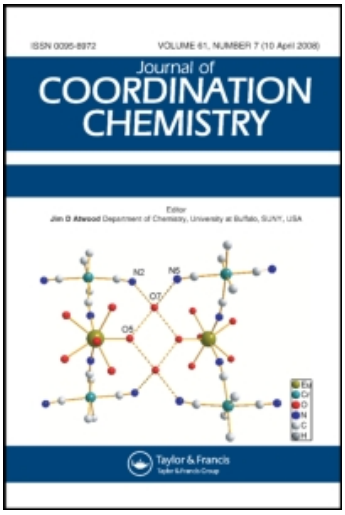

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Synthesis, Spectra and Electrochemistry of Isomeric DichloroBis-[1-Alkyl-2-(Naphthyl-(α/β)-Azo)Imidazole]Osmium(II): Single Crystal X-Ray Structure of Blue-Violet DichloroBis-[1-Ethyl-2-(Naphthyl-α-Azo) Imidazole]Osmium(II)

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SYNTHESIS, SPECTRA AND ELECTROCHEMISTRY OF ISOMERIC DICHLOROBIS-[1-ALKYL-2-(NAPHTHYL-(α/β)-AZO)IMIDAZOLE]OSMIUM(II): SINGLE CRYSTAL X-RAY STRUCTURE OF BLUE–VIOLET DICHLOROBIS-[1-ETHYL-2-(NAPHTHYL-α-AZO) IMIDAZOLE]OSMIUM(II)

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1-Alkyl-2-(naphthyl-(α/β)-azo)imidazoles (α/β-NaiR; R = Me, Et and CH_2Ph) react with $(NH_4)_2[OsCl_6]$ and complexes $OsCl_2(NaiR)_2$ are isolated in two isomeric forms: blue–violet (**3**, **4**) and red–violet (**5**, **6**). The ligand is a bidentate N (N(imidazole)), N′ (N(azo)) donor type. With reference to the pairs of Cl, Cl; N, N and N′, N′ atoms the blue–violet and red–violet isomers are assigned to *cis-trans-cis* (*ctc*) and *cis-cis-cis* (*ccc*) configurations respectively. IR spectra of the complexes show two ν(Os–Cl) bands and support the *cis*-$OsCl_2$ configuration. ^{1}H NMR spectra also support the *ctc* and *ccc*-configuration. The structure of the blue–violet complex $OsCl_2(\alpha$-NaiEt$)_2$ has been determined by X-ray crystallography and the *ctc* configuration has been confirmed. The structure shows an unusually long N=N bond length, 1.331(4) Å, which is elongated by 0.07 Å compared to the free ligand value.

Keywords: Naphthylazoimidazoles; Osmium(II); Isomers; X-ray structure; Electrochemistry

INTRODUCTION

There are numerous examples of arylazoheterocycles used in different fields of chemical science [1–12]. Modification has been carried out by changing the heterocycles and aryl group about the azo function. We have been engaged for several years on the design of new molecules containing arylazoheterocycles [10–16]. The coordination chemistry and analytical applications of 2-(arylazo)imidazoles [10,11] have encouraged us to design 2-(naphthylazo)imidazoles [14–16]. The naphthyl group is selected because of its higher

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reactivity, electron donating ability and greater steric crowding than that of the phenyl ring [17–19]. We have recently reported platinum(II) [14], ruthenium(II) [15] and palladium(II) [16] complexes of naphthylazoimidazoles. This study has now been extended to develop the chemistry of osmium(II) with these molecules. Two isomeric osmium(II) complexes of napthylazoimidazoles have been isolated and one of them has been confirmed by an X-ray diffraction study.

EXPERIMENTAL

Materials

1-Alkyl-2-naphthyl-((α/β)-azo)imidazoles (α/β-NaiR) were synthesized as before [14]. Osmium tetroxide was obtained from Johnson Matthey & Co. Ltd., UK. It was converted to $(NH_4)_2[OsCl_6]$ according to a reported method [7]. Solvent purification and reagent syntheses for electrochemical work were performed as before [13]. Commercially available silica gel (60–120 mesh) and alumina (neutral) 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 were collected using a Perkin Elmer 2400 CHN instrument. Electronic spectra were recorded using a JASCO V-570 spectrophotometer. IR spectra were obtained using a JASCO 420 spectrophotometer (KBr disks, 4000–200 cm^{-1}); ^1H NMR spectra were collected in $CDCl_3$ using a Brucker 300 MHz FT NMR spectrometer. The solution electrical conductivity was measured using a Systronics 304 conductivity meter with a solute concentration of $\sim 10^{-3}$ M in nitromethane. Electrochemical measurements were carried out under a dinitrogen atmosphere with a computer controlled EG & G PARC 270 VERSASTAT using a Pt-disk milli-working electrode. All results were collected at 298 K with the saturated calomel electrode (SCE) as reference. Reported potentials are uncorrected for junction contributions.

