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Investigation of Tetrahedral Mixed-Metal Carbonyl Clusters by Two-Dimensional ^{59}Co COSY and DQFCOSY NMR Experiments

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Two-dimensional (2D) ^{59}Co correlation spectroscopy (COSY)/double-quantum-filtered (DQF)COSY experiments are reported for three tetrahedral mixed-metal clusters $HFeCo_3(CO)_{11}L$ with L = PPh_3, $P(OMe)_3$, and PCy_3 (Cy = cyclohexyl) in which the L-substituted Co center is chemically different from the other two. The 2D ^{59}Co COSY and DQFCOSY NMR spectra of these clusters in solution prove the existence of a scalar coupling constant between the ^{59}Co nuclei. To determine this value for each cluster, 2D ^{59}Co COSY and DQFCOSY NMR spectra have been simulated by numerical density-matrix calculations. The predicted spectra mimic well the features of the experimental spectra if a scalar coupling is introduced between the Co nuclei. It was initially observed that the scalar coupling constants between the Co nuclei obtained from the 2D COSY and DQFCOSY NMR spectra differed significantly. In contrast to the 2D COSY spectra, the diagonal and cross peaks are of comparable intensity in the 2D DQFCOSY spectra, which leads to a considerable increase in the accuracy of the determination of the scalar coupling constant.

Introduction

Since its discovery in the early days of NMR spectroscopy, indirect spin−spin coupling *J* has been considered as an important structural parameter.[1−5] Because the coupling is mediated via bonding electrons, it provides fundamental information about the molecular structure and the connectivity of the mutually coupled nuclei. Indirect spin−spin coupling is responsible for the multiplet structures of NMR spectra. The determination of a coupling constant is straightforward from the observed line splitting if the nuclei involved in the scalar coupling have sufficiently long relaxation times, i.e., if the lifetime of the nuclei in these states is long compared to the inverse of the spin−spin coupling constant. However, when one of the nuclei is relaxing more rapidly, as is frequently the case for quadrupolar nuclei, the coupling pattern of the resonance lines of the other nuclei involved in the coupling is more or less hidden in the usual spectrum.[6] In these cases, the coupling constant needs to be determined indirectly.

Various one-dimensional (1D) and two-dimensional (2D) methods have been developed for the determination of coupling constants. Among the 1D techniques and for an AX spin system, where a spin $^1/_2$ nucleus A is scalar-coupled to an X quadrupolar nucleus, most methods use the fact that relaxation of the quadrupolar nucleus acts as a relaxation mechanism for the other nucleus via the scalar coupling.[7−10] Other 1D techniques involve the determination of spin coupling constants to quadrupolar nuclei by means of relaxation measurements.[11] Besides deuterium, lithium, and

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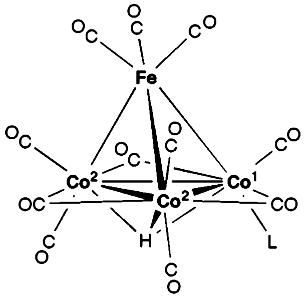
boron, to the best of our knowledge, scalar couplings between two quadrupolar nuclei have not been reported in 1D NMR studies using either of these methods.

If signals in the 1D spectrum are not resolved, the measurement of a 2D spectrum is often useful. 2D J,δ spectroscopy,[12,13] E-COSY (correlation spectroscopy),[14] Z-filtered COSY,[15] multiple-quantum-filtered COSY,[16,17] and conventional COSY[18] have proved to be efficient and powerful techniques to determine coupling constants, especially for proton spin systems. Furthermore, the COSY and double-quantum-filtered (DQF)COSY experiments have been used to prove the existence of a scalar coupling between quadrupolar nuclei. These qualitative investigations concern nuclei with small quadrupolar moments such as ^{11}B,[19−27] ^{51}V,[28] ^{2}H,[29,30] ^{6}Li,[31−33] and ^{7}Li,[32,33] which give rise to relatively narrow lines (10−150 Hz) in the conventional 1D spectrum.

