Synthesis, characterisation and redox behaviour of mixed ligand complexes of osmium(II/III/IV)-phosphines

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The reaction of [OsXnL2] [X = Cl or Br; L = 2-(1H-tolylazo)pyridine (tapy), 1; L = quinolin-8-olate (oxin), 2] with tertiary phosphine (PR3 = PPh3 or PPh2Me) bases in boiling aqueous alcohol affords complexes of the types [OsX(PR3)L2]1+ (L = tapy, Z = 1, 3; L = oxin, Z = 0, 5) and [Os(PR2)L2]2+ (L = tapy, n = 2, 4; L = oxin, n = 0, 6), which when charged isolated as their perchlorates. The osmium(IV) counterparts [OsX(PR3)(oxin)]2+ (7) and osmium(III) species [Os(PR2)(oxin)]3+ (8) of [Os(PR3)(oxin)]2+ (5) and [Os(PR2)(oxin)]3+ (6), respectively are also stable enough for isolation by oxidation with ceric sulphate of their osmium(III) and osmium(II) precursors respectively, and for characterisation. However, oxidation of tapy compounds of osmium(II), [Os(PR2)(tapy)]2+ and [Os(PR2)(tapy)]3+ results in a product of indefinite composition. The complexes provide a unique opportunity for probing redox reactions pertaining to metal-centred and/or ligand-based. The details are described below.

Experimental

The azoimine ligands (L) were prepared by the method reported earlier16. [OsXnL2] [X = Cl or Br; L = tapy8, 1; L = oxin8, 2] complexes were prepared by the literature methods. Purification of solvent (MeCN) and preparation of the supporting electrolyte ([Et4N][ClO4]) for electrochemical work were executed following published procedure11. Quinolin-8-ol, PPh3, PPh2Me and all other chemicals and solvents were of analytical grade and were used

Substantial chemistry of 2-(1H-tolylazo)pyridine (tapy)8-5 and quinolin-8-olate (oxin)8-9 ligands with Group 8 metal ions has been demonstrated in recent years. For osmium dihalogeno species of the type [OsXnL2] [X = Cl or Br; L = tapy8, 1; L = oxin8, 2] are isolated and the reactivity of the OsX moiety towards different ligands have been investigated resulting a plethora of mixed ligand complexes8,5,8,9 in varied oxidation levels of the metal ion. This work stems from our interest in the reactivity pattern of [OsXnL2] (1/2) towards tertiary phosphine (PR3 = PPh3 or PPh2Me) bases, that remains unexplored to date. Stable complexes of the type [OsX(PR3)L2]2+ (L = tapy, Z = 1, 3; L = oxin, Z = 0, 5) and [Os(PR2)L2]2+ (L = tapy, n = 2, 4; L = oxin, n = 0, 6) have been prepared, which when charged isolated as their perchlorates. The osmium(IV) counterparts [OsX(PR3)(oxin)]2+ (7) and osmium(III) species [Os(PR2)(oxin)]3+ (8) of [Os(PR3)(oxin)]2+ (5) and [Os(PR2)(oxin)]3+ (6), respectively are also stable enough for isolation by oxidation with ceric sulphate of their osmium(III) and osmium(II) precursors respectively, and for characterisation. However, oxidation of tapy compounds of osmium(II), [Os(PR2)(tapy)]2+ and [Os(PR2)(tapy)]3+ results in a product of indefinite composition. The complexes provide a unique opportunity for probing redox reactions pertaining to metal-centred and/or ligand-based. The details are described below.
without further purification. All the synthetic reactions and final work-up were done in air.

**Caution!** Perchlorates of heavy metal ions with organic ligands are potentially explosive. The syntheses described below involve the use of perchlorate ions and isolation of the complex cations as perchlorate salts. Such a procedure may present an explosion hazard and due care should be exercised to avoid this, although we have not encountered any problem taking with small quantity of the samples.

