Complexes of Osmium, Uranium, Molybdenum, and Tungsten with the Catechol Amines Adrenaline, Noradrenaline, Dopamine, Dopa, and Isoproterenol

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New complexes of the form *trans*-$[OsO_2L_2]^{2-}$ and $UO_2L{\cdot}nH_2O$ [H_2L = adrenaline (H_2ad), noradrenaline (H_2nad), dopamine (H_2dpm), dopa (H_2dp), and isoproterenol (H_2prot)] are reported, as are *cis*-$[MO_2L_2]^{2-}$ (L = nad, dp, prot for M = Mo or W, and ad for M = W), $[MO_2(Hdpm)_2]$ (M = Mo or W), and $[Mo_2O_5(Had)_2]$. The structures of these species are discussed on the basis of their Raman, infrared, ^1H, and ^{13}C n.m.r. spectra.

Catechol amines are biogenic amines which function as neurotransmitters in the brain and nervous system of mammals.[1] Although heavy-metal 'stains' such as osmium tetraoxide (OsO_4) and uranyl salts have been used to help in the location of catechol amine-rich sites in brain tissue,[2] it is not clear whether these metals are bound to the catechol amines: no characterised complexes of these ligands with osmium or uranium have been reported. We have accordingly studied the reactions of the five biologically most important catecholamines with OsO_4 and uranyl salts. We have also studied their reactions with molybdate ($[MoO_4]^{2-}$) and tungstate ($[WO_4]^{2-}$). As the generic name implies, catechol amines contain the 1,2-dihydroxyphenyl (catechol) moiety, and we have shown in earlier work that catechol and substituted catechols bind strongly to osmium,[3,4] molybdenum, and tungsten[5] *via* the deprotonated *O,O'* sites.[3-5]

There is much confusion over the nomenclature of the five catechol amines used here; in Table 1 we list their trivial and I.U.P.A.C. names, their formulae, and the abbreviations used in this paper.

The only reports on the isolation of catechol amine complexes of third-row transition elements concern *cis*-$[PtL(PPh_3)_2]$ (L = ad, nad, dpm, dp, or prot),[6] *cis*-$[Pd(dpm)(PPh_3)_2]{\cdot}CH_2Cl_2$, and *cis*-$[Pt(dpm)(PPh_3)_2]{\cdot}0.5CH_2Cl_2$.[7] Data on the interaction in solution of uranyl species with adrenaline,[8] and work on isolation and characterisation of catechol amine complexes of some first-row transition elements {*e.g.*, $[NH_4]_2[Cu(dp)_2]{\cdot}4H_2O$[9]} and of $[M(HL)_2]$ and $[Co(HL)_2]{\cdot}2H_2O$ (M = Cu or Ni, L = dp or prot),[10] are also available.

Results and Discussion

1. *Osmium Complexes.*—We have shown that osmium tetraoxide (OsO_4) reacts with catechol (benzene-1,2-diol) (H_2cat) and substituted catechols to give $[Os(cat)_3]$ and blue polymers $[\{OsO(cat)_2\}_n]{\cdot}nH_2O$; with *trans*-$K_2[OsO_2(OR)_4]$ (R = H or Me), salts of *trans*-$[OsO_2(cat)_2]^{2-}$ were isolated.[3] We find that reaction of *trans*-$K_2[OsO_2(OH)_4]$ in neutral solution with the hydrochlorides of noradrenaline (H_2nad), dopamine (H_2dpm), and isoproterenol (H_2prot), or the free bases adrenaline (H_2ad) and dopa (H_2dp), gave red-brown or blue polymeric materials, probably of the type $[\{OsOL_2\}_n]$ by analogy with the reaction product of catechol with OsO_4.[3] In basic media, however, *trans*-$K_2[OsO_2(OH)_4]$ gave deep red solutions with these catechol amines, from which the diamagnetic $K_2[OsO_2L_2]$ or $[PPh_4]_2[OsO_2L_2]$ salts were isolated. The i.r. spectra of these are listed in Table 2 (the colours of the complexes made them unsuitable for Raman studies). The very strong bands near 830 cm^{-1}, which vary little in intensity or wavenumber with L, are almost certainly due to $\nu_{asym}(OsO_2)$, the asymmetric stretch of the *trans* O=Os=O 'osmyl' moiety; bands are seen in similar positions in analogous species such as *trans*-$K_2[OsO_2(cat)_2]$[3] and $[OsO_2(trop)_2]$[11] (trop = tropolonate, 2-hydroxycyclohepta-2,4,6-trien-1-onate, $C_7H_5O_2^-$). Bands near 1 485 and 1 260 cm^{-1} may plausibly be assigned to those catecholato bands known to be sensitive to co-ordination; that near 1 485 cm^{-1} is associated with a ring stretch[5,12,13] and that near 1 260 cm^{-1} with a C–O stretch.[5,12,13] Such bands have also been observed in *cis*-$[PtL(PPh_3)_2]$ (L = ad, nad, dpm, dp, or prot).[6]

