



Original Article

Osmium(II)- Bis-chelated-arylazoimidazole-bipyridine-Complexes: Synthesis and NMR-spectral characterization

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ABSTRACT

Reaction of *ctc*-OsBr₂(RaaiR')₂ [RaaiR' = 1-alkyl-2-(arylazo)imidazole, *p*-R-C₆H₄-N=N-C₃H₂-NN-1-R', where R = H (a), Me (b), Cl (c) and R' = Me (2), Et (3) and CH₂CH₂Ph (4)] with 2,2'-bipyridine (bpy) in presence of AgNO₃ in EtOH followed by the addition of NH₄PF₆ afforded a mixed ligand complex [Os(bpy)(RaaiR')₂](PF₆)₂. Imidazole protons (4- / 4'- , 5- / 5'-) appear usually at lower δ values. Aryl-H (7-H-11'-H / 7'-H – 11'-H) appear as doublet / triplet as per spin-spin interaction pattern. The protons to primed RaaiR' (7'-H to 11'-H) are assigned to the signals those appear at lower δ values.

Keywords: Osmium, 2,2'-bipyridine, arylazoimidazole, NMR spectra.

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. Multinuclear systems of this kind

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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. A few mono and dinuclear complexes of ruthenium(II) of tptz has also been reported (Byabartta P., Pal S., Misra T.K., Sinha C., Liao F.-L., Panneerselvam K., Lu T.-H. *et al.*, (2002). However, our studies reveal that under certain experimental conditions tptz undergoes various metal-assisted reactions. 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. 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. (Saha A., Majumdar P., Peng S.-M., Goswami S., *et al.*, (2000) Byabartta P., Pal S., Misra T.K., Sinha C., Liao F.-L., Panneerselvam K., Lu T.-H., *et al.*, (2002))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 platinum metal complexes, but only a few of the above mentioned ligands have been utilized for the preparation of Os(II) complexes. 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. 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 [Tomarik P., Ratajewicz Z., *et al.*, (1985)]. 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. [Velders A.H., Keojiman H., Spek A.L., Haasnoot J.G., Vos D. de, Reedijk J., *et al.*, 1992]. Azo conjugated transition metal complexes can provide new opportunity towards redox, magnetic and optical properties originating from the d-orbitals [Pouchert J (Ed.), Cotton F A and Wilkinson G, *et al.*, 1994]. A characteristic feature of these conjugated complexes that the transition metals can interact with each other through the π -conjugated backbone to permit electronic communication. Bis-/tris-hetero chelated complexes may exhibit inter-ligand charge transferances along with some structural distortion and/or backbone deformation [Cotton F A and Wilkinson G, Greenwood N N and Earnshaw A, *et al.*, 1989]. Modification has been done substituting six membered pyridine ring by less π -acidic, biologically important five membered imidazole ring e.g., 2-(arylo)imidazole [Misra T K, Das D, Sinha C, Ghosh P K and Pal C K, *et al.*, 1998] and by increasing the number of N in pyridine ring *viz.* 2-(arylo)pyrimidine [Misra T K. and Sinha C, *et al.*, 1999]. Second modification has been carried out replacing pendent aryl group by sterically more crowded, electronically more susceptible naphthyl group from 2-(arylo)imidazole to get 2-(naphthylazo) imidazoles [Dinda J., Santra P.K., Sinha C., Falvello L. R., *et al.*, (2001)]. Pseudooctahedral $\text{OsCl}_2(\text{RaaiR}')_2$ 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 [Constable E C, Bottomley F and Mukaida M, 1982]. According to the sequence of coordination pairs of Cl, N(imidazole) and N(azo) the isomer is *cis-trans-cis*- $\text{OsCl}_2(\text{RaaiR}')_2$; 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 complexes having *cis*- OsBr_2 bonds are more labile [Perrin D D and Armarego W L F *et al.*, 1972] than analogous complexes with *cis*- OsCl_2 group and *ctc*- $\text{OsBr}_2(\text{RaaiR}')_2$ (1) has been used in this work.