Electrical conductivities (in MeCN, solute $\sim 10^{-3} M$), electronic (in MeCN, solute $\sim 10^{-5} M$), IR (KBr discs, 4000-600 cm$^{-1}$; polyethylene discs, 600-300 cm$^{-1}$) and $^1$H NMR (in CDC$_3$; Me$_4$Si as internal standard) spectra were recorded using a Systronics 304 direct reading spectrophotometer, Shimadzu UV 160A spectrophotometer, JASCO FTIR 420 and Brucker 270 MHz spectrometers, respectively. Magnetic susceptibilities were measured with a PAR 155 vibrating sample magnetometer. EPR spectra were run on a Varian 109C E-line X-band Spectrometer fitted with a varian dewar for measurements at 77 K (liquid nitrogen) and all spectra were calibrated with the help of 1,1-diphenyl-2-picryl hydrazyl (g = 2.0037). Microanalyses (C, H and N) were done with a Perkin-Elmer 2400 CHNS/O elemental analyser. Electrochemical studies were performed (in MeCN at 298 K) under dry N$_2$ with a PAR 370-4 electrochemistry system as described elsewhere. In cyclic voltammetry (CV) the following parameters and relation were used: scan rate (v), 50 mV s$^{-1}$; formal potential $E^0 = 0.5(E_{pa} + E_{pc})$ where $E_{pa}$ and $E_{pc}$ are anodic and cathodic peak potentials, respectively; $\Delta E_p$ is the peak-to-peak separation. In differential pulse voltammetry (DPV): scan rate (v), 10 mV s$^{-1}$; modulation amplitude ($\Delta E$), 25 mV; $E^0 = E_p + 0.5(\Delta E)$ where $E_p$ is the DPV peak potential. The agreement between $E^0$ data obtained by the two techniques was good (within ±5 mV). The potentials are referenced to a saturated calomel electrode (SCE) and are uncorrected for the junction contributions.

**Preparation of complexes**

All the monophosphine and diphosphine complexes (3-6) were prepared following the general procedure described below for one representative member from each group. Oxidation of 5 and 6 and the conversion of the oxidised species 7 and 8 to reduced homologues are also described.

**[OsCl(PPh$_3$(tapy)$_2$)(ClO$_4$)$_2$]**

Dinitrogen was purged for 15 min to a suspension of 0.1 g (0.153 mmol) of [OsCl$_2$(tapy)$_2$] in 30 ml MeOH$_2$:CH$_2$:OH:H$_2$:O (2:1). PPh$_3$ (0.060 g, 0.229 mmol) was added and the mixture was heated at reflux under dinitrogen for 8 h. The initial blue-violet solution gradually changed to red-violet, which was filtered through a fine glass-frit and was evaporated under reduced pressure. The residue was washed copiously with Et$_2$:O and dissolved in 10 ml ethanol-water saturated with NaClO$_4$ and was evaporated. The precipitate was collected by filtration, dried in vacuo, redissolved in a minimum of acetonitrile and was loaded on a silica gel (60-120 mesh) column (20 × 1 cm). A small blue-violet band of unreacted [OsCl$_2$(tapy)$_2$] was eluted with CH$_2$:Cl$_2$. The slow moving red-violet band of 3a was collected with CH$_2$:Cl$_2$Me-CN (4:1). A very faint orange-red band remained unmoved near the top of the column. Dark shining crystals of 3a were obtained on complete evaporation of the red-violet eluate at room temperature; yield, 0.097 g (65%). [OsBr(PPh$_3$(tapy)$_2$)(ClO$_4$)$_2$] (3b) was obtained (yield, 62%) similarly except that [OsBr(tapy)$_2$] was used instead of [OsCl$_2$(tapy)$_2$]. [OsCl(PPh$_2$:Me)(tapy)$_2$](ClO$_4$) (3c) and [OsBr(PPh$_2$:Me)(tapy)$_2$](ClO$_4$) (3d) were prepared (yield, ~60%) using PPh$_2$:Me instead of PPh$_3$ and the appropriate dihalogeno starting materials.

