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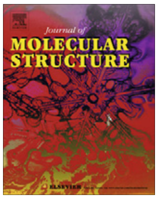

Osmium(II) bipyridine (bpy) complexes containing O,O-donor ligands and X-ray crystal structure of the acetylacetonato(acac) complex $[Os(bpy)_2(acac)](PF_6)$

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ABSTRACT

The new complexes $[Os^{11}(bpy)_2L](PF_6)$ [bpy = 2,2′-bipyridine; HL = acetylacetone (Hacac), trifluoroacetylacetone (Htfacac), hexafluoroacetylacetone, dibenzoylmethane or tropolone] have been prepared and the chemical oxidation of the $[Os^{II}(bpy)_2L]^+$ species (L = acac or tfacac) by aqueous $S_2O_8^{2-}$ solution in the presence of $(NH_4)PF_6$ gave the reddish brown complexes $[Os^{III}(bpy)_2L](PF_6)_2$. These complexes were characterized by spectroscopic measurements and also investigated by cyclic voltammetry. The X-ray crystal structure of $[Os(bpy)_2(acac)](PF_6)$ (**1**) has been determined and showed that the complex has a distorted octahedral geometry in an environment of N_4O_2 donors. The reactivity toward oxidation of benzyl alcohol by complex (**1**) using H_2O_2 or other co-oxidants has been studied and compared with that of the related ruthenium(II) complexes.

1. Introduction

Reaction of β-diketonates (dik) with $[Os^{IV}Q_2Br_2]$ (HQ = 8-quinolinol) gives the osmium(III) and (IV) complexes $[OsQ_2(dik)]^{0/+}$ [1]. We have prepared and characterized the complexes $[Ru^{II}(bpy)_2(dik)]$ (PF_6) [2], but no work has so far been reported on similar complexes of osmium(II), although analytical and electronic spectral data have been mentioned for $[Os^{II}(bpy)_2(acac)]Cl{\cdot}3H_2O$ [3,4]. Mixed complexes of osmium(II) with bipyridine and 2-(arylazo) phenolate (ON) or *o*-keto(or aldehydo) phenolate have been prepared from $[Os^{II}(bpy)_2Br_2]$ in the presence of NEt_3; the X-ray crystal structure has been determined for $[Os^{II}(bpy)_2L]^+$ (L = ON or salicyaldehyde anion) [5,6].

Mixed chelate copper(II) complexes patented and mark title registered as Casiopeinas® are potent antineoplastic agents and have general formulas. $[Cu(N–N)(O–O)]NO_3$ (**A**) and [Cu(N–N)(α-L-aminoacidato)]NO_3 (**B**), where N–N donor is an aromatic substituted diimine (1,10-phenanthroline or 2,2′-bipyridine) and the O–O donor is acac or salicylaldehydate [7]. A strong relationship between the medial inhibitory concentration (IC_{50}) and the redox potential ($E_{1/2}$) of the complexes (**A**) and (**B**) and their derivatives has been found; the most active complexes are the weaker oxidants [8]. Recently, osmium coordination compounds and its organometallic species have shown promising cytotoxic activity against human ovarian cancer cell lines, some of them as potent as cis platin and carboplatin [9].

In the present study we report a simple route for the synthesis of the new complexes $[Os^{II}(bpy)_2L](PF_6)$ [L = monoanions of acetylacetone (acac); trifluoroacetylacetone (tfacac); hexafluoroacetylacetone (hfacac); dibenzoylmethane (dbm) and tropolone(trop), 2-hydoxy-2,4,6-cyclohepta-trienone] and $[Os^{III}(bpy)_2L](PF_6)_2$ (L = acac or tfacac). We also report their rich redox and spectroscopic properties together with the X-ray crystal structure of $[Os^{II}(bpy)_2(acac)](PF_6)$ (**1**). The reactivity of the complex (**1**), as a typical example is tested towards the oxidation of alcohol, since the analogous ruthenium(II) complex [2] and $[Ru^{III}(bpy)(acac)_2](PF_6)$ [10] have been studied in this way.

2. Experimental

2.1. Physical measurements

IR spectra were measured on a Nicolet 510P FT-IR spectrometer as paraffin mulls between CsI plates or KBr discs. ^1H NMR spectra were measured on a Bruker AT-FT 100 instrument (100 MHz). The electronic spectra were measured on a Lambda 2S UV/Vis spectrophotometer. EPR spectra were recorded with a Bruker ECS 106 spectrometer. Cyclic voltammetric studies were carried out on a potentiostat/wave generator (Oxford Electrodes) using a platinum working electrode in conjunction with a Philips PM 8043 X–Y recorder. The three electrode cell comprised a reference Ag, Pt auxiliary and working electrodes, the complexes (10^{-3} M) in

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0.1 M $(n\text{-}Bu_4N)PF_6$ as supporting electrolyte were used. Magnetic measurements were made on a Johnson Matthey magnetic susceptibility balance. The thermal stability of the complexes was investigated using a Perkin–Elmer TGA7 unit (heating rate: 10 °C min^{-1}).

2.2. X-ray crystal structure analysis

Dark purple orthorhombic crystals of *[Os(bpy)$_2$(acac)](PF$_6$)*(**1**) having appropriate dimensions were measured on Bruker Kappa CCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), the unit cell dimensions and intensity data were measured at 298 K. The crystal data were collected up to 55.34° in 2θ and the structure was solved by least-squares fit of the angular setting of strong reflections based on F^2. Program used to solve structure was *SIR*92 [11] while the Program used to refine structure was maXus [12]. Integration and scaling of the reflections were performed with the HKL Denzo-Scalepack system of programs [13]. The non-hydrogen atoms were refined with anisotropic thermal parameters. Crystallographic data for (**1**) are summarized in Table 1.

