Second- and Third-row Transition-metal Complexes of Dihydroxybenzoic Acids, and the Crystal Structure of $[NMe_4]_2[MoO_2(2,3\text{-dhb})_2]\cdot1.5H_2O$ ($2,3\text{-}H_2dhb$ = 2,3-dihydroxybenzoic acid)†

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The new complexes $[MO_2L_2]^{2-}$ (H_2L = 2,3- or 3,4-dihydroxybenzoic acid, $2,3\text{-}H_2dhb$ or $3,4\text{-}H_2dhb$, M = Mo, W or Os; H_2L = 2,6-dihydroxybenzoic acid, $2,6\text{-}H_2dhb$, M = Mo), $[OsO_2(py)_2(2,6\text{-dhb})]$ (py = pyridine), $[ReOI(PPh_3)_2L]$ (H_2L = 2,3-, 3,4- or $2,6\text{-}H_2dhb$) and $[M(PPh_3)_2(2,3\text{-dhb})]$ (M = Pd or Pt) have been prepared. The crystal structure of $[NMe_4]_2[MoO_2(2,3\text{-dhb})_2]\cdot1.5H_2O$ has been determined and exhibits catecholato rather than salicylato type bonding. Infrared, Raman, ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectroscopic data for the complexes are also presented.

In earlier papers we reported a number of new complexes of second- and third-row elements with the non-innocent catechol (H_2cat) ligand; $^{13}C\text{-}\{^1H\}$ NMR spectroscopy is an excellent technique for demonstrating the presence of catecholato (cat^{2-}) bonding in such species.[1-4] More recently we have reported analogous studies on salicylato (2-hydroxybenzoic acid, H_2sal) complexes.[5,6] 2,3-Dihydroxybenzoic acid ($2,3\text{-}H_2dhb$) has the potential to function as a catecholato type ligand *via* deprotonated 2,3-oxygen atoms or as a salicylato type ligand *via* deprotonated carboxyl and 2-oxygen atom centres. Here we report a number of new complexes of $2,3\text{-}H_2dhb$ and show, by $^{13}C\text{-}\{^1H\}$ NMR and, in one instance by a crystal structure, that it functions as a catecholato type ligand in these species. We also report new complexes of 3,4-dihydroxybenzoic acid (a potential catecholato type ligand) and 2,6-dihydroxybenzoic acid (a potential salicylato type ligand).

Few complexes of these ligands have been isolated: those containing transition metals which have been characterised include $[Pd(PPh_3)_2(3,4\text{-dhb})]\cdot2C_6H_{14}$ and $[Pt(PPh_3)_2(3,4\text{-dhb})]$,[7] $[Cu(2,6\text{-Hdhb})_2(H_2O)_2]$[8] and $[Ag_2(2,6\text{-Hdhb})_2]$.[9] There do not appear to be any reported examples of crystal structure studies on transition-metal complexes containing either the 2,3- or $3,4\text{-}H_2dhb$ ligands, but there are reports for the $2,6\text{-}H_2dhb$ complexes $[Cu(2,6\text{-Hdhb})_2(H_2O)_2]$[8] and $[Ag_2(2,6\text{-Hdhb})_2]$.[9] There is evidence for the existence of $2,3\text{-}H_2dhb$ complexes of nickel(II)[10] and vanadium(IV)[11] in both catecholato and salicylato forms in solution. It is believed that the salicylato mode predominates at low pH (< 7), whilst the catecholato form is favoured at higher pH.[10,11] Complexes of $2,6\text{-}H_2dhb$ with copper have been shown to have anti-pyretic and anti-inflammatory properties[12] and $[Pt(PPh_3)_2(3,4\text{-dhb})]$ has anti-tumour activity.[13]

Results and Discussion

(*a*) *Preparations.*—The molybdenum and tungsten complexes were made from the appropriate dihydroxybenzoic acid together with $MO_3\cdot nH_2O$ or $Na_2[MO_4]$ with tetramethylammonium hydroxide or tetraphenylphosphonium chloride; the osmium complexes from *trans*-$K_2[OsO_2(OMe)_4]$ and the acid; the rhenium complexes from $[ReO_2I(PPh_3)_2]$ and the acid; and the palladium and platinum complexes from $[M(PPh_3)_2Cl_2]$ and the acid with triethylamine.

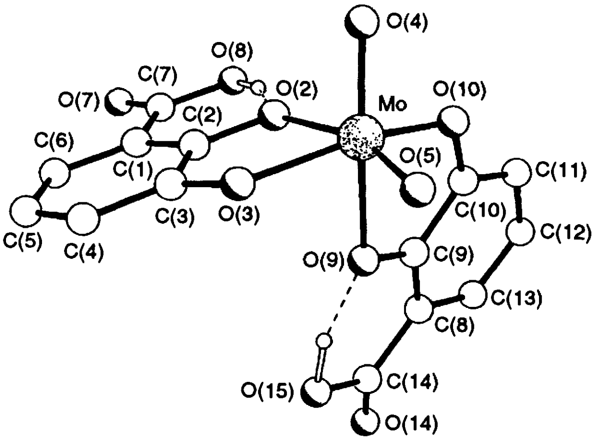

Fig. 1 Crystal structure of the anion of $[NMe_4]_2[MoO_2(2,3\text{-dhb})_2]\cdot1.5H_2O$

(*b*) *Crystal Structure of* $[NMe_4]_2[MoO_2(2,3\text{-dhb})_2]\cdot1.5H_2O$.—The orange-red crystals of this species were prepared directly by refluxing molybdic acid with 2,3-dihydroxybenzoic acid and tetramethylammonium hydroxide in water for 7 h, an adaptation of the method used by Weinland and Zimmermann[14] for the analogous salicylate (sal^{2-}) complex, $[NMe_4]_2[MoO_2(sal)_2]\cdot2H_2O$. The structure of the anion, with atom labelling, is shown in Fig. 1; fractional atomic coordinates are listed in Table 1 and selected bond lengths and angles in Table 2.

