Quantitative 2D EXSY and Dynamic ^{19}F-NMR Studies of the Dynamic Behaviour of the Bidentate Chelate Complex Ga(fox)$_3$ (fox = 5-fluoro-8-hydroxyquinoline)

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The rates of intramolecular rearrangement of the *meridional* isomer of the metal *tris*-chelate complex [Ga(fox)$_3$, fox = 5-fluoro-8-hydroxyquinoline] in DMF solution were measured using 1D NMR line shape analysis and 2D EXSY spectra. The rates of exchange k_{ab}, k_{bc} and k_{ac} between the three non-equivalent ligands **a**, **b** and **c** were determined. The values of the activation parameters were obtained. ΔH^{+} was 70.6 kJ mol^{-1} for all the rate constants. ΔS^{+} was different in each of the three cases: ΔS^{+}_{ab}, ΔS^{+}_{bc} and ΔS^{+}_{ac} were 27.7, 28.5 and 34.6 J K^{-1} mol^{-1} respectively. The interpretation of these data was related to the discrimination of different twist processes (Bailar and Rây–Dutt) for intramolecular rearrangement of the *tris*-chelate complex.

Introduction

The elucidation of the mechanisms of intramolecular rearrangements of metal chelate complexes, especially those involving metal *tris*-chelate complexes, has been studied in depth but remains a problem of continuous significance in coordination chemistry.[1] *Tris*-chelate complexes with three identical unsymmetrical bidentate ligands can exist as two *facial* (*fac*) and *meridional* (*mer*) stereoisomers, each of which exists as enantiomers Δ and Λ. Changes in stereoisomers can be observed such as inversion or racemisation (Δ ⇄ Λ) and isomerisation (*fac* ⇄ *mer*). In the literature, two categories of intramolecular mechanism have been proposed, namely those involving temporary rupture of a metal-ligand bond and those that involve ligand twisting without any bond rupture. Among the different bond rupture mechanisms, Holm et al. showed that the most probable mechanism was the one with a square-pyramidal axial transition state.[2] For those processes with concerted non-bond-breaking geometrical changes, symmetry selection rules lead to the identification of four possible mechanisms named push-through, cross-over, Bailar (transition state with D_{3h} group of symmetry for symmetrical bidentate ligands) and Rây–Dutt (transition state with C_{2v} group of symmetry for symmetrical bidentate ligands).[3–7]

Several examples in the literature show that NMR spectroscopy is well adapted for kinetic measurements of such molecular rearrangements in complexes of appropriate metal cations:[1] chromium(III) complexes with the unsymmetrical bidentate (*S*)-tryptophan (^{1}H NMR),[7] ruthenium hydrides with triphenylphosphanes as other ligands (^{31}P NMR)[8] and several *tris*(unsymmetrical bidentate ligand)-metal(III) complexes of group 13 metals such as *tris*(trifluoroacetylacetonato)-Ga(III) complexes (^{19}F NMR),[9] *tris*-(substituted-tropolonato)metal(III) complexes (^{1}H NMR),[10] *tris*[2-(2'-hydroxyphenyl)-2-oxazolino]metal(III) complexes (^{1}H and ^{27}Al NMR),[11] *tris*(2-thienoyltrifluoroacetonato)metal(III) complexes (^{1}H and ^{19}F NMR),[12] *tris*(substituted-catecholato)metal(III) complexes (^{1}H NMR).[13]

Previously, we studied a new tripodal iron chelator, *O*-Trensox, based on 8-hydroxyquinoline.[14] Subsequently, we studied, as a model, the coordination chemistry of Ga(III) [the diamagnetic analogue of Fe(III)] with a fluorine-labelled sub-unit, the 5-fluoro-8-hydroxy-quinoline (fox).[15] The presence of only one fluorine atom per ligand leads to simplified ^{19}F-NMR studies. Recently, for the Ga(fox)$_3$ species, we were able to observe the minor *facial* isomer with its C_3 axis of symmetry and the more abundant *meridi-*

