s	14·81	583 m	
$OsCl_3(NO)(SbPh_3)_2$	1805 s	14·33	600 m	328 m 315 s 299 w
$OsBr_3(NO)(SbPh_3)_2$	1810 s	14·41	582 m	229 s 216 s
$OsI_3(NO)(SbPh_3)_2$	1830 s	14·73	580 m	

In the series of stibine derivatives (VII, VIII, IX) on the contrary, the N–O stretching frequencies increase in the same order. We suggest that triphenylstibine, which is a "soft" ligand, further decreases the relatively weak "*b*" character of the Os^{II} atom, which is a "borderline case"[4], and consequently in these compounds there is only a slight tendency towards mutual stabilization by the ligands, i.e. to the so-called "symbiosis of the ligands"[5]. In other words, the ligand $Sb(C_6H_5)_3$ transfers so much negative charge to the metal that the other ligand, i.e. the halogens, must be sufficiently electronegative to compensate this charge. If this is correct, the order of stability of the stibine derivatives is: Cl > Br > I, or, in other words, the most stable situation occurs when $Sb(C_6H_5)_3$ and Cl are partners. Thus a lower ν_{NO} value would correspond to a stronger Os–Sb bond. This seems to be in agreement with both the i.r. work of Horrocks, for compounds of T_d symmetry,[6] and the kinetic measurements of Foffani[7]. A correlation between a strong, essentially covalent, $M \leftarrow L$ bond and a substantial metal-to-NO back-bonding seems evident. Further support for this view is also obtained from the force constants K_{NO}, which have been evaluated assuming the ν_{NO} as group frequencies. However, this does not mean that for our compounds the strength of the Os–*L* bond must increase in the order Os–P < Os–As < Os–Sb. In fact, since Os^{II} is a borderline case, the energy balance becomes very delicate[8], and, as indicated by Basolo[9], steric factor may become important.

4. R. G. Pearson, *J. chem. Educ.* **9**, 581 (1968).
5. C. K. Joergensen, *Inorg. Chem.* **3**, 1201 (1964).
6. G. R. VanHecke and W. De W. Horrocks, *Inorg. Chem.* **5**, 1960 (1966).
7. G. Cardaci and A. Foffani, *Inorg. chim. Acta* **2**, 252 (1968).
8. C. K. Joergensen, *Structure and Bonding*, Vol. 1, p. 234. Springer, New York (1966).
9. F. Basolo, W. H. Baddley and J. L. Burmeister, *Inorg. Chem.* **3**, 1201 (1964).

The band at ~ 600 cm^{-1} may be assigned to the Os-(NO) stretching in agreement with recent studies by Griffith[10]. Our compounds generally show two bands due to the Os$-X$ stretching vibrations, one of which is relatively strong. The structure shown in Fig. 1 requires three i.r. Os$-X$ stretchings, one of which is very weak, and may represent the structure of our derivatives.

Such structure is confirmed by the relatively low dipole moments for the compounds VII and IX [$\mu_{\text{VII}} = 2{\cdot}5$ D[1]; $\mu_{\text{IX}} = 2{\cdot}9$ D (see Experimental Section)].

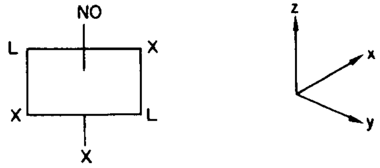

Fig. 1.

Electronic spectra

The electronic spectra of the bromo derivatives, which were the only compounds obtained in sufficient quantity for measurements, are shown in Table 3. They are almost wholly charge-transfer bands, and give little stereochemical information except that they indicate that variation of the ligand L is not sufficient to change the stereochemistry fundamentally.

