Synthesis and Molecular Structures of Novel Seven-co-ordinated Oxo- and Nitrido-rhenium(V) Complexes of 2,2′:6′,2″:6″,2‴-Quaterpyridine†

Chi-Ming Che,*[a,b] **Yu-Pey Wang,**[b] **Kap-Sun Yeung,**[a] **Kwok-Yin Wong**[a] **and Shie-Ming Peng**[b]
[a] *Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong*
[b] *Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China*

Reaction of $[ReO_2(PPh_3)_2I]$ and $[ReNCl_2(PPh_3)_2]$ with 2,2′:6′,2″:6″,2‴-quaterpyridine (L) in methanol gave $[ReO(L)(OMe)_2]ClO_4$ and $[ReN(L)(PPh_3)Cl]ClO_4$ respectively. The structures determined by X-ray crystallography revealed seven-co-ordination around rhenium with Re=O and Re≡N distances of 1.666(4) and 1.647(6) Å respectively. Intense metal-to-ligand charge-transfer transitions in the visible region and reversible Re^{VI}–Re^{V} redox couples have been observed for both complexes in acetonitrile.

High-valent d^2 metal complexes in which the metal atom is multiply bonded to a heteroatom such as oxygen and nitrogen have recently been shown to have novel physical and chemical properties.[1–3] These complexes are usually six-co-ordinated and in the cases of Re^V (ref. 1) and Os^{VI} (ref. 2), possess long-lived and emissive electronic excited states. Herein we describe the first example of seven-co-ordinated d^2 oxo- and nitrido-metal complexes with the ligand 2,2′:6′,2″:6″,2‴-quaterpyridine (L).[4] This ligand has been chosen for the design of new oxometal oxidants and photocatalysts because it is resistant towards oxidation and has low-energy π^* orbitals for metal-to-ligand charge-transfer transitions.

Experimental

The compound $KReO_4$ was obtained from Janssen Chimica; $[ReO_2(PPh_3)_2I]$,[5] $[ReNCl_2(PPh_3)_2]$[6] and 2,2′:6′,2″:6″,2‴-quaterpyridine (L)[4] were prepared by literature methods.

Preparation of $[ReO(L)(OMe)_2]ClO_4$ **1** *and* $[ReN(L)(PPh_3)Cl]ClO_4$ **2**.—A methanolic solution (30 cm^3) of $[ReO_2(PPh_3)_2I]$ (0.1 g) and excess of L (0.1 g) was heated to 50–60 °C for 0.5 h to give a violet-red solution from which $[ReO(L)(OMe)_2]ClO_4$ **1** could be obtaind by precipitation with $LiClO_4$. The complex was recrystallized by diffusion of diethyl ether into acetonitrile solution (yield ≈80%) (Found: C, 39.0; H, 3.0; N, 8.1. Calc. C, 39.2; H, 2.95; N, 8.3%). Complex **2** was similarly prepared in similar yield from $[ReNCl_2(PPh_3)_2]$ and L (Found: C, 50.1; H, 3.1; N, 7.6. Calc.: C, 50.3; H, 3.2; N, 7.7%).

Physical Measurements.—The UV/VIS absorption spectra were recorded on a Milton Roy Spectronic 3000 diode-array spectrophotometer, infrared spectra as Nujol mulls on a Nicolet 20FXC FT-IR spectrophotometer and ^1H NMR spectra on a JEOL 270 MHz FT-NMR spectrometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) model 175 universal programmer and a model 173 potentiostat. Potentials were controlled with respect to a Ag^+–Ag reference electrode in acetonitrile but are reported with respect to the ferrocenium–ferrocene couple as measured in the same solution.

