Oxo-rhenium(V) complexes with 8hydroxyquinoline derivatives

Olivier Sigouin and André L. Beauchamp

Abstract: Compounds of the types $\text{ReOCl}_2(\text{L})(\text{PPh}_3)$ and $\text{ReOCl}(\text{L})_2$ were prepared by reacting $\text{ReOCl}_3(\text{PPh}_3)_2$ with 8-hydroxyquinoline (HL) and its 2-methyl, 2-chloro, 5-chloro, 5-nitro, 5,7-dichloro, 5,7-dibromo, and 5,7-diiodo derivatives. With the bulky 2-phenyl-8-hydroxyquinoline, only $\text{ReOCl}_2(\text{L})(\text{PPh}_3)$ could be isolated, whereas the still bulkier 2*tert*-butyl derivative did not react. For $\text{ReOCl}_2(\text{L})(\text{PPh}_3)$, the coordination of the quinoline oxygen trans to the Re=O bond and the cis-dichloro arrangement in the equatorial plane were established from crystallographic studies on the 2chloro and the 5,7-dibromo complexes. From the combined data for these various derivatives, the ¹H NMR signals could be fully assigned. With both series of compounds, a complex *d*–*d* absorption pattern is observed in the visible spectra, corresponding to the excitation of a *d* electron from the interaxial *d* orbital in the equatorial plane to the empty d_{xz} and d_{yz} orbitals, which are inequivalent in these low-symmetry systems. Deconvolution revealed the presence of two very weak low-energy components (~10 000 and ~12 000 cm⁻¹), which are assigned to the two expected singlet–triplet transitions, whereas two stronger bands at higher energy (~14 000 and ~17 000 cm⁻¹) originate from the two singlet– singlet transitions. These bands are not substantially displaced by substitution on the 8-hydroxyquinoline rings.

Key words: rhenium, quinoline, crystal structure, d-d electron transitions.

Résumé : Des composés de types ReOCl₂(L)(PPh₃) et ReOCl(L)₂ ont été préparés par réaction de ReOCl₃(PPh₃)₂ avec la 8-hydroxyquinoline (HL) et ses dérivés 2-méthyl, 2-chloro, 5-chloro, 5-nitro, 5,7-dichloro, 5,7-dibromo et 5,7-diiodo. Avec le ligand encombré 2-phényl-8-hydroxyquinoline, seul ReOCl₂(L)(PPh₃) a pu être isolé, alors que le dérivé 2-*tert*butyl encore plus encombré n'a pas réagi. Pour ReOCl₂(L)(PPh₃), la coordination de l'oxygène de la quinoline en trans de la liaison Re=O et l'arrangement cis-dichloro dans le plan équatorial ont été déterminés au moyen d'études cristallographiques sur les complexes des ligands 2-chloro et 5,7-dibromo. L'ensemble des données pour ces différents dérivés a permis de faire une attribution complète des signaux RMN ¹H. Pour les deux séries de composés, un motif d'absorption *d*-*d* compliqué est observé dans le spectre visible, qui correspond à l'excitation d'un électron *d* depuis l'orbitale *d* interaxiale dans le plan équatorial vers les orbitales vacantes d_{xz} et d_{yz} , qui ne sont pas équivalentes dans ces systèmes de basse symétrie. La déconvolution révèle la présence de deux composantes très faibles à basse énergie (~10 000 et ~12 000 cm⁻¹), qui sont attribuées aux deux transitions singulet–triplet attendues, tandis que les bandes plus fortes à énergie supérieure (~14 000 et ~17 000 cm⁻¹) proviennent de deux transitions singulet–singulet. Ces bandes ne sont pas déplacées appréciablement par substitution sur le cycle de la 8-hydroxyquinoline.

Mots clés : rhénium, quinoline, structure cristalline, transitions électroniques d-d.

Introduction

Systems giving rise to electronic transitions between lowspin and high-spin states at low energy cost present considerable interest, since they may provide a basis for developing molecular switches and devices for efficient information storage. The d^2 oxo-rhenium(V) core is a stable unit in which the ground state is low-spin and diamagnetic, since the strong π bonds formed via the oxygen p_x and p_y orbitals raise the d_{xz} and d_{yz} orbitals (LUMO) above the other interaxial d orbital (HOMO) in which the two d electrons are coupled. However, if the HOMO–LUMO gap could be reduced and become comparable with the pairing energy, the molecule could adopt a high-spin triplet ground state or possess a readily accessible high-spin excited state that could be involved in spin crossover processes.

In a previous study (1), the HOMO–LUMO gap was found to be relatively small in ReOCl(P~O)₂ compounds containing bidentate mixed P~O⁻ ligands. To better understand the factors affecting the HOMO–LUMO gap, we recently examined various ReOX₃(dppe) and ReO(OR)X₂-(dppe) complexes, where the coordination sphere remained close to that of the ReOCl(P~O)₂ species and the equatorial *cis-P,P* arrangement was provided by bis(diphenylphosphino)ethane(dppe) (2). The presence of a strong π -donor RO⁻ group trans to the Re=O bond in ReO(OR)X₂(dppe) was found to produce an energy gap greater than those of the ReOX₃(dppe) compounds, where the trans position is occu-

Received 6 October 2004. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 12 May 2005.

¹Corresponding author (e-mail: andre.beauchamp@umontreal.ca).

O. Sigouin and A.L. Beauchamp.¹ Département de chimie, Université de Montréal, C.P. 6128, Succursale Centre-ville, Montréal, QC H3C 3J7, Canada.

pied by a halogen. The present study was intended to determine to what extent the energy gap is sensitive to π interactions with donor atoms in the equatorial plane. To this end, we selected the 8-hydroxyquinoline ligand. Although little is known about the influence of this ligand on *d*–*d* transitions, it was hoped that the Re(V) complexes could provide information about the interaction of its aromatic π system with the interaxial *d* orbitals: when coordinated in the equatorial plane, the π system should interact with the d_{xz} and d_{yz} orbitals, whereas coordination parallel to the Re=O direction would generate interactions with the third interaxial orbital.

We are reporting here the preparation and characterization of $\text{ReOCl}_2(L)(\text{PPh}_3)$ and $\text{ReOCl}(L)_2$ compounds with a series of variously substituted deprotonated 8-hydroxyquinolines (L^-) (I). The low-energy UV–vis spectra were found to be rather insensitive to ring substitution, but in contrast with the dppe compounds studied earlier, all four expected lowenergy *d*–*d* bands could be unraveled from the complicated spectral pattern observed.



Experimental section

Reactants and methods

8-Hydroxyquinoline (Hqn),² most of its derivatives (2methyl, 5-monosubstituted and 5,7-disubstituted), KReO₄, and all other reactants were obtained from Aldrich and used without further purification. 2-Phenyl- and 2-*tert*-butyl-8hydroxyquinoline were prepared as described by Delapierre et al. (3). The preparation of 2-chloro-8-hydroxyquinoline is described in the following. ReOCl₃(PPh₃)₂ (4) was prepared by the literature method.

