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Communication

Determination of ${}^{1}J({}^{59}Co–{}^{59}Co)$ scalar coupling constants in the tetrahedral mixed-metal cluster $HFeCo_3(CO)_{10}(PCyH_2)(PPh_2[CH_2C(O)Ph])$ using COSY-type NMR experiments

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ABSTRACT

Two-dimensional ${}^{59}Co$ correlation spectroscopy (COSY) and double-quantum-filtered (DQF) COSY NMR experiments are reported for the tetrahedral mixed-metal cluster $HFeCo_3(CO)_{10}(PCyH_2)(PPh_2[CH_2C(O)Ph])$, which consists from the point of view of ${}^{59}Co$ NMR spectroscopy, of an AMX system of three-spin $S = 7/2$. Both 2D NMR spectra prove the existence of a J scalar coupling constant between non-equivalent ${}^{59}Co$ nuclei. By contrast to what happens with the conventional 2D ${}^{59}Co$ COSY NMR spectrum, it was possible to simulate the 2D ${}^{59}Co$ DQF-COSY NMR spectrum by density matrix calculations in order to extract the values of the ${}^{1}J({}^{59}Co–{}^{59}Co)$ coupling constants. The comparison between experimental and theoretical 2D NMR spectra gives spin-couplings constants of several hundreds Hertz for this cluster.

1. Introduction

Since its discovery in the early days of NMR spectroscopy, indirect spin–spin coupling J has been considered as an important structural parameter [1–4]. Because the coupling is mediated via bonding electrons, it provides fundamental information about the molecular structure and the connectivity of the mutually coupled nuclei. Various one-dimensional (1D) [5–9] and two-dimensional (2D) NMR methods have been developed for the determination of J scalar coupling constants. If signals in the 1D spectrum are not resolved, the measurement of a 2D spectrum is often useful. 2D J, δ spectroscopy [10,11], E-COSY [12], Z-filtered COSY [13], multiple-quantum filtered COSY [14,15] and conventional COSY [16,17] have proved to be efficient and powerful techniques to determine J scalar coupling constants, especially for proton spin systems. Furthermore, the COSY and DQF-COSY experiments have been used to prove the existence of a J scalar coupling between quadrupolar nuclei. These qualitative investigations concern nuclei with small quadrupolar moments which give rise to relatively narrow lines (10–150 Hz) in the conventional 1D spectrum [18–31].

Recently, we reported the determination of J scalar coupling constants between ${}^{59}Co$ nuclei in tetrahedral mixed-metal clusters and AX_2 spin systems, even though the line widths of the peaks in the 1D ${}^{59}Co$ spectrum are greater than 1.5 kHz [32,33]. Ideal candidate molecules for such spectroscopic investigations are available in the realm of metal cluster chemistry (and maybe beyond), whose fundamental and applied multidisciplinary facets attract much attention [34–36]. 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 conceivable and sometimes isolated [35,36]. The J scalar coupling constants observed between cobalt nuclei in these clusters were more than 10 times smaller than the line widths in the 1D spectrum [32,33]. In this paper, we report the investigation and analysis of 2D ${}^{59}Co$ COSY and DQF-COSY solution NMR spectra of a tetrahedral mixed-metal cluster consisting of a three-spin $S = 7/2$ AMX system (Fig. 1) to obtain information about the coupling pattern between the chemically different ${}^{59}Co$ nuclei. This case study should demonstrate the feasibility of the NMR experiments even in the case of very broad (2.5–4.5 kHz) lines in the conventional 1D spectrum, and the determination of these coupling constants should provide very useful information on the nature of the metal–metal interactions [1].

2. Experimental

Standard Schlenk line techniques were used, and manipulations were carried out under a purified nitrogen atmosphere. Solvents

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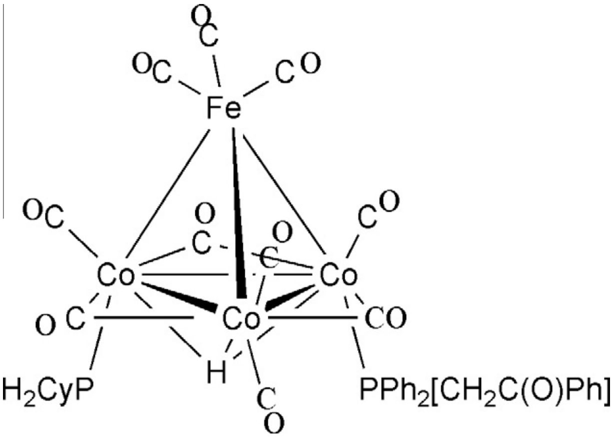

Fig. 1. Schematic of the $HFeCo_3(CO)_{10}(PCyH_2)(PPh_2[CH_2C(O)Ph])$ cluster.

were distilled before use. $HFeCo_3(CO)_{12}$ was prepared according to published procedure [37].

