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^{59}Co-NMR spectroscopy of the tetrahedral cluster $Co_4(CO)_{12}$: relaxation and exchange

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Abstract

Selective ^{59}Co-NMR inversion–recovery experiments combined with non-selective experiments on a solution of the cluster $Co_4(CO)_{12}$ at various temperatures (from 220 to 330 K) yield information about ^{59}Co relaxation data and carbonyl ligand exchange. Relaxation data characterise the motional behaviour of $Co_4(CO)_{12}$ in solution, but also provide the value of the quadrupole coupling constant of the basal cobalt nucleus ($\chi = 100$ MHz) and thus complete previous solid state NMR results. Simulations based on relaxation data confirm that the difference between the two quadrupole coupling constants accounts for the anomalous features observed in ^{13}C-NMR spectra via ^{59}Co–^{13}C scalar coupling. As far as the ligand exchange is concerned, the measurements show that all four metal centres are involved, which implies that carbonyl scrambling is complete. Experimental and simulated 2D-EXSY ^{59}Co-NMR spectra corroborate this result. Rate constants and activation parameters ($\Delta G^{\neq}$(298 K) $= 50.4 \pm 2.0$ kJ mol^{-1}; $\Delta H^{\neq} = 46.5 \pm 2.5$ kJ mol^{-1}; $\Delta S^{\neq} = -13 \pm 9$ J K^{-1} mol^{-1}) are found in the range of values reported for other tetranuclear carbonyl clusters. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Tetracobaltdodecacarbonyl; ^{59}Co-NMR; Solid state NMR; Carbonyl exchange

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1. Introduction

Among tetranuclear carbonyl clusters, $Co_4(CO)_{12}$ has provided particularly interesting challenges and controversy connected both with its structure and dynamic behaviour [1–16]. The C_{3v} structure of $Co_4(CO)_{12}$ is now agreed on in solution as in the solid state after cross checking infrared spectroscopy [6], ^{13}C-NMR [7,8,12], ^{17}O-NMR [11] and ^{59}Co-NMR [3,4,9,12] spectroscopy measurements. Fluxional behaviour was first suggested by Cotton [2] and evidenced by ^{13}C- and ^{17}O-NMR in solution [2,8,9,11,12] and by ^{13}C-NMR in the solid state [13,15,16]. Disagreements between different NMR studies are directly linked to the difficulties experienced in observing $Co_4(CO)_{12}$: effects of quadrupolar nuclei add to those of carbonyl exchange. This especially affects ^{13}C-NMR spectra [7,8,12], which have long supplied the controversy about the structure of $Co_4(CO)_{12}$. Furthermore, discrepancies exist concerning the features and interpretation of solid state ^{59}Co-NMR spectra [17,18].

We have recently shown that the cobalt nucleus provides an interesting probe to investigate tetrahedral clusters [18–24] in order to get information about their structure and dynamic behaviour in solution. We have therefore undertaken a ^{59}Co-NMR study of the cluster $Co_4(CO)_{12}$, both in solution and in the solid state. The solid state study has formed the subject of a recent publication [18]. In this paper, we report solution NMR results that aim to answer questions concerning solid state NMR and to obtain information about the dynamics and the exchange process of carbonyls in solution.

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2. Experimental

$Co_4(CO)_{12}$ was prepared by thermolysis of commercially available $Co_2(CO)_8$ in hexane.

^{59}Co-NMR inversion–recovery as well as 2D-EXSY experiments were carried out on a Bruker MSL-300 spectrometer ($B_0 = 7.1$ T) at 71.2 MHz on a saturated solution of $Co_4(CO)_{12}$ in $CDCl_3$. The temperature, ranging from 225 to 325 K, was determined by observing the proton signals of methanol placed in a sealed capillary inside the sample.

In addition to short relaxation times and exchange processes, the bandwidth provides another difficulty in observing ^{59}Co nuclei in $Co_4(CO)_{12}$. The use of a solid Bruker MAS probe with a cylindrical 7-mm-o.d. zirconia rotor was necessary to perform sufficiently short pulses, i.e. 90° pulses of 2.5 μs length. For 1D-spectra, the carrier frequency is set in the middle between the two expected resonances.

