Inorg. Chem. **2002**, *41*, 6343–6350

Inorganic Chemistry
Article

Photoinduced and Chemical Oxidation of Coordinated Imine to Amide in Isomeric Osmium(II) Complexes of N-Arylpyridine-2-carboxaldimines. Synthesis, Characterization, Electron Transfer Properties, and Structural Studies

Amit K. Ghosh,[†] Kunal K. Kamar,[†] Parimal Paul,[‡] Shie-Ming Peng,[§] Gene-Hsiang Lee,[§] and Sreebrata Goswami*,[†]

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata 700 032, India, Department of Silicates and Catalysis, Central Salt and Marine Chemicals Research Institute, Bhavnagar—364 002, India, and Instrumentation Center, National Taiwan University, Taipei, Taiwan, Republic of China

Received July 15, 2002

The reaction of *N*-arylpyridine-2-carboxaldimine [$C_5H_4NC(H)NC_6H_4R$] (HL) with ammonium hexabromoosmate $(NH_4)_2$-[$OsBr_6$] in boiling 2-methoxyethanol afforded a violet solution from which two geometrical isomers of [$OsBr_2(HL)_2$] (**1** and **2**) were isolated. These are characterized by analytical and spectroscopic data. ^{1}H NMR spectral data were used for the identification of the isomers. The blue-violet isomer, **1** (designated as ctc), has a 2-fold symmetry axis and gave rise to resonances for only one coordinated HL. The geometry of the ctc-isomer was, however, revealed from the X-ray structure determination of a representative example. The red-violet isomer (**2**, designated as ccc), on the other hand, is unsymmetrical and gave rise to a large number of proton resonances. The isomeric complexes, [$OsBr_2(HL)_2$], showed intense MLCT transitions in the visible region. This transition, in the ccc-isomer, is slightly (10 nm) red shifted in comparison to the ctc-isomer. These diimine complexes showed one metal based reversible oxidation assignable to the Os(III)/Os(II) process followed by two irreversible oxidations at more anodic potentials (>1.4 V). In addition to these, the complexes also showed two irreversible ligand reductions at high cathodic potentials (<–1.4 V). An unusual type of photochemical transformation of the azomethine function of coordinated HL in osmium compounds **1** is studied. When an air equilibrated acetonitrile solution of **1** was exposed to a xenon lamp, it underwent oxidation affording the mixed ligand, amido complexes of general formula [$OsBr_2(HL)(LO)$], **3** (LO = $C_5H_4NC(O)–N–C_6H_4R$), in an excellent yield (>95%). This transformation (**1** → **3**) was achieved chemically when H_2O_2 was used as an oxidant. Notably, the chemical oxidation with H_2O_2 also led to the formation of a tetravalent complex, [$OsBr_2(LO)_2$], **4**, as a minor product. Compound **3** was characterized by various spectroscopic and analytical techniques. The room temperature magnetic moment of **3** corresponds to a t_2^5 configuration for the osmium(III) center. EPR spectra of the amido complexes were recorded at 77 K in 1:1 dichloromethane–toluene glass, and they were anisotropic in nature. FAB mass spectra of **3** displayed intense peaks due to parent molecular ions. For example, the complex [$OsBr_2(HL^1)(L^1O)$], **3a**, showed a strong peak at *m*/*z* 729 amu. The electronic spectrum of compound **3** consisted of a broad LMCT transition (ca. 525 nm; ϵ, 3000 M^{-1} cm^{-1}). The cyclic voltammogram of compound **3** consisted of two responses, one each on the positive and negative side of SCE, corresponding to Os(IV)/Os(III) (ca. 0.8V) and Os(III)/Os(II) (ca. –0.3V) couples, respectively. There has been a large cathodic shift of potential for the Os(III)/Os(II) couple in **3** in comparison to that in the parent complex, **1**. The diamido compound [$OsBr_2(LO)_2$], **4**, is diamagnetic and insoluble in common solvents. The X-ray structure determination of a representative sample, **4a**, is reported. The molecule contains a C_2-symmetry axis with bromide ions in relative cis positions. The Os–N(amide) bond lengths are considerably shorter than the Os–N(pyridine) lengths. All other bond lengths and angles fall within the expected range.

Introduction

The chemistry of ruthenium(II) and osmium(II) complexes of α-diimino ligands has been a subject of current interest[1–3] primarily because of its relevance to the photophysical, photochemical, and redox phenomena. In this respect, the literature on the complexes of 2,2′-bipyridine and 1,10-

---

* To whom correspondence should be addressed. Fax: +91-33-473 2805. E-mail: icsg@mahendra.iacs.res.in.

[†] Indian Association for the Cultivation of Science.

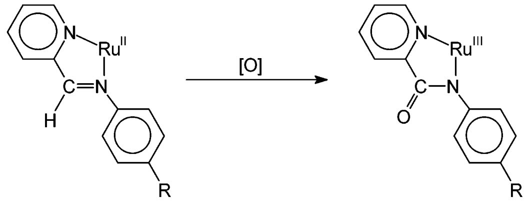
[‡] Central Salt and Marine Chemicals Research Institute.

[§] National Taiwan University.

(1) Griffith, W. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 4, p 519. (b) Schröder, M.; Stephenson, T. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G.; McCleverty, J. A.; Eds.; Pergamon: Oxford, U.K., 1987; Vol. 4, p 277.

10.1021/ic020454s CCC: \$22.00

Scheme 1

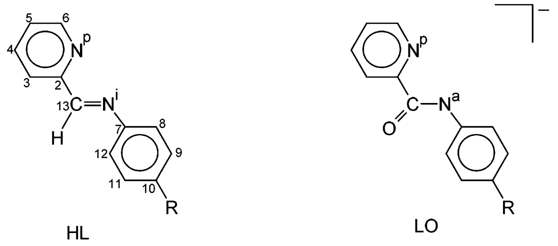


phenanthroline ligands is quite extensive and is growing rapidly. Over the past few years, we have been working[4−7] on the coordination chemistry of the Schiff base ligand, *N*-arylpyridine-2-carboxaldimines (HL). We became interested in this ligand system because of its close relationship with the much better known ligand, 2,2′-bipyridine. It may be noted here that ruthenium and osmium complexes of Schiff base ligands are relatively difficult to synthesize because these undergo hydrolyses easily.