Recently, we have reported the first theoretical investigation and quantitative analysis of 2D ^{59}Co COSY and DQFCOSY NMR spectra.[34] Ideal candidate molecules for such spectroscopic investigations are available in the realm of metal cluster chemistry, whose fundamental and applied multidisciplinary facets attract much attention.[35] In particular, the substitution of carbonyl ligands by neutral, two-electron-donor ligands such as phosphines in mixed-metal clusters is very dependent on the nature of the metal, and various chemical, geometrical, and stereochemical isomers are therefore concievable and sometimes isolated.[35b,c] Easier monitoring of the course of such substitution reactions by a direct observation at the metal nucleus, and not only at the ligands, would be of considerable synthetic interest. It should also be remembered that such ligands are often used as additives in catalytic reactions involving metal clusters (i.e., “phosphine effects”) and that precise knowledge of their fate would allow a better fine-tuning of the catalyst properties. The molecule we previously studied in solution was the tetrahedral mixed-metal cluster $HFeCo_3(CO)_{11}(PPh_2H)$, even though the line widths in the ^{59}Co 1D spectrum are around 1.5 kHz.[34] The comparison between theoretical and experimental 2D spectra in both COSY and DQFCOSY experiments led to a scalar coupling constant $^{1}J_{\mathrm{Co-Co}} = 115 \pm 20$ Hz. The coupling constant between the Co nuclei in this cluster is more than 10 times lower than the line width in the 1D spectrum. It is usually difficult to observe a cross peak in a COSY experiment when the coupling pattern is hidden in the line width. In this paper, we report the investigation and analysis of 2D ^{59}Co COSY and DQFCOSY solution NMR spectra of three heterometallic tetrahedral carbonyl clusters of the formula $HFeCo_3(CO)_{11}L$ [L = PPh_3 (**1**), $P(OMe)_3$ (**2**), and PCy_3 (**3**)] to obtain information about the coupling pattern between the chemically different ^{59}Co nuclei. A molecular mirror plane containing the atoms Fe and Co1 renders the other two Co nuclei magnetically equivalent. This case study should demonstrate the feasability of the NMR experiments, and the determination of these coupling constants should provide very useful information on the nature of the metal−metal interactions.[4]



1 L = PPh_3
2 L = $P(OMe)_3$
3 L = PCy_3

Basic Principles

Multidimensional spectra lead to off-diagonal resonances, which establish correlations between two parameters. In the

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COSY-type 2D spectra,[36] these correlations prove the existence of a scalar coupling constant. In some cases, other phenomena such as chemical exchange may also introduce correlations. In these cases, an experiment such as DQF-COSY allows suppression of all sources of correlation except the indirect coupling constant effect.

Until now, most of those sequences where applied to spin $^1/_2$ nuclei and sometime between spin $^1/_2$ nuclei coupled to quadrupolar nuclei having relatively long relaxation times. In our case, we have performed such 2D experiments between two quadrupolar nuclei with relatively large line width (1.5 kHz).

To interpret the results, a simulation program based on density-matrix calculations has been written, and the detailed theoretical background has been published previously.[34] Besides the fact that we use nuclei with spin $^7/_2$, our system contains three coupled nuclei, the first-order approximation has been used because the coupling constants are smaller than the difference in chemical shifts expressed in hertz. We used an AX_2 spin system considered as the limit of an AMX spin system where $\omega_M = \omega_X$, $J_{AM} = J_{AX}$, and $J_{MX} = 0$. We also consider that all coherences belonging to the same nucleus have the same transverse relaxation time T_2. This approach is no longer valid in the presence of multiexponential relaxation arising from degenerate transitions.[6]

