The structural chemistry of some osmium nitrosyl complexes

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Abstract

The two complexes tribromo(nitrosyl)(diethylsulfide)(diethylsulfoxide)osmium(II), $Os(NO)Br_3(Et_2S)(Et_2SO)$ and dichloro(nitrosyl)bis(diethylphenylphosphine)(2-methoxyethanoate)osmium(II), $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$, have been isolated during studies of photochemical reactions of platinum metal nitrosyl compounds. The molecular structures of these compounds have been determined by single crystal X-ray diffraction. The bright red crystals of $Os(NO)Br_3(Et_2S)(Et_2SO)$ are monoclinic $P2_1/c$; $a=13.398(3)$, $b=8.501(2)$, $c=16.199(3)$ Å, $\beta=105.69(5)°$, $V=1776.41(55)$ Å^3, $Z=4$. The structure was refined to a R factor of 0.0617 and a R_w of 0.0599. The complex is isostructural with the ruthenium analogue whose structure has been reported previously. The nitric oxide is coordinated in the linear manner (Os–N–O = 174.3(29)°) and the diethylsulfoxide ligand is oxygen bound (Os–O = 2.074(17) Å) *trans* to the NO as suggested from its infrared spectrum (ν(SO) = 940 cm^{-1}). The pale orange crystals of $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$ are also monoclinic $P2_1/c$; $a=10.869(1)$, $b=11.381(1)$, $c=22.673(2)$ Å, $\beta=102.17(10)°$, $V=2741.5(10)$ Å^3, $Z=4$. The structure was refined to an R of 0.0482 and a R_w of 0.0464. The diethylphenylphosphine ligands are coordinated in the *trans*-arrangement, and the Os–P bond lengths are identical; 2.427(3), 2.428(3) Å. The nitric oxide is coordinated in the linear manner (Os–N–O = 1.837(10) Å) and the 2-methoxyethanoate is coordinated *trans* to the nitrosyl (Os–O = 1.949(7) Å).

Introduction

Photochemical oxidation reactions of complexes of the type $Ru(NO)Br_3(R_2S)_2$ have been investigated by us previously [1–4]. Two main reaction products form, a mixed alkylsulfide and an alkylsulfoxide complex $Ru(NO)Br_3(R_2S)(R_2SO)$, and a bromine bridged dimeric complex, $[Ru(NO)Br_3(R_2SO)]_2$. The single crystal structures of some of these complexes have been determined, vis. $Ru(NO)Br_3(n\text{-}Pr_2S)_2$, $Ru(NO)Br_3(Et_2S)(Et_2SO)$ and $[Ru(NO)Br_3(Et_2SO)]$ [2, 4]. The diethylsulfide ligand is oxidised by NO_2 which is formed from the combination of NO (lost from some of the starting material) with dioxygen [2].

The work has been extended to osmium to investigate the effect of a change in the metal. However, complexes of the stoichiometric type $Os(NO)X_3(R_2S)_2$ could not be isolated. Instead small amounts of crystalline material were obtained which showed absorbances in their infrared spectra in the region expected for ν(SO) [5]. A bromo complex (R = Et) was investigated using single crystal X-ray diffraction, and was found to be isomorphous with the ruthenium complex $Ru(NO)Br_3(Et_2S)(Et_2SO)$. It appears that a similar chemistry is occurring for osmium without first forming a bis-sulfide complex.

Preparation of the complex $Os(NO)Cl_3(Et_2PPh)_2$ was attempted by treatment of a solution of $(NH_4)_2[OsCl_6]$ in 2-methoxyethanol with NO gas [6]. The ^1H NMR spectrum of the crystalline product showed additional resonances which were inconsistent with the expected stoichiometry. Also an absorbance occurred in the infrared spectrum at a position expected for ν(PO). The single crystal X-ray diffraction analysis of the product revealed that the stoichiometry of the complex was $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$ which contains a coordinated 2-methoxyethanoate ligand.

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Experimental

Preparation of the complexes

The complexes tribromo(nitrosyl)(diethylsulfide)(diethylsulfoxide)osmium(II) $Os(NO)Br_3(Et_2S)(Et_2SO)$ and dichloro(nitrosyl)bis(diethylphenylphosphine)(2-methoxyethanoate)osmium(II) $Os(NO)Cl_2(Et_2PPh)_2)(CH_3OCH_2CH_2O)$ were prepared following a similar method to that described by Baird [7] and Araneo *et al.* [6].