At low temperatures ($220 < T < 260$ K), only one signal is observed. The carrier frequency was set on resonance, so that the problem of bandwidth is irrelevant. At high temperatures ($265 < T < 330$ K), two signals are observed. Selective inversion–recovery experiments were performed with a soft 180° pulse of 30 μs length. The carrier frequency was alternatively set on resonance on each signal, so that even a hard 50° read-pulse of 2.5 μs length did not supply an homogeneous spectral coverage of both signals. The insufficiency of pulse bandwidth was taken into account in the NMR data processing.

2D-EXSY ^{59}Co-NMR experiments were performed at $290 < T < 315$ K with 90° pulses of 3.2 μs length and a spectral width of 250 kHz in both frequency domains. The carrier frequency was placed near the middle of the two resonance frequencies. Mixing times were chosen between 10 and 25 μs. 64 spectra were accumulated with 32 000 scans over 1024 points with a recycling time of 12 ms. Prior to Fourier transformation, a 90° shifted squared sine bell was applied in both domains. Simulations of 2D-EXSY ^{59}Co-NMR spectra were performed with a C program written by the authors, based on a formalism described elsewhere [25]. Loss of magnetisation due to imperfect 90° pulses was accounted for.

2D-COSY ^{59}Co spectra were acquired as described in a recent publication [26] with values for 90° pulse lengths, recycle delays and spectral widths being the same as for EXSY.

3. Results

At room temperature, the two cobalt environments in the C_{3v} structure of $Co_4(CO)_{12}$, denoted apical and basal (labelled ‘a’ and ‘b’ in Fig. 1), give two ^{59}Co-NMR signals at -670 and -2030 ppm, respectively. When the temperature is changed, the features of the spectra drastically change. The most representative spectra are shown in Fig. 2. The apical:basal ^{59}Co-NMR signal ratio does not take the expected 1:3 value at any temperature. Discrepancies about the relative intensities, which have already been pointed out by several groups [4,7,12,22], are partly due to the loss of magnetisation under the effect of transverse relaxation during the receiver dead time.

At $222 < T < 260$ K, the only observable resonance is assigned to apical ^{59}Co. The line is sharp and decreases slightly with raising temperature. Magnetisation recovery curves of inversion–recovery experiments show a monoexponential behaviour. The values of the fitted relaxation times are listed in Table 1. A graphic representation of $\ln(T_{1,a})$ versus $1/T$ is given in Fig. 3. Under the assumption that the temperature dependence of relaxation times follows the Arrhenius formula [27] $1/T_{1,a} = K\exp(E/RT)$, a linear least-squares fit affords an activation energy for molecular motion of 12 kJ mol^{-1}.

At $T > 264$ K, the trend is reversed and the line progressively broadens. At the same time, the line corresponding to basal ^{59}Co becomes observable, still very broad, but narrowing with raising temperature up to 320 K. ^{59}Co magnetisation recovery curves obtained from selective or non-selective inversion–recovery ex-

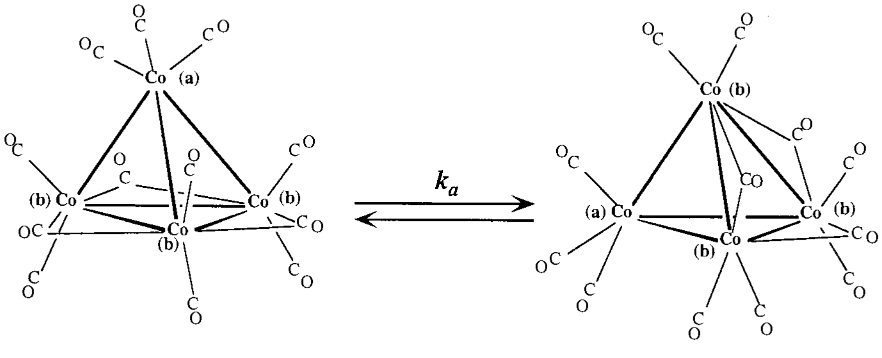

Fig. 1. Exchange process between apical (a) and basal (b) cobalt atoms in $Co_4(CO)_{12}$.