The first report[8] of the ruthenium complex of HL was by Wilson and Dose, who described the synthesis and spectral and redox properties of $[Ru(HL)_3](PF_6)_2$. Subsequently, Belser and Zelewski reported[9] the crystal structure of $[Ru(HL)(bpy)_2](PF_6)_2$. More recently, we reported the complexes of types $[RuCl_2(HL)_2]$ and $[Ru(HL)_3](ClO_4)_2$, which showed interesting spectroscopic and redox properties. An unusual type of ruthenium-promoted chemical oxidation of the coordinated imine function[10] of HL leading to the formation of mixed ligand amido ruthenium(III) complexes of type $[RuCl_2(HL)(LO)]$ was noted by us some time ago (Scheme 1). In the recent past, there have been a few reports[11] from Chakravorty's group on similar imine → amide oxidation in some related ruthenium aldimine systems.

In comparison, the corresponding osmium complexes are not available in the literature. Because the osmium(II) complexes are more easily oxidizable than the corresponding ruthenium(II) complexes, we thought it worthwhile to examine the aforesaid metal-mediated ligand oxidation reaction using the osmium analogue as a mediator. However, the chemical transformation of uncoordinated aldimines → amide is otherwise not achievable. In this paper, we wish to report synthesis, characterization, crystal structure, and redox properties of the isomeric osmium diimine complexes, $[OsBr_2(HL)_2]$. As noted, one of the primary concerns of this work was to explore the oxidation of the coordinated diimine ligand, HL, in the complexes. A novel photoinduced aerial oxidation of the coordinated imine function in $[OsBr_2(HL)_2]$ is introduced herein. Chemical oxidation, of $[OsBr_2(HL)_2]$ using H_2O_2 as an oxidant, produced an osmium(IV) complex, $[OsBr_2(LO)_2]$, along with the mixed ligand osmium(III) intermediate complex, $[OsBr_2(HL)(LO)]$. The corresponding ruthenium(IV) analogue, however, was not achievable[10] from a similar reaction. The ligands, used in this work, along with their complexes are collected in Chart 1.

Chart 1



R	HL	LO	$OsBr_2(HL)_2$, **1**	$OsBr_2(HL)(LO)$, **3**	$OsBr_2(LO)_2$, **4**
H	HL^1	L^1O	**1a**	**3a**	**4a**
Me	HL^2	L^2O	**1b**	**3b**	**4b**
OMe	HL^3		**1c**		

Results and Discussion

A. Osmium(II) Diimine Complexes. A solution of the diimine ligand, HL, in 2-methoxyethanol reacts with the salt $(NH_4)_2[OsBr_6]$ under dinitrogen and affords the complexes $[OsBr_2(HL)_2]$ via reductive substitution and chelation. On chromatographic separation, a major blue-violet (isomer ctc) (**1a**−**c**) isomer and a minor red-violet (isomer ccc) (**2a**) isomer are obtained in the case of unsubstituted HL^1. However, in the cases of the substituted ligands, HL^2 and HL^3, there is no evidence for the occurrence of the ccc-isomer. Considering the unsymmetrical bidentate chelation of HL, the pseudo-octahedral dibromo complex, $[OsBr_2(HL)_2]$, can in principle occur in five geometrically isomeric forms. The isomer description in this type of complex can best be made[4] by considering the relative orientation of the coordinating pairs of Br, N^p, and N^i in that order. Thus, a ctc-isomer means that two coordinated bromide ions and the pair of imine nitrogens (N^i) are in relative cis positions while the two pyridine nitrogens (N^p) are mutually trans. Unlike the other four isomers, only the all cis isomer (ccc) of $[OsBr_2(HL)_2]$ is completely devoid of any symmetry, which has been reflected in the complex pattern of the ^1H NMR spectrum of ccc-$[OsBr_2(HL^1)_2]$. Because this isomer is obtained as a minor product and only in the case of HL^1, we do not consider it any more in our discussion. Its physicochemical data are collected in the tables. The ctc-isomer of $[OsBr_2(HL)_2]$, **1**, is characterized by spectroscopic

---

(2) Hui, J. W.-S.; Wong, Y.-T. *Coord. Chem. Rev.* **1998**, *172*, 389. (b) Charmant, J. P. H. *Coord. Chem. Rev.* **1998**, *172*, 437. (c) Cola, L. D.; Belser, P. *Coord. Chem. Rev.* **1998**, *177*, 301. (d) Keene, F. R. *Coord. Chem. Rev.* **2002**, *187*, 121. (e) Furue, M.; Ishibashi, M.; Satoh, A.; Oguni, T.; Maruyama, K.; Sumi, K.; Kamachi, M. *Coord. Chem. Rev.* **2000**, *208*, 103. (f) van Slageren, J.; Hartt, F.; Stufkens, D. J.; Martino, D. M.; van Willigen, H. *Coord. Chem. Rev.* **2000**, *208*, 309. (g) von Zelewsky, A.; Belser, P.; Hayoz, P.; Dux, R.; Hua, X.; Suckling, A.; Stoeckli-Evans, H. *Coord. Chem. Rev.* **1994**, *132*, 75.

(3) Juris, A.; Prodi, L.; Harriman, A.; Ziessel, R.; Hissler, M.; Elghayoury, A.; Wu, F.; Riesgo, E. C.; Thummel, R. P. *Inorg. Chem.* **2000**, *39*, 3590. (b) Cocker, T. M.; Bachman, R. E. *Inorg. Chem.* **2001**, *40*, 1550. (c) Burger, P.; Fox. T. *Eur. J. Inorg. Chem.* **2001**, 795.

(4) Choudhury, S.; Kakoti, M.; Deb, A. K.; Goswami, S. *Polyhedron* **1992**, *11*, 3183.

(5) Choudhury, S.; Deb, A. K.; Goswami, S. *J. Chem. Soc., Dalton Trans.* **1994**, 1305.

(6) Goswami, S.; Choudhury, S. *Polyhedron* **1996**, *15*, 1191.

(7) Mitra, K. N.; Choudhury, S.; Goswami, S.; Peng, S.-M. *Polyhedron* **1997**, *16*, 1605.

(8) Dose, E. B.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 2660.

(9) Belser, P.; von Zelewsky, A. *Helv. Chem. Acta* **1980**, *63*, 1675.

(10) Menon, M.; Choudhury, S.; Pramanik, A.; Deb, A. K.; Chandra, S. K.; Bag, N.; Goswami, S.; Chakravorty, A. *Chem. Commun.* **1994**, 57.

