Synthesis, spectral characterization and electrochemical properties of osmium(II) complexes of 1-ethyl-2-(arylazo)imidazoles

Prithwiraj Byabartta, Sanjib Pal, Umansankar Ray & Chittaranjan Sinha
Department of Chemistry, University of Burdwan, Burdwan713104, India
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Title complexes have been synthesised on reacting 1-ethyl-2-(arylazo)imidazoles (RL, where R = H, Me, OMe, Cl) with \((\text{NH}_4)_2\text{OsCl}_6\). Two isomers, blue-violet (isomer-A) and red-violet (isomer-B) of the composition \(\text{OsCl}_2\text{(RL)}\) have been chromatographically separated. IR spectra show the presence of two \(v(\text{Os-Cl})\) (300-310 and 320-330 cm\(^{-1}\)) and suggest the complexes with cis-OsCl\(_2\) configuration. Three geometrical isomers with cis-OsCl\(_2\) configuration are possible; with consideration of co-ordination pairs in the order of Cl, N [N\(\text{imidozole}\)] and N' [N\(\text{azo}\)] they are cis/trans-cis (cct), cis/cis-cis (ccc) and cis/cis-cis (cct). The \(^1\text{H}\)NMR spectra identify isomer-A and isomer-B as ctc- and ccc-configurations, respectively. Absorption spectra exhibit multiple MLCT transitions in the visible region and the energy of transition follows the order ccc > ctc. Redox studies show Os(IV)/Os(III) and Os(V)/Os(III) couples at 0.4-0.6 V and 1.6-1.7 V versus SCE, respectively along with ligand reductions.

It is because of the biological and chemical ubiquity of imidazoles\(^1\) that we have been engaged for the last several years to explore the chemistry of 2-(arylazo)imidazoles\(^2,6\). The exobidentate character of imidazole moiety is eliminated by 1-alkylation to synthesise 1-alkyl-2-(arylazo)imidazole. The ruthenium chemistry of these ligands is known in some detail\(^3,4\). Progress in ruthenium chemistry with this ligand has encouraged us to explore the corresponding osmium chemistry. In this work we describe the synthesis, spectra and redox properties of osmium(II) complexes of 1-ethyl-2-(arylazo)imidazole complexes.

Experimental
2-(Arilazo)imidazoles and 1-ethyl-2-(arylazo)imidazoles were prepared by reported procedure\(^1\). Osmium tetroxide was obtained from Johanson Matthey & Co. U. K. It was converted to \((\text{NH}_4)_2\text{OsCl}_6\) according to reported procedure\(^1\). Solvent purification and reagent synthesis for electrochemical works were done as before\(^8\). Commercially available silica gel (60-120 mesh) from SRL was used for chromatographic purification. All other solvents and chemicals were of reagent grade and were used without further purification.

Microanalytical data (C, H, N) were collected using Perkin Elmer 2400 CHN elemental analyser. UV-Vis spectra were recorded by JASCO Model V-570 UV-VIS-NIR spectrophotometer. Infrared (IR) spectra were obtained using FTIR JASCO Model 420 spectrophotometer (KBr disk, 4000 - 200 cm\(^{-1}\)); \(^1\text{H}\) NMR spectra were collected in CDCl\(_3\) using Brucker 300 MHz FT NMR spectrometer. The solution electrical conductivity was measured using a Sytronics 304 conductivity meter with a solute concentration of \(10^{-3}\) M in nitromethane.

Electrochemical measurements were carried out under a dinitrogen environment with EG & G PARC Model 270 computer controlled, VERSASTAT using Pt-disk milli working electrode. All results were collected at 298 K with the saturated calomel electrode (SCE) as reference. The reported potentials are uncorrected for junction contribution.

Preparation of ctc- and ccc-dichloro-bis-[1-ethyl-2-(arylazo)imidazole]osmium(II), \(\text{OsCl}_2\text{(RL)}\).

