Salicylato (sal) Complexes of Second- and Third-row Transition Elements, and the Crystal Structure of $[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$ †

Catherine F. Edwards, William P. Griffith,* Andrew J. P. White and David J. Williams*
Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, UK

Salts of $[MO_2L_2]^{2-}$ [M = Mo or Os; L = salicylate(2−) (sal), 4- or 5-methylsalicylate(2−)] and $[M_2O_5(sal)_2]^{2-}$ (M = Mo or W) were prepared and their Raman, infrared, ^1H and ^{13}C-{^1H} NMR and X-ray photoelectron spectra measured. The crystal structure of $[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$ has been determined. Vibrational, ^1H and ^{13}C-{^1H} NMR spectra have also been recorded for the complexes $[Pd(sal)_2]^{2-}$, $[Pd(Hsal)_2]$ and $[Rh_2(Hsal)_4(EtOH)(H_2O)]\cdot EtOH\cdot H_2O$.

The salicylate [sal, $C_6H_4(O)(CO_2)^{2-}$] ligand, derived from salicylic acid (2-hydroxybenzoic acid, H_2sal) is unusual because it can adopt several different modes of bonding. In $[OsO_2(sal)(py)_2]$ (py = pyridine) it functions as a bidentate ligand using its deprotonated phenol and carboxylate oxygen atoms to form a six-membered ring with osmium.[1] We have shown recently that in $[Hpy][MoO_2(Hsal)(sal)]$ there are two different rings; the dianion sal^{2-} acts as in the osmium species above, whereas the monoanion $C_6H_4(O)(CO_2H)^-$ (Hsal) retains the carboxyl proton but still forms a six-membered ring with the metal.[2] In $[Cu(Hsal)_2(H_2O)_2]\cdot 2H_2O$ the monoanion $Hsal^-$ co-ordinates by one oxygen atom of the deprotonated carboxylate group,[3] while in $[Cu(Hsal)_2]\cdot 2H_2O$ one Hsal ligand co-ordinates *via* one carboxylate oxygen atom while the other bridges two adjacent copper atoms with its phenol and carboxylate oxygen atoms.[4] In $[Rh_2(Hsal)_4(EtOH)(H_2O)]\cdot EtOH\cdot H_2O$ the phenol oxygen atom is not co-ordinated, but the two carboxylate oxygen atoms span the two metal centres in the familiar lantern structure,[5] and in the manganese complex $[Mn_9O_4(O_2CPh)_4(sal)_4(Hsal)_2(py)_2]$ the sal^{2-} ligand bridges three metal atoms.[6]

The salicylate (sal^{2-}) and catecholate (cat^{2-}, dianion of benzene-1,2-diol, H_2cat) ligands are closely related and are of current interest.[6–8] In earlier work we have characterised a number of catecholato[7–11] and α-hydroxycarboxylato complexes,[12–14] and present here structural and spectroscopic studies of some new complexes of salicylic acid.

Results and Discussion

(*a*) *Preparations.*—There are early reports of salicylato complexes of molybdenum and tungsten,[15,16] but the formulae given are often unlikely, based as they are purely on elemental analyses. Thus, whereas Weinland and Zimmermann[15] report that reaction of molybdic acid, salicylic acid and tetramethylammonium hydroxide yields '$7[MoO_2(sal)_2](Me_4N)_2 + H_2sal + 16H_2O$' the product is actually $[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$. Despite many attempts we were unable to isolate salts of $[MoO_2(sal)_2]^{2-}$ with cations other than pyridinium[2] or tetramethylammonium, nor could we obtain salts of $[WO_2(sal)_2]^{2-}$ though we have isolated $[NMe_4]_2[MoO_2L_2]$ [L = 4- or 5-methylsalicylate (4- or 5-msal)]. Reaction of salicylic acid with either molybdic or tungstic acid in hot aqueous potassium hydroxide solution was said to give '$KH[MoO_2(sal)_2] + KH[MoO_3(sal)] + H_2O$'[15] or '$K[WO_2(OH)(sal)]$';[16] however we find that the products give analyses close to those expected for $K_2[M_2O_5(sal)_2]$ (M = Mo or W). These two complexes have very similar Raman and infrared spectra and we believe that they have structures analogous to those found in $[NH_4]_2[Mo_2O_5(cat)_2]$[17] and $[NH_4]_2[Mo_2O_5(nd)_2]$[18] (nd = naphthalene-2,3-diolate), with one oxygen atom from each salicylate dianion bridging the two metal atoms. These salts are insoluble in all common solvents and are decomposed by hot water, dimethylformamide and dimethyl sulfoxide.

The potassium salt $K_2[OsO_2(sal)_2]$ was first made by reaction of *trans*-$K_2[OsO_2(OH)_4]$ with aqueous salicylic acid,[19] but a better route is to treat *trans*-$K_2[OsO_2(OMe)_4]$ with salicylic acid in methanol. The salt $[PPh_4]_2[OsO_2(sal)_2]$ is soluble in organic solvents and reacts with both *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmen) and *N*,*N*′-diisopropylethylenediamine (dipen) to give $[OsO_2(sal)(tmen)]$ and $[OsO_2(sal)(dipen)]$ respectively. Surprisingly, the known complex[4] $[OsO_2(sal)(py)_2]$ could not be made from pyridine and $[OsO_2(sal)_2]^{2-}$, perhaps reflecting the stability of the chelated salicylate ring.

The known rhodium complex $[Rh_2(Hsal)_4(EtOH)(H_2O)]\cdot EtOH\cdot H_2O$[5] was made and improved procedures for the preparation of the previously reported[20] $K_2[Pd(sal)_2]$ and $[Pd(Hsal)_2]$ devised. Attempts to make platinum analogues of the latter species were unsuccessful.

