Catecholato Complexes of Ruthenium, Iridium, Rhenium, Molybdenum, and Tungsten

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Salts of the new catecholato(2−) (cat) complexes $[Ru(cat)_3]^{3-}$, $[Ir(cat)_3]^{2-}$, $[Re(cat)_3]^{2-}$, $[WO_2(cat)_2]^{2-}$, and $[W_2O_5(cat)_2]^{2-}$ are reported, a number of oxomolybdenum catecholato complexes reinvestigated and some reformulated. Infrared, Raman, and n.m.r. data are reported for the complexes.

Species containing the catechol (H_2cat) moiety have long been known to form complexes with iron[1] and other metals,[2] and we have recently reported osmium(VI) catecholato(2−) (cat) complexes,[3,4] some of which may be involved in the histochemical staining of phenolic material in plants by OsO_4.[5] In this paper we report new catecholato complexes of some second- and third-row transition elements.

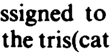
Results and Discussion

A. *Tris(catecholato) Complexes.*—Although a number of tris(catecholate) complexes of first-row transition elements is known[2] the only examples from the second and third rows are $K_3[Rh(cat)_3]\cdot H_2O$[6] and $[Os(cat)_3]$.[3,4] We find that reaction of catechol in base under anaerobic conditions in the presence of $[PPh_4]^+$ with $[Ru(acac)_3]$ (acac = acetylacetonate), $Na_2[IrCl_6]\cdot 2H_2O$ (or $IrCl_3\cdot nH_2O$), or $K_2[ReCl_6]$ gives respectively $[PPh_4]_3[Ru(cat)_3]\cdot 3H_2O$, $[PPh_4]_2[Ir(cat)_3]\cdot 3H_2O$, and $[PPh_4]_2[Re(cat)_3]\cdot H_2O$. Efforts to prepare $[Ir(cat)_3]^{3-}$ by methods similar to those used to prepare $[Rh(cat)_3]^{3-}$ (ref. 6) were not successful, though preliminary electrochemical data suggest that reduction of $[Ir(cat)_3]^{2-}$ does give $[Ir(cat)_3]^{3-}$. The complex '$H[Re(OH)_3(cat)(H_2O)]$'[7] may contain the $[Re(cat)_3]^{2-}$ ion since the preparative route for the former was somewhat similar to ours. Spectroscopic data for the complexes are given in the Table.

B. *Oxo–Catecholato Complexes.*—We have reported the oxo-osmium(VI) catecholato and substituted catecholato complexes *trans*-$[OsO_2(cat)_2]^{2-}$ and *trans*-$[OsO_2(cat)(py)_2]$(py = pyridine).[3] There are *X*-ray data on *cis*-$K_2[MoO_2(cat)_2]\cdot H_2O$,[8] $[NH_4]_2[Mo_2O_5(cat)_2]\cdot 2H_2O$,[9] $Ba[Mo_2O_5(cat)_2]\cdot H_2cat\cdot 5H_2O$,[9] and the 3,5-di-t-butylcatecholato(2−) (dtbc) complexes $[NBu^n_4]_2[Mo_2O_5(dtbc)_2]$[10] and $[\{MoO(dtbc)_2\}_2]$.[11] The 9,10-phenanthrenesemiquinonate (1−) (psq) complex $[Mo_2O_5(psq)_2]$ has a very similar structure[10] to the anions $[Mo_2O_5(cat)_2]^{2-}$ and $[Mo_2O_5(dtbc)_2]^{2-}$: there are *cis*-MoO_2 groups in all three, and a bridging oxo ligand supported by bridging from the quinonoid ligands. There are early reports of $[MoO_2(cat)_2]^{2-}$,[12] $[WO_2(cat)_2]^{2-}$,[13] $[MoO_2(cat)(OH)]^-$,[12] $[MoO_3(cat)]^{2-}$,[12] and of the pyrogallol (H_3pg) complexes $[MoO_2(Hpg)_2]^{2-}$, $[WO_2(Hpg)_2]^{2-}$, and $[MoO_2(OH)(Hpg)]^-$,[13] but *X*-ray studies show that $[NH_4]H[MoO_3(cat)]\cdot 0.5H_2O$[12] is in fact $[NH_4]_2[Mo_2O_5(cat)_2]\cdot 2H_2O$[9] and that $BaH_2[MoO_3(cat)]_2\cdot 3H_2O$[14] is $Ba[Mo_2O_5(cat)_2]\cdot H_2cat\cdot 5H_2O$.[9] The formulation $K_2[MoO_2(cat)_2]\cdot H_2O$[13] is however correct.[8]

