OSMIUM(VI) COMPLEXES OF SULPHONYL AMIDO LIGAND. CRYSTAL STRUCTURES OF $[PPh_4]_2[Os_2O_4\{C_6H_4(C_7H_7SO_2N)_2-o\}_2(\mu-OH)_2]$ AND $Os_2N_2[C_6H_4(C_7H_7SO_2N)_2-o](\mu-OH)_2$

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Abstract—Interactions of $[PPh_4]_2[OsO_2Cl_4]$ and $[Bu^n_4N][OsNCl_4]$ with Li₂L $[H_2L = 1, 2-bis(p-toluenesulphonylamido)benzene] gave binuclear osmium(VI) compounds <math>(PPh_4)_2[Os_2 O_4L_2(\mu-OH)_2]$ (1) and $Os_2N_2L_2(\mu-OH)_2$ (2), respectively. The structures of both compounds have been determined by X-ray crystallography. The crystal structure of the $[Os_2O_4L_2(\mu-OH)_2]^{2-}$ anion contains two *trans*-OsO_2(L) units bridged by two OH groups; the Os—O(oxo) bond length is *ca* 1.74 Å. The crystal structure of **2** contains two OsN(L) units bridged by two OH groups; the Os—N(nitrido) bond length is *ca* 1.56 Å.

Multianionic chelating ligands are of current interest because they can stabilize metal ions in high oxidation states. High-valent metal complexes with deprotonated amido ligands, e.g. those of manganese(V),¹ iron(IV),² cobalt(IV),³ nickel(III)⁴ and copper(III),⁵ are well documented. However, there are relatively few studies on complexes of sulphonyl amido groups. As the sulphonyl group is more electron-withdrawing than the carbonyl group one might expect that sulphonyl amido ligands can be deprotonated more readily and hence could display interesting coordination chemistry. To this end we set out to investigate the chemistry of complexes containing chelating sulphonyl amido ligands, e.g. bis-(toluenesulphonylamido)benzene (H_2L) , as shown in Fig. 1. The unique features of the ligand H_2L are: (a) it is bidentate and dianionic; (b) it can stabilize highly oxidizing metal centres due to the

strong σ -donating deprotonated sulphonyl amido groups; and (c) it is sterically bulky. Recently, the crystal structures of some copper complexes of H₂L have been described.⁶ We herein report the synthesis and crystal structures of two osmium(VI) compounds of the ligand.

EXPERIMENTAL

The ligand $H_2L_5^{6a}$ [PPh₄]₂[OsO₂Cl₄]⁷ and [Buⁿ₄N] [OsNCl₄]⁸ were prepared according to the literature procedures. Organic solvents were purified by standard methods and distilled before use. ¹H NMR spectra were recorded on a JEOL EX 400 spectrometer. Chemical shifts (δ) were reported referenced to Si(CH₃)₄. IR spectra (Nujol) were





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obtained on a Perkin-Elmer 1600 FT-IR spectrophotometer. Elemental analyses were performed by MEDAC Ltd (Middlesex, U.K.).

Preparation of $[PPh_4]_2[Os_2O_4L_2(\mu-OH)_2]$ (1)

To a suspension of H₂L (0.4 g, 0.96 mmol) in THF (20 cm³) at -40° C was added 2 equivalents of BuⁿLi (ca 1.25 cm³ of a 1.6 M solution in hexanes). The resulting mixture was warmed to room temperature and stirred for 1 h. To this solution was added $[PPh_4]_2[OsO_2Cl_4]$ (0.51 g, 0.5 mmol) under nitrogen and the reaction mixture was stirred at room temperature overnight. After the removal of volatiles the dark red residue was extracted with acetonitrile/ether. Slow evaporation of the extract at room temperature afforded red crystals, which were collected and washed with ether (yield 0.25 g). ¹H NMR (CD₃CN): 2.34 (s, 12H, p-CH₃), 5.96 (br, s, 2H, OH) and aromatic protons. IR (Nujol)/cm⁻¹: v(O-H) 3437; v(S=O) 1152, 1108; $v(OsO_2)$ 859. Found: C, 53.2; H, 4.0; N, 3.3%. Calc. for [Os₂ C₈₈H₇₈N₄O₁₄P₂S₄]: C, 53.2; H, 4.0; N, 2.8%.