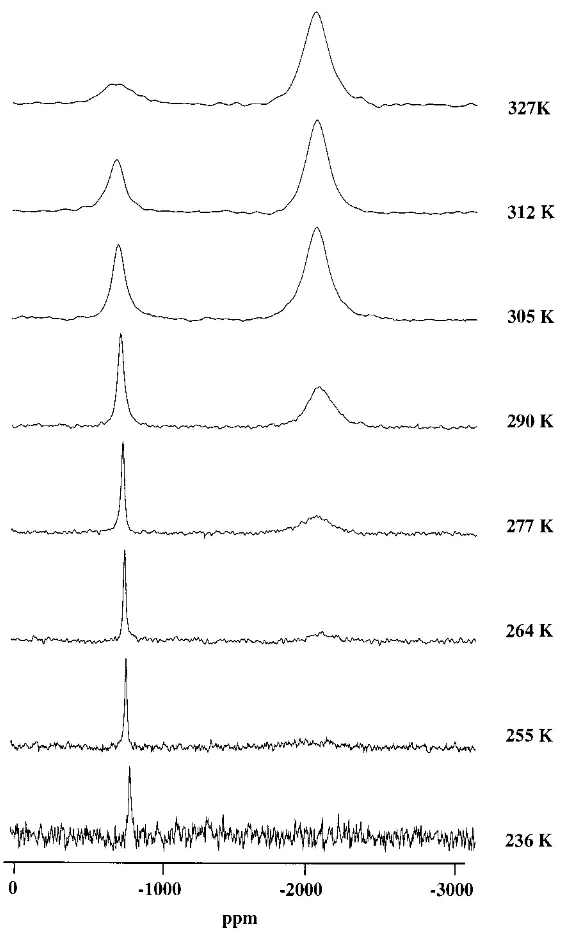

Fig. 2. Variable-temperature ^{59}Co spectra of $Co_4(CO)_{12}$ in $CDCl_3$ at 71.21 MHz.

Table 1
^{59}Co relaxation times and rate constants k_a in $Co_4(CO)_{12}$ [a]

Temperature (K)	$T_1(^{59}Co)$ (μs)		k_a (s^{-1})
	Apical	Basal	
222.0	272		
231.5	375		
238.5	455		
244.0	495		
247.5	497		
253.5	655		
291.0	1300*	21.8	6150
297.0	1450*	25.9	9300
302.0	1560*	26.8	11 500
307.0	1670*	28.1	15 600
312.0	1820*	28.6	25 600
317.0	1960*	30.3	27 400
320.0	2040*	35.0	39 500

[a] Values for Co(apical) denoted with (*) are extrapolated from low temperature measurements.

periments are not monoexponential. At $T > 320$ K, the basal line broadens again. The evolution of linewidths is easily explained by the effect of an increasing contribution of chemical exchange. The contrasting temperature dependence of apical and basal ^{59}Co signals also indicates that their relaxation times are significantly different.

Carbonyl scrambling in $Co_4(CO)_{12}$ may involve exchange of carbonyl ligands bound to basal cobalt between themselves as well as exchange with those bound to apical cobalt. However, only the last process induces a two-site exchange between apical and basal ^{59}Co nuclei, characterised by exchange rate constants k_a and k_b (Fig. 1). The longitudinal components of apical and basal magnetisations, Ia_Z and Ib_Z, are given as a function of time τ following the 180° pulse by the relationships [28] below:

$$Ia_Z(\tau) = Ia_0 + a_1 \exp(\lambda_+ \tau) + a_2 \exp(\lambda_- \tau)$$

$$Ib_Z(\tau) = Ib_0 + b_1 \exp(\lambda_+ \tau) + b_2 \exp(\lambda_- \tau) \quad (1)$$

with

$$\lambda_\pm = \frac{1}{2}\Big(-(\rho_a + k_a + \rho_b + k_b) \pm \sqrt{(\rho_a + k_a - \rho_b + k_b)^2 + 4k_a k_b}\Big)$$

$$a_{1,2} = \pm \frac{1}{\lambda_+ - \lambda_-}\big((1-\alpha_a)(\rho_a + k_a + \lambda_\mp) Ia_0 - (1-\alpha_b) k_b Ib_0\big) \quad (2)$$

$$b_{1,2} = \frac{a_{1,2}}{k_b}(\rho_a + k_a + \lambda_\pm)$$

Ia_0 and Ib_0 are the magnetisation equilibrium values. The relaxation rates, ρ_a and ρ_b, and parameters describing initial conditions, α_a and α_b, have been introduced as $\rho_i = T_{1,i}^{-1}$ and $Ii_Z(0) = \alpha_i Ii_0$, with i = a,b. An iterative non-linear least-squares fitting of the experimental recovery curves, using the Powell method [29] from the Numerical Recipes package [30], has been developed to analyse the NMR data at $290 < T < 330$ K. Computations were performed on a Silicon Graphics Computer with a C program written by the authors,