IR spectra were recorded on PerkinElmer Spectrum One (4000–400 cm⁻¹, KBr pellets) or Bio-Rad Excalibur series FTS 3000FX (4000–200 cm⁻¹, CsI pellets). The NMR spectra were measured with Bruker AV-300, AMX-300, AV-400, or ARX-400 spectrometers. For the ¹H spectra, the residual solvent signal (DMSO- d_6 (2.50 ppm), acetone- d_6 (2.17 ppm), CDCl₃ (7.26 ppm), CD₃OD (3.31 ppm)) was used as internal reference. H₃PO₄ was used as an external reference ($\delta = 0$) for the ³¹P spectra. Electronic spectra were recorded as DMSO, chloroform, or dichloromethane solutions in quartz cells with a UV–vis–near-IR Cary 5E spectrometer. Elemental analyses were run at the Laboratoire d'Analyse Élémentaire de l'Université de Montréal.

Preparation of 2-chloro-8-hydroxyquinoline

This ligand was prepared by reacting $POCl_3$ with 2,8dihydroxyquinoline obtained from Hqn via the *N*-oxide (5– 7).

In glacial acetic acid (25 mL) and 30% H_2O_2 (10 mL) were dissolved 4.00 g (27.6 mmol) of Hqn. The mixture was heated at 70 °C for 16 h and after cooling to room temperature (RT), pH was adjusted to 12 with NH₄OH. The brown solid was collected by filtration and extracted with a hexane–acetone (10:1) mixture. Solvent evaporation yielded yellow crystals of Hqn-*N*-oxide (1.47 g, yield 33%); mp 138 °C (lit. value (5) mp 138–140 °C).

The Hqn-*N*-oxide (3.85 g, 23.9 mmol) was dissolved in acetic anhydride and heated at 140 °C for 5 h. The solvent was removed under reduced pressure and the dark-gray solid was washed with ethanol to give light-yellow 8-acetoxy-2-hydroxyquinoline (1.90 g, yield 39%). ¹H NMR (CDCl₃, ppm) δ : 10.17 (br s, 1H, OH), 7.80 (d, *J* = 9.5 Hz, H4), 7.44 (dd, *J*₁ = 7.9 Hz, *J*₂ = 1.2 Hz, H5), 7.37 (dd, *J*₁ = 7.9 Hz, *J*₂ = 1.2 Hz, H7), 7.21 (t, *J* = 7.9 Hz, H6), 6.68 (d, *J* = 9.6 Hz, H3), 2.51 (s, *CH*₃COO). Anal. calcd. for C₁₁H₉NO₃ (%): C 65.02, H 4.46, N 6.89; found: C 64.89, H 4.56, N 6.83.

The 8-acetoxy-2-hydroxy derivative was dissolved in methanol with 1 equiv. of K_2CO_3 and the reaction mixture was stirred at RT for 1 h. The solvent was evaporated, the brown product was dissolved in water, and a 10% HCl solution was slowly added. Colorless 2,8-dihydroxyquinoline was collected by filtration (1.40 g, yield 93%). ¹H NMR (CD₃OD, ppm) δ : 7.99 (d, J = 9.5 Hz, H4), 7.18 (dd, $J_1 = 7.9$ Hz, $J_2 = 1.2$ Hz, H5), 7.12 (t, J = 7.8 Hz, H6), 7.02 (dd, $J_1 = 7.7$ Hz, $J_2 = 1.2$ Hz, H7), 6.66 (d, J = 9.5 Hz, H3). Anal. calcd. for C₉H₇NO₂ (%): C 67.07, H 4.38, N 8.69; found: C 66.31, H 4.22, N 8.40.

The dihydroxy compound was dissolved in excess POCl₃ (10 mL) and heated on a steam bath for 1 h. The mixture was slowly transferred into a mixture of ice (75 g) and NH₄OH (37 mL). The white solid was filtered and dissolution in concd. HCl (75 mL) gave a clear yellow solution, which was heated on a steam bath for 1 h. A Na₂CO₃ solution (1.8 mol/L, 200 mL) was then added to precipitate the light-brown solid, which was collected by filtration and purified by chromatography on silica gel with hexane - ethyl acetate (80:20) as eluent. After solvent evaporation, the solid was dissolved in methanol, water was added to cloudiness, and the mixture was placed in the freezer for a few hours. The white crystalline solid (0.68 g, yield 41%) was filtered and dried in vacuo. ¹H NMR (CDCl₃): see Table 1. Anal. calcd. for C₉H₆ClNO (%): C 60.19, H 3.37, N 7.80; found: C 59.81, H 3.17, N 7.80.

Preparation of the ReOCl₂(L)(PPh₃) compounds

These compounds were prepared following the method of Mazzi et al. (8), but benzene was replaced by THF as the solvent and reaction time was adjusted for each system.

In a typical run, $\text{ReOCl}_3(\text{PPh}_3)_2$ (0.12 mmol) was stirred in a refluxing solution of the ligand (0.12 mmol) in THF (10 mL). The colorless or yellow solution turned green first

²The neutral ligand is represented by Hqn and the coordinated deprotonated form by qn⁻. The various derivatives are identified by an appropriate prefix showing the positions of the substituents: for instance, 2-Cl-qn⁻ for the 2-chloro-8-hydroxyquinoline anion.

		manos Sundaos ana (m		(Thus company h fu			
	H-2	H-3	H-4	H-5	H-6	Н-7	H-10
du	8.84 (dd, 4.0, 1.6)	7.54 (dd, 8.4, 4.2)	8.32 (dd, 8.3, 1.6)	7.38 (dd, 8.3, 1.7)	7.44 (t, 7.7)	7.07 (dd, 7.1, 1.6)	9.83 (s, br)
2-Me-qn	2.66 (s, CH ₃)	7.41 (d, 8.4)	8.18 (d, 8.4)	7.32 (d, 6.5)	7.35 (t, 8.0)	7.04 (d, 6.6)	9.41 (s, br)
$2-CI-qn^b$		7.40 (d, 8.6)	8.10 (d, 8.6)	7.33 (dd, 8.2, 1.1)	7.47 (t, 7.9)	7.22 (dd, 7.7, 1.1)	7.68 (s, br)
2-Ph-qn ^{b,c}		7.68 (d, 8.4)	8.28 (d, 8.3)	7.37 (d, 6.6)	7.47 (dd, 7.0, 2.4)	$7.26 (d)^d$	8.68 (s, br)
2-t-Bu-qn ^b	1.47 (s, <i>t</i> -Bu)	7.55 (d, 8.7)	8.08 (d, 8.7)	7.28 (d, 8.1)	7.39 (t, 7.9)	7.15 (d, 7.4)	8.37 (s, br)
5-Cl-qn	8.95 (dd, 4.0, 1.0)	7.85 (dd, 8.4, 5.2)	8.49 (dd, 8.5, 1.5)		7.60 (d, 8.4)	7.08 (d, 8.4)	10.14 (s, br)
5-NO ₂ -qn	9.01 (d, 3.8)	7.88 (dd, 8.8, 4.1)	8.54 (d, 8.8)		9.15 (d, 8.9)	7.19 (d, 8.8)	в
5,7-Cl ₂ -qn	9.00 (dd, 4.0, 1.1)	7.77 (dd, 8.5, 4.3)	8.52 (dd, 8.5, 1.1)		7.84 (s)		в
$5,7-Br_2-qn$	8.96 (dd, 4.0, 0.9)	7.90 (dd, 8.5, 4.1)	8.45 (dd, 8.5, 1.0)		8.07 (s)		в
5,7-I ₂ -qn	8.87 (dd, 4.1, 1.0)	7.73 (dd, 8.5, 4.1)	8.29 (dd, 8.6, 1.0)		8.34 (s)		в
^a In DMSO-a	6, except when otherwise sta	ited.					