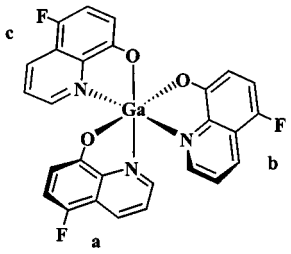

Figure 1. Structure and assignment of the sites for Ga(fox)$_3$ (fox = 5-fluoro-8-hydroxyquinoline)

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onal isomer with no elements of symmetry. In this case, the three ligands are chemically nonequivalent.[16] In addition, we were able to assign the three corresponding ^{19}F-NMR signals (using low temperature NOE experiments) as shown in Figure 1: **a** (the signal at higher frequency) assigned to the ligand perpendicular to the NGaN octahedral axis (or *antiperiplanar* to two oxygen atoms), **b** the signal at intermediate frequency, assigned to the ligand perpendicular to the OGaN axis, the first priority axis using Sloan's notation (or *antiperiplanar* to oxygen and nitrogen atoms), and **c** (the signal at lower frequency) assigned to the ligand perpendicular to the OGaO axis (second priority axis) (or *antiperiplanar* to two nitrogen atoms).[16,17]

The aim of this paper is to describe, very precisely, the stereochemical non-rigidity of the Ga(fox)$_3$ complex from the kinetic point of view and to analyse the nature of the intramolecular rearrangement mechanisms in dimethylformamide (DMF) solutions.

Results

The ^{19}F-NMR chemical shift values in ppm at low temperature (255 K, ^{1}H decoupled signals) in DMF for each fluorine of the ligands **a**, **b**, **c** in the *mer* complex were: $\delta_a = 22.80_5$, $\delta_b = 22.51_3$, $\delta_c = 21.83_8$. The corresponding chemical shift for the *fac* isomer was: $\delta = 22.28_9$.

1D Measurements versus Temperature

The line shapes of the ^{19}F Ga(fox)$_3$ signals at several temperatures are shown in Figure 2A. The exchange rates were determined by complete line shape analysis for a three-sites system (**a**, **b** and **c**). Calculated spectra are shown in Figure 2B.

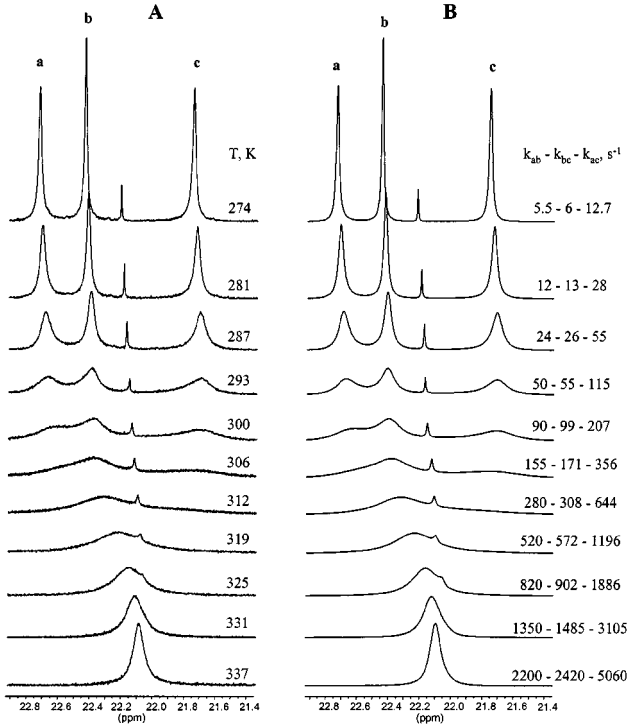


Figure 2. Variable temperature ^{19}F NMR spectra of Ga(fox)$_3$ in DMF (using ^{1}H decoupling): A – experimental, B – computer-simulated

A major problem for the refinement between experimental and calculated spectra is that the static NMR parameters were temperature dependent (chemical shifts and linewidths). Since the three populations for the different sites of exchange were equal and since all the coupling constants are suppressed, the temperature has no influence on these parameters. We also observed that the *fac* isomer intensity (5%) did not change in the explored temperature range.

(i) The temperature dependence of δ was not similar for the three signals **a**, **b** and **c**. We have recorded a set of spectra in a temperature range where the exchange effects were negligible. Assuming a linear variation of δ versus T we extrapolated the δ values at higher temperatures.

