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Short Communication

Synthesis, photophysical properties and X-ray crystal structure of a luminescent osmium(VI)–nitrido complex of bis(diphenylarsino)ethane

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Abstract

Reaction of $[Os^{VI}(N)Cl_4]^-$ with bis(diphenylarsino)ethane (As–As) in acetone gave $[Os^{VI}(N)Cl_3(As–As)]$ isolated as an orange solid. The complex (space group $P\bar{1}$ (No.2), $a=11.512(2)$, $b=14.389(2)$, $c=19.138(4)$ Å, $\alpha=102.97(1)$, $\beta=94.84(2)$, $\gamma=110.24(1)°$, $V=2852.6(9)$ Å^3, $Z=4$; $R=0.062$ for 5216 observed Mo Kα data) is a distorted octahedral with three chlorine atoms in a meridional configuration. The measured Os≡N distances of the two crystallographically independent $[Os^{VI}(N)Cl_3(As–As)]$ molecules are 1.70(1) and 1.66(2) Å. The photoluminescent properties of the osmium complex are discussed.

Introduction

For the past several years, we have been interested in the design of luminescent transition metal complexes for photo-induced electron transfer and atom transfer reactions [1–3]. Recent studies have established that the $^3[(d_{xy})^1(d_{\pi*})^1]$ ($d_{\pi*}=d_{xz}$, d_{yz}) excited states of osmium (VI)–nitrido complexes with NH_3 and CN^- as ligands are long-lived in fluid solutions and exhibit novel photochemistry [2]. For example, UV–Vis irradiation of $[Os^{VI}(NH_3)_4N]^{3+}$ in the presence of alkylbenzene has been found to lead to the formation of a μ–dinitrogen bridged diosmium (II,III) species [2c]. In an attempt to tune the redox properties and reactivities of excited states, we set forth to prepare new osmium(VI)–nitrido complexes having different auxiliary ligands. Herein is described the synthesis, spectroscopy and X-ray crystal structure of *mer*-$[Os^{VI}(N)Cl_3(As–As)]$ (As–As = bis(diphenylarsino)ethane).

Experimental

Materials

The ligand bis(diphenylarsino)ethane was purchased from Alfa Co Ltd. $[Bu_4N][Os^{VI}(N)Cl_4]$ was synthesised by published procedure [4].

$[Os^{IV}(N)Cl_3(As–As)]$

This was prepared by adding a slight excess of the As–As ligand (0.3 g) to an acetone solution of $[Bu_4N][Os^{VI}(N)Cl_4]$ (0.3 g in 30 ml), which was stirred for about 20 min at room temperature. Addition of diethyl ether to the solution gave a bright orange solid. This was filtered and recrystallised by vapour diffusion of diethyl ether into acetonitrile. Yield > 70%.

Instrumentation

UV–Vis spectra were measured on a Shimaudza UV–240 spectrophotometer. Emission spectra were measured on a Spex–Fluorolog–2–spectrofluorimeter. Lifetime measurements were conducted with a Quanta-Ray DCR-3 Nd:YAG pulsed laser system. Sample solutions were degassed by at least four successive freeze–pump–thaw cycles.

X-ray structure determination

Details of crystal parameters, data collection and structure refinement are given in Table 1. Raw intensities collected on a Nicolet R3m/V four circle diffractometer at room temperature (294 K) were processed with the profile fitting procedure of Diamond [5] and corrected for absorption using Ψ–scan data [6]. Two independent osmium atoms were located by direct phase determination and the coordinates of other non-hydrogen atoms were derived from successive difference Fourier syntheses. The carbon atoms of the phenyl groups were assigned isotropic thermal parameters and constrained to be the rigid regular hexagons with C–C bonds fixed at 1.40(1) Å. All other non-hydrogen atoms were subjected to anisotropic refinement, and the H atoms were generated geometrically (C–H bonds fixed at 0.96 Å) and assigned appropriate isotropic thermal parameters. Computations were performed using the SHELTXL-PLUS program package [7] on a DEC Micro VAX-II computer. Analytic expressions of atomic scattering

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TABLE 1. Data collection and processing parameters

