New Catecholato Oxorhenium(V) Complexes*

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The complexes $[ReO(L)(PPh_3)_2X]$ [H_2L = catechol (H_2cat), tetrachlorocatechol (H_2tccat) or tetrabromocatechol (H_2tbcat); X = Cl or I], $[NBu^n_4][ReO(L')(tccat)_2]$ (L′ = $OPPh_3$, MeOH or pyridine), $[NBu^n_4][ReO(OPPh_3)(tbcat)_2]$ and $[ReO(PPh_3)(L'')_2]I$ [HL″ = tropolone (2-hydroxycyclohepta-2,4,6-trien-1-one) or maltol (3-hydroxy-2-methylpyran-4-one)] have been isolated and their infrared, Raman, ^{31}P and ^{13}C NMR spectra are reported. The X-ray crystal structures of $[NBu^n_4][ReO(OPPh_3)(tccat)_2]$ **1** and $[NBu^n_4][ReO(MeOH)(tccat)_2]$ **2** are presented. In both molecules the co-ordination geometry about Re is very similar, being distorted octahedral with the catecholato ligands folded away from a very strongly bonded oxo ligand [1.576(8) Å in **1** and 1.653(11) Å in **2**] with weakly bound $OPPh_3$ and MeOH ligands in the *trans* positions.

Complexes of catechol (benzene-1,2-diol, H_2cat) and substituted catechols are of considerable current interest owing to their 'non innocent' nature[1] and also to their presence in many biological systems (*e.g.* as siderophoric ligands,[2] as catecholamines in the body,[3] and as phenolics in plant tissue[4]). We have previously reported catechol and substituted catechol complexes of a number of second- and third-row transition elements, *viz.* osmium,[4-6] ruthenium, iridium, rhodium, platinum, molybdenum and tungsten,[7] and also catecholamine complexes of osmium, molybdenum and tungsten.[8] We have also synthesised one rhenium catecholato complex, $[PPh_4]_2[Re(cat)_3]$,[7] and here report a number of new catechol and substituted catechol complexes of rhenium(V) and describe the related maltol (Hmalt) 3-hydroxy-2-methylpyran-4-one) and tropolone (Htrop) (2-hydroxycyclohepta-2,4,6-trien-1-one) complexes.

A number of rhenium catecholato complexes are known. Recently salts of $[ReO(cat)_2]^-$, *cis*-$[ReO_2(cat)_2]^-$ and *cis*-$[ReO_2(dbcat)_2]^-$ (H_2dbcat = 3,5-di-*tert*-butylcatechol)[9] have been isolated, and there are also reports of $[Re(dbcat)_3]$[10,11] and $[Re(tccat)_3]$ (H_2tccat = tetrachlorocatechol),[11] $[Re(\eta^5\text{-}C_5Me_5)(tccat)_2]$,[12] $[ReMeO_2(cat)X]$ (X = Cl,[13,14] Br or I[13]) and $[ReMeO_2(cat)(py)]$[14] (py = pyridine). There are X-ray crystal structures for $(NEt_4)[ReO_2(cat)_2]$,[9] $[Re(dbcat)_3]$[10,11] and $[Re(tccat)_3]$,[11] $[Re(\eta^5\text{-}C_5Me_5)(tccat)_2]$[12] and $[ReMeO_2(cat)(py)]$.[14] In this paper we investigate further the reactions of oxorhenium(V) complexes with catechols and quinones.

Results and Discussion

(*a*) *Complexes of the Type* $[ReO(L)(PPh_3)_2X]$ (X = Cl or I).—These were prepared by the reaction of $[ReO(PPh_3)_2Cl_3]$ or $[ReO_2(PPh_3)_2I]$ respectively with H_2L = catechol, tetrachlorocatechol or tetrabromocatechol (H_2tbcat). Dilworth *et al.*[9] found that the reaction of $[ReO(PPh_3)_2Cl_3]$ with catechol in refluxing ethanol and base (diethylamine) in air gave *cis*-$[ReO_2(cat)_2]^-$, while a similar procedure with triethylamine replacing diethylamine but under anaerobic conditions gave $[ReO(cat)_2]^-$. In our procedure no base was used, and it appears that the two chloro ligands have been displaced by a catecholato unit and that no redox reaction has occurred.

(*b*) *Complexes of the Type* $[NBu^n_4][ReO(OPPh_3)(L)_2]$.—When the same two rhenium precursors are treated with tetrachloro-1,2-benzoquinone or tetrabromo-1,2-benzoquinone instead of the corresponding catechols quite different products are obtained; with the addition of the cation $[NBu^n_4]^+$ complexes of the type $[NBu^n_4][ReO(OPPh_3)(L)_2]$ (L = tccat or tbcat) have been isolated. In this case it appears that two moles of the quinone (the two electron oxidised form of the corresponding catecholate) oxidises the triphenylphosphine to the oxide; one triphenylphosphine oxide molecule then co-ordinates to the metal.

The triphenylphosphine oxide group is found to be rather labile; thus by refluxing a solution of $[NBu^n_4][ReO(OPPh_3)(tccat)_2]$ in methanol a small quantity of crystalline material $[NBu^n_4][ReO(MeOH)(tccat)_2]$ was isolated, while in dichloromethane solution in the presence of a little pyridine at room temperature $[NBu^n_4][ReO(py)(tccat)_2]$ was obtained. Despite many attempts we could not isolate a product in which the site *trans* to the oxo group was vacant, such as in the complex $[NMe_4][ReO(cat)_2]$ prepared by Dilworth *et al.*[9]

(*c*) *Other Species.*—The complexes $[ReO(PPh_3)(L'')_2]I$ [HL″ = maltol (Hmalt) or tropolone (Htrop)] were prepared by the reaction of $[ReO_2(PPh_3)_2I]$ with the corresponding ligands. The compound $[ReO(PPh_3)_2Cl_3]$ however does not undergo such reactions.