Nitrogen gas was passed for 15 min through a brown-red solution of \((\text{NH}_4)_2\text{OsCl}_6\) (0.5 g, 1.14 mmol) in 2-methoxyethanol (50 ml). The solution was refluxed on oil-bath with continuous stirring for half-an hour. 1-Ethyl-2-(arylazo)imidazoles (RL, where R = H, Me, OMe, Cl) (2.28 mmol) was added pinchwise to this refluxing solution over another half-an hour. The mixture was refluxed under nitrogen and stirred magnetically for 8 h. During this period the solution turned brown-violet to blue-violet. This was concentrated slowly by bubbling N\(_2\) gas under hot condition to about 20 ml and kept in the refrigerator for 12 h. The shining dark colored crystalline precipitate was collected by filtration and washed with EtOH-H\(_2\)O (1:1,v/v) and again dried over P\(_2\)O\(_5\). The dry solid was dissolved in a small volume of CH\(_2\)Cl\(_2\) and was chromatographed on a silica-gel column. A small portion of the orange-yellow band was eluted with benzene and rejected. The blue-violet band was eluted MeCN-C\(_4\)H\(_8\) (1:4, v/v) and the red-violet band was eluted by MeOH. A violet mass
remained on the top of the column. The solution were collected separately and evaporated slowly in air. The crystals so obtained were dried over P2O5. The yields were of blue-violet, ctc-OsCl2(RL)2 40% and the red-violet ctc-OsCl2(RL)2, 12 %.

All other complexes were prepared by following the identical procedure and the yields were varied 50-60 % for the blue-violet isomers and 10-15% for the red-violet isomers. Anal.: Found: C, 39.7; H, 3.7; N, 16.7. Calcd. for OsCl2(ML)2 (%). C, 39.8; H, 3.6; N, 16.9. Anal.: Found: C, 41.8; H, 3.9; N, 16.1. Calcd. for OsCl2(MeL)2 (%). C, 41.7; H, 4.1; N, 16.2. Anal.: Found: C, 39.7; H, 3.7; N, 15.7. Calcd. for OsCl2(MeL)2 (%). C, 39.8; H, 3.9; N, 15.5. Anal.: Found: C, 35.9; H, 3.1; N, 15.5. Calcd. for OsCl2(ClL)2 (%). C, 36.1; H, 3.1; N, 15.3.

Results and discussion

1-Ethyl-2-(arylazo)imidazole, $\mu$-R-C6H5N=N-C6H4NN(1)-CH2=CH2, (RL) [where R=H (a), Me (b), OMe (c), Cl (d)] reacts with (NH2)2[OsCl6] in 2-methoxyethanol under reflux for 10 h and upon concentrating at cold condition OsCl2(RL)2 are isolated. The reaction is given in Eq. (1).

$$[\text{OsCl}_6]^2+ + 2 \text{RL} \rightarrow \text{OsCl}_2(\text{RL})_2 + 4 \text{Cl}^- \quad \ldots (1)$$

R = H (HL, 1a), Me (MeL, 1b), OMe (OMeL, 1c); Cl (ClL, 1d)

The product was purified by chromatographic separation on silica gel column; a mixture of C6H6:MeCN, 4:1 (v/v) separated a blue-violet complex (isomer A, 50-60%) and MeOH eluted red-violet complex (isomer B, 10-15%). The reduction of osmium from +4 to +2 oxidation state in Eq. (1) is probably brought about by the alcoholic solvent. All the complexes are diamagnetic in the crystalline state and are non-electrolytic in CH3NO2 and MeCN. Microanalytical data (vide supra) support the composition OsCl2(RL)2 of the complexes. Isomers are soluble in common organic solvents (C6H6, CH2Cl2, CHCl3, CH3CN etc.) to give blue-violet (isomer A) and red-violet (isomer B) solution colour. The complexes defined in the text and table are as follows: blue-violet (isomer A) is 2 and red-violet (isomer B) is 3.