X-Ray Structure Determinations.—*Crystal data.* $[ReO(L)(OMe)_2]ClO_4\cdot MeCN\cdot H_2O$, $C_{24}H_{25}ClN_5O_8Re$, $M = 733.14$, triclinic, space group $P\bar{1}$, $a = 7.787(3)$, $b = 13.832(3)$, $c = 13.999(5)$ Å, $\alpha = 119.00(2)$, $\beta = 97.14(3)$, $\gamma = 85.64°$, $U = 1308.3(8)$ Å^3, $Z = 2$, $D_c = 1.86$ g cm^{-3}, μ(Mo-Kα) = 48.6 cm^{-1}, $F(000) = 720$.

Intensities were measured at 25 °C on a Nonius diffractometer with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.709\ 30$ Å) using the θ–2θ scan mode ($2\theta_{max} = 49.8°$) with a crystal of dimensions 0.25 × 0.40 × 0.45 mm. Data reduction and structure refinement were performed using the NRCC-SDP-VAX packages, available from S.-M. Peng on request. Empirical absorption corrections (transmission factors 0.421–0.994) were applied, and of the 4599 unique reflections measured 4137 observed data [$I > 2.0\sigma(I)$] were used in structure analysis. The weighting function $w^{-1} = \sigma^2(F) + 0.0001\ F^2$ was used, leading to $R = 0.033$, $R' = 0.029$ and goodness of fit = 3.23.

$[ReN(L)(PPh_3)Cl]ClO_4\cdot MeCN$, $C_{40}H_{32}Cl_2N_6O_4PRe$, $M = 948.8$, monoclinic, space group $P2_1/n$, $a = 9.410(2)$, $b = 15.056(4)$, $c = 26.973(5)$ Å, $\beta = 94.913(2)°$, $U = 3807.1(14)$ Å^3, $Z = 4$, $D_c = 1.66$ g cm^{-3}, μ(Mo-Kα) = 34.8 cm^{-1}, $F(000) = 1880$.

Intensities measured as above; crystal dimensions 0.20 × 0.30 × 0.40 mm. Empirical absorption corrections (transmission factors 0.875–0.997) were applied, and of the 6672 unique reflections measured 4471 observed data [$I > 2.0\sigma(I)$] were used in structure analysis. The same weighting function as above was used, leading to $R = 0.035$, $R' = 0.028$ and goodness of fit = 1.74.

Tables 1 and 2 list the atomic coordinates of non-hydrogen atoms. Selected bond distances and angles are given in Table 3.

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

Results and Discussion

Both complexes **1** and **2** are air-stable diamagnetic solids. The IR spectrum of **1** shows an intense band at 947 cm^{-1} assignable to the ν(Re=O) stretch. Assignment of the ν(Re≡N) stretch of **2** is complicated by the intense stretches of the ClO_4^- ion, which occur at similar frequency. The electronic absorption spectra of the complexes show two intense absorption bands in acetonitrile [λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): **1**, 524 (2910), 654