(*b*) *Crystal Structure of* $[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$.—Yellow crystals of $[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$ suitable for X-ray study were prepared by refluxing $MoO_3\cdot nH_2O$, salicylic acid and tetramethylammonium hydroxide in water; recrystallisation was not necessary. The structure of the anion, with atom labelling, is shown in Fig. 1. Selected bond lengths and angles are listed in Table 1, atomic coordinates in Table 2.

The crystal structure shows the molybdenum to have conventional octahedral geometry with the oxo ligands *cis* [Mo–O(3) 1.714 (3), Mo–O(4) 1.701 (3) Å] consistent with the spectroscopic data (see below). Although there is an equal probability of the formation of Δ and Λ forms in the crystalline state, spontaneous resolution has occurred and in the crystal studied only molecules with the Δ configuration were present.

The two Mo–O(carboxylate) bonds *trans* to oxo [2.133(3) and 2.166(3) Å] are significantly longer than those to the two phenolic oxygens [1.967(3) and 1.971(3) Å]. This reflects the

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.
Non-SI unit employed: eV ≈ 1.60 × 10^{-19} J.

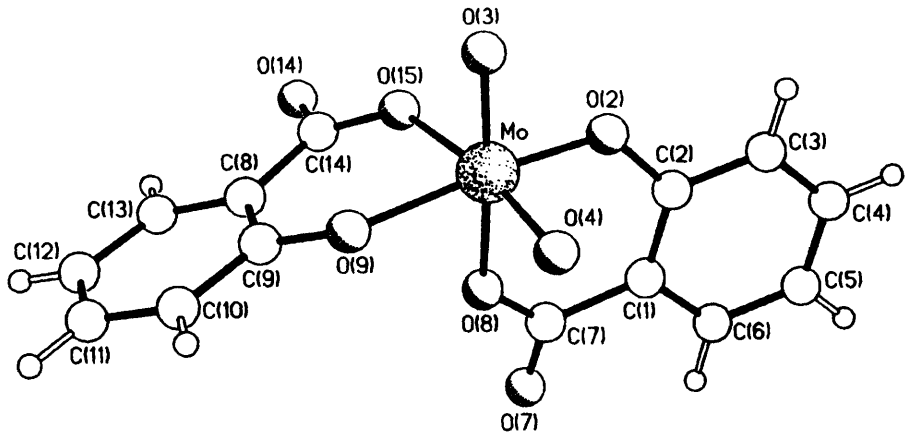

Fig. 1 Crystal structure of the anion of $[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$

Table 1 Selected bond lengths (Å) and angles (°) for $[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$ with estimated standard deviations (e.s.d.s) in parentheses

Mo–O(2)	1.967(3)	Mo–O(3)	1.714(3)
Mo–O(4)	1.701(3)	Mo–O(8)	2.166(3)
Mo–O(9)	1.971(3)	Mo–O(15)	2.133(3)
C(1)–C(2)	1.412(5)	C(8)–C(9)	1.421(6)
C(2)–O(2)	1.346(5)	C(7)–O(7)	1.243(5)
C(7)–O(8)	1.268(5)	C(9)–O(9)	1.334(5)
C(14)–O(14)	1.234(5)	C(14)–O(15)	1.285(5)
O(3)–Mo–O(4)	103.7(2)	O(3)–Mo–O(2)	92.5(1)
O(4)–Mo–O(2)	96.1(2)	O(3)–Mo–O(8)	165.3(2)
O(4)–Mo–O(8)	90.3(2)	O(2)–Mo–O(8)	81.3(1)
O(3)–Mo–O(9)	101.1(1)	O(4)–Mo–O(9)	92.6(1)
O(2)–Mo–O(9)	161.7(1)	O(8)–Mo–O(9)	82.6(1)
O(3)–Mo–O(15)	88.2(1)	O(4)–Mo–O(15)	167.6(1)
O(2)–Mo–O(15)	86.9(1)	O(8)–Mo–O(15)	78.3(1)
O(9)–Mo–O(15)	81.4(1)		

Table 2 Atomic coordinates ($\times 10^4$)

Atom	*x*	*y*	*z*
Mo	2 110(1)	3 354(1)	8 499(1)
O(3)	3 682(3)	3 395(2)	8 913(2)
O(4)	1 812(3)	2 239(2)	8 396(2)
C(1)	942(4)	3 389(3)	6 647(2)
C(2)	2 345(4)	3 343(3)	6 808(2)
O(2)	2 869(3)	3 541(2)	7 487(2)
C(3)	3 263(4)	3 157(3)	6 227(3)
C(4)	2 802(5)	3 000(3)	5 509(3)
C(5)	1 423(6)	3 029(3)	5 343(3)
C(6)	524(5)	3 223(3)	5 908(2)
C(7)	−100(4)	3 629(3)	7 218(2)
O(7)	−1 271(3)	3 815(2)	7 009(2)
O(8)	244(3)	3 656(2)	7 905(2)
C(8)	220(4)	4 995(3)	9 470(2)
C(9)	148(4)	4 081(3)	9 687(2)
O(9)	918(3)	3 438(2)	9 388(2)
C(10)	−742(4)	3 831(3)	10 265(2)
C(11)	−1 535(5)	4 456(3)	10 621(3)
C(12)	−1 487(5)	5 351(4)	10 412(3)
C(13)	−610(5)	5 604(3)	9 837(3)
C(14)	1 193(5)	5 333(3)	8 899(2)
O(14)	1 210(4)	6 140(2)	8 749(2)
O(15)	2 022(3)	4 777(2)	8 593(2)
N(20)	1 411(4)	6 132(2)	6 168(2)
C(21)	211(6)	5 892(5)	5 716(4)
C(22)	1 098(7)	6 084(4)	6 970(3)
C(23)	2 542(6)	5 505(3)	5 979(5)
C(24)	1 835(6)	7 051(3)	5 957(3)
N(30)	−1 359(3)	4 879(2)	13 230(2)
C(31)	−2 529(5)	4 294(3)	13 005(3)
C(32)	−621(6)	5 167(4)	12 536(3)
C(33)	−408(6)	4 376(3)	13 728(3)
C(34)	−1 877(4)	5 687(3)	13 625(3)
O(40)	3 086(3)	7 441(3)	8 380(2)
O(41)	4 691(4)	7 035(3)	7 136(3)

