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Complexes of EDTA in aqueous solutions. Structural aspects from a ^{13}C NMR relaxation study

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^{13}C NMR relaxation times T_1 of the carboxylate groups in EDTA and its complexes with Mg(II), Ca(II), Zn(II) and Al(III) ions in aqueous solutions were measured at different magnetic field strengths, allowing the determination of the contribution of the chemical shift anisotropy mechanism to the total relaxation rate and, consequently, the shielding tensor (chemical shift) anisotropy of these nuclei. A discussion of these values in relation to the possible structure of these species in solution and a comparison with the values obtained in the solid state were performed.

Introduction

Polyaminocarboxylate anions and, particularly, ethylenediaminetetraacetate ion ($EDTA^{4-}$) are very efficient complexing agents and are widely used in analytical chemistry as well as for applications which require a sequestering species.

EDTA complexes have been studied in the solid state, in particular by X-ray diffraction measurements[1,2] and by ^{13}C NMR.[3,4] From crystallographic studies, the coordination sphere of the metal ion is well known and, consequently, the coordination sites of the Y^{4-} ion are determined. Unfortunately, the complex structure in solution and the nature of the interactions between cations and EDTA are not yet comprehensively determined, even if it is accepted that the bonds with the carboxylate groups are essentially ionic and that those with the nitrogen atoms are rather covalent.[3] It is sometimes wondered whether EDTA acts as a penta- or a hexa-dentate ligand. A number of spectroscopic studies (NMR, IR...) have been performed in solution, showing the diversity of situations according to the different complexes, and leaving some questions unanswered.[5–8]

NMR chemical shift measurements are a means of enquiring about the perturbation induced by complexation on different ligand nuclei, but the obtained information is often only qualitative since the chemical shift represents the trace of the shielding tensor. The principal components of this tensor may be determined in the solid state. In solution, the shielding tensor ("chemical shift") anisotropy $\Delta\sigma$ can be obtained *via* T_1 relaxation measurements when the relaxation mechanism due to the chemical shift anisotropy (CSA) is efficient; in this case, experiments at different frequencies (more precisely for various magnetic field strengths) are needed to deduce the $\Delta\sigma$ value. The environment of the carbon nuclei in the CO groups is very anisotropic ($\Delta\sigma > 100$ ppm) and the relaxation of these nuclei, particularly for high magnetic fields, is partially governed by the CSA mechanism. Obtaining $\Delta\sigma$ values in solution represents further information on the local structure and on the chemical environment of the CO groups. The $\Delta\sigma$ values in solution can be compared to the values obtained in the solid state in order to see if the structure of the coordination sphere is different.[9–11]

In this paper, ^{13}C NMR relaxation measurements on the carbon nuclei of the EDTA carboxylate groups and some of its complexes with Mg(II), Ca(II), Zn(II) and Al(III) are presented. They were performed in aqueous solutions at different frequencies, enabling the CSA contribution to the total relaxation rate to be deduced and, therefore, the chemical shift anisotropy (corrected by the asymmetry factor). A discussion of the obtained values and a comparison with the values determined in the solid state were carried out.

Preliminary results for EDTA, which have been revised in this work, were reported earlier.[12]

Experimental

Aqueous solutions of EDTA were made with ethylenediaminetetraacetic acid disodium salt dihydrate from Fluka (>99%). This salt was also used for static ^{13}C NMR spectra. The pH was fixed to 12 (0.2 mol L^{-1} solutions) in order to work with the fully deprotonated form.

Ethylenediaminetetraacetic acid, magnesium disodium salt hydrate (Fluka, puriss p.a.) and ethylenediaminetetraacetic acid, calcium disodium salt hydrate (Aldrich, 98%) were used without further purification for the static ^{13}C NMR spectra and for the preparation of aqueous solutions of the MgY^{2-} and CaY^{2-} complexes; the concentration of the solutions were 0.2 mol L^{-1} and pH = 9.7. The full complexation of Mg(II) and Ca(II) ions was monitored using Eriochrome Black T as a coloured indicator.

The NMR studies of Al–EDTA and Zn–EDTA complexes were made simultaneously on the same aqueous solutions prepared with 0.1 mol L^{-1} $AlCl_3$ (Fluka, >99%) in the presence of excess EDTA (0.2 mol L^{-1}) which was titrated with Zn^{2+} ion (final concentration: 0.1 mol L^{-1}), using an identical procedure as that employed for the standard titration of aluminium(III) by EDTA (acetate buffer, pH = 5.1).

