



Proton-transfer reactions of Re(II)-nitrosyl complexes: Potentiometric studies, DFT and TD-DFT calculations

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ABSTRACT

In the present work, we investigated the proton-transfer reactions of Re(II)-nitrosyl complexes bearing halides and nicotinic acid (Hnic) or 6,6'-dinicotinic acid (H₂dinic) *trans*-coordinated to the core {ReNO}³⁺ by potentiometry and UV – Vis absorption spectroscopy in a mixture DMSO:H₂O (1:1; v:v). The presence of Hnic and H₂dinic in title complexes promotes a marked decrease in the acidity (higher pK values) compared to the non-coordinated pyridine-derived ligands. The UV – Vis measurements indicate that the absorption spectra of complexes do not show any dependence on the acidity of the medium and the number of non-coordinated carboxylic units. Time-dependent Density Functional Theory (TD-DFT) calculations are performed to understand the optical properties of complexes and their response upon deprotonation. TD-DFT studies are conducted with PBE1PBE in combination with LANL2TZ on rhenium and 6-311++G(d,p) on non-metal atoms within the C-PCM approach. This methodology shows a reasonable match between the measured and simulated spectra keeping the computational cost low. The nature of all absorption bands is ascribed to a ligand-metal-to-ligand-metal charge transfer (LMLMCT), in which negligible contribution from carboxylic units is detected.

Introduction

The coordination chemistry of rhenium has emerged as a highly active field of research in recent years. This metal, belonging to group 7, exhibits rich chemistry with complexes showing a broad palette of applications in various areas. Recently, the state-of-the-art in this discipline has been extensively reviewed by Dilworth [1]. Despite the increasing number of publications on all aspects of rhenium in the last few years [1], investigations on the oxidation state + 2 remain scarce [2]. The absence of general synthetic procedures, and the potential to be oxidized or reduced under mild conditions, make studies on this intermediate oxidation state of rhenium an excellent opportunity to foster this area of knowledge.

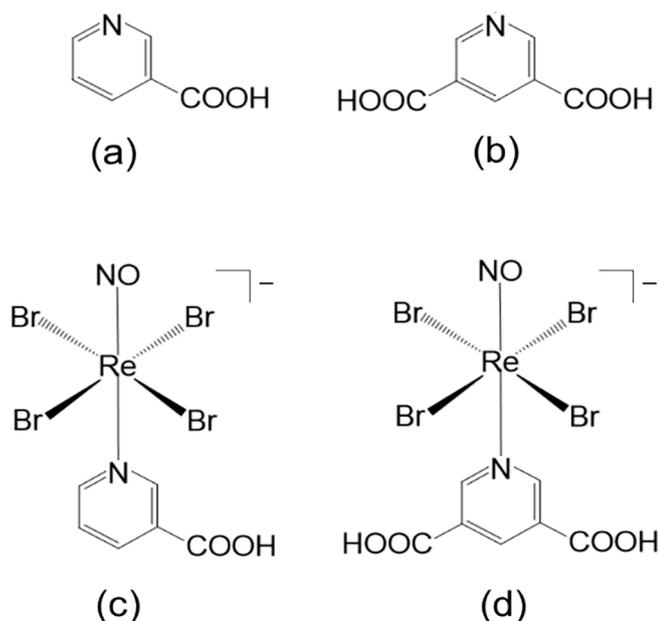
Re(II) —an ion with a d⁵ configuration— can be stabilized using π-ligands, among others. The nitrosyl group (NO) has been proven to be a suitable candidate to afford stable complexes [2]. Re(II)-nitrosyl complexes having an unpaired electron have attracted the attention of our group in the last years, and the interest is mainly focused on their magnetic properties [3–7]. Interesting complexes with potential as molecular magnets have been obtained using the so-called *complex-as-*

ligand strategy [8]. In this regard, several compounds have been successfully prepared upon deprotonation of carboxylic groups of N-coordinated ligands [4,6]. The modification in the acidity of the carboxylic groups upon coordination is expected to occur, a variable to be considered in synthetic-strategy designing. However, we are unaware of any study of the acid-base behaviour of such carboxylic units when coordinated to rhenium ions, which could contribute to choosing conditions to systematically synthesize new polynuclear complexes of rhenium(II), in particular.

Herein, we investigated proton-transfer reactions of two Re(II)-nitrosyl complexes bearing bromide ligands, and nicotinic (Hnic) or 6,6'-dinicotinic (H₂dinic) acids *trans* coordinated to the core {ReNO}³⁺ (Scheme 1). Potentiometric techniques and UV – Vis spectroscopy were selected to achieve this goal. Furthermore, TD-DFT calculations in the presence of the solvent were carried out to understand the optical properties further. The results presented in this contribution constitute an entry into the assessment of proper conditions to rationally design new polynuclear Re(II) complexes within the *complex-as-ligand* synthetic approach.

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Scheme 1. Chemical structures of (a) Hnic, (b) H₂dnic, (c) complex Re-Hnic, and (d) complex Re-H₂dnic.

Experimental

Materials

Reagents were obtained from major suppliers and used without further purifications. Complexes (NBu₄)[Re(NO)Br₄(Hnic)] and (NBu₄)[Re(NO)Br₄(H₂dnic)] (hereafter we refer to the anions as Re-Hnic and Re-H₂dnic, respectively) were afforded following reported procedures [4,6]. Standard HCl and NaOH solutions were prepared by diluting Merck standard ampoules and standardized against sodium carbonate and potassium hydrogen phthalate, respectively. These salts were dried at 100 °C and 80 °C, respectively, and stored in a desiccator before use [9]. All solutions were prepared with analytical-grade water (18 μS•cm⁻¹) and were free of carbon dioxide by bubbling with argon. In all cases, the temperature was maintained constant at 25.0 (±0.1) °C.

