

# Osmium(II) complexes of *N*-aryl-1,2-arylene diimines formed *via* *ortho*-dimerization of ArNH<sub>2</sub>: synthesis, structure and redox properties

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**A family of *ortho*-arylene diimine chelates, [OsBr<sub>2</sub>L<sub>2</sub>] (L = *N*-aryl-1,2-arylene diimine), which represent the first examples of osmium–quinonedimine complexes, are isolated from the reaction of [NH<sub>4</sub>]<sub>2</sub>[OsBr<sub>6</sub>] with aromatic amines, ArNH<sub>2</sub>.**

Here, we wish to introduce novel examples of bivalent osmium compounds of *N*-aryl-1,2-arylene diimines (L) which are formed *via* the template synthesis of L with osmium (Scheme 1). The compounds, [OsBr<sub>2</sub>L<sub>2</sub>] **1**, represent the first examples<sup>1</sup> of osmium compounds of the *o*-arylene diimine family. This class of diimine<sup>2</sup> and dioxolene<sup>3</sup> complexes exhibits many interesting properties because of their redox propensities owing to the considerable mixing between metal and ligand orbitals. It may be noted<sup>4</sup> here that the above diimine ligands cannot be formed directly from the corresponding aminoarenes (ArNH<sub>2</sub>).

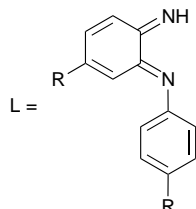
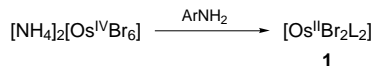
In a typical experiment 0.25 g of [NH<sub>4</sub>]<sub>2</sub>[OsBr<sub>6</sub>] was mixed with a large excess of amine, ArNH<sub>2</sub> (*ca.* 0.5 g) and the resultant mixture was heated in an oil-bath at 130–135 °C in air for 1 h. After the removal of the excess of amine, the crude product was purified on a silica gel column eluting with chloroform–acetonitrile (9 : 1). Finally, the product was recrystallized from dichloromethane–hexane. Dark shiny crystals of [OsBr<sub>2</sub>L<sub>2</sub>] **1** were obtained in *ca.* 50% yield.

The formation of **1** *via* the unusual oxidative *ortho*-dimerization reaction, ArNH<sub>2</sub> → L, has been authenticated by the structure determination of a representative example, *viz.*, [OsBr<sub>2</sub>L<sup>1</sup>]<sub>2</sub>. A view of the molecule is shown in Fig. 1. The coordination sphere consists of OsBr<sub>2</sub>N<sub>4</sub>. Two bromides are *cis* to each other and the aryl-substituted imines are also in relative *cis* positions. The imine C–N bonds<sup>5</sup> [av. 1.323(19) Å] are shorter than the two C–N single bonds [C(19)–N(4), C(7)–N(2), av. 1.437(13) Å] present in the same molecule. Moreover, the average C–C lengths [1.349(26) Å] at positions that would have localized double bonds for the diimine form of the ligands are significantly shorter than the other C–C lengths [av. 1.418(20) Å] of the same ring. It is apparent from the structural data that there is very little delocalization in the coordinated diimine

ligands with correspondingly no ambiguity in the bivalent oxidation state of osmium. The molecule approximates to overall C<sub>2</sub> symmetry. The twofold axis bisects the Br(1)–Os–Br(2) vector, as well as the N(2)–Os–N(4) vector.

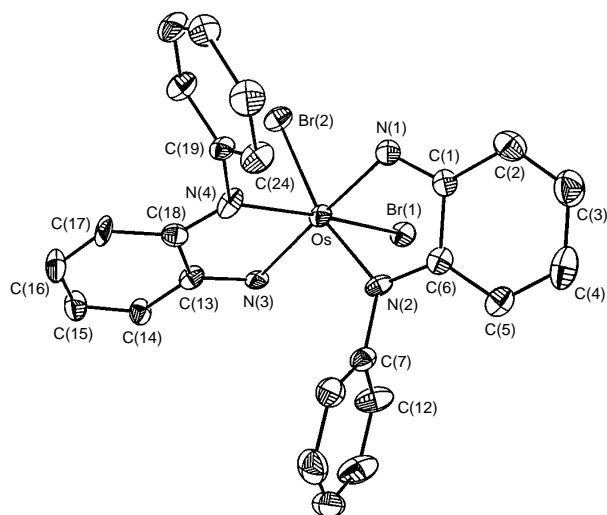
All the osmium diimine compounds analysed satisfactorily. The <sup>1</sup>H spectral features of the diamagnetic complexes consist of one relatively broad singlet resonance near δ 13.5, assignable<sup>6</sup> to NH (*e.g.* at δ 13.304 for **1b**), sharp methyl resonances (for **1b**) at δ 2.380 and 2.404 and resolved aromatic resonances in the range δ 6.5–8.0. Interestingly, each type of proton of L showed only one signal indicating magnetic equivalence of the two ligands in solution as found in the solid state. The electronic spectra of the complexes showed multiple charge-transfer transitions<sup>7</sup> occurring in the near-IR and visible regions [*e.g.* data for **1a**: λ/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 1150 (650), 900(780), 605(sh, 4310), 500(20050), 375(7290)].