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

Table 1 Atomic coordinates of $[ReO(L)(OMe)_2]ClO_4{\cdot}MeCN{\cdot}H_2O$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	0.157 02(3)	0.091 75(2)	0.227 71(2)	C(15)	0.382 7(7)	−0.118 2(5)	0.209 7(5)
O(1)	0.117 4(5)	0.124 3(3)	0.126 9(3)	C(16)	0.389 6(7)	−0.121 2(5)	0.104 7(5)
N(1)	−0.000 4(6)	0.249 4(4)	0.305 0(4)	C(17)	0.485 0(8)	−0.200 6(5)	0.022 5(5)
N(2)	0.114 0(5)	0.140 4(4)	0.404 6(4)	C(18)	0.481 7(8)	−0.199 9(6)	−0.074 3(5)
N(3)	0.288 9(5)	−0.030 8(4)	0.279 4(4)	C(19)	0.375 5(8)	−0.124 1(6)	−0.091 2(5)
N(4)	0.292 1(5)	−0.045 3(4)	0.091 3(3)	C(20)	0.283 5(8)	−0.047 2(5)	−0.006 6(5)
C(1)	−0.053 5(9)	0.303 1(6)	0.250 0(5)	C(21)	−0.063 5(8)	−0.107 0(6)	0.142 3(5)
C(2)	−0.155 7(9)	0.397 3(6)	0.289 3(6)	C(22)	0.406 8(8)	0.268 0(6)	0.378 1(5)
C(3)	−0.208 5(8)	0.436 8(6)	0.392 6(6)	O(2)	−0.052 5(4)	0.006 9(3)	0.206 0(3)
C(4)	−0.152 0(8)	0.384 6(6)	0.451 9(5)	O(3)	0.385 1(5)	0.160 5(3)	0.296 8(3)
C(5)	−0.046 8(7)	0.290 8(5)	0.406 8(5)	Cl	0.341 5(3)	0.509 3(2)	0.237 2(2)
C(6)	0.019 7(7)	0.232 6(5)	0.464 2(5)	O(4)	0.403 9(11)	0.557 1(9)	0.343 0(6)
C(7)	−0.006 8(8)	0.263 7(6)	0.571 8(5)	O(5)	0.221 2(9)	0.582 7(6)	0.222 0(5)
C(8)	0.060 8(9)	0.200 2(7)	0.617 5(5)	O(6)	0.468 3(8)	0.483 6(7)	0.171 4(6)
C(9)	0.153 2(8)	0.102 8(6)	0.556 2(5)	O(7)	0.262 7(12)	0.416 3(7)	0.210 5(11)
C(10)	0.177 6(7)	0.078 1(5)	0.450 1(4)	O(8)	−0.314 9(5)	0.065 9(4)	0.343 7(3)
C(11)	0.275 3(7)	−0.020 6(5)	0.379 6(5)	N(5)	0.793 1(10)	0.634 7(6)	0.110 0(6)
C(12)	0.348 4(8)	−0.095 1(6)	0.411 3(5)	C(23)	0.795 8(10)	0.543 2(7)	0.072 1(6)
C(13)	0.439 6(8)	−0.185 9(6)	0.338 9(6)	C(24)	0.805 4(15)	0.425 4(8)	0.022 2(8)
C(14)	0.457 2(8)	−0.194 8(6)	0.237 5(5)				