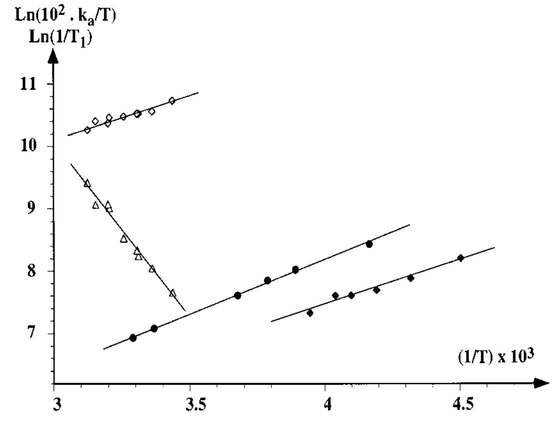

Fig. 3. Exchange rate constants k_a (△) and ^{59}Co relaxation times vs. temperature: T_1 (●) in $HFeCo_3(CO)_{12}$, $T_{1,a}$ (◆) for apical cobalt and $T_{1,b}$ (◇) for basal cobalt in $Co_4(CO)_{12}$.

based on the above analytical expressions. In the fitting process following points have been considered.

Since the magnetisation equilibrium values of the cobalt nuclei are connected by $Ib_0 = 3Ia_0$, the exchange rate constants are linked by $k_b = k_a/3$. Moreover, the contribution of $T_{1,a}$ is negligible at $T > 290$ K: the values of $T_{1,a}$ are extrapolated from the values obtained for $222 < T < 260$ K and held constant in the fitting process. Both experiments corresponding to selective inversion of each cobalt are considered simultaneously, after normalisation of the experimental recovery curves. The 1:3 ratio of equilibrium magnetisations has to be introduced artificially, so as to compensate the insufficiency of the read pulse bandwidth, which especially affects the non-inverted signal. α_a, α_b and the magnetisation equilibrium values, either Ia_0 or Ib_0, are specific to each experiment. The relevant dynamic parameters, k_a and ρ_b, are common to both experiments.

The $T_{1,b}$ and k_a values provided by the fit are listed in Table 1 with the extrapolated $T_{1,a}$ values. Ln($T_{1,b}$) versus $1/T$ and the corresponding Arrhenius fit are shown in Fig. 3. The activation energy for molecular motion is set to 12 kJ mol^{-1} provided by the relaxation of apical ^{59}Co. Fig. 3 also shows a graph of $\ln(k_b/T)$ versus $1/T$ along with the theoretical curve fitted according to Eyring equation $k_a = KT\exp(-\Delta G^{\neq}/RT)$. A linear least-squares fit affords the following activation parameters of the exchange process: $\Delta G^{\neq}$(298 K) = 50.4 ± 2.0 kJ mol^{-1}; $\Delta H^{\neq}$ = 46.5 ± 2.5 kJ mol^{-1}; $\Delta S^{\neq}$ = −13 ± 9 J K^{-1} mol^{-1}.

4. Discussion

4.1. Motional behaviour in solution

In a recent work [24] we have reported the use of ^{59}Co-NMR spectroscopy to get information about the dynamics and the molecular shape of tetrahedral clusters of formula A[MCo$_3$(CO)$_{12}$] (A = H, NEt$_4$; M = Fe, Ru) in solution. In that study, we have shown that the cobalt relaxation is dominated by the quadrupolar mechanism and that the conditions of extreme narrowing are fulfilled. We have also shown that the related tetrahedral clusters behave as rigid spherical rotors and that, as a result, their motion can be described by a single correlation time τ_C. Eq. (3) [31] gives the expression of quadrupolar relaxation times for a spin-7/2 under these conditions:

$$\frac{1}{T_{1Q}} = \frac{1}{T_{2Q}} = \frac{2\pi^2}{49} C_Q \tau_C \tag{3}$$

C_Q is a quadrupole parameter defined as $C_Q = \chi^2(1 + \eta_Q^2/3)$, $\chi = e^2qQ/h$ being the quadrupole coupling constant and $0 \leq \eta_Q \leq 1$ the asymmetry parameter of the quadrupolar tensor. This procedure has necessitated the combined use of relaxation data provided by solution NMR [24] and quadrupole parameters provided by solid state NMR [21] and has yielded conclusive results. As Co$_4$(CO)$_{12}$ has an activation energy for motional behaviour comparable with those of A[MCo$_3$(CO)$_{12}$] (see Fig. 3 for HFeCo$_3$(CO)$_{12}$), it is valid to apply the described procedure in the case M = Co.