powerful *trans* influence known to be exerted by the oxo ligand, and is consistent with the geometry observed in related salicylato complexes.[1,2] The bond distances within the salicylate ligands are comparable with those found in $[OsO_2(sal)(py)_2]$.[1] The octahedral geometry is distorted with the angles at the molybdenum in the ranges 81–104 and 162–168°. The molybdenum atom is displaced towards each oxo ligand [O(3) and O(4)] relative to the plane of the four oxygen atoms normal to these directions by 0.22 and 0.20 Å respectively. Within each ligand the carboxylate group is rotated out of the plane of its associated aromatic ring by *ca.* 12° for the C(7) carboxylate group and *ca.* 2.2° for the moiety containing C(14). In addition, the plane of each salicylate ligand is folded with respect to the plane defined by the metal and the two co-ordinated oxygen atoms. Thus, the aromatic ring C(1)–C(6) is folded by 24° to the plane defined by Mo, O(2) and O(8) and the C(8)–C(13) ring is folded by 12° with respect to the Mo, O(9) and O(15) plane. Both of the water molecules are involved in hydrogen bonding; one forms just a single hydrogen bond to the second [O(40)···O(41) 2.79 Å, O–H···O 163°]. The second water molecule, however, links the non-bonded carboxylate oxygen atom on one anion [O(40)···O(14) 2.76 Å, O–H···O 169°] to a different carbonyl oxygen atom on the opposite ligand of an adjacent anion [O(40)···O(7A) 2.81 Å, O–H···O 153°]. The pattern of hydrogen bonding extends along the crystallographic *b* direction to form infinite chains of linked anions (Fig. 2).

(*c*) *Vibrational Spectra* (*see Table* 3).—In $[NMe_4]_2[MoO_2L_2]$ (L = sal, 4- or 5-msal) the symmetric stretches $\nu_{sym}(MoO_2)$ are seen in the Raman spectrum as strong bands near 910 cm^{-1} {polarised in the solution spectrum of $[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$ as expected for a symmetric mode}, and weaker in the infrared; conversely the asymmetric stretches $\nu_{asym}(MoO_2)$ are strong in the infrared spectrum and weaker in the Raman near 880 cm^{-1}. Similar bands and assignments have been noted for other complexes containing *cis*-MO_2 units (M = Mo or W).[9,10,18] For the oxoosmium complexes the symmetric stretch $\nu_{sym}(OsO_2)$ of the centrosymmetric *trans* O=Os=O 'osmyl' unit is seen in the Raman spectrum near 880 cm^{-1}, polarised in solution and absent in the infrared spectrum, while the asymmetric stretch $\nu_{asym}(OsO_2)$ is strong in the infrared spectrum near 835 cm^{-1} and absent in the Raman. Similar bands

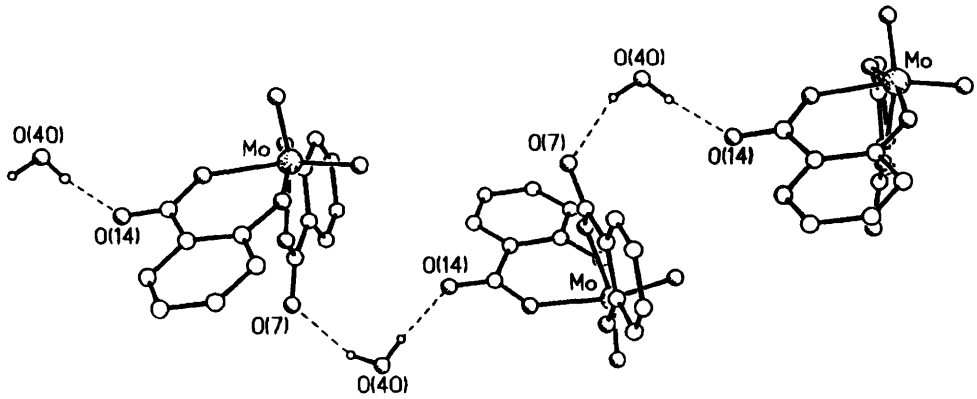

Fig. 2 Network of hydrogen-bonded linked anions in $[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$

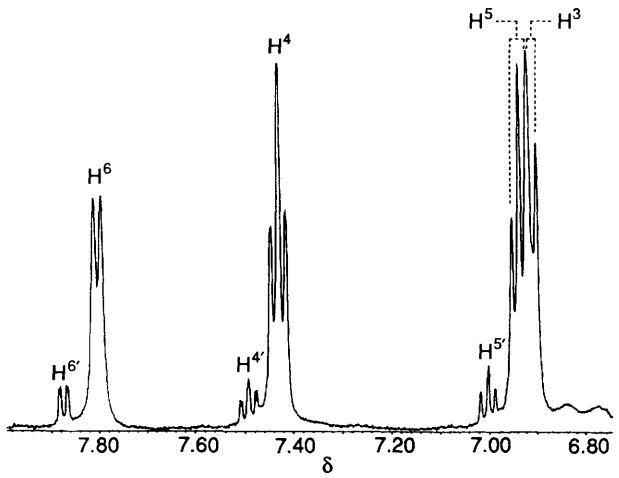

Fig. 3 Proton NMR spectrum of $[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$ (aromatic region). Peaks due to the major isomer labelled H", those due to the minor isomer labelled H"'