(11) Dirghangi, B. K.; Menon, M.; Pramanik, A.; Chakravorty, A. *Inorg. Chem.* **1997**, *36*, 1095. (b) Menon, M.; Pramanik, A.; Bag, N.; Chakravorty, A. *Inorg. Chem.* **1994**, *33*, 403.

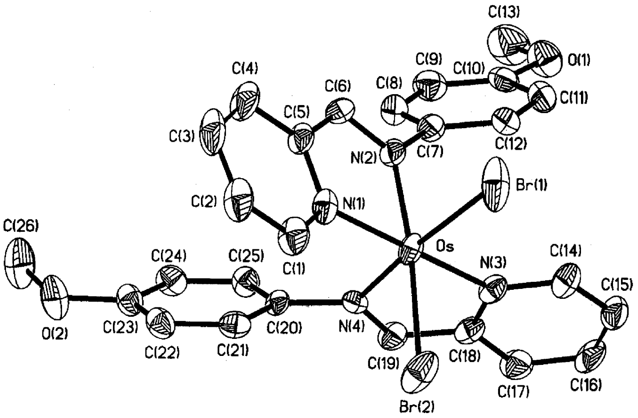


Figure 1. ORTEP plot and atom numbering scheme for ctc-$[OsBr_2(HL^3)_2]$, **1c**. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths [Å] for **1c** and **4a**

$[OsBr_2(HL^3)_2]$, **1c**		$[OsBr_2(L^1O)_2]$, **4a**	
Os−N(1)	2.057(7)	Os(1)−N(101)	2.070(4)
Os−N(2)	2.006(8)	Os(1)−N(102)	1.952(5)
Os−N(3)	2.056(7)	Os(1)−N(103)	2.079(5)
Os−N(4)	2.003(7)	Os(1)−N(104)	1.951(4)
Os−Br(1)	2.5313(12)	Os(1)−Br(11)	2.5546(7)
Os−Br(2)	2.5501(12)	Os(1)−Br(12)	2.5028(7)
C(5)−C(6)	1.410(13)	C(105)−C(106)	1.482(8)
C(6)−N(2)	1.317(10)	C(106)−O(101)	1.210(8)
C(18)−C(19)	1.427(12)	C(106)−N(102)	1.402(8)
C(19)−N(4)	1.320(10)	C(118)−C(119)	1.492(8)
		C(119)−O(102)	1.205(7)
		C(119)−N(104)	1.398(7)

data, and a definitive assignment based on the three-dimensional X-ray structure determination is made. The ^1H NMR spectra of the complexes **1a**−**c** are well resolved. A representative spectrum of **1b** is submitted as Supporting Information, Figure S1. The spectrum of **1a** consists of six aromatic resonances in the range 6.5−9.3δ. Two doublets and two triplet resonances,[4] each of which corresponds to one proton signal in the range 7.8−9.3δ, are assigned to pyridyl proton signals. The resonance at 6.55δ is a coincident doublet arising out of 8H and 12H (Chart 1). A sharp singlet at 8.85δ is assigned to 13H. The other two complexes, **1b** and **1c** of HL^2 and HL^3, respectively, showed a methyl resonance each at 2.22 and 3.72δ. The resonance due to 10H is absent in these two complexes, and the resonance due to 9H and 11H become coincident doublets. Thus, the NMR spectral pattern of the complexes **1a**−**c** clearly exhibits one signal for each proton of the ligand HL. It confirms that isolated compounds are isomerically pure and the two chelate rings are magnetically equivalent. Its geometry is finally confirmed from the X-ray crystal structure determination of the representative **1c**.

Suitable crystals of **1c** for X-ray structure determination are obtained by the slow diffusion of a dichloromethane solution of the compound into hexane. An ORTEP plot of the molecule, along with an atom numbering scheme, is displayed in Figure 1. Table 1 collects the selected bond lengths and bond angles of this compound. The coordination sphere involves $OsBr_2N_4$. The two bromide ions are cis to each other. The isomer description is cis, trans, cis, or ctc as noted before. This isomer contains a C_2 symmetry, which bisects the Br(1)−Os−Br(2) angle and also the N(2)−Os−N(4) angle. There are two types of Os−N bonds in the reference compound. Notably, the Os−N imine lengths [av 2.004(7) Å] are shorter than the corresponding Os−N(py) lengths[12] [av 2.056(7) Å]. The π^* orbital of the imine chromophore lies below[13] that of the pyridine, and hence, greater Os-(dπ)−π^*(imine) interactions are expected. Stronger π-interactions of osmium(II) and the imine function are no doubt responsible for the relatively short Os−N(imine) bond lengths in **1c**. This effect has also been reflected in the elongation of C−N bond distances in this compound. For example, the C−N length [av 1.318(10) Å] in **1c** is appreciably longer[14] than an uncoordinated C═N length observed in a Schiff base ligand. The Os−Br lengths average 2.540(12) Å, which compare well with the corresponding lengths[15] in the related dibromo systems.

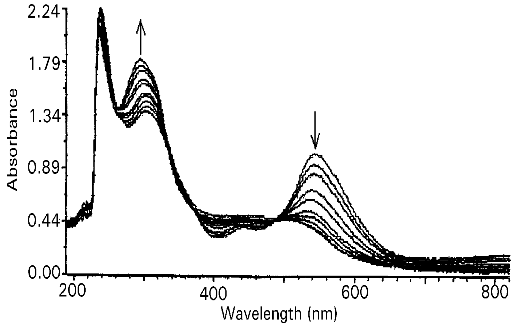


Figure 2. Spectral changes of an acetonitrile solution of ctc-$[OsBr_2(HL^1)_2]$, **1a**, as a function of time due to exposure to a xenon lamp.

