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The DQF-COSY NMR Experiment, a Way to Detect Small J Couplings in the Case of Fast Relaxing Nuclei: Application to ^{59}Co in the Tetrahedral Mixed-Metal Cluster HRuCo$_3$(CO)$_{11}$(PPh$_3$)

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Abstract

The first investigation and analysis of ^{59}Co 2D NMR homonuclear chemical shift correlation spectra for a ruthenium-based tetrahedral mixed-metal cluster HRuCo$_3$(CO)$_{11}$(PPh$_3$) are reported. For this cluster in solution and by contrast to the conventional COSY NMR experiment, the double-quantum filtered (DQF) COSY NMR spectrum proves the existence of a scalar coupling constant between ^{59}Co nuclei. In order to obtain a value of this coupling, the 2D COSY spectrum for a three-spin 7/2 AX$_2$ system has been simulated by numerical density matrix calculations. The comparison between experimental and theoretical 2D NMR COSY spectra gives a spin-coupling constant $\left| {}^{1}J\left({}^{59}Co\text{-}{}^{59}Co \right) \right| < 300$ Hz for this cluster.

Keywords

NMR, Cobalt-59, 2D COSY and DQF-COSY, Scalar Couplings, Tetrahedral Mixed-Metal Cluster

Subject Areas: Computational Chemistry, Inorganic Chemistry

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1. Introduction

The conventional COSY NMR experiment [1] is an efficient and powerful technique to prove qualitatively the existence of a coupling constant between quadrupolar nuclei. However, most of the investigations performed so far concern nuclei with small quadrupole moments such as ^{11}B [2]-[10], ^{51}V [11], ^{2}H [12], ^{6}Li [13]-[16] and ^{7}Li [14]-[16], whose lines are relatively narrow (10 - 150 Hz) in the conventional 1D spectrum. The DQF-COSY NMR experiment has only been scarcely used in the field of quadrupolar nuclei, and only when the lines were broad in the 1D spectrum [17]-[19]. Recently, we have shown theoretically the superiority of the DQF-COSY NMR experiment when trying to detect and determine relatively small J couplings in the case of fast relaxing nuclei and broad peaks in the quadrupolar nucleus 1D NMR spectrum [20]-[24]. Ideal candidates for such NMR spectroscopic investigations are available in the realm of metal cluster chemistry [25]-[27], as previously shown for HFeCo$_3$(CO)L with L = PPh$_2$H [17], PPh$_3$, P(OMe)$_3$, PCy$_3$ [18] and HFeCo$_3$(CO)$_{10}$(PCyH$_2$)(PPh$_2$)[CH$_2$C(O)Ph] [19].

Tetrahedral mixed-metal clusters containing ruthenium have been shown to have different chemical shifts and line widths in the ^{59}Co 1D NMR spectrum than their iron-based counterparts [28]. The effect of a change in the apical metal (Fe or Ru) on the ^{59}Co chemical shifts has been studied in detail on a large number of these clusters [28]. A study of the line widths has clearly shown that the apical atom plays an important role in the electron distribution at the cobalt atom [28]. This is the case for HRuCo$_3$(CO)$_{11}$(PPh$_3$) (**Figure 1**) in CDCl$_3$ which is the subject of this paper. Since we have demonstrated experimentally the feasibility of using the DQF-COSY experiment to detect and determine relatively small J$_{Co-Co}$ couplings in an iron-based tetrahedral mixed-metal cluster giving rise to broad lines in the ^{59}Co 1D NMR spectrum (2.5 - 4.5 kHz) [19], it was of interest to test the method on a ruthenium-based tetrahedral mixed-metal cluster such as HRuCo$_3$(CO)$_{11}$(PPh$_3$), because the lines in the ^{59}Co 1D NMR spectrum are even broader than those for the iron-based analog [28] [29]. Indeed, the line-widths for the iron-based cluster in CD$_2$Cl$_2$ are 1500 Hz and 1600 Hz while the linewidths for the ruthenium-based cluster in CDCl$_3$ are 5100 Hz and 2900 Hz, keeping in mind that CD$_2$Cl$_2$ and CDCl$_3$ have comparable viscosities. Furthermore, it was felt interesting to determine the J$_{Co-Co}$ scalar coupling constant and compare its value with those found previously for iron-based tetrahedral mixed-metal clusters. The J$_{Co-Co}$ coupling reported here is the first one for a ruthenium-based tetrahedral mixed-metal cluster.