Table 1. Nomenclature of catecholamines

Trivial name	Systematic name	R	Abbreviation
Adrenaline; epinephrine	4-[1-hydroxy-2-(methylamino)ethyl]benzene-1,2-diol	–CH(OH)–CH_2–NH–CH_3	H_2ad
Noradrenaline; norepinephrine	4-(2-amino-1-hydroxyethyl)benzene-1,2-diol	–C^7H(OH)–C^8H_2–NH_2	H_2nad
Dopamine; hydroxytyramine	4-(2-aminoethyl)benzene-1,2-diol	–$(CH_2)_2NH_2$	H_2dpm
Dopa; 3,4-dihydroxyphenylalanine	3-hydroxytyrosine	–C^7H_2–C^8H(NH_2)–C^9OOH	H_2dp
Isoproterenol; isoprenaline	4-[1-hydroxy-2-{(1-methylethyl)amino}ethyl]-benzene-1,2-diol	–C^7H(OH)–C^8H_2–NH–C^9H($C^{10,11}H_3$)$_2$	H_2prot

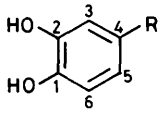

Table 2. Analytical and spectroscopic data for the complexes[a]

	Analytical data[b]			Vibrational spectra				
	C	H	N	ν(C–C)	ν(C–O)	$\nu_{sym}(MO_2)$	$\nu_{asym}(MO_2)$	^{1}H N.m.r. data
Osmium complexes								
trans-$K_2[OsO_2(ad)_2]\cdot 3H_2O$	29.7 (30.2)	2.9 (3.9)	3.8 (3.9)	1 485s	1 260s		835s	6.93 (m), 6.62 (m)
$[PPh_4]_2[OsO_2(ad)_2]$	62.3 (62.8)	5.3 (4.9)	2.6 (2.2)					
trans-$K_2[OsO_2(nad)_2]$	30.7 (30.3)	2.5 (2.8)	3.9 (4.4)	1 485s	1 260s		837s	6.69 (m) [6.96 (m)][c]
$[PPh_4]_2[OsO_2(nad)_2]\cdot H_2O$	61.9 (61.3)	4.4 (4.8)	2.6 (2.2)					
trans-$K_2[OsO_2(dpm)_2]$	31.5 (31.9)	3.0 (3.0)	4.5 (4.7)	1 490s	1 259s		833vs	6.80 (m), 6.53 (m) [6.85 (m)][c]
$[PPh_4]_2[OsO_2(dpm)_2]\cdot 2H_2O$	61.6 (62.0)	5.3 (5.0)	2.8 (2.3)					
trans-$K_2[OsO_2(dp)_2]\cdot 2H_2O$	29.3 (29.7)	2.6 (3.0)	3.8 (3.9)	1 485s	1 260s		827vs	7.37 (m), 6.60 (m) [6.95 (m)][c]
$[PPh_4]_2[OsO_2(dp)_2]\cdot 3H_2O$	58.3 (58.9)	4.3 (4.8)	2.3 (2.1)					
trans-$K_2[OsO_2(prot)_2]$	37.5 (36.8)	3.9 (4.2)	3.7 (3.9)	1 487s	1 260s		834vs	6.92 (m), 6.65 (m)
$[PPh_4]_2[OsO_2(prot)_2]$	64.5 (63.7)	5.8 (5.3)	2.4 (2.1)					
Molybdenum and tungsten complexes								
