Determination of the ^{17}O Quadrupolar Coupling Constant and of the ^{13}C Chemical Shielding Tensor Anisotropy of the CO Groups of Pentane-2,4-dione and β-Diketonate Complexes in Solution. NMR Relaxation Study

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^{13}C NMR relaxation times T_1 of the carbonyl groups of pentane-2,4-dione and β-diketonate complexes $Al(acac)_3$ and $Zr(acac)_4$ (acac: pentanedionate anion) were measured for various magnetic field strengths, allowing a determination of the contribution of the chemical shift anisotropy mechanism to the total relaxation. NOE and T_1 measurements for the ^{13}C nucleus of the central methine carbon furnished the correlation time τ_c for the reorientation of theses species. The chemical shift tensor anisotropy $\Delta\sigma$ could be deduced and compared to the values obtained in the solid state. The quadrupolar coupling constant (QCC) of the ^{17}O nucleus could also be determined by measuring the line width of the ^{17}O NMR signal and using the τ_c value. QCC values for the complexes are in the same range as for the pentane-2,4-dione molecule, indicating similar electronic distribution and symmetry around the oxygen atom of these different species. $\Delta\sigma$ for the complexes are close together, and the values obtained in solution are approximately those obtained in the solid state. They are close to the value reported in the literature for tetraacetylethane, which can be considered as a dimer of a β-diketone, but slight differences are observed for the individual components of the chemical shielding tensor.

Introduction

Many ligands are molecules which interact with metallic ions via oxygen atoms. Among them, β-diketonates and phosphorylated compounds can be mentioned. Study of the behavior, at the electronic level, of the C−O or P−O bonds when the ligand is coordinated to a cation compared to the situation where it is free can yield information on the electronic perturbation generated by the coordination. Further knowledge of these systems can be obtained by determining parameters sensitive to the electronic density and/or symmetry such as the quadrupolar coupling constant (QCC) of the ^{17}O nuclei, χ, and chemical shielding tensor anisotropy, $\Delta\sigma$, of the ^{13}C or ^{31}P nuclei. QCC is proportional to the electric field gradients and depends directly on the electronic charge symmetry around the nucleus. The components of the chemical shielding tensor are obviously related to the electronic environment of the nucleus under investigation. These two parameters can be obtained by the method we have reported in previous papers for phosphorylated compounds and their complexes;[1] QCC for the ^{17}O nucleus and $\Delta\sigma$ for the ^{31}P nucleus were determined in solution. The determination of χ and $\Delta\sigma$ requires a knowledge of τ_c, the reorientational correlation time of the molecule or of the complex, which can be obtained from a relaxation study of a rigid part of the species. $\Delta\sigma$ can be obtained only if the chemical shift anisotropy mechanism contributes significantly to the total relaxation rate; its determination requires measurements for different magnetic field strengths. This value can be compared to that obtained in the solid state when it is possible.

Several authors have also employed NMR longitudinal relaxation time measurements to estimate ^{17}O QCC and π-bond strengths in metal carbonyl complexes.[2,3] They used $\Delta\sigma$ values obtained from solid state experiments to calculate τ_c and extract $\chi(^{17}O)$.

In this paper we report a study of pentane-2,4-dione (acetylacetone), Hacac, and β-diketonate (acac) complexes of the Al(III) and Zr(IV) ions. T_1 relaxation times of the ^{13}C nuclei of the CO groups have been measured at three magnetic field strengths. T_1 and NOE factors for the central carbon were also determined. $\Delta\sigma(^{13}C)$ and $\chi(^{17}O)$ for the diketo and keto−enol forms of acetylacetone have been deduced and compared to the values obtained for the complexes. $\Delta\sigma$ values for the complexes were also measured from static NMR spectra recorded in the solid state and compared to the values obtained in solution. High-resolution solid state spectra were also recorded in order to confirm the crystallographic structure determination.

Complexes formed with cations of different valences were studied in order to determine if the charge of the cation influences the electronic repartition into the chelate ring of the β-diketonate moiety. The results were also compared to those obtained for the protonated ligand Hacac.

Experimental Section

Pentane-2,4-dione (Aldrich, 99+%), $Al(acac)_3$ (Aldrich, 99%), and $Zr(acac)_4$ (Aldrich, 98%) were used as received.