EXPERIMENTAL

Material

1-Alkyl-2-(arylo)imidazole was synthesized by the reported procedure [Bianchini C, Peruzzini *et al.*, 1995]. *ctc*- $\text{OsBr}_2(\text{RaaiR}')_2$ was prepared by known method [Pratihari J L, Bhaduri S, Pattanayak P, Patra D and Chattopadhyay S *et al.*, 2009] using $[\text{NH}_4]_2[\text{OsBr}_6]$. Commercially available neutral alumina from SRL was used for chromatographic separations. The purification of solvents for electrochemical and

spectral work and $[\text{Bu}_4\text{N}][\text{ClO}_4]$ were prepared as described earlier [Pratihari J L, Bhaduri S, Pattanayak P, Patra D *et al.*, 2009]. 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 elemental analyser. Solution electronic spectra were recorded on a JASCO UV-VIS-NIR V-570 spectrophotometer. Infrared (IR) spectra were obtained using a JASCO 420 spectrophotometer (using KBr disks, $4000\text{-}200\text{ cm}^{-1}$). The ^1H NMR spectra in CDCl_3 were obtained on a Bruker 300 MHz FT NMR spectrometer using SiMe_4 as internal reference. Solution electrical conductivities were measured using Systronics 304 conductivity meter with solute concentration $\sim 10^{-3}$ M in acetonitrile. Electrochemical work was carried out using a EG & G PARC Versastat computer controlled 250 electrochemical system. All experiments were performed under a N_2 atmosphere at 298K using a Pt-disk milli working electrode. All results were referenced to a saturated calomel electrode (SCE). Reported potentials are uncorrected for junction effect.

Preparation of complexes

$[\text{Os}(\text{bpy})(\text{MeaiMe})_2](\text{PF}_6)_2 \cdot 4\text{H}_2\text{O}$ (**2b**)

To an ethanolic suspension of *trans*- $\text{OsBr}_2(\text{MeaiMe})_2$ (0.758 g, 1.10 mmol), aqueous AgNO_3 (0.343 g, 2.02 mmol) was added and heated to reflux for 2 h. The red violet solution was filtered with G4 crucible and to the filtrate 2,2'-bipyridine (bpy) (0.195 g, 1.25 mmol) was added and again refluxed for 32 h. After reducing the volume of solution to half of its original, aqueous ammonium hexafluorophosphate was added. A brown red product was obtained which was filtered and washed with cold water followed by cold water-ethanol (1:1 v/v) mixture. The product was dried over CaCl_2 in desiccators. The dry product was dissolved in minimum volume of CH_2Cl_2 , and chromatographed over neutral alumina, a red band was eluted with $\text{MeCN-C}_7\text{H}_8$ (1:1). On slow evaporation of the eluent, the required complex was obtained in crystalline form; yield 75%. (1.028 g). The other complexes were obtained in the similar procedure, yield 70-75%. The microanalytical data of the complex are given below.