**[OsCl(PPh$_3$(tapy)$_2$)(Oxin)$_2$]**

Both dichloro and dibromo starting materials afford the same product. However, here we report with the latter as less reaction time is involved itself being better leaving group. The procedure is similar to the synthesis of 3a except that the mole ratio is changed. A 0.176 g (0.669 mmol) sample of PPh$_3$ was refluxed with 0.1 g (0.134 mmol) of [OsBr(tapy)$_2$] in 15 ml boiling MeOH$_2$:CH$_2$:OH:H$_2$:O (2:1) under dinitrogen for 12 h. The resulting orange-red solution was processed as in 3a. On slow evaporation of orange-red eluate in air, the required complex 4a was obtained in crystalline form; yield, 0.105 g (60%). The other analogous compound [Os(PPh$_2$:Me$_2$)(tapy)$_2$](ClO$_4$)] (4b) was prepared (yield, 60%) similarly as above using PPh$_2$:Me instead of PPh$_3$.

**[OsCl(PPh$_3$(oxin)$_2$]**

The procedure is similar to the synthesis of 3a except that reaction time is less. To 15 ml of deaerated MeOH$_2$:CH$_2$:OH:H$_2$:O (2:1) were added 0.1 g (0.182 mmol) [OsCl$_2$(oxin)$_2$] and 0.071 g (0.275 mmol) PPh$_3$ and the mixture was boiled at reflux
under dinitrogen for 6 h. A violet solution was obtained which, on evaporation under reduced pressure, gave a dark residue. This was washed several times with solvent ether and dried in vacuo over P₂O₅. The solid was redissolved in a minimum of CH₂Cl₂ and was chromatographed as described in 3a. Initially a green fraction of unreacted [OsCl₃(ο-toly)] was eluted out with CH₂Cl₂ followed by a slow moving band eluted with C₆H₆-MeCN (2:1). Slow evaporation of the latter results in crystals of 5a. The yield was 0.087 g, 62%. [OsBr(PPh₃)(οxin)] (5b) was obtained (yield, 65%) similarly except that [OsBr₂(οxin)] was used instead of [OsCl₂(οxin)]. [OsCl(PPh₂Me)(οxin)] (5c) and [OsBr(PPh₂Me)(οxin)] (5d) were prepared (yield, ~65%) using PPh₂Me instead of PPh₃ and the appropriate dihalogeno starting materials.

[Os(PPh₃)(οxin)] (6a)

Both dichloro and dibromo starting materials afford the same product. However, here we report with the latter as less reaction time is involved itself being better leaving group. The procedure is similar to the synthesis of 4a only the reaction time is less. A 0.206 g (0.784 mmol) sample of PPh₃ was refluxed with 0.1 g (0.157 mmol) of [OsBr₂(οxin)] in 15 ml boiling MeOCH₂CH₂OH-H₂O (2:1) under dinitrogen for 8 h. The resulting red solution was processed as in 5a. On slow evaporation of red eluate in air, the required complex 6a was obtained in crystalline form; yield, 0.094 g (60%). The other analogous compound [Os(PPh₂Me)(οxin)] (6b) was prepared (yield, 65%) similarly as above using PPh₂Me instead of PPh₃.

[OsCl(PPh₃)(οxin)]ClO₄ (7a)

A 0.1 g (0.129 mmol) sample of 5a dissolved in MeCN (20 ml) was stirred magnetically at room temperature. To this, a 10 ml aqueous Ce(SO₄)₃·4H₂O (0.052 g, 0.129 mmol) in 1 M H₂SO₄ solution was added dropwise. The violet solution immediately changed to greenish brown. After further stirring for another 15 min, this was filtered through a fine glass frit. The residue obtained upon concentrating the filtrate was extracted with dichloromethane (3×5 ml). On slow evaporation of the extractant at room temperature, dark crystals of 7a were afforded in almost quantitative yield. [OsBr(PPh₃)(οxin)]ClO₄ (7b) was prepared similarly started with [OsBr(PPh₃)(οxin)] (5b).

[Os(PPh₂Me)(οxin)]ClO₄ (8a)

This was prepared similarly using the same reaction stoichiometry and conditions as described above in 7a except that [Os(PPh₂Me)(οxin)] (6a) was used instead of 5a. The yield of the red-brown compound 8a was 75%; [Os(PPh₂Me)(οxin)]ClO₄ (8b) was also prepared (yield, 72%) similarly starting with [Os(PPh₂Me)(οxin)] (6b).