$Os(NO)Br_3(Et_2S)(Et_2SO)$

Ammonium hexabromoosmate(IV) $(NH_4)_2[OsBr_6]$ (0.25 g) was dissolved in 2-methoxyethanol (150 ml) and flushed with NO gas (prepared from the reaction of H_2SO_4 with $NaNO_3$ [8]) for 2 h. The solution was then flushed with N_2 for 1 h and the solvent removed under vacuum. The residue was taken up in ethanol, diethylsulfide (0.5 ml) was added and the solution heated under reflux. As the solution was heated the colour changed from a dark brown to a bright red, and a brown gas appeared in the condenser. The solvent was removed under vacuum, and after about two months small bright red, rectangular shaped, thin plate crystals of $Os(NO)Br_3(Et_2S)(Et_2SO)$ were obtained from the oily residue.

$Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$

Sodium hexachloroosmate(IV) $Na_2[OsCl_6]$ (0.25 g) (prepared from the ammonium salt using a cation exchange column [9]) was dissolved in 2-methoxyethanol (50 ml) and flushed with NO gas for 90 min while heating under reflux. The mixture was flushed with N_2 gas for 30 min and diethylphenylphosphine (1.0 ml) was added. The solution was heated for a further 20 min and the solvent removed under vacuum. An orange crystalline material was obtained and was washed with ethanol. The material showed two absorbances in the infrared spectrum which could be assigned to $\nu(NO)$; 1800 and 1840 cm^{-1}. An absorbance at 1090 cm^{-1} was also observed. When the crystals were examined under a microscope, two crystalline forms could be discerned; large block like orange crystals and small flakey pale orange crystals. The crystals were separated by hand and the infrared spectrum of the block shaped crystals found to contain the absorbances at 1090 and 1800 cm^{-1}. The crystals were found by single crystal X-ray diffraction to be $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$.

Structural chemistry

The data collection parameters and crystal data for the complexes are given in Table 1. All the programs used for the data collection and structure refinement are contained in the SHELXTL (version 4) package [10]. The structures were both solved using the heavy atom method after deducing the position of the osmium atom from the Patterson map. The remaining non-hydrogen atoms were located from Fourier difference maps. Absorption corrections were made using a Gaussian face indexing procedure for $Os(NO)Br_3(Et_2S)(Et_2SO)$ and using ψ-scans and an ellipsoidal model for $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$. No attempt was made to locate hydrogen atoms and the final difference map showed residual peaks only around the heavy atoms. There was no evidence for extinction.

TABLE 1. Data collection parameters and crystal data for $Os(NO)Br_3(Et_2S)(Et_2SO)$ (A) and $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$ (B)

Collection parameters	A	B
Space group	$P2_1c$	$P2_1c$
a (Å)	13.398(3)	10.869(1)
b (Å)	8.501(2)	11.381(1)
c (Å)	16.199(30)	22.673(2)
β (°)	105.69(1)	102.17(1)
μ (cm^{-1})	140.95	49.93
$F(000)$	1216	1388
Bragg angle (°)	5–55	5–50
Scan range (°)	1.20	1.60
Scan speed (° min^{-1})	4.88	9.00
Crystal dimensions (mm)	0.2×0.1×0.03	0.14×0.14×0.3
Observed reflections	1965	4123
Independent reflections	1137	2848
Transmission factors	0.243–0.652	0.583–0.679

The radiation used was Mo Kα and the temperature for both data collections was 163 K. A ω–2θ scan mode was employed to collect the data.

Results and discussion

Reaction chemistry

The method employed for the attempted preparation of the complexes of the form $Os(NO)X_3(Et_2S)$ was the same as that which proved successful for the ruthenium complexes with the same stoichiometry [7]. However, the infrared spectrum of the osmium bromo-diethylsulfide material was similar to that of the ruthenium complex $Ru(NO)Br_3(Et_2S)(Et_2O)$, and contained an absorbance at 920 cm^{-1} typical of that found for oxygen coordinated organosulfoxide ligands [5]. A similar osmium chloro complex was also obtained, but with even lower yields. The presence of the brown gas when diethylsulfide was added to the reaction mixture indicates that some NO was lost from the complex at this stage. Our previous studies of the photochemical reaction of Ru-

$(NO)Br_3(Et_2S)_2$ have shown that a small amount (less than 2%) of nitric oxide is lost from the complex when a chloroform solution of the complex is irradiated with sunlight. The liberated NO then reacted with dioxygen to form NO_2 which brought about the oxidation of the diethylsulfide to diethylsulfoxide. Therefore it seems likely that NO_2 is also the oxidising agent in the reaction involving osmium, but without the obvious formation of the bis-sulfide starting material $Os(NO)Br_3(Et_2S)_2$.