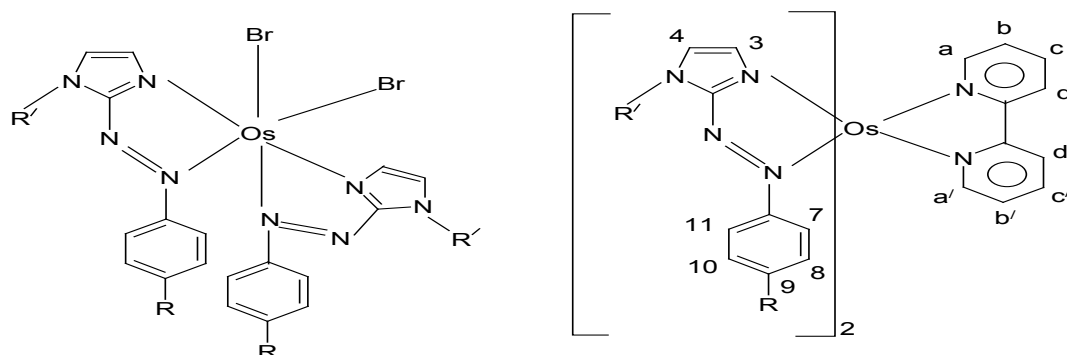
$\text{Os}(\text{bpy})(\text{HaaiMe})_2(\text{PF}_6)_2 \cdot 4\text{H}_2\text{O}$ (**2a**): *Anal.* Found: C, 33.29; H, 3.27; N, 12.88. Calc. for $\text{C}_{30}\text{H}_{36}\text{N}_{10}\text{O}_4\text{P}_2\text{F}_{12}\text{Os}$: C, 33.36; H, 3.36; N, 12.97. $\text{Os}(\text{bpy})(\text{MeaiMe})_2(\text{PF}_6)_2 \cdot 4\text{H}_2\text{O}$ (**2b**): *Anal.* Found: C, 34.55; H, 3.57; N, 12.56. Calc. for $\text{C}_{32}\text{H}_{40}\text{N}_{10}\text{O}_4\text{P}_2\text{F}_{12}\text{Os}$: C, 34.68; H, 3.64; N, 12.64. $\text{Os}(\text{bpy})(p\text{-Cl aaiMe})_2(\text{PF}_6)_2 \cdot 4\text{H}_2\text{O}$ (**2c**): *Anal.* Found: C, 31.28; H, 2.89; N, 12.07. Calc. for $\text{C}_{30}\text{H}_{34}\text{N}_{10}\text{O}_4\text{P}_2\text{F}_{12}\text{Os}$: C, 31.33; H, 2.98; N, 12.18. $\text{Os}(\text{bpy})(\text{HaaiEt})_2(\text{PF}_6)_2 \cdot 4\text{H}_2\text{O}$ (**3a**): *Anal.* Found: C, 34.56; H, 3.57; N, 12.59. Calc. for $\text{C}_{32}\text{H}_{40}\text{N}_{10}\text{O}_4\text{P}_2\text{F}_{12}\text{Os}$: C, 34.68; H, 3.64; N, 12.64. $\text{Os}(\text{bpy})(\text{MeaiEt})_2(\text{PF}_6)_2 \cdot 4\text{H}_2\text{O}$ (**3b**): *Anal.* Found: C, 35.84; H, 3.82; N, 12.25. Calc. for $\text{C}_{34}\text{H}_{44}\text{N}_{10}\text{O}_4\text{P}_2\text{F}_{12}\text{Os}$: C,

35.95; H, 3.90; N, 12.33. Os(bpy)(*p*-Cl₂Et)₂(PF₆)₂. 4H₂O (**3c**): Anal. Found: C, 32.51; H, 3.17; N, 11.78. Calc. for C₃₂H₃₈ N₈ OP₂F₁₂Os: C, 32.62; H, 3.25; N, 11.89. Os(bpy)(HaaiCH₂Ph)₂(PF₆)₂.4H₂O (**4a**): Anal. Found: C, 40.77; H, 3.48; N, 11.27. Calc. for C₄₂H₄₄N₁₀ OP₂F₁₂Os: C, 40.81; H, 3.59; N, 11.33. Os(bpy)(MeaaiCH₂Ph)₂(PF₆)₂. 4H₂O(**4b**): Anal. Found: C, 41.76; H, 3.78; N, 11.01. Calc. for C₄₄H₄₈N₁₀ OP₂F₁₂Os: C, 41.81; H, 3.83; N, 11.08. Os(bpy)(*p*-Cl₂aiCH₂Ph)₂(PF₆)₂.4H₂O (**4c**): Anal. Found: C, 38.56; H, 3.18; N, 10.65. Calc. for C₄₂H₄₂N₈ OCl₂P₂F₁₂Os: C, 38.62; H, 3.24; N, 10.73.