The solutions were prepared in $CDCl_3$ (Eurisotop) at a concentration of 33% in volume for Hacac, 0.5 mol·L^{-1} for $Al(acac)_3$, and 0.45 mol·L^{-1} for $Zr(acac)_4$.

^{13}C relaxation measurements were performed at 35 °C on WP 80 (B_0 = 1.88 T), AC 250 (B_0 = 5.88 T), CXP 300 (B_0 = 7.05 T), and

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DRX 400 (B_0 = 9.4 T) Bruker spectrometers at 20.1, 62.8, 75.5, and 100.6 MHz, respectively, using the inversion-recovery method with fast acquisition[4] or the so-called superfast method.[5] NOE factors were determined using the gated decoupling technique with frequency shift.[6] All the values given represent the average of several experiments (often at least three runs).

^{17}O NMR spectra were recorded for products in natural abundance at 54.2 MHz on a DRX 400 Bruker apparatus with a 10 mm probe. The relevant spectrometer parameters were as follows: 90° pulse duration, 19 μs; spectral width, 25 000 Hz; quadrature detection; acquisiton time, 41 ms; no field/frequency lock; sample spinning; recycling delay, 10 ms; number of scans >500 000; 2K data block with zero filling to 8K; line broadening factor of 30 Hz prior to Fourier transformation. All the chemical shifts were referenced to $H_2{}^{17}O$.

^{13}C NMR spectra in the solid state were recorded on a CXP 300 Bruker apparatus. The high-resolution spectra were obtained under magic angle spinning (4.5 kHz spinning frequency) and cross-polarization (CP) conditions with proton decoupling. The contact time was generally 1 ms, and the number of scans 500. In order to obtain the chemical shift tensor components, ^{13}C{^{1}H} static spectra were recorded, but a strong overlap between the CO and CH signals and a poor sensitivity due to a large anisotropy of the signals prevent easy extraction of these parameters. This is why the spectra were recorded under MAS conditions at a low spinning rate (~400 Hz). The CH signal was attenuated by a cross-polarization inversion sequence[7] with an additional phase inversion contact time (40−60 ms): under these conditions spectra present many rotational bands contained in an envelope that reproduces the static spectrum, but with a better signal-to-noise ratio (see Figure 1).

The 10 mm Hacac tube was degassed by the freeze and pump method and sealed under vacuum. For the two other solutions, oxygen was removed by inert gas bubbling into the tube.

Results and Discussion

Pentane-2,4-dione. This compound was studied in solution in deuteriated chloroform. Under these conditions, the molecule exists in two tautomeric forms: the diketone KK ($CH_3-CO-CH_2-CO-CH_3$) and the keto−enol KE ($CH_3-CO-CH{=}C(OH)-CH_3$) forms in a rough proportion of 1:3 at the temperature of the experiments (308 K). ^{13}C and ^{17}O NMR chemical shifts are similar to those already reported in the literature.[8,9] T_1 relaxation times and nuclear Overhauser enhancement (NOE) factors were measured at 75.47 MHz for the central carbon of the molecule, and it was verified that T_1 values do not depend on the field strength. For the CO groups, the T_1 values were measured at three frequencies (50.05, 75.47, and 100.6 MHz) and NOE factors at 75.47 MHz. ^{17}O NMR line widths were used to deduce the T_1 relaxation time of this nucleus. The results are summarized in Table 1.

It can be seen that T_1 values for the ^{13}C nuclei of CO groups depend on the field strength as a consequence of the efficiency of the chemical shift anisotropy (CSA) mechanism. This contribution to the total relaxation rate is expressed by[10]

$$T_{1,\mathrm{CSA}}{}^{-1} = {}^{2}/_{15}(\gamma B_0)^2(\Delta\sigma)^2(1 + \zeta^2/3)\tau_c \qquad (1)$$

for an isotropic motion under extreme narrowing limit conditions, where $\Delta\sigma = \sigma_{zz} - (\sigma_{xx} + \sigma_{yy})/2$, $\zeta = 3(\sigma_{yy} - \sigma_{xx})/(2\Delta\sigma)$, x, y, and z are the principal molecular axes of the shielding tensor, and τ_c is the reorientational correlation time of the species. This equation can be recast under the form

$$T_{1,\mathrm{CSA}}{}^{-1} = (8\pi^2/15)\nu^2(\Delta\sigma')^2\tau_c \qquad (2)$$

with ν the frequency and $\Delta\sigma' = \Delta\sigma(1 + \zeta^2/3)^{1/2}$.