Table 2 Atomic coordinates of $[ReN(L)(PPh_3)Cl]ClO_4{\cdot}MeCN$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	0.465 12(4)	0.139 71(2)	0.140 93(1)	C(20)	0.429 7(9)	0.342 3(5)	0.121 1(3)
P	0.705 7(2)	0.132 7(1)	0.182 07(6)	C(1A)	0.816 2(8)	0.230 6(4)	0.173 5(3)
Cl	0.252 9(2)	0.128 2(2)	0.084 07(7)	C(2A)	0.753 8(9)	0.312 2(5)	0.182 5(3)
N	0.412 1(7)	0.202 8(4)	0.185 7(2)	C(3A)	0.826 6(9)	0.390 4(5)	0.179 9(3)
N(1)	0.368 2(6)	0.030 0(4)	0.184 5(2)	C(4A)	0.966 1(11)	0.389 4(5)	0.168 6(3)
N(2)	0.507 6(6)	−0.010 9(3)	0.108 1(2)	C(5A)	1.033 2(10)	0.309 8(6)	0.161 4(4)
N(3)	0.600 9(6)	0.129 5(4)	0.066 6(2)	C(6A)	0.956 7(10)	0.231 3(5)	0.164 5(4)
N(4)	0.501 4(7)	0.271 1(3)	0.105 4(2)	C(1B)	0.725 5(8)	0.127 5(4)	0.250 3(3)
C(1)	0.289 9(9)	0.052 9(5)	0.222 4(3)	C(2B)	0.863 3(9)	0.120 9(5)	0.273 2(3)
C(2)	0.215 8(10)	−0.007 7(6)	0.248 7(3)	C(3B)	0.887 2(9)	0.120 2(5)	0.325 0(3)
C(3)	0.219 7(10)	−0.095 5(6)	0.235 9(3)	C(4B)	0.772 4(11)	0.125 6(6)	0.352 9(3)
C(4)	0.297 0(9)	−0.120 3(5)	0.197 7(3)	C(5B)	0.639 9(9)	0.134 0(6)	0.331 8(3)
C(5)	0.370 3(8)	−0.057 1(5)	0.172 1(3)	C(6B)	0.612 6(8)	0.134 7(5)	0.279 6(2)
C(6)	0.453 5(9)	−0.079 9(4)	0.131 2(3)	C(1C)	0.807 0(8)	0.035 7(5)	0.165 0(3)
C(7)	0.476 8(9)	−0.168 2(5)	0.117 1(3)	C(2C)	0.780 9(9)	−0.043 2(5)	0.189 4(3)
C(8)	0.552 3(9)	−0.182 8(5)	0.075 7(3)	C(3C)	0.843 2(10)	−0.121 6(5)	0.177 3(3)
C(9)	0.609 6(9)	−0.113 2(5)	0.052 4(3)	C(4C)	0.931 4(11)	−0.122 7(5)	0.140 5(4)
C(10)	0.584 1(8)	−0.027 2(5)	0.069 3(3)	C(5C)	0.959 9(10)	−0.045 3(6)	0.116 2(3)
C(11)	0.642 4(8)	0.052 5(5)	0.047 0(3)	C(6C)	0.891 8(9)	0.033 3(5)	0.127 2(3)
C(12)	0.729 6(10)	0.050 1(5)	0.007 8(3)	Cl(1)	0.210 04(23)	0.636 06(15)	0.103 25(8)
C(13)	0.782 1(10)	0.130 7(7)	−0.009 1(3)	O(1)	0.338 9(6)	0.632 6(4)	0.078 5(2)
C(14)	0.737 6(10)	0.208 7(5)	0.010 2(3)	O(2)	0.248 5(9)	0.649 7(7)	0.154 1(3)
C(15)	0.645 6(8)	0.205 7(5)	0.047 3(3)	O(3)	0.138 2(9)	0.559 4(5)	0.100 2(4)
C(16)	0.582 4(8)	0.286 3(5)	0.067 3(3)	O(4)	0.126 4(8)	0.705 4(5)	0.087 8(3)
C(17)	0.602 8(9)	0.370 7(5)	0.048 0(3)	N(20)	0.272 1(12)	0.358 6(9)	0.983 2(3)
C(18)	0.537 7(11)	0.441 0(5)	0.066 1(3)	C(21)	0.172 4(14)	0.372 7(12)	1.002 0(4)
C(19)	0.449 9(10)	0.426 6(5)	0.102 7(3)	C(22)	0.059 0(14)	0.371 6(12)	1.031 4(4)

(1480); **2**, 443 (3240), 558 (2300)]. The ^1H NMR spectra of **1** and **2** are much more complicated than that of the protonated form of the ligand.[4] The aromatic protons appeared as multiplets in the regions δ 7.6–9.3. For **1** the OCH_3 protons appear as a singlet at δ 3.53.