UV – Vis measurements

The UV – Vis spectroscopic measurements were obtained using a spectrophotometer Shimadzu UV – Vis 2600 in the wavelength range from 300 to 550 nm. Spectral profiles of title complexes in DMSO:H₂O (1:1; v:v) mixture were monitored for seven days at two pH values. To avoid solubility problems, concentrations in the range of 0.5–2.0 mmol•L⁻¹, and pH values of about 3 and 5 were selected. The first value was selected to avoid any precipitation. In contrast, the second one was chosen to study the stability well above the expected pH for the deprotonation of the carboxylic groups [10,11].

Potentiometric studies

First, proton-transfer reactions of neutral ligands, *i.e.*, nicotinic acid (Hnic) and 6,6'-dinitrotinic acid (H₂dnic), were investigated in DMSO:H₂O (1:1; v:v). Hnic and H₂dnic represent the neutral forms depicted in Scheme 1. A 0.250 M NaClO₄ ionic strength was selected to conduct three potentiometric titrations for each system (100–350 experimental points for each titration) in the 1–5 mM concentration range. The acid-base behaviour of title complexes (chemical structures shown in Scheme 1) was explored using the previously mentioned solvents mixture and ionic strength. Four and three potentiometric titrations were conducted for complex Re-Hnic and Re-H₂dnic, respectively. Concentrations were

in the millimolar range (up to 3.0 mM and 1.5 mM, for Re-Hnic and Re-H₂dnic, respectively) to ensure complete dissolution, and a pH interval from 2 to 10 was covered.

The solution was poured into a 50 mL titration cell in all potentiometric experiments. After thermal equilibrium was reached, hydrogen-ion concentration was determined by successive readings of EMF after incremental addition of 0.1 M NaOH, for which an automatic titrator Mettler-Toledo DL50-Graphic was used. Deviation of successive EMF readings was taken into consideration to verify equilibrium attainment. Pre-saturated argon (free of CO₂) was bubbled into the solution during titrations to eliminate atmospheric carbon dioxide, the temperature being kept at 25.0 (±0.1) °C. The cell electrode potential (*E*^o) and the acidic junction potential were determined according to the procedure of May *et al.* [12]. Independent titrations of the standard acid solution with the titrant in DMSO:H₂O (1:1; v:v) were conducted at constant ionic strength given by 0.250 M NaClO₄. This procedure allowed us to determine pH values on a free-hydrogen concentration scale. The calibration in the alkaline range was assessed by recalculating the values of *K*_w for each system. Obtained values (average log*K*_w of – 15.4) were checked to assure they were in line with results reported under the same experimental conditions [13,14]. Data were analyzed using the HYPERQUAD program [15], while species distribution diagrams were produced using the HySS program [16]. The evaluation of the goodness-of-fit of values predicted by the model to the experimental evidence was performed by estimating the parameter σ. It corresponds to the scaled sum of squared differences between the predicted and experimental values. Final models were selected to minimize σ, the model confidence level estimator (χ²), and the internal consistency of data reflected in standard deviations of the formation constants [15].

Theoretical calculations

All computational studies were undertaken at the density functional theory (DFT). Geometry optimizations were conducted starting from molecular structures determined by X-ray crystallography [3,5]. In all cases, PBE1PBE [17–19] in combination with LANL2TZ [20–24] on rhenium, and with 6–311++G(d,p) [22–26] on non-metal atoms was used (this method will hereafter be called PLTZ6311), and an ultrafine grid featured by 90 radial shells and 590 angular points per shell was considered. For rhenium, the core electrons (60) were treated through the pseudopotential (ECP) approximation as included in LANL2TZ. This basis set considers scalar relativistic effects, significant when systems containing heavy atoms are studied [27]. The nature of the stationary point was verified through vibrational analysis (no imaginary frequencies at the minimum). Vertical energy transitions at the equilibrium geometry were calculated with the time-dependent (TD-DFT) approach. We considered two hundred spin-allowed excitations in the gas phase and the presence of DMSO and H₂O as solvents. Their effects were evaluated by using the conductor-like polarisable continuum model (C-PCM) [28,29], which was chosen for the further understanding of electronic aspects of the absorptive behaviour of title complexes observed in solution (DMSO:H₂O; 1:1; v:v). Absorption spectra in the 300–550 nm range were simulated using the GAUSSSUM software [30]. All calculations reported in this contribution were conducted with the program package GAUSSIAN16, Rev. C01 [31].

Results and discussion

Stability assessment

Before proceeding with the potentiometric measurements, complex stability was assessed by recording absorption spectra in a 120-minutes period at pH values of *ca.* 3 and 5. Results obtained for the short-time range are displayed in Fig. 1, all other spectra being included in Supplementary Information (Fig. S1).