All aqueous solutions were prepared in D_2O and the pH was adjusted with NaOH.

^{13}C NMR relaxation measurements were performed at 25 °C on Bruker 200 MHz ($B_0 = 4.7$ T), AC 250 ($B_0 = 5.88$ T), CXP 300 ($B_0 = 7.05$ T) and DRX 400 ($B_0 = 9.4$ T) spectrometers at 50.3, 62.8, 75.5 and 100.6 MHz, respectively, using either the fast acquisition inversion–recovery method[13] or the so-called superfast method.[14] Non-linear least-squares procedures (exponential regression) were used for the analysis of T_1 measurements. The NOE factors were determined at 100.6 MHz by setting the decoupler on-resonance and far off-resonance in successive experiments.[15] The solutions were degassed by bubbling inert gas into the NMR tube.

^{13}C NMR static spectra on solid samples were recorded at 75.5 MHz on a Bruker CXP 300 apparatus under CP con-

Table 1 Longitudinal relaxation times T_1 and nuclear Overhauser effects η_{NOE} of the different ^{13}C nuclei of EDTA (Y^{4-}) and some of its complexes (lateral $CH_2 = CH_2N(CH_2CO_2)_2$, central $CH_2 = CH_2N(CH_2CO_2)_2$

		Y^{4-}	MgY^{2-}	CaY^{2-}	ZnY^{2-}	AlY^{-}
$T_1(CO_2)$/s	50.1 MHz	10.8	10.9	—	—	—
	62.9 MHz	9.3	10.6	7.6	11.9	—
	75.5 MHz	9.3	9.2	7.2	10.7	9.9
	100.6 MHz	6.9	7.4	5.4	9.0	7.0
$\eta_{NOE}(CO_2)$	100.6 MHz	0.86	0.92	0.86	1.02	0.86
$T_1(CH_2)$/s	Lateral CH_2 (100.6 MHz)	0.34	0.42	0.28	0.41	0.36
	Central CH_2 (100.6 MHz)	0.27	0.35	0.24	0.37	0.32
$\eta_{NOE}(CH_2)$	Lateral CH_2 (100.6 MHz)	1.83	1.91	1.97	1.97	1.86
	Central CH_2 (100.6 MHz)	1.76	1.87	1.70	1.82	1.95

ditions (contact time: 1 ms, relaxation delay: 5 s) with ≈25000 scans and a spectral width of 23 kHz (300 ppm).

^{13}C CP/MAS NMR spectra were measured on the same spectrometer at a spinning speed of ≈4.5 kHz.

The components of the chemical shift tensor were designated as δ_{11}, δ_{22} and δ_{33} with $\delta_{11} > \delta_{22} > \delta_{33}$. The chemical shift anisotropy $\Delta\delta$ and the asymmetry parameter η were calculated as follows.

As $\delta = 10^6(\sigma_{ref} - \sigma)$ (σ_{ref}: screening coefficient of the reference with respect to which the chemical shifts are measured) and as $\sigma_{33} > \sigma_{22} > \sigma_{11}$, the value of $\Delta\sigma$ (in ppm) is identical with that of $\Delta\delta$.

Results and discussion

The relaxation times T_1 of the ^{13}C nuclei of the CO_2 groups have been measured, as a function of the magnetic field B_0, for EDTA and its complexes with the cations Mg^{2+}, Ca^{2+}, Zn^{2+} and Al^{3+} (Table 1). As expected, the T_1 values depend on B_0 as a consequence of the chemical shift anisotropy (CSA) mechanism contribution to the total relaxation rate. The nuclear Overhauser effect (NOE) has also been measured and the part played by the ^{13}C–^1H dipole–dipole relaxation mechanism in the total relaxation rate was determined.

