

A novel triruthenium nitrosyl bearing a quinolinic ligand: a comparison of its spectroscopic behavior with its pyridine analogues

Nicolle Azevedo Portela dos Santos,^a Amanda Batista Silva,^a Camila Fontes Neves da Silva,^b
Anamaria Dias Pereira Alexiou,^a and Sofia Nikolaou^{*a}

^a*Departamento de Química, Laboratório de Atividade Biológica e Química Supramolecular de Compostos de Coordenação (LABIQSC²), Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Av. Bandeirantes 3900, 14040-901, Ribeirão Preto - SP, Brazil. sofia@ffclrp.usp.br.* ^b*Departamento de Bioquímica, Laboratório de Processos Fotoinduzidos e Interfaces (LPFI), Instituto de Química, Universidade de São Paulo, São Paulo, Brazil*

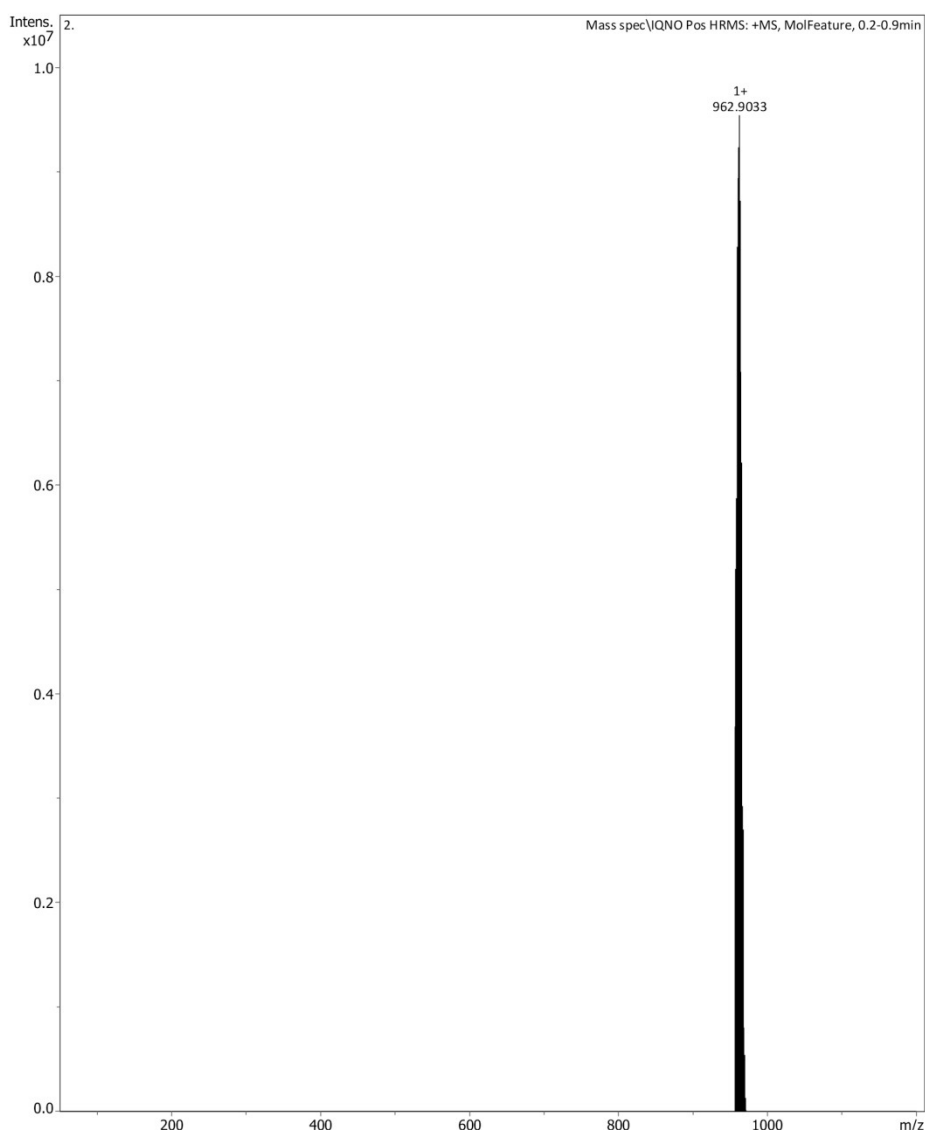
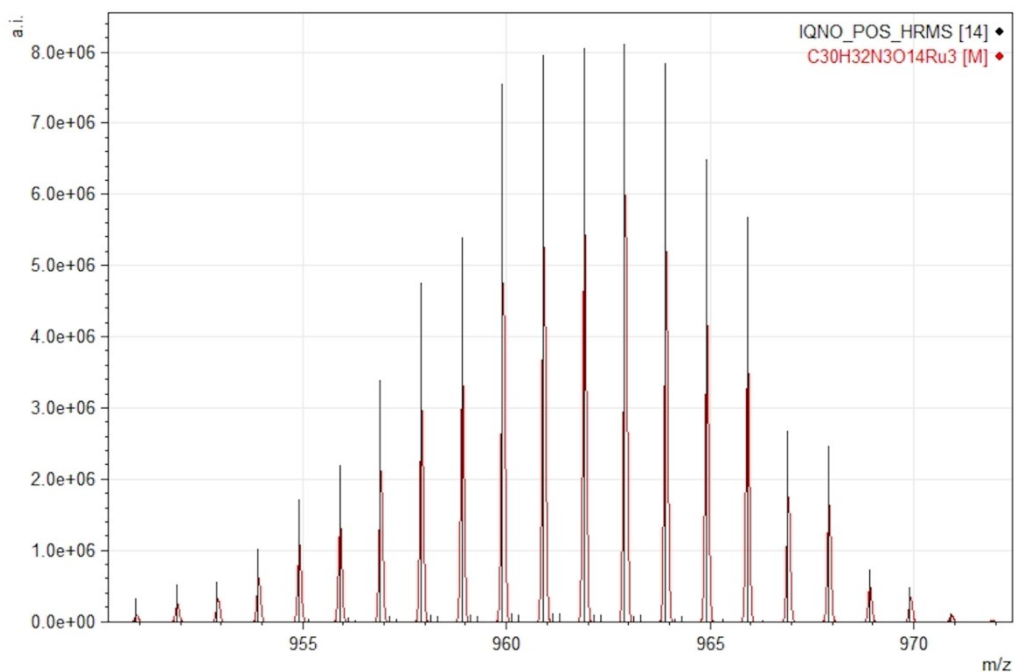
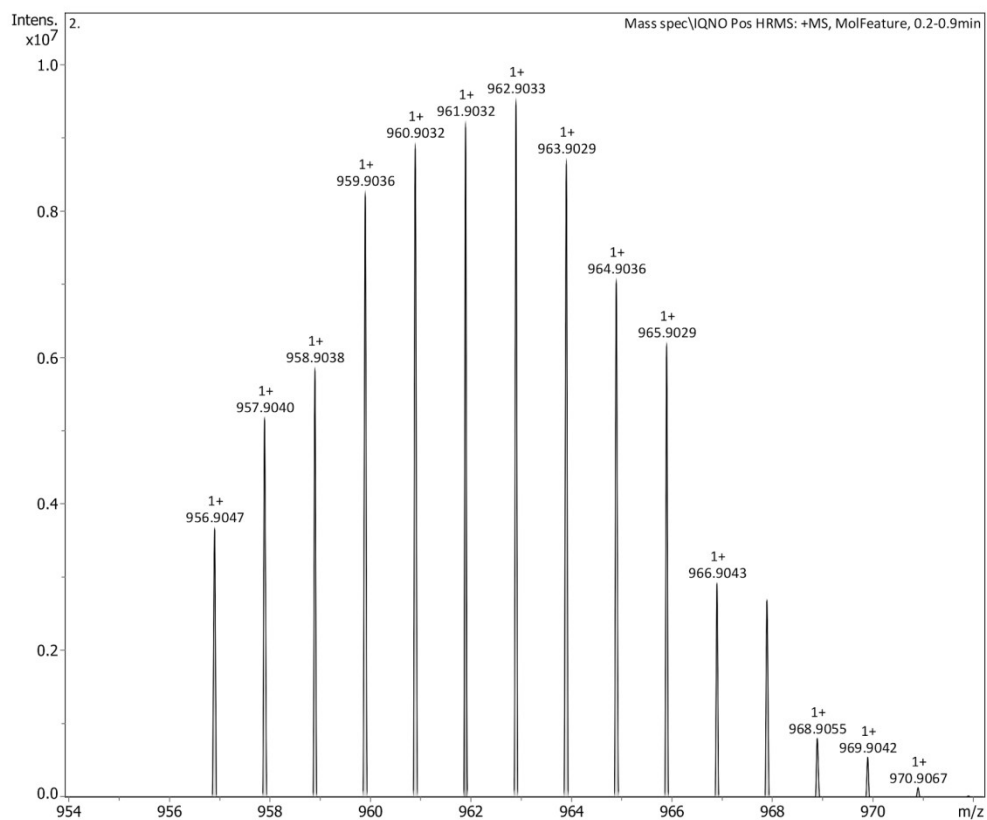


Figure ESI 1. High resolution mass spectrum of $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{iq})_2\text{NO}]\text{PF}_6$, displaying the molecular ion $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{iq})_2\text{NO}]^+$ at m/z 962; positive acquisition mode.



