Preparation and Crystal Structure of a Seven-co-ordinated Oxotungsten(IV) Complex of 2,2′:6′,2″:6″,2‴-Quaterpyridine†

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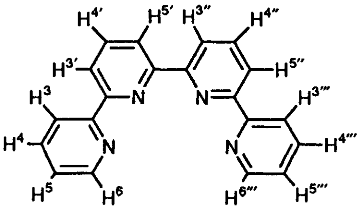
The reaction of $[WOCl_2(PMe_2Ph)_3]$ with 2,2′:6′,2″:6″,2‴-quaterpyridine (L) in ethanol gave $[WO(PMe_2Ph)_2L]^{2+}$ isolated as a BPh_4^- salt. X-Ray diffraction analysis revealed that the complex cation adopts a distorted pentagonal-bipyramidal structure with the W≡O distance being 1.696(9) Å. The spectroscopic properties and electrochemistry of this tungsten complex have been investigated.

Recently, the synthesis of 2,2′:6′,2″:6″,2‴-quaterpyridine (L) has been modified by Constable *et al.*[1] Since then a number of mononuclear metal complexes of quaterpyridine, *e.g.* of Co^{III}, Cu^{II}, Ni^{II}, Pd^{II} and Re^{V},[1–5] have been prepared and structurally characterized and the ligand was found to act as a planar tetradentate N_4 donor in most cases. Our recent study on seven-co-ordinated rhenium(V) oxo and nitrido complexes of quaterpyridine[5] stimulated our interest in the preparation and chemical properties of Group 6 metal analogues. However, only the chromium(III) complex had been synthesised.[6] Herein is described a seven-co-ordinated oxotungsten(IV) complex of quaterpyridine.



L

Experimental

2,2′:6′,2″:6″,2‴-Quaterpyridine[1] and $[WOCl_2(PMe_2Ph)_3]$[7] were prepared according to literature procedures; PMe_2Ph and $NaBPh_4$ obtained from Aldrich were used without further purification.

Preparation of $[WO(PMe_2Ph)_2L][BPh_4]_2$ **1**.—The reaction was performed under a nitrogen atmosphere using standard Schlenk-line techniques. A mixture of $[WOCl_2(PMe_2Ph)_3]$ (0.1 g) and L (0.046 g) in absolute ethanol (15 cm^3) was refluxed for 2 h during which it changed from light blue to deep violet-blue. The solution was filtered and $NaBPh_4$ (≈1 g) added to give a violet precipitate. The crude product was recrystallized by diffusion of diethyl ether into acetonitrile to give red-purple shiny needle crystals (yield = 35%) (Found: C, 70.4; H, 5.5; N, 3.70. $C_{84}H_{76}B_2N_4OP_2W$ requires C, 70.7; H, 5.3; N, 3.95%). UV/VIS (MeCN): λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 372 (1840) and 579 (590). ^1H NMR (CD_3CN): δ 1.47 [t, 12 H, $P(CH_3)_2C_6H_5$], 6.68 [m, 4 H, $P(CH_3)_2C_6H_5$], 6.84 (t, 8 H, BPh_4), 6.99 [t, 20 H, BPh_4 + $P(CH_3)_2C_6H_5$], 7.27 [m, 18 H, BPh_4 + $P(CH_3)_2C_6H_5$], 7.34–8.08 (m, 12 H, H^3–$H^{5'''}$) and 9.86 (d, 2 H, H^6 and $H^{6'''}$). IR (Nujol, cm^{-1}): 1600, 1570, 1410, 1420, 940 (W≡O), 920, 900, 780, 725s and 705s.

Physical Measurements.—The IR spectrum was recorded on a Shimadzu IR-408 spectrophotometer as a Nujol mull, the UV/VIS spectrum on a Milton Roy(Spectronic 3000 Array)-diode-array spectrophotometer and the ^1H NMR spectrum on a JEOL 270 FT-NMR spectrometer with $SiMe_4$ as internal reference. Elemental analyses were performed at the National Taiwan University.