2. Theory

For the conventional COSY experiment, the complex signal may be written as [20]

$$s^+\left(t_1,t_2\right) = C_1 \sum_{\substack{r,s \\ t>u}}^{N} \sum_{t,u}^{N} Z_{r,s,t,u} \exp\left(i\Omega_{u,t}t_1\right)\exp\left(i\Omega_{s,r}t_2\right) \times \exp\left(-t_1/T_{2(t,u)}\right)\exp\left(-t_2/T_{2(r,s)}\right) \tag{1}$$

where C_1 is a constant of proportionality. This last equation is valid for an AX system of any spin S. It is also valid for an AMX system of spins $S = 7/2$. Relaxation was introduced through relaxation of transitions (t, u) and (r, s) during evolution and detection periods, respectively. In this last equation, N is the number of the quantum states of the spin system. The complex intensity $Z_{r,s,t,u}$ is defined by [20]

$$Z_{r,s,t,u} = S_{s,r}^+ R_{90x(r,t)}^{-1} R_{90x(u,s)} \sigma_{t,u}^{(x)}\left(t_1=0\right) = S_{s,r}^+ R_{90y(r,t)}^{-1} R_{90y(u,s)} \sigma_{t,u}^{(x)}\left(t_1=0\right) \tag{2}$$
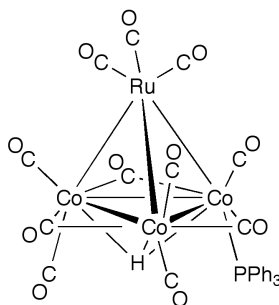

Figure 1. Schematic of the HRuCo$_3$(CO)$_{11}$(PPh$_3$) cluster.

The density matrix element $\sigma_{t,u}^{(x)}(t_1 = 0)$ represents the initial amplitude and phase of a coherence component associated with a transition $t \leftrightarrow u$ at the beginning of the evolution period. The selection rules of observation are represented by the raising operator $S_{s,r}^{+} = S_{x(s,r)} + iS_{y(s,r)}$, where S_x and S_y are the x and y components of the total angular momentum spin operator. The coherence transfer amplitude which describes the transfer of coherence from transition between two states |t> and |u> to a transition between two states |r> and |s> is equal to the product of two rotation matrix elements. The peak intensities are determined by the amplitude of coherence transfer, taking into account the limitations imposed by coherence transfer selection rules.

For the DQF-COSY NMR experiment, the complex signal may be written as a function of the same complex coefficients $Z_{r,s,t,u}$ needed to calculate the 2D COSY NMR spectrum of the same spin system [21] [22]

$$s^{+}(t_1,t_2) = C_2 \sum_{r,s}^{N} \sum_{\substack{t,u \\ t>u}}^{N} Z_{r,s,t,u} \left[\exp(-i\Omega_{u,t}t_1)\exp(-2i\Phi_{r,s,t,u}) - \exp(-i\Omega_{N+1-r,N+1-s}t_1) \right] \times$$

$$\exp(i\Omega_{s,r}t_2)\exp(-t_1/T_{2(t,u)})\exp(-t_2/T_{2(r,s)})$$

(3)

with the symbols having the same meaning as before and C_2 being a constant of proportionality.

For an AMX system of spin-7/2, there are (512) complex intensities $Z_{r,s,t,u}$ and these factors were calculated numerically with a program written in Fortran 77. The knowledge of the complex intensities allowed us to expand Equations (1) and (3) and two other programs written in C use the expressions we have obtained to compute the free induction decays for incremented values of t_1 for the conventional COSY and the DQF-COSY NMR experiments, respectively.

3. Theoretical Simulations

Figure 2 and **Figure 3** illustrate the effect of the J coupling constant on the intensities of the peaks, using, in the calculations of $s^{+}(t_1,t_2)$ a set of values corresponding to those found experimentally on our tetrahedral cluster. **Figures 2(a)-(e)** (COSY) and **Figures 3(a)-(e)** (DQF-COSY) were generated for $\omega_A = 11475$ Hz, $\omega_X = -8820$ Hz, $T_{2A} = T_{2X} = 100$ μs and $J = 20, 40, 60, 80$ and 100 Hz, respectively. Data were apodized in both dimensions and the data matrix $S(\omega_1,\omega_2)$ obtained after 2D Fourier transformation of $s^{+}(t_1,t_2)$ in both domains is drawn in the power mode as a contour plot. As expected, these 2D spectra are symmetrical about the diagonal, *i.e.* $S(\omega_1,\omega_2) = S(\omega_2,\omega_1)$ and independent of the sign of the coupling constant J.

