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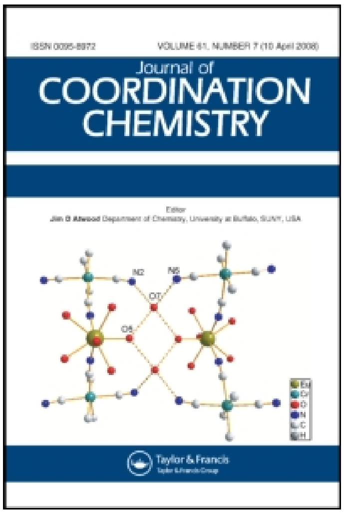

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# SYNTHESIS OF A Re(VI)-CATECHOLATO COMPLEX BY AIR OXIDATION OF OXORHENIUM(V)

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The complex [Re(ddcat)$_3$] ($H_2$ddcat = 3,5-di-*tert*-butylcatechol) was prepared by the reaction of either *cis*-[Re$^V$O$_2$I(PPh$_3$)$_2$] or (*n*-Bu$_4$N)[Re$^V$OCl$_4$] with $H_2$ddcat in toluene in air. X-ray structure determination of the product unequivocally illustrates that the bidentate chelates are in the catecholato rather than the semiquinone form and that the metal has a formal oxidation state of +VI.

*Keywords:* Rhenium(VI) complex; Rhenium(V)–oxo cleavage; Catechol; X-ray structure

## INTRODUCTION

We recently reported that the reaction of the rhenium(V) compounds *trans*-[ReO$_2$(py)$_4$]Cl and *cis*-[ReO$_2$I(PPh$_3$)$_2$] (**1**) with 1,2-diaminobenzene and its derivatives ($H_2$dab) in ethanol under aerobic conditions led to the formation of the rhenium(IV) complexes [Re(sbqdi)$_3$]X (X=Cl, I), in which the 'non-innocent' $H_2$dab ligands were oxidized by one electron each to the 1,2-benzosemiquinone diimine form sbqdi [1]. We have now extended the study to the reaction of oxorhenium(V) compounds with the 'non-innocent' ligands catechol and its derivatives, which can also undergo one-electron oxidations to semiquinone (sq) and quinone (q) [2], with a concomitant reduction of the metal center.

The reactions of oxorhenium(V) compounds with catechol ($H_2$cat) and its derivatives have been thoroughly investigated. It was found that the reaction of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] (**2**) with $H_2$cat in ethanol and diethylamine in air gave *cis*-[Re$^{VII}$O$_2$(cat)$_2$]$^-$, while a similar procedure under an inert atmosphere gave the rhenium(V) complex [ReO(cat)$_2$]$^-$ [3]. In the absence of the base Et$_2$NH, the latter procedure produced

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[$\mathrm{Re^{V}O(cat)(PPh_3)_2Cl}$] [4]. When either **1** or **2** was treated with tetrachloro-1,2-benzoquinone instead of the corresponding catechol, the compound ($n$-$\mathrm{Bu_4N}$)[$\mathrm{Re^{V}O(tccat)_2(OPPh_3)}$] was isolated. The structures of $\mathrm{(CH_3)_4N[ReO(cat)_2]}$ and $\mathrm{(CH_3)_4N[ReO(cat)_2(PPh_3)]}$, prepared from **2** and $\mathrm{H_2cat}$, were also reported [5].

In this study it was found that reaction of oxorhenium(V) compounds with 3,5-di-*tert*-butylcatechol ($\mathrm{H_2ddcat}$) in air did not lead to [$\mathrm{Re^{IV}(ddsq)_3}$]X, as was observed for the similar reaction with $\mathrm{H_2dab}$, but that only rhenium(V) was oxidized to +VI in the product [$\mathrm{Re^{VI}(ddcat)_3}$] (**3**). Complex **3** was synthesized earlier by the reaction of [$\mathrm{Re_2(CO)_{10}}$] and 3,5-di-*tert*-butyl-1,2-benzoquinone (ddq) [6], and by the catechol hydrolysis reaction of $\mathrm{ReO_4^-}$ [7].