'In CDCI₃.

Phenyl resonances: 7.49–7.62 ppm (m, 3H), 8.17 (dd, 2H, $^{3}J = 5.8$ Hz, $^{4}J = 1.6$ Hz) ⁴Interference with the CDCI₃ peak. Not observed Can. J. Chem. Vol. 83, 2005

and then became very dark. When the reaction was stopped, the solvent was evaporated to dryness, the solid was redissolved in dichloromethane (acetone for the 2-Cl-qn compound), precipitated with diethyl ether, filtered, washed with acetone and diethylether, and dried in vacuo. For the less soluble Hqn complex, a precipitate was present at the end of the reaction and solvent evaporation was unnecessary.

Details for each compound are provided in the following. In all cases, the ¹H NMR spectra showed multiplets between 7.2 and 7.5 ppm for coordinated PPh₃. The remaining signals are listed in Table 1.

$ReOCl_2(qn)(PPh_3)$

The brown precipitate was filtered from the reaction mixture after 19 h. Yield: 87%. IR (CsI, cm⁻¹): 976 (s) v(Re=O), 347 (w), 293 (w) v(Re-Cl). ³¹P NMR (DMSO- d_6) (ppm) δ : -12.5 (s). Anal. calcd. for C₂₇H₂₁Cl₂NO₂PRe (%): C 47.72, H 3.11, N 2.06; found: C 47.57, H 3.02, N 2.13.

$ReOCl_2(2-Me-qn)(PPh_3)$

Reaction time: 24 h. Green-brown solid. Yield: 77%. IR (CsI, cm^{-1}) : 972 (s) v(Re=O), 314 (w), 284 (w) v(Re-Cl). ³¹P NMR (DMSO- d_6 , ppm) δ : -17.4 (s). Anal. calcd. for C₂₈H₂₃Cl₂NO₂PRe (%): C 48.49, H 3.34, N 2.02; found: C 48.37, H 3.42, N 2.01.

$ReOCl_2(2-Cl-qn)(PPh_3)$

Reaction time: 2 h. Recrystallization in acetone gave a green solid containing one lattice acetone molecule per formula. Yield: 63%. IR (CsI, cm⁻¹): 977 (s) v(Re=O), 324 (w), 281 (w) v(Re-Cl). ³¹P NMR (DMSO- d_6 , ppm) δ: -18.0 (s). Anal. calcd. for C₃₀H₂₆Cl₃NO₃PRe (%): C 46.67, H 3.39, N 1.81; found: C 46.71, H 3.28, N 1.75.

$ReOCl_2(2-Ph-qn)(PPh_3)$

Reaction time: 23 h. Green-brown solid. Yield: 42%. IR (CsI, cm⁻¹): 974 (s) v(Re=O), 328 (w), 279 (w) v(Re-Cl). ³¹P NMR (DMSO- d_6 , ppm) δ : -16.7 (s). Anal. calcd. for C₃₃H₂₅Cl₂NO₂PRe (%): C 50.03, H 3.27, N 1.74; found: C 49.82, H 3.31, N 1.79.

$ReOCl_2(5-Cl-qn)(PPh_3)$

Reaction time: 24 h. Brown solid. Yield: 91%. IR (CsI, cm^{-1}) : 980 (s) v(Re=O), 345 (w), 296 (w) v(Re-Cl). ³¹P NMR (DMSO- d_6 , ppm) δ : -12.1 (s). Anal. calcd. for C₂₇H₂₀Cl₃NO₂PRe (%): C 45.42, H 2.82, N 1.97; found: C 45.21, H 2.75, N 2.02.

$ReOCl_2(5,7-Cl_2-qn)(PPh_3)$

Reaction time: 21 h. Brown solid. Yield: 85%. IR (CsI, cm⁻¹): 980 (s) v(Re=O), 311 (w), 282 (w) v(Re-Cl). ³¹P NMR (DMSO- d_6 , ppm) δ : -12.4 (s). Anal. calcd. for C₂₇H₁₉Cl₄NO₂PRe (%): C 43.33, H 2.56, N 1.87; found: C 43.03, H 2.57, N 1.78.

$ReOCl_2(5, 7-Br_2-qn)(PPh_3)$

Reaction time: 21 h. Brown solid. Yield: 83%. IR (CsI, cm⁻¹): 984 (s) v(Re=O), 324 (w), 279 (w) v(Re-Cl). ³¹P NMR (DMSO- d_6 , ppm) δ : -10.8 (s). Anal. calcd. for C₂₇H₁₉Br₂Cl₂NO₂PRe (%): C 38.73, H 2.29, N 1.67; found: C 37.43, H 2.07, N 1.66.

$ReOCl_2(5,7-I_2-qn)(PPh_3)$

Reaction time: 21 h. Brown solid. Yield: 93%. IR (CsI, cm⁻¹): 984 (s) v(Re=O), 324 (w), 290 (w) v(Re-Cl). ³¹P NMR (DMSO- d_6 , ppm) δ : -10.9 (s). Anal. calcd. for C₂₇H₁₉Cl₂I₂NO₂PRe (%): C 34.82, H 2.06, N 1.50; found: C 34.87, H 1.75, N 1.49.

$ReOCl_2(5-NO_2-qn)(PPh_3)$

Prepared according to Chen et al. (9). Deep-green solid. Yield: 81%. IR (CsI, cm⁻¹): 977 (s) v(Re=O), 324 (w), 285 (w) v(Re-Cl). ³¹P NMR (DMSO- d_6 , ppm) δ : –9.3 (s). Anal. calcd. for C₂₇H₂₀Cl₂N₂O₄PRe (%): C 44.76, H 2.78, N 3.87; found: C 44.71, H 2.78, N 3.87.

Preparation of the ReOCl(L)₂ compounds

These compounds were obtained according to Mazzi et al. (8), but the solvent used was THF instead of benzene. In a typical run, ReOCl₃(PPh₃)₂ (500 mg, 0.60 mmol) was added to a refluxing solution of the ligand (1.3 mmol) and Et₃N (0.2 mL, 1.44 mmol) in THF (50 mL). The mixture was stirred and the dark-brown or greenish-brown solid was filtered, washed with diethylether, rinsed with water to remove (Et₃NH)Cl, and finally dried in vacuo. Individual details are provided in the following and the ¹H NMR data are given in Table 1.

$ReOCl(qn)_2$

Reaction time: 20 h. Brown solid. Yield: 82%. IR (CsI, cm⁻¹): 968 (s) v(Re=O), 312 (w) v(Re-Cl). Anal. calcd. for $C_{18}H_{12}ClN_2O_3Re$ (%): C 41.11, H 2.30, N 5.33; found: C 40.49, H 2.20, N 5.26.

$ReOCl(2-Me-qn)_2$

Reaction time: 20 h. Brownish-green solid. Yield: 56%. IR (CsI, cm⁻¹): 970 (s) v(Re=O), 320 (w), v(Re-Cl). Anal. calcd. for $C_{20}H_{16}ClN_2O_3Re$ (%): C 43.36, H 2.91, N 5.06; found: C 42.72, H 2.88, N 4.97.

$ReOCl(2-Cl-qn)_2$

Reaction time: 3 h. Green solid. The compound recrystallized from CH_2Cl_2 contained 0.8 lattice solvent molecules per formula. Yield: 57%. IR (CsI, cm⁻¹): 968 (s) v(Re=O), 324 (w), v(Re-Cl). Anal. calcd. for $C_{18.8}H_{11.6}Cl_{4.6}N_2O_3Re$ (%): C 34.07, H 1.76, N 4.23; found: C 34.19, H 1.91, N 4.17.

