Research paper

New NMR investigation of $[RuF_5NO]^{2-}$ anion

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A B S T R A C T

The ^{15}N shift value is the main distinctive parameter to distinguish linear than angular MNO in transition metal nitrosyls by NMR spectroscopy. To get insight into the spectroscopic properties of a simple ruthenium-nitrosyl complex, the $[RuF_5NO]^{2-}$ anion, was reinvestigated. Their ^{15}N and ^{19}F nuclear magnetic resonance spectra (NMR) were analyzed and compared with the behavior observed for the geometrically related (C_{4v}) $[Fe(CN)_5NO]^{2-}$ (^{15}N and ^{13}C enriched) ion. The different *splitting and coupling constants observed* in both systems were attributed to the small change in angles and atomic distances. These results highlight the sensitivity of this spectroscopy to detect small geometrical distortion in transition metal complexes. DFT calculations predicted for both systems, shifts and coupling constant values in good agreement with the experimental results. The chemical shifts and coupling constants parameters predicted by DFT calculations for both systems are in good agreement with experimental values.

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1. Introduction

The important roles discovered for nitric oxide (NO) in biological systems in the last three decades stimulated research on transition metal complexes containing nitrosyls [1].

Their synthesis was explored with the aim of being able to release NO for biological and therapeutic applications [2,3]. Among these, ruthenium nitrosyls pay a lot of attention judging from the large number of reported investigations [2]. Sodium nitroprusside $(Na_2[Fe(CN)_5NO].2H_2O)$, Roussin's red salt $(K_2[Fe_2S_2(NO)_4])$ and black salt $(Na[(FeNOS)_4])$ are other nonheme iron nitrosyl complexes widely studied as potential NO sources [3,4] Despite the risks for cyanide release [5], sodium nitroprusside has continued to be used in cardiac hypertensive crises, vascular surgery, heart failure, pediatric surgery, and other acute applications [6].

The detailed study of NO coordinated to a metal centre is crucial to understand biological process at molecular level. Different spectroscopic and structural methods provide complementary information on the bonds nature. Among this, NMR spectroscopy is one of the most powerful and sensitive methods to explore the molecules in a solvent media. Its utility was extended to coordination chemistry to evaluate the structure and behavior of the complexes and

their ligands in solution [7,8], also in coordination supramolecular chemistry [9].

However, the simplest of all ruthenium nitrosyls $([RuF_5NO]^{2-})$ has not been sufficiently studied. The theoretical and experimental conclusions for this compound might be used as a model to understand more complex systems.

Although the number of studies on ^{15}N NMR in metal nitrosyl are few, ^{15}N chemical shift was proposed to distinguish between bent and linear M−N−O structure because bent nitrosyls appeared separated by hundreds of ppm from linear arrangements [10–12]. This behavior is also observed in solid state [13].

The aim of the present work is to get insight on the NMR study of the $[RuF_5NO]^{2-}$ ion by exploring the ^{19}F and ^{15}N spectra of $[RuF_5{}^{15}NO]^{2-}$ (^{15}N isotopic substitution >90%). This simple inorganic system is ideal to be studied by NMR spectroscopy because ^{19}F and ^{15}N (isotopically enriched) atoms are directly coordinated to the central metal and the multiplicity and coupling constant values between them can reflect conformational and structural information.

The nitroprusside ion $([Fe(CN)_5NO]^{2-})$, geometrically related to the title compound (C_{4v}), was synthesized with fully enriched ^{15}N (O) and ^{13}C isotopes in order to compare the splitting of NMR signals and coupling constant with that observed for $[RuF_5{}^{15}NO]^{2-}$.

The experimental results were supported with Density Functional Theory (DFT) calculations.

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2. Experimental section

2.1. Synthesis of $[RuF_5{}^{14/15}NO]^{2-}$ ion

The $K_2[RuF_5NO]\cdot H_2O$ complex was synthesized by a modifying method reported it in the literature [14]. The synthesis started from $K_2[RuBr_5NO]$ instead of $K_2[RuCl_5NO]$ because a better yield was achieved (60%). The solid $K_2[RuBr_5NO]$ in intimate contact with KHF_2 (at a molar ratio: complex: KHF_2, 1:5) was placed in a nickel crucible and then heated in a muffle for 30 min at 320–340 °C. The obtained solid was dissolved in the minima water volume and left for crystallization by spontaneous evaporation of the solvent at room temperature.

