not refined. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to $R = 0.049$ and $R_w = 0.042$. The final cycle of least-squares refinement contained 1442 observations and 208 variables, and a final difference Fourier map showed no feature greater than 0.16 e Å^{-3}. The atomic positional parameters obtained from the final least-squares cycle along with their estimated standard deviations are given in Table III.

Acknowledgment is made to the U.S. Army Research Office for support of this research and to the Morehead Foundation for a fellowship for M.B.H. We thank Dr. D. J. Hodgson and S. R. Wilson for crystallographic assistance.

Registry No. **1**, 79001-07-3; $[C_5Me_5(CO)_2Fe{=}CHC_6H_5]^+(OSO_2CF_3)^-$, 87101-25-5; $[C_5Me_5](CO)_2FeCH(C_6H_5)OCH_3$, 87101-26-6; $Me_3SiOSO_2CF_3$, 27607-77-8.

Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms of **1**, positional and thermal parameters for the hydrogen atoms in **1**, additional bond distances and angles in **1**, a least-squares plane calculation of the pentamethylcyclopentadienyl ligand in **1**, and observed and calculated structure factors for **1** (15 pages). Ordering information is given on any current masthead page.

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(23) Positions were calculated from d(C–H) = 0.95 Å with the program HYDRO.

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Isomeric 2-(Arylazo)pyridine Complexes of $OsCl_2$ and $OsBr_2$

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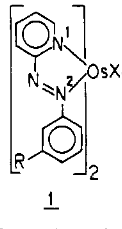
The ruthenium chemistry of unsaturated nitrogenous ligands—2,2′-bipyridine (bpy) being the prototype—has developed rapidly[1] in recent times primarily due to the relevance of this chemistry to photophysical, photochemical, and redox phenomena. In comparison to this the progress in the corresponding chemistry of osmium has been very slow.[2-5] Indications are strong, however, that this area also abounds in fascinating spectroscopic and electron-transfer phenomena.[6-9] With this background and in logical continuation to our program[10] on the chemistry of ruthenium, we have initiated research on osmium chelates of certain classes of unsaturated nitrogenous ligands. In this first report we describe the synthesis, spectra, and redox properties of the osmium(II) complexes OsX_2L_2 (**1**), where X = Cl and Br and L is 2-(phenylazo)pyridine (R = H; pap) and 2-(m-tolylazo)pyridine (R = Me; tap). The ruthenium chemistry of L has developed to a considerable extent[10-14] during the last few years, but nothing is known about the corresponding osmium chemistry.



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Results and Discussion

Synthesis. The reaction of L with $(Et_4N)_2OsX_6$ in 2-methoxyethanol

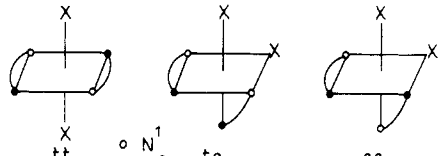
$$OsX_6^{2-} + 2L \rightarrow OsX_2L_2 + 4X^- \qquad (1)$$

proceeds slowly but smoothly. When the reaction mixture is concentrated and cooled, dark-colored crystals of composition OsX_2L_2 (isomer A) result in about 70% yield. Isomeric purity was tested by ^{1}H NMR (see below) and TLC on silica gel using 1:1 benzene–dichloromethane as developer. From the mother liquor another isomer (B) of the complex is isolated (yield 10–15%) in pure form with use of chromatographic techniques. Even when L is used in excess of 2 mol, only OsX_2L_2 is isolated from reaction 1; no OsL_3^{2+} appears to be formed.

Isomer A dissolves in common organic solvents (C_6H_6, CH_2Cl_2, CH_3CN, etc.) to give blue-violet solutions. Solutions of the isomer B are red-violet. All complexes are diamagnetic in the crystalline state and are nonelectrolytic in nitromethane and acetonitrile.

The reduction of osmium from +4 to +2 state in reaction 1 is probably brought about by the alcoholic solvent. The ruthenium complexes, RuX_2L_2, similarly arise[11] from the spontaneous reductive (+3 → +2) chelation of RuX_3 with L in methanol.

