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Synthesis, spectra and electrochemistry of isomeric dichlorobis[1-methyl-2-(13Cl-naphthyl-α/β)azo)imidazolium]osmium(II):

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ABSTRACT
*1-methyl-2-(13Cl-naphthyl-(α/β)-azo)imidazoles (α/β-NaiR where R = Me, Et and CH_2Ph) have been reacted with $(NH_4)_2[OsCl_6]$ and the complexes of composition $OsCl_2(NaiR)_2$ 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′ the blue-violet and red-violet isomers are assigned to cis-trans-cis (ctc) and cis-cis-cis (ccc) configuration, respectively. The IR spectra of the complexes show two ν(Os–Cl) bands and support cis-$OsCl_2$ configuration. The ^1H NMR spectra support the ctc and ccc-configuration. The structure of blue-violet complex of $OsCl_2(\alpha\text{-NaiEt})_2$ has been determined by X-ray crystallography and the cis-trans-cis configuration has been confirmed. The absorption spectra of the complexes exhibit high intense MLCT band at 520-590 nm along with weak multiple transitions at longer wavelength. The cyclic voltammetry show quasireversible Os(III)/Os(II) and Os(IV)/Os(III) couples at 0.55 - 0.64 V and 1.25 - 1.52 V versus SCE, respectively.*

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I. INTRODUCTION

In recent years, ruthenium(II), osmium(II) and Rh(III) complexes of polypyridyl ligands have received much attention because of their rich electrochemical and photophysical properties, and their potential applications in various supramolecular structures as electronic and photomolecular devices 1–7 . Multinuclear systems of this kind can be developed by covalent linking of building blocks with spacers which, therefore, is the key component because the size, shape and electronic nature of the bridge controls the electronic communication between the chromophores and thereby the molecule as a whole. The ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) is a potential spacer, which functions as a bis-bidentate or simultaneously as a tridentate and a bidentate bridging unit. The ligand tptz is believed to be stable towards nucleophilic attack and has been used as an analytical reagent for various metal ions 8–11. A few mono and dinuclear complexes of ruthenium(II) of tptz has also been reported 12–14. However, our studies reveal that under certain experimental conditions tptz undergoes various metal-assisted reactions 15–19. Here, we briefly account the reactivities of tptz in presence of rhodium(III), ruthenium(II) and osmium(II), stereochemistry of the products, mechanistic aspects of hydrolysis/hydroxylation and electrochemical properties. The ligands which bind the transition metal ion in a predictable way play important role in modern coordination chemistry since they may determine the reactive sites available at a metal centre and can modulate their reactivity. Fascinating chemistry of transition metal complexes incorporating ligands that are capable of binding the metal centre in facial manner, enhanced the interest on the synthesis of new tridentate ligands that are suitable for obtaining facially coordinated complexes. 1–7 Facially capped piano-stool type of platinum metal complexes have received attention due to their interesting catalytic and biological activity. Conversion of dimethyl oxalate to ethylene glycol and hydrogenation of esters to yield alcohols in homogeneous media using such metal complexes as catalyst are notable examples. 8–21 Although several tridentate facially coordinating ligands, such as 1,4,7 tri aza cyclononane, 1,4,7 trithia cyclononane, tris pyrazolyl borate, a few scorpionate and tripodal ligands, are known to form facially capped ∗For correspondence platinum metal complexes, 22–34 but only a few of the above mentioned ligands have been utilized for the preparation of Os(II) complexes. 35,36 As a consequence, chemistry of Os(II) complexes with facially coordinating ligands have not been explored considerably. Coordination chemistry of osmium incorporating azo ligands has been studied with a few bidentate (N, N and N, O donors) and tridentate (C, N, O and N, N, N donors) ligands. 37–41 Whereas the coordination chemistry of osmium with tridentate N, N, O donor ligands has not been reported so far. These background information prompted us to study the coordination chemistry of osmium incorporating the N, N, O donor azo-imine ligand system, 1. Complexes with N-heterocycles exhibit rich electrochemistry and interesting optical properties. π-Deficient nitrogen donor ligands are excellent non-innocent molecules and their complexes comprise special