B. Photochemical Oxidation of the Coordinated Azomethine Function in $[OsBr_2(HL)_2]$. It was observed that the violet solution of $[OsBr_2(HL)_2]$, **1**, on exposure to a xenon lamp (100 W) slowly became brown. The spectral change was monitored as a function of time (Figure 2). To isolate the product from this photoinduced reaction, bulk photolysis experiments on the compounds were performed at 300 K. The resulting, brown solution, upon evaporation, yielded **3** in almost quantitative yield.[16] The complexes **3a** and **3b** gave consistent elemental analysis. FAB mass spectra (Supporting Information, Figure S2) along with their elemental analyses have indeed confirmed their formulation. Complex **3a** displayed a peak due to the parent molecular ion at m/z = 729 amu, while that for **3b** appeared at m/z = 757 amu. Each of them also showed an intense peak at 650 and 678 amu, respectively, due to dissociation of a coordinated bromide ion. These complexes are paramagnetic. Room temperature (300 K) magnetic moments of the solid samples of **3** lie in the range 1.82−1.86 μ_B. Thus, the compounds are in the low spin states, that is, t_2^5 [Os(III)]. By contrast, the starting diimine complexes **1** are diamagnetic [Ru(II); t_2^6, vide supra]. EPR spectra of compounds **3** were recorded in 1:1 dichlo-

---

(12) Ghosh, B. K.; Mukhopadhyay, A.; Goswami, S.; Ray, S.; Chakravorty, A. *Inorg. Chem.* **1984**, *23*, 4633.

(13) Stufkens, D. J. *Coord. Chem. Rev.* **1990**, *104*, 39.

(14) Basuli, S.; Peng, S.-M.; Bhattacharya, S. *Inorg. Chem.* **2000**, *39*, 1120.

(15) Mitra, K. N.; Goswami, S. *Inorg. Chem.* **1997**, *36*, 1322.

(16) The mixed ligand osmium compounds are crystalline but unfortunately do not produce X-ray quality crystals. However, their identity was established, beyond doubt, on the basis of their physicochemical data.

Table 2. Characterization Data

	IR (ν, cm^{-1})[a]				EPR[c]		FAB[d]
cmpd	ν(C=N)	ν(C−N)	ν(C=O)	μ_B	g_1	g_2	(amu)
1a	1590			*b*			714
2a	1595			*b*			714
1b	1595			*b*			*e*
1c	1590			*b*			*e*
3a	1600	1100	1630	1.82	2.67	2.55	729, 650
3b	1600	1125	1635	1.86	2.72	2.50	757, 678

[a] In KBr disk. [b] Diamagnetic. [c] In 1:1 dichloromethane−toluene glass at 77 K. [d] In *m*-nitrobenzyl alcohol matrix. [e] Not measured.

romethane−toluene glass at 77 K. The spectra are anisotropic in nature with two distinct resonances (g_1 and g_2); the third resonance (g_3) was not detectable in any of the cases. The nonappearance of the g_3 signal in osmium(III) complexes was documented[17] in the literature. Selected characterization data are collected in Table 2.

Photochemical oxidation of an imine function of this type is unique, and this transformation was not observed with the uncoordinated ligand HL. The reaction occurs smoothly in air equilibrated acetonitrile. We propose that the excited state of bis-diimine complex [**1**]* is quenched by transferring an electron from the metal ion to the dissolved oxygen in solution under the experimental conditions. Molecular oxygen is one of the few molecules known[18] to quench the excited state efficiently in the case of polypyridine complexes of osmium(II) by an electron transfer. The process, therefore, resulted in the formation of [**1**]$^+$ and O_2^-. The higher oxidation of osmium in [**1**]$^+$ should have a sufficient polarizing effect on the aldimine function to make the carbon site electrophilic enough for the attack of reactive O_2^- as shown in Scheme 2. The C−H and O=O bonds in the intermediate complex then undergo photoinduced homolytic cleavage,[19] which resulted in the transformation of the ligand into an amido complex, and the $^\bullet$OH radical is generated. The formation of C=O by photochemical reaction[20] between alkane or alkene and dioxygen in the presence and absence of metal complex is documented in the literature. The hydroxy radical, thus formed, reacts to yield H_2O and O_2 (Scheme 2). This photochemical process, therefore, formed a stable osmium(III) complex with the oxidation of one ligand from the imine to the amido form. Because the osmium(III) complex is not photoactive, the transformation of the second coordinated imine ligand did not occur photochemically. However, further oxidation of the second imine ligand was achieved chemically (vide infra).

C. Chemical Oxidation of [OsBr$_2$(HL)$_2$], 1. Oxidation of the osmium(II) imine complex [OsBr$_2$(HL)$_2$], **1**, with H_2O_2 also afforded the brown trivalent complex, [OsBr$_2$(HL)(LO)], **3**, in an excellent yield. The physicochemical properties of the sample obtained from chemical oxidation exactly correspond to those of the sample obtained from the aforesaid photochemical reactions. Prolonged exposure of complex **1** to a concentrated aqueous solution of H_2O_2 led to the formation of a few insoluble dark crystals of the tetravalent complex, [OsBr$_2$(LO)$_2$], **4**, as a minor product (ca. 2%) along with trivalent complex **3** in 90% yield. For comparison, the analogous ruthenium complex, [RuCl$_2$(HL)$_2$], produces[10] only the trivalent complex, [RuCl$_2$(HL)(LO)], from a similar reaction. However, the existence of the corresponding tetravalent complex, [RuCl$_2$(LO)$_2$], was not observable.

By analogy with the proposed reaction scheme[11] for the ruthenium counterpart, we propose that the initial oxidation of the bivalent complex (**1** → **1**$^+$) followed by the addition of H_2O to the polarized aldimine function and rapid oxidation of the hydroxy-amine intermediate to **3** are the primary steps that are involved in the oxidation reaction (**1** → **3**). An identical series of reactions on **3** would, in principle, produce **4**. We, however, note here that, although conversion of **1** → **3** is facile and almost quantitative, the conversion of **3** → **4** is sluggish with the yield of **4** being poor. It may be noted here that the oxidation of **3** → **3**$^+$ is more difficult than that of **1** → **1**$^+$ (vide infra). Unfortunately, the ligand oxidation reaction with a stronger oxidant, Ce^{4+}, produced a mixture of several unidentified products, which could not be purified. We wish to note here that the transformation **1** → **4** represents the first instance[10,11] where both the coordinated imine functions in a bischelate have undergone oxidation to corresponding amide functions with concomitant 2e$^-$ oxidation of the metal center. The tetravalent compounds, **4**, are diamagnetic[17b,21] and are insoluble in all common solvents. We are fortunate to have X-ray quality crystals of representative compound **4a** directly from the reaction mixture, which allowed us to confirm its identity though its structure determination.