$K_2[RuBr_5NO]$ was prepared by a modified method reported in reference [15] $RuCl_3$ (0.070 g, 3.372×10^{-4} mol) was dissolved in 50 mL of water with addition of KNO_2 (0.0573 g, 6.744×10^{-4} mol) and HBr (2 mL, $\delta = 1.490$ g/cm³, 48%) to give a red solution which was heated to boiling point for 15 min (65% yield).

The isotopically $^{14/15}N$-substituted anion was prepared using $Na^{15}NO_2$ in the same molar proportions as described above but adding KBr (0.281 g, 2.361×10^{-3} mol) to induce the complex crystallization.

The $Na_2[Fe(^{13}CN)_5{}^{15}NO]\cdot 2H_2O$ was obtained in semimicro scale in two steps according to literature procedures. In the first one, the $Na_4[Fe(^{13}CN)_6]$ was obtained from the reaction of $FeCl_3$ with $Na^{13}CN$ [16] In the second step, $Na_4[Fe(^{13}CN)_6]$ is reacted with $Na^{15}NO_2$ to obtain the final product [17].

The purity of the prepared compounds was controlled by infrared and ^1H, ^{19}F, ^{13}C and ^{15}N NMR spectroscopies. ^1H NMR spectra showed only the residual DOH proton signal for both compounds, demonstrating that impurities containing hydrogen are not present in significant concentration. The ^{19}F NMR spectrum of the pentafluornitrosylruthenate(II) ion shows only two signals corresponding to the compound analyzed. The NMR and infrared spectra were compared with those reported in the literature showing good agreement [14,15,18].

2.2. Instruments and methods

The ^{13}C (125.8 MHz) and ^{15}N (50.7 MHz) NMR spectra of the nitroprusside ion and the ^{19}F (564.7 MHz) and ^{15}N (60.8 MHz) NMR spectra of pentafluornitrosylruthenate(II) ion were obtained with a Bruker AMX500 and a Bruker Biospin AVIII600 spectrometer, respectively. All samples were dissolved in D_2O. Chemical shifts were measured with respect to the external standard (TMS for ^{13}C and ^1H, trifluoracetic acid for ^{19}F and nitromethane for ^{15}N).

The infrared spectra of the substances as KBr pellets were recorded in the 4000–400 cm⁻¹ range on a Bruker Equinox 55 FTIR spectrometer with 4 cm⁻¹ resolution.

2.3. Computational details

The input data for the computational calculations were performed using parameters values obtained from sodium nitroprusside dihydrate and potassium pentafluoronitrosylruthenate(II) monohydrate crystal structures. The optimization of the geometries and the vibrational analysis for both complexes were carried out with the aim to get the lowest value in the potential energy surface. The calculations were performed with the DFT tools as implemented in GAUSSIAN 09 [19], using Truhlar M06L [20] functionals and a DEF2-TZVPPD basis set [21,22] for all atoms. Nuclear magnetic resonance properties for both complexes were calculated at the B3LYP/6-311++G** level of theory. This method was suggested by Cheeseman et al. [23]. using the Gauge-Including Atomic Orbital (GIAO) method [24,25] as implemented in the Gaussian 09

package. Isotropic shielding tensors of ^{13}C, ^{15}N and ^{19}F were turned into chemical shifts substracting this amounts from the references values. The chemical shifts values obtained as references are: TMS: 182.9795 ppm; CCl_3F: 174.6841 ppm, CH_3NO_2: −160.907 ppm.

3. Results and discussions

The nitroprusside anion ($[Fe(CN)_5NO]^{2-}$) is related geometrically to $[RuF_5NO]^{2-}$ because both ions can be described as a distorted octahedral characterized by short M-N distances. The symmetry of both anions is very close to the idealized C_{4v} point group. Some selected geometric parameters, extracted from the $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ [26] and $K_2[RuF_5NO]\cdot H_2O$ [27] crystallographic structures, are compared in Table 1. The ions structures are shown in Fig. 1.

Although both ions belong to the same point group of symmetry, some small structural differences can be remarked from the analysis of Table 1.