Improvement of the COSY experiments is obtained by double quantum filtration using DQFCOSY. One of the advantages of this double quantum filtration is the reduction of the intensity of the diagonal peaks relative to that of the cross peaks. This experiment eliminates also the effect of an eventual chemical exchange process between the Co atoms.[6,16,17]

Experimental Section

We have studied three tetrahedral clusters $HFeCo_3(CO)_{11}L$ with L = PPh_3 (**1**), $P(OMe_3)$ (**2**), and PCy_3 (**3**). These clusters have been synthesized from the tetranuclear mixed-metal carbonyl hydride $HFeCo_3(CO)_{12}$ by selective substitution of a Co-bound carbonyl with the ligand L, according to published procedures.[39,40] They were dissolved in $CDCl_3$, and their concentrations were between 0.01 and 0.02 mol·L^{-1}.

All ^{59}Co NMR experiments were carried out on a 7.1-T Bruker MSL 300 NMR spectrometer operating at a ^{59}Co frequency of 71.21 MHz. The ^{59}Co signal of a saturated D_2O solution of $K_3Co(CN)_6$ was used as the external frequency reference. Experiments were performed using a Bruker high-speed cross-polarization/magic angle spinning probe with cylindrical 7-mm-outer-diameter ZrO_2 rotors in order to use shorter $\pi/2$ excitation pulses (2.25 μs) necessary to cover adequately the whole spectrum. The temperature was controlled with a Bruker B-VT 1000 unit. The ^{59}Co COSY and DQFCOSY spectra were recorded using the standard ($\pi/2-t_1-\pi/2-$acquisition and $\pi/2-t_1-\pi/2-\tau-\pi/2-$acquisition) sequences, respectively. In both pulse sequences, phase cycling procedures to select the coherence transfer echo pathway were used. Most 2D data presented in this work involved the acquisition of 512 points with dwell times $\Delta t_1 = \Delta t_2 = 20$ μs; 11 200 and 26 880 scans separated by a 40-ms relaxation delay were usually collected for each t_1 increment of the COSY and DQFCOSY experiments, respectively. The total acquisition time required by the 2D NMR experiments that are illustrated below ranged between 16 and 38 h. After completing these acquisitions, the collected data were apodized in both dimensions by a squared-sine bell function with $\pi/2$ shift prior to zero-filling to 512 × 512 data points and Fourier transformation.

Table 1. Results of the Analysis of the ^{59}Co NMR Spectra of Clusters **1**−**3** with the Relaxation Times of the Cobalt Nuclei Co1 and Co2

cluster	T (K)	δ(Co1) (ppm)	δ(Co2) (ppm)	$\Delta\nu_{1/2}$ (Co1) (Hz)	$\Delta\nu_{1/2}$ (Co2) (Hz)	T_1(Co1) (μs)	T_1(Co2) (μs)
1	296	−2473	−2688	1660	1840	325 + 30	210 ± 20
1	315	−2451	−2675	1565	1730	395 + 30	260 ± 20
1	325	−2441	−2668	1505	1660	475 + 40	305 ± 20
2	296	−2766	−2706	1795	1025	310 + 30	440 ± 40
2	315	−2755	−2692	1745	955	395 + 30	585 ± 50
2	325	−2750	−2686	1665	920	440 + 40	655 ± 50
3	325	−2471	−2650	2400	1900	160 + 25	150 ± 30

^{59}Co T_1 measurements were performed using a standard inversion−recovery ($\pi-\tau-\pi/2-$acquisition) sequence. At least 42 values of τ for each relaxation experiment were used. T_1 relaxation times were deduced using a three-parameter exponential curve fit of the experimental data. The T_1 values reported in Table 1 represent the average of at least two trials, and the maximum errors are estimated to be less than 10%. The T_2 values were estimated from the line widths $\Delta\nu_{1/2}$.

