

# pH-dependent absorption and emission properties of a Re<sup>I</sup> complex working as a carboxylate ligand for Cu<sup>2+</sup>

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## Abstract

The *fac*-Re(CO)<sub>3</sub>(bipy-COOH)Cl complex (bipy = 2,2'-bipyridine) bears a carboxylic function in the 5-position of the bipy ligand: due to the kinetic inertness of the Re<sup>I</sup> center, the complex behaves as a R-COOH carboxylic acid. In aqueous solutions, it coordinates Cu<sup>2+</sup>, according to pH-dependent equilibria, to give the dimeric species Cu[*fac*-Re<sup>I</sup>(CO)<sub>3</sub>(bipy-COO)Cl]<sub>2</sub> and {Cu[*fac*-Re(CO)<sub>3</sub>(bipy-COO)Cl]<sub>2</sub>(OH)<sub>2</sub>}<sup>2-</sup>, whose formation constants have been determined by means of potentiometric titration experiments. The *fac*-Re(CO)<sub>3</sub>(bipy-R)Cl core is luminescent, and interestingly, its emitting properties are pH-dependent. In particular, its luminescence intensity increases with the formation of the {Cu[*fac*-Re(CO)<sub>3</sub>(bipy-COO)Cl]<sub>2</sub>(OH)<sub>2</sub>}<sup>2-</sup> species, visually signaling the formation of this hydroxo-containing multicenter complex.

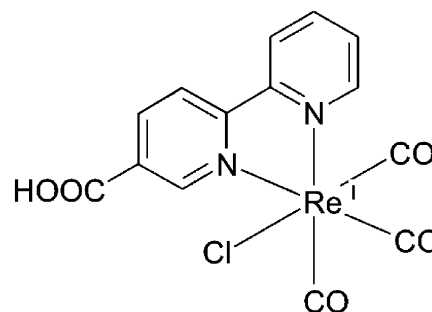
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**Keywords:** Carboxylate ligand; Cu<sup>2+</sup>; Re<sup>I</sup>

## 1. Introduction

Published studies on the solution chemistry of *fac*-Re<sup>I</sup>(CO)<sub>3</sub>(L-L)Cl compounds (in which L-L is a bidentate ligand with sp<sup>2</sup> N donors, e.g. bipy (bipy = 2,2'-bipyridine)) tend to exclude water as a solvent [1–5], despite their solubility, kinetic inertness and thermodynamic stability. We recently described [6], however, that it is possible to work in aqueous solutions where it is easy to control, by changing the pH conditions, the electrochemical, spectroscopic and photochemical properties of a series of *fac*-Re<sup>I</sup>(CO)<sub>3</sub>(L-L)Cl and [*fac*-Re<sup>I</sup>(CO)<sub>3</sub>(L-L)L']<sup>+</sup> complexes, where L-L and L' are 2,2'-bipyridine or pyridine ligands bearing ester or carboxylic functions. In this work, the complex *fac*-Re(CO)<sub>3</sub>(bipy-COOH)Cl (**1**) itself has been used as a *ligand* in aqueous solution for Cu<sup>2+</sup> ions. Thanks to the kinetic inertness [1–6] of the Re<sup>I</sup> center, compound **1** behaves as a R-COOH function and it has been possible to study its pH-dependent coordinative tendencies towards Cu<sup>2+</sup> ions by means of potentiometric titrations. Moreover,

the absorbing, emitting and electrochemical properties of the Re<sup>I</sup> core have also been studied as a function of pH, and correlated with the polynuclear Re<sup>I</sup>-Cu<sup>II</sup> complex species existing in the pertinent pH range.



## 2. Experimental

### 2.1. Materials

The complex *fac*-Re(CO)<sub>3</sub>(bipy-COOH)Cl (**1**) has been synthesized as already described [6]. All other reagents were purchased from Fluka/Aldrich and used as such.