Preparation of the complex $Os(NO)Cl_3(Et_2PPh)_2$ was attempted by an analogous procedure. However, the infrared spectrum of the large block like crystals had an absorbance at 1090 cm^{-1}, which is in the correct region reported for $\nu(CO)$ in ethers (1060–1130 cm^{-1}) [5]. The infrared spectrum for 2-methoxyethanol contained absorbances at 1065 and 1120 cm^{-1} both assignable to $\nu(CO)$. It would appear that the 2-methoxyethanoate ligand competes with a chloro ligand in the phosphine complex but not with a bromo ligand in the diethylsulfide complex.

Structural chemistry

There are little structural data available on osmium complexes of the type investigated in this work [11], and comparisons of bond length data have to be made with organometallic complexes. Comparisons can also be made with similar ruthenium complexes, as ruthenium and osmium have similar atomic radii, and structural data suggest that the M–L bond lengths are similar for the two metals when they have the same oxidation state [12].

The structure and labelling scheme for $Os(NO)Br_3(Et_2S)(Et_2SO)$ is illustrated in Fig. 1. The atomic coordinates are given in Table 2, and bond lengths and angles in Table 3. The complex is isostructural with the ruthenium analogue $Ru(NO)Br_3(Et_2S)(Et_2SO)$, and has three bromine atoms, one diethylsulfide, one diethylsulfoxide and a nitric oxide ligand coordinated to the osmium atom in an octahedral manner. The bromine atoms are coordinated to the osmium in a meridional configuration, and the diethylsulfoxide ligand is oxygen coordinated *trans* to the nitric oxide. The Os–O bond length of 2.074(17) Å is similar to that reported for other osmium compounds which lie in the range 2.06(3)–2.10(3)

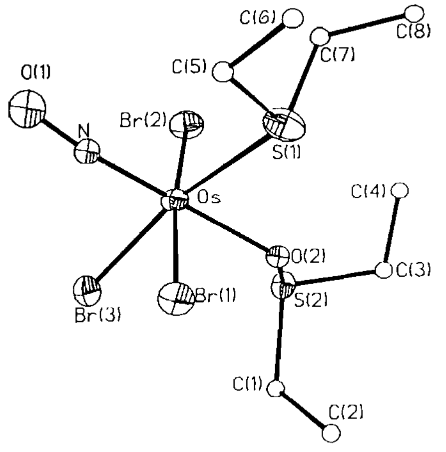

Fig. 1. Diagram of the structure of $Os(NO)Br_3(Et_2S)(Et_2SO)$ showing the labelling scheme used.

TABLE 2. Atomic coordinates ($\times 10^4$) and temperature factors ($\times 10^3$) for $Os(NO)Br_3(Et_2S)(Et_2SO)$

Atom	x	y	z	U[a]
Os	2374(1)	1804(1)	880(1)	29(1)*
Br(1)	852(3)	1973(3)	1509(2)	44(1)*
Br(2)	3976(3)	1933(3)	371(2)	47(1)*
Br(3)	3423(3)	472(3)	2213(2)	44(1)*
S(1)	1336(8)	3452(10)	−217(6)	54(4)*
S(2)	3884(7)	4399(7)	2017(5)	33(3)*
O(1)	1835(22)	−1155(25)	49(17)	57(6)
O(2)	2771(16)	3989(18)	1443(13)	26(4)
N	1990(20)	34(23)	410(15)	29(5)
C(1)	241(37)	2103(39)	−814(29)	71(10)
C(2)	−488(33)	3001(37)	−1464(27)	67(10)
C(3)	1907(34)	3960(38)	−1036(26)	59(9)
C(4)	1592(36)	5561(40)	−1411(29)	71(10)
C(5)	3677(32)	4535(33)	3119(23)	40(7)
C(6)	2754(37)	5550(44)	3195(31)	81(12)
C(7)	3914(28)	6398(27)	1734(20)	31(8)
C(8)	4187(33)	6555(36)	881(25)	54(8)

