Polyhedron 28 (2009) 2821-2830

Contents lists available at ScienceDirect

Polyhedron



journal homepage: www.elsevier.com/locate/poly

Coordination chemistry of di-2-pyridylketone. Synthesis, spectroscopic investigations, X-ray studies and DFT calculations of Re(III) and Re(V) complexes

B. Machura^{a,*}, J. Mroziński^b, R. Kruszynski^c, J. Kusz^d

^a Department of Crystallography, Institute of Chemistry, University of Silesia, 9th Szkolna St., 40-006 Katowice, Poland

^b Faculty of Chemistry, Wroclaw University, F. Joliot-Curie 14 St., 50-383 Wrocław, Poland

^c Department of X-ray Crystallography and Crystal Chemistry, Institute of General and Ecological Chemistry, Lodz University of Technology, 116 Żeromski St., 90-924 Łódź, Poland ^d Institute of Physics, University of Silesia, 4th Uniwersytecka St., 40-006 Katowice, Poland

ARTICLE INFO

Article history: Received 14 May 2009 Accepted 7 June 2009

Keywords: Rhenium complexes Di-2-pyridylketone X-ray Electronic structure DFT and TDDFT calculations Magnetic measurement

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 186 Re (1.07 MeV β -emitter, $t_{1/2}$ 90 h) and 188 Re (2.12 MeV β emitter, $t_{1/2}$ 17 h) are among the most attractive isotopes for applications in targeted radionuclide therapy [2,3]. The diazenido and dinitrogen rhenium complexes are important in view of their significance in the field of nitrogen fixation [4–6]. Methyltrioxorhenium is one of the most versatile catalysts for olefin oxidation reactions, aldehyde olefination and olefin metathesis [7,8]. The *mer,trans*- $[ReOCl_3(PPh_3)_2]$ and its derivatives catalyze the oxidation of sulfides to sulfoxides, thiols to disulfides and catalyze oxygen-transfer from sulfoxides to phosphines [8]. The [ReOCl₂(O–N)(PPh₃)] chelates with pyridinecarboxylate ligands exhibit a remarkable catalytic activity for the carboxylation of ethane by CO in the presence of $K_2S_2O_8$ to a mixture of propionic and acetic acids in a single-pot process [9]. The [CH₃ReO(pic)₂] complex is an active precursor in olefin oxidation and forms epoxides in a two-phase H₂O₂-H₂O/CH₂Cl₂ system [10].

ABSTRACT

The paper presents a combined experimental and computational study of Re(III) and Re(V) complexes containing di-2-pyridylketone and its gem-diol form – [ReCl₃(dpk-N,O)(PPh₃)] (1), [ReCl₃(dpk-N,N')(OPPh₃)] (2) and [ReOBr₃(dpk-OH)]-2(dpkH⁺Br⁻) (3). All the complexes have been characterized spectroscopically and structurally (by single-crystal X-ray diffraction). The complex 2 has been additionally studied by magnetic measurement. The magnetic behavior of 2 is characteristic of mononuclear octahedral Re(III) complex with d⁴ low-spin (³T_{1g} ground state) and arise because of the large spin–orbit coupling ($\zeta = 2500 \text{ cm}^{-1}$), which gives diamagnetic ground state. DFT and time-dependent (TD)DFT calculations have been carried out for [ReCl₃(dpk-N,N')(OPPh₃)] and [ReOBr₃(dpk-OH), and their UV-vis spectra have been discussed on this basis.

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In this context, the design, synthesis and reactivity of novel rhenium complexes has become the aim of several laboratories, including ours.

Here, we present synthesis, spectroscopic investigation, crystal and molecular structure of three rhenium complexes with di-2pyridylketone (dpk) and its gem-diol. Investigation into the properties of the ligand di-2-pyridyl ketone was first reported in 1967 by Osborne and McWhinnie and numerous reactions of di-2-pyridyl ketone with transition metals have been studied to date. The dpk can act as a bidentate, tridentate or bridging ligand. As a chelate di-2-pyridylketone can bind to the metal center ion *via* one of two modes: either through the two nitrogen atoms located in the pyridine rings or through one pyridyl nitrogen and the carbonyl oxygen [11]. The majority of metal complexes with dpk are coordinated in the N,N-mode. The N,O-coordination mode of dpk has been confirmed in [RuCl₂(DMSO)(dpk-N,O)] [12] and [Ru(Cp)(dpk-N,O)] [13].

After the initial coordination with the metal ion, the carbonyl oxygen atom of the dpk ligand can become subject to nucleophilic attack by water or alcohols, and the formation of $(2-py)_2C(OH)_2$ or $(2-py)_2C(OR)(OH)$ has been frequently observed. The deprotonated gem-diol or hemiacetal form of $(2-py)_2CO$ coordinates to the metal centers as *N*,*N'*,*O* chelates or as bridging ligands. The monoanionic form usually bridge two or three metal ions, while the dianionic form can bridge as many as five metal sites [11].

The rhenium complexes with di-2-pyridylketone have been studied relatively little [14,15]. It prompts us to explore the



^{*} Corresponding author.

E-mail addresses: basia@ich.us.edu.pl (B. Machura), jmroz@wchuwr.chem.uni. wroc.pl (J. Mroziński), rafal.kruszynski@p.lodz.pl (R. Kruszynski).

^{0277-5387/\$ -} see front matter \odot 2009 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2009.06.048

reactivity of [ReCl₃(MeCN)(PPh₃)₂] towards the dpk ligand. The [ReCl₃(MeCN)(PPh₃)₂] complex has proven to be useful precursor in the synthesis of Re(III) compounds [16–18]. The [ReCl₃(MeCN)-(PPh₃)₂] also easily reacts with di-2-pyridylketone to give [ReCl₃(dpk-N,O)(PPh₃)] (1) with rarer N,O-coordination of dpk ligand. The solid [ReCl₃(dpk-N,O)(PPh₃)] can be handled in air without significant degradation, but rapid isomerisation with oxidation of coordinated PPh₃ occurs in organic solvents at room temperature in the presence of atmospheric oxygen. In fact, the starting purple solution of [ReCl₃(dpk-N,O)(PPh₃)] in chloroform turns to dark red and crystals of [ReCl₃(dpk-N,N')(OPPh₃)] (2) with N,N-coordination of dpk ligand are deposited.

N,*N*',*O* coordination mode of monoanionic form of $(2-py)_2CO$ has been confirmed in the [ReOBr₃(dpk-OH)]·2(dpkH⁺Br⁻) (**3**), isolated from the reaction of [ReOBr₃(PPh₃)₂] with excess of di-2-pyridylketone in acetone in air.

