

¹³C Solid State CP/MAS NMR Studies of EDTA Complexes

SILVIO AIME*, ROBERTO GOBETTO, RITA NANO and ENRICA SANTUCCI

Istituto di Chimica Generale ed Inorganica dell'Università, Corso Massimo d'Azeglio 48, 10125 Turin, Italy

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Since the pioneering work of Schwarzenbach [1] and coworkers on the chelating properties of polyaminocarboxylate complexes, a huge number of papers concerning their applications in different areas of chemical research have appeared in the literature. Although many solid-state structures of these complexes have been elucidated by X-ray diffraction analysis [2], several important features concerning their dynamics and solution structures are not yet fully understood.

¹H NMR spectroscopy as well as other techniques [3] have shown that in solution the EDTA anions act mainly as penta- or sexadentate ligands toward metallic ions forming essentially ionic bonds with the four oxygens of the carboxylate groups and rather covalent bonds with the nitrogens.

Now, the availability of spectrometers operating in Cross Polarization/Magic Angle Spinning (CP/MAS Mode) allows the observation of high resolution spectra of solid samples [4], providing then a powerful bridge between solid state structures determined by diffraction techniques and solution structures proposed by several methods, primarily NMR spectroscopy.

*Author to whom correspondence should be addressed.

TABLE I. ¹³C NMR Spectral Data

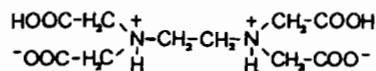
	COO ⁻	COOH	Acetate CH ₂	Ethylenic CH ₂
H ₄ -EDTA	174.8	168.8	61.3 58.5	53.4
Na ₂ H ₂ -EDTA	172.6 (169.7) ^a	170.9	61.5 (57.1) ^a	52.8 (50.6) ^a
Na ₄ -EDTA	181.3 180.5 (180.5) ^a		65.4 (59.9) ^a 63.0	54.3 (53.0) ^a
Na ₂ [Mg-EDTA]	179.2 (178.2) ^a		^b (60.0) ^a	^b (54.3) ^a
Na ₂ [Ca-EDTA]	180.7 178.9 (180.8) ^a		60.4 (61.9) ^a 57.8	51.2 (55.9) ^a
Na[La-EDTA]	179.5 (180.9) ^a		62.3 (62.9) ^a 57.7	52.1 (55.6) ^a

^aChemical shifts obtained from 0.1 M aqueous solutions. ^bAs shown in the trace (d) of Fig. 1, a broad featureless absorption at 62–57 ppm is observed for the CH₂ resonances in this complex.

Results and Discussion

In this note we report some preliminary results concerning the solid-state ¹³C NMR spectra of EDTA and its complexes with Na, Mg, Ca and La obtained in CP/MAS mode (Table I).

The spectrum of the parent EDTA compound (trace (a) in Fig. 1) shows two ¹³C NMR absorptions in the carboxylic region and three resonances in the aliphatic region respectively: we think that the two well separated carboxylate resonances reflect the zwitterionic nature of this species in which two N-atoms have been protonated [5].



The separation between the carboxylate resonances (6.0 ppm) is in good agreement with the previously reported values [6] of the protonation at the nitrogen site of glycinate and EDTA tetra-anion itself. The methylene resonances appear as singlets only slightly more broadened than the carboxylate resonances; the absence of the expected doublet due to the directly bonded N-14 as the result of not completely averaged quadrupolar splitting [7] is likely due to a decrease of the electric field gradient at the nitrogen following the protonation.

In the case of Ca-EDTA (trace (e) in Fig. 1) the carboxylate region shows two signals of equal intensity: this behaviour is probably related to the presence of two independent crystallographic sites in the unit cell rather than the unlikely occurrence of an octahedral coordination of the EDTA ligand (this type of coordination mode has been unambiguously found only for the Co(III) derivative) [8]. Actually a X-ray structure determination has been

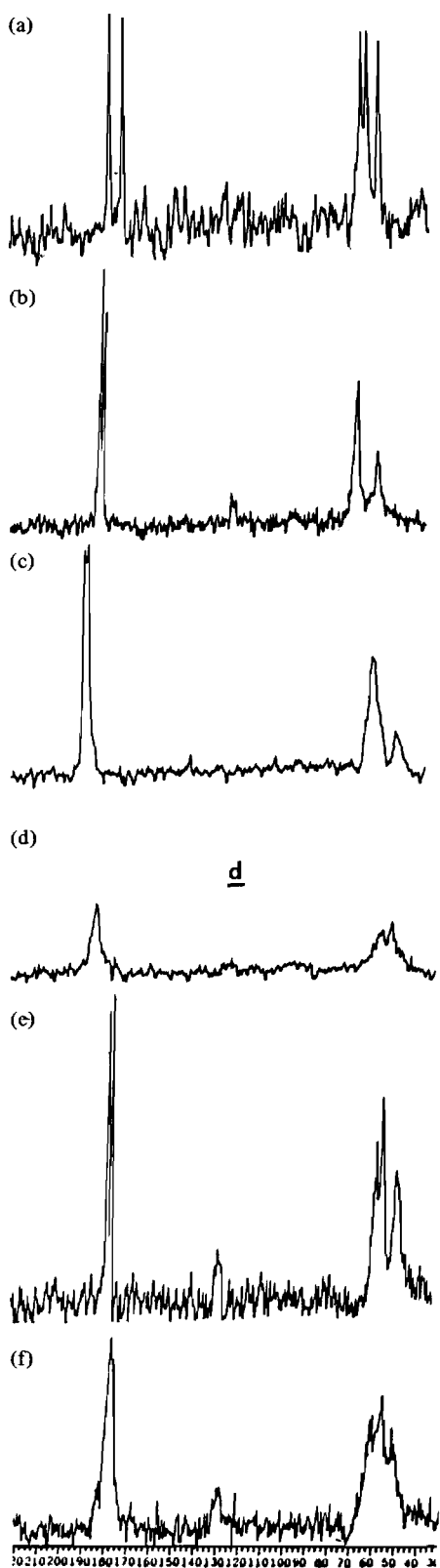
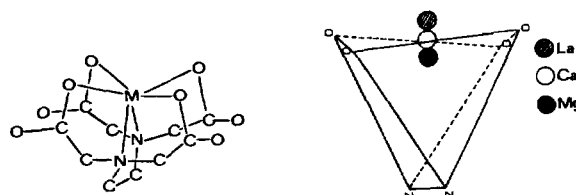