2.2.1. Syntheses of complexes

*2.2.1.1. [Os(bpy)$_2$(acac)](PF$_6$) (**1**).* A modified method to that reported for preparation of $[Os(bpy)_2(acac)](ClO_4)\cdot 2H_2O$ [3] was used as follows. The complex *cis*-$[Os(bpy)_2Cl_2]$ [14] (**C**) (0.2 g, 0.35 mmol) was dissolved in 50 cm^3 of an H_2O–EtOH mixture (1:1) under N_2, heated at 75 °C on a water bath. Acetylacetone (0.5 cm^3) and excess $CaCO_3$ (0.2 g) were added, heating continued for 5 h and then the solution filtered off from any unreacted calcium salt. The filtrate was evaporated to 30 cm^3 and the product precipitated by addition of a saturated aqueous solution of $(NH_4)PF_6$ (1 mmol), filtered off and washed with H_2O, Et_2O and dried *in vacuo* over P_2O_5 (yield, 75%). The product was recrystallized from MeOH to give dark purple crystals suitable for X-ray diffraction. The ^1H NMR data (δ, ppm) in d_6-DMSO:acetylacetonate resonances, 1.76 (s, 2Me), 5.45 (s, γ-CH); bipyridine resonances, 6.95 (t, 2H), 7.55 (m, 6H), 7.80 (t, 2H), 8.35 (d, 2H), 8.65 (m, 4H).

Table 1
Crystal data and structure refinement parameters for $[Os(bpy)_2(acac)](PF_6)$ (**1**).

$C_{25}H_{23}F_6N_4O_2OsP$	Empirical formula
746.65	Formula weight
298 K	Temperature
0.71073Å	Wavelength
Orthorhombic	Crystal system
P $2_12_12_1$	Space group
	Unit cell dimensions
10.0508(2) Å	*a*
17.6875(3) Å	*b*
29.7659 (5) Å	*c*
90.00°	$\alpha = \beta = \gamma$
5291.6 (2) $Å^3$	Volume
8	*Z*
1.874 mg m^{-3}	Density (calculated)
4.95 mm^{-1}	Absorption coefficient
2.910–27.485°	Theta range for data collection
$-12 \le h \le 12$, $-22 \le k \le 22$, $-37 \le \ell \le 37$	Index ranges
2552	Reflections collected
7096 [R(int) = 0.029]	Independent reflections
None	Absorption correction
Refinement method full-matrix least squares on F^2	Refinement method
2541/0/352	
	Reflections/restraints / parameters
	R indices [$I > 3\sigma(I)$]
0.035/0.133	R_1[a]/wR_2[b]
1.93 and −2.58 e$Å^3$	Largest diff. peak and hole

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[b] $wR_2 = \left\{ \left[w(F_o^2 - F_c^2)^2 \right] / \sum wF_o^4 \right\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2)]$.

A similar procedure was used to prepare the other osmium(II) complexes $[Os(bpy)_2L](PF_6)$, (***2***)–(***5***) with a 1:2 molar ratio of the complex (**C**) to the O,O-donor ligand, (HL) in which the acetylacetone is replaced by trifluoro/hexafluoroacetylacetone, dibenzoylmethane or tropolone. The product yield for the complexes were 75–80%. The ^1H NMR resonance data (δ, ppm) in d_6-DMSO for the complexes (**2**)–(**5**) are as follows. $[Os(bpy)_2(tfacac)](PF_6)$ (**2**): trifluoroacetylacetonate, 1.78 (s, Me), 6.07 (s, γ-CH); bipyridine, 7.20 (m, 2H), 7.75 (m, 6H), 8.05 (t, 2H), 8.30 (d, 1H), 8.45 (d, 1H), 8.75 (t, 2H), 8.90 (t, 2H). $[Os(bpy)_2(hfacac)](PF_6)$ (**3**): hexafluoroacetylacetonate, 6.24 (s, γ-CH); bipyridine, 7.16 (t, 2H), 7.65 (m, 4H), 7.81 (m, 2H), 7.95 (m, 2H), 8.08 (m, 2H), 8.87 (m, 2H). $[Os(bpy)_2(dbm)](PF_6)$ (**4**): dibenzoylmethanate, 6.85 (s, γ-CH), 7.56 (m, 8H), 7.76 (d, 2H); bipyridine, 7.10 (t, 2H), 7.34 (t, 4H), 7.67 (d, 2H), 7.83 (t, 2H), 8.31 (d, 2H), 8.67 (d, 2H), 8.77 (d, 2H). $[Os(bpy)_2(trop)](PF_6)$ (**5**): tropolonate, 7.08 (t, 3H) 7.25 (d, 2H); bipyridine, 7.60 (m, 6H), 7.70 (t, 2H), 7.95 (t, 2H), 8.53 (d, 2H), 8.72 (d, 2H), 8.90 (d, 2H).

*2.2.1.2. [Os^{III}(bpy)$_2$L](PF$_6$)$_2$ (L = acac, tfacac) (**6**), (**7**). Method (a):* To the evaporated filtrate (30 cm^3) above, $Na_2S_2O_8$ (0.48 g, 2 mmol) in H_2O (5 cm^3) was added and stirred for 0.5 h, an instantaneous brown color appears. The solution was filtered to isolate any undissolved material and the filtrate concentrated to 5–10 cm^3 on a rotary evaporator, then $(NH_4)PF_6$ (2.5 mmol) was added. The brown precipitate was filtered off, washed carefully with EtOH and Et_2O and dried *in vacuo* over P_2O_5.

The complex (**7**) was similarly prepared in which trifluoroacetylacetone replaces acetylacetone. The product yield for the complexes (**6**) and (**7**) were 70%.

Method(b): To the complex (**1**) or (**2**) (0.25 mmol) in DMF or Me_2CO (3 cm^3) was added $Na_2S_2O_8$ (2.5 mmol) in H_2O (5 cm^3) and NH_4PF_6 (1 mmol). The mixture was stirred for 15–30 min. during which a brown precipitate formed. This was filtered off, washed with little cold EtOH and then Et_2O (yield, 75%).

