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Two novel rhenium complexes derived from [ReO(OMe)Cl₂(dpphen)] – Synthesis, crystal structure, spectroscopic and magnetic properties

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ABSTRACT

The reaction of $[\text{ReO}(\text{OMe})\text{Cl}_2(\text{dpphen})]$ (dpphen = 4,7-diphenyl-1,10-phenanthroline) with triphenylphosphine has been examined and two novel rhenium complexes – $[\text{Re}^{III}\text{Cl}_3(\text{dpphen})(\text{PPh}_3)]\cdot\text{Me}_2\text{CO}$ (1) and $[\text{Re}^{IV}\text{Cl}_4(\text{dpphen})]\cdot\text{CHCl}_3$ (2) – have been obtained. The compounds have been characterised by elemental analysis, IR, UV–Vis spectroscopy, magnetic measurements and X-ray crystallography. The electronic structures of $[\text{ReCl}_3(\text{dpphen})(\text{PPh}_3)]$ and $[\text{ReCl}_4(\text{dpphen})]$ have been studied by DFT/B3LYP level calculations, and TD-DFT calculations have been employed for discussion of the electronic spectra in more detail. The magnetic behaviour of 1 is characteristic of mononuclear complexes with d⁴ low-spin octahedral Re(III) complexes (${}^{3}\text{T}_{1g}$ ground state) and arise because of the large spin–orbit coupling ($\zeta = 2500 \text{ cm}^{-1}$), which gives diamagnetic ground state. For complex 2 the results of calculations revealed value of zero-field splitting parameter $D = 10.8 \text{ cm}^{-1}$, $g_{\parallel} = 2.49$ and $g_{\perp} = 1.51$.

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1. Introduction

The coordination chemistry of rhenium is a field of current growing interest from various viewpoints. The attention of scientists concentrates on synthetic aspects, structural, physicochemical properties and reactivity, as well as on topics with an applied character such as the development of radiotherapeutic cancer agents, nitrogen fixation and catalysis [1]. The favourable nuclear properties of ¹⁸⁶Re (1.07 MeV β -emitter, $t_{1/2}$ 90 h) and ¹⁸⁸Re (2.12 MeV β emitter, $t_{1/2}$ 17 h) nuclides make the rhenium compounds with radioactive isotopes useful for applications in radioimmunotherapy [2,3]. The diazenido and dinitrogen rhenium complexes are important in view of their significance in the field of nitrogen fixation [4–6], whereas the Re=O moiety is a potentially excellent oxygen atom transfer reagent [7–12]. Transfer reactions promoted by enzymatic oxo sites based on iron, molybdenum and tungsten are important in the chemistry of life. Rhenium is not a biometal, but as an element in the periodic group next to that of molybdenum and tungsten, transfer reactions involving Re=O are of value as potential models [7–12].

Tertiary phosphines are model oxygen atom acceptors from oxo moieties such as Re^{V} =O, and chelation of nitrogenous π -acidic ligands to the Re=O moiety facilitates the transfer process *via* electron withdrawal from the metal. In this context, the complexes of the type [ReOX₃(N–N)] seem to be the most desirable. Upon

treatment with PR₃ they usually undergo facile transformation to the [ReX₃(N–N)(OPR₃)] compounds, which then react with more PR₃ forming [ReX₃(N–N)(PR₃)]. The oxygen atom transfer is believed to proceed *via* initial nucleophilic attack on the Re \equiv O π anti-bonding orbital of the oxocomplex by PR₃. On the other hand, the conversion [ReX₃(N–N)(OPR₃)] \rightarrow [ReX₃(N–N)(PR₃)] is attended with *mer* \rightarrow *fac* isomerization of the co-ordination sphere [7–12].

The reported recently [ReO(OMe)Cl₂(dpphen)] (dpphen = 4,7-diphenyl-1,10-phenanthroline) is supposed to be an excellent oxygen atom transfer reagent owing to the strong π acidity of the chelate ligand [13]. In this work we present the structure and spectroscopic characterisation of two complexes [Re^{III}Cl₃(dpphen)(PPh₃)]·Me₂CO and [Re^{IV}Cl₄(dpphen)]·CHCl₃ isolated from the reaction of [ReO(O-Me)Cl₂(dpphen)] with triphenylphosphine. The experimental studies on the Re(III) and Re(IV) complexes have been accompanied computationally by the density functional theory (DFT) and time-dependent DFT calculations. Currently density functional theory is commonly used to examine the electronic structure of transition metal complexes. It meets with the requirements of being accurate, easy to use and fast enough to allow the study of relatively large molecules of transition metal complexes [14,15].

2. Experimental

2.1. General procedure

The reactions were carried out under argon atmosphere. The reagents used to the synthesis were commercially available and were



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used without further purification. [ReO(OMe)Cl₂(dpphen)] was prepared according to the literature method [13].

IR spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 cm⁻¹ with the samples in the form of KBr pellets. Electronic spectra were measured on a spectrophotometer Lab Alliance UV–Vis 8500 in the range 1100–200 nm in deoxygenated acetonitrile solution. Elemental analyses (C, H, N) were performed on a Perkin–Elmer CHN-2400 analyzer.

