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PREPARATION AND STRUCTURAL STUDIES OF TUNGSTEN(VI)DIOLATO ADDUCTS OF PHENOL AND ANILINE

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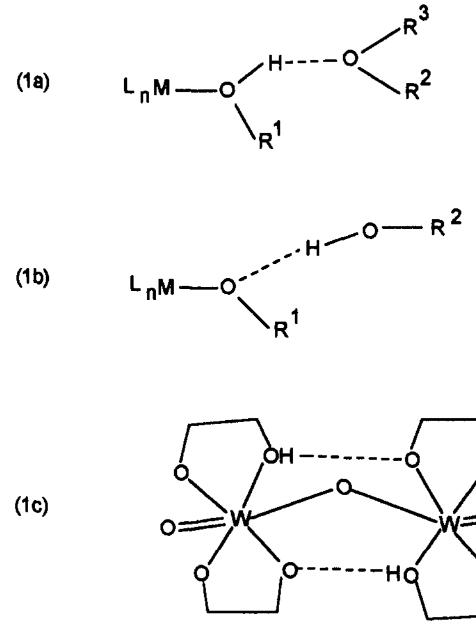
Abstract—The tungsten(VI)diolato complex, [W(eg)(pin)$_2$] (H$_2$eg = 1,2-ethanediol, H$_2$pin = 2,3-dimethyl-2,3-butanediol) forms adducts with phenol and aniline. X-ray structural studies and spectral measurements (UV and IR) show that the formation of those adducts is due to hydrogen bonding between OH or NH$_2$ groups of adductant and diolato oxygen atoms. The effect of hydrogen bonding on the octahedral WO$_6$ centre is minimal, but the conformation angles of the five-membered chelate ring change considerably. Hydrogen bonding does not promote alcoholato exchange reactions.

Hydrogen (H-) bonding is an important factor in inorganic and organometallic chemistry. In second-sphere coordination[1] H-bonding may play a dominant role.[2] This phenomenon mainly determines the solid state structure of copper(II) complexes of simple diols.[3] The H-bonding system in these compounds is shown in Scheme 1a. A similar phenomenon was found in the [WOCl(cat)(Hcat)]·Et$_2$O (H$_2$cat = 1,2-dihydroxybenzene) compound.[4]

The electron-rich late transition metal alcoholato complexes are able to associate with alcohols and phenols by H-bonds,[5,6] as shown in Scheme 1b. This association has been shown to help the alcohol exchange reactions.

Although uncharged metal phenolato complexes of early transition metals form adducts with amines and phenols,[7] reports on the alcohol (phenol) adducts of these metal alkoxides are scarce. One example is *cis*-[MoO$_2$(bud)$_2$]·2H$_2$bud (H$_2$bud = butane-2,3-diol).[8]



Scheme 1.

There are also few examples of negatively charged alcoholato complexes, in which the negative charge is compensated by trialkylammonium ions, e.g. (Et$_3$NH)$_2$[Ti(cat)$_3$] and (Et$_3$NH)$_2$[V(cat)$_3$]·CH$_3$CN. In these compounds the H-atoms of Et$_3$NH groups are attached to metal-bonded alcoholato oxygen atoms by H-bonds.[9,10]

A simultaneous first- and second-sphere coordination phenomenon occurs in dinuclear oxo tungsten(VI)diolato complexes obtained by hydrolysis of parent monomeric tungsten(VI) compounds. In

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these dinuclear complexes intramolecular H-bonds exist between coordinated OH groups and alcoholato oxygen atoms (Scheme 1c).[11]

In continuation of the studies on the reactions of tungsten(VI)diolato complexes, we have now prepared phenol (PhOH) and aniline (PhNH$_2$) adducts of [W(eg)(pin)$_2$][12] (**1**) (H$_2$eg = 1,2-ethanediol, H$_2$pin = 2,3-dimethyl-2,3-butanediol). These adducts may be useful in separation of enantiomers of tris(diolato)tungsten(VI) complexes which have shown certain inertness in their further reactions. The present paper describes the syntheses and characterization of the above-mentioned compounds by elemental analysis and spectroscopic methods. Their structures were verified by single crystal X-ray analysis.