cis-$Na_2[WO_2(ad)_2]$	34.3 (34.5)	4.2 (3.5)	4.5 (4.5)	1 485s *1 493s*	1 260s *1 272s*	904s *908s*	850s *842w*	6.65 (m)
cis-$Na_2[MoO_2(nad)_2]\cdot H_2O$	36.3 (36.5)	4.0 (3.8)	5.4 (5.3)	1 473s	1 250s	893s	850s	6.62 (m)
cis-$Na_2[WO_2(nad)_2]\cdot H_2O$	30.9 (31.3)	3.3 (3.3)	4.6 (4.6)	1 485s	1 250s	898s	845s	6.69 (m)
cis-$Na_2[MoO_2(dp)_2]\cdot H_2O$	36.5 (37.1)	3.9 (3.4)	4.4 (4.8)	1 486s *1 491s*	1 270m *1 275s*	895s *888s*	860s *855m*	6.47 (m)
cis-$Na_2[WO_2(dp)_2]\cdot 2H_2O$	31.0 (31.4)	2.9 (2.9)	3.6 (3.6)	1 495s *1 493s*	1 260s *1 272s*	905s *908s*	850vs *842w*	6.52 (m)
cis-$Na_2[MoO_2(prot)_2]\cdot H_2O$	43.6 (43.3)	5.5 (5.3)	4.6 (4.6)	1 487s *1 489s*	1 270s *1 278s*	892m *887s*	860s *854m*	6.63 (s)
$[PPh_4]_2[MoO_2(prot)_2]\cdot H_2O$[d]	68.1 (67.6)	5.9 (5.8)	2.2 (2.3)					
cis-$Na_2[WO_2(prot)_2]$	38.2 (38.8)	4.9 (4.4)	4.0 (4.1)	1 490s *1 495m*	1 270m *1 280s*	910s *909s*	850s *820m*	6.60 (m)
$[PPh_4]_2[WO_2(prot)_2]\cdot 2H_2O$[e]	62.8 (62.3)	5.9 (5.5)	2.4 (2.1)					
cis-$[MoO_2(Hdpm)_2]\cdot H_2O$	42.9 (42.7)	4.5 (4.9)	6.3 (6.3)	1 486s *1 486s*	1 268s *1 273s*	880s *879s*	837s *853m*	—
cis-$[WO_2(Hdpm)_2]\cdot H_2O$	35.4 (35.7)	3.8 (4.1)	5.1 (5.2)	1 490s *1 491m*	1 258s *1 277m*	896s *892m*	862m *848w*	—
cis-$[Mo_2O_5(Had)_2]\cdot H_2O$[f]	32.9 (33.0)	3.9 (4.0)	4.3 (4.3)	1 490s *1 493s*	1 270s *1 272s*	900vs *908s*	865s *842w*	—
Uranyl complexes								
trans-$UO_2(ad)\cdot 4H_2O$	20.4 (20.7)	2.4 (3.6)	2.2 (2.7)	1 492s	1 262s	*829s*	903vs	
trans-$UO_2(dpm)\cdot 2H_2O$	21.6 (21.0)	2.6 (2.8)	3.1 (3.1)	1 490s *1 494s*	1 265s *1 275s*	*835s*	912vs	
trans-$UO_2(dp)\cdot 2H_2O$	22.2 (21.6)	2.6 (2.0)	2.9 (2.8)	1 493s	1 262s	*834s*	915vs	
trans-$UO_2(prot)\cdot 2H_2O$	25.2 (25.6)	3.0 (3.7)	2.2 (2.7)	1 492s	1 262s	*832s*	918vs	