On the basis of analytical, and vibrational and n.m.r. spectroscopic data (see below) we reformulate $[Hpy]H[MoO_3(cat)]\cdot 1.5H_2O$[12] as $[Hpy]_2[Mo_2O_5(cat)_2]$, '$K[MoO_2(OH)(cat)]\cdot 2H_2O$'[13] as $K_2[Mo_2O_5(cat)_2]$, and $[Hpy]_2[MoO_2(cat)_2]\cdot 3H_2cat\cdot 4H_2O$[12] as $[Hpy]_2[MoO_2(cat)_2]\cdot H_2cat$; we do however confirm the formulation[13] $K_2[MoO_2(cat)_2]\cdot H_2cat\cdot H_2O$. Our attempts to prepare $Na_2[WO_2(cat)_2]$[13] gave $Na_2[W_2O_5(cat)_2]\cdot 2H_2O$, but we have prepared $[PPh_4]_2[WO_2(cat)_2]$.

C. *Spectroscopic Data.—Infrared and Raman data.* The spectra of catecholato complexes are distinguished by strong bands near 1 480 cm^{-1} (assigned to an aromatic ring stretch) and near 1 270 cm^{-1} (assigned to a C–O stretch);[15,16] such features are observed for the tris(catecholato) complexes. Bands due to the O–H stretch of free catechol[17] are of course absent in the complexes. In addition, the oxo-molybdenum and -tungsten species show bands attributable to stretches of the *cis* MO_2 groups, and Raman spectroscopy is particularly useful for observing vibrations of the highly polarisable metal–oxo vibrations. These are expected to lie in the region 870—920 cm^{-1} with the symmetric stretch $\nu_{sym}(MO_2)$ at higher frequencies than the asymmetric stretch $\nu_{asym}(MO_2)$; also $\nu_{sym}(MO_2)$ is expected to be strong in the Raman and of moderate intensity in the i.r., the reverse being the case for $\nu_{asym}(MO_2)$.[18] In the cases of $[PPh_4]_2[MO_2(cat)_2]$ (M = Mo or W) which are sufficiently soluble for i.r. and Raman spectra of the solutions to be measured, this is so, and $\nu_{sym}(MO_2)$ is polarised and $\nu_{asym}(MO_2)$ depolarised in the Raman, as expected.

Such bands are clearly discernible in all the spectra of complexes containing MO_2 or M_2O_5 moieties (M = Mo or W), and are not observed in catechol or in the tris(catecholato) complexes. They are present in $K_2[MoO_2(cat)_2]\cdot H_2O$ and $[NH_4]_2[Mo_2O_5(cat)_2]\cdot 2H_2O$, known from *X*-ray studies[8,9] to contain *cis* MoO_2 groups. The latter species is also known to contain a bridging oxo ligand;[9] this complex and the others in the Table have i.r. bands near 730 cm^{-1}, not found in catechol or in the tris(catecholato) complexes, which we tentatively assign to $\nu_{asym}(M_2O)$, the asymmetric  stretching vibration, which occurs in similar complexes in this region.[19,20]