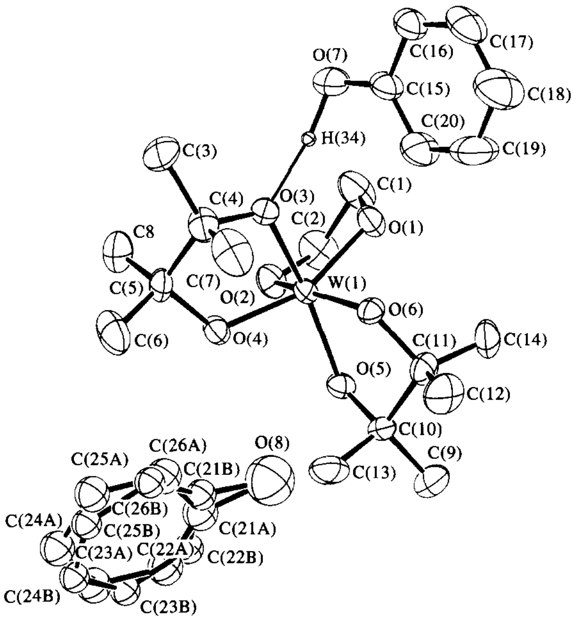

Fig. 1. ORTEP drawing of [W(eg)(pin)$_2$] · 2PhOH. Thermal ellipsoids are drawn at 30% probability.

DISCUSSION

Syntheses

The syntheses were carried out by dissolving the diolato complex and the adductant in 1 : 2 molar ratio in anhydrous protic or non-polar organic solvent. The unoptimized yields of the adducts are 60–70%. It is noteworthy that two phenol molecules cannot replace the eg ligand by the alcoholysis reaction, not even in refluxing toluene where it is easily replaced by another diol molecule. Since phenol is more acidic than H$_2$eg or H$_2$pin,[13] it is reasonable to assume that the chelate effect of diolato ligands has a crucial role in the stabilities of tris-(diolato)tungsten complexes. This finding is in line with the fact that also simple alcohols like methanol, ethanol and 2-propanol were not able to replace diol from the first coordination sphere of tris(diolato)tungsten(VI) complexes.[11]

Structures

The structures of [W(eg)(pin)$_2$] · 2PhOH (**2**) (Fig. 1) and [W(eg)(pin)$_2$] · 2PhNH$_2$ (**3**) (Fig. 2) are very similar. In both compounds the octahedral [W(eg)(pin)$_2$] units accept OH or NH hydrogens of associative molecules (phenol or aniline). The partly negatively charged oxygen atoms of the diolato ligands on the first coordination sphere of W(VI) are able to bond to the hydrogens of neutral dipole-like molecules. The hydrogen bonding seems to have a predominant role in the formation of these adducts, because toluene which is the same size as phenol or aniline does not form an adduct with **1**. In both compounds adductant molecules are attached to diolato oxygen atoms O(3) and O(5).

The O(3) ··· O(7) and O(5) ··· O(8) distances in compound **2** are 2.754(9) and 2.88(1) Å, respectively. The O(3) ··· H(34) distance is 1.64 Å and O(3) ··· H(34)—O(7) angle is 167°. These values indicate that the H-bond system is not very strong. Palladium(II) and nickel(II) phenolato complexes associate with phenol and then O ··· O distances are in the range 2.59–2.61 Å.[6] In the aniline adduct the O(3) ··· N(1) and O(5) ··· N(2) distances are 3.13 and 3.33(1) Å indicating even weaker H-bonds. This could mean that the tungsten(VI) ion has with-

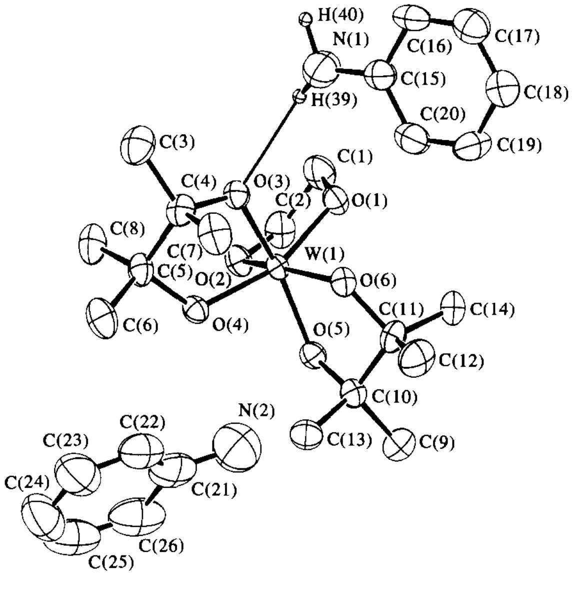

Fig. 2. ORTEP drawing of [W(eg)(pin)$_2$] · 2PhNH$_2$. Thermal ellipsoids are drawn at 30% probability.

drawn considerable negative charge from the alcoholato oxygens.