The crystal structure proves conclusively that the $2,3\text{-dhb}^{2-}$ anion functions as a catecholato ligand *via* the deprotonated hydroxyl oxygen atoms [O(2), O(3) and O(9), O(10)], Fig. 2(*a*), rather than in a salicylato mode, Fig. 2(*b*). The molecule has essentially non-crystallographic C_2 symmetry about an axis passing through the molybdenum atom and bisecting the O(4)–Mo–O(5) angle.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Fractional atomic coordinates ($\times 10^4$) for $[NMe_4]_2[MoO_2(2,3\text{-dhb})_2]\cdot 1.5H_2O$

Atom	*x*	*y*	*z*
Mo	1331(1)	3758(1)	2150(1)
O(4)	1289(2)	4161(3)	3463(4)
O(5)	1372(2)	4396(3)	1164(5)
C(1)	2103(3)	1930(3)	3800(5)
C(2)	1938(3)	2552(3)	3281(5)
O(2)	1441(2)	2796(2)	3101(4)
C(3)	2306(3)	2965(4)	2880(5)
O(3)	2106(2)	3559(2)	2395(4)
C(4)	2833(3)	2762(4)	3031(6)
C(5)	2999(3)	2151(4)	3583(6)
C(6)	2643(3)	1742(4)	3978(5)
C(7)	1726(3)	1497(4)	4229(6)
O(7)	1829(2)	956(3)	4725(5)
O(8)	1229(2)	1730(2)	4048(5)
C(8)	581(2)	2249(3)	−526(5)
C(9)	738(2)	2765(3)	320(5)
O(9)	1229(2)	3028(2)	627(3)
C(10)	364(3)	3052(3)	892(5)
O(10)	560(2)	3538(2)	1729(4)
C(11)	−162(3)	2846(3)	574(6)
C(12)	−325(3)	2349(4)	−309(6)
C(13)	40(3)	2043(3)	−833(5)
C(14)	974(3)	1920(3)	−1093(6)
O(14)	881(2)	1435(2)	−1763(4)
O(15)	1469(2)	2178(3)	−783(4)
N(30)	2441(2)	724(3)	469(4)
C(31)	2011(3)	723(4)	1149(7)
C(32)	2838(4)	213(4)	1006(8)
C(33)	2691(3)	1386(3)	526(7)
C(34)	2192(3)	568(4)	−848(6)
N(40)	0	500(4)	2500
C(41)	372(3)	111(5)	3391(8)
C(42)	287(4)	927(6)	1876(9)
N(50)	0	5613(4)	2500
C(51)	468(1)	6028(4)	2648(8)
C(52)	57(4)	5198(4)	3570(1)
O(60)	1122(3)	611(3)	−3675(5)
O(70) *	1174(5)	4267(5)	5882(9)

* Occupancy 0.50.

Table 2 Selected bond lengths (Å) and angles (°) for $[NMe_4]_2[MoO_2(2,3\text{-dhb})_2]\cdot 1.5H_2O$ with estimated standard deviations (e.s.d.s) in parentheses

Mo–O(2)	2.180(4)	Mo–O(3)	1.979(5)
Mo–O(4)	1.707(5)	Mo–O(5)	1.709(5)
Mo–O(9)	2.210(4)	Mo–O(10)	1.965(5)
C(2)–C(3)	1.412(10)	C(9)–C(10)	1.405(10)
C(2)–O(2)	1.333(8)	C(3)–O(3)	1.350(8)
C(1)–C(7)	1.468(10)	C(7)–O(7)	1.213(8)
C(7)–O(8)	1.325(9)	C(9)–O(9)	1.330(7)
C(10)–O(10)	1.354(7)	C(8)–C(14)	1.478(10)
C(14)–O(14)	1.212(8)	C(14)–O(15)	1.334(8)
O(2)–Mo–O(3)	75.8(2)	O(2)–Mo–O(4)	91.3(2)
O(2)–Mo–O(5)	162.3(2)	O(2)–Mo–O(9)	76.8(2)
O(2)–Mo–O(10)	85.3(2)	O(3)–Mo–O(4)	104.9(2)
O(3)–Mo–O(5)	90.9(2)	O(3)–Mo–O(9)	83.8(2)
O(3)–Mo–O(10)	154.8(2)	O(4)–Mo–O(5)	103.5(3)
O(4)–Mo–O(9)	163.3(2)	O(4)–Mo–O(10)	91.8(2)
O(5)–Mo–O(9)	90.4(2)	O(5)–Mo–O(10)	103.6(2)
O(9)–Mo–O(10)	75.7(2)		

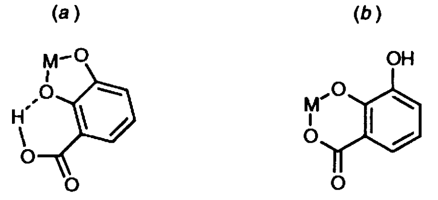

Fig. 2 Catecholato and salicylato bonding modes for 2,3-dhb^{2-}

In the complex anion the molybdenum atom has octahedral geometry with the oxo ligands *cis*, [Mo–O(4) 1.707(5), Mo–O(5) 1.709(5) Å] and with the catecholato oxygen atoms *ortho* to the carboxylic acid moieties [O(2) and O(9)] *trans* to these oxo groups.

The co-ordination geometry is distorted with the angles at molybdenum in the ranges 76–105 and 155–163°. The molybdenum atom is displaced towards each oxo ligand [O(4) and O(5)] relative to the plane of the four oxygen atoms normal to these directions by 0.27 and 0.25 Å respectively. Within each ligand the carboxylic acid group is held essentially coplanar with its associated aromatic ring by intramolecular O–H ··· O hydrogen bonds between O(8) and O(2) and between O(15) and O(9);* this hydrogen bonding pattern is similar, though not strictly comparable, to that observed in the 2,6-dihydroxybenzoic acid complex $[Cu(2,6\text{-Hdhb})_2(H_2O)_2]$.[8] The out-of-plane rotations are small with the C(7) carboxylate group rotated by *ca.* 1° and the C(14) group by *ca.* 6°.