[a] Starred items: equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 3. Bond lengths (Å) and selected bond angles (°) for $Os(NO)Br_3(Et_2S)(Et_2SO)$

Bond	Length	Bond	Length
Os–Br(1)	2.518(1)	Os–Br(2)	2.502(4)
Os–Br(3)	2.507(3)	Os–S(1)	2.393(9)
Os–N	1.712(22)	Os–O(2)	2.074(17)
S(1)–C(1)	1.952(62)	S(1)–C(3)	1.752(49)
S(2)–O(2)	1.576(21)	S(2)–C(5)	1.816(52)
S(2)–C(7)	1.764(25)	C(1)–C(2)	1.453(54)
C(3)–C(4)	1.595(55)	C(5)–C(6)	1.440(80)
C(7)–C(8)	1.607(66)	N–O(1)	1.148(31)
Bond	**Angle**	**Bond**	**Angle**
Br(1)–Os–Br(2)	172.7(1)	Br(1)–Os–Br(3)	90.3(1)
Br(2)–Os–Br(3)	88.4(1)	Br(1)–Os–S(1)	84.1(3)
Br(2)–Os–S(1)	96.1(3)	Br(3)–Os–S(1)	169.4(2)
Br(1)–Os–N	94.2(10)	Br(2)–Os–N	92.9(10)
Br(3)–Os–N	91.2(8)	S(1)–Os–N	98.1(8)
Os–S(1)–C(3)	115.0(14)	Os–N–O	174.3(29)
O(2)–S(2)–C(7)	98.3(12)		

Å [13]. The S–O bond length of the diethylsulfoxide ligand is 1.576(21) Å, relatively long compared with reported bond lengths; 1.543(8) Å for the ruthenium analogue [2], 1.541(7) Å for the dimeric ruthenium complex $[Ru(NO)Br_3(Et_2SO)]_2$ [4], and 1.461(7) Å in a dimethylsulfoxide osmium complex [14]. There is little difference in S–O bond lengths for oxygen and sulfur bound organosulfoxides, but there is a correlation between the position of the ν(SO) stretching frequency and S–O bond lengths [15]. The ν(SO) position of 940 cm^{-1} found in this complex is at the low end of the range indicative of the longer bond. The build up of electron density in an orbital that is antibonding for the oxygen–sulfur bond as a result of π-type backbonding from the osmium would be expected to influence the position of this ν(SO) absorbance and S–O bond length. However, the fact that this is not reflected in a longer bond length is indicative that factors other than bond length effect the position of the ν(SO) absorbance in the infrared spectrum. The Os–S bond length of 2.393(9) Å for the diethylsulfide ligand lies within the range reported in other compounds; 2.324(2) [14], 2.507 [16], 2.474(3) [17], 2.414(8) [18] Å. The NO group is linearly bound with the Os–N–O angle = 171.4(29)°. The Os–N bond length of 1.712(22) Å is similar to that reported for linear and bent coordinated NO in other osmium complexes; 1.776(7), 1.771(7) Å [19], although longer Os–N bond lengths (1.915(6) Å) have been reported for some bent coordinated NO groups. Also the N–O bond length of 1.48(31) Å for the NO group is similar to that found in the ruthenium analogue; 1.09(1) Å [2], and the dimeric ruthenium complex; 1.16(1) Å [4]. The Os–Br bond lengths lie within the range 2.502(4)–2.518(4) Å and are similar to those reported for other complexes; 2.481(10)–2.499(1) Å [21].

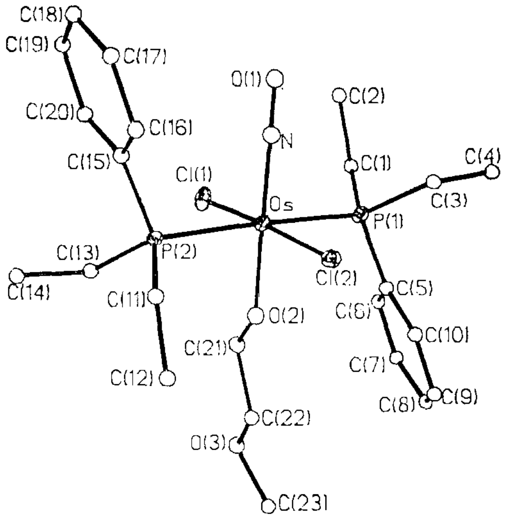

Fig. 2. Diagram of the structure of $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$ showing the labelling scheme used.