interest in coordination chemistry. Transition metal complexes of 2,2/-bipyridine (bpy) and related ligands have attracted much attention in this regard [1-5]. This has led to the modification of M-bpy system by choice of substituents and metal. Ligands have been modified by substituting electron withdrawing/donating groups or bulky groups to the aromatic backbone, substituting other heterocycles, appending extra donor centers to aromatic and/or heterocyclic rings etc. [5-17]. Azo conjugated transition metal complexes can provide new opportunity towards redox, magnetic and optical properties originating from the d-orbitals [6-34]. A characteristic feature of these conjugated complexes that the transition metals can interact with each other through the π-conjugated backbone to permit electronic communi cation. Bis-/tris–hetero chelated complexes may exhibit inter-ligand charge transferences along with some structural distortion and/or backbone deformation [17,18-27]. Modification has been done substituting six membered pyridine ring by less π-acidic, biologically important five membered imidazole ring e.g., 2-(arylazo)imidazole [12] and by increasing the number of N in pyridine ring *viz.* 2-(arylazo)pyrimidine [19]. Second modification has been carried out replacing pendent aryl group by sterically more crowded, electronically more susceptible naphthyl group from 2-(arylazo)imidazole to get 2-(naphthylazo) imidazoles [35]. Pseudooctahedral $OsCl_2(RaaiR^/)_2$ may exist, in principle, in five isomeric forms and we have isolated two isomers. One of the isomers has been structurally confirmed by X-ray diffraction measurements [12]. According to the sequence of coordination pairs of Cl, N(imidazole) and N(azo) the isomer is *cis-trans-cis*-$OsCl_2(RaaiR^/)_2$; the abbreviation is *cis-trans-cis* (*ctc*). This molecule carries *cis*-$OsCl_2$ fragment which can undergo nucleophilic substitution to synthesise mixed ligand complexes. The literature contains numerous examples of arylazoheterocycles and they have been used in the development of different field of chemical science [1 – 29]. We have been also engaged for the last several years to design new molecules belong to the family of arylazoheterocycles [22 – 32]. The modification has been carried out by changing heterocycles and aryl group about the azo function. Pyridine [17 - 21] imidazole [22 - 25] and pyrimidine [26 – 30] have been used as heterocycle backbone. The coordination chemistry and analytical application of 2-(arylazo)imidazoles [22 - 25] have encouraged us to design 2-(naphthylazo)imidazoles [31 - 32]. Naphthyl group is selected because of its higher reactivity ,electron donating ability and greater steric crowding than that of phenyl ring [33 – 37].We recently report platinum(II) [31] ruthenium(II) [32] and palladium(II) complexes of naphthyl azoimidazoles. This study has now been extended to develop the chemistry of osmium(II) of this molecule. The active function of the ligand is azoimine group, –N=N–C=N– and behaves as $N,N^/$ -chelating ligand where N refers to N(imidazole) and $N^/$ refers to N(azo)). Pseudooctahedral dichloro bis-chelated complexes, $MCl_2(N,N^/)_2$, may exist in five geometrical isomer forms[22 - 27] and with reference to the coordination pairs of Cl, N and N' the isomers have been assigned to *trans-cis-cis* (*tcc*), *cis-trans-cis* (*ctc*), *trans-trans-trans* (*ttt*), *cis-cis-trans* (*cct*) and *cis-cis-cis* (*ccc*). Osmium(II) complexes of napthylazoimidazoles have been isolated in two isomeric forms and the spectral characterisation suggests that they are of *ctc*- and *ccc*- isomers. One of the isomers has been confirmed by X-ray diffraction study.

