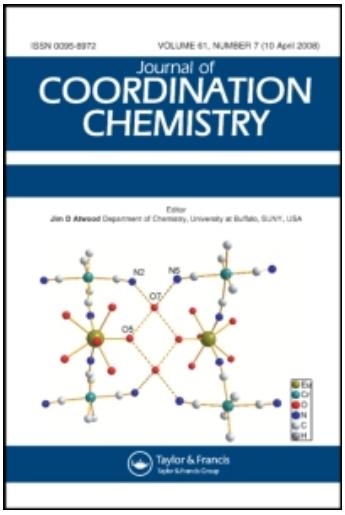

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Synthesis, Spectroscopic and Electrochemical Studies of Isomeric Dichloro-bis-[N (1)-Alkyl-2-(Arylazo)Imidazole]-Osmium(II). Single Crystal X-ray Structures of Blue-Violet Dichloro-Bis-[N (1)-Methyl-2-(Arylazo)Imidazole]-Osmium(II) Species

P. Byabartta[a]; S. Pal[a]; T. K. Misra[a]; C. Sinha[a]; F. -L. Liao[b]; K. Panneerselvam[c]; T. -H. Lu[c]
[a] Department of Chemistry, The University of Burdwan, Burdwan, India [b] Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan [c] Department of Physics, National Tsing Hua University, Hsinchu, Taiwan

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SYNTHESIS, SPECTROSCOPIC AND ELECTROCHEMICAL STUDIES OF ISOMERIC DICHLORO-BIS-[*N*(1)-ALKYL-2-(ARYLAZO)IMIDAZOLE]-OSMIUM(II). SINGLE CRYSTAL X-RAY STRUCTURES OF BLUE-VIOLET DICHLORO-BIS-[*N*(1)-METHYL-2-(ARYLAZO)IMIDAZOLE]-OSMIUM(II) SPECIES

P. BYABARTTA[a], S. PAL[a], T.K. MISRA[a], C. SINHA,[a,*] F.-L. LIAO[b], K. PANNEERSELVAM[c] and T.-H. LU[c]

[a]*Department of Chemistry, The University of Burdwan, Burdwan 713 104, India;* [b]*Department of Chemistry and* [c]*Department of Physics, National Tsing Hua University, Hsinchu, Taiwan*

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1-Alkyl-2-(arylazo)imidazoles (*p*-R-C_6H_4-N=N-$C_3H_2N_2X$, abbreviated as RaaiX, R = H(**a**), CH_3(**b**), Cl(**c**); X = N(1)-CH_3 (**1**), N(1)-CH_2-C_6H_5 (**2**)) have been reacted with $(NH_4)_2[OsCl_6]$ and $OsCl_2(RaaiX)_2$ species isolated in two isomeric forms, blue–violet (**3**, **5**) and red–violet (**4**, **6**). IR spectra show two ν(Os-Cl) modes and support a *cis*-$OsCl_2$ configuration. X-ray diffraction methods were used to determine structures of blue–violet isomers. In terms of the three coordination pairs around Os(II), Cl, Cl, N, N (N(imidazole), N) and N′, N′ (N(azo), N′) the blue–violet isomers have a *cis-trans-cis* (*ctc*) configuration.

^{1}H NMR data for the red-violet complexes (isomers B) and results concerning analogous ruthenium(II) complexes indicate isomer B to have *cis-cis-cis* (*ccc*) configuration. Absorption spectra show an intense MLCT band at *ca* 580 nm along with two weak bands at 800 and 1000 nm. Cyclic voltammetry shows *quasi*-reversible Os(III)/Os(II) and Os(IV)/Os(III) couples at 0.4–0.6 V and 1.3–1.5 V *versus* SCE and ill-defined azo reductions. The X-Ray structures show unusually long N=N bond lengths, 1.31–1.32 Å, elongated by some 0.06 Å compared to the free ligand value. Os(II) prefers to bind N(azo) (Os-N(azo), 1.98 Å) rather than N(imidazole) (Os-N(imidazole), 2.03 Å). EHMO calculations of *ctc*-$OsCl_2$(MeaaiMe) and comparison with the ruthenium(II) complex account for the MLCT transitions in terms of a metal-dominated HOMO to a ligand-dominated LUMO shift.

*Corresponding author.

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Keywords: Arylazoimidazoles; Osmium(II) complexes; Geometrical isomers; X-ray structure; Redox; MLCT transitions

INTRODUCTION

Imidazole is a ubiquitous ligand in chemical and biological systems [1]. The coupling reaction of imidazole with aryldiazonium ion gives 2-(arylazo) imidazole [2]. The molecule bears the azoimine function, -N=N-C=N-, which is π-acidic and stabilizes low valent metal redox states [2,3]. The exo-bidentate character of the imidazole moiety is eliminated by N(1)-alkylation and the ligand becomes an *N*,*N*′- chelating ligand (RaaiX) [2,3]. The high affinity of the azoimidazole ligand system for ruthenium(II) is manifested by the isolation of dichlorobis-[*N*(1)-alkyl-2(arylazo)imidazole]ruthenium(II) complexes [3]. *Pseudo*-octahedral $MCl_2(RaaiX)_2$ may exist, in principle, in five isomeric forms [3,4–7]. In $RuCl_2(RaaiX)_2$ four isomeric forms were characterized [4] and assigned on the basis of coordination pairs in the order of Cl, N(imiazole), N(azo) as *trans-cis-cis*, *cis-trans-cis*, *cis-cis-trans* and *cis-cis-cis*. The structure of the *trans-cis-cis* and *cis-trans-cis* isomers of ruthenium(II) complexes are accurately known from three-dimensional X-ray work [3]. Progress in the ruthenium chemistry of RaaiX has encouraged us to explore corresponding osmium chemistry [7]. In this report we describe the synthesis, spectra, redox properties of the osmium(II) complexes, $OsCl_2(RaaiX)_2$. The structure of one of the isomer, *cis-trans-cis*, was established by an X-ray diffraction study.

EXPERIMENTAL

Materials

2-Arylazoimidazoles and their *N*(1)-alkylated derivatives were synthesised as before [2,3]. Osmium tetroxide was obtained from Johnson Matthey & Co. Ltd., UK, and was converted to $(NH_4)_2[OsCl_6]$ according to a reported method [8]. Solvent purification and reagent synthesis for electrochemical works was performed as before [3]. Commercially available silica gel (60–120 mesh) from SRL was used for chromatographic separations. All other solvents and chemicals were of reagent grade and were used without further purification.