$ReOCl(5-Cl-qn)_2$

Reaction time: 21 h. Dark-brown solid. Yield: 31%. IR (CsI, cm⁻¹): 976 (s) v(Re=O), 324 (w) v(Re-Cl). Anal. calcd. for $C_{18}H_{10}Cl_3N_2O_3Re$ (%): C 36.34, H 1.69, N 4.71; found: C 36.29, H 1.74, N 4.34.

$ReOCl(5-NO_2-qn)_2$ and $ReOCl(5,7-X_2-qn)_2$ for X = Cl, Br, I

The dark-brown raw solids contained a small amount of $ReOCl_2(L)(PPh_3)$ that could not be totally removed by chro-

matography on silica gel. The ¹H NMR data for these 2:1 species are included in Table 1.

Crystallographic measurements and structure determination

Dark-green crystals of ReOCl₂(2-Cl-qn)(PPh₃) were obtained by slow evaporation of an acetone solution. A crystal was mounted on a Bruker SMART CCD 2K diffractometer operating with graphite-monochromatized CuKa radiation and controlled by the SMART software (10). Sets of 30 oscillation frames of 0.3° over a range of 9° were recorded in four regions of the reciprocal space, from which the reduced cell was determined by least-squares refinement. For data collection, frames were recorded for different orientations of the crystal and detector so as to cover at least 95% of the reciprocal sphere. At the end, the first 101 frames were remeasured and the intensities of the 907 reflections did not show any decomposition of the crystal. The frames were analyzed with the SAINT software (11), which determined the intensity and the position of each spot. Accurate cell parameters were obtained by least-squares refinement over the positions of the whole data set. Irregular crystal shapes precluded the calculation of an analytical correction for absorption, but an empirical correction was applied using SADABS (12).

The SHELXTL system (13) was used for all calculations and drawings. The coordinates of the Re atoms were determined by direct methods and the positions of all other nonhydrogen atoms were found by the standard Fourier method. The structures were refined on F_0^2 using all reflections. The H atoms were fixed using a riding model with $U_{iso} = 1.2 \times U_{eq}$ of the atom to which they are bonded. Crystal data are listed in Table 2.³

Brown crystals of $\text{ReOCl}_2(5,7-\text{Br}_2-\text{qn})(\text{PPh}_3)$ were obtained by recrystallization in CH₂Cl₂-pentane. The crystallographic study was carried out with an Enraf-Nonius CAD-4 diffractometer operating with CuKα radiation under the control of the CAD-4 software (14). The reduced cell was initially determined from 20-25 spots located on a preliminary rotation photograph and centered in the detector aperture. Accurate cell parameters were then determined from the positions of 25 high-angle reflections centered with the SETANG and DETTH procedures. The intensities were recorded by $\omega/2\theta$ scan. Possible crystal decomposition was monitored by measuring five standard reflections every hour. All data in the whole sphere were collected at room temperature. An absorption correction based on the crystal geometry was applied. The data were finally corrected for the effects of Lorentz and polarization, and averaged to provide the basic two-octant set.

The non-hydrogen atoms of the complex molecule were located and refined as stated previously. In the subsequent ΔF map, two regions centered on the inversion centers at (0, 0, 1/2) and (0, 0, 0), respectively, contained a number of small peaks owing to severely disordered solvent. No consis-

³ Supplementary data for this article are available on the Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 3653. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 251781 and 251782 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

	ReOCl ₂ (2-Cl-qn)(PPh ₃)	$\text{ReOCl}_2(5,7-\text{Br}_2-\text{qn})(\text{PPh}_3)$
Formula	C ₂₇ H ₂₀ Cl ₃ NO ₂ PRe	C ₂₇ H ₁₉ Br ₂ Cl ₂ NO ₂ PRe-(CH ₂ Cl ₂) _{0.75} (C ₅ H ₁₂) _{0.40}
Formula weight	713.96	929.91
Crystal shape	Dark-green blocks	Brown platelets
<i>T</i> (K)	220(2)	220(2)
Diffractometer	Smart CCD	CAD-4
Crystal system	Monoclinic	Monoclinic
Space group	<i>Cc</i> (No. 9)	$P2_1/c$ (No. 14)
<i>a</i> (Å)	9.8861(2)	16.967(8)
<i>b</i> (Å)	15.0186(3)	10.168(3)
c (Å)	17.4254(3)	18.366(6)
α (°)	90	90
β (°)	96.144(1)	96.88(3)
γ (°)	90	90
Volume (Å ³)	2572.4(1)	3146(2)
Ζ	4	4
$d_{\text{calcd}} (\text{g/cm}^3)$	1.844	1.963
Crystal dimensions (mm)	$0.40 \times 0.27 \times 0.14$	$0.46 \times 0.29 \times 0.04$
Radiation $(\lambda, \text{ Å})$	CuKa, 1.541 78	СиКа, 1.541 78
$\mu (cm^{-1})$	129.1	138.5
Rfls. measured	10 492	22 767
Rfls. independent	$4060 \ (R_{\rm int} = 0.052)$	5972 ($R_{\rm int} = 0.102$)
Rfls. obs. $(I > 2\sigma)$	3982	4579
$R^a (I > 2\sigma)$	0.0477	0.0455
$wR2^a \ (I > 2\sigma)$	0.1203	0.1080
$S^a (I > 2\sigma)$	1.056	0.965
	$(\Sigma E (E^2 - E^2)^2)/\Sigma (E^2)^2)$	$\frac{1}{2}$ G (SE (E ²) = 2) ² 1/(M M)) ^{1/2}

Table 2. Crystal data.

 ${}^{a}R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|; \ wR2 = \{ \Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma w(F_{o}^{2})^{2} \}^{1/2}; \ S = \{ \Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / (N_{obs} - N_{param}) \}^{1/2}.$

tent models for CH₂Cl₂ or pentane molecules could be assembled from these peaks. Therefore, this part of the structure was modeled by using the SQUEEZE procedure of the PLATON software (15), which indicated the presence of two cavities of 310 Å³, each occupied by 95 electrons. Considering that CH₂Cl₂ and pentane both contain 42 electrons and that their volumes are 106 and 191 Å³, respectively, each cavity should contain, on average, 0.8 pentane and 1.5 CH₂Cl₂ molecules. The contribution of the disordered solvent was calculated with the BYPASS procedure of van der Sluis and Spek (16) and a new hkl/F_0^2 list bypassing the solvent contribution was generated. The final model consisting of the ordered part only, without the disordered solvent contribution, was refined against this new data list, which is the one corresponding with the CIF file. Refinement converged normally to R = 0.0455. The solvent molecules were taken into account in the calculation of the derived quantities given in Table 2.

Results and discussion

The chemistry used by Mazzi et al. (8) to prepare $\text{ReOCl}_2(\text{qn})(\text{PPh}_3)$ and $\text{ReOCl}(\text{qn})_2$ is applied here to obtain a series of complexes with various substituted 8-hydroxy-quinolines. Refluxing equivalent amounts of the ligand and $\text{ReOCl}_3(\text{PPh}_3)_2$ leads to $\text{ReOCl}_2(\text{L})(\text{PPh}_3)$ compounds, in which one phosphine and the chlorine atom trans to the Re=O bond are displaced. By reacting 2 equiv. of ligand in the presence of 2 equiv. of Et₃N, the ReOCl(L)₂ products were obtained. No complexes could be prepared when a

bulky *tert*-butyl substituent was present α to the N atom, whereas only the 1:1 complex was isolated with the phenyl-substituted ligand.