The structures of the complexes have been characterized by X-ray crystallography. Figs. 1 and 2 show perspective views of the $[ReO(L)(OMe)_2]^+$ and $[ReN(L)(PPh_3)Cl]^+$ cations respectively with atom numbering. The structures feature the first examples of seven-co-ordinated d^2 oxo- and nitrido-metal complexes. In both **1** and **2** the co-ordination geometry about the rhenium atom is a distorted pentagonal bipyramid [O(2)–Re–O(3) 157.1(2) for **1** and Cl–Re–P 166.04(6) for **2**] with the oxo and nitrido moieties being almost coplanar with the ligand L. The measured Re=O distance in **1** and Re≡N distance in **2** are 1.666(4) and 1.647(6) Å respectively, in accord with a triple bond formulation. These values are consistent with those reported for other monooxo- and nitrido-rhenium(V) complexes (Re=O 1.63–1.71, Re≡N 1.60–1.66 Å).[7] In **1** the measured N(1)–Re–N(4) void angle of 154.5(2)° is somewhat less than the related value of 161.9(2)° in **2**. A direct comparison between the two structures with that of $[Ni(L)(MeCN)_2][PF_6]_2$[4] and $[Co(L)(H_2O)(SO_3)]NO_3{\cdot}H_2O$[8] reveals that the six-co-ordinated metal complexes have much smaller N(1)–M–N(4) void angles which are 126.0(2) and 114.3(2)° for the nickel and cobalt complexes respectively. The Re–N(2) and Re–N(3) distances of 2.479(5) and 2.474(5) Å in **2** are considerably longer than the corresponding values of 2.292(4) and 2.279(5) Å in **1** in accord with the changes in the N(1)–Re–N(4) void angles in the two structures. These Re–N(L) distances, however, are longer than the normal values for a Re–N(amine) bond. For example, the Re–N distances in *trans*-$[ReO_2(en)_2]Cl$ (en = ethane-1,2-diamine) and *trans*-$[ReO_2(py)_4]Cl$ (py = pyridine) are 2.150(9)–2.191(8) and 2.139(9)–2.166(14) Å respectively.[9]

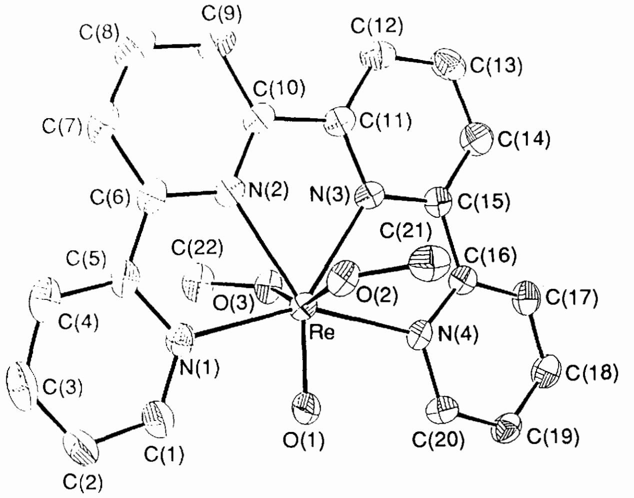

Fig. 1 Perspective view of the $[ReO(L)(OMe)_2]^+$ cation with atom numbering

Table 3 Selected bond distances (Å) and angles (°)

$[ReO(L)(OMe)_2]^+$			
Re–O(1)	1.666(4)	Re–N(4)	2.243(4)
Re–N(1)	2.250(5)	Re–O(2)	1.989(4)
Re–N(2)	2.292(4)	Re–O(3)	1.983(4)
Re–N(3)	2.279(5)		
O(1)–Re–N(1)	77.3(2)	O(1)–Re–N(4)	77.2(2)
O(1)–Re–O(2)	101.5(2)	O(1)–Re–O(3)	101.5(2)
O(2)–Re–O(3)	157.1(2)	N(1)–Re–N(4)	154.5(2)
N(1)–Re–N(2)	68.5(2)	N(2)–Re–N(3)	68.5(2)
N(3)–Re–N(4)	68.5(2)	Re–O(2)–C(21)	123.9(3)
$[ReN(L)(PPh_3)Cl]^+$			
Re–N	1.647(6)	Re–P	2.437(2)
Re–Cl	2.418(2)	Re–N(1)	2.264(6)
Re–N(2)	2.479(5)	Re–N(3)	2.474(5)
Re–N(4)	2.237(5)		
P–Re–Cl	166.04(6)	P–Re–N	91.1(2)
Cl–Re–N	102.8(2)	N(1)–Re–N(2)	66.6(2)
N(2)–Re–N(3)	62.9(2)	N(3)–Re–N(4)	66.4(2)
N(1)–Re–N(4)	161.9(2)	P–Re–N(1)	97.6(2)
N–Re–N(1)	83.1(3)		