Physical Measurements

Microanalytical data (C,H,N) were collected using a Perkin Elmer 2400 CHN instrument. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. Infrared (IR) spectra were obtained using a JASCO 420 spectrophotometer (KBr disks, 4000–200 cm^{-1}); ^1H NMR spectra were recorded for $CDCl_3$ solutions using a Brucker 300 MHz FT NMR spectrometer. Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration $\sim 10^{-3}$ M in nitromethane. Electrochemical measurements were carried out under dinitrogen with the help of an EG&G PARC 270 computer controlled Versastat using a Pt-disk milli working electrode. All results were collected at 298 K with saturated calomel electrode (SCE) as reference. Reported potentials are uncorrected for junction effects.

Preparation of *ctc*- and *ccc*-dichloro-bis-[N(1)-methyl-2-(phenylazo)-imidazole]osmium(II), $OsCl_2(HaaiMe)_2$

Nitrogen gas was passed for 15 min through a brown–red solution of $(NH_4)_2[OsCl_6]$ (0.5 g, 1.14 mmol) in 2-methoxyethanol (50 cm^3). The solution was refluxed on an oil-bath with continuous stirring for half an hour. *N*(1)-Methyl-2-(phenylazo)imidazole(HaaiMe) (0.423 g, 2.28 mmol) was added in small portions to this refluxing solution over another half an hour. The mixture was refluxed under nitrogen for 8 h. During this period the solution turned brown–violet to blue–violet. This was concentrated slowly by bubbling N_2 gas through the hot mixture to about 20 cm^3 and kept in the refrigerator for 12 h. The shining, dark coloured crystalline precipitate was collected by filtration and washed with ethanol–water (1 : 1, v/v) and 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 × 1 cm). A small orange–yellow band was eluted with benzene and rejected. A blue–violet band was eluted with MeCN–C_6H_6 (1 : 4, v/v) and a red–violet band was eluted with 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 P_4O_{10}. The yields were of blue–violet, *ctc*-$OsCl_2(HaaiMe)_2$ 40% and red–violet *ccc*-$OsCl_2(HaaiMe)_2$ 12%.

All other complexes were prepared by following identical procedures and yields were 30–50% for the blue–violet isomers and 10–15% for the red–violet isomers. Satisfactory analyses were obtained.

X-ray Crystal Structure Analysis

Crystals suitable for X-ray diffraction study of dichloro-bis[*N*(1)-methyl-2-(phenylazo)imidazole]osmium(II) ($OsCl_2(HaaiMe)_2$, **3a**, and dichloro-bis[*N*(1)-methyl-2-(*p*-tolylazo)imidazole]osmium(II) ($OsCl_2(MeaaiMe)_2$, **3b**, were grown by slow diffusion of hexane into a CH_2Cl_2 solution at room temperature. The crystal sizes were $1.0 \times 0.5 \times 0.2$ mm and $0.3 \times 0.3 \times 0.1$ mm for **3a** and **3b**, respectively. X-Ray diffraction data were collected at 293(2) K with a Siemens SMART CCD using graphite-monochromatized M_oK_α radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined from least-squares refinement of setting angles with 2θ in the range 4–56°. A summary of crystallographic data and structure refinement parameters are given in Table I of 14380 collected reflections, 5492 unique reflection for **3a**, and of 15218 collected reflections, 5716 unique reflection for **3b**, were recorded using the ω-scan technique. Data were corrected for L_p effects and for time decay. Semi-empirical absorption corrections based on ψ-scans were applied [9]. The structure was solved by heavy atom methods using SHELX-97 [10] and successive difference Fourier syntheses. All non-hydrogen

TABLE I Crystallographic data for **3a** and **3b**

	*$OsCl_2(HaaiMe)_2$ (**3a**)*	*$OsCl_2(MeaaiMe)_2$ (**3b**)*
Formula	$C_{20}H_{20}Cl_2N_8Os$	$C_{22}H_{24}Cl_2N_8Os$
Formula weight	633.54	661.59
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	9.520 (2)	9.5528 (4)
b/Å	22.017 (4)	22.7681 (10)
c/Å	11.226 (2)	11.6623 (50)
β/°	102.960 (3)	99.8330 (10)
Volume/Å^3	2293.0 (7)	2499.28 (19)
Z	4	4
ρ_{calc}/mg cm^{-3}	1.835	1.758
2θ range/deg	4–56	4–56
Index range	$-11 \le h \le 21$, $-12 \le k \le 29$, $-14 \le l \le 12$	$-12 \le h \le 6$, $-27 \le k \le 29$, $-14 \le l \le 14$
$\mu(M_oK_\alpha)$/mm^{-1}	5.819	5.342
Parameters refined	282	302
R[a], %	4.41	2.32
wR[b], %	11.30	4.67
Goodness-of-fit[c]	1.015	
Largest diff. peak and hole/eÅ^{-3}	4.676 and −2.632	0.873 and −0.663

[a] $R = \sum|F_0 - F_c|/\sum F_0$; [b] $wR = [\sum w(F_0^2 - F_c^2)/\sum wF_0^4]^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (0.0473P)^2 + 14.3394P]$, $P = (F_0^2 + 2F_c^2)/3$; [c] GOF defined as $[w(F_0 - F_c)/(n_0 - n_v)]^{1/2}$ where n_0 and n_v denote the numbers of data and variables, respectively.

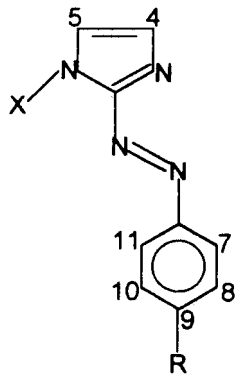
atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using a riding model. In the final difference Fourier maps the residual maximum and minimum were 4.676 and $-2.632\,e\text{Å}^{-3}$ for **3a** and 0.873 and $-0.663\,e\text{Å}^{-3}$ for **3b**, respectively. All calculations were carried out using SHELX-97 [11].