[a] Frequencies in cm^{-1}. All data measured on solids. Raman data are italicised. M = Os, Mo, W, or U as appropriate. [b] Calculated values in parentheses. [c] Aromatic multiplet from free ligand in parentheses. [d] P = 5.6 (5.0%). [e] P = 5.1 (4.6%). [f] $\nu_{asym}(Mo_2O)$ 757 cm^{-1}.

Due to limited solubility of the potassium salts in ^2H_2O, only the aromatic ^{1}H n.m.r. resonances were clearly identifiable, and are listed in Table 2. On co-ordination the multiplet pattern of the free ligand splits into two separately distinguishable multiplets in a pattern similar to that found for ABX splitting; a similar situation was observed for the ^{1}H spectra of $[OsO_2(O_2C_6H_3R\text{-}4)_2]^{2-}$ ($O_2C_6H_3R$-4 = catecholate substituted in the 4 position).[3] The protons attached to C^3 and C^6 (see Table 1) adjacent to the donor oxygen atoms are probably those shifted to higher field, near δ 6.5 p.p.m.

Table 3. ^{13}C N.m.r. of some catechol amines and their related complexes[a]

Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	$C^{10,11}$
H_2dp[b]	146.1	147.0	119.7	130.3	124.4	119.3	38.3	58.8	176.5	
$Na_2[MoO_2(dp)_2]$	158.0	159.0	117.0	128.3	121.9	116.1	39.0	59.6	177.1	
$Na_2[WO_2(dp)_2]$	157.5	158.5	118.0	128.7	122.4	117.1	38.9	59.4	177.0	
$H_2nad{\cdot}HCl$[b]	146.8		119.3	134.9	121.3	116.8	72.0	48.5		
$Na_2[MoO_2(nad)_2]$	158.0	158.1	115.5	132.0	118.6	113.2	72.7	47.7		
$Na_2[WO_2(nad)_2]$	158.1		116.6	135.8	118.8	114.6	72.5	48.1		
$H_2prot{\cdot}HCl$	147.0		119.1	135.0	121.2	116.6	71.4	53.1	53.9	21.1, 20.9
$Na_2[MoO_2(prot)_2]$	157.9	158.1	115.4	131.9	118.6	113.2	71.6	52.6	53.3	20.6, 20.2
$Na_2[WO_2(prot)_2]$	157.6		116.4	132.2	116.4	114.3	71.6	52.6	53.3	20.6, 20.2

[a] See Table 1 for atom-numbering scheme. [b] Assignments based on the work of Haran *et al.*[17]

On the basis of the i.r., n.m.r., and analytical data it seems likely that these catechol amines are bound to osmium *via* the two catechol oxygen-donor atoms rather than *via* the aliphatic side-chain donors. It therefore seems likely that the observed osmium staining at catechol amine-rich sites[1,2] could well arise, as in the analogous situation with phenolic-containing materials in plant cells,[3,14] from direct binding of osmium to the catechol oxygen donor sites in catechol amines.

2. *Uranyl Complexes.*—There is a brief report in the literature on the existence of uranyl–adrenaline complexes in solution.[6] We find that reaction of uranyl acetate with the hydrochlorides of dopamine and isoproterenol gives precipitates of $UO_2L{\cdot}nH_2O$, while the free ligands dopa and adrenaline give low yields of the analogous species. The i.r. spectra are similar in profile to the osmyl complexes discussed above [with $\nu_{asym}(UO_2)$ *ca.* 910 cm^{-1}]. Raman spectra of the solids, as expected for *trans* O=U=O species, show no vibrations coincident with the $\nu_{asym}(UO_2)$ modes but do show strong bands near 830 cm^{-1} which we assign to $\nu_{sym}(UO_2)$, the symmetric stretch of the linear O=U=O 'uranyl' moiety in these complexes.