TABLE 4. Atomic coordinates ($\times 10^4$) and temperature factors ($\times 10^3$) for $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$

Atom	x	y	z	U^a
Os	2507(0)	7301(0)	6466(0)	24(0)
Cl(1)	8037(3)	4699(2)	3784(1)	42(1)
Cl(2)	3221(3)	9274(2)	6698(1)	32(1)
P(1)	2294(3)	7290(3)	399(1)	30(1)
P(2)	2846(3)	8197(2)	2529(1)	23(1)
O(1)	−95(9)	8043(10)	6424(4)	65(4)
O(2)	4287(7)	8064(7)	1547(3)	34(3)
O(3)	6956(10)	5337(8)	6289(5)	76(5)
N	870(9)	7759(8)	6425(3)	43(3)
C(1)	1229(11)	6722(11)	4884(3)	42(3)
C(2)	−147(12)	6826(13)	4971(6)	55(5)
C(3)	1683(11)	9205(10)	5195(5)	31(4)
C(4)	1445(12)	9445(12)	4502(5)	43(5)
C(5)	3772(10)	7636(9)	5144(5)	28(4)
C(6)	4047(13)	6724(12)	4778(6)	49(5)
C(7)	5233(14)	6695(13)	4604(6)	56(6)
C(8)	6088(13)	7634(15)	4806(6)	65(6)
C(9)	5839(15)	8511(14)	5179(7)	63(7)
C(10)	4662(11)	8536(12)	5341(6)	42(5)
C(11)	3905(10)	7781(10)	8046(5)	31(4)
C(12)	5328(10)	7612(11)	7987(5)	38(4)
C(13)	3452(12)	5291(10)	7689(5)	38(5)
C(14)	3563(13)	4904(11)	8537(5)	46(5)
C(15)	1368(10)	6884(10)	7788(4)	26(4)
C(16)	1026(11)	7916(11)	8033(5)	38(5)
C(17)	−142(11)	7974(11)	8204(5)	40(5)
C(18)	−951(12)	7015(13)	8126(6)	48(5)
C(19)	−610(12)	5964(13)	7871(6)	53(6)
C(20)	577(12)	5882(11)	7710(6)	42(5)
C(21)	4880(12)	6005(11)	6391(6)	101(6)
C(22)	6297(14)	6321(13)	6498(9)	78(8)
C(23)	8173(14)	5727(13)	6177(7)	66(7)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

The structure and labelling scheme for $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$ is illustrated in Fig. 2. The atomic coordinates are given in Table 4, and the bond lengths in Table 5. The structure consists of well separated molecules in which two chlorine atoms, two diethylphenylphosphine ligands, a NO group and a 2-methoxyethanoate ligand are coordinated to the osmium atom in an octahedral manner. The diethylphenylphosphine ligands are in the *trans*-configuration, and the 2-methoxyethanoate ligand is coordinated opposite the NO group. The NO group is also linearly bound in this complex (Os–N–O 177.3(8)°), but the Os–N bond length is longer (1.837(10) Å), and the N–O bond length shorter (1.098(14) Å) than found for $Os(NO)Br_3(Et_2S)(Et_2SO)$. These values lie within the ranges reported for other structures; Os–N, 1.776(7)–

TABLE 5. Bond lengths (Å) and selected bond angles (°) for $Os(NO)Cl_2(Et_2PPh)_2(CH_3OCH_2CH_2O)$