RESULTS AND DISCUSSION

Synthesis and Isomer Characterisation

N(1)-Alkyl-2-(arylazo)imidazoles, *p*-R-$C_6H_4N=N$-$C_3H_2N_2X$ (RaaiX), (R = H (**a**), CH_3 (**b**), Cl(**c**) and X = N(1)-CH_3(**1**), N(1)-CH_2-C_6H_5(**2**)) react with $(NH_4)_2[OsCl_6]$ in 2-methoxyethanol under reflux and upon concentrating dark-coloured crystals of composition $OsCl_2(RaaiX)_2$ are isolated (1). The product was purified by chromatographic separation on silica gel; a mixture of 3 : 1 and 1 : 1 benzene–acetonitrile separated a blue–violet (isomer A, 50–60%) and red–violet (isomer B, 10–15%) complex, respectively.

$$OsCl_6 = +2RaaiX \rightarrow OsCl_2(RaaiX)_2 + 4Cl^- . \quad (1)$$



RaaiX

X = CH_3 (**1**), $CH_2C_6H_5$ (**2**)

R = H (**a**), Me (**b**), Cl (**c**)

The reduction of osmium from the +4 to the +2 state in (1) is probably brought about by the alcohol solvent [5]. Even when RaaiX is used in excess

of 2 mol only $OsCl_2(RaaiX)_2$ is isolated from reaction (1); no $Os(RaaiX)_3^{2+}$ or polynuclear complex is formed. Microanalytical data support the composition of the blue–violet complexes $OsCl_2(RaaiMe)_2$ (**3**), $OsCl_2(RaaiCH_2Ph)_2$ (**5**), and red–violet complexes $OsCl_2(RaaiMe)_2$ (**4**), $OsCl_2(RaaiCH_2Ph)_2$ (**6**). All complexes are diamagnetic in the crystalline state and are non-electrolytes in nitromethane and acetonitrile. Isomers are soluble in common organic solvents (C_6H_6, CH_2Cl_2, $CHCl_3$, CH_3CN, etc.) to give blue–violet and red–violet solutions.

Spectroscopic Studies

IR spectra of the isomers differ significantly in the region 4000–200 cm^{-1}. The endocyclic ν(C=N) band appears at 1520–1560 cm^{-1} and is also red shifted by 40–80 cm^{-1} from that of free ligand. The ν(N=N) mode in the complexes appears at 1230–1260 cm^{-1} and is red shifted by 150–170 cm^{-1} from that of free ligand values [3,12]. This supports azo-N coordination and low values are in full agreement with the Os-N(azo) π-bonding scheme. The N=N frequencies in osmium complexes are systematically lower (by 40–60 cm^{-1}) than those of the ruthenium analogues. This accounts for the relative order in $t_2 \rightarrow \pi^*$ donation as Os > Ru and is supported by bond distance data (see below). The spectra exhibit two medium intense bands at 300–310 and 320–330 cm^{-1} corresponding to two Os–Cl bonds. This supports the *cis*-$OsCl_2$ configuration in the complexes. Vibration spectra of isomer A of $OsCl_2(MeaaiMe)_2$ and *ctc*-$RuCl_2(MeaaiMe)_2$ are nearly superimposable in the above region [3] except for frequency shifting of N=N and C=N bands to lower frequency. Isomer B holds a similar relationship with spectra of *ccc*-$RuCl_2(MeaaiMe)_2$. These observations suggest that isomer A (blue–violet) has the *cis-trans-cis* (*ctc*, **3/5**) and isomer B (red–violet) the *cis-cis-cis* (*ccc*, **4/6**) configuration.

Solution electronic spectra of the complexes exhibit multiple bands and shoulders in the region 220–1100 nm in dichloromethane solution (Table II, Fig. 1). The absorptions < 400 nm are due to intraligand charge transfer and are not considered further. Major absorption at 500–600, 780–850 and 1070–1100 nm are assigned to $t_2 \rightarrow \pi^*$ charge transfer transitions where the π^* level has largely azo character. Blue–violet solutions of the *ctc* complexes have an intense band ($\varepsilon \sim 10^4\ M^{-1}cm^{-1}$) at *ca* 525 nm with a shoulder near 575 nm. In the *ccc* isomer the band is blue shifted to 515 nm and is accompanied by a shoulder at *ca* 585 nm. Bands in the 780–850 and 1040–1100 nm regions are weak ($\varepsilon \sim 10^3\ M^{-1}cm^{-1}$) and are

TABLE II Electronic spectroscopic and cyclic voltammetric[b] data for the complexes

Complexes	*Electronic spectra*	ν^{c}_{MLCT}	O_s^{III}/O_s^{II}	O_s^{IV}/O_s^{III}	*Ligand reduction*		$\Delta E^{d}_{1/2}$, V
	λ_{max} ($10^{-3}\varepsilon$, $M^{-1}cm^{-1}$)	*ev*	$E^{1}_{1/2}$,V (ΔE_p, mV)	$E^{2}_{1/2}$,V (ΔE_p, mV)	$-E^{3}_{1/2}$,V (ΔE_p, mV)	$-E^{4}_{1/2}$,V (ΔE_p, mV)	
3a	1044 (1.027)[c], 824 (0.952)[c], 579 (6.986)[c], 519 (10.856), 407 (7.905), 373 (10.509)	2.391	0.450 (70)	1.378 (160)	1.115 (170)	1.678 (230)	1.565
4a	1035 (0.834)[c], 813 (0.978)[c], 570 (6.732), 515 (8.402), 402 (6.342), 370 (9.842)	2.410	0.488 (90)	1.415 (100)	1.029 (160)	1.553 (240)	1.517
3b	1040 (0.980)[c], 815 (0.920)[c], 585 (7.307)[c], 519 (11.52), 425 (12.681), 373 (20.158)	2.391	0.433 (80)	1.349 (140)	1.149 (150)	1.713 (240)	1.582
4b	1030 (0.982)[c], 810 (0.837)[c], 565 (6.964)[c], 510 (8.394), 418 (10.343), 370 (19.941)	2.433	0.474 (100)	1.403 (160)	1.125 (160)	1.663 (210)	1.599
3c	1058 (1.235)[c], 815 (1.113)[c], 588 (9.857)[c], 524 (14.876), 416 (16.333), 370 (25.799)	2.368	0.470 (100)	1.399 (130)	1.025 (130)	1.484 (230)	1.495
4c	1054 (0.983)[c], 806 (1.002)[c], 586 (13.396)[c], 518 (21.523), 420 (38.000), 375 (24.955)	2.396	0.499 (105)	1.450 (120)	1.000 (130)	1.328 (220)	1.499
5a	1046 (1.848)[c], 814 (1.384)[c], 574 (10.757)[c], 515 (17.196), 400 (12.848), 360 (23.707)	2.410	0.534 (80)	1.410 (130)	0.986 (120)	1.532 (230)	1.520
6a	1040 (1.633)[c], 810 (1.124)[c], 568 (9.548)[c], 513 (12.334), 396 (11.346), 360 (20.094)	2.419	0.570 (70)	1.465 (140)	0.951 (130)	1.408 (210)	1.521
5b	1016 (0.874)[c], 750 (1.510)[c], 582 (5.814), 521 (7.261), 415 (9.758), 374 (12.860)	2.382	0.498 (70)	1.370 (160)	1.049 (160)	1.614 (260)	1.547
6b	1008 (0.733)[c], 745 (1.482)[c], 560 (2.580)[c], 512 (3.304), 419 (5.404), 378 (6.298)	2.424	0.544 (70)	1.416 (120)	1.009 (140)	1.481 (210)	1.553
5c	1170 (0.817)[c], 862 (1.136)[c], 592 (2.394)[c], 524 (3.936), 370 (6.159)	2.368	0.562 (70)	1.456 (150)	0.943 (130)	1.444 (220)	1.505
6c	1125 (0.434)[c], 795 (1.056)[c], 587 (3.875), 518 (7.105), 423 (9.078), 380 (12.914)	2.396	0.598 (80)	1.495 (140)	0.908 (160)	1.372 (240)	1.506