2.1. Synthesis of $HFeCo3(CO)_{10}(PCyH_2)[PPh_2\{CH_2C(O)Ph\}]$.

$HFeCo_3(CO)_{12}$ (0.384 g, 0.67 mmol) and $PPh_2CH_2C(O)Ph$ (0.206 g, 0.67 mmol) were mixed at room temperature in CH_2Cl_2 (30 ml). The color of the solution changed in 5 min from violet to dark violet and the reaction was stopped when the TLC plates indicated the presence of only the stable monosubstituted product. The solution was filtered and the solvent was removed under reduced pressure. The resulting solid was extracted with hexane and then placed at −30 °C for few days giving black crystals of $HFeCo_3(CO)_{11}[PPh_2\{CH_2C(O)Ph\}]$ (0.41 g, 0.48 mmol, 72%). Anal. Calcd. for $C_{31}H_{18}Co_3FeO_{12}P$: C, 44.01; H, 2.14. Found: C, 43.94; H, 2.25.

To a solution of the monosubstituted cluster $HFeCo_3(CO)_{11}[PPh_2\{CH_2C(O)Ph\}]$ (0.100 g, 0.12 mmol) in CH_2Cl_2 (20 ml), was added $PCyH_2$ (0.021 ml, 0.16 mmol), and the reaction mixture was stirred at room temperature. Monitoring by TLC plates indicated after 12 h the formation of a green compound. The solution was filtered, and the solvent was evaporated in vacuo. The resulting solid was extracted with a hexane/CH_2Cl_2 (8/2) mixture (20 ml), and this solution was placed at −15 °C for 2 days, giving green microcrystals of $HFeCo_3(CO)_{10}(PCyH_2)[PPh_2\{CH_2C(O)Ph\}]$. $0.5C_6H_{12}$ (0.074 g, 0.079 mmol, 67%). Anal. Calcd. for $C_{39}H_{37}Co_3FeO_{11}P$: C, 47.95; H, 3.82. Found: C, 48.32; H, 4.40.

2.2. NMR measurements

Fig. 1 presents the structure of this compound which was dissolved in $CDCl_3$. ^{59}Co NMR measurements were carried out on a Bruker Avance II 600 spectrometer operating at $B_0 = 14.1T$. The corresponding ^{59}Co Larmor frequency is 142.01 MHz. 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. The ^{59}Co COSY spectrum of $HFeCo_3(CO)_{10}(PCyH_2)(PPh_2[CH_2C(O)Ph])$ was obtained using the subprogram COSYQF from Bruker with the following parameters: $SW1 = SW2 =$ 125 kHz, acquisition time 2.0980 ms, 512 points, recycle delay 40 ms, 15360 scans, 64 decays in F1, apodization by an exponential with a line broadening of 2000 Hz and power spectra in both dimensions. The interpulse delay t_1 was incremented by twice the dwell time and the transmitter frequency was placed between *Co*1 and *Co*2 (Fig. 1). The ^{59}Co DQF-COSY spectrum was obtained using the subprogram COSYDFQF from Bruker with the same parameters as for the ^{59}Co COSY spectrum, except for the recycle delay which was equal to 10 ms, the number of decays in F1 which was equal to 32 and the number of scans which was equal to 163,840.

For T_1's measurement of ^{59}Co nuclei, the standard inversion-recovery sequence, $(\pi) - \tau - (\pi/2) - Acquisition$, was used. We have taken up to 1024 scans and 81 values of τ. The peak areas were used in a nonlinear three-parameter least-squares fit according to the usual equation: $I(\tau) = I_{eq}(1 - K\exp(-\tau/T_1))$. The maximum errors on T_1 values are estimated to be around 20%. $T_2(^{59}Co)$ values were estimated from the line widths $\Delta\nu_{1/2}$.

3. Results and discussion

The ^{59}Co spectrum of the cluster $HFeCo_3(CO)_{10}(PCyH_2)(PPh_2[CH_2C(O)Ph])$ presents three resonances having intensities in the ratio 1:1:1 (Fig. 2). As previously observed for similar tetrahedral mixed-metal clusters, there is no evidence for the existence of J scalar coupling constants between the non-equivalent ^{59}Co nuclei in the 1D ^{59}Co spectrum [32,33]. The cobalt nucleus bound to $PPh_2[CH_2C(O)Ph]$ (*Co*1) is found at −14,775 ppm, the cobalt nucleus bound to $PCyH_2$ (*Co*2) is found at −14,927 ppm while the unsubstituted cobalt nucleus (*Co*3) is observed at −15,022 ppm. The direct measurement of the longitudinal relaxation times gives the results listed in Table 1. For the three cobalt nuclei, the inversion-recovery sequence leads to a monoexponential behavior and excellent agreement between the experimental data points and the theoretical recovery curves is obtained. On the other hand, it has been shown [38,39] for tetrahedral mixed-metal clusters like the cluster under study that the cobalt relaxation times T_1 are temperature dependent but not field dependent. This indicates, in addition to the extreme narrowing conditions, that the ^{59}Co relaxation is dominated by the quadrupolar relaxation mechanism, i.e. $T_1 = T_2$, as previously observed for similar tetrahedral mixed-metal clusters [38–41]. Nevertheless, the T_2 values of *Co*1, *Co*2 and *Co*3 estimated from the line widths are between 70 and 125 µs far below the T_1 values (Table 1). As previously explained for similar clusters [32,33], this difference between T_1 and T_2 for the three cobalt nuclei comes from the scalar relaxation of the second kind where T_1 is different from T_2 [5]. This mechanism implies coupling constants and it was therefore of interest to obtain ^{59}Co 2D COSY-type NMR spectra of our cluster. As previously mentioned [33], in addition to the usual advantages that DQF-COSY NMR experiments offer compared to conventional COSY NMR experiments (observation of only-coupled spins, antiphase character of both diagonal and cross-peaks and diagonal and cross-peaks having nearly the same intensities), DQF-COSY NMR experiments have proved to be more reliable for interpretation and analysis than conventional COSY NMR experiments and this is particularly true for quadrupolar nuclei relaxing very quickly [33,42]. Therefore, the use of double quantum correlation experiments is supposed to provide information frequently obscured in the 2D COSY experiment and facilitate the analysis.