Fig. 1. ^{13}C CP/MAS NMR spectra of (a) $\text{H}_4[\text{EDTA}]$; (b) $\text{Na}_2[\text{H}_2\text{-EDTA}]$; (c) $\text{Na}_4[\text{EDTA}]$; (d) $\text{Na}_2[\text{Mg-EDTA}]$; (e) $\text{Na}_2[\text{Ca-EDTA}]$; (f) $\text{Na}[\text{La-EDTA}]$.

reported [9] for the related derivative $\text{Ca}[\text{Ca-EDTA}] \cdot 7\text{H}_2\text{O}$ which results in a structure intermediate between those of Mg^{2+} [10] and La^{3+} [11] as expected on the basis of their relative ionic radii (Mg^{2+} , 0.65; Ca^{2+} , 0.99; La^{3+} , 1.15 Å). In all three cases, EDTA^{4-} is unable to encircle the metal ion completely; however the smaller dimension of the Mg^{2+} ion allows its inclusion below the averaged plane of the four oxygens whereas the lanthanum ion is above it. The observation of two CO_2^- resonances can then be accounted for in terms of a significant departure from C_{2v} symmetry in the parameters of the coordination polyhedron as the result of asymmetric stresses exerted by the crystal-line environment.



In solution this differentiation is lost and a single carboxylate resonance is observed; only the related CyDTA chelate [12] shows two CO_2^- absorptions in solution.

The observation of two closely spaced resonances for CO_2^- functionalities in $\text{Na}_4\text{-EDTA}$ (trace (c) in Fig. 1) is consistent with the occurrence of a chelate for this metal too, as suggested from previous ^{23}Na NMR studies in solution [13]. Further support for this suggestion arises from the observation of a downfield shift of 8 ppm on going from $\text{Na}_2\text{H}_2\text{-EDTA}$ to $\text{Na}_4\text{-EDTA}$: absorptions of CO_2^- resonances close to 180 ppm (as observed for Na_4 , Na_2Mg , Na_2Ca and NaLa derivatives) may then be taken as useful probes to test the chelate formation in these species.

The carboxylate absorption of the La -chelate (trace (f) in Fig. 1) is rather broadened (350 Hz at half height) as a consequence of the residual dipolar coupling arising from the spatial proximity to the ^{139}La quadrupole ($I = 9/2$, $Q = 0.21 \cdot 10^{-24} \text{ cm}^2$) and this can mask the eventual occurrence of a splitting as observed for the Ca derivative. This view gets some support from the observation of two acetate CH_2 resonances for this compound.

The $\text{Na}_2[\text{Mg-EDTA}]$ derivative (trace (d) in Fig. 1) shows broad absorptions in both the carboxylate and methylene regions; we are unable to assess the origin of this broadening at this stage: an explanation based on a quadrupolar induced broadening as given above for the La derivative has to be ruled out since the magnetically active ^{25}Mg ($I = 5/2$) is only 10.13% naturally abundant.

Finally, comparison between solution and solid state spectra allows the evaluation of solvation

effects which can eventually be related to the release of steric stress gained in solution and/or to formation of hydrogen bonds with the solvent molecules and/or to other effects as well. Interestingly, in the cases considered in this work, the carboxylate resonances are the least affected, whereas the glycinate and ethylenic CH₂ resonances are strongly shifted in the opposite way. This behaviour seems to reflect mainly changes in the steric constraints rather than solute/solvent interactions which would be expected to be stronger at the carboxylate carbons.

Experimental

The sodium salts of ethylenediaminetetraacetic acid were obtained by dissolution of H₄EDTA with sodium hydroxide in stoichiometric quantities under good stirring. To this solution absolute ethanol was added until a persistent cloudiness was observed. The resulting solution was cooled at 10 °C for several hours. Fine white crystals separated from the solution, were recrystallized from a water-ethanol mixture and dried under vacuum.

The other salts Mg, Ca and La were prepared by addition of equimolar quantities of the corresponding chlorides to solution of Na₄-EDTA. The ¹³C CP/MAS NMR spectra were obtained on a Jeol GX 270/89 spectrometer with Chemagnetics solid-state accessories operating at 67 MHz (¹³C). The samples were packed into Kel-F rotors and the magic angle spinning was set at 3.8–3.9 KHz; a contact time of 5 ms and a pulse delay of 2 s were used. A 1000–1500

transient was usually collected employing a broadening function of 5–10 Hz in weighting the FIDs.

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