The Mo–O(2) and Mo–O(9) bond lengths, 2.180(4) and 2.210(4) Å, are significantly longer than those for Mo–O(3) and Mo–O(10), 1.979(5) and 1.965(5) Å, reflecting the *trans* effect of the oxo ligands and the intramolecular O ··· H–O hydrogen bonding (see above). The latter bond lengths are comparable with their counterparts in the *cis*-dioxo salicylato complexes $[Hpy][MoO_2(Hsal)(sal)]$[5] (py = pyridine) and $[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$.[6]

In this complex, the planarity observed for the ligand and its associated carboxylic acid moiety extends to include the co-ordinated molybdenum atom, there being only small fold angles of between 4 and 6° about a vector linking the respective pair of oxygen donor atoms [O(2) ··· O(3) and O(9) ··· O(10)]. This contrasts with the geometries observed in the two sal^{2-} complexes where there is appreciable folding with angles of 12 and 21°, and 12 and 24° in $[Hpy][MoO_2(Hsal)(sal)]$[5] and $[NMe_4]_2[MoO_2(sal)_2]\cdot 2H_2O$[6] respectively.

The average C–O$_{donor}$ bond distance of 1.34 Å observed here is very close to those reported for the two rhenium tetrachlorocatechol structures $[NBu_4][ReO(OPPh_3)(tccat)_2]$ and $[NBu_4][ReO(MeOH)(tccat)_2]$,[4] indicating catecholato rather than quinone or semiquinone co-ordination.[3]

The full-occupancy included water molecule (see below) serves to connect adjacent lattice translated complex anions *via* intermolecular hydrogen bonding to the carboxylate oxygen atoms O(7) and O(14) forming chains that extend in the crystallographic *c* direction, Fig. 3 [O(7) ··· O(60) 2.94, O(14) ··· O(60) 2.89 Å]. The partial-weight included water molecule links glide related pairs of these chains *via* hydrogen bonding to the two oxo oxygen atoms O(4) and O(5) [O(70) ··· O(4) 2.81, O(70) ··· O(5) 2.72 Å].

Centrosymmetrically related chain pairs are interleaved, there being aromatic face-to-face π–π interactions between equivalent dihydroxybenzoic acid units, Fig. 4. The mean interplanar separation between ring A and ring B is 3.31 Å and their centroid–centroid separation is 3.55 Å.

(*c*) *Vibrational Spectra.*—Infrared and Raman spectroscopic data for the free ligands and their complexes are shown in Table 3. In the molybdenum and tungsten species the symmetric metal *cis*-dioxo stretches, $\nu_{sym}(MO_2)$, are seen around 920 cm^{-1} as strong bands in the Raman, weaker in the IR, with the asymmetric stretches, $\nu_{asym}(MO_2)$, strong in the IR and weaker

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*The O–H ··· O intramolecular hydrogen-bonding geometries are as follows; O(8)–H(8A) 0.90, O(8) ··· O(2) 2.50, H(8A) ··· O(2) 1.63 Å, O–H ··· O 162°; O(15)–H(15A) 0.90, O(15) ··· O(9) 2.50, H(15A) ··· O(9) 1.69 Å, O–H ··· O 148°.

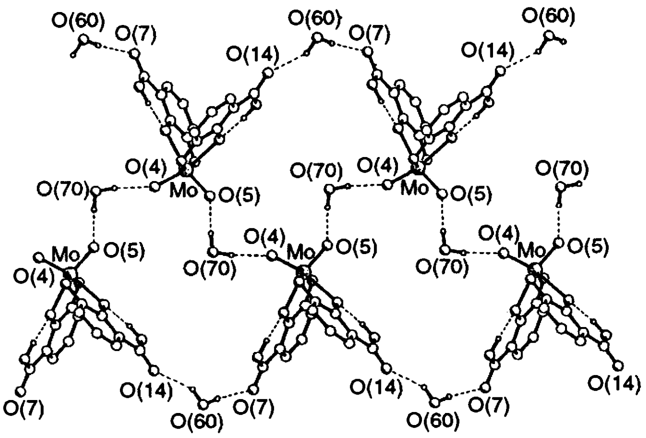

Fig. 3 Network of hydrogen-bonded linked anions in $[NMe_4]_2$-$[MoO_2(2,3\text{-dhb})_2]\cdot 1.5H_2O$

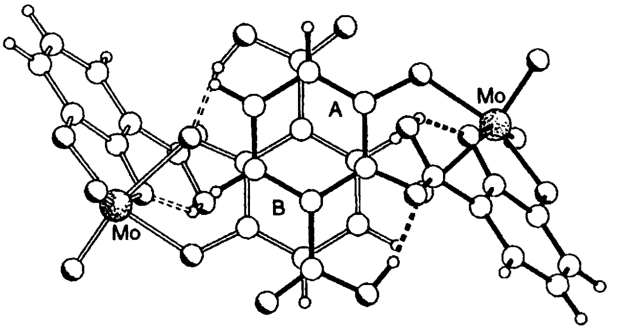

Fig. 4 π–π Overlap of dihydroxybenzoic acid residues of adjacent $[MoO_2(2,3\text{-dhb})_2]^{2-}$ anions in the structure of $[NMe_4]_2[MoO_2(2,3\text{-dhb})_2]\cdot 1.5H_2O$

in the Raman, at about 880 cm^{-1}. The complexes were too insoluble to record good quality Raman spectra of solutions, but in the case of $[NMe_4]_2[MoO_2(2,3\text{-dhb})_2]$ in water a polarised band at 919 cm^{-1} was observed, consistent with this being a symmetric mode [*i.e.* $\nu_{sym}(MoO_2)$]. Similar bands and assignments have previously been observed in other complexes containing *cis*-MO_2 moieties (M = Mo or W).[1,6,15,16] Due to the thermal instability of some of the complexes, Raman spectra of $K_2[OsO_2L_2]$ (L = 2,3-dhb or 3,4-dhb) and $[OsO_2(py)_2(2,6\text{-dhb})]$ could not be recorded but the asymmetric ν_{asym} (OsO_2) stretches are clearly seen in the IR near 845 cm^{-1}, in agreement with literature assignments for other complexes containing *trans* O=Os=O 'osmyl' units.[1,17,18]

No comprehensive assignments of the vibrational spectra of the dihydroxybenzoic acids have been published, but there are limited IR data on $[M(PPh_3)_2(3,4\text{-dhb})]$ (M = Pd or Pt)[7,19] and for $K_2(2,3\text{-dhb})$.[20] In Table 3 we select three prominent bands in the infrared and Raman which are sensitive to metal co-ordination and propose tentative assignments for these based on our earlier work on such spectra of salicylato[6] and catecholato[1,3] complexes.