An ORTEP plot of the compound [OsBr$_2$(L^{1}O)$_2$], **4a**, is shown in Figure 3, and important bond distances and angles are tabulated in Table 1. The structure analysis of **4a** has indeed confirmed its formulation. The coordination sphere involves OsBr$_2$N$_4$. The two bromide ions are cis to each other, the pair of pyridine nitrogens are trans, and two amide nitrogens are in cis orientation. So, the configuration is cis, trans, cis (ctc), which is similar to that of the parent diimine compound, **1**. It may thus be concluded that the transformations **1** → **3** → **4** are stereoretentive. There are two types of Os−N bonds in this molecule. The average of the Os(1)−N^a bond lengths is 1.951(4) Å. This value is shorter than the average Os−N^p bond length, 2.074(4) Å. The Os−N^p bond lengths in **4a** are comparable with those [av 2.056(7) Å] in the parent osmium diimine[22] compound, **1c**, whereas the Os−N^a bond lengths [av 1.951(4) Å] in **4a** are

---

(17) Majumdar, K.; Peng, S.-M.; Bhattacharya, S. *J. Chem. Soc., Dalton Trans.* **2001**, 284. (b) Lahiri, G. K.; Bhattacharya, S.; Ghosh, B. K.; Chakravorty, A. *Inorg. Chem.* **1987**, *26*, 4324.

(18) Demos, J. N.; Harris, E. W.; McBride, R. P. *J. Am. Chem. Soc.* **1977**, *99*, 3547. (b) Lin, C.-T.; Sutin, N. *J. Phys. Chem.* **1976**, *80*, 97. (c) Kurimura, Y.; Onimura, R. *Inorg. Chem.* **1980**, *19*, 3516. (d) Kalyansundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.

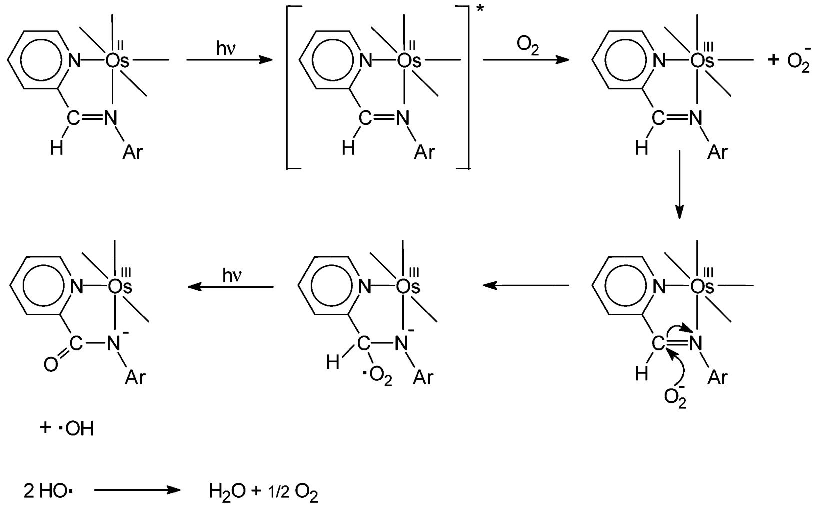
(19) Lindin, L. A.; Rabek, J. F.; Kaczmarek, H.; Kamimska, A.; Scoponi, M. *Coord. Chem. Rev.* **1993**, *125*, 125.

(20) Mansuy, D. *Coord. Chem. Rev.* **1993**, *125*, 129. (b) Maldotti, A.; Amadelli, R.; Bartocci, C.; Carassiti, V.; Polo, E.; Varani, G. *Coord. Chem. Rev.* **1993**, *125*, 143. (c) Scoponi, M.; Pradella, F.; Carassiti, V. *Coord. Chem. Rev.* **1993**, *125*, 219.

(21) Che, C.-M.; Cheng, W.-K.; Mak, T. C. W. *Inorg. Chem.* **1986**, *25*, 703.

(22) The X-ray data for **1a** is not available; however, it is reasonable to assume that the bond parameters of **1a** would be similar to those of **1c**.

Scheme 2



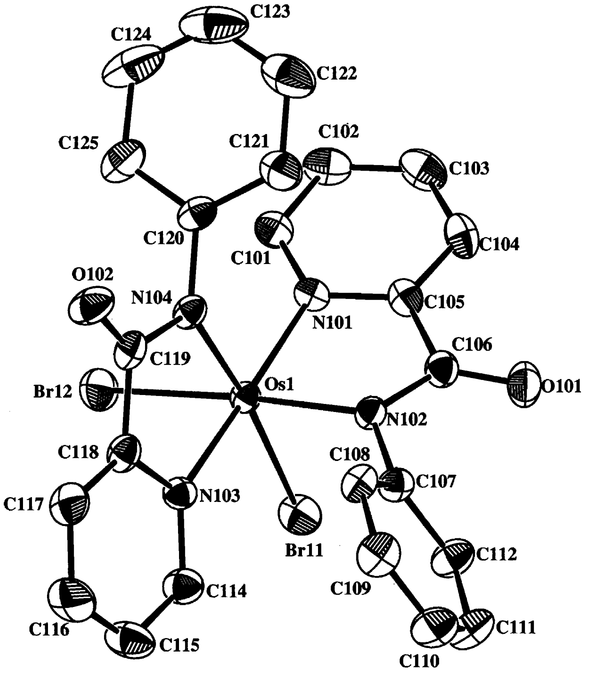
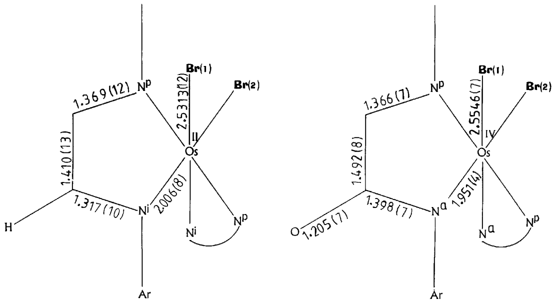


Figure 3. ORTEP plot and atom numbering scheme for $[OsBr_2(L^1O)_2]$, **4a**. Hydrogen atoms are omitted for clarity.

appreciably shorter[23] than the average Os—N^i bond length [av 2.004(7) Å] in **1c**. Shortening of these lengths may be attributed to the covalent double bond character due to dπ−pπ interactions. Notably, the two C—N^a bond lengths average 1.400(8) Å indicating a C—N single bond length.[24] By contrast, these two C—N lengths in **1c** are much shorter and indicated —HC=N^i character [av 1.318(10) Å]. The bond lengths in the coordination sphere and along the ligand backbone of the bis-diimine complex, **1c**, and the bis-diamido complex, **4a**, are shown in Figure 4 for comparison. The two Os—Br bond lengths [av 2.528(7) Å] are well within the normal range.