Preparation of $Os_2N_2L_2(\mu$ -OH)₂ (2)

The lithium salt of H_2L was prepared as for $[Os_2O_4(\mu-OH)_2]^{2-}$. To a THF solution of Li_2L (prepared from 0.41 g H_2L and 1.25 cm³ BuⁿLi) was added [Buⁿ₄N][OsNCl₄] (0.29 g, 0.5 mmol). The reaction mixture was stirred overnight and evaporated to dryness. The dark yellow residue was

extracted with THF. Careful addition of hexane to the extract afforded the crude product, which was recrystallized from THF/ether/hexane to give yellow crystals (yield 0.2 g). ¹H NMR (CD₃CN): 2.29 (s, 6H, *p*-CH₃); 6.28, 6.83, 7.06, 7.81 (all broad singlets, 12H, aroamtic protons). IR (cm⁻¹): ν (O—H) 3450; ν (S=O) 1150, 1126; ν (OsN) 986. Found: C, 61.5; H, 5.5; N, 11.0. Calc. for [Os₂C₄₀H₃₈N₆O₁₀S₄]: C, 62.3; H, 4.9; N, 10.9%.

X-ray crystallography

Diffraction measurements were performed on an Enraf-Nonius CAD-4 diffractometer. Lattice parameters of 1 were obtained from 25 reflections with 2θ angles in the range 17.00–21.00°, whereas cell dimensions of complex 2 were determined from 25 reflections with 2θ angles in the range $11.06-20.40^{\circ}$. All reflections were collected for Lorentz, polarization and adsorption effects. All data reduction and refinement were performed using the NRCC-SPD-VAX packages. The structures were solved by direct methods and refined by full-matrix leastsquares; all non-hydrogen atoms were refined with anisotropic thermal parameters. Both complexes 1 and 2 crystallize in the triclinic system with the space group $P\overline{1}$. Hydrogen atoms on the organic ligands were calculated in idealized positions and were included in the structure factor calculation. The combined data collection and refinements are given in Table 1. Selected bond lengths and angles for complexes 1 and 2 are given in Tables 2 and 3, respectively.

| Compound | 1 | 2 |
|---|---|--|
| Formula | $C_{90}H_{78}N_4O_{14}P_2Os_2 \cdot (MeCN)_2$ | $C_{40}H_{38}N_6O_{10}S_4Os_2$. (THF) $\cdot 2(H_2O) \cdot 1/2(Et_2O)$ |
| Crystal system | Triclinic | Triclinic |
| Space group | P1 (No. 2) | <i>P</i> 1 (No. 2) |
| a (Å) | 12.867(5) | 11.363(8) |
| $b(\mathbf{A})$ | 14.418(4) | 14.289(9) |
| c (Å) | 14.621(4) | 18.580(7) |
| α (°) | 66.69(3) | 109.55(5) |
| β(°) | 64.69(3) | 102.62(3) |
| γ (°) | 64.48(3) | 90.23(5) |
| $V(Å^3)$ | 2137(1) | 27,656(2) |
| Mol. wt | 2008 | 1270 |
| Ζ | 1 | 2 |
| $D_{\rm c} ({\rm g}{\rm cm}^{-3})$ | 1.608 | 1.697 |
| μ (Mo- K_{α}) (cm ⁻¹) | 31.7 | 48.0 |
| Transmission factors | 0.696–1.00 | 0.745-1.00 |
| $R; R_{w}^{b}$ | 0.043; 0.055 | 0.062; 0.062 |

Table 1. Experimental data for the X-ray diffraction studies^a

^{*a*} Features common to all determinations : $\lambda(\text{Mo-}K_{\alpha}) = 0.7107 \text{ Å}$; temperature = 297 K. ^{*b*} $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$.

| Os—O(1) 1.74 | 0(6) | S(1)-O(4) | 1.428(7) |
|--------------------|----------|-------------|-----------------------|
| Os—O(2) 1.74 | 7(7) | S(1) - N(1) | 1.646(6) |
| Os—O(3) 2.05 | 1(6) | N(1) - C(1) | 1.40(1) |
| Os—N(1) 2.02 | 2(6) | | |
| O(1)OsO(2) | 175.7(3) | Os—N(1)—C(| 1) 118.4(5) |
| O(1)—Os—O(3) | 86.7(3) | O(1)-Os-N | 1) 92.5(3) |
| O(3) - Os - O(3') | 71.3(2) | N(1)-Os-N | 2) 78.3(3) |
| O(3)—Os—N(1) | 175.7(2) | O(3)-Os-N(| 2) 105.9(2) |
| O(4) - S(1) - N(1) | 110.8(4) | N(1)S(1)C | C(7) 106.6(3) |
| Os-O(3)-Osa | 108.7(3) | O(4)-S(1)-N | I (1) 110.8(4) |
| Os-N(1)-S(1) | 123.9(4) | O(4)S(1)C | (7) 107.7(4) |
| N(1)-C(1)-C(2) | 129.1(7) | N(1)-C(1)C | C(6) 114.2(7) |
| | | | |

Table 2. Selected bond lengths (Å) and angles (°) for the $[Os_2O_4L_2(\mu - OH)_2]^{2-}$ anion