Crystal Structure of $[NBu^n_4][ReO(OPPh_3)(tccat)_2]$ **1**.—Compound **1** was prepared by the method described above and crystals suitable for X-ray study were obtained by recrystallisation from cold dichloromethane and ethanol.

The structure of the anion is shown in Fig. 1 together with the atom labelling. Selected bond lengths and angles are given in Table 1 and atomic coordinates in Table 2. Co-ordination about Re is distorted octahedral with an axial oxo ligand, two bidentate tetrachlorocatecholate ligands which are *trans* to each other, the other axial position being occupied by a weakly co-ordinated $OPPh_3$ ligand. If one neglects the weakly bound $OPPh_3$ ligand then the geometry at rhenium could be considered as distorted square pyramidal, the Re atom lying 0.34 Å above the basal plane of the four catecholate O atoms and in the direction of the apical oxygen atom. This distortion is accompanied by a mean O(oxo)–Re–O(catechol) angle of 100°. The angle subtended at Re by the four O atoms are in the range 80.7(3)–96.7(3)°, the contractions from 90° reflecting the bite of

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

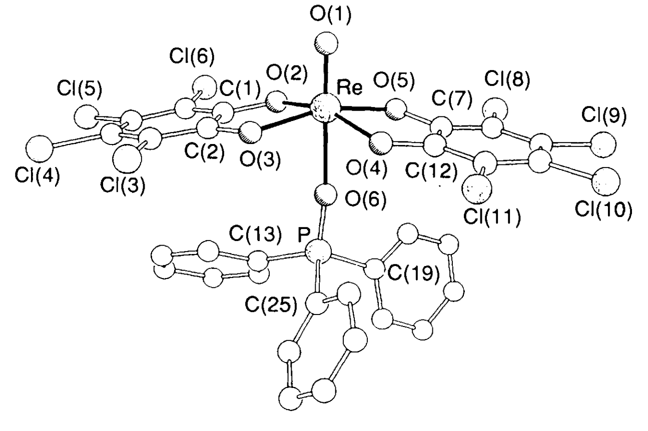

Fig. 1 Perspective view of the X-ray structure of the $[ReO(OPPh_3)(tccat)_2]^-$ anion

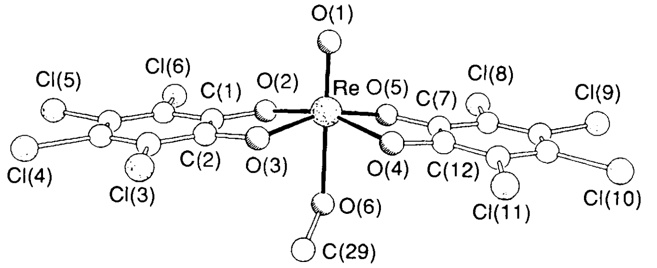

Fig. 2 Perspective view of the X-ray structure of the $[ReO(MeOH)(tccat)_2]^-$ anion

Table 1 Selected bond lengths (Å) and angles (°) for **1** with estimated standard deviations (e.s.d.s) in parentheses

Re–O(1)	1.576(8)	Re–O(2)	1.996(5)
Re–O(3)	2.015(8)	Re–O(4)	2.040(6)
Re–O(5)	2.015(7)	Re–O(6)	2.232(6)
O(2)–C(1)	1.359(13)	O(3)–C(2)	1.340(11)
O(4)–C(12)	1.338(13)	O(5)–C(7)	1.345(10)
O(6)–P	1.491(7)	P–C(13)	1.800(11)
P–C(19)	1.816(13)	P–C(25)	1.792(12)
O(1)–Re–O(2)	100.6(4)	O(1)–Re–O(3)	99.0(4)
O(2)–Re–O(3)	80.9(3)	O(1)–Re–O(4)	99.4(3)
O(2)–Re–O(4)	159.9(4)	O(3)–Re–O(4)	96.7(3)
O(1)–Re–O(5)	100.0(4)	O(2)–Re–O(5)	95.1(2)
O(3)–Re–O(5)	161.1(3)	O(4)–Re–O(5)	80.7(3)
O(1)–Re–O(6)	178.5(3)	O(2)–Re–O(6)	80.9(3)
O(3)–Re–O(6)	81.0(3)	O(4)–Re–O(6)	79.1(3)
O(5)–Re–O(6)	80.1(3)	Re–O(2)–C(1)	113.0(5)
Re–O(3)–C(2)	112.9(7)	Re–O(4)–C(12)	111.6(6)
Re–O(5)–C(7)	113.2(6)	Re–O(6)–P	172.5(5)
O(6)–P–C(13)	113.7(5)	O(6)–P–C(19)	109.6(5)
O(6)–P–C(25)	114.6(5)	C(13)–P–C(19)	108.3(5)
C(13)–P–C(25)	105.4(6)	C(19)–P–C(25)	104.5(5)

the catechol ligand. The O(oxo)–Re–$OPPh_3$ angle is close to linearity at 178.5(3)°.