The structures of all the complexes $[ReCl_3(dpk-N,O)(PPh_3)]$ (1), $[ReCl_3(dpk-N,N')(OPPh_3)]$ (2) and $[ReOBr_3(dpk-OH)]\cdot 2(dpkH^+Br^-)$ (3) have been proven by X-ray diffraction. The complexes $[ReCl_3(dpk-N,N')(OPPh_3)]$ and $[ReOBr_3(dpk-OH)]$, which are stable in solution, have been also studied by UV-vis spectroscopy. The electronic spectra of $[ReCl_3(dpk-N,N')(OPPh_3)]$ and $[ReOBr_3(dpk-OH)]$, have been discussed in detail using the density functional theory (DFT) and time-dependent DFT (TDDFT) calculations.

Currently the density functional theory (DFT) 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 [19]. Recent studies have also supported the TDDFT method to be applicable for open- and closed-shell of 5d-metal complexes giving good assignment of experimental spectra [20–22].

2. Experimental

2.1. General procedure

The reagents used to the synthesis were commercially available and were used without further purification. The $[Re(MeCN)Cl_3-(PPh_3)_2]$ [16] and $[ReOBr_3(PPh_3)_2]$ [23] complexes were prepared according to the literature methods.

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 1000– 180 nm in acetonitrile solution. Elemental analyses (CHN) were performed on a Perkin–Elmer CHN-2400 analyzer.

2.2. Preparation of [ReCl₃(dpk-N,O)(PPh₃)] (1)

 $[\text{Re}(\text{MeCN})\text{Cl}_3(\text{PPh}_3)_2]$ (0.5 g, 0.58 mmol) and di-2-pyridylketone (0.11 g, 0.60 mmol) in CH₂Cl₂ (80 cm³) were heated under argon atmosphere for 5 h. The starting material gradually dissolved and the color of the reaction solution became blue-purple. The volume of the reaction solution was condensed to 10 cm³ and allowed to cool to room temperature. Dark pink microcrystalline precipitate was formed and filtered off.

IR (KBr; v/cm^{-1}): 1646(s) $v_{C=0}$; 1608(w), 1590(m), 1572(m) and 1538(w) v_{CN} and $v_{C=C}$.

Anal. Calc. for $C_{29}H_{23}Cl_3N_2OPRe:$ C, 47.13; H, 3.14; N, 3.79. Found: C, 47.61; H, 3.42; N, 3.62%.

2.3. Preparation of $[ReCl_3(dpk-N,N')(OPPh_3)]$ (2)

A solution of [ReCl₃(dpk-N,O)(PPh₃)] in chloroform was stood for several days in air and dark red crystals were deposited. IR (KBr; ν/cm^{-1}): 1649(vs) $\nu_{C=0}$; 1609(m), 1591(m), 1575(m) and 1542(w) ν_{CN} and $\nu_{C=C}$; 1135(vs) and 1119(vs) $\nu_{R=0}$.

Anal. Calc. for C₂₉H₂₃Cl₃N₂O₂PRe: C, 46.13; H, 3.07; N, 3.71. Found: C, 46.79; H, 3.30; N, 3.45%.

2.4. Preparation of $[ReOBr_3(dpk-OH)] \cdot 2(dpkH^+Br^-)$ (3)

A mixture of $[\text{ReOBr}_3(\text{PPh}_3)_2]$ (0.50 g, 0.52 mmol), di-2-pyridylketone (0.28 g, 1.52 mmol) and acetone (100 ml) was stirred at room temperature for 12 h. Half of the solvent was removed and diethyl ether (50 ml) was added to precipitate the product as green solid, which was filtered off and dried. Yield 85%. Crystals suitable for X-ray investigation were obtained by recrystallization from acetonitrile.

IR (KBr; v/cm^{-1}): 1683(vs) $v_{C=0}$; 1599(s), 1579(s) and 1520(s) v_{CN} and $v_{C=C}$; 958(s) $v_{Re=0}$.

Anal. Calc. for $C_{33}H_{27}Br_4N_6O_5Re:$ C, 36.25; H, 2.49; N, 7.69. Found: C, 36.89; H, 2.37; N, 7.39%.

2.5. Crystal structures determination and refinement

The X-ray intensity data of 1, 2 and 3 were collected on a KM-4-CCD automatic diffractometer equipped with CCD detector and graphite monochromated Mo K α radiation (λ = 0.71073 Å). Details concerning crystal data and refinement are given in Table 1. Lorentz, polarization and absorption correction [24] 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 full-matrix, least-squares technique. The hydrogen atoms were treated as "riding" on their adjacent atoms and assigned isotropic temperature factors equal 1.2 times the value of equivalent temperature factor of the aromatic parent atoms and equal 1.5 times the value of equivalent temperature factor of the oxygen atom (OH). SHELXS97 [25], SHELXL97 [26] and SHELXTL [27] programs were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs.

2.6. Computational details

The ground states geometries of $[ReCl_3(dpk-N,N')(OPPh_3)]$ and $[ReOBr_3(dpk-OH)]$ were optimized without any symmetry restrictions with the DFT method using the hybrid B3LYP functional of GAUSSIAN-03 [28–30].

The calculations were performed using ECP basis set LANL2DZ [31] with an additional *d* and *f* function with the exponent $\alpha = 0.3811$ and $\alpha = 2.033$ [32] for rhenium and the standard 6-31G basis set for other atoms. For chloride, bromide, oxygen, nitrogen and phosphorous atoms, diffuse and polarization functions were added [33–38]. Vibrational frequencies of [ReCl₃(dpk-N,N')(OPPh₃)] and [ReOBr₃(dpk-OH)] were calculated to ensure that optimized geometries represented minima.

The electronic spectra of [ReCl₃(dpk-N,N')(OPPh₃)] and [ReOBr₃ (dpk-OH)] were calculated with the TDDFT method, and the solvent effect (acetonitrile) was simulated using the polarizable continuum model with the integral equation formalism (IEF-PCM) [39–42].

Natural bond orbital (NBO) calculations for [ReOBr₃(dpk-OH)] were performed with the NBO code [43] included in GAUSSIAN-03.

2.7. Magnetic measurement

Magnetization 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. Magnetization measurements versus magnetic field (0–5 T) were made at 2 K.

Table 1	
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Crystal data and structure refinement for 1, 2 and 3 complexes.

