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Unusual Transformation of *N*-Arylbenzohydroxamic Acids Mediated by Osmium. Formation of Organometallic Complexes of Osmium(III)

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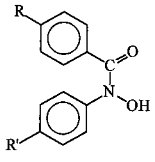
Introduction

The chemistry of transition metal hydroxamates has always been of considerable interest largely because of their bioinorganic relevance.[1] In this family of hydroxamate complexes, the iron hydroxamates have received most attention in connection with the bacterial iron transport mechanism in the life process.[2] Among the two congeners of iron, the chemistry of ruthenium hydroxamates has received some attention,[3] while that of osmium hydroxamates appears to remain totally unexplored. In the present work, which has originated from our interest in the chemistry of osmium complexed by ligands of different types,[4] our objective was to explore the chemistry of osmium hydroxamates and a group of hydroxamic acids of type **1** (see Chart 1) was chosen for this purpose. Hydroxamic acids are well-known to bind to metal ions as bidentate O,O-donor ligands forming stable five-membered chelate rings (**2**).[5] Our primary goal was restricted to the synthesis of osmium complexes containing only one hydroxamate ligand. To satisfy the remaining coordination sites of osmium, 2,2′-bipyridine (bpy) was chosen to serve as the coligand. With this strategy in mind, reactions of the *N*-arylbenzohydroxamic acids were carried out with $[Os(bpy)_2Br_2]$. However, the product obtained from these reactions has been found to be interestingly different from our expectation. The hydroxamic acids undergo unusual chemical transformation and bind to osmium as dianionic C,N-donors (as shown in **3**) affording cyclometalates of osmium(III) of type $[Os^{III}(bpy)_2(R-R')]^+$ (where R−R′ refers to the bidentate ligand in **3**). The chemistry of these complexes is described here with special reference to their formation, structure, and properties.

Chart 1



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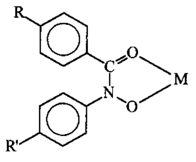

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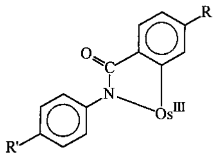

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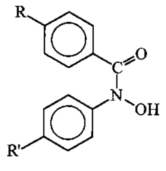

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R	R'	Ligand
H	H	H_2OH-H
Cl	H	H_2OCl-H
NO_2	H	H_2ONO_2-H
H	CH_3	H_2OH-CH_3
Cl	CH_3	H_2OCl-CH_3
NO_2	CH_3	H_2ONO_2-CH_3
H	Cl	H_2OH-Cl
Cl	Cl	H_2OCl-Cl
NO_2	Cl	H_2ONO_2-Cl

Experimental Section

Materials. Osmium tetraoxide was purchased from Arora Matthey, Calcutta, India, and was converted to $[NH_4]_2[OsBr_6]$ by reduction with hydrobromic acid.[6] $[Os(bpy)_2Br_2]$ was synthesized, starting from $[NH_4]_2[OsBr_6]$, by following a reported procedure.[7] 2,2′-Bipyridine, 4-nitrobenzene, 1-chloro-4-nitrobenzene, and 4-nitrotoluene were purchased from Loba Chemie, Mumbai, India. The nitrobenzenes were converted to the corresponding hydroxylamines by following a literature method.[8] Benzoyl chloride, 4-nitrobenzoyl chloride, and 4-chlorobenzoyl chloride were purchased from Eastgate, Whiteland, Morecambe, England. The hydroxamic acids were prepared by acylation of the hydroxylamines with the acid chlorides by following a published procedure.[9] Purification of acetonitrile and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were performed as reported in the literature.[10] All other chemicals used for the preparative works were of reagent grade and were used without further purification.