ESI 2. Expansion of the molecular ion peak at m/z 962 (top) and the match between the simulated (black line) and the experimental (red line) isotopic pattern for the ion $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{iq})_2\text{NO}]^+$ (bottom).

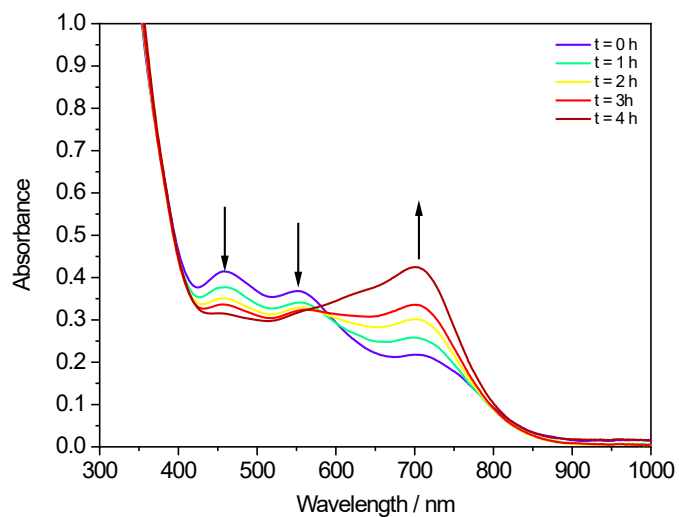


Figure ESI 3. Spectrophotometric control of a 1.98×10^{-4} acetonitrile solution of compound $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{iq})_2\text{NO}]\text{PF}_6$, kept under ambient light.

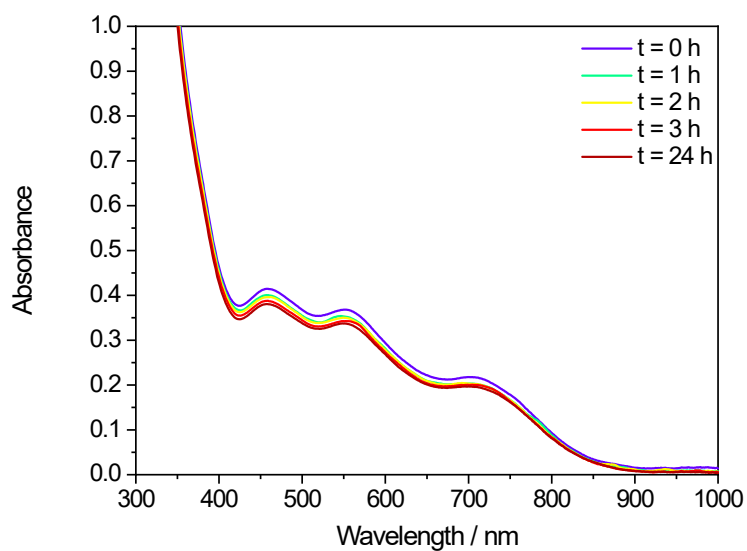


Figure ESI 4. Spectrophotometric control of a 1.98×10^{-4} acetonitrile solution of compound $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{iq})_2\text{NO}]\text{PF}_6$, kept in the absence of light.