Under the extreme narrowing limit conditions, this mechanism in the only one that depends on the frequency. Consequently it is possible to determine this contribution from the slope of the straight line $T_1{}^{-1} = f(\nu^2)$.

It was effectively verified that a straight line is obtained (correlation coefficient = 0.999 and 0.983 for the enol and ketone tautomers, respectively). The quantity $(\Delta\sigma')^2\tau_c$ is equal to 1.34×10^{-19} and 1.10×10^{-19} s for KE and KK, respectively. τ_c can be deduced from the dipole−dipole (DD) contribution to the total relaxation rate $T_1{}^{-1}$ of the central carbon:[10]

$$T_{1,\mathrm{DD}}{}^{-1} = \left(\frac{\mu_0}{4\pi}\right)^2\left(\frac{h}{2\pi}\right)^2\frac{\gamma_C{}^2\gamma_H{}^2}{r^6}N_H\tau_c = \frac{\eta}{\eta_0}T_1{}^{-1} \qquad (3)$$

where N_H is the number of hydrogen atoms bound to the considered carbon, r, the CH distance assumed to be 1.09×10^{-10} m as in the malonaldehyde molecule,[11] and η_0, the maximum NOE factor for ^{13}C−^{1}H interaction (η_0 = 1.99). τ_c is equal to 3.5×10^{-12} s for KE and to 2.3×10^{-12} s for KK, leading to $\Delta\sigma'$ = 195 and 219 ppm, respectively. These values can be compared to those reported for tetraacetylethane (TAE),[12] which consists of two acetylacetone residues, and acetone[13] from ^{13}C NMR studies in the solid state. The former compound exists in the keto−enol form in the crystal and gives rise to $\Delta\sigma'$ values equal to 176.3 and 163.9 ppm for the C=O and C−OH groups, respectively (mean value: 170.1 ppm). In solution, only one mean signal is observed for the two groups as a consequence of the existence of two symmetrical mesomers. The value obtained in solution (195 ppm) for Hacac is about 15% higher than that observed for TAE in the solid state. The same difference is observed for the KK form compared to acetone (219 against 194 ppm[13]), but in this case, the τ_c value used for the determination of $\Delta\sigma'$ is probably affected by internal rotations around the CH_2-CO bond (contrary to the KE form which is rigid); the correlation time for the reorientation of the C=O vector can be different from that of the C−H vectors of the CH_2 central group.

Table 1. ^{13}C and ^{17}O Chemical Shifts δ (ppm, Relative to TMS and H_2O, respectively), Line Widths at Half-Height of the ^{17}O Signal $\Delta\nu_{1/2}$ (Hz), Longitudinal Relaxation Times T_1 (s), and NOE Factors η for the Central Carbons and the Carbons of the CO Groups of Pentane-2,4-dione in $CDCl_3$ at 35 °C

		keto−enol form	diketone tautomer
$\delta(^{13}C)$	CH_3	24.1	30.0
	CH	100.0	58.0
	CO	191.0	201.7
$\delta(^{17}O)$		262	562
$\Delta\nu_{1/2}$		84.7	164.3
T_1(central carbon)		12.4	9.4
η(central carbon)		1.86	1.93
T_1(CO groups)	50.05 MHz	74.9	71.4
	75.47 MHz	63.7	66.2
	100.6 MHz	53.2	54.5
η(CO groups)	50.05 MHz	0.85	0.73
	75.47 MHz	0.84	0.71