The 2D ^{59}Co COSY and DQF-COSY NMR spectra are shown in Figs. 4 and 3a, respectively. In the 2D COSY NMR spectrum (Fig. 4), cross-peaks between all the resonances are weak but clearly apparent. However, it appears to be very difficult to analyse the 2D COSY spectrum and, from there, to determine the $^1J(^{59}Co–^{59}Co)$ coupling constants. One of the best proof that these cross-peaks are not arising from overlapping of the long wings of the lines is provided by the DQF-COSY NMR spectrum (Fig. 3a). This work illustrates very well the fact that it is much easier in the case of quadrupolar nuclei relaxing very quickly to obtain and analyze a 2D DQF-COSY NMR spectrum. In order to obtain a value for the $^1J(^{59}Co–^{59}Co)$ coupling constants, the 2D ^{59}Co DQF-COSY spectrum was analyzed according to the equations given elsewhere [43–45]. In this analysis, it has been assumed that (a) the ^{59}Co relaxation is

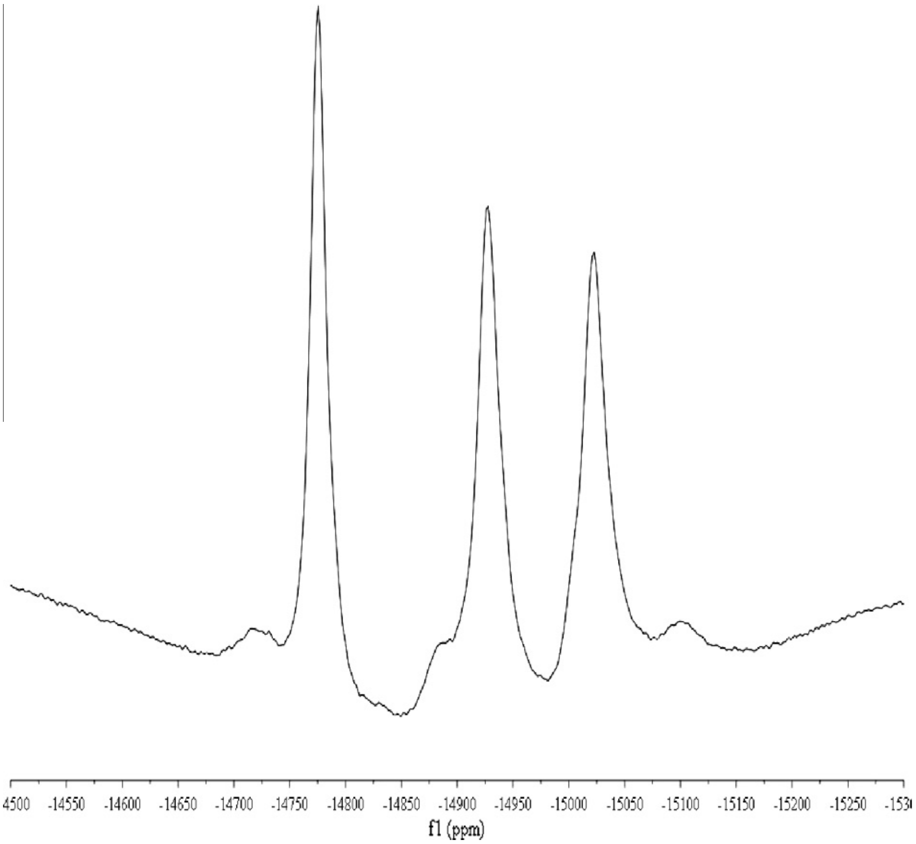

Fig. 2. ^{59}Co NMR spectrum of the cluster $HFeCo_3(CO)_{10}(PCyH_2)(PPh_2[CH_2C(O)Ph])$ in $CDCl_3$ at room temperature.