[a]Solvent: CH_2Cl_2. [b]Solvent is MeCN, supporting electrolyte Bu_4NClO_4 (0.1 M), solute concentration $\sim 10^{-3}$ M, scan rate 50 mV s^{-1}, Pt-disk working electrode, measuring and units of symbols are the same as in text. [c]$\nu_{MLCT} = 1241/\lambda_{MLCT,nm}$. [d]$\Delta E_{1/2} = E^{1}_{1/2} - E^{3}_{1/2}$ where $E^{1}_{1/2}$ refers to the Os(III)/Os(II) couple and $E^{3}_{1/2}$ refers to the first ligand reduction.

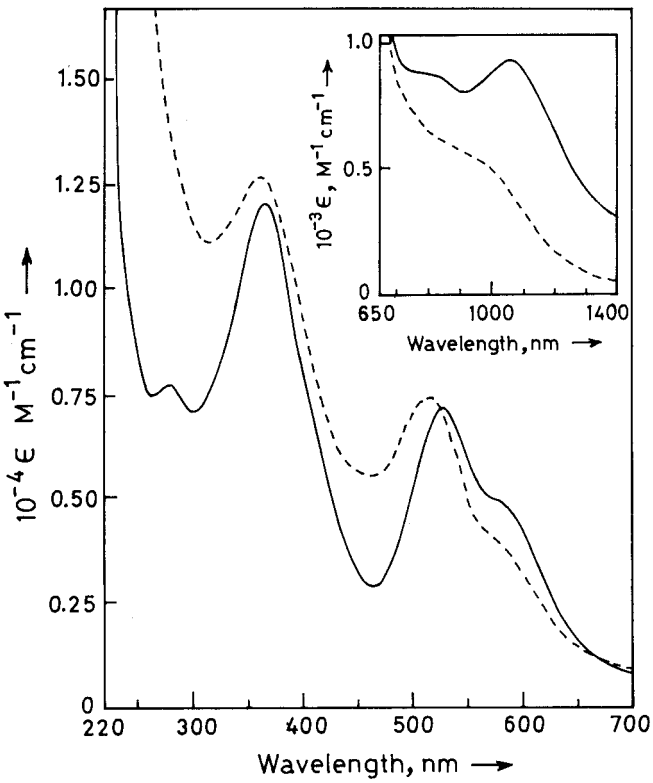


FIGURE 1 Electronic spectra of (a) *ctc*-$OsCl_2(ClaaiMe)_2$ (——) and (b) *ccc*-$OsCl_2(ClaaiMe)_2$ (-----) in CH_2Cl_2.

systematically shifted to higher energy region on going from *ctc* to *ccc* isomers. In d^6-metal complexes, multiple $t_2(Os) \rightarrow \pi^*$ charge-transfer transitions [5,13,14] can arise from low symmetry splitting of the metal level, due to the presence of more than one interacting ligand (each contributing one π^* 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 RaaiX it is observed that the transitions are blue shifted by 30–40 nm from those of analogous ruthenium complexes. This supports the notion that the t_2 orbital is more deep seated in Os than Ru. The spectroscopic behaviour is comparable with osmium(II) complexes of arylazopyridines [5,13] and absorption positions are red shifted by 10–20 nm is $OsCl_2(RaaiX)_2$. This is in agreement with the π-acidity order arylazopyridine > arylazoimidazole [5,15].

^{1}H NMR spectra of the complexes were measured for $CDCl_3$ solutions at 296 K and examined to determine isomer structures. The signals are assigned on the basis of spin–spin interaction and the effect on substitution. Data are summarised in Table III, Ar-*Me* and N(1)-*Me* or N(1)-$CH_2(C_6H_5)$ signals have been particularly useful to determine stereochemistry of isomers. The N(1)-*Me* signal appears as a singlet in isomer A, $OsCl_2(RaaiMe)_2$ (**3**) complexes at *ca* 4.1 ppm while isomer B(**4**) shows two signals of equal intensity at *ca* 4.1 and 4.2 ppm. In $OsCl_2(RaaiCH_2C_6H_5)_2$ the -C*H*$_2$- in N(1)-C*H*$_2$(C_6H_5) appears as AB quartets at 5.3 and 5.7 ppm in isomer A (**5**) and 5.3–5.5 and 5.7–5.8 ppm in isomer B (**6**) (Fig. 2). Geminal coupling constants are 14 and 24 Hz for isomers A and B, respectively. Isomer A, $OsCl_2(RaaiX)_2$ (**3**, **5**) shows a singlet for 9-*Me* at *ca* 2.3 ppm while isomer B(**4**, **6**) exhibits two signals of equal intensity of *ca* 2.1 and 2.3 ppm. The X-ray structure of isomer A (Fig. 3) and ^{1}H NMR data support the *cis-trans-cis* (*ctc*) geometry. Isomer B, $OsCl_2(RaaiX)_2$ (**4/6**) may exist as either the *cct* or *ccc* isomer. The *cct* isomer has C_2 symmetry and *ccc* isomer has C_1 symmetry. The presence of two equal intense 9-*Me*, N(1)-*Me* signals and pair of AB type quartets for N-C*H*$_2$(C_6H_5) signals identifies the *ccc*-isomer. This is also in support of similar work ruthenium(II) [3,6] and osmium(II) [13] complexes. Aryl-*H*(7-*H*-11-*H*) signals are assigned on the basis of effect of substituent; the -Me substituent (**b**) shifts 8,10-*H* signals upfield while -Cl (**c**) shifts the same downfield relative to phenyl-*H* (**a**) signals [2]. A significant difference between the NMR