The relaxation rate due to the CSA mechanism is given by eqn. (1), under the extreme narrowing conditions:[16]

$$T_{1,CSA}^{-1} = \frac{8\pi^2}{15}\nu^2\Delta\sigma^2\left(1+\frac{\eta^2}{3}\right)\tau_c \qquad (1)$$

where ν is the frequency ($2\pi\nu = \gamma B_o$); $\Delta\sigma$, the anisotropy of the shielding tensor; τ_c, the correlation time corresponding to the reorientation of the principal axis of the shielding tensor and η, the asymmetry parameter of this tensor.

$$\text{We note: } \Delta\sigma' = \Delta\sigma\left(1+\frac{\eta^2}{3}\right)^{1/2}$$

Under the extreme narrowing condition, this mechanism is the only one which depends on the frequency. The plot of $T_{1,CSA}^{-1} = f(\nu^2)$ must be a straight line, the slope of which allows the determination of the $\Delta\sigma'^2\tau_c$ term. The corresponding plots are shown in Fig. 1.

The $T_{1,CSA}^{-1}$ contribution to the total relaxation rate can be also deduced at each frequency. The $T_{1,DD}^{-1}$ contribution is also known from the NOE measurements. These values corresponding to the measurements at 100.6 MHz are reported in Table 2 where it can be seen that these two contributions represent about 90% of the total relaxation rate for Mg(II), Ca(II) and Zn(II) complexes. As concerns the Al(III) complex, the measurements are less accurate since only two points enabled the determination of the CSA contribution to the total relaxation process; a broad peak for the carboxylate carbon was observed, leading to a poorer signal to noise ratio than that obtained for the other systems. The set of the total percentages of the CSA and the DD contributions for all the studied systems (90–110%) is situated in the area of the error range expected for such measurements (see below).

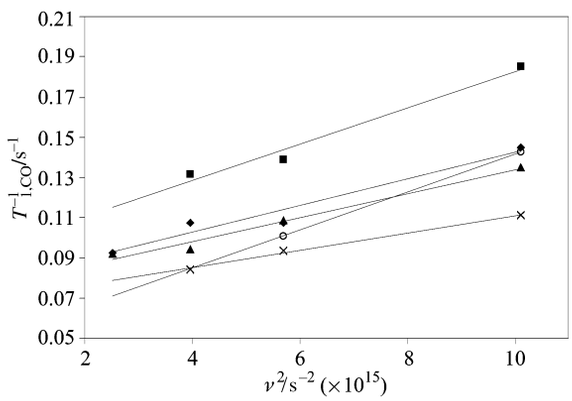

Fig. 1 Relaxation rate T_1^{-1} of the CO_2 groups in EDTA, free or complexed, as a function of ν^2 (ν, the frequency) (◆ Y^{4-}, ▲ MgY^{2-}, ■ CaY^{2-}, × ZnY^{2-}, ○ AlY^{-}).

Values of τ_c can be obtained from the relaxation times T_1 and the NOE factors η_{NOE} of the CH_2 groups of the EDTA ion which give the dipole–dipole contribution to the total relaxation time, eqn. (2):

$$T_{1,DD}^{-1} = \frac{\eta_{NOE}}{\eta_{NOE}^{o}}T_1^{-1}\ (\eta_{NOE}^{o} = 1.987)$$
$$\text{and } T_{1,DD}^{-1} = \left(\frac{\mu_o}{4\pi}\right)^2\left(\frac{h}{2\pi}\right)^2 N_H\frac{\gamma_c^2\gamma_H^2}{r_{CH}^6}\tau_c \qquad (2)$$

where γ_H and γ_c are the gyromagnetic ratios of the ^1H and ^{13}C nuclei, respectively; N_H the number of hydrogen nuclei bound to the carbon atom and r_{CH} the length of the ^{13}C–^1H vector. All these quantities are known ($r_{CH} = 1.09 \times 10^{-10}$ m) and τ_c can be computed from eqn. (2). If it is assumed that the reorientation of the ^{13}C–^1H vector and that of the principal axis of the shielding tensor are the same, the value of τ_c can be used to determine $\Delta\sigma'$. This assumption is plausible for the complexes in which the internal motions in the EDTA ion are probably blocked (or considerably slowed down) because of the coordination of the oxygen and nitrogen atoms to the cation. There are two types of CH_2 groups, and $\Delta\sigma'$ was calculated from the mean τ_c value. The results are summarized in Table 3. It can be easily verified, from the τ_c values obtained for the different complexes, that the assumption of the extreme narrowing condition: $\omega^2\tau_c^2 << 1$ where $\omega = \omega_c$, $\omega_c + \omega_H$ or $\omega_H - \omega_c$ for the dipole–dipole relaxation mechanims and $\omega = \omega_c$ for the CSA mechanisms, was correct.