These simulations show that if small scalar coupling is present between the two nuclei A and X and if the relaxation times T_{2A} and T_{2X} are short, it is not possible to detect the coupling with the conventional COSY NMR experiment because the information we are looking for is obscured in the theoretical spectrum by the overlap of the intense diagonal peaks with the very small cross peaks. On the other hand, and as previously mentioned [24], it is possible in the same situation to detect the J coupling between nuclei A and X with a 2D DQF-COSY NMR experiment, as observed in **Figures 3(a)-(f)**.

4. Experimental

The cluster $HRuCo_3(CO)_{11}(PPh_3)$ (**Figure 1**), synthesized according to the published procedure [30], was dissolved in $CDCl_3$. ^{59}Co NMR spectra were measured on a Bruker Avance II 600 spectrometer operating at 142.01 MHz. All spectra were run at room temperature. Chemical shifts are reported downfield from the external reference $Co(acac)_3$ saturated in $CDCl_3$. Experiments were performed with a $\pi/2$ pulse length of 20 μs. All experiments were performed with an $^{1}H(BB)$ 5 mm "inverse" probe-head using the standard Bruker software. Typical parameters were as follows: $SW1 = SW2 = 62.5$ kHz, acquisition time 2.0980 ms, data points 256 (F_2), 128 (F_1) (COSY)/32 (F_1) (DQF-COSY), recycle delay 40 ms (COSY)/10ms (DQF-COSY), number of scans 2048 (COSY)/16384 (DQF-COSY), exponential window function with a line broadening of 2000 Hz and power spectra in both dimensions.

T_1 relaxation times measurements have been performed on the cluster but due to the very long $\pi/2$ pulse length and also to the fact that the T_1 relaxation times are around 100 μs, it was not possible to determine these relaxation times accurately.