2.2. Preparation of [Re^{III}Cl₃(dpphen)(PPh₃)]·Me₂CO (**1**)

[ReO(OMe)Cl₂(dpphen)] (0.5 g, 0.79 mmol) and PPh₃ (0.5 g, 1.9 mmol) in a mixture of dichloromethane/acetone ($60/60 \text{ cm}^3$) were refluxed for 5 h. The volume was condensed to 20 cm³ and dark red microcrystalline solid was formed by an addition of 100 cm³ of diethyl ether. The product was washed with diethyl ether, and dried *in vacuo*. The X-ray quality crystals of **1** were obtained by recrystallization from acetone. (Yield 70%).

IR (KBr, cm⁻¹) 3057(w) 3025(w), 1621(m), 1600(m), 1558(m), 1519(m), 1475(m), 1434(m), 1424(sh), 1398(m), 1357(w), 1280(w), 1229(w), 1199(m), 1182(sh), 1118(m), 1089(m), 997(w), 970(w), 947(w), 881(w), 855(m), 766(s), 742(s), 721(s), 697(vs), 667(m), 638(m), 594(w), 577(w), 541(s), 512(w), 490(m).

Anal. Calc. for $C_{45}H_{37}N_2Cl_3OPRe:$ C, 57.17; H, 3.95; N, 2.96. Found: C, 57.31; H, 3.89; N, 2.87%.

2.3. Preparation of [ReCl₄(dpphen)]·CHCl₃ (2)

A procedure similar to that for **1** was used with [ReO(O-Me)Cl₂(dpphen)] (0.5 g, 0.79 mmol) and PPh₃ (0.5 g, 1.9 mmol) in chloroform. An orange crystalline precipitate of **2** was collected in 60% yield.

IR (KBr, cm⁻¹) 3082(w) 3007(w), 1622(m), 1601(s), 1558(s), 1518(s), 1493(w), 1445(w), 1423(s), 1400(m), 1357(w), 1297(w), 1280(w), 1229(m), 1180(w), 1102(w), 1092(w), 1076(w), 1019 (w), 968(w), 882(w), 857(s), 850(sh), 816(w), 768(vs), 737(vs), 701(vs), 666(m), 638(m), 594(w), 577(w), 548(w), 489(w), 459(w).

Anal. Calc. for C₂₅H₁₇N₂Cl₇Re: C, 38.51; H, 2.20; N, 3.59. Found: C, 38.63; H, 2.30; N, 3.47%.

2.4. Crystal structures determination and refinement

The X-ray intensity data of 1 and 2 were collected on a Gemini A Ultra diffractometer equipped with Atlas CCD detector and graphite monochromated Mo K α radiation (λ = 0.71073 Å) at room temperature. The unit cell parameters were determined from leastsquares refinement of the setting angles of 22 442 and 14 216 strongest reflections respectively for 1 and 2. Details concerning crystal data and refinement are given in Table 1. Lorentz, polarisation and empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm [16] were applied. The structures were solved by the Patterson method and subsequently completed by the difference Fourier recycling. All the non-hydrogen atoms were refined anisotropically using fullmatrix, least-squares technique. The hydrogen atoms were treated as "riding" on their parent carbon atoms and assigned isotropic temperature factors equal 1.2 (non-methyl) and 1.5 (methyl) times the value of equivalent temperature factor of the parent atom. The methyl groups were allowed to rotate about their local threefold axis. shelxs97 and shelxl97 [17] programs were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs.

Table 1

Crystal data and structure refinement for 1 and 2.

	1	2
Empirical formula	C45H37Cl3N2OPRe	C25H17Cl7N2Re
Formula weight	945.29	779.76
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	C2/c
Unit cell dimensions		
a (Å)	11.906(2)	36.043(7)
b (Å)	22.316(5)	8.3331(17)
<i>c</i> (Å)	15.092(3)	19.712(4)
β(°)	94.66(3)	112.31(3)
Volume (Å ³)	3996.6(14)	5477.1(19)
Ζ	4	8
D_{calc} (mg/m ³)	1.571	1.891
Absorption coefficient (mm ⁻¹)	3.318	5.139
F(000)	1880	3000
Crystal size (mm)	$0.024 \times 0.038 \times 0.103$	$\textbf{0.016} \times \textbf{0.055} \times \textbf{0.168}$
 θ Range for data collection (°) 	3.32-25.00	3.35-25.00
Index ranges	$-14 \le h \le 14$	$-42 \le h \le 42$
	$-25 \le k \le 26$	$-9 \le k \le 9$
	$-17 \le l \le 17$	$-23 \le l \le 23$
Reflections collected	37503	26329
Independent reflections	7021 ($R_{int} = 0.0288$)	$4800 (R_{int} = 0.0304)$
Completeness to	99.7%	99.8%
$2\theta = 25.00^{\circ}$		
Minimum and maximum transmission	0.844 and 1.000	0.293 and 1.000
Data/restraints/parameters	7021/0/480	4800/0/316
Goodness-of-fit on F^2	1.077	1.038
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0341$	$R_1 = 0.0252$
	$wR_2 = 0.0820$	$wR_2 = 0.0652$
R indices (all data)	$R_1 = 0.0442$	$R_1 = 0.0359$
	$wR_2 = 0.0842$	$wR_2 = 0.0671$
Largest difference in peak	4.270 and -2.157	0.939 and -0.643
and hole $[e Å^{-3}]$	(0.89 and 0.72 Å from Re1)	

2.5. Computational details

The gas phase geometries of $[\text{ReCl}_3(\text{dpphen})(\text{PPh}_3)]$ and $[\text{Re-Cl}_4(\text{dpphen})]$ were optimised without any symmetry restrictions with the DFT method using the hybrid B3LYP functional of GAUSS-IAN-O3 [18]. The calculations were performed using ECP LANL2DZ basis set [19] with an additional *d* and *f* function with the exponent $\alpha = 0.3811$ and $\alpha = 2.033$ [20] for the rhenium and the standard 6-31G basis set for the other atoms. For chlorine, nitrogen and phosphorous atoms diffuse and polarisation functions were added [21]. All vibrations in the calculated vibrational spectrum of [Re-Cl_3(dpphen)(PPh_3)] and [ReCl_4(dpphen)] were real, thus the both geometries correspond to true energy minimum.