2.2.2. Catalytic oxidation of benzyl alcohol

To 10 cm^3 of dichloroethane benzyl alcohol (1 cm^3, 10 mmol), complex (**1**) (0.01 g, 0.013 mmol) and Aliquat 336 (0.45 g, 1 mmol) were added. The reaction mixture was heated 70–80 °C with stirring and then 30% H_2O_2 (7.5 cm^3, 65 mmol) was added dropwise at a constant rate over 40 min. The reddish violet color changed into brown and the reaction continued for 80 min more, the organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 10 cm^3). The extracts were combined, dried over anhydrous $MgSO_4$ and evaporated to dryness. The aldehyde content was quantified as its 2,4-dinitrophenylhydrazone derivative (equivalent to 1.43 mmol of the benzaldehyde product).

3. Results and discussion

3.1. Syntheses and some physico-chemical properties

Reaction of *cis*-$[Os(bpy)_2Cl_2]$ with the O,O-donor ligands (HL) in a 50% aqueous ethanol solution under nitrogen and reflux for 5 h gave purple-dark microcrystals of the desired complexes isolated as the hexafluorophosphate salts $[Os(bpy)_2L](PF_6)$ ((***1***)–(***5***)) (yield, 75–80%). The presence of $CaCO_3$ as a heterogeneous base [1,15] allows completion of reaction to give pure products. Oxidation of $[Os(bpy)_2L]^+$ species (L = acac or tfacac) by $Na_2S_2O_8$ instead of $FeCl_3$ [3] in the presence of NH_4PF_6 gave $[Os(bpy)_2L](PF_6)_2$ (***6***) and (***7***) as

Table 2
Analytical, vibrational spectroscopic and thermal gravimetric data for complexes.

Compound	Found (Calcd.)			Λ_M (Ω^{-1} cm^2 mol^{-1})	Vibrational data (cm^{-1})[a]			Other bands	Thermal gravimetric data Deco. temp. range, °C[b,c]
	C	H	N		ν(C=O)	ν(C=C)	$\nu(PF_6)$		
[Os(bpy)$_2$(acac)](PF$_6$)	40.1	3.0	7.4	134	1544s,1396s	1519 s,1255s	844vs, 557s	1600m, 1461s, 1163w	300–380
(***1***)	(40.2)	(3.1)	(7.5)		*1541s,1320m*	*1259m*	*769w*	*1601s, 1478s, 1169s, 1023w, 674s*	14.5(13.3)
[Os(bpy)$_2$(tfacac)](PF$_6$)	37.4	2.4	6.8	139	1574s,1368m	1510m, 1257s	842vs, 556s	1602m, 1453vs, 1156s	260–370
(***2***)	(37.5)	(2.4)	(7.0)		*1539s,1319s*	*1252m*	*768w*	*1601s, 1477s, 1167s, 1021w, 672s*	18.0(19.1)
[Os(bpy)$_2$(hfacac)](PF$_6$)	34.9	2.1	6.5	148	1543m, 1333s	1520m, 1261vs	837vs, 550s	1603m, 1453vs, 1156vs	255–370
(***3***)	(35.1)	(2.0)	(6.6)		*1550s, 1318s*	*1266s*	*766w*	*1603s, 1482vs, 1170s, 1021w, 673s*	23.5(24.2)
[Os(bpy)$_2$(dbm)](PF$_6$)	48.1	3.0	6.3	145	1516vs, 1393s	1253s	842vs, 555s	1599m,1471s, 1162m	140–365
(***4***)	(48.3)	(3.1)	(6.4)						25.5(25.6)
[Os(bpy)$_2$(trop)](PF$_6$)	42.0	2.8	7.3	129	1509s, 1342s	1251s	839vs, 558s	1588s, 14625s, 1168w	300–375
(***5***)	(42.2)	(2.7)	(7.3)						15.5(15.4)
[Os(bpy)$_2$(acac)](PF$_6$)$_2$	33.6	2.5	6.2	220	1531s, 1339m	15513s, 1286m	839vs, 557s	1608s, 1451s, 1166m	230–300
(***6***)	(33.7)	(2.6)	(6.3)		*1543s, 1320s*	*1262m*	*766m*	*1600s, 1480s, 1172s, 1043m, 672s*	13.0(11.1)
[Os(bpy)$_2$(tfacac)](PF$_6$)$_2$	31.5	1.9	5.8	235	1580m	1513w, 1292 s	837vs, 550s	1608s, 1448s, 1142s	150–245
(***7***)	(31.7)	(2.1)	(5.9)						16.0(16.3)

[a] Raman bands are in italic.
[b] Refer to weight loss due to O,O-donor ligand (−1).
[c] Underlined data refer to found weight loss (Calcd.), %.

reddish-brown complexes (product yield, ~70%). Analytical data of the complexes (Table 2) are in good agreement with their compositions. Most complexes are soluble in CH_2Cl_2 and CH_3CN and the molar conductivities in the latter solvent show that the complexes, (***1***)–(***5***) behave as 1:1 electrolytes while the complexes, (***6***) and (***7***) are 1:2 electrolytes, as expected (Table 2).

Complexes (***1***)–(***5***) were found to be diamagnetic at room temperature; other complexes (***6***) and (***7***) are paramagnetic and have magnetic moments (μ_{eff}) of 1.78 and 1.92 BM, close to the spin-only value (1.73 BM) for one unpaired electron. This suggests the low-spin $d^5(t_{2g})^5$ configuration for the osmium(III) ion in an octahedral environment [6,16,17]. However, EPR studies at room temperature for the solid complexes (***6***) and (***7***) show an EPR silent as is the case for similar related osmium(III) *bis*-bipyridine complexes [5,6]. This EPR inactivity in Low-spin d^5 complexes is known to result from extensive mixing of the Kramers doublets by strong spin–orbit coupling which gives rise to short electronic relaxation time [6,18].