The ν(C=O) carboxylate stretch in the free acids we assign to the IR and Raman bands near 1670 cm^{-1}; these are little affected on co-ordination in the 2,3-dhb and 3,4-dhb complexes but shift to lower wavenumber (*ca.* 1620 cm^{-1}) in those of the 2,6-dhb ligand, as expected since the carboxyl oxygen atom is involved in co-ordination. Bands in the free acid near 1300 cm^{-1} may arise from the C–O stretch, $\nu(C\text{–}O)_c$, of the carboxyl group;[21] and are shifted to lower wavenumber in some of the complexes.

Two bands in free catechol near 1480 and 1250 cm^{-1} have been associated with the C–O stretch;[22] the latter, [ν(C–O)], is sensitive to metal co-ordination[1,4] and is listed in Table 3 for the complexes.

In addition to the above, counter-ion bands were observed in all the applicable spectra.

(*d*) *NMR Spectra.*—The ^1H, $^{13}C\text{-}\{^1H\}$ and $^{13}C\text{-}\{^1H\}$ cross-polarisation magic angle spinning (CPMAS) NMR assignments used below are based on the earlier assignments of the spectra of the related salicylato species,[6] and on the work of Scott.[23,24] (The atom numbering scheme is given in Fig. 5.)

$^{13}C\text{-}\{^1H\}$ *NMR spectra.* Data for the free acids agree well with the work of Scott;[24] $^{13}C\text{-}\{^1H\}$ NMR spectroscopic data for the ligands and those of the complexes sufficiently soluble to be studied are given in Table 4. Corresponding data from solid-state CPMAS NMR experiments are given for three of the complexes, $[PPh_4]_2[WO_2(2,3\text{-dhb})_2]\cdot 2H_2O$, $[PPh_4]_2[MoO_2(3,4\text{-dhb})_2]\cdot 5H_2O$ and $[PPh_4]_2[MoO_2(2,6\text{-dhb})_2]\cdot 3H_2O$, since they were insufficiently soluble for adequate solution spectra to be recorded.

Carbon-13 NMR spectroscopy is a good diagnostic tool for determining the mode of bonding of catechol species,[1,4,18] be it catecholato, semiquinone or quinone.[3] On co-ordination the resonances of the carbon atoms bonded to the oxygen atoms shift some 10–15 ppm downfield. In all the complexes of 2,3-H_2dhb and 3,4-H_2dhb for which we were able to measure spectra the resonances of these carbon atoms (C^2 and C^3 in the former, C^3 and C^4 in the latter) shift downfield on complexation by *ca.* 10–15 ppm. Thus, catecholato bonding is indicated, consistent with that observed in the crystal structure of $[NMe_4]_2[MoO_2(2,3\text{-dhb})_2]\cdot 1.5H_2O$ (see above).

For complexes containing the 2,6-dhb ligand the shifts are less dramatic; those nuclei which show the largest shifts are C^1, C^2 and C^7 as is observed[6] for salicylato complexes in which the carboxylate and deprotonated hydroxy oxygen atoms are involved in co-ordination.

In all the above NMR spectra, counter-ion peaks were observed wherever applicable.

Proton NMR spectra. Proton NMR data for the free acids and for their tetramethylammonium salts are given in Table 3; these data agree well with those of Scott[23] and we use her assignments here. As with spectra of some salicylato complexes, the proton NMR spectra of some of the compounds reported in Table 3 show complex splitting which may, however, be interpreted in terms of the geometrical isomers present in solution.

$[MO_2(2,3\text{-dhb})_2]^{2-}$ (M = Mo *or* W). The spectrum of $[NMe_4]_2[MoO_2(2,3\text{-dhb})_2]\cdot 1.5H_2O$ (Fig. 6) reveals the presence of two isomeric products in an approximately 2:1 ratio, with most of the minor isomer peaks downfield of their major isomer counterparts. The anion *cis*-$[MoO_2(2,3\text{-dhb})_2]^{2-}$ has three possible geometric isomers (Fig. 7). In structure **a**, the isomer found in the crystal structure of $[NMe_4]_2[MoO_2(2,3\text{-dhb})_2]\cdot 1.5H_2O$, the two *ortho* O atoms, attached to C^2 and $C^{2'}$ respectively, are *trans* to the oxo ligands; in **b** the *ortho* O atom attached to C^2 and the *meta* O atom attached to $C^{3'}$ are *trans* to the oxo ligands; while in **c** it is both the *meta* O atoms, connected to C^3 and $C^{3'}$ respectively, which are *trans* to the oxo ligands (see Fig. 5 for atom numbering scheme).

In both **a** and **c**, the protons on each of the aromatic rings are chemically equivalent, so only three resonances would be expected. In isomer **b**, however, the protons of one aromatic ring are chemically and magnetically distinct from those of the other. Consequently six distinct resonances would be expected for isomer **b**. In order for all three isomers **a**, **b** and **c** to be observed in solution, up to twelve resonances in all should be present, but the observed ^1H NMR spectrum suggests the presence of only two isomers, **a** and **b**. The first isomer shows three distinct resonances, presumably due to **a** (which would be the expected major isomer on the basis of the crystal structure) and the second isomer has six multiplets corresponding to the six unique protons of isomer **b**.

