

Osmium arylazoimidazoles: Synthesis, spectral characterisation and redox properties of the complexes

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Abstract. Arylazoimidazoles (RaaiH, *p*-R-C₆H₄N=N-C₃H₃N₂, R = H, Me, OMe, Cl and NO₂) are N,N'-chelators. On reaction with (NH₄)₂[OsCl₆], two classes of isomers blue-violet *ctc*-Os(RaaiH)₂Cl₂ and red-violet *ccc*-Os(RaaiH)₂Cl₂ have been isolated. The complexes have been characterised by elemental analyses, IR, UV-Vis and ¹H NMR spectral data. The N=N stretching is red shifted by 70–80 cm⁻¹ compared to the free ligand values and indicates *d*(Os) → π^* (azo) charge shifting. This is supported by MLCT transition in the visible region. ¹H NMR spectra suggest that blue-violet isomers are C₂-symmetric and red-violet isomers are C₁-symmetric. Redox studies show the Os(III)/(II) couple of both isomers at 0.6–0.7 V vs SCE and two successive azo reductions.

Keywords. Osmium(II); arylazoimidazole complexes; azoimines; geometric isomers; azo reduction.

1. Introduction

This work stems from our interest in the development of platinum metal chemistry^{1,2} of arylazoimidazoles (1). The molecule belongs to the azoimine, -N=N-C=N-, family. The efficiency of azoimine group in stabilising the low valent metal redox state is well established with particular reference to arylazopyridines⁴⁻¹⁰ and arylazoimidazoles¹⁻³. The ruthenium chemistry of arylazoimidazoles is now known in some detail². The ligands have unsymmetrical N,N'-donor centre N(imidazole), N,N(azo) and N'. Pseudo-octahedral dihalo species of type M(N,N')₂X₂ can, in principle, occur in five geometrically isomeric forms^{2,8,9}. Two and three of these respectively have the MX₂ group in *trans* and *cis* geometries. The geometries are assigned according to the coordination pairs X, N(imidazole) or N and N(azo) or N' as *trans-cis-cis* (*tcc*), *trans-trans-trans* (*ttt*), *cis-trans-cis* (*ctc*), *cis-cis-trans* (*cct*) and *cis-cis-cis* (*ccc*). The order of polarity of the five isomers may be *ccc* > *ctc* > *cct* > *tcc* > *ttt*. The isomeric complexes of ruthenium(II) belong to *tcc* and *ctc* geometries.

In comparison, the progress in the corresponding chemistry of osmium has been very slow¹⁰. Arylazopyridine chemistry³⁻¹⁰ of transition metals being similar has helped to probe the chemistry of arylazoimidazoles. With this background we have worked on the

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osmium chelates of arylazoimidazoles. In this report we describe the synthesis, spectra and redox properties of the osmium(II) complexes of arylazoimidazoles.

2. Experimental

2.1 Materials

2-Arylazoimidazoles are synthesised as per the literature¹. Osmium tetroxide was obtained from Johnson Matthey & Co. Ltd, UK. It was converted to $(\text{NH}_4)_2[\text{OsCl}_6]$ according to a reported procedure¹⁰. The purification of acetonitrile and preparation of $[\text{NBu}_4][\text{ClO}_4]$ for electrochemical work was done as before². All other solvents and chemicals were of reagent grade and were used without further purification.

2.2 Physical measurements

Spectroscopic data were obtained with the use of the following instruments: IR spectra (KBr disk, 4000–200 cm^{-1}), FTIR-JASCO Model 420; electronic spectra, Shimadzu UV-160A; ^1H NMR spectra (in CDCl_3 or mixture of CDCl_3 and $\text{DMSO}-d_6$ (1:1, v/v)), Bruker 300 MHz FT NMR spectrometer, while the solution electrical conductivity was measured using a Systonics 304 conductivity meter with a solute concentration of $\sim 10^{-3}$ M in methanol. Electrochemical measurements were carried out under a dinitrogen environment with the help of EG & G PARC Model 270 computer controlled, VERSASTAT using Pt-disk and glassy carbon disk 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.