The thermal stabilities of the complexes have been investigated. They are stable to 140 °C or up to 300 °C, after which temperatures the weight loss seems to correspond to loss of the coordinated O,O-donor lignad (−1) (Table 2). The complexes show less thermal stability than those of the analogous ruthenium(II) complexes [2]. The thermal data (Table 2) indicate that the osmium(II) complexes, (**1**) and (***2***) are more stable than the corresponding osmium(III) complexes, (***6***) and (***7***).

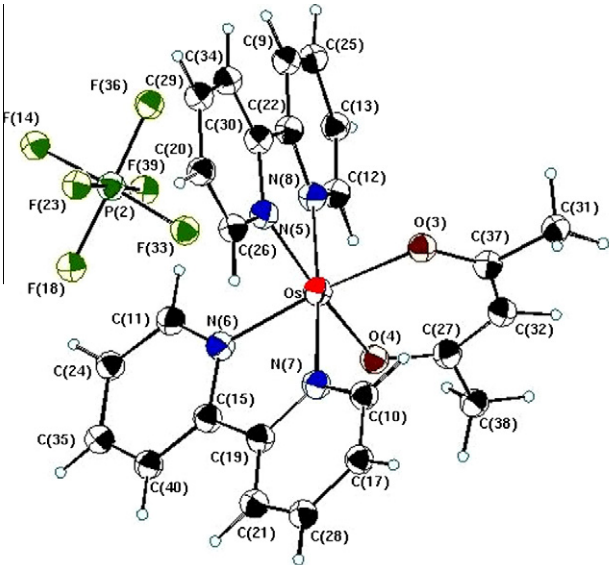


Fig. 1. ORTEP diagram of [Os^{II}(bpy)$_2$L](PF$_6$) (**1**) showing the atom-numbering scheme, with 50% ellipsoidal propability. Hydrogen atoms are shown as smaller spheres of arbitrary radii.

3.2. Molecular and crystal structure of [Os(bpy)$_2$(acac)](PF$_6$)

Molecular structure of [Os(bpy)$_2$(acac)](PF$_6$) (**1**) has been determined by X-ray crystallography. A view of the molecule is shown in Fig 1, and selected bond distances and angles are listed in Table 3. The OsN_4O_2 coordination sphere is distorted octahedral; three near linear *trans*-angles (~172.9–176.4°) and twelve *cis*-angles (~78.6–99.1°). The acetylacetonate anion (acac) is coordinated to osmium as bidentate O,O-donor with a bite angle of 91.4°, similar bond lengths have been observed for O3–C37 and O4–C27 [1.287(3) Å, 1.288(3) Å] and also for C32–C37 and C27–C32

Table 3
Selected bond lengths and angles for $[Os(bpy)_2(acac)](PF_6)$(**1**).

Bond lengths (Å)		Bond angles (°)	
Os1–O3	2.075 (2)	O3–Os1–O4	91.44 (6)
Os1–O4	2.0567 (14)	O3–Os1–N5	87.60 (6)
Os1–N5	2.014 (2)	O3–Os1–N6	173.32 (6)
Os1–N6	2.019 (2)	O3–Os1–N7	94.81 (6)
Os1–N7	2.046 (2)	O3–Os1–N8	87.17 (6)
Os1–N8	2.047 (2)	O4–Os1–N5	172.94 (7)
N8–C12	1.371 (2)	O4–Os1–N6	85.86 (6)
N8–C22	1.356 (2)	O4–Os1–N7	88.52 (6)
C22–C30	1.459 (3)	O4–Os1–N8	94.41 (6)
N5–C30	1.377 (3)	N5–Os1–N6	95.81 (6)
N5–C26	1.367 (2)	N5–Os1–N7	98.53 (7)
C12–C13	1.366 (3)	N5–Os1–N8	78.56 (7)
C20–C26	1.367 (3)	N6–Os1–N7	79.04 (7)
N6–C11	1.367 (2)	N6–Os1–N8	99.11 (7)
N6–C15	1.374 (2)	N7–Os1–N8	176.43 (9)
N7–C19	1.358 (3)	F14–P2–F18	88.98 (11)
N7–C10	1.347 (3)	F14–P2–F23	89.59 (13)
N7–C19	1.358 (3)	F14–P2–F33	177.40 (11)
C15–C19	1.475 (3)	F14–P2–F36	90.06 (12)
O3–C37	1.287 (3)	F14–P2–F39	90.18 (12)
O4–C27	1.288 (3)	F18–P2–F23	89.12 (10)
C32–C37	1.385 (3)	F18–P2–F33	88.43 (10)
C27–C32	1.386 (3)	F18–P2–F36	179.0 (2)
P2–F14	1.577 (2)	F18–P2–F39	89.13 (12)
P2–F18	1.571 (2)	F23–P2–F33	90.64 (14)
P2–F23	1.566 (2)	F23–P2–F36	90.50 (11)
P2–F33	1.575 (2)	F23–P2–F39	178.24 (12)
P2–F36	1.573 (2)	F33–P2–F36	92.53 (13)
P2–F39	1.579 (2)	F33–P2–F39	89.51 (13)
		F36–P2–F39	91.24 (12)

Table 4
Hydrogen bonding parameters (Å, °) for $[Os(bpy)_2(acac)](PF_6)$ (**1**).