Conversion of Os⁴⁺ (7) → Os⁵⁺ (5) and Os⁵⁺ (8) → Os⁶⁺ (6)

Osmium(IV) or osmium(III) compounds (0.1 mmol) was dissolved in MeCN (10 ml) and the solution was stirred magnetically at 298 K. N₂H₄·H₂O (0.15 mmol) in MeCN was then added dropwise. The greenish brown osmium(IV) solution changed to violet whereas red-brown osmium(III) solution changed to red. On evaporation under reduced pressure, dark solids deposited which were extracted with CH₂Cl₂ (3×5 ml). On slow evaporation of these extracts, pure osmium(III) and osmium(II) (whichever the case) were obtained in an almost quantitative yield. Analytically pure materials were obtained after recrystallization from MeCN-H₂O followed by drying in vacuo over P₂O₅. The composition was checked by comparing properties with authentic samples of osmium(III) and osmium(II) compounds.

Results and discussion

The reaction of PR₃ with [OsX₃L₂] (1/2) in boiling (b.p., 398 K) 2-methoxyethanol-water (2:1) through nucleophilic displacement of halide ions is of general applicability, and proceeds slowly but smoothly to form mono- and diphasphine products. Bromo compounds react faster than the chloro analogues as the former contain a better leaving group. The reaction time with PPh₂Me is less than that with PPh₃ and tapy compounds react slowly than the oxin compounds. All the crude products are tested by TLC to check the presence/absence of dihalogeno precursor. The relative yields depend on mole ratio used and the reaction time involved. However, diphasphines may be the sole product, if 5-fold excess of PR₃ is used and the reflux time is lengthened; even then during chromatographic filtration the monophosphines are eluted out to a little extent. The isomeric homogeneity of the mono- and diphasphine complexes was checked by careful column chromatography on silica gel and alumina columns. Only one isomeric form in each case was obtained by iterative separation method. The reducing behaviour of the alcoholic solvent converts osmium(IV) to osmium(III) or osmium(II) if starting with
Table 1—Analytical data of osmium complexes