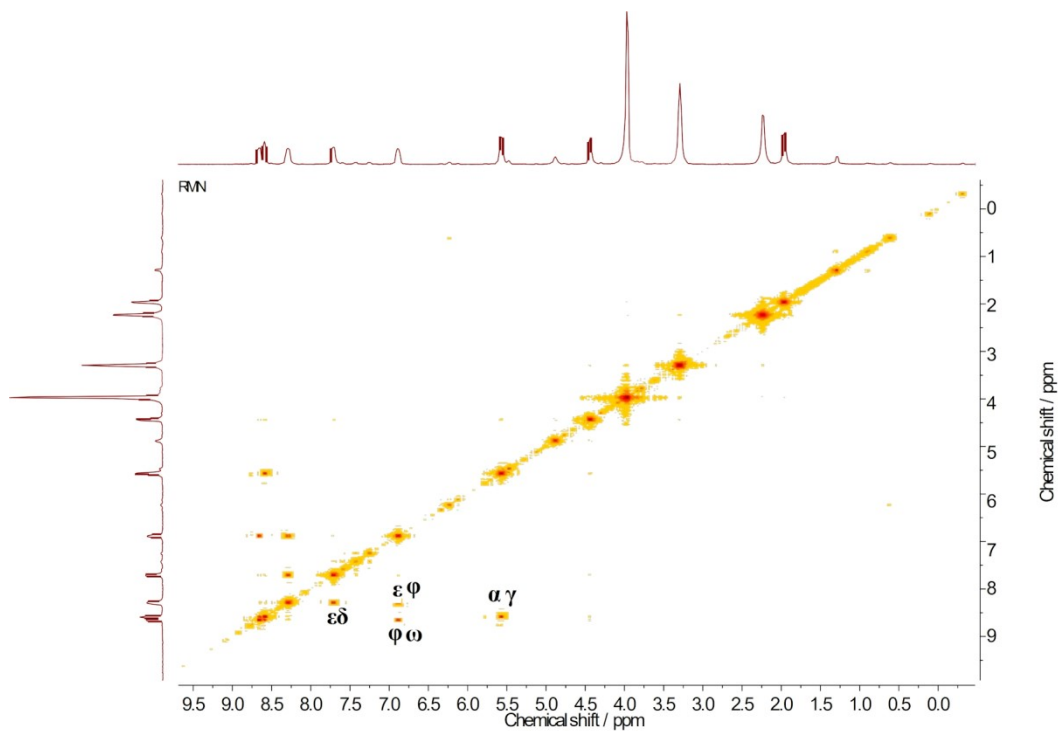
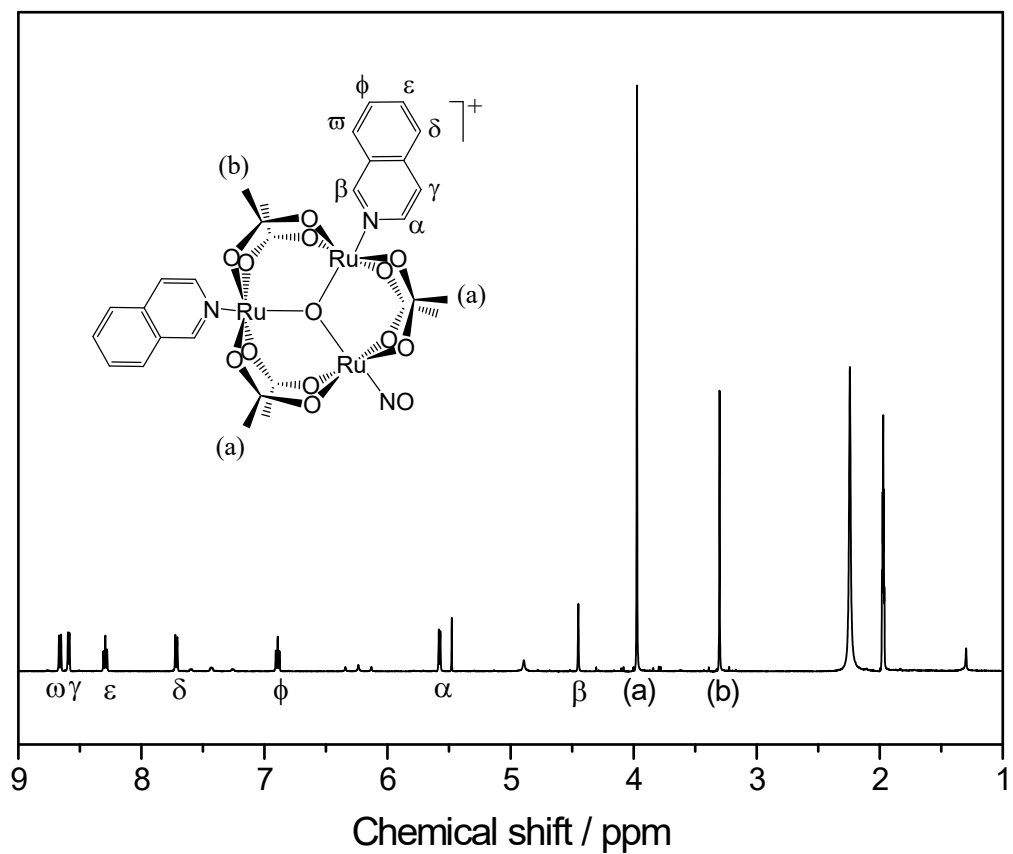


Figure ESI 5. ^1H NMR and COSY spectra of compound $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{iq})_2\text{NO}]\text{PF}_6$, registered from 1.5×10^{-2} M CD_3CN solution.

