Complexes of Pyrogallol with Molybdenum, Tungsten, Osmium, Palladium and Platinum

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Abstract

Salts of the new complexes *cis*-$[MO_2(PG)_2]^{2-}$ (M = Mo, W), *trans*-$[OsO_2(PG)_2]^{2-}$, *trans*-$OsO_2py_2(PG)$, *trans*-$UO_2(PG)\cdot 3H_2O$ and *cis*-$M'(PPh_3)_2(PG)$ (M' = Pd, Pt) with pyrogallol (H_2PG) have been prepared. Their Raman, infrared, ^1H and ^{13}C NMR spectra are reported.

Introduction

We have recently reported complexes with Group VI and Group VIII metals of the chelating *O,O'* 'non-innocent' ligand catechol (H_2 cat) [1–4], catecholamines [5], tropolone (H trop) [6], maltol (H malt) [7] and naphthalene-1,2-diol (H_2ND) [8]; such complexes often display unusual stereochemical or electrochemical features. We report now new complexes of molybdenum, tungsten, osmium, uranium, palladium and platinum with pyrogallol (1,2,3-benzenetriol), H_2PG.

There are few complexes known of the ligand with these metals. In early work Weinland *et al.* reported $M^I_2[MoO_2(PG)_2]\cdot nH_2O$ (M^I = K, NH_4, pyH, $C_5H_{11}NH$), $HM^I[MoO_2(OH)(PG)]\cdot nH_2O$ (M^I = NH_4, pyH) and $(C_5H_{11}NH)_2[WO_2(PG)_2]\cdot H_2O$ [9], and we reformulated $H(NH_4)[MoO_2(OH)(PG)]\cdot 2H_2O$ as $(NH_4)_2[Mo_2O_5(PG)_2]\cdot 2H_2O$ on the basis of analytical and spectroscopic data [1]. The salt $Na_2[WO_2(PG)_2]$ has been reported [10] and the existence of 1:1 and 2:1 uranyl pyrogallato complex in aqueous solution has been indicated by titration techniques [11, 12].

Results and Discussion

Preparation of Complexes

The sodium or potassium salts of $[MO_2(PG)_2]^{2-}$ (M = Mo, W) were made from $[MO_4]^{2-}$ and pyrogallol, and the pyridinium and tetraphenylphosphonium salts by addition of the appropriate cation. Reaction of stoichiometric quantities of OsO_4, pyridine and pyrogallol in CH_2Cl_2 gave *trans*-$[OsO_2(PG)_2]^{2-}$ and addition of pyridine to this gave $OsO_2py_2(PG)\cdot 2H_2O$. The uranyl salts $UO_2(PG)\cdot 3H_2O$ and $[UO_2(PG)_2]^{2-}$ were made from uranyl acetate and pyrogallol, and *cis*-$M'(PPh_3)_2(PG)$ from pyrogallol and *cis*-$M(PPh_3)_2Cl_2$ (M = Pd, Pt).

Vibrational Spectra

Salient features of the vibrational spectra of the complexes are listed in Table 1. The general features are similar to those observed for catecholato [1, 2] and naphthalene-1,2-diolato [8] complexes. The OH stretching frequency (ν(OH)) of pyrogallol is however still present near 3500 cm^{-1}. Strong bands in the infrared of the coordinated ligand near 1480 cm^{-1} are assigned, by analogy with catecholato [1, 2] and tropolonato [6] ligands to an aromatic ring stretch and that near 1270 cm^{-1} to a predominantly ν(C–O) stretch. For the molybdenum and tungsten complexes strong bands near 870 and 910 cm^{-1} are assigned to asymmetric and symmetric stretches respectively of a *cis*-MO_2 unit, the higher frequency being polarised for solutions of the complexes suggesting that it arises from a symmetric stretch, as in other complexes of this type [1, 2, 5–8]. For the osmyl and uranyl species strong infrared bands near 830 and 935 cm^{-1} respectively are likely to arise from asymmetric stretches $\nu^{as}(MO_2)$ of the *trans* O=M=O moiety with the strong Raman bands near 880 and 840 cm^{-1} respectively being assigned to $\nu^s(MO_2)$.