The Re–O distances are in the range 1.576(8) to 2.232(6) Å. The Re–O(oxo) distance at 1.576(8) Å is exceptionally short (Re–O distances in mono-oxo complexes are usually within the range 1.63–1.71 Å[15]) and this suggests a high degree of π-overlap within the bond probably due to the electrophilic effect of the tetrachlorocatechol ligands. The mean Re–O(catechol) distance is 2.02 Å, comparable with that found in $[Re(\eta\text{-}C_5Me_5)(tccat)_2]$.[12] Conversely the distance to the $OPPh_3$ ligand is appreciably longer at 2.232(6) Å. In, for example, $[Re(NO)(OPPh_3)(NPPh_3)Cl_3]$[16] and $[Re(O)I_2(PPh_3)(OPPh_3)(OReO_3)]\cdot 0.5C_6H_6$[17] where the $OPPh_3$ is *trans* to nitrosyl and triphenylphosphine groups respectively, the Re–O(phosphine oxide) distances are considerably shorter at 2.092(6) and 2.075(9) Å respectively. The Re–O–PPh_3 angle is nearly linear at 172.5(5)°, an unusual situation in complexes containing $OPPh_3$ as a ligand; in $[Re(NO)(OPPh_3)(NPPh_3)Cl_3]$[16] and $[Re(O)I_2(PPh_3)(OPPh_3)(OReO_3)]\cdot 0.5C_6H_6$[17] this angle is appreciably bent at 148.7(4)° and 151.5(6)° respectively. It is not clear why the Re–O–P angle is so large in our complex.

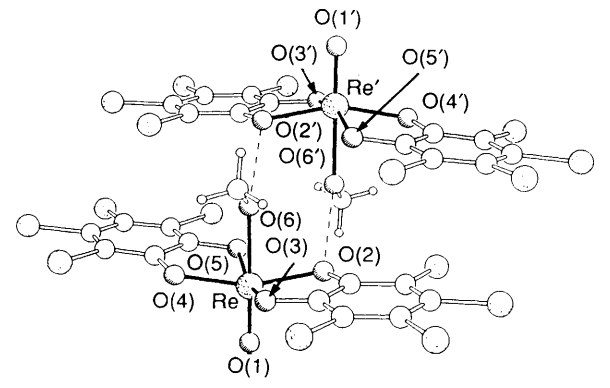

Fig. 3 The hydrogen bonding between centrosymmetrically related pairs of anions in the crystal structure of **2**

The tetrachlorocatecholato ligands in complex **1** have an average C–C distance of 1.39 Å while the average C–O bond length is 1.35 Å; these values are very close to those found in $[Re(tccat)_3]$[11] and suggest that these ligands are indeed bound in the catecholato mode. Both catechol ligands are essentially coplanar with the rhenium atom; the maximum deviation for that containing O(5) and O(4) being 0.14 Å and for that containing O(2) and O(3) 0.09 Å. The dihedral angle between the two rhenium catechol planes is 164°.

Crystal Structure of $[NBu^n_4][ReO(MeOH)(tccat)_2]$ **2**.—Compound **2** was prepared from **1** by recrystallisation from methanol. The structure of the anion is shown in Fig. 2 with the atom labelling. Selected bond lengths and angles are given in Table 3 and atomic coordinates in Table 4.

As in the case of **1** the co-ordination about Re is distorted octahedral, the $OPPh_3$ ligand in **1** being replaced by a MeOH molecule. Neglecting the MeOH ligand and as previously for **1** considering the geometry at Re as distorted pyramidal, the Re atom lies 0.36 Å above the basal plane of the four catechol O atoms in the direction of the apical oxygen atom. Here the mean O(oxo)–Re–O(catechol) angle is *ca.* 100°. The angles subtended at Re by the four basal O atoms are 81.4(4), 82.3(4), 93.5(4) and 95.2(4)°, the two acute angles being those associated with the catecholato ligands. The O(oxo)–Re–O(MeOH) angle is linear [179.2(4)°].

The Re–O distances are in the range 1.653(11)–2.289(11) Å. The Re–O(oxo) distance of 1.653(11) Å, although short, is noticeably longer than that observed in **1**; this may arise from the increased electron density at Re brought about by the MeOH ligand which is likely to be more nucleophilic than $OPPh_3$. The mean Re–O(catechol) distance is 2.00 Å, and the Re–O(MeOH) distance is 2.289(11) Å, even larger than that observed to the $OPPh_3$ ligand in **1**. The mean C–C and C–O distances in **2** are very similar to those in **1** which again confirms the catecholato nature of the ligand. As with **1** the catecholate ligands are essentially coplanar with the Re atoms, there being a dihedral angle of 163° between their mean planes. Within the crystal each $[ReO(MeOH)(tccat)_2]^-$ unit is linked to its centrosymmetrically related partner *via* two O–H · · · O hydrogen bonds (2.73 Å), effectively creating hydrogen-bonded 'back to back' dimer pairs (Fig. 3).