Preparation of *ctc*- and *ccc*-dichloro-bis-[1-methyl-2-(naphthyl-α-azo)imidazole]osmium(II), $OsCl_2(\alpha\text{-NaiMe})_2$

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. 1-Methyl-2-(naphthyl-α-azo)imidazole (α-NaiMe) (0.55 g, 2.33 mmol) in methanol was added dropwise to this refluxing solution over another half an hour. The mixture was refluxed under nitrogen, stirring magnetically for 8 h. During this period, the solution turned from brown–violet to blue–violet. It was concentrated slowly by bubbling N_2 gas to about 20 cm^3 and kept in a 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 an alumina column (30 × 1 cm). A small orange–red band of free ligand was eluted first with benzene and rejected. The blue–violet band was eluted by MeCN–C_6H_6

(1 : 4, v/v) and a red–violet solution was eluted by MeOH. A violet mass remained on the top of the column. The solutions were collected separately and evaporated slowly in air and the crystals so obtained were dried over P_4O_{10}. Yields were of blue–violet, *ctc*-$OsCl_2(\alpha\text{-NaiR})_2$, 35% and red–violet *ccc*-$OsCl_2(\alpha\text{-NaiR})_2$, 8%.

All other complexes were prepared by following an identical procedure and the yields varied between 30–40% for the blue–violet isomers and 8–14% for the red–violet isomers. Satisfactory analytical data for the complexes were obtained.

X-Ray Crystal Structure and Analysis

Crystal suitable for X-ray diffraction study of dichloro-bis-[1-ethyl-2-(naphthyl-α-azo)imidazole]osmium(II) ($OsCl_2(\alpha\text{-NaiEt})_2$, **(3b)** were grown by slow diffusion of hexane into a CH_2Cl_2 solution at room temperature. The selected crystal size was $0.35 \times 0.30 \times 0.30\,mm^3$. X-Ray diffraction data were collected at 295(2) K with a Siemens SMART CCD using graphite-monochromatized MoK_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 is given in Table I. Atomic coordinates for the non-hydrogen atoms are given in Table II. Of 17807 collected reflections, 6706 unique reflections 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 [20]. The structure was solved by heavy atom methods using SHELX-97 and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed geometrically and refined using a riding model. In the final difference Fourier maps the residual maximum and minimum were 1.009 and -0.597 e Å^{-3}. All calculations were carried out using SHELX-97 [21].

TABLE I Crystallographic data for *ctc*-$[OsCl_2(\mathbf{1b})_2]$ **(3b)**

Crystal parameters	
Formula	$C_{30}H_{28}Cl_2N_8Os$
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.0186(17)
b/Å	22.700(4)
c/Å	13.164(2)
β/°	113.264(3)
V/Å^3	3024.9(8)
λ/Å	0.71073
ρ_{calcd}/gm cm^{-3}	1.848
Z	4
T/K	295(k)
μ ($M_0 - K_\alpha$)/mm^{-1}	4.448
Refined parameters	370
R^a ($I > 2\sigma(I)$)%	2.36
wR^b%	7.29
GOF[c]	0.622

[a] $R = \sum |F_0 - F_c| / \sum F_0$; [b] $wR_2 = [\sum w(F_0^2 - F_c^2) / \sum wF_0^4]^{1/2}$, $w = 1/[\sigma^2(F_0^2) + (0.0473P)^2 + 14.3394P]$, $P = (F_0^2 + 2F_c^2)/3$; [c] GOF (Goodness of Fit) is defined as $[w(F_0 - F_c)/(n_0 - n_v)]^{1/2}$ where n_0 and n_v denote the number of data and variables, respectively.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *ctc*-[$OsCl_2$(**1b**)$_2$] (**3b**). *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Os	3036(1)	1497(1)	3564(1)	35(1)
C1(1)	3390(1)	1487(1)	5483(1)	49(1)
C1(2)	985(1)	1007(1)	3203(1)	49(1)
N(1)	2476(3)	1618(1)	1955(3)	41(1)
N(2)	2102(3)	2284(1)	3294(2)	41(1)
N(3)	1694(3)	2057(1)	1443(2)	48(1)
N(4)	858(4)	2919(1)	2022(3)	63(1)
N(5)	4910(3)	1754(1)	4068(2)	42(1)
N(6)	4018(3)	736(1)	3670(2)	41(1)
N(7)	5876(3)	1357(2)	4361(3)	49(1)
N(8)	5967(3)	296(2)	4157(3)	51(1)
C(1)	1515(4)	2399(2)	2205(3)	46(1)
C(2)	1806(4)	2749(2)	3819(3)	52(1)
C(3)	1049(5)	3134(2)	3044(4)	68(1)
C(4)	71(8)	3164(3)	905(5)	117(3)
C(5)	177(12)	3731(6)	809(9)	198(6)
C(6)	1823(4)	933(2)	348(3)	43(1)
C(7)	2251(4)	562(2)	−320(3)	51(1)
C(8)	4133(4)	1185(2)	1420(3)	52(1)
C(9)	468(4)	982(2)	111(3)	53(1)
C(10)	1263(5)	251(2)	−1197(4)	64(1)
C(11)	−441(5)	671(2)	−759(4)	65(1)
C(12)	2824(4)	1245(2)	1225(3)	43(1)
C(13)	4525(5)	813(2)	756(4)	67(1)
C(14)	3610(5)	514(2)	−84(4)	68(1)
C(15)	−16(6)	309(2)	−1414(4)	71(1)
C(21)	5326(4)	816(2)	4115(3)	44(1)
C(22)	3822(4)	156(2)	3393(3)	49(1)
C(23)	5017(5)	−120(2)	3700(3)	57(1)
C(24)	7396(5)	213(2)	4545(4)	71(1)
C(25)	7875(6)	239(5)	3647(5)	121(3)
C(26)	5388(4)	2349(2)	4216(3)	45(1)
C(27)	6310(4)	2548(2)	5267(3)	52(1)
C(28)	6820(4)	3130(2)	5327(4)	58(1)
C(29)	6357(6)	3490(2)	4386(5)	68(1)
C(30)	4947(4)	2717(2)	3339(3)	57(1)
C(31)	5432(5)	3297(2)	3418(4)	69(1)
C(32)	6701(5)	2207(2)	6242(4)	72(1)
C(33)	7788(5)	3323(3)	6358(5)	80(2)
C(34)	7623(6)	2427(3)	7222(4)	90(2)
C(35)	8186(6)	2975(3)	7267(5)	92(2)