Isomer Characterization. RuX_2L_2 occurs in three isomeric forms[10,13] designated as trans–trans (tt, **2**), trans–cis (tc, **3**) and cis–cis (cc, **4**) on the basis of the relative positions within the pairs N^1,N^1 and N^2,N^2. The structures of the tc and cc isomers of $RuCl_2(pap)_2$ are accurately known from three-dimensional X-ray work.[10,12] The IR spectra of the three isomers differ significantly in the region 4000–300 cm^{-1}.



tt **2** tc **3** cc **4**

The vibration spectra of the isomer A of $OsCl_2(pap)_2$ and tc-$RuCl_2(pap)_2$ (**3**) are nearly superposable in the above region except for frequency shifts particularly in the $\nu_{N=N}$ region

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Table I. Infrared, Visible-Ultraviolet, and ^{1}H NMR Spectral and Analytical Data

compd	IR,[a] cm^{-1} ν_{OsCl}[b]	$\nu_{N=N}$	vis-UV[c] λ_{max}, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})	^{1}H NMR[d] δ_{Me}	anal. data[e] % C	% H	% N
tc-$OsCl_2(pap)_2$	306, 320	1280	975 (0.99), 795 (0.81),[f] 568 (7.9),[f] 518 (11.9), 364 (13.75),[f] 314 (26.0)		41.95 (42.11)	3.05 (2.89)	13.56 (13.39)
cc-$OsCl_2(pap)_2$	304, 312	1278	845 (1.29), 580 (3.8),[f] 510 (11.7), 344 (15.0),[f] 306 (16.0), 230 (22.0)		42.23 (42.11)	3.10 (2.89)	13.49 (13.39)
tc-$OsCl_2(tap)_2$	308, 320	1280	980 (0.97), 800 (0.81),[f] 572 (6.8),[f] 520 (10.17), 364 (13.65),[f] 316 (20.98)	2.10	44.27 (43.97)	3.20 (3.38)	12.48 (12.82)
cc-$OsCl_2(tap)_2$	307, 315	1278	838 (1.05), 580 (3.4),[f] 510 (11.5), 344 (13.85),[f] 306 (14.0), 232 (21.8)	2.20, 2.31	43.45 (43.97)	3.50 (3.38)	12.52 (12.82)
tc-$OsBr_2(tap)_2$		1280	990 (1.07), 792 (0.86),[f] 568 (7.13),[f] 518 (9.3), 364 (13.96),[f] 314 (24.3)	2.11	39.01 (38.72)	3.05 (2.98)	11.26 (11.29)
cc-$OsBr_2(tap)_2$		1278	830 (1.17), 576 (3.53),[f] 512 (11.2), 344 (13.8),[f] 308 (15.15), 232 (26.0)	2.23, 2.33	38.61 (38.72)	3.15 (2.98)	10.99 (11.29)

[a] All bands are sharp and strong. [b] In polyethylene disk (400–200 cm^{-1}). [c] In acetonitrile. [d] In $CDCl_3$. [e] Calculated values are in parentheses. [f] Shoulder.

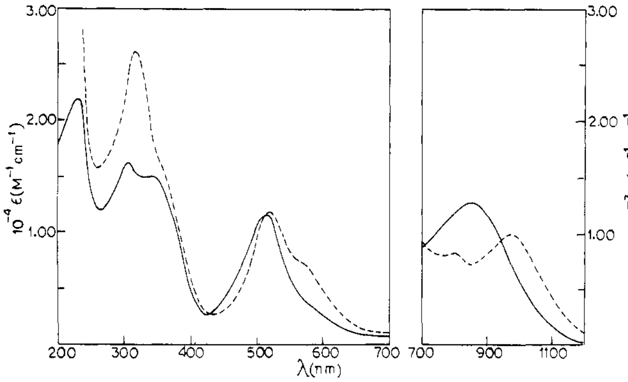

Figure 1. Electronic spectra of *tc*-$OsCl_2(pap)_2$ (- - -) and *cc*-$OsCl_2(pap)_2$ (—) in CH_3CN.

Table II. Cyclic Voltammetric Data[a,b] at 298 K

compd	$E°_{298}$, V (ΔE_p, mV)[c] Os(III)–Os(II)	Os(IV)–Os(III)	E_{pc}, V[d] ligand redn
tc-$OsCl_2(pap)_2$	0.96 (60)	1.72 (150)	−0.58, −0.85, −1.53, −1.91
cc-$OsCl_2(pap)_2$	0.94 (60)	1.79 (180)	−0.71, −1.00, −1.62, −1.94
tc-$OsCl_2(tap)_2$	0.96 (60)	1.74 (180)	−0.60, −0.85, −1.50, −1.92
cc-$OsCl_2(tap)_2$	0.94 (60)	1.79 (160)	−0.72, −1.01, −1.65, −1.85
tc-$OsBr_2(tap)_2$	0.96 (60)	1.71 (150)	−0.58, −0.83, −1.57, −2.20
cc-$OsBr_2(tap)_2$	0.94 (60)	1.80 (160)	−0.71, −0.90, −1.61, −1.90

[a] Meaning of symbols are the same as in the text. [b] Conditions: solvent, acetonitrile (0.1 M in TEAP); solute concentration, ~10^{-3} M; scan rate, 50 mV s^{-1}. [c] Working electrode is platinum. [d] Working electrode is glassy carbon.