	1	2	3
Empirical formula	C ₂₉ H ₂₃ Cl ₃ N ₂ OPRe	C ₂₉ H ₂₃ Cl ₃ N ₂ O ₂ PRe	C33H27Br4N6O5Re
Formula weight	739.01	755.01	1093.45
Temperature (K)	293(2)	293(2)	120(1)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	triclinic
Space group	$P2_1/n$	$P2_{1}2_{1}2_{1}$	PĨ
Unit cell dimensions (Å, °)	a = 11.621(2)	a = 9.9643(3)	a = 8.98070(10)
	b = 12.505(3)	b = 13.9694(5)	b = 13.0557(2)
	<i>c</i> = 18.938(4)	<i>c</i> = 19.7787(6)	c = 16.2930(2) $\alpha = 69.0060(10)$
	$\beta = 90.12(3)$		$\beta = 81.8530(10)$ $\gamma = 79.3880(10)$
Volume (Å ³)	2752.1(10)	2753.10(15)	1747.05(4)
Ζ	4	4	2
D_{calc} (mg/m ³)	1.784	1.822	2.079
Absorption coefficient (mm ⁻¹)	4.791	4.794	8.102
F(000)	1440	1472	1044
Crystal size (mm)	$0.05\times0.08\times0.19$	$0.04 \times 0.18 \times 0.20$	$0.183 \times 0.181 \times 0.176$
θ Range for data collection (°)	3.22-25.00	2.90-25.00	1.76-25.05
Index ranges	$-13 \leqslant h \leqslant 13$	$-9 \leqslant h \leqslant 11$	$-10 \leqslant h \leqslant 10$
	$-10 \leqslant k \leqslant 14$	$-15 \leqslant k \leqslant 16$	$-15 \leqslant k \leqslant 15$
	$-22 \leqslant l \leqslant 22$	$-23 \leqslant l \leqslant 23$	$-19 \leqslant l \leqslant 19$
Reflections collected	15 206	17 510	17 564
Independent reflections	4710 (<i>R</i> _{int} = 0.0471)	4852 (<i>R</i> _{int} = 0.0556)	$6200 (R_{int} = 0.0272)$
Completeness to 2θ (%)	98.6	99.8	99.9
Maximum and minimum transmission	0.792 and 0.641	0.822 and 0.405	0.259 and 0.241
Data/restraints/parameters	4710/0/334	4852/0/343	6200/0/443
Goodness-of-fit (GOF) on F^2	0.857	1.083	1.050
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0294, wR_2 = 0.0506$	$R_1 = 0.0260, wR_2 = 0.0722$	$R_1 = 0.0217, wR_2 = 0.0533$
R indices (all data)	$R_1 = 0.0681, wR_2 = 0.0554$	$R_1 = 0.0303, wR_2 = 0.0731$	$R_1 = 0.0264, wR_2 = 0.0550$
Largest difference in peak and hole (e $Å^{-3}$)	1.210 and -0.739	0.927 and -0.985	0.593 and -1.432

Corrections are based on subtracting the sample – holder signal and contribution $\chi_{\rm D}$ estimated from the Pascal constants [44] and equal – 376 × 10⁻⁶ for complex Re(III). The effective magnetic moment was calculated from the equation, $\mu_{\rm eff} = 2.83 (\chi_{\rm M}^{\rm corr} \times T)^{1/2}$ B.M.

3. Results and discussion

3.1. Preparation and infrared data

The [ReCl₃(dpk-N,O)(PPh₃)] (**1**) complex was prepared in good yield by ligand exchange reaction starting from [ReCl₃(MeCN)-(PPh₃)] and di-2-pyridylketone (dpk):

 $[\text{ReCl}_3(\text{MeCN})(\text{PPh}_3)_2] + \text{dpk} \rightarrow [\text{ReCl}_3(\text{dpk-N}, O)(\text{PPh}_3)] + \text{PPh}_3 + \text{MeCN}$

The solid [ReCl₃(dpk-N,O)(PPh₃)] can be handled in air without significant degradation, but rapid isomerisation with oxidation of coordinated PPh₃ occurs in organic solvents at room temperature in the presence of atmospheric oxygen. The [ReCl₃(dpk-N,N')-(OPPh₃)] (**2**) compound has been isolated during crystallization of [ReCl₃(dpk-N,O)(PPh₃)] from chloroform in air.

The $[ReOBr_3(dpk-OH)] \cdot 2(dpkH^+Br^-)$ (**3**) compound has been obtained in the reaction of $[ReOBr_3(PPh_3)_2]$ with excess of di-2-pyridylketone in acetone in a system open to the atmosphere. In this case the carbonyl oxygen atom of the di-2-pyridylketone is subject to nucleophilic attack by water and *gem*-diol form of dpk is formed.

The elemental analyses of the **1**, **2** and **3** complexes are in good agreement with their formulation. The selected frequencies observed in the IR spectra of **1**, **2** and **3** complexes are given in Section 2.

A band due to the v(C=0) vibration of dpk appears at 1646, 1649 and 1683 cm⁻¹ for **1**, **2** and **3**, respectively. In the case of **3** this band is consequence of v(C=0) vibration of the protonated ligand present in the outer coordination sphere. The characteristic bands corresponding to the v(CN), v(C=C) modes of dpk and dpk-OH are observed in the range 1610–1500 cm⁻¹. The strong

v(Re=O) stretching band of **3** is found at 958 cm⁻¹. The medium intensity band at 3045 cm⁻¹ assignable to v(OH) vibrations confirms the monoanionic *gem*-diol form of *dpk* in the coordination sphere of **3**. The strong bands at 1135 and 1119 cm⁻¹ in the IR spectrum of **2** confirm the presence of the coordinated OPPh₃ molecule [45].

3.2. Crystal structures

The crystallographic data of the **1**, **2** and **3** complexes are summarized in Table 1. The short intra- and intermolecular contacts [46,47] detected in the **1**, **2** and **3** are gathered in Table 2. The perspective drawings of **1**, **2** and **3** are presented in Figs. 1–3, and the selected bond distances and angles of **1**, **2** and **3** are collected in Tables 3–5, respectively.

The overall structure of **1** can be considered as a distorted octahedral with the largest deviation from the expected 90° bond angles coming from the bite angle di-2-pyridylketone coordinated in N,O-mode. It equals to 76.08(14)°, and it is similar to that reported for the related [Ru(Cp)(dpk-N,O)] (78.38(7)°) [13]. The bite angles O–M–N in the structures with α -iminoketo chelate ligands bounded to transition metals depend mainly on the size of the metal center, the smallest values (down to 67°) were found for Ag^I complexes and the largest angles (up to 85°) were observed for compounds with Cu^{II} [48].

The electron rich central ion of **1** shows larger affinity towards the less basic but strongly π accepting carbonyl oxo atom, and the Re–O(1) is slightly shorter than the Re–N(1) bond (Table 3). The pyridyl rings of dpk ligand are planar in the range of experimental error and they are inclined at 5.9(3)°.

The chloride ions of **1** are arranged in a *facial* fashion, typical of the [ReX₃(L–L)(PPh₃)] compounds with bipy-like ligands [49]. In the [ReX₃(L–L)(PPh₃)] complexes with two excellent π acceptor ligands coordinated to π -donor rhenium(III) center the back-bonding

Table 2Hydrogen bonds for 1, 2 and 3 complexes.