Table 1
Parameters obtained from the analysis of the 1D ^{59}Co spectrum for the three nuclei, along with the results of the relaxation time measurements of cobalt nuclei, *Co*1, *Co*2 and *Co*3 (See Fig. 1) in the cluster $HFeCo_3(CO)_{10}(PCyH_2)(PPh_2[CH_2C(O)Ph])$ and $^1J(^{59}Co–^{59}Co)$ scalar coupling constants determined from the simulation of the ^{59}Co DQF-COSY NMR spectrum.

	Ligand	σ^{59}_{Co} (ppm)	$\Delta\nu_{1/2}$ (Hz)	T_2 (μs)[a]	T_1 (μs)[b]	$^1J(^{59}Co_i–^{59}Co_j)$ (Hz)[c]
*Co*1	$PPh_2[CH_2C(O)Ph]$	−14,775 ± 10	2540 ± 200	125	220 ± 40	(1 − 2) = 600 ± 150
*Co*2	$PCyH_2$	−14,927 ± 10	3800 ± 200	84	125 ± 25	(2 − 3) = 450 ± 100
*Co*3	unsubstituted	−15,022 ± 10	4600 ± 200	69	130 ± 25	(3 − 1) = 350 ± 100

[a] Calculated from the line width of each signal.
[b] Measured directly by the inversion-recovery method.
[c] Determined from the simulation of the ^{59}Co DQF-COSY NMR spectrum.

described with the assumptions of extreme narrowing and single correlation time, (b) the decay of coherences for nuclei, A, M and X is described by a single transverse relation time T_{2A}, T_{2M} and T_{2X}, respectively and (c) the couplings between ^{31}P and ^{59}Co nuclei (some values of $^1J_{Co–P}$ couplings in tetrahedral mixed-metal clusters of general formula $HFeCo_3(CO)_{11}L$ have been reported previously in the literature: $^1J_{Co–P} = 450$ Hz with $L = PPh_2H$ [38,40], $^1J_{Co\text{-}P} = 446$ Hz with $L = PCy_2H$ [40], $^1J_{Co\text{-}P} = 573$ Hz with $L = PPh_3$ [40], $^1J_{Co\text{-}P} = 830$ Hz with $L = [P(OMe)_3]_3$ [39] and $^1J_{Co\text{-}P} = 750$ Hz with $L = [P(OMe)_3]$ [33,46]) and between ^{57}Fe and ^{59}Co nuclei (there is no value of a coupling $^1J_{Co\text{-}Fe}$ 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 $^1J(^{59}Co–^{59}Co)$ coupling constants [32,33].

Experimental and simulated DQF-COSY NMR spectra for the related cluster are shown in Fig. 3a and b, respectively. The $^1J(^{59}Co–^{59}Co)$ couplings obtained from the simulation, along with the chemical shifts and T_1's used for the simulation are given in Table 1. The experimental uncertainty is reported on the basis of the accuracy estimated from simulation observations. The experimental uncertainty limit is probably underestimated in view of unknown errors due to the assumptions used in the simulation. Note that the experimental and simulated spectra are very similar, except for diagonal peaks and especially the one of *Co*3 but this maybe due to an irradiation problem because of the very long $\pi/2$ pulse length of 20 μs. In this case, it will definitively be useful to use solid-state NMR transmitters and probes to obtain very short pulses, as was done previously [32,33]. However, as can be seen in Fig. 3a and b, the experimental spectrum mimics well the features of the predicted spectrum in the presence of *J* scalar coupling constants between cobalt nuclei.

It is of interest to compare the $^1J(^{59}Co–^{59}Co)$ couplings obtained in this work with the previously determined $^1J(^{59}Co–^{59}Co)$ couplings, the only ones which are known were determined in similar tetrahedral mixed-metal clusters. The $^1J(^{59}Co–^{59}Co)$ couplings determined previously were surprisingly very small compared to the $^1J(^{59}Co–^{59}Co)$ couplings determined in this work: $^1J(^{59}Co–^{59}Co)=(115 \pm 20)$ Hz for $HFeCo_3(CO)_{11}(PPh_2H)$ [32], $^1J(^{59}Co – ^{59}Co)= 140$ Hz for $HFeCo_3(CO)_{11}(PPh_3)$ [33], $^1J(^{59}Co–^{59}Co)=(165 \pm 15)$ Hz