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<th>Comp. (Mol formula)</th>
<th>Found (Calc)</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; nm (ε, dm&lt;sup&gt;3&lt;/sup&gt; mol&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
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<td>51.6 3.7 8.9</td>
<td>860 (970), 710° (1,920), 660° (2,380), 600 (3,020), 505 (13,280), 360° (27,100), 324 (44,460), 250° (28,010)</td>
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<td>48.8 3.5 8.4</td>
<td>862 (950), 715° (1,850), 665° (2,210), 600 (2,860), 505 (12,770), 364° (26,240), 325 (42,830), 252° (27,440)</td>
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<td>47.9 3.6 9.2</td>
<td>865 (990), 705° (1,770), 668° (2,150), 595 (2,710), 510 (12,310), 368° (25,190), 328 (42,590), 250° (27,610)</td>
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<td>45.8 3.7 8.5</td>
<td>870 (860), 702° (1,680), 670° (2,100), 595 (2,590), 510 (12,010), 370° (24,570), 328 (42,100), 250° (2,130)</td>
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<td>54.7 4.0 6.3</td>
<td>830° (1,060), 760° (1,450), 520 (11,020), 416° (20,830), 370 (25,480), 330 (26,210), 284 (19,830), 240° (11,020)</td>
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<td>55.1 4.0 6.4</td>
<td>842° (850), 764° (1,270), 520 (11,490), 420° (20,060), 372 (24,110), 330 (25,470), 288 (18,240), 240° (10,220)</td>
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<td>55.4 3.5 3.4</td>
<td>720° (650), 585° (3,340), 420 (8,560), 362 (7,870), 325 (13,420), 275 (12,540)</td>
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<td>52.4 3.1 3.3</td>
<td>725° (610), 588° (3,180), 420 (8,410), 364 (7,510), 326 (13,050), 275 (12,110)</td>
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<td>51.8 3.6 4.2</td>
<td>732° (560), 590° (2,740), 422 (7,970), 368 (7,010), 328 (12,240), 278 (11,430)</td>
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<td>48.9 3.3 3.6</td>
<td>735° (650), 595° (2,090), 422 (7,700), 368 (7,290), 328 (11,910), 278 (12,070)</td>
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<td>64.4 4.1 3.0</td>
<td>690° (740), 545° (4,210), 415 (9,020), 360 (8,980), 320 (14,100), 270 (13,120)</td>
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<td>60.4 4.3 3.1</td>
<td>700° (630), 548° (3,820), 415 (8,440), 364 (8,110), 320 (13,640), 272 (12,550)</td>
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<td>49.1 3.0 3.4</td>
<td>680 (7,020), 500° (4,560), 355 (19,240), 315 (13,760), 272 (16,200)</td>
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<td>49.4 3.1 3.2</td>
<td>680 (7,020), 500° (4,560), 355 (19,240), 315 (13,760), 272 (16,200)</td>
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<td>46.3 3.0 3.1</td>
<td>685 (6,780), 505° (4,010), 358 (18,120), 315 (13,010), 274 (15,310)</td>
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<td>59.1 4.0 2.4</td>
<td>655° (970), 502° (4,860), 405 (8,020), 352 (9,940), 314 (15,050), 265 (13,200)</td>
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<td>54.3 3.8 2.7</td>
<td>660° (880), 505° (4,130), 405 (7,440), 355 (9,170), 316 (14,330), 268 (12,320)</td>
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<td>54.0 3.9 2.9</td>
<td>660° (880), 505° (4,130), 405 (7,440), 355 (9,170), 316 (14,330), 268 (12,320)</td>
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The presence of water is, however, invariably needed for such mixed ligand complex formation. Oxidation of violet \([\text{Os}^{II}]X(\text{PR}_3)(\text{oxin})_2\) (5) and red \([\text{Os}^{III}]X(\text{PR}_3)(\text{oxin})_2\) (6) by aqueous cerium(IV) furnishes respectively greenish-brown \([\text{Os}^{IV}]X(\text{PR}_3)(\text{oxin})_2\) (7) and red-brown \([\text{Os}^{IV}]X(\text{PR}_3)(\text{oxin})_2\) (8): conversion of these to their corresponding precursor complexes can be achieved with hydrazine hydrate. Both oxidative and reductive steps are facile and using appropriate reagents converts one into the other at room temperature.

The complexes were characterized using microanalytical, spectroscopic, magnetic and electrochemical results (Table 1). Analytical data of all the complexes are consistent with the calculated values. The air-stable moisture-insensitive complexes are highly soluble in a range of common organic solvents, such as dichloromethane, acetonitrile, methanol but are moderately soluble in water. In acetonitrile solutions they show the expected non-electrolytic (5-8 \(\Omega^{-1} \text{cm}^2 \text{mol}^{-1}\)) or 1:1 (120-130 \(\Omega^{-1} \text{cm}^2 \text{mol}^{-1}\)) electrolytic behaviour as indicated by their wide range of \(\Lambda_M\) values. The perchlorate salts display characteristics of perchlorate bands at \(~1090\) (\(v_1\)) and \(620\) (\(v_2\)) cm\(^{-1}\), \(v(C=\text{N})\) band at \(~1590\) cm\(^{-1}\) is invariably seen in all complexes. In \([\text{Os}^{IV}]X(\text{PR}_3)(\text{tapy})_2\)ClO\(_4\) (3) and \([\text{Os}^{II}]X(\text{PR}_3)(\text{tapy})_2\)ClO\(_4\) (4) complexes azo modes are observable respectively at \(~1290\) and \(~1300\) cm\(^{-1}\); with more and more \(\text{PR}_3\) substitution the mode shifted to higher wave number reflecting competition of \(\text{PR}_3\) to withdraw \(\delta\)-electron on it which reduces back bonding towards tapy. Large shift (140 cm\(^{-1}\)) towards lower energy than the free ligand value (1425 cm\(^{-1}\))\(^{10}\) is indicative of strong \(\pi\)-bonding of osmium(II) through an azo nitrogen. Phenolic \(\nu(C=\text{O})\) in oxin complexes is observable at \(~1100\) cm\(^{-1}\). All other characteristic \(\text{PR}_3\) and \(L\) vibrations are present in the 1600-600 cm\(^{-1}\) range.