RESULTS AND DISCUSSION

Synthesis and Formulation

1-Alkyl-2-(arylo)imidazole (RaaiR') have been reacted with [NH₄]₂[OsBr₆] in 2-methoxyethanol under reflux for 8h. Two isomers, blue-violet (≥45%) and red-violet (<10%), are separated by chromatography. The blue-violet compound belongs to *cis-trans-cis* and red-violet compound is *cis-cis-cis*-(*ccc*)-OsBr₂(RaaiR')₂. The structure of blue-violet complex in case of OsCl₂(MeaaiMe)₂ has been established as *cis-trans-cis* by X-ray diffraction study [Pratihari J L, *et al.*, 2009]. The abbreviation *cis-trans-cis* (*ctc*) stands for the sequence of coordination of X (X = Cl or Br), N(imidazole) and N(azo) in the complex. The Ag⁺-assisted Br-substitution from *ctc*-OsBr₂(RaaiR')₂ in ethanol followed by filtration in sintered crucible (G4) has synthesized [Os(EtOH)₂(RaaiR')₂]²⁺. Upon treatment of solvated species with 2,2'-bipyridine (bpy) under refluxing condition and addition of [NH₄][PF₆] has isolated [Os(bpy)(RaaiR')₂](PF₆)₂. The composition of the compounds was formulated by elemental analyses. The diamagnetic (t_{2g}⁶) complexes are 1:2 electrolyte in MeCN (230-280 Ω⁻¹cm⁻¹mol⁻¹) and show characteristic absorptions of coordinated RaaiR' and bpy in their spectroscopic data.



ctc-OsBr₂(RaaiR')₂ (**1**)

R = H (**a**), ¹²OMe (**b**), NO₂ (**c**)

R' = ¹²Me (**2**), ¹²CH₂ ¹³CH₃ (**3**), ¹²CH₂ (¹⁴⁻¹⁸)Ph (**4**)

Scheme-1

Spectra and bonding mode

¹H-NMR spectroscopy

¹H-NMR spectra have been used extensively to determine the coordination mode of bpy and RaaiR'. The atom numbering pattern is shown in Scheme 1. The resonances are assigned to hydrogen nuclei of coordinated ligands on comparing with the spectra of free ligands, OsCl₂(RaaiR')₂ and ruthenium complexes, [Ru(bpy)(RaaiR')₂]²⁺. Besides the spin-spin interaction and the effect of substitution helps to identify the NMR signals. The substituent Ar-Me and 1-R' (Me, Et, CH₂Ph) are particularly useful to identify conformational nature of the complex. There is a possibility of existence of diastereomeric forms, however, we have not been able to isolate / separate them. There is a singlet signal corresponding to Ar-OMe group at 2.40-2.44 ppm. This is due to C₂-symmetry in the molecule. However, 1-Me in [Os(bpy)(OMeaaR')₂]²⁺ shows two singlets, the methylene signals of 1-CH₂(CH₃) and 1-CH₂(Ph) appear as set of multiplets and quartets, respectively. Imidazole protons (4- / 4'-, 5- / 5'-) appear usually at lower δ values. Aryl-H (7-H- 11'-H / 7'-H – 11'-H) appear as doublet / triplet as per spin-spin interaction pattern. The protons to primed RaaiR' (7'-H to 11'- H) are assigned to the signals those appear at lower δ values (Table 2, Figure 1).

I.R. spectra

The infrared spectra of the complexes have been compared with the spectra of OsCl₂(RaaiR')₂ and [Ru(bpy)(RaaiR')₂](ClO₄)₂.H₂O and the following conclusions have been drawn. The ν(N=N), ν(C=N), and ν(H₂O) appear at 1370-1390, 1590-1610 and 3420-3460 cm⁻¹ respectively. The hexafluorophosphate (PF₆) exhibits strong stretching at 840-850 cm⁻¹.