5. Results and Discussion

The ^{59}Co NMR spectrum of the cluster $HRuCo_3(CO)_{11}(PPh_3)$ consists of two resonances having intensities in the
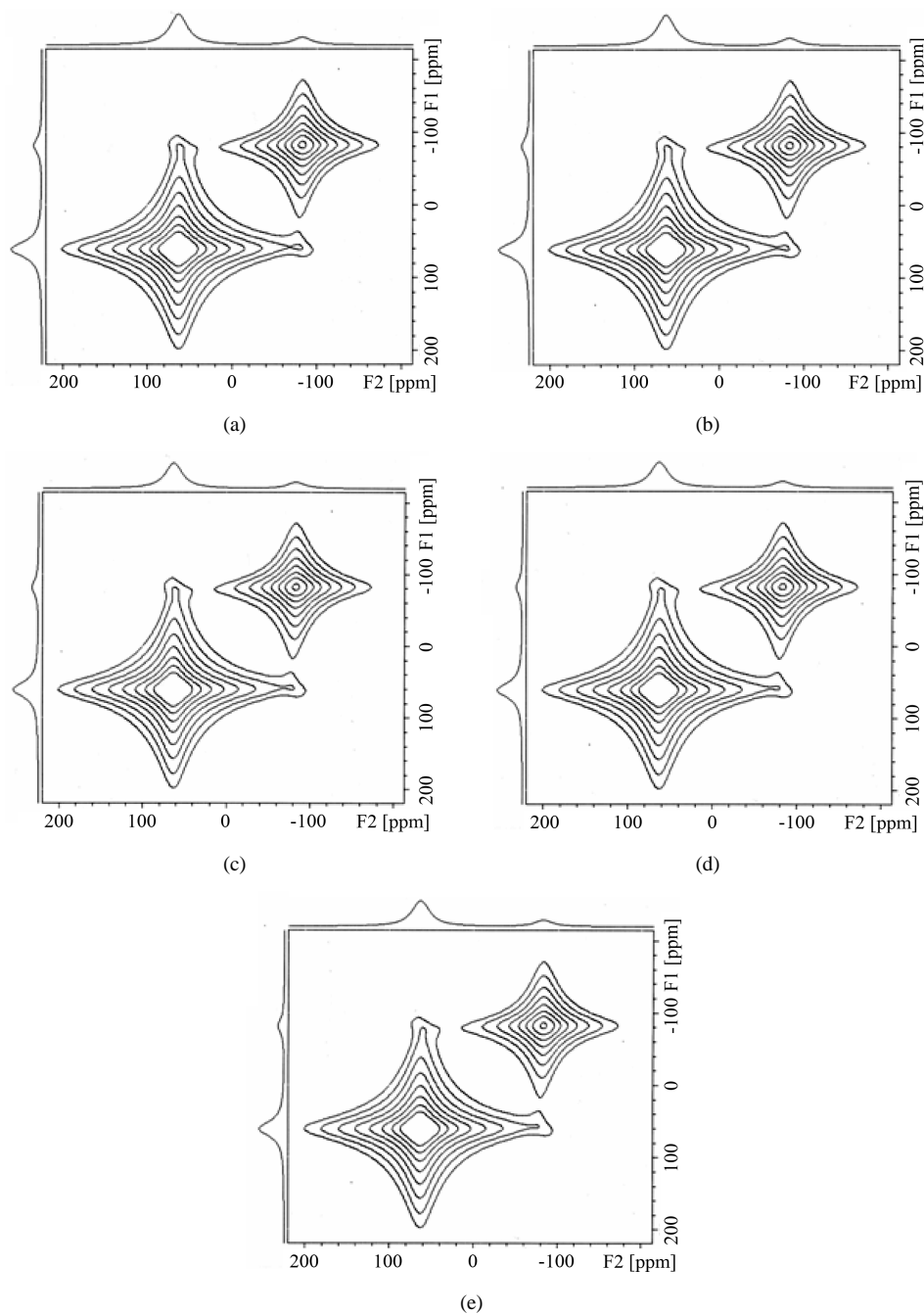
Figure 2. 2D NMR COSY calculated power spectra with $\omega_A = 11475$ Hz, $\omega_X = -8820$ Hz, $T_{2A} = T_{2X} = 100$ μs and **(a)** J = 20 Hz **(b)** J = 40 Hz **(c)** J = 60 Hz **(d)** J = 80 Hz and **(e)** J = 100 Hz.