In both cases the coordination spheres of tungsten(VI) ions are almost identical to those found in a monomeric tris(diolato)tungsten(VI) complex **1** (see bonding parameters in Table 1). The torsion angles (Table 2) reveal that the configuration $\Delta(\lambda\lambda\lambda)lel_3$ of **1** prevails in **2** and **3**.

The W—O bond lengths vary from 1.889(6) to 1.924(6) Å in pure $[W(eg)(pin)_2]$ and from 1.884(6) to 1.936(5) Å in **2** and from 1.886(4) to 1.901(4) Å in **3**. The average of the W—O distances are 1.905, 1.903 and 1.894 Å for **1**, **2** and **3**, respectively. The W(1)—O(3) bond of **1** is slightly shorter than that of **2** but longer than that of **3**. These facts indicate that H-bonding to the alcoholato oxygens does not significantly affect the W—O bonds. However, while the HO hydrogen of phenol bonded to O(3) and O(5) lengthens the W(1)—O(3) and W(1)—O(5) bonds, the less acidic hydrogen of the aniline NH_2 group bonded to O(3) and O(5) shortens the relevant bonds.

The bond angles show similar trends as bond lengths. As seen in Table 1, only O(2)—W(1)—O(5) and O(2)—W(1)—O(6) bond angles are about 2–3° smaller in the adducts than in the parent compound. The greatest effect of the first sphere coordination is on the torsion angles of five-membered chelate rings (Table 2). Especially the first three torsion angles in [W(1)—O(1)—C(1)—C(2)—O(2)] rings are affected. For example, the differences of the torsion angles in this ring can be 9° between **1** and **2**. The corresponding torsion angles in **2** and **3** are similar.

The M—O distances and the M—O—C angles in alcoholato complexes can reflect the degree of π-bonding between the oxygen *p* orbital and metal *d* orbital.[14,15] In **2** and **3** both distances and angles are similar as in the parent complex **1**, so the formation of the H-bond hardly affects the W—O π-bond and does not facilitate ligand exchange. The W—O distances and W—O—C angles in diolato complexes of tungsten(VI) are mainly controlled by steric effects, and it seems that in tris(diolato)tungsten(VI) adducts with phenol and aniline packing forces play a role in chelate ring reformation.

Table 1. Selected bonding parameters (Å,°) for **1**, **2** and **3**

	1	2	3
W(1)—O(1)	1.924(6)	1.898(6)	1.898(4)
W(1)—O(2)	1.889(6)	1.899(6)	1.896(4)
W(1)—O(3)	1.919(5)	1.936(5)	1.895(4)
W(1)—O(4)	1.898(6)	1.888(6)	1.886(4)
W(1)—O(5)	1.902(6)	1.913(5)	1.901(4)
W(1)—O(6)	1.896(6)	1.884(6)	1.888(4)
O(1)—C(1)	1.40(1)	1.44(1)	1.421(8)
O(2)—C(2)	1.46(1)	1.42(1)	1.440(8)
O(3)—C(4)	1.45(1)	1.45(1)	1.452(8)
O(4)—C(5)	1.44(1)	1.44(1)	1.455(8)
O(5)—C(10)	1.45(1)	1.44(1)	1.438(8)
O(6)—C(11)	1.45(1)	1.44(1)	1.439(8)
O(1)—W(1)—O(2)	79.2(3)	78.6(3)	79.0(2)
O(1)—W(1)—O(3)	88.6(2)	86.9(2)	89.3(2)
O(1)—W(1)—O(4)	159.6(3)	158.2(3)	160.3(2)
O(1)—W(1)—O(5)	105.3(2)	107.1(2)	105.6(2)
O(1)—W(1)—O(6)	88.8(2)	89.4(3)	89.4(2)
O(2)—W(1)—O(3)	105.7(3)	107.7(3)	107.3(2)
O(2)—W(1)—O(4)	89.2(3)	91.2(3)	90.0(2)
O(2)—W(1)—O(5)	90.1(3)	87.5(2)	87.6(2)
O(2)—W(1)—O(6)	160.9(3)	157.9(3)	158.8(2)
O(3)—W(1)—O(4)	78.4(2)	77.9(2)	78.3(2)
O(3)—W(1)—O(5)	160.8(2)	161.3(2)	160.9(2)
O(3)—W(1)—O(6)	88.6(2)	89.9(3)	90.1(2)
O(4)—W(1)—O(5)	91.4(3)	91.5(2)	90.1(2)
O(4)—W(1)—O(6)	106.4(2)	105.9(3)	105.7(2)
O(5)—W(1)—O(6)	78.7(2)	78.2(2)	78.3(2)
W(1)—O(1)—C(1)	118.3(6)	118.5(6)	120.3(4)
W(1)—O(2)—C(2)	118.6(6)	118.0(6)	117.4(4)
W(1)—O(3)—C(4)	118.6(5)	119.2(5)	120.2(4)
W(1)—O(4)—C(5)	120.6(5)	121.5(5)	121.3(4)
W(1)—O(5)—C(10)	120.1(5)	120.1(5)	119.2(4)
W(1)—O(6)—C(11)	120.5(5)	120.9(5)	120.5(4)