D–H–A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
C34–H34···F14$^{(i)}$	0.960(2)	2.629(2)	3.279(3)	122.7(2)
C29–H29···F14$^{(i)}$	0.960(2)	2.702(2)	3.306(3)	121.4(2)
C17–H17···F18$^{(ii)}$	0.960(2)	2.563(2)	3.283(3)	131.9(2)
C10–H10···F23$^{(ii)}$	0.960(2)	2.832(2)	3.583(3)	135.7(2)
C38–H38A···F39$^{(iii)}$	0.960(3)	2.801(2)	3.614(3)	143.0(2)
C32–H32···F39$^{(iii)}$	0.960(2)	2.817(2)	3.574(3)	136.39(14)

Symmetry codes: (i) 2 – *x*, –*y*, –*z*; (ii) 3/2 – *x*, 1/2 – *y*, *z*; (iii) 5/2 – *x*, 1/2 – *y*, *z*.

[1.385(3) Å, 1.386(3) Å] which are indicating the resonating structure of the coordinating acac ligand. Similar coordination and structural data have been found for $[Os^{II}(bpy)_2(sal)](ClO_4)$ [sal = O,O-donor of salicylaldhydate(−1)] [6], but a square pyramidal structure of $[Cu(bpy)(acac)(H_2O)]NO_3.H_2O$ has been recently reported [19]. Table 3 shows that the hexafluorophosphate anion in the complex (**1**) is a slightly distorted octahedral structure; the 12 *cis*-angles are near 90° (~88.4–92.5°) and the six P–F bond lengths are similar .

The PF_6^- ions are involved in the intermolecular hydrogen bonding interactions, the fluorine atoms interact with hydrogen atoms of H–C (bpy) and H–C(acac). Medium–weak contacts of lengths in the range 3.279(3)–3.614(3) Å have been observed (Table 4).

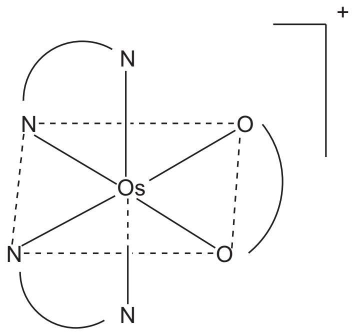
3.3. Spectroscopic properties

The vibrational spectral data (IR and Raman, Table 2) are consistent with the proposed structures for complexes and indicate that the O,O-donor ligand (HL) is coordinated in the normal manner through O,O-donor sites [2,10,17,20–22].

The electronic spectra (Table 5) in $(CH_2Cl)_2$ for complexes showed several intense absorptions for each in the visible region. These bands are probably due to either a metal (d) → ligand (π*) charge-transfer for the complexes, (**1**)–(**5**) [5,6,23–26,27a] or ligand (π) → metal (d) charge-transfer (MLCT) for complexes (**6**) and (**7**) [5,6,26]. It was pointed out by Lever [27b] that for a MLCT transition involving the bpy π* orbital, a molar extinction coefficient of ~4000 $M^{-1}\ cm^{-1}$ per bpy ligand is expected. So, the bands in the range 490–550 nm for the complexes $[Os^{II}(bpy)L](PF_6)$ are assigned to MLCT transition from the $Os^{II}(d\pi)$ to π*(bpy), while the lower energy bands in 647–780 nm region are probably arising from $Os^{II}(d\pi)$ to π*(L) transition. Each of these MLCT transitions are shifted to a higher wavelength in the order of L = hfacac < tfacac < acac < trop, as those found for X = CN < Br < Cl in the complexes $[Ru^{II}L'X_2]$(L′ = N4-tetradentate neutral ligand) [27c]. The bands or shoulders below 300 nm are of the interligand π → π* type [25,26,28,29]. The complexes (**1**) and (***6***) showed similar spectra to those previously reported for $[Os(bpy)_2(acac)]^+$ [4] and $[Os(bpy)_2(acac)]^{2+}$ [30], respectively.

The ^{1}HNMR spectra of the complexes $[Os(bpy)_2L](PF_6)$ **(1)-(5)** were recorded in d_6-DMSO (data in Section 2.2.1) and are in accordance with the structures suggested previously for analogous ruthenium(II) complexes [2].

On the basis of different analytical and spectroscopic data above together with the structural data of $[Os(bpy)_2(acac)](PF_6)$ (**1**), the structures of osmium complexes are expected to be formulated as shown below. The non-isomeric nature of these complexes is in contrast to those observed for $[M^{II}(PPh_3)_2(tfacac)_2]$ (M = Ru or Os) [31].



N-N = 2,2′-bipyridine

O-O = O,O- donor ligand (-1)

3.4. Redox properties

The electron transfer properties of the complexes have been studied by cyclic voltammetric techniques. Voltammetric data *vs.* a silver electrode for 0.1 M (*n*-Bu_4N)PF_6-dichloroethane solutions (containing 10^{-3} M of the complex) are presented in Table 5 and Fig. 2 as a representative example. These are compared with $[Fe(C_5H_5)_2]^{0/+}$, $E_{1/2}$ = +0.42 V, Δ*E* = 65 mV for the cell used under the same conditions. The voltammogram for each of the complexes, (***1***)–(***5***) shows a redox wave at positive potential (+0.07–+0.67 V) which is assigned to the Os^{II}/Os^{III} oxidation (equation below), similar to that reported for $[Os^{II}(bpy)_2(sal)](ClO_4)$ [6]. The peak separation (Δ*E*) for each complex is close to that anticipated for a Nernstian one electron-process (59 mV) [32], and remains unaltered upon changing the scan rate (10–50 mV s^{-1}). The anodic peak current (i_{pa}) is almost equal to the cathodic peak current (i_{pc}) as expected for a reversible couple.

$$[Os^{II}(bpy)_2L]^+ \rightleftharpoons [Os^{III}(bpy)_2L]^{2+} + e$$

For the complexes (**1**) and (***5***) a further an irreversible peak (E_{pa} = +1.36 V) or a quasi-reversible oxidation wave ($E_{1/2}$ = +1.28 V, Δ*E* = 120 mV) is observed; each has the same current

Table 5
UV/Vis spectroscopic and cyclic voltammetric data for complexes.