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## 2.2. Potentiometric titrations and data fitting

Potentiometric titrations were carried out in water/dioxane mixtures (1:4 v/v) 0.1 M of sodium perchlorate. In a typical experiment 50 cm<sup>3</sup> of solvent were used, containing 1 × 10<sup>-3</sup> M Cu(ClO<sub>4</sub>)<sub>2</sub>, 2 × 10<sup>-3</sup> M *fac*-Re(CO)<sub>3</sub>(bipy-COOH)Cl (i.e. Cu<sup>2+</sup>:ligand = 1:2) and excess perchloric acid. Standard NaOH was added, under a nitrogen atmosphere, in a cell thermostated at 25 °C. 50–70 points were recorded, spanning the 3–11 pH range (prior to each experiment, the pH scale was calibrated by the Gran method [7]). Potentiometric data (e.m.f. vs. volume of added base) were then refined using the Hyperquad package [8,9]. A value of 5.39 was used for p*K*<sub>a</sub> in the equilibrium *fac*-Re(CO)<sub>3</sub>(bipy-COOH)Cl ⇌ [*fac*-Re(CO)<sub>3</sub>(bipy-COO)Cl]<sup>-</sup> + H<sup>+</sup>, as determined in reference 6 under experimental conditions identical to those employed in this work. Fit between calculated and experimental e.m.f. data was evaluated through the  $\sigma$  and  $\chi^2$  parameters [9], whose values, in each treatment, were found to be 1 (±0.2) and <8%, respectively. The calculated log *K* values, which are reported in the text, bear an uncertainty lower than ±0.02.

### 2.2.1. Physical and spectroscopic measurements

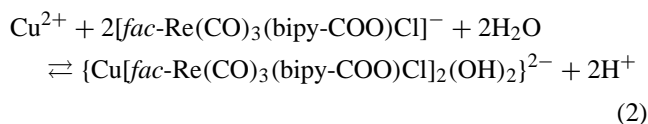
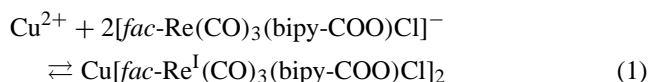
Mass spectra (ESI) were obtained on a Finnigan LCQ ion trap instrument, using negative ions mode (trace quantities of NaCl were added to favor negative ions formation). UV-Vis absorption spectra were taken with a Hewlett-Packard HP 8453 diode array spectrophotometer or with a Perkin Elmer lambda 16 spectrophotometer. Uncorrected emission and corrected excitation spectra were obtained with a Perkin Elmer LS 50 spectrofluorimeter. The fluorescence lifetimes (uncertainty ±5%) were obtained with an Edinburgh single-photon counting apparatus, in which the flash lamp was filled with D<sub>2</sub>.

Spectrophotometric and fluorimetric titrations were carried out as elsewhere described [10].

## 3. Results and discussion

Cu<sup>2+</sup> ions can form 2:1 or 1:1 copper:ligand complexes, which could be [11] of square planar (or distorted tetragonal) geometry, with carboxylate groups acting either as bidentate or monodentate ligands; in the latter case with water molecules completing the coordination sphere. For potentiometric titration experiments on the system *fac*-Re(CO)<sub>3</sub>(bipy-COOH)Cl + Cu<sup>2+</sup>, we chose a 2:1 rhenium complex:copper cation molar ratio, in order to allow the system to observe complexes of the above mentioned stoichiometries. From potentiometric data, two different *fac*-Re(CO)<sub>3</sub>(bipy-COOH)Cl/Cu<sup>2+</sup> complexes have been identified, according to Eqs. (1) and (2), and their formation constants have been calculated (log *K* = 5.36 and log *K* = -5.44 for equilibrium 1 and 2, respectively), with a good

agreement among the experimental and calculated data:



A much poorer agreement was instead observed when the formation of complexes of 1:1 *fac*-Re(CO)<sub>3</sub>(bipy-COOH)Cl/Cu<sup>2+</sup> stoichiometry and of the monohydroxy {Cu[*fac*-Re(CO)<sub>3</sub>(bipy-COO)Cl]<sub>2</sub>(OH)}<sup>-</sup> species were taken into account. As a consequence, we discarded the hypothesis that these species can form in solution under these experimental conditions.

The values obtained for the association constants of Eqs. (1) and (2), and the already known value of the dissociation constant of [*fac*-Re(CO)<sub>3</sub>(bipy-COOH)Cl] [6], allowed us to draw the complete distribution diagram of the various species present in solution (Fig. 1).