The electronic spectra of $[ReCl_3(dpphen)(PPh_3)]$ and $[Re-Cl_4(dpphen)]$ were calculated with the TD-DFT method [22], and the solvent effect (acetonitrile) was simulated using the polarisable continuum model with the integral equation formalism (IEF-PCM) [23].

2.6. Magnetic measurement

Magnetisation measurements of polycrystalline samples were carried out with a Quantum Design SQUID magnetometer (MPMSXL-5-type) at a magnetic field of 0.5 T over the temperature range 1.8–300 K. Magnetisation measurements versus magnetic field (0–5 T) were made at 2 K.

Corrections are based on subtracting the sample, holder signal and contribution χ_D estimated from the Pascal constants [24] and equal, $573\times10^{-6}\,cm^3\,mol^{-1}$ for 1 and $400\times10^{-6}\,cm^3\,mol^{-1}$

for **2**. The effective magnetic moment was calculated from the equation, $\mu_{eff} = 2.83(\chi_M T)^{1/2}$ (B.M.).

3. Results and discussion

3.1. Preparation

The $[Re^{III}Cl_3(dpphen)(PPh_3)]\cdot Me_2CO$ (1) and $[ReCl_4(dpphen)]\cdot CHCl_3$ (2) complexes have been obtained in the reaction of [ReO



Fig. 1. The molecular structure of 1. Displacement ellipsoids are drawn at 50% probability.



Fig. 2. The molecular structure of 2. Displacement ellipsoids are drawn at 50% probability.

(OMe)Cl₂(dpphen)] with triphenylphosphine in a mixture dichloromethane/acetone and chloroform, respectively.

Formation of the Re(III) complex in the reaction of [ReO(O-Me)Cl₂(dpphen)] with PPh₃ in a mixture dichloromethane/acetone can be easily explained on the basis of the previous studies on the oxygen atom transfer reactions between monooxorhenium(V) reagents and tertiary phosphines [7-12]. Upon treatment with PPh₃ the oxocompound [ReO(OMe)Cl₂(dpphen)] in CH₂Cl₂ undergoes facile transformation to [Re^{III}Cl₃(dpphen)(OPPh₃)] which then react with more PPh₃ forming [Re^{III}Cl₃(dpphen)(PPh₃)]. Another course of the reaction of [ReO(OMe)Cl₂(dpphen)] with PPh₃ is observed in chloroform. It can be supposed that the Re(III) complex formed in the first reaction step undergoes the halogenation reaction by CHCl₃ to give [ReCl₄(dpphen)]·CHCl₃. The chemistry of Re(IV) with *N*-heterocyclic chelate ligands is scarcely developed compared with that of other oxidation states. In fact, only a few Re(IV) complexes containing bidendate heterocyclic ligands have been reported, naming $[ReX_4(bipy)]$ (X = Cl, Br; bipy = 2,2'-bipyridine), $[ReCl_4(pyim)]$ ·DMF (pyim = 2-(2'-pyridyl)imidazole), [Re- $Cl_4(biimH_2)$]·2DMF ((biimH_2 = 2,2'-biimidazole), [ReX_4(bpym)] $(bpym = 2,2'-bipyrimidine), [ReCl_4(pbimz)] \cdot OPPh_3$ (2(2'-pyridyl)benzimidazole) and [ReCl₄{ η^2 -HC(pz)₃}] [25–29].

3.2. IR spectra

The characteristic bands corresponding to the v(CN), v(C=C) modes of the dpphen ligand appear in the range 1630–1510 cm⁻¹ in the IR spectrum of **1** and **2**. The absence of the characteristic strong v(Re=O) band in the range 900–1000 cm⁻¹ is clear indication that there is no oxo-Re(V) starting material left in the samples **1** and **2** [30].

3.3. Crystal structures

The molecular structures of **1** and **2** are depicted in Figs. 1 and 2, and the crystallographic details are given in Table 1. The short intra- and intermolecular contacts detected in the examined complexes are listed in Table 2. The classical hydrogen bonds can not be found, only some $C-H\cdots X$, $C-H\cdots O$ and $C-H\cdots N$ weak interand intramolecular hydrogen bonds exist in the structures **1** and **2** [31,32]. The selected bond lengths and angles of **1** and **2** are collected in Tables 3 and 4.

The pseudooctahedral environment of Re center in [Re-Cl₃(dpphen)(PPh₃)] shows clear distortions, induced by the bite angle of the chelating dpphen ligand. The chloride ions of [ReCl₃(dpphen)(PPh₃)] are arranged in a *facial* fashion. This geometry of the ReX₃ fragment it is affected by π acidity of the phosphine ligand [7–12].