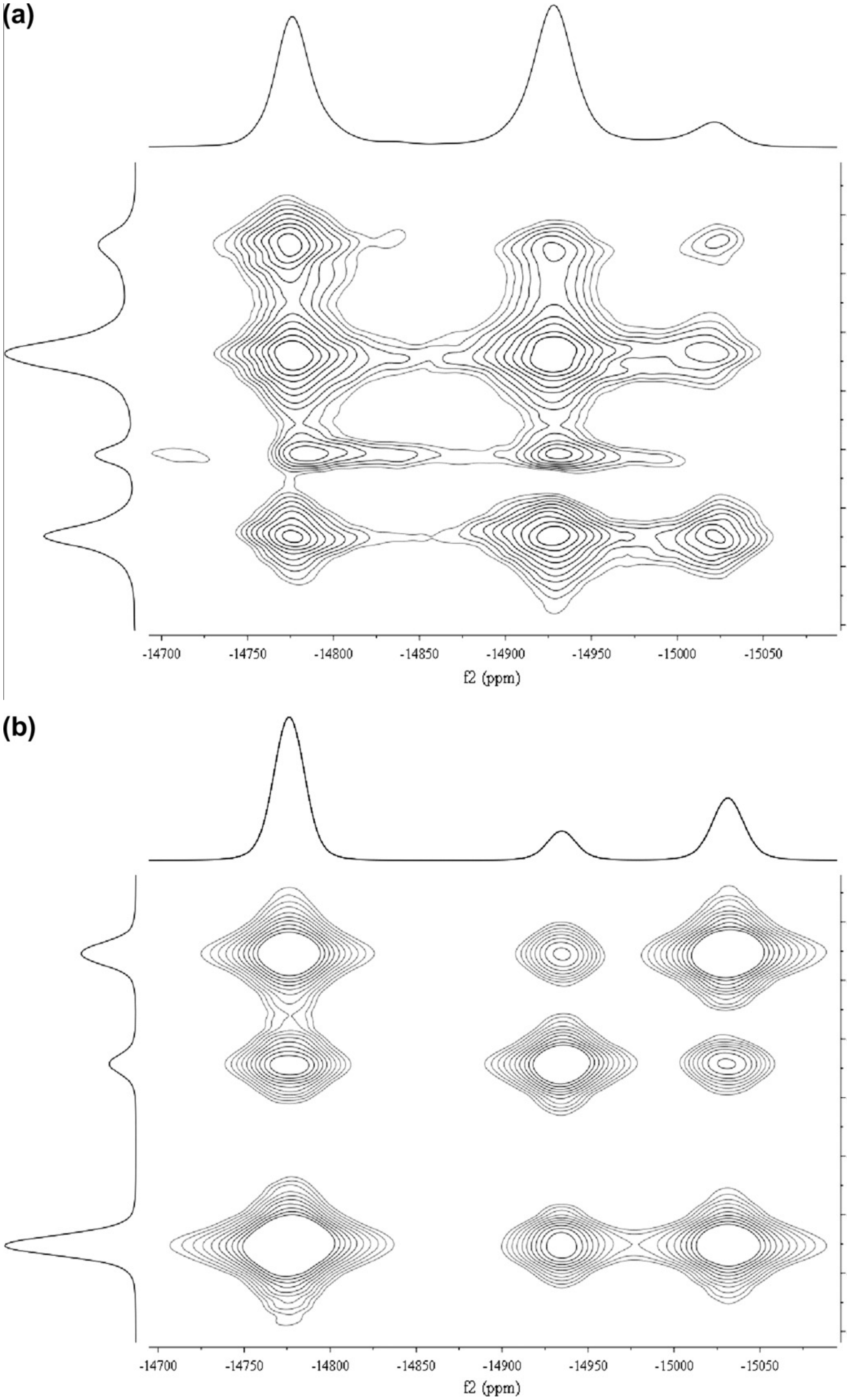

Fig. 3. ^{59}Co 2D NMR DQF-COSY power spectra of the cluster $HFeCo_3(CO)_{10}(PCyH_2)(PPh_2[CH_2C(O)Ph])$. (a) Experimental spectrum in $CDCl_3$ at room temperature. Note the presence of artefacts in the 2D experimental spectrum due to the bad suppression of the career frequency in the F1 dimension. (b) Theoretical spectrum with the chemical shift and the T_1 and the $^1J(^{59}Co–^{59}Co)$ values listed in Table 1.

for $HFeCo_3(CO)_{11}[P(OMe)_3]$ [33] and $^1J(^{59}Co–^{59}Co) = 45$ Hz for $HFeCo_3(CO)_{11}(PCy_3)$ [33]. To explain this difference, we have to take into account the fact that the ligands are different in the cluster studied in this paper (and, therefore, the chemical situation is