Molecular formula	$OsNCl_3[(C_6H_5)_2AsCH_2]_2$
Molecular weight	796.89
Color and habit	orange prism
Unit cell parameters	
a (Å)	11.512(2)
b (Å)	14.389(2)
c (Å)	19.138(4)
α (°)	102.97(1)
β (°)	94.84(2)
γ (°)	110.24(1)
V (Å^3)	2852.6(9)
Z	4
F (000)	1520
Density (calc.) (g cm^{-3})	1.855
Space group	$P\bar{1}$ (No.2)
Radiation, λ (Å)	graphite-monochromatized Mo $K\alpha$, 0.71073
Standard reflections	$(24\bar{1})$, $(4\bar{4}0)$
Intensity variation (%)	± 4
Absorption coefficient (cm^{-1})	70.70
Crystal size (mm)	$0.10 \times 0.24 \times 0.36$
Mean μr	0.825
Transmission factors	0.263–0.344
Scan type; rate (° min^{-1})	ω–2θ; 3.01–15.63
Scan range	0.65° below $K\alpha_1$ to 0.65° above $K\alpha_2$
Back ground counting	stationary counts for one-fifth of scan time at each end of scan range
Collection range	$h, \pm k, \pm l$; $2\theta_{max} = 45°$
Unique data measured	7500
Observed data with $\lvert F_o \rvert > 6\sigma(\lvert F_o \rvert)$, n	5216
No. of variables, p	260
$R_F = \Sigma \lvert \lvert F_o - \lvert F_c \rvert \rvert / \Sigma \lvert F_o \rvert$	0.062
Weighting scheme, w	$[1 - \exp(-4\sin^2\theta/\lambda^2][\sigma^2(F_o) + 0.0008\lvert F_o \rvert^2]^{-1}$
$R_G = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$	0.072
$S = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/(n-p)]^{1/2}$	1.025
Residual extrema in final difference map (e Å^{-3})	+2.77 to −2.11

factors were employed, and anomalous dispersion corrections were incorporated [8]. The maxima in the last difference map all lie in the neighborhood of the osmium atoms. In addition, another residual peak of height 2.59 e Å^{-3} appeared in a void at (0,1/2,1/2), whose nearest neighbours are C(15) at 3.551 Å and C(65; x, $1+y$, z) at 3.879 Å. However, inclusion of a water molecule at this site with a small occupancy factor of 1/4 yielded an unreasonably high thermal parameter and was therefore not pursued. The final atomic coordinates for $[Os^{VI}(N)Cl_3(As\text{–}As)]$ are listed in Table 2. Selected bond distances and angles are given in Table 3.

Results and discussion

Dawson and Griffith previously reported the synthesis of $[Os^{VI}(N)Cl_3(Ph_3As)_2]$ (**1**) by the reaction of $[Os^{VI}(N)Cl_4]^-$ with Ph_3As in acetone [9]. In this work, a similar reaction with the As–As ligand gave a bright orange solution, from which $[Os^{VI}(N)Cl_3(As\text{–}As)]$ (**2**) was isolated. Complex **2** is an air-stable orange crystalline solid. It is diamagnetic and displays an intense IR band at 1080 cm^{-1} attributed to the ν(Os≡N) stretch. It is soluble and stable in aprotic solvents, from which crystals can easily be obtained. Its structure has been established by X-ray crystallography. Figure 1 shows perspective view of the molecule with the atom numbering. The structure features a six-coordinated osmium-nitrido complex [2b, 10]. The title compound consists of discrete molecules and there are two crystallographically independent molecules I and II in an asymmetric unit; the orientations of their phenyl groups are different. Each osmium atom is surrounded by a nitrogen, two arsenic and three *cis* chlorine atoms in a distorted octahedral coordination environment. The measured As(1)–Os(1)–Cl(1) and As(2)–Os(1)–Cl(2) angles of 167.2(1) and 171.7(1)° do not severely deviate from 180°. The short Os≡N distances of 1.70(1) and 1.66(2) Å are consistent with a triple bond formation [2b, 10]. Similar Os≡N distances have also been found in other related complexes such as in *cis*–[Os(N)(CH$_2$-

TABLE 2. Atomic coordinates ($\times 10^5$ for Os, $\times 10^4$ for other atoms) and equivalent isotropic temperature factors ($Å^2 \times 10^4$ for Os and As, $\times 10^3$ for other atoms)