TABLE III ^{1}H NMR data for the complexes

Compd	*4-H*[a]	*5-H*[a]	*7,11-H*[b]	*8,10-H*	*9-H*[c]	*N(1)-CH$_3$*	*N(1)-CH$_2$*[d]	*9-CH$_3$*	*13–17-H*[c]
3a	7.49	7.40	7.11	6.66[c]	7.06	4.11			
4a	7.53	7.42	7.16	6.70[c]	7.10	4.08, 4.18			
3b	7.69	7.42	6.87	6.59[b]		4.09		2.25	
4b	7.52	7.38	6.93	6.63[b]		4.10, 4.17		2.13, 2.29	
3c	7.57	7.48	7.09	6.71[b]		4.14			
4c	7.56	7.45	7.20	6.80[b]		4.11, 4.18			
5a	7.55	7.38	7.14	6.73[c]	7.13		5.26, 5.74		7.30–7.45
6a	7.55	7.40	7.21	6.78[c]	6.74		5.38, 5.46		7.35–7.50
							5.72, 5.80		
5b	7.60	7.42	6.80	6.55[b]			5.30, 5.71	2.28	7.10–7.50
6b	7.60	7.42	6.87	6.66[b]			5.36, 5.45	2.24	7.40–7.50
							5.80, 5.89	2.33	
5c	7.63	7.43	6.95	6.58[b]			5.33, 5.71		7.40–7.50
6c	7.58	7.41	7.00	6.65[b]			5.40, 5.45		7.40–7.50
							5.77, 5.82		

[a]Doublet, J = 4.0–5.0 Hz. [b]Doublet, J = 8.0–9.0 Hz. [c]Triplet, J = 8.0–9.0 Hz. [d]AB type quartet, J = 14.0 Hz (**5**) and 24.0 Hz (**6**). [e]Phenyl protons.

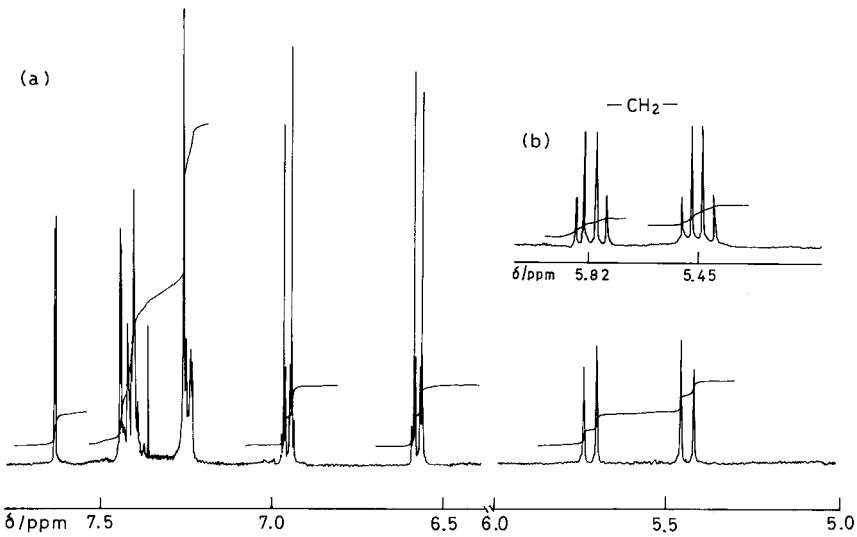


FIGURE 2 ^{1}H NMR spectra of (a) *ctc*-$OsCl_2(ClaaiCH_2C_6H_5)_2$ and (b) -CH_2-(C_6H_5) part of *ccc*-$OsCl_2(ClaaiCH_2C_6H_5)_2$ in $CDCl_3$ at 298 K.

spectra of the osmium(II) complexes with those of ruthenium(II), palladium(II) complexes is that the aryl-*H*(7-*H*-11-*H*) signals in the present complexes are shifted upfield by > 1.00 ppm and downfield shifting is observed for imidazole 4- and 5-*H*. This may be due to the stronger π-back bonding of the azo function with osmium d-orbitals compared to ruthenium and palladium in their complexes. Because of the relativistic effect, 5d orbitals in Os(II) are perturbed more effectively than 4d orbitals [16] of isoelectronic Ru(II) complexes by the π^*(azo) orbitals. This leads to increase in electron density in azoaryl rings and is manifested by upfield shifting or aryl-*H*(7-*H*-11-*H*) signals and consequently opposite effects for imidazole 4- and 5-*H* signals.

Structure of Blue–violet $OsCl_2(HaaiMe)_2$ (3a) and $OsCl_2(MeaaiMe)_2$ (3b)

X-ray quality crystals of $OsCl_2(HaaaiMe)_2$ (**3a**) and $OsCl_2(MeaaiMe)_2$ (**3b**) were grown by slow diffusion of dichloromethane solution into hexane. A view of the molecular structures are given in Fig. 3. The coordination sphere around osmium is approximately octahedral, and the atomic arrangement indeed corresponds to *cis-trans-cis* configuration (C_2 symmetry). Selected bond parameters are listed in Table IV.