The six resonances due to isomer **b** have been assigned on the basis of homodecoupled ^1H NMR spectra. The chemical shift of H^{6b} (7.13) is similar to that of H^6 in isomer **a** (δ 7.11),

Table 3 Analytical, vibrational and ^{1}H NMR spectroscopic data for complexes of dihydroxybenzoic acids

	Analysis^a (%)			Vibrational spectra^{b,c} (cm^{-1})					^{1}H NMR data^e (δ)				
Compound	C	H	N	ν(C=O)	ν(C–O)$_c$	ν(C–O)	ν_{sym}(MO$_2$)^d	ν_{asym}(MO$_2$)	H^2	H^3	H^4	H^5	H^6
2,3-Dihydroxybenzoic acid				1658vs	1301vs	1234vs			—	—	7.00	6.72	7.35
				1669(3)	*1298(2)*	*1233(3)*							
[NMe$_4$]$_2$[2,3-dhb]									—	—	6.68	6.48	7.02
3,4-Dihydroxybenzoic acid				1602vs	1297vs	1236vs			7.44	—	—	6.80	7.43
				1605(9)	*1308(4)*	*1241(1)*							
[NMe$_4$]$_2$[3,4-dhb]									7.32	—	—	6.54	7.27
2,6-Dihydroxybenzoic acid				1686vs	1293s	1235vs			—	6.41	7.28	6.41	—
				1684(4)	*1294(3)*	*1238(2)*							
[NMe$_4$]$_2$[MoO$_2$(2,3-dhb)$_2$]·1.5H$_2$O	42.7	5.7	4.5	1694vs	1301s	1251s	907s	867s	—	—	6.74^f	6.49^f	7.11^f
	(42.9)	(5.9)	(4.5)	*1702(2)*	*1307(1)*	*1258(4)*	*919(9)*	*885(3)*	—	—	6.69^g	6.54^g	7.13^g
									—	—	6.81^g	6.58^g	7.32^g
[PPh$_4$]$_2$[WO$_2$(2,3-dhb)$_2$]·2H$_2$O	60.4	4.1	—	1705vs	1299s	1253s	937s	891s	—	—	6.72^f	6.44^f	7.02^f
	(60.3)	(4.2)	—	*1705(1)*	*1295(1)*	*1258(2)*	*938(6)*	*892(2)*	—	—	6.72^g	6.57^g	7.13^g
									—		6.82^g	6.58^g	7.33^g
K$_2$[OsO$_2$(2,3-dhb)$_2$]·2H$_2$O	26.2	2.1	—	1710s	1315vs	1249m	—	851m	—	—	7.06^h	6.82^h	7.39^h
	(26.3)	(1.9)	—										
[ReOI(PPh$_3$)$_2$(2,3-dhb)]	51.3	3.3	—	1722vs	1290s	1222vs	953s	—	—	—	6.09^i	6.02^i	6.90^i
	(51.4)	(3.4)	—										
[Pd(PPh$_3$)$_2$(2,3-dhb)]·EtOH	64.5	4.4	—	1721vs	1277vs	1262vs	—	—	—	—	6.39^i	6.44^i	7.11^i
	(65.2)	(4.9)	—	—	*1277(1)*	*1262(1)*	—	—					
[Pt(PPh$_3$)$_2$(2,3-dhb)]·EtOH	58.2	3.8	—	1718vs	1278vs	1264vs	—	—	—	—	6.47^i	6.41^i	7.06^i
	(58.9)	(4.4)	—	*1722(2)*	*1276(1)*	*1263(3)*	—	—					
[PPh$_4$]$_2$[MoO$_2$(3,4-dhb)$_2$]·5H$_2$O	62.0	4.2	—	1688s	1274vs	1263(sh)	924 m	897s	7.14^j	—	—	6.35^j	7.21^j
	(62.0)	(4.9)	—	*1697(2)*	*1284(3)*	*1265(2)*	*929(3)*	*904(3)*					
[N(C$_6$H$_{13}$)$_4$]$_2$[WO$_2$(3,4-dhb)$_2$]·3H$_2$O	58.2	8.7	2.3	1665s	1278vs	1219m	921 m	873m	7.20^f	—	—	6.55^f	7.35^f
	(58.0)	(9.3)	(2.2)	*1624(5)*	*1284(4)*	*1224(2)*	*920(3)*	*872(1)*					
K$_2$[OsO$_2$(3,4-dhb)$_2$]·2H$_2$O	26.2	2.1	—	1661m	1327m	1193vs	—	838m					
	(26.3)	(1.9)	—										
[ReOI(PPh$_3$)$_2$(3,4-dhb)]	50.2	3.4	—	1710s	1299vs	1261(sh)	954s	—	6.44^i	—	—	6.27^i	6.98^i
	(51.4)	(3.4)	—										
[PPh$_4$]$_2$[MoO$_2$(2,6-dhb)$_2$]·3H$_2$O	64.0	4.2	—	1626vs	1288m	1228vs	911vs	891s	—	6.17	7.01	6.17	—
	(63.9)	(4.7)	—	*1628(1)*	*1297(3)*	—	*919(4)*	*896(2)*					
[OsO$_2$(py)$_2$(2,6-dhb)]	38.7	2.6	5.2	1622vs	1261vs	1212vs	—	856vs	—	6.46^j	7.41^j	6.49^j	—
	(38.3)	(2.7)	(5.3)										
[ReOI(PPh$_3$)$_2$(2,6-dhb)]	51.2	3.3	—	1626s	1263s	1232vs	946vs	—	—	5.39^i	6.69^i	6.14^i	—
	(51.4)	(3.4)	—										

^{a} Calculated values in parentheses. ^{b} Raman data in italics. ^{c} Subscripted 'c' indicates a motion of a carboxyl group. ^{d} ν(Re=O) for rhenium complexes. ^{e} Spectra in CD$_3$OD solution unless otherwise stated; chemical shifts in δ *vs.* SiMe$_4$ or sodium 4,4-dimethyl-4-silapentane-1-sulfonate (dss). ^{f} Peak due to isomer **a**. ^{g} Peak due to isomer **b**. ^{h} In D$_2$O solution. ^{i} In CDCl$_3$ solution. ^{j} In (CD$_3$)$_2$CO solution.