Table 3. Electronic spectra of compounds $OsBr_3(NO)L_2^*$

	Frequencies (cm^{-1})†			
	T	W	A	B
Compound	$xy \rightarrow \pi^*(NO)$	$xz, yz \rightarrow \pi^*(NO)$	$\sigma(L) \rightarrow \pi^*(NO)$	$\sigma(L) \rightarrow x^2-y^2$
$OsBr_3NOL_2'$	20,000	25,000	31,746	34,130
	174	*353*	*6400*	*15,600*
$OsBr_3NOL_2''$	19,608	24,096	31,646	33,784
	178	*501*	*15,625*	*26,800*
$OsBr_3NOL_2'''$	19,231	23,810	28,329	30,488
	229	*100*	*14,300*	*26,800*

*Run in chloroform solution at room temperature.

†The numbers in italic type refer to molar extinction.

In our compounds, the electronegativity difference, and the very different position of the ligands L and X in the spectrochemical series, very probably lead to an anisotropy of the ligand field in the xy plane (Fig. 1). However no symmetry lower than tetragonal is clearly indicated by the spectra of these compounds, which show only rather broad bands. Therefore, the assignment of the spectra may be based on the theoretical analysis performed by Gray[11] on tetragonal cyanonitrosyl derivatives, and confirmed by experimental data.

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10. M. J. Cleare and W. P. Griffith, *J. chem. Soc.* **A**, 372 (1969).
11. P. T. Manobaran and H. B. Gray, *Inorg. Chem.* **5**, 823 (1966).

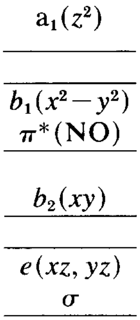

Fig. 2.

Nevertheless, band T, W, A and B may be attributed tentatively according to Table 3 (see also the schematic monoelectronic energy diagram in Fig. 2.)
If the spectra of the bromo, arsine and stibine derivatives are compared (as in Table 3), it is seen that our assignment of bands A and B is in agreement with the optical electronegativity values for these ligands, which decrease on going from $As(C_6H_5)_3$ to $Sb(C_6H_5)_3$ [12, 13].

The absorption bands of type B of the three stibine derivatives have values:

$OsCl_3(NO)L_2'''$	32468 cm^{-1}
$OsBr_3(NO)L_2'''$	30488 cm^{-1}
$OsI_3(NO)L_2'''$	29851 cm^{-1}.

As is evident, these values are in agreement with the position of the halogens in the spectrochemical series. On the other hand, a comparison of the bromo, phosphine and arsine derivatives (Table 3) shows that the absorpton maxima are almost coincident while the intensities are distinctly different.

However, to explain the results, it is not necessary to assume that $P(C_6H_5)_3$ and $As(C_6H_5)_3$ behave in the same manner. It is possible that the coincidence of the absorption maxima in the spectra of these two compounds is due to the fortuitous balancing of various factors: on the one hand the greater ligand field strength of triphenylphosphine [12] and its higher π-acceptor character (on which, possibly, depends the higher positions of bands T and W); on the other, the lower electronegativity of the phosphine itself which facilitates ligand–metal charge-transfer processes.

EXPERIMENTAL

Melting points were determined on a Leit apparatus and are uncorrected. I.R. spectra were recorded on Perkin Elmer 237 or 621 spectrometers employing Nujol mulls. Electronic spectra were recorded on a Beckman DK 2A instrument.

Starting materials

$OsCl_3[Sb(C_6H_5)_3]_3$, was prepared as previously described [1].

$OsBr_3[Sb(C_6H_5)_3]_3$, for which some data are already available [14], was made in a similar manner to $OsCl_3[Sb(C_6H_5)_3]_3$, by adding a solution of $(NH_4)_2OsBr_6$ (0·5 g) in ethanol (25 ml) to a boiling solu-

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12. C. K. Joergensen, *Inorganic Complexes* p. 160. Academic Press, New York (1963).
13. V. Valenti, A. Sgamellotti, F. Cariati and A. Arăneo, *Gazz. Chim. Ital.* **98**, 983 (1968).
14. L. Vaska, *Chem. Ind.* 1402 (1961).

tion of $Sb(C_6H_5)_3$ (2 g) in ethanol (100 ml). After reflux (*ca.* 2 hr) a dark precipitate (*ca.* 1·1 g) was filtered off, and then crystallized from chloroform-ethanol. (Found: C, 54·1; H, 3·34. Calc. for $C_{54}H_{45}Br_3OsSb_3$: C, 45·7; H, 3·02%).