Hydrogen-1 and carbon-13 n.m.r spectra. The ^1H n.m.r. spectrum of catechol, an A_2B_2 system, shows a single resonance at δ 6.83 p.p.m.† in acetone;[21] in C^2HCl_3 we also observe a resonance at δ 5.22 p.p.m. with an intensity half of that of the 6.83 p.p.m. resonance. This is likely to be due to the hydroxyl groups and disappears on complexation of the ligand. The δ 6.83 p.p.m. aromatic ring resonance in general shifts to higher field on complexation; this has been ascribed to the decreased electron density in the aromatic ring consequent upon co-ordination of the ligand.[6] The resonance is generally observed as a complex multiplet. The species formulated by Weinland and Gaisser[12] as $K_2[MoO_2(cat)_2]\cdot H_2cat\cdot H_2O$[14] shows two resonances, at δ 6.79 and 6.59; the former has half the intensity

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† All values are quoted relative to low-field of $SiMe_4$.

Table. Spectroscopic data for catecholato and related complexes

	Infrared and Raman[a] data (cm^{-1})					N.m.r. data (^1H, ^{13}C, in ^2H_2O)			
	ν(C–C)	ν(C–O)	$\nu_{sym}(MO_2)$	$\nu_{asym}(MO_2)$	$\nu_{asym}(M_2O)$	phenyl H	$C^{1,2}$	$C^{4,5}$	$C^{3,6}$
Catechol	1 607s	1 257m				6.83m[b]	146.6	123.6	118.9[c]
	(1 594s)	(1 265s)							
$[PPh_4]_3[Ru(cat)_3]\cdot 3H_2O$	1 485vs	1 253vs							
$[Os(cat)_3]$[d]	1 580s	1 180s				6.4—6.68m	171.5	124.0	117.1[e]
$K_3[Rh(cat)_3]\cdot H_2O$	1 514	1 280[f]				6.44—6.69m[f]	165.0	118.4	118.2
$[PPh_4]_2[Ir(cat)_3]\cdot 3H_2O$	1 477s	1 250vs							
$[Pt(cat)(PPh_3)_2]$	1 570	1 267[g]				6.24m[g]	163.0	115.7	115.3[e]
$[PPh_4]_2[Re(cat)_3]\cdot H_2O$	1 485s	1 253s							
$K_2[MoO_2(cat)_2]\cdot H_2O$	1 482s	1 264s	890vs	872vs		6.72s	158.8	121.5	116.4
			(900s)	(871w)					
$[PPh_4]_2[MoO_2(cat)_2]\cdot H_2O$		1 260s	905m	880s					
			900s	*875s*					
	(1 487s)	(1 262w)	(906s)	(888m)					
			(*900p*)	(*878dp*)					
$K_2[MoO_2(cat)_2]\cdot H_2cat\cdot H_2O$	1 480s	1 256s	890vs	873vs		6.59m	158.7	121.4	116.3
						6.79m	147.0	124.0	119.4
$[NH_4]_2[Mo_2O_5(cat)_2]\cdot 2H_2O$	1 485s	1 260s	920vs	872vs	733s	6.32m	157.1	122.4	117.2
$[Hpy]_2[Mo_2O_5(cat)_2]$	1 482s	1 255s	920m	972vs	740s	*h*			
$K_2[Mo_2O_5(cat)_2]$	1 486s	1 260s	920vs	870vs	730s				
$Na_2[W_2O_5(cat)_2]\cdot 2H_2O$	1 490s	1 264vs	915vs	864vs	770s	6.76m	158.3	121.9	117.4
$Cs_2[WO_2(cat)_2]$		1 250s	904s	870w					
$[PPh_4]_2[WO_2(cat)_2]$	*h*	1 260w	909vs	875m					
	1 480m	*h*	*h*	880w					
	(1 491s)		(909vs)	(864m)					
			(910p)	(880dp)					
$[NH_4]_2[Mo_2O_5(Hpg)_2]\cdot 2H_2O$	1 496s	1 247s	928s	882s	720s				
trans-$K_2[OsO_2(cat)_2]$		1 250s		824vs[e]		6.87m[e]	167.7	121.1	118.2
			(864vs)						