^1H and ^{13}C NMR Spectra

The ^1H shifts are listed in Table 1 and ^{13}C shifts in Table 2; the numbering scheme for carbon nuclei is shown in Fig. 1. There seem to be no literature data on spectra of the ligand or its complexes apart from a reference to the ^1H shift of the hydroxy groups at δ 7.16 in acetone [13].

The ^1H NMR spectrum of pyrogallol in $(C^2H_3)_2CO$ shows a triplet at δ 6.53 with a doublet at δ 6.38 ppm, this having twice the integral of the triplet. These we assign to the H_5 and $H_{4,6}$ protons respectively. A broad singlet at δ 7.16, which disappears

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TABLE 1. Vibrational and ^1H NMR spectroscopic data of pyrogallolato complexes

Compound	Vibrational spectra[a]				^1H NMR data				Solvent
	$\nu(C-C)$	$\nu(C-O)$	$\nu^{as}(MO_2)$	$\nu^{s}(MO_2)$	H_5	H_4	H_6	H_{OH}	
$H_2(PG)$					6.53 (t, H)	6.38 (d, 2H)		7.16s	$(C^2H_3)_2CO$
cis-$K_2[MoO_2(PG)_2]\cdot 4H_2O$	1460s $\underline{1496s}$ $\underline{1461m}$	1250s $\underline{1254m}$ $\underline{1295m}$	888s $\underline{868m}$ $\underline{859w, b^*}$	905m $\underline{910s}$ $\underline{896s, p^*}$	6.54t	6.27d			^2H_2O
cis-$(PPh_4)_2[MoO_2(PG)_2]\cdot 2H_2O$	obsc.	1238m	854s $\underline{851m}$	895m $\underline{881s}$ $\underline{893s}$					
cis-$(PyH)_2[MoO_2(PG)_2]\cdot H_2O$	1490s	1250s	875s $\underline{842m}$	917m $\underline{877s}$					
cis-$Na_2[WO_2(PG)_2]\cdot C_2H_5OH$	1455s	1245s	850s $\underline{861w, b}$ $\underline{855w, b}$	912 $\underline{916s}$ $\underline{908s, p^*}$	6.60 (t, 2H)	6.35 (d, 4H)			$^2H_2O^b$
cis-$(Ph_4P)_2[WO_2(PG)_2]\cdot 2H_2O$	1485s	1237m	860s	905m					
trans-$[OsO_2(PG)(py)_2]\cdot 2H_2O$	1480s	1240m	840s	$\underline{879s}$	6.57 (t, H)	6.48 (d, H)	6.30 (d, H)		C^2HCl_3 [c]
trans-$(Ph_4P)_2[OsO_2(PG)_2]\cdot 2H_2O$	obsc.	1262m	830s	$\underline{865s}$					
trans-$UO_2(PG)\cdot 3H_2O^d$	obsc.	1245m	935s	$\underline{837s, b}$					
trans-$(Ph_4P)_2[UO_2(PG)_2]\cdot 2H_2O^d$	1480s $\underline{1488s}$	1265	900s	$\underline{804s}$ $\underline{808s, p^{++}}$					
cis-$Pd(PPh_3)_2(PG)$	1480s	1268m			6.28 (t, H)	6.07 (d, 2H)		4.84 (s, H)	C^2HCl_3
cis-$Pt(Ph_3P)_2(PG)$	1480s $\underline{1483m}$	1268m $\underline{1264m}$			6.32 (t, H)	6.16 (d, H)	6.05 (d, H)	4.70 (s, H)	C^2HCl_3

Frequencies in cm^{-1}, chemical shifts (δ) in ppm relative to $Si(CH_3)_4$. [a]Raman bands underlined; other bands infrared. Data on solids or * in H_2O, ++ or in DMF. [b]^1H NMR shifts at δ 3.66 and 1.15 ppm due to C_2H_5OH also observed. [c]^1H NMR shifts at δ 8.89, 8.01 and 7.61 ppm also observed, due to pyridine. [d]Medium band at 250 cm^{-1} also observed in uranyl complexes attributed to $\delta(UO_2)$ as in ref. 12.