Preparation of the $[Os(bpy)_2(R-R')]ClO_4$ Complexes. The $[Os(bpy)_2(R-R')]ClO_4$ complexes were synthesized by following two

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Table 1. Crystallographic Data for $[Os(bpy)_2(H-H)]ClO_4$

empirical formula	$C_{33}H_{25}ClN_5O_5Os$
fw	797.23
space group	orthorhombic, $P2_12_12_1$
a, Å	10.660(5)
b, Å	14.990(4)
c, Å	18.662(3)
V, Å^3	2982.1(17)
Z	4
λ, Å	0.710 73
cryst size, mm	0.27 × 0.12 × 0.11
T, K	297(2)
μ, mm^{-1}	4.418
R1[a]	0.0558
wR2[b]	1253
GOF[c]	1.032

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)\}]^{1/2}$. [c] $GOF = [\sum(w(F_o^2 - F_c^2)^2)/(M - N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

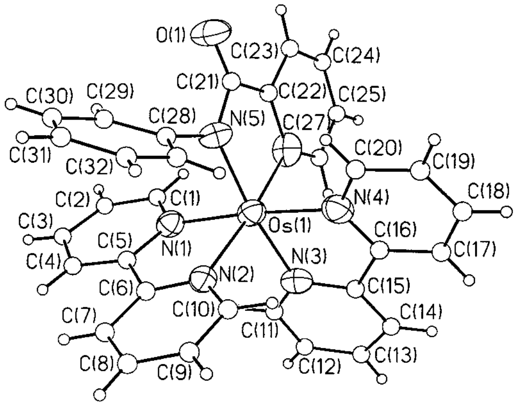

Figure 1. View of the $[Os(bpy)_2)(H-H)]^+$ complex.

Table 2. Selected Bond Distances and Bond Angles for $[Os(bpy)_2(H-H)]ClO_4$

Bond Distances (Å)			
Os(1)−N(5)	2.041(15)	C(21)−C(22)	1.45(3)
Os(1)−N(4)	2.047(14)	C(22)−C(27)	1.40(3)
Os(1)−C(27)	2.06(2)	C(22)−C(23)	1.41(3)
Os(1)−N(1)	2.076(14)	C(23)−C(24)	1.36(3)
Os(1)−N(3)	2.091(15)	C(24)−C(25)	1.33(3)
Os(1)−N(2)	2.186(14)	C(25)−C(26)	1.38(3)
N(5)−C(21)	1.38(2)	C(26)−C(27)	1.37(3)
C(21)−O(1)	1.20(2)		

Bond Angles (deg)			
N(4)−Os(1)−N(1)	175.2(6)	C(27)−Os(1)−N(2)	174.4(7)
N(5)−Os(1)−N(3)	172.0(6)		
N(5)−Os(1)−N(4)	97.0(6)	C(27)−Os(1)−N(3)	94.4(7)
N(5)−Os(1)−C(27)	78.4(7)	N(1)−Os(1)−N(3)	97.5(6)
N(4)−Os(1)−C(27)	83.6(7)	N(5)−Os(1)−N(2)	96.8(6)
N(5)−Os(1)−N(1)	87.3(6)	N(4)−Os(1)−N(2)	100.1(6)
C(27)−Os(1)−N(1)	99.6(7)	N(1)−Os(1)−N(2)	77.0(6)
N(4)−Os(1)−N(3)	78.6(6)	N(3)−Os(1)−N(2)	90.5(6)

general procedures. Yields varied in the range of 60−70%. Specific details are given below for one complex.

$[Os(bpy)_2(H-H)]ClO_4$. Method A. $[Os(bpy)_2Br_2]$ (100 mg, 0.15 mmol) was dissolved in 3:1 ethanol−water (40 cm^3), and to it was added *N*-phenylbenzohydroxamic acid (32 mg, 0.15 mmol) followed by triethylamine (50 mg, 0.50 mmol). The solution was heated at reflux for 8 h to produce a dark brown solution. After this solution was cooled to room temperature, a saturated aqueous solution of $NaClO_4$ (0.5 cm^3) was added to it followed by a large volume (∼60 cm^3) of water. The brown solution was then extracted repeatedly with dichloromethane, and the extract was concentrated to ∼10 cm^3 by evaporation under reduced pressure. The concentrate was then triturated with 10 cm^3 of benzene causing precipitation of $[Os(bpy)_2(H-H)]ClO_4$ as a dark brown microcrystalline solid, which was collected by filtration and dried in air. Yield: 62%.