ratio 1:2 (**Figure 4**). There is no evidence in the 1D [59]Co NMR spectrum for the existence of a J scalar coupling constants between the non-equivalent [59]Co nuclei, as previously observed for iron-based tetrahedral mixed-metal clusters [17] [18]. The cobalt nucleus bound to PPh$_3$ (Co$_1$) resonates at −14,888 ppm while the two equivalent cobalt nuclei (Co$_2$) are observed at −15,028 ppm. The $T2$ values of Co$_1$ and Co$_2$ estimated from the line widths are equal to 110 and 60 μs, respectively, while it was not possible to measure the T_1 relaxation times because of the very long $\pi/2$ pulse and at the same time the very short T_1 relaxation times (around 100 μs). As previously explained for similar clusters [17] [18], there should be a difference between T_1 and T_2 for the two cobalt nuclei due to the scalar relaxation of the second kind where T_1 is different from T_2 [31]. This mechanism implies the
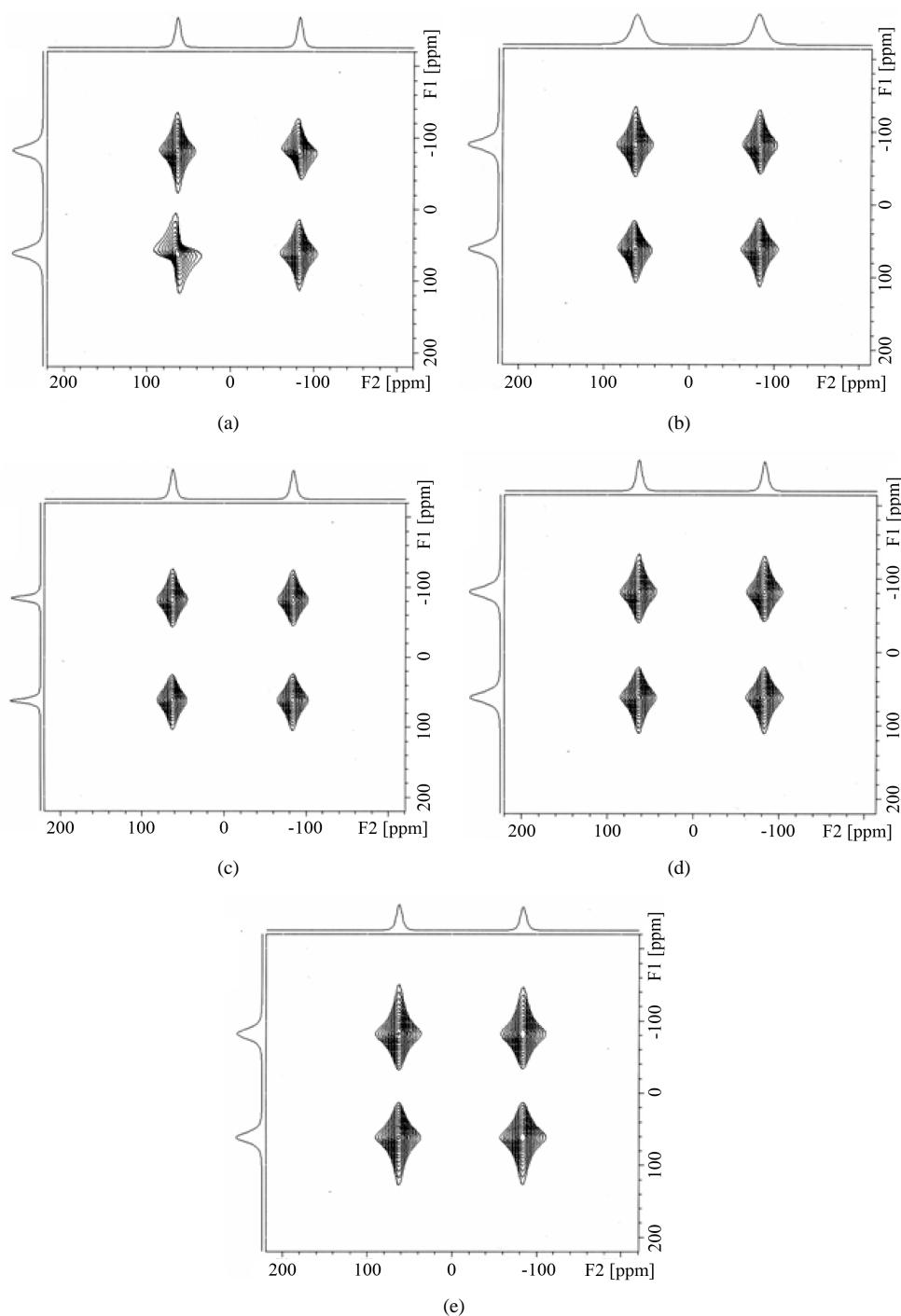
Figure 3. 2D NMR DQF-COSY calculated power spectra with $\omega_A = 11475$ Hz, $\omega_X = -8820$ Hz, $T_{2A} = T_{2X} = 100$ μs and **(a)** J = 20 Hz **(b)** J = 40 Hz **(c)** J = 60 Hz **(d)** J = 80 Hz and **(e)** J = 100 Hz.

existence of coupling constants and the fact that T_1 and T_2 are comparable indicates that the J coupling in our case, if it exists, is small but hopefully still detectable by using DQF-COSY NMR experiments, as highlighted in the theoretical simulations part of this paper. It was therefore of interest to obtain ^{59}Co 2D COSY-type NMR spectra of our cluster.

The 2D ^{59}Co COSY and DQF-COSY NMR spectra are shown in **Figure 5(a)** and **Figure 5(b)**, respectively. In the 2D COSY NMR spectrum (**Figure 5(a)**), cross peaks between the two resonances are not visible by contrast
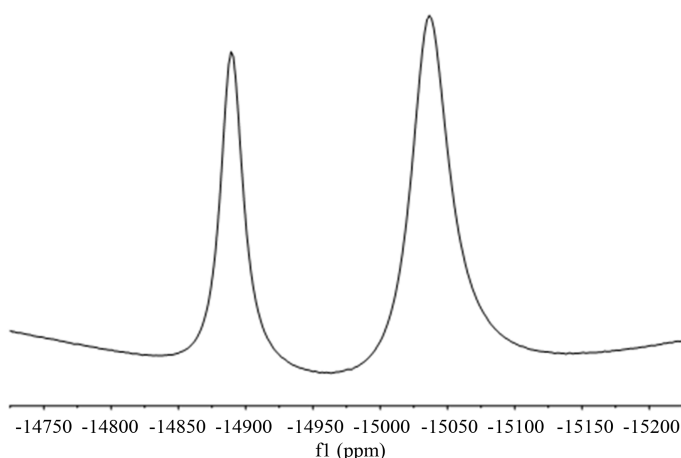
Figure 4. ^{59}Co NMR spectrum of the cluster HRuCo$_3$(CO)$_{11}$(PPh$_3$) in CDCl$_3$ at room temperature.