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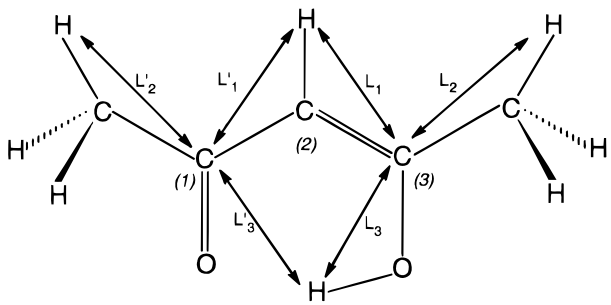
The measurement of the NOE factor for the CO groups allows us to calculate the dipole−dipole $^{13}C-^{1}H$ contribution to the total relaxation rate ($T_{1,DD}^{-1} = 6.2 \times 10^{-3}$ s $^{-1}$ for the keto−enol form, average value for two experiments at 50.05 and 75.47 MHz). The ^{13}C nuclei of the CO groups interact with the central hydrogen atom, the O−H hydrogen, and the hydrogen atoms of the methyl groups which are rapidly rotating around the H_3C-CO bond. $T_{1,DD}^{-1}$ can be computed according to

$$T_{1,DD}^{-1} = K\{\frac{1}{2}\left[\left(\frac{3}{L_2^6} + \frac{3}{L'^6_2}\right)J(\omega) + \left(\frac{1}{L_1^6} + \frac{1}{L_3^6} + \frac{1}{L'^6_1} + \frac{1}{L'^6_3}\right)\tau_c\right] \quad (4)$$

where L_1, L_2, L_3, L'_1, L'_2, and L'_3 are the distances defined in the following scheme



with $L_1 = 2.10$, $L_2 = 2.17$, $L_3 = 1.77$, $L'_1 = 2.17$, $L'_2 = 2.11$, and $L'_3 = 2.19$ Å as calculated from the crystallographic data[14] and $K = 3.6 \times 10^{-50}$ m^6 s^{-2}.

As only one CO carbon is observed, an average was obtained over the two theoretically computable T_1^{-1} values. $J(\omega)$ is the spectral density function for the dipole−dipole interaction with the CH_3 hydrogen nuclei:

$$J(\omega) = \frac{B_{00}}{6D_0} + \frac{B_{10}}{6D_0 + D_1} + \frac{B_{20}}{6D_0 + 4D_1} \quad (5)$$

where B_{00}, B_{10} and B_{20} are coefficients (squared reduced Wigner rotation matrix elements[15]) and D_0 and D_1, the isotropic diffusion constants related to the reorientation of the whole molecule and to the internal rotation.

$$B_{00} = {}^1/_4(3\cos^2\beta - 1)^2; \quad B_{10} = 3\sin^2\beta\cos^2\beta; \quad B_{20} = {}^3/_4\sin^4\beta$$

where β is the angle between the $C(O)-C(H_3)$ bond and the $C(O)-H_{CH_3}$ vector, estimated to 30°.

As $\tau_c = (6D_0)^{-1}$ $\tau_1 = (6D_1)^{-1}$ and $\rho = \tau_c/\tau_1$, eq 5 is recast in the form

$$J(\omega) = B_{00}\tau_c + B_{10}\frac{6\tau_c}{6+\rho} + B_{20}\frac{3\tau_c}{3+2\rho} \quad (6)$$

The calculation leads to $\rho \sim 13$. This value will further be useful to estimate $T_{1,DD}^{-1}$ for the CO groups in the complexes.

Finally it can be noted that the CSA and dipole−dipole mechanisms do not fully explain the relaxation behavior of the CO groups. At 75.47 MHz, for the keto−enol form, CSA and DD mechanisms contribute 26 and 42%, respectively, to the total relaxation rate. The remaining 32% are probably due to spin-rotation interactions.

Table 2. ^{13}C and ^{17}O NMR Chemical Shifts δ (ppm), Line-Widths at Half-Height of the ^{17}O NMR Signal $\Delta\nu_{1/2}$ (Hz), Longitudinal Relaxation Times T_1 (s), and NOE Factors η for the Central Carbons and the Carbons Belonging to the Carbonyl Groups of $Al(acac)_3$ and $Zr(acac)_4$ Complexes in $CDCl_3$ at 35 °C

		$Al(acac)_3$	$Zr(acac)_4$
$\delta(^{13}C)$	CH_3	29.4	26.3
	CH	100.7	101.9
	CO	191.0	188.1
$\delta(^{17}O)$		268	336
$\Delta\nu_{1/2}$		911	1097
T_1(central carbon)		1.10	0.94
η(central carbon)		1.83	1.89
T_1(carbonyl)		20.11 MHz: 18.1	20.11 MHz: 13.2
		75.47 MHz: 10.0	62.87 MHz: 9.9
		100.6 MHz: 8.1	100.6 MHz: 7.2
η(carbonyl)		0.6	not measured