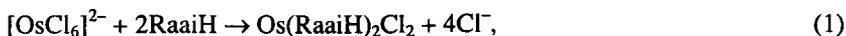
2.3 Preparation of *ctc*- and *ccc*-dichlorobis((2-phenylazo)imidazole)osmium(II). $\text{Os}(\text{HaaiH})_2\text{Cl}_2$

Nitrogen gas was bubbled 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 with continuous stirring for half an hour. 2-(Phenylazo)imidazole (RaaiH) (0.4 g, 2.33 mmol) was added pinch-wise to this refluxing solution over another half an hour time period. The mixture was refluxed under nitrogen, stirring magnetically for 8 h. During this period the solution turned to reddish-violet with the separation of a dark precipitate. The solvent was then distilled off from the reaction mixture and washed with water (30 ml \times 5). The residue was dried and washed with ethanol–water (1:1, v/v) and again dried over P_4O_{10} . The dry solid was dissolved in a small volume of CH_2Cl_2 and was chromatographed on a silica gel column (30 \times 1 ml). A small portion of the orange-yellow band was eluted with benzene and rejected. The blue-violet band was eluted by 20% $\text{MeCN}-\text{C}_6\text{H}_6$ (v/v) and the red-violet band was eluted by MeOH . A violet mass remained on the top of the column. The solutions were collected separately and evaporated in air. The crystals so obtained were dried over P_4O_{10} . The yields were of blue-violet, *ctc*- $\text{Os}(\text{HaaiH})_2\text{Cl}_2$, 32% and the red-violet, *ccc*- $\text{Os}(\text{HaaiH})_2\text{Cl}_2$, 18%.

All other compounds were prepared by following the same method. The yields were *ctc*-isomers, 30–35% and *ccc*-isomers, 20–25%.

3. Results and discussion

2-Arylazoimidazoles (RaaiH) are N,N'-chelating ligands. They may either act as N(3), N(a) or N(1), N(a) chelating molecules, N(a), azo-N to maintain a five-membered chelate structure. N(1) is a soft donor and N(3) is a hard donor centre. The reaction of RaaiH with $(\text{NH}_4)_2[\text{OsCl}_6]$ in 2-methoxyethanol under reflux has yielded dark-coloured $\text{Os}(\text{RaaiH})_2\text{Cl}_2$ type complexes. The complexes arise from spontaneous reductive (+4 \rightarrow +2) chelation of $[\text{OsCl}_6]^{2-}$ with RaaiH in 2-methoxyethanol. The reduction of osmium +4 to +2 state in reaction 1 is probably brought about by the alcoholic solvent.



On chromatographic purification over silica gel, two isomers separated approximately in 3:2 mole proportion; a violet band was eluted, with 20% $\text{CH}_3\text{CN}-\text{C}_6\text{H}_6$ (v/v), followed by a red-violet band with CH_3OH . The difference in polarity of the complexes may be due to their symmetry²; the isomer of C_2 -symmetry is less polar than that of C_1 -symmetry. Out of the five geometrical isomers, two are isolated and the 2-(arylo)pyridine-Os(II) complexes¹⁰ serve as guides to establish the structure of the present series of complexes. The composition of complexes $\text{Os}(\text{RaaiH})_2\text{Cl}_2$, is supported by elemental analyses data. All complexes are diamagnetic and nonelectrolyte in acetonitrile.