Method B. To a mixture of *N*-phenylbenzohydroxamic acid (32 mg, 0.15 mmol) and Na_2CO_3 (100 mg, 0.94 mmol) were added 2-methoxyethanol (40 cm^3) and $[Os(bpy)_2Br_2]$ (100 mg, 0.15 mmol). The resulting mixture was heated at reflux for 72 h under a N_2 atmosphere to produce a dark brown solution. After the solution was cooled to room temperature, a saturated aqueous solution of $NaClO_4$ (0.5 cm^3) was added to it. Upon partial evaporation $[Os(bpy)_2(H-H)]ClO_4$ precipitated as a brown solid, which was collected by filtration, washed with ice-cold water, and dried in air. Purification of the product was done by recrystallization from dichloromethane-benzene solution. Yield: 68%.

Physical Measurements. Microanalyses (C, H, N) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra were obtained on a Perkin-Elmer 783 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on JASCO V-570 and Hitachi 330 spectrophotometers. Solution electrical conductivities were measured using a Philips PR 9500 bridge with a solute concentration of 10^{-3} M. Magnetic susceptibilities were measured using a PAR 155 vibrating-sample magnetometer fitted with a Walker scientific L75FBAL magnet. ESR spectral studies were carried out with a Varian model 109C E-line X-band spectrometer fitted with a quartz dewar for measurements at 77 K (liquid dinitrogen). Electrochemical measurements were made using a PAR model 273 potentiostat. A platinum-disk working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. A graphite working electrode was also used for scanning the negative side of SCE. A platinum wire gauze working electrode was used in the coulometric experiments. A RE 0089 X−Y recorder was used to trace the voltammograms. Electrochemical measurements were made under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

Crystallography of $[Os(bpy)_2(H-H)]ClO_4$. Single crystals were grown by slow diffusion of benzene into a dichloromethane solution of the complex. Selected crystal data and data collection parameters are given in Table 1. The unit cell dimensions were determined by a least-squares fit of 25 centered reflections. Data were collected on an Enraf Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) by $\omega-\theta$ scans within the angular range $2.18 < \theta < 24.98°$. Three standard reflections were used to check the crystal stability toward X-ray exposure, and they showed no significant intensity variation over the course of data collection. X-ray data reduction, structure solution, and refinement were done using the SHELXS-97 and SHELXL-97 packages. The structure was solved by the direct methods.

Results and Discussion

Nine hydroxamic acids have been used in the present study, which are abbreviated in general as H_2OR-R', where H_2 stands for the two protons that undergo dissociation upon complexation, O stands for the hydroxy oxygen, and R and R′ stand for the two substituents. The ligands along with their individual abbreviations are shown in **4** (Chart 1). Reaction of these hydroxamic acids with $[Os(bpy)_2Br_2]$ proceeds smoothly in 1:3 aqueous−ethanol medium in the presence of triethylamine to afford brown solutions of $[Os(bpy)_2(R-R')]^+$. Reactions carried out in refluxing 2-methoxyethanol in the presence of Na_2CO_3 also yield the same complexes. The complex cations have been isolated as perchlorate salts in the solid state. Identity of these complexes has been revealed by structure determination of a representative member of this family, viz. $[Os(bpy)_2(H-H)]ClO_4$. The structure is shown in Figure 1, and selected bond parameters are listed in Table 2.

