Acetato-complexes of Osmium(II, III, and IV)

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Summary The osmium(III) acetate $[OsCl(O_2CMe)_2]_n$ has been prepared from Na_2OsCl_6; it is a useful source of other mono-or bi-nuclear osmium complexes that have the metal in oxidation states II, III, and IV.

Although ruthenium carboxylates of the types $Ru_2(O_2CR)_4$-Cl[1] and $[Ru_3O(O_2CR)_6L_3]^+$, L = H_2O, pyridine (py), *etc.*,[2] are known, the osmium analogues are not. Attempts to synthesise triosmium oxo-centred species have so far been unsuccessful but by the interaction of sodium hexachloro-osmate(IV) in acetic acid containing acetic anhydride and a little concentrated hydrochloric acid we have obtained in high yield the brown osmium(III) chloro acetate of stoichieiometry $[OsCl(O_2CMe)_2]_n$ (**1**). This compound is so in-soluble in common organic solvents that the molecular weight cannot be determined but it may have a structure similar to that found for the 2-hydroxypyridinato (hp) complex $Os_2Cl_2(hp)_4$.[3] Thus, complex (**1**) has i.r. bands at 1645 and 1480 cm^{-1} characteristic[4] for symmetrically bridging acetato-groups. In diethyl ether suspension complex (**1**) reacts with triphenylphosphine and sodium amalgam to give the binuclear species $Os_2(O_2CMe)_4(PPh_3)_2$ which again has i.r. bands for bridging acetate groups and presumably has the common tetra-acetato-bridged structure with PPh_3 end groups; the ruthenium analogue is known.[5] With neat trimethylphosphine complex (**1**) undergoes a cleavage and disproportionation reaction to give an osmium(IV) salt, $[Os(O_2CMe)_3(PMe_3)_3Cl]$, which has unidentate[4] acetato-groups, in $< 50\%$ yield plus an as yet unidentified soluble species. Interaction of complex (**1**) with t-butyl isocyanide gives the purple octahedral $OsCl(O_2CMe)_2(CNBu^t)_3$ also with unidentate acetate groups according to its i.r. spectra. The interaction of complex (**1**) with pyridine in ethanol leads to reduction to a binuclear species, $Os_2(O_2CMe)_4(Cl)(py)$, in which osmium has the mean oxidation state of 2·5 [similar to ruthenium in $Ru_2(O_2CMe)_4Cl$ (ref. 1)]; the acetate groups are bridging (i.r.) and py and Cl are terminal.

The complex (**1**) dissolves readily in neat pyridine and from the red solution so obtained can be isolated $[Os(O_2CMe)_2(py)_2]Cl$ which has chelate acetate groups (i.r.). This red solution provides a useful source of a variety of osmium(III) compounds which appear to be octahedral with either unidentate or chelate acetato-groups, as appropriate, ccording to the i.r. criteria.[4]

a

The red solution reacts with (a) carbon monoxide to give $OsCl(O_2CMe)_2(CO)(py)_2$, (b) hydrogen to give blue $OsCl(O_2CMe)_2(py)_3$, and (c) gaseous ammonia to give $OsCl(O_2CMe)_2(NH_3)_2(py)$. With nitric oxide, reduction to give formally an osmium(II) species of stoicheiometry $[Os(O_2CMe)(NO)_2(py)_2]Cl$ occurs. Although the red solution is unaffected on refluxing with silver acetate, with silver trifluoroacetate oxidation occurs and the neutral mixed carboxylate osmium(IV) complex, $[OsCl(O_2CMe)(O_2CCF_3)_2(py)_2]$, is obtained as dark blue crystals; the i.r. spectrum indicates unidentate carboxylate groups. Satisfactory analytical data for the new compounds have been obtained.

Studies on the replacement of chlorine in these species by hydrido, alkyl, aryl, and other groups are in progress.

It may be noted that although several of these osmium species should have an odd electron and be paramagnetic, nevertheless, quite sharp ^1H n.m.r. spectra can be obtained. E.s.r. studies on frozen solutions of $[OsCl(O_2CMe)_3(PMe_3)_3]Cl$, $Os_2(O_2CMe)_4(Cl)(py)$, and $OsCl(O_2CMe)_2(py)_3$ show only very weak signals in the $g = 2$ region and this weakness is probably due to fast spin–lattice relaxations at the temperatures used (*ca.* 100 K).

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