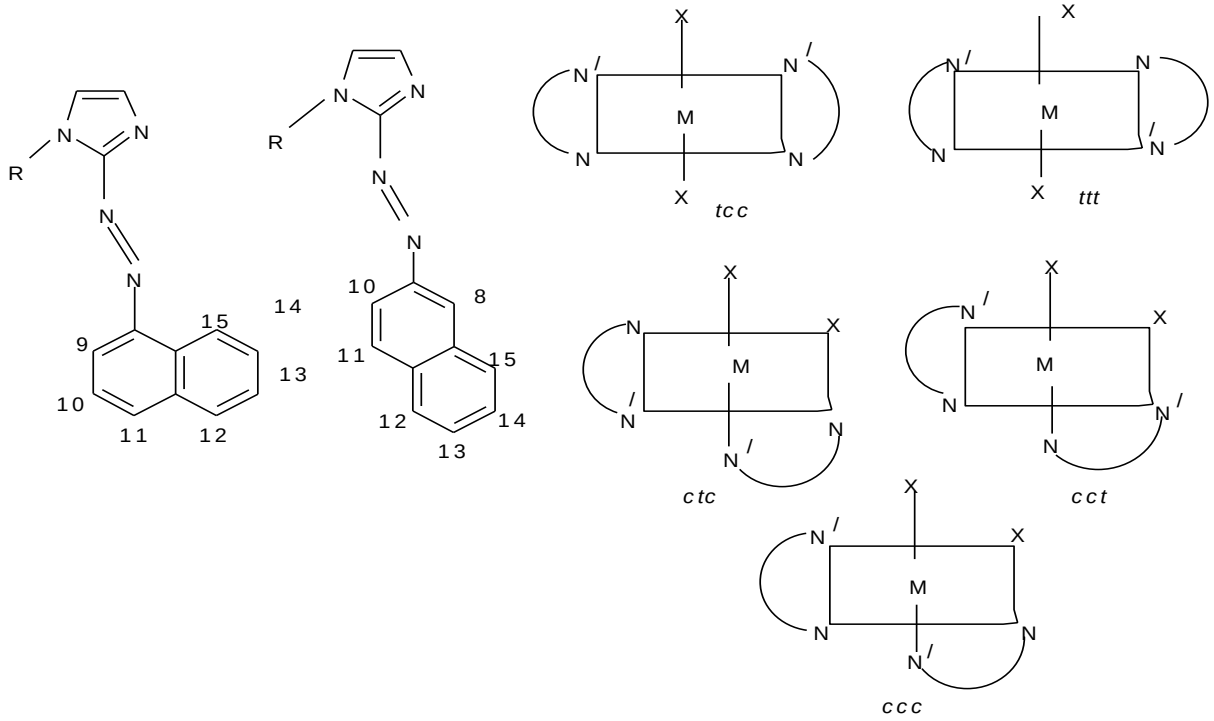
II. RESULTS AND DISCUSSION

Ligands and Complexes Synthesis

Two classes of ligands have been used in this work: 1–alkyl–2–(13Clnaphthyl-α-azo)imidazoles[(α-$C_{10}H_7$–N=N–$C_3H_2N_2$–1–R (abbreviated α–NaiR,**1**) and 1-alkyl–2–(13Clnaphthyl-β-azo)imidazoles [β-$C_{10}H_7$–N=N-$C_3H_2N_2$–1–R (abbreviated β–NaiR, **2**) (where R = Me (**a**), Et (**b**) and CH_2Ph (**c**)). The active function is the azoimine group, -N=N-C=N-, and is designated as $N,N^/$ chelates where N(imidazole) refers to N and N(azo) refers to $N^/$ [31]. They react with $[NH_4]_2[OsCl_6]$ in 2-methoxy- ethanol (**Equation 1**) under refluxing condition at inert atmosphere (N_2) and afford the complexes of composition $[OsCl_2(NaiR)_2]$ *via* spontaneous reductive chelation. On chromatographic purification blue-violet and red-violet isomers have been separated. Micro-analytical data (*vide supra*) confirms the composition of the complexes. The X-ray crystal structure study in one case confirms the structure of blue-violet isomer. Isomers are abbreviated in this chapter are as follows; blue-violet complexes $[OsCl_2(\alpha–NaiR)_2]$(**3**), $[OsCl_2(\beta–NaiR)_2]$(**4**); red-violet complexes $[OsCl_2(\alpha–NaiR)_2]$(**5**),$[OsCl_2(\beta–NaiR)_2]$(**6**). All the complexes are characterised by elemental analyses (**Table VIII. 1**), IR, UV-VIS-NIR and ^{1}H NMR spectral data.

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

(3 – 6)



α–NaiR, **1** β–NaiR, **2**

R = Me (**a**),

VIII. 2. B. Spectral studies

VIII. 2. B. (i) IR Spectra

A sharp band at 1400-1410 cm^{-1} in the free ligands corresponds to ν(N=N) have been shifted to 1210-1240 cm^{-1} in the complexes which is shown in **Figure VIII. 1**. The endocyclic C=N appears at 1530-1540 cm^{-1} in the complexes. The red shift of N=N stretching is corroborated with N(azo) coordination [18,43-45] and may be attributed to Os (dπ)→π* charge transition. The complexes exhibit two Os-Cl stretches at 320-310 and 300-290 cm^{-1} and suggest the present of *cis*-$OsCl_2$ configuration (**Table VIII. 1**.)