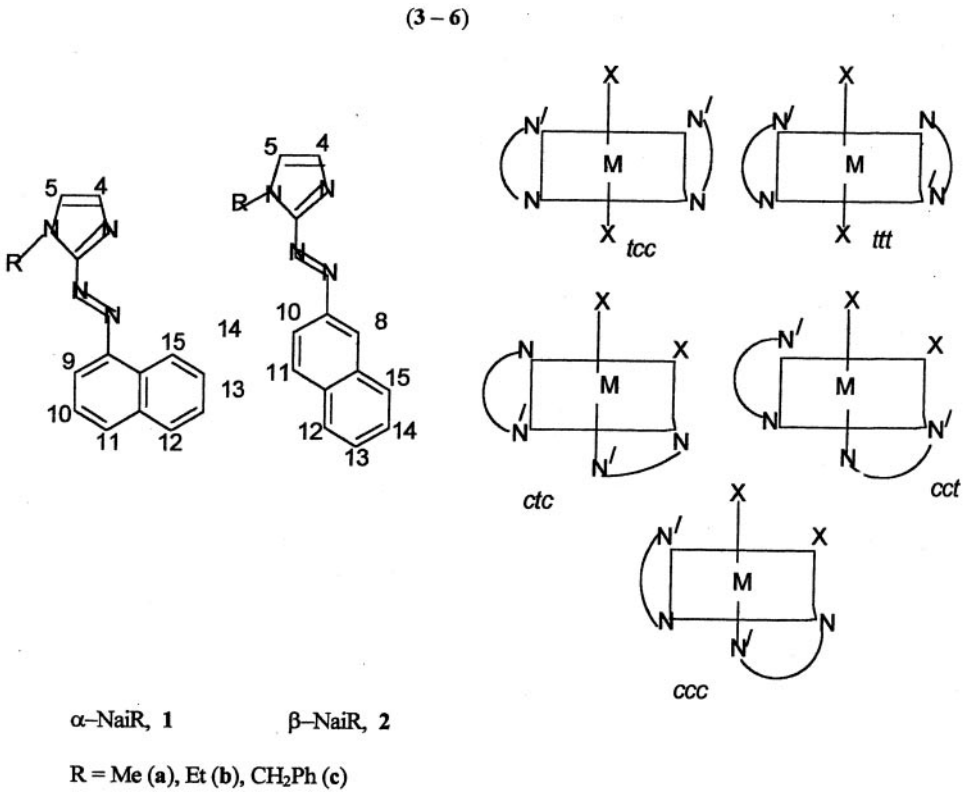
RESULTS AND DISCUSSION

Synthesis and Isomer Characterization

1-Alkyl-2-(naphthyl-α-azo)imidazoles [α-$C_{10}H_7$–N=N–C_3 H_2N_2-1-R] (abbreviated α-NaiR, **1**) and 1-alkyl-2-(naphthyl-β-azo)imidazoles [β-$C_{10}H_7$–N=N–C_3 H_2N_2-1-R] (abbreviated β-NaiR, **2**) (where **R** = Me (**a**), Et (**b**) and CH_2Ph (**c**)) have been used in this work. The active function is the azoimine group, $-$N=N–C=N–, and they are designated as N,N′ chelates where N(imidazole) refers to N and N(azo) refers to N′. They react with $[NH_4]_2[OsCl_6]$ in 2-methoxyethanol under refluxing conditions under

N_2 and afford complexes of composition $[OsCl_2(\mathbf{1}/\mathbf{2})_2]$ via spontaneous reductive chelation (Eq. (1)). On chromatographic purification blue–violet and red–violet isomers have been separated.