N^i = N(imine) N^a = N(amide)
N^p = N(pyridine) N^p = N(pyridine)

Figure 4. Comparison of selected bond distances in ctc-$[OsBr_2(HL^3)_2]$, **1c**, and $[OsBr_2(L^1O)_2]$, **4a**.

Table 3. Electronic and Cyclic Voltammetric Data

cmpd	absorption λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})^a	oxidation, $E_{1/2}$ (V)^b	reduction, $E_{1/2}$ (V)^b
1a	540(8300), 440^c(3000), 300(17000)	0.23, 1.40,^{d} 1.70^d	−1.38,^{e} −1.45^e
2a	550(9700), 445^c(5500), 300(18100)	0.24, 0.73,^{d} 1.40^d	−1.40,^{e} −1.45^e
1b	545(9000), 445^c(3500), 310(17500)	0.24, 1.40,^{d} 1.68^d	−1.38,^{e} −1.46^e
1c	540(9000), 440^c(3450), 320(15100)	0.20, 1.47, 1.65	−1.40,^{e} −1.46^e
3a	525^c(3200), 320(9000), 250^c(13500)	0.80	−0.34
3b	530^c(3000), 320(9400), 250^c(13100)	0.82	−0.34

[a] Data in CH_3CN. [b] Experiments were carried out in CH_3CN at 298 K using TEAP as supporting electrolyte. The reported data corresponds to a scan rate of 50 mV s^{-1}. [c] Shoulder. [d] Irreversible anodic response, the potential corresponds to E_{pa}. [e] Irreversible cathodic response, the potential corresponds to E_{pc}.

D. Electronic Spectra and Redox Properties. Solution spectral data of the osmium complexes are collected in Table 3. The free ligand HL^1 displays absorption bands at 310 nm (ϵ, 3250 M^{-1} cm^{-1}) and 270 nm (ϵ, 5900 M^{-1} cm^{-1}). The solution color of compound **1** is blue-violet while that of its isomer **2a** is red-violet. Both of them display a broad band and a shoulder in the visible region of the spectra. For

---

(23) Che, C.-M.; Cheng, W.-K.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1986**, 200. (b) Dutta, S.; Bhattacharya, P. K.; Tiekink, E. R. T. *Polyhedron* **2001**, *20,* 2027.

(24) Ray, M.; Mukherjee, R.; Richardson, J. F.; Mashuta, M. S.; Buchanan, R. M. *J. Chem. Soc., Dalton Trans.* **1994**, 965. (b) Dutta, S.; Bhattacharya, P. K.; Horn, E.; Tiekink, E. R. T. *Polyhedron* **2001**, *20,* 1815.

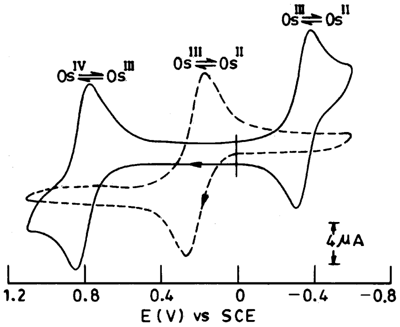


Figure 5. Voltammograms of ctc-[$OsBr_2(HL^1)_2$], **1a**, and [$OsBr_2(HL^1)(L^1O)$], **3a**, in acetonitrile.

example, complex **1** shows an intense band (ϵ, ca. 9000 M^{-1} cm^{-1}) near 540 nm, which was associated with a shoulder at 440 nm. Its isomer, compound **2**, has a similar intense transition at 550 nm and a shoulder at 445 nm. The absorptions occurring above 440 nm are assigned to the $t_2(Os) \rightarrow \pi^*(HL)$ transition (MLCT), where the π^* level has predominantly azomethine character.[25] It may be noted here that in d^6-metal ions, multiple $t_2 \rightarrow \pi^*$ charge transfer transitions can arise because of many reasons[26] including (i) low symmetry splitting of the metal level, (ii) the presence of more than one interacting ligands, and (iii) mixing of singlet and triplet configurations in the exited state via spin−orbit coupling. Similar multiple charge transfer transitions were noted[4] in the corresponding ruthenium(II) complexes. The osmium(II) complexes also showed allowed transitions in the UV region, which are of ligand origin. The solution color of the trivalent osmium compound, [$OsBr_2(HL)(LO)$], **3**, is brown. The spectrum consists of a shoulder of medium intensity near 530 nm. The rest of the transitions occur in the UV region. A comparison between the spectrum of **1** with that of **3** indicates that the MLCT transition in **1** near 540 nm is replaced by a broad transition of relatively lesser intensity in **3** (near 530 nm). It is probable that this broad transition may actually be the combination of more than one transition. These are tentatively assigned to ligand(π) → metal(t_2) charge transfer (LMCT). We wish to note here that such multiple LMCT transitions are noted by others[27] in some related mixed ligand osmium(III) complexes.

The redox behavior of osmium complexes in acetonitrile solution was examined cyclic voltammetrically at a platinum disk working electrode, and the potentials, reported herein, are referenced to the SCE. Results are collected in Table 3, and representative voltammograms are shown in Figure 5. The voltammograms of [$OsBr_2(HL)_2$] complexes display multiple responses in the potential range 2.0 to −1.5 V. Among these, the response near 0.25 V is a reversible (peak to peak separation 60−65 mV) oxidative response, which is assigned as the Os(III)/Os(II) couple. It may be noted here that the oxidation in the corresponding ruthenium(II) analogue appeared[4] in the range 0.25−0.50 V. There are two high potential irreversible anodic responses near 1.4 and 1.7 V, respectively. Notably, the current height of the response at 1.7 V is very large and is ascribed to ligand oxidation. The response near 1.4 V may be due to the Os(III) → Os(IV) process, which displays a cathodic shift by ca. 0.6 V and becomes electrochemically reversible in the mixed ligand amido complex, **3** (see later). The amido complexes, **3**, show two reversible one-electron cyclic voltammetric responses near 0.8 and −0.3 V versus SCE. The couple on the positive of the SCE is oxidative and is assigned to an Os(IV)/Os(III) oxidation process whereas that on the negative side of the SCE is due to the reductive couple of Os(III)/Os(II). Thus, the couples, Os(III)/Os(II) and Os(IV)/Os(III) of the diimine complex, **1**, both displayed cathodic shifts by nearly 0.6 V in the mixed ligand amido complex, **3**. This is due to the strong stabilization effect of the higher valent osmium(III) state[23] by the hard amido ligand. Because of the high formal charge on the osmium ion in **3**, the response due to ligand oxidation shifts further toward the anodic side and is not observable within our experimentally accessible range.