## EXPERIMENTAL

### Reagents

*cis*-[$\mathrm{ReO_2I(PPh_3)_2}$] [8a] and ($n$-$\mathrm{Bu_4N}$)[$\mathrm{ReOCl_4}$] [8b] were synthesized by literature methods. $\mathrm{H_2ddcat}$ was obtained commercially (Aldrich). Solvents were purified and dried before use.

### Synthesis of [Re(ddcat)$_3$] (3)

A mixture of 100 mg (115 µmol) of *cis*-[$\mathrm{ReO_2I(PPh_3)_2}$] and 77 mg (346 µmol) of $\mathrm{H_2ddcat}$ in 30 cm$^3$ of toluene was heated at reflux conditions in air for 1 h. During this time the color of the solution turned purple. After cooling to room temperature, the volume was reduced under vacuum to about 5 cm$^3$, and a purple residue filtered off. This was recrystallized from 2 : 1 dichloromethane : ethanol to give purple rods, suitable for X-ray studies. They were washed with ethanol and diethylether, and dried under vacuum. Yield 63%; mp 178°C. Anal. Calcd. for $\mathrm{C_{42}H_{60}O_6Re}$(%): C, 59.13; H, 7.09. Found: C, 59.36; H, 7.00. IR (KBr): $\nu$(*tert*-$\mathrm{CH_3}$) 2967, 2905, 2868; $\nu$(C–O) 1203; $\nu$(Re–O) 514. UV–Vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ ($\varepsilon$, $\mathrm{M^{-1}\,cm^{-1}}$): 276 (15 800), 495 (21 300), 595 (16 100). Complex **3** was also isolated by using ($n$-$\mathrm{Bu_4N}$)[$\mathrm{ReOCl_4}$] as starting material under these experimental conditions, albeit in a lower yield of 54%.

### Physical Measurements

The instrumentation used in this study is the same as that reported previously [8c]. Cyclic voltammetry was performed in dichloromethane with an Epsilon C3 instrument, using ($n$-$\mathrm{Bu_4N}$)$\mathrm{PF_6}$ as electrolyte, with $\mathrm{Ag^+/AgCl}$ as reference at a scan rate of 100 mV s$^{-1}$. The ferrocene/ferrocenium couple was used as internal standard.

### X-ray Data Collection, Structure Solution and Refinement

A Nonius Kappa CCD with Mo K$\alpha$ radiation was used for the data collection for complex **3**. The structure was solved by direct methods and refined by full-matrix least-squares procedures using SHELXL97 [8d]. All nonhydrogen atoms were refined anisotropically. The crystal data and details of the structure determination are given in Table I, and selected bond distances and angles are shown in Table II.

TABLE I Crystal data and structure refinement details for [Re(ddcat)$_3$] (**3**)

| | |
|---|---|
| Empirical formula | $C_{42}H_{60}O_6Re$ |
| Formula weight | 847.13 |
| Temperature (K) | 200(2) |
| Radiation (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| Unit cell dimensions (Å, °) | $a = 15.8455(3)$<br>$b = 15.8343(3)$<br>$c = 16.3301(3)$<br>$\beta = 93.334(1)$ |
| Volume (Å$^3$) | 4090.3(1) |
| $Z$ | 4 |
| Density (calc.) (Mg m$^{-3}$) | 1.376 |
| Crystal size (mm) | 0.02 × 0.04 × 0.33 |
| Absorption coefficient ($\mu$) (mm$^{-1}$) | 3.013 |
| $F$(000) | 1740 |
| Theta min.–max. | 3.15–27.45 |
| Limiting indices | $-20 \le h \le 20$; $-20 \le k \le 20$; $-21 \le l \le 21$ |
| Reflections collected/unique | 59087/9325 |
| Observed data [$I > 2.0\sigma(I)$] | 7074 |
| $N$ref, $N$par | 9325/442 |
| $R$, $wR2$, $S$ | 0.0385, 0.0756, 1.048 |
| Min. and max. resol. dens. (e Å$^{-3}$) | −1.403, 0.985 |