IR and NMR spectroscopies

Beside the large number of vibrations because of the quinolinate and PPh₃ ligands, all compounds show strong IR bands in the 968–984 cm⁻¹ range for the Re=O stretching mode. Weaker features at ~325 and ~285 cm⁻¹ are likely due to Re-Cl stretching, bands in this region being commonly found for similar systems (17).

The ¹H NMR signals of the free ligands are listed in Table 1 and identified following the numbering scheme **I**. Except for the 2-substituted compounds, a typical doublet of doublets is observed for H-3 at 7.4–7.9 ppm with couplings of 4 to 5 and 8 to 9 Hz, respectively. From the coupling constants and the COSY spectrum of Hqn, the adjacent protons are identified at 8.1–8.6 ppm (J = 8 to 9 Hz) and 8.8–9.0 ppm (J = 4 to 5 Hz). The latter signal must originate from H-2, since it disappears for the 2-substituted derivatives, whereas the remaining doublets for H-3 and H-4 show the larger coupling. Systematically, the H-2 and H-4 protons appear downfield from H-3, as expected from the mesomeric effect in the six-membered nitrogen heterocycle.

For the 5,7-disubstituted compounds, the remaining C-H signal is a singlet obviously due to H-6. When the phenol ring is not substituted, H-6 usually appears as a pseudo-triplet at \sim 7.4 ppm, resulting from roughly equal couplings (7–9 Hz) to two adjacent protons at \sim 7.1 and \sim 7.35 ppm, respectively. The latter signal is assigned to H-5, since it

Table 3. ¹H NMR chemical shifts (ppm) and coupling constants (Hz) for the quinolinate signals in the complexes.^a

	H-2	H-3	H-4	H-5	H-6	H-7
ReOCl ₂ (L)(F	PPh ₃)					
qn	8.37 (d, 5.0)	7.70 (dd, 8.3, 5.2)	8.21 (d, 8.3)	b	b	6.79 (d, 7.7)
2-Me-qn ^c	2.87 (s, CH ₃)	7.70 (d, 8.0)	8.11 (d, 8.1)	b	b	6.62 (d, 7.1)
2-Cl-qn		7.89 (d, 8.6)	8.26 (d, 8.6)	b	b	6.81 (d, 7.1)
2-Ph-qn	7.04-7.10 (m, Ph)	7.68 (d, 8.4)	8.28 (d, 8.3)	b	b	6.70 (7.1)
5-Cl-qn	8.51 (d, 5.0)	7.85 (dd, 8.4, 5.2)	8.23 (d, 8.3)		7.57 (d, 8.3)	6.82 (d, 8.3)
5,7-Cl ₂ -qn	8.61 (d, 4.9)	7.89 (dd, 8.4, 5.3)	8.26 (d, 8.4)		7.79 (s)	
5,7-Br ₂ -qn	8.59 (d, 5.0)	7.90 (dd, 8.4, 5.2)	8.16 (d, 8.4)		7.99 (s)	
5,7-I ₂ -qn	8.52 (d, 5.1)	7.84 (dd, 8.5, 5.2)	7.99 (d, 8.2)		8.21 (s)	
5-NO ₂ -qn	8.63 (d, 5.0)	8.00 (dd, 8.7, 5.2)	8.49 (d, 8.8)		8.88 (d, 8.8)	6.90 (d, 8.8)
$\operatorname{ReOCl}(L)_2^d$						
qn	8.88 (d, 4.7)	8.00 (dd, 8.2, 5.2)	8.27 (m, H-2'/H-4)	7.42 (d, 8.1)	7.51 (t, 7.9)	6.61 (d, 7.6)
	8.27 (m, H-2'/H-4)	7.71 (dd, 8.2, 5.2)	8.83 (d, 8.2)	7.64 (d, 8.0)	7.86 (t, 8.0)	7.62 (d, 7.4)
2-Me-qn	3.56 (s, CH ₃)	7.96 (d, 8.5)	8.18 (d, 8.4)	7.31 (m)	7.31 (m)	6.40 (dd, 6.5, 2.2)
•	2.34 (s, CH ₃)	7.55 (d, 8.4)	8.48 (d, 8.4)	7.47 (d, 8.3)	7.74 (t, 8.0)	7.49 (d, 7.9)
2-Cl-qn		8.14 (d, 8.6)	8.41 (d, 8.6)	7.45 (m)	7.45 (m)	6.67 (dd, 6.7, 2.1)
		7.81 (d, 8.6)	8.77 (d, 8.8)	7.64 (d, 8.7)	7.85 (t, 8.0)	7.66 (d, 8.4)
5-Cl-qn	8.99 (d, 4.8)	8.15 (dd, 8.6, 5.1)	8.34 (d, 8.3)		7.62 (d, 8.6)	6.62 (d, 8.4)
	8.48 (d, 4.9)	7.83 (dd, 8.5, 5.1)	8.90 (d, 8.6)		8.06 (d, 8.4)	7.66 (d, 8.6)
5,7-Cl ₂ -qn	9.02 (d, 4.3)	8.19 (dd, 8.5, 5.2)	8.41 (d, 8.5)		7.94 (s)	
	8.62 (d, 5.1)	7.88 (dd, 8.5, 5.2)	8.96 (d, 7.4)		8.34 (s)	
5,7-Br ₂ -qn	9.01 (d, 4.7)	8.19 (dd, 8.5, 5.2)	8.32 (d, 8.6)		8.14 (s)	
	8.57 (d, 5.1)	7.88 (dd, 8.5, 5.2)	8.88 (d, 9.3)		8.55 (s)	
5,7-I ₂ -qn	8.93 (d, 5.0)	8.14 (dd, 8.4, 5.1)	8.16 (d, 8.4)		7.99 (s)	
	8.40 (d, 5.0)	7.90 (dd, 8.6, 5.0)	8.70 (d, 8.2)		8.74 (s)	
5-NO ₂ -qn	9.11 (d, 4.3)	8.32 (dd, 8.9, 5.2)	8.59 (d, 8.9)		8.95 (d, 8.9)	6.73 (d, 8.9)
	8.77 (d, 4.1)	8.04 (dd, 8.9, 5.1)	9.04 (d, 8.8)		9.53 (d, 8.9)	7.77 (d, 8.8)

^{*a*}In DMSO-*d*₆, except when otherwise stated.

^bMasked by PPh₃ multiplets.

^{*c*}In acetone- d_6 .

^{*d*}For the ReOCl(L)₂ complexes, the signals in the first line are assigned to the axial ligand.

shows a proximity to H-4 in the NOESY spectrum. For the 5-substituted molecules, the doublet at 7.0–7.2 ppm is assigned to H-7, by comparison with the unsubstituted rings. As expected, the remaining H-6 resonance is found to be very sensitive to the presence of the adjacent electron-attracting substituents: for instance, introducing a 5-nitro group induces a large 1.8 ppm downfield shift. In the free molecules, small couplings of 1 to 2 Hz are generally observed between nonadjacent protons on either ring. Also, in most cases, a broad resonance appears at low field for the OH proton.