TABLE 2. ^{13}C NMR spectra of pyrogallol and its complexes in ^2H_2O

Compound	δ (ppm)					
	C_1	C_2	C_3	C_4	C_5	C_6
H_2PG	148.0	135.1	148.0	111.2	123.1	111.2
cis-$K_2[MoO_2(PG)_2]\cdot 4H_2O$	152.9	153.1	147.2	109.7	123.1	109.7
cis-$Na_2[WO_2(PG)_2]\cdot C_2H_5OH$	159.5	159.5	146.4	110.5	123.2	110.5

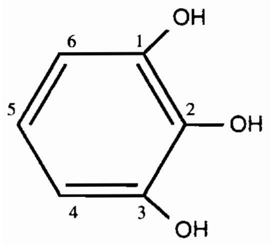

Fig. 1. Atom numbering scheme for pyrogallol.

if ^2H_2O is used as solvent, is assigned to the hydroxyl protons. On coordination de $H_{4,6}$ and H_5 protons shift slightly, and the resonance from the former $H_{4,6}$ protons splits into two doublets in some cases.

The ^1H decoupled ^{13}C spectrum of the free ligand shows four peaks, as expected. Those at lower field, at δ 148.0 and 135.1 ppm, are likely to arise from $C_{1,3}$ and C_2 resonances; since the former has twice the intensity of the latter it seems likely that the δ 148.0 shift arises from $C_{1,2}$. The C_4 and C_6 nuclei adjacent to the 1,3-hydroxy groups are likely to resonate at higher field and to be of higher intensity compared with that of C_5. The peaks at δ 111.2 and 123.1 ppm are assigned to C_4/C_6 and C_5 resonances respectively.

On complexation involving the 1,2-dihydroxy groups the pyrogallol molecule loses symmetry. The C_1/C_2 pair is likely to resonate at lower field and C_3, which is attached to the remaining hydroxy group, is also expected to give a low intensity peak at a lower field. The remaining C_4, C_5 and C_6 nuclei are little affected. Table 2 summarises ^{13}C NMR spectra of pyrogallol and its complexes.

Cyclic Voltammetric Data

In CH_2Cl_2 both $Pd(PPh_3)_2(PG)$ and $Pt(PPh_3)_2(PG)$ using 0.2 M $(Bu^n_4N)PF_6$ as supporting electrolyte and an Ag/AgCl reference electrode show a one electron oxidation process. For the former complex, a quasi-reversible oxidation wave was observed at a potential $E_{1/2} = +0.31$ V, $\Delta E = 90$ mV while the platinum complex showed a reversible oxidation wave at $E_{1/2} = +0.45$ V, $\Delta E = 60$ mV. These may arise from oxidation of M^{II} to M^{III} (M = Pd, Pt).

Experimental

Preparation of Pyrogallolato Complexes

(a) cis-$M^I[MoO_2(PG)_2]\cdot nH_2O$ (M^I = K, n = 4; Y = PPh_4, n = 2)

To potassium molybdate (0.96 g, 4 mmol) in water (5 cm^3) was added pyrogallol (1.2 g, 9.5 mmol) in water (5 cm^3). A deep red solution was obtained, the volume of which was reduced by evaporation *in vacuo*. It was then left to stand at room temperature for a few hours until precipitation occurred, and ethanol was then added. The precipitate was filtered off and washed with ether to remove excess pyrogallol. It was finally dried *in vacuo*. *Anal.* Calc. for $K_2[MoO_2(PG)_2]\cdot 4H_2O$: C, 27.4; H, 3.1. Found: C, 26.8; H, 2.9%.

The tetraphenylphosphonium salt was prepared by adding an aqueous solution of Ph_4PCl (Ph_4PCl:M 2:1) to the reactant red solution before evaporation. *Anal.* Calc. for $(Ph_4P)_2[MoO_2(PG)_2]\cdot 2H_2O$: C, 66.1; H, 4.8. Found: C, 65.7; H, 4.7%.