Atom	x	y	z	U_{eq}[a]
Molecule I				
Os(1)	18841(6)	52414(5)	14441(4)	421(3)
As(1)	490(1)	3778(1)	1847(1)	419(7)
As(2)	3624(2)	4825(1)	1986(1)	449(7)
Cl(1)	3357(4)	6826(3)	1342(3)	54(2)
Cl(2)	246(4)	5778(4)	1103(3)	57(2)
Cl(3)	1954(4)	6084(4)	2751(3)	58(2)
N(1)	1843(12)	4390(11)	655(8)	45(6)
C(1)	1596(15)	3385(15)	2417(10)	51(8)
C(2)	2795(15)	3472(12)	2104(9)	41(7)
C(11)	−771	3879	2407	48(4)
C(12)	−1442(14)	4499(11)	2318(7)	69(6)
C(13)	−2369	4544	2734	96(8)
C(14)	−2625	3970	3239	91(7)
C(15)	−1953	3349	3329	117(10)
C(16)	−1026	3304	2913	85(7)
C(21)	−402	2606	1035	43(4)
C(22)	−432(12)	1628(9)	1034(6)	65(5)
C(23)	−1094	790	434	71(6)
C(24)	−1726	931	−164	74(6)
C(25)	−1696	1909	−163	79(6)
C(26)	−1034	2746	437	52(4)
C(31)	4594	5693	2911	47(4)
C(32)	4738(13)	5273(8)	3488(7)	64(5)
C(33)	5422	5915	4166	88(7)
C(34)	5963	6976	4269	88(7)
C(35)	5820	7396	3692	114(10)
C(36)	5135	6754	3014	104(8)
C(41)	4862	4704	1409	49(4)
C(42)	4724(15)	3747(10)	965(11)	132(12)
C(43)	5640	3659	550	133(12)
C(44)	6693	4528	578	79(6)
C(45)	6831	5486	1022	144(13)
C(46)	5915	5574	1437	154(14)
Molecule II				
Os(2)	21218(6)	8656(5)	33322(4)	404(3)
As(3)	701(1)	−951(1)	2751(1)	414(7)
As(4)	3833(1)	247(1)	3032(1)	429(7)
Cl(4)	1879(4)	824(3)	2008(2)	49(2)
Cl(5)	3516(5)	2621(3)	3641(3)	64(2)
Cl(6)	395(5)	1406(4)	3401(3)	67(2)
N(2)	2288(14)	571(11)	4114(9)	54(7)
C(3)	1765(14)	−1613(14)	2315(10)	50(7)
C(4)	3034(15)	−1228(12)	2837(12)	53(8)
C(51)	−735	−1298	2027	51(4)
C(52)	−728(12)	−1716(12)	1296(7)	75(6)
C(53)	−1791	−1985	771	101(8)
C(54)	−2861	−1835	978	103(8)
C(55)	−2868	−1417	1709	100(8)
C(56)	−1805	−1149	2233	97(8)
C(61)	42	−1629	3466	42(4)
C(62)	−318(13)	−1091(7)	4054(7)	63(5)
C(63)	−757	−1555	4596	76(6)
C(64)	−837	−2557	4551	82(7)
C(65)	−476	−3095	3964	71(6)
C(66)	−37	−2631	3421	61(5)
C(71)	5244	674	3795	48(4)
C(72)	5303(13)	1299(12)	4480(8)	84(7)
C(73)	6327	1567	5032	111(9)
C(74)	7292	1210	4899	92(7)
C(75)	7233	585	4214	122(10)
C(76)	6209	317	3662	101(8)
C(81)	4565	519	2212	47(4)
C(82)	5162(14)	1544(8)	2210(7)	81(6)
C(83)	5787	1779	1642	103(8)
C(84)	5815	990	1074	90(7)
C(85)	5218	−34	1076	89(7)
C(86)	4593	−269	1645	66(5)

[a] U_{eq} defined as one third of the trace of the orthogonalized U tensor.