In the ReOCl₂(L)(PPh₃) compounds, the phosphine gives rise to ¹H multiplets in the 7.2–7.5 ppm range and to a ³¹P singlet lying between –9 and –12.5 ppm, except for the 2-substituted ligands, where this signal is shifted to ca. –17 ppm. The signals for the coordinated quinolinate are listed in Table 3. Assignments in the pyridine ring are straightforward, based on multiplicity and couplings. For the phenolate ring, the lowest-field signal, whose position is very substituent-sensitive, originates from H-6. When the ring is not substituted, two of the protons are masked by those of PPh₃, and the only resolved signal at 6.6–6.8 ppm is assigned to H-7 by comparison with the 5-substituted ligands.

The ReOCl(L)₂ compounds exhibit two sets of ¹H signals, showing that the two ligands are inequivalent, in agreement

with the structure (II) observed by Chen et al. (9) for ReOCl(NO₂-qn)(NH₂-qn). From the COSY spectrum of ReOCl(qn)₂, two sets of connected H-2/H-3/H-4 signals were defined, in which the H-2 and H-4 doublets could be identified individually from their respective coupling constants. Two H-5/H-6/H-7 sets could also be assembled, but the similar coupling constants made it impossible to identify H-5 and H-7 individually at this stage. This could be done, however, from a NOESY spectrum, where each H-4 proton showed a cross peak with a proton in the other ring, which identified the latter proton as H-5 and established the connection between the H-2/H-3/H-4 and the H-5/H-6/H-7 sets belonging to the same ligand.



There is no direct evidence to associate a given complete set to either the axial or the equatorial ligand. The tentative identification proposed in Table 3 is based on the assumption that the phenol ring signals for the axial ligand in $ReOCl(L)_2$ should be similar to those of the equally axial ligand in ReOCl₂(L)(PPh₃), since this ring should be similarly influenced by the very large electronic effect of the oxo ligand via the trans O=Re-O unit and it should not be greatly affected by the anisotropy or other features of the equatorial ligands. With the assignment proposed, the average δ [axia] $\text{ReOCl}(L)_2$] – $\delta[\text{ReOCl}_2(L)(\text{PPh}_3)]$ difference is 0.13 ppm for H-6 and -0.18 ppm for H-7, whereas these values would be 0.56 and 0.85 ppm, respectively, for the alternate possibility. In contrast, the pyridine ring signals of these axial ligands show larger differences: 0.45 ppm for H-2, 0.29 ppm for H-3, and 0.12 ppm for H-4. Since these differences are systematically positive, they may reflect the anisotropy effect of the PPh3 rings in ReOCl₂(L)(PPh3), which is no longer present in ReOCl(L)₂. Also consistent with this interpretation is the fact that the H-2 or 2-CH₃ protons of the equatorial ligand appear at a much higher field than those of the axial one. For instance, the chemical shifts of H-2 in ReOCl(qn)₂ are 8.27 ppm (equatorial) vs. 8.88 ppm (axial), whereas those of the 2-CH₃ groups in ReOCl(2-Me-qn)₂ are 2.34 ppm (equatorial) vs. 3.56 ppm (axial). This could be ascribed to the fact that these protons lie in the cone of anisotropy of the axial pyridine ring (III). Thus, these various effects are consistent with the structure proposed for ReOCl(L)₂, which should be the one favored electronically, since two π -donor ligands lie trans to weakly π -accepting pyridine rings.



X-ray diffraction studies

The ReOCl₂(5,7-Br₂-qn)(PPh₃) and ReOCl₂(2-Cl-qn)(PPh₃) molecules are shown in Figs. 1 and 2, respectively. In both compounds, the rhenium atom has a distorted octahedral coordination, created by an oxo ligand, two chlorine atoms, a phosphine, and a *N*,*O*-coordinated quinolinate. In agreement with a general trend in mono-oxo Re(V) chemistry, the quinolinate oxygen donor lies trans to the Re=O bond, which results in the quinolinate plane being roughly parallel to the Re=O direction. The PPh₃ group is found to be cis to the nitrogen atom in the equatorial plane. This arrangement has also been reported for ReOCl₂(5-nitro-qn)(PPh₃) (9).

Selected distances and angles are presented in Table 4. The Re=O bond lengths (1.656(8) and 1.671(4) Å) are in good agreement with the value expected for Re(V) monooxo complexes (18). The trans influence of PPh₃ makes the opposite Re—Cl(1) bond 0.05 Å longer than the other in both complexes. The Re—O(2) distances (1.999(6) and 2.021(4) Å), which are ~0.1 Å longer than the typical value **Fig. 1.** ORTEP drawing of the ReOCl₂(5,7-Br₂-qn)(PPh₃) molecule. Ellipsoids correspond to 30% probability.



Fig. 2. ORTEP drawing of the ReOCl₂(2-Cl₂-qn)(PPh₃) molecule. Ellipsoids correspond to 40% probability.



for Re—OR bonds (2), reflect the constraint imposed by the five-membered chelate ring.

The oxo ligand tends to produce a general displacement of the adjacent bonds in the opposite direction, which results in the Re atom lying above the plane defined by the four equatorial donor atoms. The distances of rhenium to the PNCl₂ plane are 0.23 and 0.28 Å for the 5,7-Br-qn and 2-Cl-qn complexes, respectively. Additional distortion is introduced by the bidentate coordination of the quinolinate ligand, whose O(2)-Re-N bite angle is ~76°. This small angle af-

	ReOCl ₂ (2-Cl-qn)(PPh ₃)	ReOCl ₂ (5,7-Br ₂ -qn)(PPh ₃)
Bond distances (Å)		
Re=O(1)	1.656(8)	1.671(4)
Re—O(2)	1.999(6)	2.021(4)
Re—N	2.183(8)	2.130(6)
Re—Cl(1)	2.390(2)	2.371(2)
Re—Cl(2)	2.334(2)	2.327(2)
Re—P	2.485(2)	2.469(2)
Bond angles (°)		
O(1)-Re-O(2)	163.2(3)	160.2(2)
O(1)-Re-N	93.2(3)	86.7(2)
O(2)-Re-N	76.2(3)	75.5(2)
O(1)-Re-Cl(1)	100.0(3)	99.8(2)
O(2)-Re-Cl(1)	92.5(2)	87.24(13)
N-Re-Cl(1)	87.1(2)	84.76(14)
O(1)-Re-Cl(2)	102.3(3)	105.67(17)
O(2)-Re-Cl(2)	89.5(2)	92.79(13)
N-Re-Cl(2)	164.0(2)	167.15(14)
Cl(1)-Re-Cl(2)	86.42(10)	89.59(7)
O(1)-Re-P	86.3(3)	91.18(16)
O(2)-Re-P	81.1(2)	81.86(13)
N-Re-P	91.3(2)	94.35(14)
Cl(1)-Re-P	173.58(8)	168.92(6)
Cl(2)-Re-P	93.49(8)	88.98(7)
Re-O(2)-C(6)	118.7(5)	119.4(4)
Re-N-C(1)	131.1(8)	127.2(5)
Re-N-C(5)	112.0(6)	115.4(4)

Table 4. Selected distances (Å) and angles (°) in the ReOCl₂(L)(PPh₃) compounds.

fects mainly the O(1)-Re-O(2) unit, which is definitely nonlinear: $163.2(3)^{\circ}$ for 2-Cl-qn and $160.2(2)^{\circ}$ for 5,7-Br₂-qn. The Re=O bond is displaced away from the chloro ligands, as evidenced from the Cl-Re=O angles (100° - 106°) being systematically greater than the N-Re=O and P-Re=O angles (87° - 94°).