RESULTS AND DISCUSSION

Interaction of $[PPh_4]_2[OsO_2Cl_4]$ with 2 equivalents of the lithium salt of H_2L [$H_2L = 1,2$ -bis(*p*-toluenesulphonylamido)benzene] in THF gave the air-stable binuclear hydroxo-bridged osmium(VI)-dioxo compound (1), isolated as its $[PPh_4]^+$ salt. A monomeric compound could not be obtained even when excess ligand was used, presumably because the ligand is too bulky for formation of a planar bischelate complex. The IR spectrum of 1 does not show any sharp N—H band, indicating that the sulphonyl amido group is in the deprotonated form. The broad band near 3470 cm⁻¹ can be assigned to the v(O-H) stretch. The Os=O stretch at 845 cm⁻¹ is within the range expected for *trans*-OsO₂ compounds.

The binuclear structure of 1 was confirmed by an X-ray diffraction study. A diagram of the $[Os_2O_4L_2(\mu-OH)_2]^{2-}$ anion is shown in Fig. 2; selected bond lengths and angles are given in Table 2. The geometry around each osmium is best described as octahedral with the two oxo groups as axial ligands and L and two hydroxo groups as equatorial ligands. The two *trans*-OsO₂L units are bridged by the two hydroxo ligands with the Os—O(H)—Os' bond angle of *ca* 108.7°. A similar structure has been observed for the binuclear oxobridged Os₂O₆py₄.⁹ The Os—O(oxo) bond lengths (*ca* 1.74 Å) are normal by comparison with *trans*osmium(VI)-dioxo compounds. The Os—N(sulphonyl amido) bond length of *ca* 2.03 Å is similar to that for Os—N(amido) found in a related osmium(VI)-nitrido compound of a tetradentate amido ligand.¹⁰ Of note, the four toluenesulphonyl groups of the ligands adopt a "two-up–two-down" geometry.

Treatment of $[Bu^n_4N][OsNCl_4]$ with 2 equivalents of Li₂L gave the neutral dimeric osmium(VI)nitrido compound **2**. Again, the steric bulk of the ligand L precludes the formation of the monomeric bischelate complex. The presence of the bridging hydroxo group is indicated by the broad IR band at 3450 cm⁻¹. The Os—N stretch at 986 cm⁻¹ is

Table 3. Selected bond lengths (Å) and angles (°) for $Os_2N_2L_2(\mu$ -OH)₂ (2)

| Os(1)—O(9) 1.99(2 | 2) | S(1)-N(1) | 1.60(2) |
|---------------------|----------|---------------------|-----------------|
| Os(1)-N(1) 1.97(2 | | S(1)-O(1) | 1.46(2) |
| Os(1)-N(5) 1.52(2 | | N(1) - C(1) | 1.47(3) |
| Os(2)—N(6) 1.61(2 | 2) | | |
| O(9)-Os(1)-O(10) | 74.5(7) | O(1)—S(1)—P | N(1) 105(1) |
| O(9) - Os(1) - N(1) | 92.4(7) | O(1)S(1)C | C(7) 108(1) |
| O(9) - Os(1) - N(2) | 140.2(7) | N(1)—S(1)—(| C(7) 106(1) |
| O(9) - Os(1) - N(5) | 110.0(9) | Os(1)O(9) | -Os(2) 104.2(7) |
| N(1) - Os(1) - N(2) | 85.6(7) | Os(1) - N(1) - N(1) | -S(1) 124(1) |
| N(1) - Os(1) - N(5) | 113.1(9) | Os(1)-N(1)- | -C(1) 116(2) |
| N(2) - Os(1) - N(5) | 109.5(9) | N(1) - C(1) - C(1) | C(2) 126(2) |
| N(1)-C(1)-C(6) | 112(2) | S(1)C(7)C | C(8) 120.7(8) |
| | | | |



Fig. 2. A perspective view of the $[Os_2O_4L_2(\mu-OH)_2]^{2-1}$ anion.

normal for nitrido compounds. The ¹H NMR spectrum of **2** is consistent with the solid-state structure.

The structure of 2 has been determined by Xray crystallography. An ORTEP drawing of 2 is shown in Fig. 3 and selected bond lengths and angles are given in Table 3. The geometry around each osmium is square pyramidal with the nitrido group as an axial ligand. The two Os(N)L units are bridged by the two hydroxo ligands with the two nitrido ligands on the same side. The Os(1)—O(H)—Os(2) bond angle of 104.2° and Os—N(amido) bond length of 1.973 Å are similar to those for 1. The Os—N(nitrido) bond length is normal for osmium(VI)-nitrido compounds.¹¹ It might be noted that this is the first structure of a binuclear osmium-nitrido compound.

The reactivity of these two osmium complexes is being studied.



Fig. 3. A perspective view of 2.

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