(ii) The linewidth was also an important parameter to determine in order to obtain accurate rate constants from the simulated spectra. The low temperature spectra allowed the determination of the relationship between the Ga(fox)$_3$ and C_6F_6 signals linewidth (lw). This ratio lw(*Ga(fox)$_3$*)/lw(*C_6F_6*) was approximately 1.6 in DMF. So, we evaluated the natural Ga(fox)$_3$ line from the C_6F_6 linewidth measured for each temperature, assuming that this pertinent ratio was constant for all the temperature range. We were comforted by the observation that the ratio between the width of the free ligand (fox) line and that of the C_6F_6 line was constant over the temperature range.

The exchange rates between the three ligands of the Ga(fox)$_3$ complex were determined by complete lineshape analysis for the 3-sites system through the " WIN-DYNAMICS " software (see Experimental Section). We differentiated three different exchange rates: k_{ab}, k_{bc} and k_{ac} corresponding to the **a** ⇄ **b**, **b** ⇄ **c** and **a**<->**c** ligand exchange respectively. The kinetics of exchange involving the *fac* isomer only occurred for temperatures higher than 319 K, so, its contribution in the main range was negligible. All the values are reported for the 262–350 K temperature range, along with their standard errors on the fit, in Table 1.

2D Measurements versus Temperature

2D EXSY experiments with appropriate mixing times were carried out. Figure 3 shows a contour plot of the spectra obtained in DMF at 273 K with $\tau_m = 30$ ms as a mixing time. From the volume of the cross-peaks, according to the methodology developed in the Experimental Section, we obtained a new set of reaction rates for three temperatures (249, 255 and 268 K). These values, with standard deviation higher than with 1D measurements, are also reported in Table 1. The aim of these experiments was to extend towards the low temperature range and to show clearly that the exchange rate k_{ac} was larger than the other rates, thus demonstrating the greater efficiency of the transfer of magnetization between **a** and **c**.

Table 1. Values of rate constants (s^{-1}) for exchange derived from 1D (lineshape analysis) and 2D EXSY ^{19}F-NMR spectra as a function of temperature (K)

T, K	k_{ab}, s^{-1}	k_{bc}, s^{-1}	k_{ac}, s^{-1}
249	0.17 (± 0.04)[a]	0.19 (± 0.04)[a]	0.39 (± 0.08)[a]
255	0.5 (± 0.05)[a]	0.55 (± 0.06)[a]	1.15 (± 0.1)[a]
262	1.2 (± 0.1)	1.3 (± 0.1)	2.8 (± 0.2)
268	2.5 (± 0.1)	2.75 (± 0.1)	5.75 (± 0.2)
268	2.7 (± 0.3)[a]	3 (± 0.3)[a]	6.2 (± 0.6)[a]
274	5.5 (± 0.4)	6 (± 0.4)	12.7 (± 0.8)
281	12 (± 1)	13 (± 1)	28 (± 2)
287	24 (± 1)	26 (± 1)	55 (± 2)
293	50 (± 4)	55 (± 4)	115 (± 9)
300	90 (± 4)	99 (± 4)	207 (± 8)
306	155 (± 5)	171 (± 5.6)	356 (± 11)
312	280 (± 9)	308 (± 10)	644 (± 21)
319	520 (± 14)	572 (± 16)	1196 (± 33)
325	820 (± 19)	902 (± 21)	1886 (± 45)
331	1350 (± 90)	1485 (± 104)	3105 (± 217)
337	2200 (± 170)	2420 (± 180)	5060 (± 380)
344	3600 (± 280)	3960 (± 315)	8280 (± 660)
350	7200 (± 650)	7920 (± 710)	16560 (± 150)

[a] 2D results.