(a)   (b)
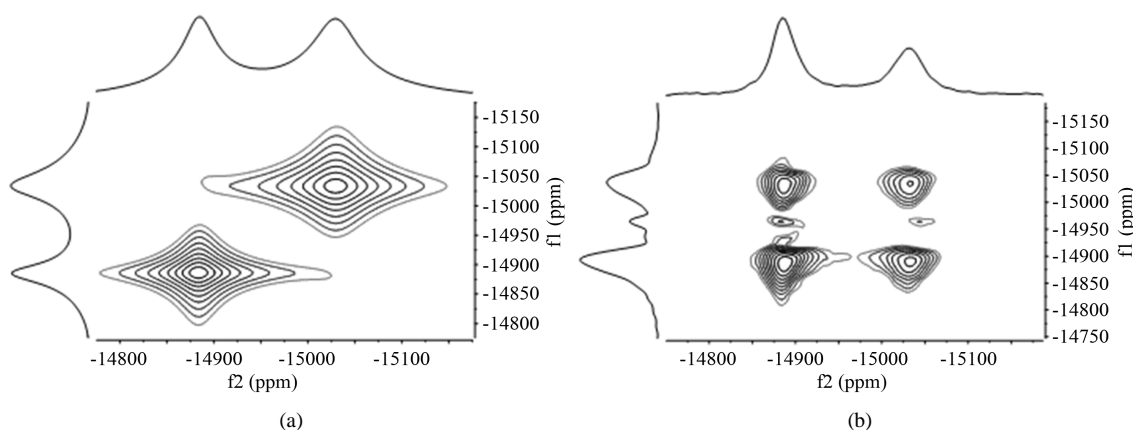
Figure 5. ^{59}Co 2D NMR power spectra of the cluster HRuCo$_3$(CO)$_{11}$(PPh$_3$) in CDCl$_3$ at room temperature. **(a)** Experimental COSY NMR spectrum. **(b)** Experimental DQF-COSY NMR spectrum.

to what happen in the DQF-COSY NMR spectrum (**Figure 5(b)**). This illustrates very well the fact that it is much easier in the case of quadrupolar nuclei relaxing very quickly to detect a relatively small J coupling in a 2D DQF-COSY NMR spectrum. In order to obtain a value for the ^{1}J(^{59}Co-^{59}Co) coupling constant, the 2D ^{59}Co COSY spectrum was analyzed according to the equations given above. In this analysis, it has been assumed that 1) the ^{59}Co relaxation is described with the assumptions of extreme narrowing and single correlation time, 2) the decay of coherences for nuclei, A and X is described by a single transverse relation time T_{2A} and T_{2X}, respectively, and 3) the couplings between the ^{31}P and ^{59}Co nuclei (some values of ^{1}J$_{Co-P}$ couplings in tetrahedral mixed-metal clusters of general formula HFeCo$_3$(CO)$_{11}$L have been reported previously in the literature: ^{1}J$_{Co-P}$ = 450 Hz with L = PPh$_2$H [32] [33], ^{1}J$_{Co-P}$ = 446 Hz with L = PCy$_2$H [33], ^{1}J$_{Co-P}$ = 573 Hz with L = PPh$_3$ [33] and ^{1}J$_{Co-P}$ = 750 Hz with L = [P(OMe)$_3$] [18] [34]) and between ^{99}Ru and ^{59}Co nuclei (there has been no value of a ^{1}J$_{Co-Ru}$ coupling reported in the literature before, to the best of our knowledge) are neglected. Note that according to our experience, taking into account the coupling between ^{31}P and ^{59}Co nuclei, as was previously done, does not change the final result for the ^{1}J(^{59}Co-^{59}Co) coupling constants [17] [18].

