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Synthesis, Characterization and DFT Studies of $(Hdmphen)(H_2dmphen)_{0.5}[ReBr_4(mal)]\cdot(dmphen)\cdot2H_2O$

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ABSTRACT

Polynuclear Re^{IV}–M^{II} (M^{II} = first-row transition-metal ion) complexes are usually obtained from an halide-based rhenium(IV) precursor acting as ligand against a 3*d* transition metal ion. This synthetic strategy seems not to proceed as expected when $[ReBr_4(mal)]^{2-}$ and Fe^{2+} are considered. Indeed, the reaction of $(PPh_4)_2[ReBr_4(mal)]$ with $Fe(ClO_4)_2\cdot6H_2O$ in the presence of 2,9-dimethyl-1,10-phenanthroline (dmphen) in acetonitrile unexpectedly afforded the complex $(Hdmphen)(H_2dmphen)_{0.5}[Re^{IV}Br_4(mal)]$. The metal ion is observed in a slight distorted octahedral coordination environment in which malonato exhibits a boat conformation. Protonation of two dmphen provides the charge to balance the anionic complex. One of them is resolved as monoprotonated, the other one beingobserved as diprotonated but located on a two-fold symmetry axis of the space group.The crystallographic structure shows several non-covalent interactions, namely, π-π stacking and different H-bonds connecting water molecules of crystallization. Theoretical Density Functional (DFT) studies on geometry and electronic properties were performed employing B3LYP and PBE1PBE. The general trends observed in the crystallographic data are well reproduced in the calculations. Calculated bond lengths and angles reasonably match the values obtained from the X-ray diffraction study. Time-dependent DFT (TD-DFT) calculations helped us in assigning the origin of all absorption bandsexperimentally observed.

KEYWORDS

Rhenium complexes;
Malonato ligands;
X-ray structure;
DFT calculation;
TDDFT studies.

INTRODUCTION

The study of the coordination chemistry of Re^{IV} has received considerable attention in the past few years[1].Polynuclear complexes with first-row transition-metal ions have aroused particular interests due to their magnetic properties derived from the presence of 5*d* and 3*d* metallic centres. Such systems are featured by a very important degree of orbital-diffuseness and high spin–orbit coupling of the 5*d*spin carriers[2].The synthetic path of such complexes is not straightforward.It is usually accomplished by the preparation of a Re^{IV} complex stable enough to be used as a ligand to coordinate an appropriate 3*d* ion.Positions of the coordination environment of the last one are often blocked by the use of a polydentate ligand. Examples of this "blocking ligand" are 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-penanthroline (dmphen), 2,2′-bipyridine (bpy), and 2,2′:6′,2′′-terpyridine (terpy). This synthetic strategy has been successfully assayed in affording polynuclear complexes with several 3*d* ions by employing $[ReX_4(ox)]^{2-}$ ($X^- = Cl^-, Br^-$; ox^{2-} = oxalate)[3], $[ReCl_5(L_1)]^-$ (L_1 = pyrazine (pyz)[4], 2-pyrazinecarboxylic acid (Hpyzc)[5]), *trans*-$[ReCl_4(CN)_2]^{2-}$[6], and $[ReX_4(mal)]^{2-}$ (mal^{2-} = malonate)[7] as building blocks. In particular, the use of malonate-containing complexes firstly prompted us to assess the versatility of this dicarboxylato ligand as bridging unit, situation representing an extension of the well-know behavior of oxalate. In this regard, the complexes $[ReCl_4(\mu\text{-mal})M(L_2)]$ ($M^{2+} = Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$; L_2 = phen, bpy, dmphen) were obtained, and their structural and magnetic properties were studied in detail[7b]. When the halide of the rhenium-containing precursor is changed from Cl^- to Br^-, the aforementioned synthetic strategy does not proceed as expected in the presence of Fe^{2+}.

Herein, we describe the synthesis and structural characterization of a new Re^{IV} complex in trying to obtain a polynuclear complex employing $[ReBr_4(mal)]^{2-}$ as a ligand toward Fe^{2+}, and dmphen as a "blocking ligand". To the best of our knowledge, we are not aware of any X-ray diffraction result of mononuclear bromide-based Re^{IV} complex with malonato ligands.To go insight into the electronic properties of the title complex, studies at the Density Functional Theory (DFT) level of calculation were also performed.