Cyclic voltammetry was performed on a Princeton Applied Research (PAR) model 173/179 potentiostat/digital coulometer equipped with positive-feedback *IR*-compensation and a model 175 universal programmer.

Crystal Structure Determination.—*Crystal data.* $[WO(PMe_2Ph)_2L][BPh_4]_2$, $C_{84}H_{76}B_2N_4OP_2W$, M = 1424.99, monoclinic, space group $C2/c$, a = 18.622(2), b = 13.796(2), c = 26.799(3) Å, β = 99.29(1)°, U = 6794.6(1.0) $Å^3$, Z = 4, D_c = 1.394 g cm^{-3}, μ(Mo-Kα) = 18.3 cm^{-1}, $F(000)$ = 2920.

A crystal of dimensions 0.1 × 0.15 × 0.15 mm was used for data collection at 25 °C on a Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.710 73 Å) using a ω–2θ scan. Intensity data ($2\theta_{max}$ = 45°, h 0–20, k 0–14, l −28 to 28; three standard reflections measured every 2 h showed no decay) were corrected for Lorentz and polarization effects and empirical absorption based on a ψ scan of four strong reflections. Upon averaging the 4828 reflections, 4475 of which were measured once, 4352 independent ones were obtained. 2924 Reflections with $F_o \geqslant 3.0\sigma(F_o)$ were observed and used in the structural analysis. The space group was determined from systematic absences and the structure solved by Patterson and Fourier methods and subsequent refinement by full-matrix least squares using the Enraf-Nonius programs[8] on a Micro VAX II computer. The W, P, O, N, C and B atoms were refined anisotropically, and the H atoms at calculated positions with isotropic thermal parameters equal to 1.3 times those of the attached C atoms were not refined. Convergence for 425 variables by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.04F_o^2)^2]$ for reflections with $I \geqslant 1.5\sigma(I)$, was reached at R = 0.048, R' = 0.046 and S = 1.119 for the 2924 reflections; $(\Delta/\sigma)_{max}$ = 0.02. A final Fourier difference map was featureless, with maximum positive and negative peaks of 0.97 and 0.67 e $Å^{-3}$ respectively. Atomic coordinates of non-hydrogen atoms are listed in Table 1, selected bond distances and angles in Table 2.