$$OsCl_6^{2-} + 2NaiR \longrightarrow OsCl_2(NaiR)_2 + 4Cl^- \quad (1)$$



Pseudooctahedral dichlorobis-chelated complexes, $MCl_2(N,N')_2$, may exist in five geometrical isomer forms [10,11] and with reference to the coordination pairs of Cl, N and N′ the isomers have been assigned as *trans-cis-cis* (*tcc*), *cis-trans-cis* (*ctc*), *trans-trans-trans* (*ttt*), *cis-cis-trans* (*cct*) and *cis-cis-cis* (*ccc*). Microanalytical data (*vide supra*) confirm the composition of the complexes. The X-ray crystal structure study in the case of the blue–violet isomer suggests the *ctc* configuration. Isomers are abbreviated in this article are as follows; blue–violet complexes $[OsCl_2(\mathbf{1})_2]$ (**3**), $[OsCl_2(\mathbf{2})_2]$ (**4**); red–violet complexes $[OsCl_2(\mathbf{1})_2]$ (**5**), $[OsCl_2(\mathbf{2})_2]$ (**6**).

X-Ray Crystal Structure of Blue–Violet Dichloro-bis-[1-ethyl-2-(naphthyl-α-azo)imidazole]osmium(II)

A view of the molecular unit of $[OsCl_2(\mathbf{1b})_2](\mathbf{3b})$ is shown in Fig. 1 and selected bond parameters are listed in Table III. The atomic arrangement around osmium invokes

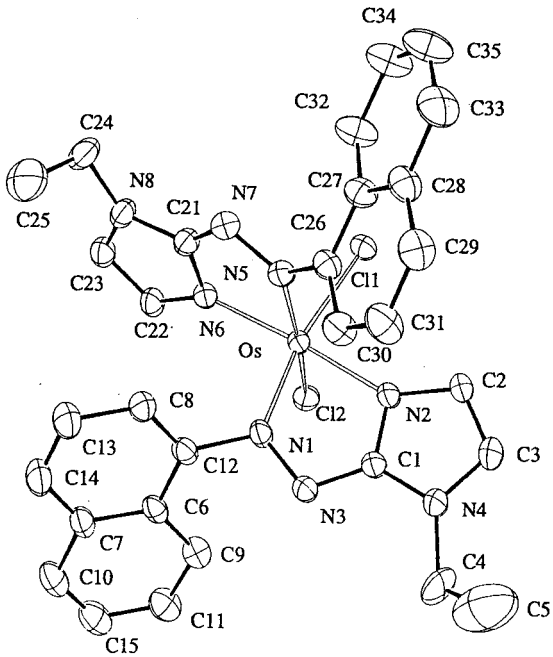


FIGURE 1 ORTEP plot and atom labelling scheme for *ctc*-$OsCl_2(\alpha\text{-NaiCH}_2CH_3)_2$.

TABLE III Selected bond distances (Å) and angles (°) for *ctc*-$[OsCl_2(\mathbf{1b})_2]$ (**3b**) with estimated standard deviations

Distances (Å)		*Angles* (°)			
Os–N(1)	1.977(3)	N(1)–Os–N(2)	76.55(11)	N(2)–Os–Cl(1)	93.03(8)
Os–Cl(1)	2.3995(10)	N(5)–Os–N(6)	76.74(12)	N(2)–Os–Cl(2)	90.01(9)
Os–N(2)	2.022(3)	Cl(1)–Os–Cl(2)	87.27(4)	N(2)–Os–N(5)	100.88(12)
Os–Cl(2)	2.3932(10)	N(1)–Os–Cl(1)	168.91(9)	N(2)–Os–N(6)	173.01(12)
Os–N(5)	1.990(3)	N(1)–Os–Cl(2)	88.93(10)	N(5)–Os–Cl(1)	86.33(9)
N(1)–N(3)	1.315(4)	N(1)–Os–N(5)	99.22(13)	N(5)–Os–Cl(2)	167.63(9)
Os–N(6)	2.013(3)	N(1)–Os–N(6)	97.24(12)	N(3)–N(1)–Os	121.3(2)
N(5)–N(7)	1.331(4)	N(6)–Os–Cl(1)	93.37(8)	N(6)–Os–Cl(2)	93.10(9)
		N(7)–N(5)–Os	120.2(3)		

sequentially two *cis*-chlorine, *trans*-N(imidazole)[N] and *cis*-N(azo),[N′] atoms and corresponds to the *ctc* configuration. Atomic arrangements Os, Cl(1), N(6), N(1), N(2) (plane-1) and Os, Cl(2), N(2), N(5), N(6) (plane-2) separately constitute two planes (mean deviation < 0.1 Å) and are orthogonal (dihedral angle 88.30°). The planarity of atoms groups Os, Cl(1), Cl(2), N(1), N(5) (plane-3) is not good and deviation of N(5), Cl(2), Cl(1) from the best plane are 0.24 Å (downward), 0.14 Å (downward) and 0.42 Å (upward), respectively. This plane makes dihedral angles with plane-1 and plane-2 of 94.64 and 79.41°, respectively. Distortion from octahedral geometry is due to acute chelate bite angles, N(1)–Os–N(2) 76.55(11)° and N(5)–Os–N(6) 76.74(12)°. Azo-nitrogen N(1) (deviation -0.063 Å), and N(5) (deviation, -0.056 Å) are responsible for this distortion more than imidazole nitrogen,