The cyclic voltammogram of complex **1** in acetonitrile displays a reversible couple at 0.39 V *vs.* ferrocenium–ferrocene assignable to the Re^{VI}–Re^{V} couple (Fig. 3). For **2** the cyclic voltammogram shows a similar reversible Re^{VI}–Re^{V} couple at 0.75 V. These observations suggest that seven-co-ordinated oxo- and nitrido-rhenium(VI) complexes of L are stable in the time-scale of cyclic voltammetric scans. An irreversible reduction wave at −1.58 V was also observed for **2** in acetonitrile.

Seven-co-ordinated metal complexes are usually thought to involve a large metal ion in order to reduce the coulombic and steric repulsion. The present study suggests a large covalent radius of the rhenium atom in oxo- and nitrido-rhenium(V) despite its high oxidation state. Previous works by Conry and Mayer[10] indicated that rhenium(III) complexes of polypyridine ligands are potent reagents for oxygen-, nitrogen- and sulfur-atom abstraction reactions. Thus it is not unreasonable to speculate that similar chemistry may be encountered in six-co-ordinated rhenium(III) complexes of ligand L.

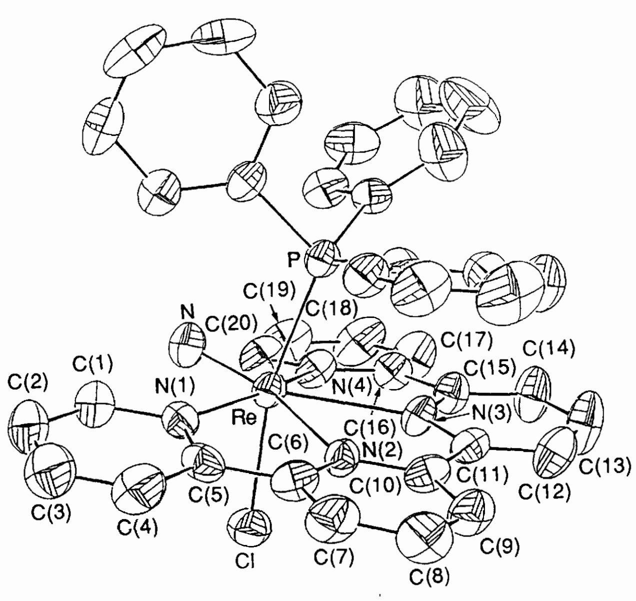

Fig. 2 Perspective view of the $[ReN(L)(PPh_3)Cl]^+$ cation with atom numbering

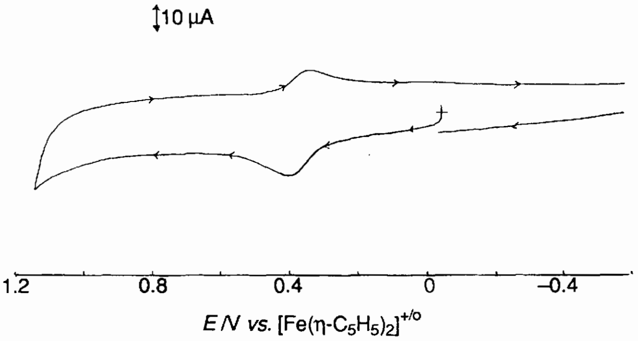

Fig. 3 Cyclic voltammogram of $[ReO(L)(OMe)_2]ClO_4$ in acetonitrile with 0.1 mol dm^{-3} tetrabutylammonium fluorophosphate as supporting electrolyte. Working electrode: edge-plane pyrolytic graphite. Scan rate: 100 mV s^{-1}

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