IR spectra of the complexes are compared with the IR spectra of free ligands and analogous ruthenium complexes9. The spectra of the isomers differ significantly in the region 4000-200 cm$^{-1}$. The $\nu$(N=N) in OsCl2(RL)2 appears at 1230-1250 cm$^{-1}$ and is red shifted by 150-160 cm$^{-1}$ from that of free ligand values. This supports the N(azo) (N1) coordination. Imidazole-N(N) in the endocyclic C=N exhibits stretching frequency at 1520-1550 cm$^{-1}$ and is red shifted by 40-70 cm$^{-1}$ from that of free ligand values. The significant red shifting of $\nu$(N=N) in the complexes are in full agreement with the Os-N(azo) $\pi$-back bonding9. The N=N frequency in OsCl2(RL)2 are systematically lower (by 40-50 cm$^{-1}$ than those of the ruthenium analogues. This accounts that the relative order of $t_2 \rightarrow \pi^*$ charge donation is Os > Ru. The IR spectra of the isomer A (2) of OsCl2(MeL)2 and ctc-RuCl2(MeL)2 are nearly superimposable in the above region except for frequency shifting of N=N and C=N stretching bonds to the lower frequency region. Isomer B (3) holds the similar relationship with the spectra of ctc-RuCl2(MeL)2. This suggests that isomer A has the cis-trans-cis (etc, 2) and isomer B has cis-cis-cis (ccc, 3) geometry. Two Os-Cl stretching are observed at 320-330 and 300-310 cm$^{-1}$ and is the support of the presence of cis-OsCl2 configuration in the complexes9.

The solution absorption spectra of the complexes were taken in CHCl3 in the region 200-1200 nm. The absorptions < 400 nm are due to intraligand charge transfer transition and are not considered further. The spectra exhibit major absorption at 500-600, 800-850 and 1010-1050 nm (Table 1) and are assigned to $t_2 \rightarrow \pi^*$ charge transfer transitions where the $\pi^*$ level has large azo character9. Blue-violet solution of ctc-OsCl2(RL)2 complexes have an intense band ($\epsilon \sim 10^4$ M$^{-1}$ cm$^{-1}$) at ca 525 nm with a shoulder near 575 nm. In ccc-OsCl2(RL)2, the band is blue shifted to 515 nm and is accompanied by a shoulder at ca 585 nm. The bands in the 780-850 and 1040-1100 nm are weak ($\epsilon \sim 10^3$ M$^{-1}$ cm$^{-1}$) and are systematically shifted to higher energy region on going from ctc to ccc isomers. In d$^2$-metal complexes, multiple $t_2$(Os) $\rightarrow \pi^*$ charge-transfer transitions10,12 can arise from low symmetry splitting of the metal level, from the presence of more than one interacting ligands (each contributing one $\pi^*$ orbital).
and from mixing of singlet and triplet configurations in the excited state via spin-orbit coupling. On comparing the electronic spectra of the present series of complexes of RL with analogous ruthenium complexes it is observed that the transitions are blue shifted by 30-40 nm. This supports that the t2 orbital is deep seated in Os than Ru. The spectral behaviour is comparable with osmium(II) complexes of aryiazopyridines and the absorption positions are red shifted by 10-20 nm in the present complexes. This is in agreement with the π-acidity order, aryiazopyridine > aryloazimidazole.

The ¹H NMR spectra of the complexes were collected in CDCl₃ and examined to determine bonding and isomer structures. The atom numbering pattern is shown in structure 1. The signals are assigned on the basis of spin-spin interaction and the effect of substitution at the ligand. Ar-Me (9-Me), Ar-OMe (9-0Me) and N(1)-CH₂-CH₃ signals have been particularly useful to determine stereochemistry of the isomers.