In the visible region, the compounds display three absorption bands

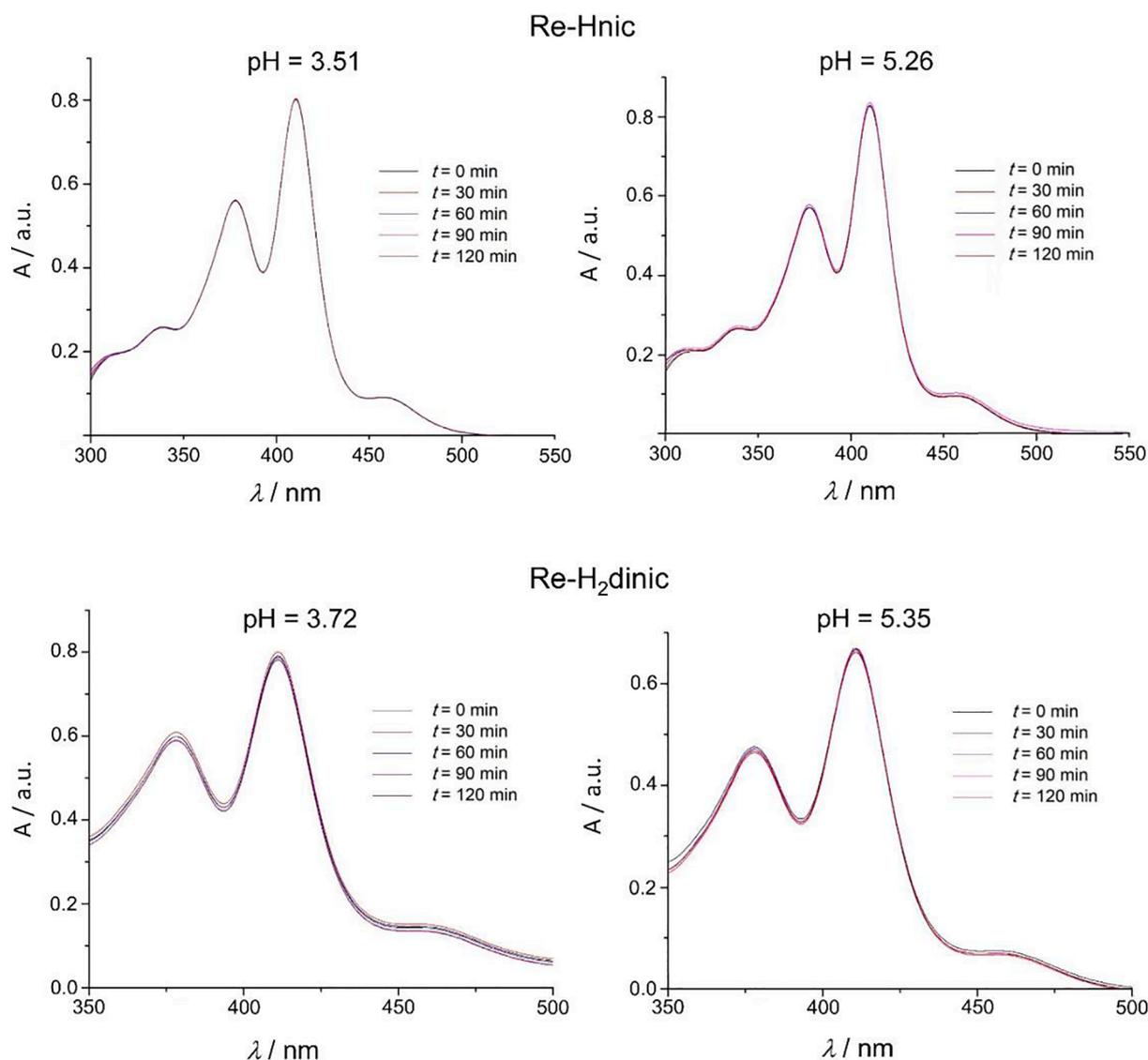


Fig. 1. Absorption UV – Vis spectra of Re-Hnic (top) and Re-H₂dinic (bottom) at two pH values recorded in the period 0–120 min in a solution of DMSO:H₂O (1:1; v:v) at ambient temperature.

Table 1

Successive dissociation constants expressed as pK values determined at 25.0 °C, $I = 0.25$ M NaClO₄ in a mixture DMSO:H₂O (1:1; v:v). The parameter σ represents the scaled sum of square differences between predicted and experimental values. Values given in parentheses are the 1σ statistical uncertainties in the last digit of the constant.

System	pK _{a1}	pK _{a2}	pK _{a3}	σ
Hnic	2.05(4)	4.162(9)		0.4
H ₂ dinic	1.2(5)	3.35(7)	4.30(4)	0.8
Re-Hnic	4.56(4)			0.8
Re-H ₂ dinic	3.08(5)	4.25(4)		0.7

at 460, 411 nm, and 380 nm, showing no dependence on pH. In addition, no significant shifts were detected with time, and this observation allowed us to assume the stability of complexes under our experimental conditions. This finding, and the fact that the position of bands emerges as independent of carboxylic groups (number and acid-base status), seems to be in line with bands arising from electronic transitions with no contribution from the protic groups worth to be highlighted.

Potentiometric studies

Proton-transfer reactions for the simplest system (Hnic) are described by Eqs. (1) and (2):



It is worth mentioning that Hnic strictly represents the neutral specie (depicted in Scheme 1) and the zwitterionic form arising from a proton-transfer from the carboxylic group to the pyridine unit. The neutral form for both ligands is expected to predominate in DMSO-rich mixtures, while the charged zwitterionic species is stabilized as the water content increases [32]. Previous results on ligand Hnic (and similar systems) led to a wide variation of protonation constants, which can be rationalized from differences in solvation and charge-stabilization ability of H₂O and DMSO, and the lower potential of DMSO to establish H-bonds compared to H₂O. Nevertheless, variations in values are small, at least for H₂O-rich mixtures [10,11,32]. For acids Hnic and H₂dinic and their Re(II) complexes, pK_a values determined in this work at 25.0 °C in the presence of a mixture DMSO:H₂O (1:1; v:v; ionic strength of 0.25 M in NaClO₄) are shown in Table 1.