This diagram shows that different trimetallic species exist at pH > 4. In particular, the neutral species Cu[*fac*-Re<sup>I</sup>(CO)<sub>3</sub>(bipy-COO)Cl]<sub>2</sub> reaches 70% of relative abundance at pH 5.9, while the molar fraction of {Cu[*fac*-Re(CO)<sub>3</sub>(bipy-COO)Cl]<sub>2</sub>(OH)<sub>2</sub>}<sup>2-</sup> becomes greater than 0.95 at pH > 8.6. A residual percentage of uncomplexed [*fac*-Re(CO)<sub>3</sub>(bipy-COO)Cl]<sup>-</sup> can be found between pH 4 and 8, reaching a maximum of 18% at pH 6.1. The formation constant that we have calculated for Cu[*fac*-Re(CO)<sub>3</sub>(bipy-COO)Cl]<sub>2</sub> is fully consistent with the data reported in literature for Cu<sup>2+</sup> complexes with carboxylate anions bearing substituents of similar shape and properties. For example, benzoic acid displays a log *K* value of 3.24 for 1:1 complexation in 1:1 v/v water:dioxane, and similar values are found for a series of carboxylates bearing aromatic bulky groups [11]. Unfortunately, we were not able to grow crystals of this species suitable for X-ray diffraction studies, so that its structure can only be hypothesized. However, the 2:1 ligand:metal molar ratio and the typical d-d band in the absorption spectrum (690 nm, very broad) suggest a tetragonal geometry. To further support the hypothesis of an authentic 2:1 complex instead of an oligomeric mixture with 2:1 stoichiometry, mass spectra experiments were carried out with ESI technique on solutions containing *fac*-Re(CO)<sub>3</sub>(bipy-COOH)Cl and Cu<sup>2+</sup> in a 2:1 stoichiometric ratio at pH 5.9, i.e. when Cu[*fac*-Re(CO)<sub>3</sub>(bipy-COOH)Cl]<sub>2</sub> reaches its maximum percentage. Beside a peak at *m/z* = 505, relative to the free [*fac*-Re(CO)<sub>3</sub>(bipy-COO)Cl]<sup>-</sup> species, which is still present at pH 5.9, the main peak was found at *m/z* = 1108, as expected for {Cu[*fac*-Re(CO)<sub>3</sub>(bipy-COO)Cl]<sub>2</sub> + Cl<sup>-</sup>} (less intense peaks at 1106, 1110 and 1112 cm<sup>-1</sup> were also found, due to the isotopic distribution of Cu and Re). No peaks were observed at higher mass values.

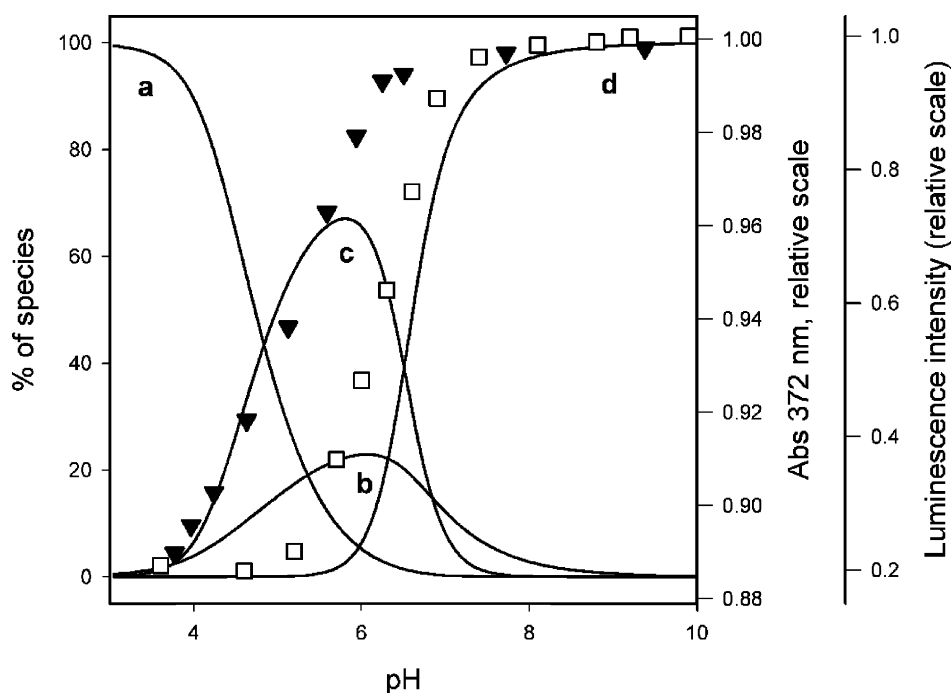


Fig. 1. Distribution diagram (percentage of species vs. pH) for the system  $fac\text{-Re}(\text{CO})_3\text{Cl}(\text{bipy-COOH})/\text{Cu}^{2+}$ , molar ratio 2:1, in water:dioxane 1:4 v/v: (a)  $fac\text{-Re}(\text{CO})_3\text{Cl}(\text{bipy-COOH})$ ; (b)  $fac\text{-Re}(\text{CO})_3\text{Cl}(\text{bipy-COO})^-$ ; (c)  $\text{Cu}[fac\text{-Re}(\text{CO})_3\text{Cl}(\text{bipy-COO})]_2$ ; (d)  $\{\text{Cu}[fac\text{-Re}(\text{CO})_3\text{Cl}(\text{bipy-COO})]_2(\text{OH})_2\}^{2-}$ . Black triangles:  $A_{372}$  vs. pH, relative scale (right vertical axis). White squares:  $I_{625}$  vs. pH, relative scale (right displaced axis).