The π -accepting ability of the azoimidazoles is proved following the isolation of the Cu(I), Ru(II) complexes^{2,3}. In the case of Ru(II)-complexes of N(1)-alkyl-2-arylazoimidazoles, two isomers are structurally characterised as *tcc*- and *ctc*-isomers. The average Ru-N(azo) bond (2.00 Å) is systematically shorter than Ru-N(imidazole) bond (2.04 Å)^{2(a)}. The azo orbitals are thus strongly involved in the π -interaction. Diagnostic evidence of the existence of this interaction is the shift of $\nu(\text{N}=\text{N})$ to lower frequencies in going from the free state to its complexes. A sharp intense single band at 1400–1410 cm^{-1} which corresponds to the N=N stretch in the free ligand is shifted to 1300–1340 cm^{-1} in the complexes and indicates N(azo)-coordination. Large red shifting may be the indication of $d(\text{Os}) \rightarrow \pi^*(\text{azo})$ charge shifting. The N=N frequencies of $\text{Os}(\text{RaaiH})_2\text{Cl}_2$ are the lowest among those of all RaaiH complexes reported so far¹⁻³ and follow the order $\text{Os} < \text{Ru}$ in corresponding complexes. Clearly, osmium(II) is a stronger $d\pi$ -donor than ruthenium(II) complexes of RaaiH. The exocyclic C=N appears at 1500–1520 cm^{-1} . Complexes exhibit two sharp stretches at 320–330 and 300–315 cm^{-1} respectively in agreement with *cis*- OsCl_2 configuration¹⁰. There are three probable isomers with *cis*- OsCl_2 configuration: *ctc*, *cct* and *ccc*, out of which two are isolated.

Solution absorption spectra of the complexes are taken in methanol between 200–900 nm. The transition below 400 nm are due to intraligand charge transfer transition and are not considered further. Two or three absorption peaks are observed at longer wave length >400 nm and are assigned to $t_2 \rightarrow \pi^*$ charge transfer transitions where π^* level has large azo character. In the complexes d^6 metal ions with π -acidic ligands, multiple $t_2 \rightarrow \pi^*$ charge transfer transitions can arise^{2,9,10,12} from low symmetry splitting of the metal level, from the presence of more than one interacting ligands and from mixing of singlet and triplet configurations in the excited state *via* spin-orbit coupling¹³. The blue-violet complexes exhibit two intense absorptions ($\epsilon \sim 10^4$) in the region 572 ± 5 and 505 ± 5 nm. Red-violet isomer exhibits a weak transition at a longer wave length region, 760 ± 20 nm along with two other transitions as blue-violet isomer at higher energy sites.