Spectral studies

FTIR studies support the above conclusions as the IR spectra of the adducts below 1700 cm^{-1} closely resemble the sum of the spectra of both pure components. The greatest spectral differences of **1** and its adducts are seen in the range of 3000–4000 cm^{-1} where the bands due to OH or NH stretchings are seen.

^1H NMR spectra of **1** with 0.5, 1.0, 2.0 and 6.0 equivalents of PhOH in $CDCl_3$ show only one singlet for phenolic OH hydrogen at 6.10 ppm (free PhOH at 6.11 ppm).

The solid state UV spectra of **1** shows a broad band at 300 nm. The relevant band for **2** is at 300 and at 290 nm for **3**. All had a weak shoulder at 320–330 nm. As the UV spectral changes are minimal, the H-bonding hardly affects the W—O bond strength. Although **3** is pale yellow it does not absorb more than **1** or **2** at 300–400 nm.

CONCLUSIONS

Hydrogen bonding plays a dominant role in the formation of $[W(eg)(pin)_2]\cdot 2PhX$ (X = OH or

Table 2. Selected torsion angles (°) for compounds **1**–**3**

	1	**2**	**3**
O(1)—C(1)—C(2)—O(2)	34(1)	41(1)	37.6(7)
C(1)-C(2)-O(2)—W(1)	−27.6(9)	−38(1)	−35.6(7)
C(2)—O(2)—W(1)—O(1)	9.6(6)	18.0(7)	16.5(5)
O(2)—W(1)—O(1)—C(1)	13.3(6)	9.5(7)	9.3(5)
W(1)—O(1)—C(1)—C(2)	−31(1)	−32(1)	−29.5(7)
O(3)—C(4)-C(5)—O(4)	39.6(8)	37(1)	37.2(6)
C(4)—C(5)—O(4)—W(1)	−34.9(8)	−32.6(9)	−32.1(6)
C(5)—O(4)—W(1)—O(3)	14.1(6)	13.0(6)	12.0(4)
O(4)—W(1)—O(3)—C(4)	14.1(6)	13.5(7)	15.3(4)
W(1)—O(3)—C(4)—C(5)	−34.9(8)	−33(1)	−34.8(6)
O(5)—C(10)—C(11)—O(6)	36.1(9)	38.6(8)	39.5(6)
C(10)—C(11)—O(6)—W(1)	−32.3(8)	−35.8(8)	−33.9(6)
C(11)—O(6)—W(1)—O(5)	13.3(6)	15.8(6)	12.9(4)
O(6)—W(1)—O(5)—C(10)	12.7(6)	12.7(6)	15.6(4)
W(1)—O(5)—C(10)—C(11)	−31.7(9)	−33.1(8)	−36.2(6)

NH_2) compounds. The effect of coordinated hydrogen donors to the structural parameters of tris-(diolato)tungsten(VI) complexes in the solid state is quite small. Also spectral data support the idea that W—O bonds are similar in pure tungsten(VI)diolato complexes and phenol and aniline adducts. The formation of H-bonds does not facilitate the alcoholato exchange reaction of **1** with phenol, aniline and simple alcohols. The reason for this is the electron deficient tungsten(VI) ion, which does not allow alcohol exchange reactions to occur as easily as electron-rich late transition metal ions.

EXPERIMENTAL

Phenol (Merck) and aniline (Merck) were used as purchased. Solvents were purified by standard methods and stored over 4 Å molecular sieves. [W(eg)(pin)$_2$] was prepared as described earlier.[12] The IR spectra were measured on a Mattson Galaxy FTIR spectrometer and the solid state UV spectra on a Cary 5E spectrophotometer as Nujol mulls. ^{1}H NMR spectra were recorded on a Jeol GSX-400 spectrometer in $CDCl_3$. Elemental analyses were performed by a Perkin–Elmer Series II analyser.