CONCLUSION

A novel series of tris chelated osmium complexes were synthesised from its dichloro precursor. This follows a heteroleptic tris-chelated complex formation pathway. Imidazole protons (4- / 4'-, 5- / 5'-) appear usually at lower δ values. Aryl-H (7-H- 11'-H / 7'-H – 11'-H) appear as doublet / triplet as per spin-spin interaction pattern. The protons to primed RaaiR' (7'-H to 11'- H) are assigned to the signals those appear at lower δ values

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REFERENCES

- Akasaka T., Otsuki J., Araki K., (2002). *Chem. Eur. J.* 130
- Au Y.-K., Cheung K.-K., Wong W.-T., (1995) *Inorg. Chim. Acta.* 238 193.
- B. Mondal, H. Paul, V.G. Puranik, G.K. Lahiri, *J. Chem. Soc., Dalton Trans.* 481(2001).
- Bock H., Dienelt R., Schodel H., Van T.T.H., (1998). *Struet. Chem.* 9 279
- Byabartta P, Jasimuddin Sk, Ghosh B K, Sinha C, Slawin A M Z and Woollins J D, 2002 *New J. Chem.*, 26, 1415.
- Byabartta P, Pal S, Misra T K, Sinha C, Liao F -L, Panneerselvam K and Lu T -H, 2002 *J. Coord. Chem.*, 55(5), 479.
- Byabartta P, Pal S, Ray U and Sinha C, 2001, *Indian J. Chem.*, 40A, 896.
- Byabartta P, Santra P K, Misra T K, Sinha C and Kennard C H L, 2001 *Polyhedron*, 20, 905.
- Byabartta P., Pal S., Misra T.K., Sinha C., Liao F.-L., Panneerselvam K., Lu T.-H., (2002) *J. Coord. Chem.* 55 479 and reference therein.
- Byabartta P., Jasimuddin Sk, Ghosh B.K., Sinha C., Slawin A.M.Z., Woollins J.D., (2002). *New J. Chem.* 26 1415
- Byabartta. P, Dinda J, Santra P K, Sinha C, Panneerselvam K, Liao F -L and Lu T - H, 2001 *J. Chem. Soc., Dalton Trans.*, 2825.
- Campagna S., Serroni S., Puloriero F., Pietro C. Di, (2001) in *Electron Transfer in Chemistry* (Ed.), V. Balzani, (vol. 5)VCH-Wiley, Weinheim,
- Constable E C, 1989 *Coord. Chem. Rev.*, 93, 205; Bottomley F and Mukaida M, 1982 *J. Chem. Soc., Dalton Trans.*, 1933.
- Constable E.C., (1989). *Coord. Chem. Rev.* 93 205
- Cotton F A and Wilkinson G, *Advanced Inorganic Chemistry*, 5th Edn, Wiley-Interscience, 1994, p-338; Greenwood N N and Earnshaw A, *Chemistry of the Elements*, Pergamon Press, 1989 Oxford, p-519.
- Das D, *Ph. D. Thesis*, 1998, Burdwan University, Burdwan; Saha A, Das C, Goswami S and Peng S -M, 2001, *Indian J. Chem*, 40A, 198;
- Deb A.K., Goswami S., (1993). *Polyhedron* 12 1419
- Deb A.K., Paul P.C., Goswami S., (1988). *J. Chem. Soc., Dalton Trans.* 2051
- Dinda J., Santra P.K., Sinha C., Falvello L. R., (2001). *J. Organomet. Chem.* 629, 28
- Fees J., Hausen H.D., Kaim W., *Naturoforsch Z.* (1995).50B 15
- Ghosh B.K., Chakravorty A., (1989). *Coord. Chem. Rev.* 95 239
- Ghosh P, Pramanik A, Bag N, Lahiri G K and Chakravorty A, 1993 *J. Organomet. Chem.*, 454, 237.
- Goswami S., Chakravorty A.R., A. Chakravorty, (1982). *J. Chem. Soc., Chem. Commun.* 1288
- Grover N, Gupta N and Thorp H H, 1932 *J. Am. Chem. Soc.*, 114, 3390 .