Table 4 ^{13}C-{^1H} NMR spectroscopic data for complexes of dihydroxybenzoic acids[a]

Compound	Chemical shift (δ) C¹	C²	C³	C⁴	C⁵	C⁶	C⁷
2,3-Dihydroxybenzoic acid	114.1	151.5	146.8	121.4	119.5	121.8	173.6
3,4-Dihydroxybenzoic acid	123.3	117.9	146.1	151.6	115.9	124.1	170.3
2,6-Dihydroxybenzoic acid	101.8	162.5	108.8	136.9	108.8	162.5	173.2
$[NMe_4]_2[MoO_2(2,3\text{-dhb})_2]\cdot1.5H_2O$	114.2	162.1	158.5	118.2	117.0	121.4	172.8
$[PPh_4]_2[WO_2(2,3\text{-dhb})_2]\cdot2H_2O$[b]	113.1	161.2	157.3	120.3	118.7	121.1	170.4
$[ReOI(PPh_3)_2(2,3\text{-dhb})]$[c]	115.4	157.6	157.0	117.8	116.6	122.6	167.0
$[Pd(PPh_3)_2(2,3\text{-dhb})]\cdot EtOH$[c]	116.1	164.1	163.1	117.4	117.2	118.8	169.4
$[Pt(PPh_3)_2(2,3\text{-dhb})]\cdot EtOH$[c]	116.1	163.1	162.4	118.0	117.7	119.4	168.7
$[PPh_4]_2[MoO_2(3,4\text{-dhb})_2]\cdot5H_2O$[b]	117.3	*d*	158.3	163.2	*d*	*d*	167.7
$[N(C_6H_{13})_4]_2[WO_2(3,4\text{-dhb})_2]\cdot3H_2O$	114.4	116.7	157.2	162.0	116.1	124.6	172.5
$[PPh_4]_2[MoO_2(2,6\text{-dhb})_2]\cdot3H_2O$[b]	107.9	167.7	110.5	137.4	110.5	164.2	174.8
$[OsO_2(py)_2(2,6\text{-dhb})]$[e]	109.1	166.1	110.9	135.9	110.9	165.8	172.1
$[ReOI(PPh_3)_2(2,6\text{-dhb})]$[c]	108.2	164.0	110.2	133.6	110.2	157.2	169.6

[a] Spectra in CD_3OD solution unless otherwise stated; chemical shifts in δ *vs.* $SiMe_4$ or dss. [b] Spectra measured as ^{13}C-{^1H} CPMAS solid-state NMR. [c] In $CDCl_3$ solution. [d] Peak obscured. [e] In $(CD_3)_2CO$ solution.

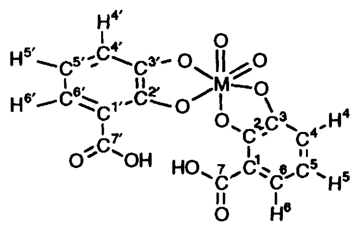

Fig. 5 Atom numbering scheme

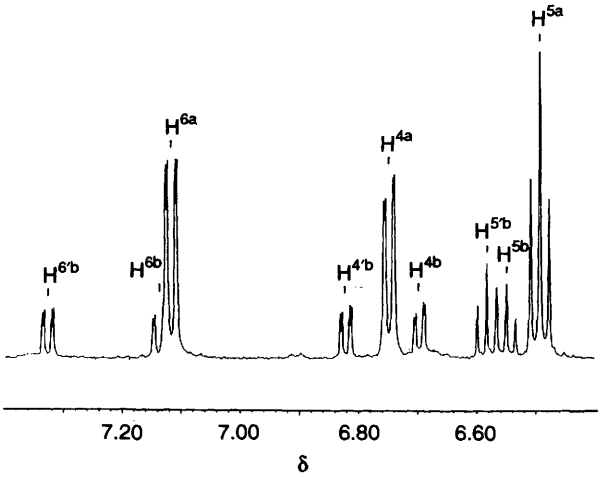

Fig. 6 Proton NMR spectrum of $[MoO_2(2,3\text{-dhb})_2]^{2-}$ (aromatic region)

suggesting that the resonance corresponds to an aromatic ring bound to the metal as in isomer **a**. Homodecoupled ^1H NMR experiments showed that H^{6b} was coupled only to the multiplets at δ 6.54 and 6.69, corresponding to H^{5b} and H^{4b}. Similarly, the resonance at δ 7.32 ($H^{6b'}$) is coupled exclusively to the multiplets at δ 6.58 and 6.81, assigned as $H^{5'b}$ and $H^{4'b}$.

Variable-temperature experiments over the range −40 to +65 °C in CD_3OD showed that the six multiplets attributed to isomer **b** progressively broadened with increasing temperature (with coalescence temperatures in the range 38 to 63 °C); equivalent pairs such as H^{6b} and $H^{6'b}$ coalesce at the same temperature. This is consistent with our assignment of the spectrum.

Similar results have been obtained for $[PPh_4]_2[WO_2(2,3\text{-dhb})_2]\cdot2H_2O$ (see Table 3).

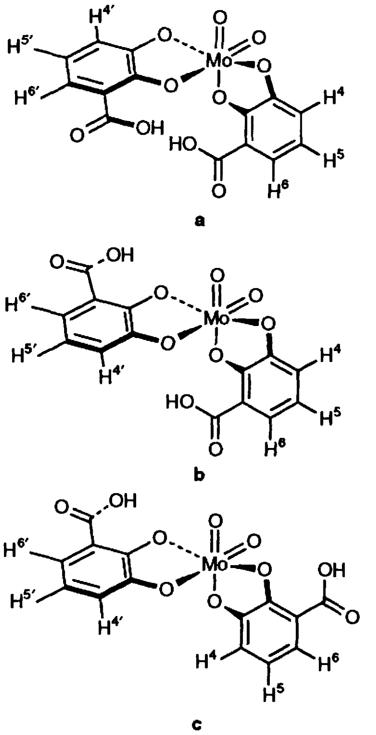

Fig. 7 Geometric isomers of *cis*-$[MoO_2(2,3\text{-dhb})_2]^{2-}$

$[MoO_2(3,4\text{-dhb})_2]^{2-}$. The ^1H NMR spectra show splitting attributable to the presence of only one isomer in solution, probably the analogue of **a** in Fig. 7; the numbering scheme is similar to that in Fig. 5 except that the protons involved are now H^2, H^5 and H^6. There are in addition several extra, non-assigned, weak resonances (not listed in Table 3). The ^1H NMR spectrum of $[N(C_6H_{13})_4]_2[WO_2(3,4\text{-dhb})_2]\cdot3H_2O$ is of poor quality; provisional assignments for the major isomer of type **a** are listed in Table 3.