Bond	Length	Bond	Length
Os–Cl(1)	2.390(3)	Os–Cl(2)	2.398(3)
Os–P(1)	2.427(3)	Os–P(2)	2.428(3)
Os–O(2)	1.949(7)	Os–N	1.837(10)
N–O(1)	1.098(14)	O(2)–C(21)	1.236(16)
C(21)–C(22)	1.550(18)	O(3)–C(22)	1.461(17)
O(3)–C(23)	1.467(16)	P(1)–C(1)	1.851(7)
P(1)–C(3)	1.838(6)	P(1)–C(5)	1.821(6)
P(2)–C(11)	1.836(5)	P(2)–C(13)	1.851(5)
C(1)–C(2)	1.554(14)	C(3)–C(4)	1.562(12)
C(5)–C(6)	1.400(18)	C(6)–C(7)	1.443(22)
C(7)–C(8)	1.427(21)	C(8)–C(9)	1.372(23)
C(9)–C(10)	1.402(22)	C(10)–C(5)	1.415(16)
C(11)–C(12)	1.592(15)	C(13)–C(14)	1.557(18)
C(15)–C(16)	1.384(17)	C(16)–C(17)	1.404(19)
C(18)–C(19)	1.411(21)	C(19)–C(20)	1.417(20)
C(20)–C(5)	1.416(17)		
Bond	Angle	Bond	Angle
Cl(1)–Os–Cl(2)	175.2(1)	P(1)–Os–P(2)	175.9(1)
O(2)–Os–N	175.2(3)	Os–N–O	177.3(8)
P(1)–Os–Cl(2)	89.9(1)	P(1)–Os–O(2)	91.1(2)
P(1)–C(3)–C(1)	104.1(4)	P(2)–Os–N	93.4(3)
P(1)–C(1)–C(2)	111.3(3)	P(1)–C(3)–C(4)	112.9(5)
P(1)–C(5)–C(6)	122.7(3)	C(5)–C(6)–C(7)	119.9(12)
C(8)–C(9)–C(10)	119.0(14)	P(2)–C(11)–C(12)	111.3(4)
P(2)–C(13)–C(14)	113.9(4)	P(2)–C(13)–C(11)	106.8(3)
C(15)–C(16)–C(17)	119.1(11)	C(18)–C(19)–C(20)	120.2(13)

1.915(6) Å [19–21]; N–O, 1.09(1)–1.16(1) Å [2–4]. Whereas most of the reported bond length values for Os–N lie at the lower end and the N–O values at the higher end of the ranges the reverse occurs for the present compound. The infrared spectrum for the complex has an absorbance at 1800 cm^{-1} assigned to the NO stretching frequency. The value lies in the middle of the range reported for absorbances for linearly coordinated NO, and the position of the absorbance is not directly related to the N–O bond length [22]. The two Os–P bond lengths, Os–P = 2.427(3), 2.428(3) Å are similar to reported values [20, 21]. The two phosphines are in the *trans*-arrangement, as in fact occurs for most complexes containing two tertiary phosphine ligands [1, 23–26]. Few complexes are reported with the ligands in the *cis*-arrangement, viz. $Ru(NO)Cl_3(Me_2EPh)_2$ for E = As and P [27]. The most likely reason for this is the steric bulk of the ligands inhibiting the formation of the *cis*-isomer [27]. This explanation is supported by the fact that the known *cis*-complexes are those with less bulky ligands. The *cis*-isomer has been detected in solution when the *trans*-isomer is irradiated with UV–Vis light using NMR spectroscopy [1, 12, 28]. The 2-methoxyethanoate ligand is coordinated opposite the NO group. The Os–O bond length of 1.949(7) Å is significantly shorter than other reported values which lie in the range 2.3036(3)–2.10(3) Å [11, 29]. It is of interest that the 2-methoxyethanoate ligand rather than chloride coordinates opposite the NO group. Ligands that are good σ-donors and poor π-acceptors usually coordinate opposite NO [22]. In this complex there are two such ligands; chloride and 2-methoxyethanoate, and the fact that the latter coordinates opposite NO may mean that it is a better σ-donor but poorer π-acceptor than chloride. Also oxygen is significantly smaller than Cl^- and is a harder base, again favouring it being *trans* to NO. This preference is also seen in the compound $(NH_4)[Ru(NO)Cl_4(H_2O)]Cl \cdot H_2O$ which has the oxygen atom of the coordinated water molecule opposite the NO group [29]. Shortening of the M–L bonds opposite NO has been described previously [2, 4, 22].

It is assumed that the 2-methoxyethanoate is coordinated in the deprotonated form as this would lead to formal oxidation state of two for the osmium, which is the more common oxidation state for osmium complexes containing tertiary phosphine ligands [30]. The absence of evidence of paramagnetism in the ^{1}H NMR spectrum supports this assumption.

Supplementary material

Tables of atomic thermal parameters, and structure factors are available as supplementary material from author J.E.F.

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