D	Α	H···A	$D{\cdots}A$	D−H···A
1				
C(8)	Cl(2)	2.69	3.444(5)	138.2
C(8)	0(1)	2.59	3.150(6)	119.5
C(18)	Cl(2)	2.73	3.539(6)	146.2
C(26)	N(2)	2.29	2.899(7)	122.3
C(29)	Cl(1)	2.69	3.286(7)	123.0
2				
C(9)	Cl(2)#1	2.68	3.506(8)	148.5
C(15)	Cl(3)#2	2.73	3.474(7)	137.6
C(27)	O(1)#3	2.48	2.886(8)	106.7
C(18)	Cl(2)	2.77	3.683(7)	166.8
3				
O(3)	Br(99)	2.36	3.175(2)	171.5
N(22)	Br(98)	2.39	3.153(3)	148.6
N(22)	0(21)	2.25	2.620(4)	106.0
N(42)	N(41)	2.08	2.685(4)	126.5
C(28)	N(21)	2.30	2.919(5)	123.3
N(42)	Br(99)#4	2.68	3.377(3)	138.8
C(11)	Br(2)#5	2.90	3.787(4)	159.4
C(29)	Br(98)#6	2.91	3.715(4)	145.7
C(51)	O(2)#4	2.46	3.316(4)	153.7

#1: 0.5 + x, 1.5 - y, 1 - z; #2: 0.5 - x, 2 - y, -0.5 + z; #3: -0.5 + x, 2.5 - y, 1 - z; #4: 1 - x, 1 - y, 1 - z; #5: 2 - x, -y, -z; and #6: 3 - 1 + x, y, z.

effect is maximized in the *facial* disposition, which ensures minimum competition between the two ligands for identical metal orbitals.

The *fac* geometry of chloride ions are also confirmed in complex **2**. However, in this case *facial* arrangement seems to be sustained by steric advantages. Phosphine oxides are purely donor in character, and lack acceptor properties favor the meridional configuration of chloride ligands in the complexes $[ReX_3(L-L)(OPPh_3)]$ with approximately planar L–L ligands. The di-2-pyridylketone is coordinated to the Re(III) center of **2** in a nonplanar N,N-mode, and nonplanarity seems to be responsible for *fac* Chloride arrangement in **2**. Upon coordination of di-2-pyridylketone to the rhenium *via* two nitrogen atoms, a six-membered cycle is formed, and the formed ring shows a *boat* conformation with the rhenium and the carbonyl group off the plane defined by the two nitrogen and

two carbon atoms. The planar in the range of experimental error pyridyl rings are inclined at $51.3(2)^{\circ}$. By forming a six-membered chelate ring dpk allows Re(III) center to achieve a geometry that is closer to octahedral than is possible for α -iminoketo which form five-membered chelate.

The asymmetric unit of **3** contains one complex molecule [Re-OBr₃(dpk-OH)], two bromide anions and two 2-pyridyl-2-pyrydiniumketone cations. In complex molecule of **3** monoanionic gem-diol form $(2-py)_2C(OH)O^-$ coordinates to the Re(V) center through the deprotonated hydroxy group and two pyridyl nitrogen atoms. The coordination sphere of [ReOBr₃(dpk-OH)] is completed by two bromide and terminal oxo ligands, and the geometry about Re(V) can be described as a very distorted octahedral.

The oxygen atom of dpk-OH is coordinated in *trans* position to the terminal oxo ligand. The high concentration of electronic density along the Re–O axis strongly influences the positions of the adjacent halogen atoms, which are pushed away. The planar in the range of experimental error pyridyl rings of the diol are inclined at $72.72(10)^{\circ}$. Aromatic rings of cations are inclined at distinctly smaller angles: $24.8(2)^{\circ}$ and $22.4(2)^{\circ}$. The pyridine ring is in *trans* arrangement to the pyrydinium ring in one of cations and *cis* in second one.

The Re–N bond lengths of **1** and **2** are similar to those found for the rhenium(III) polypyridyl compounds ([ReCl₂(bipy)₂]PF₆ – 2.094(5) and 2.096(5) Å [50] and in the [ReL(terpy)₂]²⁺ (L = Cl, OH, NCS) complexes – about 2.10 Å [51]) and significantly shorter than comparable distances of **3**, where metal-to-ligand π -back bonding is not possible.

The Re–Cl(3) distance of **1** is affected by *trans* influence of triphenylphospine and is longer than the Re–Cl(1) and Re–Cl(2) bond lengths located in *trans* positions to the dpk ligand.

The Re–O_t bond length of **3** falls in the range 1.639–1.76 Å, which is typical of mononuclear complexes of rhenium(V) having [ReO]³⁺ core, and indicates the presence of a triple bond Re \equiv O [52]. The interatomic distance between the rhenium atom and the oxygen atom of dpk-OH ligand is somewhat shorter in comparison with an ideal single Re–O bond length (ca. 2.04 Å) [53], and indicates small delocalization in the O(2)–Re(1)–O(1) moiety. In keeping with that, the O(1)–Re(1)–O(2) angle is equal 157.10(11), notably less than 180°.



Fig. 1. The molecular structure of 1.



Fig. 2. The molecular structure of 2.

In all the compounds the molecules (and ions in **3**) are connected via intermolecular interaction to the three-dimensional nets, however, in compounds **1** and **2** the intermolecular bonds are weak due to absence of strong hydrogen bond donors. In **3** the medium strength hydrogen bonds link molecules and ions to the $[ReOBr_3(dpk-OH)]\cdots Br^{-}\cdots Hdpk^+$ trimers and $Br^{-}\cdots Hdpk^+$ dimers and these clusters are connected via weak C-H···A hydrogen bonds to the three-dimensional net.

3.3. Magnetic properties

The magnetic properties of **2** under the form molar magnetic susceptibility (χ_M) and $\chi_M T = f(T)$ are shown in Fig. 4.

The complex **2** shows in the whole temperature range lowering of the magnetic moment from 2.59 B.M. at 300 K up to 0.91 B.M. at 1.8 K.

