Novel Five-co-ordinate Osmium–Oxo Complex Stabilized by Diaminato Ligands. Synthesis, Reactivities, and *X*-Ray Crystal Structure of $[OsO\{NHC(Me)_2C(Me)_2NH\}\{NH_2C(Me)_2C(Me)_2NH\}]ClO_4$

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The six-co-ordinate *trans*-$[Os(L)_2(O)_2]^{2+}$ [L = $NH_2C(Me)_2C(Me)_2NH_2$] and five-co-ordinate $[OsO\{NHC(Me)_2C(Me)_2NH\}\{NH_2C(Me)_2C(Me)_2NH\}]^+$ complexes are in equilibrium in solution; the *X*-ray structure of the five-co-ordinate square pyramidal Os^{VI}–oxo complex has been determined with a measured Os=O distance of 1.72(2) Å.

We have been studying the design and reactivities of high-valent ruthenium and osmium–oxo complexes. There has been much work done on the oxidation of these compounds with chelating tertiary amines,[1] but there are few reports of related studies with primary and secondary amine ligands. This is because the co-ordinated primary and secondary amines would easily undergo oxidative dehydrogenation to imines, equation (1),[2] rendering the formation of ruthenium and osmium–oxo complexes difficult.

We anticipate that the problem of oxidative dehydrogenation could be overcome if the chelating diamine ligand did not have α(C–H) groups. Herein we describe the synthesis and reactivities of osmium–oxo complexes of 2,3-dimethyl-2,3-diaminobutane (L). The deprotonated forms of L, which are strong σ-donors, have been found to stabilize an unusual five-co-ordinate osmium(VI)–oxo complex.

Reaction of $Na_2[OsCl_6]$ with L in refluxing ethanol, in the presence of tin plates, for 1 day gave *trans*-$[Os(L)_2Cl_2]^+$, which was oxidized to *trans*-$[Os(L)_2(O)_2]^{2+}$ (**1**) with H_2O_2 in water. Complex (**1**) was isolated as a yellow crystalline perchlorate salt. As expected, it is diamagnetic and exhibits an intense IR $\nu_{as}(OsO_2)$ stretch at $\sim$870 cm^{-1}. In acidic solutions, its UV–VIS absorption spectrum displays two distinct vibronic structured absorption bands centred at 310 and 350 nm, which are the characteristic spin-allowed and spin-forbidden $(d_{xy})^2 \rightarrow (d_{xy})^1(d_{\pi^*})$ ($d_{\pi^*} = d_{xz}, d_{yz}$) transitions of *trans*-dioxotetraamineosmium(VI).[3] In basic solutions, such as acetonitrile with collidine, (**1**) is rapidly converted to a new species (**2**) having an intense absorption band at 390 nm (Figure 1). Complex (**2**) can also be prepared by the reaction of $K[Os(O)_3(NBu^t)]$ with L in methanol and isolated as a red crystalline perchlorate salt. Magnetic susceptibility measurements by Evan's method indicated that it is diamagnetic. Its IR spectrum displays an intense ν(Os=O) stretch at 920 cm^{-1}. The structure of (**2**) has been determined by *X*-ray crystallography to be $[OsO\{NHC(Me)_2C(Me)_2NH\}\{NH_2C(Me)_2C(Me)_2NH\}]ClO_4$.† Figure 2 shows a perspective view of the complex cation. The structure features one of the few examples of