Attempts to analyze this 2D DQF-COSY NMR spectrum (not shown) did not give satisfactory results. This may be due to an irradiation problem because of the very long π/2 pulse length of 20 μs. In this case, it will definitively be useful to use solid-state NMR transmitters and probes and work with very short pulses as previously done [17] [18].

Attempts to analyze the 2D COSY NMR spectrum (not shown) show that the cross peaks start to be visible for ^{1}J(^{59}Co-^{59}Co) = 300 Hz. Therefore, as cross peaks are not visible on the experimental spectrum, this value is

Table 1. Parameters obtained from the analysis of the 1D ^{59}Co spectrum of cobalt nuclei Co$_1$ and Co$_2$ in the cluster HRuCo$_3$(CO)$_{11}$(PPh$_3$) and the ^{1}J(^{59}Co-^{59}Co) scalar coupling constant determined from the simulation of the ^{59}Co COSY NMR spectrum.

	Ligand	δ_{Co}^{59} (ppm)	$\Delta\nu_{1/2}$ (Hz)	T_2 (µs)[a]	^{1}J(^{59}Co$_i$-^{59}Co$_j$) (Hz)[b]
Co$_1$	PPh$_3$	−14,888 ± 10	2870 ± 200	111	(1-2) < 300
Co$_2$	Unsubstituted	−15,028 ± 10	5110 ± 200	62	

[a]Calculated from the line width of each signal. [b]Determined from the simulation of the ^{59}Co COSY NMR spectrum.

an upper limit for the ^{1}J(^{59}Co-^{59}Co) coupling (**Table 1**). Note that we supposed in the simulations that $T_1 = T_2$, T_2 being obtained from the line widths, and this hypothesis is supported by the fact that the J$_{Co-Co}$ coupling is small in our case.

It is of interest to compare the value of the ^{1}J(^{59}Co-^{59}Co) coupling constant obtained in this work with those previously determined. The only ones known were determined in iron-based tetrahedral mixed-metal clusters and are surprisingly of the same order of magnitude compared to the ^{1}J(^{59}Co-^{59}Co) coupling determined in this work: ^{1}J(^{59}Co-^{59}Co) = (115 ± 20) Hz for HFeCo$_3$(CO)$_{11}$(PPh$_2$H) [17], ^{1}J(^{59}Co-^{59}Co) = 140 Hz for HFeCo$_3$(CO)$_{11}$(PPh$_3$) [18], ^{1}J(^{59}Co-^{59}Co) = (165 ± 15) Hz for HFeCo$_3$(CO)$_{11}$[P(OMe)$_3$] [18], ^{1}J(^{59}Co-^{59}Co) = 45 Hz for HFeCo$_3$(CO)$_{11}$(PCy$_3$) [18] and ^{1}J(^{59}Co-^{59}Co) = (600 ± 150) Hz, ^{1}J(^{59}Co-^{59}Co) = (450 ± 100) Hz, ^{1}J(^{59}Co-^{59}Co) = (350 ± 100) Hz for HFeCo$_3$(CO)$_{10}$(PCyH$_2$)(PPh$_2$[CH$_2$C(O)Ph]) [19]. This could be explained by the similarities between the phosphorous ligands used. Note that large differences were also observed for ^{1}J(^{59}Co-^{31}P) scalar coupling constants in iron-based tetrahedral mixed-metal clusters [18] [32]-[35].

6. Conclusion

It has been shown in this paper that it is possible to detect cross peaks in a 2D DQF-COSY NMR spectrum when the relaxation times T_1 are very short and the lines in the conventional 1D NMR spectrum are consequently very broad. This is not the case for the conventional COSY NMR experiment. This case study demonstrates the feasibility of 2D DQF-COSY NMR experiments even in the case of very broad (2.9 - 5.1 kHz) lines in the conventional 1D NMR spectrum. The present data complement the previously reported ^{59}Co-^{59}Co J coupling constants and therefore refer to a quadrupolar nucleus. It is believed that other metal-to-metal scalar coupling constants involving quadrupolar nuclei may be obtained by simulation of COSY-type 2D NMR spectra. Particularly, this work opens up the possibility of investigating other ruthenium-based tetrahedral mixed-metal clusters with very broad peaks in the conventional 1D ^{59}Co NMR spectrum. It is also believed that the methodology described in this paper will be applicable to study metal clusters of biological relevance.

Acknowledgements

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