The second trimetallic, copper containing species existing in solution,  $\{\text{Cu}[fac\text{-Re}(\text{CO})_3(\text{bipy-COO})\text{Cl}]_2(\text{OH})_2\}^{2-}$ , is obtained by coordination of two  $\text{OH}^-$  ions to  $\text{Cu}[Re^I(\text{CO})_3(\text{COO})\text{Cl}]_2$  or by deprotonation of two water molecules already coordinated to the copper center. The obtained complexation constants allowed us to calculate a  $\log K$  of  $-13.02$  for the process  $2\text{H}_2\text{O}(\text{coordinated}) \rightleftharpoons 2\text{OH}^-(\text{coordinated}) + 2\text{H}^+$ . Mass spectra carried out at pH 9.5 revealed a more complex nature for this species, since the expected molecular peak for  $\{\text{Cu}[fac\text{-Re}(\text{CO})_3(\text{bipy-COO})\text{Cl}]_2(\text{OH})_2\}^{2-}$  ( $m/z = 554$ , i.e. molecular ion mass/2) was missing, while peaks were found at higher ( $m/z = 1033$ ) and lower masses. These latest peaks, anyway, did not match any rational fragmentation pattern for  $\{\text{Cu}[fac\text{-Re}(\text{CO})_3(\text{bipy-COO})\text{Cl}]_2(\text{OH})_2\}^{2-}$ . Significantly, the isotopic distribution of the peak at 1033 excludes the presence of Cu atoms, while it suggests the presence of two Re centers. Moreover, this peak does not appear if mass spectra are carried out on solutions at pH 9.5 which contain only  $[fac\text{-Re}(\text{CO})_3(\text{bipy-COO})\text{Cl}]^-$  (i.e. with no  $\text{Cu}^{2+}$ ), this indicates: (i) that the species responsible of the 1033 peak is reasonably formed during the ionization process in the mass spectrometer; (ii) that it is not due to the high energy reaction of the  $\text{OH}^-$  ions which are present in the bulk with the  $[fac\text{-Re}(\text{CO})_3(\text{bipy-COO})\text{Cl}]^-$  molecule; (iii) that it comes from an intramolecular reaction of the hydroxy anions coordinated to  $\text{Cu}^{2+}$  on the Re centers coordinated through  $-\text{COO}^-$  to the same copper cation.

Unfortunately, on the basis of these data, due to the lack of the appropriate molecular peak, the structure of

the  $\{\text{Cu}[fac\text{-Re}(\text{CO})_3(\text{bipy-COO})\text{Cl}]_2(\text{OH})_2\}^{2-}$  complex remains not completely defined. As a matter of fact, for this species both a definite  $\text{Re}_2\text{Cu}$  and a multicenter oligomeric structure with  $\text{OH}^-$  acting as bridging ligand can be postulated, this latter being not uncommon for  $\text{Cu}^{2+}$  complexes in aqueous solution. In this latter case, the formula  $\{\text{Cu}[fac\text{-Re}(\text{CO})_3(\text{bipy-COO})\text{Cl}]_2(\text{OH})_2\}^{2-}$ , determined through potentiometric titration experiments, would give account only of the stoichiometry of this complex and not of its real structure.

Coupled pH-metric and spectrophotometric or spectrofluorimetric titrations were carried out with the same  $fac\text{-Re}(\text{CO})_3(\text{bipy-COOH})\text{Cl}/\text{Cu}^{2+}$  molar ratio (2:1), following the changes of the MLCT band [3–5,12–14] of the rhenium complex. As far as the absorption is concerned, we observed a shift of  $\lambda_{\text{max}}$  from 390 (neutral  $fac\text{-Re}(\text{CO})_3(\text{bipy-COOH})\text{Cl}$ ,  $\epsilon = 3150 \text{ M}^{-1} \text{ cm}^{-1}$ ) towards shorter wavelengths upon addition of base. The maximum of MLCT band reached its minimum value of 372 nm ( $\epsilon = 3590 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>1</sup> at pH 6.2 and did not shift further on addition of more base. Superimposition to the distribution diagram of the profile of the  $A_{372}$  vs. pH (Fig. 1, black triangles) indicates that the variation of the MLCT band maximum follows exactly the depro-