As T_1 values can be presumed to be measured with an accuracy of ± 5%, the error in $\Delta\sigma'$ values can be evaluated to 7–8%.

The τ_c values obtained for the two kinds of CH_2 groups are very similar indicating that the reorientation of the EDTA ion and of the complexes is isotropic.

It should be noted that the τ_c value for the Al^{3+} complex is of the same order of magnitude as that obtained for the other complexes, suggesting that this complex is monomeric and not dimeric as sometimes suggested.[17]

Table 2 Relaxation rates T_1^{-1} for the ^{13}C nucleus in the CO group of EDTA and some of its complexes and the different contributions to the total relaxation rate at 100.6 MHz; $T_{1,CSA}^{-1}$, the shielding anisotropy contribution, $T_{1,DD}^{-1}$, the ^{1}H–^{13}C dipole–dipole contribution (percentage of these contributions in parentheses)

	T_1^{-1}/s^{-1}	$T_{1,CSA}^{-1}/s^{-1}$	$T_{1,DD}^{-1}/s^{-1}$
Y^{4-}	14.4×10^{-2}	6.5×10^{-2} (45%)	6.2×10^{-2} (43%)
MgY^{2-}	13.5×10^{-2}	6.1×10^{-2} (45%)	6.3×10^{-2} (47%)
CaY^{2-}	18.5×10^{-2}	9.2×10^{-2} (50%)	8.2×10^{-2} (43%)
ZnY^{2-}	11.1×10^{-2}	4.3×10^{-2} (39%)	5.7×10^{-2} (51%)
AlY^{-}	14.3×10^{-2}	9.6×10^{-2} (67%)	6.2×10^{-2} (43%)

The $\Delta\sigma'$ values obtained for the Mg^{2+} and Ca^{2+} complexes are very similar and slightly higher than that obtained for the Y^{4-} ion.

This result suggests that the coordination of EDTA to Mg^{2+} and Ca^{2+} ions does not greatly perturb the electronic distribution around the carbon nucleus in the carboxylic groups, contrary to what was observed for the ^{31}P nucleus in the phosphoryl bond for phosphine oxide complexes.[18] In the case of the carboxylic group, there are two oxygen atoms which interact with the ion (although it is likely that only one is coordinated at a given time), which probably undergo a rapid exchange. This leads to a weaker electronic perturbation than for a P=O bond which has only one interacting oxygen. Moreover, for the Mg^{2+} complex, its study in the solid state showed that the O–Mg^{2+} distances are relatively long[2] (partially explaining the relatively low value obtained for the stability constant, log $K = 8.7$, compared to that of the calcium salt, log $K = 10.7$).[19] This explains the weak perturbations undergone by the carbon nuclei. For the Ca^{2+} complex, which presents a high stability constant, the Ca^{2+} ion is more adapted than the Mg^{2+} ion to the geometrical constraints due to the multidentate character of the EDTA ion. However, its larger size (0.99×10^{-10} m *cf.* 0.66×10^{-10} m for the Mg^{2+} ion)[20] gives rise to a weaker charge density and, consequently, a weaker electric field on the oxygen atom than would the Mg^{2+} ion at equivalent distances.

The $\Delta\sigma'$ values for the Al^{3+} and Zn^{2+} complexes are appreciably different from the other values. These two complexes are more stable (log $K = 16.1$ and 16.5 for the Al and Zn complexes, respectively)[19] than the others. In the case of the Zn^{2+} ion, this is probably due to a good adaptation to the size of the chelate ring, as already noted[2] for Mn(II) compared to Mg(II) (the ionic radii and the stability constants of some complexes are summarized in Table 4). This situation leads to a favourable interaction between this ion and EDTA, which is reflected by a modification of the electronic environment of the carbon atom, which triggers change in the $\Delta\sigma'$ value.

The $\Delta\sigma'$ value of the Al(III)–EDTA complex is noticeably higher than the other values. The charge of this ion and its small size should induce a stronger perturbation than in the case of the other ions for complexes with similar structures. Whereas $\Delta\sigma'$ of the ZnY^{2-} complex is lower than that of the AlY^{-} complex, its larger value compared to those of the EDTA complexes of Mg(II) and Ca(II), could mean that the structure of the AlY^{-} complex is different from the three others, as already mentioned by Sawyer and Tackett[17] who suggested as a possible structure $Al(HY)(OH)^{-}$. The existence of a protonated carboxylate group among the four groups, which would give only a mean resonance in the NMR spectra, should have some consequences on the shielding tensor of the carbon-13 nuclei.