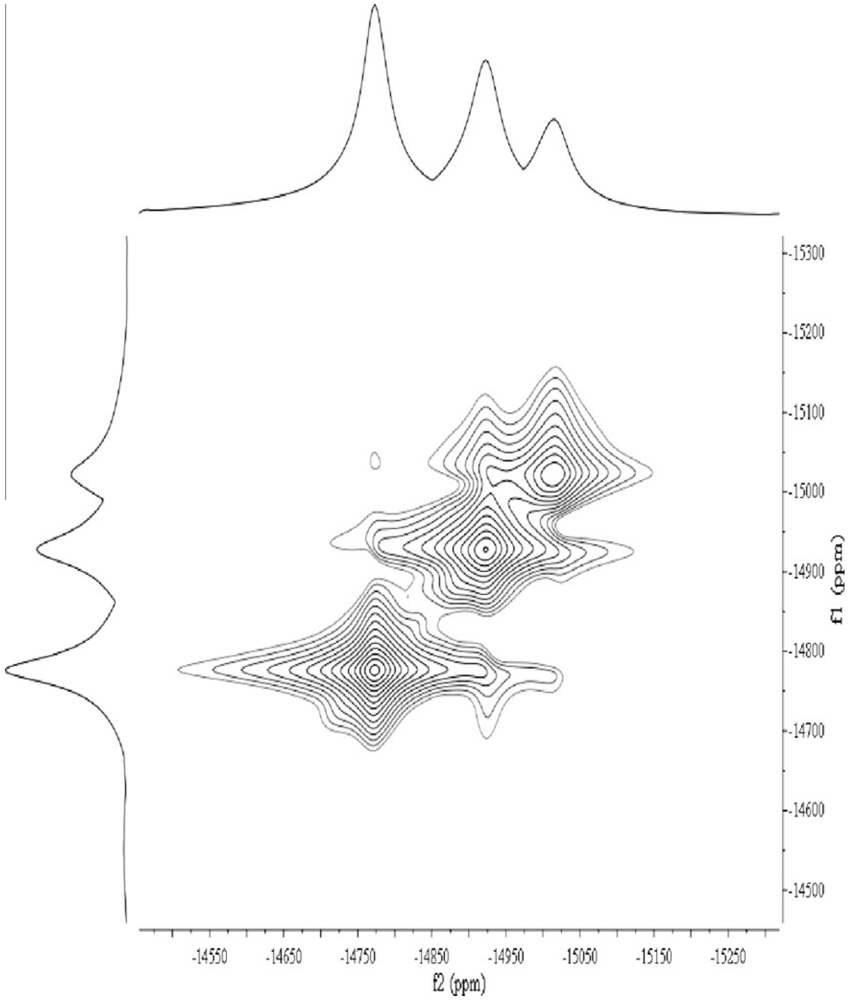

Fig. 4. ^{59}Co 2D NMR COSY power spectra of the cluster $HFeCo_3(CO)_{10}(PCyH_2)(PPh_2[CH_2C(O)Ph])$ in $CDCl_3$ at room temperature.

not the same). Note that large differences were also observed for $^1J(^{59}Co–^{31}P)$ scalar coupling constants in similar tetrahedral mixed-metal clusters [33,38–40,46]. The fact that the $^1J(^{59}Co–^{59}Co)$ couplings observed in this work are larger than the ones previously determined is fortunate as relaxation times for ^{59}Co in the cluster under study are very short and the fact that the $^1J(^{59}Co–^{59}Co)$ couplings are of the order of several hundred Hertz makes it possible to observe them using 2D COSY-type NMR experiments.

4. Conclusion

It was not obvious that 2D COSY-type NMR experiments would be instructive in the case of the cluster $HFeCo_3(CO)_{10}(PCyH_2)(PPh_2[CH_2C(O)Ph])$. Not only are the ^{59}Co–^{59}Co coupling constants not resolved in the 1D spectrum but also relaxation times for ^{59}Co nuclei are very short (and, consequently, the lines very broad), suggesting that relaxation would average the spin–spin coupling interaction to zero. Nevertheless, this case study demonstrates the feasibility of 2D DQF-COSY NMR experiments even in the case of very broad (2.5–4.5 kHz) lines in the conventional 1D spectrum. The present data complement the previously reported ^{59}Co–^{59}Co J coupling constants and also the 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 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. The determination of scalar coupling constants should be useful to better characterize the nature of the metal–metal interactions in complex molecules and clusters.

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References

[1] C.J. Jameson, Spin–spin coupling, in: J. Mason (Ed.), Multinuclear NMR, New York, pp. 89–131.
[2] J.N. Murell, The theory of nuclear spin–spin coupling in high-resolution NMR spectroscopy, Prog. NMR Spectrosc. 6 (1970) 1–60.
[3] J. Kowalewski, Calculations of nuclear spin–spin couplings, Annu. Rep. NMR Spectrosc. 12 (1982) 81–176.
[4] M. Eberstadt, G. Gemmeker, D.F. Mierke, H. Kessler, Scalar coupling constants – their analysis and their application for the elucidation of structures, Angew. Chem., Int. Ed. Engl. 34 (1995) 1671–1695.
[5] A. Abragam, The Principles of Nuclear Magnetism, Oxford University Press, Oxford, UK, 1961.
[6] J.A. Pople, The effect of quadrupolar relaxation on nuclear magnetic resonance multiplets, Mol. Phys. 1 (1958) 168–174.
[7] M. Suzuki, R. Kubo, Theoretical calculation of NMR spectral line shapes, Mol. Phys. 7 (1964) 201–209.
[8] N.C. Pyper, Theory of nuclear magnetic resonance line shapes for multispin system containing a single quadrupolar nucleus, Mol. Phys. 19 (1970) 161–167.
[9] V. Mlynarik, Measurement of spin coupling constants to quadrupolar nuclei via relaxation studies, Prog. NMR Spectrosc. 18 (1986) 277–305.

[10] W.P. Aue, J. Karhan, R.R. Ernst, Homonuclear broad band decoupling and two-dimensional J-resolved NMR spectroscopy, J. Chem. Phys. 64 (1976) 4226–4227.