- Hartmann H., Scheiring T., Fiedler J., Kaim W., (2000). *J. Organomet. Chem.* 604 267
- Kaes C., Katz A., Hosseini M.W., (2000). *Chem. Rev.* 100 3553,
- Kaim W., Kohlmann S., Jordanov J., Fenske D., (1991). *Z. Anorg. Alleg. Chem.* 598/599 217
- Kalyansudaram K., (1992). *Photochemistry of Polypyridine and Porphyrine complexes*, Academic press, London,
- Menon M., Pramanik A., Chakravorty A., (1995). *Inorg. Chem.* 34 3310
- Misra T K. and Sinha C, 1999 *Indian J. Chem.*, 38A, 346; 1999. *Transition Met. Chem.*, 24
- Misra T.K., Das D., sinha C., Ghosh P.K., Pal C.K., (1998). *Inorg. Chem.* 37 1672
- Mondal B, Paul H, Puranik V G and Lahiri G K, 2001 *J. Chem. Soc., Dalton Trans.*, 481.
- Otsuki J., Sato K., Tsujino M., Okuda N., Araki K., Seno M., (1996). *Chem. Lett.* 847
- Pal S, Misra T K, Sinha C, Slawin A M Z and Woollins J D, 2000 *Polyhedron*, 19, 1925.
- Pal S., Misra T.K., Sinha C., Slawin A.M.Z., Woollins J.D., (2000). *Polyhedron* 19 1925
- Perrin D D and Armarego W L F 1988 *Purification of laboratory chemicals*, 3rd edn.; New York:
- Pouchert J (Ed.), *The Aldrich library of NMR spectra*, Vol 2, Aldrich Chem Co Inc, USA 1993;
- Pramanik K., Shivakumar M., Ghosh P., Chakravorty A., (2000). *Inorg. Chem.* 39 195
- Pramanik K., Shivakumar M., Ghosh P., Chakravorty A., (2000). *Inorg. Chem.* 39 195
- Saha A., Majumdar P., Peng S.-M., Goswami S., (2000) *Eur. J. Inorg. Chem.* 2631 and references therein.
- Samanta R, Munsu P, Santra B K and Lahiri G K, 1999 *Polyhedron* 19, 995;
- Santra B.K., Lahiri G.K., *Proc. (1999) Indian Acad. Sci (Chem Sci).* 111 509 and references therein.
- Santra P.K, Roy R., Sinha C., (2000). *Proc. Indian Acad. Sci. (Chem. Sci).* 112 523
- Santra P.K., Byabartta P., Chattopadhyay S., Falvello L.R., Sinha C., (2002) *Eur. J. Inorg. Chem.* 1124
- Santra P.K., Das D., Misra T.K., Ray R., Sinha C., Peng S.-M., (1999). *Polyhedron* 18 1909
- Seal A and Ray S, 1984 *Acta Crystallogr., Sect C : Struct. Commun.*, C40, 929.
- Shivakumar M., Pramanik K., Bhattacharya I., Chakravorty A., (2000). *Inorg. Chem.* 39 4332
- Shivakumar M., Pramanik K., Ghosh P., Chakravorty A., (1998). *Chem. Chommun.* 2103