N(2) (deviation, − 0.042 Å) and N(6) (deviation, − 0.046 Å). The angles N(1)–Os–N(5), 99.22(13)° and N(2)–Os–N(6) 173.01(12)° are far from orthogonal. Each chelate ring is a good plane and no atom deviates by > 0.06 Å; for the chelate rings the dihedral angle is 76.20°. The pendent naphthyl ring is planar and is inclined at an angle of about 60° with the parent chelate plane. Two naphthyl rings of α-NaiEt are nearly orthogonal (dihedral angle, 87.48°). Os–N(imidazole) [Os–N(2) = 2.022(3), Os–N(6) = 2.013 Å] bond lengths are longer than Os–N(azo) [Os–N(1) = 1.977(3), Os–N(5) = 1.990(3) Å] bond lengths (Table III). N=N distances are 1.32–1.33 Å, elongated by 0.07 Å compared to the free ligand value (1.26 Å)] [22]. The elongation of the N–N distance and shortening of Os–N(azo) bond length are an indication of considerable Os–L π-bonding with major involvement of the azo group [7]. A comparison of bond parameters in the chelate ring of *tcc*-$RuCl_2$(α-NaiEt)$_2$ [15] and *ctc*-$OsCl_2$(α-NaiEt)$_2$ is shown in Fig. 2. N–N distances are elongated by ~0.03 Å in the osmium(II) complex as compared to the ruthenium(II) complex. C–N distances vary in a characteristic manner; in the imidazole ring the endocyclic C–N(imine) distance is elongated by ~0.03 Å while the exocyclic C–N (azo) distance is shortened by ~0.03 Å in osmium(II) complexes compared with analogous ruthenium(II) complexes. N=N and C=N distances follow the order Os > Ru and are elongated by ~0.03 Å. This means that the M–L π-interaction order is Ru < Os.

The observable difference between the structure of ruthenium(II) and osmium(II) complexes of 1-ethyl-2-(naphthyl-α-azo)imidazole may be due to relativistic effects [23] on Os as compared to Ru and their different isomeric structures, *tcc*-$RuCl_2$(α-NaiEt)$_2$ and *ctc*-$OsCl_2$(α-NaiEt)$_2$. In the *tcc* configuration two azoimine functions are present in a square plane and a π* orbital of the ligand shares the same metal-d orbital whereas in the *ctc* configuration they are oriented *cis* and π* orbitals use different metal d-functions.

Spectroscopic Studies

A sharp band at 1400–1410 cm^{-1} in the free ligands corresponding to ν(N=N) is shifted to 1210–1240 cm^{-1} in the complexes. Endocyclic C=N appears at 1530–1540 cm^{-1} in the complexes. The red shift of N=N stretching is correlated with N(azo) coordination [7,23–25] and may be attributed to Os (dπ) → π* charge transfer. The complexes exhibit

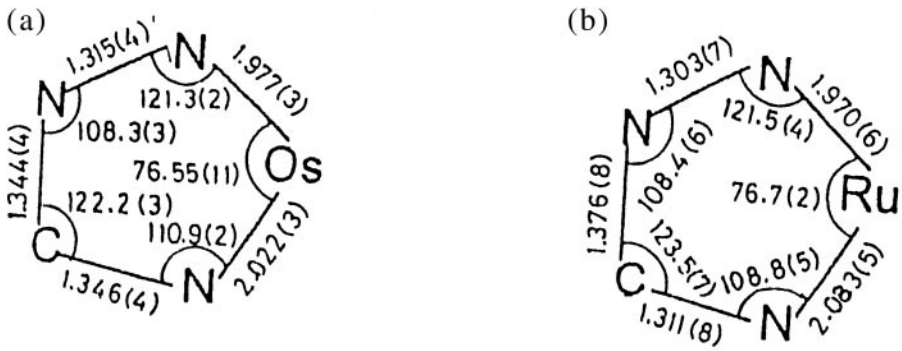


FIGURE 2 Dimensions of chelate rings with esd of (a) *ctc*-$OsCl_2$(α-NaiEt)$_2$ and (b) *tcc*-$RuCl_2$(α-NaiEt)$_2$.

two Os–Cl stretches at 320–310 and 300–290 cm^{-1} and suggest the presence of the *cis*-$OsCl_2$ configuration.