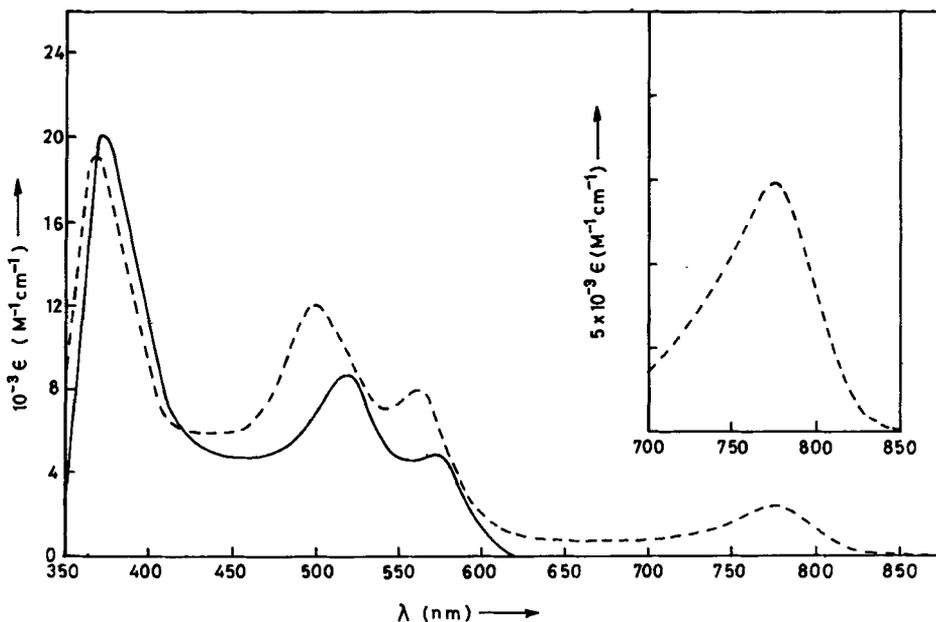
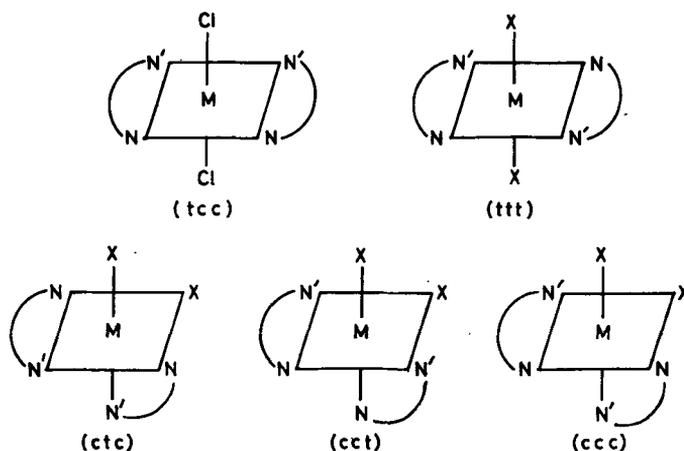
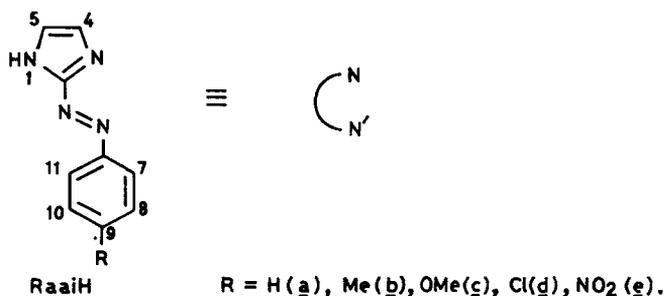


Figure 1. Electronic spectra of *ctc*-Os(*p*-ClaiiH)₂Cl₂ (—) and *ccc*-Os(*p*-ClaiiH)₂Cl₂ (----) in MeOH.

The high energy transitions in blue-violet isomers appear comparatively at longer wavelength region compared to red-violet isomers (figure 1). On comparing the results with analogous Os-complexes^{10,11}, we may conclude red-violet isomer is less symmetric than blue-violet isomers. The low symmetry environment in the *ccc*-isomer may be the reason for strong polarisation of Os singlet-triplet mixing and leading to strong spin-orbit coupling². Hence the weak transition in the low energy region 740–780 nm. Thus red-violet isomer may be suggested as *ccc*-Os(RaaiH)₂Cl₂. The second isomer may be either *ctc* or *cct* type.

The structural elucidation of the complexes are carried out by ¹H NMR data. All the proton signals have been carried out on the basis of spin-spin structure and changes therein on substitution. The proton numbering scheme is shown in scheme 1 and the prime is assigned to the respective protons in the second ligand of the complexes Os(RaaiH)₂Cl₂. The spectra are taken in CDCl₃ and in some cases using a mixture of CDCl₃-DMSO-*d*₆ mixture (4:1 v/v). The structural confirmation of the isomers have been carried out by comparison with the reported results for similar compounds and X-ray structures of some of the complexes reported elsewhere¹⁰. The appearance of a single Ar-CH₃ and Ar-OCH₃ signal in blue-violet isomers suggests the C₂-symmetry of the complexes, while in red-violet isomers, they exhibit two signals of equal intensities (figure 2). This confirms that red-violet complexes belong to *ccc*-Os(RaaiH)₂Cl₂ isomers. Blue-violet isomers have C₂-symmetry and comparing the X-ray and other spectral reports of similar complexes¹⁰ we conclude they belong to *ctc*-Os(RaaiH)₂Cl₂.