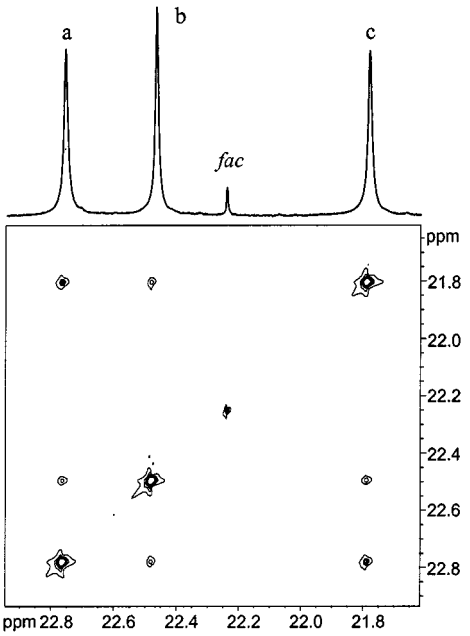


Figure 3. Contour plot of 2D EXSY ^{19}F NMR spectrum of $Ga(fox)_3$ in DMF obtained at 273 K with 30 ms as a mixing time

Rate Constants versus Temperature

For each temperature, the **a** ⇄ **b** exchange is the slowest, **b** ⇄ **c** is slightly faster and the **a** ⇄ **c** is the fastest (ratio of the rate constants k_{ab}, k_{bc} and k_{ac} were 1, 1.1 and 2.3 respectively).

The plots of $\log(kij/T)$ of these rate constants versus the reciprocal of temperature gave three straight lines (for the three lines, $r = 0.9997$) according to the Eyring formula (Figure 4):

$$\log(k/T) = \log(k_B/h) - \Delta H^{\#}/RT + \Delta S^{\#}/R$$

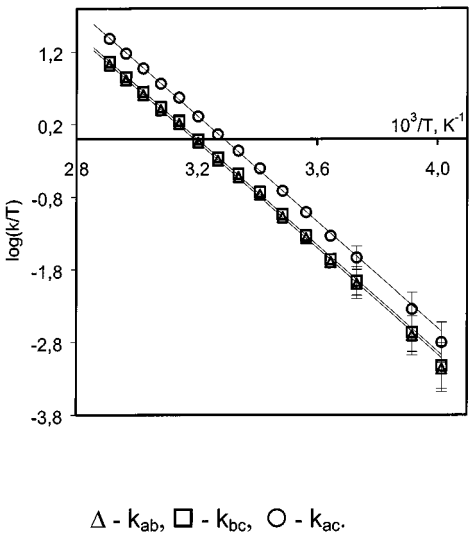


Figure 4. Eyring plot of $\log(k_{ij}/T)$ *versus* 1/T for ligand exchanges in $Ga(fox)_3$ in DMF

The activation parameters (enthalpy, entropy and free enthalpy at 293 K) are reported in Table 2.

Table 2. Activation parameters for the ligand exchanges for $Ga(fox)_3$ in DMF

Exchange	$\Delta H^{\#}$, kJ mol^{-1}	$\Delta S^{\#}$, J K^{-1} mol^{-1}	$\Delta G^{\#}$, kJ mol^{-1} (293 K)
a ⇄ b	70.6 ± 0.5	27.7 ± 2	62.3 ± 1.5
b ⇄ c	70.6 ± 0.5	28.5 ± 2	62.1 ± 1.5
a ⇄ c	70.6 ± 0.5	34.6 ± 2	60.2 ± 1.5

The slopes of the Eyring plot are, within the experimental errors, the same. The ratio ($k_{ac}/k_{ab} = 2.3$) between the fastest and the slowest rate constants can be described as an "extra" entropy effect of about 6.5 J mol^{-1} K^{-1}.

Discussion

The three main features of our kinetic results are:

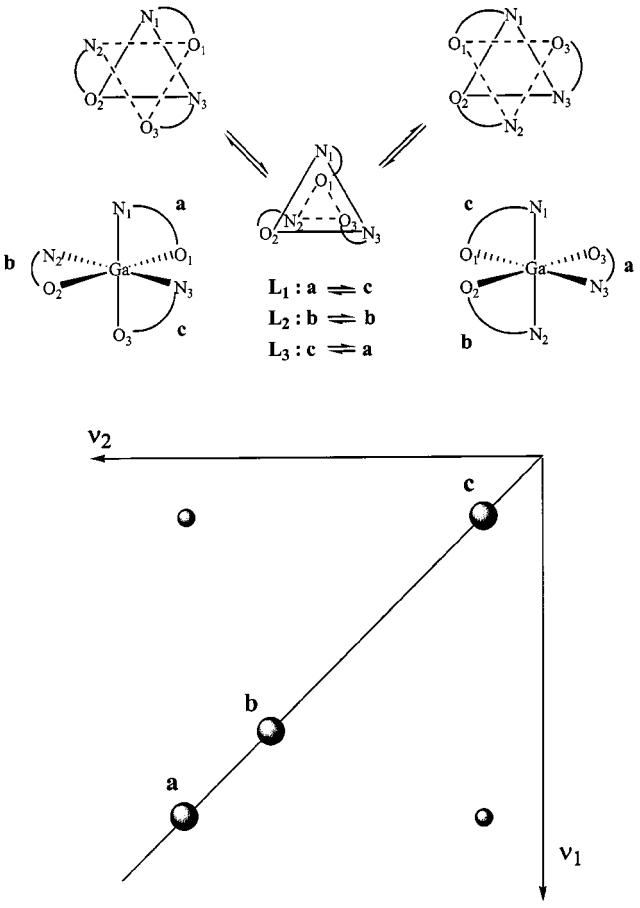
(i) For each temperature, the ratio of the exchange reaction rates between the three sites are 1:1.1:2.3 for $k_{ab}/k_{bc}/k_{ac}$ respectively. This effect is particularly clear as shown in Figure 3 where the cross-peak from the **a** and **c** signals was larger than the two others involving the ligand **b**.

(ii) The kinetics of exchange involving the *fac* isomer among the exchange between the three sites of the *meridional* isomers was negligible.

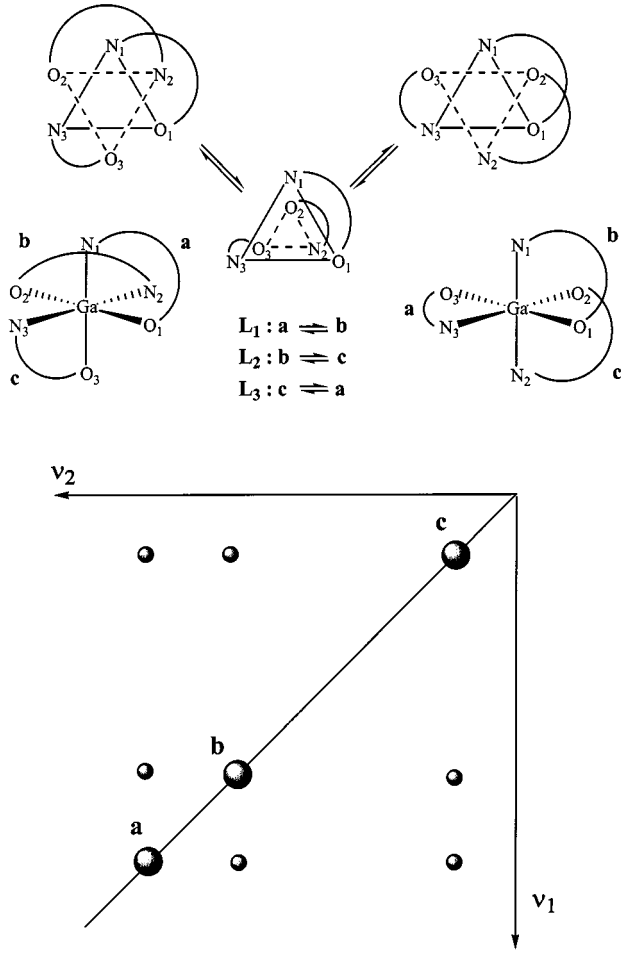
(iii) The enthalpies of activation are, within the experimental errors, the same (70.6 kJ mol^{-1}) and the value of k_{ac} in comparison of the k_{bc} and k_{ab} can be described as an "extra" entropy effect of about 6.5 J mol^{-1} K^{-1}.