[11] G. Bodenhausen, R. Freeman, G.A. Morris, D.L. Turner, NMR spectra of some simple spin systems studied by two-dimensional Fourier transformation of spin echoes, J. Magn. Reson. 31 (1978) 75–95.

[12] C. Griesinger, O.W. Sørensen, R.R. Ernst, Two-dimensional correlation of connected NMR transitions, J. Am. Chem. Soc. 107 (1985) 6394–6396.

[13] H. Oschkinat, A. Pastore, P. Pfändler, G. Bodenhausen, Two-dimensional correlation of directly and remotely connected transitions by z-filtered COSY, J. Magn. Reson. 69 (1986) 559–566.

[14] A.J. Shaka, R. Freeman, Simplification of NMR spectra by filtration through multiple-quantum coherences, J. Magn. Reson. 51 (1983) 169–173.

[15] U. Piantini, O.W. Sørensen, R.R. Ernst, Multiple quantum filters for elucidating NMR coupling networks, J. Am. Chem. Soc. 104 (1982) 6800–6801.

[16] J. Jeener, Ampere International Summer School, Basko Polje, Yugoslavia, 1971.

[17] W.P. Aue, E. Bartholdi, R.R. Ernst, Two-dimensional spectroscopy. Application to nuclear magnetic resonance, J. Chem. Phys. 64 (1976) 2229–2246.

[18] D. Reed, Applications of two-dimensional nuclear magnetic resonance for the boron chemist. A COSY study of some polyhedral boranes, J. Chem. Res. (1984) 198–199.

[19] T.L. Venable, W.C. Hutton, R.N. Grimes, Two-dimensional boron-11–boron-11 nuclear magnetic resonance spectroscopy as a probe of polyhedral structure: application to boron hydrides, carboranes, metallaboranes and metallacarboranes, J. Am. Chem. Soc. 106 (1984) 29–37.

[20] P.J. Domaille, The 1- and 2-dimensional tungsten-183 and vanadium-51 NMR characterization of isopolymetalates and heteropolymetalates, J. Am. Chem. Soc. 106 (1984) 7677–7687.

[21] T.L. Venable, W.C. Hutton, R.N. Grimes, Atom connectivities in polyhedral boranes elucidated via two-dimensional J-correlated boron-11-boron-11 FT NMR: a general method, J. Am. Chem. Soc. 104 (1982) 4716–4717.

[22] S. Hermanek, J. Fusek, B. Stibr, J. Plesek, T. Jelinek, Elucidation of structures of nido-y-CB_8 H_{12} and B_9 $H^-{}_{12}$ by two-diemnsional^{11} B-^{11} B NMR spectroscopy, Polyhedron 5 (1986) 1873–1879.

[23] G.B. Jacobsen, D.G. Meina, J.H. Morris, C. Thomson, S.J. Andrews, D. Reed, A.J. Welch, D.F. Gaines, Studies of 2,5;6,10;8,10-tri-μ-hydro-nonahydro-nonaborate(1$^-$), [B_9 H_{12}]$^-$: preparation, crystal and molecular structure, nuclear magnetic resonance spectra, electrochemistry and reactions, J. Chem. Soc. Dalton Trans. (1985) 1645–1654.

[24] X.L.R. Fontaine, H. Fowkes, N.N. Greenwood, J.D. Kennedy, M. Thornton-Pett, Pentamethylcyclopentadienylrhodaborane chemistry. Part 1. High-yield planned synthesis, molecular structure and nuclear magnetic resonance properties of the ten-vertex nido-6-rhodadecaborane [(η^5-C_5 Me_5)RhB_9 H_{13}], J. Chem. Soc. Dalton Trans. (1986) 547–552.

[25] X.L.R. Fontaine, H. Fowkes, N.N. Greenwood, J.D. Kennedy, M. Thornton-Pett, Pentamethylcyclopentadienylrhodaborane chemistry. Part 2. The reaction of [6-(η^5-C_5 Me_5)-nido-6-RhB_9 H_{13}] with dimethyl phenylphosphine and the characterization of [5-(η^5-C_5 Me_5)-nido-5-RhB_9 H_{11}-7-(PMe_2Ph)], [2-(η^5-C_5 Me_5)-closo-2-RhB_9 H_7-3,10-(PMe_2 Ph)$_2$], and [2-(η^5-C_5 Me_5)-nido-2-RhB_8 H_{10} -5-(PMe_2 Ph)] by X-ray diffraction analysis and nuclear m.agnetic resonance spectroscopy, J. Chem. Soc., Dalton Trans. (1987) 1431–1443.

[26] X.L.R. Fontaine, N.N. Greenwood, J.D. Kennedy, P. MacKinnon, Boron-11 and proton nuclear magnetic resonance study of anti-B_{18} H_{22} and its anions, anti-[B_{18} H_{21}]$^-$ and anti-[B_{18} H_{20}]$^{2-}$. The crystal and molecular structure of [NMe_4]$_2$ [anti-B_{18} H_{20}], J. Chem. Soc., Dalton Trans. (1988) 1785–1793.