Experimental

X-Ray Crystallography.—Crystal data for $[NMe_4]_2[MoO_2(2,3\text{-dhb})_2]\cdot1.5H_2O$, $C_{22}H_{32}MoN_2O_{10}\cdot1.5H_2O$, M = 607.5, monoclinic, space group $C2/c$, a = 25.698(15), b = 19.974(8), c = 11.221(5) Å, β = 104.80(2)°, U = 5569(5) Å^3, Z = 8, D_c = 1.45 g cm^{-3}, Mo-Kα radiation, λ = 0.710 73 Å, μ(Mo-Kα) = 5.3 cm^{-1}, $F(000)$ = 2520. Orange-red trapezoidal plates, crystal dimensions 0.33 × 0.40 × 0.13 mm.

Data collection and processing. Data were measured on a Siemens P4/PC diffractometer with Mo-Kα radiation (graphite monochromator) using ω-scans. 4908 Independent reflections were measured ($2\theta > 50°$) of which 2818 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors.

Structure analysis and refinement. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. One of the counter ions was found to occupy a general position and was well defined. The remaining counter ion was found to be distributed about two independent two-fold positions within the unit cell. One of these partial-weight counter ions was severely disordered and thus its geometry was optimised (alternative fractional occupancy orientations for this group could not be identified). There was also slight disorder in the second partial-weight counter ion and therefore its geometry was constrained. A ΔF map revealed the presence of both a full- and a partial-weight included water molecule; the latter was estimated to have an occupancy of 0.50. The hydrogen atoms of the water molecules and of the carboxylic acid groups were refined isotropically, $U(\text{H}) = 1.2U_{\text{eq}}(\text{O})$, subject to an O–H distance constraint. The positions of the remaining hydrogen atoms were idealised (C–H 0.96 Å), assigned isotropic thermal parameters, $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares to give $R = 0.058$, $R' = 0.055$ $[w^{-1} = \sigma^2(F) + 0.0007F^2]$. The maximum and minimum residual electron densities in the final ΔF map were 0.66 and -0.34 e Å^{-3} respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.016 and 0.272 respectively.

Computations were carried out on a 50 MHz 486 computer using the SHELXTL PC program system.[25]

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. The compound $MoO_3 \cdot nH_2O$ and the three dihydroxybenzoic acids were bought from Aldrich, Na_2MoO_4 and Na_2WO_4 were supplied by BDH and $WO_3 \cdot nH_2O$ was obtained from Fluka and each of these materials were used without further purification; *trans*-$K_2[OsO_2(OMe)_4]$,[26] $[ReO_2I(PPh_3)_2]$,[27] $[Pd(PPh_3)_2Cl_2]$[28] and $[Pt(PPh_3)_2Cl_2]$[29] were made by the respective literature procedures. The rhenium complexes were made *via* an adaptation of the literature method for the analogous catecholato species.[4] The palladium and platinum complexes were made *via* an adaptation of the literature method for the analogous 6,7-dihydroxycoumarin species.[30]

$[NMe_4]_2[MoO_2(2,3\text{-dhb})_2] \cdot 1.5H_2O$. This complex was made *via* an adaptation of Weinland and Zimmermann's method[14] for the corresponding salicylato complex.

Molybdic acid, $MoO_3 \cdot nH_2O$ (0.144 g, 0.982 mmol) was refluxed for 6–8 h with 2,3-dihydroxybenzoic acid (0.462 g, 3.00 mmol) and tetramethylammonium hydroxide pentahydrate (0.544 g, 3.00 mmol) in water (10 cm^3). The deep red solution was then hot filtered and the filtrate evaporated to half volume. On overnight refrigeration, deep red crystals formed and these were filtered off and air dried. Yield = 0.418 g, 0.679 mmol, 68%.

$[PPh_4]_2[WO_2(2,3\text{-dhb})_2] \cdot 2H_2O$. To an aqueous solution (5 cm^3) of sodium tungstate dihydrate (0.330 g, 1.00 mmol) was added 2,3-dihydroxybenzoic acid (0.308 g, 2.00 mmol). The resulting yellow solution was filtered and then an aqueous solution (10 cm^3) of tetraphenylphosphonium chloride (0.750 g, 2.00 mmol) was added to the filtrate. The white precipitate was filtered off, washed with copious quantities of water and air dried. Yield = 1.04 g, 0.844 mmol, 84%.

$K_2[OsO_2(2,3\text{-dhb})_2] \cdot 2H_2O$. To a stirred solution of *trans*-$K_2[OsO_2(OMe)_4]$ (0.200 g, 0.470 mmol) in methanol (15 cm^3) was added a methanolic solution (1 cm^3) of 2,3-dihydroxybenzoic acid (0.145 g, 0.941 mmol). The deep red solution was left stirring for about 5 min, and then a copious quantity of diethyl ether was added. The solution turned black, and upon filtration a black solid was isolated. This was washed with diethyl ether and air dried. Yield = 0.205 g, 0.320 mmol, 68%.

$[ReOI(PPh_3)_2(2,3\text{-dhb})]$. To a stirred suspension of $[ReO_2I(PPh_3)_2]$ (0.174 g, 0.20 mmol) in methanol (30 cm^3) was added 2,3-dihydroxybenzoic acid (0.062 g, 0.40 mmol). The resulting suspension was refluxed for 30 min with stirring. A dark red solution was obtained and filtered after cooling. After 8 days in the fridge the dark brown crystals formed were filtered off and dried in a desiccator over silica gel. Yield = 0.098 g, 0.097 mmol, 49%.

$[Pd(PPh_3)_2(2,3\text{-dhb})] \cdot EtOH$. To a stirred suspension of $[Pd(PPh_3)_2Cl_2]$ (0.351 g, 0.50 mmol) in ethanol (10 cm^3) was added a methanolic solution (4 cm^3) of 2,3-dihydroxybenzoic acid (0.154 g, 1.00 mmol) and triethylamine (0.28 cm^3, 2.00 mmol). The resulting yellow suspension was stirred for 2 days and a violet suspension was obtained. It was centrifuged and a violet solid isolated and dried in a desiccator over silica gel. Yield = 0.309 g, 0.373 mmol, 75%.