[W(eg)(pin)$_2$]·2PhOH. [W(eg)(pin$_2$] (480 mg, 1.0 mmol) and phenol (200 mg, 2.1 mmol) were dissolved by warming in dry hexane (5.0 cm^3). The solution was allowed to cool and then kept at −18°C for 4 days. Colourless crystals (490 mg) were separated and washed with petroleum ether (yield 72%). Found: C, 46.5; H, 6.1; $C_{26}H_{40}O_8W$ requires C, 46.8; H, 6.0. IR: 3271(br)s, 1939w, 1852w, 1790w, 1721w, 1605s, 1601s, 1505s, 1468s, 1370s, 1265s, 1219(br)s, 1136(br)s, 1055(br)m, 1005m, 959s, 887s, 814m, 754s, 718s, 694s, 629(br)s, 519m.

[W(eg)(pin)$_2$]·2PhNH$_2$. [W(eg)(pin)$_2$] (240 mg, 0.50 mmol) and aniline (0.10 cm^3, 1.1 mmol) were dissolved in dry methanol (2.0 cm^3) and the solution was kept at −18°C for a week. Pale yellow crystals (210 mg) were separated and washed with petroleum ether (yield 63%). Found: C, 46.7; N, 4.1; H, 6.3; $C_{26}H_{42}O_6N_2W$ requires C, 46.9; N, 4.2; H, 6.3. IR: 3464s, 3358s, 3219m, 2029w, 1934w, 1848w, 1790w, 1717w, 1628s, 1603s, 1503s, 1468s, 1387m, 1366s, 1292s, 1248m, 1225m, 1200m, 1140(br)s, 1069(br)m, 1005m, 993m, 963s, 887(br)s, 750s, 733m, 710s, 696s, 619(br)s, 513(br)m.

Crystal structure determination

Single-crystal X-ray measurements were carried out on a Rigaku AFC5S diffractometer with graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71069 Å). The data obtained were corrected for Lorentz and polarization effects. Absorption (ψ scan) and decay corrections (−11% for **2** and −18% for **3**) were also taken into account. The crystal data and experimental details are shown in Table 3.

The lattice parameters were calculated by least-squares refinements of 25 reflections for **2** and **3**. The structures were solved by direct methods using MITHRIL[16] and DIRDIF[17] programs and refined by full-matrix least-squares techniques to an R-value of 0.030 (R_W = 0.038) for **2** and 0.020 (0.025) for **3**. One phenol group of **2** was disordered and

Table 3. Crystal data and experimental details

Compound	2	3
Formula	$C_{26}H_{40}O_8W$	$C_{26}H_{42}N_2O_6W$
M_r	664.45	662.48
Crystal dimensions (mm)	0.25 × 0.20 × 0.20	0.30 × 0.25 × 0.25
Crystal appearance	Bright, plate	Yellow, prism
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	P-1 (no. 2)
a (Å)	17.578(6)	13.004(4)
b (Å)	8.836(2)	13.289(4)
c (Å)	18.636(3)	9.094(3)
α (°)	90	101.91(3)
β (°)	92.10(2)	106.56(3)
γ (°)	90	81.50(3)
U (Å^3)	2892(1)	1467.3(9)
Z	4	2
D_c (g cm^{-3})	1.526	1.499
μ (cm^{-1})	41.18	40.56
$F(000)$	1336	1064
R_{int}	0.025	0.038
Measured reflections	5668	5407
Unique reflections	5478	5156
Obs. reflections with $I > 2\sigma(I)$	2734	2091
Min., max. transmission coefficients	0.65, 1.00	0.84, 1.00
No. of parameters	271	316
R^a	0.030	0.020
$R_w{}^b$	0.038	0.025
Goodness of fit	1.46	1.19
Maximum $\Delta(\sigma)$	0.03	0.02
Maximim, minimum $\Delta\rho$ (e Å^{-3})	+1.20, −0.51	+0.41, −0.46

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

was refined isotropically as a rigid group in two positions (A and B). The rest of the heavy atoms were refined anistropically, and the CH hydrogen atoms were included in calculated positions (0.95 Å) with fixed temperature factors. The OH hydrogen of another phenol molecule was kept as it was found from the difference Fourier map of **2**. The other OH hydrogen was not found. Compound **3** was not disordered and was refined in the same way, except that two NH_2 hydrogens of another aniline molecule were refined with fixed temperature parameter. The NH_2 hydrogens of the other aniline molecule were not found. Neutral atomic scattering and dispersion factors were taken from Cromer and Waber.[18] All calculations were performed using the TEXSAN[19] crystallographic software. Figures were drawn with ORTEP.[20]

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