Results and Discussion

The ^{59}Co 1D spectra of the three clusters (not shown) present two resonances having intensities in the ratio 2:1. There was no evidence for the existence of a scalar coupling constant between the nonequivalent Co nuclei in the 1D spectra. In agreement with previous results,[41] substitution of a phosphine ligand by a phosphite ligand results in a significant change of the chemical shift of the substituted cobalt site Co1, as observed in Table 1 when comparing **1** or **3** with **2**. On the other hand, the chemical shift of the unsubstituted cobalt nuclei Co2 remains almost unperturbed. For cluster **2**, it is interesting to note that the resonance of the phosphite-substituted cobalt site Co1 is shifted to a lower frequency than that of the two unsubstituted equivalent cobalt nuclei Co2. As usual in transition-metal NMR,[42,43] the ^{59}Co chemical shift in these clusters is temperature-dependent. The line widths at half-height $\Delta\nu_{1/2}$ of the corresponding spectra are given in Table 1, along with the experimental T_1 longitudinal relaxation times. For the three compounds, the inversion−recovery sequence leads to a monoexponential behavior, and an excellent agreement between experimental data points and the theoretical recovery curves is obtained.

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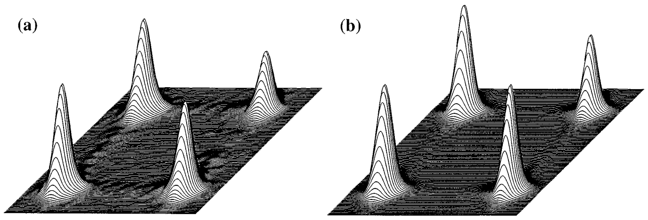

Figure 1. 2D ^{59}Co DQFCOSY NMR power spectra of cluster **1**. Experimental spectrum (a) in $CDCl_3$ at $T = 296$ K. Theoretical spectrum (b) obtained with the chemical shifts and relaxation times listed in Table 1, with $^1J_{Co1-P} = 575$ Hz and $^1J_{Co1-Co2} = 140$ Hz.

As was already mentioned,[44-47] this result indicates that the ^{59}Co relaxation may be described by the extreme narrowing conditions, i.e., $T_1 = T_2$. However, for the three clusters, the T_2 values of Co1 and Co2 obtained from the line width ($T_2 = 1/\pi\Delta\nu_{1/2}$) ranged between 135 and 345 μs, less than the T_1 values. This is not surprising because additional line broadening must be produced by scalar *J* couplings between the ^{59}Co and ^{31}P nuclei. A previous analysis of the ^{31}P NMR saddle-shaped solution spectra has given the following results: $^1J_{Co1-P} = 573$ Hz in cluster **1**[44] and 750 Hz in cluster **2**.[48] As was previously mentioned for the tetrahedral cluster $HFeCo_3(CO)_{11}(PPh_2H)$,[34] these values cannot explain the differences observed between T_1 and T_2. This result indicates the existence of other unresolved couplings in the ^{59}Co spectra. It was therefore of interest to obtain the 2D ^{59}Co COSY and DQFCOSY NMR spectra of these clusters and to compare them to the corresponding theoretical spectra in order to estimate the coupling constants between the Co nuclei. To take into account the coupling between the ^{59}Co and ^{31}P nuclei, calculations were performed by considering a free induction decay equal to the sum of two terms corresponding to the two resonances arising from the coupling to the P atom. They were calculated with a shift of the offset frequency corresponding to the Co nucleus bound to the ligand equal to $+\pi^1J_{Co1-P}$ and to $-\pi^1J_{\,Co1-P}$.[34]

Cluster 1. Figure 1 shows the experimental and calculated ^{59}Co DQFCOSY spectra of cluster **1** at 296 K. Experiments carried out at 315 and 325 K led to similar spectra (see Figure S-1 of the Supporting Information). The cross and diagonal peaks in the experimental spectra are of comparable intensities, as was expected when using multiple quantum filtration.[16] Indeed, these spectra clearly prove the existence of a scalar coupling constant between the Co nuclei. To simulate the spectra, we used the chemical shifts and the longitudinal relaxation times listed in Table 1. An excellent agreement between the experimental and theoretical spectra was obtained at all temperatures. The best simulations led to the same value for the coupling constant between the two Co atoms: $^1J_{Co1-Co2} = 140$ Hz.