EXPERIMENTAL

Materials and procedures

All chemicals and solvents were purchased from commercial sources. *N,N*-dimethylformamide (DMF) and triethylamine were dried over 4 Å molecular sieves, the last one being also distilled over calcium hydride prior to use. $(PPh_4)_2[ReBr_4(mal)]$ **(1)** was prepared by employing a reported procedure[7a]. Elemental analyses (C, H, N) were performed on a Carlo Erba 1108 elemental analyzer. IR spectrum was recorded on a Bomen MB-102 FTIR spectrometer as KBr pellets. UV-vis absorption spectrum was measured on a UV-1603 Shimadzu spectrophotometer.

Synthesis of $(Hdmphen)(H_2dmphen)_{0.5}[ReBr_4(mal)]\cdot(dmphen)\cdot 2H_2O$

A solution of 1 (16 mg, 0.0125 mmol) in acetonitrile (5 mL) was added dropwise to a solution of $Fe(ClO_4)_2\cdot 6H_2O$ (4.6 mg, 0.0125 mmol) and 2,9-dimethyl-1,10-phenanthroline monohydrate (7.8 mg, 0.0375 mmol) in acetonitrile (5 mL). The reaction mixture was allowed to stand by three days at ambient temperature. Green crystals (10 mg, 0.081 mmol, 65%), suitable for X-ray diffraction studies, were filtered-off and washed with acetonitrile (3 x 2 mL). IR (KBr) ν_{max} (cm^{-1}): 3423 (νOH_w), 1666 ($NH_{Hdmphen}^+$), 1369 ($NH_{Hdmphen}^+$), 850 and 730 ($C{-}C_{dmphen}$). Anal.Calcd.for $C_{38}H_{38}Br_4N_5O_6Re$: C, 39.1; H, 3.3; N, 6.0. Found: C, 38.9; H, 3.1; N, 5.9. All values are given in percentages.

X-ray data collection and structure refinement

Diffraction data for $(Hdmphen)(H_2dmphen)_{0.5}[ReBr_4(mal)]\cdot(dmphen)\cdot 2H_2O$ were collected with a Rigaku AFC-7S diffractometerat 293 K using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Diffraction data were collected over the range $13 \geq h \geq -1$, $22 \geq k \geq -1$, $57 \geq l \geq -57$, and were corrected for absorption. The data reduction was performed with the MSC/AFC[8] program package. A structure solution was found with the SHELXS-97[9] package using the heavy-atom method and was refined with SHELXL-97[10] against $|F^2|$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions. DIAMOND[11] software was used for drawings.Selected crystal data, collection procedures, and refinement results are summarized in TABLE 1.

TABLE 1 : Selected crystallographic data, and structure refinement for (Hdmphen)(H_2dmphen)$_{0.5}$ [$ReBr_4$(mal)]·(dmphen)·$2H_2O$.

Formula	$C_{76}H_{68}Br_8N_{10}O_{12}Re_2$
Formula weight	2325.02
Crystal system	Monoclinic
Space group	*C*2/*c*
a, *b*, *c* (Å)	10.069(6), 17.735(4), 44.270(3)
α, β, γ (°)	90, 92.897(18), 90
V (Å^3)	7895(5)
Z	4
D_{calc} (g cm^{-3})	1.956
μ (Mo-Kα) (mm^{-1})	7.18
Data collection	
Radiation (Å)	Mo-Kα 0.71073
θ Min–Max (°)	2.3–27.5
Tot., Uniq. Data, *R* (int)	11318, 9075, 0.102
Refinement	
R, *wR*^{2}	0.064, 0.217