Room-temperature solid-phase magnetic susceptibility measurements show that the osmium(II) complexes \([\text{Os}X(\text{PR}_3)(\text{tapy})_2]\)ClO\(_4\) (3), \([\text{Os}X(\text{PR}_3)(\text{tapy})_2]\)ClO\(_4\) (4) and \([\text{Os}(\text{tapy})_2(\text{oxin})_2]\) (6) are uniformly diamagnetic \((\mu_{\text{eff}}=0\) \(\mu_B\)) and osmium(III) compounds \([\text{Os}X(\text{tapy})_2(\text{oxin})_2]\) (5) and \([\text{Os}(\text{tapy})_2(\text{oxin})_2]\)ClO\(_4\) (8) have moments \((\mu_{\text{eff}}=1.78-1.81 \text{ BM})\) close to the spin-only value, 1.73 BM, expected for mononuclear low-spin \((t_{2g}^5\) idealised, \(S=1/2\)) six coordinate \(d^5\) complexes. Osmium(IV) complexes \([\text{Os}X(\text{PR}_3)(\text{oxin})_2]\)ClO\(_4\) (7) exhibit a subnormal magnetic moment \((\mu_{\text{eff}}=1.12-1.15 \text{ BM})\): such a low value with \(t_{2g}^4\) configuration is characteristic of heavy metal osmium in octahedral environment\(^{13}\). All the osmium(II) and osmium(IV) complexes are EPR-silent at room temperature and liquid nitrogen in MeCN-PhMe solution and glass, respectively as expected\(^{14,15}\) for \(d^0\) and \(d^2\) metal ions, respectively. On the other hand, in MeCN-PhMe glass at liquid nitrogen temperature (77 K), two resonances are observable for the osmium(III) complexes (5a: 2.554, 2.154; 5b: 2.545, 2.168; 5c: 2.558, 2.149; 5d: 2.542, 2.174; 8a: 2.561, 2.147; 8b: 2.544, 2.167). The inability to observe an expected third resonance is often a characteristic feature\(^{16,17}\) of an anisotropic environment in low-spin \(d^0\)-osmium complexes. No ligand hyperfine structure could be resolved in any of the spectra.

\(^1H\ NMR investigation of selected complexes was made to solve the stereochemical problem of these mixed ligand complexes. The methyl signal of tapy in type 3/4 complexes and of \(\text{PPh}_3\)Me in type 6 compounds is particularly useful in diagnosing the geometry of \([\text{Os}X]^{2+}\) (\(Z=\text{Os}-2\)) radical. A single sharp methyl signal in \([\text{Os}(\text{PPh}_3)(\text{tapy})_2]\)ClO\(_4\) (4a) at \(~2.2\) ppm is in line with the fact that the gross stereochemistry of Os(tapy)_2^2^- moiety in 4a and by inference in 4b and type 3 compounds is the same as in the dihalo precursor 1. Similarly, 6b shows single \(\delta_{\text{Me}}\) (of \(\text{PPh}_3\)Me) at \(~2.3\) ppm; this implies that during substitution of halides by phosphines Os(oxin)_2 fragment in type 6 complexes and by inference in type 5 retains the gross structure as in 2. It is then reasonable to assume that the reactions proceed in a stereo-retentive manner and the effective \(C_2\) (\(C_2\) in 1 and \(C_2\) in 2) symmetry is retained. The facile interconversions of the pairs 5 and 7, and 6 and 8 along with the closely similar electroactivity (\(E'_{pa}, E''\) and \(E'\) values) strongly suggest that 7 and 8 adopt same gross geometry as in 2.

The complexes exhibit several absorption bands and shoulders in the 200-1000 nm region (Table 1). The high intensity bands below 400 nm are presumably of ligand origin assignable to intraligand \(\pi-\pi^*\) and \(\pi-\pi^*\) transitions. Above this wavelength the transitions are LMCT for osmium(III)/osmium(IV) complexes and MLCT type for osmium(II) members. The intense transitions are spin-allowed whilst the weaker ones at longer wavelengths could be of spin-forbidden being partially allowed through strong spin-orbit coupling by heavy element osmium\(^{18,19}\). In each set the systematic shift of bands to higher frequencies...
on progressive PR₃ coordination is understandable, since PR₃ is expected to stabilise the t₂ level better than X due to Os→PR₃ π retrodictive bonding. This is also consistent with the increase in metal redox potential on PR₃ coordination, as discussed below.