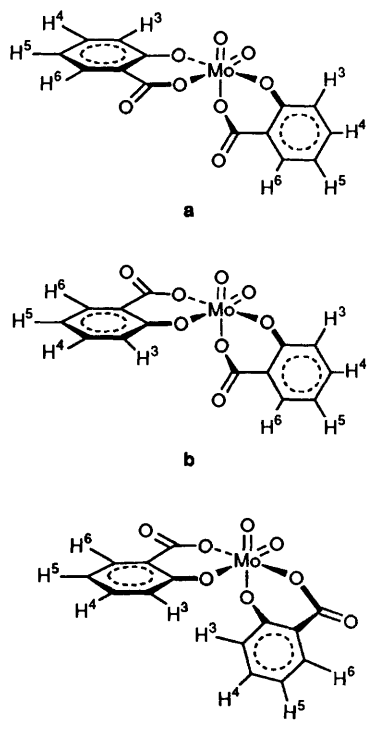

Fig. 4 Isomers of $[MoO_2(sal)_2]^{2-}$

have been noted for other complexes containing *trans*-OsO_2 units.[9,11,12]

Salicylic acid[21,22] and salicylato complexes[23,24] have been studied by Raman and infrared spectroscopy and modes assigned; there is also a recent surface enhanced Raman spectroscopy (SERS) study of salicylate adsorbed on a silver colloid.[25] We use the commonly accepted assignments[21-24] for the asymmetric and symmetric modes $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$: in the infrared spectrum $\nu_{asym}(CO_2)$ is a strong band near 1615 cm^{-1} while $\nu_{sym}(CO_2)$ appears as a moderately strong band between 1325 and 1380 cm^{-1}. In general $\nu_{asym}(CO_2)$ occurs at lower frequencies for the complexes than for salicylic acid while $\nu_{sym}(CO_2)$ occurs at higher frequencies.

The salicylate ligand is known to remain protonated at the hydroxyl group in $[Rh_2(Hsal)_4(EtOH)(H_2O)]\cdot EtOH\cdot H_2O$,[5] and a very strong broad infrared band at 1385 cm^{-1} may be due to the CO stretch ν(COH) of this group, which probably obscures $\nu_{sym}(CO_2)$. The salicylate in $[Pd(Hsal)_2]$ is also likely to retain its hydroxyl proton and the band at 1341 cm^{-1} {not observed in the spectrum of $K_2[Pd(sal)_2]$} is also likely to arise from ν(COH).

(d) Proton and ^{13}C-$\{^1H\}$ *NMR Spectra of the Complexes.*—Salicylic acid with its atomic numbering scheme is as shown.

^1H *NMR.* Proton NMR data for salicylic acid, its 4- and 5-methyl derivatives, and complexes thereof, are given in Table 3; the data for salicylic acid are in agreement with literature data.[26,27] The spectrum of sal^{2-} suggests that all the protons are more shielded than in the free acid.

The spectrum of $[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$ (Fig. 3) shows the presence of two isomeric products in approximately 6:1 ratio with all the minor isomer peaks downfield of their major isomer counterparts. For the major isomer the resonances of the two protons H^3 and H^5 are very similar and a second-order multiplet is observed, while for the minor isomer the resonances of these protons occur at fields sufficiently different that their signals do not overlap. The signal due to $H^{3'}$ is, however, obscured by the resonances of H^3 and H^5.

The anion *cis*-$[MoO_2(sal)_2]^{2-}$ has three possible geometric isomers (Fig. 4). Structure **a** is that seen for the anion in the solid state (see above), **b** is the mixed isomer with one carboxylate oxygen atom and one phenolic oxygen atom *trans* to the oxo groups, while **c** has two phenolic oxygen atoms in these positions. In **b** the protons on each of the aromatic rings are in different chemical environments, so more than four resonances

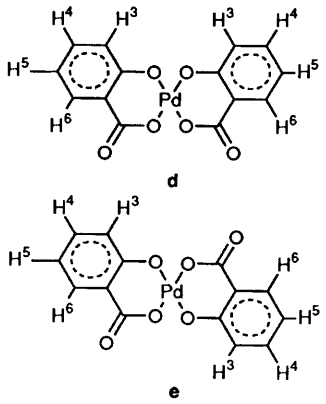

Fig. 5 Isomers of $[Pd(sal)_2]^{2-}$

would be expected. For it to be present, therefore, some minor isomer peaks would have to be directly under the major isomer peaks. A resolution enhancement of the spectrum only revealed part of the $H^{3'}$ doublet under the H^3 and H^5 resonances of the major isomer, and so **b** is unlikely to be present. Space-filling molecular models (Corey–Pauling–Koltun, CPK) show that whereas in **c** it is possible for the two aromatic rings to come close to each other this is not so in **a**. The result of this proximity is that the anisotropic local magnetic field produced by one ring can influence the chemical shifts of the protons on the second ring. The resonances of $H^{4'}$, $H^{5'}$ and $H^{6'}$ are observed to be shifted to lower field than that of their major isomer counterparts, and this is consistent with **c** where these three protons are in an area of space where the local field enhances the applied field. The resonance due to $H^{3'}$, however, is relatively unaffected, again consistent with **c**. Thus, we conclude that in solution the major isomer is **a** and the minor isomer is **c**.

The spectra of the methylated analogues $[NMe_4]_2[MoO_2(4\text{-msal})_2]\cdot 3H_2O$ and $[NMe_4]_2[MoO_2(5\text{-msal})_2]$ also show two isomers in 7:1 and 13:1 ratios respectively. By analogy with the parent compound above, the two isomers present are believed to be the two symmetric complexes, again with **a** as the major species.