Solution electronic spectra of the complexes exhibit absorptions at 300–1400 nm (Table IV). Multiple transitions are observed at longer wavelengths and are absent in the free ligand; these are assigned to MLCT transitions. In general $[OsCl_2(\mathbf{1})_2]$ complexes exhibit absorption at higher energy compared with $[OsCl_2(\mathbf{2})_2]$. Major absorptions at 420–480, 500–600, 700–800 and 1050–1150 nm are assigned to $t_2 \rightarrow \pi^*$ charge transfer where the π^* level has largely azo character. Blue–violet solutions of the *ctc*-isomer have an intense band ($\varepsilon \sim 10^4\ M^{-1}\ cm^{-1}$) at *ca.* 525 nm with a shoulder at *ca.* 575 nm. In the red–violet complexes (*ccc*-isomer) the bands are blue shifted to 510 nm accompanied by a shoulder at *ca.* 580 nm. Bands in the 700–850 and 1050–1150 nm regions are weak ($\varepsilon \sim 10^3\ M^{-1}\ cm^{-1}$) and systematically shifted to higher energy on going from *ctc* to *ccc*-isomer. In d^6-metal complexes, multiple charge transitions can arise from low-symmetry splitting of the metal levels, from the mixing of singlet and triplet configurations in excited states via spin-orbit coupling and from the presence of more than one interacting ligand, each contributing one π^* level [23–26]. The absorption properties of the present complexes have been compared with the spectra of ruthenium(II) analogues and it is concluded that the bands are blue shifted by 80–100 nm in the osmium(II) complexes along with appearance of a low energy band in the near-IR region. This accounts the stronger interaction of osmium(II) t_2-orbitals

TABLE IV Electronic spectra[a] and cyclic voltammetric data[b] for $[OsCl_2(NaiR)_2]$

Compound	*Electronic spectra*	Os^{III}/Os^{II}	Os^{IV}/Os^{III}	*Ligand reductions*
	λ_{max}, nm($10^{-3}\varepsilon M^{-1}cm^{-1}$)	$E^1_{1/2}$, V (ΔE_p, mV)	$E^2_{1/2}$, V (ΔE_p, mV)	$E^3_{1/2}$, V (ΔE_p, mV)
ctc-$[OsCl_2(\mathbf{1a})_2](\mathbf{3a})$	1058(0.211)[c], 734(0.852)[c], 550(4.182), 524(3.668), 425(8.495)	0.594(80)	1.347(170)	−0.655(120), −0.774[d], −1.50[d]
ctc-$[OsCl_2(\mathbf{1b})_2](\mathbf{3b})$	1057(1.083)[c], 730(1.655)[c], 558(4.754), 522(5.060), 420(11.907)	0.576(80)	1.291(160)	−0.703(130), −1.10[d], −1.58[d]
ctc-$[OsCl_2(\mathbf{1c})_2](\mathbf{3c})$	1052(1.648)[c], 740(1.003)[c], 590(4.625), 525(7.246), 440(7.022)	0.619(95)	1.453(130)	−0.639(110), −0.780[d], −1.35[d]
ccc-$[OsCl_2(\mathbf{1a})_2](\mathbf{5a})$	1056(0.748)[c], 710(1.637)[c], 583(5.009), 512(7.597), 445(8.048)	0.622(100)	1.468(120)	−0.538(110), −0.749[d], −1.42[d]
ccc-$[OsCl_2(\mathbf{1b})_2](\mathbf{5b})$	1048(0.899)[c], 710(1.420)[c], 590(4.423), 518(7.903), 448(6.765)	0.590(85)	1.361(140)	−0.750(110), −1.05[d], −1.54[d]
ccc-$[OsCl_2(\mathbf{1c})_2](\mathbf{5c})$	1048(0.934)[c], 740(1.567)[c], 584(4.768), 522(6.929), 438(6.862)	0.638(105)	1.540(130)	−0.540(110), −0.744[d], −1.45[d]
ctc-$[OsCl_2(\mathbf{2a})_2](\mathbf{4a})$	1072(0.204)[c], 750(0.539)[c], 570(5.094), 530(3.749), 440(9.058)	0.560(95)	1.247(140)	−0.725(130), −1.073[d], −1.63[d]
ctc-$[OsCl_2(\mathbf{2b})_2](\mathbf{4b})$	1064(0.843)[c], 750(1.008)[c], 572(6.193), 535(7.243), 440(10.448)	0.548(90)	1.214(150)	−0.734(120), −1.113[d], −1.60[d]
ctc-$[OsCl_2(\mathbf{2c})_2](\mathbf{4c})$	1068(0.914)[c], 762(1.359)[c], 580(7.318), 538(6.918), 440(10.309)	0.589(85)	1.360(130)	−0.668(130), −0.910[d], −1.44[d]
ccc-$[OsCl_2(\mathbf{2a})_2](\mathbf{6a})$	1058(0.616)[c], 815(0.579)[c], 726(0.904)[c], 594(4.382), 530(9.527), 445(12.677)	0.603(110)	1.367(120)	−0.654(140), −0.900[d], −1.48[d]
ccc-$[OsCl_2(\mathbf{2b})_2](\mathbf{6b})$	1052(0.953)[c], 810(1.032)[c], 740(1.179)[c], 598(8.101), 525(9.701), 446(10.094)	0.564(100)	1.278(160)	−0.730(100), −0.984[d], −1.49[d]
ccc-$[OsCl_2(\mathbf{2c})_2](\mathbf{6c})$	1044(0.783)[c], 795(0.849)[c], 730(1.356)[c], 590(7.318), 530(9.048), 450(11.349)	0.624(95)	1.518(130)	−0.544(120), −0.754[d], −1.48[d]