TABLE 3. Selected bond distances and bond angles

I		II	
Os(1)–As(1)	2.491(2)	Os(2)–As(3)	2.485(2)
Os(1)–As(2)	2.491(2)	Os(2)–As(4)	2.486(2)
Os(1)–Cl(1)	2.386(4)	Os(2)–Cl(5)	2.381(4)
Os(1)–Cl(2)	2.368(6)	Os(2)–Cl(6)	2.375(7)
Os(1)–Cl(3)	2.504(5)	Os(2)–Cl(4)	2.511(5)
Os(1)–N(1)	1.70(1)	Os(2)–N(2)	1.66(2)
As(1)–Os(1)–As(2)	84.7(1)	As(3)–Os(2)–As(4)	84.7(1)
As(1)–Os(1)–Cl(1)	167.2(1)	As(3)–Os(2)–Cl(5)	168.3(1)
As(2)–Os(1)–Cl(1)	90.7(1)	As(4)–Os(2)–Cl(5)	92.2(2)
As(1)–Os(1)–Cl(2)	94.4(1)	As(3)–Os(2)–Cl(6)	91.8(1)
As(2)–Os(1)–Cl(2)	171.7(1)	As(4)–Os(2)–Cl(6)	170.2(1)
Cl(1)–Os(1)–Cl(2)	88.4(2)	Cl(5)–Os(2)–Cl(6)	89.4(2)
As(1)–Os(1)–Cl(3)	78.1(1)	As(3)–Os(2)–Cl(4)	78.3(1)
As(2)–Os(1)–Cl(3)	82.4(1)	As(4)–Os(2)–Cl(4)	82.6(1)
Cl(1)–Os(1)–Cl(3)	89.5(2)	Cl(4)–Os(2)–Cl(5)	90.2(2)
Cl(2)–Os(1)–Cl(3)	89.3(2)	Cl(4)–Os(2)–Cl(6)	87.8(2)
As(1)–Os(1)–N(1)	89.0(5)	As(3)–Os(2)–N(2)	89.2(4)
As(2)–Os(1)–N(1)	86.5(5)	As(4)–Os(2)–N(2)	86.5(6)
Cl(1)–Os(1)–N(1)	102.6(5)	Cl(5)–Os(2)–N(2)	101.9(4)
Cl(2)–Os(1)–N(1)	101.7(6)	Cl(6)–Os(2)–N(2)	102.6(6)
Cl(3)–Os(1)–N(1)	163.7(6)	Cl(4)–Os(2)–N(2)	164.0(6)

$SiMe_3)_2(2\text{–}S\text{–}NC_5H_4)]_2$ (1.63(1) Å) [10a], $[Os(N)(CH_2SiMe_3)_4]^-$ (1.631 Å) [10a] and $[Os(N)(CN)_5]^{2-}$ (1.64 Å) [2b]. The unusual long Os(1)–Cl(3) and Os(2)–Cl(5) distances of 2.504(5) and 2.511(5) Å, respectively, are undoubtedly due to the structural *trans* effect of the nitrido group. The Os–Cl(*trans* to As–As) and Os–As distances are normal.

The UV–Vis absorption spectrum of **2** in acetonitrile is featureless, showing an intense band tailing from 310 (ϵ_{max}, 5×10^3 mol^{-1} dm^3 cm^{-1}) to 400 nm. Very weak and broad absorption at around 460 nm (ϵ_{max}, 200 mol^{-1} dm^3 cm^{-1}) has also been found. The complex displays room temperature photoluminescence, the excitation and emission spectra of which in degassed acetonitrile are shown in Fig. 2. Cooling the sample

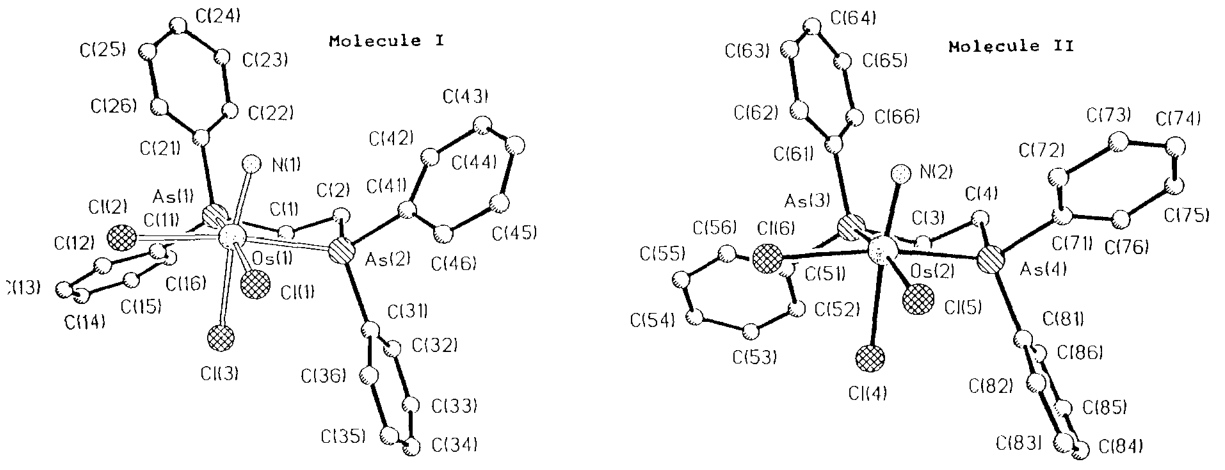

Fig. 1. A perspective view of the $[Os^{VI}(N)Cl_3(As\text{–}As)]$ molecule (molecule I), showing the atom numbering scheme.

