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Multinuclear NMR and DFT studies of the structure and fluxionality for M^{III}–ethylenediamine-tetraacetate complexes ($M(EDTA)^-$, M = Al, Ga and In) in solution

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Abstract

Multinuclear NMR studies of $M(EDTA)^-$ complexes (M = Al, Ga and In) by ^1H, ^{13}C and ^{27}Al NMR in solution while varying the temperature, pH or using different solvents have been done. The features of the high-field NMR spectra show that the complexes have similar structure in solution and solid state, i.e., the Al(III) and Ga(III) are octahedrally coordinated by the hexadentate EDTA ligand, whilst In(III) is seven-coordinated in a trigonal prismatic fashion by a hexadentate EDTA and one water molecule. $M(EDTA)(OH)^{2-}$ complexes (M = Ga, In) have also been detected, pK values in D_2O are 6.08 ± 0.06 and 9.17 ± 0.07, respectively. In the case of the octahedral Al(III) and Ga(III) complexes, the fluxional rearrangement of the chelate rings can be followed by ^1H NMR, but $In(H_2O)(EDTA)^-$ does not show fluxionality for structural reasons. The exchange between the *axial* and *equatorial* acetate arms of $Al(EDTA)^-$, located at different N-atoms of the ligand, could be a proton-catalyzed reaction assisted with water molecule(s). Density functional theory (DFT) calculations have been carried out to reveal the effect of protonation and the role of solvent.

Keywords: EDTA; NMR; DFT; structure; fluxionality; Al; Ga; In

1. Introduction

Interest in metal–aminopolycarboxylate complexes dates back several decades [1]. Fueled by the need for analytical chemistry and different applications in industry and medicine, the equilibria of the complexes including group 13 elements (M = Al, Ga, In and Tl) have been studied [2]. The stability constants of the parent complexes, $M(EDTA)^-$ are in the range of log K = 16–37, and protonated M(HEDTA) and mixed $M(EDTA)(OH)^{2-}$ complexes are also known. Migration of metal ions, especially in the case of EDTA-containing, radioactive waste waters, has renewed the research interest in the chemistry of this classical ligand [2–4]. The transport of metal complexes in the environment, i.e., the interaction of these species with the components of soil (for example by surface complexation) might be related among others to the hydration and the fluxionality of dissolved complexes.

The dilemma of the actual denticity of the potentially hexadentate EDTA ligand and the coordination number of the M(III) ions (M = Al and Ga) in solution is discussed in several papers [5–9], although the molecular structure shows distorted, octahedrally coordinated Al, Ga by hexadentate ligand in the isostructural $M^IM^{III}(EDTA)\cdot 2H_2O$ solid crystals (M^I = K, NH_4, M^{III} = Al, Ga) [8,10,11], with no water molecules in the inner sphere of the central ions. In the $Na[In(EDTA)(H_2O)]\cdot 2H_2O$ crystal, [12] the structure features seven-coordinated In^{3+} and hexadentate $EDTA^{4-}$ ligand.

High-resolution NMR spectroscopy is excellent for studying the symmetry of complexes in solution, but there is an obvious need to take into account the intra-molecular isomerization/fluxionality of the complexes, because fast rearrangement of the donor atoms (including the water) in the inner sphere might apparently increase the symmetry. The aim of this paper is to

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reinvestigate the $M(EDTA)^-$ systems (M=Al, Ga and In) in solution by ^1H, ^{13}C and ^{27}Al NMR while varying the temperature, pH or using different solvents to change the rate of the fluxionality. Structures and relative stabilities of various forms of $Al(EDTA)^-$ involved in carboxylate exchange processes have also been examined using density functional theory calculations.

2. Experimental procedure

2.1. Materials

$Al(NO_3)_3 \cdot 6H_2O$, Na_2H_2EDTA, NaOH, $In(NO_3)_3 \cdot 6H_2O$ (Reanal, reagent grade) came from commercial sources. $GaCl_3$ and solutions were prepared from 99.99% Ga (Aluminium Work, Ajka, Hungary). $KAl(EDTA) \cdot 2H_2O$ was supplied by Dojin (Japan).

2.2. Preparation of the complexes

Solid complexes $NaAl(EDTA) \cdot 2H_2O$, $NaGa(EDTA) \cdot 2H_2O$ and $Na[In(EDTA)(H_2O)] \cdot 2H_2O$ were crystallized from about 0.1 mol dm^{-3} solutions (containing EDTA and M(III) in a 1:1 molar ratio at pH=4) by adding an excess (at least four volumes) of ethanol. The solid was filtered, washed with 96% ethanol and dried in air. ^1H NMR spectra showed the signals of only the complexes.

2.3. pH measurements

The electrode was calibrated [13a] as $pH = -\log[H^+]$; therefore, the derived constants were stoichiometric constants. In D_2O, pD was calculated as $pH_{reading} + 0.4$ [13b]. The speciation diagram was calculated using the Medusa program [14].