$OsI_3[Sb(C_6H_5)_3]_3$, triiodotristriphenylstibineosmium (II) (new compound) was prepared in the same way as the analogous $OsBr_3[Sb(C_6H_5)_3]_3$ from $(NH_4)_2OsI_6$ (0·3 g) and $Sb(C_6H_5)_3$ (1·2 g). Yield *ca.* 0·6 g, m.p. 225°. (Found: C, 41·28; H, 2·9. Calc. for $C_{54}H_{45}I_3OsSb_3$: C, 40·0; H, 2·9%).

Nitrosyl derivatives

They are moderately soluble in benzene, chloroform, methylene chloride, insoluble in ethanol, ethyl ether, hexane.

Analytical data are reported in Table 4. The mol. wt. determination on the compound IX was carried out in chloroform solution (1%) on a Mechrolab Osmometer 301 A. The other compounds were not sufficiently soluble in the appropriate solvent for molecular weight determination.

(1) $OsCl_3(NO)[P(C_6H_5)_3]_2$, *trichloronitrosylbis(triphenylphosphine) osmium(II).* A solution of Na_2OsCl_6(0·25 g) in 2-methoxyethanol (50 ml) was purged by nitrogen, and then treated with a stream of nitric oxide, while refluxing till a red colour appeared (*ca.* 2 hr). Nitrogen was bubbled again and a solution of $P(C_6H_5)_3$ (1; 5 g) in 2-methoxyethanol (25 ml) was added drop wise to the refluxing mixture. After refluxing for 2 hr, the crystalline product (0·25 g) obtained, was filtered off and recrystallized from benzene solution by addition of ethanol.

Table 4. Analytical data

		C%		H%		N%		X%	
	Formula	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
I	$C_{36}H_{30}Cl_3NOOsP_2$	50·7	51·67	3·50	3·80	1·60	1·49	12·34	11·30
II	$C_{36}H_{30}Br_3NOOsP_2$	43·9	44·3	3·05	3·23	1·42	1·53	24·39	24·18
III	$C_{36}H_{30}I_3NOOsP_2$	38·40	38·90	2·66	2·61	1·24	1·43	33·80	33·01
IV	$C_{36}H_{30}As_2Cl_3NOOs$	46·05	46·92	3·19	3·38	1·49	1·44	11·02	11·52
V	$C_{36}H_{30}As_2Br_3NOOs$	40·3	40·9	2·79	2·81	1·3	1·6	22·38	22·3
VI	$C_{36}H_{30}As_2I_3NOOs$	35·61	35·9	2·47	2·56	1·15	1·60	31·44	31·9
VIII	$C_{36}H_{30}Br_3NOOsSb_2$	37·05	37·9	2·57	2·74	1·2	1·0	20·58	20·05
VIX	$C_{36}H_{30}I_3NOOsSb_2$	33·05	33·67	2·30	2·42	1·07	1·11	29·13	29·7

(2) $OsBr_3(NO)[P(C_6H_5)_3]_2$, *tribromonitrosylbis(triphenylphosphine)osmium(II).* This compound was obtained in the same way as compound I, from a solution of $(NH_4)_2OsBr_6$ (0·5 g) in 2-methoxyethanol (100 ml), by bubbling nitric oxide and then adding a solution of $P(C_6H_5)_3$ (1 g) in 2-methoxyethanol (100 ml)(Yield 0·48 g).

(3) $OsI_3(NO)[P(C_6H_5)_3]_2$, *triiodonitrosylbis(triphenylphosphine)osmium(II).* Similarly to the compound I from $(NH_4)_2OsI_6$ (0·3 g) and $P(C_6H_5)_3$(0·5 g). (Yield 0·25 g).