Vibrational Spectroscopy.—The complexes all contain a

Table 2 Atomic coordinates (× 10^4) for **1** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Re	2 364(1)	2 500	2 311(1)
O(1)	2 576(7)	1 526(5)	2 348(4)
O(2)	583(6)	2 595(7)	1 400(3)
O(3)	3 216(7)	2 757(5)	1 368(4)
O(4)	4 081(8)	2 841(4)	3 240(4)
O(5)	1 412(6)	2 652(5)	3 230(4)
O(6)	2 122(7)	3 884(4)	2 283(4)
C(1)	825(11)	2 724(5)	648(6)
C(2)	2 245(11)	2 795(7)	635(6)
C(3)	2 590(13)	2 899(7)	−106(7)
Cl(3)	4 324(4)	2 966(3)	−108(2)
C(4)	1 467(15)	2 958(8)	−846(7)
Cl(4)	1 922(5)	3 110(3)	−1 769(2)
C(5)	99(15)	2 914(7)	−811(7)
Cl(5)	−1 258(5)	3 002(3)	−1 731(2)
C(6)	−246(12)	2 770(7)	−74(7)
Cl(6)	−1 972(3)	2 619(4)	−45(2)
C(7)	2 324(11)	2 839(6)	3 961(6)
C(8)	1 930(12)	2 905(6)	4 689(6)
Cl(8)	145(3)	2 836(2)	4 650(2)
C(9)	2 951(13)	3 054(7)	5 429(6)
Cl(9)	2 412(5)	3 145(2)	6 332(2)
C(10)	4 367(14)	3 109(8)	5 447(6)
Cl(10)	5 622(5)	3 246(3)	6 375(2)
C(11)	4 764(12)	3 071(7)	4 715(7)
Cl(11)	6 499(3)	3 179(3)	4 693(2)
C(12)	3 747(12)	2 929(6)	3 960(6)
P	2 026(3)	4 805(2)	2 164(2)
C(13)	1 015(13)	5 118(7)	1 148(7)
C(14)	−232(13)	5 570(8)	993(9)
C(15)	−963(18)	5 758(10)	163(10)
C(16)	−468(18)	5 487(9)	−502(10)
C(17)	750(20)	5 036(10)	−318(9)
C(18)	1 514(16)	4 847(8)	485(7)
C(19)	1 223(11)	5 268(7)	2 920(7)
C(20)	611(12)	4 793(8)	3 375(8)
C(21)	24(14)	5 095(8)	3 972(7)
C(22)	19(14)	5 925(9)	4 074(8)
C(23)	623(15)	6 462(9)	3 629(9)
C(24)	1 255(15)	6 116(9)	3 048(9)
C(25)	3 700(12)	5 322(7)	2 326(7)
C(26)	4 839(13)	4 963(9)	2 885(9)
C(27)	6 205(17)	5 367(10)	3 104(11)
C(28)	6 286(17)	6 082(11)	2 702(12)
C(29)	5 217(16)	6 449(11)	2 131(10)
C(30)	3 891(15)	6 035(9)	1 953(10)
N	7 189(4)	1 188(2)	2 620(2)
C(31)	6 684(6)	2 067(2)	2 611(4)
C(32)	7 401(14)	2 597(2)	2 104(7)
C(33)	7 197(18)	3 494(2)	2 295(7)
C(34)	7 550(21)	4 038(5)	1 655(8)
C(35)	6 943(5)	883(4)	1 745(2)
C(36)	5 427(9)	1 035(15)	1 289(5)
C(37)	5 191(11)	745(3)	412(3)
C(38)	4 844(29)	−167(5)	372(16)
C(39)	8 742(3)	1 158(3)	3 034(4)
C(40)	9 255(9)	280(4)	3 083(14)
C(41)	10 820(8)	266(7)	3 492(12)
C(42)	11 268(11)	−613(5)	3 718(18)
C(43)	6 401(6)	644(3)	3 064(4)
C(44)	6 535(14)	962(11)	3 919(4)
C(45)	5 354(12)	599(13)	4 229(4)
C(46)	5 672(16)	730(17)	5 142(4)

Table 3 Selected bond lengths (Å) and angles (°) for **2** with e.s.d.s in parentheses

Re–O(1)	1.653(11)	Re–O(2)	1.989(9)
Re–O(3)	2.015(10)	Re–O(4)	2.005(9)
Re–O(5)	1.989(11)	Re–O(6)	2.289(11)
O(2)–C(1)	1.357(18)	O(3)–C(2)	1.366(17)
O(4)–C(12)	1.360(19)	O(5)–C(7)	1.373(18)
O(6)–C(29)	1.340(25)		
O(1)–Re–O(2)	101.0(5)	O(1)–Re–O(3)	100.9(5)
O(2)–Re–O(3)	81.4(4)	O(1)–Re–O(4)	100.2(5)
O(2)–Re–O(4)	158.8(4)	O(3)–Re–O(4)	95.2(4)
O(1)–Re–O(5)	99.9(5)	O(2)–Re–O(5)	93.5(4)
O(3)–Re–O(5)	159.1(5)	O(4)–Re–O(5)	82.3(4)
O(1)–Re–O(6)	179.2(4)	O(2)–Re–O(6)	79.6(4)
O(3)–Re–O(6)	79.6(4)	O(4)–Re–O(6)	79.2(4)
O(5)–Re–O(6)	79.6(4)	Re–O(2)–C(1)	112.8(9)
Re–O(3)–C(2)	112.6(9)	Re–O(4)–C(12)	111.2(8)
Re–O(5)–C(7)	111.5(9)	Re–O(6)–C(29)	126.8(13)

terminal Re=O group and this gives a characteristic stretch in the IR spectrum in the region 935–990 cm^{-1}; this mode is also seen as a very strong band in the Raman spectrum. The stretching frequency tends to be higher for those complexes in which the site *trans* to the oxo group is occupied by the weakly bound $OPPh_3$. When this is replaced by pyridine in the complex $[NBu^n_4][ReO(py)(tccat)_2]$ the Re=O stretch shifts to lower wavenumber indicating a weakening of this bond, probably attributable to the presence of empty π-acceptor orbitals on pyridine. The phosphine oxide complexes may be identified by the presence in the IR of a medium strength band at *ca.* 1170 cm^{-1} which is not seen for the PPh_3 complexes.