Imidazolic protons, 4- and 5-H appear as doublet and the upfield signal is referred to 5-H which is consistent with coordination *via* N(3). The N(1)-H appears as a broad band



Scheme 1.

at 13.3 to 13.4 ppm and disappears on shaking with D₂O. Presence of a trace amount of water in DMSO-*d*₆ also reduces the signal intensity suggesting proton exchange with the solvent. The aryl protons 8,10-(8',10')H resonate symmetrically at a single position while 7-(7')H and 11-(11')H resonate asymmetrically indicative of magnetic inequivalence of the protonic positions. The 11-(11')H is assigned as stereochemically nearer than 7-(7')H to the metal centre (figure 2a and b). The larger steric interaction in *ccc*-isomer induces more distortion than *ctc*-isomer and is reflected from greater separation^{2(a)} in signal resonance of 11-(11')H and 7-(7')H. The values are 20 and 45 Hz for *ctc* and *ccc*-isomers, respectively.

The redox behaviour of the complexes in acetonitrile solution was examined cyclic voltammetrically at a platinum working electrode and the potentials are reported with reference to SCE. The voltammograms display metal oxidations at the positive side and the ligand reductions at the negative side to the SCE. The results are in table 1 and a representative voltammogram is shown in figure 3.

In the potential range 0.0 to 1.5 V at the scan rate 50 mVs⁻¹ in acetonitrile, one reversible to quasireversible (peak-to-peak separation, $\Delta E = 60\text{--}80\text{ mV}$) oxidative response (0.54–0.73 V vs SCE) was observed corresponding to the couple (2).

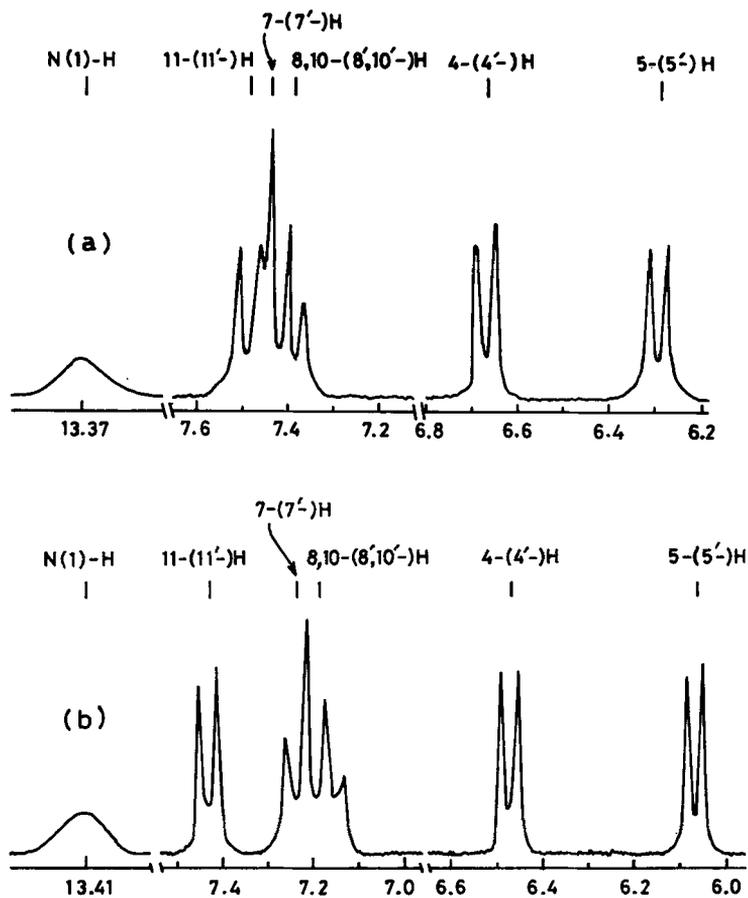


Figure 2. ^1H NMR spectra of (a) $\text{ctc-Os}(p\text{-ClaiiH})_2\text{Cl}_2$ and (b) $\text{ccc-Os}(p\text{-ClaiiH})_2\text{Cl}_2$ in CDCl_3 .