The intramolecular rearrangement processes of the $Ga(fox)_3$ complex are described as an inversion without isomerisation. The inversion proceeds by two energetically favourable twist mechanisms that are easily discriminated through the structure of their transition state:[1]

(i) Bailar's transition state, which has a C_3 axis of symmetry (trigonal prismatic geometry, Scheme 1). There is only one such transition state, and



Scheme 1. Intramolecular rearrangement through a Bailar transition state and predicted cross-peak intensity in a 2D EXSY experiment



Scheme 2. Intramolecular rearrangement through a Rây–Dutt transition state and predicted cross-peak intensities in a 2D EXSY experiment

(ii) Rây–Dutt's transition state, which has no element of symmetry (the group of symmetry for the corresponding complex with a symmetrical bidentate ligand would be C_{2v} with the C_2 axis perpendicular to the ligand joining the two planes in Scheme 2). There are three such transition states depending on the nature of the ligand (1, 2 or 3) perpendicular to the plane of the drawing.

If the internal rearrangement only consisted of a Bailar-type mechanism then Scheme 1 shows that ligand 1 (with the heteroatoms N and O labelled as 1 in the starting structure), which has an environment **a** (from the electronic distribution in the neighbourhood and has a high frequency ^{19}F chemical shift named site **a**), is moving to give, in the final structure, the site **c**. From the same scheme, ligand 2 (site **b**) and ligand 3 (site **c**) move to sites **b** and **a** respectively. We can predict that the transfer of magnetization occurs only between **a** and **c** as shown in the bottom part of Scheme 1. If the internal rearrangement consisted only of a Rây–Dutt type mechanism, Scheme 2 shows that ligand 1 with the environment **a** (named site **a**) is moving to give, in the final structure, the site **b**. Similarly, from Scheme 2, sites **b** and **c** move to **c** and **a** sites respectively. We can predict that the transfer of magnetization occurs as a permutation between **a**, **b** and **c**. The same permutation occurs for the two other Rây–Dutt transition states. The prediction of the cross-peak intensities is shown in the lower part of Scheme 2. So, as we observe non-equal magnetization transfers between the three **a**, **b** and **c** signals, we suggest that two mechanisms for internal rearrangement occur: a Rây–Dutt mechanism giving equal magnetization transfers between the three signals (at the origin of the almost equal k_{ab} and k_{bc} reaction rates) and an almost equal contribution (1.3) by a Bailar mechanism, at the origin of the higher k_{ac} reaction rate value (~ 2.3 k_{ab}).

The activation parameters of the two mechanisms seem to be the same. The $\Delta H^{\neq}$ value was 70.6 kJmol^{-1}, which is of the same order of magnitude as values obtained in dipolar aprotic solvents and reported in the literature.[13] A positive moderate $\Delta S^{\neq}$ value (28.1 J K^{-1} mol^{-1}) for the two processes (Bailar and Rây–Dutt) implies more disorder in the transition states than in the initial states. The apparent increase of entropy of 6.5 J K^{-1} mol^{-1} is only due to the contribution of the two mechanisms ($2.2 = e^{6.5/8.32}$). The activation parameters for the two processes were almost the same as no predominance of one of the two mechanisms was evidenced at one of the edges of the temperature range.

This fact suggests that the bond modifications from the initial state to the transition state are almost the same around the C_3 axis for the Bailar twist or the *pseudo*-C_3 axis for the Rây–Dutt twists. The same types of interactions of the initial and transition states with the solvent are at the origin of the same activation entropy values. These facts also confirm that a bond-rupture mechanism with a pendant axial ligand did not occur, as the entropy of activation should not be the same for a mechanism with temporary rupture of a metal-ligand bond and those with twisting without any bond rupture.[4,12]