We tentatively suggest that these complexes contain the uranyl group with the catechol amines bound *via* the *O,O'*-donor atoms, with co-ordinated water molecules giving at least octahedral co-ordination to the metal atom [as in $UO_2(cat){\cdot}2H_2O$[15]].

3. *Molybdenum and Tungsten Complexes.*—(*a*) *cis*-$[MO_2L_2]^{2-}$. Reaction of sodium molybdate or tungstate $\{Na_2[MO_4]\}$ in neutral solutions with the hydrochlorides of noradrenaline, dopa, and isoproterenol gave species which analysed as $Na_2[MO_2L_2]$; the $[PPh_4]^+$ salts of the isoproterenol complexes were also isolated. The i.r. spectra of these salts are very similar in profile to those of $K_2[OsO_2L_2]$ (L = nad, dp, or prot) with catecholato vibrations near 1 480 and 1 260 cm^{-1}. In place of the $\nu_{asym}(OsO_2)$ bands near 830 cm^{-1} and $\nu_{asym}(UO_2)$ bands near 910 cm^{-1}, two strong bands near 890 and 850 cm^{-1} are observed, the latter being stronger than the former. The Raman spectra all exhibit the same pair of bands but with reversed intensities. We assign the band at higher wavenumber to the symmetric stretch, $\nu_{sym}(MO_2)$, and the lower to the asymmetric stretch, $\nu_{asym}(MO_2)$, of *cis*-MO_2 units. Similar bands and assignments were made for salts of *cis*-$[MO_2(cat)_2]^{2-}$[5] and *cis*-$[MO_2(trop)_2]$[11] (M = Mo or W),[5] for which the *X*-ray crystal structure of $K_2[MoO_2(cat)_2]$[16] and of *cis*-$[MoO_2(trop)_2]$[11] confirms the *cis*-dioxo geometry. The Raman spectra of the complexes also show catecholato ligand bands near 1 480 and 1 270 cm^{-1}, as observed in other catecholato complexes.[5,13]

The ^1H n.m.r. spectra of $[MO_2L_2]^{2-}$ show little change in the pattern of aromatic resonances from those of the free ligand, apart from a shift to higher field by *ca.* 0.4 p.p.m., while the aliphatic side chains also show little change in position and no change in pattern. This behaviour is similar to that observed for the ^1H n.m.r. spectra of *cis*-$Na_2[MoO_2(cat)_2]$[5] and suggests that, as in the latter case, the ligands are bound in the catecholato mode.

These salts are sufficiently soluble in ^2H_2O for their ^{13}C proton-decoupled n.m.r. spectra to be measured, and these are listed for *cis*-$[MO_2L_2]^{2-}$ (M = Mo or W; L = nad, dp, or prot) in Table 3, together with the ^{13}C n.m.r. spectra of the corresponding ligands. The ^{13}C spectra of adrenaline,[17,18] noradrenaline,[17,18] dopamine,[17,18] and dopa[17] have been published and the shifts assigned. In all cases, as with catechol itself, the carbon nuclei adjacent to the catecholato oxygen atoms resonate at lower fields (*ca.* δ 145 p.p.m. *vs.* $SiMe_4$)[17,18] than the others. Our spectra for noradrenaline and dopa agree well with the literature data;[17,18] although no data on isoproterenol seem to have been published we find that its spectrum is similar to other catechol amines. Our ^{13}C spectra of the complexes *cis*-$[MO_2L_2]^{2-}$ (M = Mo or W) containing co-ordinated noradrenaline, dopa, and isoproterenol show clearly that the shifts arising from C^1 and C^2 (those attached to the catechol hydroxy groups) are shifted downfield by at least 10 p.p.m. upon co-ordination. There are minimal shifts in the carbon nuclei of the side chains, again suggesting that co-ordination occurs through the catecholato groups. We observed a similar effect on the δ 146.6 p.p.m. shifts in free catechol upon co-ordination in *cis*-$[MoO_2(cat)_2]^{2-}$ and in $[W_2O_5(cat)_2]^{2-}$, both shifting to lower field in these complexes.[5]