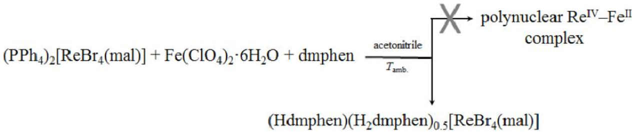
Computational details

All computational studies have been undertaken at the density functional level of theory (DFT). All geometries were optimized starting from the molecular structure determined by X-ray crystallography. The nature of the stationary point was verified through a vibrational analysis (no imaginary frequencies). It has been reported[12] that PBE1PBE in combination with the so-called STMIDI basis set (see further in text for details) has shown a good performance in studying electronic features of rhenium complexes. PBE1PBE is composed of the Perdew, Burke, Ernzerhof[13–15] exchange and a correlation functional with 25 % HF exchange. The valence electrons for non-metal atoms in STMIDI were treated with MIDI!,[16] those for the metal being described by a basis set (8s7p6d2f1g)/[6s5p3d2f1g][17]. The inner electrons were replaced by Stuttgart effective core pseudopotentials[17,18].The electronic UV–vis spectra were studied in the framework of the time-dependent DFT (TD-DFT) method by means of B3LYP[19–21] in combination with LANL2DZ. For the metallic atom, the core electrons (60) were treated through the pseudopotential approximations (ECP) as included in the LANL2DZ basis set. LANL2DZ and STMIDI take scalar relativistic effects into account, especially important when systems with heavy atoms are studied[22]. Fifty vertical transitions in the gas phase and in a CH_3CN solution have been calculated with TD-DFT. The effect of the solvent was described by the conductor-like polarizable continuum model (C-PCM)[23,24], which is a valid model to take the effects of the solvent into account as long as speciûc interactions between the solute and the solvent are not of signiûcant importance. Electronic UV–vis spectra were simulated by means of the GAUSSSUM software[25] considering all calculated transitions. Natural population analysis (NPA) calculations were performed with the NBO code[26–29] including in the program package Gaussian 03, Rev. D.02[30], which has been used for all theoretical studies reported in this work.

RESULTS AND DISCUSSION

Synthesis and crystal structure

Usually, polynuclear complexes of Re^{IV} and 3*d* divalent cations are obtained by a one-step reaction starting from a rhenium-containing precursor acting as a ligand toward a first-row metallic centre. Polidentate auxiliary ligands are often employed to block several coordination positions of the last one. Unlike different polynuclear complexes have been obtained starting from [$ReBr_4$(mal)]$^{2-}$[7a], the simple abovementioned synthetic path seems not to proceed as expected with Fe^{2+}. We have reacted $(PPh_4)_2$[$ReBr_4$(mal)] with $Fe(ClO_4)_2·6H_2O$ in acetonitrile in the presence of dmphen (as a source of "blocking ligand"). Unexpectedly, the salt (Hdmphen)(H_2dmphen)$_{0.5}$ [$ReBr_4$(mal)]·(dmphen)·$2H_2O$ was obtained (Scheme 1).



Scheme 1 : Synthesis of complex (Hdmphen)(H_2dmphen)$_{0.5}$ [$ReBr_4$(mal)]

The X-ray diffraction structure analysis (Figure 1) shows the metal ion residing in a slight distorted octahedral coordination environment. The malonato ligand acts as bidentate through the carboxilato groups. The Re–Br distances fall in the range from 2.478 to 2.516 Å, and the Re–O bond lengths are 2.016 and 2.038 Å. Both metric parameters are in agreement with those obtained from the X-ray diffraction studies of [ReBr$_4$(μ-mal)]M(L$_3$)]·Y (M = Co^{2+}, Cu^{2+}; L$_3$ = phen, dmphen; Y = MeCN, ¼H$_2$O)[7b]. It deserves to be mentioned that the geometric features of the anionic bromide-based complex are also in line with the observations made for the crystallographic structure of [ReCl$_4$(mal)]$^{2-}$ in (AsPh$_4$)(HNEt$_3$)[ReCl$_4$(mal)] and (AsPh$_4$)$_{1.5}$(HNEt$_3$)$_{0.5}$[ReCl$_4$(mal)][7a].