[a]Solvent: $CHCl_3$; [b]Shoulder; [c]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, units of symbols same as in text, $\Delta E_p = |E_{pa} - E_{pc}|$, mV; [d]$E_{pa}$, V.

with ligand π^*-functions than with ruthenium(II) complexes. The behavior is comparable with osmium(II) complexes of arylazopyridines [7] and 1-alkyl-2-(arylazo)-imidazoles [24,25] and the band position are red shifted by 20–30 nm in the present complexes. This is in agreement with the π-acidity order arylazopyridine > arylazoimidazole > naphthylazoimidazole. The presence of an additional aromatic ring in naphthyl derivatives may increase the electron density in the molecule and is one reason for reduced π-acidity [26,27].

^{1}H NMR spectra of the complexes were examined to determine isomeric structure. Signals are assigned on the basis of spin–spin interaction, and comparison between the integration of aliphatic and aromatic regions, chemical shift data and on comparing with reported results [14,15]. Some characteristic NMR data serving to distinguish isomers are summarized in Table V. The 1-Me signal appears as a singlet in the blue–violet isomer at 3.8–3.9 ppm and is shifted downfield by 0.1–0.2 ppm compared to free ligand values [14,15]. Red–violet $OsCl_2(NaiCH_3)$ exhibits two equally intense signals at 3.90 and 4.07 ppm correspond to the 1-Me group. The methylene signal of 1-$CH_2(CH_3)$ appears as an AB type sextet at around 4.3 and 4.4 ppm in the blue–violet $OsCl_2(NaiCH_2CH_3)_2$ complex (Fig. 3). Red–violet $OsCl_2(NaiCH_2CH_3)_2$ exhibits a pair of AB type complex multiplets at 3.6–3.7, 3.8–3.9; 4.3–4.4 and 4.5–4.6 ppm (1-CH_2-protons). Separation of resonances of –CH_2-protons is found to be higher in red–violet isomers than in blue–violet cousin. In $OsCl_2(NaiCH_2Ph)_2$, the –CH_2–, group shows AB type quartets at 5.4–5.5 and 5.5–5.6 ppm in the blue–violet isomer while a pair of quartets are observed in red–violet isomers at 5.4, 5.5; 5.6, 5.7 ppm. This suggests that the red–violet isomer is less symmetric than the blue–violet partner. On comparing with the result of ruthenium(II) complexes of 1-alkyl-2-(naphthtylazo)-imidazoles [15] and osmium(II) complexes of 1-alkyl-2-(arylazo)imidazoles [25] we conclude that blue–violet and red–violet isomers belong to *ctc*- and *ccc*-configurations, respectively. The proton signal pattern in the aliphatic region (4.0–6.0 ppm) supports molecular dissymmetry in the complexes and extent of distortion is more evident in red–violet (*ccc*-isomer) complexes. Imidazolyl 4- and 5-H signals appear at 7.0–7.2 and 6.9–7.0 ppm and are up-field shifted by ≥ 0.1 ppm relative to analogous ruthenium(II) complexes. The β-naphthyl ring shows a characteristic broad singlet resonance corresponding to 8-H and indicates inter-ring coupling, which is absent in the α-NaiR group. All other naphthyl ring protons exhibit multiple coupling and are assigned on comparing with reported results [14,15].

TABLE V Characteristic ^{1}H NMR data[a] for isomeric $OsCl_2(NaiR)_2$ species in the aliphatic region

	δ, ppm (J, Hz)											
Compound[b]	**3a**	**3b**	**3c**[f]	**5a**	**5b**	**5c**[f]	**4a**	**4b**	**4c**[f]	**6a**	**6b**	**6c**[f]
1-Me[c]	3.81			4.07 3.91			3.90			4.09 3.90		
1-CH_2[d]-		4.31 4.41			4.41, 3.68 4.55, 3.78	5.37, 5.50 5.62, 5.71		4.31 4.43			3.57, 3.80 4.40, 4.55	5.41 5.76
1-(CH_2)CH_3[e]		1.55	5.40(14.0) 5.49(14.0)		1.55 1.50			1.53	5.45(15.0) 5.57(15.0)			

[a]Solvent: $CDCl_3$; [b]4-H: 7.0–7.2, 5-H: 6.9–7.0, 8-H: 7.3–7.9, 9-H: 7.7–7.8, 10-H: 7.4–7.8, 11-H: 7.4-7.5, 12-H–14-H: 7.2–7.4, 15-H: 7.5–7.8 ppm; [c]Singlet; [d]Sextet; [e]Triplet; [f]Phenyl protons, (1-CH_2)-Ph appears at 7.25–7.30 (for **3c** and **4c**), 7.30–7.40 for (**5c** and **6c**).