(Table I). A similar relationship holds between the spectra of *cc*-$RuCl_2(pap)_2$ and the isomer B of $OsCl_2(pap)_2$. These observations suggest that the isomer A has the *tc* (**3**) while isomer B has the *cc* (**4**) configuration.

In both *tc* and *cc* forms the $OsCl_2$ fragment is cis. The two expected OsCl stretches are observed in the region 300–320 cm^{-1}. That these are not OsN stretches is inferred from their absence in $OsBr_2L_2$. Finally, *tc*-$OsX_2(tap)_2$ (C_2 symmetry) shows only one ^{1}H methyl signal while the *cc* isomer (C_1 symmetry) shows two (Table I).

We have no evidence for the existence of the *tt* isomer of OsX_2L_2 in any of our preparations. This is a major distinctive feature between RuX_2L_2 and OsX_2L_2.

π-Bonding. The ability of L to act as a relatively strong (compared to e.g. bpy) π-acceptor toward metal ions in relatively low oxidation states—Cu(I),[15] Fe(II),[16] Ru(II)[10,14]—is now well documented. In the cases of *tc*- and *cc*-$RuCl_2(pap)_2$ the average Ru–N^2 bond (1.98 Å) is systematically shorter than the average Ru–N^1 bond (2.05 Å).[10] The azo orbitals are thus strongly involved in the π-interaction. A diagnostic test[10,14] for the existence of this interaction is the shift of $\nu_{N=N}$ to lower frequencies in going from free L to its complexes. The N=N frequencies (Table I) of OsX_2L_2 are the *lowest* among those of all L complexes reported so far. In particular the N=N frequencies systematically follow the order Os < Ru in corresponding complexes. Clearly, osmium(II) is a stronger π-donor than ruthenium(II) in complexes of L.

Charge-Transfer Spectra. Spectral data in CH_3CN are in Table I and Figure 1. Major absorption peaks occur in three distinct regions: <400, 500–600, and 800–1000 nm. The allowed transitions below 400 nm are probably of ligand origin and are not considered any further.

Blue-violet solutions of the *tc* complexes have an intense band ($\epsilon \approx 10^4$ M^{-1} cm^{-1}) at ~520 nm with a clearly defined shoulder near 570 nm. In the *cc* isomer the band is blue shifted to 510 nm and is accompanied by an ill-defined shoulder at ~580 nm.

The bands in the 800–1000-nm region are the weakest with $\epsilon \approx 1000$. Here also the absorption of the *tc* isomer has two distinct components while that of the *cc* isomer is almost structureless but broad.

The bands in the 500–600- and 800–1000-nm regions are assigned to MLCT transitions Os(t_2) → L(π*). The more intense bands at higher energies are believed to be spin-allowed singlet–singlet transitions while the weaker bands at lower energies could be the corresponding singlet–triplet transitions made partially allowed by the strong spin–orbit coupling in osmium. In RuX_2L_2 the spin-allowed MLCT bands occur (in CH_3CN) at 580 nm (*tc*) and 570 nm (*cc*), respectively. No spin-forbidden band is observed, however. The situation is analogous[4,6,7] to that of the bpy complexes, which also display two types of MLCT transitions only in the case of osmium.

Electron Transfer. Electrochemical data are in Table II and Figure 2. The complexes were examined by cyclic voltammetry at a platinum working electrode in acetonitrile (0.1 M in TEAP) on the positive side of the SCE. The osmium(III)–osmium(II) couple (2) is nearly reversible[17] with peak-to-peak separations of 60 mV. The formal potential, $E°_{298}$,

$$OsX_2L_2^+ + e^- \rightleftharpoons OsX_2L_2 \qquad (2)$$

calculated as the average of peak potentials, lies close to 1 V.