2.4. NMR measurements

^1H NMR spectra were recorded at 200, 360, 400 and 500 MHz. ^{13}C NMR spectra were recorded at 50, 90, 100 and 125 MHz using Bruker AM200, Avance 360, AM400, DMX500 spectrometers using 5 mm inverse probes (except the Avance 360 with QNP probe) in locked mode. Typical acquisition parameters for ^1H (and ^{13}C) NMR spectra were flip angle ~5 (13) µs (30°), pulse repetition time 0.2–0.5 (15) s, spectral window 210–1100 (25,250) Hz, number of scans 8–32 (256–8000). Some ^{13}C NMR spectra were collected with power gated or, for quantitative purposes, with the inverse gated decoupling pulse sequence. The chemical shifts are reported in ppm relative to TMS* ($\delta = 0.00$ ppm) as an external standard. Spectral analyses were done using the Bruker WIN-NMR software. The temperature of the probe heads was checked by the methanol-thermometer method [15].

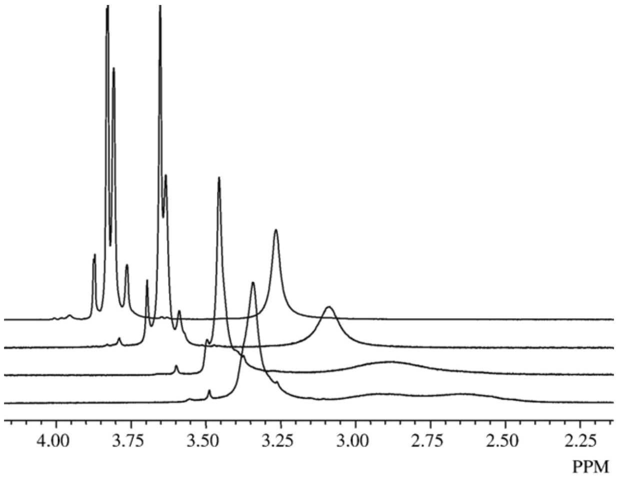

Fig. 1. The temperature dependence of 400 MHz ^1H NMR spectra in a sample of 0.1 M NaAl(EDTA), (self pD≈4, D_2O solvent). The temperature values from the top to the bottom are 323, 301, 283 and 273 K.

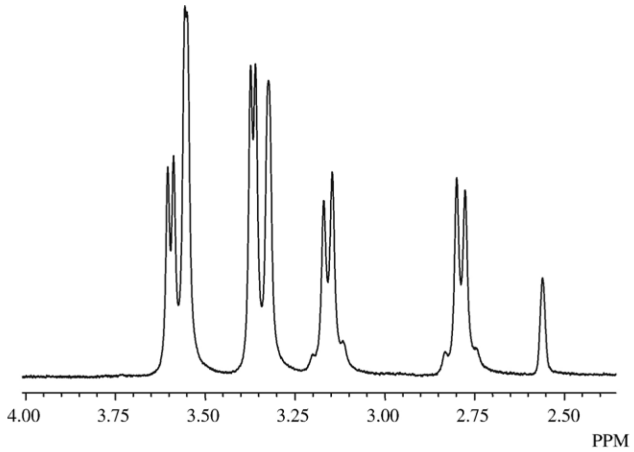

Fig. 2. 400 MHz ^1H NMR spectrum of 0.1 M NaAl(EDTA) in D_2O (20%)–DMSO-d_6 (80%) at 281 K. (The signal at 2.65 ppm belongs to the DMSO solvent.)

104.23 MHz ^{27}Al NMR spectra were recorded on a JEOL 400 instrument. The chemical shift refers to 0.01 M $AlCl_3$ solution containing 0.01 M HCl, $\delta = 0$ ppm. Some 400 MHz ^1H NMR spectra were also recorded using this equipment.

2.5. DFT calculations

The structures of the investigated complexes have been fully optimized at the B3LYP/6-31G* level of DFT, where B3LYP refers to the applied exchange-correlation functional [16–18] and 6-31G* is the standard split-valence basis set. The relative energies reported in the paper have been obtained at the same level of theory. The calculations have been carried out using the Gaussian 03 software package [19].

3. Results and discussion

3.1. NMR study of $M(EDTA)^-$ complexes

3.1.1. $Al(EDTA)^-$ complex

The free EDTA ligand shows two singlet ^1H NMR signals, one of the acetate arms (8H) and one of the ethylenic group (4H), and three ^{13}C NMR signals, assigned to the already mentioned groups and another to the carboxylate carbons. However, ^1H and ^{13}C NMR spectra of $Al(EDTA)^-$ show different pattern at different fields indicating the presence of exchange processes, i.e.,