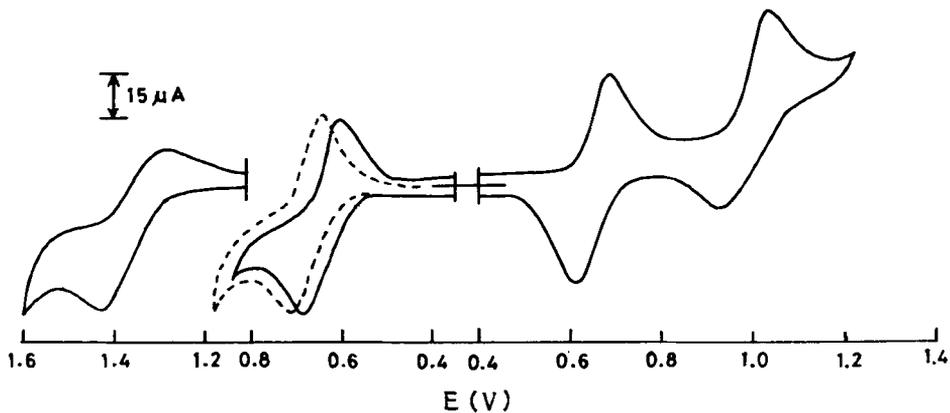


Figure 3. Cyclic voltammogram in MeCN (0.1 M TBAP) at Pt-bead working electrode. Solute concentration and scan rate are 10^{-3} M and 50 mVs^{-1} respectively of $\text{ctc-Os}(p\text{-ClaiiH})_2\text{Cl}_2$ (—) and only $\text{Os}^{\text{III/II}}$ couple of $\text{ccc-Os}(p\text{-ClaiiH})_2\text{Cl}_2$ (---).

Table 1. Elemental analyses^a, UV-VIS spectral^b and cyclic voltammetric data of complexes