Complex	UV/Vis data λ_{max} (ε, M^{-1} cm^{-1})	Voltammetric data (V)					
		Oxidations			Reductions		
		$E_{1/2}$	E_{pa}	ΔE	$E_{1/2}$	E_{pc}	ΔE
(***1***)	765(4770), 525(11,180), 443(10,640)	+0.22		0.060		−1.28	
	373(11,320), 297(50,960), 247(30,600)		+1.36				
	749(4010), 521(10,300), 438(9470)[a]			0.060			
	375(10,200), 295(48,100), 275, 244(28,800)[a]						
(***2***)	723(4200), 506(9500), 415(10,700)	+0.32		0.060	−1.73		0.060
	380(8600), 296(44,050), 246(20,450)			0.060			
(***3***)	647(5950), 490(16,800), 420(12,200)	+0.67		0.060		−1.43	
	355(8100), 293(69,000), 245(29,900)						
(***4***)	750(5600), 514(14,150), 438(17,000)	+0.07		0.060		−1.27	
	332(32,250), 297(72,850), 247(41,650)						
(***5***)	780(3050), 706(3150), 550(9850)	+0.08		0.060		−1.40	
	438(11,850), 298(38,750), 240(32,500)	+1.28		0.120			
(***6***)	5105h(1500), 389(5150), 286(27,350)				+0.22		0.060
	252(26,000)						
	505sh, 413sh, 384(4610), 283(21,200)[b]						
	264(22,200), 250(22,500)[b]						
(***7***)	700(1300), 487(4880), 402(5110)				+0.32		0.060
	380(5180), 291(26,380), 245(21,740)						

[a] In MeOH solvent Ref. [4].

[b] In H_2O solvent Ref. [30].

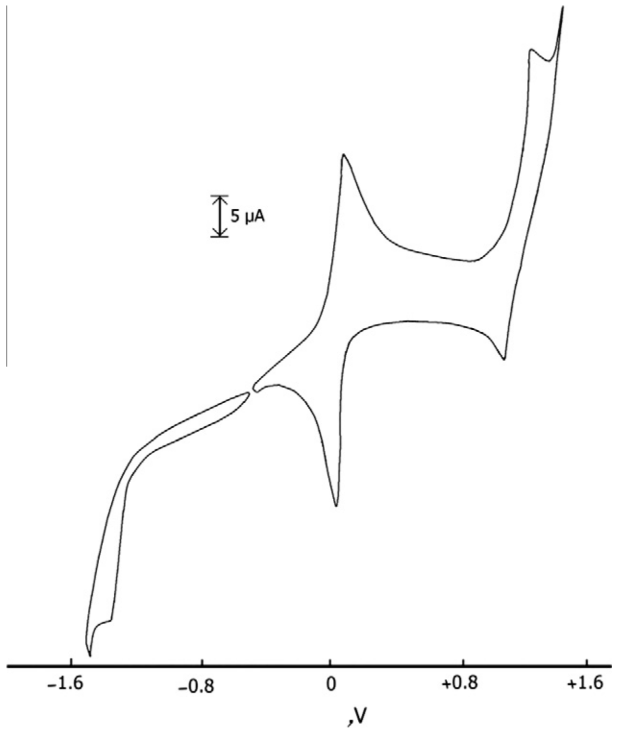


Fig. 2. Cyclic voltammogram, volts *versus* Ag electrode, scan rate 50 mV s^{-1} for $[Os^{II}(bpy)_2(trop)](PF_6)$ (***5***). (10^{-3} M) in dichloroethane –0.1 M ($(n\text{-}Bu_4N)PF_6$) solution.

height as that of the Os^{II}/Os^{III} couple. This peak or wave is probably arises from Os^{III}/Os^{IV} oxidation as similarly found for $[Os^{II}(bpy)_2Cl_2]$ [14] and $[Ru^{II}(PPh_3)_2L_2]$ [L = O,O-donor ligand(−1)] [33,34].

There is a gradual decrease in redox potentials of the Os^{II}/Os^{III} couple in the series $[Os(bpy)_3]^{2+}$, +0.81 V [35]; $[Os(bpy)_2(acac)]^+$, +0.22 V; $[Os(acac)_3]$, −1.244 V [36]. This is similar to that observed for the Ru^{II}/Ru^{III} couple in $[Ru(bpy)_n(acac)_{3-n}]$ (n = 0,1,2,3) [10] and also in $[Ru(bpy)_n(L)_{3-n}]$ (L = O,N-donor ligand (−1)] [37,38]; the Os^{II}/Os^{III} redox potentials have lower values than those of the corresponding Ru^{II}/Ru^{III} couples.

Comparison of the Os^{II}/Os^{III} redox potentials, $E_{1/2}$ (Table 5) for the present complexes $[Os^{II}(bpy)_2L](PF_6)$, (***1***)–(***5***) with that of the Ru^{II}/Ru^{III} couple in the analogous ruthenium(II) complexes [2] shows that these potentials are lower in the osmium complexes compared to those of ruthenium. This indicates that the osmium(II)–osmium(III) oxidation is easier than that of ruthenium(II)–ruthenium(III) as the case for $[M(bpy)_2(sal)]^+$ (M = Ru or Os) [6,39].

The oxidation potential, $E_{1/2}$ for the Os^{II}/Os^{III} couple is sensitive to the nature of the substituent in the O,O-donor ligand. It is shifted to lower or higher values (Table 5) relative to the $[Os^{II}(bpy)_2(acac)](PF_6)$, reflecting an increase of basicity with lower $E_{1/2}$ values corresponding to O,O-donor ligand (L) in the order;

$$\text{hfacac} < \text{tfacac} < \text{acac} < \text{trop} \approx \text{dbm}$$

The reversibility of the Os^{II}/Os^{III} couple for $[Os^{II}(bpy)_2L](PF_6)$ (L = acac or tfacac) at relatively low positive potentials ($E_{1/2}$ = +0.22, +0.33 V) points to the possibility of the oxidized complexes $[Os^{III}(bpy)_2L](PF_6)_2$, (***6***) and (***7***), being stable and isolable in the solid state.