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[17] Coulometric confirmation of 1e stoichiometry was not possible due to continuous accumulation of coulombs at the required high (>1 V) potentials. The cyclic voltammetric peak heights are, however, the same as those of typical 1e processes.[10-12]

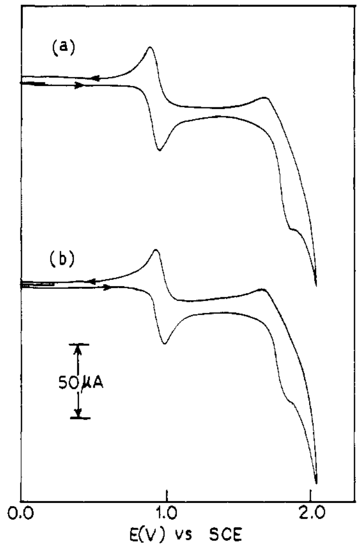

Figure 2. Cyclic voltammograms of (a) *cc*-$OsCl_2(tap)_2$ and (b) *tc*-$OsCl_2(tap)_2$ in CH_3CN (0.1 M TEAP) at a platinum electrode vs. SCE; scan rate 50 mV s^{-1}.

Between the two isomers the order of $E°_{298}$ is *tc* > *cc*.

A second one-electron (on the basis of current height) anodic response occurs (~1.8 V) close to the solvent cutoff limit. The corresponding cathodic peak is observed, but it is not as well-defined as the anodic peak and its height is smaller. It is logical[18,19] to assign this response to the osmium(IV)-osmium(III) couple. The diminished height of the cathodic response indicates that the osmium(IV) species may not be very stable.

The negative side of the SCE was scanned with use of a glassy-carbon working electrode. Four successive cathodic reductions are observed (Table II). On scan reversal the corresponding anodic peaks either are not seen at all or are very ill-defined. These reductions are believed to correspond to successive electron transfers to the two azoimine functions.[10-12]

Concluding Remarks

OsX_2L_2 is isolated in two isomeric forms (*tc* and *cc*) differing in orientation of the OsL_2 fragment only. In contrast to the case for RuX_2L_2, no evidence for the existence of the *tt*-OsX_2L_2 isomer has been obtained. In the extent of M-L π-back-bonding the order is Os-L > Ru-L. The MLCT spectra of OsX_2L_2 is richer than those of RuX_2L_2 due to marked allowedness of the singlet-triplet transitions in the former. Very few data on osmium(III)-osmium(II) formal potentials of chelates of OsX_2 are available in the literature.[9,19] The values of OsX_2L_2 are the highest among those reported so far. In particular, these values are nearly 1 V more positive than the corresponding value[18,19] of $OsCl_2(bpy)_2$. The strong Os-L π-bonding undoubtedly plays an important role here. Studies on the chemical reactions of OsX_2L_2 and their utilization for the synthesis of other Os-L complexes are in progress.

Experimental Section

Materials. 2-(Arylazo)pyridine was prepared as before.[11] Osmium tetraoxide was obtained from Johnson Matthey & Co. Ltd., London. It was converted to $(NH_4)_2OsX_6$ (X = Cl, Br) according to a reported procedure.[20] The salt $(NEt_4)_2OsX_6$ was prepared by matathesis of $(NH_4)_2OsX_6$ and tetraethylammonium perchlorate (TEAP) in aqueous solution. The purification of acetonitrile and preparation of TEAP for electrochemical work were done as before.[11] All other solvents and chemicals used were of reagent grade and were used without further purification.

Measurements. Spectroscopic data were obtained with use of the following instruments: electronic spectra, Cary 17D or Pye Unicam SP8-150 spectrophotometer; IR spectra (KBr disk, 4000-400 cm^{-1}; polyethylene disk, 400-200 cm^{-1}), Perkin-Elmer IR-597 spectrophotometer; ^1H NMR spectra (in $CDCl_3$), Varian T-60A spectrometer. Solution electrical conductivity was measured with use of a Philips PR9500 bridge with a solute concentration of ~10^{-3} M. Electrochemical measurements wee carried out under a dinitrogen atmosphere with the help of a PAR Model 370-4 electrochemistry system as described elsewhere.[10] A Beckman Model 39273 platinum electrode and PAR G0021 glassy-carbon electrode were used as working electrodes. All results were collected at 298 K and are referenced to the saturated calomel electrode (SCE). The reported potentials are uncorrected for junction contribution.