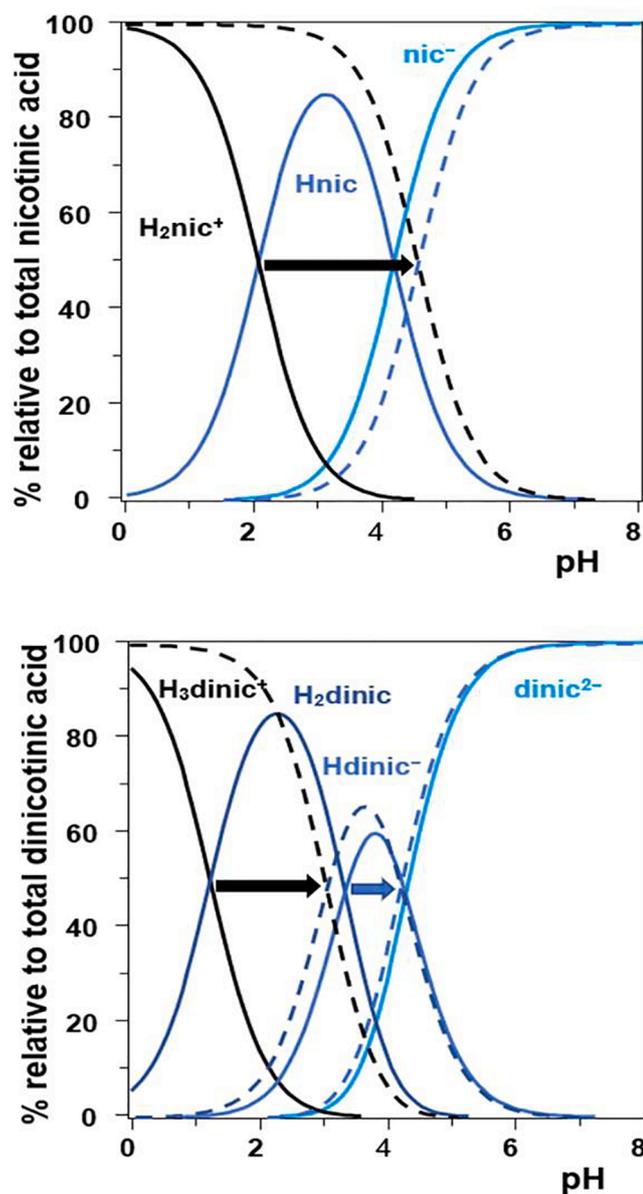


Fig. 2. Distribution species diagrams of Hnic (top) and H₂dinic (bottom). Species are calculated from the data in Table 1. Dashed lines represent the corresponding processes for the coordinated ligand.

Results for ligands are in excellent agreement with previous values [32–34]. For nicotinic acid, the pK_{a1} value corresponds to the dissociation of the carboxylic group, whereas pK_{a2} corresponds to the deprotonation of the pyridine residue [32]. Analogously, for dinicotinic acid, two carboxylic groups, pK_{a1} and pK_{a2} , are associated with the successive deprotonation of acidic groups, and pK_{a3} corresponds to the deprotonation of pyridine. The first dissociation occurs at a very acidic pH, making the experimental error significant. In addition, available reports on potentiometric measurements could not detect this constant [33,34].

Nicotinic and dinicotinic acid coordinate Re(II) by the pyridinic nitrogen atom. As stated in the previous section, the absorption spectra of complexes remain unchanged with time. This observation allowed the study of their acid-base behaviour, assuming the carboxylic ligands to be effectively bound to the metal-ion during the experiments (lasting up to 120 min). Since pyridine nitrogen cannot be protonated in this situation due to coordination, measured dissociation constants are linked only to proton transfers from carboxylic groups. Results for Re-Hnic and Re-H₂dinic are summed up in Table 1. As can be seen, coordination effects

directly decrease the acidity of carboxylic groups (greater values of pK ; Fig. 2) in comparison to the uncoordinated ligands. This fact can be intuitively rationalized by the different charges of the conjugate acid-base pairs and their relative stabilization in the employed solvent mixture.

Theoretical calculations

To gain insight into electronic aspects of the UV – Vis evidence, time-dependent DFT (TD-DFT) calculations in the presence of the solvent were carried out. Even when TD-DFT investigations to interrogate the nature of optical features (absorption and emission) on Re(II)-complexes are available [35,36], we are not aware of any TD-DFT reports dealing with Re(II)-nitrosyl complexes bearing halides and *trans*-coordinated N-ligands.

Optimizations starting from the crystallographically determined molecular structure [4,6] led to a minimum as a stationary point. Selected optimized parameters are presented in Supplementary Information (Figs. S2 and S3). The general trends observed in the crystallographical data are well reproduced in the calculations. Calculated bond lengths and angles reasonably match the values obtained from the X-ray diffraction reports.

The absorption spectra of title complexes and their deprotonation products were calculated in vacuum, and in the presence of H₂O and DMSO within the C-PCM approach with the methodology TD-PLTZ6311. This method enabled all calculations to be conducted with a low computational cost [37–39]. Fig. 3 displays results for Re-Hnic and Re-nic (taken as an example), while spectra for complexes Re-H₂dinic, Re-Hdinic, and Re-dinic are included in Supplementary Information (Fig. S4).