The 2-chloro substituent enhances the distortion of the octahedron. This group further displaces the Re=O bond toward PPh₃, as evidenced from the O(1)-Re-P angle of 86.3(3)°, compared to 91.2(2)° in the 5,7-Br₂-qn complex. The angle between the Cl(2)-Re-O(1) plane and the mean plane through the quinolinate ligand increases from 10.5° for the dibromo complex to 22.2° here. The distortion is also illustrated by the sum of the deviations of the Cl, P, and N atoms from their least-squares plane: these atoms are virtually coplanar for the dibromo complex, but the mean deviation is 0.69 Å for ReOCl₂(2-Cl-qn)(PPh₃).

In both complexes, intramolecular π -stacking interactions exist between one of the phosphine phenyl rings (C(31)-C(36)) and the quinolinate ligand, which are roughly parallel (dihedral angles of 11.7° and 12.9° for the 5,7-Br₂-qn and 2-Cl-qn complexes, respectively) and separated by ~3.42 Å.

The molecules are packed individually in the unit cell, with normal van der Waals contacts, including some intermolecular π stacking.

UV-vis spectroscopy

The low-energy (8 000–20 000 cm^{-1}) region of the UV– vis absorption spectra was recorded for all complexes, gen-

Fig. 3. UV–vis spectra of $\text{ReOCl}_2(qn)(\text{PPh}_3)$ in DMSO (full line). Dashed lines correspond to the four components obtained by deconvolution.



erally in CHCl₃. For a few less soluble complexes, DMSO was used to improve the quality of the spectra. The DMSO solutions were stable and the spectral features were similar to those of the weaker spectra in CHCl₃, showing that the same species was present in both solvents. The spectra of $\text{ReOCl}_2(\text{qn})(\text{PPh}_3)$ and $\text{ReOCl}(\text{qn})_2$ are illustrated in Figs. 3 and 4, respectively. In each case, four individual compo-

	$[\mathrm{S} \to \mathrm{T}^*]$	$[S \to T^{**}]$	$[\mathrm{S} \to \mathrm{S}^*]$	$[\mathrm{S} \to \mathrm{S}^{**}]$
ReOCl ₂ (qn)(PPh ₃) ^b	9.6 (29)	12.1 (150)	14.3 (381)	16.2 (299)
ReOCl ₂ (2-Me-qn)(PPh ₃) ^b	10.0 ^c (17)	12.6 (73)	14.8 (235)	16.4 (241)
$\operatorname{ReOCl}_2(2-\operatorname{Cl}-\operatorname{qn})(\operatorname{PPh}_3)^b$	10.9 ^c (8)	12.6 (29)	14.9 (97)	16.6 (99)
$\text{ReOCl}_2(5\text{-}\text{Cl}\text{-}\text{qn})(\text{PPh}_3)^d$	9.8 (18)	12.1 (149)	14.3 (407)	16.3 (310)
$\operatorname{ReOCl}_2(5-\operatorname{NO}_2-\operatorname{qn})(\operatorname{PPh}_3)^e$	10.0 ^c (22)	11.8 (195)	14.2 (544)	17.5 (430)
$\text{ReOCl}_2(5,7\text{-}\text{Cl}_2\text{-}\text{qn})(\text{PPh}_3)^d$	9.8 (16)	11.8 (142)	14.3 (389)	16.6 (290)
$\text{ReOCl}_2(5,7-\text{Br}_2-\text{qn})(\text{PPh}_3)^d$	10.0 ^c (18)	11.8 (166)	14.4 (430)	16.6 (312)
$\text{ReOCl}_2(5,7-I_2-qn)(\text{PPh}_3)^d$	10.0 ^c (16)	11.8 (160)	14.2 (424)	16.5 (320)
$\operatorname{ReOCl}(qn)_2^d$	9.8 (24)	11.6 (120)	13.7 (243)	17.7 (181)
$\text{ReOCl}(2\text{-Me-qn})_2^d$	9.5 (38)	12.2 (185)	14.4 (441)	17.7 (360)
$\text{ReOCl}(2\text{-}\text{Cl}\text{-}\text{qn})_2^d$	_	12.5 (153)	14.6 (346)	18.3 (226)
$\text{ReOCl}(5\text{-}\text{Cl}\text{-}\text{qn})_2^d$	9.4 (6)	11.7 (51)	13.8 (111)	_
$\text{ReOCl}(5-\text{NO}_2-\text{qn})_2^d$	_	12.0 ^c (230)	14.5 ^c (466)	17.5 ^c (970)
$\operatorname{ReOCl}(5,7-\operatorname{Cl}_2-\operatorname{qn})_2^d$	_	12.0 ^c (263)	14.0 ^c (480)	17.5 ^c (754)
$\operatorname{ReOCl}(5,7-\operatorname{Br}_2-\operatorname{qn})_2^d$		12.0 ^c (140)	14.0 ^c (283)	17.0 ^c (460)
$\text{ReOCl}(5,7-\text{I}_2-\text{qn})_2^d$		12.0 ^c (433)	14.0 ^c (780)	17.0 ^c (1270)

Table 5. Transition energy $(cm^{-1} \times 10^{-3})$ and absorption coefficient^{*a*} (M⁻¹ cm⁻¹, within parentheses) of the low-energy components of the electronic spectra.

^aThe ε values listed are those obtained at the indicated wavelength from the nondeconvoluted spectra. ^bIn DMSO.

^cPeak position estimated visually.

Fig. 4. UV–vis spectra of $\text{ReOCl}(qn)_2$ in DMSO (full line). Dashed lines correspond to the four components obtained by deconvolution.



nents were obtained by deconvolution using ORIGIN (19). The data are listed in Table 5.

Since these complexes have no symmetry, the d_{yz} and d_{xz} orbitals, which are degenerate under D_{4h} symmetry, become inequivalent. For consistency with the recent study of Da Re and Hopkins (20) on the isoelectronic oxo-Mo(IV) core, d_{yz} will be assumed to lie at lower energy than d_{xz} . The five lowest-energy electronic states expected are depicted in Fig. 5, in increasing order of energy.

Both series of complexes show a strong maximum between 13 700 and 14 900 cm⁻¹. For the ReOCl(L)₂ compounds, another strong peak is visible at 17 000–18 300 cm⁻¹,

whereas the related band is present as an unresolved component at slightly lower energy for the $ReOCl_2(L)(PPh_3)$ compounds. These absorptions are assigned to the spinallowed $[S \rightarrow S^*]$ and $[S \rightarrow S^{**}]$ transitions, respectively. On the low-energy side, there is a distinct dissymmetry in the main peak and a rather long tail before intensity falls off to zero. Two weak features are revealed by deconvolution, which are assigned to the two anticipated singlet-triplet transitions. These transitions being spin-forbidden, their extinction coefficients are expected to be ~10, and this is indeed the case for the first transition $(d_{xy})^2 \rightarrow (d_{xy})^1 (d_{yz})^1$ [S \rightarrow T*] at ~10 000 cm⁻¹. The coefficient is much higher (~100) for the second transition $(d_{xy})^2 \rightarrow (d_{xy})^1 (d_{xz})^1 [S \rightarrow T^{**}]$ at ~12 000 cm⁻¹, but enhanced intensity could be due to mixing between the higher-energy triplet state and the lowestenergy singlet states (20), as a result of strong spin-orbit couplings commonly found for third-row transition metals. The separations (Table 6) between the two triplet states, the two singlet states, and the second triplet – first singlet states (roughly 2000 cm⁻¹) are in good agreement with the values calculated by Da Re and Hopkins (20).