The spectrum of $K_2[Pd(sal)_2]$ shows the presence of two isomers in an approximate 6:1 ratio; the protons of the minor isomer are less shielded than those of the major isomer. For the former, peaks due to H^3 and H^5 appear as a complex multiplet while for the latter they differ sufficiently so that discrete signals are seen for each. The *cis* and *trans* isomers are shown in Fig. 5. The magnetic anisotropy of the carbonyl group is likely to be an important factor affecting its neighbouring atoms, with protons in the same plane as a carbonyl group deshielded by it. In **d**, protons H^3 and H^5 on one ring are both remote from the carbonyl group on the other ring and so should be relatively unaffected, while in **e** H^3 is directed in the same way as the carbonyl group on the opposite ligand and may therefore be deshielded by it. There is then a greater difference between the environments of H^3 and H^5 in **e**, suggesting that this isomer is the major one. In the spectrum of $[Pd(Hsal)_2]$ all the peaks are deshielded compared with those of the potassium salt and an extra signal, due to the 'added' proton, is observed at δ 10.9.

For $[OsO_2(sal)_2]^{2-}$, $[OsO_2(4\text{-msal})_2]^{2-}$ and $[OsO_2(5\text{-msal})_2]^{2-}$ the spectra each show the presence of two isomers in approximately 4:1, 3:1 and 3:1 ratios respectively. In each case, the protons of the major isomer are deshielded with respect to those of the minor isomer. By analogy with the relative shifts of the two isomers for $K_2[Pd(sal)_2]$ (see above) it is tentatively suggested that the *cis* isomer is the one which predominates (*i.e.* the form shown for the palladium analogue in Fig. 5, **d**; the osmium complexes will in addition have two *trans* oxo ligands).

The spectrum of $[Rh_2(Hsal)_4(EtOH)(H_2O)]\cdot EtOH\cdot H_2O$ shows a peak due to the hydroxyl proton at δ 10.3. The aromatic region of the spectrum is rather complex and suggests that there are indeed two different salicylate orientations in the molecule (as shown by its crystal structure),[5] giving rise to similar signals.

$^{13}C\text{-}\{^1H\}$ *NMR*. The $^{13}C\text{-}\{^1H\}$ NMR data for salicylic acid and the complexes are given in Table 4; the data for the acid agree closely with those given by Breitmayer and Voelter[28] and by Scott.[29] There are seven resonances corresponding to the seven different carbon atoms of the molecule for which we have made assignments following those of Yamamoto and co-workers.[30] For sal^{2-} the spectrum shows that deprotonation of the carboxylate group primarily affects C^1 and C^7, the resonances of which are both shifted to lower fields.

It is clear from Table 4 that $^{13}C\text{-}\{^1H\}$ NMR spectroscopy is less effective for the determination of modes of bonding in salicylato complexes than it is for complexes of aliphatic hydroxy acids[12,13] or catecholates:[8,9,11] chemical shifts occurring upon complexation are quite small and are thus less reliable indicators of co-ordination sites.

In the spectrum of $[MoO_2(sal)_2]^{2-}$ there is again evidence for two isomers. For the major isomer a set of seven peaks is observed. In comparison with salicylic acid, the only resonances which have significantly shifted are those of C^1 and C^7, which are both deshielded for the complex, while the position of the resonance of the phenolic carbon atom (C^2) is little altered. Peaks due to the minor isomer are much weaker (due to the 6:1 ratio); data had to be accumulated for 2–3 d before these resonances were observed. Even so, those of the quaternary carbon atoms are so weak that they are not visible above the background noise.

In the cases of $[NMe_4]_2[MoO_2(4\text{-msal})_2]\cdot 3H_2O$ and $[NMe_4]_2[MoO_2(5\text{-msal})_2]$, similar features are observed as for the complex of the unsubstituted ligand; the replacement of a proton by a methyl group causes the resonance of the substituted ring carbon to shift to lower field by approximately 10 ppm. (Minor isomer peaks were not observed for these two complexes due to the shorter accumulation times.)

The spectrum of $[Pd(sal)_2]^{2-}$ shows fourteen peaks, indicating the presence of two isomeric products. For the *cis* isomer, Fig. 5, **d**, C^2 resonates at lower field than in **e** by 0.6 ppm. This may be because in **d** C^2 is opposite to the electron-withdrawing carboxylate group. In these palladium complexes C^2 is deshielded compared with salicylic acid while C^7 is not. For $[Pd(Hsal)_2]$ only seven peaks appear. Surprisingly the protonation has affected the carboxylate carbon (C^7), which is deshielded more than the phenoxyl carbon (C^2), so it appears possible that the proton is on the carboxyl group as in $[Hpy][MoO_2(Hsal)(sal)]$, though we were unable to obtain crystals of $[Pd(Hsal)_2]$ in order to confirm this.

The spectrum of $K_2[OsO_2(sal)_2]$ also suggests the existence of two isomers since there are fourteen peaks; the ^1H NMR spectrum (see above) suggested that the isomers are present in a 4:1 ratio. For $K_2[OsO_2(4\text{-msal})_2]\cdot H_2O$ and $K_2[OsO_2(5\text{-msal})_2]\cdot H_2O$ the spectra show sixteen peaks, the additional two from the ring-substituted methyl groups in the two isomers. The $^{13}C\text{-}\{^1H\}$ NMR spectrum of the rhodium complex $[Rh_2(Hsal)_4(EtOH)(H_2O)]\cdot EtOH\cdot H_2O$ showed the presence of two salicylate ligands in different orientations.

(*e*) *X-Ray Photoelectronic Spectroscopy and Cyclic Voltammetry*.—X-Ray photoelectronic measurements for $K_2[OsO_2L_2]$ (L = sal, 4- or 5-msal) showed Os $4f_{\frac{7}{2}}$ binding energies of 55.1, 55.0 and 55.1 eV respectively, which, as with previous osmium(VI) α-hydroxycarboxylato complexes studied by this method,[12] suggests that the osmium is indeed in the VI oxidation state.