Catechol has recently been the subject of a full vibrational assignment.[18] Co-ordinated catechols typically show strong bands attributed to the ring stretch of the C–C bond between the two donor oxygen atoms and assigned to the C–O stretch.[19,20] For complexes of unsubstituted catechol these occur near 1480 and 1250 cm^{-1} respectively[7] and such bands are seen in our complexes $[ReO(cat)(PPh_3)_2X]$. For the halogeno substituted catechol complexes the C–O stretching frequencies are similar to those above while the C–C stretches are considerably lower; others have reported that in tccat complexes a strong band near 1250 cm^{-1} is observed.[11] Similar bands are seen for the complexes $[NBu^n_4][ReO(L')(tccat)_2]$ (L′ = $OPPh_3$, MeOH or py) prepared from quinones, which, like the X-ray data, suggests that the ligands are bound in the catecholato rather than the quinonoid form and have been reduced during the course of the reaction. There is no evidence for bands attributable to ν(O–H) confirming that the catechol ligands are completely deprotonated.

For the maltol complex the band at 1615 cm^{-1} is assigned to ν(C=O), a fall of 32 cm^{-1} from the corresponding band in to the free ligand[21] due to co-ordination. This may be explained by a lowering of the carbonyl bond strength when the group donates to the metal atom; bands due to mixed ν(C=O) and ν(C=C) modes at 1560 and 1540 cm^{-1} have also shifted considerably. Similar effects were noted in a number of maltol complexes.[21]

For the tropolone complex we follow the assignments of Redington and Redington[22] and propose that a strong band at 1434 cm^{-1} arises from the ν(C–C) ring stretch while that at 1318 cm^{-1} is likely to be due to the ν(C–O) stretch.

^{13}C *and* ^{13}P *NMR Studies*.—Solutions of the complexes have been studied by ^{13}C and ^{31}P NMR spectroscopy.

$[ReO(L)(PPh_3)_2Cl]$ (L = *cat, tccat or tbcat*). Proton-decoupled ^{13}C NMR spectra for these complexes show two single peaks due to $C^{3,6}$ and $C^{4,5}$ for the catechol ligands (Table 5) which are shifted only very slightly upfield from their values for the free ligands. The $C^{1,2}$ resonances however are shifted

Table 4 Atomic coordinates (× 10^4) for **2** with e.s.d.s in parentheses

Atom	x	y	z
Re	2293(1)	479(1)	72(1)
O(1)	3694(9)	208(6)	139(6)
O(2)	1352(9)	−314(5)	−583(5)
O(3)	1897(10)	1077(5)	−848(6)
O(4)	2619(9)	1394(5)	712(5)
O(5)	2061(10)	−14(5)	942(5)
O(6)	363(10)	861(6)	−6(6)
C(1)	1081(14)	−110(9)	−1283(8)
C(2)	1375(14)	639(9)	−1434(7)
C(3)	1154(16)	903(10)	−2120(9)
Cl(3)	1483(5)	1830(3)	−2260(3)
C(4)	670(17)	392(12)	−2672(9)
Cl(4)	396(6)	725(4)	−3555(3)
C(5)	380(16)	−342(11)	−2551(9)
Cl(5)	−161(5)	−967(4)	−3250(3)
C(6)	580(15)	−620(9)	−1863(9)
Cl(6)	273(4)	−1522(3)	−1664(2)
C(7)	2403(14)	459(9)	1526(8)
C(8)	2546(16)	229(9)	2228(9)
Cl(8)	2196(5)	−718(3)	2352(3)
C(9)	2907(17)	715(12)	2780(9)
Cl(9)	3182(5)	400(4)	3650(3)
C(10)	3135(17)	1449(13)	2641(9)
Cl(10)	3567(6)	2119(4)	3340(3)
C(11)	3013(15)	1710(9)	1945(8)
Cl(11)	3251(5)	2656(3)	1762(3)
C(12)	2693(14)	1202(8)	1400(8)
C(29)	−203(20)	1481(14)	−341(12)
N	462(7)	2707(4)	−5073(4)
C(13)	−870(7)	2591(6)	−5096(6)
C(14)	−1364(12)	1850(9)	−5486(11)
C(15)	−2671(11)	1723(9)	−5458(13)
C(16)	−2978(22)	873(10)	−5526(21)
C(17)	963(11)	3405(5)	−4605(5)
C(18)	1041(17)	3239(6)	−3819(4)
C(19)	1172(19)	3995(7)	−3402(5)
C(20)	1536(21)	3835(10)	−2593(5)
C(21)	571(11)	2832(6)	−5831(4)
C(22)	−192(16)	3512(8)	−6194(6)
C(23)	−13(20)	3621(14)	−6947(8)
C(24)	−853(30)	4254(16)	−7346(10)
C(25)	1197(9)	1995(5)	−4748(6)
C(26)	2526(9)	2093(7)	−4743(10)
C(27)	3228(12)	1359(10)	−4451(15)
C(28)	4573(11)	1464(12)	−4396(14)

considerably downfield upon co-ordination of the catechol to rhenium; this has been observed in other catecholato complexes[7] and is attributable to removal of electron density from the adjacent oxygen atoms to the metal.

The ^{31}P NMR spectrum for [ReO(tccat)($PPh_3)_2$Cl] shows just a single peak at δ −15.3. The corresponding catechol and tetrabromocatechol complexes show similar strong peaks at δ −17.2 and −15.4 respectively but also three other minor peaks suggesting the presence of isomeric products in small quantities.