TABLE II Selected bond distances (Å) and angles (°) for **3**

| | | | |
|---|---|---|---|
| Re–O(1) | 1.923(3) | Re–O(4) | 1.927(3) |
| Re–O(2) | 1.936(3) | Re–O(5) | 1.926(3) |
| Re–O(3) | 1.932(3) | Re–O(6) | 1.940(3) |
| C(1)–O(1) | 1.361(5) | C(2)–O(2) | 1.371(5) |
| C(15)–O(3) | 1.364(5) | C(16)–O(4) | 1.356(5) |
| C(29)–O(5) | 1.361(5) | C(30)–O(6) | 1.363(5) |
| C(1)–C(2) | 1.381(5) | C(1)–C(6) | 1.395(6) |
| C(2)–C(3) | 1.383(6) | C(3)–C(4) | 1.378(6) |
| C(4)–C(5) | 1.407(6) | C(4)–C(11) | 1.552(6) |
| C(5)–C(6) | 1.393(6) | C(6)–C(7) | 1.536(6) |
| O(1)–Re–O(2) | 79.2(1) | O(1)–Re–O(5) | 86.1(1) |
| O(3)–Re–O(4) | 78.9(1) | O(1)–Re–O(4) | 106.1(1) |
| O(5)–Re–O(6) | 78.9(1) | O(1)–Re–O(3) | 87.9(1) |
| C(1)–O(1)–Re | 117.2(2) | C(2)–O(2)–Re | 116.6(2) |
| C(15)–O(3)–Re | 117.3(2) | C(30)–O(6)–Re | 117.1(2) |
| O(1)–C(1)–C(2) | 113.0(4) | C(12)–C(11)–C(13) | 110.2(5) |

## RESULTS AND DISCUSSION

Reaction of *cis*-[Re$^{V}$O$_2$I(PPh$_3$)$_2$] with H$_2$ddcat in benzene under reflux conditions gave the product [Re$^{VI}$(ddcat)$_3$] (**3**) in a reasonable yield. The reaction is described by the following equation.

$$[\mathrm{ReO_2I(PPh_3)_2}] + 3\mathrm{H_2ddcat} + \frac{1}{2}\mathrm{O_2} \xrightarrow{\Delta} [\mathrm{Re(ddcat)_3}] + 2\mathrm{PPh_3} + 3\mathrm{H_2O} + \mathrm{I^-}$$

Complex **3** could also be prepared by the reaction of ($n$-Bu$_4$N)[ReOCl$_4$] with H$_2$ddcat. The complex is air-stable and a nonelectrolyte in DMF, and is soluble in a wide variety of solvents such as acetone, acetonitrile, dichloromethane, DMF, chloroform and tetrahydrofuran.

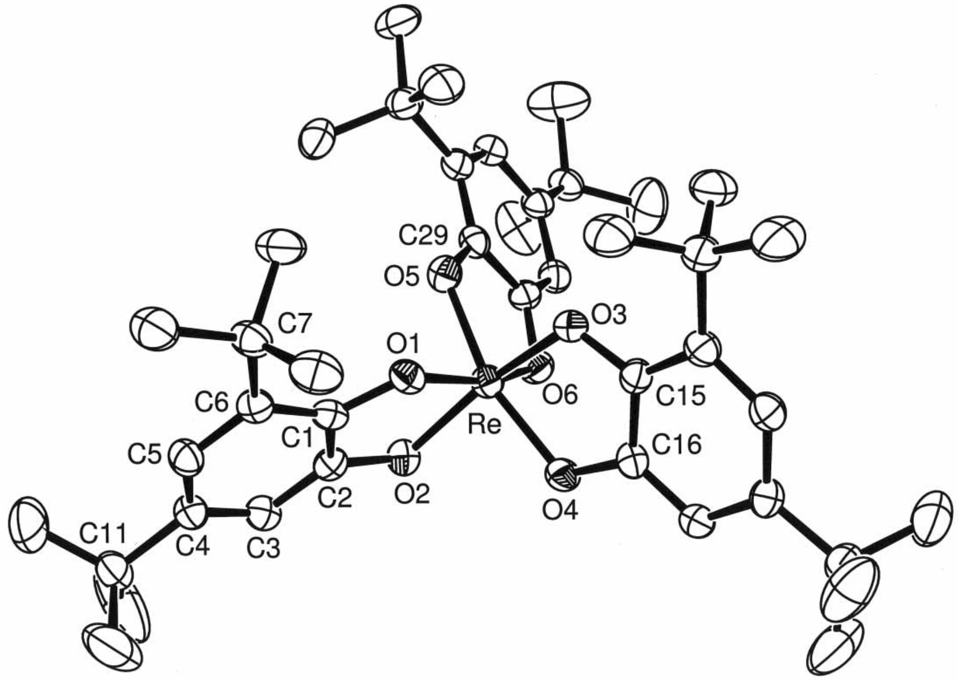

FIGURE 1 An ORTEP view of [Re(ddcat)$_3$] (**3**) showing the atom-labeling scheme and 40% probability ellipsoids.