The Re–N, Re–Cl and Re–P bond lengths of **1** are unexceptional, they agree well with appropriate values found previously in the

Table 2					
Hydrogen	bonds	for	1	and	2.

D	А	D–H [Å]	H⊷A [Å]	D· · ·A [Å]	D−H···A [°]
1					
C1	Cl2	0.93	2.70	3.304(5)	123.2
C5	098_#1	0.93	2.55	3.160(9)	123.3
C6	098_#1	0.93	2.55	3.159(9)	123.2
C10	Cl1	0.93	2.75	3.346(5)	122.8
C36	Cl2	0.93	2.78	3.455(6)	130.3
2					
C1	Cl2	0.93	2.75	3.318(4)	120.5
C10	Cl1	0.93	2.78	3.352(4)	121.2
C99	Cl2	0.98	2.60	3.512(7)	154.9

+11 - x, -y, 2 - z.

Table 3
The experimental and optimised bond lengths (Å) and angles (°) for 1 .

	Experimental	Optimised
Bond lengths		
Re(1)-N(2)	2.084(4)	2.101
Re(1)-N(1)	2.087(4)	2.100
Re(1)-Cl(2)	2.3618(13)	2.431
Re(1)-Cl(1)	2.3666(13)	2.432
Re(1)-Cl(3)	2.3954(16)	2.452
Re(1)-P(1)	2.4683(16)	2.507
Bond angles		
N(2)-Re(1)-N(1)	77.04(14)	76.91
N(2)-Re(1)-Cl(2)	170.33(10)	169.35
N(1)-Re(1)-Cl(2)	93.30(11)	92.52
N(2)-Re(1)-Cl(1)	94.64(11)	93.42
N(1)-Re(1)-Cl(1)	171.15(11)	170.04
Cl(2)-Re(1)-Cl(1)	95.03(5)	97.07
N(2)-Re(1)-Cl(3)	88.84(12)	86.47
N(1)-Re(1)-Cl(3)	87.37(11)	86.28
Cl(2)-Re(1)-Cl(3)	91.25(6)	91.52
Cl(1)-Re(1)-Cl(3)	89.45(6)	90.78
N(2)-Re(1)-P(1)	90.73(11)	96.26
N(1)-Re(1)-P(1)	92.01(11)	96.00
Cl(2)-Re(1)-P(1)	89.08(6)	86.12
Cl(1)-Re(1)-P(1)	91.12(5)	87.34
Cl(3)-Re(1)-P(1)	179.31(5)	176.77

Table 4

The experimental and optimised bond lengths (Å) and angles (°) for 2.

	Experimental	Optimised
Bond lengths		
Re(1)-N(2)	2.111(3)	2.146
Re(1)-N(1)	2.122(3)	2.146
Re(1)-Cl(1)	2.3088(11)	2.369
Re(1)-Cl(3)	2.3203(12)	2.369
Re(1)-Cl(2)	2.3217(14)	2.408
Re(1)-Cl(4)	2.3350(12)	2.407
Bond angles		
N(2)-Re(1)-N(1)	77.26(12)	76.69
N(2)-Re(1)-Cl(1)	94.67(9)	94.15
N(1)-Re(1)-Cl(1)	171.57(9)	170.83
N(2)-Re(1)-Cl(3)	86.93(9)	85.93
N(1)-Re(1)-Cl(3)	89.28(9)	85.93
Cl(1)-Re(1)-Cl(3)	92.74(4)	93.46
N(2)-Re(1)-Cl(2)	170.87(9)	170.83
N(1)-Re(1)-Cl(2)	93.66(9)	94.15
Cl(1)-Re(1)-Cl(2)	94.45(4)	95.02
Cl(3)-Re(1)-Cl(2)	92.03(5)	93.46
N(2)-Re(1)-Cl(4)	88.40(9)	85.98
N(1)-Re(1)-Cl(4)	85.51(10)	85.98
Cl(1)-Re(1)-Cl(4)	91.91(5)	93.51
Cl(3)-Re(1)-Cl(4)	173.66(4)	169.68
Cl(2)-Re(1)-Cl(4)	91.90(4)	93.51

related Re(III) compounds. Namely, the Re–N distances are in good agreement with those found for the rhenium(III) polypyridyl compounds: in [ReCl₂(bipy)₂]PF₆ – 2.094(5) and 2.096(5) Å [33] and in the [ReL(terpy)₂]²⁺ (L = Cl, OH, NCS) complexes – about 2.10 Å [34]. These values are significantly shorter than comparable distances for saturated amine complexes, where metal-to-ligand π -back bonding is not possible, for instance, the Re–NH₂ distance in the [Re(N₂)(ampy)(tbpy)(PPh₃)]PF₆ compound is 2.197(7) [35]. The Re–Cl(3) distance of **1** is affected by *trans* influence of triphenyl-phosphine and is therefore longer than the Re–Cl(1) and Re–Cl(2) bond lengths located in *trans* positions to the dpphen ligand.