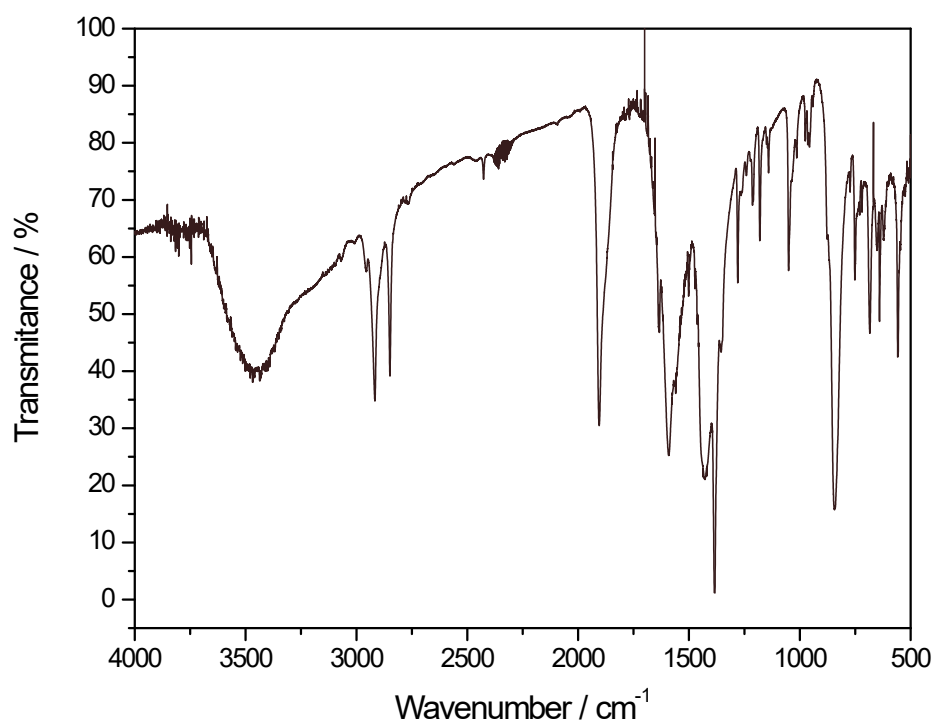


Figure ESI6. Infrared spectrum of compound $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{iq})_2\text{NO}]\text{PF}_6$, collected from KBr pellets.

Table ESI 1. Infrared data observed for compound $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{iq})_2\text{NO}]\text{PF}_6$, collected from KBr pellets.

| $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{iq})_2\text{NO}]\text{PF}_6$ | $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{iq})_3]\text{PF}_6^a$ | Tentative assignement |
|---|--|--|
| 2956vw; 2917m, 2849m | 3095w; 3064w; 2931w | $\nu(\text{CH})$ |
| 1904s | - | $\nu(\text{NO})$ |
| 1636m | 1633m | ν aromatic ring; $\nu_{\text{as}}(\text{COO}^-)$ |
| 1590s | 1598m | $\nu(\text{CC})$; $\nu(\text{CN})$ aromatic ring |
| 1560w | 1556w | $\nu_{\text{as}}(\text{COO}^-)$ |
| 1430s | 1427s | $\nu_s(\text{COO})$ |
| 1385vs | 1387w | $\nu(\text{CC})$ aromatic ring |
| 1355sh | | $\delta_{\text{ip}}(\text{CH}_3)$ |
| 1279w; 1213w; 1180w | 1274w; 1215w; 1180w | $\delta_{\text{ip}}(\text{CH})$ aromatic ring |
| 843s | 844s | $\nu(\text{PF}_6)$ |
| 751w; 684w; 640w | 741w; 683w; 639w | $\delta_{\text{oop}}(\text{CH})$ aromatic ring |

^afrom reference [1], vw = very weak; w = weak; m = medium; s = strong; vs = very strong; ν = stretching; ν_s = symmetric stretching; ν_{as} = antisymmetric stretching; δ_{ip} = in plane bending; δ_{oop} = out of plane bending; sh=shoulder