The $[RuF_5NO]^{2-}$ ion is more symmetric (closer to an octahedral geometry) than $[Fe(CN)_5NO]^{2-}$. The N-Ru-Fax (Fax refers to axial position) angle is linear while in nitroprusside (N-Fe-Cax) it is slightly bent. The N-M-Xeq (Feq refers to equatorial position) angle is slightly larger in nitroprusside ion than in $[RuF_5NO]^{2-}$. Equatorial groups are slightly bent towards the fifth axial ligand in both ions, but the Ceq-Fe-Ceq angle (for opposite Ceq) is smaller than the equivalent FeqRuFeq ones. It is interesting to test whether the smaller structural differences between ions are evidenced in the NMR spectra.

The $[Fe(CN)_5NO]^{2-}$ ion was intensely studied by Butler and coworkers [28] using ^{13}C and ^{15}N NMR spectroscopy, including partial and total isotopic substitution.

In order to compare the splitting and coupling constants between ^{15}N and ^{19}F in $[RuF_5NO]^{2-}$ with those of ^{13}C and ^{15}N in nitroprusside ion, the ^{13}C and ^{15}N NMR spectra of natural $[Fe(CN)_5NO]^{2-}$ and ^{13}C and ^{15}NO enriched samples were measured in this work.

Fig. 2 compares the ^{13}C NMR spectra of the nitroprusside anion measured at natural abundance $[Fe(CN)_5NO]^{2-}$, with $[Fe(CN)_5{}^{15}NO]^{2-}$ (>90% ^{15}N enrichment) and with $[Fe(^{13}CN)_5{}^{15}NO]^{2-}$ (>90% ^{15}N and ^{13}C isotopically enriched samples).

As expected, the coupling constant value (J) between nitrosyl nitrogen and axial ^{13}C ($^{13}C_{ax}$-^{15}N = 13 Hz) is larger than equatorial ^{13}C ($^{13}C_{eq}$-^{15}N = 4 Hz) due to geometrical considerations (see Fig. 2B and C).

The ^{15}N NMR chemical shift singlet of $[Fe(CN)_5{}^{15}NO]^{2-}$ at −8.83 ppm (Fig. 3A) is in good agreement with the reported values (−9.9 ppm) [28]. This signal becomes a double quintet when the sample

Table 1
Selected angles and atomic distances for $[Fe(CN)_5NO]^{2-}$ and $[RuF_5NO]^{2-}$ ions taken from their crystals structures: $Na_2[Fe(CN)_5NO]\cdot H_2O^{26}$ and $K_2[RuF_5NO]\cdot H_2O^{27}$.

Angles (°)	$[Fe(CN)_5NO]^{2-}$	$[RuF_5NO]^{2-}$
N-M-Xeq[#]	95.46 (Av)	94.3
XeqMXax[#]	84.52 (Av)	85.7
XeqMXeq [(op)]	169.05 (5)	171.4
MNO	176.2 (2)	180.0
N-M-Xax	176.89 (7)	180.0
Atomic distances (Å)		
d(NO)	1.129 (2)	1.17
d(M-N)	1.660 (2)	1.696
d(M-Xax)	1.928 (2)	1.896
d(M-Xeq)	1.941 (Av)	1.954

M = Ru, Fe; X = C or F; (op): referred to opposite ligands in equatorial plane; Av: average value.

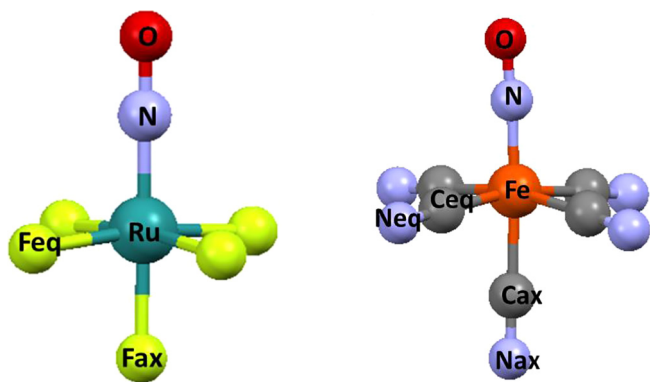[#] Xax or Xeq is referred to the axial or equatorial position relative to NO for the CN or F ligands.