Cyclic voltammetric measurements were made for the complex $[PPh_4]_2[OsO_2(sal)_2]$. The voltammogram showed an oxidation and a reduction at +0.50 and −2.42 V respectively

Table 3 Analytical and spectroscopic data for metal salicylato complexes

	Analysis[a] (%)				Vibrational spectra[b] (cm^{-1})				^1H NMR data[c] (δ)				
Complex	C	H	N	X	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	$\nu_{sym}(MO_2)$	$\nu_{asym}(MO_2)$	H^3	H^4	H^5	H^6	CH_3
Salicylic acid					1661vs	1325m			6.91[d]	7.45[d]	6.88[d]	7.85[d]	
					1634(7)	*1323(5)*							
Sodium salicylate					1582vs	1318m			6.92	7.43	6.94	7.79	
					1586(3)	*1303w*							
Salicylate(2−) (pH 14)									6.28	6.81	6.17	6.96	
4-Methylsalicylic acid					1625vs	1325w			6.74[d]	—	6.69[d]	7.71[d]	
					1640(10)	*1330(7)*							2.31[d]
5-Methylsalicylic acid					1661vs	1328m			6.80[d]	7.27[d]	—	7.64[d]	
					1638(7)	*1325(7)*							2.26[d]
$[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$	45.3	6.2	4.7		1598vs	1359vs	913m	881s	6.91[e]	7.43[e]	6.94[e]	7.80[e]	
	(45.2)	(6.2)	(4.8)		*1591(4)*	*1357w*	*908(10)*	*875(3)*	6.92[f]	7.49[f]	7.00[f]	7.87[f]	
$[NMe_4]_2[MoO_2(4\text{-msal})_2]\cdot 3H_2O$	45.0	5.8	4.7		1596vs	1387m	904s	875vs	6.75[e]	—	6.77[e]	7.67[e]	
	(45.7)	(6.7)	(4.4)		*1596(2)*	*1384(1)*	*902(10)*	*881(3)*	6.76[f]	—	6.84[f]	7.76[f]	2.29[e]
$[NMe_4]_2[MoO_2(5\text{-msal})_2]$	49.5	6.5	4.7		1634vs	1384m	903s	873s	6.82[e]	7.27[e]	—	7.61[e]	2.32[f]
	(50.0)	(6.3)	(4.9)		*1631(2)*	*1383(1)*	*901(10)*	*869(3)*	6.75[f]	7.33[f]	—	7.67[f]	2.25[e]
$K_2[Mo_2O_5(sal)_2]$	29.0	1.6		11.5[g]	1596s	1362s	935s	896s					2.29[f]
	(27.0)	(1.3)		(12.6)									
$K_2[W_2O_5(sal)_2]$	22.1	1.3		9.6[g]	1600s	1361s	943s	901s					
	(21.1)	(1.0)		(9.8)									
$K_2[OsO_2(sal)_2]$	29.0	1.5		13.3[g]	1639vs	1341s		835s	6.98[e]	7.40[e]	6.85[e]	8.00[e]	
	(29.4)	(1.4)		(13.7)			*885s*		6.91[f]	7.31[f]	6.78[f]	7.68[f]	
$K_2[OsO_2(4\text{-msal})_2]\cdot H_2O$	30.4	2.0			1634vs	1387m		830vs	6.95[e]	—	6.81[e]	7.99[e]	
	(31.1)	(2.3)							6.88[f]	—	6.79[f]	7.68[f]	2.34[e]
$K_2[OsO_2(5\text{-msal})_2]\cdot H_2O$	30.6	2.1			1634vs	1385w (sh)		835m	7.05[e]	7.39[e]	—	7.94[e]	2.31[f]
	(31.1)	(2.3)							6.98[f]	7.30[f]	—	7.90[f]	2.38[e]
$[OsO_2(sal)(tmen)]$	32.8	4.0	5.8		1625s	1325s		843s					2.37[f]
	(32.9)	(4.2)	(5.9)				*880s*						
$[OsO_2(sal)(dipen)]$	35.6	4.6	5.6		1620s	1330s		838s					
	(35.8)	(4.8)	(5.6)				*882s*						
$[Rh_2(Hsal)_4(EtOH)(H_2O)]\cdot EtOH\cdot H_2O$	43.6	4.0			1590s	1385vs			6.75[e]	7.28[e]	6.75[e]	7.75[e]	
	(43.6)	(4.1)			*1586w*	*1379vs*			6.95[f]	7.55[f]	6.95[f]	7.91[f]	
$K_2[Pd(sal)_2]$	37.0	1.9		16.8[g]	1590vs	1378s			6.61[e]	7.06[e]	6.54[e]	7.55[e]	
	(36.8)	(1.8)		(17.1)	*1575s*	*1368m*			6.75[f]	7.25[f]	6.75[f]	7.60[f]	
$Na_2[Pd(sal)_2]$	39.9	2.0		10.4[h]									
	(39.6)	(1.9)		(10.8)									
$[Pd(Hsal)_2]$	44.0	2.7			1596s	1380s			6.80	7.48	6.76	7.73	
	(44.2)	(2.6)											

[a] Calculated values in parentheses. [b] Raman data in italics. [c] Spectra in D_2O solution unless otherwise stated; chemical shifts in δ *vs.* $SiMe_4$. [d] In CD_3OD solution. [e] Peak due to major isomer. [f] Peak due to minor isomer. [g] Potassium analysis. [h] Sodium analysis.