(4) $OsCl_3(NO)[As(C_6H_5)_3]_2$, *trichloronitrosylbis(triphenylarsine)osmium(II).* (a) By a similar method to that used for compound I, a reddish precipitate (0·5 g) was obtained from Na_2OsCl_6 (0·5 g) and $As(C_6H_5)_3$ (1 g). The i.r. spectrum of the crude product shows two bands at 1840 and 1810 cm^{-1}. Its benzene solution (250 ml) was eluted with anhydrous benzene by column chromatography (600 × 10 mm), on neutral Al_2O_3 Woehm (activity I). The first fraction (70 ml) of the eluted solution was concentrated under reduced pressure and, on addition of ethanol, an orange-yellow crystalline compound (0·2 g) was obtained. I.R. spectrum: a single band at 1810 cm^{-1}. (b) A solution of Na_2OsCl_6 (0·25 g) in ethanol (25 ml) was added drop wise to a stirred and boiling solution of $As(C_6H_5)_3$ (1 g) in ethanol (50 ml). After refluxing *ca.* 4hr, a brown solid product (0·5 g) was obtained, which was filtered off. Elemental analysis gave a composition very near to $OsCl_4[As(C_6H_5)_3]_2$. (Found: C, 46·75; H, 3·75; Cl, 13·56. Calc. for $C_{36}H_{30}As_2Cl_4Os$: C, 45·75; H, 3·17; Cl, 15·10%).

The solution of this product (0·4 g) in 2-methoxyethanol (80 ml) after purging with nitrogen, was treated with an NO stream and refluxed till a red colour appeared. After again purging with nitrogen and concentrating under reduced pressure, the red-orange crystalline $OsCl_3(NO)[As(C_6H_5)_3]_2$ (0·2 g) was obtained. I.R. spectrum: a band at 1840 cm^{-1}.

(5) $OsBr_3(NO)[As(C_6H_5)_3]_2$, *tribromonitrosylbis(triphenylarsine)osmium(II).* Similarly to the compound II, from $(NH_4)_2OsBr_6$ (0·5 g) and $As(C_6H_5)_3$ (1 g). Yield, after crystallization from benzene-ethanol, 0·45 g.

(6) $OsI_3(NO)[As(C_6H_5)_3]_2$, *triiodonitrosylbis(triphenylarsine)osmium(II).* Similarly to the compound I, from $(NH_4)_2OsI_6$ (0·25 g) and $As(C_6H_5)_3$ (1 g). Yield, after recrystallization from benzene-ethanol, 0·22 g.

(7) $OsCl_3(NO)[Sb(C_6H_5)_3]_2$, *trichloronitrosylbis(triphenylstibine)osmium(II).* See [1].

(8) $OsBr_3(NO)[Sb(C_6H_5)_3]_2$, *tribromonitrosylbis(triphenylstibine)osmium(II).* A solution of $OsBr_3[Sb(C_6H_5)_3]_2$, (1 g) in benzene (100 ml), after purging with nitrogen, was treated with NO and refluxed *ca.* 2 hr. After another nitrogen sweep, on addition of ethanol, a crystalline precipitate was formed, which was filtered off and crystallized from benzene-ethanol. (Yield 0·55 g).

(9) $OsI_3(NO)[Sb(C_6H_5)_3]_2$, *triodonitrosylbis(triphenylstibine)osmium(II).* Obtained analogously to the above compound VIII from $OsI_3[Sb(C_6H_5)_3]_3$ (0·5 g). Yield 0·2 g. M.W., Found 1230; Calc. 1307. Dipole moment was determined according to Chatt's procedure[15]: $M = 1{\cdot}2\ 10^{-2}$; $P_M = 193$; $\mu = 2{\cdot}9$ D.

15. J. Chatt, *J. chem. Soc.* 3066 (1951).