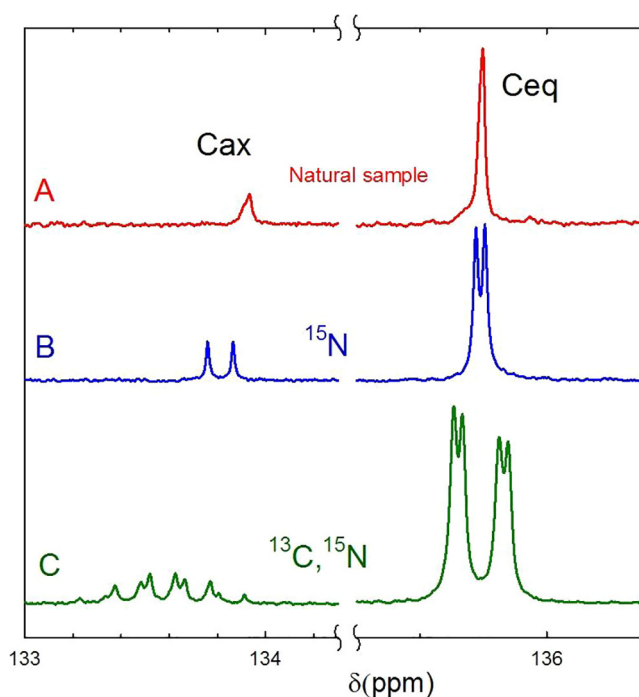**Fig. 1.** $[RuF_5NO]^{2-}$ and $[Fe(CN)_5NO]^{2-}$ C_{4v} ions geometry taken from crystal structures.

Fig. 2. ^{13}C NMR spectra of the nitroprusside anion: (A) natural sample $[Fe(CN)_5NO]^{2-}$, (B) (^{15}NO: >90%) $[Fe(CN)_5^{15}NO]^{2-}$ and (C) (^{15}NO and ^{13}C: >90%) $[Fe(^{13}CN)_5^{15}NO]^{2-}$.

Fig. 3. ^{15}N NMR spectra of nitroprusside anion: (A) $[Fe(CN)_5^{15}NO]^{2-}$ sample (^{15}N enrichment >90%) and (B) $[Fe(^{13}CN)_5^{15}NO]^{2-}$ (^{13}C and ^{15}N isotopically enrichment >90%).

is ^{13}C enriched $[Fe(^{13}CN)_5^{15}NO]^{2-}$ (Fig. 3B). The measured heteronuclear coupling constants (J_{NC}) were 13 and 3.6 Hz, for axial and equatorial carbons, respectively (see Fig. 3B).

For the title complex, some spectroscopic properties, such as the ^{19}F NMR spectrum were published before. This study includes time decomposition processes monitored by this spectroscopy [18]. Our data shows two spin systems, a quintet (integrating for one F) at −411.1 ppm, and a doublet (integrating for four F) at −140.5 ppm. Those multiplicities indicate the axial and equatorial fluorine atoms, respectively. The same signals were reported at −409.5 and −142.2 ppm [18].

To evaluate the effect of the isotopic substitution, the ^{19}F spectra of a natural sample ($[RuF_5NO]^{2-}$) and an enriched one (^{15}N > 90%) are shown in Fig. 4. As consequence of the ^{15}N substitution the axial fluorine should be split in a double quintet, but instead of this, the observed multiplicity is a sextet because of the similar coupling constant values ($J_{Fax-Feq}$ = 71 Hz; $J_{Fax-^{15}N}$ = 67 Hz). Other important feature is the lack of heteronuclear coupling for the
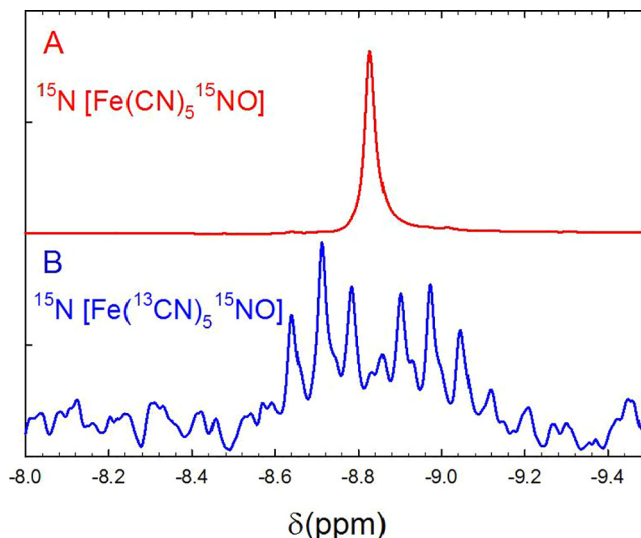
equatorial fluorine atoms after ^{15}N enrichment, suggesting that these atoms are in a geometric arrangement close to 90° and then with the smallest coupling magnitude.