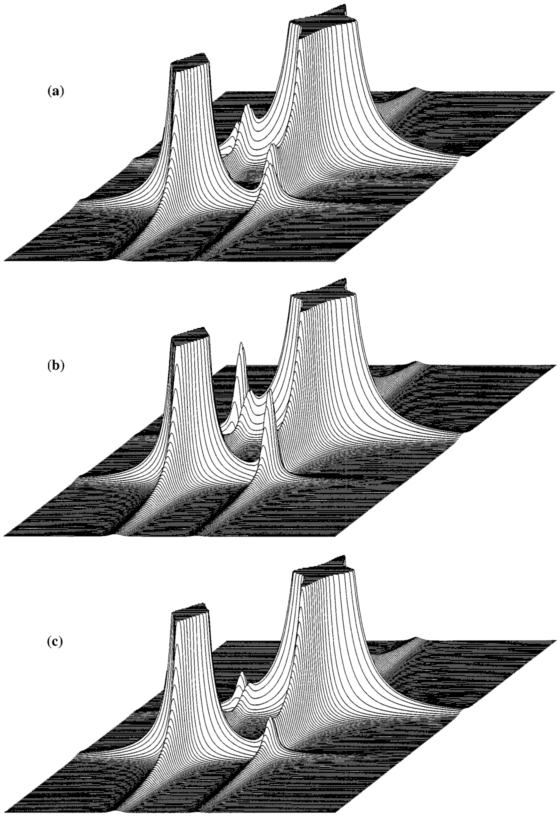

Figure 2. ^{59}Co COSY NMR power spectra of cluster **1**. Experimental spectrum in $CDCl_3$ at $T = 325$ K (a). Theoretical spectra obtained with the chemical shifts and relaxation times listed in Table 1, with $^1J_{Co1-P} = 575$ Hz and $^1J_{Co1-Co2} = 140$ Hz (b) or $^1J_{Co1-Co2} = 70$ Hz (c).

The ^{59}Co COSY spectra of cluster **1** at 296, 315, and 325 K, reproduced in Figure 2, exhibit cross peaks having very low intensities. Only the spectrum at 325 K has been analyzed. The positions of the two weak cross peaks are slightly shifted from their normal positions at (ω_A, ω_X) and (ω_X, ω_A). This is a consequence of the interferences of these cross peaks with the long tail of the feet of the diagonal peaks.[34] The simulation of the COSY spectrum, using the same parameters as those used previously and a scalar coupling constant of 140 Hz between the Co atoms as deduced from the DQFCOSY spectra, leads to cross-peak intensities larger than the experimental ones. If lower $^1J_{Co1-Co2}$ values are used for the simulation, a better agreement between the theoretical and experimental spectra is obtained, with the best value being $^1J_{Co1-Co2} = 70$ Hz.

We also notice that the envelopes of the diagonal peaks in the experimental and theoretical spectra present some significant differences. The experimental lines have a larger envelope than the calculated spectrum. This difference arises from the fact that we have assumed that all coherences belonging to the same ^{59}Co nucleus have the same transverse relaxation time. However, it has long been recognized that transverse relaxation coherences of degenerate transitions cannot be described by a single relaxation time T_2. This leads to the fact that, for a quadrupolar nucleus, the line widths of the "outer" lines of a multiplet arising from a coupling pattern