(b) cis-$M^I_2[WO_2(PG)_2]\cdot n$ (M^I = Na, n = C_2H_5OH; M^I = Ph_4P, n = $2H_2O$)

Similar procedures were used in which $Na_2[WO_4]$ replaced $K_2[MoO_4]$ and the resulting yellow solution was evaporated to near dryness followed by addition of ethanol. The yellow precipitate was filtered off and treated as above. *Anal.* Calc. for $Na_2[WO_2(PG)_2]\cdot C_2H_5OH$: C, 30.2; H, 2.5. Found: C, 29.3; H, 2.5%. Calc. for $(Ph_4P)_2[WO_2(PG)_2]\cdot 2H_2O$: C, 61.1; H, 4.5. Found: C, 60.7; H, 4.4%.

(c) cis-$(pyH)_2[MoO_2(PG)_2]\cdot H_2O$

This was prepared by the literature method [9] for '$H(pyH)[MoO_2PG(OH)]$'. *Anal.* Calc. for $(pyH)_2[MoO_2(PG)_2]\cdot H_2O$: C, 47.7; H, 4.0; N, 5.1. Found: C, 47.5; H, 4.0; N, 5.1%.

(d) trans-$[OsO_2(PG)(py)_2]\cdot 2H_2O$ and trans-$(Ph_4P)_2[OsO_2(PG)_2]\cdot 2H_2O$

The literature method in ref. 2 was used for preparation of the corresponding catecholato complexes. *Anal.* Calc. for $[OsO_2(PG)(py)_2]\cdot 2H_2O$: C, 35.6; H, 3.4; N, 5.2. Found: C, 35.4; H, 3.0; N, 5.1%. Calc. for $(Ph_4P)_2[OsO_2(PG)_2]\cdot 2H_2O$: C, 60.8; H, 4.4. Found: C, 60.5; H, 4.1%.

(e) trans-$UO_2PG\cdot 3H_2O$ and trans-$(Ph_4P)_2UO_2PG\cdot 2H_2O$

The complex $UO_2PG\cdot 3H_2O$ was prepared by mixing equimolar solutions of pyrogallol and uranyl acetate in ethanol and refluxing for 3 h. The solution was reduced by evaporation and precipitation occurred after cooling, the brown precipitate filtered off, washed with ether and dried *in vacuo*. *Anal.* Calc. for $UO_2PG\cdot 3H_2O$: C, 16.0; H, 2.3. Found: C, 15.6; H, 2.0%.

The salt *trans*-$(Ph_4P)_2UO_2PG\cdot 2H_2O$ was prepared by mixing equimolar aqueous solutions of both pyrogallol and uranyl acetate. The complex precipitated out immediately on addition of Ph_4PCl. *Anal.* Calc. for $(Ph_4P)_2UO_2(PG)_2\cdot 2H_2O$: C, 58.4; H, 4.2. Found: C, 58.1; H, 4.2%.

(f) $M(PPh_3)_2(PG)$ (M = Pd, Pt)

These reactions were carried out as for the naphthalene-2,3-diolate complexes above using Gandolfi's method [14] of reacting *cis*-$M(PPh_3)_2Cl_2$ with the ligand. Greenish (Pd) and yellow (Pt) precipitates were formed. *Anal.* Calc. for $Pd(PPh_3)_2(PG)$: C, 66.8; H, 4.5. Found: C, 67.4; H, 4.5%. Calc. for $Pt(PPh_3)_2(PG)$: C, 59.8; H, 4.1. Found: C, 59.7; H, 4.0%.

Raman spectra were measured on a Spex Ramalog 5 instrument with a Coherent Radiation Innova 90 krypton-ion laser with excitation at 6471 (red) or 5682 (yellow) Å, as spinning discs with a KBr base for solids or in sealed capillaries for solutions. Infrared spectra were measured in liquid paraffin films between caesium iodide plates on a Perkin-Elmer 683 instrument. NMR spectra were measured on a Jeol FX 90 Q spectrometer.

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