Table 4 ^{13}C-{^1H} NMR data for salicylato complexes

Compound		Chemical shift (δ) C^1	C^2	C^3	C^4	C^5	C^6	C^7	CH_3
Salicylic acid[a]		113.8	162.7	118.0	136.6	120.2	131.5	173.6	
Salicylate(2−) (pH 14)		114.5	168.5	123.3	133.3	130.9	132.1	181.2	
4-Methylsalicylic acid[b]		111.1	162.7	118.1	148.3	121.5	131.4	173.6	21.8
5-Methylsalicylic acid[b]		113.3	160.2	117.9	137.6	129.7	131.1	173.6	20.4
$[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$	*c*	120.1	162.3	119.0	136.9	122.1	133.2	177.7	
	d	*e*	*e*	123.3	136.6	122.4	133.7	*e*	
$[NMe_4]_2[MoO_2(4\text{-msal})_2]\cdot 3H_2O$		118.3	162.6	119.3	148.2	123.1	133.3	177.9	23.4
$[NMe_4]_2[MoO_2(5\text{-msal})_2]$		119.2	160.2	120.3	137.6	131.9	133.3	177.3	22.2
$K_2[OsO_2(sal)_2]$	*c*	122.0	174.0	122.9	136.7	123.3	135.8	176.9	
	d	122.1	173.9	122.6	137.1	123.5	133.2	177.9	
$K_2[OsO_2(4\text{-msal})_2]\cdot H_2O$	*c*	119.7	173.9	122.4	148.6	124.5	135.9	177.3	23.5
	d	119.3	173.8	123.3	149.0	124.8	133.9	178.2	23.3
$K_2[OsO_2(5\text{-msal})_2]\cdot H_2O$	*c*	118.7	172.1	123.1	137.5	132.7	135.2	176.9	22.0
	d	119.4	172.0	122.8	137.1	133.0	134.5	177.9	21.7
$[Rh_2(Hsal)_4(EtOH)(H_2O)]\cdot EtOH\cdot H_2O$	*c*	115.9	162.2	118.1	135.6	119.9	131.0	171.7	
	d	113.3	163.1	117.9	136.7	119.5	131.3	*e*	
$K_2[Pd(sal)_2]$	*c*	119.5	165.8	116.5	133.3	120.1	132.6	173.0	
	d	119.3	166.4	116.2	133.9	120.4	132.5	172.8	
$(Pd(Hsal)_2]$		120.7	165.6	120.8	139.4	122.7	133.9	175.3	

Spectra in D_2O solution unless otherwise stated; chemical shifts in δ *vs.* $SiMe_4$. [a] In CD_3OD solution. [b] In $(CD_3)_2CO$ solution. [c] Major isomer. [d] Minor isomer. [e] Peak not observed.

(in dichloroethane with ferrocene–ferrocenium as 0.0 V and 0.1 mol dm^{-3} $NBu^n_4PF_6$) both of which were irreversible (as is often observed for *trans* osmyl complexes).[31–35] The complex $[OsO_2(sal)(py)_2]$ was also found to give irreversible features only,[5] *viz.* an oxidation at +1.58 and reductions at −0.88 and −1.54 V; the more positive potentials required for this complex may reflect its neutral charge, which should make it more difficult to oxidise and easier to reduce. The complex $[Pd(Hsal)_2]$ in acetonitrile showed an oxidation at +0.8 V and a reduction at −1.78 V, both irreversible; $[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$ underwent no electrochemical changes.

Experimental

Crystallography.—Crystal data. $C_{22}H_{36}MoN_2O_{10}$, M = 584.5, orthorthombic, space group $P2_12_12_1$, a = 9.846(2), b = 14.931(4), c = 17.765(4) Å, U = 2612 Å^3, Z = 4, D_c = 1.49 g cm^{-3}, Mo-Kα radiation, λ = 0.710 73 Å, μ(Mo-Kα) = 5.6 cm^{-1}, $F(000)$ = 1216. Yellow plates, crystal dimensions 0.11 × 0.41 × 0.67 mm.

Data collection and processing. Data were measured on a Siemens P4/PC diffractometer with Mo-Kα radiation (graphite monochromator) using ω scans. 2614 Independent reflections were measured ($2\theta \leqslant 50°$) of which 2428 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors; a numerical absorption correction (face-indexed crystal) was applied; maximum and minimum transmission factors were 0.891 and 0.768 respectively.

Structure analysis and refinement. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. A ΔF map revealed the presence of two individual water molecules and of disorder in the counter ions. The geometries of the counter ions were optimised and they were refined as rigid bodies. The hydrogen atoms of the water molecules were refined isotropically subject to an O–H distance constraint (0.85 Å). The positions of the remaining hydrogen atoms (determined from a ΔF map) were idealised (C–H 0.96 Å), assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares to give R = 0.029, R' = 0.031 [$w^{-1} = \sigma^2(F) + 0.0010F^2$]. The absolute structure was determined by an R-factor test (R_+ = 0.029, R_- = 0.031). The maximum and minimum residual electron densities in the final ΔF map were 0.27 and −0.29 e Å^{-3} respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.012 and 0.103:1 respectively.

Computations were carried out on an IBM PS/2 model 70 386 computer using the SHELXTL PC program system.[36]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Preparation of Complexes.—General. GPR grade molybdic acid ($MoO_3\cdot nH_2O$) was obtained from BDH, tungstic acid ($WO_3\cdot H_2O$) from Fluka Chemie and platinum metals were kindly lent by Johnson Matthey. Salicylic acid, 4- and 5-methylsalicylic acid, sodium salicylate, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and *N*,*N*′-diisopropylethylenediamine were supplied by the Aldrich Chemical Company. All chemicals were used without prior purification.