$[\mathrm{NBu^n_4}][\mathrm{ReO(OPPh_3)(L)_2}]$ (L = *tccat or tbcat*). These complexes have resonances for the catecholato carbon atoms in their ^{13}C NMR spectra which are very close to the values in the previously described [ReO(L)($PPh_3)_2$Cl] complexes. The ^{13}C resonances for these complexes together with those of the free catechols and quinones are listed in Table 5. For these species the spectra suggest that the ligand is co-ordinated in the catecholato rather than the quinonoid form, as the X-ray structure of $[\mathrm{NBu^n_4}][\mathrm{ReO(OPPh_3)(tccat)_2}]$ also shows. The $C^{3,6}$ and $C^{4,5}$ resonances are little shifted from those of the free catechols but are quite different from those for the quinones. The $C^{1,2}$ resonances are however shifted downfield by *ca.* 20 ppm from those of the free catechols, as in [ReO(L)($PPh_3)_2$Cl]. There are relatively few data in the literature on the ^{13}C NMR of complexes containing co-ordinated catecholate (or quinone) and it seems that ^{13}C NMR may be a useful way of distinguishing the bonding modes of the ligands in such complexes. The ^{31}P NMR spectra in $C^2H_2Cl_2$ each contain one signal near δ 35 suggesting that the $OPPh_3$ group remains associated with the rhenium in solution at room temperature; free $OPPh_3$ in the same solvent has a resonance at δ 28.

Experimental

Crystallography.—Crystal data. $[\mathrm{NBu^n_4}][\mathrm{ReO(OPPh_3)(tccat)_2}]$ **1**, $C_{46}H_{51}Cl_8NO_6PRe$, M = 1214.7, monoclinic, a = 9.783(1), b = 16.046(2), c = 16.759(3) Å, β = 105.34(1)°, U = 2537 Å^3, space group $P2_1$, Z = 2, D_c = 1.59 g cm^{-3}, μ(Cu-Kα) = 92 cm^{-1}, λ = 1.541 78 Å, F(000) = 1216. Green, air-sensitive thin needles, crystal dimensions 0.03 × 0.15 × 0.36 mm.

$[\mathrm{NBu^n_4}][\mathrm{ReO(MeOH)(tccat)_2}]$ **2**, $C_{29}H_{40}Cl_8NO_6Re$, M = 968.4, monoclinic, a = 11.534(2), b = 17.573(4), c = 19.484(4) Å, β = 106.56(3)°, U = 3785 Å^3, space group $P2_1/n$, Z = 4, D_c = 1.70 g cm^{-3}, μ(Cu-Kα) = 118 cm^{-1}, λ = 1.541 78 Å, F(000) = 1920. Green, air-sensitive prisms, crystal dimensions 0.12 × 0.13 × 0.20 mm.

Data collection and processing. Nicolet R3m diffractometer, ω-scan method (2θ ⩽ 116°), graphite monochromated Cu-Kα radiation. For compounds **1** and **2** 3576 and 5336 independent reflections were measured; 3284 and 3939 respectively, considered observed $[|F_o| > 3\sigma(|F_o|)]$, corrected for Lorentz and polarisation factors. For both **1** and **2** a Gaussian absorption correction (face-indexed crystal) was applied, minimum and maximum transmission factors 0.26 and 0.76 for **1** and 0.24 and 0.37 for **2**.

Structure analysis and refinement. Both structures **1** and **2** were solved by the heavy-atom method. All remaining non-hydrogen atoms were located from subsequent ΔF maps and refined anisotropically. In each case ΔF maps revealed severe disorder in the cations. Their geometries were optimised and they were refined subject to N–C and C–C distance constraints. The methyl groups were refined as rigid bodies. The polarity of structure **1** was detemined unambiguously by an R-factor test. In **1** the positions of the hydrogen atoms were idealized (C–H 0.96 Å), assigned isotropic thermal parameters, $U(\mathrm{H}) = 1.2U_{eq}(\mathrm{C})$, and allowed to ride on their parent carbons. In **2** the position of the methoxy hydrogen atom could not be located. The positions of the remaining hydrogens were idealised, assigned isotropic thermal parameters, U = 0.08 Å^2 and allowed to ride on their parent carbon atoms. Refinement was, for **1**, by block-cascade full-matrix least squares to give R = 0.039, R' = 0.040 $[w^{-1} = \sigma^2(F) + 0.000\ 72F^2]$, and for **2**, by full-matrix least squares to give R = 0.077, R' = 0.075 $[w^{-1} = \sigma^2(F) + 0.000\ 50F^2]$ $(R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$ and $R' = \Sigma[(|F_o| - |F_c|)w^{\frac{1}{2}}]/\Sigma[|F_o|w^{\frac{1}{2}}]$. The maximum residual electron densities in the final ΔF maps were 0.53 and 3.45 e Å^{-3} for **1** and **2** respectively. The largest residual electron density peak in **2** was close to the rhenium atom and could not be reduced despite many different absorption corrections. The mean and maximum shift/error ratios in the final refinement cycle were: for **1**, 0.07 and 0.44; and for **2**. 0.01 and 0.11. Computations were carried out: for **1** on an Eclipse S140 computer using the SHELTXL program system;[26] and for **2** on a IBM PS/2 Model 70 386 using SHELTXL PC program system;[27] both using published scattering factors.[28] Selected bond lengths and angles for **1** and **2** are listed in Tables 1 and 3 respectively, and atomic co-ordinates are given in Tables 2 and 4.

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

Preparations.—The complexes [ReO($PPh_3)_2Cl_3$][29] and [Re$O_2(PPh_3)_2$I][30] were both prepared by literature methods.