(*b*) *cis*-$[MO_2(Hdpm)_2]$. Reaction of $[MoO_4]^{2-}$ or $[WO_4]^{2-}$ with dopamine hydrochloride in water gave orange (Mo) or yellow (W) precipitates, rather than the expected water-soluble *cis*-$[MO_2L_2]^{2-}$ found with noradrenaline, dopa, and isoproterenol. The precipitates contain no sodium, analyse as $[MO_2(Hdpm)_2]{\cdot}H_2O$, and are diamagnetic. Their insolubility prevented n.m.r. measurements but the i.r. and Raman spectra showed catecholato bands, as well as bands assignable to $\nu_{sym}(MO_2)$ and $\nu_{asym}(MO_2)$ of *cis*-MO_2 units. We tentatively suggest that these are best formulated as containing co-ordinated *O,O'*-catechol amines in which only one proton has been removed from the two catechol hydroxy groups. A similar situation has been proposed for $[M(Hdpm)_2]$ (M = Cu, Co, or Ni),[10] and the Schiff-base complex [Fe(salen)(Hcat)] [salen = *N,N'*-ethylenebis(salicylideneiminate)] contains monodentate catechol in which the unco-ordinated oxygen atom is protonated.[19]

(*c*) $[Mo_2O_5(Had)_2]$. Reaction of $Na_2[WO_4]$ with adrenaline in dilute HCl gave *cis*-$Na_2[WO_2(ad)_2]$, but the corresponding reaction with $Na_2[MoO_4]$ gave a deep red material which contained no sodium. The Raman and i.r. spectra gave bands

suggestive of the presence of *cis*-MoO_2 units; an extra i.r. band at 757 cm^{-1} could arise from the asymmetric stretch $\nu_{asym}(Mo_2O)$ of a bent Mo<O>Mo bridge, as observed in the spectra of $[NH_4]_2[Mo_2O_5(cat)_2]\cdot 2H_2O$,[5] known from *X*-ray studies[20] to contain such a bridge together with bridging catecholato ligands. The complex has limited solubility in $(C^2H_3)_2SO$ and in this solvent, although not all the ^{13}C resonances could be seen, the shifts due to the nuclei bound to catecholato oxygen atoms at δ 145 p.p.m.[18] remained in the same position in the complex, suggesting that there is no binding from the catecholato part of the ligand. We tentatively suggest a structure akin to that established for $[NH_4]_2[Mo_2O_5(cat)_2]\cdot 2H_2O$[20] with, in this case, the bridging five-membered rings being provided by the deprotonated β-hydroxy group and the secondary amine group of the aliphatic side chain, *i.e.* –CH(OH)–CH_2–*N*H–CH_3, of adrenaline. An analogous mode of bonding, albeit in a mononuclear complex, has been proposed for $[Cu(Hdp)_2]\cdot H_2O$, in one form of which the aliphatic side chain rather than the catecholato moiety is bonded to the metal.[9]

4. *Other Studies.*—Despite many attempts, no crystals suitable for an *X*-ray study of any of the complexes could be obtained. Cyclic voltammetric studies on the complexes were made but gave ill defined waves in the cases of *trans*-$[OsO_2L_2]^{2-}$ and *cis*-$[MoO_2L_2]^{2-}$ (M = Mo or W).

Experimental

Preparations.—The catechol amines (Aldrich Chemical Co.) were used as the free bases (adrenaline, dopa) or as the hydrochlorides (dopamine, noradrenaline, isoproterenol).