Solid state ^{59}Co-NMR studies performed on Co$_4$(CO)$_{12}$ led to different results [17,18]. Eguchi et al. [17] observed two resonances with comparable widths (30 kHz). They reported following quadrupole parameters determined from nutation experiments: $\chi = 15 \pm 3$ MHz, $\eta_Q = 0.8$ for apical ^{59}Co and $\chi = 9 \pm 2$ MHz, $\eta_Q = 0$ for basal ^{59}Co. We observed two signals of very different widths (50 and 350 kHz) [18]. A method based on two-pulse Hahn-echo experiments yielded $\chi = 12.4 \pm 2$ MHz and $\eta_Q = 0.32$ for apical ^{59}Co. No quadrupole parameter could be determined for the broad signal assigned to basal ^{59}Co. The quadrupole coupling constants for apical ^{59}Co determined by both groups ($\chi = 15$ [17] and 12.4 MHz [18]) are compatible. Using Eq. (3) it is thus possible to get an estimation of τ_C in CDCl$_3$ at 298 K. With T_1(apical) = 1460 μs, extrapolated from the Arrhenius law, and the above solid state result $\chi = 12.4$ MHz [18] for apical ^{59}Co, $\tau_C = 11 \pm 4$ ps. This value is coherent with the values found for the series of tetrahedral clusters [24] for which $20 < \tau_C < 30$ ps in either CHCl$_3$ or CH$_2$Cl$_2$, noting that at 298 K both solvents have comparable viscosities [32].

4.2. Quadrupole parameters and solid state NMR

Solid state NMR results diverge as basal ^{59}Co is concerned [17,18]. Solution NMR results allow to reach the quadrupole parameters of the basal ^{59}Co. As τ_C characterises the motion of the cluster, τ_C is the same for apical and basal ^{59}Co, leading to following relationship deduced from Eq. (3):

$$C_Q(\text{basal}) = C_Q(\text{apical})\sqrt{T_1(\text{apical})/T_1(\text{basal})} \tag{4}$$

At $T = 298$ K, $\chi = 100 \pm 20$ MHz if $\eta_Q = 0$. The assumption that η_Q is negligible is based on solid state NMR results [18,24], which yielded $\eta_Q < 0.5$ for A[MCo$_3$(CO)$_{12}$]. In fact η_Q induces a maximum relative error on χ of 15%. χ(basal) is one order of magnitude greater than χ(apical), contrary to what was asserted by Heaton et al. [16]. As an indication, χ values of the same order of magnitude measured by NQR have been reported for carbonyl cobalt compounds: Co$_2$(CO)$_8$ ($\chi = 90$ MHz) [33] and RCCo$_3$(CO)$_9$ ($67 < \chi < 83$ MHz) [34]. Solid state ^{59}Co-NMR simulations at 71.2 MHz predict a linewidth of the order of 1 MHz with similarly large coupling constant values. Such a signal would be undetectable. The assignments [17,18] of basal ^{59}Co are therefore questionable. As the signal ratio of the broad