In the structure of **2** the distorted octahedral Re environment is formed by four chloride ligands and two nitrogen atoms of the heterocyclic ligand. The N(1), N(2), Cl(1) and Cl(2) set of atoms constitute the best equatorial plane around Re with the largest deviation from planarity being 0.0336(14)Å for N(1). The Re atom is practically placed in this plane. The phenyl rings of the coordinated 4,7-diphenyl-1,10-phenanthroline are inclined to the 1,10-phenanthroline moiety at 56.11(8)° and 81.40(18)°. Similar to the Re(III) complex the main distortion of the ideal octahedral geometry of **2** is due to the short bite angle of the bidentate dpphen ligand. The Re–Cl and Re–N bond distances are in agreement with those found in the literature for Re(IV). In comparison with the Re(III) complex, the Re–N distances of **2** are longer, indicating a stronger bond in the lower oxidation state. It can be explained on the basis of the π -acceptor character of dpphen. The higher affinity of Re(III) for dpphen stabilizes oxidation state III relative to IV. Furthermore, due to the back bonding of the chelate ligand the Re–Cl bond lengths in *trans* relation to the nitrogen donors are slightly shorter than those in *cis* positions.

3.4. Magnetic properties

The magnetic properties of complex **1** under the form molecular magnetic susceptibility $\chi_{\rm M} = f(T)$ and magnetic moment $\mu_{\rm eff} = f(T)$ are shown in Fig. 3. The complex shows in the whole temperature range lowering of the magnetic moment from 1.81 B.M. at 300 K up to 0.50 B.M. at 1.8 K. This behaviour is characteristic for mononuclear Re(III) pseudooctahedral complexes with d⁴ low-spin configuration [36–41]. It seems that at room temperature accordance Boltzmann's distribution, it is populated higher magnetic state, which is depopulated with temperature lowering and decreasing of the magnetic moment is observed.



Fig. 3. Experimental magnetic data plotted as χ_M (\bigcirc) and μ_{eff} (\bullet) versus *T* for complex **1**.



Fig. 4. Experimental magnetic data plotted as χ_M (•) and $\chi_M T$ (\bigcirc) versus *T* for complex **2.** The solid line is the calculated curve for $\chi_M T$ versus *T*.

The variation of the magnetisation M versus the magnetic field H for **1** at 2 K very slowly increases and indicates value of the magnetisation only 0.06 B.M. at 5 T, confirms pure diamagnetic ground state of the complex.

The magnetic properties of the Re(IV) complex as relations of $\chi_{\rm M} = f(T)$ and $\chi_{\rm M}T = f(T)$ are shown in Fig. 4. The complex shows in the whole temperature range lowering of the magnetic moment from 3.63 B.M. at 300 K up to 2.40 B.M. at 1.8 K.

The magnetisation M versus the magnetic field H for **2** at 2 K increases and value of the magnetic moment 1.72 B.M. at 5 T, confirms low spin ground state of the rhenium(IV) complex at the lowest temperatures.

The octahedral crystal field around the rhenium cations Re⁴⁺ gives the t_{2g}^3 electronic configuration with the ${}^4A_{2g}$ ground term. The combined action of the axial ligand field and spin–orbit coupling removed the orbital degeneration of the ${}^4A_{2g}$ state and split the ground term of two Kramers doublets $\pm 3/2$, $\pm 1/2$ separated of $2D = 8\lambda^2 (1/\Delta_{\perp} - 1/\Delta_{\parallel})$, where *D* is the zero field-splitting parameter, λ the spin–orbit coupling constant [42]. Formally, this behaviour can be treated as an *S* = 3/2 spin state. In the absence of magnetic exchange, the magnetic properties are described to sufficient accuracy by the Hamiltonian [43–45]:

$$H = 2D[S_z^2 - 1/3S(S+1)] + g_{||}\beta H_z S_z + g_{\perp}\beta (H_x S_x + H_y S_y)$$



where DS_z^2 represents the splitting into two Kramers doublets in the absence of magnetic field.

The parallel and perpendicular zero field susceptibilities for S = 3/2 with an axial crystal field distortion are:

$$\begin{split} \chi_{\parallel} &= \frac{N\beta^2}{4kT} g_{\parallel}^2 \frac{1+9\exp\left(-\frac{2D}{kT}\right)}{1+\exp\left(-\frac{2D}{kT}\right)} \\ \chi_{\perp} &= \frac{N\beta^2}{4kT} g_{\perp}^2 \frac{4+6\frac{kT}{2D}\left[1-\exp\left(-\frac{2D}{kT}\right)\right]}{1+\exp\left(-\frac{2D}{kT}\right)} \end{split}$$

where $g_{(||,\perp)} = (2(1 - \lambda)/\Delta_{(||,\perp)})$, *N* the Avogadro number, *g* the spectroscopic splitting factor, β the Bohr magneton, k the Boltzman constant and *T* is absolute temperature.

The average magnetic susceptibility is equal to $\chi_{av} = 1/3\chi_{||} + 2/3\chi_{\perp}$. In the frame of this model, the best parameters obtained

by a least-squares fit are as follows: $D = 10.8 \text{ cm}^{-1}$, $g_{||} = 2.49$, $g_{\perp} = 1.51$ and $R = 4.94 \times 10^{-4}$ where

$$R = \frac{\sum_{i=1}^{n} (T_i \chi_i^{\exp} - T_i \chi_i^{\operatorname{calc}})^2}{\sum_{i=1}^{n} (T_i \chi_i^{\exp})^2}$$

3.5. Geometry optimisation and electronic structure

The geometries of [ReCl₃(dpphen)(PPh₃)] and [ReCl₄(dpphen)] were optimised in a triplet and quartet state respectively using the DFT method with the B3LYP functional. The optimised geometric parameters of [ReCl₃(dpphen)(PPh₃)] and [ReCl₄(dpphen)] are given in Tables 3 and 4. In general, the predicted bond lengths and angles are in good agreement with the values based upon the X-ray crystal structure data, and the general trends observed



Fig. 6. The molecular diagram of [ReCl₄(dpphen)].

in the experimental data are well reproduced in the calculations. The largest differences are found for the Re–Cl and Re–P bond distances. It may come from the basis sets which are approximated to a certain extent or may indicate the influence of the crystal packing on the values of the experimental bond lengths. The theoretical calculations do not consider the effects of chemical environment.