[27] B.H. Goodreau, J.T. Spencer, Small heteroborane cluster systems. 5. Factors affecting the 2D^{11} B-^{11} B (boron-11) COSY NMR spectra of terminal- and bridge-substituted pentaborane cluster systems, Inorg. Chem. 31 (1992) 2612–2621.

[28] H. Günther, D. Moskau, R. Dujardin, A. Maercker, ^{6} Li-^{6} Li-COSY-a new tool for structure determinations of lithium organic compounds in solution, Tetrahedron Lett. 27 (1986) 2251–2254.

[29] H. Günther, D. Moskau, P. Bast, D. Schmalz, Modern NMR spectroscopy of organolithium compounds, Angew. Chem. Int. Ed. Engl. 26 (1987) 1212–1220.

[30] D. Moskau, W. Frankmölle, O. Eppers, H.-E. Mons, H. Günther, Homonuclear correlation experiments with quadrupolar nuclei, Proc. Indian Acad. Sci. 106 (1994) 1471–1480.

[31] D. Moskau D, H. Günther, 2H,2H-COSY and 2H,2H,13C-RELAY NMR experiments for the analysis of deuterated compounds, Angew. Chem. Int. Ed. Engl. 26 (1987) 156–157.

[32] P. Kempgens, J. Raya, K. Elbayed, P. Granger, J. Rosé, P. Braunstein, Theoretical study of two-dimensional COSY experiments for $S = 7/2$ spins: application to^{59} Co in the tetrahedral cluster $HFeCo_3$ $(CO)_{11}$ PPh_2 H, J. Magn. Reson. 142 (2000) 64–73.

[33] P. Kempgens, K. Elbayed, J. Raya, P. Granger, J. Rosé, P. Braunstein, Investigation of tetrahedral mixed-metal carbonyl clusters by two-dimensional^{59} Co COSY and DQFCOSY NMR experiments, Inorg. Chem. 45 (2006) 3378–3383.

[34] P. Braunstein, L.A. Oro, P.R. Raithby, Metal Clusters in Chemistry, vols. 1–3, Wiley-VCH, Weinheim, Germany, 1999.

[35] P. Braunstein, J. Rosé, Catalysis and related reactions with compounds containing heteronuclear metal–metal bonds, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, 2nd ed., Pergamon Press, Oxford, UK, 1995, vol. 10, Chap. 7, pp. 351–385.

[36] P. Braunstein, J. Rosé, Heterometallic clusters in catalysis, in: P. Braunstein, L.A. Oro, P.R. Raithby (Eds.), Metal Clusters in Chemistry, Wiley-VCH, Weinheim, Germany, 1999, vol. 2, pp. 616–677.

[37] P. Chini, L. Colli, M. Peraldo, Gazz. Chim. Ital. 90 (1960) 1005–1020.

[38] K. Elbayed, P. Kempgens, J. Raya, P. Granger, J. Rosé, Differential line broadening in the presence of quadrupolar-CSA interference, J. Magn. Reson. 130 (1998) 209–216.

[39] P. Kempgens, J. Hirschinger, K. Elbayed, J. Raya, P. Granger, J. Rosé, Multinuclear NMR Study of μ3-HFeCo3(CO)9[P(OCH3)3]3 in the solid state and in solution, J. Phys. Chem. 100 (1996) 2045–2052.

[40] P. Granger, K. Elbayed, J. Raya, P. Kempgens, J. Rosé, ^{31} P Differential line broadening in the presence of the^{59} Co quadrupolar-CSA interference in tetrahedral clusters, J. Magn. Reson. A 117 (1995) 179–185.

[41] P. Granger, T. Richert, K. Elbayed, P. Kempgens, J. Hirschinger, J. Raya, J. Rosé, P. Braunstein, Microdynamic motion of tetrahedral clusters studied by 59Co and 99Ru NMR relaxations, Mol. Phys. 92 (1997) 895–902.

[42] P. Kempgens, The COSY and DQF-COSY NMR spectra of an AX system of spins $I = 3/2$, Concepts Magn. Reson. Part A, in press.

[43] P. Kempgens, The theory of COSY NMR experiments revisited: application to an AX spin system of quadrupolar nuclei, Concepts Magn. Reson. Part A 36A (2010) 170–177.

[44] P. Kempgens, The theory of DQF-COSY NMR experiments. Part I: Amplitude modulation of the signal, Concepts Magn. Reson. Part A 36A (2010) 341–346.

[45] P. Kempgens, The theory of DQF-COSY NMR experiments. Part II: Phase modulation of the signal. A simple relationship between the coefficients needed to calculate the COSY and DQF-COSY NMR spectra of an AX spin system of quadrupolar nuclei, Concepts Magn. Reson. Part A 36A (2010) 394–399.

[46] C. Carpenter, P. Kempgens, J. Hirschinger, K. Elbayed, J. Raya, P. Granger, J. Rosé, in: 13th European Experimental NMR Conference, Paris, 1996.