Osmium Complexes, trans-$X_2[OsO_2L_2]$ (X = K^+ *or* PPh_4^+). —Potassium osmate, *trans*-$K_2[OsO_2(OH)_4]$, was prepared by the literature method.[21]

To a solution of potassium hydroxide (0.1 g, 2 mmol) in water (5 cm^3) was added a solution of *trans*-$K_2[OsO_2(OH)_4]$ (0.2 g, 0.5 mmol) in water (10 cm^3), followed by addition of the catechol amine hydrochloride (1 mmol) in saturated solution. In the case of the free bases dopa and adrenaline the solids were added to the reaction mixture. The solutions were immediately reduced in volume on a rotary evaporator and the deep red-brown potassium salts recrystallised from water–ethanol (1:1). The tetraphenylphosphonium salts were formed by addition of excess of aqueous $[PPh_4]Cl$ to the reactant solution.

Uranyl Complexes, $UO_2L\cdot nH_2O$.—To hydrated uranyl acetate (0.14 g, 0.33 mmol) in water (10 cm^3) was added the ligand hydrochloride (1 mmol) in water (10 cm^3). The solution immediately became dark brown and a flocculent brown precipitate soon separated out, was filtered off, washed with ethanol and diethyl ether, and dried over concentrated H_2SO_4. In the case of adrenaline, which is far less water soluble than the hydrochlorides, the free base (1 mmol) was stirred with water (100 cm^3) for a few hours and the solution filtered into the uranyl acetate; dopa (1 mol) was dissolved in water (25 cm^3) by warming and stirring and was then added to uranyl acetate. The dopamine complex was made by mixing ethanolic solutions of the ligand and uranyl acetate in a molar ratio of 1:2 and refluxing for 0.5 h.

Molybdenum and Tungsten Complexes.—(*i*) *cis*-$Na_2[MO_2L_2]$ (M = Mo *or* W). For L = noradrenaline, isoproterenol, or adrenaline, the base hydrochloride (1.3 mmol) in water (5 cm^3) was added to sodium molybdate or sodium tungstate (0.66 mmol) in water (10 cm^3). A deep red colour was immediately observed; the solid products were isolated by evaporation on a rotary evaporator followed by recrystallisation from a water–ethanol (1:1) mixture. The dopa complex was made by dissolving the free base in water (25 cm^3) by warming and stirring. The tetraphenylphosphonium salts of $[MO_2(prot)_2]^{2-}$ (M = Mo or W) were also made by addition of $[PPh_4]Cl$ to the appropriate red solutions.

(*ii*) $[MO_2(Hdpm)_2]\cdot nH_2O$. Sodium molybdate or tungstate (0.66 mmol) was dissolved in water (10 cm^3) and dopamine hydrochloride (1.3 mmol) in water (5 cm^3) was added. An orange (Mo) or yellow (W) precipitate formed immediately and was filtered off, washed with ethanol and diethyl ether, and dried over concentrated H_2SO_4.

(*iii*) $[Mo_2O_5(Had)_2]\cdot H_2O$. Adrenaline (0.26 g, 1.4 mmol) was dissolved in 2 mol dm^{-3} HCl (10 cm^3) and added to a solution of sodium molybdate (0.16 g, 0.66 mmol) in water (10 cm^3). A deep red colour was observed immediately, followed 1 h later by formation of a deep red precipitate. This was filtered off, washed with ethanol and diethyl ether, and dried over concentrated H_2SO_4.

Infrared spectra were measured on a Perkin-Elmer 683 spectrometer as liquid paraffin mulls between CsI plates. Raman spectra were measured as KBr discs with 6 471 or 5 682 Å krypton-ion laser excitation on a Spex Ramalog 5 instrument. Proton and ^{13}C n.m.r. spectra were recorded on a Bruker WM 250 MHz instrument. Microanalyses were performed by the microanalytical department at Imperial College.

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