The ^{15}N NMR spectra of $[RuF_5^{15}NO]^{2-}$ sample is observed as a doublet at −36.5 ppm due to the coupling with the axial fluorine (see Fig. 5). Again, the spectrum does not show the coupling with the equatorial fluorine atoms.

Due to the geometric analogy between the nitroprusside and $[RuF_5NO]^{2-}$ ions, similar NMR splitting signal are expected. The spectra of Figs. 2 and 3 (nitroprusside ion) compared with those shown in Figs. 4 and 5 ($[RuF_5NO]^{2-}$) reveals different splitting patterns and coupling constant values. In the nitroprusside ion a coupling of smaller magnitude between ^{15}N and equatorial atoms than ^{15}N Cax was detected, but the corresponding ^{15}N Feq splitting was not observed in ($[RuF_5NO]^{2-}$).

This distinctive behavior could be explained by the few geometric differences highlighted above (see Table 1).

To provide theoretical support to this interpretation, DFT calculations were carried out to evaluate the coupling constants in both complexes, starting from the crystallographic parameters and optimizing them.

Table 2 compares the experimental coupling constants for the nitroprusside and $[RuF_5^{15}NO]^{2-}$ ions with those predicted by the DFT calculations. The theoretical calculations predict for $[RuF_5^{15}NO]^{2-}$ the lowest coupling constant value (1.1 Hz) between ^{15}N and equatorial groups, a fact that is observed in experimental spectra ($J_{15N-Feq}$ not observed), while this coupling constants rise to 78.8 Hz (observed $J_{15N-Fax}$ = 67 Hz) for axial group.

^{15}N RMN spectra shows signals between 200 and −50 ppm (nitromethane as reference) for linear transition metal nitrosyls [11]. Our spectra show a doublet at −36.5 ppm, close to the values observed for similar Ru-complexes (−48 ppm for $[RuCl_5NO]^{2-}$ and −29 ppm for $[Ru(NH_3)_5NO]^{2-}$) with linear geometry [29].

Table 3 compare experimental and calculated chemical shifts (δ) of $[Fe(^{13}CN)_5^{15}NO]^{2-}$ and $[RuF_5^{15}NO]^{2-}$ ions. Calculated δ are in reasonable agreement with experimental values with exception of the values of ^{15}N NMR. As is known, the ^{15}N NMR chemical shift depends strongly on the experimental conditions of measurement. In this communication no effort was made in evaluate the effect of the change in some variables such as solvent, temperature or sample concentration.
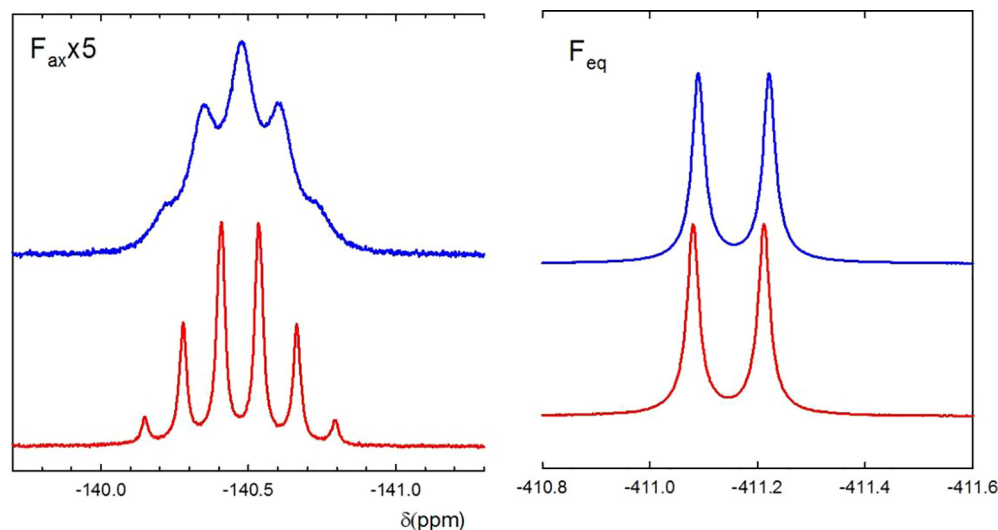
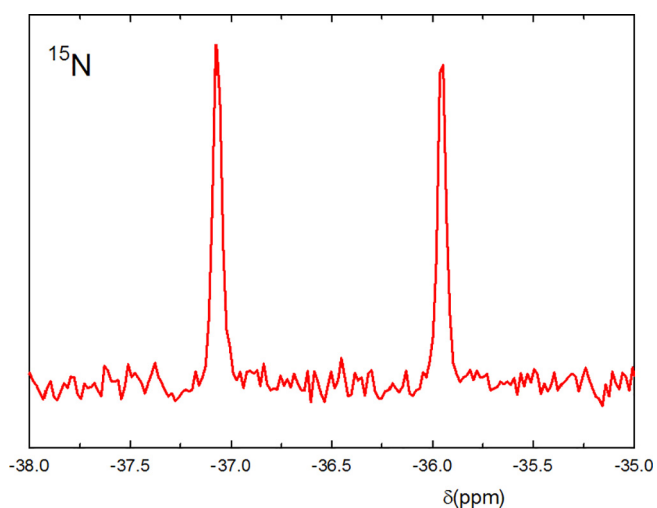**Fig. 4.** ^{19}F NMR spectra of $[RuF_5NO]^{2-}$ and $[RuF_5^{15}NO]^{2-}$.