Table 4 Ionic radii r of the studied ions and of the Mn^{2+} ion and their stability constants K with EDTA (20 °C, ionic strength: 0.1 mol L^{-1})

	r/Å[20]	log K[19]
Al^{3+}	0.51	16.1
Mg^{2+}	0.66	8.7
Zn^{2+}	0.74	16.5
Ca^{2+}	0.99	10.7
Mn^{2+}	0.80	13.8

At this stage, it is not known whether the anisotropy of the shielding tensor determined in solution differs from that in the solid state. With this in mind, we compared the values obtained in solution (this work) with both those determined from ^{13}C NMR static spectra on the following solid samples: H_2Y^{2-},$2Na^{+}$ CaY^{2-},$2Na^{+}$ and MgY^{2-},$2Na^{+}$ and those obtained by Alam *et al.*[4] Experiments on solid samples allows the determination of the principal components of the shielding tensor and, from these values, $\Delta\sigma$, η and $\Delta\sigma'$ were deduced. The results are shown in Table 5; they are limited to the observation of the carbon-13 nuclei of the carboxylate groups.

Alam *et al.*[4] performed shielding tensor analysis by computer simulation of the spinning side bands in the spectra recorded with a low spinning speed. In our case the δ_{xx} values have been directly read on the static spectra. Examples of such spectra are shown in Fig. 2. There is no particular problem with the compound H_2Y^{2+},$2Na^{+}$, as the carboxylate groups give only one signal. For the Mg(II) and Ca(II) complexes, three different signals are observed in the CP-MAS high resolution spectra for the CO_2^{-} groups in the intensity ratio 1 : 0.5 due to either the presence of different independent crystallographic sites in the unit cell (for instance, $Z = 2$ for the Mg(II) complex)[2] or the inequivalence of the carboxylate groups in the solid complex (for the MgY^{2-},$2Na^{+}$ complex, two long and two short Mg–O bonds are observed),[2] as already reported by Alam *et al.*[4] It should be noted that we obtained high-resolution NMR spectra of the solid complexes similar to those reported in ref. 4 and different from those previously reported.[3] The presence of three resonances (close together within a range of 2.5 ppm) do not significantly affect the measurements of the principal components on the static spectra. For instance, the shape of the signal around the δ_{22} value does not show the presence of several bands (Fig. 2). This can also be concluded from the results which were previously reported[4] on the same complexes and also from a study on glycine crystals which showed that the principal values of the shielding tensor of the carboxylate groups of the two independent molecules in the unit cell do not differ much from each other.[21]

In Table 5 it can be seen that the δ_{11} and δ_{33} components are very similar for the three species. A difference in the δ_{22} values is noted between H_2Y^{2-},$2Na^{+}$ on the one hand and the other two complexes on the other (about 20 ppm). The $\Delta\sigma'$ values are nevertheless very similar, indicating that the difference in the electrostatic interactions between the various ions and the

Table 3 Dipole–dipole contribution $T_{1,DD}^{-1}$ to the total relaxation rate of the CH_2 carbons, correlation time of reorientation of the C–H vectors in EDTA and in some of its complexes (τ_c) and $\Delta\sigma'$ values for the ^{13}C nucleus of the carboxylate group, calculated from the mean τ_c value (arithmetic average of the two τ_c values)

		Y^{4-}	MgY^{2-}	CaY^{2-}	ZnY^{2-}	AlY^{-}
$T_{1,DD}^{-1}/s^{-1}$	Lateral CH_2	2.7	2.3	3.5	2.4	2.6
	Central CH_2	3.2	2.7	3.6	2.5	3.0
τ_c/ps	Lateral CH_2	64	53	82	57	60
	Central CH_2	75	62	84	58	70
$\Delta\sigma'$/ppm		132	141	144	119	165

Table 5 ^{13}C isotropic chemical shift δ_{iso} of the CO_2^- groups (with respect to TMS), principal values of the shielding tensor, δ_{11}, δ_{22} and δ_{33} (with respect to TMS), chemical shift anisotropy $\Delta\delta$, asymmetry parameter η and $\Delta\delta' = \Delta\delta\ (1 + \eta^2/3)^{1/2}$ for EDTA and its Mg(II) and Ca(II) complexes in the solid state