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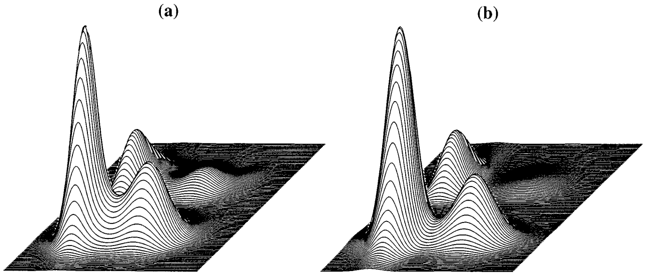

Figure 3. 2D ^{59}Co DQFCOSY NMR power spectra of cluster **2**. Experimental spectrum (a) in $CDCl_3$ at $T = 296$ K. The corresponding theoretical spectrum (b) was obtained with the chemical shifts and relaxation times listed in Table 1, with $^1J_{Co1-P} = 750$ Hz and $^1J_{Co1-Co2} = 180$ Hz.

are larger than the "inner" and "central" ones.[49] This is consistent with the difference observed between the experimental and simulated spectra.

It has been shown that the COSY spectrum leads to less accurate coupling constant values than the DQFCOSY experiment,[34] and we will therefore only use the latter.

Cluster 2. The experimental and calculated 2D ^{59}Co DQFCOSY spectra of cluster **2** at 296 K are shown in Figure 3 and those at 315 and 325 K, which are similar, in Figure S-2 (Supporting Information). Relatively intense cross peaks were observed. The spectrum did not change with increasing temperature, although the relaxation time shows significant variations, as shown in Table 1. The simulations were performed with the parameters given in Table 1, and the best agreement between the experimental and theoretical spectra was obtained for the following coupling constants: $^1J_{Co1-Co2} = 180$ Hz at 296 K, $^1J_{Co1-Co2} = 165$ Hz at 315 K, and $^1J_{Co1-Co2} = 150$ Hz at 325 K. The variations of $^1J_{Co1-Co2}$ values as a function of the temperature are outside the experimental errors estimated to be less than 10%.

The 2D ^{59}Co COSY spectra of cluster **2** have been measured at 296 and 315 K (see Figure S-3 of the Supporting Information). The best simulations obtained with the parameters of Table 1 led to the following coupling constants: $^1J_{Co1-Co2}(296\text{ K}) = 120$ Hz and $^1J_{Co1-Co2}(315\text{ K}) = 125$ Hz. As previously, the scalar coupling constant between the two Co atoms was deduced from the visually optimized fits of the 2D COSY spectra: $^1J_{Co1-Co2} = 120 \pm 5$ Hz, which is lower than that obtained from the corresponding 2D DQFCOSY, where $^1J_{Co1-Co2} = 165 \pm 15$ Hz. As for cluster **1**, the diagonal and cross peaks in the 2D DQFCOSY spectra are of comparable intensities, which leads to a more accurate fitting and estimate of the scalar coupling constant than that obtained from the COSY experiments where the cross peaks are of low intensity when compared to the intense diagonal peaks.[34]

Cluster 3. The 2D DQFCOSY spectra of cluster **3** at 296 and 325 K exhibit cross peaks of intensities similar to those of the diagonal peaks, which shows again why double quantum filtration is interesting. The simulation of the 2D experiment at 325 K, done as previously with the parameters of Table 1 and $^1J_{Co1-P} = 450$ Hz, led to a coupling constant $^1J_{Co1-Co2}$ of 45 Hz. This smaller value compared to those for clusters **1** and **2** and $HFeCo_3(CO)_{11}PPh_2H$, where $^1J_{Co1-Co2} = 115 \pm 20$ Hz,[34] may arise from a partial decoupling because the Co relaxation times of cluster **3** are about 3 times shorter than those for clusters **1** and **2** (see Table 1). We notice the similarity of T_1 and $T_2 = 1/\pi\Delta\nu_{1/2}$ for this cluster, which indicates that there is a small contribution of the scalar coupling constant to the line width.