Preparation of Complexes. *tc*-Dichlorobis(2-(phenylazo)pyridine)osmium(II), *tc*-$OsCl_2(pap)_2$. Dinitrogen was passed for 15 min through a suspension of 330 mg (0.5 mmol) of $(Et_4N)_2OsCl_6$ in 40 mL of 2-methoxyethanol. Following this 200 mg (1.09 mmol) of 2-(phenylazo)pyridine in 5 mL of 2-methoxyethanol was added. The mixture was then heated to reflux under a dinitrogen atmosphere for 8 h. During this period the suspension dissolved, producing a blue-violet solution. This was then concentrated slowly under dinitrogen atmosphere to about 10 mL and kept in the refrigerator for 12 h. The shining dark-colored crystalline precipitate was collected by filtration. The filtrate was saved for isolating the *cc* isomer (see below). The precipitate was washed thoroughly with water and finally with diethyl ether. It was dried under vacuum over P_4O_{10}. The yield was 250 mg (66.1%).

***cc*-Dichlorobis(2-(phenylazo)pyridine)osmium(II), *cc*-$OsCl_2(pap)_2$.** The filtrate collected from the preparation of *tc*-$OsCl_2(pap)_2$ was evaporated nearly to dryness on a water bath, and the mass was washed thoroughly with water and then with diethyl ether. It was dried under vacuum over P_4O_{10}. The dried mass was dissolved in 5 mL of 1:1 benzene-dichloromethane and was subjected to chromatography on a silica gel (60-120 mesh, S.D. India) column (30 × 1 cm). A small blue-violet band (*tc* isomer) was first eluted with dichloromethane. Finally the slower moving red-violet band was eluted with 9:1 benzene-acetonitrile. On slow evaporation at room temperature crystals started depositing. The yield was 40 mg (10.6%).

The **2-(*m*-tolylazo)pyridine analogues** were prepared with use of the same reaction stoichiometry and conditions starting with $(Et_4N)_2OsCl_6$ and 2-(*m*-tolylazo)pyridine.

***tc*-Dibromobis(2-(*m*-tolylazo)pyridine)osmium(II), *tc*-$OsBr_2(tap)_2$.** To a dinitrogen-flushed suspension of 465 mg (0.5 mmol) of $(Et_4N)_2OsBr_6$ in 40 mL of 2-methoxyethanol was added 200 mg (1.09 mmol) of 2-(*m*-tolylazo)pyridine, and the mixture was heated to reflux for 7 h. Gradually the solution turned blue-violet. Here the reaction proceeded faster than in the case of the chloro analogue. The solution was concentrated and processed as in the case of *tc*-$OsCl_2(pap)_2$. The yield of the highly crystalline complex was 220 mg (68.7%).

***cc*-Dibromobis(2-(*m*-tolylazo)pyridine)osmium(II), *cc*-$OsBr_2(tap)_2$.** This was isolated from the mother liquor left after crystallization of *tc*-$OsBr_2(tap)_2$ exactly as in the case of *cc*-$OsCl_2(pap)_2$. The yield was 50 mg (15.6%).

Acknowledgment. Financial support received from the Department of Science and Technology, Government of India, New Delhi, is gratefully acknowledged.

Registry No. *tc*-$OsCl_2(pap)_2$, 87114-20-3; *tc*-$OsCl_2(pap)_2^+$, 87114-23-6; *tc*-$OsCl_2(pap)_2^{2+}$, 87114-26-9; *cc*-$OsCl_2(pap)_2$, 87172-01-8; *cc*-$OsCl_2(pap)_2^+$, 87172-04-1; *cc*-$OsCl_2(pap)_2^{2+}$, 87172-07-4; *tc*-$OsCl_2(tap)_2$, 87114-21-4; *tc*-$OsCl_2(tap)_2^+$, 87114-24-7; *tc*-$OsCl_2(tap)_2^{2+}$, 87114-27-0; *cc*-$OsCl_2(tap)_2$, 87172-02-9; *cc*-$OsCl_2(tap)_2^+$, 87172-05-2; *cc*-$OsCl_2(tap)_2^{2+}$, 87172-08-5; *tc*-$OsBr_2(tap)_2$, 87114-22-5; *tc*-$OsBr_2(tap)_2^+$, 87114-25-8; *tc*-$OsBr_2(tap)_2^{2+}$, 87114-28-1; *cc*-$OsBr_2(tap)_2$, 87172-03-0; *cc*-$OsBr_2(tap)_2^+$, 87172-06-3; *cc*-$OsBr_2(tap)_2^{2+}$, 87172-09-6.

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(18) Free L and RuX_2L_2 (the ruthenium(III)-ruthenium(II) couple at ~1 V) do not display any oxidative response up to 2 V. Hence the response with osmium complexes can hardly be due to ligand oxidation. Analogy with $OsCl_2(bpy)_2$ is also helpful: it shows osmium(III)-osmium(II) and osmium(IV)-osmium(III) coupled at -0.04 and +1.35 V in dichloromethane.[19]

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