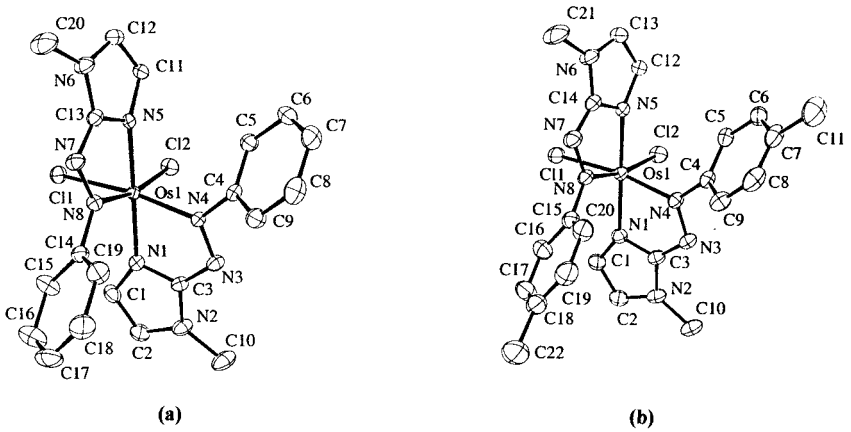


FIGURE 3 ORTEP plot and atom-labelling scheme for (a) *ctc*-$OsCl_2(HaaiMe)_2$ and (b) *ctc*-$OsCl_2(HaaiMe)_2$.

TABLE IV Selected bond distances (Å) and angles (°) for complexes **3a** and **3b**, along with their estimated standard deviations

	Distances			*Angles*	
	3a	**3b**		**3a**	**3b**
Os-N(1)	2.024 (5)	2.033 (3)	N(1)-Os-N(4)	79.2 (2)	76.5 (1)
Os-N(4)	1.986 (4)	1.972 (2)	N(5)-Os-N(8)	76.4 (2)	76.2 (1)
Os-N(5)	2.028 (5)	2.041 (2)	N(1)-Os-Cl(1)	94.7 (1)	92.8 (1)
Os-N(8)	1.979 (4)	1.974 (2)	N(1)-Os-Cl(2)	88.4 (1)	88.5 (1)
Os-Cl(1)	2.382 (1)	2.3876 (8)	N(5)-Os-Cl(1)	85.5 (1)	88.4 (1)
Os-Cl(2)	2.394 (1)	2.3980 (8)	N(5)-Os-Cl(2)	93.7 (1)	93.3 (1)
N(3)-N(4)	1.306 (6)	1.323 (3)	N(4)-Os-N(5)	104.0 (2)	102.3 (1)
N(7)-N(8)	1.316 (6)	1.319 (3)	N(3)-N(4)-Os	122.0 (4)	121.2 (2)
			N(4)-Os-Cl(1)	170.5 (1)	169.3 (1)
			N(4)-Os-Cl(2)	90.3 (1)	90.0 (1)
			N(1)-Os-N(5)	177.9 (2)	177.8 (1)
			N(4)-Os-N(8)	96.5 (2)	95.4 (1)
			Cl(1)-Os-Cl(2)	88.0 (5)	89.1 (1)
			N(8)-Os-Cl(1)	86.7 (1)	87.3 (1)
			N(8)-Os-Cl(2)	169.1 (1)	169.0 (1)
			N(8)-Os-N(1)	101.5 (2)	102.1 (1)
			N(7)-N(8)-Os	121.2 (4)	121.2 (2)

The two atomic groups Os, Cl(1), N(1), N(4), N(5) and Os, Cl(2), N(5), N(8), N(1) separately constitute excellent planes (mean deviation < 0.04 Å) and are orthogonal. The planarity of the group Os, Cl(1), Cl(2), N(4), N(8) is not good (deviation ~ 0.16 Å) and deviation of N(4) and N(8) from the best plane is ~ 0.19 Å. Distortion from octahedral

geometry is certainly due to the acute chelate bite angle ($\sim 76^\circ$), whereas the imidazole nitrogen occupy nearly ideal axial positions (N(1)-Os-N(5), 178°). Each chelate ring is planar with no atom deviating by more than 0.08 Å. The dihedral angle between the chelate ring and the corresponding pendant aryl ring is in the range 53–65°.

Os-N distances are different for imidazole-N (Os-N(1)/N(5)) and azo-N (Os-N(4)/N(8)). Os-N(imidazole) bond lengths are longer than Os-N(azo) bonds by 0.03–0.04 Å (Table IV). N=N distances are 1.31–1.32 Å, longer by 0.06 Å compared to the free ligand value (1.26 Å) [8,13]. Coordination can lead to a decrease in the N-N bond order due to both σ-donor and π-acceptor characters of the ligand, the later having a more pronounced effect [17]. The elongation in the N-N distance in these complexes is thus an indication of the existence of considerable Os-RaaiX π-bonding with major involvement of the azo group.

A comparison of bond distances between ruthenium(II) [3] and osmium(II) (Fig. 4) complexes reveals that the N-N distance is elongated by only 0.01–0.02 Å in the latter complexes and the C-N distances vary only slightly. The systematic shortening of the M-N(azo) distance compared to the M-N(imidazole) distance in ruthenium [3] and osmium complexes of the ligand is a further indication of the presence of stronger M-azo π-bonding. The π-interaction follows the order Os > Ru as is evident from the shortening of the Os-N (azo) bond length by 0.02 Å compared with that of the Ru complex.

Electrochemistry

The electrochemical properties of the complexes were examined by cyclic voltammetry at a platinum working electrode in acetonitrile (0.1 M

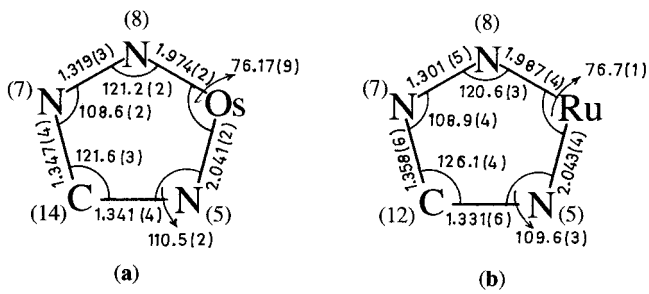


FIGURE 4 Dimensions of chelate rings with esd of (a) *ctc*-$OsCl_2(MeaaiMe)_2$ and (b) *ctc*-$RuCl_2(MeaaiMe)_2$.