[a] Raman data are in parentheses. All data on solids except those in italic, for which CH_3CN solutions were used; p = polarised, dp = depolarised. [b] Ref. 21. [c] Ref. 22. [d] Ref. 3. [e] In C^2HCl_3. [f] Ref. 6. [g] Ref. 25. [h] Obscured (by solvent or ligand mode).

of the latter and this, together with its position, suggests that it arises from free catechol, in agreement with its original formulation. The *X*-ray crystal structure of $Ba[Mo_2O_5(cat)_2]\cdot H_2cat\cdot 5H_2O$[9] shows that 'catechol of crystallisation' does occur in some complexes.

The only ^{13}C data reported for catecholato complexes are for $[Os(cat)_3]$.[3] The proton-decoupled ^{13}C n.m.r. spectrum of free catechol shows three resonances at δ 146.6, 123.6, and 118.9 p.p.m. assigned respectively to $C^{1,2}$, $C^{4,5}$, and $C^{3,6}$.[22] On co-ordination there is a considerable low-field shift of the δ 146.6 p.p.m. resonance while the other two remain relatively unaffected, and this is clearly characteristic of co-ordination. It is interesting that the largest shift[3] occurs in $[Os(cat)_3]$ which formally involves osmium(VI); in the other hexavalent species in which the strongly π-donating oxo ligand is also present the shift is less pronounced, suggesting that there is perhaps less electron drainage from the catecholato oxygen-donor atoms in these cases than with $[Os(cat)_3]$. The complex $K_2[MoO_2(cat)_2]\cdot H_2cat\cdot H_2O$ shows two sets of such resonances; those at δ 147.0, 124.0, and 119.4 p.p.m. are likely to arise from free catechol.

Experimental

Tris(catecholato) Complexes.—All preparations were carried out under anaerobic conditions with degassed solvents.

Tetraphenylphosphonium tris(catecholato)ruthenate(III), $[PPh_4]_3[Ru(cat)_3]\cdot 3H_2O$. Tris(acetylacetonato)ruthenium(III) (0.1 g, 0.5 mmol) was dissolved in methanol (5 cm^3). Potassium hydroxide (0.1 g, 0.3 mmol), dissolved in water (5 cm^3), was added to a solution of catechol (0.2 g, 2 mmol) in ethanol (5 cm^3) and this mixture was immediately added to the ruthenium solution. The dark red solution was stirred and warmed for 1 h and tetraphenylphosphonium chloride (0.56 g, 0.7 mmol) in water (5 cm^3) then added. No colour change was seen, so warming and stirring of the solution was continued. After standing overnight the resulting dark red solid was filtered off under nitrogen, and then dried in a desiccator over concentrated sulphuric acid (Found: C, 72.3; H, 5.3; P, 6.7. $C_{90}H_{78}O_9P_3Ru$ requires C, 72.2; H, 5.3; P, 6.2%), yield 35%.

Tetraphenylphosphonium tris(catecholato)iridate(IV), $[PPh_4]_2[Ir(cat)_3]\cdot 3H_2O$. The methods used were adapted from those described for $K_3[Cr(cat)_3]$[23] and $K_3[Fe(cat)_3]$.[24]

Method 1. Sodium hexachloroiridate (0.5 g, 1 mmol) and catechol (0.33 g, 3 mmol) were dissolved in water (10 cm^3). Sodium hydroxide (0.4 g, 0.01 mol) in water (5 cm^3) was added to the iridium(IV) solution which then became very dark green. It was left to stand for 15 min and tetraphenylphosphonium chloride (0.75 g, 2 mmol) in degassed water (10 cm^3) added. The solution was left to stand until a thick green precipitate formed; after standing for *ca.* 2 h, the solid was filtered off. The product was washed with water, then dried under a nitrogen stream, then in a desiccator over concentrated sulphuric acid.