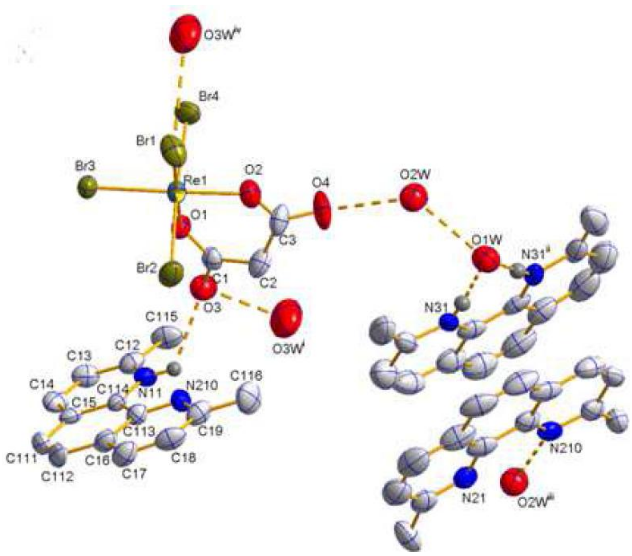


Figure 1 : Molecular structure of (Hdmphen)(H$_2$dmphen)$_{0.5}$ [ReBr$_4$(mal)]·(dmphen)·2H$_2$O with the atomic numbering scheme. Hydrogen atoms, except the ones of Hdmphen$^+$ and H$_2$dmphen^{2+}, have been omitted for clarity. Selected bond lengths (Å) and angles (°): Re–O1 2.016(7), Re–O2 2.038(7), Re–Br1 2.4778(13), Re–Br2 2.5165(17), Re–Br3 2.4820(12), Re–Br4 2.5112(17); O1–Re–O2 87.1(3), Br1–Re–Br2 91.26(5), Br1–Re–Br3 91.03(4), Br1–Re–Br4 92.20(5), Br1–Re–O1 177.6 (2), Br1–Re–O2 91.25(19), Br3–Re–O1 90.67(18), Br3–Re–O2 176.3(2). (For interpretation of references to color, the reader is referred to the web version of this article)

Atoms O2, C3, and O4 define a plane, as O1, C1, and O3 do. The dihedral angles C1O1ReO2 and C3O2ReO1 are of about 33° and 14°, respectively, while the one involving C2, C1, O1, and Re measures 18°. The bidentate ligand, which displays a boat conformation, leads to an angle at the metallic centre (O1–Re–O2) of about 87°. This finding is in accord to that found in the abovementioned dinuclear complexes, in which malonatealso acts as bridge.

The rhenium complex of the title complex is completed by three crystallographically independent dmphen molecules —one of them being located at a two-fold symmetry axis—, and three independent crystallization water molecules. The latter have been located as follow: over at two-fold axis (O1W), in a general position (O2W), and in a half-occupied general position (O3W) adding up to a total of two water molecules per rhenium centre.

The protonation of two dmphen provides the charge to balance the anionic complex. One of them has been resolved as monoprotonated, while one half of a second unit is proposed as protonated leading to a diprotonaded molecule. It is worth mentioning that π-π stacking interactions involving these residues have been found in the crystallographic structure of the title complex (Figure 2). While such interactions connect the monoprotonateddmphen at a distance of 3.46 Å (average value), the diprotonated one stacks with the unprotonated molecule in an alternating pattern at 3.36 Å (average value).

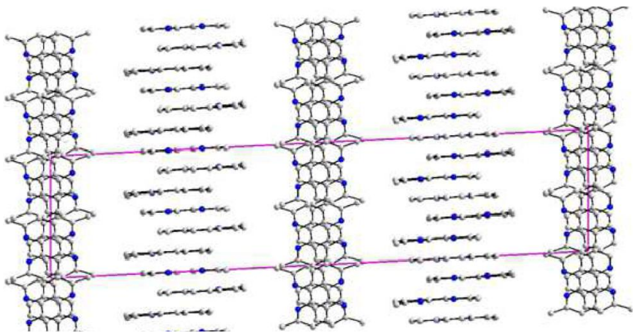


Figure 2 : Packing of dmphen molecules viewed along the *b* axis. Molecules dmphen and H$_2$dmphen^{2+} are disposed lying parallel to the line of sight of the figure in the *ab* plane

Several interactions *via* H-bond involving the complex, the counterions, and both crystallization water molecules have been detected (Figure 1). Selected structural parameters are gathered in TABLE 2. Both oxygens of the malonato ligand act as acceptors. While an H-bond involves N11–H and O3, O4 is connected to the water molecule labeled as O2W, which also interacts with the second crystallization water (O1W). This water molecule is observed in turn H-bonded to the diprotonateddmphen, for which the formation of the

O1W···H–N31 and O1W···H–N31^{ii} bondsis proposed (symmetry code = x–½, y–½, z).The title complex was further characterized by means of absorption spectroscopy. The assignment of the origin of all observed absorption bands is discussed in detail in the section *Electronic Spectra*.