Table 5 Analytical, vibrational and NMR spectroscopic data for rhenium catecholato complexes

	Analysis[a] (%)					Vibrational data[b]			^{13}C NMR (catechol)[c]		
Complex	C	H	N	P	Halide	ν(CC)	ν(CO)	ν(ReO)	$C^{1,2}$	$C^{4,5}$	$C^{3,6}$
Catechol						1620s	1256vs		146.6	123.6	118.9[23]
1,2-Benzoquinone									180.4	139.7	130.8[24]
Tetrachlorocatechol									143.6	123.1	120.2
Tetrachloro-1,2-benzoquinone									168.8	143.8	131.9[25]
Tetrabromocatechol									144.8	118.2	113.8
Tetrabromo-1,2-benzoquinone									168.6	128.2	142.2
$[ReO(cat)(PPh_3)_2Cl]$	57.9	3.8	—	6.85	4.4	1463s	1253s	936vs	161.3	120.4	115.6
	(57.95)	(3.9)		(7.1)	(4.1)	*1460w*	*1245w*	*939vs*			
$[ReO(cat)(PPh_3)_2I]$	51.7	3.4	—	6.55	13.1	1461s	1254s	935s			
	(52.4)	(3.6)		(6.45)	(13.2)						
$[ReO(tccat)(PPh_3)_2Cl]$	50.2	3.0	—	6.1	17.8	1433vs	1257s	945vs	163.8	121.4	118.0
	(50.0)	(3.0)		(6.1)	(17.6)						
$[ReO(tbcat)(PPh_3)_2Cl]$	42.4	2.4	—	5.0		1419vs	1254s	937s	160.1	115.9	112.1
	(42.5)	(2.55)		(5.2)			1240m				
$[NBu^n_4][ReO(OPPh_3)(tccat)_2]$	45.4	4.2	1.2	2.4	23.2	1406vs	1246m	966s	167.3	121.8	117.5
	(45.5)	(4.2)	(1.15)	(2.55)	(23.35)	*1419s*	*1255m*	*965vs*			
$[NBu^n_4][ReO(MeOH)(tccat)_2]$	35.7	4.3	1.4	—	29.2	1402vs	1248s	967vs			
	(36.0)	(4.2)	(1.45)		(29.3)		1238m				
$[NBu^n_4][ReO(py)(tccat)_2]$	39.2	4.2	2.9	—	27.7	1408vs	1249s	950s			
	(39.0)	(4.1)	(2.8)		(27.9)						
$[NBu^n_4][ReO(OPPh_3)(tbcat)_2]$	34.8	3.1	0.9	2.0	40.4	1396vs	1267s	983s	164.4	116.6	113.0
	(35.2)	(3.25)	(0.9)	(2.0)	(40.7)						
$[ReO(PPh_3)(malt)_2]I$	42.6	3.1	—	3.4	14.7	1560s	1615s	986vs			
	(42.8)	(3.0)		(3.7)	(15.0)	1540s					
$[ReO(PPh_3)(trop)_2]I$	46.2	2.9	—	3.75	14.8	1434vs	1318m	987vs			
	(46.1)	(3.0)		(3.7)	(15.2)						

[a] Calculated values are given in parentheses. [b] Frequencies in cm^{-1}; Raman data are italicised. [c] ^{13}C NMR shifts in ppm relative to $Si(CH_3)_4$.

$[ReO(cat)(PPh_3)_2Cl]$. To $[ReO(PPh_3)_2Cl_3]$ (0.15 g, 0.18 mmol) in ethanol (30 cm^3) was added catechol (0.04 g, 0.36 mmol). This suspension was gently warmed and stirred and the reagents gradually dissolved to give a deep red solution. Upon cooling the compound deposited as a red-brown powdery solid. It was recrystallised from dichloromethane–ethanol to give a crystalline product.

Analogous procedures yielded the complexes $[ReO(tccat)(PPh_3)_2Cl]$ and $[ReO(tbcat)(PPh_3)_2Cl]$.

$[ReO(cat)(PPh_3)_2I]$. This was prepared in a similar manner to $[ReO(cat)(PPh_3)_2Cl]$ but with $[ReO_2(PPh_3)_2I]$ in place of $[ReO(PPh_3)_2Cl_3]$ and with methanol as the solvent.

$[NBu^n_4][ReO(OPPh_3)(tccat)_2]$. To $[ReO(PPh_3)_2Cl_3]$ (0.15 g, 0.18 mmol) in ethanol (25 cm^3) was added tetrachloro-1,2-benzoquinone (0.089 g, 0.36 mmol). This suspension was stirred with gentle heating for 3 h after which time a clear green solution was obtained. This was allowed to cool and $[NBu^n_4]PF_6$ (0.14 g, 0.36 mmol) dissolved in ethanol (5 cm^3) was added. After reduction of the volume to *ca.* 10 cm^3 the product crystallised out and was recrystallised from dichloromethane–ethanol. The complex $[NBu^n_4][ReO(OPPh_3)(tbcat)_2]$ was prepared in a similar manner.

The same complexes were also be prepared by following a similar method with $[ReO_2(PPh_3)_2I]$ in place of $[ReO(PPh_3)_2Cl_3]$ and using methanol as solvent. The reaction proceeded without the application of heat.

$[NBu^n_4][ReO(MeOH)(tccat)_2]$. A solution of $[NBu^n_4][ReO(OPPh_3)(tccat)_2]$ in methanol (25 cm^3) was boiled on a hot-plate until a solid began to deposit. This dark green crystalline compound was isolated from the still warm solution and found to be $[NBu^n_4][ReO(MeOH)(tccat)_2]$. The further quantity of precipitate which formed from the fully cooled solution was mainly $[NBu^n_4][ReO(OPPh_3)(tccat)_2]$.