From all these experiments, the quadrupolar coupling constant χ of the ^{17}O nucleus can be deduced. Indeed, quadrupolar relaxation $T_{1,Q}$ is predominant for this nucleus and is described by the equation[10]

$$T_{1,Q}^{-1} = T_{2,Q}^{-1} = \frac{3\pi^2}{10}\frac{2I+3}{I^2(2I-1)}\left(1 + \frac{\xi^2}{3}\right)\chi^2\tau_c \quad (7)$$

where $I = {}^5/_2$, ξ is the asymmetry parameter of the electric field gradient tensor ($0 < \xi < 1$), and τ_c is the reorientational correlation time. T_{1Q}^{-1} and T_{2Q}^{-1} are related to the signal line width by

$$T_{1Q}^{-1} = T_{2Q}^{-1} = \pi\,\Delta\nu_{1/2} \quad (8)$$

As ξ is not determined in our experiments, the following χ values are found: $7.9 < \chi < 9.1$ MHz for the keto−enol form and $13.3 < \chi < 15.4$ MHz for the keto−keto form. For the latter form, the value of χ is higher than those found for various ketones[16] ($\chi \sim 10.3-11$ MHz), probably for the same reasons as those given above in order to explain the difference between the $\Delta\sigma'$ values. The value corresponding to the keto−enol form is lower, comparable to those reported for aromatic OH groups.[16]

Complexes. ^{13}C and ^{17}O NMR chemical shifts were measured on $CDCl_3$ solutions of $Al(acac)_3$ and $Zr(acac)_4$. The values agree with those reported in the literature.[17,18] T_1 relaxation measurements were performed for the central methine carbon and the CO carbons (at several frequencies in the latter case) as well as NOE factor determinations. All the results are summarized in Table 2. T_1 of the CO carbons strongly depends on the frequency (CSA mechanism). The graph $T_1^{-1} = f(\nu^2)$ gives a linear plot, the slope of which provides the quantity $(\Delta\sigma')^2\tau_c$. The correlation time τ_c can be obtained from the T_1 and NOE values of the methine carbon (eq 3) allowing the determination of $\Delta\sigma'$ and χ, the QCC value of the ^{17}O nuclei, from eq 7. These values are reported in Table 3.

From Table 2, the $T_{1,DD}^{-1}$ contribution of the ^{13}CO group for $Al(acac)_3$ can be computed: $T_{1,DD}^{-1} = 0.038$ s^{-1}. This value can be also determined theoretically from the equation

$$T_{1,DD}^{-1} = K\left[\frac{3J'(\omega)}{L''^6_2} + \frac{\tau_c}{L''^6_1}\right] \quad (9)$$

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Table 3. Correlation Times τ_c, ^{17}O Quadrupolar Coupling Constants χ, and Anisotropies of the ^{13}C Chemical Shielding Tensors for the Complexes $Al(acac)_3$ and $Zr(acac)_4$ and for Acetylacetone, Hacac (Keto−Enol, First Line; Diketone Form, Second Line)

	$Al(acac)_3$	$Zr(acac)_4$	Hacac
$10^{12}\tau_c$, s	39[a]	47	3.5 2.3
χ, MHz	$7.6 < \chi < 8.8$	$7.6 < \chi < 8.8$	$7.9 < \chi < 9.1$ $13.3 < \chi < 15.4$
$\Delta\sigma'$,[b] ppm	186 ± 13	161 ± 12	195 ± 14 219 ± 16

[a] Detcher et al.[19] report a value of 4.5×10^{-11} s at 33.9 °C for the complex dissolved in toluene. [b] Propagated errors on $\Delta\sigma'$ were estimated at 7−8% at the maximum.

where $L''_2 = (L'_2 + L_2)/2$, $L''_1 = (L_1 + L'_1)/2$, and $\tau_c = 3.9 \times 10^{-11}$s. $J'(\omega)$ is calculated from eq 6 where B_{00}, B_{10}, and B_{20} are considered to be the same as the parameters for Hacac and $\rho \sim 150$, the τ_1 value for the rotation of the methyl groups being assumed to be the same in the complex as in the KE form of Hacac. The calculation leads to $T_{1,DD}^{-1} = 0.035$ s^{-1}, a value very close to that determined experimentally, indicating that the rotation of the methyl groups of the ligands is not much affected, compared to that of free Hacac.