At the negative potentials a reversible wave ($E_{1/2}$ = −1.73 V) for complex (***2***) or an irreversible cathodic peak (E_{pc}) for the other complexes is observed indicating a reduction of one bpy molecule as shown in the equation below. A similar reduction wave was found for $[Os(bpy)_2Cl_2]$ ($E_{1/2}$ = −1.6 V) [14,35] while in $[Ru^{II}(bpy)_2L]^+$ two successive-one electron reductions were observed [2,40].

$$[Os^{II}(bpy)_2L]^+ + e \rightleftharpoons [Os^{II}(bpy)(bpy^-)L]$$

It is concluded that in the *tris*-acetylacetonato complex, the trivalent state of osmium is highly stabilized and has a low value of $E_{1/2}$ for the Os^{III}/Os^{II} couple. This also indicates that chelation by O,O-donors alone can not stabilize the +2 state of osmium, and in order to have a stable complex containing O,O-donor ligand of osmium(II), strong π-acid ligands are needed to be in the coordination sphere, e.g. bpy ligands which are familiar stabilisers of osmium(II) and cause a positive shift to the $E_{1/2}$ for Os^{II}/Os^{III} couple.

A linear correlation exists on combining the Os^{II}/Os^{III} oxidation potential ($E_{1/2}$) with those of the MLCT energy in both the regions 490–550 nm and 647–780 nm. For a higher potential $E_{1/2}$, the MLCT transition energy becomes higher for the complexes $[Os^{II}(bpy)_2L](PF_6)$ in the order L = hfacac > tfacac > acac > trop. This correlation has already been reported for many ruthenium (II) systems [27].

3.5. Reactivity towards benzyl alcohol oxidation

We have found that $[Ru^{II}(bpy)_2(acac)](PF_6)$ acts as a good catalytic oxidant in the presece of t-butylhydroperoxide (t-BuOOH) as a co-oxidant for selective oxidation of primary and secondary alcholols to the corresponding aldehydes and ketones [2]. The use of the complex $[Os(bpy)_2(acac)](PF_6)$ (**1**) has been tried for such catalytic oxidation with t-BuOOH or N-methylmorpholine N-oxide as co-oxidants, but no oxidation products were obtained over 3–4 h of the reaction time under the similar conditions. Use of the osmium (II) complex (**1**) with H_2O_2 as a co-oxidant (Section 2.2.2) in the presence of Aliquat 336 as a phase transfer catalyst in dichloroethane solution (at 80 °C) for 2 h was effective for the selective oxidation of benzyl alcohol to benzaldehyde with a catalytic turnover of 110, lower than obtained by $[Ru^{II}bpy(acac)_2](PF_6)/H_2O_2$ (turnover = 480) [10]. Here we have used a half equivalent amount of H_2O_2 (30%) than that mentioned for $RuCl_3{\cdot}nH_2O/H_2O_2$ system in which benzoic acid was completely formed [41]. Under the same conditions, cyclohexanol was not oxidized at all. In the absence of Aliquat 336 or when using MeCN as a solvent [42], no oxidation products were obtained and this suggests that the phase transfer catalyst brings both the osmium catalyst and H_2O_2 to the organic layer where reaction occurs. The low reactivity of the osmium complex (**1**) in comparison with the ruthenium complexes is perhaps not surprising, thus $[RuO_4]^-$ and $[Ru^{III}(PPh_3)_2Cl_2(acac)]$ are much better oxidants than those of $[OsO_4]^-$ and $[Os(PPh_3)_2Cl_2(acac)]$ [10,43,44].

4. Conclusion

Careful synthesis of the complexes $[Os^{II}(bpy)_2L](PF_6)$ was performed under N_2 and use of the heterogeneous base catalyst ($CaCO_3$), otherwise impure and unidentified osmium(II) complexes containing some paramagnetic Os(III) species are obtained. The redox Os^{II}/Os^{III} potentials ($E_{1/2}$) for these osmium(II) complexes are shifted to more lower values compared with those of analogous ruthenium(II) complexes [2]. These electrochemical data showed that the O,O-donor ligand (L) stabilizes the high oxidation state of osmium(III) and confirms that Os^{II} is easier to oxidize than Ru^{II} [45] and the general trend is consistent with the inherent stability of the third-row *vs* second-row transition metals in higher oxidation states. As expected, osmium complexes are weaker oxidants than those of ruthenium because the 5d electrons in the third-row transition element, osmium are less tightly held by the nucleus than the 4d electrons in its congener, ruthenium. Analytical and spectroscopic data together with the structural data of osmium complex (**1**) supported the structural formulations of complexes .

5. Supplementary data

Crystallographic data for the structure analysis been deposited with the Cambridge Crystallographic Data Center, CCDC No. 795957 for $[Os^{II}(bpy)_2(acac)](PF_6)$. Copy of information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit @ccdc.com.ac.uk or http://www.ccdc.cam.ac.uk).