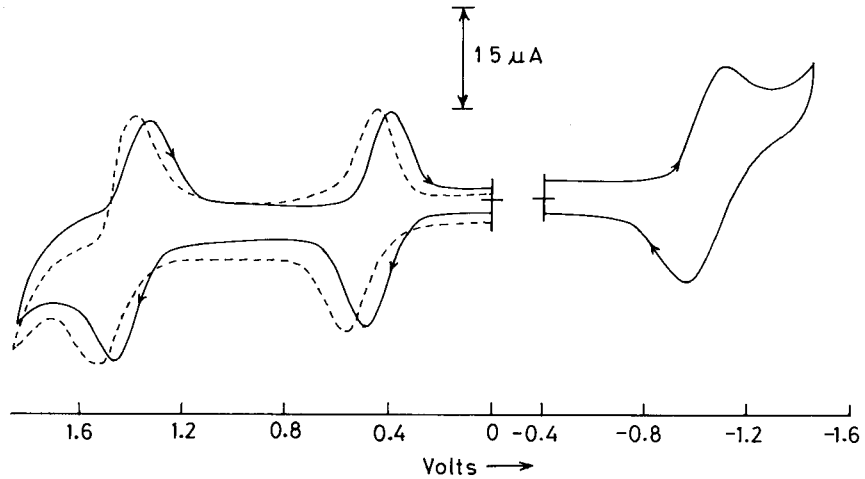


FIGURE 5 Cyclic voltammogram of *ctc*-$OsCl_2(ClaaiMe)_2$ (———) and *ccc*-$OsCl_2(ClaaiMe)_2$ (----) in MeCN using a Pt-disk milli electrode at 298 K, SCE reference and TBAP (0.1 M) supporting electrolyte.

TBAP). In the potential range +1.0 to +2.0 V two oxidation responses are observed (Table II, Fig. 5). The first at 0.40 to 0.60 V is referred to the osmium(III)–osmium(II) couple (2),

$$OsCl_2(RaaiX)_2^+ + e \rightleftharpoons OsCl_2(RaaiX)_2 \qquad (2)$$

and is nearly reversible with peak-to-peak separation of 60–70 mV. The current height ratio $i_{pa}/i_{pc} \sim 1.0$ refers to a one-electron oxidation couple. The second couple at 1.6 to 1.7 V is also a one-electron response (on the basis of current height) and is *quasi*-reversible in character ($\Delta E_p \geq 100$ mV). This is assigned to the osmium(IV)–osmium(III) couple (3).

$$OsCl_2(RaaiX)_2^{2+} + e \rightleftharpoons OsCl_2(RaaiX)_2^+ \qquad (3)$$

The negative side of the SCE shows three or four successive reduction responses. On scan reversal the corresponding anodic peak of the first response is observed at $\Delta E_p \sim 120$–170 mV and the second response appears at a separation of > 200 mV; other anodic peaks are ill-defined. These reductions are believed to successive electron addition to the two azoimine functions [3,5]. The substituent in the ligand frame perturbs both metal oxidation and ligand reduction potentials. The potential changes linearly with the Hammett constant σ of the substituent. A decrease in σ-donor capacity of the substituent increases both the Os(III)/Os(II) and the first

bound ligand reduction potentials [17]. The extent of perturbation is found to be more pronounced in the ligand reduction potential values, and this 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 ($\Delta E_{1/2} = E^1_{1/2} - \Delta E^3_{1/2}$) may be correlated with the MLCT transition energy ν_{CT} (Table II) and follows Eq. (4). A similar

$$\nu_{CT} = 0.304\ \Delta E_{1/2} + 1.932 \tag{4}$$

correlation has been observed for α-diimine [19] and azoimine [3,17–19] complexes of ruthenium(II).

Frontier Orbitals, Spectra, Redox Property of Osmium (II) Complexes and Comparison with Analogous Ruthenium(II) Complexes

In order to gain insight into the approximate composition of the frontier orbitals in osmium(II) complexes of arylazoimidazoles extended Hückel calculations were performed on a model complex of *ctc*-dichloro-bis-[1-methyl-2(*p*-tolylazo)imidazole]osmium(II). Similar calculations have also been carried out on the ruthenium(II) analogue so as to compare the physical properties with osmium(II) complexes. Crystallographic data were used [3] as the parameters for bond distances and angles. The HOMO and LUMO of the complexes are depicted in Fig. 6. In the osmium(II) complex the HOMO is constituted by metal d_{z^2} (22%) and d_{xy} (54%) orbitals where as the LUMO is constructed by 65% of ligand orbitals of which the azoimine function has contributed 42%. In the ruthenium(II) complex the HOMO is 70% metal d-orbital (18% d_{z^2}, 52% d_{xz}) and the LUMO is constructed by 74% ligand contribution (azoimine function shares 48%). The ruthenium HOMO lies ~ 0.07 eV above than the osmium HOMO and the LUMOs are closely spaced. This supports our proposition of π-interaction order Os > Ru.

Some experimental findings may be rationalized on the basis of EHMO results. The highest occupied HOMO and the lower orbitals, HOMO-1, HOMO-2 *etc*., are predominantly of metal character and LUMO, LUMO+1, LUMO+2 are basically of π^*-ligand character. Several charge transitions may be observed [13,20]. Cyclic voltammetry exhibits both oxidation and reduction couples and they correspond to metal oxidation and ligand reductions, respectively. The oxidation involves electron extraction from HOMO which is metal-d-orbital dominated and the reduction involves electron accommodation at LUMOs. Because of the strong Os-π^*(azo) interaction the reductions are *quasi*-reversible to irreversible in nature.