- Shivakumar M., Pramanik K., Ghosh P., Chakravorty A., (1998). *Inorg. Chem.* 37 5968
- Srinivasan B R, Sarkar S, 1990 *Inorg. Chem.*, 29, 3898. Chattopadhyay S, Ghosh K, Pattanayak S and Chakravorty A, 2001 *J. Chem. Soc., Dalton Trans.*, 1259.
- Tomarik P., Ratajewicz Z., . (1985). *The Chemistry of Heterocyclic Compounds: part 6, Pyridine Metal Complexes, (vol.14).* Wiley
- Velders A.H., Keojiman H., Spek A.L., Haasnoot J.G., Vos D. de, Reedijk J., (2000). *Inorg. Chem.* 39 2966.
- Vliet. P M, Haasnoot J G and Reedijk J, 1994, *Inorg. Chem.* 33, 1934. Misra T K, Das D, Sinha C, Ghosh P K and Pal C K, 1998 *Inorg. Chem.*, 37, 1672.
- Ward M.D., Mc Cleverty J.A., (2002). *J. Chem. Soc., Dalton Trans.* 275
- Wong W.Y., Cheung S.–H., Lee S.–M., Leung S.Y., (2000). *J. Organomet. Chem.* 596 36
- Wu F., Chamchoumis C.M., Thummel R. P., (2000). *Inorg. Chem.* 39 584

Table 1: ¹H-Nmr Spectra Of The Complexes, [Os(bpy)(RaaiR')₂](PF₆)₂ IN MECN

Compound	δ, ppm (J, Hz)													
	4-H 4'- H ^b	5-H 5'-H ^b	7-H 7'-H ^b	8,10- (8'-10')- H	9-(9')- H	11- (11') ^b - H	a,a'-H ^b	b,b'-H ^c	c,c'-H ^c	d,d'-H ^b	9- Me	1- Me	13-Me	12- CH ₂
2a	7.11 (5.2)	6.92 (5.2)	7.24 (7.0)	7.87 ^e	7.87 ^e	7.41 (7.0)	8.49 (8.0)	8.12 (8.0)	7.90 (8.0)	7.55 (8.0)		4.34, 4.40 ^e		
2b	6.66 (6.0)	6.31 (7.0)	7.18 (7.0)	7.19 ^b (8.0)		7.30 (7.5)	8.52 (8.0)	8.11 (8.0)	7.83 (8.0)	7.60 (8.0)	2.40	4.34, 4.36 ^e		
2c	7.10 (6.0)	6.95 (6.0)	7.18 (7.0)	7.95 ^b (8.0)		7.45 (7.0)	8.50 (8.0)	8.14 (8.0)	7.90 (8.0)	7.60 (8.0)		4.35, 4.40 ^e		
3a	7.11 (5.0)	6.86 (5.0)	7.28 (7.0)	7.82 ^e	7.82 ^e	7.41 (7.0)	8.48 (8.0)	8.11 (8.0)	7.85 (8.0)	7.59 (8.0)			1.34	3.52
3b	6.74 (6.0)	6.44 (6.0)	7.30 (7.0)	7.20 ^b (8.0)		7.34 (7.5)	8.53 (8.0)	8.14 (8.0)	7.91 (8.0)	7.62 (8.0)	2.44		1.42	3.92
3c	7.12 (6.5)	6.90 (6.5)	7.12 (7.0)	7.95 ^b (8.0)		7.47 (7.0)	8.50 (8.0)	8.10 (8.0)	7.86 (8.0)	7.50 (8.0)			1.44	4.30, 4.14
4a	7.09 (5.4)	6.94 (5.4)	7.30 (7.0)	7.90 ^e	7.90 ^e	7.46 (7.0)	8.50 (8.0)	8.12 (8.0)	7.88 (8.0)	7.60 (8.0)				5.53, 5.60 ^d
4b	7.02 (6.0)	6.81 (6.0)	7.11 (7.0)	7.17 ^b (8.0)		7.31 (7.0)	8.54 (8.0)	8.11 (8.0)	7.88 (8.0)	7.58 (8.0)	2.40			5.56, 5.61 ^d
4c	7.11 (6.0)	6.94 (6.0)	7.18 (7.0)	7.92 (8.0)		7.49 (7.0)	8.52 (8.0)	8.14 (8.0)	7.85 (8.0)	7.54 (8.0)				5.55, 5.60 ^d

^a in CD₃CN, ^b Doublet; ^cTriplet; ^d Phenyl protons; ^e multiplet; δ 7.35-7.50, -CH₂- shows AB type quartets.