This behavior is characteristic of mononuclear Re(III) complexes $({}^{3}T_{1g}$ ground state) with d⁴ low-spin octahedral [54–62] and arise

Table 3

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

Bond lengths	Experimental	Bond angles	Experimental
Re(1)-O(1)	1.997(3)	O(1)-Re(1)-N(1)	76.08(14)
Re(1) - N(1)	2.091(4)	N(1)-Re(1)-Cl(1)	93.88(12)
Re(1)-Cl(1)	2.3314(15)	N(1)-Re(1)-Cl(2)	168.94(12)
Re(1)-Cl(2)	2.3524(15)	N(1)-Re(1)-Cl(3)	86.62(12)
Re(1)-Cl(3)	2.3979(15)	O(1)-Re(1)-Cl(1)	169.79(10)
Re(1)–P(1)	2.4469(15)	O(1)-Re(1)-Cl(2)	93.77(10)
		O(1)-Re(1)-Cl(3)	89.52(10)
		Cl(1)-Re(1)-Cl(2)	96.38(5)
		Cl(3)-Re(1)-Cl(2)	88.95(6)
		Cl(3)-Re(1)-Cl(1)	91.74(6)
		O(1)-Re(1)-P(1)	90.43(10)
		N(1)-Re(1)-P(1)	95.04(12)
		Cl(1)-Re(1)-P(1)	88.61(5)
		Cl(2)-Re(1)-P(1)	89.33(5)
		Cl(3)-Re(1)-P(1)	178.28(5)

from the large spin–orbit coupling ($\zeta = 2500 \text{ cm}^{-1}$ [63]),which gives diamagnetic ground state. It seems that in room temperature, in accordance Boltzmann's distribution, it is populated higher magnetic state, which is depopulated with temperature lowering and decreasing of the magnetic moment is observed.

The variation of the magnetization M versus the magnetic field H for complex **2** at 2 K is shown in Fig. 5.

The magnetization versus magnetic field curve for complex very slowly increases and indicates value of the magnetization 0.36 B.M at 5 T, confirms that the ground state of the complex is diamagnetic.

3.4. Geometry optimization

The geometries of [ReCl₃(dpk-N,N')(OPPh₃)] and [ReOBr₃(dpk-OH)] complexes were optimized by the DFT method with the B3LYP functional. The geometry of [ReCl₃(dpk-N,N')(OPPh₃)] was optimized in triplet and singlet states, and geometry of [Re-OBr₃(dpk-OH)] – in singlet state. For complex [ReCl₃(dpk-N,N')(OPPh₃)] the energy of the triplet state is of 22.12 kcal/mol smaller in comparison with the singlet state. It is in good agreement with the magnetic measurements. The effective magnetic moment of [ReCl₃(dpk-N,N')(OPPh₃)] is equal to 2.59 B.M. at 300 K and decreases with temperature lowering (to 0.91 B.M. at 1.8 K). This behavior is characteristic of mononuclear octahedral Re(III) complex with d⁴ low-spin (³T_{1g} ground state). The optimized geometric parameters of [ReCl₃(dpk-N,N')(OPPh₃)] (triplet state)



Fig. 3. The molecular structure of 3.

Table 4

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

Bond lengths	Experimental	Optimized	Bond angles	Experimental	Optimized
Re(1)-O(2)	2.061(4)	2.080	N(2)-Re(1)-N(1)	87.3(2)	86.93
Re(1)-N(2)	2.055(5)	2.082	O(2)-Re(1)-N(1)	87.8(2)	87.57
Re(1)-N(1)	2.079(6)	2.080	N(1)-Re(1)-Cl(1)	175.85(15)	174.95
Re(1)-Cl(1)	2.3831(15)	2.442	N(1)-Re(1)-Cl(2)	90.55(15)	89.97
Re(1)-Cl(2)	2.3792(17)	2.441	N(1)-Re(1)-Cl(3)	89.35(17)	90.78
Re(1)-Cl(3)	2.3315(17)	2.383	N(2)-Re(1)-Cl(1)	88.69(17)	90.07
O(2)-P(1)	1.513(5)	1.537	N(2)-Re(1)-Cl(2)	172.67(17)	176.02
			N(2)-Re(1)-Cl(3)	92.18(17)	90.23
			O(2)-Re(1)-Cl(1)	90.82(13)	89.45
			O(2)-Re(1)-Cl(2)	87.78(13)	89.73
			O(2)-Re(1)-Cl(3)	176.17(13)	176.48
			Cl(2)-Re(1)-Cl(1)	93.30(6)	92.84
			Cl(3)-Re(1)-Cl(1)	91.86(6)	93.30
			Cl(3)-Re(1)-Cl(2)	94.80(6)	92.33
			N(2)-Re(1)-O(2)	85.1(2)	87.57
			P(1)-O(2)-Re(1)	158.8(3)	150.54

Table	5
	~

The experimental and optimized bond lengths (Å) and angles (°) for ${\bf 3}.$

Bond lengths	Experimental	Optimized	Bond angles	Experimental	Optimized
Re(1)-O(1)	1.681(2)	1.680	O(1)-Re(1)-O(2)	157.10(11)	154.81
Re(1) - O(2)	1.961(2)	2.022	O(1)-Re(1)-N(1)	88.21(11)	88.66
Re(1)-N(1)	2.144(3)	2.196	O(2)-Re(1)-N(1)	74.38(9)	72.99
Re(1)-N(2)	2.151(3)	2.197	O(1)-Re(1)-N(2)	89.88(11)	88.72
$\operatorname{Re}(1)-\operatorname{Br}(1)$	2.4858(4)	2.536	O(2)-Re(1)-N(2)	74.16(9)	72.98
$\operatorname{Re}(1)-\operatorname{Br}(2)$	2.4796(4)	2.536	N(1)-Re(1)-N(2)	85.02(10)	85.14
			O(1)-Re(1)-Br(2)	103.30(9)	103.37
			O(2) - Re(1) - Br(2)	93.65(6)	94.11
			N(1)-Re(1)-Br(2)	168.02(7)	167.08
			N(2)-Re(1)-Br(2)	91.62(7)	90.35
			O(1) - Re(1) - Br(1)	102.69(8)	103.39
			O(2) - Re(1) - Br(1)	92.47(6)	94.04
			N(1)-Re(1)-Br(1)	90.71(7)	90.35
			N(2)-Re(1)-Br(1)	166.61(7)	167.00
			Br(2)-Re(1)-Br(1)	89.967(13)	91.41



Fig. 4. Experimental magnetic plotted as $\chi_M(\bullet)$ and $\chi_M T(\bigcirc)$ versus *T* for complex **2.**

and [ReOBr₃(dpk-OH)] (singlet state) are gathered in Tables 4 and 5, respectively. Generally, the predicted bond lengths and angles are in agreement with the values based upon the X-ray crystal structure data, and the general trends observed in the experimental data are well reproduced in the calculations.

3.5. Molecular orbitals

The energies and characters of several highest occupied and lowest unoccupied molecular orbitals of [ReCl₃(dpk-N,N')(OPPh₃)]



Fig. 5. Field dependence of the magnetization for complex 2.

and $[ReOBr_3(dpk-OH)]$ are presented in Tables 6 and 7, respectively. The selected contours of frontier orbitals of $[ReCl_3(dpk-N,N')(OPPh_3)]$ and $[ReOBr_3(dpk-OH)]$ are presented in Figs. 6 and 7, respectively.