	$H_2Y^{2-},2Na^+$	$MgY^{2-},2Na^+$	$CaY^{2-},2Na^+$
δ_{iso}/ppm	173.0	178.7, 180.1, 180.9	177.3, 178.8, 179.7
δ_{11}/ppm	245 (246)[a]	239 (235, 239, 237)[a]	246 (240)[a]
δ_{22}/ppm	167 (167)[a]	191 (190, 190, 195)[a]	187 (188)[a]
δ_{33}/ppm	108 (104)[a]	108 (108, 110, 107)[a]	110 (110)[a]
$\Delta\sigma$/ppm	107 (110)[b]	107 (104, 104, 110)[b]	106(104)[b]
η	0.82 (0.85)[b]	0.67 (0.65, 0.70, 0.55)[b]	0.83 (0.75)[b]
$\Delta\delta'$/ppm	119 (123)[b]	115 (112, 113, 115)[b]	118 (113)[b]

[a] Values from the literature.[4] [b] Values calculated from the literature results.[4]

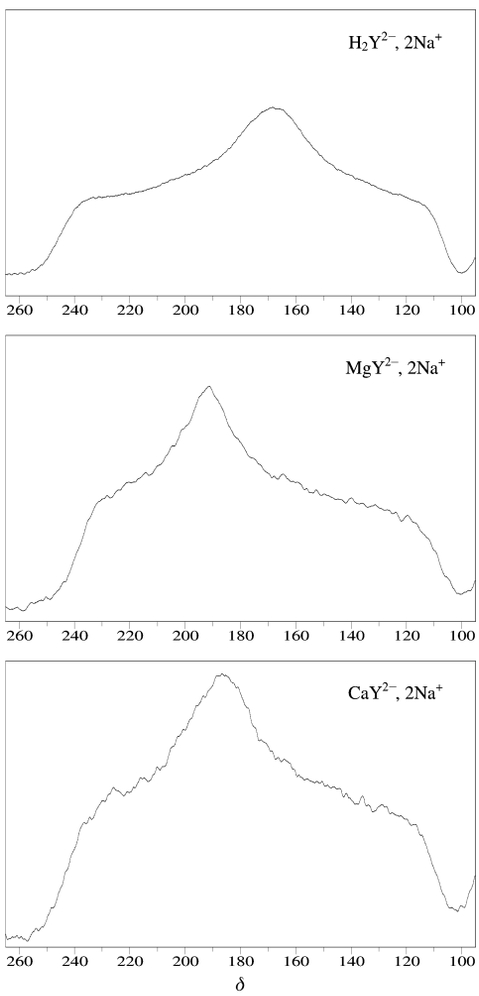

Fig. 2 ^{13}C CP-NMR static spectra of the solid samples, $H_2Y^{2-},2Na^+$; $MgY^{2-},2Na^+$ and $CaY^{2-},2Na^+$ at 75.5 MHz (signals of carboxylic groups only).

carboxylate groups has little influence on the electronic surrounding of the carbon atoms of the carboxylate groups (for H_2Y^{2-}, the nitrogen atoms are protonated and all the carboxylate groups are ionized).

The $\Delta\sigma'$ values obtained in the solid state are noticeably smaller than those determined in aqueous solutions, this being more so for the complexes (≈25 ppm). This could be due to the fact that, in the solid, the Na^+ ions are close to the oxygen of the carboxylate group whereas, in solution, they are solvated by water molecules and more "separated" from the counter ions. As generally considered, if the interactions between the carboxylate groups and the metallic ions are essentially electrostatic in character, the CO_2^- groups are subjected to the charge of a M^{2+} cation and two Na^+ cations in the solid state but are only under the direct influence of the M^{2+} cation in solution.

Conclusion

Contrary to what was observed for the phosphorus atom in the phosphoryl bond in the case of the phosphine oxide ligands and its complexes,[18] the chemical shift anisotropy of the carboxylate groups is not very different for the calcium(II) and magnesium(II) EDTA complexes in aqueous solutions, compared to that observed for free EDTA (sodium salt dissolved in water). A noticeable difference exists for this parameter between solid samples and the corresponding complexes dissolved in aqueous solutions. The shielding tensor of the carbon-13 nuclei in the carboxylic group seems to be less sensitive to the variations in the local structure and chemical environment than expected, as already noted for acetylacetonate complexes.[11]

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