It can be noted that the χ values are included in the same range for the complexes as for Hacac. As χ is related to the electric gradients around the oxygen nucleus, it can be concluded that the coordination of the enolate ligand to the Al^{3+} or Zr^{4+} cations does not induce a significant perturbation of the electronic distribution around the oxygen atom in comparison with that of Hacac in the keto−enol form. It must be also kept in mind that the complexes are neutral and that the ratio of the charge of the cation to the number of ligands is always 1. Hacac could also be considered as a cation H^+ coordinated to the enolate ligand; this could explain the fact that the χ values are similar.

In order to verify whether the $\Delta\sigma'$ values obtained in solution are identical to the values in the solid state, we carried out a ^{13}C NMR study on solid samples. We recorded static spectra in order to extract the different components of the chemical shielding tensor. Actually, as an overlap between the CH and CO bands occurs and as the sensitivity is poor due to the large anisotropy of the carbonyl chemical shift tensor, the spectra were recorded according to the MAS conditions at a low spinning rate (∼400 Hz), and with attenuation of the CH signal as described in the Experimental Section. Under these conditions, spectra, with many side spinning bands, contained in an envelope which reproduces the static spectrum, but with a better signal-to-noise ratio, are obtained (Figure 1). σ_{xx}, σ_{yy}, and σ_{zz} are easily determined, the knowledge of $\sigma_{iso} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$ allowing a more accurate determination, if necessary. The results are reported in Table 4 with those corresponding to TAE.[12] $\Delta\sigma'$, obtained in solution, is very close to $\Delta\sigma'$ in the solid state for both complexes (the divergence is less than 8%), indicating that the relaxation experiments at variable frequency to obtain $\Delta\sigma'$ are valid and can be useful when $\Delta\sigma'$ cannot be determined in the solid state (spectra with many overlapping bands, liquid sample, ...). The comparison with the results obtained for TAE (average value for the C=O and C−OH groups) leads to the conclusion that the $\Delta\sigma'$ values are very similar. Moreover $\Delta\sigma'$ for the complexes are closer for the KE form of Hacac in solution ($\Delta\sigma' = 195$ ppm) than for the KK tautomer ($\Delta\sigma' = 219$ ppm). This was already reflected by the isotropic ^{13}C chemical shifts of the complexes in solution which are very similar to those of the KE form of Hacac.

Nevertheless, if the σ_{ii} values are observed in detail, a significant difference in the σ_{yy} values of TAE and the complexes can be noted. According to ref 9, the *y* direction corresponds to the C_2-C_3 or C_2-C_1 direction (see scheme). The σ_{yy} value for the complexes is closer to that of the COH carbon than to that of the CO carbon of TAE. This could be due either to a slight perturbation into the electronic distribution of complexes relatively to that of the protonated ligand (actually TAE) or to the variation in the geometry of the chelate ring (the angles OCC are larger in the complexes than in Hacac[20−22]).

The differences between the two complexes are very small, probably for the same reason as that given above for the χ values.