Among the highest occupied MOs of [ReCl₃(dpk-N,N')(OPPh₃)] the largest numbers constitute π orbitals of the phenyl rings with a contribution from Cl atoms. The rhenium d_{xz} , d_{yz} and d_{xy} orbitals make main contributions into the HOMO–2, HOMO–1 and HOMO with α spin and HOMO, LUMO and LUMO+1 with β spin. In all these molecular orbitals, the rhenium d_{xz} , d_{yz} and d_{xy} orbitals bear

Table 6

The energy and character of the selected molecular orbitals with α and β spins for [Recl₃(dpk-N,N')(OPPh₃)].

	MOs with α spin		MOs with	nβspin
	E (eV)	Character	<i>E</i> (eV)	Character
HOMO-5	-7.256	π(Ph)	-7.366	$\pi(Ph)$
HOMO-4	-7.113	$\pi(Ph)$	-7.282	$\pi(Ph)$
HOMO-3	-7.062	$\pi(Ph)$	-7.248	$\pi(Ph)$
HOMO-2	-6.388	$d_{xz}(\text{Re}), \pi(\text{Cl}), \pi(O_{\text{OPPh}_3})$	-7.106	$\pi(Ph)$
HOMO-1	-6.230	$d_{yz}(\text{Re}), \pi(\text{Cl}), \pi(O_{\text{OPPh}_3})$	-7.045	$\pi(Ph), \pi(Cl)$
НОМО	-5.853	$d_{yz}(\text{Re}), \pi(\text{Cl}), \pi(\text{dpk})$	-5.081	d_{xy} , $\pi(dpk)$, $\pi(Cl)$
LUMO	-2.856	$\pi^{*}(dpk), d_{xy}$	-2.997	$d_{xz}(\text{Re}), \pi(\text{dpk})$
LUMO +1	-1.667	$\pi^{*}(dpk)$	-2.978	$d_{vz}(\text{Re}), \pi^{*}(\text{dpk})$
LUMO+2	-1.438	$\pi^{*}(\text{OPPh}_{3}), \pi^{*}(\text{dpk}), d_{z}^{2}$	-2.734	$\pi^*(dpk), d_{vz}$
LUMO+3	-1.308	$\pi^{\circ}(dpk), d_{7}^{2}, \pi^{\circ}(OPPh_{3})$	-1.552	$\pi^*(dpk), d_{xz}$
LUMO+4	-1.194	$\pi^{*}(\text{OPPh}_{3})$	-1.355	$\pi^{*}(dpk), \pi^{*}(OPPh_{3})$
LUMO+5	-0.876	$\pi^{*}(OPPh_{3})$	-1.236	$\pi^{*}(dpk), \pi^{*}(OPPh_{3})$
LUMO+6	-0.792	$\pi^*(dpk), d_z^2$	-1.178	$\pi^*(\text{OPPh}_3)$
LUMO+7	-0.735	d_z^2	-0.862	$\pi^{*}(\text{OPPh}_{3})$

 Table 7

 The energy and character of the selected molecular orbitals for [ReOBr₃(dpk-OH)].

	<i>E</i> (eV)	Character
HOMO-5	-8.123	π (dpk-OH), π (Br), π (O _t)
HOMO-4	-7.932	$\pi(Br), \pi(O_t)$
HOMO-3	-7.648	π (dpk-OH), π (Br), π (O _t)
HOMO-2	-7.550	$\pi(Br), \pi(dpk-OH)$
HOMO-1	-7.291	$\pi(Br)$
НОМО	-6.264	$d_{yz}(\text{Re}), \pi(\text{Br})$
LUMO	-3.066	$d_{yz}, \pi(O)$
LUMO+1	-2.860	$d_{yz}, \pi(O)$
LUMO+2	-1.903	π^* (dpk-OH), d_{yz}
LUMO+3	-1.532	$\pi^{*}(dpk-OH), d_{x^{2}-y^{2}}$
LUMO+4	-1.378	$d_{x^2-y^2}$
LUMO+5	-1.349	$\pi^{*}(dpk-OH)$
LUMO+6	-0.673	$\pi^{*}(dpk-OH)$
LUMO+7	-0.270	d_z^2

antibonding character towards the p_{π} orbitals of the chloride ions and oxygen donor. The d_z^2 rhenium orbital has a significant contribution in the LUMO+7 with α spin and the LUMO+11 with β spin, whereas the LUMO+10 with α spin and the LUMO+13 with β have predominantly $d_{x^2-y^2}$ character. Among the lowest unoccupied MOs of[ReCl₃(dpk-N,N')(OPPh₃)], the largest numbers constitute π orbitals of the dpk ligand. The π phenyl ring orbitals of the triphenylphosphine oxide ligand participate in the higher unoccupied orbitals.

The HOMO of [ReOBr₃(dpk-OH)] is mainly localized on the d_{xy} rhenium orbital and p_{π} chloride orbitals. The LUMO and LUMO+1 are also to a large extent formed by rhenium $d\pi$ atomic orbital (d_{xz} and d_{yz} orbitals) with some contribution of p_{π} oxygen orbitals. The LUMO+4 is of $d_{x^2-y^2}$ character, and d_z^2 rhenium orbital contributes to the LUMO+7.

3.6. NBO analysis

The nature of rhenium-terminal oxygen interaction in [Re-OBr₃(dpk-OH)] has been studied by NBO analysis. The occupancy and composition of the calculated Re–O_t natural bond orbitals (NBOs) are given in Table 8. Each natural bond orbital (NBO) σ_{AB} can be written in terms of two directed valence hybrids (NHOs) h_A and h_B on atoms A and B:

$$(1)\sigma_{\rm AB} = c_{\rm A}h_{\rm A} + c_{\rm B}h_{\rm B},$$

where c_A and c_B are polarization coefficients. Each valence bonding NBO must in turn be paired with a corresponding valence *anti*bonding NBO:

$$(2)\sigma_{AB}^* = c_B h_A - c_A h$$

to complete the span of the valence space. The Lewis-type (donor) NBOs are thereby complemented by the non-Lewis-type (acceptor) NBOs that are formally empty in an idealized Lewis picture. The interactions between 'filled' Lewis-type NBOs and 'empty' non-Le-



Fig. 6. The selected HOMO and LUMO orbitals with α and β spin for [ReCl₃(dpk-N,N')(OPPh₃)].



Fig. 7. The selected HOMO and LUMO orbitals for [ReOBr₃(dpk-OH)].

Table 8

The occupancy of the calculated natural bond orbitals (NBOs) between the rhenium and the oxo ligand for [ReOBr₃(dpk-OH)].

BD	Occupancy	Composition of NBO	BD⁺	Occupancy
Re–O _t	1.994	$0.566(d)_{Re} + 0.825(p)_{O}$	$0.825(d)_{Re} - 0.566(p)_{O}$	0.255
Re-O _t	1.984	$0.566(d)_{Re} + 0.824(p)_{O}$	$0.824(d)_{Re} - 0.566(p)_{O}$	0.307

^{*}Denotes antibond NBO.