Conclusion

Successful isolation and characterization of osmium complexes involving the Schiff base diimine ligand, *N*-arylpyridine-2-carboxaldimine, together with the studies on oxidation of coordinated diimine ligands are the two major issues of this report. It has been demonstrated that the diimine function of the ligand (HL), upon coordination to an osmium(II) center, is susceptible to oxidation. Along with the oxidation of one ligand, the metal oxidation state (z) increases to ($z + 1$). Thus, the partial oxidation of the bivalent complex [$Os^{II}Br_2(HL)_2$], **1**, resulted in a trivalent complex, [$Os^{III}Br_2(HL)(LO)$], **3**, while a tetravalent complex, [$Os^{IV}Br_2(LO)_2$], **4**, resulted because of complete oxidation of two coordinated ligands. This novel transformation was also brought about by the photochemical oxidation reaction, using O_2 as the reactant. Such chemical transformations are scarce in the literature. The reaction concerning us here, −CH=NR → −C(=O)NHR, in principle, could open a convenient route for converting aldehydes (via Schiff base) to amides.

Experimental Section

Physical Measurements. The starting compound $(NH_4)_2[OsBr_6]$ was prepared following a reported procedure.[28] Solvents and chemicals used for synthesis were of analytical grade.

The IR spectra were obtained with a Perkin-Elmer 783 spectrophotometer, and the ^1H NMR spectra, on a Bruker Avance DPX 300 spectrophotometer with $SiMe_4$ as an internal standard. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C, H, N). A Shimadzu UV 2100 UV−vis spectrometer was used to record electronic spectra. Magnetic susceptibilities of

---

(25) Ghosh, B. K.; Goswami, S.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 3358. (b) Ghosh, B. K.; Mukhopadhyay, A.; Goswami, S.; Ray, S.; Chakravorty, A. *Inorg. Chem.* **1984**, *23*, 4633.

(26) Pankuch, B. J.; Lacky, D. E.; Crosby, G. A. *J. Phys. Chem.* **1980**, *84*, 2061. (b) Ceulemans, A.; Vanquickenborne, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 2238. (c) Decurtins, S.; Felix, F.; Ferguson, J.; Güdel, H. U.; Ludi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4102. (d) Kober, E. M.; Caspan, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4587.

(27) Bryant, G. M.; Fergusson, J. E. *Aust. J. Chem.*, **1971**, *24*, 275. (b) Haga, M.; Isobe, K.; Boone, S. R.; Pierpont, C. G. *Inorg. Chem.* **1990**, *29*, 3795. (c) Barthram, A. M.; Reeves, Z. R.; Jeffery, J. C.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **2000**, 3162.

(28) Dwyer, F. P.; Hogarth, J. W. *Inorg. Synth.* **1957**, *5*, 204.

samples were measured on a PAR 155 vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet. Electrochemical measurements were performed[25] at 298 K under a dry nitrogen atmosphere on a PC controlled EG&G PAR model 273A electrochemistry system. All potentials were uncorrected for junction potentials and referenced to the saturated calomel electrode (SCE). The value of the ferrocenium−ferrocene couple under our conditions was 0.42 V. FAB mass spectra were recorded on a JEOL SX 102/DA 6000 model mass spectrometer system using NBA (*m*-nitrobenzyl alcohol) as the matrix. EPR spectra were recorded on a Varian model 109 C E-line X-band spectrometer fitted with a quartz Dewar for measurement at 77 K (liquid nitrogen), and the spectra were calibrated against the spectrum of DPPH ($g = 2.0037$). Steady state photolysis of complexes was carried out in an air equilibrated purified acetonitrile solution. The solution was taken in a spectrophotometer quartz cell and exposed to a xenon lamp (100W) in Laser Kinetic Spectrometer equipment, and the progress of the reaction was monitored by the UV−vis spectral change using a diode array spectrophotometer (Hewlett-Packard, model 8452A).

Synthesis of Complexes. [$OsBr_2(HL^1)_2$], 1a, and 2a. $(NH_4)_2$-[$OsBr_6$] (100 mg, 0.14 mmol) was added to 20 mL of freshly distilled 2-methoxyethanol in a three-neck flask, and N_2 gas was bubbled into the mixture for 15 min. To this yellow-brown suspension was added, under N_2 atmosphere, a mixture of pyridine-2-carboxaldehyde (0.032 g, 0.3 mmol) and aniline (0.032 g, 0.3 mmol) in 25 mL of ethanol, which was refluxed separately for 30 min. The entire mixture was then refluxed in an oil bath under N_2 atmosphere at 120 °C for 3 h. A dark violet solution resulted, which was evaporated to dryness. The precipitate, thus obtained, was dissolved in dichloromethane and subjected to column chromatography on a silica gel column (1 cm × 50 cm). Two bands, a red-violet band followed by a blue-violet band, were collected using a dichloromethane−acetonitrile mixture in the ratios 20:1 and 15:1, respectively. The separated products were finally recrystallized from a 1:1 dichloromethane−hexane mixture.

The yields and analytical data for **1a** and **2a** follow. [$OsBr_2(HL^1)_2$], **1a**: yield 60%. Anal. Calcd for $C_{24}H_{20}N_4Br_2Os$: C, 40.33; H, 2.80; N, 7.84. Found: C, 40.59; H, 2.79; N, 7.95. [$OsBr_2(HL^1)_2$], **2a**: yield 20%. Anal. Calcd for $C_{24}H_{20}N_4Br_2Os$: C, 40.33; H, 2.80; N, 7.84%. Found: C, 40.26; H, 2.82; N, 7.81.

The osmium complexes of HL^2 and HL^3 were prepared similarly. However, no red-violet ccc-isomer was obtained in these two cases.

[$OsBr_2(HL^2)_2$], **1b**: yield 65%. Anal. Calcd for $C_{26}H_{24}N_4Br_2Os$: C, 42.04; H, 3.23; N, 7.54. Found: C, 42.19; H, 3.26; N, 7.64. [$OsBr_2(HL^3)_2$], **1c**: yield 60%. Anal. Calcd for $C_{26}H_{24}N_4O_2Br_2Os$: C, 40.31; H, 3.10; N, 7.23. Found: C, 40.57; H, 3.16; N, 7.31.