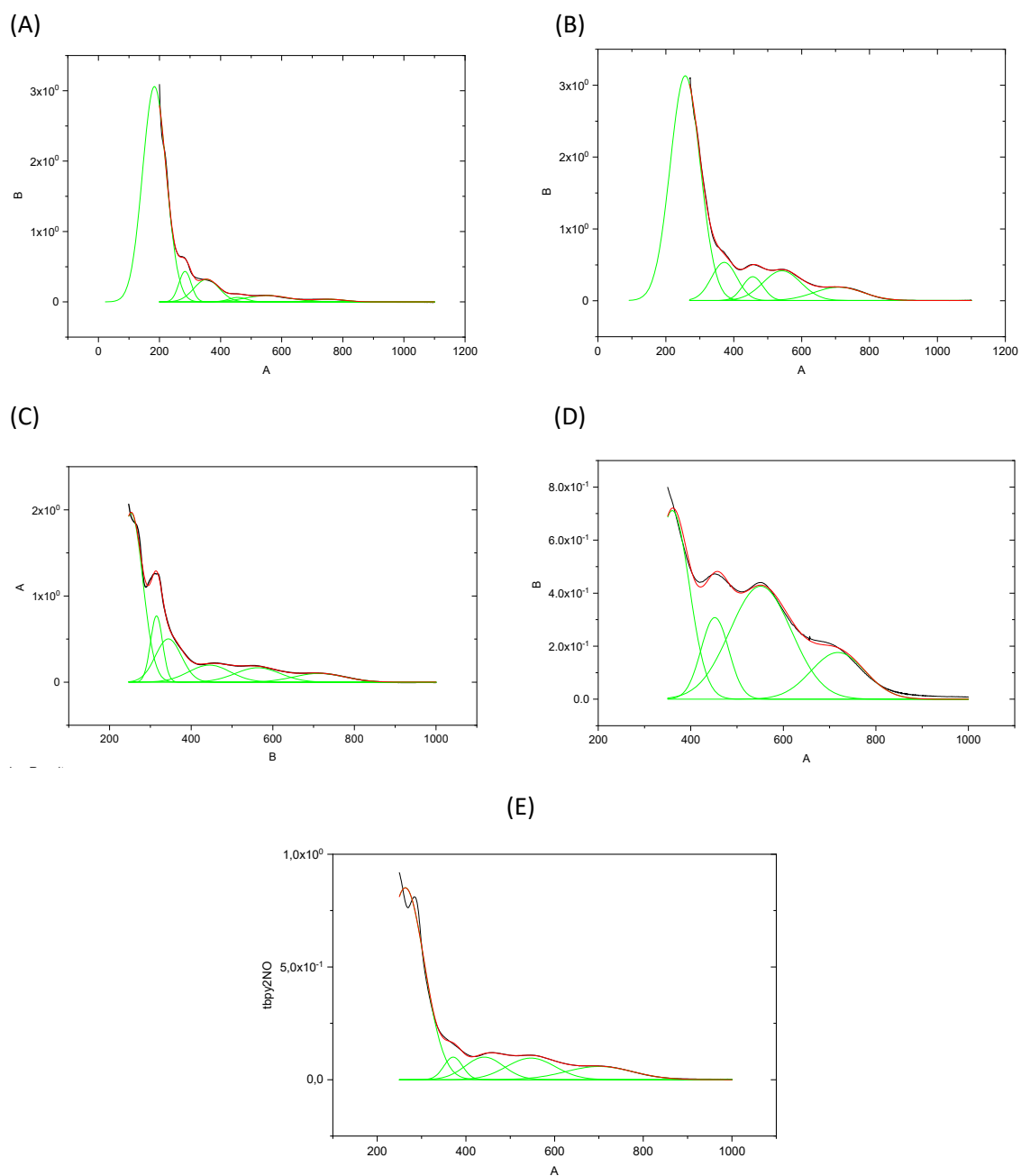


Figure ES17. Deconvoluted electronic spectra of compounds $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{L})_2\text{NO}]\text{PF}_6$ where L = (A) 4-acetylpyridine; (B) 3-methylpyridine; (C) isoquinoline; (D) 4-methylpyridine and (E) 4-terpyridine. Deconvolutions were performed using Origin® 2020.

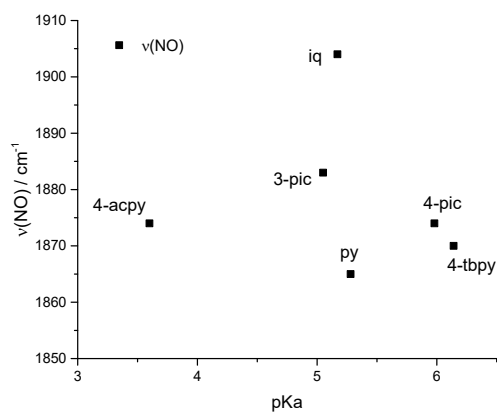


Figure ES18. Dependence of the $\nu(\text{NO})$ stretching frequency with the pKa of the ancillary ligands L for the nitrosyl clusters of general formula $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{L})_2\text{NO}]\text{PF}_6$.

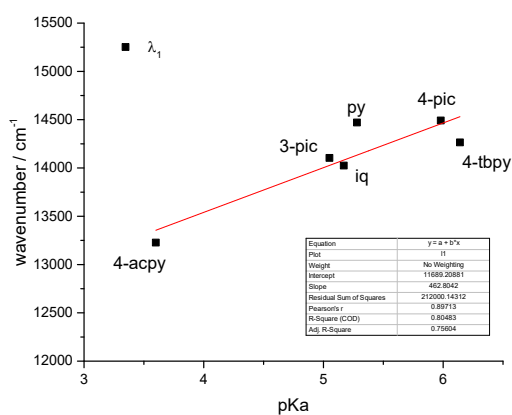


Figure ES19. Dependence of the IC band energy (λ_1) with the pKa of the ancillary ligands L for the nitrosyl clusters of general formula $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{L})_2\text{NO}]\text{PF}_6$.