Infrared spectra were recorded as KBr discs on a Perkin-Elmer 1720 FT instrument. Raman spectra were obtained on a Spex Ramalog 5 instrument, with a Datamate data-acquisition unit, as spun discs on a KBr matrix with excitation at 647.1 nm by a Coherent Radiation Innova 90 krypton-ion laser and on a Perkin-Elmer 1760 X FT-IR instrument fitted with a 1700 X NIR FT-Raman accessory (Spectron Nd:YAG laser, 1064 nm excitation). Proton and ^{13}C-{^1H} NMR spectra were recorded on Brüker WM-250 FT (^1H, 250.13; ^{13}C, 62.9 MHz), JEOL EX-270 (^1H, 270.05; ^{13}C, 67.94 MHz) and Brüker AM-500 FT spectrometers (^1H, 500.13; ^{13}C, 125.76 MHz). The XPS measurements were made on powdered samples mounted on a sample stub using chlorine-free, double-sided adhesive tape and analysed using Mg-Kα radiation at 15 kV and 10 mA using 6 mm slits on a Kratos XSAM 800 instrument. Cyclic voltammograms were measured on an Oxford Electrodes PVSU potentiostat and microanalyses were by the Microanalytical Department, Imperial College.

The complex $[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$ was prepared by a modification of the literature method for '$7[MoO_2(sal)_2]\cdot(Me_4N)_2 + H_2sal + 16H_2O$'.[15] To a stirred suspension of $MoO_3\cdot nH_2O$ (0.72 g, 4.9 mmol) and salicylic acid (2.1 g, 15 mmol) in water (20 cm^3) was added tetramethylammonium

hydroxide pentahydrate (2.7 g, 15 mmol). The mixture was refluxed for 6–8 h, the intense yellow solution filtered whilst hot and the filtrate reduced in volume by 50%. Yellow crystals of the product were formed on standing overnight (yield 2.22 g, 76%). The complexes $[NMe_4]_2[MoO_2(4\text{-msal})_2]\cdot 3H_2O$ (yield 85%) and $[NMe_4]_2[MoO_2(5\text{-msal})_2]$ (yield 70%) were prepared similarly.

The complex $K_2[Mo_2O_5(sal)_2]$ was prepared by the literature method for '$KH[MoO_2(sal)_2]$ + $KH[MoO_3(sal)]$ + H_2O',[15] using $MoO_3\cdot nH_2O$, salicylic acid and aqueous KOH on a water-bath (yield 60%); $K_2[W_2O_5(sal)_2]$ was prepared by the literature method for '$K[WO_2(OH)(sal)]$'[16] from $WO_3\cdot H_2O$, salicylic acid and aqueous KOH on a water-bath (yield 72%).

The complex $K_2[OsO_2(sal)_2]$ was prepared by three methods. (*a*) The method of Barbieri,[19] involving salicylic acid and potassium osmate, *trans*-$K_2[OsO_2(OH)_4]$ (yield 59%). (*b*) To a stirred solution of $K_2[trans\text{-}OsO_2(OMe)_4]$[37] (0.20 g, 0.47 mmol) in methanol (15 cm^3) was added salicylic acid (0.13 g, 0.94 mmol) in methanol (5 cm^3). The deep red solution that resulted was left to stir until the product precipitated as a shiny brown-red precipitate. This was filtered off and washed with methanol and diethyl ether (yield 0.17 g, 62%). (*c*) To a stirred solution of osmium tetraoxide (0.15 g, 0.59 mmol) in tetrachloromethane (10 cm^3) was added sodium salicylate (0.28 g, 1.8 mmol) in ethanol. The resulting suspension was stirred for 4 h during which time its colour changed through yellow to deep red. The product was filtered off and washed with ethanol and diethyl ether (yield 0.15 g, 56%).

The complexes $K_2[OsO_2(4\text{-msal})_2]\cdot H_2O$ (yield 75%) and $K_2[OsO_2(5\text{-msal})_2]\cdot H_2O$ (yield 18%) were prepared similarly by method (*b*).

$[PPh_4]_2[OsO_2(sal)_2]$. To a stirred solution of $K_2[trans\text{-}OsO_2(OMe)_4]$[37] (0.15 g, 0.34 mmol) in methanol (10 cm^3) was added salicylic acid (0.094 g, 0.68 mmol) dissolved in methanol and water (8 + 2 cm^3). This gave a red solution which was filtered into an aqueous solution (10 cm^3) of PPh_4Cl (0.31 g, 0.83 mmol). The methanol was evaporated off and the salt precipitated from the solution as a green powder. This was recrystallised twice from dichloromethane and diethyl ether (yield 0.19 g, 46%).

$[OsO_2(sal)(tmen)]$. To a solution of $[PPh_4]_2[OsO_2(sal)_2]$ (0.20 g, 0.18 mmol) in dichloromethane was added *N,N,N',N'*-tetramethylethylenediamine (0.5 cm^3) and this solution was then refrigerated until the product precipitated as a brown powder (yield 0.05 g, 63%). The complex $[OsO_2(sal)(dipen)]$ was prepared similarly (yield 47%).

The complex $K_2[Pd(sal)_2]$ was prepared by two methods. (*a*) By use of the method of Barbieri[20] from $K_2[PdCl_4]$ and salicylic acid (yield 59%). (*b*) A solution of potassium carbonate (1.0 g, 7.2 mmol) and salicylic acid (1.0 g, 7.2 mmol) in water was heated until all effervescence had ceased. Then palladium dichloride (0.33 g, 1.9 mmol) was added with stirring. This gradually dissolved to give a yellow solution which upon cooling yielded the product as a bright yellow powder. This was filtered off and washed with ethanol (yield 0.51 g, 59%). The complex $Na_2[Pd(sal)_2]$ was prepared similarly (yield 54%).

$[Pd(Hsal)_2]$. This complex was prepared by a modification of the literature method.[20] To a solution of $Na_2[Pd(sal)_2]$ (0.20 g, 0.47 mmol) in water (5 cm^3) was added dilute sulfuric acid (dropwise) until no more off-white precipitate formed. This was filtered off and washed with water (yield 0.09 g, 52%).

The complex $[Rh_2(Hsal)_4(EtOH)(H_2O)]\cdot EtOH\cdot H_2O$ was prepared by the literature method[5] from rhodium trichloride and salicylic acid under reflux (yield 58%).

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