For cluster **3** at 296 K, no cross peaks are observed in the experimental 2D ^{59}Co COSY spectrum. The relaxation processes are too efficient and suppress all of the effects of the coupling constant. One could also argue that exchange processes could be responsible for this cross-peak collapse. To address this issue, we performed 2D ^{59}Co exchange spectroscopy (EXSY) experiments on all of the clusters under study. As stated elsewhere in the study of $Co_4(CO)_{12}$, 2D ^{59}Co EXSY experiments are possible on these kinds of systems and lead to observations of cross peaks when exchange processes take place.[50] None of the clusters **1**, **2**, or **3** features any cross peak in such experiments. This leads to the conclusion that only relaxation processes are responsible for the weakness of the $^1J_{Co1-Co2}$ coupling in cluster **3**. At 325 K, the 2D COSY spectrum presents very weak cross peaks, and their intensities are too low to allow a precise determination of the $^1J_{Co1-Co2}$ coupling constant from spectral simulation. This result confirms the apparently low value of the Co−Co coupling constant in this cluster.

Conclusion

The major significance of the present work resides in the experimental proof by 2D ^{59}Co NMR of a scalar coupling constant of ca. 150 Hz between the Co atoms of the tetrahedral mixed-metal clusters $HFeCo_3(CO)_{11}L$ with L = PPh_3, $P(OMe)_3$, and PCy_3, despite the fact that its magnitude is about 10 times lower than the line widths in the 1D spectra. In most cases, simulation of the 2D COSY and DQFCOSY spectra with a single relaxation time for each Co atom leads to ambiguous results; i.e., the scalar coupling between the Co nuclei deduced from both experiments differs significantly. The fact that the experimental diagonal peaks are broader than those predicted by theory may be interpreted as the result of the existence of degenerate transitions in the three-spin-$^7/_2$ AX_2 system, which leads to multiexponential transverse relaxation. To our knowledge, our results are the first dealing with multiexponential relaxation effects in the 2D COSY and DQFCOSY NMR spectra of a quadrupolar nucleus. Theoretical interpretations of such results would require precise quantum-mechanical calculations using Redfield's relaxation theory,[37] which are not accessible at this time for a three-spin-$^7/_2$ AX_2 spin system. Our work shows that DQFCOSY gives better results for the determination of $^1J_{Co-Co}$ values than simple COSY experiments.

It is difficult at this stage to discuss further the values found for $^1J_{Co1-Co2}$ and compare them with other coupling constants in tetrahedral clusters because no such data have been measured. Nevertheless, our data are consistent with

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the rare values of coupling constants reported for similar transition-metal nuclei.[51] With much heavier nuclei, relativistic effects considerably increase these values. The values we found for $^{1}J_{\mathrm{Co1-Co2}}$ represent a lower limit because we do not know the extent of the decoupling arising from the relaxation processes. The small value obtained for $^{1}J_{\mathrm{Co1-Co2}}$ in cluster **3** may be explained by such an effect.

The present data complement the previously reported transition-metal-to-transition-metal scalar coupling constants of spin $^{1}/_{2}$ nuclei such as ^{103}Rh, ^{109}Ag, and ^{195}Pt. However, the scalar coupling constants determined in this paper refer to quadrupolar nuclei. It is believed that other metal-to-metal scalar coupling constants involving quadrupolar nuclei may be obtained by simulation of 2D COSY and multiple-quantum-filtered COSY NMR spectra. On the basis of the present work, detection of scalar couplings for $S = {}^{7}/_{2}$ nuclei should be possible when the ratio $\Delta\nu/J$ is at least ca. 50. The determination of scalar coupling constants should be useful to better characterize the nature of the metal–metal interactions in complex molecules such as mixed-metal clusters.

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Supporting Information Available: Figures of 2D ^{59}Co DQFCOSY NMR power spectra of clusters **1** and **2** and 2D ^{59}Co COSY NMR power spectra of cluster **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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