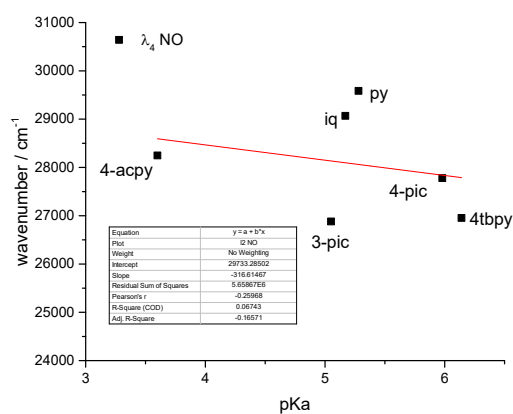


Figure ES10. Dependence of the CLCT band energy (λ_4) with the pKa of the ancillary ligands L for the nitrosyl clusters of general formula $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{L})_2\text{NO}]\text{PF}_6$.

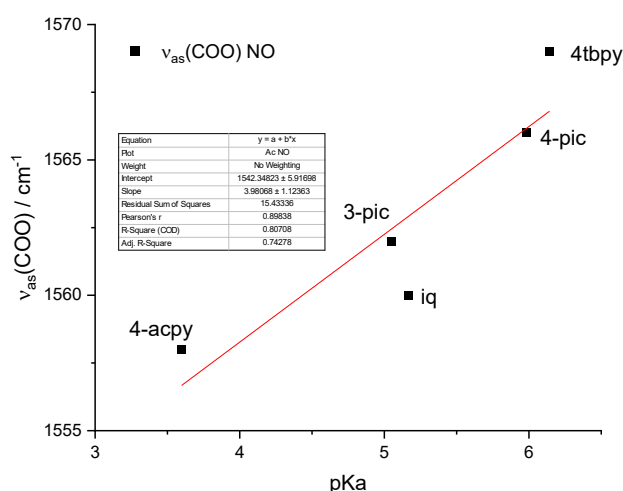


Figure ESI11. Dependence of the $\nu_{as}(\text{COO})$ stretching frequency with the pKa of the ancillary ligands L for the nitrosyl clusters of general formula $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{L})_2\text{NO}]\text{PF}_6$.

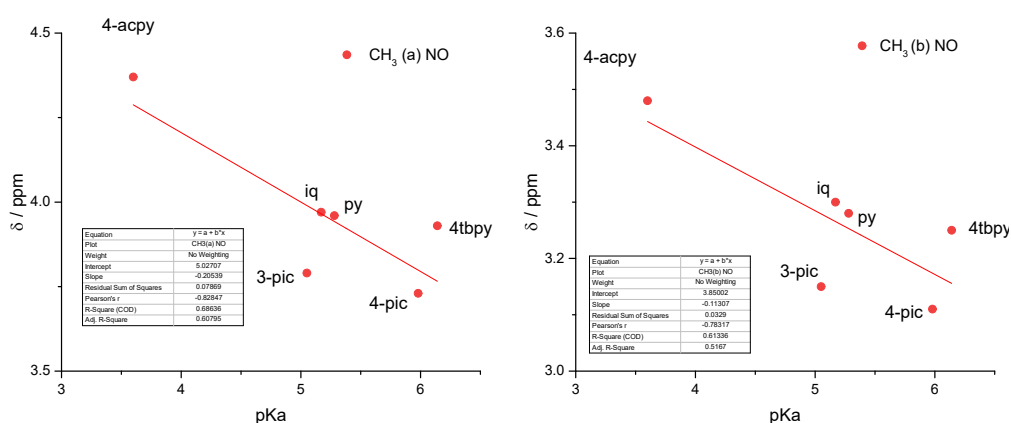
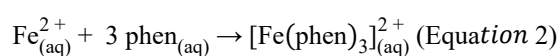
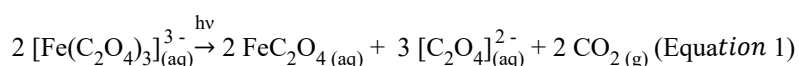


Figure ESI12. Dependence of the $\delta(\text{CH}_3)$ chemical shifts with the pKa of the ancillary ligands L for the nitrosyl clusters of general formula $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{L})_2\text{NO}]\text{PF}_6$.