Cyclic voltammetry of [OsBr<sub>2</sub>L<sub>2</sub>] showed two oxidations and one reduction wave in the potential range 2.0 to –1.8 V *vs.* SCE. The two responses on the positive potentials are reversible (Δ*E*<sub>p</sub> 60–65 mV, *i*<sub>pa</sub> = *i*<sub>pc</sub>) and assigned to successive one-electron transfers at the metal centre. The irreversible ligand reductions occur at negative potential. The potentials of the above couples shift anodically as the electron withdrawing ability of the substituent increases. For example, the potential of the Os<sup>III</sup>–Os<sup>II</sup> couple shifts from 0.70 V for **1a** to 0.94 V for **1c**. This potential, 0.94 V for an Os<sup>III</sup>–Os<sup>II</sup> couple, is one of the highest reported<sup>8</sup> in [OsX<sub>2</sub>L'<sub>2</sub>] (X = Cl, Br; L' = bidentate



|    |                |           |
|----|----------------|-----------|
| R  |                |           |
| H  | L <sup>1</sup> | <b>1a</b> |
| Me | L <sup>2</sup> | <b>b</b>  |
| Cl | L <sup>3</sup> | <b>c</b>  |

Scheme 1



**Fig. 1** Molecular structure of [OsBr<sub>2</sub>L<sup>1</sup>]<sub>2</sub> showing the atom numbering scheme. Selected distances (Å) and angles (°): Os–Br(1) 2.519(2), Os–Br(2) 2.523(3), Os–N(1) 1.998(11), Os–N(2) 2.000(11), Os–N(3) 1.994(10), Os–N(4) 2.017(11), N(1)–C(1) 1.317(19), N(2)–C(6) 1.338(19), N(2)–C(7) 1.417(15), N(3)–C(13) 1.325(19), N(4)–C(18) 1.312(20), N(4)–C(19) 1.458(11); Os–N(1)–C(1) 116.7(7), Os–N(2)–C(6) 115.5(8), N(1)–C(1)–C(6) 113.6(12), N(2)–C(6)–C(1) 114.1(12), N(1)–Os–N(2) 77.9(4), N(3)–Os–N(4) 76.6(4), Os–N(3)–C(13), 118.2(6), Os–N(4)–C(18) 117.5(7), N(3)–C(13)–C(18) 112.8(12), N(4)–C(18)–C(13) 113.8(13).

ligand) systems. This may be attributed to the very strong  $\pi$  interactions between the metal and low-lying acceptor-ligand orbitals. This effect is also reflected in the short Os–N distance<sup>7</sup> (av. 2.002 Å) in [OsBr<sub>2</sub>L<sub>2</sub>].

One-electron coulometric oxidation of **1a** at 0.9 V afforded a brown solution which can be quantitatively reduced to **1a** by electrolysis at 0.5 V. The brown solution of **1a**<sup>+</sup> displayed a rhombic EPR spectrum with three distinct resonances at  $g = 2.693, 2.401$  and  $1.638$  indicating<sup>9</sup> the trivalent d<sup>5</sup> state of osmium in **1a**<sup>+</sup>.

The formation of L from ArNH<sub>2</sub> involves the transfer of four electrons and four protons. Therefore, a total of eight electrons and eight protons are released for the formation of two L in **1**. In contrast, the metal oxidation levels in [NH<sub>4</sub>]<sub>2</sub>[OsBr<sub>6</sub>] and **1** differ only by two units. The mechanism of the above reaction is, as yet, not established. However, we wish to note here that the above reaction does not proceed in an N<sub>2</sub> atmosphere in the absence of O<sub>2</sub>. Presumably, *cis*-coordination of two aniline molecules followed by oxidative dimerization with the formation of a C–N bond in the presence of O<sub>2</sub> would be a plausible path for the formation of L in the above reaction. Osmium promoted oxidation of amine to imine by O<sub>2</sub> is known<sup>10</sup> in the literature. Interestingly, and as expected, 2,6-dimethylaniline did not react with [OsBr<sub>6</sub>]<sup>2-</sup> under identical conditions.

Preliminary experiments indicate that compounds **1** serve as excellent starting materials for the syntheses of tris-chelates of osmium(II) diimines, the photochemistry and electrochemistry of which are of interest in contemporary research.<sup>11</sup> Detailed studies are in progress and will be reported elsewhere.

We are grateful to Professor A. Chakravorty and thank Dr P. Ghosh, IACS, Calcutta for their help in the X-ray analysis of **1a**. Financial support received from the UGC, New Delhi is acknowledged.

#### Footnotes

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‡ *X-Ray structure determination*: X-ray quality crystals (0.4 × 0.3 × 0.25 mm) of [OsBr<sub>2</sub>L<sub>2</sub>] were obtained by slow diffusion of a dichloromethane solution of the complex into hexane. Cell parameters were obtained by least-square fits of 30 machine centred reflections. Data were collected (3 ≤ 2θ ≤ 43°) on a Nicolet R3 m/V diffractometer (295 K) with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Two check reflections were measured after 198 reflections did not show any significant change in intensity over 25 h exposure to X-rays. Data were corrected for Lorentz-polarization effect and absorption (azimuthal scan). Of the 2953 reflections collected 2858 were unique and 2386 reflections satisfying  $I > 2\sigma(I)$  were

used for structure solution by the Patterson heavy atom method using the SHELXTL-PLUS program<sup>12</sup> package on a MicroVax II computer. Refinement was done by the full-matrix least-squares method. All non-hydrogen atoms were made anisotropic. Hydrogen atoms were added at calculated positions and refined with fixed  $U = 0.08 \text{ \AA}^2$ .

*Crystal data for 2a*: C<sub>24</sub>H<sub>20</sub>Br<sub>2</sub>N<sub>4</sub>Os,  $M = 712.2$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.464(6)$ ,  $b = 11.778(6)$ ,  $c = 12.595(10)$  Å,  $\alpha = 103.86(5)$ ,  $\beta = 112.72(6)$ ,  $\gamma = 107.79(4)^\circ$ ,  $U = 1245.3(10)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.991$  g cm<sup>-3</sup>,  $R = 0.046$ ,  $R' = 0.0521$ .

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/298.

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Received, 27th September 1996; Com. 6/06623B