In the gas phase, calculations could not detect three bands either for Re-Hnic or Re-nic, as experimentally observed. Three bands were detected only when the continuum polarizable as solvent was considered, whose position is independent of the solvent (no solvatochromism effects). The band at 510 nm (λ_1) was calculated bathochromically shifted (+60 nm) in comparison to the experimental data. Bands in the blue-region (λ_2 and λ_3 at 382 and 324 nm, respectively) were detected hypsochromically shifted, the displacement being of –29 nm (λ_2) and –56 nm (λ_3). Deprotonation of Re-Hnic does not promote significant changes, and this observation is in line with the experimental findings.

The methodology shows performance in the case of complex Re-H₂dinic in vacuum. In contrast to the system Re-Hnic, results for Re-H₂dinic accounted for a well-defined band at 470 nm and a strong one at 355 nm, while a shoulder at 390 nm was also simulated (further details in Fig. S2). The inclusion of the solvent resulted in improvements keeping the results in vacuum in mind. Three absorption bands were calculated, with the one at the lowest-energy part of the spectrum being +49 nm shifted (exp. value of 460 nm). The blue-portion of the spectrum shows two bands, which were simulated at 383 and 330 nm. Both were hypsochromically detected with shifts of –28 nm and –50 nm, respectively (Fig. S3).

Deprotonation of complex Re-H₂dinic led to results with no systematic behaviour. Furthermore, including a polarizable continuum to simulate solvent effects rather than improve results sometimes worsens them. To obtain better agreement between TD-DFT results and experiments, the inclusion of explicit solvent emerges as a natural variable. This approach seems to be more important for systems with two carboxylic groups. However, the need for highly accurate calculations should be evaluated appropriately since the ultimate goal of DFT results is to complement experimental observations. The qualitative match between simulated and experimental spectra of Re-Hnic and Re-nic allows us to use TD-PLTZ6311/C-PCM as a tool to shed light on the absorptive response of title complexes upon changes in pH, keeping the computational cost low.

The analysis of molecular orbitals (MOs) is important to gain insight into optical properties. As noted above, the general features of the

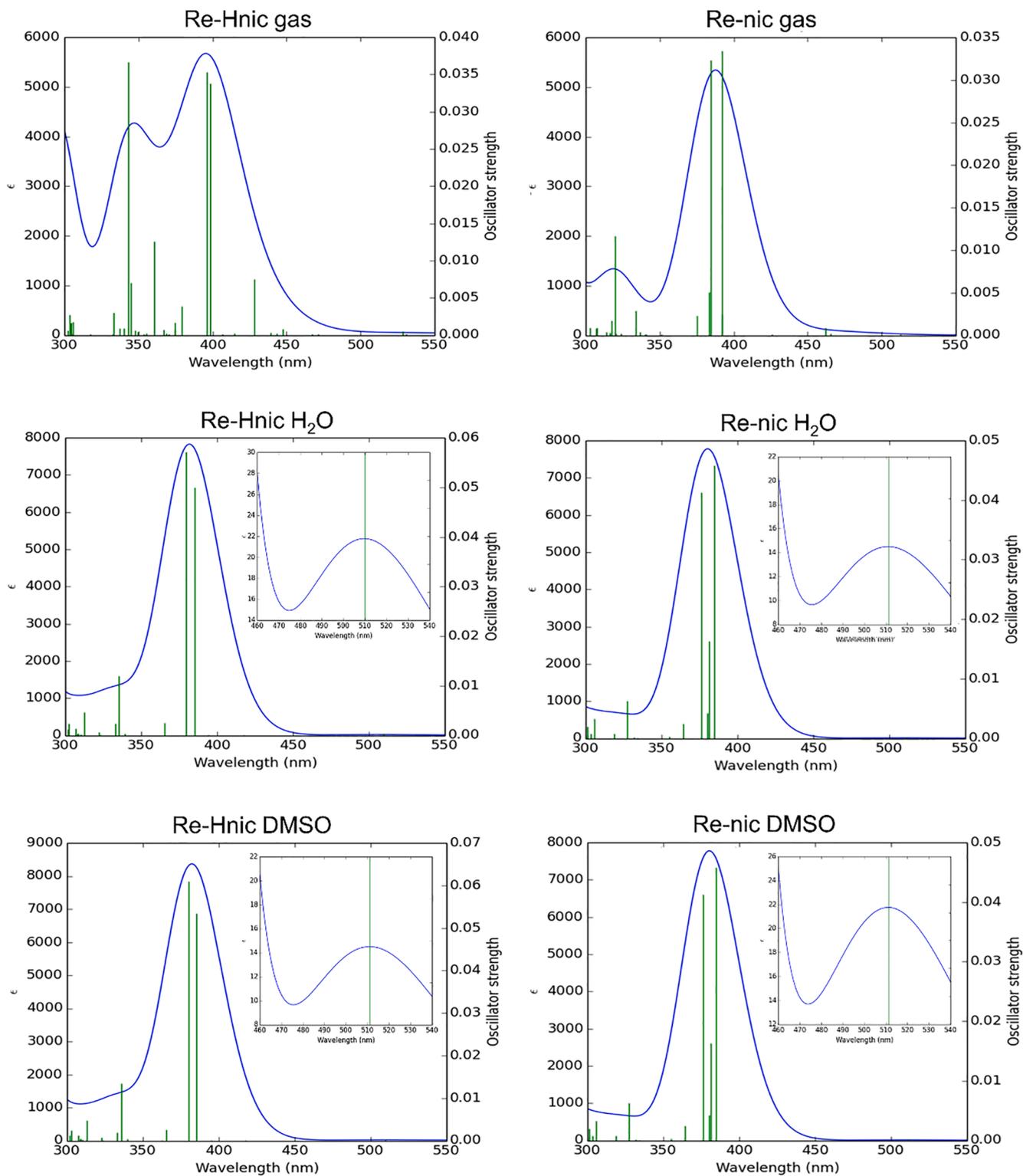


Fig. 3. GAUSSSUM plots of UV – Vis spectra of Re-Hnic and Re-nic as calculated with the method TD-PLTZ6311 in the gas phase, in the presence of H₂O and DMSO ($T = 298$ K).