Photochemical Synthesis of *cis*-[$OsBr_2(HL^1)(L^1O)$], 3a, from ctc-[$OsBr_2(HL^1)_2$], 1a. The ctc-isomer of [$OsBr_2(HL^1)_2$] (100 mg, 0.14 mmol) was dissolved in 200 mL of AR grade acetonitrile, and the blue-violet solution was irradiated internally through a water-cooled quartz immersion well with a xenon lamp (100 W) for 30 min. The color of the solution changed to brown. The solvent was evaporated in a rotary evaporator, and the precipitate was redissolved in dichloromethane and subjected to column chromatography on a silica gel column (1 cm × 30 cm). An intense brown band was eluted as a major fraction with a (20:1) dichloromethane−acetonitrile mixture. Evaporation of the eluate, followed by recrystallization from the dichloromethane−hexane mixture, yielded the brown crystalline product in 96% yield. Compound **1b** upon exposure to light produced **3b** in 93% yield.

Chemical Oxidation of ctc-[$OsBr_2(HL^1)_2$], 1a, to [$OsBr_2(HL^1)(L^1O)$], 3a, and [$OsBr_2(L^1O)_2$], 4a. To a 30 mL acetonitrile solution of ctc-[$OsBr_2(HL^1)_2$], **1a**, (100 mg, 0.14 mmol) was added 30% aqueous H_2O_2 (10 mL), and then, the mixture was stirred at room temperature for 1 h. The initial blue-violet color of the solution changed to brown. The brown solution was kept in a refrigerator overnight when a few dark small crystals of complex **4a** deposited, which were carefully isolated by filtration. These crystals were insoluble in all common organic solvents. The brown mother liquid was evaporated, and the brown precipitate was recrystallized from a dichloromethane−hexane mixture. The spectral properties of this brown compound exactly corresponded to compound **3a** obtained from the photochemical transformation. The yields of **3a** and **4a** were 90% and 2%, respectively. These gave satisfactory analyses. [$OsBr_2(HL^1)(L^1O)$], **3a**. Anal. Calcd for $C_{24}H_{19}N_4OBr_2Os$: C, 39.50; H, 2.60; N, 7.68. Found: C, 39.59; H, 2.63; N, 7.51. [$OsBr_2(L^1O)_2$], **4a**. Anal. Calcd for $C_{24}H_{18}N_4O_2Br_2Os$: C, 38.68; H, 2.42; N, 7.52. Found: C, 38.85; H, 2.40; N, 7.64.

Table 4. Crystallographic Data of Compounds **1c** and **4a**

	1c	**4a**
empirical formula	$C_{26}H_{24}Br_2N_4O_2Os$	$C_{24}H_{18}Br_2N_4O_2Os$
molecular mass	774.51	744.44
temp [K]	295(2)	150(1)
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a [Å]	8.8976(12)	13.0690(4)
b [Å]	18.370(4)	11.8825(4)
c [Å]	15.956(3)	15.8787(5)
α [deg]	90	90
β [deg]	94.53(2)	105.2290(10)
γ [deg]	90	90
V [Å^3]	2600.00(8)	2379.25(13)
Z	4	4
D_{calcd} [Mg/m^3]	1.979	2.078
cryst dimens [mm^3]	0.50 × 0.50 × 0.20	0.40 × 0.25 × 0.20
θ range for data collection [deg]	1.69−25.00	2.17−27.50
GOF	1.003	1.032
wavelength [Å]	0.71073	0.71073
reflns collected	4581	20469
unique reflns	2930	4325
largest diff between peak and hole [eÅ^{-3}]	1.694, −1.533	1.826, −1.471
final R indices [$I > 2\sigma I$)]	R1 = 0.0429 wR2 = 0.1018	R1 = 0.0301 wR2 = 0.0774

Complexes **3b** and **4b** were obtained similarly from **1b**. Yields and analyses follow. [$OsBr_2(HL^2)(L^2O)$], **3b**: yield 85%. Anal. Calcd for $C_{26}H_{23}N_4OBr_2Os$: C, 41.21; H, 3.03; N, 7.39. Found: C, 41.38; H, 3.03; N, 7.47. [$OsBr_2(L^2O)_2$], **4b**: yield 2%. Anal. Calcd for $C_{26}H_{22}N_4O_2Br_2Os$: C, 43.90; H, 2.68; N, 6.83. Found: C, 44.01; H, 2.70; N, 6.69.

X-ray Structure Determination.[29,30] The crystal data of representative compounds **1c** and **4a** are collected in Table 4.

(i) [$OsBr_2(HL^3)_2$], 1c. Dark colored X-ray quality crystals (0.50 × 0.50 × 0.20 mm^3) of **1c** were obtained at room temperature by slow diffusion of a dichloromethane solution of the compound into hexane. The data were collected on an Enraf-Nonius CAD 4 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 295 K. A total of 4581 unique reflections were collected of which 2930 reflections satisfied the [$I > 2\sigma(I)$] criterion. The structure was refined by full-matrix least-squares based on F^2 using SHELXS-97.

(ii) [$OsBr_2(L^1O)_2$], 4a. A rod-shaped dark colored crystal (0.40 × 0.25 × 0.20 mm^3) was obtained directly from the reaction

---

(29) Sheldrick, G. M. *SHELXS-97, Program for the refinement of crystal structures*; University of Gottingen: Gottingen, Germany, 1997.

(30) Sheldrick, G. M. *SHELXS-93, Program for the solution of crystal structures*; University of Gottingen: Gottingen, Germany, 1993.

mixture. The data were collected on a Bruker SMART CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 150 K. A total of 20469 reflections were collected, of which 4325 reflections satisfied the [$I > 2\sigma(I)$] criterion. Employing the SHELXL-93 program package solved the structure and refined it by full-matrix least-squares based on F^2.

Acknowledgment. We thank the Council of Scientific and Industrial Research and the Department of Science and Technology, New Delhi, for financial support. Thanks are due to RSIC, Lucknow, for providing mass spectra.

Supporting Information Available: X-ray crystallographic details, in CIF format, of two compounds, NMR spectrum for **1b**, and FAB mass spectrum for **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC020454S