<sup>1</sup> The molar extinction coefficient is here calculated taking into account the total concentration of the rhenium-containing species, i.e. the initial analytical concentration of the  $fac\text{-Re}(\text{CO})_3(\text{bipy-COOH})\text{Cl}$  species. The  $\epsilon$  values for the dimeric  $\text{Cu}[fac\text{-Re}(\text{CO})_3(\text{bipy-COO})\text{Cl}]_2$  and  $\{\text{Cu}[fac\text{-Re}(\text{CO})_3(\text{bipy-COO})_2\text{OH}]_2\}^{2-}$  species can then be calculated as the double of the reported values.

tonation of the –COOH group, being complete when all *fac*-Re(CO)<sub>3</sub>(bipy-COOH)Cl is in its deprotonated form, both as a free species or coordinated to Cu<sup>2+</sup>. The blue shift of the band is a consequence of the more energy-demanding transition of an electron from the rhenium center to the negatively charged (instead of neutral) bipy-COOH fragment, while the deprotonation of the water molecules coordinated to Cu<sup>2+</sup> with the consequent formation of {Cu[*fac*-Re<sup>I</sup>(CO)<sub>3</sub>Cl(bipy-COO)]<sub>2</sub>(OH)<sub>2</sub>}<sup>2-</sup> does not further significantly affect the MLCT band.

A different behavior was instead observed for the emission band of the Re fluorophore, which has its maximum at 625 nm. We have recently reported [6] that the *fac*-Re(CO)<sub>3</sub>(bipy-COOH)Cl is very weakly luminescent ( $\Phi = 1 \times 10^{-4}$ ) in its protonated form, while a 10-fold more intense luminescence band ( $\Phi = 1 \times 10^{-3}$ ) is observed at pH values above 6.5, where this complex is deprotonated. Superimposition to the distribution diagram of the profile of the emission intensity at 625 nm (Fig. 1, white square symbols) vs. pH clearly indicates that Cu[*fac*-Re<sup>I</sup>(CO)<sub>3</sub>(bipy-COO)Cl]<sub>2</sub> does not contribute at all to the overall luminescence intensity at 625 nm. The increase of luminescence expected from the presence of the free deprotonated form in the pH range 5–7 is in fact counterbalanced by the lack of luminescence from this trimetallic complex. A global luminescence increase is only observed when the {Cu[*fac*-Re<sup>I</sup>(CO)<sub>3</sub>(bipy-COO)Cl]<sub>2</sub>(OH)<sub>2</sub>}<sup>2-</sup> species is obtained at higher pH. The intensity value in the plateau region (pH above 9), such as the excited state lifetime, is very similar to that observed in the absence of copper ions. This finding can only be explained supposing that the luminescence of the Re complex is strongly quenched in Cu[*fac*-Re<sup>I</sup>(CO)<sub>3</sub>(bipy-COO)Cl]<sub>2</sub>, and not in {Cu[*fac*-Re<sup>I</sup>(CO)<sub>3</sub>(bipy-COO)Cl]<sub>2</sub>(OH)<sub>2</sub>}<sup>2-</sup>. The observed quenching can be ascribed in theory to an energy transfer process to the d–d states centered on the copper atom or to an electron transfer process from the Re complex to the Cu center. Formation of the hydroxy species is expected to make both processes slower, unfavoring them from a thermodynamical point of view by making more negative the reduction potential of the copper center and by rising the energy of the Cu centered state. Unfortunately, no indication could come from low temperature experiments, since the large change in temperature shifts all the equilibria involved in an unpredictable way, being the pH window for the presence of {Cu[*fac*-Re<sup>I</sup>(CO)<sub>3</sub>(bipy-COO)Cl]<sub>2</sub>} very small. In addition, the dioxane–water mixture forms an opaque ma-

trix that makes difficult to compare luminescence intensity values.

#### 4. Conclusions

According to our results, it has to be stressed that absorption, emission and coordination properties of *fac*-Re<sup>I</sup>(CO)<sub>3</sub>(bipy-COOH)Cl indicate that this complex can be an useful ligand for the signaling (e.g. through coupled UV spectrum and fluorescence changes) of the pH-dependent formation of multicenter complexes with transition metal cations.

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