Table 2

Selected electronic transitions of Re-Hnic and Re-nic (taken as an example) calculated in H₂O and DMSO using the TD-PLTZ6311/C-PCM method.

System	Most important excitations ^a	λ (nm)	f	λ_{exp} (nm) ^b
Re-Hnic-H ₂ O	H-1(α) \rightarrow L + 3(α), H(β) \rightarrow L + 3(β)	509.9	0.0003	460
	H-3(β) \rightarrow L(β)	385.1	0.0499	411
	H-4(β) \rightarrow L(β)	379.8	0.0572	
	H-2(α) \rightarrow L(α), H-1(β) \rightarrow L + 1(β)	335.3	0.0119	380
	H(α) \rightarrow L + 5(α), H-1(β) \rightarrow L + 1(β)	312.5	0.0047	
Re-Hnic-DMSO	H-1(α) \rightarrow L + 3(α), H(β) \rightarrow L + 3(β)	509.9	0.0003	460
	H-3(β) \rightarrow L(β)	385.5	0.0535	411
	H-4(β) \rightarrow L(β)	380.3	0.0610	
	H-2(α) \rightarrow L(α), H-1(β) \rightarrow L + 1(β)	335.7	0.0134	380
	H(α) \rightarrow L + 5(α), H-1(β) \rightarrow L + 1(β)	312.9	0.0047	
Re-nic-H ₂ O	H-2(α) \rightarrow L + 2(α), H(β) \rightarrow L + 2(β)	509.9	0.0003	460
	H-7(β) \rightarrow L(β)	384.4	0.0458	411
	H(α) \rightarrow L(α), H-8(β) \rightarrow L(β)	381.4	0.0163	
	H-3(α) \rightarrow L(α), H-2(α) \rightarrow L + 2(α), H-1(β) \rightarrow L + 1(β)	327.2	0.0063	380
	H-1(β) \rightarrow L + 1(β)			
	H(α) \rightarrow L + 5(α)	305.65	0.0033	
Re-nic-DMSO	H-2(α) \rightarrow L + 2(α), H(β) \rightarrow L + 2(β)	511.2	0.0003	460
	H-7(β) \rightarrow L(β)	384.9	0.0484	411
	H(α) \rightarrow L(α), H-8(β) \rightarrow L(β)	376.7	0.0424	
	H-3(α) \rightarrow L(α), H-2(α) \rightarrow L + 2(α), H-1(β) \rightarrow L + 1(β)	327.3	0.0066	380
	H-1(β) \rightarrow L + 1(β)			
	H(α) \rightarrow L + 5(α)	305.8	0.0035	

^a H = HOMO; L = LUMO.

^b λ_{exp} refers to the maximum of absorption bands detected in H₂O:DMSO (1:1; v:v).

simulated spectra for all Re(II)-nitrosyl monoanionic complexes in the presence of the solvent are reasonably consistent with those experimentally observed. Calculated spin-allowed electronic transitions in H₂O and DMSO of Re-Hnic and Re-nic (taken as an example) are presented in Table 2. For all transitions, only orbital contributions larger than 15 % were considered.

The inclusion of H₂O or DMSO did not promote differences in the electronic transitions responsible for the absorption bands simulated with TD-PLTZ6311/C-PCM. The band at the red-part of the spectrum of Re-Hnic was simulated due to transitions from the HOMO – 1(α) and HOMO(β) to the LUMO + 3(α) and LUMO + 3(β), respectively. The features exhibited by these MOs lead the character for this band to be LMLMCT (ligand-metal-to-ligand-metal charge transfer) (Fig. 4), for which no contribution from the pyridine-carboxylic unit was detected. Furthermore, the deprotonation reaction to form Re-nic did not induce changes in the origin of this band according to the contours of MOs involved in the excitations (HOMO – 2(α), HOMO(β), LUMO + 2(α), and LUMO + 2(β)) (Fig. 5). Therefore, the origin of the band peaked at 460 nm for Re-nic is also labelled as LMLMCT, for which a negligible contribution from –COO[–] was detected in HOMO – 2(α).

At the blue-part of the spectrum, an intense band at 382 nm was calculated, for which an in-plane charge-density rearrangement involving the unit {ReBr₄} was simulated. The analysis of all MOs responsible for excitations (HOMO – 3(β), HOMO – 4(β), and the LUMO (β)) pointed the nature of this band also to an LMLMCT. This origin also remains upon the deprotonation event, although the additional excitation LUMO(α) \leftarrow HOMO(α) is also required to produce the absorption at 382 nm of Re-nic.

Several orbitals participate in the excitations giving place to the

weak band simulated at the highest-energy part of the spectrum (at 324 nm). Transitions from HOMO – 2(α), HOMO – 1(β), and HOMO(ν) to the LUMO(α), LUMO + 1(β), and LUMO + 5(α) enables assigning an LMLMCT character for the abovementioned band, for which a minor contribution from the –COOH group was detected in LUMO(α) and LUMO + 1(β).