VIII. 2. B. (ii) UV-VIS Spectra

The solution electronic spectra of the complexes exhibit absorptions 300-1400 nm (**Table VIII. 2, Figure VIII. 2**). The allowed transition at <400nm are due to intraligand charge transfer transition [31,32] and are not considered further. Multiple transition are observed at longer

wavelength region those are absent in free ligand and have been assigned to MLCT transition. In general $[OsCl_2(\alpha\text{–NaiR})_2]$ complexes exhibit absorption on higher energy region compared with $[OsCl_2(\beta\text{–NaiR})_2]$. Major absorption at 420-480, 500-600, 700-800 and 1050-1150 nm are assigned to $t_2 \rightarrow \pi^*$ charge transfer transition where the π^* level has large azo character. Blue-violet solution of the *ctc*-isomer has 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 and is accompanied by a shoulder at *ca* 580 nm. The bands in the 700-850 nm and 1050-1150 nm are weak ($\varepsilon \sim 10^3$ $M^{-1}cm^{-1}$) and are systematically shifted to higher energy region on going from *ctc* to *ccc*-isomer. In d^6-metal complexes, multiple charge transition can arise from low symmetry splitting of the metal level, from the mixing of singlet and triplet configuration in excited state *via* spin-orbit coupling and from the presence of more than one interacting ligand, each contributing one π^* level [43-46]. The absorption properties of the present complexes have been compared with the spectra of ruthenium (II) analogous and it is concluded that the bands are blue shifted by 80-100 nm in the osmium (II) complexes along with appearance of low energy band at near-IR region. This account the stronger interaction of osmium (II) t_2-orbitals with ligand π^*-functions than that of ruthenium (II) complexes. The spectral behavior is comparable with osmium (II) complexes of arylazopyridines [18], 1-alkyl-2-(arylazo)imidazoles [44,45] 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 additional aromatic ring in naphthyl derivative may increase the electron influx in the molecule and is the reason of reduced π-acidity [46,47].

VIII. 2. B. (iii) ^{1}H NMR Spectra

The ^{1}H NMR spectra of the complexes were examined to determine isomeric structure. The signals are assigned on the basis of spin-spin interaction, and comparison between the integration of aliphatic and aromatic region, chemical shift data and on comparing with reported results.[31,32] The signals correspond to the spectral data are summarized in **Table VIII. 3** and representative spectra is given **Fig. VIII. 3**. ^{1}H NMR spectra have been particularly useful to determine stereochemistry of isomers. The observation is given below. The 1-Me signal appears as a singlet in blue-violet isomer at 3.8-3.9 ppm and is downfield shifted by 0.1 - 0.2 ppm compared to the free ligand values.[31,32] The red-violet, $OsCl_2(NaiCH_3)$ exhibit two equally intense signals at 3.90 and 4.07 ppm correspond to 1-Me group. The methylene signal of 1-$CH_2(CH_3)$ appears as AB type sextet at around 4.3 and 4.4 ppm in blue-violet $OsCl_2(NaiCH_2CH_3)_2$ complex (Fig. 4). Red-violet $OsCl_2(NaiCH_2CH_3)_2$ exhibits 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 corresponds to 1-CH_2- protons. The separation of resonance of -CH_2- protons is found to be higher in red-violet isomers than that of blue-violet cousin. In $OsCl_2(NaiCH_2Ph)_2$, -CH_2-, group shows AB type quartets at 5.4-5.5 and 5.5-5.6 ppm in blue-

violet isomer while pair of quartets are observed in red-violet complexes at 5.4, 5.5; 5.6, 5.7 ppm. This suggests that the red-violet isomer is less symmetric than blue-violet partner. On comparing with the result of ruthenium (II) complexes of 1-alkyl-2-(naphthtylazo)imidazoles [32] and osmium(II) complexes of 1-alkyl-2-(arylazo)imidazoles [44, 45] we may conclude that blue-violet and red-violet isomers belong to *ctc*-and *ccc*-configuration, respectively. The proton signal pattern in the aliphatic region (4.0 - 6.0 ppm) supports molecular dissymmetry in the complexes and the extend of distortion is more meaningful in red-violet (*ccc*-isomer) than blue-violet (*ctc*-isomer) complexes. Imidazolyl 4- and 5- H appears at 7.0-7.2 and 6.9-7.0 ppm and they are up field shifted by ≥ 0.1 ppm relative to analogous ruthenium(II) complexes. β-Naphthyl ring shows characteristic broad singlet resonance corresponds to 8-H and this indicates inter-ring coupling, which is, absent in α-NaiR group. All other naphthyl ring protons exhibit multiple couple and are assigned on comparing with reported result [31-32].