TABLE 2.H-bonds of (Hdmphen)(H_2dmphen)$_{0.5}$ [ReBr$_4$(mal)]·(dmphen)·2H_2O (all values in Å).^{a}

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N11–H11···O3	0.86	2.43	3.023(11)	126
N31–H31···O1W	0.86	1.99	2.845(13)	174
O1W···O2W			2.744(11)	
O1W···O2W^{i}			2.744(11)	
O2W···N21O^{ii}			2.861(11)	
O2W···O4			2.865(12)	
O3W···O3^{iii}			2.79(3)	
O3W···Br1^{iv}			3.33(3)	

^{a}**symmetrycodes: (i) –*x*+1, *y*, –*z*+½; (iii) *x*+½, *y*–½, *z*; (iv) *x*+1, *y*, *z*.**

Geometry optimization, electronic structure and NPA analysis

The use of PBE1PBE in combination with STMIDI (see *Computational Details*) has been successfully employed in studying electronic properties not only in mononuclear rhenium complexes but also in large transition-metal complexes[12]. This DFT method has proven to be a good performer to describe rhenium–non-metal bonds keeping the computational cost very low. DFT investigations of oxidorhenium(V) coordination compounds, of rhenium(V) self-assembled helicates with thiolato ligands[12a,12d], of Re^{IV} complexes with thiocyanto ligands[12b], and of Re^{III}chalcogenide clusters have been conducted by means of PBE1PBE/STMIDI[12c]. Besides the study of the electronic features of [ReBr$_4$(mal)]$^{2–}$, it is also our aim to assess the feasibility of PBE1PBE/STMIDI in studying coordination compounds of rhenium bearing different donor-atoms. Therefore, we also included in this work DFT studies of the analogous of chloride, namely, [ReCl$_4$(mal)]$^{2–}$. As aforementioned, this rhenium precursor has been employed in obtaining a Re^{IV}–Fe^{II}polynuclear complex[7a].

The optimizations starting from the crystallographically determined molecular structure lead to a minimum as stationary point. Selected optimized parameters are presented in TABLE 3.

TABLE 3 : Selected bond parameters calculated for [ReBr$_4$(mal)]$^{2–}$ by employing PBE1PBE/STMIDI (T = 298 K).^{a}

Bond	*d* (Å)	Angle	∠ (°)
Re–O1	2.008	O1–Re–O2	88.8
Re–O2	2.008	Br1–Re–Br2	90.3
Re–Br1	2.506	Br1–Re–Br3	92.5
Re–Br2	2.531	Br1–Re–Br4	91.2
Re–Br3	2.505	Br1–Re–O1	177.9
Re–Br4	2.505	Br1–Re–O2	89.4
		Br3–Re–O1	89.4
		Br3–Re–O2	177.7

^{a}**for atom numbering see Figure 1**

The general trends observed in the crystallographic data are well reproduced in the calculations. Calculated bond lengths and angles reasonably match the values obtained from the X-ray diffraction study. It is to be noted, that all calculations have been conducted at the gas phase, for which the influence of crystal-packing effects and presence of counterions is not taken into account.The optimized structure of [ReBr$_4$(mal)]$^{2–}$ displays identical Re–Br (with the exception of Re–Br2) and Re–O bonds with distances of 2.505 and 2.008 Å, respectively. The bond angles values displayed in TABLE 3 account for a slight distorted octahedral environment around rhenium in which the malonato ligand is calculated in a boat conformation (Figure 3). The geometric parameters obtained for [ReCl$_4$(mal)]$^{2–}$ (further details in the Supplementary Information) are also in good agreement with those experimentally found[7c]. Its equilibrium geometry shows malonate also in a boat conformation. These finding point to PBE1PBE/STMIDI to be a reasonable performer in studying geometric aspect of rhenium(IV) complexes bearing halide and oxygen donor-atoms ligands keeping the computational cost very low.