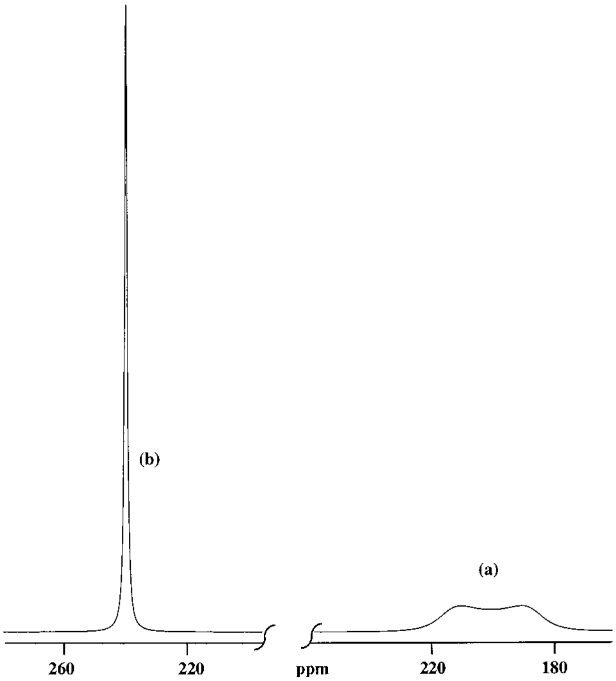

Fig. 4. Predicted NMR signals at 233 K and 100 MHz of apical (a) and basal (b) cobalt-bound ^{13}C nuclei. The plot corresponds to theoretical spectra for a spin-1/2 J-coupled to a spin-7/2 nucleus with $J = 300$ Hz, $T_1 = 360$ μs (a) and $T_1 = 8$ μs (b).

and sharp signals we observed is greater than 3:1 [18], the broad signal may correspond to satellite transitions [31] of apical ^{59}Co. As for the signal interpreted as basal ^{59}Co by Eguchi et al. [17], it may also be assigned to apical ^{59}Co, which is supported by the reported quadrupole coupling constant value. The difference in the magnitude of relaxation times, which led to these conclusions, is also supported by the ^{13}C-NMR spectra behaviour.

4.3. Influence of the quadrupolar cobalt nucleus on ^{13}C-NMR relaxation

The C_{3v} structure of $Co_4(CO)_{12}$ implies four carbonyl environments (one apical, two types of basal terminal and one basal bridging). However, ^{13}C-NMR spectra obtained by several groups [7–9,12] at $T < 243$ K in the absence of carbonyl exchange present only three resonances of the same intensities. This result was initially interpreted as supporting a D_{2d} structure [7,8]. Reinvestigation of the solution structure by Aime et al. [12] has shown that the missing line, assigned to apical carbonyl, is very broad. He suggested that ^{13}C–^{59}Co J coupling is responsible for the missing line and that scalar relaxation of the second kind governs ^{13}C relaxation. ^{13}C-NMR lineshape simulations at 233 K were carried out with the Quad_CSA program [35], using ^{59}Co relaxation times extrapolated from the results above: $T_{1,a} = 380$ μs and $T_{1,b} = 9$ μs. $J = 300$ Hz ($J =$ 287 Hz is reported for tetracarbonyl cobaltate [3] $[Co(CO)_4]^-$) was taken as an order of magnitude estimate for both apical and basal sites. Other values of J^{13}C–^{59}Co [36,37] are reported in the range 60–300 Hz. A sharp line is obtained for a ^{13}C nucleus bound to a basal ^{59}Co nucleus, whereas a broad saddle-like line is obtained for a ^{13}C nucleus bound to an apical ^{59}Co nucleus (Fig. 4). This is in agreement with experimental spectra at 233 K [7–9,12] and indicates that basal ^{13}C nuclei are thermally decoupled from basal ^{59}Co nuclei whereas ^{13}C nuclei are near the decoupling limit if bound to an apical ^{59}Co nucleus. These results confirm that ^{13}C-NMR spectra are normal and that the difference in lineshapes at low temperatures essentially arises from the difference in ^{59}Co relaxation times (at 233 K, $T_{1,a} = 42 * T_{1,b}$).

4.4. Carbonyl scrambling

Several studies performed on homo- and heterometallic carbonyl clusters as well as on their derivatives with one or several carbonyl ligands established that carbonyl exchange is an ubiquitous phenomenon in those compounds [38–45]. Variable-temperature ^{13}C-NMR spectra and 2D-exchange ^{13}C-NMR spectra of ^{13}C-enriched samples were usually performed to obtain information about rate constants, activation parameters and mechanisms [38–45]. The difficulties encountered in observing the ^{13}C-NMR signal of $Co_4(CO)_{12}$ prevented a thorough study of carbonyl scrambling, although exchange involving all four carbonyl types was evidenced [8,9,11,12].

To our knowledge carbonyl exchange processes have never been studied by NMR of quadrupolar nuclei before, i.e. ^{59}Co-NMR inversion–recovery in the case of $Co_4(CO)_{12}$. Variable-temperature ^{59}Co-NMR spectra (Fig. 2) clearly indicate exchange between basal and apical cobalt atoms. This result is also confirmed by 2D-EXSY ^{59}Co-NMR experiments. Contour plots of experimental and simulated 2D-EXSY ^{59}Co-NMR spectra at 307 K are shown in Fig. 5. The values of relaxation times and rate constants used in the simulation were extrapolated from Table 1. The agreement between experimental and calculated spectra confirms the reliability of the inversion–recovery method. As ^{59}Co COSY experiments do not show any cross peak for $Co_4(CO)_{12}$, contrary to $HFeCo_3(CO)_{11}PPh_2H$ [26], it can be asserted that the cross peaks of 2D-EXSY ^{59}Co-NMR spectra do not arise from scalar coupling between apical and basal cobalt.