The relative importance of the Bailar mechanism can also be interpreted in relation with the metal-chelating heteroatom distances in the complex. We were unable to obtain sufficiently good crystals of $Ga(fox)_3$ for X-ray crystallography, but in the literature we have data for closely related complexes $Fe(ox)_3$ and $Ga(ox)_3$ (where ox is for 8-hydroxyquinoline or oxine).[18,19] Table 3 gives selected values of metal-oxygen, metal-nitrogen and oxygen-nitrogen bond lengths for these two complexes. We can see that the metal-nitrogen$_b$ bonds are the shortest in relation with the **b** site, which "sees" no change in the Bailar-type process. More precisely, as discussed in several papers,[4,7] the pertinent parameter for these studies is the bite size (also called the normalised bite), defined as the ratio of the distance between the donor atoms of the chelate ring divided by the metal-donor atom distance. When this value is less than 1.5, the Bailar twist is energetically preferred over a Rây–Dutt twist.[4,7] From literature data in Table 3, this bite value is included in 1.244 to 1.384 values for the gallium complex and 1.212 and 1.360 for the iron one. These values are calculated as: the higher ratio for gallium (1.384) was obtained as the ratio of the highest distance between the donor atoms (265.8 pm) divided by the smallest metal-donor atom distance (192.1 pm); the lowest ratio (1.244) was obtained as the ratio of the shortest distance between the donor atoms (263.3 pm) divided by the largest metal-donor atom distance (211.6 pm), and the same for the iron case. Arguments developed by Rodger and Johnson show that a Bailar twist was energetically preferred over a Rây–Dutt twist for bite values less than 1.5.[4] We suggest that both mechanisms are plausible because the bite values for our system are not too far from 1.5.

Table 3. Selected bond lengths (pm) for $M(ox)_3$ complexes [M = Ga(III) or Fe(III)] from the literature[18,19]

Bond	Distance (pm) for Ga[19]	Distance (pm) for Fe[18]
M–Oa	192.9	195.6
M–Ob	195.6	199.6
M–Oc	192.1	193.6
M–Na	211.6	216.6
M–Nb	206.7	212.5
M–Nc	209.1	217.2
Oa–Na	263.3	262.5
Ob–Nb	264.8	262.8
Oc–Nc	265.8	263.3

We were also able to undertake experiments on the same complex in methanol as a solvent instead of DMF. The data obtained were not as detailed, especially from evaluation of the experimental errors, as linewidths for the complex were not so easily related to those of C_6F_6 as they were in DMF. Nevertheless, we can make some comments on the data. Assignment of the fluorine signals is the same for site **c** but the reverse for sites **a** and **b**. The enthalpies of activation are almost the same ($\Delta H^{\neq} = 72.5$ kJ mol^{-1}) as in DMF, but the entropies of activation are much lower ($\Delta S^{\neq}$ about 22 J K^{-1} mol^{-1}) than for DMF as the reaction rates at the same temperatures were slower in methanol than in DMF. This smaller positive entropy value in methanol than in DMF can be related with closer interactions between the transition state and the highly ordered protic solvent methanol. More work has to be done using this solvent for more detailed analysis of the rate constants for exchange between the three sites.

Conclusion

To our knowledge, this work constitutes one of the first measurements of three different rates of exchange between the three sites **a**, **b** and **c** in this type of complex. We were able to discriminate, from the kinetic point of view, the different twist processes (Bailar and Rây–Dutt) for intramolecular rearrangement in *tris*-chelate complexes of metal cations such as Ga(III) in solution, using 1D NMR line shape analysis and 2D EXSY measurements.

Experimental Section

Preparation of $Ga(fox)_3$: To a solution of 5-fluoro-8-hydroxyquinoline (denoted fox) (0.05 g, 0.31 mmol) in methanol (10 mL) was added $Ga(NO_3).9\ H_2O$ (0.36 g, 0.088 mmol) in methanol/water (10:1), followed by slow addition of 3.3 equivalents of sodium hydroxide (1 M). The resulting mixture was stirred for 15 min and evaporated to dryness.

Apparatus: The 1D ^{19}F- and 2D phase-sensitive ^{19}F-EXSY-NMR spectra of $Ga(fox)_3$ in DMF were recorded at 376.42 MHz on a Bruker AM 400 spectrometer at various temperatures. The ^{19}F chemical shifts are expressed in ppm with respect to the C_6F_6 line used as the internal reference. The ^{19}F-NMR chemical shifts for ^1H decoupled signals at 255 K in DMF were: $\delta = 22.80_5$ (s, F_a), $\delta = 22.51_3$ (s, F_b), $\delta = 21.83_8$ (s, F_c), $\delta = 22.28_9$ (s, F_{fac}). The variable-temperature accessories were calibrated with methanol and ethylene glycol samples. The measurement was repeated three times for each point of calibration. The NMR tubes were left in the probe during at least 20 minutes in order to obtain an equilibrium and were not spinning.