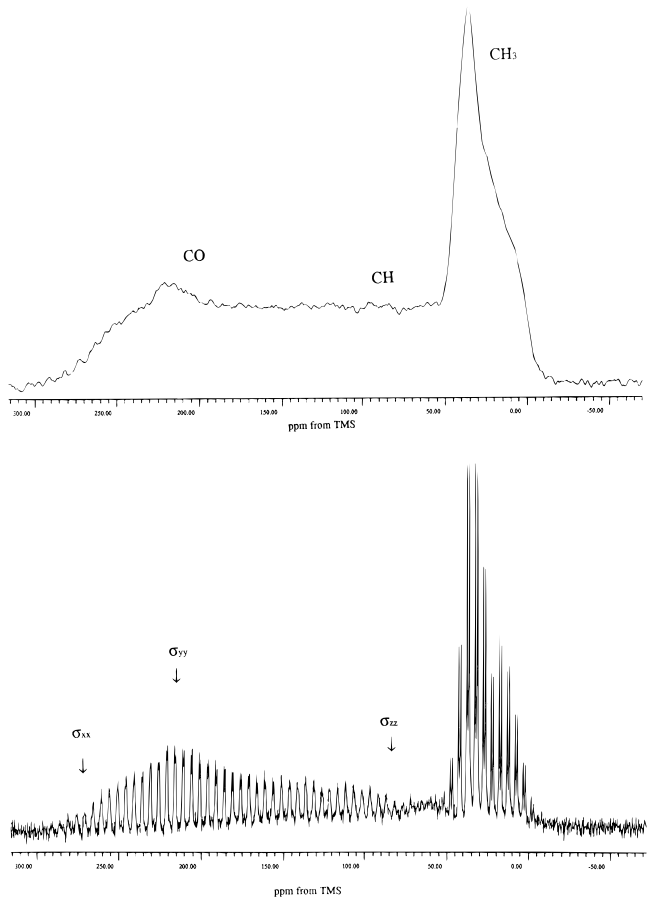

Figure 1. $^{13}C\{^1H\}$ NMR spectra of the solid complex $Al(acac)_3$: top, static spectrum; bottom, spectrum recorded with a low spinning frequency (375 Hz). The CH signal has been attenuated by using an appropriate pulse sequence (see text).

Table 4. Isotropic Chemical Shifts σ_{iso}, Principal Components of the Chemical Shift Tensors, σ_{xx}, σ_{yy}, and σ_{zz}, Anisotropies of the Chemical Shift Tensors $\Delta\sigma$, Asymmetry Parameters of the Shielding Tensors ζ, $\Delta\sigma' = \Delta\sigma(1 + \zeta^2/3)^{1/2}$, and $\Delta\sigma'$ Values Obtained in Solution ($\Delta\sigma'_{sol}$) for the Complexes $Al(acac)_3$ and $Zr(acac)_4$ and for Tetraacetylethane TAE[12]

			TAE		
	$Al(acac)_3$	$Zr(acac)_4$	C=O	C−OH	av
σ_{iso}, ppm	191.1	188	200.9	190.6	195.7
σ_{xx}, ppm	276	273	277.6	270.0	273.8
σ_{yy}, ppm	215	210	239.7	215.9	227.8
σ_{zz}, ppm	82	81	85.4	85.9	85.6
$\Delta\sigma$, ppm	164	160	173.3	157.1	165.2
ζ	0.56	0.59	0.328	0.517	
$\Delta\sigma'$, ppm	172	169	176.3	163.9	170.1
$\Delta\sigma'_{sol}$, ppm	186	161			

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Finally high-resolution ^{13}C NMR spectra of the solid complexes $Al(acac)_3$ and $Zr(acac)_4$ are in full agreement with the crystallographic structures. For $Zr(acac)_4$, three signals are observed for the CO group (one is twice higher than the others), two for CH, and three for the methyl groups when the crystallographic data[20] indicate that there are four inequivalent CO groups, two CH groups, and four CH_3 groups according to the cell symmetry. The crystal structure of $Al(acac)_3$[22] indicates six inequivalent CO groups, three CH groups, and six CH_3 groups; the NMR spectrum exhibits only two, three, and two signals for the CO, CH, and CH_3, groups respectively.

Conclusion

This study shows clearly that much information can be obtained from the determination of quadrupolar coupling constants or chemical shielding tensor anisotropy in complexes. Variation in electronic distribution can be detected relative to the situation of the free ligand. Measurements on nuclei, the relaxation of which depends on the chemical shift anisotropy mechanism, allow the determination of $\Delta\sigma$ in solution which can be compared to the value obtained for the solid.

In the case of β-diketonate complexes, we have shown that there is no large difference between their ^{17}O QCC and $\Delta\sigma$ values and those of Hacac. The charge of the cation has little influence probably because the total charge of the complexes is zero. Hacac could be considered as an ion H^+ interacting with the enolate anion. We attempted to extend our study to complexes with monovalent (K^+) or divalent (Mg^{2+}) cations, but our efforts failed because of the low solubility of the species and/or the difficulty in obtaining compounds with a well-defined stoichiometry.

This work is the starting point of structural studies on molecules having CO groups (amides, amino acids, peptides, ...) which potentially interact with acids or metal ions, for instance. The evolution of the structural parameters χ and $\Delta\sigma$ as functions of this interaction may yield much information regarding its nature (electrostatic character, covalency, ...).

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