Natural Population Analysis (NPA) results show rhenium supporting a charge considerable lower than the formal charge of +4 as a result of significant electronic density donation from the donor atoms. The charge of the metal ion is of +0.75, while the halides and oxygen atoms end with a charge of –0.40 and –0.64, respectively. These results suggest that the charge donation from the malonato ligand is more important than the one from the bromides. The NPA results for

$[ReCl_4(mal)]^{2-}$ ($Re^{+0.89}$, $Cl^{-0.45}$, $O^{-0.65}$) are in line with the comments already made for the bromide-containing precursor.

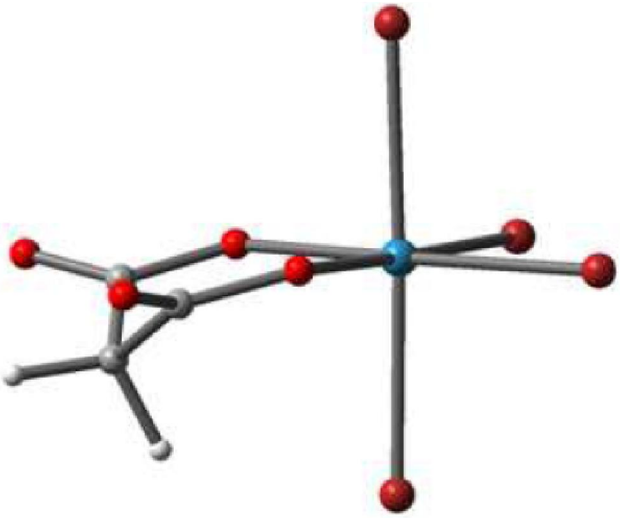


Figure 3 : Calculated structure of $[ReBr_4(mal)]^{2-}$ as obtained with PBE1PBE/STMIDI (T = 298 K). For atom numbering see Figure 1

Electronic spectra

The electronic UV–vis spectrum of $[ReBr_4(mal)]^{2-}$ simulated in the presence of the solvent (CH_3CN) by means of TD-B3LYP/LANL2DZ is depicted in Figure 4 (the experimentally one is also included). Calculated spin-allowed excitations in the visible region are displayed in TABLE 4. For all transitions, only orbital contributions larger than 10% were considered. No significant shifts were detected in going from the gas phase to the solvent.

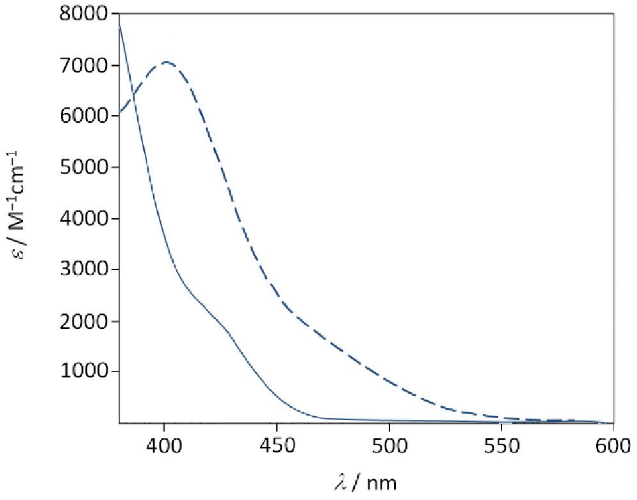


Figure 4 : Electronic absorption UV-vis spectrum of $[ReBr_4(mal)]^{2-}$ (broken line) as calculated with B3LYP/LANL2DZ in the presence of CH_3CN (experimental spectrum in solid line)