The molecular diagrams of $[ReCl_3(dpphen)(PPh_3)]$ and $[Re-Cl_4(dpphen)]$ are presented in Figs. 5 and 6, respectively. The selected contours of the frontier orbitals of $[ReCl_3(dpphen)(PPh_3)]$ and $[ReCl_4(dpphen)]$ are depicted in Figs. 7 and 8, respectively.

The rhenium d_{π} atomic orbital (d_{xz} , d_{yz} and d_{xy}) and π orbitals of the chloride ligands being in anti-bonding arrangement make main contributions into the HOMO–2, HOMO–1 and HOMO of α spin and HOMO, LUMO and LUMO+1 with β spin. The LUMO of α spin is predominately localised on the dpphen ligand. The d_z^2 rhenium orbital has a significant contribution in the LUMO+2 of α spin and the LUMO+5 of β spin, whereas the LUMO+7 of α spin and the LUMO+15 of β have predominantly $d_{x^2-y^2}$ character. It confirms d⁴ low-spin configuration of the rhenium atom in [ReCl₃(dpphen) (PPh₃)]. Among the lowest unoccupied MOs of [ReCl₃(dpphen)



Fig. 7. The selected HOMO and LUMO orbitals of α - and β -spin for [ReCl₃(dpphen)(PPh₃)]. Positive values of the orbital contour are represented in blue (0.04 au) and negative values – in yellow (-0.04 au). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 8. The selected HOMO and LUMO orbitals of α- and β-spin for [Recl₄(dpphen)]. Positive values of the orbital contour are represented in blue (0.04 au) and negative values – in yellow (-0.04 au). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(PPh₃)], the largest numbers constitute π orbitals of the dpphen ligand and π phenyl ring orbitals of the triphenylphosphine.

The rhenium atom of [ReCl₄(dpphen)] possesses $(d_{xz})^1(d_{yz})^1$ $(d_{xy})^1$ configuration. The d_{xz} , d_{yz} and d_{xy} rhenium orbitals make main contributions into the HOMO–6, HOMO–5 and HOMO–4 of α spin and LUMO, LUMO+1 and LUMO+2 of β spin. In all these MOs, the rhenium d_{xz} , d_{yz} and d_{xy} orbitals bear anti-bonding character towards the p_{π} orbitals of the chloride ligands. The contribution from



Fig. 9. The experimental (black) and calculated (red) electronic absorption spectra of 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 10. The experimental (black) and calculated (red) electronic absorption spectra of 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the rhenium d orbitals is also visible in the two highest occupied molecular orbitals of α spin, but it is much smaller in comparison with HOMO–6, HOMO–5 and HOMO–4. The HOMO–1 and HOMO are mainly π orbitals of the dpphen. The d_z^2 rhenium orbital has a significant contribution in the LUMO+2 of α spin and the LUMO+5 of β spin, whereas the LUMO+3 of α spin and the LUMO+7 of β have predominantly $d_{x^2-v^2}$ character.

3.6. Electronic spectra

The experimental and calculated electronic spectra of **1** and **2** are presented in Figs. 9 and 10, respectively. Each calculated transition for **1** and **2** is represented by a gaussian function $y = ce^{-bx^2}$

with the height (*c*) equal to the oscillator strength and *b* equal to 0.04 nm^{-2} . The TD-DFT results obtained by using B3LYP in combination with the LANL2DZ basis set are in good agreement with the experimental spectra.

Tables 5 and 6 present the most important electronic transitions calculated with the TD-DFT method assigned to the observed absorption bands of **1** and **2**, respectively. The assignment of the calculated orbital excitations to the experimental bands was based on an overview of the contour plots and relative energy to the occupied and unoccupied orbitals involved in the electronic transitions. The investigated complexes are of large size; the number of basis functions is equal 808 and 526 for **1** and **2**, respectively. 110 electron transitions calculated by the TD-DFT method do not

Table 5

The energy and molar absorption coefficients of experimental absorption bands and the electronic transitions calculated with the TDDFT method for [ReCl₃(dpphen)(PPh₃)].