Chemical Actinometry

A actinometer is defined by IUPAC as “a chemical system or physical device by which the number of photons in a beam absorbed in a defined space of a chemical reactor can be determined integrally or per unit of time”.⁶ A chemical actinometer is a chemical system that has a known quantum yield and, therefore, is subjected to a photoinduced reaction in order to determine parameters of the equipment used, such as the intensity of the radiation used. The chemical actinometers are still preferred over a physical actinometer due to the accessibility and reproducibility achieved for these systems.⁷

The ferrioxalate actinometer consists of two reactions, described in equations 1 and 2: the first being a photoinduced reaction of reduction of Fe³⁺ from the ferrioxalate to Fe²⁺ and the second, occurring in acid buffered medium, consisting of the reaction of the Fe²⁺ ion with 1,10-phenanthroline, generating a complex that allows the measurement of absorbance at its maximum absorption at 510 nm ($\epsilon_{510\text{ nm}} = 11100\text{ L mol}^{-1}\text{ cm}^{-1}$).⁸ Thus, since the quantum yield of the process is known for different wavelengths, from absorbance measurements of the complex generated in equation 2, it is possible to determine the intensity of the irradiated light – which will be applied in a subsequent photochemical process.



To determine the intensity of the light irradiated in the NO photorelease experiment at 365 nm, the ferrioxalate actinometer was employed. For the procedure, three solutions were used: a) K₃[Fe(C₂O₄)₃].3H₂O, 6 mmol L⁻¹; b) an acidic solution of H₂SO₄ and H₃CCOONa prepared by mixing 600 mL of a 1 mol L⁻¹ sodium acetate aqueous solution and 360 mL of a 1 mol L⁻¹ H₂SO₄ solution, followed by dilution to 1 L; c) 0.1% 1,10-phenanthroline solution. For the measurements, 2 mL of the potassium ferrioxalate solution were placed in a 10 mL volumetric flask (control sample) and 3 mL (V1) were placed in a quartz cell. This cell containing the solution was subjected to gentle agitation and 5 minutes of irradiation at 365 nm by Boitton/Lucamat lamps 6W T-5-BL8. After an interval of 5 minutes, 2 mL of this irradiated solution (V2) was transferred to another 10 mL volumetric flask (V3). To the two prepared flasks, 2.5 ml of the acid solution and 1 ml of the phenanthroline solution were added and the flasks volume were completed with distilled water. The solutions were shaken and stored in the dark for 1 hour and absorbance measurements were made for these solutions using the Agilent Technologies Cary 60 UV-Vis spectrophotometer. This procedure was performed in triplicate. It was observed that after a period of 1 hour, the control solution remained green, while the irradiated solution presented an orange color, corresponding to the Fe²⁺-phen complex.

The intensity of the used lamp is given by equation 3 and the parameter nFe (number of Fe²⁺ ions generated) is determined by equation 4:^{9,10}

$$I = \frac{n\text{Fe}}{\Phi_{\text{Fe}} \cdot t \cdot (1 - 10^{-A})} \text{ (Equation 3)}$$

I = intensity of light at 365 nm

nFe = number of moles of Fe²⁺

ΦFe= quantum yield of Fe²⁺ formation (1.25)

t = irradiation time (5 minutes)

A= absorbance of the control solution at the irradiation wavelength

$$n\text{Fe} = \frac{A_{510} \cdot V_1 \cdot V_3}{V_2 \cdot I \cdot \epsilon} \text{ (Equation 4)}$$

nFe = number of moles of Fe²⁺ ions

A₅₁₀ = absorbance of the irradiated solution at 510 nm

V₁ = volume of the irradiated sample (3 x 10⁻³ L)

V₂ = volume of the irradiated aliquot used in the dilution (2 x 10⁻³ L)

V₃ = volume of the diluted solution (10 x 10⁻³ L)

I = light path (1 cm)

ε = molar absorptivity coefficient of the Fe²⁺-phen complex at 510 nm (1.11 x 10⁴ L mol⁻¹ cm⁻¹)

Then, a 7.0 x 10⁻² mmol L⁻¹ solution of the [Ru₃O(CH₃COO)₆(iq)₂NO]PF₆ cluster was prepared in acetonitrile and 3 mL of this solution was irradiated at 365 nm for 6 minutes. The absorbance of the solution was measured before and after irradiation, and thus, the quantum yield of the photorelease of NO was determined from equation 5.

$$\Phi\text{NO} = \frac{n\text{NO}}{I \cdot t \cdot (1 - 10^{-A})} \text{ (Equation 5)}$$

nNO = amount of NO released by the photochemical reaction determined by the changing in the absorption band of the complex at 458 nm (ε= 1703 L mol⁻¹ cm⁻¹)

I = incident light intensity

t = photolysis time

A = absorbance of the sample at the wavelength of the irradiation

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