Method 2. Hydrated iridium chloride (0.1 g, 0.3 mmol) was dissolved in water (10 cm^3) by warming, and catechol (0.1 g, 10 mmol) added. Potassium hydroxide (0.2 g, 25 mmol) in water (5 cm^3) was added anaerobically to the green iridium solution, which immediately turned red. Tetraphenylphosphonium chloride (0.33 g, 0.9 mmol) in water (5 cm^3) was added. A cloudiness with a fine flocculent precipitate appeared and after 1 h the precipitate was filtered off under nitrogen, and washed with a little water. It was dried by passing nitrogen over it, then in a desiccator over concentrated sulphuric acid. The precipitate became green even before it was totally exposed to the air (Found: C, 63.3; H, 4.6. $C_{66}H_{58}IrO_9P_2$ requires C, 63.5; H, 4.7%).

Tetraphenylphosphonium tris(catecholato)rhenate(IV), $[PPh_4]_2[Re(cat)_3]\cdot H_2O$. A similar method to that described for the iridium(IV) catecholato complex was used. A solution of $K_2[ReCl_6]$ (0.02 g, 0.04 mmol) and catechol (0.14 g, 0.1 mmol) in water (5 cm^3) was mixed with potassium hydroxide (0.3 g, 4 mmol) in water (5 cm^3). The light green solution immediately became very dark green; tetraphenylphosphonium chloride (0.49 g, 1.1 mmol) in water (10 cm^3) was added. After standing in the refrigerator overnight the resulting purplish solid was filtered off under nitrogen, washed with water, and dried under nitrogen (Found: C, 65.4; H, 4.5; P, 4.5. $C_{66}H_{54}O_7P_2Re$ requires C, 65.7; H, 4.5; P, 5.1%), yield 20%.

Oxo-Catecholato Complexes.—Dipotassium cis-*bis(catecholato)dioxomolybdate*(VI), $K_2[MoO_2(cat)_2]\cdot H_2O$. The preparation of this complex is described in the literature,[13] but the following modification was found to be more satisfactory.

Molybdenum trioxide (0.7 g, 5 mmol) was added to a solution of potassium hydroxide (0.55 g, 1.0 mmol) in water (7.5 cm^3), and dissolved by gentle warming and stirring. This solution was filtered into a flask containing catechol (1.1 g, 10 mmol). A deep red solution formed immediately as the solid dissolved. It was heated gently and left to stand for several days. The red product was filtered off, washed with a little ethanol and diethyl ether, dried in a desiccator over concentrated sulphuric acid, and then recrystallised from water (Found: C, 32.7; H, 2.0. $C_{12}H_{10}K_2MoO_7$ requires C, 32.7; H, 2.3%). The *pyridinium salt* was similarly prepared as orange-red crystals (Found: C, 52.5; H, 4.0; N, 5.6. $C_{22}H_{20}MoN_2O_6$ requires C, 52.4; H, 4.0; N, 5.6%). The *tetraphenylphosphonium salt* was prepared in analogous fashion from $K_2[MoO_4]$ (1.17 g, 5 mmol) in water (10 cm^3) and catechol (1.1 g, 10 mmol). To the deep red solution was added tetraphenylphosphonium chloride (3.80 g in 25 cm^3 of water) and the red product filtered off (Found: C, 68.8; H, 4.7; P, 5.8. $C_{60}H_{50}MoO_7P_2$ requires C, 68.1; H, 4.7; P, 5.8%).

Potassium cis-*bis(catecholato)dioxomolybdate*(VI), *with catechol of crystallisation*, $K_2[MoO_2(cat)_2]\cdot H_2cat\cdot H_2O$. The method for the preparation of this complex is described in the literature.[13] However, in this work, it was found more successful to use the method described for the formation of $K_2[MoO_2(cat)_2]$[14] but using excess catechol.