The most important orbital excitations	Character	λ [nm]	E [eV]	f	Experimental Λ [nm] (E [eV]) ε
$H(\beta) \rightarrow L+2(\beta)$	$d/\pi(Cl) \rightarrow \pi^*(dpphen)/d$	639.7	1.94	0.0316	624.3 (1.99) 4415
$H(\beta) \rightarrow L+3(\beta)$	$d/\pi(Cl) \rightarrow \pi^*(dpphen)/d$	573.7	2.16	0.0178	
$H(\alpha) \rightarrow L(\alpha)$	$d/\pi(Cl)/\pi(dpphen) \rightarrow \pi^*(dpphen)/d$	462.2	2.68	0.1696	492.0 (2.52) 2300
$H(\alpha) \rightarrow L+1(\alpha)$	$d/\pi(Cl)/\pi(dpphen) \rightarrow \pi^*(dpphen)$	458.8	2.70	0.0477	451.5 (2.75) 2345
$H-2(\beta) \rightarrow L(\beta)$	$\pi(\text{dpphen})/\pi(\text{PPh}_3) \rightarrow d/\pi^*(\text{dpphen})$	430.8	2.88	0.0678	
$H-6(\beta) \rightarrow L(\beta)$	$\pi(\text{PPh}_3)/\pi(\text{dpphen}) \rightarrow d/\pi^*(\text{dpphen})$	381.8	3.25	0.0412	378.8 (3.27) 5160
$H-2(\alpha) \rightarrow L+7(\alpha)$	$\pi(Cl)/d \rightarrow d$	321.5	3.86	0.0579	282.5 (3.39) 26400
$H-10(\beta) \rightarrow L+1(\beta)$	$\pi(\text{dpphen})/\pi(\text{PPh}_3) \rightarrow d$	320.7	3.87	0.0588	
$H-16(\beta) \rightarrow L(\beta)$	$\pi(Cl)/\pi(PPh_3) \rightarrow d/\pi^*(dpphen)$				
$H-4(\alpha) \rightarrow L+1(\alpha)$	$\pi(\text{dpphen})/\text{d} \rightarrow \pi^*(\text{dpphen})$				
$H(\beta) \rightarrow L+8(\beta)$	$d/\pi(Cl) \rightarrow \pi^*(dpphen)/\pi^*(PPh_3)$	314.6	3.94	0.0813	
$H-6(\alpha) \rightarrow L(\alpha)$	$\pi(\text{dpphen})/\pi(\text{PPh}_3) \rightarrow \pi^*(\text{dpphen})/d$	307.6	4.03	0.0322	
$H-4(\beta) \rightarrow L+2(\beta)$	$\pi(\text{dpphen}) \rightarrow \pi^*(\text{dpphen})/\text{d}$				
$H(\alpha) \rightarrow L+3(\alpha)$	$d/\pi(Cl)/\pi(dpphen) \rightarrow \pi^*(dpphen)$	307.1	4.04	0.0382	
$H-5(\alpha) \rightarrow L+4(\alpha)$	$\pi(\text{PPh}_3) \rightarrow \pi^*(\text{PPh}_3)$	281.9	4.40	0.0337	
$H-7(\alpha) \rightarrow L+4(\alpha)$	$\pi(\text{PPh}_3)/\pi(\text{dpphen})/\pi(\text{Cl}) \rightarrow \pi^*(\text{PPh}_3)$				
$H-5(\beta) \rightarrow L+3(\beta)$	$\pi(\text{PPh}_3)/\pi(\text{Cl}) \rightarrow \pi^*(\text{dpphen})/\text{d}$				
$H-12(\beta) \rightarrow L+2(\beta)$	$\pi(\text{dpphen}) \rightarrow \pi^*(\text{dpphen})/d$				
$H(\alpha) \rightarrow L+6(\alpha)$	$d/\pi(Cl)/\pi(dpphen) \rightarrow \pi^*(dpphen)$	281.2	4.41	0.0738	
$H(\alpha) \rightarrow L+5(\alpha)$	$d/\pi(Cl)/\pi(dpphen) \rightarrow \pi^*(PPh_3)$				
					206.8 (6.00) 45800

 ε – molar absorption coefficient [dm³ mol⁻¹ cm⁻¹]; f – oscillator strength; H – highest occupied molecular orbital; L – lowest unoccupied molecular orbital.

Table 6

The energy and molar absorption coefficients of experimental absorption bands and the electronic transitions calculated with the TDDFT method for [ReCl₄(dpphen)].