VIII. 2. D. Electrochemistry

The electrochemical properties of the complexes were examined by cyclic voltammetry at glassy-carbon working electrode in dry MeCN (0.1M TBAP) under N_2 atmosphere and the potentials are reported with reference to the SCE. In the potential range 0.0 to 2.0 V at the scan rate of 50 mVS^{-1} two oxidative responses are observed (**Table VIII. 2, Fig. VIII. 7**). First redox response at 0.55-0.65 and the second couple at 1.2-1.5 V versus SCE are referred to osmium (III)-osmium (II) (Equation 2) and osmium (IV)- osmium (III) (Equation. 3), respectively.

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

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

Second couple shows wider peak-to-peak separation (120-170 mV) than that of first couple (ΔE_p = 80-110 mV). First couple shows well-defined peak potentials than that of second couples (**Fig. VIII. 7**). Bulk electrolysis by coulometric method at 0.75 V *vs* SCE of $[OsCl_2(\alpha\text{–}NaiMe)_2]$ (**3a**) shows one-electron stoichiometry (n = 1.04). Dark blue-violet solution colour changes to orange-red. The negative side of the SCE shows three successive redox responses. First reductive response exhibits well-defined anodic peak on scan reversal while other peaks are illdefined. These reductions are believed to successive electron feeding into the two-azoimine function.[17,18,31,32] The data (**Table VIII. 2**) reveal that the red-violet complexes *ccc*-$OsCl_2(NaiR)_2$ exhibit higher redox potential by ~0.1 V than that of blue-violet isomer. This may be due to the lower symmetry in *ccc*-isomer (C_1-symmetry) than that of *ctc*-isomer (C_2-symmetry). Besides, 1-alkyl-2- (naphthtylazo) imidazole complexes of osmium (II) (**4b**) exhibit lower Os(III)/Os(II) redox couple than that of α-naphthyl analogous (**3**, **5**). This is also reflected from the solution spectral behavior of the complexes: α-naphthylazoimidazole–osmium (II) complexes show higher absorption energy than that of β-naphthylazoimidazole–osmium (II) complexes. This may be due to better thermodynamic stability of β-naphthyl derivatives compared to α-naphthyl derivatives [36,37].

VIII. 3. Experimental

VIII. 3. A. Materials

1-Alkyl-2-naphthyl-(α/β)-azo)imidazoles (α/β-NaiR) (**Chapter – II**) were synthesised as before [31]. Osmium tetroxide was obtained from Johnson Matthey & Co. Ltd., UK. It was converted to $(NH_4)_2[OsCl_6]$ according to a reported method [38]. Solvent purification and reagent synthesis for electrochemical works were

done as before [31]. Commercially available silica gel (60 - 120 mesh) and alumina (neutral) from SRL was used for chromatographic separation. All other solvents and chemicals were of reagent grade and were used without further purification.

VIII. 3. B. Physical Measurements

Microanalyses and spectral measurements and electrochemical studies were carried out as in **Chapter 1.**

VIII. 3.C. Preparation of Compounds

VIII. 3. C. (i) Synthesis of the ligands

Synthesis of the ligands are described in **Chapter II**.

VIII. 3. C. (i) Preparation of ctc- and ccc- dichloro-bis-[1-methyl-2-(naphthyl-α-azo)imidazole] osmium(II), $OsCl_2(\alpha$-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 mL). The solution was refluxed on oil-bath with continious stirring for half-an hour. 1-Methyl-2-(naphthyl-α-azo)imidazole (α-NaiMe) (0.55 g, 2.33 mmol) in methanol was added in drops 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 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 coloured crystalline precipitate was collected by filtration 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 an alumina column (30 × 1 mL). A small portion of the 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 MeOH eluted the red-violet band. 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*-$OsCl_2(\alpha$-NaiR$)_2$ 35% and the red-violet *ccc*- $OsCl_2(\alpha$-NaiR$)_2$, 8 %.

All other complexes were prepared by following the identical procedure and the yields were varied 30-40 % for the blue-violet isomers and 8-14% for the red-violet isomers. Microanalytical data is given in **Table VIII. 1**.