$[NBu^n_4][ReO(py)(tccat)_2]$. The compound $[NBu^n_4][ReO(OPPh_3)(tccat)_2]$ (0.5 g, 0.4 mmol) was dissolved in dichloromethane (20 cm^3) and pyridine (0.1 g) was added. The solution became a somewhat brighter shade of green. It was kept at −20 °C for 2 d and the complex precipitated as bright green crystals.

$[ReO(PPh_3)(malt)_2]I$. A suspension of $[ReO_2(PPh_3)_2I]$ (0.2 g, 0.23 mmol) in methanol (25 cm^3) was stirred while maltol (0.063 g, 0.5 mmol) was added. After several hours at ambient temperature a green-brown solution was obtained. A small amount of insoluble material was removed by filtration and the volume of the solution reduced until the product precipitated as green crystals.

The compound $[ReO(PPh_3)(trop)_2]I$ was prepared similarly.

Characterisation.—Infrared spectra were measured on a Perkin-Elmer 1720 infrared Fourier transform spectrometer with samples as KBr discs. Raman spectra were measured on a Spex Ramalog 5 instrument with a Datamate data acquisition unit as spinning discs on a KBr matrix, or as solutions in dichloromethane, using the green 5415 Å line of an Innova 70 CRL argon-ion laser. ^{13}C NMR spectra were measured in $C^2H_2Cl_2$ or C^2HCl_3 on a Bruker WM 250 Fourier transform spectrometer. Microanalyses were provided by the Microanalytical Department of Imperial College and by the University of Strathclyde.

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References

1 C. G. Pierpont and R. M. Buchanan, *Coord. Chem. Rev.*, 1981, **38**, 43.

2 *Development of Iron Chelators for Clinical Use*, eds. A. E. Martell, W. F. Anderson and D. G. Badman, Elsevier, Amsterdam, 1981.

3 T. Stabler, *J. Med. Tech.*, 1986, **3**, 351.

4 A. J. Nielson and W. P. Griffith, *J. Histochem. Cytochem.*, 1978, **76**, 138.

5 A. J. Nielson and W. P. Griffith, *J. Chem. Soc., Dalton Trans.*, 1978, 1501.

6 M. B. Hursthouse, T. Fram, L. New, W. P. Griffith and A. J. Nielson, *Transition Met. Chem.*, 1978, **3**, 253.

7 W. P. Griffith, C. A. Pumphrey and T. A. Rainey, *J. Chem. Soc., Dalton Trans.*, 1986, 1125.

8 A. M. El-Hendawy, W. P. Griffith and C. A. Pumphrey, *J. Chem. Soc., Dalton Trans.*, 1988, 1817.

9 J. R. Dilworth, S. K. Ibrahim, S. R. Khan, M. B. Hursthouse and A. A. Karaulov, *Polyhedron*, 1990, **9**, 1323.

10 L. A. deLearie and C. G. Pierpont, *J. Am. Chem. Soc.*, 1986, **108**, 6393.

11 L. A. deLearie, R. C. Haltiwanger and C. G. Pierpont, *Inorg. Chem.*, 1987, **26**, 817.

12 W. A. Herrmann, U. Kürsthardt and E. Herdtweck, *J. Organomet. Chem.*, 1985, **294**, C33.

13 J. Takacs, N. R. Cook, P. Kiprof, J. G. Kuchler and W. A. Herrmann, *Organometallics*, 1991, **10**, 316.

14 J. Takacs, P. Kiprof, J. Riede and W. A. Hermann, *Organometallics*, 1990, **9**, 782.

15 K. A. Conner and R. A. Walton, *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 4, ch. 43, pp. 177–185.

16 N. Mronga, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1983, **502**, 35.

17 G. Ciani, A. Sironi, T. Beringhelli, G. D'Alfonso and M. Freni, *Inorg. Chim. Acta*, 1986, **113**, 61.

18 S. J. Greaves and W. P. Griffith, *Spectrochim. Acta, Part A*, 1991, **47**, 133.

19 P. A. Wicklund and D. G. Brown, *Inorg. Chem.*, 1976, **15**, 396.

20 L. Que and R. H. Heistland, *J. Am. Chem. Soc.*, 1979, **101**, 2219.

21 S. J. Greaves and W. P. Griffith, *Polyhedron*, 1988, **7**, 1973.

22 L. D. Redington and T. E. Redington, *J. Mol. Spectrosc.*, 1979, **78**, 229.

23 L. Johnson and W. C. Jankowski, *Carbon-13 NMR Spectra*, Wiley, New York, 1972.

24 R. Hollenstein and W. Van Philipsborn, *Helv. Chim. Acta*, 1973, **56**, 320.

25 S. T. Berger and A. Rieker, *Tetrahedron*, 1972, **28**, 3123.

26 G. M. Sheldrick, SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data, University of Göttingen, 1978; revision 4.1, 1983.

27 SHELXTL PC, Release 4.1, May 1990, Siemens Analytical X-Ray Instruments, Inc. Madison, W.I.

28 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99–149.

29 N. P. Johnson, C. J. Lock and G. Wilkinson, *J. Chem. Soc.*, 1964, 1054.

30 G. Ciani, G. D'Alfonso, P. Romiti, A. Sironi and M. Freni, *Inorg. Chim. Acta*, 1983, **72**, 29.

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