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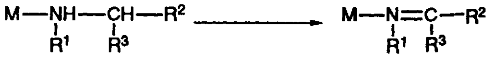
† *Crystal data*: $OsO(C_6H_{14}N_2)(C_6H_{15}N_2)\cdot ClO_4$, $M = 535.05$, space group *Pnma* (No. 62), $a = 13.331(3)$, $b = 7.9087(7)$, $c = 17.840(4)$ Å, $U = 1880.9(6)$ Å^3, $Z = 4$, $D_c = 1.893$ g cm^{-3}, μ(Mo-K_α) = 69.54 cm^{-1}, $F(000) = 1068$, no. of variables (p) 116, no. of unique data measured 2323, no. of observed data with $|F_o| \geqslant 6\sigma(|F_o|)$ (n) 1613, $R_F = 0.055$, $R_G = 0.075$. The residual extremes in the final difference map were 2.31 to -2.04 e Å^{-3}. Raw intensities collected on a Nicolet R3m/V four-circle diffractometer at room temperature (294 K) were processed with the profile fitting procedure of Diamond and corrected for absorption using ψ-scan data. The osmium atom was located by the Patterson method and the co-ordinates of the other non-hydrogen atoms were derived from successive difference Fourier syntheses. The C atoms in both non-planar chelate rings exhibited two-fold disorder as dictated by the space group, and distance constraints of 1.48(2) and 1.55(2) Å were applied to the C–N and C–C bonds in order to overcome correlation problems caused by overlapping atoms. The Os, Cl, O, and N atoms were refined anisotropically and the C atoms isotropically. Hydrogen atoms were not included in the refinement and structure-factor calculation. Computations were performed using the SHELTXL-PLUS program package on a DEC MicroVAX-II computer. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.


$$\underset{R^1}{M-NH}-\underset{R^3}{CH}-R^2 \longrightarrow \underset{R^1}{M-N}=\underset{R^3}{C}-R^2 \quad (1)$$

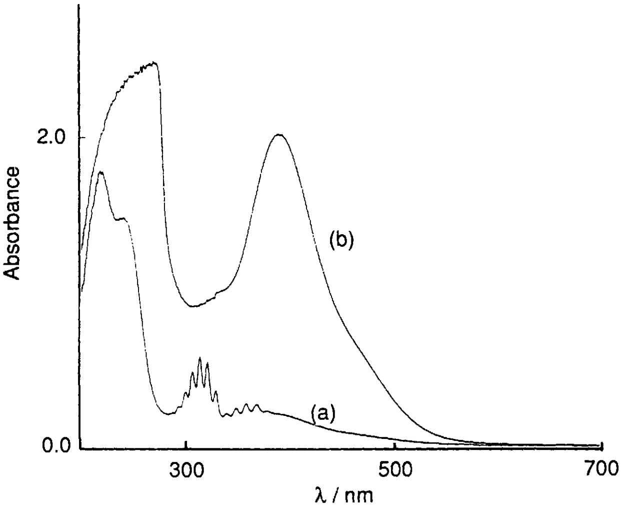


Figure 1. UV-VIS spectra of (a) (**1**) and (b) (**2**) in acetonitrile.

five-co-ordinate osmium(VI)–oxo complexes.[4] In the crystalline compound, both the complex cation and the perchlorate ion occupy sites of crystallographic mirror symmetry. The hydrocarbon moiety in each organic ligand has two equally populated conformations related by mirror symmetry, so that every carbon atom has a site occupancy factor of 1/2. As illustrated in Figure 2, the osmium atom is surrounded by the oxo O(1) atom and four nitrogen atoms from two organic ligands in a square-pyramidal co-ordination environment. The four co-planar nitrogen atoms constitute a basal plane with edges of 2.35(2) Å [N(1) ··· N(1a)] and 2.65(2) Å [N(1) ··· N(2)]. The osmium atom is displaced 0.67(1) Å from the basal plane toward O(1) and the angle between the plane normal and the Os(1)–O(1) bond is 2.5(5)°. This is structurally similar to the square pyramidal oxobis(ethane-1,2-diolato)osmium(VI) complex, in which the osmium atom is 0.64 Å above the base of the pyramid.[4] The measured Os–O distance of 1.72(2) Å is in accord with a metal–oxygen double bond. This value is similar to that found in the *trans*-dioxo-osmium(VI) system, but slightly longer than the value of 1.670 Å in $[OsO(O_2C_2H_4)_2]$.[4]