Single crystals of **3** of X-ray quality were grown from a 2 : 1 mixture of dichloromethane/ethanol. An ORTEP perspective view of the asymmetric unit, together with the atom-numbering scheme, is given in Fig. 1. The complex crystallizes in the monoclinic $P2_1/n$ space group with four molecules per unit cell. The rhenium atom is at the center of a highly distorted octahedron. The six Re–O distances are all similar within experimental error, with an average of 1.931(3) Å; this is shorter than the expected value of 2.04 Å for a Re(V)–O single bond [9], but larger than the values of 1.76–1.78 Å for a Re(V)–O double bond [10]. For the formally $ReO_6$ system in **3**, with filled $\pi$-orbitals on the oxygens perpendicular to the ligand plane, $O \rightarrow Re$ $\pi$-bonding is to be expected. The Re–O(catecholate) bond distances in a series of oxorhenium(V)–catecholate complexes vary in the range 1.96–2.02 Å [5]. The average bite angle of the chelating catecholate ligands is 79.0(1)°, which is slightly smaller than the average of 80.8° in $[Re^VO(tccat)_2(OPPh_3)]^-$ [4]. The compression of these bite angles from 90° causes the octahedron to be trigonally twisted along the threefold axis. The average Re–O–C bond angle is 117.2(2)°.

The bond distances in the chelating catecholato ligands provide an indication of their specific form, i.e. ddcat, ddsq or ddq. The six C–O bond lengths are all equal within standard deviations, with an average value of 1.363(5) Å. This value compares well with the range of 1.34–1.38 Å found in a series of rhenium(V) complexes containing catecholate as ligand [4,5]. It is longer than the C–O bond lengths in semiquinone and quinone compounds, which average around 1.30 and 1.22 Å, respectively [11].

The C–C bond distances in the ligands provide additional evidence of the presence of ddcat chelates. In all three rings there are delocalized C=C double bonds, with averages of 1.390(6), 1.393(6) and 1.396(6) Å. The average C–C bond length in the *tert*-butyl groups is 1.528(7) Å. A comparison of the torsion angles in the phenyl rings shows very little deviation from planarity, thereby indicating their aromaticity. The crystallographic data thus justify the assignment of an oxidation state of +VI to rhenium in complex **3**, and with the chelates existing in the dinegative catecholate form.

In the IR spectrum of **3**, *tert*-butyl stretching frequencies occur at 2967, 2905 and 2868 $\mathrm{cm^{-1}}$. There are also two intense absorptions at 1462 $\mathrm{cm^{-1}}$ (ring stretch of the C–C bond between the two oxygen donor atoms) and 1203 $\mathrm{cm^{-1}}$ (C–O stretch). There are no assignable $\nu$(O–H) frequencies in the 3300–3600 $\mathrm{cm^{-1}}$ region, indicating that the catecholate ligands are deprotonated. The electronic spectrum reveals typical intraligand $\pi$–$\pi^*$ transitions at 276 nm, while a ligand-to-metal change transfer band and a d–d transition are observed at 495 and 595 nm, respectively. Voltammetry of **3** showed a reversible one-electron reduction at −0.601 V (*vs* $\mathrm{Fc^+/Fc}$), and a reversible oxidation at 0.580 V. These values agree well with those found earlier for **3** [6].

Although Re(VI) coordination complexes are known, they are not very common. They are generally prepared by the reduction of Re(VII) or by substitution of Re(VI) precursors, and mostly contain alkoxide or diolate ligands [12,13]. Their synthesis through the oxidation of Re(V) complexes, as shown in this study, is highly unusual.

## Supplementary data

Full lists of crystallographic data are available from the authors.

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