The signal 9-Me (9-0Me) of OsCl₂(MeL/OMeL)₂ appears as a single resonance in isomer A (2b/2c) at 2.62 (3.85) ppm while isomer B (3b/3c) shows a pair of equal intense signals at 2.32 and 2.24 (3.80, 3.88) ppm. The methylene of N(1)-CH₂-CH₃ exhibits a pair of AB type multiplets in both the isomers of OsCl₂(RL₂). The AB type complex multiplets in the complexes may be the result of the geminal coupling of the inequivalent CH₂ protons. The geminal coupling constant for isomer A (J = 20-25 Hz) is less than that of isomer B (J = 35-40 Hz). In free ligand, RL, the methylene, 1-CH₂-CH₃ proton exhibits a quartet at 4.6 ppm. There are, however, neither neighbouring chiral centres nor any appreciable bond rotation barrier but there does exist a distorted coordination around the metal centre. The geminal coupling constant is the measure of distortion due to stereochemical orientation of the groups around the metal centre. This suggests that the isomer B is less symmetric than isomer A. 2-(Arylazo)pyridine complexes of osmium(II) are known in two isomeric structures, etc- and ctc-geometry. The structure of ctc isomer of 2-(arylazo)pyridin-osmium(II) is established by X-ray study. This serves as a guide along with the spectra of analogous ruthenium(II) complexes to establish

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electronic Spectra</th>
<th>Cyclic voltammetry</th>
<th>ΔEₚ Consortium V</th>
<th>( \bar{ν}_{CT} ) ev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>osC₂H₂(L), (2a)</td>
<td>1048(1.262), 839(1.077), 580(9.708), 522(15.561), 407(10.315), 368(25.271)</td>
<td>E₁₃₂ = 1.369, E₁₃₂ = 1.015, E₁₃₂ = 1.534, ΔEₚ = 1.423, ( \bar{ν}_{CT} ) = 2.377</td>
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<tr>
<td>osC₂H₂(MeL), (2b)</td>
<td>1040(1.153), 837(0.979), 582(8.295), 520(13.69), 405(9.042), 370(21.639)</td>
<td>E₁₃₂ = 1.450, E₁₃₂ = 1.044, E₁₃₂ = 1.458, ΔEₚ = 1.042, ( \bar{ν}_{CT} ) = 2.387</td>
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<tr>
<td>osC₂H₂(OMeL), (2c)</td>
<td>1032(1.008), 820(0.892), 572(7.385), 515(11.851), 400(9.536), 375(20.540)</td>
<td>E₁₃₂ = 1.314, E₁₃₂ = 1.118, E₁₃₂ = 1.613, ΔEₚ = 1.422, ( \bar{ν}_{CT} ) = 2.410</td>
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<tr>
<td>osC₂H₂(OL), (2d)</td>
<td>1054(0.893), 838(0.784), 584(7.094), 527(12.831), 408(13.016), 372(18.845)</td>
<td>E₁₃₂ = 1.385, E₁₃₂ = 0.934, E₁₃₂ = 1.449, ΔEₚ = 1.378, ( \bar{ν}_{CT} ) = 2.355</td>
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<tr>
<td>osC₂H₂(OMeL), (2e)</td>
<td>1040(0.984), 822(0.856), 575(7.229), 519(11.672), 400(7.935), 356(16.863)</td>
<td>E₁₃₂ = 1.383, E₁₃₂ = 0.935, E₁₃₂ = 1.449, ΔEₚ = 1.392, ( \bar{ν}_{CT} ) = 2.391</td>
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<tr>
<td>osC₂H₂(OMeL), (2f)</td>
<td>1012(0.813), 772(1.148), 585(3.392), 518(5.506), 419(8.048), 377(10.767)</td>
<td>E₁₃₂ = 1.352, E₁₃₂ = 1.021, E₁₃₂ = 1.552, ΔEₚ = 1.423, ( \bar{ν}_{CT} ) = 2.395</td>
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<tr>
<td>osC₂H₂(OMeL), (2g)</td>
<td>1018(0.892), 809(0.784), 570(6.488), 510(10.058), 402(8.159), 365(16.689)</td>
<td>E₁₃₂ = 1.328, E₁₃₂ = 1.085, E₁₃₂ = 1.551, ΔEₚ = 1.434, ( \bar{ν}_{CT} ) = 2.433</td>
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<tr>
<td>osC₂H₂(OMeL), (2h)</td>
<td>1045(0.738), 832(0.634), 572(6.096), 512(11.485), 400(14.345), 362(19.283)</td>
<td>E₁₃₂ = 1.407, E₁₃₂ = 0.911, E₁₃₂ = 1.405, ΔEₚ = 1.420, ( \bar{ν}_{CT} ) = 2.453</td>
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stereochemistry of the present complexes. The ctc-geometry belongs to C2-symmetry and ccc-geometry has C1-symmetry. Thus, extent of stereochemical distortion will be higher in magnitude in ccc- than ctc-geometry. The existence of two equal intense signals of 9-Me(9-OMe) in isomer B of OsCl5(MeL/OMeL)2 supports the lowering of symmetry than isomer A system. Hence, we may conclude that isomer A is ctc-OsCl5(RL)2 and isomer B is ccc-OsCl5(RL)2. The signals of aryl-H (7-H–11-H) are assigned on the basis of substituent 9-R; -Me(MeL)/-OMe(OMeL) substituent shifts 8,10-H signal to upfield side with reference to HL because of +I effect of the group2. Imidazole 4- and 5-H exist as weak doublet (coupling constant, J = 3.0–4.0 Hz) and appear at downfield portion of the spectrum. This is just reverse of previously reported results of ruthenium(II)3 and palladium(II) complexes2 of 2-(arylazo)imidazoles. Aryl-H (7-H–11-H) are upfield shifted in the present complexes by > 1.00 ppm and the reverse case is seen for imidazole 4- and 5-H compared to ruthenium(II) analogues. This may be due to the involvement of π-back bonding of azo function with osmium d-orbitals more efficiently than that of ruthenium and palladium d-orbitals13. Because of the relativistic effect, 5d-orbitals of osmium are perturbed strongly than that of 4d-orbitals in isoelectronic ruthenium by the π (azo) orbitals16. This leads to increase in electron density at azoaryl motif and is manifested by upfield shifting of aryl-H signals and consequently opposite effect to imidazole 4- and 5-H signals is observed.