VIII. 4. Epilogue

Synthesis, spectral characterization and redox studies of dichloro-bis-[1-alkyl-2-(naphthyl-(α/β)azo]imidazoleosmium(II) are described . The complexes have been isolated in two isomeric forms; with consideration of coordination pairs of Cl, N(imidazole), and N(azo) around osmium(II) these two isomers are cis-trans-cis and cis-cis-cis. The isomers are characterized by ^{1}H NMR data. In one case, the structure of cis-trans-cis isomer is confirmed by X-ray crystallography. The solution electronic spectra show multiple MLCT transitions and redox properties exhibit Os(III)/Os(II) and Os(IV)/Os(III) couples along with illdefined azo reductions.

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Table. VIII. 1. Microanalytical [a] and IR spectral data.

Compounds	Elemental analysis (%)			IR data [b] (cm^{-1})	
	C	H	N	ν (N=N)	ν (Cl)
ctc-[$OsCl_2$(13Clα–NaiMe)$_2$](**3a**)	45.43 (45.90)	3.27 (3.22)	15.28 (15.21)	1240	290, 310
ccc-[$OsCl_2$(13Clα–NaiMe)$_2$](**5a**)	45.43 (45.87)	3.27 (3.31)	15.28 (15.33)	1235	292, 312
ctc-[$OsCl_2$(13CLβ–NaiMe)$_2$](**4a**)	45.43 (45.90)	3.27 (3.22)	15.28 (15.21)	1237	290, 312
ccc-[$OsCl_2$(13Clβ–NaiMe)$_2$](**6a**)	45.43 (45.90)	3.27(3.22)	15.28 (15.21)	1235	294, 316

[a] Calculated values are in the parentheses. [b] In KBr disc.

Table VII. 2. Electronic spectra [a] and cyclic voltammetric data [c] of [$OsCl_2(NaiR)_2$]

Compds.	Electronic spectra $\lambda_{max,}$ nm (10^{-3} ε M^{-1} cm^{-1})	Os^{III}/Os^{II} $E^1_{1/2}$, V (ΔE_p, mV)	Os^{IV}/OS^{III} $E^2_{1/2}$, V (ΔE_p, mV)	Ligand reductions $E^3_{1/2}$, V (ΔE_p, mV)
(**3a**)	1058(0.211) [b], 734(0.852) [b], 550(4.182), 524(3.668), 425(8.495)	0.594(80)	1.347 (170)	-0.655(120), -0.774[d], -1.50[d]
(**5a**)	1056(0.748)[b],710(1.637)[b],583(5.009), 512(7.597), 445(8.048)	0.622(100)	1.468 (120)	-0.538(110), -0.749[d], -1.42[d]
(**4a**)	1072(0.204)[b], 750(0.539)[b], 570(5.094), 530(3.749), 440(9.058)	0.560(95)	1.247 (140)	-0.725(130), -1.073[d], -1.63[d]
(**6a**)	1058(0.616)[b], 815(0.579)[b],726(0.904)[b], 594(4.382), 530(9.527),445(12.677)	0.603(110)	1.367 (120)	-0.654(140), -0.900[d], -1.48[d]

[a] Solvent $CHCl_3$, [b] Shoulder, [c] Solvent is MeCN, supporting electrolyte Bu_4NClO_4 (0.1 M), solute concentration ~10^{-3} M, scan rate 50 mVS^{-1}, Pt-disk working electrode, measuring and units of symbols are the same as in text, $\Delta E_p = |E_{pa} - E_{pc}|$, mV and [d] E_{pa}, V.

Table VIII. 3. ^{1}H NMR spectral data of isomeric $OsCl_2(NaiR)_2$ in $CDCl_3$

Compounds	δ, ppm (J, Hz)										
	4-H[d]	5-H[a]	8-H[b]	9-H[a]	10-H	11-H[d]	12-14H[d]	15-H[a]	1-Me		
(**3a**)	7.19 (6.0)	6.97 (6.0)		7.77 (8.1)	7.70[c] (9.0)	7.42	7.20-7.30	7.65 (8.0)	3.81		
(**5a**)	7.13 (6.0)	7.00 (6.0)		7.76	7.70[c]	7.40[c]	7.20-7.36	7.70	4.07, 3.91		
(**4a**)	7.03 (6.0)	6.91 (6.0)	7.91		7.44[a] (9.0)	7.38	7.20-7.38	7.51	3.90		
6a)	7.18 (6.0)	7.00 (6.0)			7.75[a]	7.42	7.22-7.40	7.64	4.09, 3.90		

[a] doublet, [b] brought singlet, [c] triplet, [d] multiplet, [e] sextet (J= 12-16 Hz), [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**).