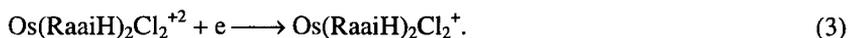
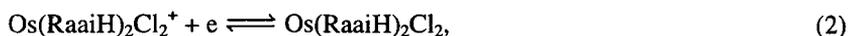
| Compound | Elemental analyses, Found/calculated | | | UV-VIS spectral data | | CV data ^d | |
|---|---|----------------|------------------|---|-----------------------------------|---|--|
| | C | H | N | λ_{\max} , nm ($10^{-3}\epsilon$, M ⁻¹ cm ⁻¹) | E_{M}^0 , V(ΔE_p , mV) | $-E_L^0$, V(ΔE_p , mV) | |
| <i>ctc</i> -Os(HaaiH) ₂ Cl ₂ | 35.66 (35.70) | 2.58 (2.64) | 18.55 (18.51) | 568 (10.95), 508 (15.95), 362 (21.70), 261 (17.26), 218 (23.07) | 0.618 (68), 1.40 ^e | 0.65 (75), 0.95 (100) | |
| <i>ctc</i> -Os(<i>p</i> -MeaaiH) ₂ Cl ₂ | 37.95 (37.91) | 3.10 (3.16) | 17.76 (17.69) | 580 (4.52), 514 (7.44), 327 (11.77), 270 (9.04), 236 (8.18) | 0.590 (60), 1.38 ^e | 0.703 (80), 0.92 (90) | |
| <i>ctc</i> -Os(<i>p</i> -OMeaaaiH) ₂ Cl ₂ | 36.02 (36.09) | 3.08 (3.01) | 16.77 (16.84) | 586 (4.61), 522 (6.86), 387 (20.80), 268 (10.36), 234 (11.67) | 0.53 (66), 1.36 ^e | 0.78 (90), 1.15 (100) | |
| <i>ctc</i> -Os(<i>p</i> -ClaaiH) ₂ Cl ₂ | 32.10 (32.04) | 2.03 (2.07) | 16.69 (16.62) | 576 (5.59), 514 (8.82), 373 (20.142), 371 (10.85), 233 (12.58) | 0.656 (76), 1.40 ^e | 0.65 (90), 0.96 (110) | |
| <i>ctc</i> -Os(<i>p</i> -NO ₂ aaaiH) ₂ Cl ₂ | 31.13 (31.08) | 2.07 (2.01) | 20.08 (20.14) | 640 (3.26), 498 (7.65), 371 (11.02), 270 (11.71), 236 (9.82) | 0.704 (82), 1.45 ^e | 0.51 (65), 0.80 (85) 1.33 ^f | |
| <i>ccc</i> -Os(HaaiH) ₂ Cl ₂ | 35.62 (35.70) | 2.58 (2.64) | 18.44 (18.51) | 745 (1.08) ^g , 576 (5.63), 502(7.07), 366 (10.11), 236 (11.64) | 0.630 (72), 1.47 ^e | 0.61 (70), 0.91 (80) | |
| <i>ccc</i> -Os(<i>p</i> -MeaaiH) ₂ Cl ₂ | 37.95 (37.91) | 3.11 (3.16) | 17.60 (17.69) | 740 (0.96), 566 (5.10), 500 (6.65), 378 (10.24), 272 (7.52), 234 (6.56) | 0.611 (70), 1.44 ^e | 0.68 (80), 1.01 (100) | |
| <i>ccc</i> -Os(<i>p</i> -OMeaaaiH) ₂ Cl ₂ | 36.16 (36.09) | 3.07 (3.01) | 16.79 (16.84) | 740 (1.15) ^g , 573 (4.69), 508 (5.96), 390 (13.70), 270 (9.26), 234 (10.89) | 0.542 (70), 1.41 ^e | 0.74 (80), 1.18 (130) | |
| <i>ccc</i> -Os(<i>p</i> -ClaaiH) ₂ Cl ₂ | 32.10 (32.04) | 2.01 (2.07) | 16.60 (16.62) | 780 (2.67) ^g , 560 (8.26), 500 (12.10), 367 (19.15), 272 (15.29), 236 (13.08) | 0.673 (70), 1.48 ^e | 0.60 (75), 0.90 (100) | |
| <i>ccc</i> -Os(<i>p</i> -NO ₂ aaaiH) ₂ Cl ₂ | 31.00 (31.08) | 1.95 (2.01) | 20.10 (20.14) | 750 (1.87) ^g , 614 (2.41), 487 (4.84), 368 (11.98), 268 (12.69) | 0.73 (80), 1.54 ^e | 0.48 (80), 0.74 (90) 1.26 ^f | |

^aCalculated values are given in parentheses; ^bsolvent MeOH; ^cshoulder; ^dsolvent MeCN, solute concentration $\sim 10^{-3}$ M, scan rate 50 mV s⁻¹, working electrode glassy carbon disk, potentials are reference to SCE, supporting electrolyte TBAP (0.1M); ^eEpa, corresponding to Os(IV)/(III); ^freduction response of -NO₂ group

Table 2. ¹H NMR spectral data of [Os(RaaiH)₂Cl₂] in CDCl₃.