$[Pt(PPh_3)_2(2,3\text{-dhb})] \cdot EtOH$. To a stirred suspension of $[Pt(PPh_3)_2Cl_2]$ (0.395 g, 0.50 mmol) in ethanol (10 cm^3) was added a methanolic solution (4 cm^3) of 2,3-dihydroxybenzoic acid (0.154 g, 1.00 mmol) and triethylamine (0.28 cm^3, 2.00 mmol). The resulting white suspension was stirred overnight and a yellow suspension was obtained. It was centrifuged and a yellow solid isolated and dried in a desiccator over silica gel. Yield = 0.386 g, 0.421 mmol, 84%.

$[PPh_4]_2[MoO_2(3,4\text{-dhb})_2] \cdot 5H_2O$. To an aqueous solution (5 cm^3) of potassium molybdate (0.238 g, 1.00 mmol) was added 3,4-dihydroxybenzoic acid (0.308 g, 2.00 mmol). The resulting dark red solution was filtered and then an aqueous solution (10 cm^3) of tetraphenylphosphonium chloride (0.750 g, 2.00 mmol) was added to the filtrate. The orange precipitate was filtered off, washed with copious quantities of water, and air dried. Yield = 0.850 g, 0.707 mmol, 71%.

$[N(C_6H_{13})_4]_2[WO_2(3,4\text{-dhb})_2] \cdot 3H_2O$. To an aqueous solution (5 cm^3) of sodium tungstate (0.330 g, 1.00 mmol) was added 3,4-dihydroxybenzoic acid (0.308 g, 2.00 mmol). The resulting yellow solution was filtered and then an aqueous solution (10 cm^3) of tetrahexylammonium bromide (0.869 g, 2.00 mmol) was added to the filtrate. The yellow precipitate was filtered off, dissolved in ethanol, reprecipitated with water and then centrifuged to give a yellow oil. The upper, colourless solution was decanted off and the yellow oil air dried. The yellow solid was then washed with diethyl ether (which was allowed to evaporate off) and dried *in vacuo* over silica gel. Yield = 0.816 g, 0.635 mmol, 64%.

$K_2[OsO_2(3,4\text{-dhb})_2] \cdot 2H_2O$. To a stirred solution of *trans*-$K_2[OsO_2(OMe)_4]$ (0.200 g, 0.470 mmol) in methanol (15 cm^3) was added a methanolic solution (1 cm^3) of 3,4-dihydroxybenzoic acid (0.145 g, 0.941 mmol). The blue-black solution was left stirring for about 5 min, and then a copious quantity of diethyl ether was added. The solution turned black, and upon filtration a black solid was isolated. This was washed with diethyl ether and air dried. Yield = 0.186 g, 0.291 mmol, 62%.

$[ReOI(PPh_3)_2(3,4\text{-dhb})]$. To a stirred suspension of $[ReO_2I(PPh_3)_2]$ (0.174 g, 0.20 mmol) in methanol (30 cm^3) was added 3,4-dihydroxybenzoic acid (0.062 g, 0.40 mmol). The resulting suspension was refluxed for 1 h with stirring. A dark brown solution was obtained and filtered after cooling. After 8 days in the fridge the dark brown solid formed was filtered off and dried in a desiccator over silica gel. Yield = 0.023 g, 0.023 mmol, 11%.

$[PPh_4]_2[MoO_2(2,6\text{-dhb})_2] \cdot 3H_2O$. To an aqueous solution (5 cm^3) of potassium molybdate (0.238 g, 1.00 mmol) was added 2,6-dihydroxybenzoic acid (0.308 g, 2.00 mmol). The resulting dark red solution was filtered and then an aqueous solution (10 cm^3) of tetraphenylphosphonium chloride (0.750 g, 2.00 mmol) was added to the filtrate. The pale yellow precipitate was filtered off, washed with copious quantities of water, and air dried. Yield = 0.954 g, 0.819 mmol, 82%.

[$OsO_2(py)_2$(2,6-dhb)]. To a solution of OsO_4 (0.064 g, 0.25 mmol) in carbon tetrachloride (10 cm^3) was added an ethanolic solution (6 cm^3) of [Hpy][2,6-Hdhb] (0.116 g, 0.50 mmol). The resulting light yellow solution was stirred for 3 h and a dark brown solution was obtained. After 2 days in the fridge the dark brown crystals formed were filtered off, washed with diethyl ether and dried in a desiccator over silica gel. Yield = 0.078 g, 0.146 mmol, 59%.

[ReOI($(PPh_3)_2$(2,6-dhb)]. To a stirred suspension of [$ReO_2I(PPh_3)_2$] (0.174 g, 0.20 mmol) in methanol (30 cm^3) was added 2,6-dihydroxybenzoic acid (0.062 g, 0.40 mmol). The resulting suspension was refluxed for 2 h with stirring. An orange solution and a suspended violet solid was obtained, and filtered after cooling to remove the remains of the violet starting material. After eight days in the fridge no solid was formed and the yellowish brown solution was rotary evaporated to half volume. After a further 5 days in the fridge the dark brown solid formed was filtered off and dried in a desiccator over silica gel. Yield = 0.016 g, 0.016 mmol, 8%.

Instrumentation.—Infrared spectra were measured as KBr discs on a Perkin-Elmer 1720 FT instrument. Raman spectra were recorded on as spun discs on a KBr matrix on a Spex Ramalog 5 instrument, with a Datamate data acquisition unit using excitation at 647.1 nm from a Coherent Radiation Innova 90 krypton-ion laser, and as powders 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 measured on a Brüker WM-250 FT spectrometer (^1H, 250.13 MHz), a JEOL EX-270 spectrometer (^1H, 270.05 MHz) and a Brüker AM-500 FT spectrometer (^1H, 500.13 MHz). Solid-state NMR spectra were recorded by the ULIRS service at University College, London by Dr. Patrick Barrie. Microanalyses were measured by the Microanalytical Department, Imperial College.

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