The electroactivity of the complexes was examined in MeCN solutions using voltammetry (CV and DPV) and coulometry at platinum and glassy carbon electrodes. The DPV technique is particularly useful for observing responses close to solvent cut-off regions. The representative voltammograms are shown in Fig. 1. Essentially, the same voltammogram is observable irrespective of whether the bulk solution of mixed PR₃-oxin complexes is on an osmium(II) or osmium(III) and an osmium(III) or osmium(IV) levels as are the cases. In acetonitrile two successive nearly reversible CV responses are observed for these mixed ligand complexes which correspond to osmium(III)-osmium(II) and osmium(IV)-osmium(III) couples, whereas the mixed PR₃-tapy complexes show only the former couple. The responses (Eqs 1 and 2, shown with L = oxin, PR₃ = PPh₃ or PPh₃Me) are:

\[ \text{[Os}^{II}(PR₃)₂(oxin)₂]⁺ + e⁻ \rightarrow \text{[Os}^{II}(PR₃)₂(oxin)₂]^{\text{0}} \quad \ldots (1) \]
\[ \text{[Os}^{IV}(PR₃)₂(oxin)₂]²⁺ + 2e⁻ \rightarrow \text{[Os}^{III}(PR₃)₂(oxin)₂⁺]²⁺ \quad \ldots (2) \]

reproducible with no trace of decomposition after a number of cycles. One-electron nature of couple 1 was confirmed from constant-potential electrolysis (n = 1.02) and that of 2 from a comparison of current height with couple 1 in DPV experiments.

The most striking observation is the almost 2 V positive shift of the potential in osmium(III)-osmium(II) couple in passing from oxin complexes to tapy compounds. The more the substitution of tertiary phosphines, the greater is the anodic shift of the potentials. This is in accord with argument that dπ(t₂) level (HOMO) of metal orbital in tapy complexes is most stabilised. Strong π-back donation of the metal to the excellent π-acceptor azomine ligand is no doubt the prime factor in making E⁰ of the metal-based electrode reactions high. Although the overall charges have some effect, the trend in such E⁰ values dictates the order of π-acceptor ability of oxin<tapy.

The presence of one pyridine N (π-acceptor centre) and one phenolic O (with almost no π-acceptance property) in oxin and one pyridine N (π-acceptor centre) and one azo N (excellent π-acceptor centre) in tapy may presumably control the π-acceptor ability.

The negative side of SCE was scanned using a glassy carbon electrode. The LUMO (π⁰ level) of tapy can accommodate up to two electrons. Four successive one-electron reductions are therefore expected for Os(tapy)₂⁰⁺ moiety. In the potential range −0.3 to −2.3 V three reductions are seen in CV but all the four expected reductions are clearly observable in careful DPV experiments in dry solvents. The first two reductions are reproducible (in CV) with current heights comparable to that of couple 1 indicating involvement of one-electron transfer. The redox processes are depicted in Eqs (3) and (4). The fourth reduction is irreversible in CV, which may be due to some kind of chemical assistance connected with the charge transfer steps at such lower potentials. The reductions involve azoimine (−N=N−) over imine (−C=N−) is the major responsible factor in stabilising LUMO of tapy.
complexes. It is to note that the free ligands oxin and PR₃ do not show any response in the whole potential window used in studying the complexes, which is helpful in assigning the responses on the negative of oxin complexes to be metal centred.

We conclude that this note has addressed a comparative account of oxin and tapy towards Os-PR₃ binding. Spectral and electrochemical properties reflect that with more and more PR₃ donor centres osmium(II) is better stabilised. The $E^0$ values reflect that azoimines stabilise osmium(II) better than quionolin-8-olate. To our knowledge this work demonstrates the first example where the comparative view of osmium-PR₃ binding in different oxidation states of the metal has been examined in combination with azoimine and quionolin-8-olate.

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