BD: denotes two-center bond.

wis NBOs lead to loss of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals, and they are referred to as 'delocalization' corrections to the zeroth-order natural Lewis structure [43].

The detected natural Re–O_t bond orbitals of **3** are π orbitals – the p_x and p_y oxygen orbitals and d_{xz} and d_{yz} rhenium orbitals are involved in their formation. Not detected $\sigma_{\text{Re-O_t}}$ bond has character

of predominant Coulomb-type interactions between the central ion and ligands [64]. The terminal oxo ligand of **1** has two lone pair orbitals, and electron density from one of them is strongly delocalized into non-Lewis rhenium orbital. Accordingly, NBO analysis confirms a triple bond between the rhenium and the terminal oxygen ligand.



Fig. 8. The experimental (black) and calculated (red) electronic absorption spectra of the solution of **2** in acetronitrile. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 9. The experimental (black) and calculated (red) electronic absorption spectra of the solution of **3** in acetronitrile. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.7. Electronic spectra

The experimental and calculated electronic spectra of [ReCl₃(dpk-N,N')(OPPh₃)] and [ReOBr₃(dpk-OH)] are presented in Figs. 8 and 9, respectively. Each calculated transition 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.

Tables 9 and 10 present the most important electronic transitions calculated with the TDDFT method assigned to the observed absorption bands of [ReCl₃(dpk-N,N')(OPPh₃)] and [ReOBr₃(dpk-OH)]. For the high energy part of the spectrum, only transitions with oscillator strengths larger than 0.020 are listed in Tables 9 and 10. 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 orbitals HOMO and LUMO involved in the electronic transitions. As seen in Figs. 8 and 9, TDDFT/PCM calculations well reproduce the absorption spectra of [ReCl₃(dpkN,N')(OPPh₃)] and [ReOBr₃(dpk-OH)] in terms of the energy of the experimental bands and calculated transitions.

3.8. [ReCl₃(dpk-N,N')(OPPh₃)]

The low-energy absorption band at 761.0 nm originates from the transition between HOMO and LUMO+2 with β spins. As can be seen from the Fig. 6, the β HOMO is delocalized on central ion, chloride ions and dpk ligand, whereas the β LUMO+2 are formed of d_{Re} orbitals and π -bonding orbitals of dpk ligand. Accordingly, the transition can be seen as a delocalized MLLCT (*Metal–Ligand-to-Ligand CT*) transition. The same character can be assigned to the experimental absorptions at 487.1, 372.7 and 266.9 nm.

The investigated complex is of large size; the numbers of basis functions are equal to 646. The calculated electron transitions (100) do not comprise all the experimental absorption bands; the

Table 9

The energy and molar absorption coefficients of experimental absorption bands and the electronic transitions calculated with the TDDFT method for [ReCl₃(dpk-N,N')(OPPh₃)].

The most important orbital excitations	Character	λ (nm)	<i>E</i> (eV)	f	Experimental Λ [nm] (E [eV]) ϵ
$H(\beta) \rightarrow L+2(\beta)$	$d/\pi(Cl)/\pi(dpk) \rightarrow \pi^{*}(dpk)/d$	969.6	1.28	0.0184	897.2 (1.38) 200
					761.0 (1.63) 1050
$H(\alpha) \rightarrow L(\alpha)$	$d/\pi(Cl)/\pi(dpk) \rightarrow \pi(dpk)/d$	526.7	2.35	0.0753	487.1 (2.55) 1750
$H(\beta) \rightarrow L+3(\beta)$	$d/\pi(Cl)/\pi(dpk) \rightarrow \pi^{*}(dpk)/d$	476.6	2.60	0.0394	
$H(\alpha) \rightarrow L+1(\alpha)$	$d/\pi(Cl)/\pi(dpk) \rightarrow \pi^{\circ}(dpk)$	374.4	3.31	0.0525	372.7 (3.33) 1580
$H-8(\beta) \rightarrow L+1(\beta)$	$\pi(\text{Cl})/\pi(\text{dpk}) \rightarrow \text{d}/\pi^{\circ}(\text{dpk})$	333.7	3.72	0.0339	266.9 (4.65) 42 700
$H-1(\alpha) \rightarrow L+1(\alpha)$	$d/\pi(Cl)/\pi(O_{OPPh_2}) \rightarrow \pi^*(dpk)$	331.6	3.74	0.0241	
$H-1(\alpha) \rightarrow L+3(\alpha)$	$d/\pi(Cl)/\pi(O_{OPPh_2}) \rightarrow \pi^*(dpk)/\pi^*(OPPh_3)/d$	300.9	4.12	0.0511	
$H-12(\beta) \rightarrow L+1(\beta)$	$\pi(dpk)/\pi(Cl)/\pi(O_{OPPh_2}) \rightarrow d/\pi^*(dpk)$				
$H-12(\alpha) \rightarrow L(\alpha)$	$\pi(\text{Cl})/\pi(\text{dpk}) \rightarrow \pi^*(\text{dpk})/\text{d}$	286.0	4.34	0.0229	
$H-10(\beta) \rightarrow L+2(\beta)$	$\pi(\text{Cl})/\pi(\text{dpk})/\pi(O_{\text{OPPh}_2}) \rightarrow \pi^*(\text{dpk})/\text{d}$				
$H-14(\alpha) \rightarrow L(\alpha)$	$\pi(dpk)/\pi(Cl)/\pi(O_{OPPh_2}) \rightarrow \pi^*(dpk)/d$	277.8	4.46	0.0301	
$H(\beta) \rightarrow L+15(\beta)$	$d/\pi (dpk)/\pi (Cl) \rightarrow \pi (dpk)$	269.4	4.60	0.0205	
$H-13(\beta) \rightarrow L+2(\beta)$	$\pi(dpk)/\pi(Cl) \rightarrow \pi^*(dpk)/d$				202.0 (6.14) 131 600

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

Table 10

The energy and molar absorption coefficients of experimental absorption bands and the electronic transitions calculated with the TDDFT method for [ReOBr₃(dpk-OH)].