By proton-transfer reaction, this band in complex Re-nic also became LMLMCT in nature due to excitations from HOMO – 3(α), HOMO – 2(α), HOMO – 1(β), and HOMO(α) to LUMO(ν), LUMO + 2(α), and LUMO + 1(β), respectively. It is worth emphasizing that deprotonation promotes the contribution from the –COO[–] group to be negligible, as can be seen in HOMO – 2(α) (Fig. 5).

Concluding remarks

In this contribution, proton-transfer reactions of Re(II)-nitrosyl halide-complexes bearing nicotinic (Hnic) or 6,6'-dinicotinic acid (H₂dinic) were investigated using UV – Vis spectroscopy and potentiometric measurements. Experimental studies were conducted in the presence of a mixture DMSO:H₂O (1:1; v:v) to avoid solubility problems. No changes in absorptive behaviour were detected for complexes upon pH changes and with time. Potentiometric results accounted for excellent agreement for non-coordinated ligands taking previous reports into account. In addition, constant pK_{a1} of 1.2(5) associated with the first deprotonation of H₂dinic at very acidic conditions was detected for the first time. Coordination effects directly affect the acidity of carboxylic groups: pK_a markedly decreased compared to the free ligands. This finding was intuitively rationalized on the different charges of the conjugate acid-base pairs and their relative stabilization in the employed solvent mixture. A value of 4.56(4) was calculated for the first deprotonation constant (pK_{a1}) of Re-Hnic, and values of 3.08(5) and 4.25(4) were observed for the successive deprotonation constants pK_{a1} and pK_{a2} of complex Re-H₂dinic, respectively.

The no dependence of the absorptive response of complexes on changes in pH motivated an investigation of their features by theoretical calculations. TD-DFT studies with PBE1PBE in combination with LANL2TZ on rhenium and 6-311++G(d,p) on non-metal atoms were undertaken. To better understand the origin of all absorption bands experimentally observed in a DMSO:H₂O (1:1; v:v), a spectra simulation was conducted, taking the effects of DMSO and H₂O as solvents within the C-PCM approach into consideration.

The method was able to detect three bands as the experimental evidence for Re-Hnic by the inclusion of the solvent. The methodology also shows a reasonable match between the measured and simulated spectra of complex Re-nic. In contrast, studies on Re-H₂dinic and its deprotonation products led to non-systematic results, and higher accuracy calculations by the inclusion of explicit solvent seemed to be required. However, the qualitative match between simulated and experimental spectra of Re-Hnic and Re-nic allows us to propose TD-PLTZ6311/C-PCM as a reasonable tool to shed light on the absorptive response of title complexes upon changes in pH, keeping the computational cost low.

The band simulated at the lowest-energy region is originated in LMLMCT. At the blue-part of the spectrum, an intense band was detected, keeping the same nature. This origin was also assigned to the third absorption band. In all of them, the contribution arising from carboxylic units is negligible.

Finally, we hope our work will represent a new entry into the assessment of conditions to obtain new polymetallic species starting from complexes bearing uncoordinated carboxylic groups following a *complex-as-ligand* synthetic path.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