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

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Positional parameters and their estimated standard deviations for $[WO(PMe_2Ph)_2L][BPh_4]_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	0.000	0.157 23(5)	0.250	C(20)	0.425 8(5)	0.079 5(7)	0.454 1(3)
P	−0.131 3(1)	0.171 6(2)	0.260 62(8)	C(21)	0.400 7(5)	0.010 6(7)	0.484 6(3)
O	0.000	0.034 3(6)	0.250	C(22)	0.338 2(5)	0.026 3(7)	0.504 0(3)
N(1)	−0.024 5(3)	0.296 1(5)	0.202 0(2)	C(23)	0.301 6(6)	0.110 9(7)	0.492 9(4)
N(2)	−0.041 9(4)	0.123 1(5)	0.167 2(3)	C(24)	0.326 9(5)	0.181 0(7)	0.461 9(4)
C(1)	−0.013 0(4)	0.386 4(6)	0.223 5(3)	C(25)	0.387 3(5)	0.354 9(7)	0.407 7(3)
C(2)	−0.026 2(5)	0.469 7(7)	0.194 9(4)	C(26)	0.422 8(5)	0.434 1(7)	0.433 4(3)
C(3)	−0.049 9(5)	0.461 6(7)	0.143 5(4)	C(27)	0.389 9(5)	0.521 4(7)	0.436 9(4)
C(4)	−0.063 0(5)	0.372 8(7)	0.121 4(4)	C(28)	0.278 6(5)	0.458 0(7)	0.392 3(4)
C(5)	−0.049 6(5)	0.289 7(7)	0.151 4(3)	C(29)	0.317 1(5)	0.534 7(7)	0.417 4(4)
C(6)	−0.062 7(5)	0.191 9(7)	0.132 3(3)	C(30)	0.313 7(5)	0.371 4(7)	0.388 2(3)
C(7)	−0.093 3(5)	0.172 2(9)	0.082 2(3)	C(31)	0.599 1(4)	0.209 8(7)	0.156 3(3)
C(8)	−0.104 1(6)	0.076 5(9)	0.068 3(4)	C(32)	0.627 4(5)	0.154 4(8)	0.259 8(3)
C(9)	−0.085 2(5)	0.004 7(9)	0.104 1(4)	C(33)	0.609 1(5)	0.249 0(8)	0.246 4(4)
C(10)	−0.053 5(5)	0.029 8(8)	0.152 8(4)	C(34)	0.595 0(5)	0.277 1(8)	0.196 5(4)
C(11)	−0.157 1(5)	0.258 6(7)	0.303 6(3)	C(35)	0.633 1(5)	0.089 1(8)	0.222 7(3)
C(12)	−0.209 5(5)	0.328 5(8)	0.290 2(4)	C(36)	0.619 1(4)	0.116 7(6)	0.171 8(3)
C(13)	−0.228 6(6)	0.395 7(8)	0.327 1(4)	C(37)	0.511 4(5)	0.248 3(6)	0.416 7(3)
C(14)	−0.195 0(6)	0.393 5(8)	0.374 3(4)	C(38)	0.547 5(5)	0.262 9(7)	0.466 1(3)
C(15)	−0.140 6(5)	0.324 5(8)	0.388 9(3)	C(39)	0.622 8(5)	0.268 2(7)	0.479 8(4)
C(16)	−0.123 6(5)	0.259 9(7)	0.354 1(3)	C(40)	0.666 3(5)	0.259 8(7)	0.443 2(4)
C(17)	−0.194 9(5)	0.190 9(8)	0.202 0(3)	C(41)	0.634 5(5)	0.242 0(8)	0.394 1(4)
C(18)	−0.158 7(5)	0.055 1(7)	0.284 0(4)	C(42)	0.558 3(5)	0.238 5(7)	0.381 1(4)
C(19)	0.391 0(4)	0.167 9(8)	0.440 7(3)	B	0.420 6(6)	0.244 1(8)	0.402 5(4)

Table 2 Selected bond distances (Å) and angles (°) for $[WO(PMe_2Ph)_2L]^{2+}$

W–P	2.515(2)	W–N(1)	2.311(7)
W–O	1.696(9)	W–N(2)	2.277(7)
N(1)–C(1)	1.37(2)	N(1)–C(5)	1.36(1)
N(2)–C(6)	1.35(1)	N(2)–C(10)	1.36(1)
C(5)–C(6)	1.45(1)		
P–W–O	94.51(6)	P–W–N(1)	83.7(2)
P–W–N(2)	86.6(2)	O–W–N(2)	78.1(2)
O–W–N(1)	146.0(2)	N(1)–W–N(2)	68.0(2)
N(1)–C(5)–C(6)	115.0(8)	N(2)–C(6)–C(5)	113.4(7)