Comparison of the data within each series reveals that ring substitution does not introduce dramatic effects on the spectra: the strongly electron-attracting 5-nitro substituent seems to slightly increase the $[S \rightarrow S^{**}]$ transition energy in the ReOCl₂(L)(PPh₃) series, but the effect is modest and no recognizable trend can be detected. Thus, the HOMO– LUMO gap is not substantially affected by ligand substitution in these systems.

The spin-allowed $[S \rightarrow S^*]$ and $[S \rightarrow S^{**}]$ bands in both series are observed at somewhat lower energy than for the ReO(OR)X₂(dppe) compounds studied earlier, where they were found at ~16 500 and 20 000 cm⁻¹, respectively (2). This can be explained by the lower electron-donating ability

^{*d*}In CHCl₃. ^{*e*}In CH₂Cl₂.

Fig. 5. Low-energy electron configurations for the $\text{Re}(V) d^2$ systems.



Table 6. Energy separation $(cm^{-1} \times 10^{-3})$ between the low-energy states from the electronic spectra.

	$\Delta[\mathrm{T}^* \to \mathrm{T}^{**}]$	$\Delta[\mathrm{S}^* \to \mathrm{S}^{**}]$	$\Delta[\mathrm{T}^{**}\to\mathrm{S}^*]$	$\Delta[\mathrm{T}^* \to \mathrm{S}^{**}]$
ReOCl ₂ (qn)(PPh ₃)	2.5	1.9	2.2	6.6
ReOCl ₂ (2-Me-qn)(PPh ₃)	2.6	1.6	2.2	6.4
ReOCl ₂ (2-Cl-qn)(PPh ₃)	1.7	1.7	2.3	5.7
ReOCl ₂ (5-Cl-qn)(PPh ₃)	2.3	2.0	2.2	6.5
ReOCl ₂ (5-NO ₂ -qn)(PPh ₃)	1.8	3.3	2.4	7.5
ReOCl ₂ (5,7-Cl ₂ -qn)(PPh ₃)	2.0	2.3	2.5	6.8
$\text{ReOCl}_2(5,7-\text{Br}_2-\text{qn})(\text{PPh}_3)$	1.8	2.3	2.6	6.6
$\text{ReOCl}_2(5,7-I_2-qn)(\text{PPh}_3)$	1.8	2.2	2.4	6.5
ReOCl(qn) ₂	1.8	2.3	2.1	7.9
ReOCl(2-Me-qn) ₂	2.7	4.0	2.2	8.2
$ReOCl(2-Cl-qn)_2$	_	3.3	2.1	_
$ReOCl(5-Cl-qn)_2$	2.3	3.7	2.1	_
ReOCl(5-NO ₂ -qn) ₂	_	3.0	2.5	_
$\text{ReOCl}(5,7\text{-}\text{Cl}_2\text{-}\text{qn})_2$	_	3.5	2.0	_
$\text{ReOCl}(5,7\text{-Br}_2\text{-qn})_2$		3.0	2.0	_
$\text{ReOCl}(5,7-I_2-qn)_2$	_	3.0	2.0	_

of the quinolinate oxygen compared to alkoxo groups, considering that donation from the ligand trans to the Re=O bond was previously identified as a very sensitive factor. However, this reduction is not large enough to bring the energies below those of the ReOX₃(dppe) compounds (~12 000 and ~16 400 cm⁻¹).

Concluding remarks

Homologous series of $\text{ReOCl}_2(L)(\text{PPh}_3)$ and $\text{ReOCl}(L)_2$ compounds were prepared with various 8-hydroxyquinolines bearing substituents with different steric and electronic properties. Comparisons between these related compounds allowed us to fully interpret their ¹H NMR spectral features. The positions of the UV–vis bands used to estimate the HOMO–LUMO gap failed to reveal a large effect of ring substitution on electronic transitions, but it confirmed that the donor ability of the ligand trans to the Re=O band plays a major role. On the other hand, the fact that the spinforbidden singlet–triplet bands were readily observed makes these systems attractive for future in-depth spectroscopic studies to improve our understanding of the low-lying excited states and the spin-crossover processes, whose control is crucial for the eventual development of optically or magnetically tunable materials (1, 21).

Acknowledgments

We wish to thank M. Palardy for his participation in the preparative work, Dr. M. Simard and F. Bélanger-Gariépy for assistance in the interpretation of the X-ray diffraction data, and the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support.

References

- U. Oetliker, C. Savoie, S. Stanislas, C. Reber, F. Connac, A.L. Beauchamp, F. Loiseau, and M. Dartiguenave. J. Chem. Soc. Chem. Commun. 657 (1998).
- F. Baril-Robert and A.L. Beauchamp. Can. J. Chem. 81, 1326 (2003).
- 3. G. Delapierre, J.M. Brunel, T. Constantieux, and G. Buono. Tetrahedron Asymmetry, **12**, 1345 (2001).
- 4. J. Chatt and G.A. Rowe. J. Chem. Soc. 4019 (1962).
- 5. G.R. Pettit and M.V. Kalnins. J. Org. Chem. 25, 1365 (1960).
- J.J. Plattner, R.D. Gless, and H. Rapoport. J. Am. Chem. Soc. 94, 8613 (1972).

- 7. W.C. Fleming and G.R. Pettit. J. Org. Chem. 36, 3490 (1971).
- 8. U. Mazzi, E. Roncari, R. Rossi, V. Bertolasi, O. Traverso, and L. Magon. Transition Met. Chem. 5, 289 (1980).
- X. Chen, F.J. Femia, J.W. Babich, and J. Zubieta. Inorg. Chim. Acta, **308**, 80 (2000).
- SMART. Release 5.059 [computer program]. Bruker AXS Inc., Madison, Wisconsin, USA. 1999.
- SAINT. Release 6.06 [computer program]. Bruker AXS Inc., Madison, Wisconsin, USA. 1999.
- G.M. Sheldrick. SADABS [computer program]. Bruker AXS Inc., Madison, Wisconsin, USA. 1996.
- G.M. Sheldrick. SHELXTL. Release 5.10 [computer program]. Bruker AXS Inc., Madison, Wisconsin, USA. 1997.
- CAD-4. Version 5.0 [computer program]. Enraf-Nonius, Delft, The Netherlands. 1989.

- 15. A.L. Spek. PLATON. July 1995 version [computer program]. University of Utrecht, Utrecht, The Netherlands. 1995.
- 16. P. van der Sluis and A.L. Spek. Acta Crystallogr. A46, 194 (1990).
- 17. A.M. Lebuis and A.L. Beauchamp. Can. J. Chem. 71, 441 (1993).
- Cambridge Structural Database. Version 5.4, November 2002 release with February 2003 updates. Cambridge University, Cambridge, UK.
- 19. ORIGIN 6.1, 6.1052 (B232) [computer program]. OriginLab Corporation, Northampton, UK. 2000.
- 20. R.E. Da Re and M.D. Hopkins. Inorg. Chem. 41, 6973 (2002).
- 21. C. Savoie and C. Reber. J. Am. Chem. Soc. 122, 844 (2000).