Potassium hydroxide (1.4 g, 25 mmol) was added to a solution of $[NH_4]_6[Mo_7O_{24}]\cdot 4H_2O$ (2.1 g, 12 mmol) in water (10 cm^3), and the solution heated for 30 min to expel ammonia. It was then filtered into a flask containing catechol (2.6 g, 24 mmol). The solution immediately became deep red in colour, and was heated until solid appeared on the surface. It was then left to stand, and the resulting solid filtered off, washed with a little water, and dried in a desiccator (Found: C, 39.7; H, 2.8. $C_{18}H_{16}K_2MoO_9$ requires C, 39.3; H, 2.9%).

Pyridinium cis-*bis(catecholato)dioxomolybdate*(VI), *with catechol of crystallisation*, $[Hpy]_2[MoO_2(cat)_2]\cdot H_2cat$. The method used was that described in the literature for the preparation of $[Hpy]_2[MoO_2(cat)_2]\cdot 3H_2cat\cdot 4H_2O$.[12]

Molybdenum trioxide (1.4 g, 0.01 mol), catechol (5.5 g, 0.05 mol) and pyridine (8 cm^3) were refluxed in water (50 cm^3). After 30 min the solution was filtered hot and left to stand. The orange-red crystalline precipitate was filtered off and washed with a little ethanol and diethyl ether. It was dried in a desiccator over concentrated sulphuric acid (Found: C, 54.2; H, 4.1; N, 4.6. $C_{28}H_{26}MoN_2O_8$ requires C, 54.7; H, 4.3; N, 4.6%).

*Potassium bis(catecholato)-μ-oxo-bis[*cis*-dioxomolybdate*(VI)], $K_2[Mo_2O_5(cat)_2]$. The literature method for $K[MoO_2(OH)(cat)]\cdot 2H_2O$[13] was followed. Molybdenum trioxide (1.4 g, 0.01 mol) and potassium hydroxide (0.6 g, 0.01 mol) were dissolved by warming in water (20 cm^3). The solution was filtered into a flask containing catechol (1.1 g, 0.01 mol). The resulting dark orange-red solution was reduced in volume slightly by heating and left to stand. The red-brown precipitate that formed was filtered off, washed with ethanol and diethyl ether, and dried in a desiccator {Found: C, 25.1; H, 1.7. $K[MoO_2(OH)(C_6H_4O_2)]\cdot 2H_2O$ requires C, 24.7; H, 1.4. $K_2[Mo_2O_5(C_6H_4O_2)_2]$ requires C, 25.5; H, 1.4%}.

*Ammonium bis(catecholato)-μ-oxo-bis[*cis*-dioxomolybdate*(VI)], $[NH_4]_2[Mo_2O_5(cat)_2]\cdot 2H_2O$. The method used was that described for $[NH_4]H[MoO_3(cat)]\cdot 0.5H_2O$.[12] This was subsequently shown to be $[NH_4]_2[Mo_2O_5(cat)_2]\cdot 2H_2O$ by *X*-ray crystallographic studies.[9]

$[NH_4]_6[Mo_7O_{24}]\cdot 4H_2O$ (1.96 g, 0.01 mol) was dissolved in water (20 cm^3) by warming, the solution filtered, and catechol (1.1 g, 0.01 mol) in water (10 cm^3) added. The colourless solution became dark red; it was reduced in volume by heating until solid first started to appear, and was left to cool. The resulting dark red solid was filtered off, washed with ethanol and diethyl ether, and dried in a desiccator (Found: C, 25.8; H, 3.6; N, 5.1. $C_{12}H_{20}Mo_2N_2O_{11}$ requires C, 25.7; H, 3.6; N, 5.0%).