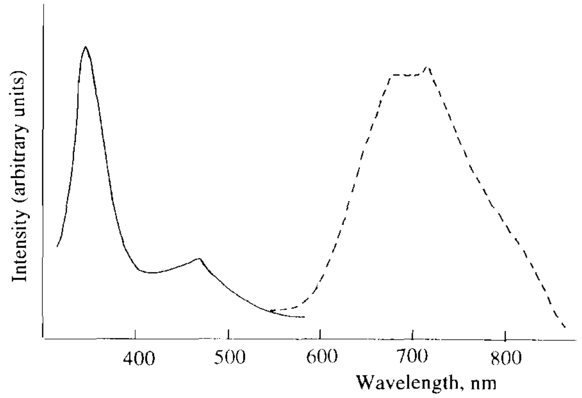

Fig. 2. Excitation (——) and emission (– – –) spectra of $[Os^{VI}(N)Cl_3(As\text{–}As)]$ in degassed acetonitrile and at room temperature.

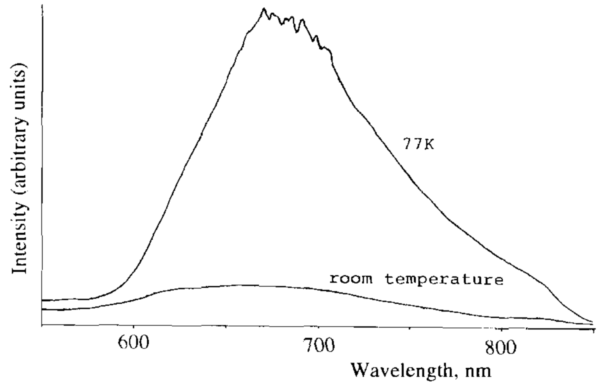

Fig. 3. Solid state emission spectra of $[Os^{VI}(N)Cl_3(As\text{–}As)]$ at room temperature and 77 K. Excitation 350 nm.

from 298 to 77 K leads to an enhancement of the emission intensity but no distinct vibronic feature is observed (Fig. 3). Quantum yield of the emission in degassed acetonitrile is 1.5×10^{-3} at a complex concentration of 1.49×10^{-3} mol dm^{-3} at room temperature. The measured emission lifetime of 2.8 μs (solid sample, 298 K) suggests that the emission is due to phosphorescence. With reference to previous works [2] we assign the emission to the $^3[(d_{xy})^1(d_{xz},d_{yz})^1]$ triplet excited state. Thus the two bands at 350 and 460 nm in the excitation spectrum are due to the spin-allowed and spin-forbidden $(d_{xy})^2 \longrightarrow (d_{xy})^1(d_{xz},d_{yz})^1$ transitions, respectively. As in the case of $[Os(CN)_5N]^{2-}$ and $[Os(NH_3)_4N]^{3+}$ [2], the emission lifetime of **2** in fluid solution depends on the concentration of the osmium complex. A linear Stern-Volmer plot of 1/lifetime versus [Os] has been obtained from which the τ_0 (lifetime at infinite dilution) and k_q (self-quenching rate constant) values have been determined to be 0.70 μs and 1.7×10^8 M^{-1} s^{-1}, respectively, in acetonitrile and at room temperature. In dichloromethane solution, the τ_0 and k_q values are 0.54 μs and 6×10^8 M^{-1} s^{-1}, respectively.

The present work further demonstrates a new osmium(VI)–nitrido complex, apart from $[Os^{VI}(NH_3)_4N]^{3+}$ [2a] and $[Os^{VI}(CN)_5N]^{2-}$ [2b], which also has a long-lived electronic excited state in fluid solution at room temperature. Thus photoluminescence is perhaps a general property of the Os(VI)≡N system. Previous spectroscopic studies established that the Os≡N bond in the excited state is about 0.09 Å longer than that in the ground state [3c]. Thus it is not difficult to envisage that luminescent osmium(VI)–nitrido complexes should find useful applications in the study of photo-induced nitrogen atom transfer reactions.

Supplementary material

Tables of H-atom coordinates, thermal parameters, bond distances and angles, and structure factors are available from the authors upon request.

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