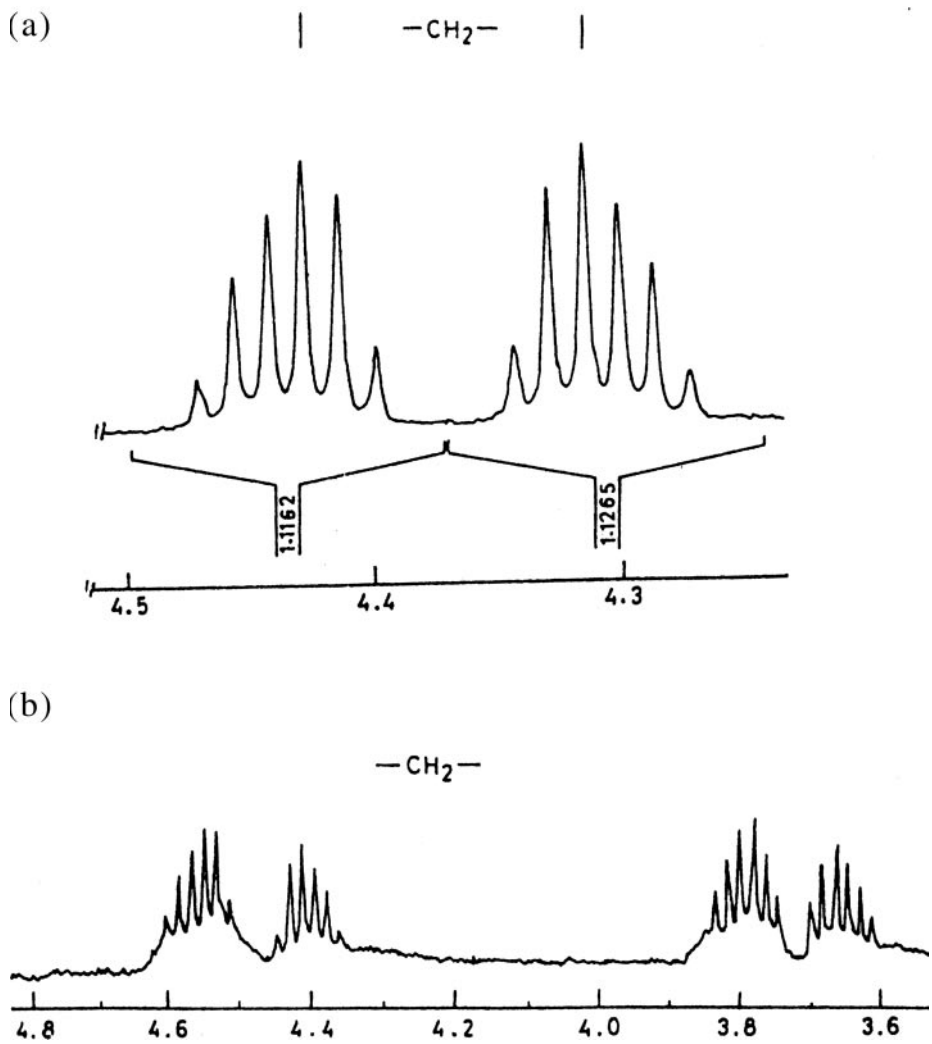


FIGURE 3 ^{1}H NMR spectra of (a) $-CH_2-(CH_3)$ region of *ctc*-$OsCl_2(\alpha$-NaiEt$)_2$ and (b) $-CH_2-(CH_3)$ region of *ccc*-$OsCl_2(\alpha$-NaiEt$)_2$ in $CDCl_3$ at 295 K.

Electrochemistry

Cyclic voltammetric of the complexes gives two oxidative responses positive to SCE and three successive couples negative to SCE (Table IV). Potentials at 0.55–0.65 and 1.2–1.5 V *versus* SCE refer to osmium(III)–osmium(II) (Eq. (2)) and osmium(IV)–osmium(III) (Eq. (3)), respectively. The reductions are believed to be due to successive electrons feeding into the two azoimine functions [6,7,14,15].

$$OsCl_2(NaiR)_2^+ + e \rightleftharpoons OsCl_2(NaiR)_2 \quad (2)$$

$$OsCl_2(NaiR)_2^{2+} + e \longrightarrow OsCl_2(NaiR)_2^+ \quad (3)$$

It is observed that *ccc*-$OsCl_2(NaiR)_2$ exhibits a higher redox potential by ~ 0.1 V than *ctc*-$OsCl_2(NaiR)_2$. This may be due to the lower symmetry of the *ccc*-isomer (C_1-symmetry) than that of *ctc*-isomer (C_2-symmetry). In addition, $OsCl_2(\beta\text{-}NaiR)_2$ exhibits a lower Os(III)–Os(II) redox couple than $OsCl_2(\alpha\text{-}NaiR)_2$. This may be due to the greater thermodynamic stability of β-naphthyl derivatives as compared to α-naphthyl derivatives [19].

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Supplementary Data

Full lists of crystallographic data are available from the authors upon request.

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