The electrochemical properties of the complexes were examined by cyclic voltammetry at platinum working electrode in acetonitrile (0.1 M TBAP). In the potential range +1.0 to +2.0 two oxidative responses are observed (Table 1, Fig. 1). The first response at 0.40 to 0.60 V is referred to osmium(III)–osmium(II) couple (Eq. 2) and is nearly reversible with peak-to-peak separation 60–70 mV.

\[
\text{OsCl}_5(\text{RL})_2^{+} + e \rightarrow \text{OsCl}_5(\text{RL})_2 \quad \ldots \quad (2)
\]

\[
\text{OsCl}_5(\text{RL})_2^{2+} + e \rightarrow \text{OsCl}_5(\text{RL})_2^{+} \quad \ldots \quad (3)
\]

The current height ratio \(i_\text{ma} / i_\text{pe} \sim 1.0\) refers to one-electron oxidation couple. The second couple at 1.6 to 1.7 V is also an one-electron response (on the basis of current height) and is quasireversible in character (\(\Delta E_p \geq 100 \text{ mV}\)). This is assigned to osmium(IV)–osmium(III) couple (Eq. 3). The negative side of SCE shows two successive reductive responses. On scan reversal the corresponding anodic peak of the response is observed at \(\Delta E_p = 120–170 \text{ mV}\). These reductions are believed to give successive electron feeding into the two azoimine functions19. The substituent at the ligand frame perturbs both metal oxidation and ligand reduction potentials. The potential changes linearly with Hammett \(\sigma\) of the substituent. A decrease in the \(\sigma\)-donor capacity of the substituent increases both the Os(III)/Os(II) and the first bound-ligand reduction potentials17. The extent of perturbation is found to be more pronounced in the ligand reduction potential values, which may be due to direct bonding of the substituent in the ligand frame. The difference in two successive redox potentials positive and negative to SCE (\(\Delta E_{1/2} = E_{1/2}^+ - E_{1/2}^-\)) may be correlated with the MLCT transition energy \(v_{\text{CT}}\) (Table 1) and follows the Eq. 4.

\[
v_{\text{CT}} = 1.093 \Delta E_{1/2} + 0.857 \quad \ldots \quad (4)
\]

A similar correlation has been observed for \(\alpha\)-diimine12 and azoimine18,17 complexes of ruthenium(II).

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