TABLE 4 : Electronic transitions of $[ReBr_4(mal)]^{2-}$ calculated in DMF using the TD-BLDZ DFT method

most important orbital excitations[a]	λ (nm)	f	λ_{exp}(nm)[b]
H(β) → L(β)	485.7	0.0032	
H–1(β) → L+1(β)	473.8	0.0023	423 (sh)
H–2(α) → L(α), H(α) → L(α)	470.0	0.0018	
H–1(β) → L(β), H(β) → L+1(β)	462.2	0.0098	
H–3(β) → L(β), H–2(β) → L+2(β)	420.3	0.0202	
H–4(β) → L(β), H–3(β) → L+1(β)	404.6	0.0437	
H–5(β) → L(β)	393.9	0.0127	not detected
H(α) → L+1(α), H–5(β) → L+1(β)	391.0	0.0106	
H(α) → L+1(α), H–3(β) → L+2(β)	386.8	0.0047	
H–4(β) → L+2(β)	382.9	0.0030	

[a]H = HOMO, L = LUMO; [b] sh = shoulder

The TD-B3LYP method in combination with LANL2DZ has been successfully employed in studying absorptive properties of rhenium complexes in different oxidation states bearing different donor-atoms[12a,12b,12d,13]. The general features of the experimental spectrum of $[ReBr_4(mal)]^{2-}$ are well reproduced by the simulated one in the presence of CH_3CN. A relative weak absorption band at the low-energy part of the spectrum was experimentally observed as a shoulder peaked at 423 nm. This band was simulated also as a shoulder, for which a bathochromic shift of about +55 nm was obtained. The excitations are originated in the HOMO–2(α), HOMO–1(β), HOMO(α), and HOMO(β), and show the LUMO(α), LUMO(β), and LUMO+1(β) as destination molecular orbitals (MOs). The HOMO(β)-derivatives are 100 % ligand in composition, while both the HOMO(α)-derivatives and the LUMOs show an important charge delocalization among rhenium and the ligands (Figure 5). These observations allow the assignment of this transition to be metal-ligand-to-metal-ligand charge transfer (MLMLCT). It is worth mentioning that the *d-d* degree of the aforementioned excitations is in line with the low molar absorption coefficient (ε) experimentally observed.

In going to the blue-part of the spectrum, a relative weak absorption band was also simulated. This band, which has been experimentally not detected, is originated in several excitations. In this case the charge is moving from the HOMO–5(β), HOMO–4(β), HOMO–3(β), HOMO–2(β), HOMO(β), and HOMO(α), to the LUMO(α), LUMO+1(α), LUMO+1(β), and LUMO+2(β) MOs. When the contours depicted in Figure 5 are taken into account, the origin of this absorption band may be attributed also to a MLMLCT. In this case however, the contribution from the ligands seems to be more important than in the other band, which leads to a greater value of ε than the one of the band peaked at 423 nm.

CONCLUSIONS

In this work, we have reported an experimental and theoretical study of a bromide-containing Re^{IV} complex with malonato ligand. This complex has been unexpectedly obtained during the attempt to preparepolynuclear complexes of Re^{IV} and 3*d* transition metals. In our case, the reaction of $[ReBr_4(mal)]^{2-}$ as a ligand in the presence of Fe^{2+}, and dmphen as "blocking ligand" seems not to proceed as expected. The crystallographic results show the rhenium ion in a slight distorted octahedron, in which the malonato ligand is observed in a boat conformation. The charge of the complex is balance through the protonation of two