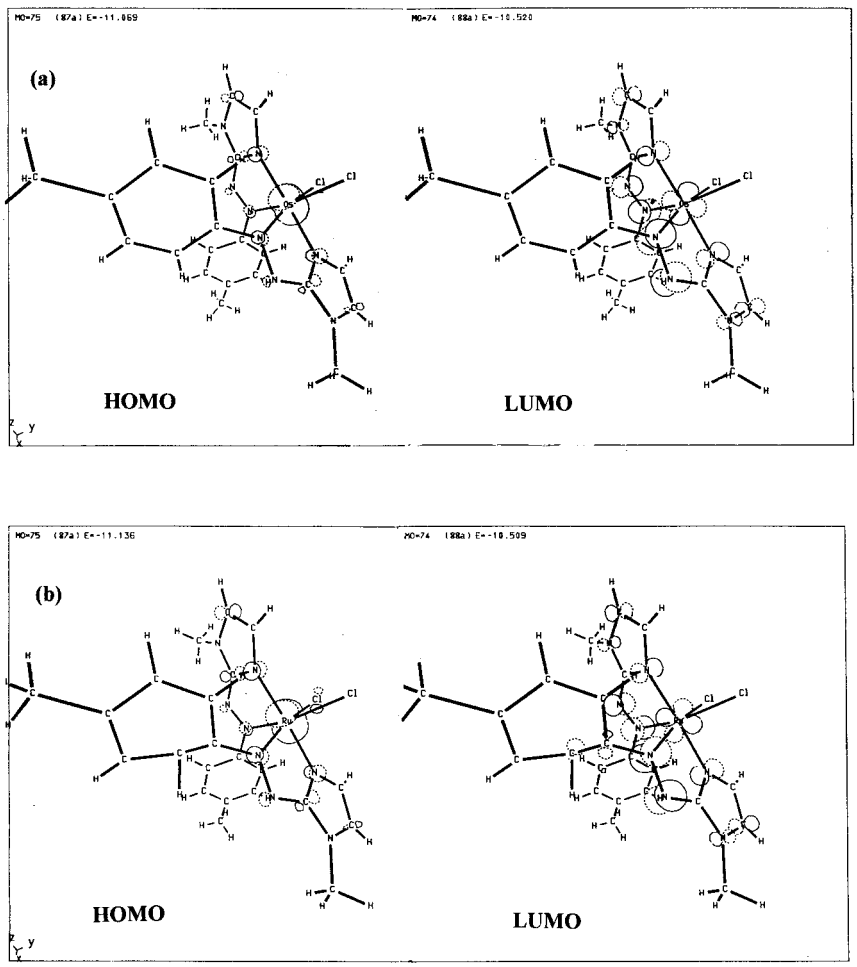


FIGURE 6 Frontier orbitals, HOMO and LUMO of (a) *ctc*-$OsCl_2(MeaaiMe)_2$ and (b) *ctc*-$RuCl_2(MeaaiMe)_2$.

The interaction is also supported by the elongation of the N=N bond compared to free ligand values. Ruthenium(II) and osmium(II) complexes are isoelectronic and isostructural. Solution spectra and redox property of these two series of *N*(1)-alkyl-2-(arylazo)imidazoles show two geometrical of five possible isomers in both cases. Two isomers in dichloro-bis[1-alkyl-2-(arylazo)imidazole]ruthenium(II) [$RuCl_2(RaaiX)_2$] exist in *trans-cis-cis* and *cis-trans-cis* forms while $OsCl_2(RaaiX)_2$ exists in *cis-trans-cis* and *cis-cis-cis* structures. Bond parameters in the chelate ring of osmium(II)

complexes differ significantly from that of ruthenium(II) analogues (Fig. 4). Solution electronic spectra show multiple transitions in the higher energy region for $OsCl_2(RaaiX)_2$ unlike the ruthenium(II) complexes (Table II). Cyclic voltammetric data suggest that osmium(II) system are more easily oxidisable than the ruthenium(II) complexes. The most significant difference is observed in the ^1H NMR spectra of the complexes. The comparison of *ctc*-isomers shows that aryl-H (7-H-11-H) and imidazole-H (4- and 5-H) have significantly altered chemical shift data in $OsCl_2(RaaiX)_2$ with respect to $RuCl_2(RaaiX)_2$ [3]. In the present examples, aryl-H signals have been shifted to upfield and imidazole-H (4 and 5-H) downfield compared with analogous ruthenium(II) complexes. Aryl-H signals are shifted by > 1.00 ppm upfield side in osmium(II) complexes. The difference in these properties may be explained by comparing the mean light-atom bond parameters in the chelate rings of the *ctc*-isomer of $OsCl_2(MeaaiMe)_2$ and $RuCl_2(MeaaiMe)_2$ as in Fig. 4. The Os-N(azo) [Os-N(4)/N(8), 1.97 Å] bond length is shorter than Ru-N(azo) [Ru-N(4)/N(8), 1.99 Å] by 0.02 Å while Os-N(imidazole) [Os-N(1)/N(5), 2.03/2.04 Å] is comparable to that of Ru-N(imidazole) [Ru-N(1)/N(5), 2.03/2.04 Å]. The N=N and C=N distances follow the order Os > Ru and are elongated by 0.02 and 0.01 Å respectively. This demonstrates that M-L π-interactions change in the order Ru < Os and that the interaction is primarily localized in the M-azo fragment. The systematic shortening of the M-N(azo) distance compared to the M-N(imidazole) distance in ruthenium and osmium complexes of RaaiX is a further indication of the presence of stronger M-azo π-bonding. Thus charge density movement from the metal-to-ligand (azoaryl) function is more significant in osmium complexes than in $RuCl_2(RaaiX)_2$ and may be the reason for the reversal of NMR signal positions.

TABLE V Comparison of EHMO, Spectroscopic and Redox Data for $OsCl_2(MeaaiMe)_2$ and $RuCl_2(MeaaiMe)_2$

Compound	*EHMO data*				*UV–Vis data*	*Redox data*	
	HOMO	*Energy,* eV	*LUMO*	*Energy,* eV	λ_{max} ($10^{-3}\,\varepsilon$, $M^{-1}\,cm^{-1}$)	$M^{III/II}$, V	*azo/azo,* V
$OsCl_2(MeaaiMe)_2$	76%	−11.069	65%	−10.520	1040 (0.98), 815 (0.92), 585 (7.32), 519 (11.56)	0.433	−1.149
$RuCl_2(MeaaiMe)_2$	70%	−11.136	74%	−10.509	858 (0.97), 590 (11.15)	0.746	−0.868

Dichloro-bis[2-(arylazo)pyridine]osmium(II), ($OsCl_2(aap)_2$) complexes were also known in *cis-trans-cis* and *cis-cis-cis* isomeric forms [13]. The spectra and redox behaviour of $OsCl_2(aap)_2$ are comparable with present series of complexes, $OsCl_2(RaaiX)_2$ and the magnitude of Os(III)/Os(II) couple is shifted to more positive potential and the MLCT bands are blue shifted on going from azoimidazole to azopyridine-osmium(II) complexes. This is because of the decreased π-acidity of the five-membered heterocycle imidazole compared to six-membered pyridine [21].

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Supplementary material

Full crystallographic data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request and the deposition numbers are CCDC 147713 (for **3a**) and CCDC 147714 (for **3b**).

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