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Synthesis and Molecular Structure of Dichlorotetrakis(benzamidato)diosmium(III)

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Several years ago the first compound containing a triple bond between osmium atoms was discovered in this laboratory. However, the chemistry of multiply bonded diosmium complexes has until recently been very limited, comprising only hydroxypyridinate [1, 2] and tetracarboxylate compounds [3–6]. Recently we reported [7] the orthometallated diosmium species, $Os_2(O_2CCH_3)_2(Ph_2PC_6H_4)_2Cl_2$, having mixed bridging ligands. However, in view of the very fruitful and important chemistry that has been developed for other dimetal species (*e.g.*, Cr_2^{4+} [8], Mo_2^{4+} [9], Ru_2^{5+} [10] and Rh_2^{4+} [11]) by introducing bridging amidato ligands, we have been seeking to prepare such compounds for the Os_2^{6+} unit.

In this note we describe the first such compound, $Os_2(PhCONH)_4Cl_2$, which has been obtained from the reaction of $Os_2(O_2CCH_3)_4Cl_2$ with 10 g molten benzamide ($PhCONH_2$) at 140 °C for 72 h under dinitrogen atmosphere. The excess ligand was removed by sublimation. The yield was quantitative. During the reaction, the colour of the reaction mixture changed from brown (colour of the starting $Os_2(O_2CCH_3)_4Cl_2$) to dark-green. The complex[†] is only sparingly soluble in common organic solvents other than Me_2SO in which it displays bands at 750 nm (ϵ = 1050 dm^3 mol^{-1} cm^{-1}) and 635 nm (1665) in the visible region of the electronic spectrum (Fig. 1).

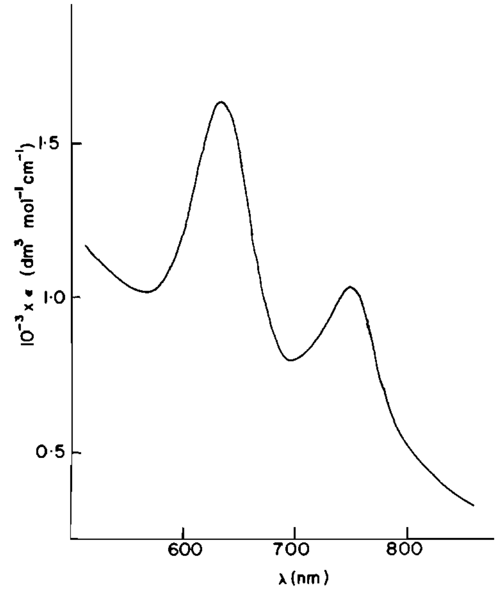

Fig. 1. Electronic spectrum of $Os_2Cl_2(PhCONH)_4$ in Me_2SO.

Suitable crystals for X-ray analysis[‡] were obtained by slow diffusion of MeOH containing $[(C_2H_5)_4N]Cl$ into a solution of the complex in Me_2SO. The crystals belong to the triclinic system and there are two molecules in the unit cell residing on the inversion centers at (0,0,0) and (½,½,½). The asymmetric unit thus consists of half of each molecule. The structure of one molecule (the other is substantially identical) with the atom labelling scheme is shown in Fig. 2. Each molecule is dinuclear with each osmium atom having an $OsClN_2O_2$ ligand set that is essentially octahedral in shape. The Os–Os–Cl angles are 175.1(3) and 172.4(3)°. The Os–Os–O and Os–Os–N angles lie in the ranges 88.7(6)–93.5(7)° and 86.5(8)–89.2(6)°, respectively. The average O–C–N angle is 121°. The Os–N and Os–O bond distances are similar to the corresponding Ru–N and Ru–O distances in $Ru_2(PhCONH)_2(NC(Ph)OPPh_2)_2(Ph)_2$ [12].

The osmium–osmium distances, 2.371(3) and 2.364(3) Å (average distance = 2.368(3) Å), are higher in the present complex compared to other reported diosmium species. $[Os_2(hp)_4Cl_2\cdot 2CH_3CN$ [2], 2.357 Å; $Os_2(O_2CCH_3)_4Cl_2$ [6], 2.314 Å; $Os_2(O_2CCH_3)_2(Ph_2PC_6H_4)_2Cl_2$ [7], 2.271 Å]. The average Os–Cl bond length is 2.485 Å which is comparable to the Os–Cl distance in $Os_2(hp)_4Cl_2\cdot 2CH_3CN$ (2.505 Å) [2] but considerably higher than that found [4–7] in orthometallated species (2.372 Å) and in carboxylato complexes (2.417–2.448 Å).

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[†] Ir spectrum in the KBr phase: 3300br, 3020m, 1640m, 1595m, 1505s, 1450vs, 1235s, 1185m, 1155w, 1115s, 1025s, 1000s, 845s, 695vs, 615w, 545s, 470w, 390m, 345w, 290w (cm^{-1}).