1D ^{19}F-NMR Spectra: The temperature range variations were 224–368 K for DMF (with a variation of 6 K by step). The ^{19}F spectra of $Ga(fox)_3$ were acquired with ^1H decoupling in Waltz mode, using a spectral width of 11.6 kHz, 32 K memory size, 3.4 s total recycling delay and 256 scans. The series of spectra were realised at low temperatures (without chemical exchange effects) in order to study the chemical shift variations as a function of temperature. For the control of the magnetic field stability, an accurate measurement of the linewidth of the C_6F_6 signal was carried out for each temperature. We evaluated the $Ga(fox)_3$ linewidth from the measured C_6F_6

linewidth multiplied by the ratio lw($Ga(fox)_3$)/lw(C_6F_6) (approximately evaluated to be 1.6). The final spectra were obtained after Fourier transformation using "1D Win-NMR" software. The simulation of 1D NMR exchange spectra was performed using the Bruker "Win-Dynamics" software.[20] We treated the data with the model of three exchanging sites on only one non-coupled spin 1/2.

2D ^{19}F-EXSY Spectra: 2D ^{19}F-EXSY spectra were recorded in DMF at 258, 263 and 273 K using a conventional NOESY *90° – t1 – 90° – τ_m – 90° – acq* phase sensitive pulse sequence[21] with time-proportional phase incrementation (TPPI). The 90° pulse length was calibrated at low temperature. The following parameters were used: spectral width 1104 Hz, with a size of 512 × 1024 data points, 512 time incrementations, 56 scans, total recycling delay of 2.9 s. The used mixing times (τ_m) were 0.2, 0.4, 0.6, 0.8 and 1 s at 258 K; 40, 60, 80 ms at 263 K and 10, 20, 30, 40, 50 ms at 273 K. Each EXSY spectrum required approximately 20 h of accumulation. Both FID's were apodized by a shifted sine-bell window function, with a shift of 2 to minimise the truncature, and was zero filled in t_1 dimensions to build a 1024 × 1024 points matrix. The auto- and cross-peak volumes were determined using "2D Win-NMR" Bruker software after phase and baseline corrections in both dimensions. The calculations of matrix elements were performed with "Mathematica" software on a Unix computer.

Rate Constant Calculation for Treatment of 2D Data: To calculate the rate constants we used the method of Perrin, Gipe and Dwyer,[22,23] improved on several examples by Willem,[24,25] which consists of determining the matrix of exchange (**L**) from all peak volumes obtained from an experiment at a single mixing time: $\mathbf{L} = (1/\tau_m)\ln\mathbf{A} = (1/\tau_m)\mathbf{U}\ln\ \mathbf{U}^{-1}$, where the elements of the matrix **A** are defined as $A_{kj}(\tau_m) = V_{kj}(\tau_m)/x_j$ (**U** and λ are the matrices of the eigenvectors and eigenvalues of **A**). $V_{kj}(\tau_m)$ represents the integrated auto-peak (k = j) or cross-peak (k ≠ j) volume and x_j is the molar chemical equilibrium fraction of the species associated with resonance j (in our case of intramolecular exchange $x_a = x_b = x_c$). We prefer to use this method rather than the one with matrix $A_{kj}(\tau_m) = V_{kj}(\tau_m)/M_j^0$, where M_j^0 is the volume of the corresponding auto-peak for $\tau_m = 0$). The substitution of M_j^0 by x_j affects only the exchange matrix **L** diagonal part and leads to the loss of the information about the longitudinal relaxation rate (containing in L_{jj} diagonal elements calculated with M_j^0). This method, however, allows the avoidance of comparison between auto- and cross-peak volumes from different EXSY spectra with important error in the case of instrumental instabilities during the rather long times of experiments (instability accentuated by necessity of work at low temperature). The same calculations were performed with replacement of cross-peak volumes V_{kj} and V_{jk} in matrix **A** by symmetrical value $(V_{kj} + V_{jk})/2$ in order to "smooth out" experimental error.[24–26] The rate constant obtained for each temperature was averaged from the data obtained at different mixing time and given with its standard deviation.

Acknowledgments

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