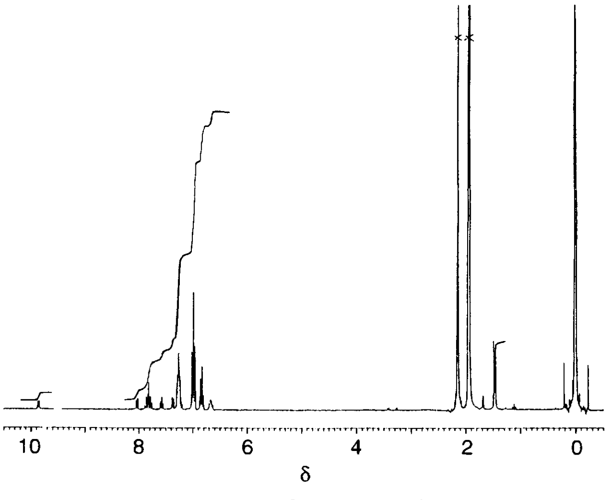

Fig. 1 Proton NMR spectrum of $[WO(PMe_2Ph)_2L][BPh_4]_2$

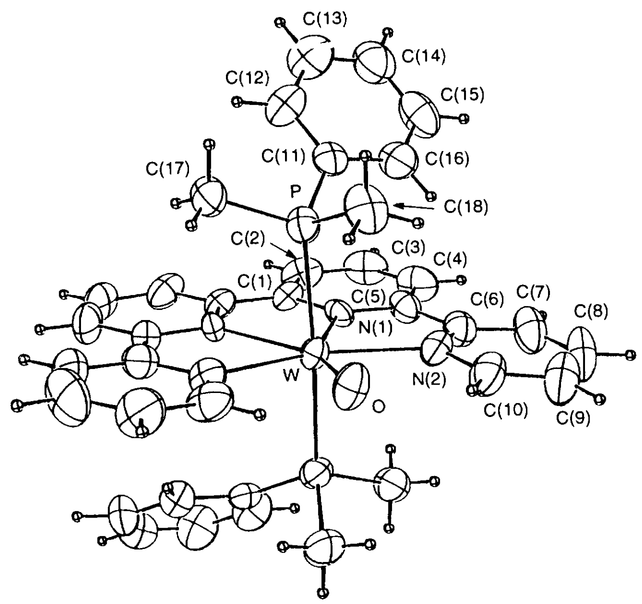

Fig. 2 A perspective drawing of the $[WO(PMe_2Ph)_2L]^{2+}$ cation

Results and Discussion

Complex **1** is diamagnetic and stable both in the solid state and in solution. No detectable decomposition was found under ambient conditions. It is soluble in acetonitrile or dimethylformamide, slightly soluble in dichloromethane. Its IR spectrum shows an intense band at 940 cm^{-1}, which could be tentatively assigned to a W≡O stretch.[9] The UV/VIS absorption spectrum in acetonitrile shows two bands at 372 and 579 nm. The small ε_{max} value of the latter suggests that it is possibly a d–d transition and an assignment would be $(d_{xy})^2 \longrightarrow (d_{xy})^1(d_{xz},d_{yz})^1$. The intense band at 372 nm is likely to be metal-to-metal charge transfer in nature. Interpretation of the ^1H NMR spectrum in Fig. 1 is complicated due to the overlapping of resonances of the aromatic protons of PMe_2Ph and BPh_4^-. Nevertheless, the doublet at δ 9.86 corresponds to H^6 and $H^{6'''}$ of L. Furthermore, the virtual triplet at δ 1.47 indicates that the two PMe_2Ph are orientated in *trans* configuration.

Fig. 2 shows a perspective drawing of the complex cation. It features a distorted pentagonal bipyramid with the W≡O moiety almost coplanar with the ligand L. This is quite different from the structure of seven-co-ordinated tungsten(II) carbonyls which were reported to be either capped octahedral or capped trigonal prismatic.[10b,c] Although seven-co-ordinated tungsten complexes are not uncommon in the literature, this is the first example of a mononuclear oxotungsten(IV) complex having a pentagonal-bipyramidal structure.[10a] The measured W≡O distance of 1.696(9) Å is in accord with a triple bond formulation and is consistent with values reported for other monooxotungsten(IV) complexes.[11] It is, however, slightly longer than that of 1.666(4) Å in $[WOCl_2(PMe_2Ph)_3]$.[12] The two PMe_2Ph ligands are bent away from the W≡O moiety, as revealed by the P–W–O angle of 94.51(6)°. The measured N(2)–W–N(2′) void angle of 156.2(2)° is similar to that of $[ReO(L)(OMe)_2]^+$.[5] The structure of **1** is another example of a seven-co-ordinated d^2 oxometal complex.[5]

The cyclic voltammogram of complex **1** in dimethylformamide exhibits an irreversible oxidation wave at +0.63 V *vs.* a AgCl–Ag electrode. This irreversible wave is tentatively assigned to the oxidation of W^{IV} to W^V.

We have demonstrated once again that quaterpyridine is a good ligand for the generation of a seven-co-ordinated metal complex.[5] The chemistry of complex **1** and the preparation of low-valent metal complexes of quaterpyridine are under active investigation.

Acknowledgements

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