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References

[1] B. Roy, T.K. Mallick, P.K. Das, B.K. Ghosh, Transition Met. Chem. 18 (1993) 89.
[2] A.M. El-Hendawy, A.H. Al-Kubaisi, H.A. Al-Madfa, Polyhedron 16 (1997) 3039.
[3] D.A. Buckingham, F.P. Dwyer, H.A. Goodwin, A.M. Sargeson, Aust. J. Chem. 17 (1964) 325.
[4] G.M. Bryant, J.E. Fergusson, H.K.J. Powell, Aust. J. Chem. 24 (1971) 257.
[5] F. Basuli, S.-M. Peng, S. Bhattacharya, Polyhedron 18 (1999) 391.
[6] F. Basuli, S.-M. Peng, S. Bhattacharya, Polyhedron 17 (1998) 2191.
[7] (a) L. Ruiz-Azuara, United States Patent 1996, vol. 5, 576, 326.;
(b) L. Ruiz-Azuara, United States Patent 1992, vol. RE35, 458, February 18, 1997.
[8] M.E. Bravo-Gomez, J.C. Garcia-Ramos, I. Gracia-Mora, L. Ruiz-Azuara, J. Inorg. Biochem. 103 (2009) 299.
[9] (a) G.E. Buchel, I.N. Stepanenko, M. Hejl, M.A. Jakupec, V.B. Arion, B.K. Keppler, Inorg. Chem. 48 (2009) 10737;
(b) A.M. Pizarro, A. Habtemariam, P.J. Sadler, Top Organomet. Chem. 32 (2010) 21.
[10] A.M. El-Hendawy, S.Y. Alqaradawi, H.A. AL-Madfa, Transition Met. Chem. 25 (2000) 572.
[11] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Cryst. 27 (1994) 435.
[12] S. Mackay, C. Gilmore, C.J. Edwards, N. Stewart, K. Shankland, maXus Computer Program for the Solution and Refinement of Crystal Structures. Bruker Nonius, The Netherlands, MacScience, Japan and The University of Glasgow, 1999.
[13] Z. Otwinowski, W. Minor, in: C.W. Carter Jr., R.M. Sweet (Eds.), Methods in Enzymology, vol. 276, Academic Press, New York, 1997, pp. 307–326.
[14] E.M. Kober, J.V. Caspar, B.P. Sullivan, T.J. Meyer, Inorg. Chem. 27 (1988) 4587.
[15] B.K. Ghosh, A. Mukhopadhyay, S. Goswami, S. Ray, A. Chakravorty, Inorg. Chem. 23 (1984) 4633.
[16] J. Chatt, G.J. Leigh, D.M.P. Mingos, R. Paske, J. Chem. Soc. (A) (1968) 2636.
[17] A.M. El-Hendawy, Polyhedron 9 (1990) 2309.
[18] Z. Shirin, R.N. Mukherjee, Polyhedron 11 (1992) 2625.
[19] O.O.E. Onawumi, O.O.P. Faboya, O.A. Odunola, T.K. Prasad, M.V. Rajasekharan, Polyhedron 27 (2008) 113.
[20] M.M. Finnegan, T.G. Lutz, W.O. Nelson, A. Smith, C. Orvig, Inorg. Chem. 26 (1987) 2171.
[21] G.T. Behnke, K. Nakamoto, Inorg. Chem. 6 (1967) 433.
[22] W.P. Griffith, C.A. Pumphrey, C.A. Skapski, Polyhedron 6 (1987) 891.
[23] S.P. Copper, Y.B. Koh, K.N. Raymond, Inorg. Chem. 104 (1982) 5092.
[24] R.B. Von Dreele, R.C. Fay, J. Am. Chem. Soc. 94 (1972) 7935.
[25] T.W. Hambley, C.J. Hawkins, T.A. Kabanos, Inorg. Chem. 26 (1987) 3740.
[26] C.J. Hawkins, T.A. Kabanos, Inorg. Chem. 28 (1989) 1084.
[27] (a) D. Mishra, S. Naskar, B. Adhikary, R.J. Butcher, S.K. Chattopadhyay, Polyhedron 24 (2005) 201;
(b) A.B.P. Lever, P.R. Auburn, E.S. Dodsworth, M.-a. Haga, W. Lui, M. Melnik, A. Nevin, J. Am. Chem. Soc. 110 (1988) 8076;
(c) K. Mizushima, M. Nakaura, S-B Park, H. Nishiyama, K. Harada, M.-a. Haga, Inorg. Chim. Acta 261 (1997) 175.
[28] A.M. El-Hendawy, Inorg. Chim. Acta 179 (1991) 223.
[29] A.M. El-Hendawy, Polyhedron 10 (1991) 2511.
[30] G.M. Bryant, J.E. Fergusson, Aust. J. Chem. 24 (1971) 275.
[31] M.A. Queiros, S.D. Robinson, Inorg. Chem. 17 (1978) 310.
[32] R.S. Nicholson, I. Shain, Anal. Chem. 36 (1964) 706.
[33] J. Chakravarty, S. Bhattacharya, Polyhedron 15 (1996) 257.
[34] A.M. El-Hendawy, Transition Met. Chem. 17 (1992) 250.
[35] T. Matsumura-Inoue, T. Tominaga-Morimoto, J. Electroanal. Chem. 93 (1978) 127.
[36] G.S. Patterson, R.S. Holm, Inorg. Chem. 11 (1972) 2285.
[37] N.C. Pramanik, S. Bhattacharya, Polyhedron 16 (1997) 1755.
[38] N.C. Pramanik, S. Bhattacharya, J. Chem. Research (S) (1997) 98.
[39] N. Bag, G.K. Lahiri, S. Bhattacharya, L.R. Falvello, A. Chakravorty, Inorg. Chem. 27 (1988) 4396.
[40] S. Bhattacharya, Polyhedron 12 (1993) 235.
[41] G. Barak, J. Dakka, Y. Sasson, J. Org. Chem. 53 (1988) 3553.
[42] G.B. Shul'pin, G.Suss-Fink, L.S. Shul'pina, Chem. Commun. (2000) 1131.
[43] A.C. Dengel, A.M. EL-Hendawy, W.P. Griffith, A.D. White, Transition Met. Chem. 14 (1989) 230.
[44] A.M. El-Hendawy, M.S. El-Shahawi, Polyhedron 8 (1989) 2813.
[45] H. Taube, Pure Appl. Chem. 51 (1979) 901.