The most important orbital excitations	Character	λ [nm]	E [eV]	f	Experimental Λ [nm] (<i>E</i> [eV]) ε
$H(\beta) \rightarrow L(\beta)$	$\pi(\text{dpphen}) \rightarrow d/\pi^*(\text{dpphen})$	568.3	2.18	0.0434	456.5 (2.72) 60
$H(\beta) \rightarrow L+2(\beta)$	$\pi(dpphen) \rightarrow d$	522.0	2.38	0.0173	
$H-1(\beta) \rightarrow L+2(\beta)$	$\pi(dpphen) \rightarrow d$	456.4	2.72	0.0216	
$H(\alpha) \rightarrow L+1(\alpha)$	$d/\pi(dpphen) \rightarrow \pi^*(dpphen)$	444.0	2.79	0.0262	
$H(\alpha) \rightarrow L(\alpha)$	$d/\pi(dpphen) \rightarrow \pi^*(dpphen)$	411.7	3.01	0.0531	412.1 (3.01) 2030
$H-8(\beta) \rightarrow L+1(\beta)$	$\pi(Cl) \rightarrow d$	363.6	3.41	0.0267	
$H(\beta) \rightarrow L+3(\beta)$	$\pi(dpphen) \rightarrow \pi^*(dpphen)/d$	346.4	3.58	0.0901	290.3 (4.27) 28230
$H(\beta) \rightarrow L+4(\beta)$	$\pi(\text{dpphen}) \rightarrow \pi^*(\text{dpphen})$	338.3	3.67	0.2764	
$H-10(\beta) \rightarrow L+2(\beta)$	$\pi(Cl) \rightarrow d/\pi^*(dpphen)$	336.1	3.69	0.0756	
$H-1(\alpha) \rightarrow L+1(\alpha)$	$\pi(\text{dpphen})/\text{d} \rightarrow \pi^*(\text{dpphen})$	318.6	3.89	0.0835	
$H-11(\beta) \rightarrow L(\beta)$	$\pi(Cl)/\pi(dpphen) \rightarrow d$	315.2	3.93	0.0485	
$H-3(\beta) \rightarrow L+3(\beta)$	$\pi(\text{dpphen}) \rightarrow d/\pi^*(\text{dpphen})$				
$H-12(\beta) \rightarrow L+2(\beta)$	$\pi(\text{Cl})/\pi(\text{dpphen}) \rightarrow d/\pi^*(\text{dpphen})$	278.8	4.45	0.0878	
$H-15(\beta) \rightarrow L+1(\beta)$	$d/\pi(Cl)/\pi(dpphen) \rightarrow d$				
$H-14(\beta) \rightarrow L+1(\beta)$	$\pi(\text{dpphen})/\pi(\text{Cl}) \to \text{d}$	271.2	4.57	0.0870	
$H-5(\beta) \rightarrow L+4(\beta)$	$\pi(\text{dpphen}) \rightarrow \pi^*(\text{dpphen})/d$	270.6	4.58	0.0538	
$H-2(\alpha) \rightarrow L+2(\alpha)$	$\pi(\text{dpphen}) \rightarrow d$	269.4	4.60	0.0484	
$H-13(\beta) \rightarrow L+2(\beta)$	$\pi(\text{Cl})/\pi(\text{dpphen}) \rightarrow d/\pi^*(\text{dpphen})$	266.8	4.65	0.1790	
$H-8(\alpha) \rightarrow L(\alpha)$	$\pi(\text{dpphen}) \rightarrow \pi^*(\text{dpphen})$				
$H-6(\beta) \rightarrow L+3(\beta)$	$\pi(\text{Cl}) \rightarrow d/\pi^*(\text{dpphen})$	254.1	4.88	0.0344	
					219.5 (5.65) 50425

 ε – molar absorption coefficient [dm³ mol⁻¹ cm⁻¹]; f – oscillator strength; H – highest occupied molecular orbital; L – lowest unoccupied molecular orbital.

comprise all the experimental absorption bands, thus the shortest wavelength experimental bands of **1** and **2** are not assigned to the calculated transitions. As the solution spectra of PPh₃ and 4,7-diphenyl-1,10-phenanthroline exhibit intense absorption bands in 300-200 nm region, some additional intraligand and interligand transitions are expected to be found at higher energies in the calculations for **1** and **2**.

In the visible region complex **1** displays multiple transitions of moderate intensity in the form of peaks and shoulders. The broad and asymmetric longest wavelength experimental band with maximum at 624.3 nm is assigned to the transitions of $d/\pi(Cl) \rightarrow \pi^*(dpphen)/d$ type. They can be seen as mixed $d_{Re} \rightarrow \pi^*(dpphen)$ (*MLCT*), $d \rightarrow d$ (*LF*) and $\pi(Cl) \rightarrow \pi^*(dpphen)$ (*MLCT*) or a delocalised *MLLCT* (metal–ligand-to-ligand CT) description can be used. The transitions leading to the experimental bands at 492.0 and 451.5 nm have also delocalised *MLLCT* character. The experimental absorption bands at 378.8 and 282.5 nm is mainly attributed to *Ligand–Ligand Charge Transfer* and interligand (*IL*) transitions. However, some contribution of the *Ligand–Metal Charge Transfer* from the triphenylphosphine, chloride and dpphen orbitals to the *d* rhenium orbitals in these bands is also confirmed by the calculations.

The rhenium(IV) complex in which MLCT transitions are expected to shift to much higher energies, do not display any band in the visible region except for two weak shoulders around 450 and 410 nm. The transitions leading to these absorptions can be assigned to *Ligand–Metal Charge Transfer* transitions occurring from the Cl and dpphen ligands to the *d* rhenium orbitals and *Ligand–Ligand Charge Transfer* transitions (π (dpphen)) $\rightarrow \pi^*$ (dpphen)). The absorption band at 290.3 nm results from *Ligand–Ligand Charge Transfer* and interligand (*IL*) transitions.

4. Conclusions

The oxochelate [ReO(OMe)Cl₂(dpphen)] has been shown to be an excellent oxygen atom transfer reagent. In a mixture dichloromethane/acetone it undergoes facile transformation to [Re-Cl₃(dpphen)(PPh₃)]·Me₂CO, whereas the same reaction carried out in chloroform leads to [ReCl₄(dpphen)]·CHCl₃. The Re(III) and Re(IV) compounds have been characterised structurally and spectroscopically, as well as by magnetic measurements. The magnetic behaviour of [Re^{III}Cl₃(dpphen)(PPh₃)]·Me₂CO is characteristic of mononuclear complexes with d⁴ low-spin octahedral Re(III) complexes (³T_{1g} ground state) and arise because of the large spin–orbit coupling. For complex [ReCl₄(dpphen)]·CHCl₃ the results of calculations revealed value of zero-field splitting parameter $D = 10.8 \text{ cm}^{-1}$, $g_{II} = 2.49$ and $g_{\perp} = 1.51$.

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Appendix A. Supplementary data

CCDC 793303 and 793304 contains the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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