[‡] Crystal data: For $Os_2Cl_2(PhCONH)_4$, M = 931.83, triclinic, $P\bar{1}$, a = 10.840(6) Å, b = 14.381(7) Å, c = 10.682(7) Å, α = 110.91(4)°, β = 105.80(6)°, γ = 68.10(6)°, U = 1424(1) Å^3, D_c = 2.17 g cm^{-3}, μ(Mo-Kα) = 91.43 cm^{-1}, Z = 2, λ = 0.71073 Å, crystal dimensions 0.15 × 0.1 × 0.1 mm^3, present R factor is 0.089 for 2019 reflections with $F > 3\sigma(F)$ collected at 25 °C on an Enraf-Nonius CAD-4 diffractometer. Full details and a discussion of the problems in X-ray analysis will be reported in the full paper. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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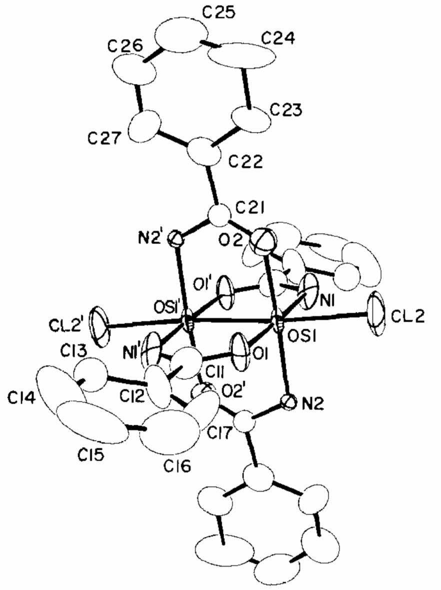
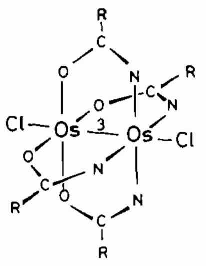


Fig. 2. An ORTEP drawing at the 50% probability level of the molecular structure of $Os_2Cl_2(PhCONH)_4$. Only one molecule out of two in the asymmetric unit is shown. The other molecule is essentially the same. Selected bond distances (Å) and angles (°) in both molecules are: Os(1)–Os(1)′, 2.371(3); Os(2)–Os(2)′, 2.364(3); Os(1)–Cl(2), 2.504(9); Os(2)–Cl(1), 2.466(9); Os(1)–O(1), 2.03(2); Os(1)–O(2), 1.96(2); Os(1)–N(1), 2.01(3); Os(1)–N(2), 2.04(2); Os(2)–O(3), 1.97(3); Os(2)–O(4), 1.88(2); Os(2)–N(3), 2.02(3); Os(2)–N(4), 1.94(3); Os(1)–Os(1)–Cl(2), 175.1(3); Os(1)–Os(1)–O(1), 88.7(6); Os(1)–Os(1)–O(2), 88.8(7); Os(1)–Os(1)–N(1), 88.5(9); Os(1)–Os(1)–N(2), 89.2(6); Cl(2)–Os(1)–O(1), 90.7(7); Cl(2)–Os(1)–O(2), 86.3(7); Cl(2)–Os(1)–N(1), 92.0(9); Cl(2)–Os(1)–N(2), 95.7(7); O(1)–Os(1)–O(2), 86.7(9); O(1)–Os(1)–N(1), 177.0(1); O(1)–Os(1)–N(2) 91.0(9); O(2)–Os(1)–N(1), 92.0(1); O(2)–Os(1)–N(2), 177.0(9); N(1)–Os(1)–N(2), 90.0(1); Os(2)–Os(2)–Cl(1), 172.4(2); Os(2)–Os(2)–O(3), 88.9(7); Os(2)–Os(2)–O(4), 93.5(7); Os(2)–Os(2)–N(3), 88.7(8); Os(2)–Os(2)–N(4), 86.5(8); Cl(1)–Os(2)–O(3), 90.7(8); Cl(1)–Os(2)–O(4), 94.0(8); Cl(1)–Os(2)–N(3); 92.1(9); Cl(1)–Os(2)–N(4), 85.8(9); O(3)–Os(2)–O(4), 87.0(1); O(3)–Os(2)–N(3), 176.0(1); O(3)–Os(2)–N(4), 91.0(1); O(4)–Os(2)–N(3), 91.0(1); O(4)–Os(2)–N(4), 177.0(1); N(3)–Os(2)–N(4), 92.0(1).

The molecule $Os_2Cl_2(PhCONH)_4$ can exist in four possible isomeric forms (*1–4*). In absence of any substituent on the nitrogen it is very difficult to assign the atom positions. We have tried all four possibilities and the best fit was observed with the structural arrangement *4* below. The high *R* factor and several large vibrational amplitudes indicate the existence of some sort of disorder in this molecular frame. A similar type of arrangement was observed [13] in $Rh_2(CF_3CONH)_4(py)_2$. Further studies on the present complex and related species are now in progress.



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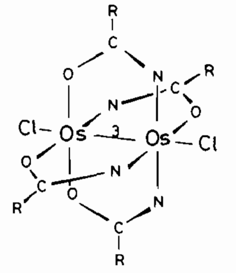

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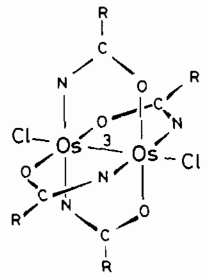

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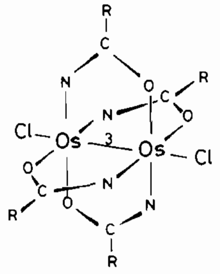

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Acknowledgement

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