Apical and basal cobalt exchange implies that carbonyl scrambling is complete and corresponds to exchange of basal and apical faces as previously suggested by Cotton. Such an exchange was observed in other tetranuclear carbonyl clusters with values of rate constants and activation parameters in the range of values

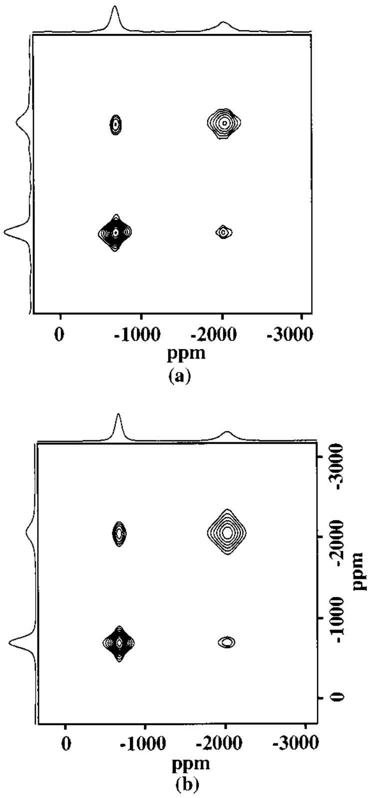

Fig. 5. Experimental (a) and calculated (b) 2D-EXSY ^{59}Co-NMR spectra of $Co_4(CO)_{12}$ in $CDCl_3$ at 307 K with a mixing time of 20 μs.

found for $Co_4(CO)_{12}$ (at 298 K, $\Delta G^{\neq} = 42.8 \pm 0.4$ kJ mol^{-1} for $Rh_4(CO)_{12}$ [45], 57.9 ± 0.6 for $IrRh_3(CO)_{12}$ [45], 51.2 ± 0.4 for $Ir_2Rh_2(CO)_{12}$) [41].

However, ^{59}Co-NMR spectroscopy is unsuitable for the distinction between the detailed mechanisms established for clusters: the so-called merry-go-round proposed by Cotton [2], which involves concerted bridge opening and closing of the carbonyl ligands, or Johnson and Benfield's theory of initial icosahedral arrangement of ligands rearranging via a cubo-octahedral transition state [10]. In the same way, the existence of a process involving three metal centres belonging to the basal face [38,41,42,45] cannot be excluded on the basis of our results, since the probed nucleus is unaffected by this process. Complementary ^{13}C- and ^{17}O-NMR experiments would answer these questions.

5. Conclusions

In this paper we have shown that the cobalt nucleus provides an interesting probe for the study of the tetrahedral cluster $Co_4(CO)_{12}$. Measurements of relaxation times and rate constants have been performed at various temperatures using selective and non-selective inversion–recovery experiments. Given previous controversy in this area, an analysis of the experimental conditions and modelling procedures is presented to obtain information about the dynamics and the exchange process of carbonyls. Relaxation data answer questions concerning the NMR solid state and resolve previous interpretations of the ^{59}Co spectrum of $Co_4(CO)_{12}$. Also, on the basis of relaxation data, simulations clearly confirm that the ^{13}C-NMR spectra are perfectly normal and that the anomalous features of the latter are ascribed to the effects of the quadrupolar ^{59}Co nuclei, i.e. the difference of relaxation times and therefore of quadrupole parameters.

As far as the exchange is concerned, the measurements show that this exchange process involves four metal centres, which implies that carbonyl scrambling is complete. This result, confirmed by experimental and calculated 2D-EXSY ^{59}Co-NMR spectra, agrees with the suggestion made by Cotton [2] and observations reported by Aime et al. [11]. The values of the rate constants and activation energy are reported.

In conclusion, we believe that NMR spectroscopy is useful to observe and study cobalt clusters. However, great care must be taken before any claim is made. The case of $Co_4(CO)_{12}$ is not an exception: similar difficulties are encountered in preliminary investigations performed on derivatives of $Co_4(CO)_{12}$.

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