*Pyridinium bis(catecholato)-μ-oxo-bis[*cis*-dioxomolybdate*(VI)], $[Hpy]_2[Mo_2O_5(cat)_2]$. The method used was that described in the literature for $[Hpy]H[MoO_3(cat)]\cdot 1.5H_2O$.[13]

Molybdenum trioxide (1.4 g, 0.01 mol), catechol (1.1 g, 0.01 mol) and pyridine (1.6 cm^3) were refluxed in water (50 cm^3). After 20 min the solution was filtered hot and left to stand. The resulting orange-red precipitate was filtered off, washed with a little cold water, and dried in a desiccator over concentrated sulphuric acid {Found: C, 39.1; H, 3.1; N, 4.0. $[Hpy]H[MoO_3(C_6H_4O_2)]\cdot 1.5H_2O$ requires C, 39.9; H, 2.7; N, 4.2. $[Hpy]_2[Mo_2O_5(C_6H_4O_2)_2]$ requires C, 38.8; H, 3.0; N, 4.1%}.

*Sodium bis(catecholato)-μ-oxo-bis[*cis*-dioxotungstate*(VI)], $Na_2[W_2O_5(cat)_2]\cdot 2H_2O$. Sodium tungstate (0.29 g, 1 mmol) was dissolved in water (10 cm^3). A solution of catechol (0.11 g, 1 mmol) in water (5 cm^3) was added. The colourless solution immediately became yellow-green on mixing. The mixture was evaporated until solid was first seen to form; the yellow-green precipitate was filtered off, washed with ethanol and diethyl ether and dried *in vacuo* (Found: C, 19.4; H, 1.9. $C_{12}H_{12}Na_2O_{11}W_2$ requires C, 19.3; H, 1.6%).

Tetraphenylphosphonium cis-*bis(catecholato)dioxotungstate*(VI), $[PPh_4]_2[WO_2(cat)_2]$. Sodium tungstate (0.58 g, 2 mmol) was dissolved in water (20 cm^3) and a solution of catechol (0.44 g, 4 mmol) in water (15 cm^3) added. Tetraphenylphosphonium chloride (1.5 g) in water (10 cm^3) was mixed with the solution and the yellow product filtered off (Found: C, 63.9; H, 4.2; P, 6.1. $C_{60}H_{48}O_6P_2W$ requires C, 63.8; H, 4.2; P, 5.5%).

*Ammonium μ-oxo-bis[pyrogallolato(2−)]bis[*cis*-dioxomolybdate*(VI)], $[NH_4]_2[Mo_2O_5(Hpg)_2]\cdot 2H_2O$. The literature method described for $[NH_4][MoO_2(OH)(Hpg)]$[13] was used. Pyrogallol (0.3 g, 0.02 mol) was added to a solution of ammonium molybdate (4.2 g, 0.02 mol) in water (15 cm^3). The very dark solution was reduced in volume slightly by heating. After standing for 1 d, the resulting product was filtered off, washed with ethanol and diethyl ether, and dried in a desiccator {Found: C, 24.5; H, 2.8; N, 4.3. $[NH_4][MoO_2(OH)(C_6H_4O_3)]$ requires C, 25.1; H, 3.2; N, 4.9. $[NH_4]_2[Mo_2O_5(C_6H_4O_3)_2]\cdot 2H_2O$ requires C, 24.2; H, 3.0; N, 4.8%}.

The following complexes were prepared as described in the literature: $[Pt(cat)(PPh_3)_2]$[25] and $K_2[OsO_2(cat)_2]$.[3]

Infrared spectra were measured on a Perkin-Elmer 683 instrument as Nujol mulls between CsI plates, and Raman spectra on a Spex Ramalog 5 instrument as spinning discs on KBr, using a krypton-ion laser. ^1H N.m.r. spectra were measured on a Perkin-Elmer R32 90-MHz instrument and ^{13}C spectra on a 62.9-MHz JEOL FX 90Q Fourier-transform spectrometer at 22.51 MHz.

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