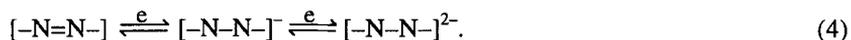
| Compound | δ, ppm (J, Hz) | 4-(4'-)H ^a | 5-(5'-)H ^a | 7-(7'-)H ^a | 8,10-(8';10'-)H | 11-(11'-)H ^a | N(1)-H ^b | 9-R |
|--|----------------|-----------------------|-----------------------|-------------------------|-----------------|-------------------------|---------------------|-----|
| <i>cis</i> -Os(HaaiH) ₂ Cl ₂ | 6.64 (7.0) | 6.28 (7.0) | 7.38 (8.0) | 7.32 ^c | 7.44 (8.0) | 13.33 | | |
| <i>cis</i> -Os(<i>p</i> -MeaaiH) ₂ Cl ₂ | 6.62 (6.5) | 6.30 (6.5) | 7.34 (8.0) | 7.25 ^a (8.0) | 7.41 (8.0) | 13.35 | 2.32 | |
| <i>cis</i> -Os(<i>p</i> -OMeaaiH) ₂ Cl ₂ | 6.60 (6.5) | 6.24 (6.5) | 7.30 (8.0) | 6.88 (8.0) | 7.37 (8.0) | 13.30 | 3.64 | |
| <i>cis</i> -Os(<i>p</i> -ClaaiH) ₂ Cl ₂ | 6.66 (6.0) | 6.29 (6.0) | 7.43 (8.0) | 7.38 (8.0) | 7.50 (8.0) | 13.37 | | |
| <i>cis</i> -Os(<i>p</i> -NO ₂ aaiH) ₂ Cl ₂ | 6.72 (6.5) | 6.34 (6.5) | 7.54 (8.0) | 7.67 (8.0) | 7.61 (8.0) | 13.35 | | |
| <i>ccc</i> -Os(HaaiH) ₂ Cl ₂ | 6.46 (6.0) | 6.14 (6.0) | 7.30 (8.0) | 7.10 ^c | 7.44 (8.0) | 13.38 | | |
| <i>ccc</i> -Os(<i>p</i> -MeaaiH) ₂ Cl ₂ | 6.42 (7.0) | 6.11 (7.0) | 7.18 (8.0) | 7.00 (8.0) | 7.34 (8.0) | 13.39 | 2.25, 2.48 | |
| <i>ccc</i> -Os(<i>p</i> -OMeaaiH) ₂ Cl ₂ | 6.49 (6.5) | 6.14 (6.5) | 7.14 (8.0) | 6.77 (8.0) | 7.30 (8.0) | 13.35 | 3.56, 3.77 | |
| <i>ccc</i> -Os(<i>p</i> -ClaaiH) ₂ Cl ₂ | 6.47 (6.0) | 6.08 (6.0) | 7.24 (8.0) | 7.18 (8.0) | 7.42 (8.0) | 13.41 | | |
| <i>ccc</i> -Os(<i>p</i> -NO ₂ aaiH) ₂ Cl ₂ | 6.58 (6.5) | 6.21 (6.5) | 7.40 (8.0) | 7.58 (8.0) | 7.56 (8.0) | 13.40 | | |

^aDoublet; ^bbroad; ^cmultiplet



The one-electron behaviour of the couple is defined by current height measurement along with a quasireversible response ($\Delta E = 160\text{--}220$ mV) at high potential site, $E_{\text{pa}} \geq 1.40$ V for the couple (3). The data reveal that the *ccc*-Os(RaaiH)₂Cl₂ exhibits Os^{III/II} couple at higher values by 0.1–0.2 V than that of *ctc*-isomer. In conjunction with spectral data (*vide supra*) it may be concluded that in *ccc*-isomer two *cis*-oriented azo functions may perform better back-bonding interaction with two different *dπ*-orbitals compared to *trans*-azo configuration in *ctc*-isomer.

Osmium(III)/(II) redox potential of the present examples is less than that of analogues arylazopyridine complexes. This is corroborated with the π -acidity order of the ligands, azoimidazole < azopyridine. In the potential range 0.0–1.5 V reductive responses are observed under similar conditions using glassy-carbon electrode.



The reduced species appears to be less stable, and on scan reversal, multiple anodic responses are observed. The reduction is referred to electron accommodation in the LUMO of RaaiH dominated by azo function. The potential movement follows the usual successive substituent effects.

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