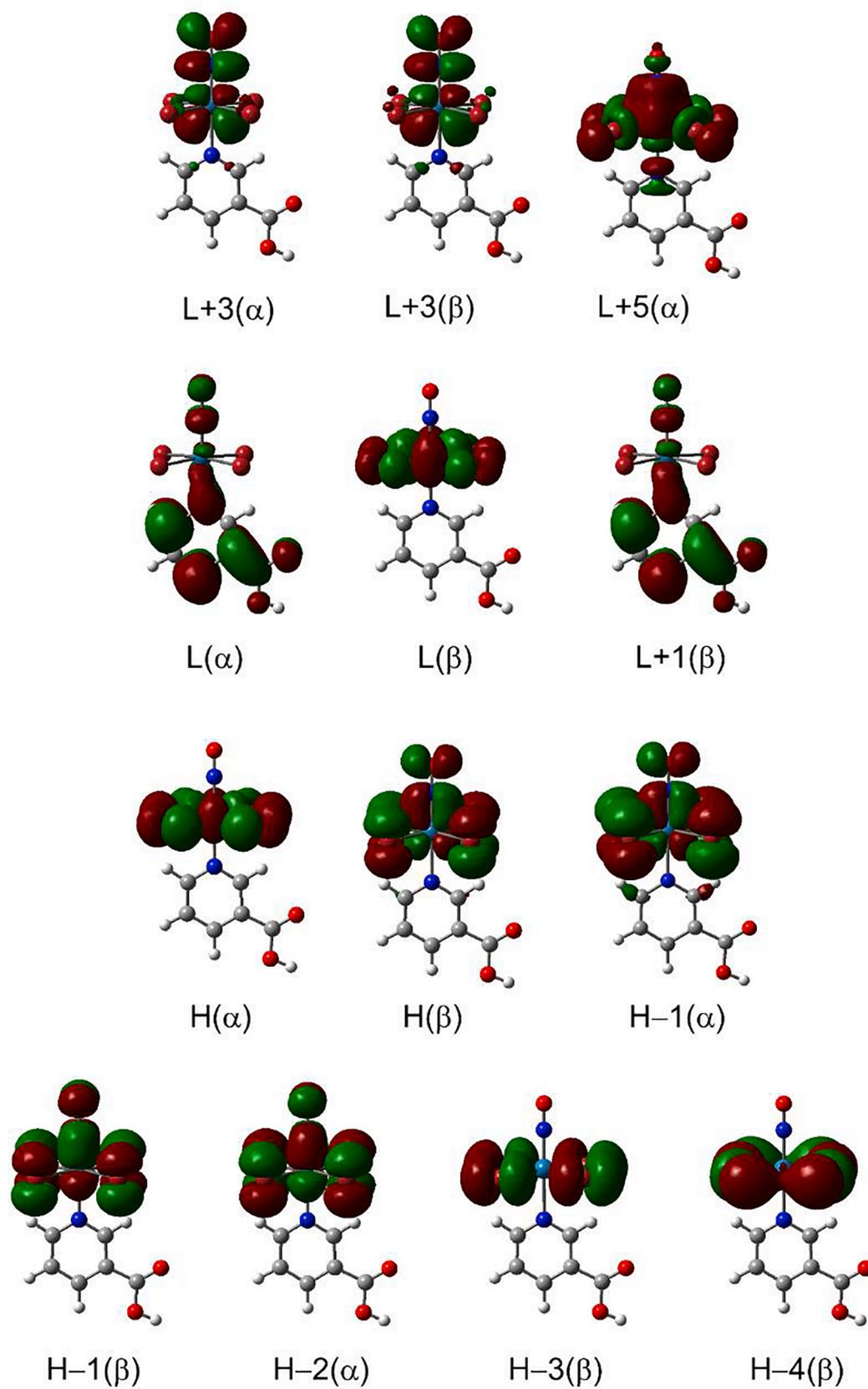


Fig. 4. Contours of selected MOs of Re-Hnic in the presence of H₂O (taken as an example) calculated with PLTZ6311/C-PCM (isovalue of 0.025 e•V⁻³; H = HOMO; L = LUMO).

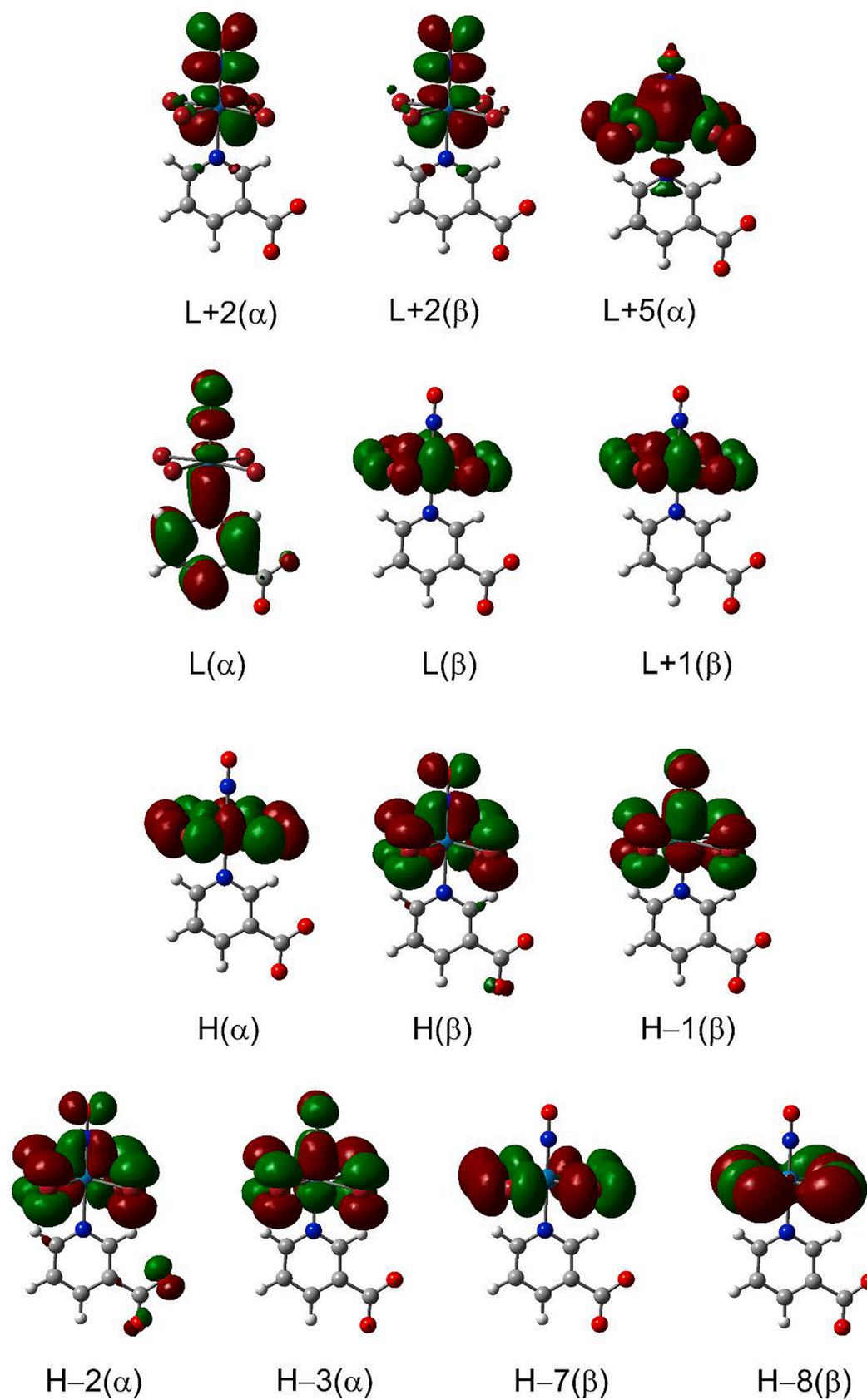


Fig. 5. Contours of selected MOs of Re-nic in the presence of H₂O (taken as an example) calculated with PLTZ6311/C-PCM (isovalue of 0.025 e \bullet V⁻³; H = HOMO; L = LUMO).

the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rechem.2022.100455>.

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