The most important orbital excitations	Character	λ (nm)	<i>E</i> (eV)	f	Experimental Λ [nm] (E [eV]) ε
$H \rightarrow L$	$d/\pi(Br) \rightarrow d$	721.7	1.72	0.0014	794.1 (1.56) 50
$H \rightarrow L+1$	$d/\pi(Br) \to d$	640.0	1.94	0.0003	623.6 (1.99) 230
$ \begin{array}{l} H \rightarrow L+2 \\ H-2 \rightarrow L \end{array} $	$d/\pi(Br) \rightarrow \pi^*(dpk-OH)/d \pi(Br)/\pi(dpk-OH) \rightarrow d$	339.2	3.66	0.0781	367.4 (3.37) 7300
$\begin{array}{l} H-2 \rightarrow L+1 \\ H-4 \rightarrow L \end{array}$	$\begin{array}{l} \pi(Br)/\pi(dpk\text{-}OH) \rightarrow d \\ \pi(Br)/\pi(O_t) \rightarrow d \end{array}$	330.3 318.5	3.75 3.89	0.0127 0.0248	
$ \begin{array}{l} H \rightarrow L + 3 \\ H - 4 \rightarrow L \\ H \rightarrow L + 5 \\ H - 3 \rightarrow L + 2 \end{array} $	$\begin{aligned} d/\pi(Br) &\to \pi^*(dpk\text{-OH})/d \\ \pi(Br)/\pi(O_t) &\to d \\ d/\pi(Br) &\to \pi^*(dpk\text{-OH}) \\ \pi(Br)/\pi(dpk\text{-OH})/\pi(O_t) &\to \pi^*(dpk\text{-OH})/d \end{aligned}$	308.3 296.6 293.8 243.0	4.02 4.18 4.22 5.10	0.0430 0.0147 0.0531 0.0707	278.1 (4.46) 82 000
$H-4 \rightarrow L+2$ $H-3 \rightarrow L+5$ $H-7 \rightarrow L+2$ $H-5 \rightarrow L+3$ $H-1 \rightarrow L+7$ $H-8 \rightarrow L+2$ $H-10 \rightarrow L+3$ $H-2 \rightarrow L+6$	$\pi(Br)/\pi(O_t) \rightarrow \pi^*(dpk-OH)/d$ $\pi(Br)/\pi(dpk-OH)/\pi(O) \rightarrow \pi^*(dpk-OH)$ $\pi(Br)/\pi(dpk-OH)/\pi(O) \rightarrow \pi^*(dpk-OH)/d$ $\pi(dpk-OH)/\pi(O)/\pi(Br) \rightarrow \pi^*(dpk-OH)/d$ $\pi(Br) \rightarrow d$ $\pi(dpk-OH) \rightarrow \pi^*(dpk-OH)/d$ $\pi(Br)/\pi(dpk-OH)/\pi(O_t) \rightarrow \pi^*(dpk-OH)/d$ $\pi(Br)/\pi(dpk-OH) \rightarrow \pi^*(dpk-OH)$	229.5 216.4 214.0 209.8 202.4 198.1 197.6	5.40 5.73 5.79 5.91 6.13 6.26 6.27	0.0229 0.0283 0.0507 0.0376 0.1187 0.1226 0.0552	204.0 (6.08) 105 300
$\begin{array}{l} H = 7 \rightarrow L + 5 \\ H = 10 \rightarrow L + 2 \\ H = 16 \rightarrow L + 1 \\ H = 9 \rightarrow L + 4 \\ H = 10 \rightarrow L + 3 \\ H = 3 \rightarrow L + 7 \\ H = 11 \rightarrow L + 2 \\ H = 4 \rightarrow + 6 \\ H = 13 \rightarrow L + 2 \end{array}$	$\begin{aligned} \pi(\mathrm{Br})/\pi(\mathrm{dpk-OH})/\pi(\mathrm{O_t}) &\rightarrow \pi^*(\mathrm{dpk-OH})\\ \pi(\mathrm{Br})/\pi(\mathrm{dpk-OH})/\pi(\mathrm{O_t}) &\rightarrow \pi^*(\mathrm{dpk-OH})/\mathrm{d}\\ \pi(\mathrm{O_t})/\pi(\mathrm{dpk-OH})/\pi(\mathrm{O_t}) &\rightarrow \mathrm{d}\\ \pi(\mathrm{Br})/\pi(\mathrm{dpk-OH})/\pi(\mathrm{O_t}) &\rightarrow \mathrm{d}\\ \pi(\mathrm{Br})/\pi(\mathrm{dpk-OH})/\pi(\mathrm{O_t}) &\rightarrow \mathrm{d}\\ \pi(\mathrm{Br})/\pi(\mathrm{dpk-OH})/\pi(\mathrm{O_t}) &\rightarrow \mathrm{d}\\ \pi(\mathrm{Br})/\pi(\mathrm{dpk-OH}) &\rightarrow \pi^*(\mathrm{dpk-OH})/\mathrm{d}\\ \pi(\mathrm{Br})/\pi(\mathrm{dpk-OH}) &\rightarrow \pi^*(\mathrm{dpk-OH})/\mathrm{d} \end{aligned}$	195.1 192.6 189.5 189.2 187.7 186.3 185.5 185.4 185.4 184.7	6.35 6.44 6.54 6.55 6.60 6.66 6.68 6.69 6.71	0.0625 0.0258 0.0625 0.3537 0.0656 0.0440 0.0322 0.0234 0.0281	
$H-8 \rightarrow L+5$	$\pi(dpk-OH) \rightarrow \pi^*(dpk-OH)$	184.4	6.72	0.0559	

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

UV-vis spectrum was calculated to \sim 270 nm. Thus the shortest wavelength experimental band of **2** is not assigned to the calculated transitions; some intraligand and interligand transitions are expected to be found at higher energies in the calculations for **2**.

3.9. [ReOBr₃(dpk-OH)]

The two longest wavelength experimental bands of **3** originate in the HOMO–LUMO and HOMO–LUMO+1 transitions, respectively. As can be seen from the Fig. 7, the LUMO and LUMO+1 orbitals are mainly formed from rhenium *d* atomic orbitals, the HOMO orbital is delocalized among rhenium ion and bromide orbitals. Accordingly, the transitions assigned to the experimental bands at 794.1 and 623.6 nm can be seen as mixed bromide \rightarrow Re (*Ligand-Metal Charge Transfer; LMCT*) and d \rightarrow d (*Ligand Field; LF*) transitions.

The experimental absorption band at 367.4 nm can be assigned to *Ligand-Metal Charge Transfer* transitions occurring from the bromide, oxo, and dpk-OH ligands to *d* rhenium orbitals.

The absorption bands at 278.1 and 204.0 nm result mainly from *Ligand-Ligand Charge Transfer* and interligand (*IL*) transitions, but participation of *Ligand-Metal Charge Transfer* into this band is also confirmed by the calculations.

Supplementary data

CCDC 731661, 731662 and 731663 contain the supplementary crystallographic data for $C_{29}H_{23}Cl_3N_2OPRe$, $C_{29}H_{23}Cl_3N_2O_2PRe$ and $C_{33}H_{27}Br_4N_6O_5Re$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

The GAUSSIAN-03 calculations were carried out in the Wrocław Center for Networking and Supercomputing, WCSS, Wrocław, Poland, http://www.wcss.wroc.pl, under calculational Grant No. 51/ 96.

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