Fig. 5. ^{15}N NMR spectra of ^{15}N (>90%) substituted $[RuF_5^{15}NO]^{2-}$.

Table 2
Experimental and theoretical coupling constant for $[Fe(^{13}CN)_5^{15}NO]^{2-}$ and $[RuF_5^{15}NO]^{2-}$ ions.

Coupling atoms	$[Fe(^{13}CN)_5^{15}NO]^{2-}$		$[RuF_5^{15}NO]^{2-}$	
	Calc	Expt	Calc	Expt
^{15}N(O)-Xax	7.6	13.1	78.8	67
^{15}N(O)-Xeq	6.4	3.6	1.1	0
Xeq-Xax	32.7	17.9	74.5	71

Table 3
Experimental and calculated chemical shifts (δ) for $[Fe(^{13}CN)_5^{15}NO]^{2-}$ and $[RuF_5^{15}NO]^{2-}$ ions.

$[Fe(^{13}CN)_5^{15}NO]^{2-}$			$[RuF_5^{15}NO]^{2-}$		
δ(ppm)	Calc	Expt	δ(ppm)	Calc	Expt
^{15}N(O)	47.6	−8.8	^{15}N(O)^1	11.1	−36.5
^{13}Ceq	149.6	135.8	^{9}Fax	−83.4	−140.5
^{13}Cax	150.5	133.9	^{19}Feq	−404.5	−411.38

4. Conclusions

The ^{15}N shift value is the main distinctive parameter to distinguish linear than angular MNO in transition metal nitrosyls by NMR spectroscopy, and in the case of the compounds under study, they belong to linear nitrosyl complexes (MNO angles close to 180°). Although the symmetry of both, the nitroprusside and pentacianenitrosylruthenate(II) ions is similar and consequently the same type of coupling between the nuclei located in axial and equatorial positions are expected, the parameters observed in the NMR spectra, however, reveals some significant differences. The differential behavior in the magnitude of the heteronuclear coupling constant value between equatorial ligands and ^{15}N nitrosyl axial group is attributed to the small geometric differences in angles and distances observed in both complexes.

Since equatorial groups are more bent towards the fifth axial ligand in $[Fe(CN)_5NO]^{2-}$ than in $[RuF_5NO]^{2-}$ and Cax-Fe-N angle is lower than the equivalent Fax-Ru-N ones, these two geometrical differences allowed a small coupling constant for the first detected by the NMR spectroscopy. This experimental result was supported by DFT calculation. However, the less distorted pentafluornitrosylruthenate(II) ion precludes the experimental observation of this coupling. These results points towards the sensitivity of the NMR spectroscopy as an analytical tool with sensitivity to detect small differences in molecular geometry of this kind of complexes. All spectroscopic results were accompanied by DFT calculations. Coupling constants obtained by theoretical calculation are in good agreement with experimental results observed for both ions, supporting these conclusions.

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