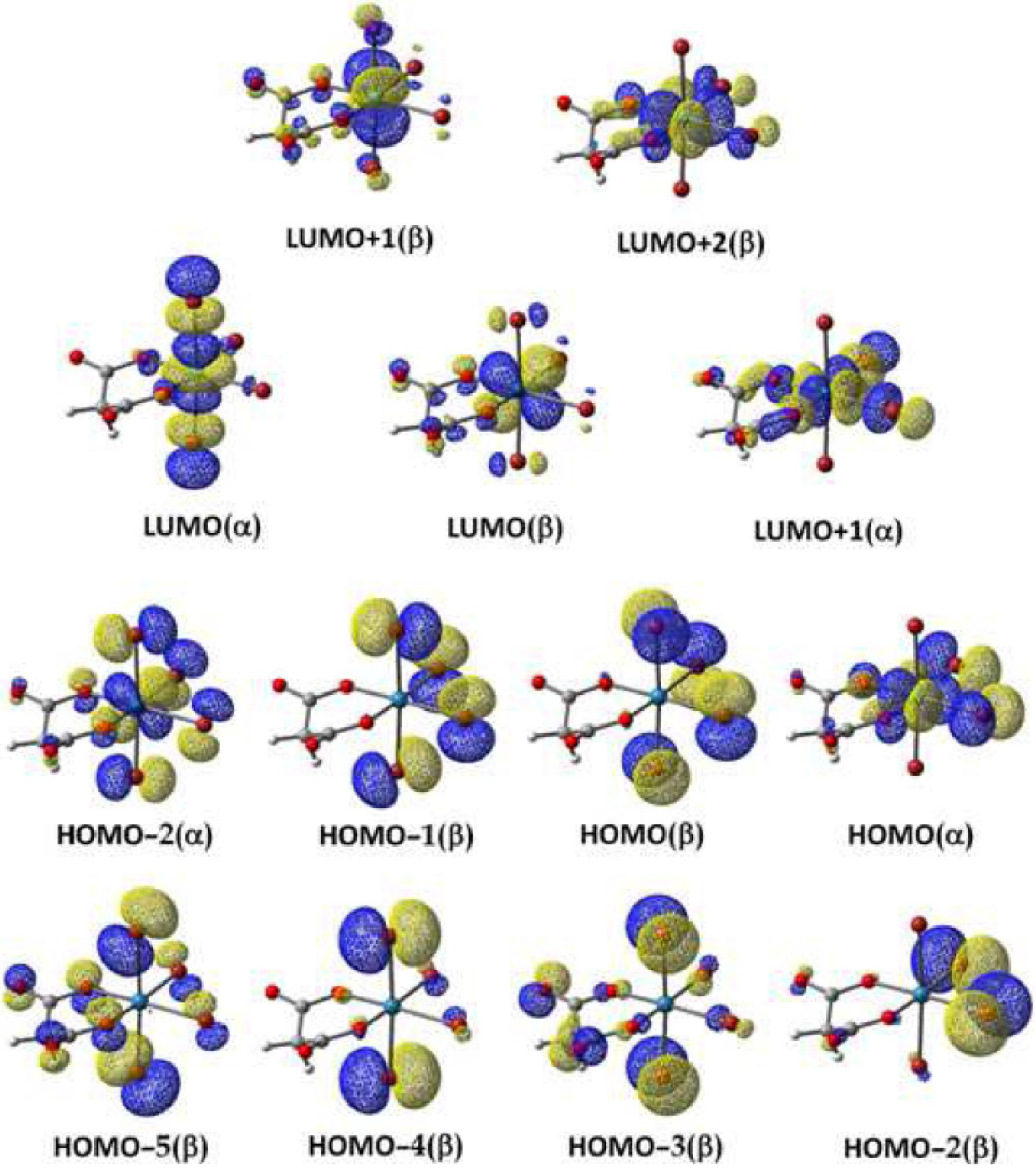


Figure 5 : Contour of selected MOs of $[ReBr_4(mal)]^{2-}$ as obtained from the B3LYP/LANLDZ methodology

dmphen, for which stacking interactions have been observed.

Calculations of structure and electronic properties have been conducted by means of DFT methods. The general trends of the crystallographic data are well reproduced by employing PBE1PBE in combination with MIDI!, and the Stuttgart energy-consistent pseudopotentials. The B3LYP/LANL2DZ method has proven to be appropriate in reproducing the electronic visible spectrum of the title complex. The solvent effects are successfully described, which enable the prediction of the absorption band experimentally observed. A MLMLCT origin has been assigned for the band simulated at the lowest-energy part of the spectrum. The same assignation has been considered for the one simulated in the high-energy region, which has been experimentally not observed.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC number 898158. A copy of this information may be obtained via http://www.ccdc.cam.ac.uk or from The Director, CCDC 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336 033; e-mail: de-posit@ccdc.cam.ac.uk.Details of DFT calculations of $[ReBr_4(mal)]^{2-}[ReCl_4(mal)]^{2-}$ are also included.

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