It is very interesting to find out that the *N*-phenylbenzohydroxamic acid has undergone oxygen loss from the NOH function and is coordinated to osmium, via loss of two protons, as a dianionic bidentate C,N-donor ligand forming a five-membered chelate ring (as in **3**) with a bite angle of 78.4(7)°. As the coordinated ligand is equivalent to a doubly deprotonated benzanilide, the organic transformation may be regarded as conversion of *N*-phenylbenzohydroxamic acid to benzanilide. Precedence of metal-assisted reduction of *N*-phenylbenzohydroxamic acid to benzanilide is avilable in the literature.[11] However, in all these examples the hydroxamic acid served as a mere oxidizing agent for the metal and itself was reduced to benzanilide, which never participated in complexation and was aways obtained as a byproduct. In our present case, the striking difference is that the reduced hydroxamic acid (viz. benzanilide) remains coordinated to the oxidized metal (viz. osmium(III)), which appears to be unprecedented in the literature. The mechanism of the observed transformation of hydroxamic acid is not clear to us. However, prior coordination of the hydroxamic acid to osmium(II) followed by intramolecular redox reaction between the coordinated hydroxamic acid and osmium(II) finally leading to formation of the organometallic complex seems probable. It is interesting to note that such cyclometalates of osmium(III) are scarce in the literature.[4h,12] Within the Os(C−N) chelate, the Os−C length is comparable to the Os^{III}−C distances observed by us before[12b] and the Os−N(5) distance is also normal.[13] The C(21)−O(1) distance (1.20(2) Å) indicates the double bond character of the carbonyl function. Distances within the $Os(bpy)_2$ fragment are quite usual, as observed in structurally characterized osmium(III) complexes having the $Os^{III}(bpy)_2$ moiety.[13] However, the Os−N(2) bond, which is trans to the Os−C bond, is noticeably longer than the other four Os−N bonds. The $OsCN_5$ core is significantly distorted from ideal octahedral geometry, as reflected in the bond parameters around osmium. As all the nine $[Os(bpy)_2(R-R')]ClO_4$ complexes have been synthesized similarly and as all these complexes exhibit similar properties (vide infra), the other eight complexes are assumed to have similar structure as $[Os(bpy)_2(H-H)]ClO_4$. Elemental (C, H ,N) analytical data of all the complexes are consistent with their compositions.

Magnetic susceptibility measurements show that the $[Os(bpy)_2(R-R')]ClO_4$ complexes are one-electron paramagnetic ($\mu_{eff} = 1.87-1.93\ \mu_B$), which corresponds to the +3 state of osmium (low-spin d^5, $S = 1/2$) in these complexes. However, ESR studies show that these $[Os(bpy)_2(R-R')]^+$ complexes are ESR-silent. ESR inactivity in low-spin d^5 complexes is quite common and is known to result from extensive mixing of the Kramers doublets by strong spin−orbit coupling which gives rise to short electronic relaxation time.[4b,d,14] Infrared spectra of the $[Os(bpy)_2(R-R')]ClO_4$ complexes show many strong vibrations below 1700 cm^{-1}. The ν(C=O) stretch is uniformly displayed as a strong band by all the complexes near 1600 cm^{-1}. Two intense bands are observed near 1110 and 625 cm^{-1} in all the complexes, and these are attributed to the perchlorate ion. The $[Os(bpy)_2(R-R')]ClO_4$ complexes are soluble in solvents such as dichloromethane, acetonitrile, acetone, etc., producing intense brown solutions. Conductance measurement in acetonitrile solution shows that these complexes behave as 1:1 electrolytes ($\Lambda_M = 140-150\ \Omega^{-1}\ cm^2\ M^{-1}$), as expected. Electronic spectra of the $[Os(bpy)_2(R-R')]ClO_4$ complexes have been recorded in acetonitrile solution. Each complex shows seven absorptions, two in the near-infrared region, three in the visible region, and two in the ultraviolet region. The two absorptions in the near-infrared region are weak in intensity, and these are assignable to the two possible transitions within the three split components of the t_2 orbitals, which are known to occur at low energies.[15] The absorptions in the visible region are of high intensity, and they are probably due to allowed ligand-to-metal charge-transfer transitions. The absorptions in the ultraviolet region are very intense and are assignable to transitions within the ligand orbitals.