The Os–N distances are an interesting structural feature of the complex cation. There are two independent Os–N bond distances, namely Os–N(1) and Os–N(2). The measured Os–N(1) distance of 1.85(1) Å is substantially shorter than the Os–N distances of 2.10 and 2.12 Å for *trans*-$[Os^{VI}(en)_2(O)_2](HSO_4)_2$ (en = 1,2-diaminoethane),[5] but close to the value of 1.896(7) Å for the Os–N(1,2-ethanediaminato)$^-$ distance in *cis*-$[Os^{IV}(en)_2(enH)]Br_2$.[6] This suggests that N(1) belongs to an amido group, where the N(2) and N(2a) atoms belong to the monodeprotonated form of L. The measured Os–N(2) distance of 1.99(1) Å is also substantially lower than a normal Os^{VI}–N(amine) single bond, which is around 2.1 Å.[5] The symmetry of the complex may require that the average values of the Os–N(NH_2) and Os–N(NH) distances are equivalent. This equivalence may also arise if one H atom of the NH_2– group is disordered owing to, *e.g.*, H-bonding interaction. As the distance between O(1) and N(2b) (symmetry transformation: $-x$, $-y$, $-z$) is 3.30(2) Å and the related angles are 124.7(5) [Os(1)–O(1) ··· N(2b)], 106.9(5) [O(1) ··· N(2b)–Os(1b)], and 132.3(5)° [O(1) ··· N(2b)–C(7b)], there may be a weak hydrogen bond interaction between O(1) and N(2b).

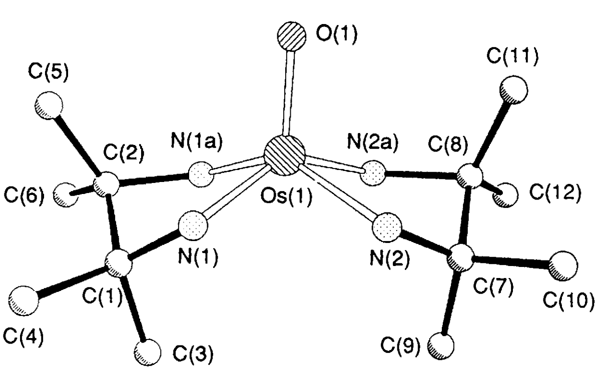


Figure 2. Perspective view of the $[OsO\{NHC(Me)_2C(Me)_2NH\}\{NH_2C(Me)_2C(Me)_2NH\}]^+$ cation with atom numbering. Os(1)–N(2) 1.99(1), Os(1)–N(1) 1.85(1), Os(1)–O(1) 1.72(2) Å. O(1)–Os(1)–N(1) 113.1(5), O(1)–Os(1)–N(2) 107.8(5), N(1a)–Os(1)–N(2) 139.0(5), N(1)–Os(1)–N(1a) 79.0(4), N(1)–Os(1)–N(2) 87.5(5), N(2)–Os(1)–N(2a) 77.8(4)°.

Complexes (**1**) and (**2**) are in equilibrium in solution. Addition of acid to a solution of (**2**) would regenerate (**1**) (Figure 1). This finding explains previous work by Malin *et al.*[5] who reported that the ^{18}O exchange rate of *trans*-$[Os^{VI}(en)_2(O)_2]^{2+}$ is very slow in acidic solution but becomes very fast in alkaline solution. We attribute the interconversion between a six-co-ordinate *trans*-dioxo-osmium(VI) and a five-co-ordinate mono-oxo-osmium(VI) through deprotonation of the amine ligands, to be the reason for the fast ^{18}O exchange rate. We have demonstrated that the ligand L and its deprotonated forms are oxidation resistant and capable of stabilizing high-valent metal–oxo complexes. The strong σ-donor strength and oxidative stability of the doubly deprotonated form of L suggests that this is an important ligand in the oxidation chemistry of high-valent metal complexes.

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