Electrochemical properties of the $[Os(bpy)_2(R-R')]ClO_4$ complexes have been studied in acetonitrile solution (0.1 M TEAP) by cyclic voltammetry. Each complex shows an oxidative response on the positive side of SCE and three reductive responses on the negative side. The oxidative response, observed within 0.76 to 0.92 V, is assigned to osmium(III)−osmium(IV) oxidation. This oxidation is quasi-reversible in nature, characterized by a slightly larger anodic peak current (i_{pa}) than the cathodic peak current (i_{pc}). One-electron stoichiometry of this oxidation has been established by comparing its current height (i_{pa}) with that of standard ferrocene−ferrocenium couple under identical experimental conditions. The first reductive response, observed within −0.32 to −0.18 V, is assigned to the osmium(III)−osmium(II) reduction. This reduction is reversible, characterized by a peak-to-peak separation (ΔE_p) of 60 mV, and the anodic peak current (i_{pa}) is almost equal to the cathodic peak current (i_{pc}). The one-electron nature of this reduction has been established by comparing its current heights with the anodic peak current (i_{pa}) of the oxidative response. In $[Os(bpy)_3]^{2+}$, the osmium(II)−osmium(III) couple appears at 0.84 V.[16] This large negative shift of the osmium(III)−osmium(II) potential upon replacing one bpy by one R−R′ ligand shows the hard character of these R−R′ ligands and their efficiency in stabilizing the higher oxidation states of osmium. Potentials of both the osmium(III)−osmium(IV) and osmium(III)−osmium(II) couples are found to be sensitive to the nature of the two substituents (R and R′) on the R−R′ ligands. The potentials increase as electron-withdrawing character of the substituents increase. Two successive one-electron reductions are displayed by all these complexes at potentials below −1.6 V vs SCE, which are assigned to reductions of the two bpy ligands. It is well-known that each bpy can successively accept two electrons in the lowest unoccupied molecular orbital.[17] Hence in these $[Os(bpy)_2(R-R')]^+$ complexes, four successive reductions are expected. Only two of these have been experimentally observed, and the other two have not been observed because of solvent cutoff.

The reversible character of the osmium(III)−osmium(II) reduction, together with its relatively low potential, suggest that the reduced complexes, viz. $[Os^{II}(bpy)_2(R-R')]$, should be fairly stable. To investigate this, a representative complex, viz. $[Os^{III}(bpy)_2(H-H)]ClO_4$, has been coulometrically reduced at −0.5 V vs SCE in acetonitrile solution (0.1 M TEAP). The reduction has been smooth and quantitative yielding a green solution {electronic spectral data [λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)]: 600 (5800), 490^{sh} (6000), 420^{sh} (7400), 380 (7900); sh = shoulder}. The voltammetric behavior of the reduced complex has been found to be identical with that of the parent osmium(III) complex,

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except that the osmium(II)−osmium(III) couple appears as an oxidative response. The same reduction has also been achieved chemically by adding hydrazine to an acetonitrile solution of the $[Os(bpy)_2(R-R')]ClO_4$ complexes. While exposed to air, green solutions of the $[Os^{II}(bpy)_2(R-R')]$ complexes undergo oxidation to regenerate brown solutions of the $[Os^{III}(bpy)_2(R-R')]^+$ complexes, which have been identified by their respective electronic spectrum. This shows that the $[Os^{II}(bpy)_2(R-R')]$ complexes, though they can be generated easily by reduction of their osmium(III) precursors, are susceptible to aerial oxidation.

Conclusions

The present study shows a very unusual transformation of *N*-arylbenzohydroxamic acids (**1**) mediated by an osmium complex, viz. $[Os(bpy)_2Br_2]$, affording a family of cyclometalates of osmium(III) where the transformed hydroxamic acids are coordinated as doubly deprotonated benzanilides (**3**). The findings of the present study indicate that benzanilides should be capable, in principle, of functioning as bidentate C,N-donor ligands, and such a possibility is currently being explored. Efforts are also being made to discover the right experimental condition for binding the hydroxamic acids (**1**) to osmium in the usual fashion (**2**).

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Supporting Information Available: Figures giving the electronic spectrum of $[Os(bpy)_2(Cl-Cl)]ClO_4$ and cyclic voltammogram of $[Os(bpy)_2(H-H)]ClO_4$ and tables containing analytical data, electronic spectral data, and cyclic voltammetric data of the $[Os(bpy)_2(R-R')]ClO_4$ complexes and crystal data and details of structure determination, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for $[Os(bpy)_2(H-H)]ClO_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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